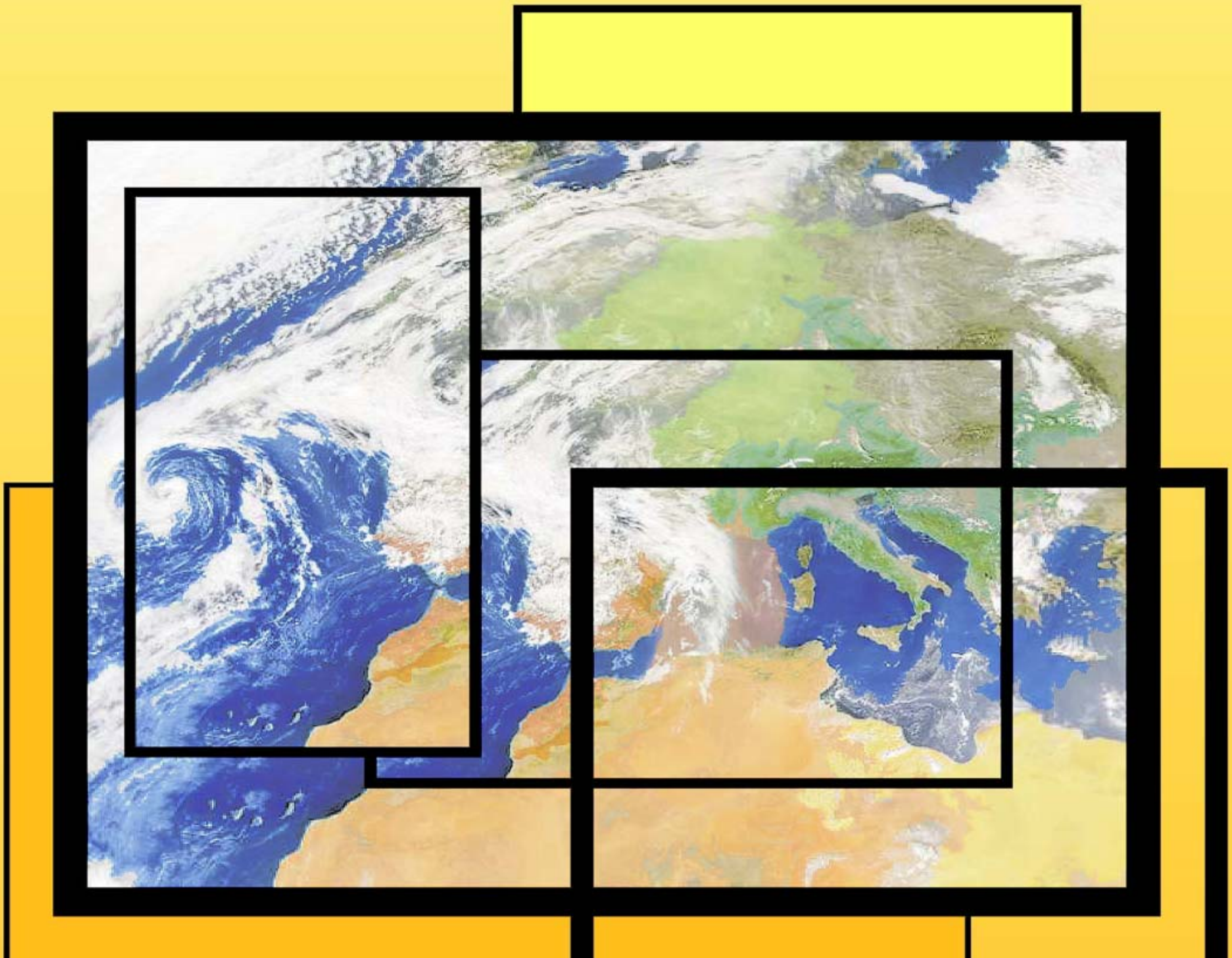
UNIVERSITAT DE BARCELONA

Suspended particulate matter and wet deposition fluxes in regional background stations of the Iberian Peninsula: a detailed study of African dust outbreaks

Miguel Escudero Tellechea

SUSPENDED PARTICULATE MATTER AND WET DEPOSITION FLUXES IN REGIONAL BACKGROUND STATIONS OF THE IBERIAN PENINSULA

A DETAILED STUDY OF AFRICAN DUST OUTBREAKS



MIGUEL ESCUDERO TELLECHEA

BARCELONA 2006

Cover and back design by Javier Escudero, 2006
Front image SeaWIFS 13-10-2001 (modified)

Suspended particulate matter and wet deposition fluxes in regional background stations of the Iberian Peninsula

A detailed study of African dust outbreaks

A dissertation submitted by Miguel Escudero Tellechea to the department of Astronomia i Meteorologia in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Barcelona.

Memoria de tesis presentada por Miguel Escudero Tellechea en el departamento de Astronomia i Meteorología para optar al grado de Doctor por la Universidad de Barcelona

Barcelona, April of 2006

Thesis supervisors:

Dr. Xavier Querol Carceller
Instituto de Ciencias de la Tierra “Jaume Almera” (CSIC)

Dr. Ánna Avila Castells
Centre de Recerca Ecològica i Aplicacions Forestals

Dr. Emilio Cuevas Agulló
Observatorio Atmosférico de Izaña (INM)

Thesis tutor:

Dr. Ángel Redaño Xipell
Departament de Astronomia i Meteorologia (UB)

External reviewers:

Dr. George Kallos
School of Physics, University of Athens

Dr. Francisco Ferreira
Facultade de Ciências e Tecnología, Universidade Nova de Lisboa

A mis padres María José y Tomás

Por vuestro apoyo y comprensión
Os quiero

AGRADECIMIENTOS

Al terminar un trabajo de la dimensión de una tesis doctoral sopesas qué habría sido de ti sin la ayuda de mucha gente. A decir verdad, considero que este trabajo ha sido más un éxito colectivo que personal y así lo quiero reconocer. Por ello me gustaría agradecer su colaboración a mucha gente e instituciones:

A mis tres directores de tesis el Dr. Xavier Querol (Instituto de Ciencias de la Tierra "Jaume Almera", CSIC), la Dra. Anna Ávila (CREAF) y el Dr. Emilio Cuevas (Observatorio Meteorológico de Izaña, INM) por la confianza depositada en mí para llevar a feliz término este estudio. A Xavi me gustaría agradecerle su ayuda permanente así como su cercanía humana, he aprendido mucho trabajando con un científico de su capacidad y confío en seguir aprendiendo. A Anna por su confianza en mi trabajo y su disponibilidad personal y profesional. A Emilio por sus buenos consejos y su buena orientación en los aspectos meteorológicos del estudio. Con vosotros nunca me ha faltado un buen consejo profesional o personal. Ha sido un placer trabajar con los tres.

He realizado la mayor parte de mi trabajo dentro del grupo de geoquímica ambiental del Instituto de Ciencias de la Tierra "Jaume Almera" del CSIC. Me gustaría destacar el gran nivel científico y humano de todos los miembros de este grupo lo que ha ayudado decisivamente en el cumplimiento de las tareas asociadas a mi proyecto de investigación. Muchas son las personas en este grupo a las que tengo que agradecer cosas:

A Sonia Castillo (Frigiliana power), mi compañera becaria dentro del proyecto desde el 2002. Empezamos juntos el trabajo y terminamos casi juntos. Creo que esto ha creado una gran empatía entre nosotros porque sé que ambos hemos pasado por dificultades. Gracias por los buenos ratos que hemos pasado y por la colaboración que me has prestado en muchos momentos para esta tesis. Que seas muy feliz en Granada junto a vibro.

Al Dr. Andrés Alastuey por su ayuda para que un físico como yo llegase a comprender un poco mejor el complicado mundo de la química de aerosoles.

A la Dra. Mar Viana mi vecina en el despacho durante tanto tiempo, cuya paciencia puse a prueba tantas veces que nos hicimos amigos. Su colaboración ha sido inestimable para la realización de esta tesis en muchos aspectos.

A la Dra. Natàlia Moreno, la reina madre, por las muchas y buenas conversaciones y las muchas y buenas risas. Un encanto de persona.

A Oriol Font por los buenos y divertidos momento que hemos pasado durante estos años. Ha sido un placer aunque no hayamos colaborado directamente.

A mis compañeros de despacho y grupo Jorge Pey y Mari Cruz Minguillón por la cantidad de favores que me han hecho mientras estaba en Atenas o Zaragoza, siempre con una gran voluntad para ayudarme. Espero no haber sido muy pesado, gracias.

A la Dra. Teresa Moreno por su colaboración para descifrar los diagramas triangulares y al Dr. Wes Gibbons por sus consejos para mejorar el inglés de esta tesis.

A otros compañeros de mi grupo de trabajo como Silvia Rico, Sandra Toro y Patricia Ávila (las chicas del laboratorio), el Dr. Ángel López, el Dr. Felicià Plana, el Dr. Sergi Diez, Noemí Pérez, la Dra. María Izquierdo, la Dra. Esther Álvarez y el Dr. Sergio Rodríguez con los que, por razones profesionales, he interactuado menos pero con los que también he compartido grandes momentos y he recibido valiosos consejos.

Otros compañeros del Instituto "Jaume Almera" también merecen mi más sincera gratitud:

A mis amigos de Raman (los quita-picos) David Pastor, y Esther Alarcón, buena gente y grandes amigos.

A Isaac Flecha (un hacha en LINUX), al Dr. Sergi Hernández (también quita-picos), Mapi Asta (compatriota zaragozana) y Tobías Rötting (tecnología alemana sobre bici) por hacer que me plantee seriamente si podía haber caído en un despacho mejor. Ellos, junto a todos los componentes de mi grupo con los que he compartido despacho (Natalia, Mar, Jorge y Mari Cruz), han sido de fundamental ayuda personal y profesional en muchos momentos. Tras cuatro años de trabajo es difícil llevarse tan bien con todos y me queda la sensación de haber tenido la dosis justa de diversión que ayuda a trabajar mejor.

A mis compañeros conserjes Xavi Pascual, Amelia Salas y Joana Sáenz por siempre hacer su trabajo con una gran sonrisa y amabilidad y, a Pepi López por los buenos ratos bromeando en el despacho.

No me gustaría olvidar a compañeros del CREAF y mostrar mi gratitud a todos aquellos con los que compartí esos primeros meses en Barcelona.

En particular me gustaría agradecer a Marta Barceló su gran disposición y efectividad para resolver problemas, a Carlos Carreño por ayudarme siempre con los problemas informáticos, a la gente de administración (Nuria Colás, Silvia Querol, Charo del Hoyo y Ramón María Pardinas) por su colaboración y a buenos compañeros como Xavi Roijals, Anabel Sánchez, Quique, Laura Alvadalejo y la Dr. Corina Basnou con los que pasé grandes momentos.

A los Drs. Jerónimo Lorente y Ángel Redaño (tutor de esta tesis) y a José Ramón Rodríguez por su buena disposición para colaborar en la resolución de los trámites departamentales así como a todo el Departament de Astronomia i Meteorologia de la Facultat de Física de la Universitat de Barcelona por permitirme presentar esta tesis.

A la Dra. Marta Alarcón por su inestimable colaboración científica en la realización de mi primer artículo científico.

A la Dra. Begoña Artíñano, el Dr. Pedro Salvador, la Dra. Mar Viana, Sonia Castillo, al Dr. Sergio Rodríguez y la Dra. Ana Sánchez por la suministro de información muy útil sobre origen de retro-trayectorias sobre distintas zonas de la Península Ibérica.

También me gustaría mencionar en esta sección a una serie de entidades que han colaborado decisivamente en la realización de la tesis:

En primer lugar al Ministerio de Ciencia y Tecnología (actualmente englobado en el Ministerio de Educación y Ciencia) por haber financiado tanto el proyecto REN2001-0659 como mi beca FPI.

Al Ministerio de Medio Ambiente de España por el suministro de los datos de la Red EMEP de calidad del aire. En concreto, me gustaría agradecer a Santiago Jiménez y a Alberto González su disponibilidad ante las peticiones de datos de dichas estaciones.

Al Gobierno Vasco por el suministro de los datos de las estaciones de Valderejo e Izki.

A ENDESA por la provisión de los datos de la estación de Monagrega.

A la Generalitat de Catalunya y a la Generalitat Valenciana por el suministro de datos de estaciones de sus redes calidad del aire.

A Meteocat por los datos de precipitación de Santa María de Palautordera.

To the Naval Research Laboratory (NRL) for the supply of NAAPs aerosol maps.

To the SeaWIFS Project (NASA) for supplying satellite imagery.

To the NASA/Goddard Space Flight Center for the provision of TOMS-AI maps.

To the NOAA-CIRES Climate Diagnostics Center and to the NOAA Air Resources Laboratory (ARL) for providing meteorological maps.

I would like express my gratitude to the Atmospheric Modeling & Weather Forecasting Group (AM&WFG) in the University of Athens for the SKIRON/Eta model outputs and for accepting as visitor. In my time there, I developed a very useful work with SKIRON/Eta model which improved my thesis greatly. I would like to stress the high scientific level of the AM&WFG and the hospitality of all the group members. In particular I would like to thank Dr. George Kallos as director of the group for accepting my visit and for his very important suggestions which helped to improve my work, and to my cicerone in the world of SKIRON/Eta, Christos Spyrou. Thank you to all my friends in Athens: Marina, Petroula, Petros, Ioannis, Ermioni, Antigoni, Georgos…

I would like to express my gratitude to Dr Francisco Ferreira from the Universidade Nova de Lisboa for the very useful comments and suggestions derived from the revision of this dissertation.

I also would like to thank Drs. Roland Draxler and Ariel Stein from the NOAA-ARL for introducing me to the very useful tool of HYSPLIT4. I acknowledge the important support and help I have received from both when working with this model. I also would like to thank the Centro de Estudios Ambientales del Mediterráneo (CEAM) for inviting me to the HYSPLIT training seminar held in Valencia (October, 2004).

Para terminar me gustaría también hacer mención a personas muy cercanas a mí de fuera de mi ámbito laboral que, pese a ello, han sido fundamentales en este tiempo por su apoyo personal. Así me gustaría reconocer:

A mis padres Maria José y Tomás y a mis hermanos, Javier e Isabel, por su apoyo, compañía e interés en todo este tiempo. Estoy orgulloso de pertenecer a esta familia y de haber recibido la educación y los valores que me han transmitido. En concreto me gustaría agradecer a mi hermano Javier por el diseño y realización de la portada de esta tesis.

A los miembros de la familia Marco-Lacoma: Manolo, Angelines, Isabel, Manolo y Goya, y los de la familia Vicente-Marco: Jorge, María, las nenas Isabel y Julia (que va venir), por haberme aceptado y haberme abierto las puertas tan sinceramente.

A tantos amigos tanto del local como del maca que me han ayudado mucho a divertirme y a desconectar en ocasiones del trabajo.

To my favourite couple in Athens, Andreas and Dora, for hosting me in Athens. You deserve the best and you will always have a friend in me.

A mis compañeros de piso Michel y Luis por el respeto y la colaboración que me han mostrado durante este tiempo y por los muchísimos viajes por la A2 y la AP2. Me han demostrado lo que es saber convivir.

He querido dejar al final mi agradecimiento más especial a mi compañera Isabel. Todo lo que me has ayudado y apoyado ha sido esencial para mí y tu compañía y comprensión han sido mi sustento más importante. Mereces el reconocimiento más grande por todo esto, te quiero.

En definitiva me gustaría resaltar que la calidad de cualquier trabajo de investigación va en consonancia con la capacidad de la gente que ha colaborado en su realización. Esto da validez a una máxima que siendo niño escuché en la televisión cuando aún enseñaba algo: “Tú solo no puedes, con amigos sí”. Gracias de corazón a todos.

RESUMEN

La presencia de partículas sólidas y/o líquidas en la atmósfera (aerosol atmosférico) tiene diversas implicaciones sobre el clima, la visibilidad, la salud de los humanos y diversos ciclos biogeoquímicos. Debido a todos estos efectos, el estudio de este material se está llevando a cabo por una comunidad científica de marcado carácter interdisciplinar.

El efecto en la salud del material particulado (MP) atmosférico en modo de incremento en mortalidad por afecciones cardiovasculares y respiratorias, por el carácter carcinógeno de algunas especies y el importante impacto en la salud de niños y fetos, impulsó a la Comisión Europea a aprobar en el año 1999 la Directiva Hija 1999/30/EC de Calidad del Aire en donde se establecían unos estándares de calidad del aire de obligado cumplimiento por parte de los Estados Miembros. Esta directiva establece un valor límite anual de 40 µgPM10 m^{-3} en 2005 y de 20 µgPM10 m^{-3} en 2010, y el valor límite diario de 50 µgPM10 m^{-3} que no podrá ser superado en un número superior a 35 días $año^{-1}$ en 2005 y 7 días $año^{-1}$ en 2010. Esta Directiva está en revisión actualmente (2006) y la Comisión Europea ha emitido una versión preliminar que propone mantener los valores límite establecidos en la Directiva 1999/30/EC para 2005 y, además añadir un valor de concentración tope anual de PM2.5 para 2015 de 25 µg m^{-3}. Además se propone establecer un valor objetivo de reducción a la exposición de la población a PM2.5 que consistirá en la reducción en el 20% de la media tri-anual de PM2.5 obtenida en estaciones de fondo urbano entre 2008-2010 y 2018-2020.

En Europa en general y en España en particular, control de los niveles de contaminación atmosférica por MP así como estudios de especiación química de dichos contaminantes se lleva a cabo con frecuencia en las ciudades para obtener medidas representativas de la exposición de la población. Sin embargo no se han estudiado con tanta precisión los niveles de fondo regional de estos contaminantes. Tampoco se ha detallado la caracterización meteorológica de los distintos episodios que explican la variabilidad estacional y geográfica de los niveles de MP en estaciones de fondo regional de la Península Ibérica.

El trabajo con estaciones de fondo regional (aquellas localizadas fuera de la influencia directa de fuentes antropogénicas locales de MP) permite la detección y el estudio de una serie de episodios naturales y antropogénicos de aporte de aerosoles que tendrán una influencia importante en todo tipo de estaciones de medida de la Península Ibérica. Entre estos eventos se encuentran las intrusiones de polvo atmosférico Africano. Estas entradas de masas de aire Africanas con alta carga de material crustal provocan unos incrementos importantes en los niveles de MP especialmente en los rangos de tamaño gruesos (TSP y PM10) que puede producir superaciones de los niveles limite establecidos en la Directiva 1999/30/CE. Cabe recordar que, de acuerdo con esta directiva, las superaciones asociadas a episodios de resuspensión natural podrán ser descontadas si son justificadas adecuadamente. El polvo mineral Africano constituye además una fuente importante de alcalinidad que reduce la incidencia de la lluvia ácida en el Mediterráneo. Debido a estos dos efectos, se han llevado a cabo de manera independiente trabajos para el estudio, por un lado, de los niveles de MP durante intrusiones Africanas y, por otro lado, de los flujos de deposición de polvo Africano. Sin embargo, hasta ahora, no se había incluido en un mismo trabajo el estudio de estos dos procesos.

El objetivo principal de este trabajo es el desarrollo de un modelo conceptual para la interpretación de los episodios que tienen un impacto tanto en los niveles de MP como en los flujos de deposición en el fondo regional en el de la Península Ibérica. Para ello

se cubrirán otros sub-objetivos, como son la interpretación de los escenarios meteorológicos que dan lugar a episodios con impacto en niveles de MP en el fondo regional y la interpretación de la variabilidad temporal y geográfica de estos niveles en la Península Ibérica. También se llevará a cabo el estudio detallado de las intrusiones de polvo Africano incluyendo su variabilidad estacional, impacto en niveles de MP y en los flujos de deposición en zonas de fondo regional, así como la especificación de las áreas fuente de polvo que preferentemente contribuyen a las plumas de polvo que alcanzan la Península Ibérica.

Para ello se obtuvieron datos de MP atmosférico en estaciones de fondo regional de la Península Ibérica del periodo 1998-2003. Se utilizaron datos de TSP (partículas totales en suspensión), PM10 (partículas en suspensión con diámetro aerodinámico menor de 10 μm) y PM2.5 (partículas en suspensión con diámetro aerodinámico menor de 2.5 μm) de estaciones pertenecientes a la red EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe) de distintas zonas de la Peninsula (Noia, Niembro-Llanes y O Saviñao en el noroeste; Logroño en el norte; Roquetas, Cabo de Creus y Els Torms en el noreste; San Pablo de los Montes, Risco Llano, Campisábalos y Peñausende en el centro; Zarra en el este, Bancarrota en el suroeste y Víznar en el sureste). Además se utilizaron datos de TSP y PM10 de dos estaciones del norte peninsular pertenecientes a la red de calidad del aire del Gobierno Vasco (Valderejo e Izki) y datos de PM10 de una estación situada del noreste peninsular perteneciente a la red de control de calidad ambiental de ENDESA (Monagrega). De estas estaciones se seleccionaron las que se consideraron representativas del fondo regional en cada zona. En las estaciones EMEP se realizan las medidas usando el método gravimétrico, en Valderejo e Izki se utiliza el método de atenuación β y en Monagrega se utiliza el método TEOM. Se identificó el tipo de episodio que afecta a las distintas zonas de la Península Ibérica cada día del periodo de estudio (1998-2003) así como los escenarios meteorológicos que dan lugar esos episodios y se evaluó su impacto en los niveles de TSP, PM10 y PM2.5. Esto se hizo utilizando llevando a cabo una metodología que incluyó el cálculo de retro-trayectorias con el modelo de dispersión HYSPLIT4, la inspección de imágenes de satélite (SeaWIFS), de mapas de índice de aerosoles (TOMS), de mapas de modelos de predicción de aerosoles (SKIRON/Eta y NAAPs) y la consulta de mapas meteorológicos. Así, se distinguieron los siguientes episodios de MP:

a) **Episodios Atlánticos**: Se producen muy frecuentemente en todas las zonas de la Península Ibérica pero con un gradiente decreciente del noroeste al sureste (del 72 al 36% de los días) y con una duración elevada (con una media de entre 4 y 7 días de duración en todas las zonas de España). El verano es el periodo con menor frecuencia relativa de episodios Atlánticos. En general se registran bajos niveles de MP en el fondo regional (con medias anuales de 11-34 μgTSP m^{-3}, 7-18 μgPM10 m^{-3}, 5-11 μgPM2.5 m^{-3} para este tipo de episodios en las distintas estaciones de fondo regional). Esto se debe a la renovación de masas de aire y al lavado atmosférico que provoca la lluvia durante los episodios Atlánticos. Esta lluvia está asociada al frecuente paso de sistemas frontales durante los episodios Atlánticos. Además, las masas de aire Atlánticas tienen una baja carga de partículas. Los niveles se pueden asociar por ello a contribuciones locales o regionales.

Se reconocieron dos escenarios meteorológicos que explican la llegada de masas de aire Atlánticas sobre la Península Ibérica. Uno asociado a la presencia de el anticiclón de las Azores y la baja de Islandia en sus posiciones estándar (escenario AZH-NAtD) y otro debido a la presencia de una depresión sobre el Atlántico (escenario

AD(ATL)). La segunda de las situaciones es mucho menos frecuente y lleva asociada lluvia con más frecuencia que la primera. Este segundo factor generalmente da lugar a niveles de MP más bajos.

b) **Episodios Africanos**: Las intrusiones de polvo Africano sobre la Península Ibérica se producen con una frecuencia desigual en distintas zonas geográficas. En el noroeste sólo se llega al 8% de los días mientras que en sureste se registran intrusiones en un 27% de los días. El verano es periodo de máxima frecuencia de intrusiones con otros periodos con alta frecuencia como el trimestre Enero-Marzo y Octubre. La duración de estos eventos es moderada (3-4 días de media). Los niveles de MP durante las intrusiones de masas de aire africanas son generalmente altos debido a la importante carga de material crustal en estas masas (29-62 µgTSP m^{-3}, 21-35 µgPM10 m^{-3}, 11-18 µgPM2.5 m^{-3} como rangos de media anual en las diferentes estaciones seleccionadas). Los niveles de partículas son elevados con respecto al resto de episodios no sólo en TSP y PM10 sino también en PM2.5.

Se identificaron cuatro escenarios meteorológicos que dan lugar a situaciones de transporte desde el norte de África. Dos de ellos están asociados a la presencia de depresiones sobre el Atlántico (escenario AD(NAF)) o sobre el norte de África (escenario NAD) y en consecuencia con probabilidad relativamente alta de lluvia. Los otros dos están asociados a la presencia de un anticiclón sobre la Península Ibérica en niveles superficiales atmosféricos (escenario NAH-S) o en niveles elevados de la atmósfera (escenario NAH-A). Estos últimos son los más frecuentes. Los NAH-S se dan en el periodo Enero-Marzo y los NAH-A en verano. Estos dos escenarios son secos, y por ello provocan un alto impacto en los niveles de MP. Esto es más intenso en el caso de los episodios NAH-A por las condiciones meteorológicas predominantes en verano.

c) **Episodios Europeos**: Estos episodios afectan con frecuencia al flanco norte de la Península y mucho menos frecuentemente a la zona sur (10-17% de los días en el norte y 3-5% en el sur). El transporte de masas de aire europeas es un proceso que típicamente se produce en la época fría del año. La duración de estos episodios es moderada (2-4 días de media). Durante los episodios Europeos los niveles de MP en zonas de fondo regional son moderadamente altos en el norte y bajos en el sur (las medias anuales en las diferentes estaciones seleccionadas varían en los siguientes rangos 13-43 µgTSP m^{-3}, 10-25 µgPM10 m^{-3}, 7-16 µgPM2.5 m^{-3}). Esto se debe a la dispersión y dilución de los contaminantes en el trayecto hasta llegar al sur peninsular.

Existen dos escenarios sinópticos que causan el transporte de masas de aire Europeas sobre la Península Ibérica. Uno está asociado a la presencia de un anticiclón sobre el continente Europeo o sobre el Atlántico norte (escenario EUH) y el otro a la presencia de una depresión sobre el área Mediterránea (escenario MD). El primer escenario se da más frecuentemente que el segundo, además, tiene más impacto en los niveles de MP debido a la bajo frecuencia de lluvia comparada con el escenario MD.

d) **Episodios Mediterráneos**: Estos periodos se caracterizan por estar asociados a la presencia de precipitaciones en especial en el flanco este de la Península Ibérica. Se dan con poca frecuencia (por debajo del 6% de los días en todas las zonas geográficas), tienen una duración baja (2 días de media en todas las zonas) y, debido a la alta frecuencia de precipitación, los niveles de MP son bajos (13-39 µgTSP m^{-3}, 9-24 µgPM10 m^{-3}, 6-16 µgPM2.5 m^{-3} como rangos de media anual en las diferentes estaciones seleccionadas). Los periodos del año en los que se produce este tipo de transporte es primavera y otoño.

Se distinguieron dos escenarios meteorológicos que causan advección Mediterránea sobre la Península Ibérica, uno caracterizado por la presencia de un anticiclón sobre el continente Europeo o el Mediterráneo (escenario EUH-MH) y otro con la presencia de una depresión sobre el norte de África o el Mediterráneo occidental (escenario NAD-MD).

e) **Episodios sin advección dominante**: Estos son periodos que se dan con alta frecuencia durante el verano aunque también en invierno. La zona este y centro peninsular se ve afectada por este tipo de episodios con más frecuencia que el norte y el oeste (23-29% y 9-16% de los días respectivamente). Estos episodios tienen una duración moderada (3 días de media en todas las regiones).

Se distinguen dos escenarios meteorológicos que explican la existencia de este tipo de episodios con falta de advección dominante. En invierno, bajo el efecto de una anticiclón que cubre la Península Ibérica (escenario WIA) se producen frecuentemente situaciones de inversión térmica que reducen el transporte de contaminantes de zonas urbanas e industriales hasta zonas de fondo regional. Así los niveles de MP son bajos en situaciones WIA (15-32 µgTSP m^{-3}, 10-23 µgPM10 m^{-3}, 7-14 µgPM2.5 m^{-3} como rangos de media anual en las diferentes estaciones seleccionadas). En verano la falta de advección está unida al desarrollo de la baja térmica peninsular debido al fuerte calentamiento (escenario ITL). El desarrollo de esta baja y las condiciones típicas de verano genera las condiciones ideales para el envejecimiento de masas de aires, la generación fotoquímica de contaminantes secundarios y la dispersión de contaminantes hacia zonas de fondo regional. Por estas razones los niveles de MP son elevados en situaciones ITL (las medias anuales en las diferentes estaciones seleccionadas varían en los siguientes rangos 25-54 µgTSP m^{-3}, 21-30 µgPM10 m^{-3}, 14-21 µgPM2.5 m^{-3}).
Combinando información sobre la frecuencia y los niveles de MP asociados a cada escenario se puede estimar el impacto de cada uno de los episodios en los niveles medios anuales. Se puede entonces determinar el porcentaje de la media anual atribuible a aportes de cada tipo de episodio. Esto se hizo definiendo un índice de impacto (II). Esta variable tiene una gran variabilidad geográfica. Debido a la alta frecuencia de los episodios Atlánticos su II es mayoritario en casi todas las zonas salvo en el sureste (30-50% en el norte y oeste y 20-30% en el este y sureste), el impacto de los episodios Africanos es dominante en el sureste (40-50% con respecto a 15-20% en ele noroeste) y los episodios Europeos sólo tienen una influencia relevante en el flanco norte (15-20% en el norte y 5-10% en el sur y centro). Los episodios con falta de advección dominante tienen un II moderadamente alto en todas las zonas pero en el este en mayor medida (10-15% in el noroeste y 15-40% en el resto de las zonas).

Centrándonos en los episodios de intrusión de polvo Africano, se llevó a término una evaluación del impacto de estos eventos en los niveles de MP atmosférico y en la deposición húmeda en el este Peninsular en el periodo 1996-2002. Para ello, se interpretaron series temporales de TSP y PM10 de distintas estaciones de monitoreo de la calidad del aire de la zona levantina y se complementó este análisis con el cálculo de retro-trayectorias con HYSPLIT4 y la consulta de imágenes de satélite (SeaWIFS), mapas de índice de aerosoles (TOMS), modelos de predicción de polvo mineral (SKIRON/Eta y NAAPs) y mapas meteorológicos. Las muestras de deposición húmeda se obtuvieron de un muestreo semanal de lluvia en una estación rural (La Castanya, Barcelona) para el periodo 1996-2002 en las que se identificó una señal química africana (altos pH y concentraciones de Ca^{2+}). Se identificaron 112 episodios Africanos (16 episodios año^{-1}). En 93 de los 112 episodios (13 episodios año^{-1}) la influencia del polvo Africano causó altos niveles de MP. En 49 de los 112 (7 episodios año^{-1}) se recogió deposición húmeda de polvo y la química de la lluvia quedó influenciada por éste. Existe una clara tendencia estacional con una frecuencia superior de intrusiones secas de polvo Africano en Mayo-Agosto con modas secundarias en Marzo y Octubre.

Los episodios de deposición húmeda tienen una evolución diferente con un marcado máximo de frecuencia en Mayo. Exceptuando un único episodio, en Diciembre no se registraron intrusiones de ninguno de los dos tipos en el periodo de estudio sobre el Noreste de la Península Ibérica. Basándonos en patrones meteorológicos estacionales se llevó a cabo una interpretación de los escenarios meteorológicos que causan el transporte de polvo Africano. Se evaluó la estacionalidad de los cuatro escenarios mencionados con anterioridad (NAH-S, AD(NAF), NAD, NAH-A). Se evaluó también el impacto de los distintos tipos de intrusiones de polvo en los niveles de PM10 obtenidos en una estación rural (Monagrega, Teruel) en el periodo 1996-2002.

Para hacer un estudio detallado de los episodios de deposición húmeda de polvo mineral, se seleccionaron las 16 lluvias de barro (agua de lluvia que deja un residuo insoluble rojizo o marrón al evaporarse o al ser filtrada) Africanas más intensas que tuvieron lugar en el noreste de la Península Ibérica del muestreo semanal de lluvia en la estación rural de La Castanya (Barcelona) en dos periodos de muestreo (1983-2000 y 2002-2003). Estos son los episodios en los que se depositó más de 1000 mg m^{-2} de polvo insoluble y suponen más del 80% de la cantidad total de polvo insoluble depositado por vía húmeda en los dos periodos de muestreo. Estos eventos se simularon con el modelo SKIRON/Eta para su estudio detallado.
La existencia de estos episodios se debe al efecto de depresiones localizadas o bien sobre el Atlántico al oeste o suroeste de la costa de Portugal (escenario AD), o sobre norte de África o el oeste del Mediterráneo (escenario NAD). Adicionalmente, en algunos episodios puede ocurrir que una depresión, originalmente sobre el Océano Atlántico, evolucione atravesando el norte de África a modo de episodio híbrido (escenario AD→NAD). La marcada estacionalidad de estos escenarios (ocurren principalmente en otoño y final de invierno-primavera) y los flujos de deposición asociados a ambas situaciones se describieron.
Se utilizaron también estos 16 episodios intensos de deposición para llevar a cabo una validación cualitativa y cuantitativa del modelo SKIRON/Eta. La detección cualitativa de estos episodios fue correcta (probabilidad de detección del 79%) como se comprobó tras la comparación de los mapas de concentración de polvo del SKIRON/Eta con imágenes de satélite del SeaWIFS y los mapas de índice de aerosoles del TOMS. Se utilizaron los datos de TSP y PM10 disponibles de estaciones de calidad del aire de fondo regional para su comparación con las concentraciones de polvo mineral obtenidas del modelo, mostrando una infravaloración moderada de los niveles. Esta infravaloración es lógica porque el modelo no da cuenta de contribuciones locales o regionales. Los flujos de material depositado por vía húmeda también se infravaloraron por SKIRON/Eta debido a una suma de factores que incluyen limitaciones del método de muestreo (se utiliza una sola estación de muestreo para la comparación y pueden existir contribuciones locales) y errores en la predicción de la lluvia, en el transporte de polvo y en el ratio de lavado atmosférico.
Se obtuvieron mapas de flujo de emisión de polvo del SKIRON/Eta y se utilizaron para identificar las áreas fuente de polvo Africano más activas durante los episodios de lluvia de barro. Las zonas fuente de polvo del norte de África se activan siempre en las horas de máximo calentamiento debido al incremento en convección. No es descartable, sin embargo, que debido a una humidificación esporádica debido a precipitación de alguna zona desértica no se produzca levantamiento de polvo incluso en las horas de máxima convección. Solapado al ciclo diario de emisión debido a los procesos convectivos, el efecto de los vientos de escala sinóptica dispara la inyección de polvo sobre el Mediterráneo. La combinación de estos dos procesos genera que durante los 16

episodios simulados las áreas fuente del norte de África (norte y centro de Argelia y Túnez) sean, de manera casi exclusiva, las zonas emisoras.

Otro objetivo planteado en este trabajo es la detección de las áreas fuente del polvo Africano que llega a la Península Ibérica y tiene un impacto en niveles de MP así como la evaluación de la señal química de este polvo en las muestras recogidas en zonas de fondo regional. Para ello se diseñó una metodología para estimar la contribución de distintas regiones del desierto norteafricano en los niveles de PM10 registrados en diversas estaciones de la Península Ibérica. Para ello se utilizó el modelo de dispersión de contaminantes HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) para estimar las proporciones de polvo originadas en zonas concretas del desierto durante una intrusión de polvo sobre la Península Ibérica. Se configuró el modelo para reproducir los altos niveles de PM10 recogidos en tres estaciones EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe) del centro de la Península Ibérica durante un episodio de intrusión Africana del 12 al 15 de Marzo del 2003. Se utilizaron diferentes configuraciones para la determinación de los parámetros del modelo que dieran lugar al mejor ajuste con las concentraciones observadas en las estaciones. Una vez configurado el modelo, se ejecutó el episodio restringiendo la emisión a nueve áreas fuente concretas del norte de África consideradas potencialmente como zonas emisoras posibles contribuyentes implementó de polvo Africano. Una vez hecho esto, la proporción de polvo originaria de cada zona en las concentraciones de PM10 en las zonas receptoras se utilizó para estimar la contribución de fuentes. Para el episodio de Marzo 2003 las contribuciones de polvo a los niveles de PM10 en el centro de la Península Ibérica son las siguientes: 20-30% del polvo en PM10 se originó en Mauritania y el Sahara occidental, 15-20% de la zona de Malí, Mauritania y la zona oeste de las montañas Ahaggar y 55-60% de otras zonas del noroeste africano.

Utilizando la metodología expuesta en el se simularon 7 intrusiones de polvo Africano con importante impacto en los niveles de PM10 de fondo regional registradas en 13 estaciones de muestreo a lo largo de estos periodos con el módulo de polvo del HYSPLIT4. En primer lugar, se llevó a cabo una validación cualitativa y cuantitativa. La comparación entre los mapas de concentración de polvo producidos por HYSPLIT4 y las imágenes de SeaWIFS mostraron una buena predicción cualitativa de las intrusiones sobre la Península Ibérica (probabilidad de detección del 96% en esos 7 eventos). Los niveles de PM10 registrados en estaciones de fondo regional de la Península Ibérica durante los 7 episodios simulados fueron más altos que los simulados por HYSPLIT4 aunque esto no significa necesariamente una infravaloración porque, según la configuración usada, el modelo sólo dio cuenta del transporte a larga distancia desde África así que la fracción local/regional de PM10 no se calculó y pudo dar lugar a esta infravaloración.

Este estudio refleja un papel predominante de las zonas norte y oeste de África (Túnez, Argelia, Mauritania y el Sahara occidental) contrasta con la despreciable contribución de zonas de fuerte emisión como la depresión del Bodelé, Libia, Níger y Sudán. Durante estos episodios, el material de estas zonas se transportó persistentemente a través del Océano Atlántico pero no hacia Europa occidental. El TSP que llegó al noreste de la Península Ibérica durante estos 7 episodios se muestreó en La Castanya (Barcelona) y se analizó químicamente. Aunque otros autores encontraron diferencias químicas en el polvo de diferentes áreas fuente sobre el norte de África, la composición del polvo es monotónica durante los episodios de estudio debido a la mezcla de polvo de distintas áreas fuente. Únicamente se encuentran ligeras diferencias en los ratios de Ca/Al que se observaron en algunas muestras principalmente explicadas por la segregación de las partículas de polvo más gruesas (carbonatos de calcio) con respecto a las partículas de arcillas (más ricas en aluminio) de más que por diferencias en el origen del polvo.

ABSTRACT

The presence of solid/liquid particles in the atmosphere (atmospheric aerosol) has diverse implications on climate, visibility, humans' health and biogeochemical cycles. Owing to all these effects, the study of this material is being carried out by a scientific community of a marked interdisciplinary character.

The health effects of atmospheric particulate matter (PM) in the form of increment in morbidity by cardiovascular and pulmonary diseases, the carcinogenic character of some species and the important impact in the health of children and fetuses, motivated the European Commission to issue in 1999 the Daughter Directive 1999/30/EC on Air Quality where standards of air quality to be met by the Estate Members were established. This Directive imposed an annual limit value of 40 µgPM10 m^{-3} in 2005 and of 20 µgPM10 m^{-3} in 2010, and the daily limit value of 50 µgPM10 m^{-3} which should not be exceeded more than 35 days $year^{-1}$ in 2005 and 7 days $year^{-1}$ in 2010. This Directive is in revision (2006) and the European Commission has issued in September 2005 a draft version of a new Air Quality Directive where it is proposed to maintain the limit values established for 2005 in de Directive 1999/30/EC and, in addition, to add an annual cap value of PM2.5 for 2015 of 25 µg m^{-3}. Furthermore, it is proposed to establish a PM2.5 exposure reduction target consisting in the 20% reduction of the tri-annual PM2.5 means obtained for urban background sites of a State Member between 2008-2010 and 2018-2020

In Europe, in general, and in Spain, in particular, the control of levels of atmospheric pollution by PM and the studies on chemical speciation of these pollutants are often carried out in cities to provide representative measurements of the population exposure. However, the regional background PM levels have not been studied so precisely. The meteorological characterisation of the meteorological scenarios which explain the seasonal and geographical variability of PM levels in the regional background of the Iberian Peninsula has not been done.

The use of data from regional background stations (those located out of the direct influence of local anthropogenic sources) allows the detection and study of a number of natural and anthropogenic PM episodes which will have an important impact on the levels of all types of monitoring stations in the Iberian Peninsula. Within these episodes we can find the African dust outbreaks. These intrusions of African air masses heavy loaded with crustal matter cause increases in PM levels especially in the coarse size ranges (TSP and PM10) which may result in exceedances of the daily limit value established in the 1999/30/EC Directive. It is worth reminding that, according to this Directive, the exceedances associated to natural episodes of re-suspension can be discounted after an adequate justification. The African mineral dust also constitutes an important source of alkalinity which reduces the acidity of rain in the Mediterranean basin. Owing to these two effects, studies have been carried out treating separately, on one hand, the ambient PM levels during African intrusions and, on the other hand, the deposition fluxes of dust. However, this far, no study has been carried out including these two processes.

The main objective of this work is the development of a conceptual model for the interpretation of the episodes with an impact on both PM levels and deposition fluxes in regional background areas of the Iberian Peninsula. Towards this end, other sub-objectives will be covered such as the interpretation of the meteorological scenarios causing episodes with impact on PM levels in the regional background and the description of the seasonal and geographical variability of these levels within the Iberian Peninsula. Furthermore, a detailed study of the African dust outbreaks including

seasonal variability, impact on PM levels and in the deposition fluxes in regional background areas and the identification of the dust source areas which preferably contribute to dust plumes reaching the Iberian Peninsula.

Data of atmospheric PM levels from regional background stations of the Iberian Peninsula in the period 1998-2003 were used. Data on TSP (total suspended particles), PM10 (suspended particles with aerodynamic diameter lower than 10 μm) and PM2.5 (suspended particles with aerodynamic diameter lower than 2.5 μm) from stations belonging to the EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe) from different areas of Iberia were used (Noia, Niembro-Llanes and O Saviñao from the northwest; Logroño from the north; Roquetas, Cabo de Creus and Els Torms from the northeast; San Pablo de los Montes, Risco Llano, Campisábalos y Peñausende from the centre; Zarra from the east, Bancarrota from the southwest and Víznar from the southeast). Moreover, data on TSP and PM10 from two northern stations belonging to the air quality monitoring network of the Basque Country (Valderejo and Izki), and data on PM10 from a northeastern stations belonging to the air quality monitoring network of ENDESA (Monagrega) were used. From these stations, only those considered representative of the regional background were employed. In the EMEP stations the determination of PM levels was carried out using the gravimetric method, in Valderejo and Izki the β-attenuation method was used and in Monagrega the TEOM methodology was employed. The PM episode type affecting the different regions of Iberia each day of the study period (1998-2003) so as the synoptic scenario giving rise to these events were identified. The impact on TSP, PM10 and PM2.5 of these events was evaluated. This was made carrying out a methodology which included the computation of back-trajectories with HYSPLIT4 dispersion model, the inspection of satellite imagery (SeaWIFS), aerosol index maps (TOMS), aerosol prediction maps (SKIRON/Eta and NAAPs), and the study of meteorological maps. The following PM episodes were distinguished:

a) **Atlantic episodes**: These episodes occur very frequently in all the regions of Iberia, but with a decreasing gradient from northwest to southeast (72 to 36% of the days respectively) with a long duration (a mean duration of 4-7 days depending on the region). Summer is the period with the lowest relative frequency of Atlantic events. In general low PM levels are registered in regional background stations (with annual means of 11-34 μgTSP m^{-3}, 7-18 μgPM10 m^{-3}, 5-11 μgPM2.5 m^{-3} for this type of episodes in the different regional background stations). This occurs owing to the renovation of air masses and to the atmospheric wash out of pollutants caused by rain during Atlantic events. This rain is associated with the passage of frontal systems during Atlantic events. Moreover, the Atlantic air masses have a low concentration of aerosols. Thus, the PM levels can be associated with local/regional contributions.

Two meteorological scenarios were recognised to cause the arrival of Atlantic air masses to Iberia. One is associated with the presence of the Azores anticyclone and the Iceland low over their standard locations (AZH-NAtD scenario); another is caused by the location of a depression over the Atlantic (AD(ATL) scenario). The second scenario is considerably less frequent and is associated with a higher frequency of rain than the first one. This second characteristic generally results in lower PM levels.

b) **African episodes**: The African dust outbreaks over the Iberian Peninsula occur with uneven frequency in different geographical regions of the Iberian Peninsula. Over the northwest the occurrence of African events reaches only 8% of the days while in the southeast it reaches 27% of the days. The summer period has the highest frequency of occurrence with other periods of high frequency such as January-March and October.

The duration of these episodes is moderate (3-4 days on average). The levels of PM recorded during African intrusions are generally high owing to the high load of crustal matter in these air masses (29-62 μgTSP m^{-3}, 21-35 μgPM10 m^{-3}, 11-18 μgPM2.5 m^{-3} as annual mean ranges in the different stations selected for the study). PM levels are high with respect to the other episodes not only in TSP and PM10 but also in PM2.5.

Four transport scenarios giving rise to African transport were identified. Two of them are associated with the presence of depressions over the Atlantic Ocean (AD(NAF) scenario) and over northern Africa (NAD scenario) and, in consequence, with high probability of rain. The other two are associated with the presence of an anticyclone over the Iberian Peninsula at surface levels (NAH-S scenario) or in high atmospheric levels (NAH-A scenario). The last one is the most frequent situation. NAH-S episodes occur in the period January-March and the NAH-A in summer. These two scenarios are dry, which results in a high impact on PM levels. This is more intense in the case of NAH-A events owing to the dominant meteorological conditions prevailing in summer.

c) **European episodes**: These events affect frequently the northern flank of the Iberian Peninsula and less frequently the south (10-17% of the days in the north and 3-5% in the south). The transport of European air masses typically occurs in the cold seasons of the year. The duration of these episodes is moderate (2-4 days on average). During the European events the PM levels in the regional background areas are moderately high in the north and low in the south (the annual means in the selected stations vary in the ranges 13-43 μgTSP m^{-3}, 10-25 μgPM10 m^{-3}, 7-16 μgPM2.5 m^{-3}). This is due to the dispersion and dilution of pollutants on their transect towards the south of Iberia.

There are two synoptic scenarios causing the transport of European air masses over the Iberian Peninsula. One is associated with the presence of an anticyclone over the European continent or over the north Atlantic (EUH scenario), and the other due to the presence of a depression over the Mediterranean area (MD scenario). The first scenario is more frequent than the second and, in addition, has higher impact on PM levels due to the low frequency of rain compared with the MD scenario.

d) **Mediterranean episodes**: These periods are characterised by a high frequency of precipitation especially over the eastern flank of the Iberian Peninsula. These episodes have a low frequency of occurrence (below 6% of the days in al the regions), have a long duration (2 days on average in all regions) and, owing to the high frequency of precipitation, the PM levels are low (13-39 μgTSP m^{-3}, 9-24 μgPM10 m^{-3}, 6-16 μgPM2.5 m^{-3} as annual mean ranges in the selected stations). The periods of the year in which this transport occurs are spring and autumn.

Two transport scenarios causing Mediterranean advection over the Iberian Peninsula, one characterised by the presence of an anticyclone over the European continent or the Mediterranean Sea (EUH-MH scenario), and another by the presence of a depression over northern Africa or the Mediterranean Sea (NAD-MD).

e) **Episodes without dominant advective conditions**: These are periods which occur with high frequency during summer, but also in winter. The eastern and central regions of Iberia are affected by these events more frequently than the north and west (23-29% and 9-16% of the days respectively). These episodes have a moderate duration (3 days on average in all the regions of Iberia).

Two synoptic scenarios which explain the occurrence of the events with lack of advective conditions are differentiated. In winter, under the effect of an anticyclone covering the Iberian Peninsula (WIA scenario) thermal inversions frequently develop over urban or industrial sites reducing the transport of pollutants towards rural areas.

Therefore, the PM levels at regional background stations are low during WIA episodes (15-32 µgTSP m^{-3}, 10-23 µgPM10 m^{-3}, 7-14 µgPM2.5 m^{-3} as annual mean ranges in the different stations). In summer the lack of advection is associated with the development of the Iberian thermal low owing to the high heating of the surface (ITL scenario). The development of this low and the typical summer conditions generate the ideal conditions for the aging of air masses, the recirculation of air masses (especially over the east), the photochemical generation of secondary aerosols, and the dispersion of pollutants towards regional background areas. Due to these reasons, PM levels are high during ITL situations (annual means in the selected stations ranking in 25-54 µgTSP m^{-3}, 21-30 µgPM10 m^{-3}, 14-21 µgPM2.5 m^{-3}).
Combining information about the frequency and PM levels associated with each scenario, the impact of these episodes on the annual PM levels can be estimated. That is, the proportion of the annual mean attributable to contributions of each episode type can be determined. This was made by defining an impact index (II). This parameter has a large geographical variability. Owing to its high frequency of occurrence, the II of Atlantic episodes is dominant in almost all regions except in the southeast (30-50% in the north and west, and 20-30% in the east and southeast), the impact of the African episodes is dominant over the southeast (40-50% with respect to 15-20% over the northwest) and the European episodes only reach relatively high II in the northern flank (15-20% compared with 5-10% in the south and centre). The events with lack of advective conditions have an II moderately high in all the regions, but over the east in a greater extent (10-15% in the northeast and 15-40% in the rest of the areas).

Focusing on the episodes of intrusion of African dust, the impact of the African dust on levels of atmospheric suspended PM and on wet deposition was evaluated in eastern Iberia for the period 1996-2002. An effort was made to compile both the SPM and wet episodes. To this end, the time series of levels of TSP and PM10 in Levantine air quality monitoring stations were interpreted and complemented with the computation of HYSPLIT4 back-trajectories, satellite images (SeaWIFS), aerosol index maps (TOMS), mineral dust prediction models (SKIRON/Eta and NAAPs), and meteorological analysis. Wet deposition frequency was obtained from weekly collected precipitation data at a rural background station (La Castanya, Barcelona) during the study period in which the African chemical signature was identified (mainly pH and Ca^{2+} concentrations). A number of African dust episodes (112) were identified (16 episodes $year^{-1}$). In 93 out of the 112 (13 episodes $year^{-1}$) the African dust influence caused high SPM levels. In 49 out of 112 (7 episodes $year^{-1}$) wet deposition was detected and the chemistry was influenced by dust. There is a clear seasonal trend with higher frequency of dust outbreaks in May-August, with second modes in March and October. Wet events followed a different pattern, with a marked maximum in May. Except for one event, in 1996-2003, December was devoid of African air mass intrusions over northeastern Iberia. Based on seasonal meteorological patterns affecting the Iberian Peninsula, an interpretation of the meteorological scenarios causing African dust transport over Iberia was carried out. The seasonality of the four scenarios previously mentioned (NAH-S, AD(NAF), NAD, NAH-A) was evaluated. The impact of the different dust outbreak scenarios on the levels of PM10 recorded at a rural site (Monagrega, Teruel) in the period 1996-2002 was also evaluated.

With the objective of carrying out a detailed study of the episodes of wet deposition of dust, the 16 most intense "red rains" (rainwater which leaves a reddish-brownish insoluble residual when filtered or evaporated) occurred at the Northeastern Iberian

Peninsula were selected from the weekly precipitation records obtained at the rural site of La Castanya (Barcelona, Northeastern Spain) in two sampling periods (1983-2000 and 2002-2003). These were events in which more than 1000 mg m^{-2} of insoluble dust was deposited, and contributed with more than 80% of the total amount of insoluble material deposited during all the African events in two sampling periods. These episodes were simulated with SKIRON/Eta model.
The occurrence of these events was associated with the effect of depressions over the Atlantic Ocean located off west the Portuguese coast (AD scenario) or over northern Africa or the western Mediterranean (NAD scenario). Moreover, in a number of events, a depression, originally over the Atlantic Ocean, evolved across northern Africa which constituted a hybrid type transport scenario (AD→NAD scenario). The seasonal evolution of these scenarios (mainly occurring in autumn and late winter-spring) and the chemical patterns of the material deposited in both the soluble (high pH, alkalinity and Ca^{2+} concentrations) and the insoluble fraction (rich in metals such as Si, Al and Fe characteristic of clay minerals) were described.
A validation of the performance of the SKIRON/Eta model simulating these 16 "red rains" was carried out showing a correct qualitative detection of the dust plumes (probability of detection of 79%) as proved by means of a comparison with satellite imagery (from SeaWIFS), and TOMS aerosol index maps. TSP and PM10 levels recorded at regional background monitoring stations were compared with the dust concentration levels obtained from the model outputs showing a moderate underestimation of PM levels by the model. This underestimation is logical since the model does not compute local/regional contributions. The wet deposition fluxes were also underestimated by SKIRON/Eta probably owing to a sum of errors in the prediction of rain, dust loads and the washing out ratio, and to the contribution of resuspension in the quantification of deposition fluxes and also to sampling limitations (only one station is used for the comparison, and local contributions cannot be discarded).
Dust flux maps provided by SKIRON/Eta model were used to identify the most active dust source areas during the "red rains". Northern African dust sources were always activated at the time of maximum heating owing to the enhanced convection. However, it cannot be discarded that, owing to a sporadic moistening of certain areas of the north African desert, dust may not be mobilised even at the time of maximum convection. Coupled with the emission resulting from convective processes, synoptic winds trigger the injection of dust over the Mediterranean. Owing to this combination of effects, during the simulated events, source areas almost exclusively from northern Africa (northern and central Algeria and Tunisia) showed the largest contribution.

Another objective of this work was to identify source areas of African dust reaching the Iberian Peninsula having an important impact on PM levels and the evaluation of the chemical signature in samples collected in regional background areas. For this, a source apportionment methodology was implemented to estimate the contribution from different arid geographical areas to the levels of PM10 recorded in several regional background stations of the Iberian Peninsula. Towards that end, the HYbrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT4) was used to quantify the proportions of mineral dust originated from specific geographical areas in Northern Africa. HYSPLIT4 simulates the transport, dispersion, and deposition of dust plumes as they travel from the source areas to the receptors. This model was configured to reproduce high daily ambient PM10 levels recorded at three Spanish EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe) regional background monitoring stations, located over the Central Iberian Peninsula, during a North African dust outbreak from 12th to 15th March 2003. Different model set ups were utilized to determine the best suite of parameters needed to better represent the observed concentrations. Once the model was configured, the model was run for individual scenarios which include eight specific source areas over Northern Africa considered as possible contributors to the PM10 levels measured at the monitoring stations. One additional run was carried out to account for the rest of the dust sources in Northern Africa. Furthermore, the fractional contribution to the PM10 air concentrations at the receptors from each run was used to estimate the source apportionment. According to these calculations, the contribution from each area to the PM10 recorded over Central Iberia for the March 2003 episode can be detailed as follows: 20-30% of the PM10 dust originated in Mauritania and the Western Sahara, 15-20% from Mali, Mauritania and the Western Flanks of the Ahaggar Mountains, and 55-60% from other Northwestern African sources within the rest of the desert source area.

Using the methodology just presented, 7 North African dust outbreaks yielding high PM10 levels at 13 Spanish regional background stations were simulated with the dust module of HYSPLIT4 model. Firstly, the performance of HYSPLIT4 dust module was validated qualitative and quantitatively. The comparison between dust concentration maps produced by HYSPLIT4 and SeaWIFS imagery showed the good qualitative performance of the model predicting African dust outbreaks over Iberia (probability of detection of 96%). The PM10 levels recorded at regional background stations all over the Iberian Peninsula during the 7 episodes were higher than those simulated by HYSPLIT4, although this does not mean necessarily a quantitative underprediction of the model since, in these simulations, only long range transport of dust from Africa were taken into account, and consequently the important local/regional part of PM10 was not computed.

The dominant role of northern and western source areas (Tunisia, Algeria, Mauritania and the Western Sahara) contrasted with the negligible contribution of major emission source areas such as the Bodelé depression, Libya, Niger and Sudan. Material from these regions is persistently transported across the Atlantic but not towards Western Europe during the 7 simulated events. Total suspended particles during these 7 events were sampled at La Castanya rural station (Montseny, northeastern Spain) and analysed chemically. Although other studies found chemical differences in dust from different areas of northern Africa, the composition of the dust turned out to be quite monotonic for the study events since the mixing of dusts from various source areas is common. Only slight differences Ca/Al ratios were found in a number of samples mainly explained by the segregation of coarser dust particles (Ca-carbonate) with respect to clay minerals (relatively richer in Al) rather than by the different origin of the dust.

INDEX

1. Introduction

1. INTRODUCTION

The solid and/or liquid (except pure water) particles which enter the atmosphere by natural and anthropogenic causes are called atmospheric aerosols or atmospheric particulate matter (PM). They play an important role especially in the troposphere (the lower 10-15 kms of the atmosphere). Aerosols affect several atmospheric processes and cause various effects:

- Affect climate by absorbing or/and scattering radiation, and acting as cloud condensation nuclei (CCN).
- Visibility degradation.
- Influence atmospheric acidity.
- Affect humans' health and material lifetime.
- Contribute to formation of deep-sea sediments.
- Affect several biogeochemical cycles.

1.1 Classification of aerosols

In order to describe the complex features of atmospheric particles, scientists needed to classify aerosols following distinct approaches depending on their research interest. They can be *anthropogenic* or *natural* depending on whether human activities are responsible for their formation or not. They can also be sorted in terms of their formation processes, size distribution or chemical composition. These characteristics are associated with particular emission sources (EC, 2004). One of the classical classifications of the aerosols is as *primary* or *secondary*. Primary particles are those emitted from the source directly to the atmosphere. Secondary particles are those that are formed in the atmosphere from gaseous precursors.

1.1.1 Size classification

Aerosols' diameters range from several nanometres (nm or 10^{-9} m) to tenths of micrometres (μm or 10^{-6} m). They are distributed in modes or size fractions. The physical and chemical formation mechanisms of the aerosols determine their size. Four modes are distinguished: *nucleation*, *Aitken*, *accumulation* and *coarse* modes (sorted by increasing dimension).

The ***nucleation mode*** extends below 20 nm (Figure 1.1). The origin of these particles is the condensation of gaseous precursors when the vapour pressure of the condensing gases is sufficiently high. Meteorological conditions can influence this process. Decreases in temperature and/or increases in the relative humidity (apart from higher concentrations of precursor gases) favour this process (eastern and Peter, 1994). This mode presents the maximum number-density of particles around 5-15 nm.

The basic concepts of nucleation are presented by Hidy (1994). Two processes occur: *homogeneous* and *heterogeneous* nucleation. In both cases gas-phase reactions lead to the formation of particles but in the homogeneous nucleation only gases are present whereas for the heterogeneous nucleation the presence of pre-existing particles is needed in order to provide a surface on which the reaction takes place.

Homogeneous nucleation is a major mechanism for the formation of sulphate and other organic aerosols in the atmosphere. According to the classical theory of homogeneous nucleation, the supersaturation degree needed to obtain homogeneous nucleation of a single specie is so high that it is never reached in the atmosphere. However, the system H_2SO_4(g)-H_2O(g) does lead to nucleation even when the condensing gases are undersaturated. That is why nucleation of sulphates is possible in the atmosphere. Moreover, light radiation exerts a striking influence on nucleation in the atmosphere.

The heterogeneous nucleation is efficient when the nucleus (particle) is soluble in the liquid phase of the condensing gases. This should turn our attention to the classic solvent in the atmosphere, water, and to particles that are soluble in water.
The lifetime of nucleation mode particles is short (hours). In general, particles tend to coalescence because the sticking probability at normal humidity is 1, this means that any collision results in a larger particle (Warneck, 1988). Therefore, nucleation mode particles rapidly coagulate to form particles in the accumulation mode.

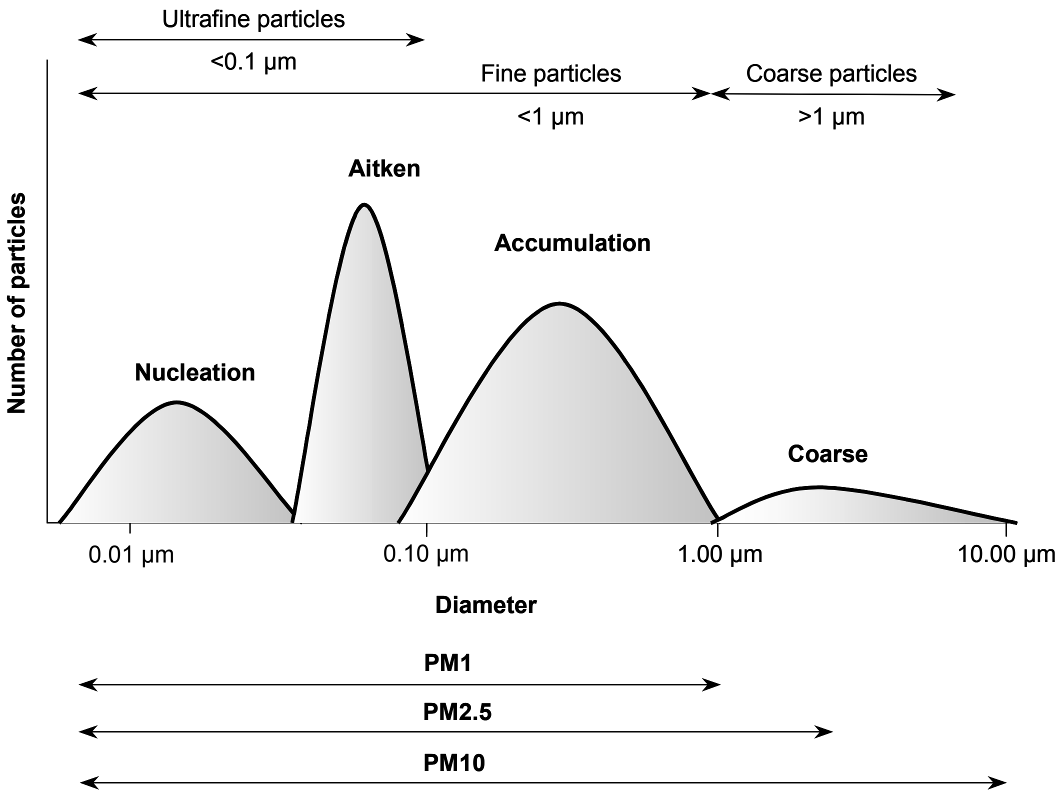


Figure 1.1. Size distribution of atmospheric particles (modified from EPA, 1996)

The ***Aitken mode*** is comprised between 20-100 nm (Figure 1.1). Secondary Aitken particles come from coagulation of nucleation mode aerosols, from condensation or as result of liquid phase reactions of inorganic compounds. Furthermore, they can consist of primary particles of anthropogenic and natural origin. Soot is a major primary product of combustion processes and contributes mainly to this size range mainly in diameters between 30 and 100 nm (Matter et al., 1999). Studies dealing with Aitken mode aerosols suggest that they are stable and are present in all locations (from rural to pure urban areas) (Tunved et al., 2002).
Nucleation and Aitken modes are grouped and designated as *ultrafine particles* (Figure 1.1). These two modes contribute greatly to the number of particles but poorly to the aerosol mass. Therefore, in order to study ultrafine particles, number oriented studies will be more useful than research efforts regarding mass measurements.
The ***accumulation mode*** is constituted by particulates from the nucleation mode that grow by coagulation or by vapour condensation on their surfaces. Liquid phase reactions control the formation of particles in this mode. Their size ranges from 0.1 µm to 1 µm (Figure 1.1) with a peak number concentration around 150-250 nm (EC, 2004).
Coagulation is due to Brownian (thermal) motion of particles. Collisions between small particles form larger aggregations. Particles with diameters below 10 nm do not last in the atmosphere more than a few hours because simultaneous growth of particles is

inexistent. For an initial density number distribution principally made up of ultrafine particles, coagulation would decrease the number and increase the size of particles. Thus, the number concentration of accumulation mode particles is lower than in the case of ultrafine particles but their mass contribution is higher (Warneck, 1988).
The other process contributing greatly to generate particles in the accumulation size range is condensation. This process consists on the condensation as the deposition of vapour-phase material directly onto pre-existing particles. Assuming a sticking probability of one, the rate of condensation depends on the number of molecules of the condensable gas impacting the particle per unit time (Warneck, 1988). As water vapour is the characteristic condensable molecule in the atmosphere, condensation of water onto solid particles is a common process.
Particles with diameters smaller than 1 μm are known as *fine particles*. Oppositely, those with diameters larger then 1 μm make up the *coarse mode* (Figure 1.1). The aerosols in this mode have a mechanical origin such as the disintegration of Earth's surface (by natural or anthropogenic processes). Sea spray and vegetation are also important sources of coarse particles. Coarse mode particles are characterised by low number concentration but by a high mass.
A very important feature that characterises aerosols is that there is a natural 'barrier' around 1 μm. Particles formed by means of mechanical processes rarely acquire sizes < 1 μm, while secondary aerosol formation in the range > 1 μm are not dominant (EC, 2004).

1.1.2 Natural and anthropogenic particles

Aerosols can also be classified as anthropogenic or natural depending on whether they are a product of human or natural emissions. A sub-classification in primary or secondary aerosols will be used in order to complete the description of atmospheric particles.

Natural aerosols

Oceans, disintegration of soils, volcanoes and biogenic emissions are major sources of both primary and secondary natural aerosols in the atmosphere.

SEA SPRAY

Particles emitted by the oceans make up a considerable proportion of the natural emissions of aerosols. Most of them are primary. However, marine phytoplankton emits dimethyl sulphide (DMS), S-containing compound which turns out to be a natural gaseous precursor of sulphate in oceanic regions. Although, for obvious reasons, the load of marine aerosols is higher in coastal areas, these are also found in appreciable levels in continental areas far from the oceans. This means that marine particles are transported over long distances (Pósfai and Molnár, 2000). Several estimations of the global marine aerosol emissions have been presented. Blanchard (1985) estimated it in 10^4 Tg yr^{-1} and Erickson and Duce (1988) in 10^4 to $3 \cdot 10^4$ Tg yr^{-1}. Focusing on the particle number, Blanchard (1969) concluded that the global annual emission was 10^{28} particles yr^{-1}.
Wind is responsible for the release of sea particles. Whitecaps are produced by agitation of the ocean surface due to wind and bursting of bubbles occurs within them. Figure 1.2 shows the sea spray formation mechanism. Each collapsing bubble forms a jet of water that ejects 1-10 jet drops (2-4 μm of diameter) of seawater up to 15 cm above the surface together with a group of film drops (< 1 μm of diameter) caused by the bursting of the water film covering the bubble as it reaches the surface. These drops are then

lofted to higher altitudes where water evaporates (though not completely) due to lower values of relative humidity. By then, the drop has lost three quarters of its diameter (Warneck, 1988).

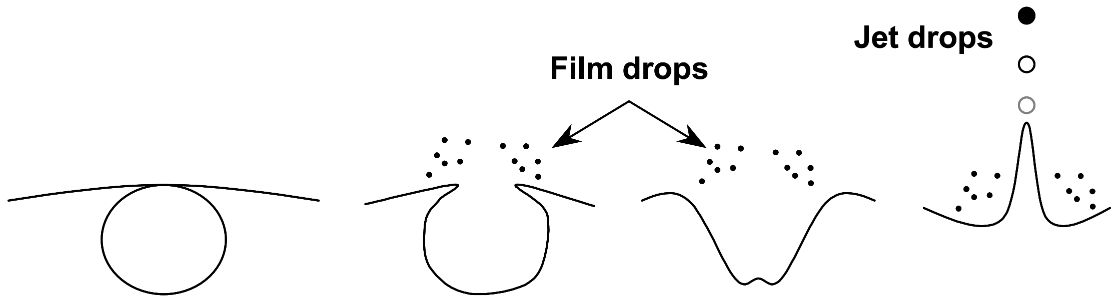


Figure 1.2. Formation of marine aerosols (from Warneck, 1988).

Sea spray typically contributes to the coarse fraction of the aerosols (Figure 1.3). Bursting produces small droplets with sizes typically between 2-4 μm (Woodcock, 1972). However, sizes of 0.05 μm were found for marine particles (Mészarós and Vissy, 1974).
Marine aerosols are mainly sea salts. The dominant species are sodium and chlorine but sulphate, potassium, magnesium and calcium are typical ions in sea salts. More precisely, sea spray is mainly made up by NaCl and sulphate species such as Na_2SO_4, $MgSO_4$ or K_2SO_4 (EC, 2004).
Organic compounds are also found in sea particles. Their origin are the microorganisms suspended near the sea surface that are encountered by rising film drops (Warneck, 1988).
Marine phytoplankton is a natural producer of DMS (dimethyl sulphide - $(CH_3)_2S$). This is oxidised to SO_2 which is capable to produce natural sulphate particles. These are considered biogenic emissions.
Sea salt reacts with gaseous species in the atmosphere. SO_2 reacts inside water containing sea salt and Na_2SO_4(solid) is formed and HCl(g) is released. Sea salt is then a sink of sulphur dioxide mainly in marine environments. NO_x and HNO_3 can also react with sea salt forming $NaNO_3$(solid) and releasing HCl(g).
Sea salt also interacts with other aerosol species by aggregation with mineral particles especially with clays. This aggregation takes place in the clouds because both sea salt and clays can act as CCN. If the cloud evaporates without forming precipitation aggregations of sea salt and mineral particles can be formed (Andreae et al., 1986).

CRUSTAL MATERIAL
Another important part of primary particles arises from crustal soil emissions. Arid and semiarid areas are major sources for this material but any soil can become potentially a source. An annual production of 10^3-$2 \cdot 10^3$ Tg of mineral soil particles has been estimated (Duce, 1995).
The crustal material susceptible to be blown off the soil comes from two processes: (1) Division of crust in small grains and (2) uplift of those small grains. The first process comprises several mechanisms such as weathering, leaching of soluble elements, and freezing of water inside rocks' pores. Once the grains acquire sizes below 1000 μm of diameter, they can be moved by wind roll and provoke *sandblasting*. This is a process by which fine particles encrusted onto larger grains or on the surface are broken off and loosened by the impact of large grains. Particles with diameters below 100 μm can

remain airborne (Warneck, 1988). Thus, as soon as wind reaches a certain threshold velocity mineral grains are ejected from soils to the atmosphere.

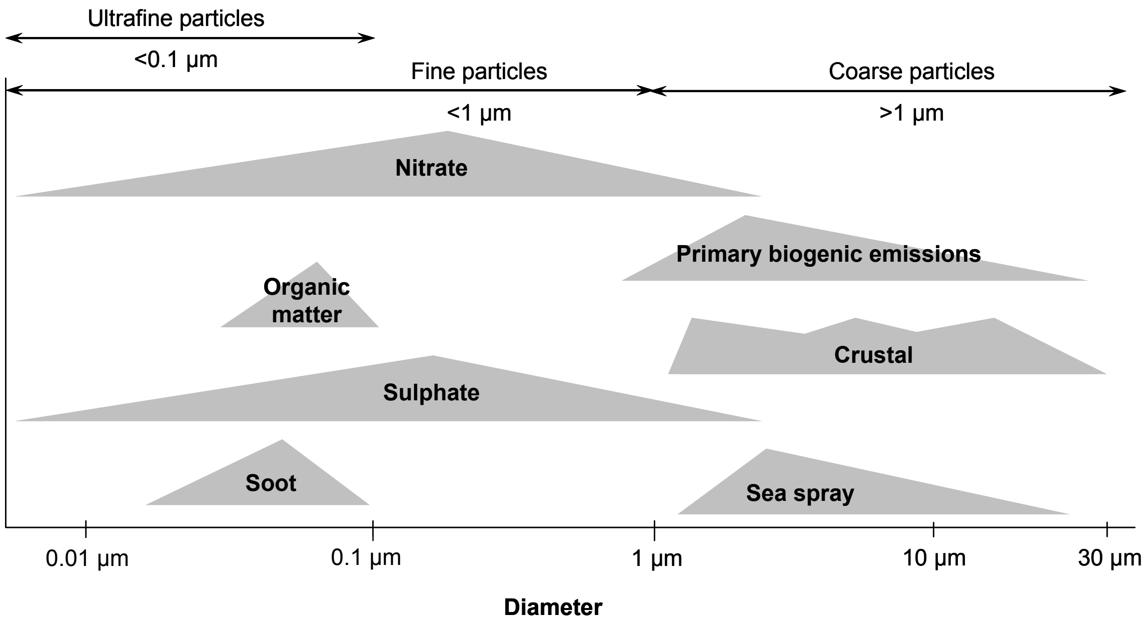


Figure 1.3. Size distribution of particles from different origins.

Table 1.1 shows the classification for size ranges of soil particles by Weast (1978). According to Alfaro et al. (1998), three modes make up the size distributions of crustal aerosols recently produced. They fall approximately in 1.5, 7 and 15 µm of diameter, which correspond to silt and clay size ranges (Figure 1.3, Table 1.1). Friction velocity of wind is the factor that determines the relative abundance of each of those modes. Low friction velocities result in the emission of large particles formed from the aggregation of soil particles while with high wind speeds the finer modes are also released. This happens because high speeds confer enough energy to break the aggregates so production of smaller particles is possible (Lu and Shao, 1999). However, these distributions may change when long range transport of crustal material occurs due to gravitational settling of coarser particles and also by chemical reactions of mineral grains with gaseous molecules or ionic species.
Crustal material is made of a variety of rock forming minerals, consequently this has a solely primary origin. However, mineralogy of airborne dust is highly dependent on the distance to the source area and the geology of the source areas. EC (2004) presented the most common chemical composition of crustal material as follows:

(1) Silicate minerals: Quartz (SiO_2), clays (kaolinite-$Al_2Si_2O_5(OH)_4$ and illite-$K(Al,Mg)_3SiAl_{10}(OH)$) and feldspars ($KalSi_3O_8$ and $(Na,Ca)(AlSi)_4O_8$).
(2) Carbonate minerals: Calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$).
(3) Minor amounts of calcium sulphate ($CaSO_4 \cdot 2H_2O$) and iron oxide (Fe_2O_3).

Table 1.1. Classification system for size ranges of soil particles (by Weast, 1978).

Diameter (µm)	Nomenclature
<2	Clay
2-20	Silt
20-200	Fine sand
200-2000	Coarse sand
>2000	Gravel

At a global scale crustal particulate atmospheric emissions are mostly originated in arid or semiarid areas where enormous amounts of dust are available. Deserts such as the Sahara, the Sahel and the Gobi are persistent sources of dust particles. The process of long range transport of dust (especially from north Africa) including specific source areas, meteorological scenarios of transport, seasonality of production and transport and other features such as mineralogy, chemical reactions and climate related effects of dust will be deeply treated later in this introductory chapter.

VOLCANIC EMISSIONS

Volcanoes are natural sources of primary and secondary aerosols. Their effect is limited to the occurrence of great eruptions but large amounts of particles are emitted during these episodes (Brimblecombe, 1996).

The primary emissions of aerosols from eruptions are made up of crustal material made of Al-Si glass with minor proportions of crystalline phases. These volcanic ashes tend to be coarse (1-10 μm) but the size range in a volcanic plume is wide. Very high concentrations of PM, up to 10^5 μg m^{-3}, have been found under the effect of volcanic plumes (Brimblecombe, 1996). In addition of the primary aerosols emitted in volcanic eruptions, volcanoes release large amounts of SO_2 that can contribute to the formation of secondary sulphate in the troposphere (Möller, 1995).

PARTICLES DERIVED FROM LIGHTNING

Lightning is known to be a source of NO_x ($NO+NO_2$) in the atmosphere and, consequently, of natural secondary nitrate particles.

When a lightning stroke takes place, the air is heated (up to 4000° K in the discharge channel) and the following reaction happens:

$$N_2 + O_2 \rightarrow 2NO \qquad (1.1)$$

And rapidly NO can be oxidised to NO_2

Though it is not clear the bulk production of atmospheric nitrate via this process, it has been estimated that 8 Tg yr^{-1} of NO_x are formed by this mechanism (Brimblecombe, 1996).

BIOGENIC EMISSIONS

Biomass is responsible for a large amount of gaseous and particulate emissions. Vegetation and some types of microorganisms contribute to the total aerosol content by generating primary and secondary particles.

Primary natural particles that are emitted by vegetation and microorganisms are known as *biological aerosols* or *bioaerosols*. As they are organic matter the main element in their composition is carbon. Biogenic particles are responsible for the spread of some diseases and act as droplets and ice condensation nuclei in clouds (Schnell and Vali, 1976).

Disintegration and dispersion of plant material consisting of viruses, bacteria, pollen, protozoa, algae and leaf debris are examples of such aerosols. They generally belong to the coarse fraction (Figure 1.3) with sizes ranging 1-250 μm (Delany et al, 1967). Even giant pollen grains of 30-55 μm can be transported thousands of kilometres (Campbell et al., 1999). Sea surfaces are sources of biogenic particles. Bacteria living in water, diatom and coccolith fragments are found in the marine aerosol (Pósfai et al., 1994, Sievering et al., 1999).

Many organic gases are released by vegetation. Among them, hydrocarbons such as isoprene (C_5H_8) and terpenes (α-pinene and β-pinene) are the most common species. After a complex set of secondary reactions, they form organic particles. Warneck (1988) summarises some of these reactions.
Marine phytoplankton is a natural producer of DMS ($(CH_3)_2S$). DMS is a natural gaseous precursor of secondary aerosols in the atmosphere. DMS is oxidised into SO_2 through intermediaries forming sulphuric acid at the end of the process. DMS and SO_2 oxidation is highly dependent on photochemical processes and consequently the amount of sulphate derived from DMS oxidation varies with solar radiation (Pósfái and Molnár, 2000).

Anthropogenic aerosols
Humans' influence in aerosols generation is clear. Traffic, industrial processes and other anthropogenic activities such as agriculture and waste recycling and composting plants are well known sources of atmospheric particles. Both anthropogenic primary and secondary aerosols are present in the troposphere. Anthropogenic particles are unevenly distributed in the troposphere being the dense populated areas where the greatest concentration of such particles is found. However, long range transport occurs and anthropogenic particles may reach remote locations. Forest fires provoked by humans can release large quantities of particles affecting broad areas as well (Levine, 1990, Crutzen and Andreae, 1990).

TRAFFIC
Road traffic, especially in urban environments, is a major source of primary and secondary aerosols. These particles have a wide range of sizes and chemical composition depending on the mechanism involved in their formation. Vehicles emit through their exhaust pipe a mixture of gaseous precursors and ultrafine primary carbonaceous particles (*soot* or *Black carbon, BC*) but road erosion and abrasion of brakes and tires also contribute with aerosols to the urban atmospheres (EC, 2004).
Vehicles also re-suspend coarse particles deposited on pavement. Northern European countries suffer of peak PM episodes of coarse particles generated by re-suspension of sand and salt used to prevent freezing in winter time and the usage of studded tires (EC, 2004).
Another group of primary particles included in traffic emissions are present in the fine range. Products from the incomplete combustion of fossil fuels and from the new particle formation processes during combustion are released to the atmosphere not only from vehicles but also from other industrial activities. These products are known as soot (this concept will be also extensively used when referring to forest fires or combustion processes in general). They are mainly made of carbon and have sizes of tens of nanometers (Figure 1.3, Colbeck et al., 1997). Automobiles using diesel engines release most of soot particles in urban areas.
Metals such as aluminium (Al) and silicon (Si) are present in the atmosphere in relatively high concentrations. Other metals (V, Cr, Mn, Fe, Cu, Pb, Cd, Zn) are present in much lower concentrations. Although most of these metals may have a partial natural load, usually the anthropogenic (traffic, high temperature industrial processes and others) contribution predominates. Trace metals participate in the regulation of chemical reactions in liquid phase and, under highly polluted atmospheres, they may cause a risk for health (Mészáros, 1999).
Lead was used as an anti-knock agent in motor fuels. Lead concentrations in ambient air in London reached 3 $\mu g\ m^{-3}$ (Brimblecombe, 1996) in the 1970's. These concentrations

declined in the last decades as a consequence of the use of unleaded fuels. Zinc is added to oil and is also present in tires. Cadmium is also present in oils used in vehicles. Vanadium and Nickel are present in highly loads in fuel oil used for power generation.
It is known that aircrafts (together with forest fires) can contribute to a veil of BC that may penetrate beyond the tropopause and, therefore, remain for a long period there due to the stability of the stratosphere. In occasions, these particles return back to the lower troposphere (Pueschel et al., 1992, Blake and Kato, 1995).
Nitrogen oxides are gaseous precursors for nitrates. Traffic is the main source of NO_x in urban environments. NO_x is oxidised to nitric acid (HNO_3) and, later, can be neutralised into NH_4NO_3 and $NaNO_3$.
Nitrate species tend to be in the gaseous phase above temperatures of 15-20 °C (Seidl et al., 1996). Thus, nitrate predominates in particulates in winter and in vapour phase in summer (Mészáros and Horvárth, 1984).
Other types of nitrate are also present in the atmosphere. When Na or Ca are present in high concentrations in ambient air, $NaNO_3$ and $Ca(NO_3)_2$ can be respectively found. While ammonium nitrate is present mainly in the fine mode, calcium and sodium nitrate form on coarse particles due to the size of crustal and marine aerosols involved in the reaction (Warneck, 1988, Harrison and Kito, 1990, Wakamatsu et al., 1996).

INDUSTRIAL ACTIVITIES
Primary particles are released from industrial activities. Cement, ceramic, brick manufacture, and smelter industries emit large quantities of primary aerosols. Ni, V, Mn and Cu are commonly released by smelters (Pacyna, 1998). V and Ni are also emitted by fuel-oil combustion in different industrial processes. Cement, ceramic and brick manufacture industries mainly release coarse mineral aerosols (EC, 2004).
Humans' activities can produce primary biological particles as well. In fact, biological aerosols are also present in areas of anthropogenic influence and they can contribute up to 30% of the aerosol number (Matthias-Maser and Jaenicke, 1994). Bacteria and fungi are released by waste recycling and composting plants (Marchand et al., 1995). Furthermore, in Los Angeles, 1-3% of the total fine aerosols originate from urban vegetative detritus (Hildemann et al., 1996).
Coal combustion in power plants releases primary particles (*fly ashes*). They are composed of the residual products included in coal (clay, sulphides, carbonates, chlorides and trace metals) and unburned coal (char). These are mainly spherical spongy and coarse carbonaceous particles (Biermann and Ondov, 1980).
Power generation from fossil fuels is a very important source of gaseous precursors of secondary PM. In fact, human activities generate 60 to 80 % of sulphur emissions in the atmosphere (Chuang et al., 1997). Power plants, where S-containing fuels might be used, are well known sources of acidity in polluted atmospheres. Nevertheless, action for the abatement of SO_2 emissions in north America and Europe has been undertaken in the last decades, and this has successfully mitigated the problem of acid rain in those territories.
The formation of sulphuric acid in gas phase via the oxidation of sulphur dioxide by OH radicals is described by Mészáros (1999):

$$SO_2 + OH \rightarrow HSO_3 \quad (1.2)$$
$$HSO_3 + O_2 \rightarrow HO_2 + SO_3 \quad (1.3)$$
$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (1.4)$$

A key process in the atmosphere for the generation of secondary sulphate is nucleation. A typical example of homogeneous nucleation of sulphate in the atmosphere is the formation of sulphuric acid solution droplets by the condensation of water molecules and sulphuric acid in vapour phase. Sulphate can also be generated from reactions onto other particles' surfaces. This is known as heterogeneous nucleation. Soot from combustion is a good surface for sulphate nucleation (Novakov, 1984). These mixed aerosols change their optical and chemical with respect to pure sulphates.
The rapid condensation of sulphuric acid in minute droplets of solution of sulphuric acid allows the reaction with basic species. Sulphuric acid is neutralised by various basic species: ammonia (NH_3), ammonium (NH_4^+), calcium carbonate ($CaCO_3$) or sodium chloride (NaCl). The most abundant sulphates in the atmosphere are $(NH_4)_2SO_4$ above continental areas (due to the high concentration of NH_3). This compound is found mainly in the fine range with sizes of 0.2-0.5 μm (Figure 1.3, Mildford and Davidson, 1985). Other common sulphate species present in the atmosphere are: NH_4HSO_4, $CaSO_4 \cdot 2H_2O$ Na_2SO_4 and $Ca(NH_4)_2(SO_4)_2$ (EC, 2004). They are commonly found in atmospheres with high concentration of sea-salts and crustal elements with respect to ammonium (Querol et al., 1996, Querol et al., 1998). As for nitrate, Ca and Na sulphate occur in the coarse mode (> 1 μm) due to the original size of crustal and marine particles (Mildford and Davidson, 1985).

BIOMASS BURNING
Biomass fires can be a natural source of aerosols. However, forests clearing in order to use land for agriculture is estimated to account $5 \cdot 10^2$-10^3 Tg C yr^{-1}(Levine, 1990, Crutzen and Andreae, 1990). Thus, biomass burning produced by humans is very important.
We will refer to *black carbon (BC)* or, alternatively, *soot* to the matter produced during the incomplete combustion of fossil fuels and biomass. Therefore we have to understand soot as a mixture of elemental (graphitic) carbon and organic compounds generated in the combustion. BC constitutes just 4 - 40 % of the particles emitted in the combustion of biomass (Crutzen and Andreae, 1990, Andreae et al., 1998).
Large areas of forests are burned every year in Sub-Saharan Africa (maximum intensity in January), south Africa, south America (in both areas a maximum in August and September) and southeast Asia (between August and September) (Levine, 1991).
The chemical composition of soot is highly influenced by the material that is burned. Soot from biomass burning contains K (Andreae, 1983, Turn et al., 1997), soot from coal burning contains different metals (Ramsden and Shibaoka, 1982) and soot from oil combustion contains V and Ni.

1.2. Social and scientific interest

After describing and classifying aerosols, it is important to highlight the relevance of understanding the physical and chemical properties of PM matter. Aerosols are considered to influence climate by altering the radiation balance of the atmosphere and to affect humans' health. Other effects on building materials, soil and fresh water acidification, eutrophication and visibility degradation have been demonstrated.

1.2.1 Health effects

Atmospheric aerosol is a complex mixture in which particles with different chemical composition, size and origin are present. Moreover, PM is far from being homogenously distributed in all locations. For instance, particulates in urban environments differ in concentration, size and chemical composition from aerosols in rural environments. The

sensibility of individuals to develop cardiopulmonary diseases derived from particulate pollutants is an important factor to be taken into account. Consequently, effects of particulate pollutants on humans' health vary widely.
Particles are inhalated through the respiratory system. Particles with diameters above 10 μm are retained in the airways outside the thorax. Particles with diameters below 10 μm (PM10) make up the thoracic fraction. However, only particles with diameters below 2.5 μm (PM2.5) are able to reach the alveoli and, through them, to the blood (Figure 1.4 from http://www.epa.gov). Epidemiological studies have used PM mass (TSP, PM10 or PM2.5) as the factor to be controlled. However, some studies have suggested that number or surface concentration could correlate better with health effects (Peters et al., 1997). Ultrafine particles have been studied lately and evidences have been found that relate the number concentration in this size range and asthma exacerbations and mortality (WHO, 2003).
Studies focused in the long term effects of particulate air pollution in cities have found a relationship between this type of contamination and mortality especially due to lung and cardiopulmonary diseases (Lave and Seskin, 1970, Özkaynak and Thurston, 1987, Dockery et al., 1993, Pope et al., 1999). Pope et al. (2002) found that each 10 μg m^{-3} increase in fine particulate concentration accounts for increases in cardiopulmonary (6% increase) and lung cancer (8% increases) deaths. However, we should also consider that other risk factors such as smoking are principal causes of this type of illnesses.
As stated above, particle size is basic in terms of effects on health. Fine particles are more hazardous than larger ones. The study by Dockery et al., (1993) showed that health effect of particulate pollution becomes stronger as the size decreases from TSP to PM10 and to PM2.5.
There is also enough knowledge to associate particulate air pollution with increased risk in cardiovascular diseases (Pope et al., 1999, Dockery, 2001). In particular, increased heart rate, increased cardiac arrhythmias, myocardial and cerebral infarctions and ventricular fibrillations are effects related to PM concentrations. Exacerbation of asthma, pneumonia and decreased respiratory functions are health related effects also described (Schwarzt, 1996, Lippmann, 1999). Even thrombosis risk could be increased by PM pollution (Nemmar et al., 2002).
Focusing on the sources of aerosols, diesel soot emissions contain, on one hand, carcinogenic polycyclic aromatic hydrocarbons (PAH). On the other hand they are the major source of ultrafine particles in heavy polluted ambient. Combustion of coal, oil and biomass are other important sources of hazardous particles (WHO, 2003). Metals are present in emissions released in burning processes and are an important cause of toxicity (Burnett et al., 2000). Lungs and airways inflammation is produced by metals as Fe, V, Ni, Zn and Cu, the last two having the greatest effect on health (Prieditis and Adamson, 2002). Secondary acidic aerosols formed by chemical transformation of SO_2 released in burning processes (mainly H_2SO_4) can affects asthmatics (Utell et al., 1991). Finally, some bacterial endotoxins can cause inflammatory effects (Monn and Becher, 1999).

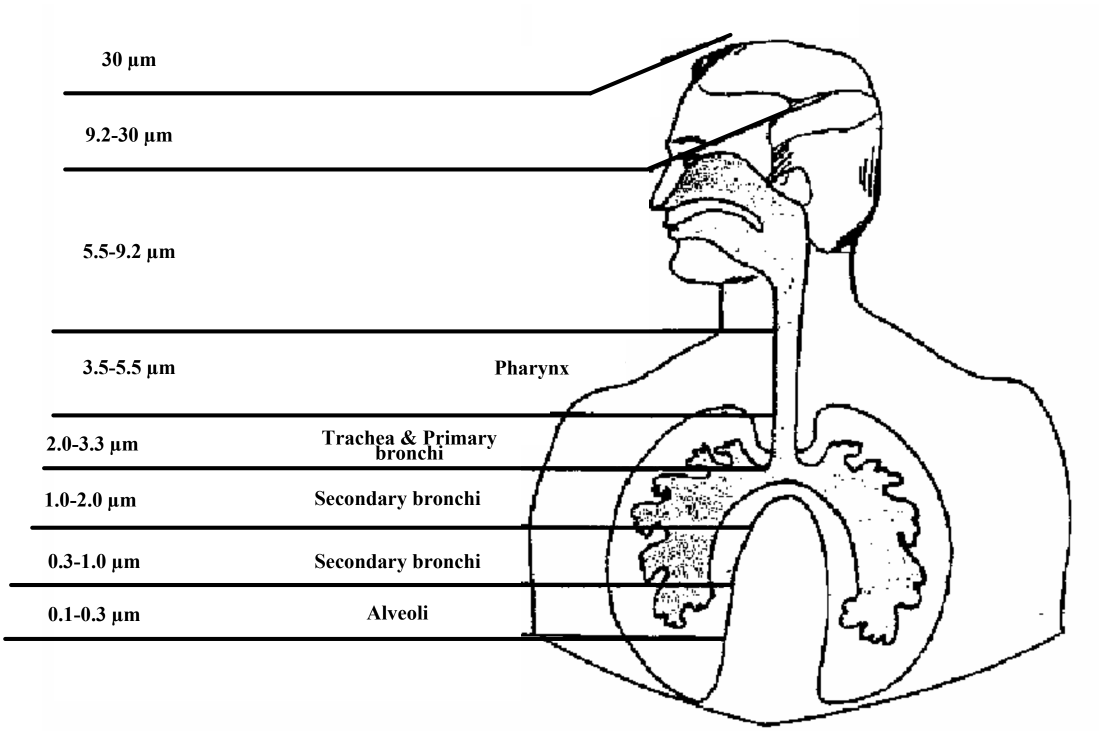


Figure 1.4. Scheme of the respiratory system and the size of particles capable to reach each region (from http://www.epa.gov).

1.2.2 Optical and climatic properties of aerosols

Aerosol particles can affect climate *directly* and *indirectly*. Direct effects are those related with the interaction of aerosols with solar and terrestrial radiation. Particles act as cloud condensation nuclei (CCN) so they also alter the radiation budget via the formation of clouds, this is known as indirect effect.

Aerosols interact directly with incoming solar radiation in two ways: (1) *scattering* and (2) *absorbing* radiation. The term *scattering* means that light is re-irradiated without changing its wavelength. *Absorption* is a process in which particles re-irradiate light with a different wavelength or in a different form.

For the treatment of optical properties an *extinction* or *attenuation* coefficient (σ_{ext}) is defined as the sum of *scattering* (σ_{scat}) and *absorption* (σ_{abs}) coefficients. These are the ratios of the amount of light scattered or absorbed respectively to the energy received by particles.

If we divide the scattering coefficient by the extinction coefficient we obtain the so called *single-scatter albedo* (w_0). The value of this factor represents the importance of scattering processes in light attenuation and it is widely used in literature concerning optical features of aerosols.

Extinction by particles depends on two factors:

- **Optical size(x):** A parameter depending on the size of the particles and the incident wavelength. The mathematical expression is:

$$x = \pi d_p / \lambda \qquad (1.5)$$

- **Refractive index (RI or m):** This is a complex number in which the real part represents scattering and the imaginary part represents absorption. This is:

$$m = Re(m) + Im(m)I \qquad (1.6)$$

If a certain specie has Im(m) = 0, it does not absorb and only scatters.
Particles with diameters between 0.1-2 μm (mostly in the accumulation mode) have the largest extinction efficiency. In addition, accumulation mode aerosols have the longest atmospheric lifetime (IPCC, 2001). However also marine and crustal coarse particles may dominate light scattering in the absence of minor particles (Whitby, 1978, O'Dowd and Smith, 1993).
Indirect climate forcing of aerosols is defined as the overall process by which aerosols perturb the Earth-atmosphere radiation balance by modulation of cloud albedo and cloud density (IPCC, 2001).
The hygroscopic behaviour of aerosols, that is, their hygrophobic or hygrophilic character, affects greatly the ability of some types of particles to act as CCN. For the formation of clouds in the atmosphere the presence of solid particles is essential since the condensation of water takes place exclusively on them (Pósfái and Molnár, 2000).
As the relative humidity (RH) increases the solid particle grows by adsorption of water molecules on its surface. At a certain value of the RH the solid soluble particle is solubilised in a water droplet because the saturated solution is in equilibrium with the ambient. That point is defined as the critical supersaturation value. It depends on the size and the composition of the aerosol. When the critical supersaturation point is lower or equal than the supersaturation in the forming cloud a new droplet is formed (Götz, 1991).
Two main indirect forcing processes are described in IPCC (2001). The first is linked with the change in abundance of droplets due to the increase in number of CCN that generally decreases droplets radius. This results in an increase in cloud albedo of optically thick clouds but a decrease in albedo for optically thin clouds (Han et al., 1998). The second is associated to the change in precipitation efficiency and, consequently, an increase in clouds lifetime (Liou and Cheng, 1989, Rosenfeld, 2000). Also cold clouds (where ice droplets are present) play a role in climate (Senior and Mitchell, 1993, Fowler and Randall, 1996).
On one hand, marine aerosols can act as CCN due to their hygroscopic behaviour (Hudson and Da, 1996). On the other hand they have a high efficiency scattering solar radiation. These two features confer this type of aerosol a net cooling effect (Pósfái and Molnár, 2000). Moreover, in areas such as the southern Ocean, sea salt is the main contributor to mean clear-sky energy budget, being responsible for 80 % of the light scattered and accounts for 60 % of the CCN (Murphy et al., 1998).
Pure sulphate species do not absorb radiation, they exclusively scatter light. This is because they are mostly in the sub-micron range where aerosols scatter very efficiently. Apart from the direct effect, sulphates and other inorganic acids act often as CCN (Hudson and Da, 1996). The direct global-mean climate forcing exerted by anthropogenic sulphate in the troposphere from pre-industrial (1975) to present day (2000) is approximately –0.4 Wm^{-2} with an uncertainty range of –0.2 to –0.8 Wm^{-2}. Thus a net cooling effect is exerted by the scattering of radiation of tropospheric sulphates. The first indirect effect (change in abundance of droplets due to the increase in number of CCN) due to sulphate aerosols is estimated to range from –0.3 to 1.8 Wm^{-2}. The second indirect effect (change in precipitation efficiency and, consequently, an increase in clouds lifetime) alone ranges between –0.53 and 2.29 Wm^{-2}. The combined effect (first and second indirect effects) give estimates from 0.0 to –4.8 Wm^{-2} as global mean (Figure 1.6 and Figure 1.5).

Volcanic gaseous and primary particulate emissions reach very high altitudes, even beyond the tropopause. Therefore, important climatic effects by a decrease of global temperature can be noticed in the years following a great volcanic eruption (Michalsky et al., 1990, Lacis and Mishchenko, 1995).
Nitrate is also able to act as CCN (Hudson and Da, 1996). When concentrations of nitrate aerosols exceed those of sulphate, as it occurs at a regional scale (Europe, India, north America), direct forcing of nitrate can be very important (ten Brink et al, 1996). There are few estimates of global-mean direct radiative forcing for nitrate and the uncertainty is high. However, a range of –0.02 to –0.22 Wm^{-2} is estimated (IPCC, 2001). Indirect effects on climate produced by nitrate are not evaluated in IPCC (2001).
Optically, black carbon is a strong absorber of solar radiation especially in the visible part of the spectrum. The energy is released in the atmosphere as thermal radiation, increasing the ambient temperature. The net climatic forcing of soot is positive (Haywood and Ramaswamy, 1998). Modelling studies have estimated the climatic effects of BC and organic carbon (OC) released from fossil fuels and biomass burning processes (IPCC, 2001). The global-mean direct climatic effects of BC from fossil fuels is +0.2 Wm^{-2} with an uncertainty range of +0.1 to +0.4 Wm^{-2} (Figure 1.5). Conversely to BC emitted when fossil fuels are burned, the absorption of OC aerosols released in those processes is negligible. Regarding only the direct climatic effects, scattering dominates over absorption and a net global-mean cooling of –0.1 Wm^{-2} has been estimated for the direct forcing of OC from fossil fuels burning processes. The direct climate forcing of biomass burning aerosols has been estimated without differentiating BC and OC. A value of -0.2 Wm^{-2} with an uncertainty range of –0.07 to –0.6 Wm^{-2} was found (Figure 1.5).
In addition to the direct forcing, carbonaceous particles can also act as CCN which can affect climate indirectly. A forcing of –1.51 Wm^{-2} for the first indirect effect is exerted by BC+OC particles according to the study of Chuang et al. (2002). Lohmann et al. (2000) obtained a radiative impact from –0.9 to –1.3 Wm^{-2}.
Primary biogenic particles may act both as cloud droplet and ice nuclei (Schnell and Vali, 1976) and also absorb radiation especially in the UV-B region of the spectrum (Ultraviolet with wavelength ranging from 280 to 315 nm).
The study of the radiative forcing of mineral dust is important owing to the important uncertainty of the estimations of the radiative forcing of mineral dust. In fact, it is the only factor which could exert positive or negative forcing (Figure 1.5). Furthermore, the optical properties can be modified by the interaction of mineral dust with local pollution. Thus, the optical and climatic properties of mineral dust will be discussed in section 1.7.1.

1.2.3 Other effects

Other effects caused by particulate matter have been studied. Rain acidification, reduction of visibility and effects on construction materials have been reported.
Acid species can be incorporated to cloud water and be deposited with rainfall. Acid deposition disturbs ecosystem functioning. It has been an important environmental concern for the last 3 decades for wide areas in the northern hemisphere due to freshwater and terrestrial ecosystem acidification (Likens and Bormann, 1974, Cogbill and Likens, 1974). Several measures were taken in Europe in the early 1990's in order to establish ceiling limits for emissions of sulphur compounds which resulted in a decrease of S deposition in the last decades (Buishand et al., 1988, Matzner and Meiwes, 1994, Hovmand and Kemp, 1996, Irwin et al., 2002). However, neutralisation of rain acidity may occur due to mineral dust. This has been proved to be important in

southern Europe (Löye-Pilot, 1986, Losno et al., 1991, Rodà et al., 1993, Alastuey et al., 1999, Avila and Alarcón, 1999).

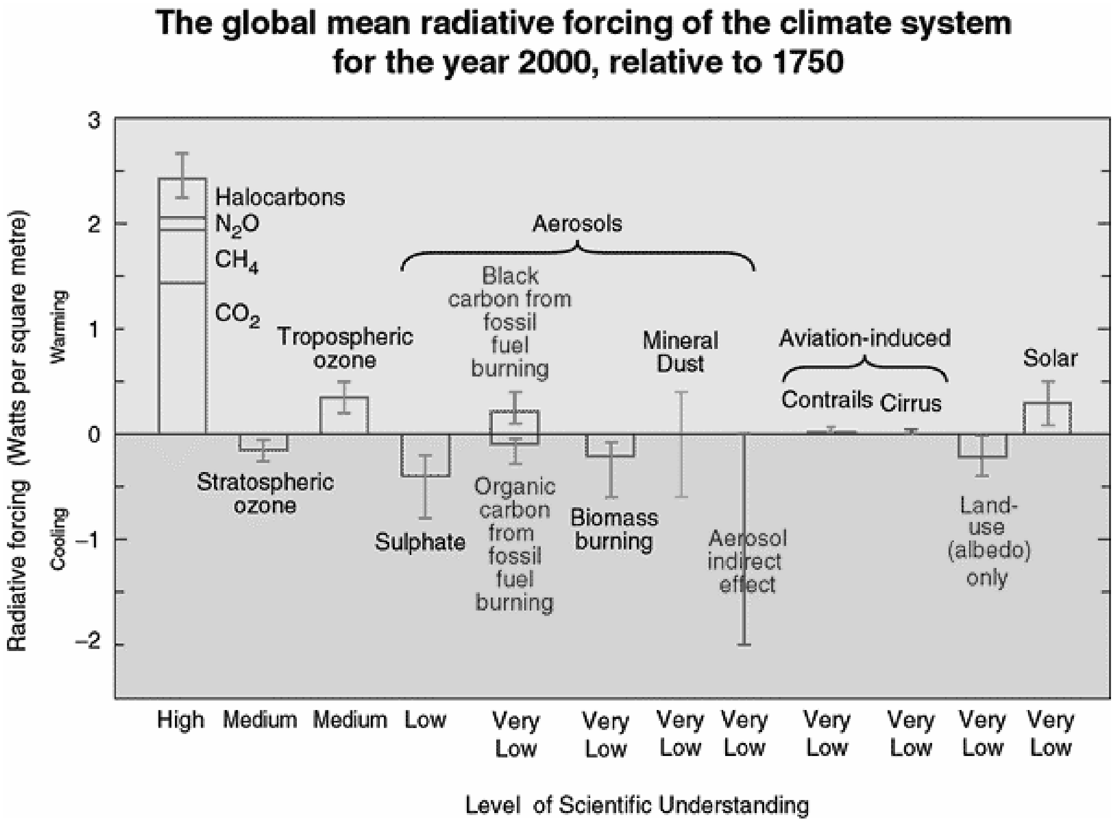


Figure 1.5. Global mean radiative forcing of different factors affecting climate (from IPCC, 2001). The bars represent estimates of the contributions of these forcing. The line above or below the bars indicates a range of estimates, guided by the spread in the published values of the forcing and physical understanding. A line without a bar denotes a forcing for which estimations are difficult to obtain can be given owing to large uncertainties. The indirect effect of aerosols shown is their effect on the size and number of cloud droplets. A second indirect effect of aerosols on clouds, namely their effect on cloud lifetime, which would also lead to a negative forcing, is not shown.

Visibility is altered by the dispersion of visible radiation. This is especially dramatic in and around urban atmospheres where visibility ranges from 10 to 100 km (WHO, 2003) whereas, for clean ambients, mean visibility is around 337 km (Horvath, 1992).
The deposition of atmospheric reactive pollutants in urban areas may result in the degradation and weathering of building materials and monuments (Alastuey, 1994). The most common reaction takes place between the sulphate and calcium carbonate present in construction materials (Laurenzi Tabasso and Marabelli, 1992). The rock is the obscured by a gypsum cover. Furthermore, metal structures can be corroded by the effect of some type of particles and result in a decrease of the lifetime of constructions.

1.2.4 Legislation

Due to the above mentioned effects of PM and especially due to the health risk of high levels of PM exposure, limit values for PM have been proposed by different environmental agencies. In Spain, before July 2001 Black smoke (BS) and TSP were monitored following the Royal Decrees 1613/1985 and 1321/1992 (BOE nº 219 and 289 of 12/09/85 and 02/12/92 respectively, incorporating the European directives 80/779/CEE and 89/427/CEE). After that date the European Air Quality Directive

1999/30/CE (daughter Directive of the 96/62/CE Directive and transposed by the Royal Decrees 1073/2002) established limit values for PM10. This resulted in a change of the parameter to be monitored in Spain and in more restrictive limit values permitted. The new directive established two stages with increasing restrictive values for 2005 and 2010. Together with the reference parameter change, the limit value for the annual mean changed from 150 $\mu gTSPm^{-3}$ to 40 $\mu gPM10m^{-3}$ in 2005 and to 20 $\mu gPM10m^{-3}$ in 2010. The number of exceedances per year of the daily limit value changed from 18 exceedances per year of 300 $\mu gTSPm^{-3}$ to 35 (in 2005) and 7 (in 2010) exceedances of 50 $\mu gPM10m^{-3}$ in the two directive stages (Table 1.2).
The change in the monitoring parameter was undertaken principally because of the important non thoracic PM present in TSP, but at the same time, this change enables a better control of the anthropogenic emissions because natural contributions to TSP are very important compared to PM10. However, in the 1999/30/CE the influence of natural events on PM10 levels is recognised. This is particularly important in some countries in Europe where African dust outbreaks are common. In the article 2.15 of the Directive, natural event is defined as "*volcanic eruptions, seismic activities, geothermal activities, wild-land fires, high-wind events or the atmospheric re-suspension or transport of natural particles from dry regions*". In section 5.4 also states that when PM10 limit values are exceeded due to natural events, Member States should inform the Commission providing the necessary justification to demonstrate that such events are due to natural causes. In such cases, the limit exceedances registered in periods in which natural events (as defined in article 2.15) occur can be discounted from the total number of exceedances. Thus, the Directive aims to control the exceedances owing to causes other than natural events.
Although this legislation establishes limit values for PM10, numerous epidemiological studies (Dockery et al, 1993, Lippmann, 1998) suggest that the harmful effects of PM10 are mainly due to the finer fraction (PM2.5). Consequently, PM2.5 is being measured at air quality monitoring networks. In particular, the Environmental Protection Agency (EPA) responsible for setting the limit values for particle pollutants in the USA, recently established standards for PM2.5 together with PM10 standards (EPA, 1996). In 1987 the National Ambient Air Quality Standard (NAAQS) established limits for the annual mean of PM10 of 50 $\mu gPM10\ m^{-3}$ and a daily limit of 150 $\mu gPM10\ m^{-3}$ which should not be exceeded more than 1% of the days of a year (4 days). The legislation was revised in 1997 and the metric was changed from PM10 to PM2.5. For the annual mean a limit value of 15 $\mu gPM2.5\ m^{-3}$ was adopted. However, this value should not be exceeded during three consecutive years. The daily limit changed to 65 $\mu gPM2.5\ m^{-3}$. This limit should not be exceeded in more than 2% of the days of the year (7 days). More recently, in 2003, the EPA issued recommendations for future NAAQS. The recommended annual limit value for PM2.5 would be in the range 12 to 15 $\mu gPM2.5\ m^{-3}$. The suggestion for the annual limit value for PM2.5 would be in the range 30-50 $\mu gPM2.5\ m^{-3}$ (which should not be exceeded in more than 7 days per year). Moreover, the establishment of daily limit value for PM2.5-10 (particles with diameters between 2.5 and 10 µm) is also recommended. This would be a value in the range 30 to 75 $\mu gPM2.5\ m^{-3}$ which should not be exceeded more than 4 days (1% of the days of the year). An annual target value (optional) for PM2.5-10 in the range 13 to 30 $\mu gPM2.5\text{-}10\ m^{-3}$ is also suggested.
Also the European Commission recognised the importance of measuring PM2.5. Consequently, the Working Group on PM, part of the CAFE (Clean Air For Europe) programme, issued in 2004 the II PM Position paper on particulate matter (EC, 2004). The Position Paper recommended a change in the reference parameter from PM10 to

PM2.5 recommending a daily limit value of 35 μgPM2.5 m^{-3} (that should not be exceeded more than 10% of the days of the year, that is, 35 times per year). Furthermore, an annual limit value in the range 12-20 μgPM2.5 m^{-3} was also suggested. More recently, a draft for a new air quality directive (AQD) was issued by the EC in September 2005. In this new AQD, the recommendation of the II position paper of setting a daily limit value for PM2.5 was not taken into account. The 2005 PM10 limit values fixed by the Air Quality Directive 1999/30/CE would remain fixed, whereas the 2010 indicative limit values will be replaced by a PM2.5 annual cap value of 25 μg m^{-3} to be met by all types of stations by the 1st of January 2015. Furthermore, the new AQD will establish a PM2.5 exposure reduction target consisting in the 20% reduction of the tri-annual PM2.5 means obtained for urban background sites of a State Member between 2008-2010 and 2018-2020.

Table 1.2. Annual and daily limit values and limit number of exceedances of the daily limit value in Spain from 1992 to 2001, the future values arising from the air quality 1999/30/CE Directive and PM2.5 limit values recommended in the II PM position paper of the CAFE programme (EC, 2004) and the draft for a new air quality Directive issued in September 2005.

	Old legislation	**AQ Directive 1999/30/CE**		**II PM position paper recommendations**
		Phase I	**Phase II**	
	1992-2001	**2005**	**2010**	
Reference parameter	TSP	PM10	PM10	PM2.5
Limit value for annual mean (μg m^{-3})	150	40	20	12-20
Limit value for daily mean (μg m^{-3})	300	50	50	35
Annual limit of exceedances of the daily limit (days)	18	35	7	35

	AQ Directive draft September 2005		
Since	**2005**	**2015**	**2020**
Parameter	**PM10**	**PM2.5**	**PM2.5**
Limit/cap value for annual mean (μg m^{-3})	40	25	-
Limit value for daily mean (μg m^{-3})	50	-	-
Annual limit of exceedances of the daily limit (days)	35	-	-
Exposure reduction target from 2010 to 2020	-	-	20%*

*Reduction in the tri-annual PM2.5 means of the urban background stations of a monitoring network from 2008-2010 to 2018-2020.

1.3 Atmospheric removal processes

Particulate matter is removed from the atmosphere by means of *wet* and *dry deposition*. The removal processes by which particles are extracted from the atmosphere is studied in order to evaluate the residence time of aerosols in the atmosphere. If the aerosols are scavenged by precipitation we refer to a wet deposition whereas if they undergo dry fallout we refer to dry deposition. Particles in different size ranges are removed by different mechanisms (Jaenicke, 1978).

Ultrafine particles are removed by coagulation to enter in the accumulation mode. The rate of coagulation is determined by the mobility of ultrafine particles and by the number concentration of the entire aerosol population. Wet deposition is the main removal process for aerosols in the 0.1-10 μm size range as particles in this size range have the highest efficiency acting as CCN. This range covers also coarse particles. Dry deposition or sedimentation becomes important for particles coarser than 10 μm.

1.3.1 Wet deposition

Atmospheric particles may act as CCN. When clouds precipitate, deposition of the CCN particles occurs. This removal mechanism of particles is known as *in-cloud scavenging (or rain out)*. Moreover, additional particles present in the atmosphere are washed out by precipitation. This process is termed *below-cloud scavenging (or wash out)*.The in-cloud scavenging occurs when aerosol particles (and also gases) are removed from the atmosphere by condensation. The majority of sulphate mass is removed from the air in the process of formation of clouds (Mészáros, 1999).

In the below-cloud mechanism, particles in the atmosphere can be removed by two processes. Particles with diameters below 0.5-1 μm are removed by diffusion due to their Brownian motion, whereas coarser particles are removed by their inertial deposition onto drop or snow crystals (Mészáros, 1999).

Due to the in-cloud and below-cloud scavenging, precipitation water contains chemical species which affect the precipitation acidity. Precipitation is considered acidic when pH is lower than 5.6, the equilibrium pH of pure water and CO2 atmospheric concentrations (Granat, 1972). Acid rain damages vegetation, building materials and affects the biogeochemical functioning of ecosystems. Sulphuric acid is the main contributor to acidity in rain but also nitric acid can contribute to acidification. Figure 1.6 shows a schematic representation of the formation of acid rain.

1.3.2 Dry deposition

We define dry deposition or sedimentation as the downward movement of PM due to gravitational settling. The *sedimentation velocity* (v_s) can be obtained by equating the drag force (air resistance force) and the weight of particles:

$$v_s = \frac{d_p^2 \rho_p g}{18\eta} \tag{1.7}$$

where η is the dynamic viscosity, d_p is the particle diameter, g is the gravitational acceleration (9.8 m s^{-2}) and ρ_p is the particle density. This velocity only becomes important for particles coarser than 10 μm. If the sedimentation velocity is divided by the concentration near the surface C_p we obtain *the dry deposition velocity* (v_d). The dry deposition rate D_d is then defined as the number or mass of the PM deposited per surface area during a unit time:

$$D_d = v_d\, M \tag{1.8}$$

where M is the mass concentration immediately adjacent to the surface (Mészáros, 1999).

1.4 The general circulation of the atmosphere

The general circulation in the atmosphere is the result of an uneven distribution of income solar radiation arriving to the Earth's surface. The solar radiation arriving to the equatorial zones is higher than that arriving to the polar areas, whereas the radiation emitted by the Earth is approximately equal in the equator and in the poles. This establishes an energetic deficit in the poles and an energetic surplus in the equator (Figure 1.7). Therefore, horizontal winds are the materialization of the necessary energy transfer between the equator towards the poles to neutralize that energy difference. Thus a net matter northward flux should be established.

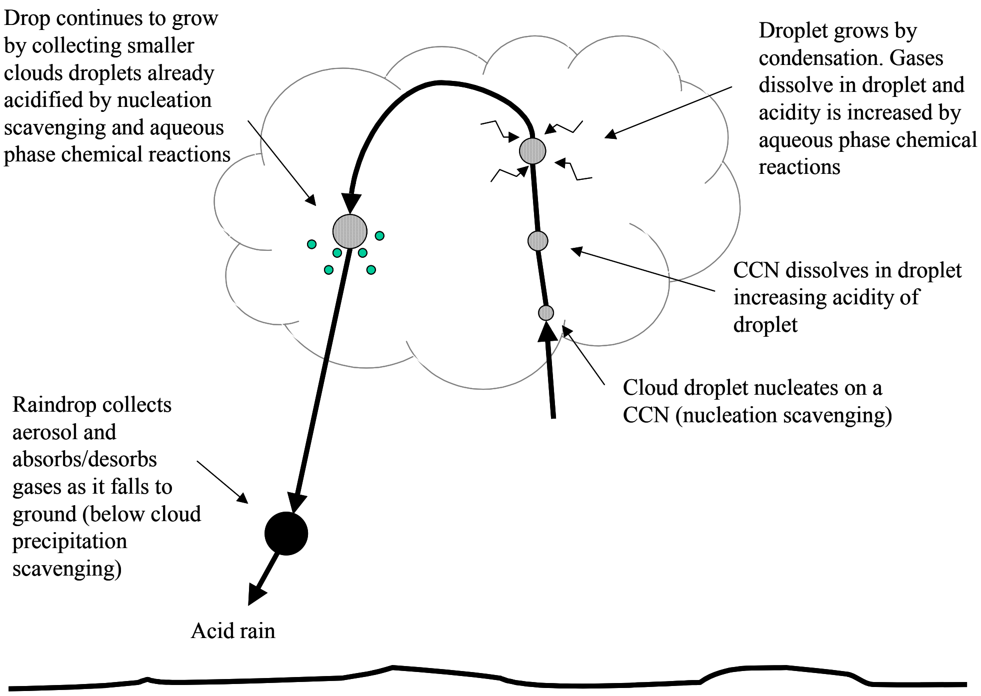


Figure 1.6. Schematic representation of acid rain formation (according to Hobbs, 1993).

When the equator is heated most of the energy is used to evaporate water. Most of the surface in these regions is oceanic, and the rest is vegetated. Some of the radiation is also used to heat the surface. The result is the presence of warm and moist air near the surface. This air is less dense than the air in the layers above the surface and makes the atmosphere more unstable. As a result, the moist and unstable air above the surface has a tendency to rise. As it rises, the water vapour condensates and cumulonimbus clouds with strong vertical development are formed. This vertical movement of air leads to a low pressure belt on surface known as the Inter Tropical Convergency Zone (ITCZ). This region is characterized by great amounts of clouds and precipitation. As the lower atmospheric air rises, it is replaced by air moving from the north and south. The rising air eventually spreads poleward as it ascends, it cools by radiation emission, and eventually sinks to the surface about 30º N and 30º S. In this manner the so called 'Hadley cells' are formed as a circulation system ranging from the equator to 30º degrees N and S (Figure 1.8). The air subsiding at those latitudes is warm and dry because of the latent heat released in the clouds formed above the ITCZ. This subsiding air produces warm and dry climates. Consequently, many of the deserts on Earth are located at these latitudes. This subsiding air also creates an area of high pressures on surface at those latitudes and a horizontal divergence of air masses poleward and equatorward. The air over the poles is very cold and dense, and flows towards the equator. At some point it must meet the air flowing towards the pole. At about 60º N and S the dry, cold and dense polar air encounters warmer and moister air flowing towards the pole. This collision of two different air masses at surface induces the rising of air masses and, consequently, a low pressure area is established there. The rising air diverges in altitude towards the pole and latitudes around 30º N and S were it sinks. In this way four more circulation cells are formed, the ‘Ferrel cells’ between 30º and 60º N and S and the ‘polar cells’ between 60º N and S and the poles (Figure 1.8).

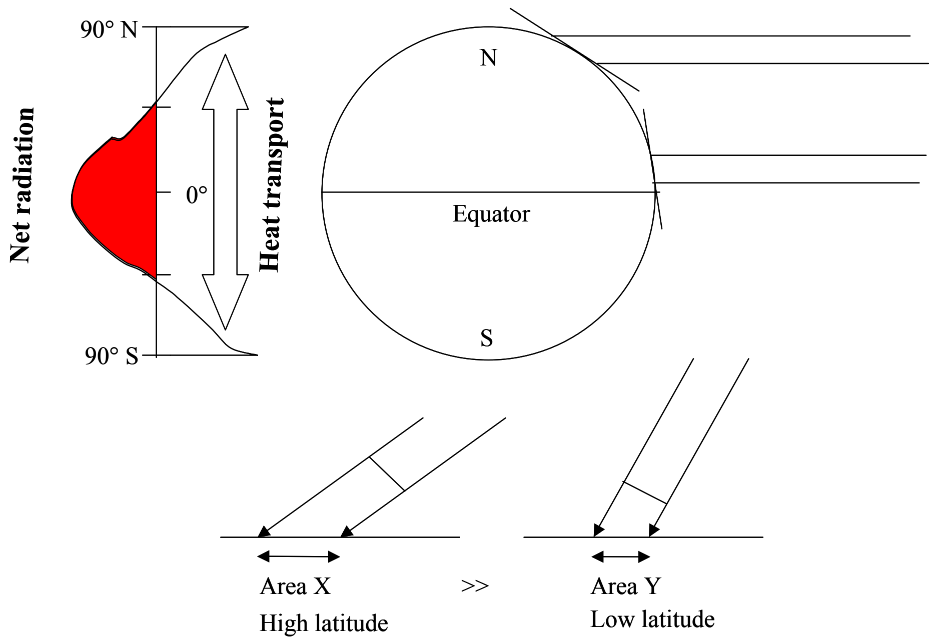


Figure 1.7. Latitudinal imbalance in the net radiation reaching the Earth.

There is another factor playing a key role in the general circulation of the atmosphere. The Earth rotation around its axis is the responsible of the Coriolis force. It is not a real physical force but an apparent acceleration due to the insistence of following a straight line onto a rotating sphere. That is, this acceleration only affects to bodies in motion and it is perceived as a deflection in the movement of the body to its right in the northern hemisphere and to its left in the southern hemisphere. We will not go deeply into the physics of the Coriolis acceleration but it is defined as follows:

$$\mathbf{a}_{cor} = 2\,(\mathbf{v} \times \mathbf{\Omega}) \qquad (1.9)$$

where **v** is the velocity vector and **Ω** is the angular velocity. It is important to remark that on the equator the Coriolis acceleration vanishes and reaches to its maximum intensity over the poles.

Owing to the Coriolis effect, in the tropics, the air moving into the ITCZ from the north and south will be gently deflected by the Coriolis effect, which is small in the tropics. The resulting winds are known as the ‘Trade winds’, and blow from the northeast in the northern Hemisphere and southeast in the southern Hemisphere (Figure 1.8). As the air from the Hadley Cell moves poleward, it is deflected by the Coriolis effect, and becomes the ‘westerlies’ in each hemisphere. Finally, the air moving away from the poles is deflected by the Coriolis effect, to become the ‘Polar easterlies’ (Figure 1.8).

As a consequence of these global atmospheric dynamics four areas of semi-permanent calm conditions in the northern hemisphere (as in the southern hemisphere) are differentiated: the ITCZ or ‘equatorial lows belt’ (marking the climatic equator), the ‘subtropical highs belt’ (at 30º), the ‘subpolar lows belt’ (at 60º) and the polar highs (over the pole). Between these zones three areas with prevailing winds exist: the eastern ‘Trade winds’ between the ITCZ and the ‘subtropical highs belt’, the ‘westerlies’ from the ‘subtropical highs belt’ to the ‘subpolar lows belt’ and the ‘Polar easterlies’ blowing from the pole towards the ‘subpolar lows belt’ (Figure 1.8).

1.5 Climate and meteorology in the Iberian Peninsula

For the purpose of this thesis it is essential to describe the climate and the meteorological patterns of the Iberian Peninsula. Owing to its location between two different air masses (the subtropical and the subpolar air masses), its orography and its peninsular character, Iberia has complex climatic patterns. Two excellent texts dealing with these topics are Capel (2000) and Font (2000).

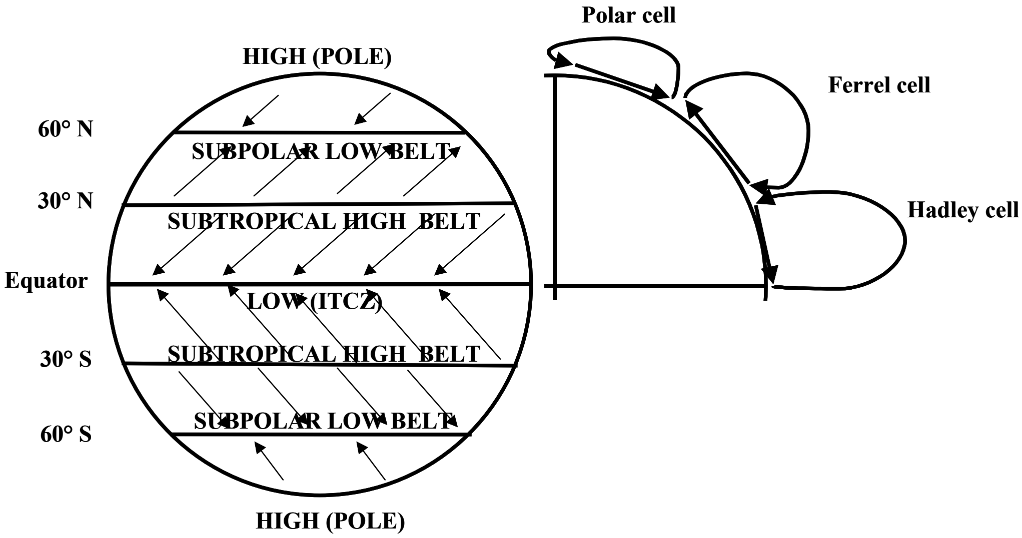


Figure 1.8. Idealised global airflow and the Hadley, Ferrel and Polar cells.

1.5.1 Factors affecting the Iberian climate

Font (2000) identifies four major factors controlling the climate of a given region: a) The location of the region in the context of the general circulation of the atmosphere, b) the distribution of oceans and continents in the area, c) the orography of the area and d) the sea surface temperature. The Iberian Peninsula is located between 44° N and 36° N in latitude and 3° E and 9° 30’ W. That is, in the temperate area between the ‘subpolar lows belt’ and the ‘subtropical highs belt’. The meteorological manifestations of these belts in this area are the Iceland low and the Azores high respectively (Figure 1.9).

The Iberian Peninsula is sufficiently large and compact to yield continental climate patterns, obviously, in a lesser degree than the large Eurasian continent. Furthermore, it is surrounded by mountain ranges which confer a certain degree of isolation of the continental Iberia from the marine influence. On the western flank, the Atlantic Ocean with temperate waters and strong evaporation during the whole year is a source of heat and humidity that affects the entire peninsula. On the eastern flank, the Mediterranean Sea presents high temperatures during the summer, so it becomes a source of heat and humidity for the eastern areas of the Iberian Peninsula. From the northeastern flank European air masses overcome the Pyrenees and may affect the Iberian Peninsula modifying its climatic conditions. This is especially relevant in winter when cold waves coming from northern and central Europe decrease temperatures in Iberia.

The temperature of the ocean waters surrounding the Iberian Peninsula are higher than it would be expected according to its latitude due to the influence of the Gulf stream that transports warm waters across the Atlantic Ocean towards Europe. Figure 1.10 shows the isotherms of the mean sea surface temperature in February and August 2003. In winter, the mean sea surface temperature ranges from 12° to 15° C in the Mediterranean and from 12° to 18° C over the Atlantic Ocean. In summer (and in general throughout the year except from the period January-March), the temperatures of the Mediterranean are higher than the Atlantic Ocean, although temperatures increase greatly in both water masses with respect to winter. Despite it is noticed in the whole Peninsula, owing to the continental features of the Iberian Peninsula and the high degree of isolation produced by the mountain ranges surrounding Iberia, the influence of the oceans on the air masses over the Iberian Peninsula is mainly restricted to a more or less broad coastal band.

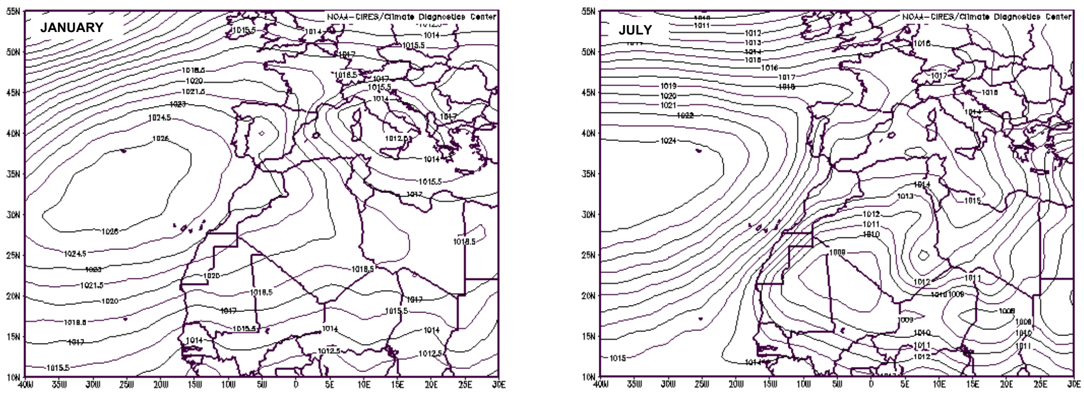


Figure 1.9. Mean sea surface pressure in the months of January and July 2003 (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov/).

The Iberian Peninsula is one of the most mountainous areas in Europe with an average altitude of 500 metres (Font, 2000). This feature enhances greatly the climatic diversity of Iberia and influences its meteorological dynamics. The Iberian Peninsula (Figure 1.11) is orographically characterised by the presence of two elevated plateaus (divided by the central range) in the centre of the Peninsula and by a group of mountain ranges (the Galaico-Cantabrian range, the Pyrenees, the central range, the Iberian range, the Toledo mountains, Sierra Morena and the Penibetic range) which, in general, run following the parallels with the exception of the Iberian range.
These mountainous systems delimit large river basins: Duero, Tajo, Guadiana and Guadalquivir basins on the west and Ebro, Segura and Jucar basins on the east. The climatic influence of these mountain ranges is linked to the blocking they offer against the passage of air masses originated over the oceans or over the European continent:

- The Galaico-Cantabrian range and the Pyrenees range block the Iberian Peninsula from the maritime air masses coming from the northwestern Atlantic Ocean. This blocking is enhanced in the southeast by the central range.
- The basins of the rivers flowing into the Atlantic Ocean (Duero, Duero, Guadiana and Guadalquivir) offer the path for the Atlantic air masses to penetrate Iberia. This is especially relevant from October to May.
- The eastern Iberian Peninsula is influenced by the Mediterranean Sea. The Mediterranean air masses only find paths to penetrate towards the central areas of the Peninsula through the major river basins (Ebro, Segura and Jucar).
- The Pyrenees tend to block the transport of cold continental air from Europe although sometimes those intrusions of European air enter from the east of Iberia through the Jucar basin affecting southeastern Spain.

1.5.2 Climatic elements

Climatic element is defined as a property or condition of the atmosphere which defines the physic state of the climate in a certain place and for a certain period of time (Font, 2000). There are many climatic elements but in this section we will deal with the elements that are relevant to the aim of this study: air temperature, precipitation and air pressure. Thus we will investigate the normal values of these elements and their seasonal variations over Iberia.

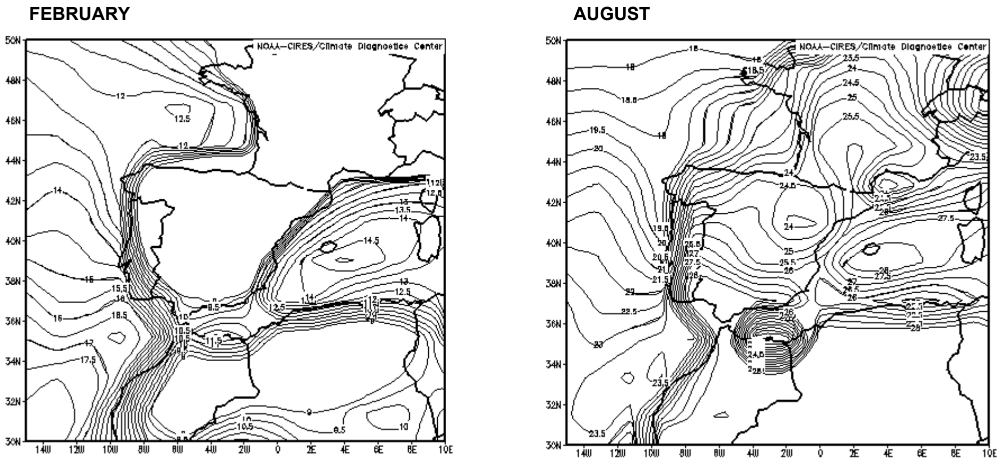


Figure 1.10. Mean sea surface isotherms around the Iberian Peninsula in February and August 2003 (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov/).

Owing to the complex orography of the Iberian Peninsula the air temperature varies widely with altitude as shown in Figure 1.12. It is noticeable that there is a latitudinal gradient between the northern and the southern coast of around 4° C and a longitudinal positive gradient between the Mediterranean and the Atlantic coasts of 4° C in winter and 6° C in summer (Figure 1.12). The influence of the penetration of coastal conditions through the river basins is evident in the rivers flowing into the Atlantic Ocean and, to a lesser degree in the rivers flowing into the Mediterranean. Thus the warmer air masses of the coastal areas are transported towards inner Iberia.

The air temperature varies greatly between seasons. In winter, there is a decrease in temperature from the coasts towards the inner regions. There is a clear gradient from south to north and a slight one from west to east although this does not stand for coastal areas where Mediterranean areas are slightly warmer than Atlantic areas (Figure 1.12). In summer the highest temperatures are recorded over central areas especially on the Guadiana basin. The Mediterranean coast is warmer than the Atlantic coast and, in general, there is a decreasing gradient south-north. Temperatures over the central plateaus are fairly uniform (Figure 1.12).

The precipitation can be studied by the number of precipitation days or the volume of precipitation (or rainfall regime). These two values show similar annual variation but different geographical variation over the peninsula. The number of days with precipitation > 10 mm is shown in Figure 1.13. There is a great variation from more than 60 days in the Cantabrian coast down to less than 10 days in the southeast.

The rainfall regime constitutes the most characteristic feature of the climate of a region. In the Iberian Peninsula the geographical and seasonal variability of the rainfall regime is high. From Figure 1.14 we can highlight the following features:

- The annual rainfall increases from south to north and from east to west.

- The rainfall increases with altitude.
- Annual precipitations of more than 2000 mm are found in Galicia, northern Portugal and elevated locations such as the Cantabrian range, the central range and locally in the Grazalema range.
- The driest areas of the Iberian Peninsula occur in the southeast with an annual rainfall lower than 300 mm.

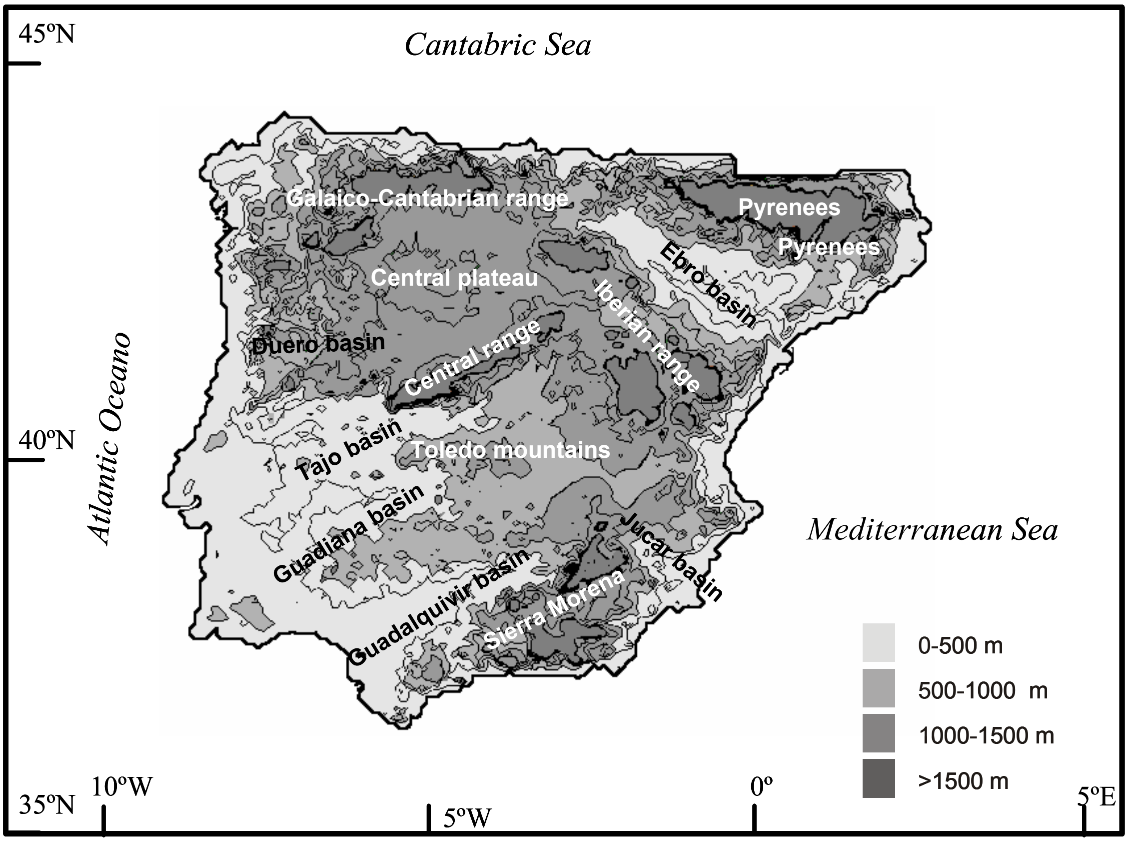


Figure 1.11. The Iberian Peninsula and the major orographic accidents.

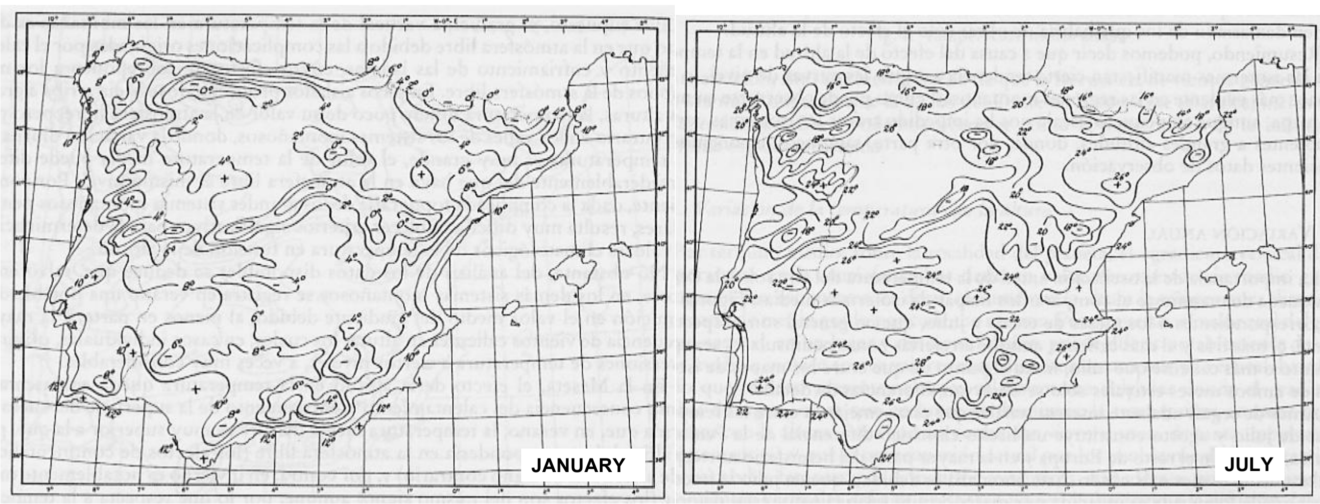


Figure 1.12. Mean isotherms in the Iberian Peninsula at surface level in January and July (from Font, 2000).

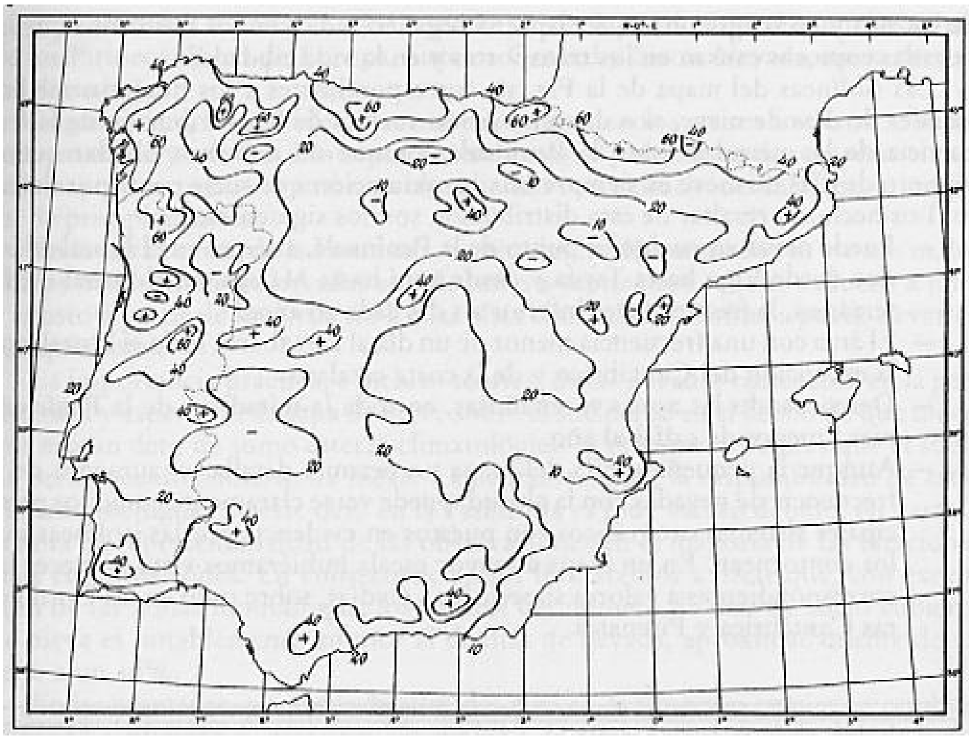


Figure 1.13. Mean annual number of days with precipitation > 10 mm in the Iberian Peninsula (from Font, 2000).

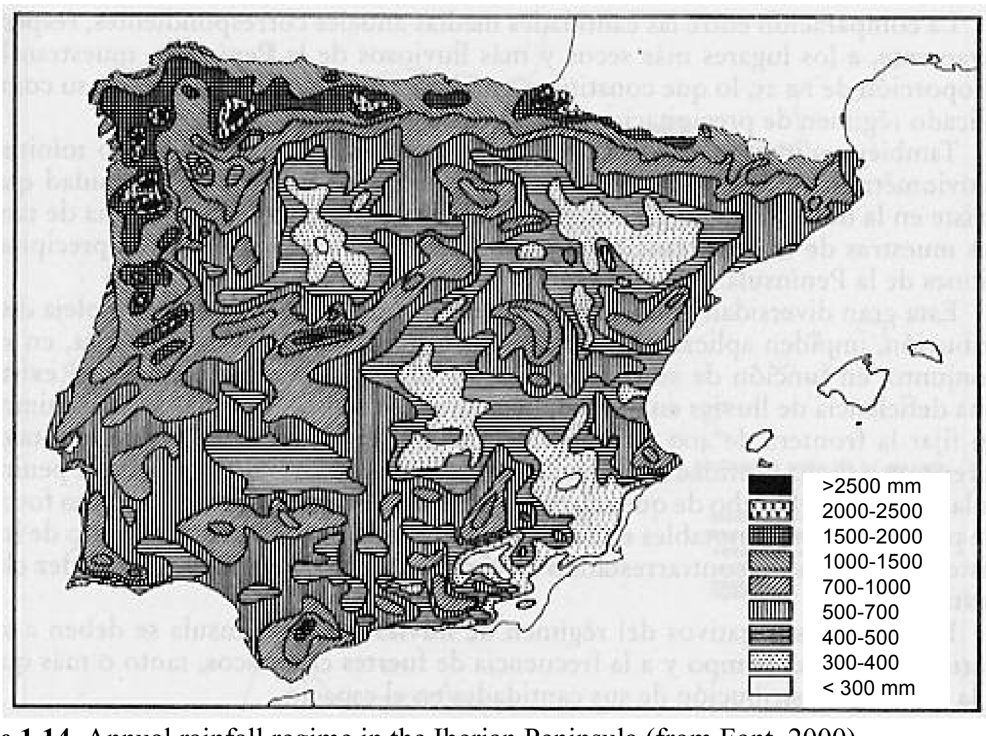


Figure 1.14. Annual rainfall regime in the Iberian Peninsula (from Font, 2000).

However this rainfall distribution is variable in intensity and seasonally. In fact, long droughts and heavy precipitations coexist in the same areas of Iberia. Figure 1.15 shows the monthly mean precipitation in several locations over the Iberian Peninsula. At all sites, the minimum values of precipitation are found in summer. In the Atlantic Iberia (La Coruña, Beja and Valladolid) March has a maximum of precipitation but this does not occur over eastern Iberia. In the Mediterranean area (Valencia) an autumn rainfall maximum is frequent due to heavy precipitations known as the 'cold drop'. These precipitations may be extreme, with 400 mm in less than 6 hours (Font, 2000). Continental areas of the Iberian Peninsula (Zaragoza, Teruel and Valladolid) present a winter rainfall minimum. Summarising, summer is dry in all the Iberian Peninsula, whereas spring and autumn are the wet seasons in the eastern Iberian Peninsula. Furthermore winter is the wettest season in the western Iberian Peninsula.

1.5.2 Synoptic climate: Weather types

The climate of a region is determined by the characteristics, the frequency and the development of the great variety (we could say unlimited) of atmospheric situations that can occur in that region. Thus, the climate can be studied by analysing those atmospheric situations. Therefore, an effort has been made in synthesising the atmospheric situations in a comprehensive bunch of synoptic scenarios (in the same manner as the common weather charts are presented) by several authors such as Sánchez (1993), Capel (2000) and Font (2000). Based on these three references the common synoptic situations affecting Iberia will be revised below. A summary of the different types of air masses reaching the Iberian Peninsula will be also presented.

Air mass is defined as a large extension of air with differentiated physical properties. Air masses are formed in a certain region and adopt the properties of that region but as they move they export those properties (modified by transport processes) to other areas. The general circulation of the atmosphere determines the physical properties of air masses. Thus, air masses at the same latitudes tend to have similar physical features. Furthermore, air masses can have their physical properties modified by the surface over which they are located. Differences in variables such as temperature, humidity, visibility and aerosol content in air masses depend on whether it was formed over the continent or over the ocean. The air masses that affect the Iberian Peninsula and the months in which they are more frequent are shown in Table 1.3 and their usual routes towards Iberia are shown in Figure 1.16.

The marine air masses are referred with the letter 'm' and the continental air masses are referred with the letter 'c'. In addition, it is common in meteorology to denote the warm air masses with the letter 'T' (Tropical) and the cold air masses with the letters 'P' (Polar) or 'A' (Artic). The cold air masses have their origin on the European continent (Russia and Siberia) or over the ocean (Greenland and the Artic Ocean). The first (cP) are cold and dry and are created by the Russian-Siberian anticyclone in winter. The rest (mP or mA) are moist and cold masses that affect Iberia all throughout the year but mainly in winter. The mA air masses are somewhat colder and drier than the mP air masses but they generally provoke instability and rain over Iberia. As regards the warm air masses we can differentiate the dry, hot and calm north African continental air masses (cT), and the temperate and moist tropical and subtropical marine air masses (mT and mT(sub)). The mT is related to transport over Iberia from the southwestern Atlantic ocean and mT(sub) air masses to the transport from the western and northwestern Atlantic Ocean. These two marine air masses can produce a variety of weather features in different areas of the Peninsula. The cT air masses reach the Iberian Peninsula mainly in summer but the can be present in the whole year. In occasions, the Mediterranean Sea is crossed by the cT air masses. This results in enrichment with water of the African air masses.

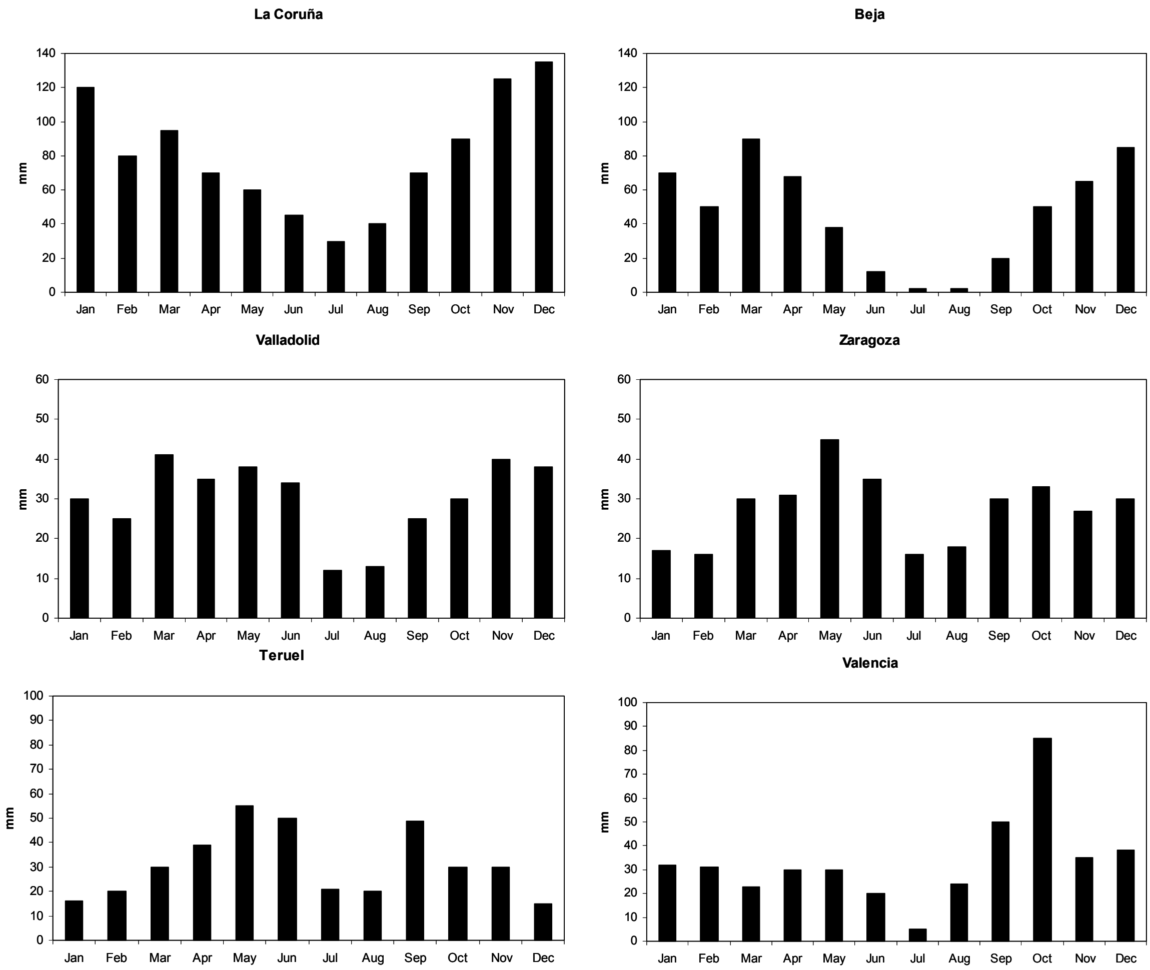


Figure 1.15. Monthly mean precipitation on 6 sites in the Iberian Peninsula (adapted from Font, 2000).

Table 1.3. Air masses that affect the Iberian Peninsula (from Font, 2000)

Nature	Origin	Nomenclature	Months of occurrence
Cold masses			
Marine	Arctic Ocean	mA	winter and April
	Greenland and northern Canada	mP	winter and occasionally the rest of the year
Continental	Russia and Siberia	cP	February, December and January
Warm masses			
Marine	Subtropical Atlantic Ocean	mT(sub), mT	summer and occasionally the rest of the year
	Tropical Atlantic Ocean		autumn, winter and occasionally spring
Continental	northern Africa	cT	summer and occasionally the rest of the year

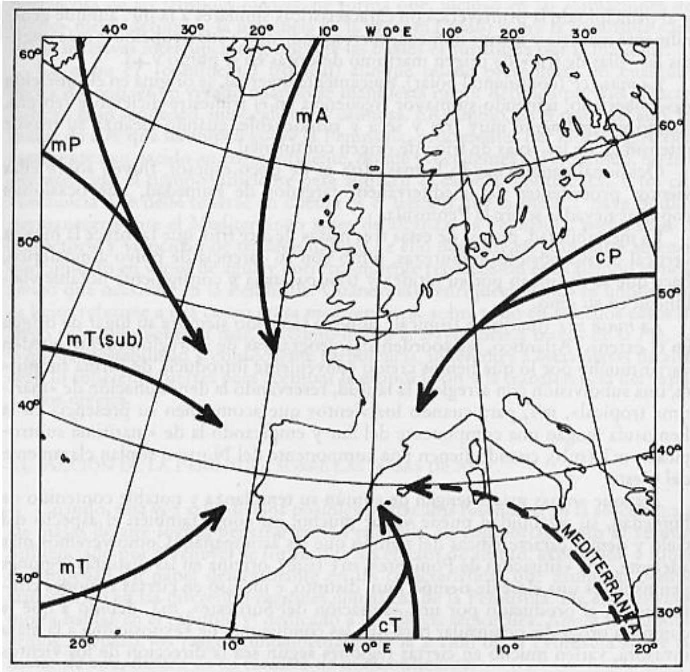


Figure 1.16. Trajectories of air masses reaching the Iberian Peninsula (from Font, 2000).

The Iberian Peninsula is large enough and is exposed to enough solar radiation to generate its proper air masses as well. In winter an anticyclone is frequently located over Iberia and the resulting air masses are cold especially if the anticyclone occurs after the arrival of a cold continental air mass. In summer, continental tropical air masses can be generated when weak gradient conditions occur over Iberia (Sánchez, 1993).

After studying the different air mass transport scenarios that can affect the Iberian Peninsula the synoptic situation that causes the transport are reviewed below:

a) **Transport from Europe**: The cP air masses reach the Iberian Peninsula from the European continent. The synoptic situations that induce European transport are:

a.1) Depression over the Gulf of Genoa or Majorca (Figure 1.17): The Mediterranean is a typical area for cyclogenesis. The dominant air mass is continental but also northern Atlantic air masses can affect the western part of the Iberian Peninsula or Mediterranean air masses can affect the eastern part of Iberia when these two situations occur. The mean duration of these episodes is 3-10 days being less persistent the depressions in the Gulf of Genoa (Font, 2000). These depressions develop in any period of the year but in summer these are sporadic and do not last long. Although the cP air masses are generally dry, precipitations are common in the eastern Peninsula and, in occasions, in the whole Peninsula when depressions in the Mediterranean occur in autumn. This is due to the warmness of the sea surface and the relatively low temperatures of the upper atmosphere that make up the 'clod drop' phenomenon.

a.2) Anticyclone over the British islands or Atlantic-European anticyclone (Figure 1.17): These two synoptic situations provoke transport from Europe although Mediterranean transport may occur as well. If the transport is Mediterranean, these scenarios can lead to intense precipitations especially in the east and southeast. These situations are typical from the period November-March and their duration ranges from 3 to 10 days (Font, 2000).

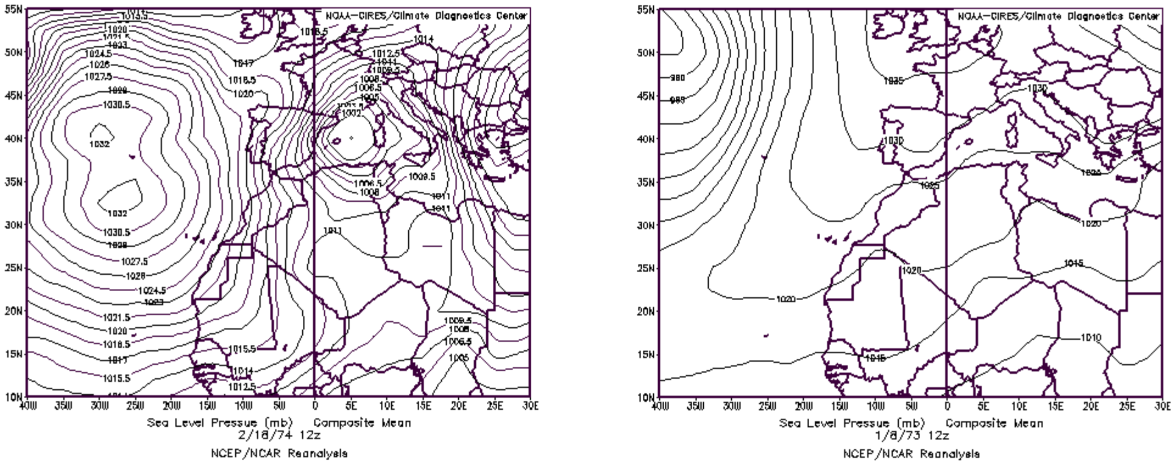


Figure 1.17. Sea level pressure maps of situations of the type a.1 (18-February-1974) and a.2 (8-January-1973) (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov/).

b) **Transport from the north and northwestern Atlantic Ocean**: The north and northwestern Atlantic air masses (mP and mA) are cold. There are two situations that induce transport of cold marine air masses over Iberia:

b.1) Anticyclone over the Azores Islands (Figure 1.18): When the subtropical anticyclone is located far west the Iberian Peninsula and over the Azores Islands the predominant air masses that arrive to the Peninsula are mP. These air masses may have their polar conditions moderated by the long transect over the Atlantic Ocean. Under this situation the entire Peninsula is generally affected by the frontal systems linked to these air masses. Precipitation occurs over most areas of Iberia. These episodes last up to 15 days with a minimum duration of 5 days (Font, 2000). These episodes occur all through the year but the frequency decreases in summer and increases in winter.

b.2) Depression over the Gulf of Biscay or the British Islands (Figure 1.18): These situations take place only in winter and in the early spring. Their duration ranges from 3 to 6 days. Although the first air mass that affects the Iberian Peninsula is mT, after the passage of the associated front, it is followed by mP and mA air masses with a marked change in the weather. In the first stage of these episodes, when the mT mass is advected, precipitations are common in the south and in the Pyrenees. Once the front crosses the Iberian Peninsula, the northern Iberian Peninsula is affected by cold and unstable weather. If the depression is located over the British Islands the mP and mA air masses dominate and lead to cold and unstable weather in the north of the Iberian Peninsula.

c) **Transport from the west and southwestern Atlantic Ocean**: Air masses reaching the Iberian Peninsula from the west and southwest of the Atlantic Ocean are mT(sub) and mT. There are a variety of synoptic situations leading to this type of adevctive conditions

c.1) Atlantic-Mediterranean anticyclone (Figure 1.19): A situation similar to the above b.1 (‘Anticyclone over the Azores Islands’) can result in transport of mT(sub) type. The circulation is dominated by the subtropical anticyclone. The main difference has to do with the extension of the Azores high over the western Mediterranean. The duration ranges from 5 to 10 days but it can reach up to 30 days

(Font, 2000). These situations occur all throughout the year. Furthermore, during summer a thermal depression may develop over Iberia. This situation is treated below.

c.2) Azores high combined with a thermal low over the central plateau (Figure 1.19): If the circulation on the eastern flank of the Azores high is intense the thermal low is substituted by a trough. These situations can be persistent lasting more than two weeks in occasions. The presence of these situations is restricted to the period May-September. The temperatures are usually very high. The mT(sub) air mass is conducted by the Azores high affecting only the Cantabrian and the Atlantic areas of Iberia. The rest of the Peninsula is affected by cT air masses or/and autochthonous air masses.

c.3) Atlantic Iberian depression (Figure 1.20): A cold depression placed over the Atlantic Ocean opposite to the Portuguese coast is the typical scenario for the transport of mT air masses over Iberia. However, also mP air masses are advected under these scenarios. These last between 3 and 12 days and they can be present in all the months of the year except from June to August (Font, 2000). The main meteorological characteristics in these situations are the instability and the high precipitation occurrence.

c.4) Cold depression over the Peninsula (Figure 1.20): Depressions detached from the subpolar vortex can reach to the latitude of the Iberian Peninsula and remain there for some days. These lows advect mT or mT(sub) wet air masses. The instability under these scenarios is great and intense precipitations are generalised over the Iberian Peninsula. These situations are short (not exceeding 5 days) and scarcely produced along the year, especially in the cold season.

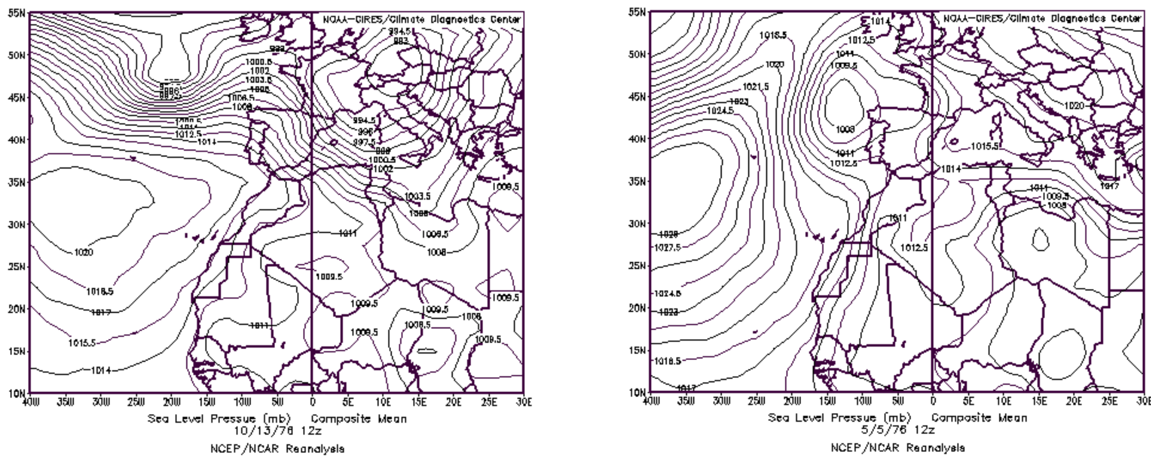


Figure 1.18. Sea level pressure maps of situations of the type b.1 (13-October-1976) and b.2 (5-May-1976) (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov).

d) **Iberian air masses**: The formation of the regional Iberian air masses occurs under the following synoptic situations:

d.1) Peninsular winter anticyclone (Figure 1.21): The Azores anticyclone often moves over Iberia in winter (from December to March). These situations can last from 5 up to 30 days (Font, 2000). The original air mass is mT(sub) but it gradually cools over Iberia until it becomes colder and drier. Under these scenarios strong episodes of pollution are present in urban and industrial locations due to the subsidence regime leading to frequent formation of inversion layers over cities which result in high stability low dispersive conditions (Font, 2000).

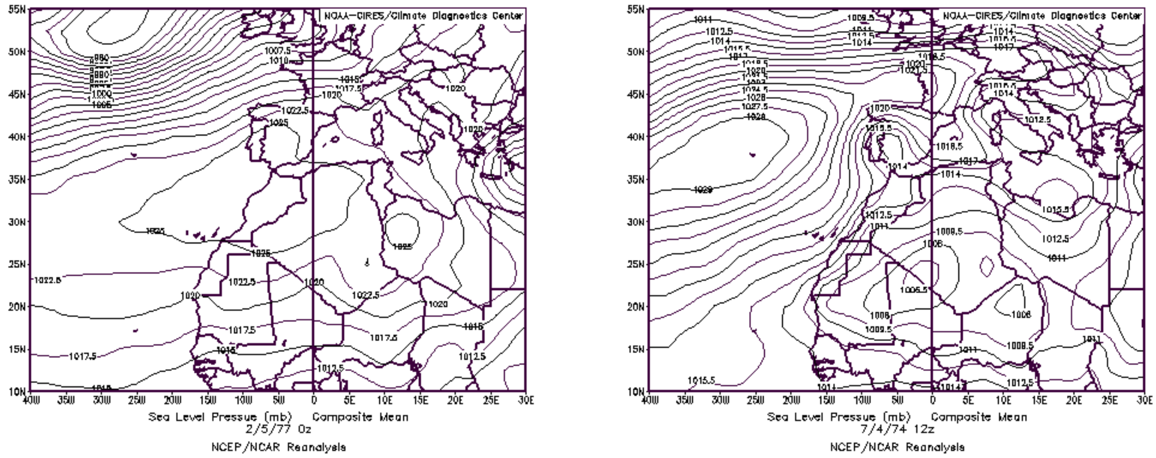


Figure 1.19. Sea level pressure maps of situations of the type c.1 (5-February-1974) and c.2 (4-July-1974) (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov).

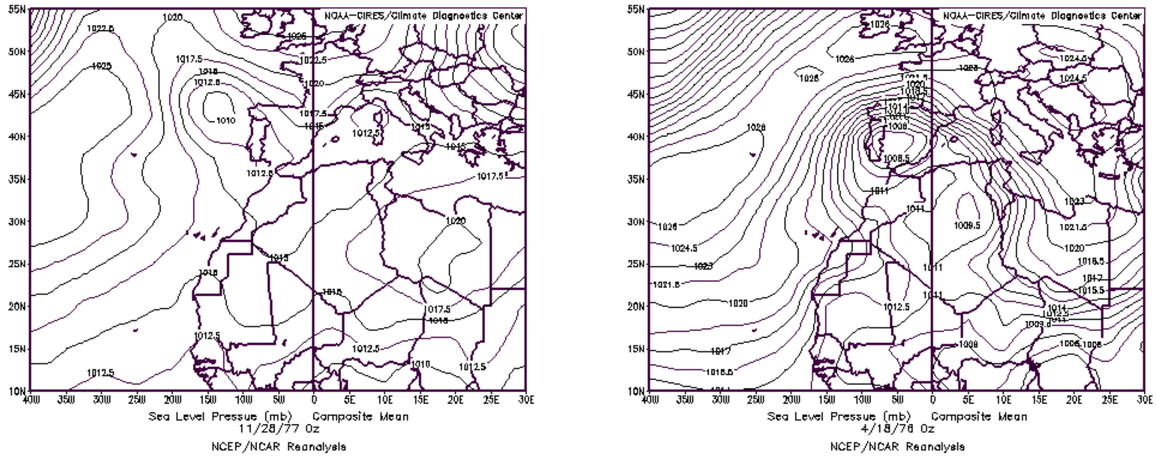


Figure 1.20. Sea level pressure maps of situations of the type c.3 (28-November-1977) and c.4 (18-April-1976) (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov).

d.2) High pressures over the Atlantic and Europe (Figure 1.21): This situation is characterised by the shift of the Azores high towards the west and the influence of high pressures over the Mediterranean basin and Europe. This is a situation that typically occurs in summer and has duration of a week (Font, 2000). The lack of pressure gradients synoptic winds results in the formation of a warm air mass that extends over the Iberian Peninsula. Temperatures are very high owing to the strong heating of the surface. These situations produce strong heat events in the Peninsula.

d.3) Azores high extending from the British Islands to the Canary Islands producing weak barometric gradient over the Iberian Peninsula (Figure 1.21): The prevalence of these conditions occurs in summer and the duration varies between 3 and 15 days (Font, 2000). The original air mass is of the type mT(sub) but it can be modified substantially through the days and results in an regional air mass. Temperatures are quite high and precipitation is associated with convective showers in the north and the Mediterranean flank of the Iberian Peninsula. With this scenario and the previous one, the formation of thermal depressions in the central plateaus of the Iberian Peninsula is favoured by the strong heating of surface and the lack of air masses renewal (Millán et al, 1997, Rodríguez et al., 2003). In the following section a description of these processes is carried out.

Summer conditions in the Iberian Peninsula: *The Thermal low*

At this point we should turn our attention to the characteristics of the summer circulation in the Iberian Peninsula. It is driven by the development of a thermal low located in the central plateau and the convergence of winds from the coastal areas, through natural passes, towards the centre of the Peninsula. Figure 1.22 shows an example of the development of the thermal low occurred on June 25th 1987.

Three consecutive projects studied the summer atmospheric circulation and its relationship with photooxidant pollution cycles in the Iberian Peninsula (MECAPIC in 1988-1991), the west and central Mediterranean basin (RECAPMA in 1990-1991) and the whole Mediterranean basin (SECAP in 1992-1995). These resulted in a number of papers describing the principles of atmospheric dynamics under summer conditions in the Mediterranean (Millán et al., 1991, 1996 and 1997, Salvador et al., 1997 and Kallos et al., 1998 among others).

As regards the Iberian situation, the weather, the surface properties and the mountain ranges that surround the basin favour the formation of deep convective cells and thermal lows over the major land masses as well as the development of sea breezes. The thermally driven mesoscale processes have a marked diurnal cycle (Lalas et al., 1983, Millán et al., 1984 and 1987).

The formation of the thermal low is associated with the convergence of surface winds inland and the strong convection over the central plateau. These processes are accompanied by a compensatory subsidence over the surrounding areas (Mediterranean and the Atlantic Ocean). Thus, Millán et al. (1996 and 1997) made use of O_3 as tracer to document atmospheric dynamics in the central plateau and Mediterranean flank of Iberia.

The structure of the thermal low dynamics can be described by three cells as shown in Figure 1.23. The first cell is formed by the combination of the sea breeze and the up-slope winds over the eastern Iberia Peninsula. The transport reaches 100 km inland (Millán et al., 1996). This is especially relevant when no orographic blocking is present, that is, through the main river basins (Ebro, Segura and Jucar). As this process occurs, the leading edge of the incoming breeze can return over the sea transported by the generalised northwestern upper flow. This mechanism injects pollutants at altitudes between 2 and 3 km and the subsidence over the sea creates 'stratified reservoir layers' of aged pollutants that re-enter in the circulation cells the following days. During the night a weak 'morning subsidence inversion' creates a breeze circulation in the opposite direction (towards the sea). The air masses with origin in the coastal Mediterranean areas re-circulate with the breeze to re-enter the cycle 2 or 3 days later (Millán et al., 1997).

The second cell occurs in the central plateau. One or various relatively deep convective cells develop during the day reaching to 3.5-5 km in height. By these means, pollutants either originated in the Madrid area or previously transported by the coastal cells, are injected into the middle troposphere (Millán et al., 1996). Finally, a third coastal cell over the western coast is expected to occur in the west aided by the subsidence over the Atlantic Ocean (Millán et al., 1997).

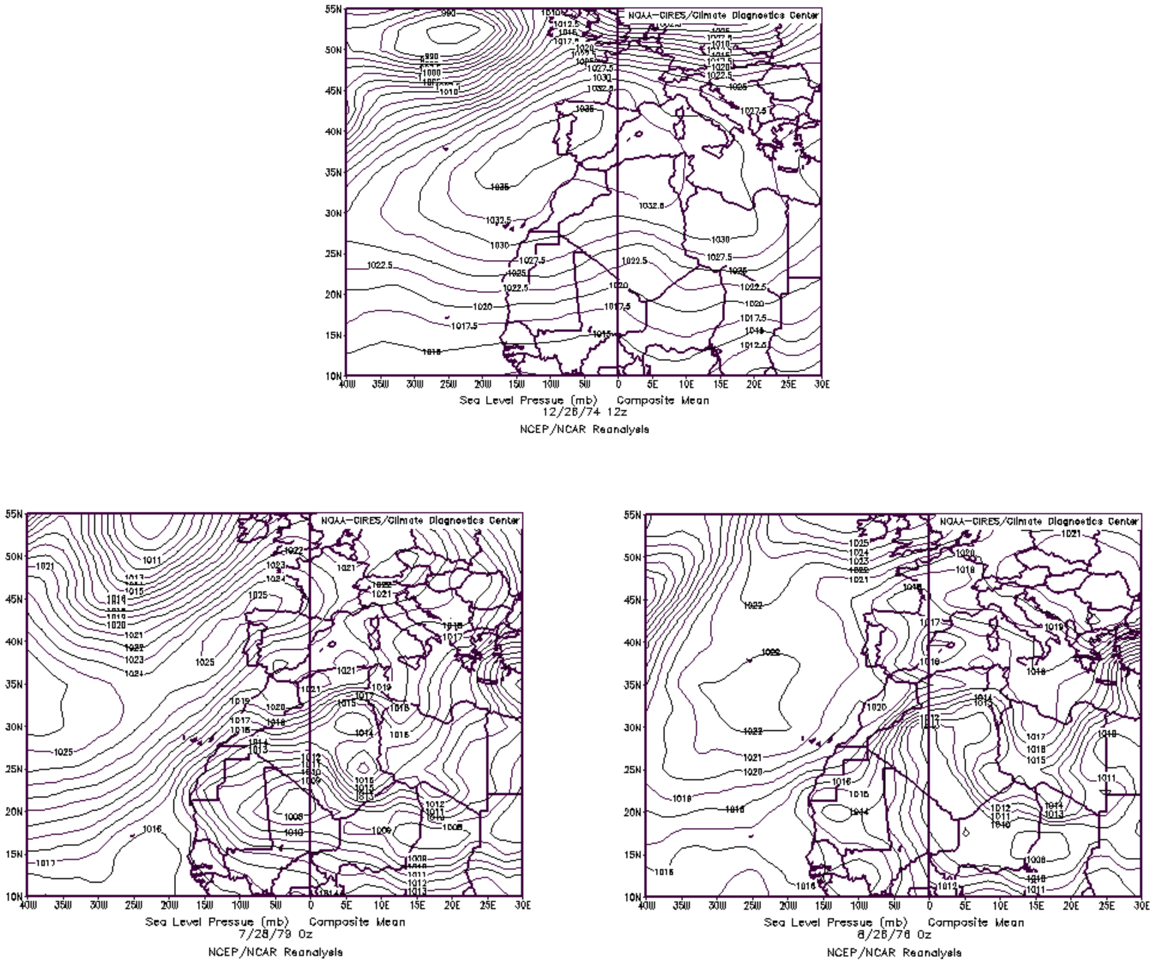


Figure 1.21. Sea level pressure maps of situations of the type d.1 (26-December-1974), d.2 (28-July-1979) and d.3 (26-August-1976) (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov).

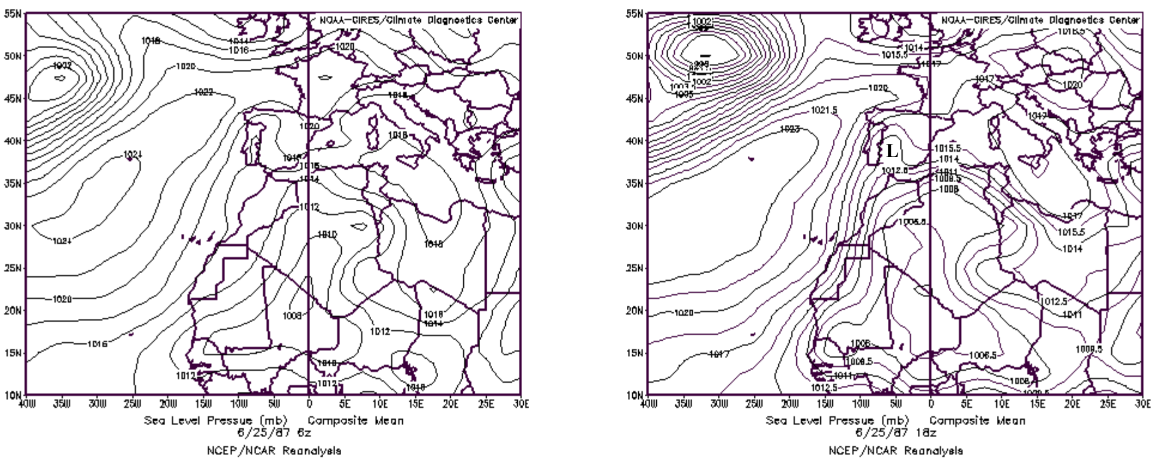


Figure 1.22. Sea level pressure charts showing the formation of the thermal low over the Iberian Peninsula on 25 June 1987 (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov).

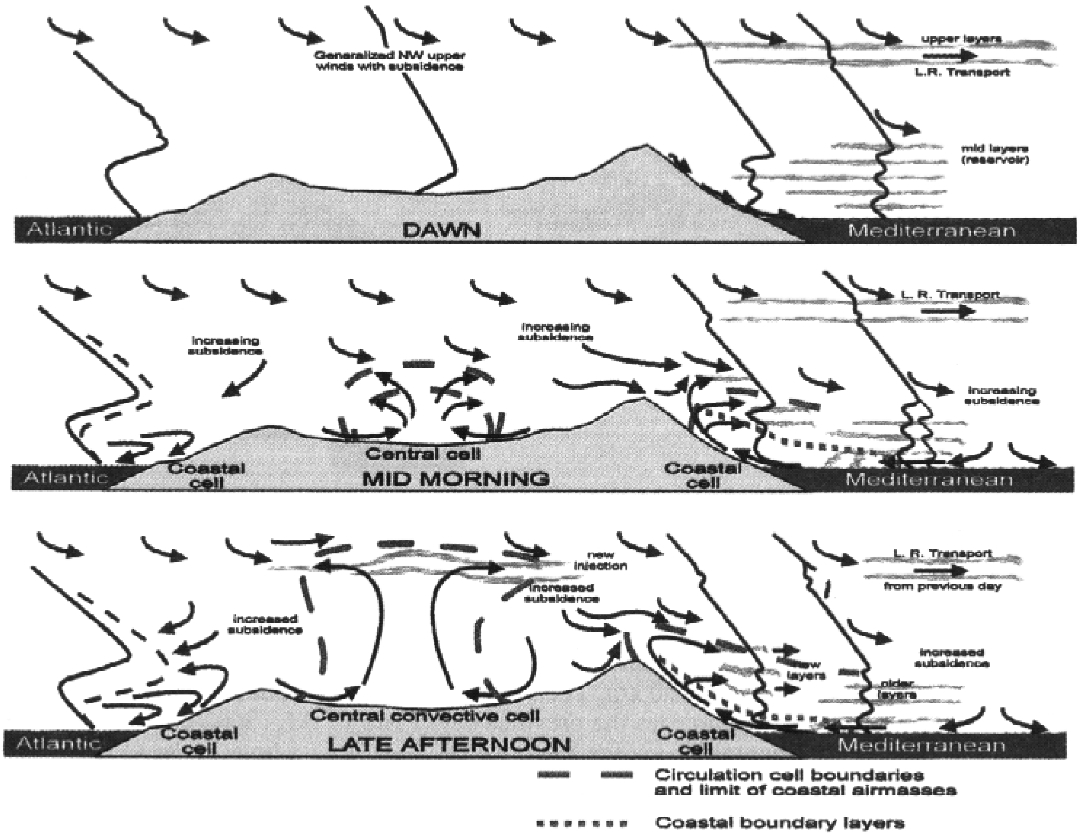


Figure 1.23. Schematic cross section of the Iberian thermal low circulation (from Millán et al., 1997).

Combined with the circulation of the three cells, the following interregional and long range transport scenarios were identified (Millán, 1997):

- The first scenario is the transport of the pollutants injected into the middle troposphere by the convective cells of the central Iberian Peninsula towards the European continent. This is possible owing to the prevailing winds at those altitudes which have northwestern direction.

- The second scenario combines the effect of a quasi-permanent high pressure area in the Gulf of Lion, the mountain ranges that surround the Mediterranean basin and the nocturnal coastal processes. In particular, the movement of air masses are parallel to the coastline and in a southern direction during the night. During the day, the air flow driven by the breeze is perpendicular to the coastline. Thus, the reservoir layers formed during the day move along the Mediterranean coast and can reach the Atlantic via the strait of Gibraltar after several cycles of re-entry and layering during the day Figure 1.24.

- Pollutants that may have been injected by convective processes in France, the Low Countries and Germany may also be transported towards the Atlantic Ocean passing over the western coast of Spain and Portugal.

The summary of both the documented and the hypothesised mesoscale summer circulations in the Mediterranean basin is shown in Figure 1.24.

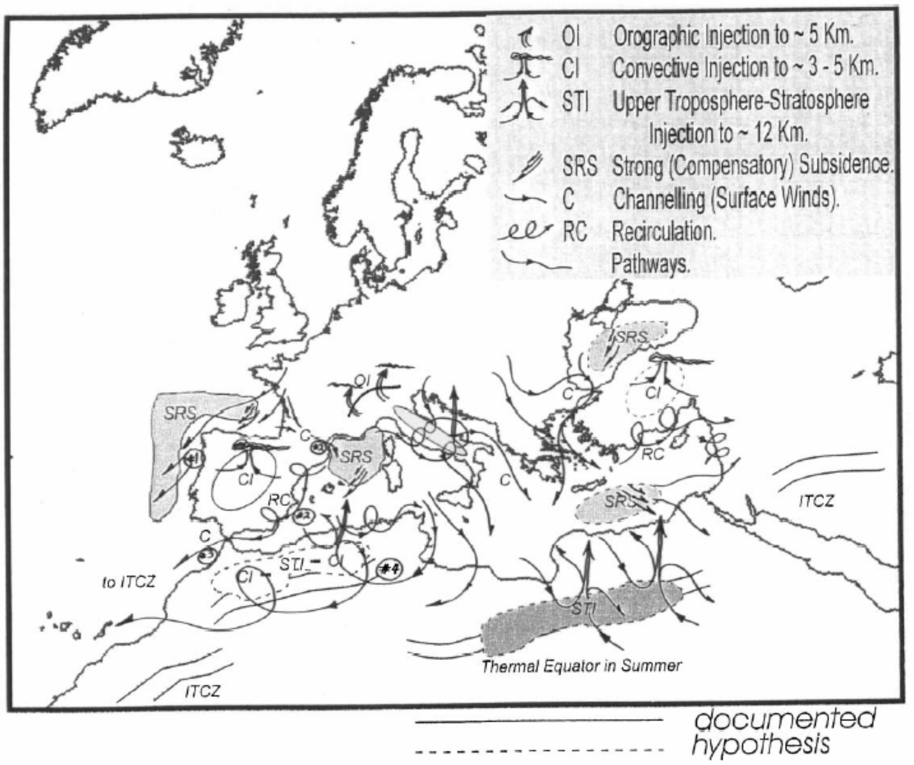


Figure 1.24. Schematic presentation of the observed and postulated circulations for the whole Mediterranean (from Millán et al., 1997).

e) **Transport from north Africa**: In this section attention will be paid to the cT air masses that have their origin over the African continent. The complete description of the African dust outbreaks over the Iberian atmosphere is one of the objectives of this thesis. Further discussion concerning scenarios of African dust transport will be presented later in this introduction and in the development of the study. The unique scenario proposed by Font (2000) under which African transport occurs is the following:

e.1) Azores anticyclone and thermal low (Figure 1.25): This situation leads to the formation of an Iberian regional air mass as explained above but also a cT air mass that affects the entire Iberian Peninsula except the north and the northwest. As we will see in the results section this transport takes place in high levels of the atmosphere (850 hPa or above). These situations are persistent and may last more than two weeks almost exclusively in summer. The precipitation is linked to local episodic summer storms.

1.6 Climate in north Africa

North Africa is located in the latitudes affected by the 'subtropical highs belt' (around 20-30º N). Dry and warm subsiding air from the 'Hadley cell' circulation establishes areas of high pressures were arid zones are common. At a global scale, north African deserts are the most important on Earth. In this section we will describe the climate and the meteorological patterns of north Africa having an influence on dust emissions will be reviewed.

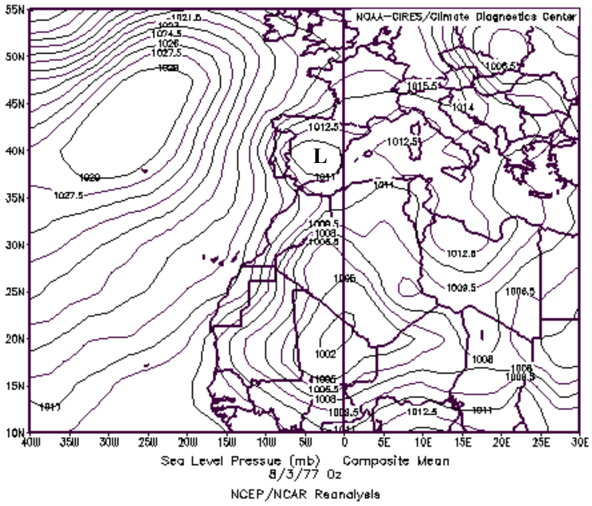


Figure 1.25. Sea level pressure maps of situations of the type e.1 (3-August-1977) (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov).

The Sahara is the most important hot desert on Earth because, in addition to the latitudinal location in the area of influence of the 'subtropical highs belt', it is a vast continental area well isolated from ocean influence. This creates a large continental air mass with extremely dry conditions. The Atlas range is an efficient barrier for Atlantic winds as the mountains in Ethiopia and Kenya are a barrier for south-eastern transport from the Indian Ocean and the continental air masses over the Asian continent avoid transport from the northeast. The Mediterranean basin is an area where formation and transport of cyclones commonly occur. Therefore, humid air from the Atlantic Ocean travels towards the east or the northeast and reaches the Mediterranean. From the southwest the monsoon winds rarely penetrate further than 20º N because the Coriolis force deflects them sufficiently to blow from the west (Font, 1955).

The oscillation of the ITCZ influences strongly the climate and the seasonal pattern of meteorological variables, such as temperature, pressure and wind intensity and direction. This is a belt of low pressure centres where the 'Trade winds' converge and strong convective conditions are found. In fact we could understand it as the 'thermal equator' although it does not necessarily follow the geographical equator. The ITCZ follows the apparent movement of the sun with a time lag of six weeks to two months (Dubief, 1979). In winter this belt of low pressure is placed over the gulf of Guinea in the west side of Africa and somewhat lower at the east side of the African continent. In summer it is placed over the Sahara. In north Africa the ITCZ separates two air masses with different characteristics, therefore it is sometimes known as the Intertropical Front (ITF). Below the ITF there is a warm and moist maritime air mass known as the Sudanese monsoon. Above the ITF there is a very dry air mass that changes its properties during the year: in winter it is cold in the Sahara but warm in Sudan, and in summer it is always warm (Dubief, 1979).

The general wind pattern in north Africa is closely related to the ITCZ oscillation. The relevant winds in winter are northerly in the northern part of Africa and gradually turn easterly and increases in intensity with decreasing latitudes. This wind is known as 'Harmattan' in Sudan (Figure 1.26) and it consists of a dry air mass transport from the southern Sahara and the Sahel (Dubief, 1979). During the summer the ITF is situated near the Tropic of Cancer pushed by the Monsoon winds. Only the Azores high persists affecting the European continent. Thus, northern winds known as the 'Etesian winds' enter north Africa through the eastern Mediterranean. In the same manner as the Harmattan in winter, in the southern Sahara and in the Sahel, Etesian winds turn gradually east, drying out and increasing their speed giving rise to drought in the northern and central Sahara (Figure 1.27). Over the Atlantic, the cool and moist 'Trade winds' are persistent all year long (Figures 1.26 and 1.27). From spring to autumn the Harmattan winds may be replaced by higher latitude air due to the influence of depressions crossing north Africa and the Mediterranean (Dubief, 1979).

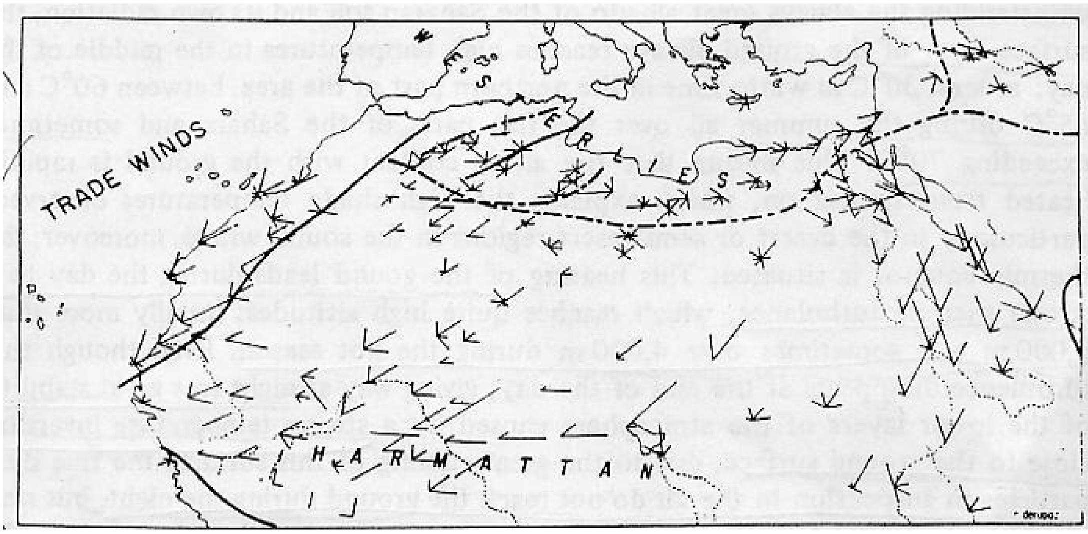


Figure 1.26. Prevailing winds in January in north Africa (from Dubief, 1979).

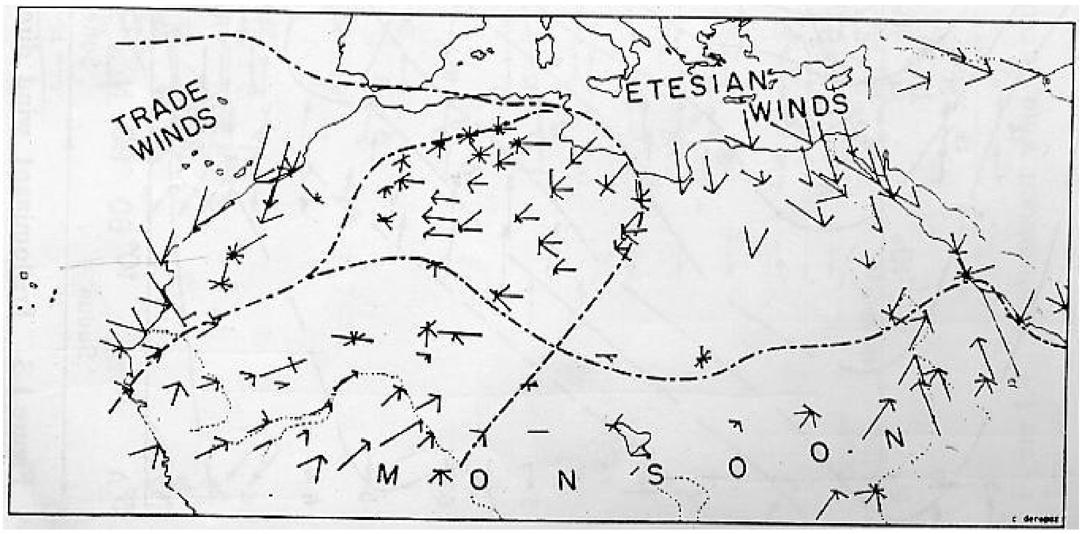


Figure 1.27. Prevailing winds in August in north Africa (from Dubief, 1979).

The average flows over Africa at 850 hPa (or mb) level were studied by Newell and Kidson (1979). They studied the zonal (u) and the meridional (v) components of the wind speed, that is, the components of the wind speed parallel to the parallels and to the meridians respectively. In winter 'u' exhibits the maximum variation with easterly winds at 10° N and 20° S and westerly winds north of 25° N, south 30° N and in the range 0-15° S (Figure 1.28) with maximum values to the north and the south of the Sahara. In summer, there are substantial variations and westerly winds across the Sahara occur with maximum values at about 25° N near the Greenwich meridian (Figure 1.28).

The study of the meridional component 'v' leaded to the following conclusion: the flow over the Sahara is towards the equator in the east and towards the pole in the west (Figure 1.29). Consequently, the prevailing winds in Africa would not lead to transport of African air masses towards the Mediterranean basin, thus, we should turn our attention to meteorological anomalous processes which are responsible of northward transport of air masses.

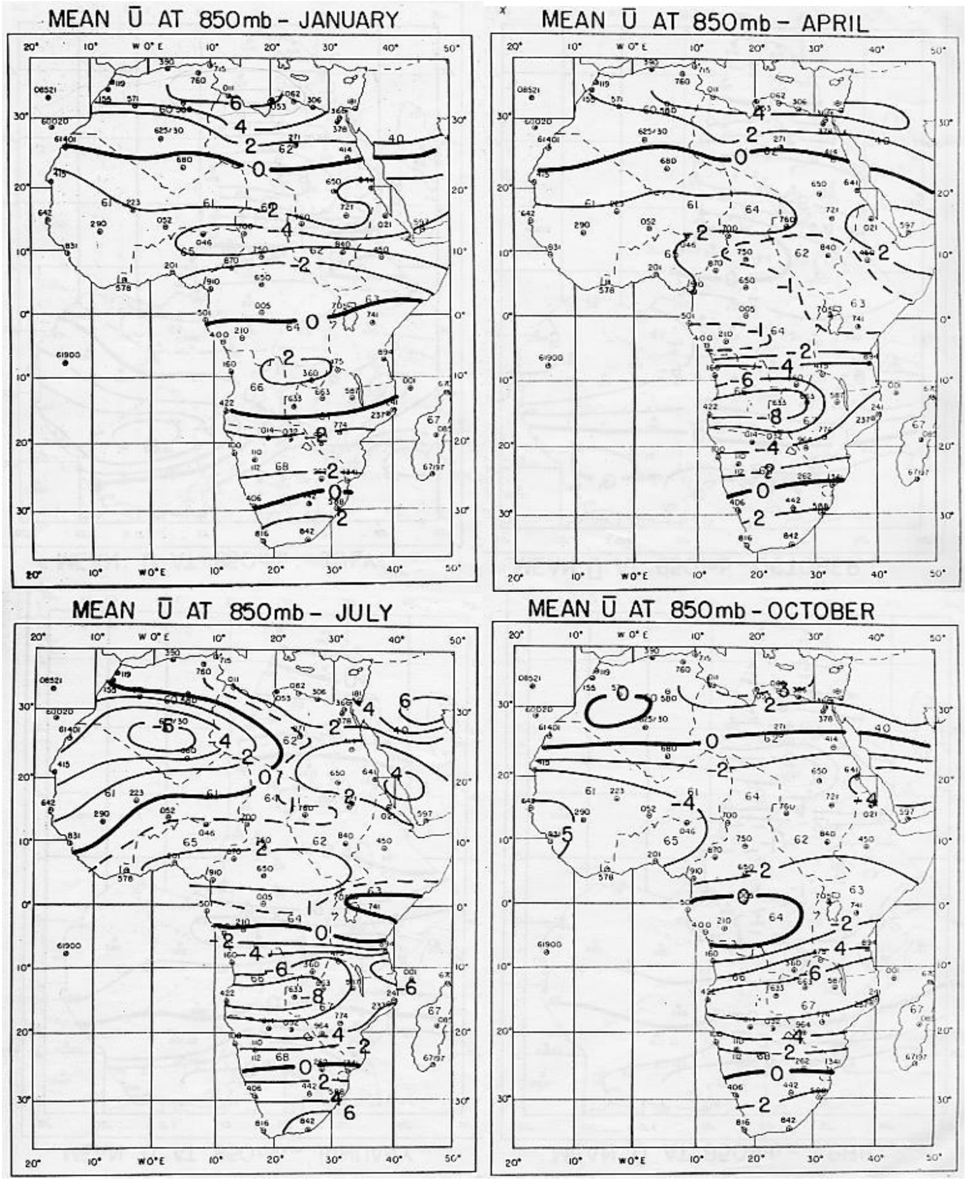


Figure 1.28. Monthly mean zonal wind component at 850 hPa level for January, April, July and October (from Newell and Kidson, 1979).

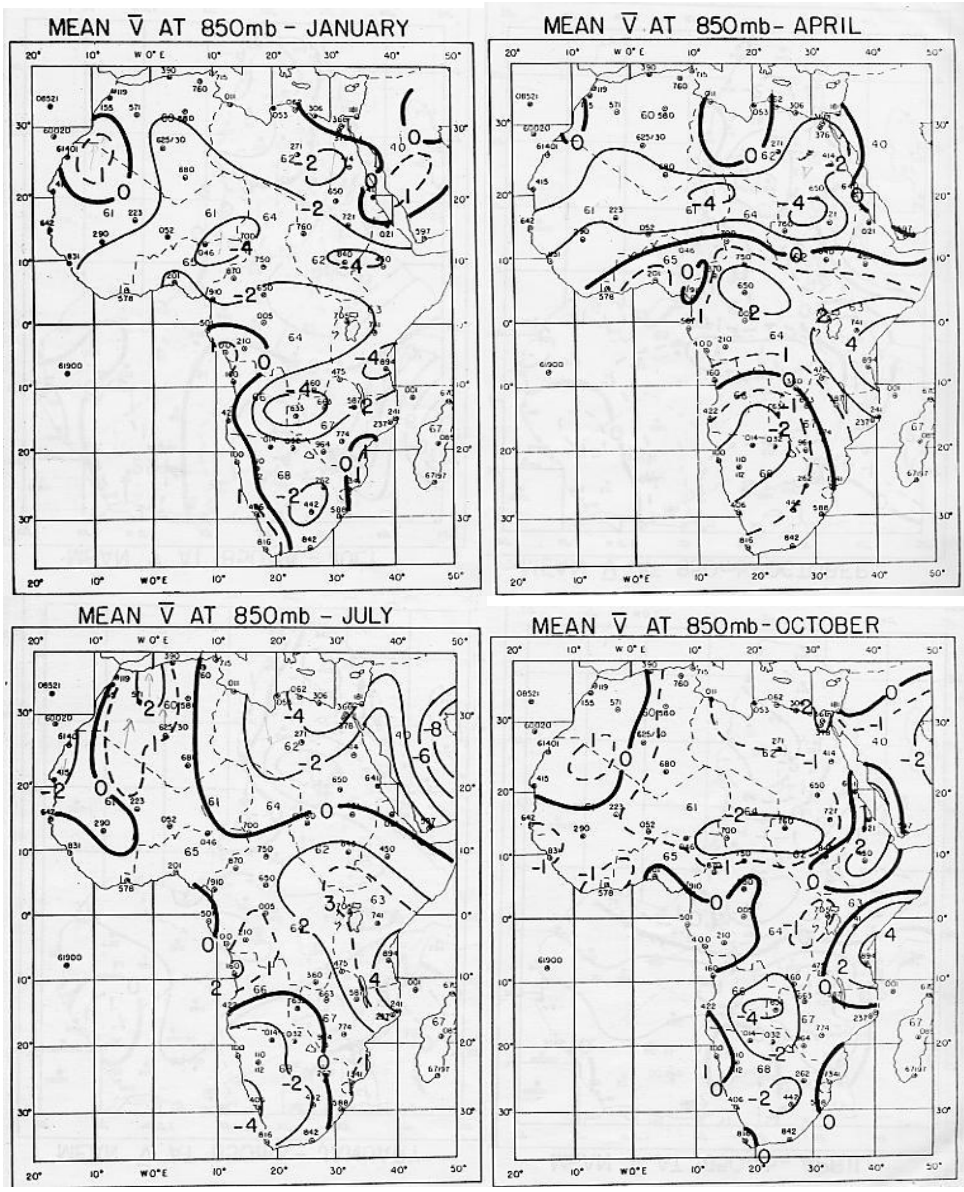


Figure 1.29. Monthly mean meridional wind component at 850 hPa level for January, April, July and October (from Newell and Kidson, 1979).

Rainfall over desert areas in north Africa is extremely low and has irregular seasonal intensity and duration. In the western part of the Sahara precipitation occurs in 1/100 days and only for a few hours. In the other part, the 'absolute desert', this frequency only reaches 2/1000 days (Dubief, 1979). Figure 1.30 shows the rainfall distribution in north Africa and illustrates the extensive band of extremely low precipitation that crosses the continent from west to east. The width of this band increases from west to east. In the northern Sahara drought occurs mainly in summer while in the southern Sahara and the Sahel the dry period is centred in winter and the rain is associated with the monsoon and takes place from May to September. It is characteristic of north Africa that, regardless the latitude, it is in autumn when the maximal precipitation is recorded. This is mainly governed by the activity of the Sudano-Saharan depressions (Font, 1955). The role of these and other depressions frequently responsible for the dust transport over the Mediterranean and the Iberian Peninsula will be treated in section 1.7.

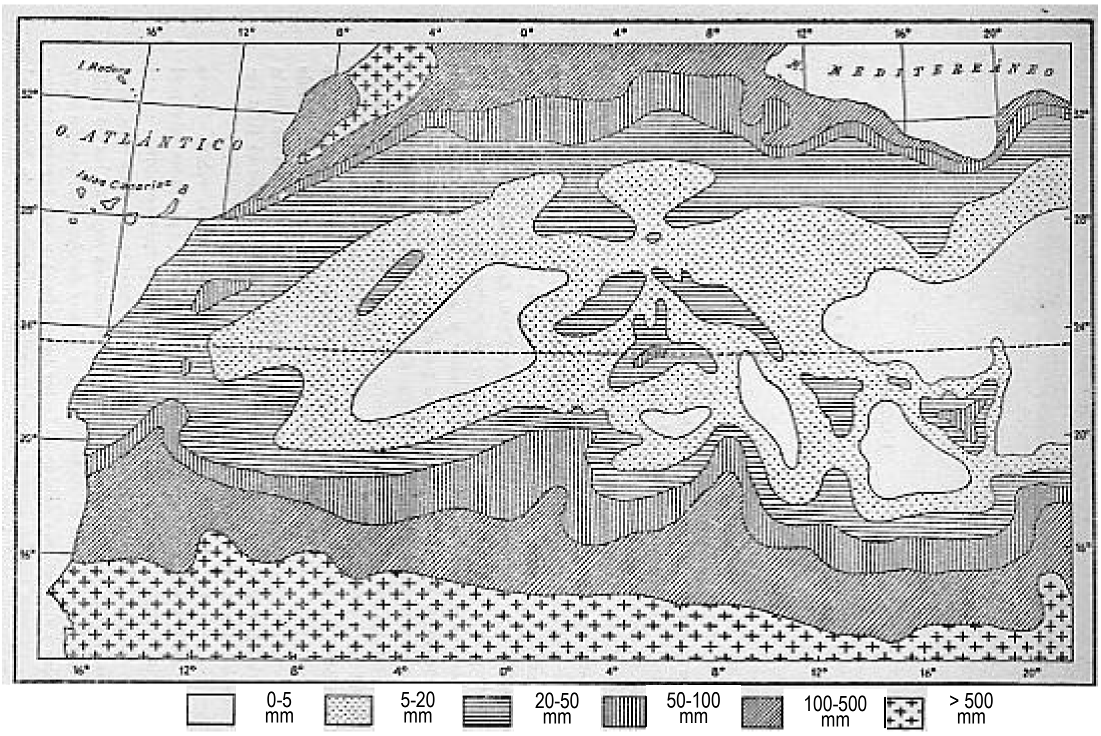


Figure1.30. Annual rainfall regime in north Africa (from Font, 1955).

Due to the small angle of incidence of sun's radiation, the long duration of the days, the long duration of summers with respect to winters and the pronounced dryness of the atmosphere, the surface is intensively heated in north Africa. Furthermore, because of the large albedo (percentage of solar energy reflected by a surface) of the Saharan surface, the lower layers of the atmosphere over the north African deserts always reach very high temperatures in the middle of the day (at least 30° C in the northern part of the area and sometimes exceeding 70° C in summer, Dubief, 1979). This heating of the ground leads to a strong thermal diurnal turbulence followed by a strong nocturnal temperature decrease near the ground. The ground temperature can decrease near 0° C in the first hours of the day (Font, 1955). This mechanism creates a thermal inversion near the surface at night that is responsible of the formation of the semi-permanent dust layer at altitudes up to 7000 metres (Prospero and Carlson, 1981). This is known as the 'dry haze'. The seasonal variation of the surface temperatures over north Africa is linked with the oscillation of the ITCZ as explained above. It is interesting to review where, in north Africa, the highest temperatures are found. In these zones the strongest thermal convection would take place and the 'dry haze' could be formed. The highest temperatures in late autumn and early winter (November and December) occur over the Atlantic Ocean at low latitudes (0-10º N). In late winter (February and March), the highest temperatures are found over the gulf of Guinea and the Sahel whereas in summer (July and August) the highest temperatures are centred over the Sahara desert (Figure 1.31).
In the following sections attention will be paid to the major episodes that have been proved to influence PM levels and precipitation features in a regional scale in the Iberian Peninsula. These are mesoscale or synoptic scale processes such as long range transport of aerosols and regional recirculation episodes.

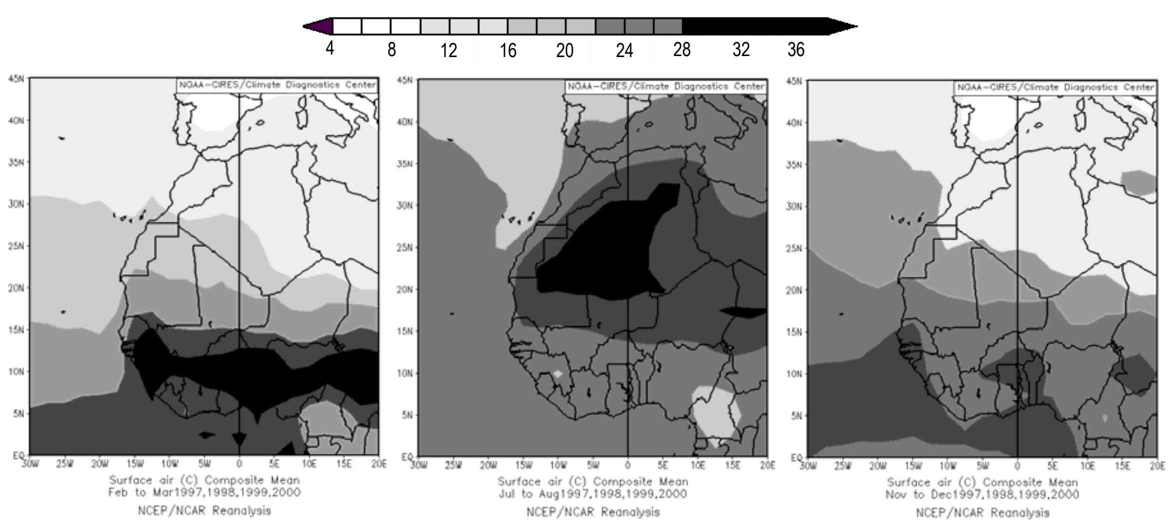


Figure 1.31. Mean surface air temperature in north Africa in February-March, July-August and October-November for the period 1997-2000 (calculated from the reanalysis of the NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov/).

1.7 Dust episodes

The emissions of crustal material from arid areas have been widely studied. Great amounts of dust are released from arid or semiarid areas around the globe. Among all dust sources the Sahara desert is the major contributor to the total amount of dust suspended in the atmosphere (Goudie and Middleton, 2001). Provided the objectives of this thesis, the Saharan and the Sahelian contributions will be treated more deeply.

Mineral dust interacts with the atmosphere, the hydrosphere and the lithosphere in a number of important processes. It alters the radiation balance of the Earth-Atmosphere system (Figure 1.32), provides reaction surfaces for reactive gas species, neutralises atmospheric acidity and releases Fe that acts as fertilising agent for phytoplankton. As regards air quality control in Europe, dust outbreaks are natural events (as defined in European directive 1999/30/CE) that have an impact on levels of PM recorded in air quality monitoring stations. This may cause exceedances of the daily limit value that can be discounted by the State Members if the occurrence of such events is adequately supported. Thus, there is great interest in controlling and in forecasting dust intrusions over Europe especially in southern Europe.

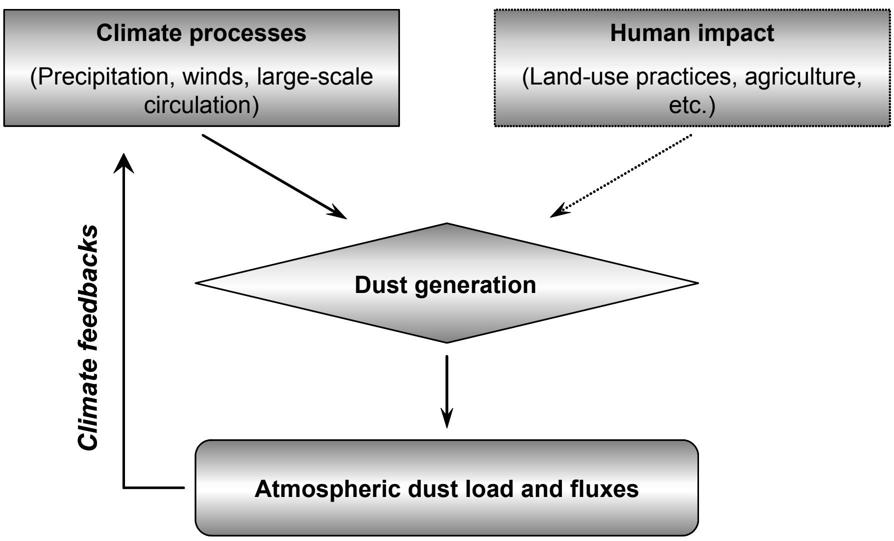


Figure 1.32. Dust-climate connections (modified from Arimoto, 2001).

The estimates of soil dust emissions show a large range (Table 1.4). These large differences can be attributed to the differences in the assumptions made in the different models, such as the rate of scavenging. The interval of variation goes from 500 to 5000 million tonnes of dust per year although recent studies suggest a range of 1000 to 3000 million tonnes per year. As mentioned above, the Sahara desert is the major contributor to suspended dust in the Earth's atmosphere. The strength of the Saharan dust source has been estimated in several studies showing also a wide range of emissions values (Table 1.4). The dust emitted in the Sahara estimated by different authors ranges between 130 and 760 million tonnes per year though most estimations are in the range 260-710 million tonnes per year. These data confirm the importance of the north African deserts on the global scale.

Table 1.4. Estimates of the global dust emissions and of the Saharan dust emissions (from Goudie and Middleton, 2001).

Global dust emissions		**Saharan dust emissions**	
Author(s)	**Annual quantity (millions of Tn)**	**Author(s)**	**Annual quantity (millions of Tn)**
Schütz (1980)	Up to 5000	Callot et al. (2000)	760
Tegen and Fung (1994)	3000	D'Almeida (1986)	630-710
D'Almeida (1986)	1800-2000	Marticorena and Bergametti (1996)	586-665
Duce (1995)	1000-2000	Swap et al. (1996)	130-460
Andreae (1995)	1500	Jaenicke (1979)	260
Peterson and Junge (1971)	500	Schütz et al. (1981)	260
		Prospero (1996)	170

The emissions and/or transport of dust can have great regional and time variability due to the possible interactions of dust production with climatic cycles. For example, the dust transported to Barbados was found to be more intense in El Niño years (Prospero and Nees, 1986) and the dust export towards the Mediterranean shows correlation with the north Atlantic Oscillation (Moulin et al., 1997).

1.7.1 Climate and mineral dust

In section 1.2.2 the optical properties of the aerosols and the climatic consequences of those properties have been revised. The mineral aerosols influence the climate mainly by scattering and absorption of radiation. The mineral grains may act as CCN as Levin et al. (1996) suggested.

The single scattering albedo of dust is significantly below one. Thus, the resulting forcing is small due to partial cancellation of solar and thermal forcing as well as cancellation of positive and negative forcing over different geographic regions (Tegen and Lacis, 1996). Mineral dust has different radiative forcing for short and long-wave radiation. Dust aerosols also exert different radiative forcing above oceans and above land. Over dark surfaces such as the ocean, dust exerts a cooling effect because the scattering effect of dust increases the planetary albedo, thus, less radiation reaches the surface. In contrast, over bright surfaces such as in arid regions the forcing of dust at thermal wavelengths, which is always positive, dominates over scattering effects (Arimoto, 2001). The size of dust aerosols and the fact of being lofted to high altitudes cause the dust to have a significant interaction with long-wave radiation in addition to the interaction with short-wave radiation. For example, Sokolik and Toon (1996) estimated the short-wave radiative forcing in –0.25 Wm^{-2} over ocean and –0.6 Wm^{-2} over land leading to a global forcing of –0.46 Wm^{-2}. With the estimations of these and

other authors a range of –0.6 to 0.4 Wm^{-2} can be adopted as the direct radiative forcing of dust, though efforts are being made to obtain a better estimate (IPCC, 2001). As the radiative forcing of dust is positive for thermal wavelengths, the net effect is to cool dark surfaces (such as the oceans) and to heat bright surfaces (such as deserts).
The indirect climatic effects of mineral dust cannot be quantified because it has nor been investigated enough. However, Levin et al. (1996) observed dust grains coated with sulphate which may have its origin in the condensation of SO_2 onto dust followed by oxidation. The presence of this soluble material (which may have anthropogenic origin) coating dust grains converts them in effective CCN.

1.7.2 Chemistry and grain size of dust

In section 1.1.2 the main chemical species present in crustal material are detailed. Silicates (especially aluminium silicates such as clay minerals), carbonates and minor amounts of calcium sulphates and iron oxides are the common species in crustal material. This is not different for soil material originated in deserts. The dominant species in dust are SiO_2 and Al_2O_3. Saharan dust is known to be rich in Fe_2O_3, MgO, and CaO (Goudie and Middleton, 2001) and $CaCO_3$ that has been proved to act increasing the pH of rain in the Mediterranean (Löye-Pilot et al., 1986, Caboi et al., 1992, Rodà et al., 1993, Avila et al., 1997, Avila and Alarcón, 2003, Singer et al., 2003). The chemical or mineralogical differences of dust reaching sampling stations may provide knowledge about source areas even in the same geographical areas. However, no elements have been found to be uniquely tracers for specific regions. The common approach is to make use of ratios of the concentrations of elements of desert dust such as: aluminium, calcium, iron, potassium, magnesium, scandium and silica (Coudé-Gaussen et al., 1987, Bergametti et al., 1989a, Chiapello et al., 1997). For the case of north Africa, Lafon et al., (2004) found a significant difference in the percentages of free iron relative to the total estimated aerosol mass for samples of the Sahel (5.0%) and the Sahara (2.8%).
The dust, while transported over remote locations, can interact chemically with species of different origin that are not present in the desert environment. In particular, it is important the effect of dust on oxidant cycles (Arimoto, 2001). Apart from small effects on oxidants such as O_3 and HO_2 (hydroperoxyl radical), the reactions of mineral matter with gaseous nitrogen and sulphur compounds (NO_2, HNO_3, SO_2 and H_2SO_4) are important.
These gaseous precursors may give rise to nitrates or sulphates by reacting onto soil particles. Through this interaction these gaseous precursors are removed and consequently the homogeneous nucleation of new particles decreases. These reactions require the presence of water because they are heterogeneous reactions. Dust-laden air is dry and these reactions need a certain degree of humidity to become important. Thus, only after the mixing of dry air mass with humid air the reactions take place. The reaction that results in the neutralisation of atmospheric acidity caused by nitrogen compounds can be as follows (Arimoto, 2001):

$$HNO_3(g) + CaCO_3 \rightarrow Ca^{2+}NO_3^- + HCO_3^- \quad (1.10)$$
$$HNO_3(g) + Ca^{2+}NO_3^- + HCO_3^- \rightarrow Ca(NO_3)_2 + H_2O + CO_2 \quad (1.11)$$

Equivalent reactions occur for the neutralisation case of the conversion of calcite ($CaCO_3$) to gypsum ($CaSO_4 \cdot 2H_2O$) also leading to a neutralisation of acidity of sulphuric acid.

Also sea salts may interact with dust particles. Dust aerosols have been found to be coated with sea salts after long range transport across the Mediterranean (Levin et al., 1996). These particles are thought to act as cloud condensation nuclei.
Caquineau et al. (1998) and Avila et al. (1997) detected variations in the mineralogy of clays in desert dust on the basis of the different source areas. The north and west Sahara exhibited the highest illite/kaolinite proportion, whereas kaolinite is predominant for Sahelian contributions and also in contributions from southern and central Sahara. In addition to these clay minerals, paligorskite was also frequent. Lacustrian diatoms and minerals such as quartz, carbonates (calcite) and feldspars have been found in African desert dust plumes (Alastuey et al., 2005).
The size distribution of dust particles transported to remote locations is highly dependent on the distance to the source area. This is due to the segregation of fine particles by mechanical processes during transport. As regards mass concentration of dust plumes, material with median sizes ranging between 5 and 30 μm is the dominant (Goudie and Middleton, 2001). Thus, in Tanezrouft, in the central Sahara the median diameter of the suspended particles (contributing to the mass) is 72 μm (Coudé-Gaussen, 1981) whereas in Catalonia, the median diameter for three rain-dust events was 11.1 μm (A.Avila, com.pers), and in Barbados (Talbot et al., 1986), Bermuda (Arimoto et al, 1997) and the USA (Perry et al., 1997) it may be lower than 5 μm Saharan dust also includes biological particles. Griffin et al., (2001) found bacteria and fungi in the dust arriving to the Virgin Islands in the Caribbean. Therefore, the concentration of cultivatable airborne microorganisms can be 2-3 times higher during dust events than in the absence of such dust events.

1.7.3 Source areas of mineral dust

On a global scale, most of the mineral dust is released to the atmosphere in arid or semiarid areas. However, on a local scale, mineral dust emitted by human activities such as roads erosion, and agricultural activities may be important. Several studies have dealt with the identification of dust sources (Kalu, 1979, D'Almeida, 1986, N'Tchayi et al., 1997) but a recent study by Prospero et al. (2002) gives details of all source areas distributed around the world. The major dust source areas are located in arid climates (with rainfall < 200-250 mm/year) in the so called 'dust belt' associated with topographical lows (caused by ephemeral playa-lakes, rivers, lakes and streams) and in the proximity of mountains. Dust emission source areas in north Africa are closed continental drainage basins in which large amounts of PM is accumulated due to the erosion of arid zones during the wet seasons (characterised with torrential rains). In the dry seasons this material is exposed to re-suspension processes (Querol et al., 2002). The 'dust belt' is located at the latitudes of the subtropical high (only in the northern hemisphere) and extends from the west coast of north Africa, over the Middle east, central and south Asia to China. The southern hemisphere is almost devoid of dust activity.
Dust events have also been observed in Asia (Middleton 1989, 1991, Littmann 1991). Asian dust is transported to Hawaii and other sites of north Pacific (Duce et al., 1980, Tsunogai and Kondo, 1982, Uematsu et al., 1983, Braaten and Cahill, 1986, Gao et al., 2001), Alaska (Rahn, 1981) and the western United States (Husar et al., 2001), the Arabian sea (Savoie et al., 1987, Tindale and Pease, 1999). The dust sources are distributed in the whole Asian continent. From west to east these are the main source areas in Asia (Prospero et al., 2002):

- Middle East: Dust activity peaks take place in summer in this area with minimum activity in winter. There are three regions where the dust is released: a) the

Arabian Peninsula (with two defined active areas in the eastern side of the peninsula and near the coast of Oman), b) Oman and c) the Tigris and Euphrates Basin (Middleton, 1986, Ackerman and Cox, 1989).

- Central and south Asia: The activity of the source areas in this region starts in March-April and extends until September when it weakens. However, owing to the summer monsoon in India, dust activity is practically inexistent in south India after June (Middleton, 1986, 1989, Ackerman and Cox, 1989, Golitsyn and Gillette, 1993). Prospero et al. (2002) identifies three major dust sources in this area: a) The Caspian Sea and the Aral Sea region, b) Iran and Pakistan basins and c) the Indian subcontinent.

- China and Mongolia: Large quantities of dust are generated in China (Middleton, 1989, 1991, Littmann, 1991) and the Gobi desert in Mongolia (Goudie, 1983). The dust activity begins in February-March, reaches to its peak in April-May and ends in September. According to Prospero et al. (2002), two are the main source areas: a) Tarim Pendin and the Takla Makan desert and b) The Gobi desert on the Mongolian Plateau. Also the loess Plateau and deserts such as the Mu Us, the Badain Juran, Ulan Buh, Hobq and Tengger are dust source areas in this region (Zhang et al., 2003).

There are other regions in which dust is released but they have weaker activity than Asian and north African source areas. Regions from the southern hemisphere such as the Lake Eyre and the great Artesian Basin in Australia, the region of Makgadikgadi Pans in Botswana, the region of Etosha Pan in Namibia, the Altiplano in Bolivia and the Patagonia in Argentina emit dust. Also in the northern hemisphere there are 'weak' source areas in western United States and Mexico (Prospero et al., 2002). As stated above, the reason for this weaker activity is the lack of extent areas of closed continental drainage basins in these areas which are present in north Africa and Asia.

As mentioned above, north Africa is a major emission source of atmospheric mineral dust. The formation of the 'dry haze' is the common phenomenon that permits the transport of great quantities of dust. Dubief (1979) defines the 'dry haze' as an 'almost inexhaustible reservoir of airborne dust particles'. The regions in which dust is more frequently injected in northern Africa is controlled by the yearly oscillation of the ITCZ where strong convective processes occur during the day alternated with thermal inversions during the night. During the winter it is situated along the latitude of the gulf of Guinea in the west and at somewhat lower latitudes in the east. During the summer it shifts towards the Sahara. Thus, in winter, in the Sahel and in the southern Sahara the thermal turbulence creates the 'dry haze' (more or less mingled with ash from forest fires occurring in that area in winter) while in summer the maximum injection processes take place in the Sahara (Dubief, 1979).

The strength of the source areas in north Africa is then highly influenced by the position of the ITCZ. According with the review of emission sources by Prospero et al. (2002), the Iberian Peninsula could receive dust from the following source areas (figure 1.24):

- Tunisia and northeast Algeria: The dust activity takes place in a system of dry lakes (sabkhas) and salt lakes (chotts) situated south to the Atlas Mountains. The most intense dust activity is in the area 33-35° N and 6-8.5° E from April to September.

- eastern Libyan Desert: The Al Jabar and Al Akhdar hills are the natural sources of material for a group of wadis (dry valleys intensively flooded during the wet season). This source area is persistent during the whole year but reaches it is especially active in May and June. The area is located from 22 to 23° N of latitude and from 15 to 17° E of longitude.

- Egypt: This source becomes active in March and ceases its activity in October. The material is emitted mainly from depressions in central Egypt in the period March-

October. This source area is located in 24-27° N and 29-33° E but it tends to merge with the Libyan source as the active season progresses.

- Mauritania and Western Sahara: This is a permanent source that comprises areas from the Western Sahara to northwestern Mauritania. The maximum activity is reached in the period June-September. The geographical limits of this area are 21-27° N of latitude and 6-16° W.

- Mali, Mauritania and the western flanks of the Ahaggar Mountains: The alluvial playas situated west of the Ahaggar Mountains and north of the Niger River. The activity of these sources is persistent all year long but the low activity of the period October-March is followed by a high activity period from April to September. The location of this large source area falls between 17 and 26° N and 0-10° W.

- Niger and the southern flanks of the Ahaggar Mountains: The limits of this region are 18 to 23° N and 3 to 6° E characterised by low-lying areas between mountain slopes. This area shows activity during the whole year with maximum in the period April-September.

- Lake Chad and the Bodele depression: This is known as the most intense dust source in the world. It is active during all the months of the year. The large drainage basin of the Lake Chad is the surface from which large amounts of dust are emitted. Two active areas can be distinguished: a) The Bodele depression and the erg du Djourab (16-18° N and 15-19° E) and b) the erg du Bilma (17.5° N and 13-14° E). In winter this area is the unique responsible of the dust transport towards the Gulf of Guinea (Kalu, 1979) and, subsequently, towards America (Prospero and Carlson, 1981, Swap et al., 1992) and also towards western Europe forming a curved dust plume known as Atlantic arch (Querol et al., 2002).

Other source areas in north Africa are Sudan and the Flanks of Ethiopian Highlands and the Ethiopia Rift Valley and Djibouti. These sources do not likely contribute to dust outbreaks in the Iberian Peninsula.

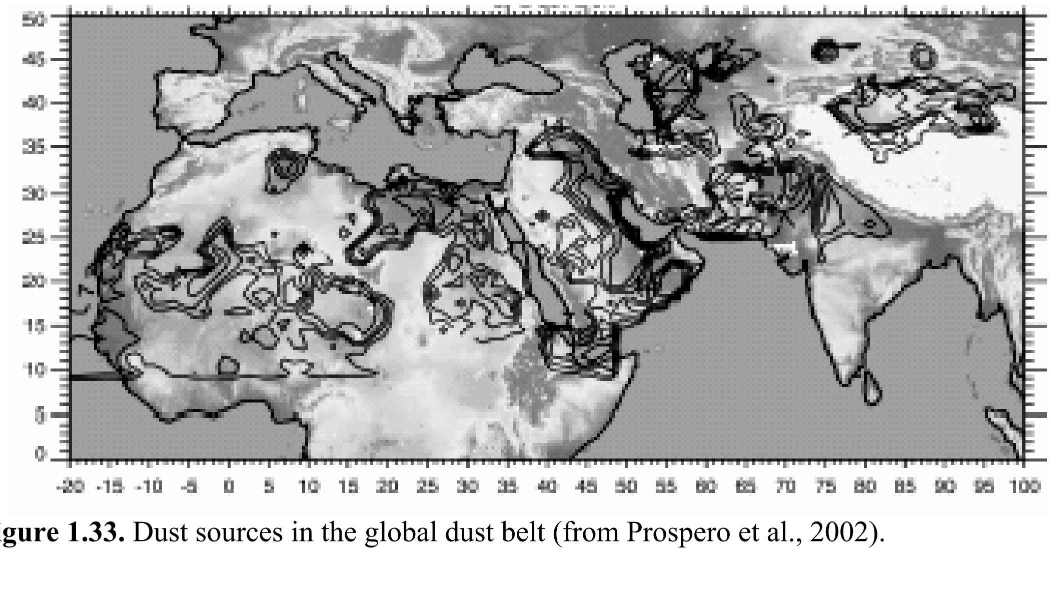


Figure 1.33. Dust sources in the global dust belt (from Prospero et al., 2002).

1.7.4 Transport of north African dust

Long range transport of dust has been documented for Asian and north African source areas. Attention will be paid here to the long range transport of north African dust for the objective of this thesis.

The transport of north African dust towards the American continent is associated to synoptic scale processes and presents a marked seasonality (Swap et al., 1996). The prevailing winds in the free troposphere over northeastern Africa and the subtropical Atlantic Ocean (trade winds) favour the transport towards the west. The transport takes place in the free troposphere and it is also favoured by the increasing velocity of the wind at the upper levels and the increase in residence time due to lower scavenging at those altitudes. A number of studies have documented the transport of north African dust to distant locations in America: south-eastern United States (Perry et al., 1997, Prospero, 1999), the Caribbean (Carlson and Prospero, 1972, Prospero and Carlson, 1972, Westphal et al., 1987), Bermuda (Arimoto et al., 1995) and south America (Prospero et al., 1981, Swap et al., 1992). Dust is also commonly transported to Atlantic islands such as Cape Verde (Chiapello et al., 1995, 1997, Caquineau et al., 1998), the Canary Islands (Coudé-Gaussen, 1987, Bergametti et al., 1989a, Prospero et al., 1995, Bustos et al., 1998, Torres et al., 2001, Viana et al, 2002) and northwestern Europe (Martín Vide and Moreno, 1985, Reiff et al., 1986, Avila et al., 1997, Rodríguez et al., 2001, Ryall et al., 2002). The seasonality in the transport of dust towards the west Atlantic Ocean depends on the oscillation of the ITCZ. Airborne dust in south America show maximums early in the year (when the ITZC is in its most southerly position around 5° N), while in north America summer concentrations of suspended north African dust reach values 10 to 100 times greater than in winter. This is due to the position of the ITCZ in summer (between 20 and 30° N) (Prospero and Carlson, 1981). Thus, as shown by Husar et al. (1997) with data from NOAA AVHRR (National Oceanic and Atmospheric Administration Advanced very High Resolution Radiometer) by means of the analysis of the optical depth over the ocean, the origin and the amount of the dust transported over the Atlantic has a clear seasonality. As shown on Figure 1.34 transport over the north Atlantic Ocean is maximum in spring and summer and minimum in autumn. An intensive flow off the gulf of Guinea occurs also in winter. Owing to the quasi-permanent subsidence conditions at those latitudes and the presence of the trade winds, a strong temperature inversion develops (located at 1400 m.a.s.l. in average, Rodríguez, 1999). This inversion separates the warm and dry African air mass and the relatively fresh and moist marine boundary layer air mass and impeaches the mixing between the two layers. Under these circumstances, the transport of dust over the American continent takes place above the 850 hPa (approximately 1500 m). Over Barbados, the upper African dust layer has PM concentrations three times higher than the surface layer (Prospero and Carlson, 1972).

Due to the geographical location of the Canary Islands (100 km from the African coast at around 28° N and 16° W), African dust outbreaks have a high influence on the air quality of these islands. The occurrence of these episodes results in numerous exceedances of the daily PM10 limit value established by the EU directive 1999/30/EC (Viana et al., 2002). The contributions of dust over the Canary Islands have different origins and impact on surface PM levels depending on the season. The following three scenarios were differentiated by Viana et al., (2002):

(a) Winter (February-March) events: The presence of an anticyclone over north Africa, or sometimes over the Mediterranean basin, induces transport from the Sahel at low altitudes (from surface up to 2 km). The low altitude of this transport result in sharp increases of the PM levels in air quality monitoring stations (daily means of up to 600-700 μgPM10 m^{-3}).

(b) Summer (June-August) events: The north African anticyclone is relocated above 850 hPa as a consequence of the development of the thermal low which develops at surface levels over the Sahara desert. Summer intrusions over the Canary Islands occur in altitude and provoke persistent high background PM levels but with less intensity than the winter intrusions (daily means < 75 μgPM10 m^{-3}).

(c) Autumn-winter (October-November) events: These episodes respond to local phenomena such as dust storms. They have strong influence on PM levels (up to daily means of 400-500 μgPM10 m^{-3}) because they are surface processes.

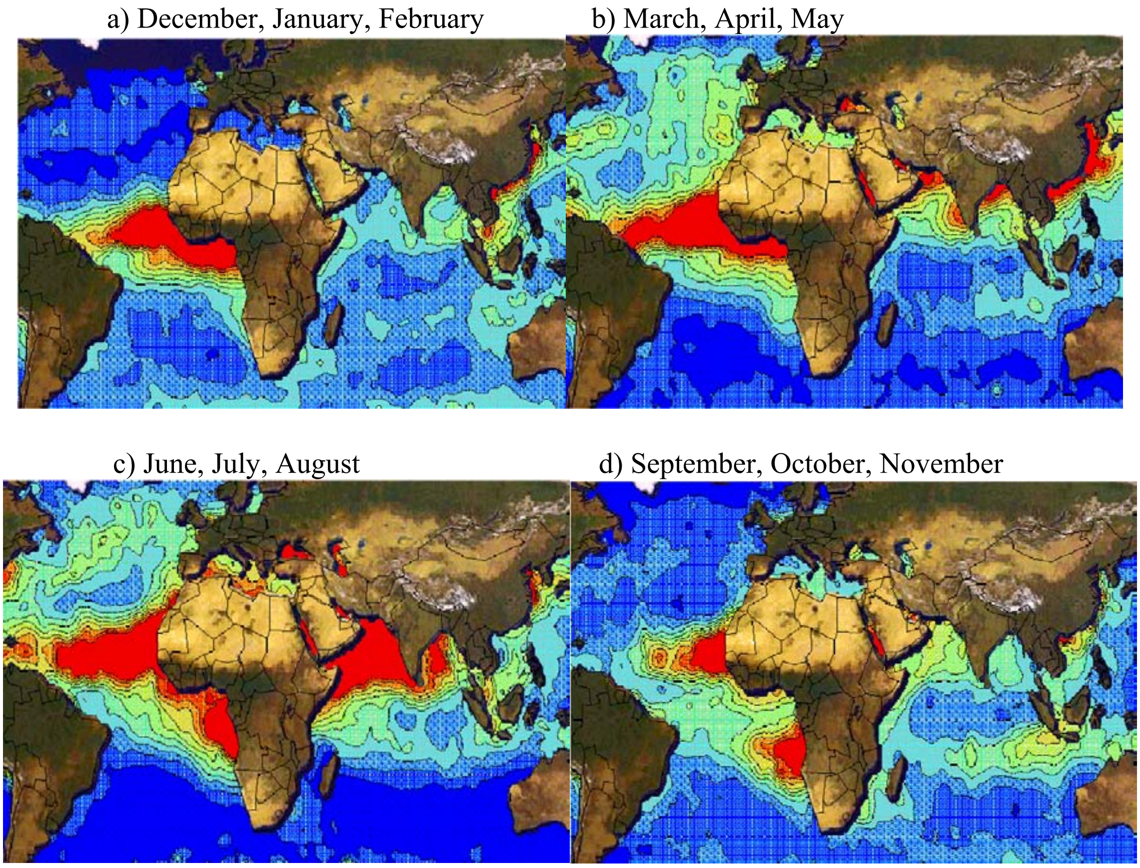


Figure 1.34. Seasonal maps of aerosol optical thickness for the period July 1989 to June 1991. The red colour denotes maximum concentration of aerosols (from Husar et al., 1997).

The dust originated in north Africa may be also transported towards the Mediterranean basin. The low precipitation in the Mediterranean basin favours the long residence time of PM in the atmosphere with the consequent impact on air quality. There are numerous studies on the phenomenology of dust outbreaks over the Mediterranean basin (Joseph and Wolfson, 1975, Prodi and Fea, 1979, Ganor and Mamane, 1982, Sequeira, 1982, Martín Vide and Moreno, 1985, Löye-Pilot et al., 1986, Bergametti et al., 1989b, Dayan et al., 1991, Dulac et al., 1992, Samara et al., 1992, Alpert and Ganor, 1993, 2001, Camarero and Catalán, 1993, Carratalá, 1993, Chester et al., 1993, Molinaroli et al., 1993, Rodà et al., 1993, Guerzoni et al., 1995a, 1997, Avila, 1996, Avila et al., 1997, 1998, Kubilay et al., 1997, Moulin et al., 1997, 1998, Querol et al., 1998, Alastuey et al., 1999, Avila and Alarcón, 1999, Hamonou et al., 1999, Rodríguez et al., 2001, Özsoy et al., 2001, Avila and Rodà, 2002, Singer et al., 2003, Viana et al., 2003, Salvador et al., 2004). While the transport of African dust across the Atlantic is semi-permanent due to the trade winds, the transport over southern Europe is less frequent and is linked to specific meteorological situations (north African depressions or anticyclones) which not necessarily follow the general patterns of the circulation over north Africa (Figures 1.27 and 1.28).

Dust can be transported towards the Mediterranean by means of the numerous depressions that come across the region during the year (Alpert et al., 1990). However, dust outbreaks due to the influence of anticyclones also occur over the western Mediterranean (Rodríguez et al., 2001). According to Moulin et al. (1998), spring and the beginning of summer is the preferred period for the development of depressions (Sharav cyclones) that have their origin in the great thermal gradient existing between the sea and the continent on that time. These cyclones cross north of Africa towards the Mediterranean Sea reaching Libya and Egypt. In these situations dust transport towards the central and the eastern Mediterranean occurs. In summer, the presence of the semi-permanent anticyclone over Libya prevents the depressions to develop across the northern flank of Africa and they only reach Tunisia. The combination of these two systems creates the ideal conditions for the transport of dust over the central Mediterranean and eastern Mediterranean.
More particularly, the transport over the Iberian Peninsula is attached to depressions off the south-eastern coast of the Iberian Peninsula or strong anticyclones over the Mediterranean (Rodriguez et al., 2001). As regards the transport of dust over the Iberian Peninsula, there are three characteristic periods (Querol et al., 2002):
Late autumn-Early winter: In this period important precipitations occur in the ITCZ (located between 3° N and 12° N) which prevent the re-suspension and injection of dust in the upper layers of the atmosphere over north Africa. The concentration of atmospheric aerosols in November in northern Africa is low and the highest temperature is registered over the Atlantic Ocean (Figure 1.31). The relative low temperature in north Africa in those months inhibits dust re-suspension. The occurrence of dust outbreaks over Iberia in this period is scarce. Querol et al. (2002) did not find any episode of transport of dust with high impact on PM levels over the Iberian Peninsula in November or December in the period 1996-2000. However, sporadic wet deposition of dust (red rains) has been documented over eastern Spain in autumn by Avila et al. (1997, 1998). These two facts are not in contradiction because these wet dust deposition episodes are caused by intense depressions which cause heavy rains and strong winds, thus PM levels are not affected.
Late winter-Early spring: The ITCZ is located around 10° N and the intense heating in the Sahel desert (over which the highest temperatures are registered in this part of the year, Figure 1.31) results in the vertical injection of dust in the free troposphere where it can be transported towards the Iberian Peninsula by two meteorological situations:

a) The presence of depressions located opposite to Portugal or at a lower latitude between the Cape of San Vicente, the Canary Islands and the strait of Gibraltar. These events are characterised by sharp (2-3 days) peaks in the PM daily time series (reaching up to 147 μgPM10 m^{-3} in the rural station of Carboneras in the south of Iberia, Rodríguez et al., 2001). The levels of PM suffer a sharp increase due to the plume-like behaviour of the African intrusion under this scenario. At the end of these events there is a rapid decrease of the PM levels due to the rain events following most of these events. An example of one of these episodes is shown in Figure 1.35.

b) An anticyclone over the Iberian Peninsula and north Africa produces narrow convex plumes that depart from the coast of the Sahel and travel over the Canary Islands and reach the Iberian Peninsula from its western part. These episodes have less frequency (1-2 events per year in the period 1996-2000) than the previous ones (4-5 events per year in the same period). These events are responsible for high levels of PM in the Canary Islands (Viana et al., 2002) and in the Basque Country (Viana et al., 2003). Reiff et al., (1986) studied examples of these types of dust transport episodes over the western coasts of Europe. Hermann (1903) reported a dust event that affected the Canaries, the Azores, Great Britain and central Europe while Spain was not affected. An example of one of these events is shown in Figure 1.36.

Late spring-summer: The displacement of the ITCZ towards higher latitudes induces the intense heating of the Sahara (Figure 1.31) and the consequent development of the north African thermal low and the considerable vertical growth of the boundary layer. This convective system pumps dust up to 5000 m.a.s.l. Once the dust is injected into the mid-troposphere it may be transported towards Iberia by the eastern branch of the high present over north Africa (lifted to upper atmospheric levels with respect to the winter scenarios, Rodríguez et al., 2001). In these cases the air masses are heavily loaded with dust and are transported towards the north covering most of the western Mediterranean basin and Iberia, with a wide plume of dust. Given that the transport of dust is carried out at a considerable altitude, a number of studies have documented episodes of dust transport over Europe reaching altitudes of up to 6 km without impact on the low atmospheric levels (Ansmann et al., 2003). Thus, although the transport takes place in high levels of the atmosphere (above 1500 meters), impact on PM levels in Iberia has been documented (Rodríguez et al., 2001, Viana et al., 2003, Salvador et al., 2004). An example of a summer dust event is presented in Figure 1.37.

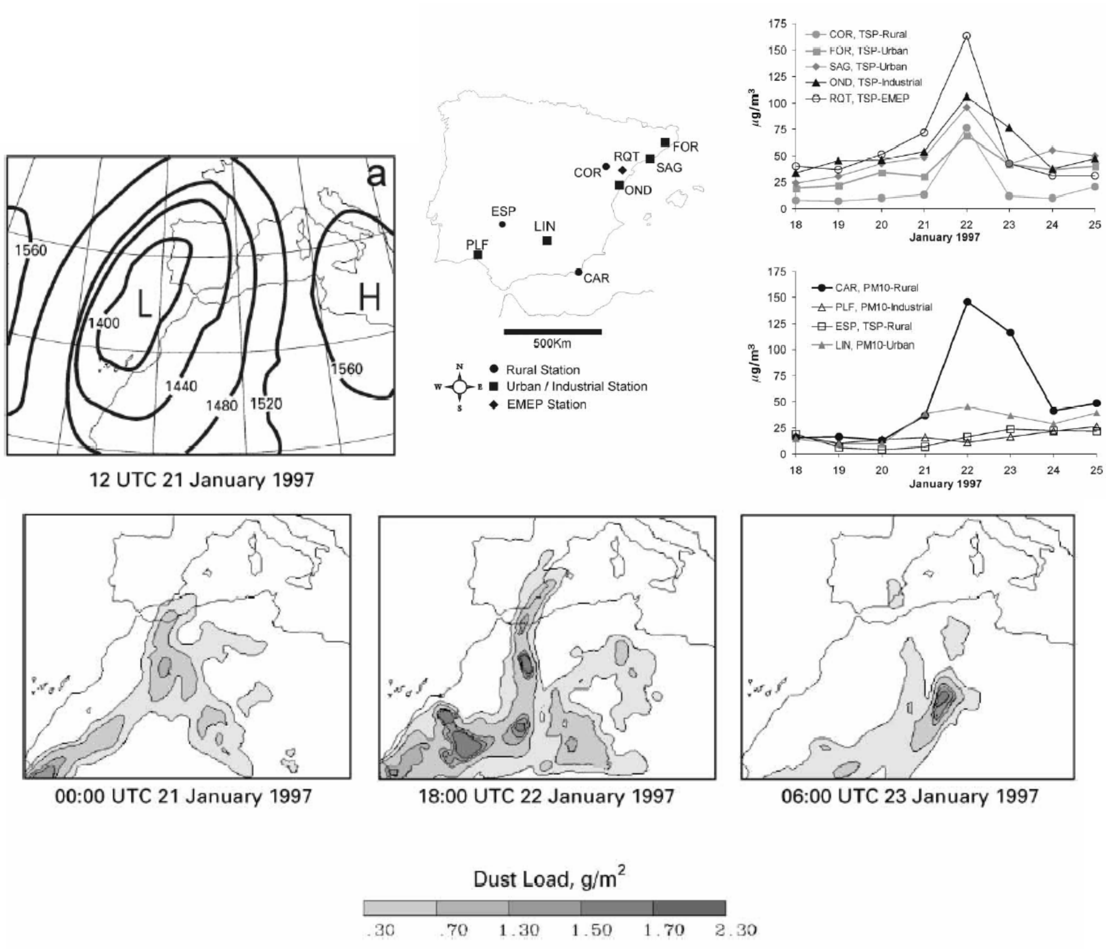


Figure 1.35. Example of dust outbreak in the Iberian Peninsula originated by the presence of a depression placed off southwest Portugal. This Figure shows the 850 geopotential height maps, the SKIRON dust load maps and the impact in PM levels in several air quality monitoring stations in Spain (from Rodríguez et al., 2001).

1.8 Long range transport of European air masses

Another source of PM that has been documented affecting PM levels in Spain due to long range transport precesses is the European continent. Central Europe is a highly populated and industrialised region and, as a consequence, an important source of anthropogenic aerosols and gaseous precursors. The effects of transboundary pollution within Europe and the associated problems such as acidification and eutrophication forced the European authorities to create the Convention on Long-range Transboundary Air Pollution in 1979. Initially, acidification and eutrophication were the two main problems investigated but, later, tropospheric O_3, persistent organic pollutants (POP's), heavy metals and particulate matter were introduced in the programmes in order to assess the transboundary transport of those pollutants.

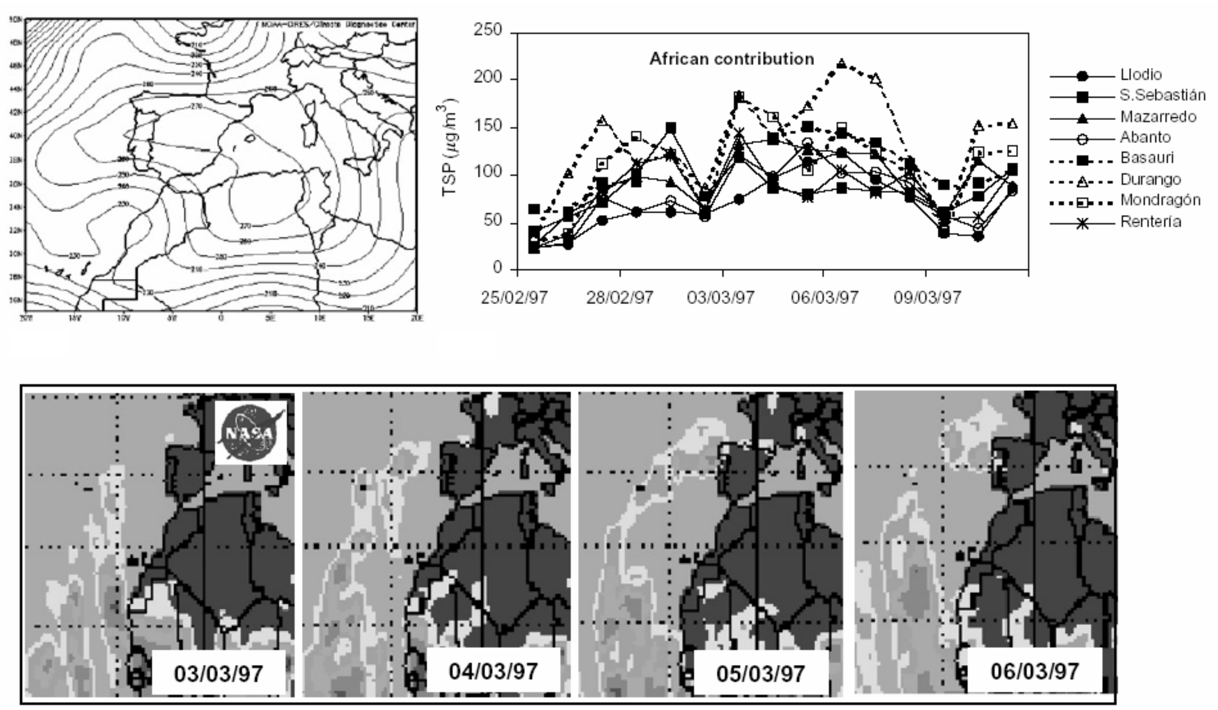


Figure 1.36. Example of a winter dust outbreak in the Iberian Peninsula originated by the presence of an anticyclone at surface level over the Iberian Peninsula. This Figure shows the 1000 hPa map of geopotential height for 04/03/97, the NASA-TOMS aerosol index maps and time series of PM levels in several air quality monitoring stations in the Basque Country (north of Spain) (from Viana et al., 2003).

As regards particulate matter transboundary pollution within Europe, Putaud et al., (2002) derived a European continental background concentration for PM10 and PM2.5 averaging annual mean concentrations measured at around 30 sites across central and northern Europe background. They obtained values of 7.0 ± 4.1 µg m^{-3} for PM10 and 4.8 ± 2.4 µg m^{-3} for PM2.5. This background includes both natural and anthropogenic contributions. The PM originated in the European continent even reaches to remote locations such as the Canary Islands where peaks of non sea salt sulphate of more than 4.4 µg m^{-3} in both the marine boundary layer and the free troposphere have been recorded. These peaks were attributed to long range transport of pollutants from the European continent (McGovern et al., 1999).

In the Iberian Peninsula, the northern areas are more exposed to intrusions of European air masses loaded with particulate matter (mainly sulphate and other secondary inorganic pollutants). European PM events have been described by Viana et al. (2003) but other authors also integrated the transport of pollutants from the European continent over the north of the Iberian Peninsula (Alonso et al., 2000, Gangoiti et al., 2002). The meteorological scenarios that are suggested to be responsible of European pollutants over Spain are: a) A high pressure over northern Europe (UK, Poland, Denmark) and b) a low pressure system over southeastern Europe (Italy, Greece). The first is more frequent than the latter, and the transport of European pollutants is more intense also for the first scenario. Nevertheless, the scenario giving rise to the European PM transport also favours the formation of the typical local and regional winter pollution episodes owing to the presence of an anticyclone over the Bay of Biscay. Thus, it is unclear the proportion of the high PM levels measured under this scenario that can be attributed to long range transport from Europe or to local/regional emissions (Viana et al., 2003). The European episodes in the Basque Country occur mainly in winter but they can also occur in summer (Alonso et al., 2000, Gangoiti et al., 2002). An example of a European PM event is shown in Figure 1.38.

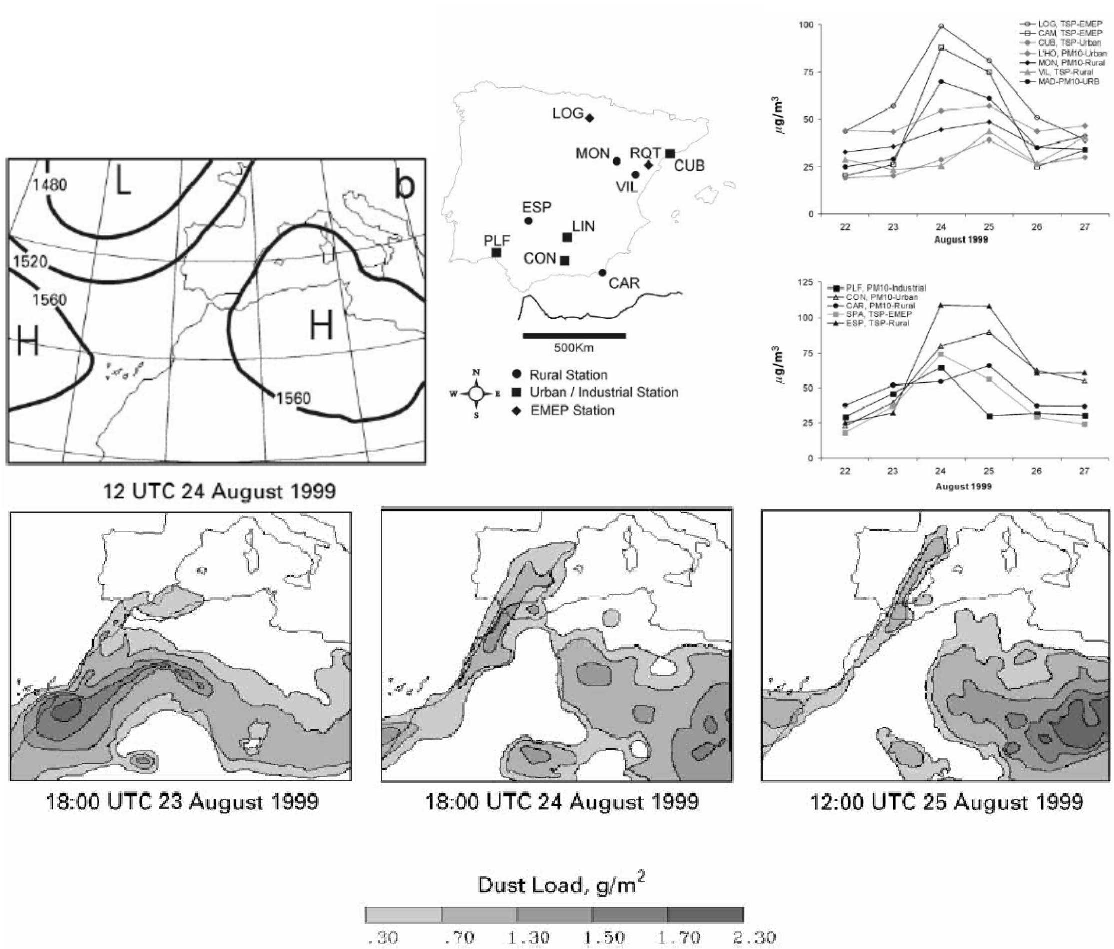


Figure 1.37. Example of a summer dust outbreak in the Iberian Peninsula originated by the presence of an anticyclone placed over Algeria and Tunisia. This Figure shows the 850 hPa map of geopotential height, the SKIRON dust load maps and the impact in PM levels in several air quality monitoring stations in Spain (from Rodríguez et al., 2001).

1.9 Regional episodes

A number of studies have reported summer maximum PM levels in rural stations in the Mediterranean basin (Bergametti et al., 1989b, Kubilay and Saydam, 1995, Querol et al., 1998, Rodríguez et al., 2003) but this does not stand for central and northern Europe (Monn et al., 1995, Turnbull and Harrison, 2000). The consistent behaviour of the levels of PM in rural stations located in a, more or less, broad region has to respond to synoptic scale processes or, at least, to mesoscale processes. Four main can explain this behaviour: a) the increased summer frequency of north African dust outbreaks in the area, b) increase of re-suspension by summer convective dynamics, c) the decreasing frequency of rain episodes in the area, and d) the aging and recirculation of polluted air masses.

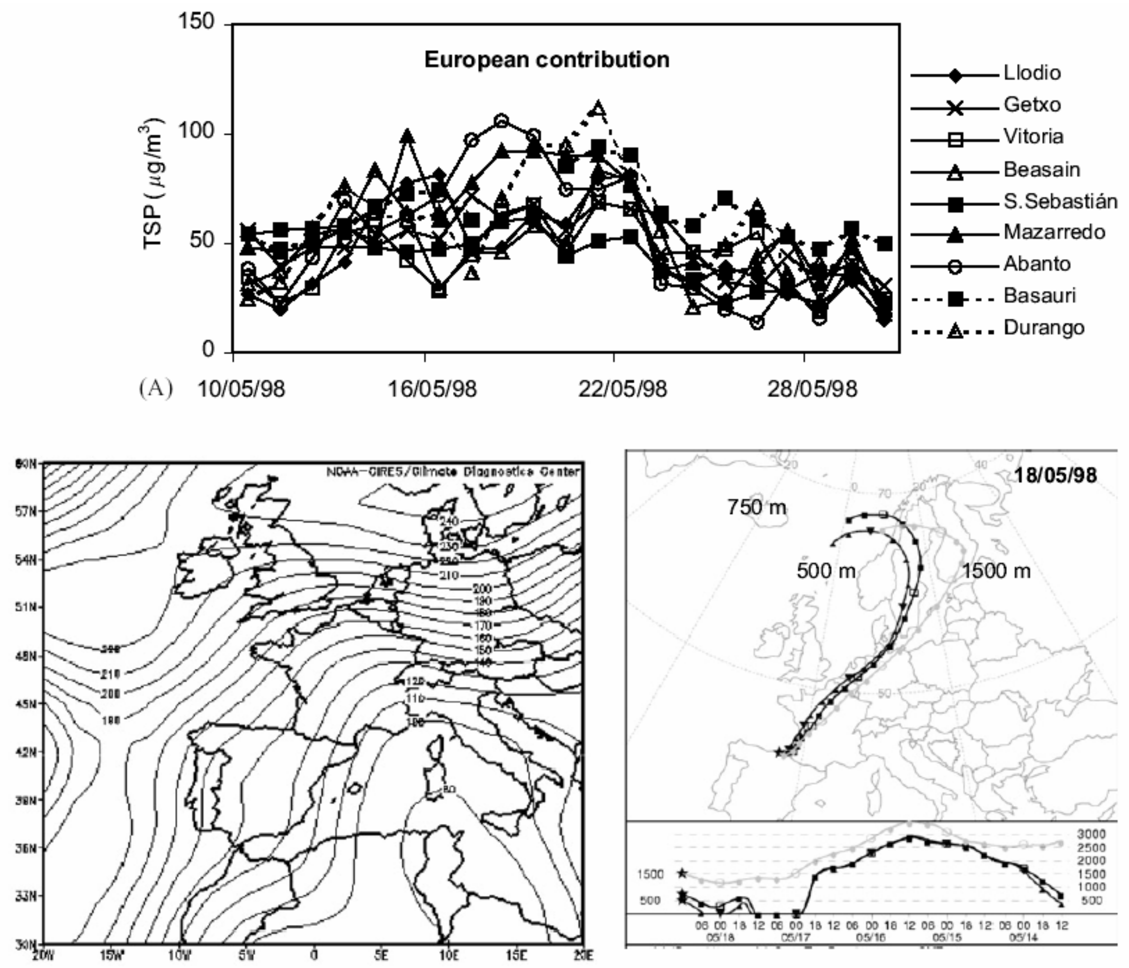


Figure 1.38. Example of a European PM episode in the Basque Country (north of Spain). This Figure shows the PM time series in several air quality monitoring stations during the episode, the 1000 hPa map of geopotential height for 18/05/98 and the 5-days back-trajectories at 500, 750 and 1500 m.a.s.l. (from Viana et al., 2003).

The synoptic conditions over the Iberian Peninsula in summer often show a weak pressure gradient and, often, the development of the ‘Iberian Thermal Low’. Under these circumstances, the transport of polluted air masses is driven by local circulations such as the breeze dynamics. By means of the circulation of the breezes, anthropogenic pollutants originated in urban or industrial environments reach the rural sites where high levels of O_3 and PM are recorded in summer (Millán et al., 1997, Alonso et al., 2000, Gangoiti et al., 2001, Rodríguez et al., 2003, Viana et al., 2003).
The regional episodes occur in all locations of the Iberian Peninsula but the impact of these events on PM levels is particularly important in the eastern flank of the Peninsula.

The dynamics (see section 1.5.2) results in the injection of pollutants at altitudes between 2 and 3 km and the subsidence over the sea creates 'stratified reservoir layers' of aged pollutants that re-enter in the circulation cells of the following days. The air masses with origin in the coastal Mediterranean areas re-circulate with the breeze to re-enter the cycle 2 or 3 days later (Millán et al., 1997). These mechanics and the poor renewal of air masses due to the low of synoptic flows, result increases in O_3 and PM concentrations in eastern Spain (Figure 1.39, Rodríguez et al., 2003). This meteorological context can persist for several days (up to 2 weeks) in summer, resulting in the atmospheric accumulation of airborne particulates driven by the sea breeze circulation. This results in an elevation of the background levels of PM in a regional scale. These regional events have more temporal persistence but less intensity than PM episodes with an African origin. Rodríguez et al. (2003) documented regional episodes as the second highest PM episode in eastern Spain after dust outbreaks.
Studies dealing with air pollution in the north of Spain also reveal the occurrence of regional episodes with marked daily cycles (not exactly in the same sense as in the Mediterranean area because they do not include re-circulation processes) that affect rural environments. The mesoscale processes linked with the development of the ITL are responsible of this increase (and of other photochemical pollutants such as O_3) in rural sites in the Basque Country during summer (Alonso et al., 2000, Gangoiti et al., 2002, Viana et al., 2003). A striking consequence of the regional episodes is that the grain size of PM in the Basque Country is finer in the summer months when 80% of the PM10 is PM2.5. The intense photochemical production of aerosols and the lack of air masses renewal during the regional episodes in summer induce the multiplication of fine range species such as sulphate aerosols. The higher re-suspension of coarser crustal size during summer is not enough to reduce the PM2.5/PM10 ratio (Viana et al., 2003).

1.10 PM deposition episodes

Aerosols are extracted from the atmosphere by deposition. Two extracting pathways are possible: wet and dry deposition. The first has to do with scavenging of particles by rain. The latter has to do with the fallout of particles due to gravitational reasons, or with deposition by inertial impaction and with surface adsorption or absorption (Lovett, 1994).
The British Isles, Germany, Poland and Czechoslovakia in Europe and important areas of north America emitted large amounts of acidic sulphur compounds during the 70's and the 80's. In this context, pH of rainfall reached values near 4 in northern Europe. After the adoption of several protocols in Europe and north America to reduce sulphur emissions (by changes in types of fuel, desulphurisation and abatement measures) recent studies showed a decline in S deposition owing to a reduction in SO_2 emissions among others (Buishand et al., 1988, Butler and Likens, 1991, Matzner and Meiwes, 1994, Hovmand and Kemp, 1996, Irwin et al., 2002, Avila and Alarcón, 2003). However, NO_x emissions (mainly by traffic) do not follow the same trend and the importance of nitric acid in the acidity of precipitation is increasing. Acid rain has been found to be responsible of soil and freshwater acidification and forest decline (Drablos and Tollan, 1980, Hutchinson and Havas, 1980), effects on human health (Speizer, 1989) and damage of building materials (Laurenzi Tabasso and Marabelli, 1992, Alastuey, 1994). Nowadays southeast Asia is in rapid industrialization process and turns out to be a major sulphur emission source. Acid rain episodes in Australia can be attributed to S emissions in this region. Other countries as Venezuela and Nigeria are major contributors for acidity in precipitation in the world (Brimblecombe, 1996).

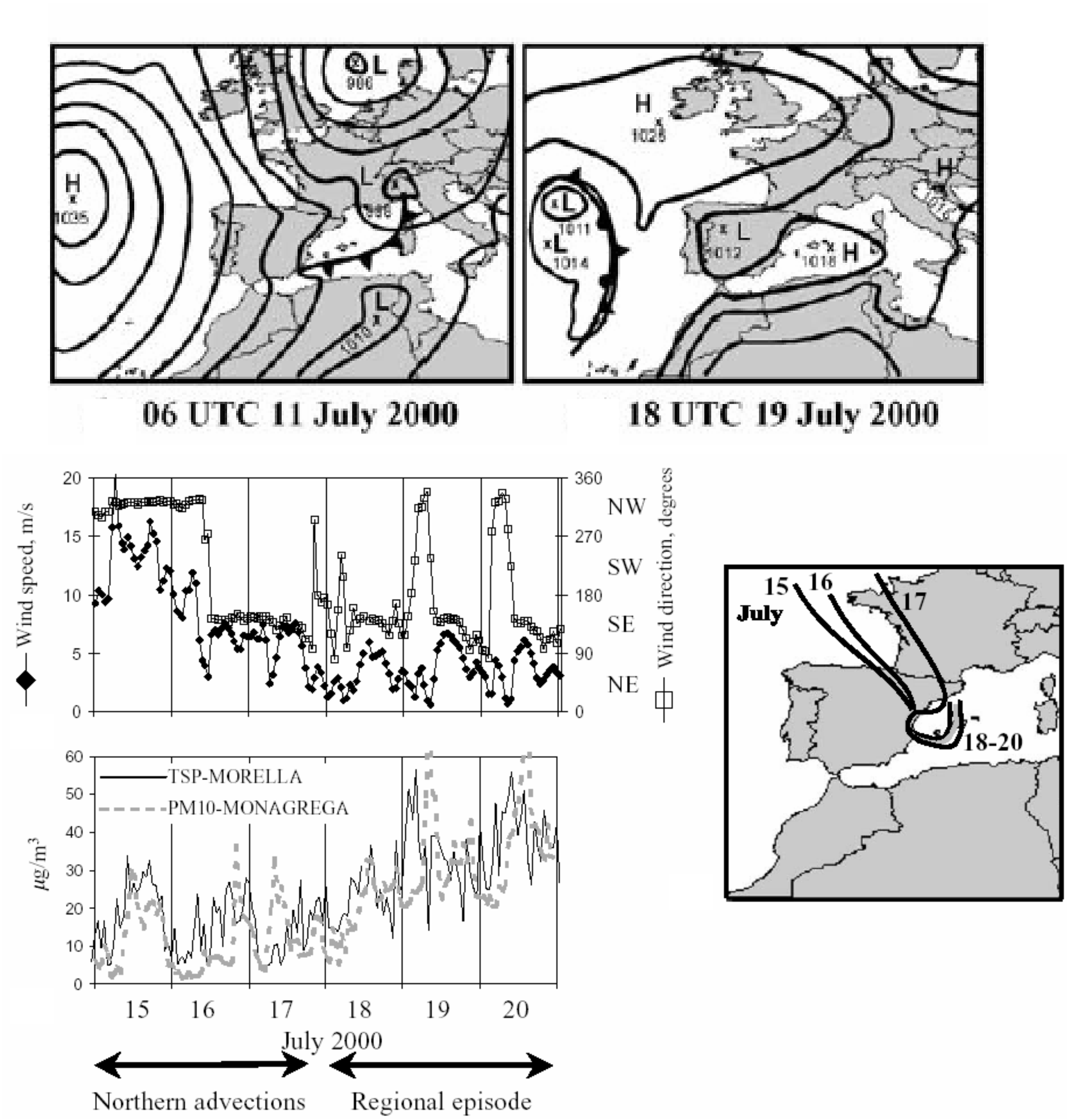


Figure 1.39. Example of a regional re-circulation PM episode in eastern Spain from Rodríguez et al. (2002). The regional episode is preceded by Atlantic advection. The figure shows the sea level pressure charts for a day in the Atlantic episode (11/06/2000) and another in the regional episode (19/07/2000), the hourly values of wind speed and direction and the hourly values of PM in two rural sites in eastern Spain (Morella and Monagrega) and the 3-days back-trajectories for 1000 m.a.s.l. during the period 15-20 July 2000.

Besides the anthropogenic emissions from northern and central Europe, rainfall characteristics in the Mediterranean basin are highly influenced by the presence of the north African deserts which represent a source of alkalinity (crustal aerosols).
With these two influences (in addition to the influence of the Atlantic Ocean and the Mediterranean Sea) the chemistry of precipitation in Europe shows differences with latitude. Sulphate and nitrate rain concentrations in southern Europe (sampled in rural background locations) are remarkable, despite the emissions of the gaseous precursors of those acidifying compounds (SO_2 and NO_x) are maximum in central Europe. This can be explained by the important role of photochemistry in the secondary aerosol formation in southern Europe which increases the speed and intensity of the chemical

transformation of SO_2 and NO_x into sulphate and nitrate (Gimeno and Hernández, 1997). Therefore, in spite of the high sulphate and nitrate concentrations, no severe acidification of rain water (Löye-Pilot et al., 1986, Losno et al., 1991, Rodà et al., 1993, Alastuey, 1999, Avila and Alarcón, 1999) or in lakes (Camarero and Catalán, 1998) has been reported in the Mediterranean basin. The alkalinity character of the crustal aerosol (especially the carbonate minerals) results in the neutralisation of acidity, a fact that affects southern Europe and particularly the Iberian Peninsula as can be seen in the report on the rain chemistry in rural locations around Europe in Table 1.5. The transport from different regions results in different chemical signals in the rainwater. Using back-trajectory analysis Avila and Alarcón (2003) studied the differences in the chemistry of rainwater under transport scenarios from four different regions: a) African, b) European, c) Oceanic and d) Local (Table 1.6). According to these results the African rains are less acidic (pH=6.70), the local rains as neutral (pH=5.27) and Oceanic and European rains as acidic (pH=4.98 and 4.67 respectively). The distributions of pH for rains from the four different origins are shown in Figure 1.40. Additionally, an increase in alkalinity in rainwater in the period 1983-2000 regardless the provenance of those rains (even for the African provenance) was detected and attributed to the effects of abatement strategies for SO_2 emissions in Europe (Avila and Rodà, 2002).

Table 1.7 summarises the annual deposition rates of African dust in several locations in Europe. The clear dependency of the dust deposition fluxes on the distance to the source is clear. Löye-Pilot et al. (1986) estimated in $3.9{\cdot}10^6$ tonnes yr^{-1} the total annual deposition flux of dust in the Mediterranean basin. In particular in Spain, the 11-years record of “red rains” presented by Avila et al. (1996) produced an annual mean dust deposition of 5.1 g m^{-2} yr^{-1}. This value is intermediate between the records by Löye-Pilot et al. (1986) and Bergametti et al. (1989b) who reported values of annual dust deposition of 12-13 g m^{-2} yr^{-1} for Corsica and 1 g m^{-2} yr^{-1} by Bücher and Lucas (1984) for central France.

The episodes of wet deposition of dust have a characteristic high alkalinity and high calcium concentration. This has been proved by several authors (Löye-Pilot et al., 1986, Caboi et al., 1992, Rodà et al., 1993, Avila et al., 1997, Singer et al., 2003). In general these rains contain a high load of dissolved ions. In northeastern Spain the red rains account for high percentages of total annual wet deposition: 46% for Ca^{2+}, between 20 and 25 % for Na^+, Cl^-, and Mg^{2+} and between 7 and 16 % for SO_4^{2-}, NO_3^- and NH_4^+, despite the fact that only 11% of the rain events were red rains. In addition to these species also important proportions of deposition fluxes of P, Al, Fe and K^+ are supplied with these rains. The deposition fluxes of some of these species are basic nutrients in northeastern Spain, and account for 27% of K^+, 45% of Ca^{2+} and 84% of Mg^{2+} of the fluxes needed for the biomass annual increment in that region (Avila et al., 1998).

The typical scenarios causing wet deposition of dust in the western Mediterranean (Martín Vide and Moreno, 1985, Bergametti et al., 1989b, Avila and Alarcón, 1999) are associated to the presence of a depression over southern Portugal or north Africa at low levels and an anticyclone over central or northern Europe. Studies on dust deposition in the Mediterranean basin are often based on collecting bulk deposition samples, that is, wet plus dry sedimenting deposition. In some cases, it is assumed that bulk deposition corresponds basically to wet deposition (Löye-Pilot et al., 1986, Camarero y Catalán, 1993, Avila et al., 1997, Avila and Alarcón, 1999). In particular, in Sardinia approximately 75% of the Saharan dust is deposited with precipitation (Guerzoni et al., 1992). Furthermore, a few wet episodes account for most (60-80 %) of the annual flux of dust particles (Löye-Pilot et al., 1986, Guerzoni et al., 1995b). In opposition to the maximum transport of suspended dust over the Mediterranean in summer, the deposition of dust is maximum in spring and autumn in close correlation with the wet seasons (Löye-Pilot et al., 1986, Avila et al., 1997, Guerzoni et al., 1997, Singer et al., 2003), while minimums are found in summer and winter. The summer minimums are not due to the lack of dust export over the Mediterranean (actually it is the period of maximum dust transport to the basin) but to the lack of precipitation and the strong upward movement of dust leading to a lower deposition rate than expected. Nevertheless, in case of long dust outbreaks dry deposition can be important (Dulac et al., 1989). An example of the estimations of dry deposition of dust is given by Singer et al. (1993) who estimated the annual dry deposition of dust in the north of Israel in 6 g m^{-2} yr^{-1} while the estimations of total annual fallout of dust is in the range 30-60 g m^{-2} yr^{-1}.

Table 1.5. Mean concentration of major ions in stations around Europe. Units for ionic concentrations are in µeq L^{-1}. The sampling period of each study is indicated (compiled by Carratalá and Bellot, 1998).

Author(s)	Site, Country	Period	pH	NO_3^-	SO_4^{2-}	NH_4^-	Ca^{2+}
Chaves (2001)	Albalate, Spain	1996-1998	6.2	38	73	47	179
Chaves (2001)	Cerollera, Spain	1996-1998	5.9	21	49	37	82
Chaves (2001)	Torre Miró, Spain	1996-1998	6.0	24	59	75	62
Chaves (2001)	Carrascales, Spain	1996-1998	5.8	30	74	61	80
Chaves (2001)	Sénia, Spain	1996-1998	5.3	35	56	94	69
Pedersen et al. (1992)	Birkenes, Norway	1990	4.4	34	27	33	7
Conlan and Longhurst (1993)	Manchester, UK	1990	4.9	24	111	19	74
Pedersen et al. (1992)	Witteven, Netherlands	1990	4.8	51	87	139	19
Pedersen et al. (1992)	Illmtz, Austria	1990	4.5	41	73	56	96
Pedersen et al. (1992)	Ispra, Italy	1990	4.3	62	35	71	17
Pedersen et al. (1992)	Kamernicki, Yugoslavia	1990	5.1	36	75	87	82
Pedersen et al. (1992)	Iraty, France	1990	5.1	22	23	57	21
Pedersen et al. (1992)	Braganza, Portugal	1990	5.4	10	25	18	34
Pedersen et al. (1992)	Aliartos, Greece	1990	4.8	47	159	158	204
Camarero and Catalán (1993)	Pyrenees, Spain	Aug87-Aug88	5.3	18	51	22	94
Bellot and Golley (1989)	Prades, Spain	Aug81-Jun88	5.0	20	69	28	66
Roda et al. (1993)	Zaragoza, Spain	Mar86-Feb87	6.8	34	76		81

Table 1.6. Mean ionic concentration in bulk deposition for four meteorological provenances at the Montseny (NE Spain) for the period 1 August 1983 to 31 July 2000. VWM indicates the Volume-weighted mean and VWsd indicates the volume-weighted standard deviation. Units for conductivity are in µS cm^{-1} and units for ionic concentrations are in µeq L^{-1} (from Avila and Alarcón, 2003).

	Cond.	pH	Alk.	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-
					African						
VWM	35.1	6.70	98.4	40.3	6.3	143.0	17.4	19.1	24.0	52.4	47.9
VWsd	13.7		59.9	10.4	2.3	57.4	4.2	5.2	5.7	10.3	9.9
					European						
VWM	39.5	4.67	-22.5	24.7	4.5	51.0	11.7	55.6	44.5	74.7	29.4
VWsd	14.2		12.3	11.5	1.7	24.3	6.3	16.9	13.4	27.5	13.8
					Local						
VWM	17.7	5.27	8.3	17.0	3.9	47.6	8.7	31.3	26.0	51.0	21.2
VWsd	8.3		16.3	7.8	1.7	14.5	3.6	8.0	6.3	12.4	9.7
					Oceanic						
VWM	10.2	4.98	-8.9	17.6	2.8	23.5	6.5	18.4	17.3	32.3	22.4
VWsd	4.4		11.0	5.1	0.8	4.1	1.2	3.2	2.0	5.4	6.0

Table 1.7. Dust deposition amounts (compiled by Goudie and Middleton, 2001).

Author(s)	**Location**	**Annual deposition (g m^{-2})**
Drees et al. (1993)	SW Niger	200
Herut and Krom (1996)	Israeli coast	72
Nihlen and Olsson (1995)	Aegean Sea	11.2-36.5
Le Bolloch et al. (1996)	southern Sardinia	6-13
Löye-Pilot et al. (1986)	Corsica	12.5
Bergametti et al. (1989b)	Corsica	12
Avila et al. (1996)	NE Spain	5.1
Bücher and Lucas (1984)	central France	1
Wagenbach and Geis (1989)	Swiss Alps	0.4

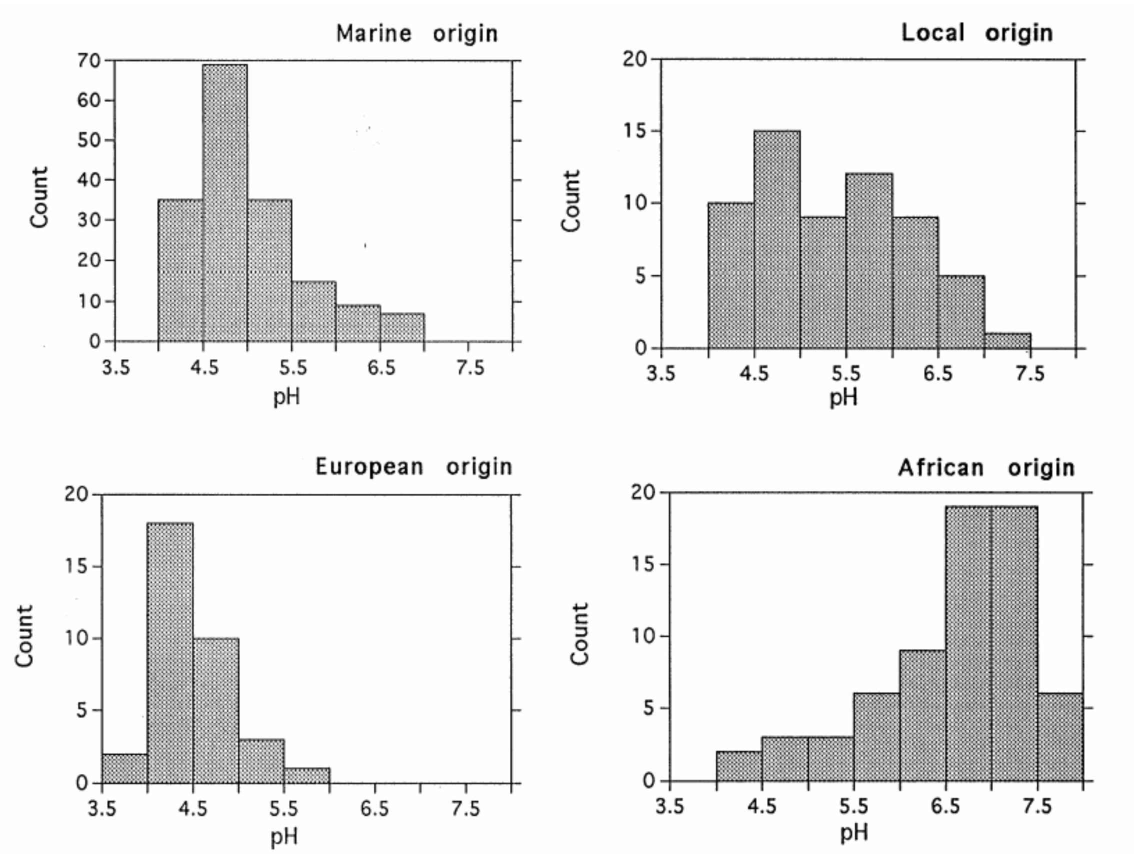


Figure 1.40. pH of rain in northeastern Spain classified as a function of the air mass origin (from Avila and Alarcón, 1999).

2. Objectives

2. OBJECTIVES

PM play an important role in the troposphere affecting ecosystems and biogeochemical cycles:

- Affect climate by scattering and absorbing radiation and by acting as CCN.
- Degrade visibility.
- Affect humans' health.
- Influence atmospheric acidity.
- Contribute to the formation of sediments.
- Damage building materials and monuments.
- Serve as nutrient to biogenic species such as phytoplankton

African high dust air mass intrusions over Spain, episodes such as long range transport of pollutants from the European continent and the development of regional pollution episodes exert an important influence on the above factors on a regional scale.

PM may be extracted from the atmosphere by wet and dry deposition. There are large uncertainties in the quantification of PM deposition fluxes. Furthermore, the meteorological scenarios which cause wet deposition events have not been described in detail.

Owing to the health effects of PM, the forecasting of episodes of high levels of suspended PM is an important task to be undertaken. For this purpose it is essential to determine factors such as the meteorological scenarios that provoke long range transport, the transport seasonality and the impact of such events on different regions of the Iberian Peninsula.

Different research groups in Spain have undertaken studies evaluating the impact of African, European and regional episodes on ambient air levels of suspended PM (Querol et al., 1998; Millán et al., 1997; Rodríguez et al., 2001; Rodríguez et al., 2003; Viana et al., 2002; Viana et al., 2003; Salvador et al., 2004) while others have studied the impact of such events on the chemistry of rainwater (Avila et al,. 1997; Avila and Alarcón, 2003). Given that most PM events accompanied by rain episodes lead to a decrease in the levels of suspended PM, studies focusing solely on suspended PM levels would not detect the occurrence of such 'wet episodes'. Conversely if only wet deposition is evaluated the 'dry episodes' would not be detected. To our knowledge no study has been developed integrating the evaluation of levels of PM and the deposition fluxes in regional background stations. Furthermore these studies do not cover the entire Iberian Peninsula but focus on specific regions.

Moreover, a number of studies have been carried out in stations located in the free troposphere where mixing with anthropogenic emissions is not treated, while others have been developed in areas highly influenced by local emissions where contributions of long range transport processes such as African dust outbreaks or European PM events cannot be discriminated.

In this interdisciplinary research project the main objective is to develop a conceptual model for the characterisation and description of the episodes which exert an influence on the regional background suspended PM and deposition patterns in the Iberian Peninsula. This will allow to link source areas, transport scenarios and deposition with the levels of suspended and deposited PM at different regions. To this end, African high dust air mass intrusions from north Africa will be deeply treated, but other episodes such as European PM long range transport, regional events and Atlantic PM transport will be also studied in detail. The main sub-objectives are:

1- To obtain a complete database of daily PM episodes affecting the regional background in different areas of Iberia in order to describe the spatial and temporal patterns of the different PM episodes over the Iberian Peninsula. The determination of the meteorological scenarios accounting for each type of episode will be also undertaken. Especial attention will be paid to the meteorological scenarios inducing wet deposition episodes. The temporal and the spatial variability will be described with the objective of determining the periods and geographical areas in which these events occur more frequently.

2- To evaluate the impact of these PM events on the air quality monitoring stations located in rural areas (regional background). This is valuable for future studies and for air quality monitoring. The impact of the PM events on different size fractions of the PM (TSP, PM10 and PM2.5) will be evaluated. In this context it is important to highlight the possible responsibility of these events in the exceedances of the daily and annual limit values established by the EU/1999/30 European Directive and in the draft of the AQ Directive of September 2005.

3- To evaluate the influence of the African events in the time series of wet deposition registered in regional background sites.

The information obtained from this study will is useful for the following applications:

A- To discriminate the impact of the differentiated PM episodes on the PM levels measured by the air quality monitoring stations in the Iberian Peninsula. Differences between geographical-climate areas and seasonal periods with higher probability of occurrence of specific events can be evaluated with the results of this study. It is important to note that the EU/1999/30 Directive contemplates the possibility for derogation of the exceedances of the limit value registered in periods in which natural events ("*volcanic eruptions, seismic activities, geothermal activities, wild-land fires, high-wind events or the atmospheric re-suspension or transport of natural particles from dry regions*") occur, if these are adequately demonstrated. This study will give information on natural events such as African air mass intrusions over the Iberian Peninsula.

B- To predict dust outbreaks and other PM episodes over the Iberian Peninsula. In particular, the validation of numerical models which incorporate aerosol modules. One of the main objectives of these models is to issue forecasts of PM episodes. This will help future efforts in modelling PM episodes over the Iberian Peninsula with especial interest in the transport of dust from north Africa.

C- To determine fluxes of nutrients in the Iberian Peninsula and the seasonal and geographical patterns of those fluxes.

An important issue still to be covered by the scientific community is the identification of African dust source areas and the evaluation of the impact of the different dust sources on PM levels recorded at sampling sites at the Iberian Peninsula (located far away from the desert).

3. Methodology

3. METHODOLOGY

In order to complete the above objectives a methodology strategy has been designed with the following stages:

1- Selection of time series of PM levels and particulate deposition chemistry covering the different climatic areas of the Iberian Peninsula:

1.a- PM from regional background EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe) air quality monitoring network (AQMN).

1.b- PM from two rural stations, Valderejo (which belongs to the AQMN of the Autonomous Government of the Bask Country) and Monagrega (which belong to the AQMN of ENDESA).

1.c- Wet deposition chemistry from a rural station in La Castanya (northeast Spain).

The selection of time series from regional and rural background stations was made in order to avoid the direct anthropogenic influence, and consequently to undertake a study with the evaluation of regional background levels.

2- Study of correlations in the daily time series between gaseous pollutants and PM levels on a daily basis. The levels of gaseous pollutants such as SO_2 and $NO_x(NO+NO_2)$ measured at the EMEP stations were so close to the detection limit of the instrumentation that made the correlation impossible in most cases. On the contrary, levels of O_3 were correlated with PM levels seeking for episodes related with regional events.

3- Interpretation of the origin of air masses and the synoptic scenarios which cause such transport using:

3.a- Meteorological maps of different variables such as mean sea level pressure (MSLP), geopotential height and accumulated precipitation obtained from the NOAA FNL meteorological gridded data archive and from the NOAA-CIRES Climate Diagnostics Center.

3.b- Calculation of back-trajectories using the HYSPLIT4 model (Draxler and Rolph, 2003)

4- The identification of African dust episodes was made using:

4.a- Maps of the TOMS (Total Ozone Mapping Spectrometer) aerosol index (Herman et al., 1997).

4.b- Maps of desert dust models as NAAPS (by the NRL-Naval Research Laboratory, http://www.nrlmry.navy.mil/aerosol/) with global coverage and SKIRON/Eta (Kallos et al., 1997, Nickovic et al., 2001, http://forecast.uoa.gr) with coverage of the Mediterranean basin.

4.c- "True color" images from the NASA SeaWIFS project (http://seawifs.gsfc.nasa.gov/SEAWIFS.html, McClain et al., 1998).

5- Identification of possible European PM episodes using the sulphate maps of NAAPS.

Developing this methodology a group of archives have been constructed detailing the type of PM episode occurring in each of the seven regions on a daily basis. These files serve as basis for carrying out other studies included in this thesis.

3.1 Measurement of levels of PM and wet deposition sampling

Provided the great climatic differences existing across the Iberian Peninsula, for a study of this type it is required to divide the Iberian Peninsula in different areas. Thus, seven areas were selected according to the following criteria:

- Gographical location: The proximity to the European continent, the oceans or the African continent could influence PM characteristics and the frequency of occurrence of PM events for a given area.
- Climate: Factors such as the rainfall regime, the advection of air masses in the synoptic scale and the development of mesoscale circulations (sea breezes) exert an important influence on PM episodes. Also the different soil cover of the different regions has a high influence on the resuspension of soil-derived particles.

The seven areas differentiated for the study are shown in Figure 3.1.

Figure 3.1. Geographical areas differentiated for the study.

These geographical zones in the Spanish Iberian Peninsula were defined and selected with the aim of covering the following climatic conditions:

- NW is a humid and well ventilated area frequently affected by westerly winds and frontal systems.
- N is adjacent to the Cantabrian coast in the north is likely to be affected by European air mass transport due to its vicinity to the European continent but, in general, its climatic characteristics do not differ from those of the NW area.
- NE on one hand is adjacent to the European continent and due to its location European air mass transport may occur easily. On the other hand, this area bordering the Mediterranean Sea is dominated by the coastal circulations interacting with topography frequently resulting in atmospheric layering and recirculation of polluted air masses (Gangoiti et al., 2001, Millán et al., 1997 and 2000).
- E climatic characteristics are similar to those described for NE but its location reduces the possible occurrence of European air mass transport.
- Central area (C) in the plateau is an elevated area which acts as the core of thermal low pressure systems in summer.
- SE is influenced by the Mediterranean Sea but also by the vicinity of the African continent as a source of crustal aerosols.
- SW is also close to the African continent but differs from the SE area in a higher ventilation due to the influence of the Atlantic Ocean.

The Convention on Long Range Transboundary Air Pollution (LRTAP), signed in 1979 has addressed some of the major environmental problems of the UE region. The EMEP programme provides parties under the LRTAP Convention with qualified scientific

information to support the development and further evaluation of the international protocols on emission reductions.
Initially, the EMEP programme focused on assessing the transboundary transport of species causing acidification and eutrophication. Subsequently, the scope of the programme widened to address the formation of ground level ozone, persistent organic pollutants (POPs), heavy metals and PM.
The EMEP monitoring network is built up of 150 stations from 35 countries covering the European continent. These stations have the following characteristics:

- They must be placed in rural areas.
- They must be placed at least 40 km away from building areas.
- They must be placed at least 40 km away from industrial sources of pollutants.
- They must not be placed neither in valleys nor in mountains peaks.
- The setting of the stations must not be placed in a place with strong wind.

The location of the stations selected for this study is shown in Figure 3.2. Table 3.1 reports on the coordinates and the altitude of the stations and the data availability for each station. Views of the EMEP stations from which PM and wet deposition data used in this study are shown in Figure 3.3 (when available at http://www.emep.int/). Photographs of Noia, O Saviñao, Risco Llano, Peñausende and Els Torms stations were not available.
In the EMEP stations meteorological measurements are also carried out. These measurements comprise precipitation data which will be used for characterising the synoptic scenarios causing the different PM events over the Iberian Peninsula (chapter 4). These measurements are validated after although these are not issued as official meteorological data.

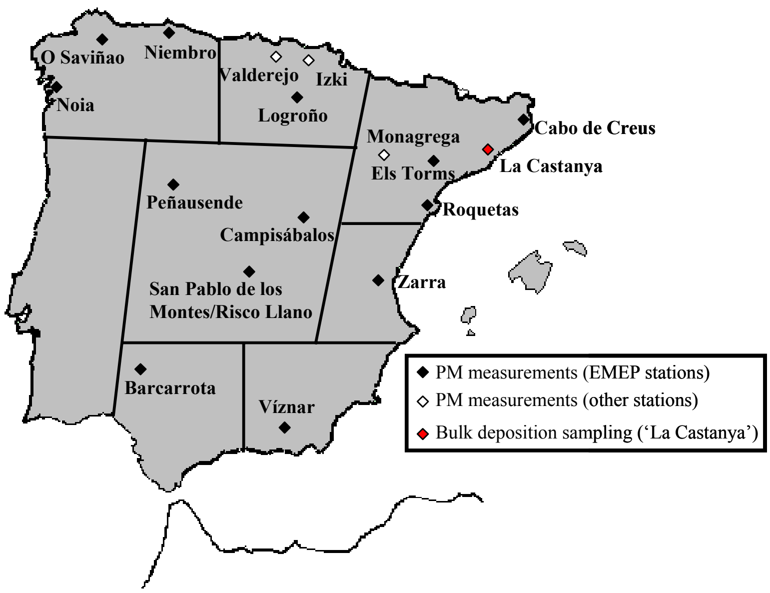


Figure 3.2. Location of the measurement stations used in the study in the seven areas differentiated.

In addition to PM data from the EMEP stations, data from three rural stations measuring PM10 were also used for this study (Valderejo, Izki and Monagrega). The first two belong to the AQMN of the Autonomous Government of the Basque Country, the latter belongs to the AQMN of ENDESA. An image of the Monagrega station is shown in Figure 3.3.
The measurement of PM in the EMEP stations was made by the gravimetric method. This is a reference method defined in EU Directive 1999/30/EC for the determination of

the mass concentration of PM as the European Standardisation Organisation (CEN) designed for PM10 measurements in EN 1234-1 (CEN, 1998). Although a reference method is not yet adopted for PM2.5, also the gravimetric method will be probably recommended (Lazaridis et al., 2002). It consists on the sampling of air through a suitable filter and subsequent evaluation of the sampled mass by pre- and post-weighing. An example of the instrument which is the reference high volume sampler of the CEN standard (1998) for PM measurements, is the high volume sampler Sierra–Andersen/GMW model 1200 shown in Figures 3.4 and 3.5. Without any special inlet on the high volume sampler the cut-off size is between 50-100 μm, termed as total suspended particle matter (TSP). If PM10 or PM2.5 is measured, a sampling inlet with a cut off of 10 or 2.5 μm should be used. When ambient air is drawn into the inlet, the acceleration nozzles fractionate particles larger than the defined size. The air containing the desired particle fraction is channelled through to the filter holder. A constant flow rate of 68 $m^3 h^{-1}$ is needed for a standard high volume sampler with the design of the EN1234 reference method. However, the high volume samplers used in the Spanish EMEP stations are high volume PM1025 MCV models. These samplers follow the same working principles as the Sierra-Andersen with the only exception of the constant flow rate which is set to 30 $m^3 h^{-1}$ instead of 68 $m^3 h^{-1}$. The filters are made of quartz or glass fibre due to the good retention properties. However, the gravimetric method is also subject to a number of sampling artefacts and losses of volatile components, such as ammonium nitrate when the ambient temperature is high. The gravimetric method allows chemical analysis of the filters after weighing. SO_4^{2-}, NO_3^-, NH_4^-, Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^- are analysed from the filters obtained in the EMEP stations by ion chromatography (see details in EMEP, 2001) although these chemical data will not be used in this work.

PM10 measurements at Monagrega were performed continuously with TEOM (tapered element oscillating microbalance) instrumentation. These instruments incorporate an inertial balance that directly measures the mass collected on an exchangeable filter cartridge by monitoring the corresponding frequency changes of a tapered element (Figure 3.6). In Valderejo and Izki continuous measurement of PM10 was made with the β-attenuation method. This is based on monitoring the attenuation of β-radiation during one hour through the filter where the PM is continuously being filtered (Figure 3.7). TEOM and β-attenuation instruments have been proved to underestimate PM10 mass in winter due to the loss of species (such as NH_4NO_3 and specific semi-volatile organic compounds) due to the difference of temperature between ambient conditions and the heated inlet (50°C to prevent water condensation) (Allen et al., 1997). The underestimation of measurement of PM10 levels at Monagrega station was quantified by means of a comparison with DIGITEL DH-80 gravimetric equipment for 143 measurement days (Rodríguez, 2002). A relation of TEOM = 1.01 x DIGITEL with $R^2 = 0.85$ was found for spring, summer and autumn whereas for winter the relation was TEOM = 0.77 x DIGITEL with $R^2 = 0.73$. This results in an underestimation of PM10 mass in winter of 23%.

In certain occasions PM data from a continuous sampling carried out at La Castanya during 2002-2003 will be used. This sampling is part of the work carried out by Sonia Castillo in her PhD thesis within the same scientific project of this work (financed by the Spanish Ministry of Science of Technology, project REN2001-0659). The work of Sonia Castillo treats on the chemical characterisation and source apportionment of atmospheric aerosols with particular interest on African dust. Chemical analyses of PM filters collected at La Castanya were also performed in her work and a complete description of the sampling methodology and the chemical analyses are presented in the

PhD thesis dissertation of Sonia Castillo (Castillo, 2006). Nevertheless a brief description of the methodology followed is presented here.
The sampling was performed using a high volume captor (DIGITEL DH80) for 24 h periods, three consecutive times per week since March 2002 until September 2003. Atmospheric particulates were collected on quartz microfibre filters (Schleicher and Schuell, QF20). Once sampled, filters were weighed and TSP concentrations were determined by gravimetry.
The chemical composition of the material collected on the filters was analysed with the procedure stated below. In general two of the three weekly samples were analysed. However, when the three samples corresponded to African dust outbreaks, the chemical composition was obtained for all of them.
A fraction of the filter was acid digested (HF; HNO_3; $HClO_4$) following the methodology described by Querol et al. (2001). The solution obtained was used for the determination of concentrations of major and trace elements in TSP by means of ICP-AES and ICP-MS. The water soluble fraction was extracted with distilled water. Solutions obtained were utilised for determinations of the concentrations of water soluble anions (sulphate, nitrate and chloride) by capillary electrophoresis and levels of NH_4^+ by means of Colorimetry FIA. In addition for selected samples, levels of major soluble cations (Na^+, Ca^{2+}, Mg^{2+} and K^+) were determined in the water leachates by ICP-AES. Levels of total carbon were determined by LECO. In addition, levels of elemental carbon (EC) and organic carbon (OC) were determined by a thermal/optical method (NIOSH method 5040).
Data on chemical analyses of aerosols will be used as a complementary tool in chapter 8 of this dissertation with the objective of detecting a chemical signal in African dust reaching the Iberian Peninsula from different African dust source areas. In no case the chemical description of the aerosols is an objective of this work.
Weekly data of bulk deposition from the rural station at La Castanya station will be also used in this study (Figure 3.2, Table 3.1). At La Castanya bulk deposition was collected with an open bulk (Figures 3.8 and 3.9) deposition collector (placed 1.5 m above the ground) which consisted of a 19-cm diameter-polyethylene funnel connected by tygon tubing to a 10 L polyethylene bottle. A clean nylon sieve was placed in the neck of the funnel to prevent sample contamination from insects or particle debris.
The deposition samples were filtered (Millipore filters 0,45 μm pore size) and then the soluble fraction was analysed and concentrations of the major ions (SO_4^{2-}, NO_3^-, NH_4^-, Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-) were analysed. pH and conductivity were analysed at CREAF. Avila (1996) gives details of the methods used for chemical analysis of the deposition samples at La Castanya (Table 3.2). At La Castanya the insoluble fraction of heavy loaded simples was weighted and, if enough material was available, it was analysed for mineralogy (X-ray diffraction with Siemens D500 diffractometer) and elemental composition (following the procedure described in Avila et al., 1998). These data are used to identify a chemical signal of each type of episode. The details of the chemical signal of each episode will be discussed in the results section.

Table 3.1. Coordinates, altitude and data availability at the PM measurement stations used in this study.

Station name	Longitude (º E)	Latitude (º N)	Altitude (m.a.s.l.)	PM measurements	Wet deposition sampling
EMEP Network (Daily levels, PM with gravimetric method)					
San Pablo de los Montes	- 4º 20'	39º 23'	917	1985-2000 (TSP)	
Roquetas	0º 29'	40º 49'	44	1987-2000 (TSP)	
Logroño	- 2º 30'	42º 27'	445	1988-2000 (TSP)	
Noia	- 8º 55'	42º 44'	683	1993-2000 (TSP)	
Viznar	- 3º 28'	37º 14'	1230	1995-2002 (TSP) 2001 > (PM10, PM2.5)	
Niembro	- 4º 51'	43º 27'	134	1999-2002 (TSP) 2001 > (PM10, PM2.5)	
Campisábalos	- 3º 09'	41º 17'	1360	1999-2002 (TSP) 2001 > (PM10, PM2.5)	
Cabo de Creus	3º 19'	42º 19'	23	1999-2002 (TSP) 2001 > (PM10, PM2.5)	
Barcarrota	- 6º 55'	38º 29'	393	1999-2002 (TSP) 2001 > (PM10, PM2.5)	
Zarra	- 1º 06'	39º 05'	885	1999-2002 (TSP) 2001 > (PM10, PM2.5)	
Peñausende	- 5º 52'	41º 17'	985	2000-2002 (TSP) 2001 > (PM10, PM2.5)	
Els Torms	0º 43'	41º 24'	470	2000-2002 (TSP) 2001 > (PM10, PM2.5)	
Risco Llano	- 4º 21'	39º 31'	1241	2000-2002 (TSP) 2001 > (PM10, PM2.5)	
O Saviñao	- 7º 42'	43º 14'	506	2001-2002 (TSP) 2001 > (PM10, PM2.5)	
Air quality monitoring network of the Basque Country (Daily levels, PM with β-attenuation method)					
Valderejo	-3º 14'	42º 53'	911	1999 (TSP) 2000 > (PM10)	
Izki	-2º 30'	42º 39'	835	2001 > (PM10)	
Air quality monitoring station of ENDESA (Daily levels, PM with TEOM method)					
Monagrega	-0º 12'	40º 30'	600	1996 > (PM10)	
Estació biologica de La Castanya (Weekly sampling, bulk wet deposition)					
La Castanya	02º 21'	41º 46'	700	2002-2003 (Chemical analyses of TSP)	1983-2000 & 2002-2003

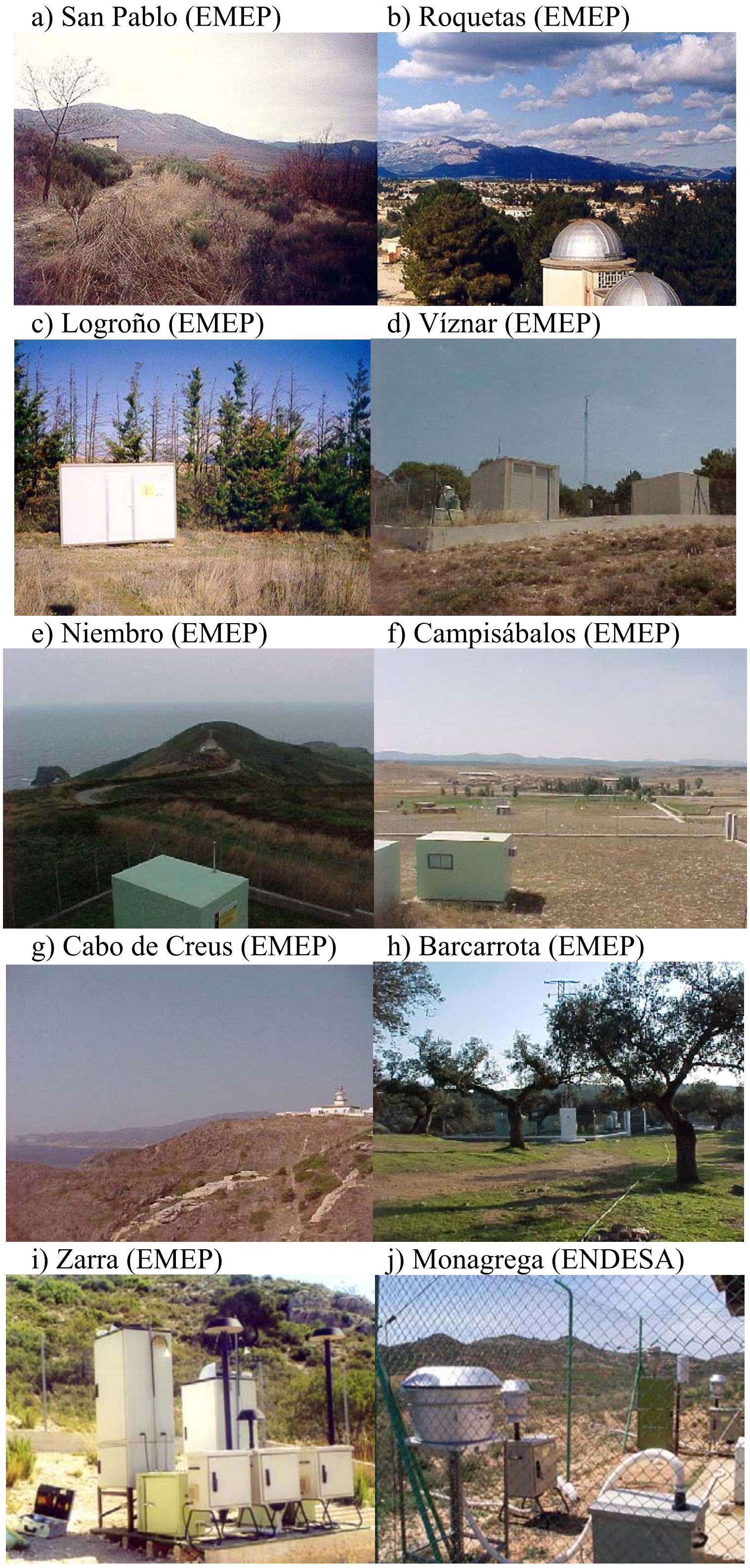


Figure 3.3. Views of some of the monitoring stations where PM data used in this study were recorded (from http://www.emep.int/ and Rodríguez, 2002).

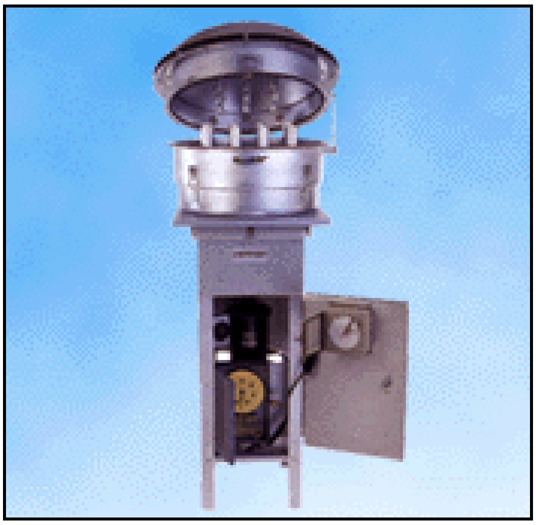


Figure 3.4. Image of a PM high volume sampler.

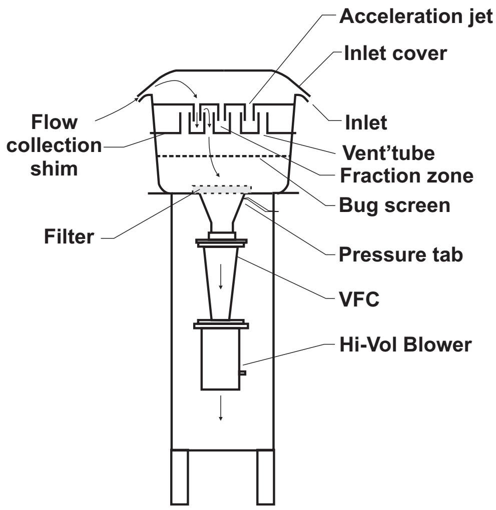


Figure 3.5. Scheme of a PM10 high volume sampler which is the high volume reference sampler according to CEN standard. This model is the Sierra–Andersen/GMW-1200 (from EMEP, 2001).

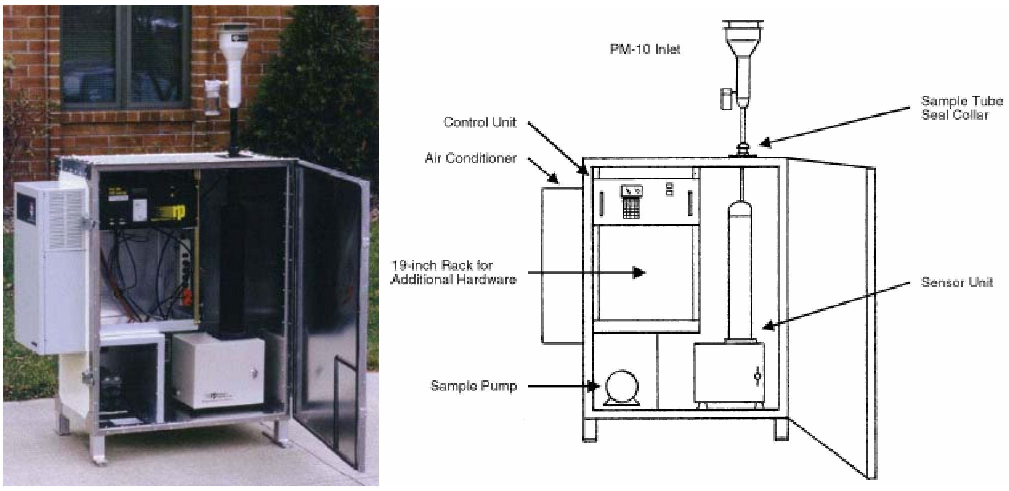


Figure 3.6. Image and scheme of the typical installation of a Rupprecht & Patashnick TEOM instrument model 1400a (from http://www.rpco.com/).

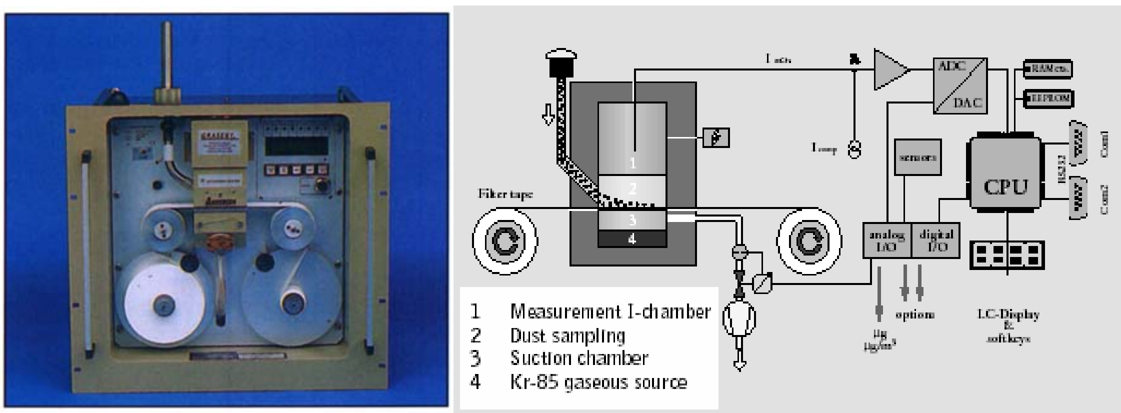


Figure 3.7. Image and scheme of an Andersen β-attenuation instrument model FH62I-N (from http://www.esm-online.de/andersen/).

Figure 3.8. Image of the bulk deposition sampler at La Castanya.

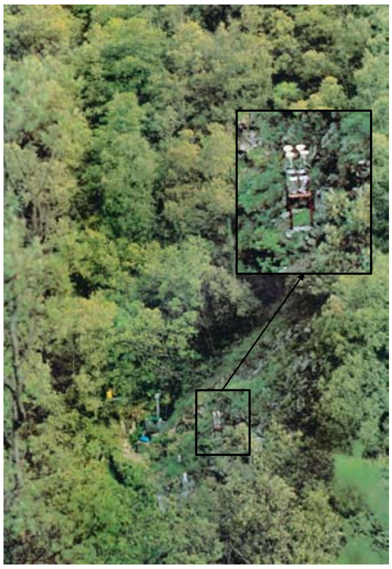


Figure 3.9. Image of La Castanya bulk deposition sampling station. The image of the bulk deposition collector is enlarged.

Table 3.2. Analytical methods for determination of major ions concentrations in wet deposition samples from La Castanya. From Avila (1996).

Specie	Sampling method
Sulphate	Ion chromatography
Nitrate	Ion chromatography
Ammonium	Flow injection analysis
Magnesium	Atomic absorption
Sodium	Atomic emission
Chloride	Ion chromatography
Calcium	Atomic absorption
Potassium	Atomic absorption
Conductivity	Conductivity meter
pH	pH meter
Alkalinity	Gran Titration

3.2 Methodology used for the identification of PM episodes

One of the objectives of this work was to integrate in one study the interpretation of time series of ambient air levels of PM and deposition fluxes recorded at regional background sites of Spain. For the sake of simplicity, the term PM event (or PM episode) will be used indistinctly to refer to both types of episodes.

The first step is to make a daily classification of the type of PM event occurring on each of the 7 regions in the period January 1998 to December 2003. Eight different source areas of air masses are considered for a given day (Figure 3.10):

- Atlantic Ocean north (AN)
- Atlantic Ocean northwest (ANW)
- Atlantic Ocean west (AW)
- Atlantic Ocean southwest (ASW)
- north Africa (NAF)
- Mediterranean Sea (MED)
- European continent (EU)

- Regional origin without a clear advective scenario (REG)

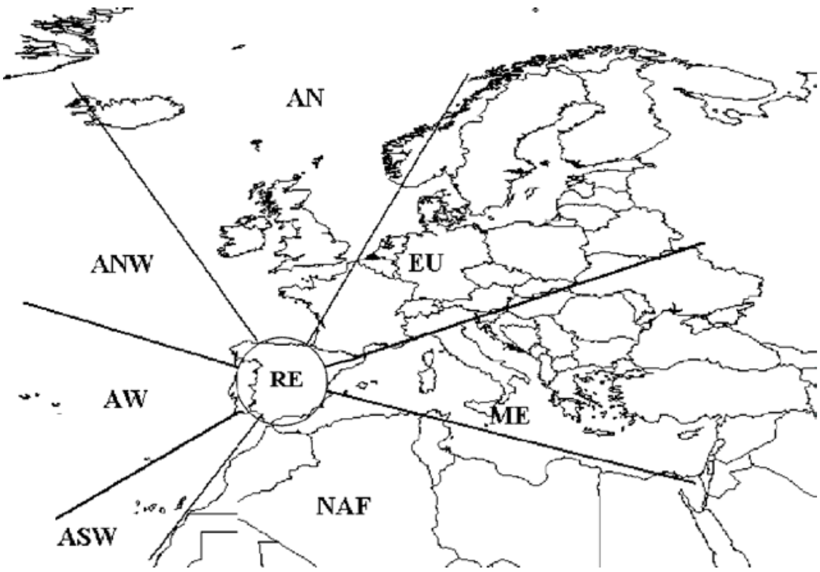


Figure 3.10. Air mass source areas considered in this study for interpretation of the time series of PM levels and deposition fluxes.

For this objective, back trajectories were calculated with HYSPLIT4 for each of the regions and for each day of the study period (January 1998- December 2003). SKIRON/Eta, NAAPS, TOMS maps and SeaWIFS images were used to evaluate the possible occurrence of north African or anthropogenic European PM episodes. The correlation between increases in temperature, O_3 and PM levels helped to detect summer regional episodes (Rodríguez et al., 2003). The interpretation was confirmed by an analysis of the gridded meteorological data. Maps of synoptic variables such as mean sea level pressure and geopotential heights at 850 and 700 hPa were used for that purpose.
The meteorological scenarios for each episode were analysed with the support of the meteorological maps. Factors such as the altitude of transport and the occurrence or not of rainfall together with the PM transport were also analysed. For dust outbreaks, an evaluation of the source areas was undertaken based on the information supplied by previous studies (Prospero et al., 2002).
Once the PM episodes are described in terms of the meteorological scenarios which cause them, the frequency of occurrence and the seasonal and interannual variability of those episodes (distinguishing between meteorological scenarios) in the seven regions is examined. Geographical differences are detailed.
The impact of the different episodes and the distinguished meteorological scenarios on PM levels in different regions was studied. The seasonal and interannual variability of this impact and the differences between regions was also treated.
A number of tools were used for the identification of PM and wet deposition events. These tools are data from satellite sensors, numerical models of dispersion and deposition of aerosols and meteorological charts. All these tools have limitations but the combination of the information obtained from all of them allows an adequate description of PM events.

- **Meteorological gridded data**

The National Weather Service's National Centers for Environmental Prediction (NCEP) runs a series of computer analyses and forecasts operationally. One of the operational systems is the Global Data Assimilation System (GDAS). Analysis and forecasts of a large set of global meteorological variables are grouped as the FNL (Final run) data set. It consists of a 6-hourly archive with data since January 1997. These are available at http://www.arl.noaa.gov/ready/amet.html. In this study, maps of meteorological fields such as sea level pressure, geopotential height at different altitudes and 6-hour accumulated precipitation (Figure 3.11) are used in order to examine the meteorological synoptic scenarios causing PM events at the altitude of PM transport. FNL is the meteorological data set used to feed HYSPLIT4.

The NOAA-CIRES Climate Diagnostics Center (CDC) issues meteorological maps in http://www.cdc.noaa.gov/Composites/Hour/. All the data plotted there belong to the NCEP/NCAR reanalysis project. The NCEP/NCAR Reanalysis project is using a state-of-the-art analysis/forecast system to perform data assimilation using past data from 1948 to the present. A large subset of this data is available from CDC in its original 4 times daily format and as daily averages. That data was done at 8 times daily in the model, because the inputs available in that era were available at 3Z, 9Z, 15Z, and 21Z, whereas the 4x daily data has been available at 0Z, 6Z, 12Z, and 18Z. These latter times were forecasted and the combined result for this early era is 8x daily. The local ingestion process took only the 0Z, 6Z, 12Z, and 18Z forecasted values, and thus only those were used to make the daily time series and monthly means in the web site of CDC (Figure 3.11).

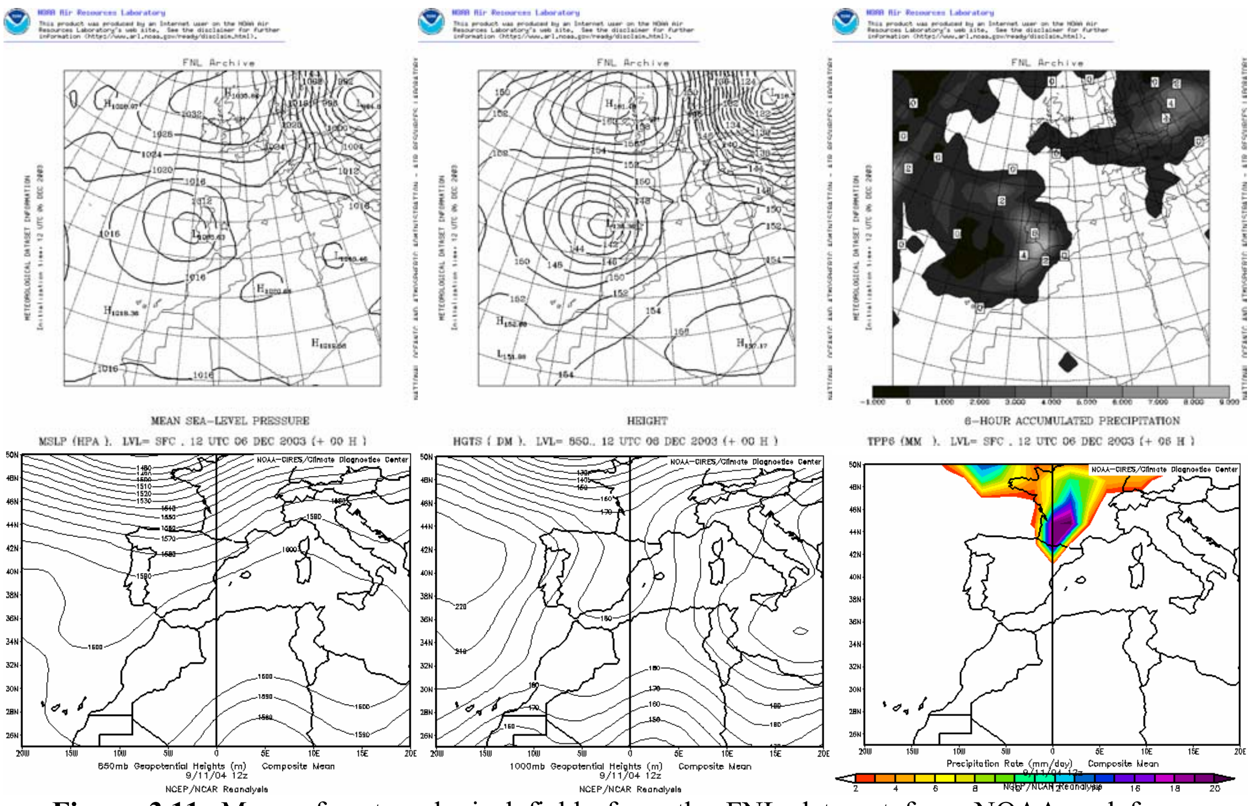


Figure 3.11. Maps of meteorological fields from the FNL data set from NOAA and from NCEP/NCAR Reanalysis project data set from Climate Diagnostics Center (from http://www.arl.noaa.gov/ready/amet.html and http://www.cdc.noaa.gov/Composites/Hour/).

- Hybrid Single-Particle Lagrangian Integrated Trajectories versión 4 (HYSPLIT4)

HYSPLIT4 is the fourth version of the HYSPLIT dispersion model (Draxler and Rolph, 2003). This model was designed to study the temporal evolution of atmospheric

pollutants concentrations, that is, trajectories, dispersion, and deposition of pollutants. In this study HYSPLIT4 is used to calculate back trajectories and consequently study the source areas of the air masses reaching the Iberian Peninsula. For its operation HYSPLIT4 is fed with gridded meteorological data from either analysis or short-term forecasts. The HYSPLIT4 model is operational from the National Oceanic and Atmospheric Administration's (NOAA) Air Resource Laboratory (ARL) web site http://www.arl.noaa.gov/ready/hysplit4.html (Figure 3.12). 5-days back trajectories are calculated at three altitudes (500, 1500 and 2500 m.a.s.l.) for each day and for each of the seven regions distinguished at 12 hours GTM. The vertical velocities calculated by the model are used to calculate the back trajectories.
For the purpose of the application of this tool in this study the main disadvantage is the resolution of the model's grid (90 km, Draxler, 1995). This model cannot be used for estimating source areas and transport patterns during episodes of weak pressure gradient conditions due to the consequent lack of advection.

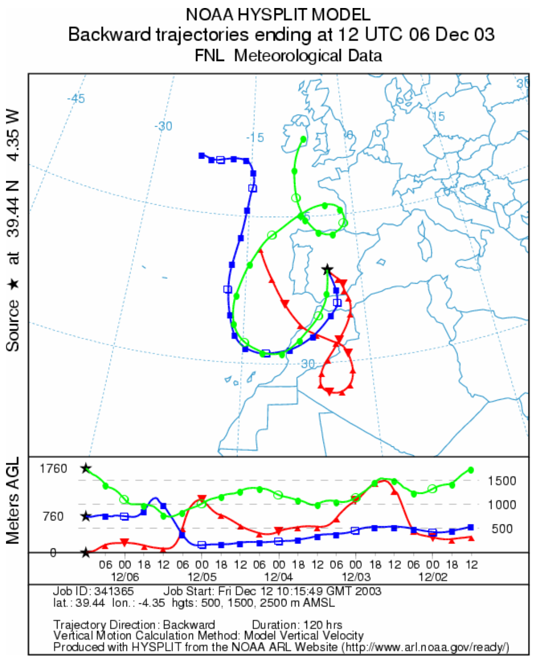


Figure 3.12. Plots of the 5-days back trajectories at 500, 1500 and 2500 m.a.s.l. calculated by HYSPLIT4 using model vertical velocity (from http://www.arl.noaa. gov/ready/hysplit4.html).

Apart of the calculation of back trajectories for the identification of the origin of the air masses with HYSPLIT4, this model also contains a dust module which simulates all the steps of dust outbreaks such as dust mobilisation, transport and deposition. This part of HYSPLIT4 will be used for the determination of the African dust source areas and the contribution of these to the PM10 levels recorded at regional background stations over the Iberian Peninsula in section 8. Following, a brief description of the technical aspects of this dust module is presented.

HYSPLIT4 Description – a Lagrangian Dispersion Model
In an Eulerian modeling approach, air concentrations are computed for every grid cell by integrating the pollutant fluxes at each grid cell interface due to diffusion and advection. On the other hand, in a Lagrangian modeling approach, air concentrations are computed by summing the contribution of each pollutant "puff" that is advected through the grid cell as represented by its trajectory. Under the later approach, modeling the growth of the pollutant puff's 2^{nd} moments or explicitly modeling the growth of a

cluster of particles can simulate dispersion. Contrary to its acronym, HYSPLIT4 can simulate a pollutant distribution starting with a single particle or puff, or by following the dispersive motion of a large number of particles. A detailed model description can be found in Draxler and Hess (1997 and 1998). Only a brief description of the model follows below.

If we assume that a particle passively follows the wind, then its trajectory is just the integration of the particle position vector in space and time (t). The final position is computed from the average velocity (V) at the initial position (P) and first-guess position (P'). Namely,

$$P(t+\Delta t) = P(t) + 0.5\,[\,V(P,t) + V(P',t+\Delta t)\,]\,\Delta t \qquad (3.1)$$
$$P'(t+\Delta t) = P(t) + V(P,t)\,\Delta t \qquad (3.2)$$

A puff following a single trajectory cannot properly represent the growth of a pollutant cloud when the wind field varies horizontally and vertically. In these situations, the single-puff must either split into multiple-puffs or the simulation must be conducted using many pollutant “particles”. In HYSPLIT4, there are three main configurations that can be set to represent the dispersive growth of the pollutant elements. In the “puff” mode the element is a fully 3-D cylindrical puff, having a defined concentration distribution in the vertical and horizontal. Puffs grow horizontally and vertically according to the dispersion rules for puffs, and split if they become too large. In the “particle” mode the element (an infinitely small particle) is a point mass of contaminant. Under this mode, a fixed number of particles are released. They are moved by a wind having mean and random components. They never grow or split. On the other hand, in the “hybrid” approach the element is a circular 2-D object (planar mass, having zero vertical depth), in which the horizontal contaminant has a “puff” distribution. There are a fixed number of these in the vertical because they function as particles in that dimension. In the horizontal dimension, they grow according to the dispersion rules for puffs, and split if they get too large.

To compute air concentrations it is necessary to explicitly follow all the particles or know the particle distribution (the definition of a puff) about the mean trajectory path. In the particle approach, this is accomplished by adding a random component to the mean advection velocity to define the dispersion of the pollutant cloud. For example, in the horizontal, the particle dispersion can be represented by the following equations:

$$X(t+\Delta t)=X_{mean}(t+\Delta t)+U'(t+\Delta t)\,\Delta t \qquad (3.3)$$
$$U'(t+\Delta t)=R(\Delta t)\,U'(t)+U''(\,1-R(\Delta t)^2\,)^{1/2} \qquad (3.4)$$
$$R(\Delta t)=\exp(-\Delta t/T_{Lx}) \qquad (3.5)$$
$$U''=\sigma_u\,\lambda, \qquad (3.6)$$

where U’ is the random velocity component, X_{mean} is the original position due to only advection by the mean winds, R is the turbulent velocity autocorrelation, σ_u is the standard deviation of the turbulent velocity, T_{Lx} a constant Lagrangian time scale, and λ is a computer generated random number with 0 mean and σ of 1. Additional terms to account for gradients in the turbulent velocity near the ground are required for vertical particle dispersion.

The growth of the particle distribution, or the “puff” mode, is represented by a much simpler formulation, where the growth rate of the horizontal standard deviation of the particles is given by

$$d\sigma_h/dt = (2\,\sigma_u)^{1/2} \qquad (3.7)$$

The dispersive growth rate for particles or puffs is controlled by the standard deviation of the turbulent velocity. Many different formulations can be found in the literature, but a simplified form is used in HYSPLIT4 such that

$$\sigma_u = (K_x / T_L)^{1/2} \tag{3.8}$$

where K_x represents the turbulent diffusivity and T_L a constant Lagrangian time scale. For vertical turbulence and within the boundary layer K_x is a function of height and surface stability. Above the boundary layer it depends upon the local stability, a ratio of the wind shear and thermal stratification. Horizontal turbulence is computed from the deformation of the wind field.
Air concentrations are computed by summing each particle's mass as it passes over the concentration grid. In the particle model mode (3D particle), the concentration grid is treated as a matrix of cells, each with a volume defined by the grid dimensions. Therefore the concentration increment is just the particle mass divided by the cell volume.

$$\Delta c = q\ (\Delta x\ \Delta y\ \Delta z)^{-1} \tag{3.9}$$

In the hybrid mode, the vertical component to the concentration calculation is still computed from the cell depth, however in the horizontal the grid is now composed of nodes rather than cells, and if a node is within the particle distribution, then the concentration is computed for that node. Two different horizontal distributions may be assumed. In the traditional Gaussian (GS) formulation, the change in concentration added by a puff to each grid point would be

$$\Delta c = q\ (2\ \pi\ \Phi_h^2\ \Delta z)^{-1} \exp(-0.5\ x^2/\sigma h^2) \tag{3.10}$$

A simplified top-hat (TH) distribution can also be assumed, in which the grid point is either in the puff or outside of the puff. There is no variation of concentration within the puff. The concentration within the puff is equal to the average concentration in the equivalent Gaussian puff.

$$c = q\ (\pi\ r^2 \Delta z)^{-1} \tag{3.11}$$

HYSPLIT4 Dust Emission Module
A model for the emission of PM10 dust has been constructed (Draxler et al., 2001) using the concept of a surface roughness dependent threshold friction velocity. This surface roughness is correlated with soil properties. A dust emission rate is computed from each model grid cell when the local wind velocity exceeds the threshold velocity for the soil characteristics of that emission cell. The dominant mechanism for the PM10 emission is "sand-blasting". The emitted material is dispersed and transported using HYSPLIT4. The model was initially tested over Kuwait, Iraq, and Saudi Arabia (Draxler et al., 2001), where it predicted about the right number of dust events (18%). The model results also agreed quantitatively with measurements at four locations in Saudi Arabia and one in Kuwait for one major dust event (>1000 $\mu g\ m^{-3}$). However, for several smaller scale dust events (200-1000 $\mu g\ m^{-3}$) the model substantially over-predicted the air concentrations. Part of the over-prediction was attributed to the model's sensitivity to the threshold friction velocity and the surface soil texture

coefficient (the soil emission factor), and the difficulty in accurately representing these parameters in the model.
In the model configuration applied over Kuwait, the source algorithm of Marticorena et al. (1997) was used to compute the PM10 dust injections. The vertical mass flux,

$$F = K \rho g^{-1} u_* (u_*^2 - u_{*t}^2) \qquad (3.12)$$

is calculated from the friction velocity and the threshold friction velocity. Gillette et al. (1997) found that for sand soils, the soil texture coefficient (K) had a value of $5.6x10^{-4}$ m^{-1}.
In this application, the model is applied over other domains where detailed digital soil characteristics are not available. The emission module has been modified (Draxler, 2002) to use HYSPLIT4's one-degree land-use file by assuming that a "desert" land-use grid cell corresponds to the Kuwait "active sand sheet" soil type category. To compensate for the greater number of potential dust emission cells the original PM10 flux equation has been replaced by a relationship not dependent upon soil type and with a substantially lower emission flux. In the revised version of the emission module, the flux ($g\ m^{-2}$) equation,

$$F = 0.01\ u_*^4 \qquad (3.13)$$

used by westphal et al. (1987) replaces the Marticorena equation. In both approaches, dust emissions only occur during dry days when the friction velocity exceeds the threshold value (0.28 m/s for an active sand sheet as determined by Draxler et al., 2002). Over the typical range of wind speeds that result in dust emissions, the emission flux is about a factor of 10 lower using the westphal equation.

- **Total Ozone Mapping Spectrometer (TOMS)**
TOMS was designed to measure the total Ozone column using backscattered ultraviolet (UV) radiance in six wavelengths (313, 318, 331, 340, 360 and 380 nm). Data from TOMS can be used to map the distribution of absorbing aerosols although nonabsorbing aerosols can also be detected (Herman et al., 1997). Aerosol measurements are made in the three longest wavelengths (340, 360 and 380 nm) where gaseous absorption is weak and backscattered radiation is controlled by molecular (Rayleigh) scattering, aerosol and clouds (Mie) scattering and surface reflection. As UV albedo of continental surfaces is low, TOMS can detect absorbing aerosols over land and over water. This feature is of great importance for the detection of dust episodes in the Iberian Peninsula. The algorithm of TOMS for the detection of aerosols is described by Herman et al. (1997) and Torres et al. (1998). Briefly, an aerosol index (AI) is defined based on the differences between measured backscattered radiances (I_{meas}) and calculated backscattered radiances assuming a pure gaseous atmosphere (I_{calc}) at two wavelengths (340 and 380 nm):

$$AI = -100 \log_{10}[(I_{340}/I_{380})_{meas} - (I_{340}/I_{380})_{calc}] \qquad (3.14)$$

Absorbing aerosols yield positive values of AI and non absorbing aerosols yield negative values of AI.
TOMS began measuring in November 1978 so a long record of real measurements of aerosols is available from that date to present time. TOMS AI data are available in the internet at http://toms.gsfc.nasa.gov/aerosols/aerosols.html. Daily absorbing AI maps

for the Mediterranean region are available in ftp://jwocky.gsfc.nasa.gov/pub/tmp/ meduse/ (Figure 3.13).
For the purpose of the application of this tool in this study, the main advantages drawn from the usage of TOMS data are:

-These data consist on real measurements of aerosols.

-TOMS provides global coverage, thus, dust source areas and transport patterns can be evaluated with TOMS data.

For the purpose of the application of this tool in this study, the main disadvantages of TOMS are three:

-TOMS gives estimates of the total aerosol column and consequently information on aerosols layers altitude is not available.

-TOMS aerosols measurements are based on the perturbation of the UV upwelling flux from backscatter from the gaseous constituents in the atmosphere. Consequently, aerosols at the upper layers of the troposphere will yield larger values of the AI than an equal amount of aerosols at lower layers. In fact, TOMS cannot detect aerosols below 1000 m (Torres et al., 1998).

-TOMS detects absorbing aerosols without distinction between black carbon, mineral aerosol and volcanic ashes.

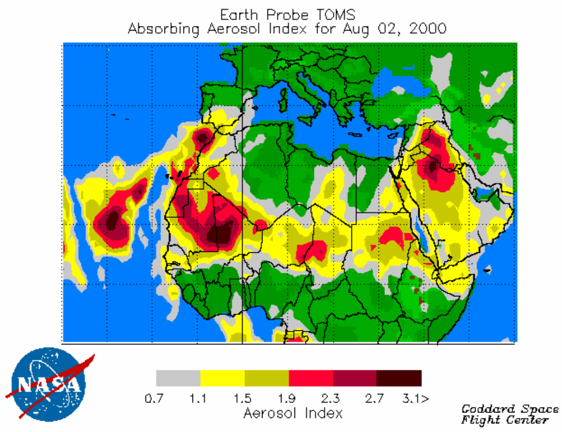


Figure 3.13. TOMS aerosol index map (from ftp://jwocky.gsfc.nasa.gov /pub/tmp/meduse/).

- NAAPS

The Naval Research Laboratory (NRL) developed NAAPS a near-operational system for predicting the distribution of tropospheric aerosols. This model uses meteorological fields at 6-hour intervals and 24 vertical levels also providing surface information. Inventories of emissions of different components are used in the model:

-Sulphur compounds: SO_2 and DMS.

-Smoke and products from forest fires: Smoke emissions in NAAPS are based on geostationary satellite and MODIS fire products.

-Dust: Including land cover characteristics database which differentiates eight dust-producing categories. Dust emission occurs whenever the friction velocity exceeds a threshold value, snow depth is less than a critical value, and the surface moisture is less than a critical value. The flux is scaled to include only particles with radii smaller than 5 µm. The flux is injected into the lowest two layers of the model. The threshold friction velocity is set to infinity except in known dust-emission areas.

NAAPS supplies regional plots of 120 hours forecasts with a temporal resolution of 6 hours of the following variables (Figure 3.14):

-Optical depth at a wavelength of 550 nm for three components: Sulphate, dust and smoke.

-Sulphate concentration at surface level in $\mu g\ m^{-3}$.
-Dust concentration at surface level in $\mu g\ m^{-3}$.
-Smoke concentration at surface level in $\mu g\ m^{-3}$.

Additional plots of the vertical profile of dust concentration (in $\mu g\ m^{-3}$) along (Figure 3.14):

-The 0 meridian from 0 to 39º N.
-The 20º N parallel from 29º E to 49º W.
-The 20º W meridian from 0 to 39º N.

All these plots and detailed information about the model are available at http://www.nrlmry.navy.mil/aerosol/.

For the purpose of the application of this tool in this study the strengths of this model are:

-The global coverage allows the identification of aerosols' source areas and transport patterns.

-Sulphate and smoke maps are available which allows the identification of anthropogenic European PM and biomass burning episodes respectively.

-NAAPS offers information on surface concentration of dust, sulphate and smoke.

For the purpose of the application of this tool in this study the weaknesses of NAAPS are the following points:

-It is a model and not real data (such as TOMS AI data).
-This model does not provide data on deposition fluxes.
-The resolution of this model is lower than mesoscale models such as SKIRON/Eta.

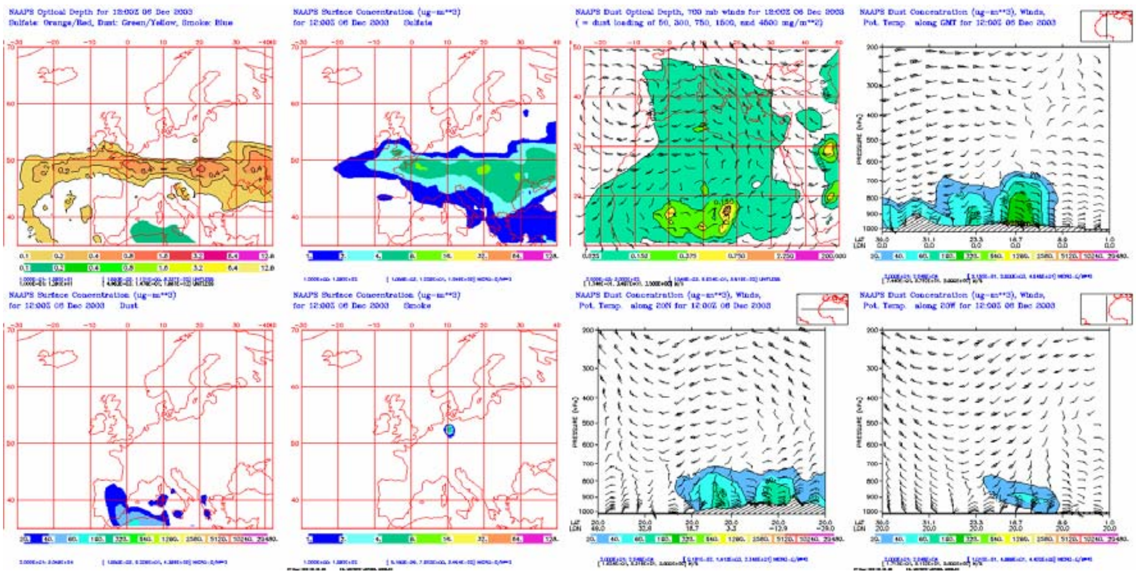


Figure 3.14. NAAPS maps for the European window including aerosol optical depth, surface concentrations of dust, sulphate and smoke and vertical concentration of dust (from http://www.nrlmry.navy.mil/aerosol/).

- **SKIRON/Eta**

The Project SKIRON is a system for operational regional weather prediction designed and developed at the Hellenic National Meteorological Service (HNMS) and the University of Athens (Kallos et al., 1997, http://forecast.uoa.gr). SKIRON/Eta is a pluggable component of the Eta limited-area weather forecasting model (Nickovic et al., 2001) that predicts the atmospheric life cycle of the eroded desert dust. The Eta model is

a state-of-the-art limited area model which is used as a short-range forecasting tool. The parameterisation of mountain effects in the Eta model is very useful in the Mediterranean area where steep mountain ranges are frequent. The preprocessing part of the system prepares the input data for the model. After the model execution, the postprocessing uses the model output data for visualization and other specific applications. One major application concerns the linking with a dust uptake-transport-deposition module in order to simulate dust transport in the Mediterranean region.
SKIRON/Eta model provides 6-hourly forecasts for the following 72 hours for the following variables (Figure 3.15):

-Dust load in g m^{-2}.

-Dry and wet deposition of dust, both in mg m^{-2}.

For the purpose of the application of this tool in this study the advantages of this model are:

-This is a mesoscale model centred in the European region. Consequently, the spatial resolution of this model is better than NAAPS's.

-The model also offers information on wet and dry deposition fluxes.

For the purpose of the application of this tool in this study the weaknesses of this model are:

-It is a model (not real data).

-The model only offers data for the European region and dust transport patterns and source areas cannot be studied.

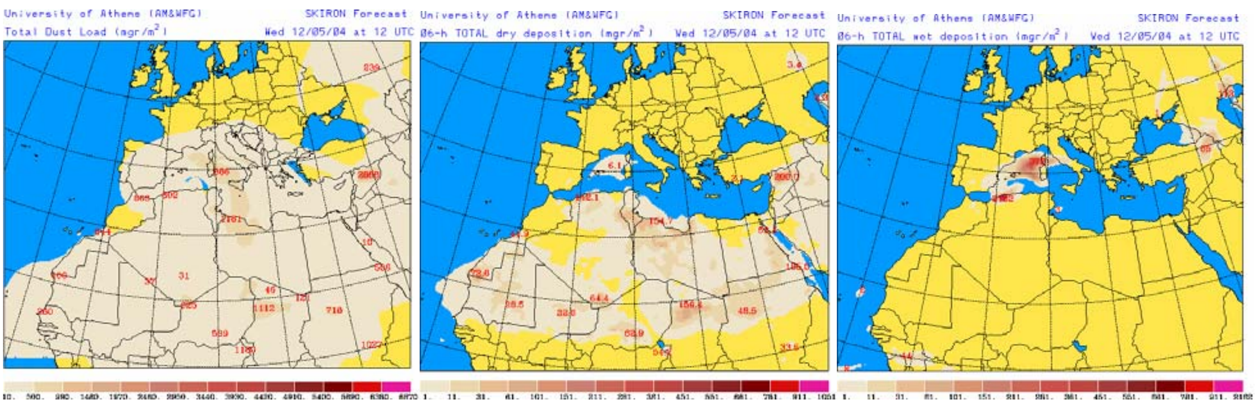


Figure 3.15. SKIRON/Eta maps including dust load, dry deposition and wet deposition of dust (from http://forecast.uoa.gr).

In section 7 SKIRON/Eta model is used for simulating intense wet deposition events of African dust over the northeastern Iberian Peninsula. This requires a short section detailing the main technical characteristics of this regional model.
The SKIRON/Eta system with the dust capabilities has been developed at the University of Athens by the Atmospheric Modeling and Weather Forecasting Group (AM&WFG), at the framework of MEDUSE and ADIOS projects. It is based on the regional atmospheric model Eta/NCEP (NCEP–National Centers for Environmental Prediction). The Eta model is well-documented and detailed descriptions of its dynamics and physics components can be found in several studies (Mesinger et al., 1988, Janjic, 1994, and references therein). The main advantage of SKIRON/Eta modeling system is that dust module is directly coupled with the atmospheric model, resulting in the computation of the dust cycle at every time step. Comparison of the model outputs with the available observations indicates that the model is capable to reproduce the dust

sources, the evolution of the aerosol size distribution, the dust transport and the 3-D mass concentration on a satisfactory way.
The dust module was initially developed at the University of Athens (AM&WFG), and incorporated into the SKIRON integrated limited area forecasting system (Nickovic et al., 1997). The system has been further developed from the AM&WFG during the last years and the current model version incorporates state-of-the-art parameterizations of all the major phases of the atmospheric dust lifecycle such as production, diffusion, advection and removal, including the effects of particle size distribution on aerosol dispersion and deposition. A detailed description of the dust module can be found in Nickovic et al., 2001 and references therein. In particular, the wet removal of dust in SKIRON/Eta is carried out using the model precipitation rate, thus, for each model grid, the rate of dust scavenged by rainfall is

$$\left(\frac{\partial C}{\partial t}\right) = -\Phi \frac{\partial}{\partial z}\left(C \frac{\partial P}{\partial t}\right) \qquad (3.15)$$

where and $\partial P/\partial t$ is the precipitation rate and Φ is the constant washout parameter which has a value of $5x10^5$. The deposition on surface calculated by

$$\left(\frac{\partial C}{\partial t}\right)_{SINKwetdep} = -\Phi\left(\frac{C}{\Delta z}\frac{\partial P}{\partial t}\right)^{LM} \qquad (3.16)$$

where LM denotes the lowest model level and Δz is the depth of the lowest model layer.
The SKIRON system with the dust component has been in operational use at the University of Athens since 1998 providing 72-hour weather and dust transport and deposition forecasts for the Mediterranean region. These forecasts are available from the Internet site http://forecast.uoa.gr. The SKIRON/Eta model, coupled with the dust module, has been extensively used in a number of studies (e.g. in the study of the trans-Atlantic Saharan dust transport, Kallos et al., 2006).

- Sea-viewing Wide Field-of-view Sensor (SeaWIFS)
The SeaWiFS Project from NASA (http://seawifs.gsfc.nasa.gov/SEAWIFS.html, McClain et al., 1998) develops and operates a research data system that will process, calibrate, validate, archive and distribute data received from an Earth-orbiting ocean colour sensor. SeaWIFS offers daily “true colour” images (resembling visible images) in which dust plumes can be appreciated clearly, especially when clouds are not present (Figure 3.16). SeaWIFS project is offering daily images since September 1997 to present time.

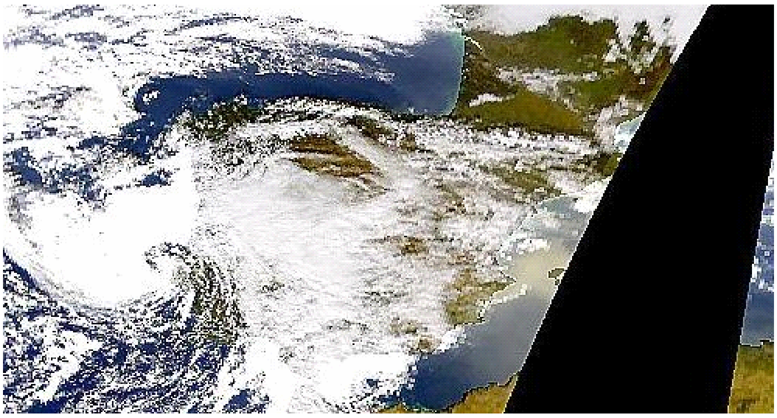


Figure 3.16. SeaWIFS visible image of a dust outbreak over the Iberian Peninsula occurred on 06/12/2003 (from http://www.nrlmry.navy.mil/aerosol/).

For the purpose of the application of this tool in this study using "true color" images provided by SeaWIFS has the following advantages:

- Dust plumes can be directly observed especially over the oceans and the shape of such plumes can be described.
- Owing to the global coverage of the images, dust transport patterns can be observed.

For the purpose of the application of this tool in this study SeaWIFS "true color" images have these disadvantages:

- Dust is hard to be distinguished over land so the detection of dust source areas is difficult.
- In occasions, clouds interfere with the observation of dust.
- The altitude of the dust transport cannot be evaluated.

3.3 Specific methodological aspects of the study on dry and wet African dust episodes over eastern Spain presented in section 6

High PM events

In order to study the impact of African dust outbreaks on ambient PM levels, 1996-2002 time series of levels of TSP and PM10 (total suspended particles, and suspended particles <10 μm, respectively) from 18 air quality monitoring stations from the eastern Iberian Peninsula (from the Autonomous Governments of Catalonia and Valencia, and one station belonging to ENDESA) were selected. Selection criteria were based on data availability, geographical location, pollution level and type of emission sources influencing the monitoring stations. TSP and PM10 time series were then inter-correlated, showing that nine of them exhibited parallel trends for the selected period. Consequently, nine stations (Monagrega, Morella, Coratxar, Hospitalet, Igualada, Sagrera, Fornells, Penyeta and Onda, Figure 3.17) were finally chosen for this study. The Monagrega rural station was chosen to represent regional background levels because of its location (rural area in the Calanda desert in the semi-arid Ebro basin), far from the direct influence of anthropogenic emissions.

TSP measurements were carried out by the β-attenuation method (FAG and Dasibi instruments) at all sites, with the exception of Monagrega where measurements of PM10 were performed with TEOM (oscillating microbalance method) instrumentation.

After identifying a number of simultaneously recorded concentration peaks in the TSP and PM10 time series, the possible attribution to an African dust episode and the transport mechanisms which generate it were investigated by means of the evaluation of the sources of information presented above.

Wet deposition events

Data on the chemical composition of bulk deposition were used to identify wet African episodes. To this end, a weekly sampling was carried out at La Castanya (Montseny, Barcelona, 41° 46' N, 02° 21' E, 700 m.a.s.l.) from January 1996 to the end of September 2000, and at a nearby station at the base of the Montseny mountains (Santa Maria de Palautordera, 41° 41' N, 02° 27' E, 200 m.a.s.l., 7 km from La Castanya in southern direction) from October 2000 to December 2002.

After sampling, the rainwater was taken to the laboratory where conductivity, pH, alkalinity were measured and the major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^- and Cl^-) were analysed with the techniques detailed in section 3.1.

African wet episodes were defined as rainfall events that gave a reddish-brownish colour to the rainwater filters (red rains). The chemistry of these episodes is characterised by very high pH and high concentrations of Ca^{+2}. The identification of African events was confirmed by means of back trajectory analysis. Given that the sampling was carried out on a weekly basis, the identification of the exact dates of the African rain episode was obtained from the precipitation records of the La Castanya station and from the Santa María de Palautordera (the latter belonging to the meteorological service of Catalonia, Meteocat).

Once the time series of wet deposition and high PM levels were obtained, these were combined to create a time series of dust outbreaks. The meteorological scenarios causing these episodes, the duration, the seasonal trends and the levels of PM recorded in regional background sites were then investigated. To this end, each dust event was studied using three parameters: a) geopotential height for 850, b) geopotential height for 700 hPa and c) mean sea level pressure (MSLP) with data files obtained from the NOAA Air Research Laboratory. The African dust outbreaks occurred under certain synoptic scenarios. Following the classification of events, geopotential height and MSLP data were averaged and plotted using the data of the first day of each dust episode. Thus, an average map was obtained for each African scenario.

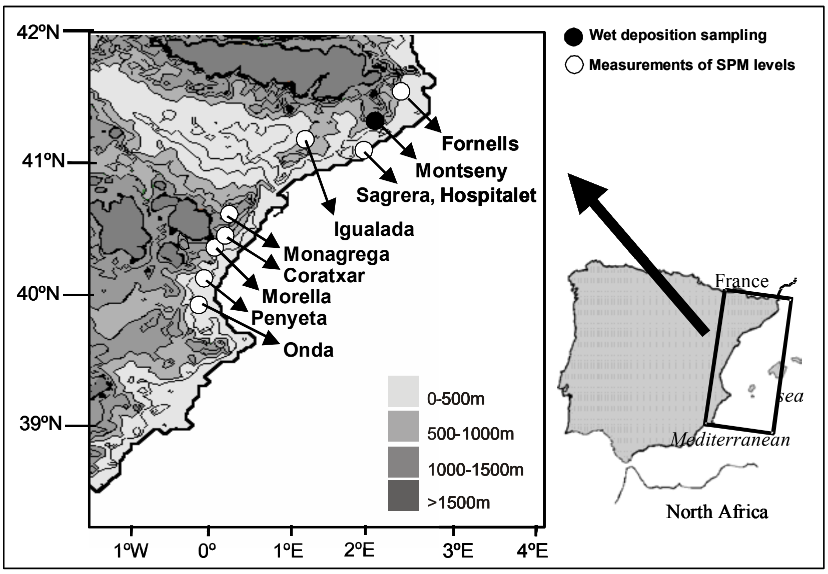


Figure 3.17. Location of the stations measuring levels of atmospheric suspended particles (PM), and the Montseny (La Castanya and Santa María de Palautordera) for wet deposition sampling.

3.4 Specific methodological aspects of the study on intense African "red rains" occurred in the period 1983-2003 over northeastern Spain simulated with SKIRON/Eta model presented in section 7

The 16 most intense African "red rains" (rainwater which leaves a reddish-brownish insoluble residual when filtered or evaporated) occurred at the northeastern Iberian Peninsula were selected from the weekly precipitation records obtained at La Castanya rural site in two sampling periods (1983-2000 and 2002-2003). All these events (Table 3.3), in which more than 1000 mg m^{-2} of insoluble dust deposited, were simulated with SKIRON/Eta since these episodes contributed with more than 80% of the total amount of insoluble material deposited during all the African events during the two sampling periods.

For these experiments the SKIRON/Eta model was integrated over a domain comprised from 10 to 56º N and from -35 to 25º E. This area covers north Africa, Europe, the Mediterranean Sea, and the eastern Atlantic Ocean. In the vertical, 32 levels were used stretching from the ground to the model top (15800 m). In the horizontal, a grid increment of 0.2º was applied. The timestep used was 90 seconds.

The events were simulated taking into account the rainy days at La Castanya. Outputs were obtained every 6 hours for a period covering the rainy days and one day before and one day after them. For the initial and the boundary meteorological conditions the European Center for Medium range Weather Forecasts (ECMWF) objective analysis gridded data were used, with a 0.5º horizontal grid increment and for 11 standard pressure levels. The initial dust concentration was obtained by performing a 3-days dust generation simulation ending on the starting time of the episode to be modeled, the initial dust fields were taken from that previous simulation.

Finally, the dust source areas active during the intense wet deposition episodes were identified by means of dust flux maps provided by SKIRON/Eta.

Table 3.3. Intense events of dust deposition in La Castanya (NE Spain).

Sampling date	Rainy days	Total precipitation (mm)
12/11/1984	9-11	49.7
25/04/1985	21,22,25	30.8
04/11/1987	28,29	42.5
05/12/1987	3,4,5	70.9
09/05/1988	6,7,8	5.3
11/03/1991	5,6	26.9
28/03/1991	24,25	169.0
16/10/1991	9,10,11	15.4
11/03/1992	4-6,8	22.6
21/11/1996	11-17	256.0
03/05/1999	28,29,2,3	5.3
14/06/1999	9,12,13	19.8
15/11/1999	11-12	80.3
27/02/2003	19-21,24-26	165.0
13/05/2003	6-7	27.0
27/11/2003	21-24,26	56.3

3.5 Specific methodological aspects of the study on the determination of the contribution of northern Africa dust source areas to PM10 concentrations over the Iberian Peninsula using the HYSPLIT4 model presented in section 8

Configuration of HYSPLIT4 and methodology test

In this section, we present a methodology that quantitatively estimates the contribution of north African dust sources using the HYbrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT4, Draxler and Rolph, 2003) as the main tool.

Using the sources of information presented above an African dust outbreak (occurred over the Iberian Peninsula in March 2003, see section 8 for case study) was analysed in order to confirm the impact of this event in the PM10 levels of regional background stations of Spain. Once this episode was analysed, it was simulated with HYSPLIT4 to estimate PM10 concentrations over the Iberian Peninsula.

The source area was chosen to cover all northern Africa and several simulations were performed in order to determine the set of model parameters that best fit the measured data. Parameters such as the concentration grid resolution, the number of particles emitted per simulation cycle, and the particle type (3D, Gaussian or Top-hat particles) were modified in the search of the best performance of the model. Furthermore, wet and dry deposition were incorporated later in order to obtain a more realistic behavior of the model.

Once the best suites of parameters were determined, nine simulations were executed. Eight of these simulations were performed constraining the emission area to the regions identified by Prospero et al. (2002) as source areas over northern Africa. These regions are (Figure 3.18): (1) Tunisia and northeast Algeria, (2) eastern Libyan Desert, (3) Egypt, (4) Sudan and the Flanks of Ethiopian Highlands, (5) Lake Chad and the Bodele depression, (6) Niger and the southern flanks of the Ahaggar Mountains, (7) Mali, Mauritania and the western flanks of the Ahaggar Mountains and (8) Mauritania and western Sahara. The Ethiopia Rift Valley and Djibouti source area were not taken into consideration as it might not contribute to dust plumes arriving to the Iberian Peninsula. The last simulation was performed constraining the emission of dust to the "rest of the desert" source (black area in Figure 3.18). This region comprises all the regions considered as desert in the soil type map used by HYSPLIT4 which are not explicitly mentioned in the work by Prospero et al., (2002). In this area there must be dust susceptible to be mobilised although this may not be an intense emission region as those identified by Prospero et al. In this manner, the contribution of each source area can be evaluated by calculating the portion of the PM10 concentration at a receptor site estimated from each individual model run. It is important to note that this methodology is not only applicable to north African deserts but also to any other desert areas in the world.

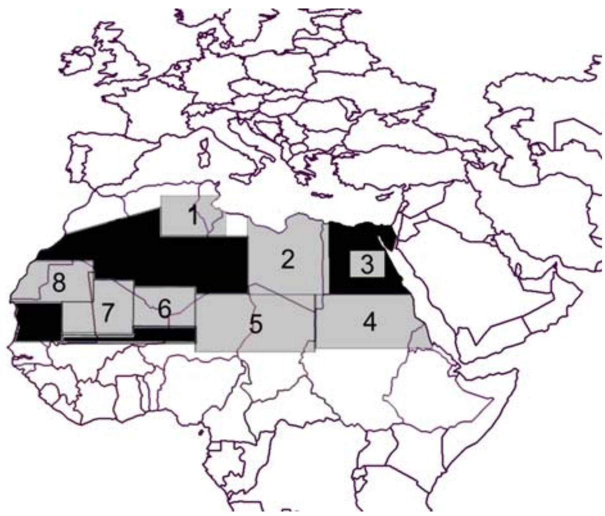


Figure 3.18. Source areas of dust over northern Africa. The source areas identified by Prospero et al. (2002) are highlighted in grey. The rest of the desert is highlighted in black.

Source apportionment of African dust over Spain

Seven north African dust outbreaks yielding high PM10 levels at Spanish regional background stations were simulated with the dust module of HYSPLIT4 model with the objective of determining the source areas of dust mainly contributing in African episodes over Spain. This source apportionment was carried out using the methodology just presented.

The final model adjustment and configuration found in that study was adopted in this work with just a modification in the source areas taken into account. In the initial methodology presented above the north African source areas considered were those determined by Prospero et al. (2002): (a) Tunisia and northeast Algeria (~30 to 35° N and 3 to 12° E), (b) Eastern Libyan Desert (~22 to 33° N and 15 to 26° E), (c) Egypt (~24 to 27° N and 29 to 33° E), (d) Mauritania and Western Sahara (~21 to 27° N and 6 to 16° W), (e) Mali, Mauritania and the western flanks of the Ahaggar Mountains (~17 to 26° N and 0 to 10° W), (f) Niger and the southern flanks of the Ahaggar Mountains (~18 to 23° N and 0 to 7° E), (g) Lake Chad and the Bodele depression (~14 to 22° N and 7 to 24° E) and (h) Sudan and the Flanks of Ethiopian Highlands (~15 to 22° N and 24 to 39° E), plus another covering all the remaining regions considered as desert in the soil type map used by HYSPLIT4. For this study, this large area was divided in three independent regions named as (i) Western Algeria (~27 to 31° N and 0 to 11° W), (j) Eastern Algeria (~24 to 32° N and 0 to 14° E) and (k) Western Mauritania (~17 to 20° N and 11 to 17° W) which gives a more reasonable coverage of the African continent for the purposes of this work. All these regions are presented in Figure 3.19.

The source apportionment methodology was applied to 7 African dust outbreaks occurred over the Iberian Peninsula between in 2002 and 2003 (Table 3.4) previously identified with the tools presented above. All these events yielded considerably high daily PM levels in regional background stations all over the Iberian Peninsula.

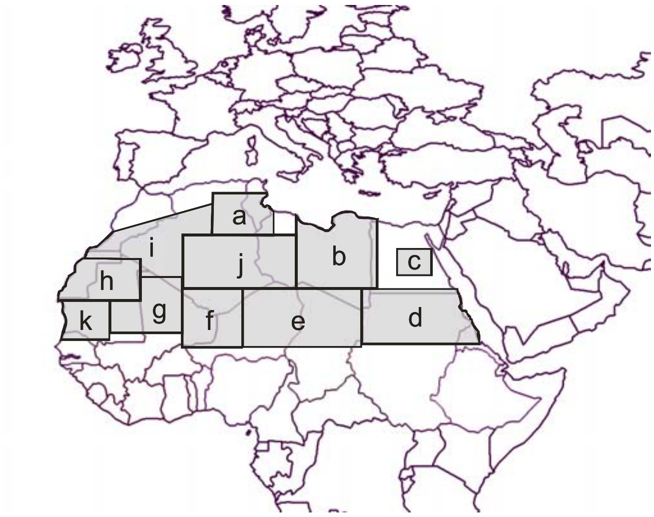


Figure 3.19. Eleven predefined north African dust source areas considered in the source area apportionment study presented in section 8 of this dissertation.

Table 3.4. African dust outbreaks simulated with HYSPLIT4 for this study. The dates within these periods for which TSP was sampled at La Castanya and analysed chemically are also shown.

Period of simulation	Dates with chemical analyses of TSP available at La Castanya
17-23 March 2002	22, 23
17-23 June 2002	17, 18, 21, 22, 23
22-28 June 2002	26, 27, 28
20-26 March 2003	24, 25, 26
8-14 June 2003	10, 11, 12, 13
21-27 June 2003	26
16-22 July 2003	18, 19, 20, 21

4. Meteorological characteristics of episodes influencing ambient air PM levels in regional background areas of the Iberian Peninsula

4. METEOROLOGICAL CHARACTERISTICS OF EPISODES INFLUENCING AMBIENT AIR PM LEVELS IN REGIONAL BACKGROUND AREAS OF THE IBERIAN PENINSULA

Using all the sources of information described in the methodology chapter, each day in each of the regions was associated with an air mass transport episode. The objective of this chapter is to define and characterise the meteorological scenarios causing air mass transport from different source areas to the Iberian Peninsula. The rainfall regime associated to each of the transport scenarios is discussed.

It is important to bear in mind that we are not treating with pure situations and, in many occasions, air masses with origin in a certain area may cross regions with different conditions on its transect towards the Iberian Peninsula capturing properties from this second area. For example, a dry African air mass may cross the Mediterranean Sea before reaching Iberia and increase its moisture. Furthermore, a certain synoptic situation may result in different PM episodes over different regions of Iberia, thus, some scenarios may cause different PM events. In any case, a greater or lower local/regional PM contribution will always exist regardless the transport episode.

In the period 1998-2003 daily precipitation and temperature data were available in the EMEP stations for the following periods: in O Saviñao since March 2001, in Niembro-Llanes since October 1998, in Logroño from February 1998 to January 2001, in Cabo de Creus since January 1998, in Els Torms since November 2000, in Risco Llano since November 2000, in Campisábalos since January 1998, in Peñausende since August 2000, in Zarra since January 1998, in Barcarrota since March 1999 and in Víznar since January 1998.

The occurrence of rain events differed in the seven regions. The proportion of rainy days in the EMEP stations (Table 4.1) was high in the northwest (>40%), moderate in the southwest, the centre and the north (around 30%) and scarce over the eastern flank (around 20%). The mean daily rainfall also varied within the EMEP stations, within 7 mm in Víznar and 3 mm in Logroño (Table 4.1).

Table 4.1. Proportion of rain days and mean daily rainfall (mm) recorded in EMEP stations of the Iberian Peninsula in 1998-2003.

1998-2003	*northwest*		*north*	*northeast*	
	O Saviñao	**Niembro-Llanes**	**Logroño**	**Cabo de Creus**	**Els Torms**
% rain days	41	44	28	18	22
Mean daily rainfall	6.1	4.7	3.3	4.5	3.9

1998-2003	*centre*			*east*	*southwest*	*southeast*
	Risco Llano	**Campisábalos**	**Peñausende**	**Zarra**	**Barcarrota**	**Víznar**
% rain days	30	34	32	19	27	22
Mean daily rainfall	5.4	3.8	3.5	4.0	6.1	7.1

4.1. Atlantic episodes

4.1.1. Mean pressure fields

Based on the evaluation of different sources of information (synoptic meteorological charts, dispersion and transport models), two synoptic transport scenarios were differentiated for the episodes of advection of Atlantic air masses over the Iberian Peninsula. The first meteorological scenario was characterised by the presence of the

Azores high and the Iceland low in their standard positions (AZH-NAtD scenario). This situation induces the transport of air masses from the north, Norwestern or western Atlantic Ocean over Iberia, depending on the relative positions of the Azores high and the Iceland low. As shown in Figure 4.1 (a), (b) and (c), this pattern is clear at different altitudes in the troposphere (1000 hPa, 850 hPa and 700 hPa approximately equivalent to surface level, 1500 and 3000 m.a.s.l.).
The second transport scenario is characterised by the presence of a relatively deep low pressure centre over the Atlantic by the Portuguese coast (AD(ATL) scenario). This feature is present in all altitude levels from surface to 3000 m.a.s.l. (Figure 4.1 (d), (e) and (f)). The origin of the air masses reaching the Iberian Peninsula during these situations may be the west or southwest of the Atlantic Ocean.

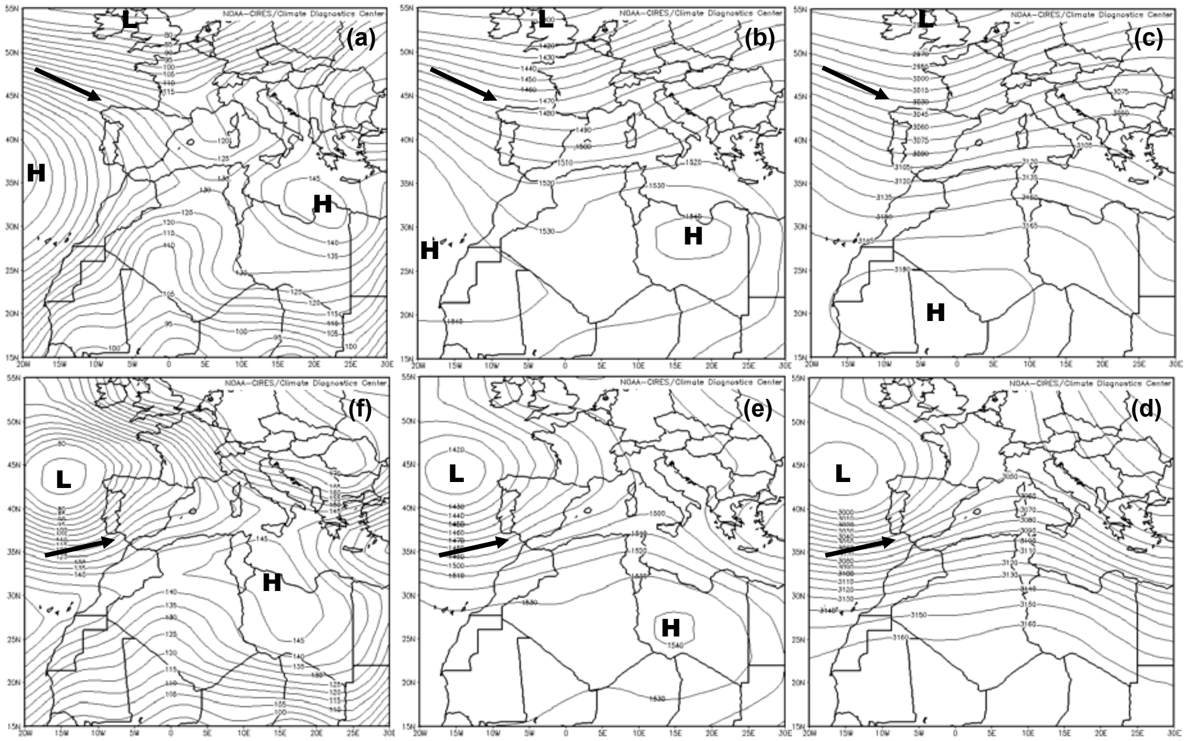


Figure 4.1. Mean geopotential height for 1000, 850 and 700 hPa calculated using data from the first day of AZH-NAtD (a, b and c) and AD(ATL) (d, e, f) episodes in 2003.

4.1.2. Precipitation

The frequency of occurrence of rain during Atlantic episodes is higher in all the regions (40-50% in the northwest and the centre, around 35% in the southeast, southwest and north and around 20% in the east, Table 4.2) compared with the frequency of occurrence of rain in 1998-2003 (41-44% in the northwest, 28% in the north, 18-22% in the northeast, 30-34% in the centre, 19% in the east, 27% in the southwest and 22% in the southeast). The mean daily precipitation recorded during Atlantic episodes (Table 4.2) is comparable with the mean daily rainfall amount in 1998-2003 with the exception of the stations in the northeast and the east of the Iberian Peninsula where the precipitation amounts were lower. This reflects the importance of Atlantic events in the annual precipitation of all the regions of Iberia with the exception of the east and the northeast.
As shown in Figure 4.2, rainfall occurred less frequently during AZH-NAtD events in all the regions of the Iberian Peninsula (rain frequencies of 36-50% in the northwest and the centre, around 30% in the north, southwest and southeast and around 20% in the northeast and the east) than during AD(ATL) episodes (rain frequencies between 47-

82% in the northwest, in the two southern areas and in the centre and between 23-48% in the north and the east). While during AD(ATL) episodes the Iberian Peninsula is under the effect of an Atlantic depression commonly associated with rain, during AZH-NAtD episodes the influence of the Azores high reduces the frequency of the precipitation. The daily mean precipitation recorded during AD(ATL) episodes (Figure 4.2) was, usually, of the same order or higher than during AZH-NAtD events. In both cases the precipitation intensity was moderately high.

Table 4.2. Mean daily precipitation (mm) and % of rain days recorded during episodes with Atlantic advection in EMEP stations in Spain for the period 1998-2003.

ATL EPISODES	*northwest*		*north*	*northeast*	
	O Saviñao	**Niembro-Llanes**	**Logroño**	**Cabo de Creus**	**Els Torms**
% rain days	50	50	33	21	21
Mean daily precipitation	6.3	4.7	3.2	3.6	2.3

ATL EPISODES	*Centre*			*east*	*southwest*	*southeast*
	Risco Llano	**Campisábalos**	**Peñausende**	**Zarra**	**Barcarrota**	**Víznar**
% rain days	42	46	45	20	35	35
Mean daily precipitation	5.5	3.7	3.7	3.2	6.1	7.6

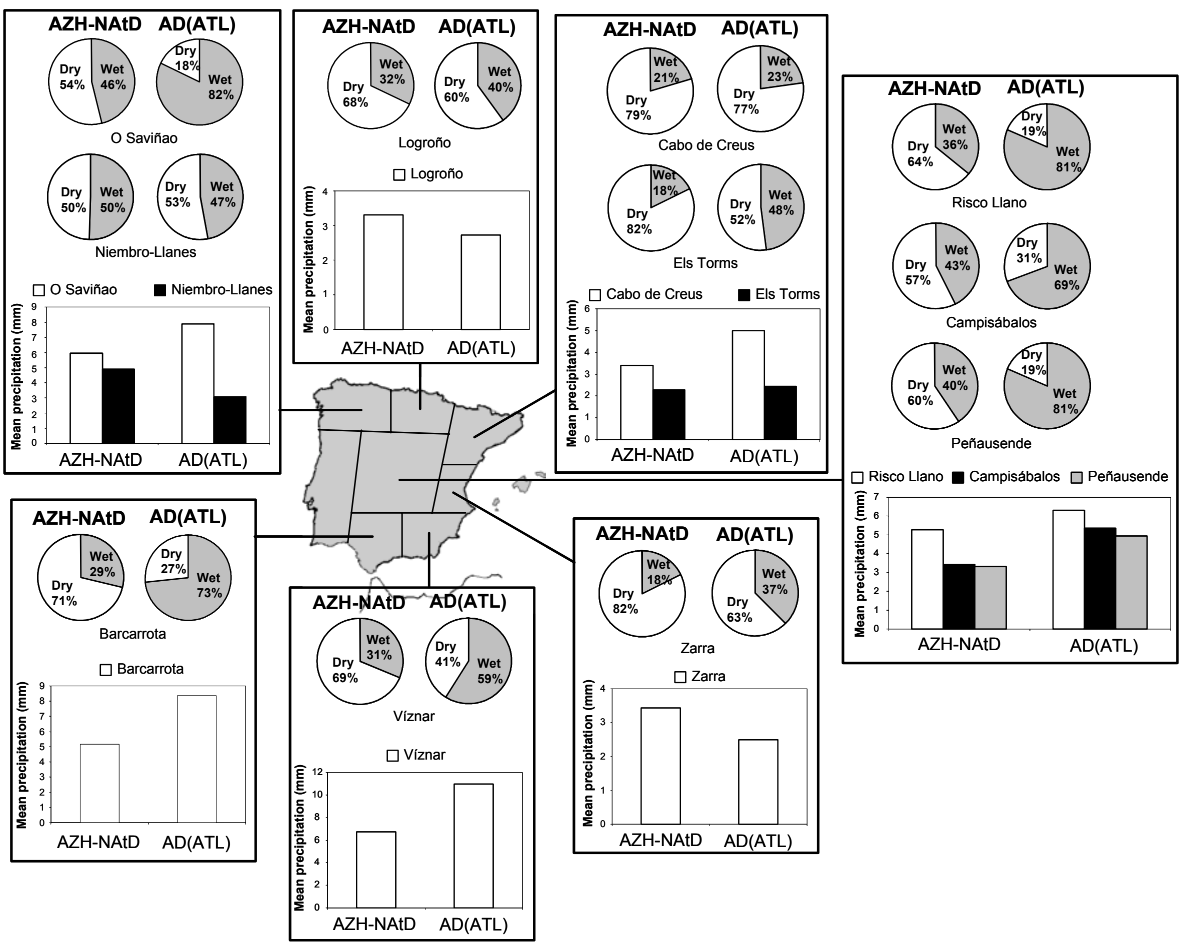


Figure 4.2. Mean daily precipitation and % of wet and dry days recorded during AZH-NAtD and AD(ATL) Atlantic events in EMEP stations in Spain for the period 1998-2003.

Summarising, during AD(ATL) scenario rainfall was more frequent and more intense than during AZH-NAtD. These factors may account for a different impact of these two scenarios on PM levels recorded at the regional background sites owing to the washing out of pollutants by precipitation.

4.2. African episodes

4.2.1. Mean pressure fields

Four different meteorological scenarios were observed to cause air mass transport from northern Africa towards Iberia. The first transport scenario is characterised by the no-presence of the quasi-permanent Azores high. In fact, the transport is caused by an anticyclone located over north Africa or the Iberian Peninsula (north African High-Surface, NAH-S scenario). This feature is well detected at ground level and 850 hPa as shown in Figure 4.3 (a), (b) and (c). At 700 hPa the anticyclone is found displaced towards the south. This scenario induces the transport of African air masses from the western Sahara, Mauritania, Mali and the Sahel towards the western flank of the Iberian Peninsula after a relatively long transect over the Atlantic Ocean.

The second African air mass transport scenario is caused by the development of a relatively deep low pressure (observed from sea level to 850 hPa but not at 700 hPa) centred off west the Portuguese coast with an associated high or ridge over the European continent or the central Mediterranean (Atlantic Depression, AD(NAF) scenario, Figure 4.3 (d), (e) and (f)). This anticyclone may also be the cause of the reinforcement of the African air mass transport over the Iberian Peninsula. In these situations western regions of north Africa (Mauritania, Mali, Morocco) may be the main emission areas.

The third synoptic scenario is characterised by the slight shift of the Azores high to the west of its normal position while a depression is centred over Morocco, Algeria, Tunisia, or even the western Mediterranean (north African Depression, NAD scenario). This meteorological scenario favours the transport of African air masses towards Iberia across the Mediterranean. The low pressure centred is well marked from surface to 700 hPa (Figure 4.3 (g), (h) and (i)). According to this scenario, the dust sources may be regions from Algeria, Tunisia, Libya and Chad.

The fourth scenario causing dust outbreaks over Iberia is produced by the intense heating of the Sahara in summer and the consequent development of the north-African thermal low (Figure 4.3 (j), (k) and (l)) and the considerable vertical growth of the boundary layer. This convective system pumps dust up to 5000 m a.s.l. Once the dust is injected into the mid-troposphere it may be transported towards Iberia by the western branch of the high present over north Africa at altitudes above 1000-1500 m (north African High-Altitude, NAH-A scenario). Thus, this scenario is similar to NAH-S but this one only occurs in summer and the transport trakes place in altitude. In these cases the air masses are heavily loaded with dust and are transported towards the north over most of the western Mediterranean basin and Iberia, forming a wide plume of dust.

4.2.2. Precipitation

The rain occurrence during African events is low in most regions (mean proportion of rainy days in EMEP stations during African events between 24 and 30% in the northwest, the north and the centre and between 15 and 30% in the northeast, the east, the southwest and the southeast, Table 4.3) when compared with the rain frequency in 1998-2003 (41-44% in the northwest, 14% in the north, 18-22% in the northeast, 30-34% in the centre, 19% in the east, 27% in the southwest and 22% in the southeast). The mean daily precipitation registered at the EMEP stations during wet African events (Table 4.3) is higher than the mean daily rainfall in 1998-2003. This indicates that, on average, the rainfall intensity associated with African air mass transport is relatively high.

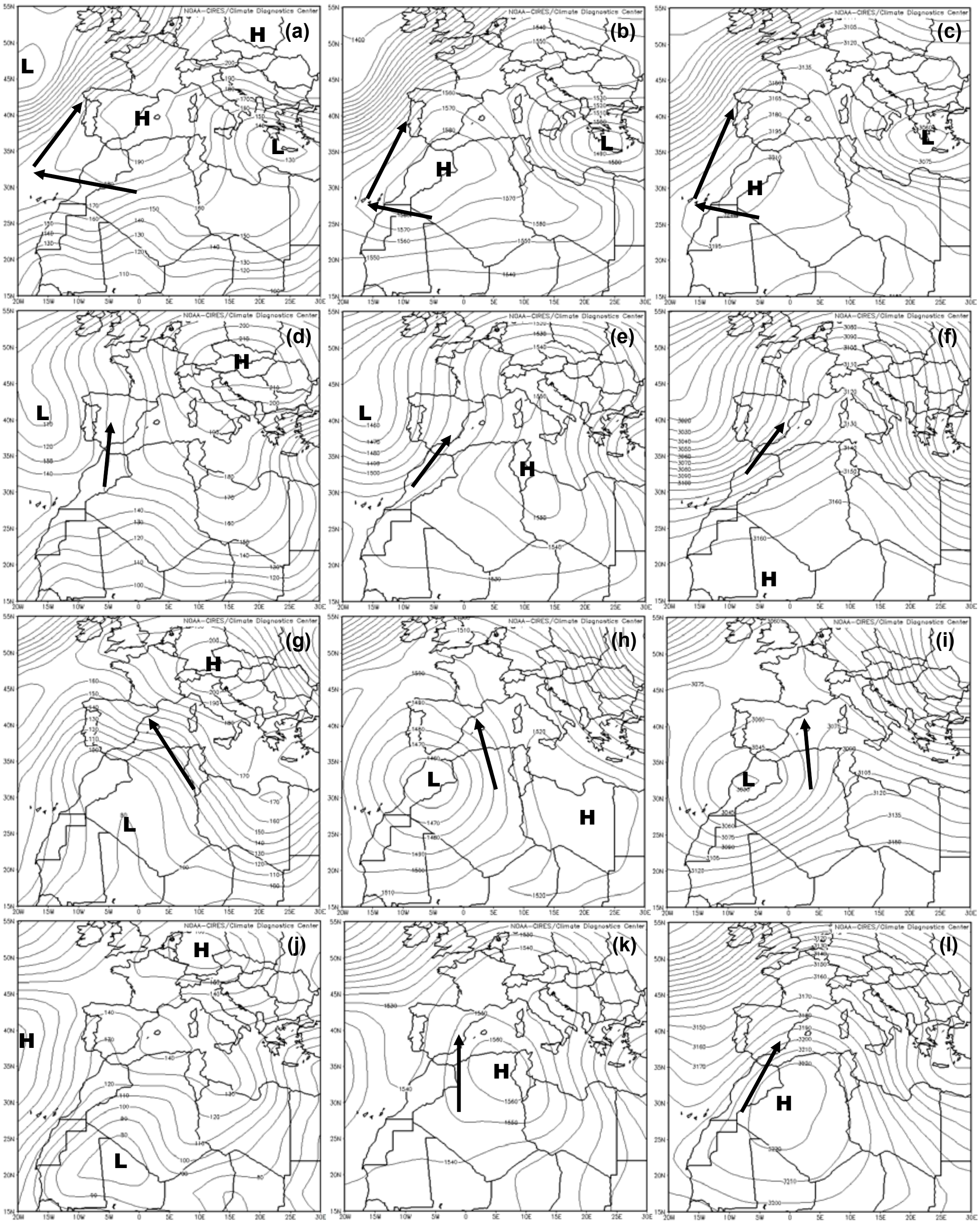


Figure 4.3. Mean geopotential height for 1000, 850 and 700 hPa calculated using data from the first day of NAH-S (a, b and c), AD(NAF) (d, e, f), NAD (g, h, i) and NAH-A (j, k and l) episodes in 2003.

Table 4.3. Mean daily precipitation (mm) and % of rain days recorded during episodes with African advection in EMEP stations in Spain for the period 1998-2003.

NAF EPISODES	*northwest*		*north*	*northeast*	
	O Saviñao	**Niembro-Llanes**	**Logroño**	**Cabo de Creus**	**Els Torms**
% rain days	28	26	29	15	30
Mean daily precipitation	6.1	5.2	4.5	4.8	4.8

NAF EPISODES	*centre*			*east*	*southwest*	*southeast*
	Risco Llano	**Campisábalos**	**Peñausende**	**Zarra**	**Barcarrota**	**Víznar**
% rain days	24	26	30	20	19	17
Mean daily precipitation	6.6	5.0	2.9	6.5	7.3	7.6

Among the African transport scenarios, the occurrence of precipitation in the EMEP sites is clearly more frequent during AD(NAF) than during NAD events (frequency of occurrences of daily precipitation between 23 and 58% in the different regions during AD(NAF) episodes and between 21 and 48% in the different areas during NAD events, Figure 4.4) than during NAH-S and NAH-A events (frequency of occurrences of daily precipitation between 6-37% in the different regions of Iberia during NAH-S episodes and between 4 and 42% in the different areas of Iberia during NAH-A events, Figure 4.4). With respect to the intensity of precipitation differences can be observed between AD(NAF) and NAD episodes (Figure 4.4). In some stations the mean daily precipitation was higher during AD(NAF) events while in others the opposite stands (Figure 4.4). Except in Logroño the rainfall intensity during AD(NAF) and NAD events was higher than during NAH-S and NAH-A episodes (Figure 4.4).

Thus, precipitation associated with AD(NAF) and NAD African events was considerably more frequent and intense than during NAH-S and NAH-A episodes. AD(NAF) and NAD are associated with rainfall because the transport is caused by depressions and because the African air masses may acquire humidity when crossing above the Mediterranean Sea. In fact, the precipitation intensity during AD(NAF) and NAD is intense as generally occurs over the Iberian Peninsula under Mediterranean transport. These factors may account for a different impact of these two groups of scenarios on PM levels recorded at the regional background sites owing to the washing out of pollutants by precipitation.

4.3. European episodes

4.3.1. Mean pressure fields

The transport of European air masses over the Iberian Peninsula occurs under two different synoptic scenarios. During these events a transboundary transport of pollutants from central Europe across the Pyrenees may occur. The first is associated with the presence or development of an anticyclone over the European continent or the north Atlantic Ocean (EUropean High, EUH scenario). This is present from surface to 700 hPa (Figure 4.5 (a), (b) and (c)). The presence of a low centre over the eastern Mediterranean basin may intensify the transport from the European continent. In the second scenario the most outstanding feature is the displacement of the Azores high towards the northwestern Atlantic Ocean and the development of a depression over the western Mediterranean (Mediterranean Depression, MD scenario). This is clearly present at surface and 850 hPa but not at 700 hPa (Figure 4.5 (d), (e) and (f)). The Mediterranean is a region of cyclogenesis so these Mediterranean depressions are common.

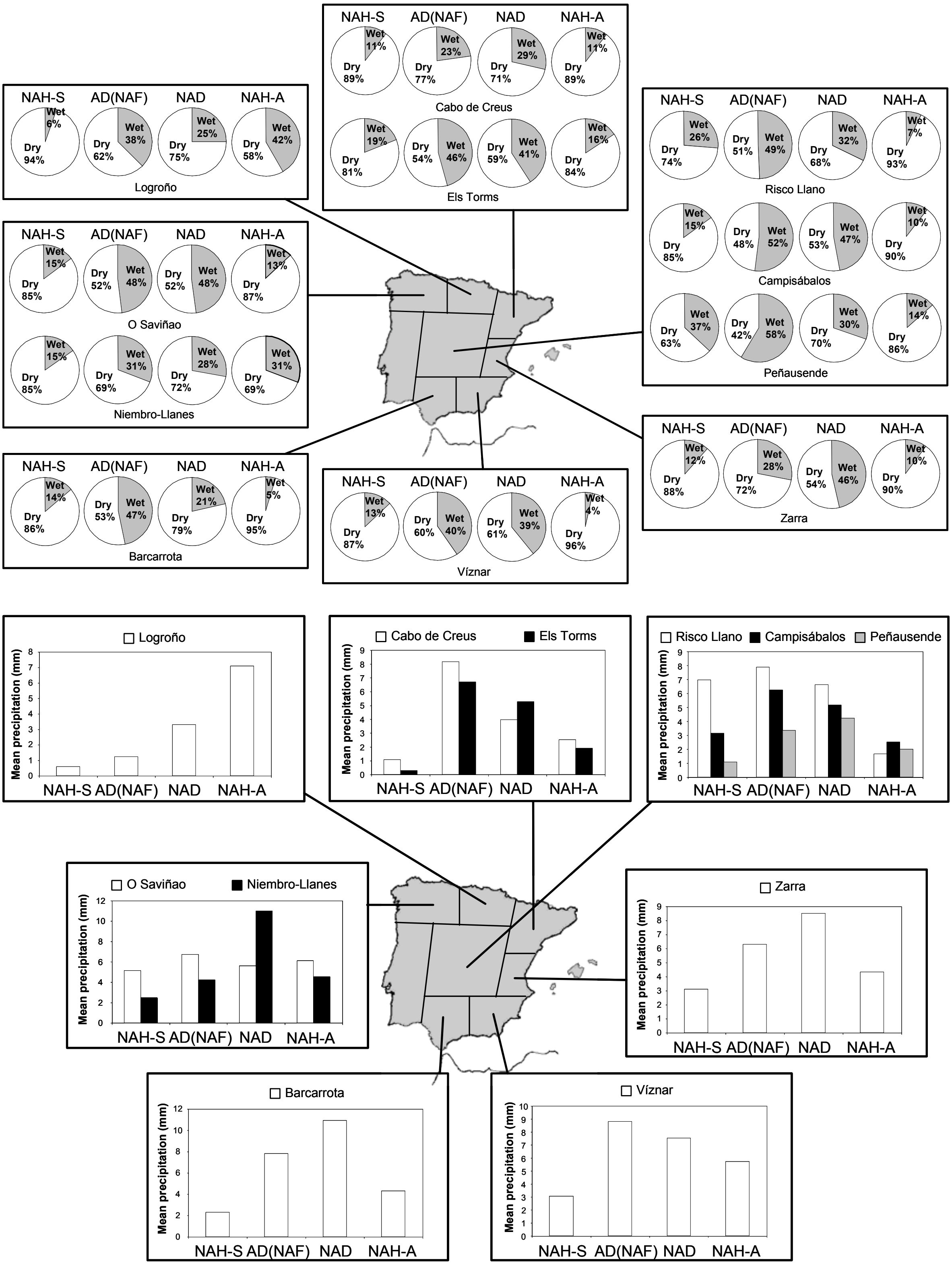


Figure 4.4. Mean daily precipitation and % of wet and dry days recorded during NAH-S, AD(NAF), NAD and NAH-A African events in EMEP stations in Spain for the period 1998-2003.

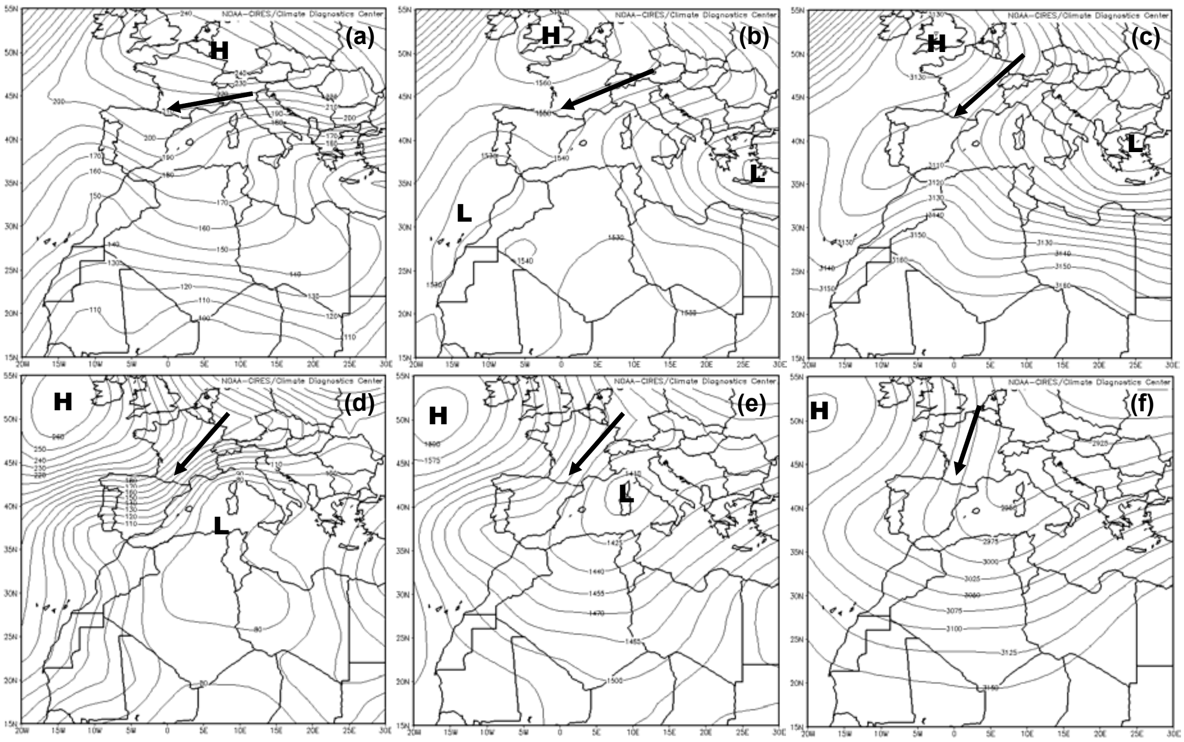


Figure 4.5. Mean geopotential height for 1000, 850 and 700 hPa calculated using data from the first day of EUH (a, b and c), and MD (d, e and f) episodes in 2003.

4.3.2. Precipitation

The European episodes were associated with a low rainfall frequency in the EMEP stations (between 7 and 34% of the days with European advection in the different regions of Iberia, Table 4.4) when compared with the mean rain frequency in 1998-2003 (41-44% in the northwest, 28% in the north, 18-22% in the northeast, 30-34% in the centre, 19% in the east, 27% in the southwest and 22% in the southeast). The mean daily precipitation recorded during European episodes was lower than the mean rainfall volume registered in 1998-2003 (Table 4.4).

Table 4.4. Mean daily precipitation (mm) and % of rain days recorded during episodes with European advection in EMEP stations in Spain for the period 1998-2003.

EU EPISODES	***northwest***		***north***	***northeast***	
	O Saviñao	**Niembro-Llanes**	**Logroño**	**Cabo de Creus**	**Els Torms**
% rain days	18	34	20	20	14
Mean daily precipitation	4.5	5.1	2.4	6.5	4.4

EU EPISODES	***centre***			***east***	***southwest***	***Southeast***
	Risco Llano	**Campisábalos**	**Peñausende**	**Zarra**	**Barcarrota**	**Víznar**
% rain days	13	14	12	20	7	24
Mean daily precipitation	2.6	2.6	3.0	2.4	1.1	5.9

As shown in Figure 4.6, the frequency of occurrence of rain associated with EUH episodes in the EMEP sites (between 7-18% in all the regions of Iberia) was, generally, lower than during MD events (between 5 and 62% in the different areas of Iberia) with the exception of southwestern Iberia (8 and 5% during EUH and MD episodes respectively). The higher frequency of rain during MD episodes is logical since this scenario is associated with the presence of a depression while EUH is caused by an anticyclone. However, in both cases, the original European air masses are dry since these

are continental masses. As shown in Figure 4.6, the mean volumes of precipitation collected during EUH episodes were similar or lower than those recorded during MD episodes with only one exception of Barcarrota.
Consequently, precipitation was, in general, more frequent and more intense during MD events than during EUH episodes. This can be explained by the effect of the Mediterranean depression acting in MD scenario. This may cause differences on the PM levels recorded at the regional background sites during these two scenarios.

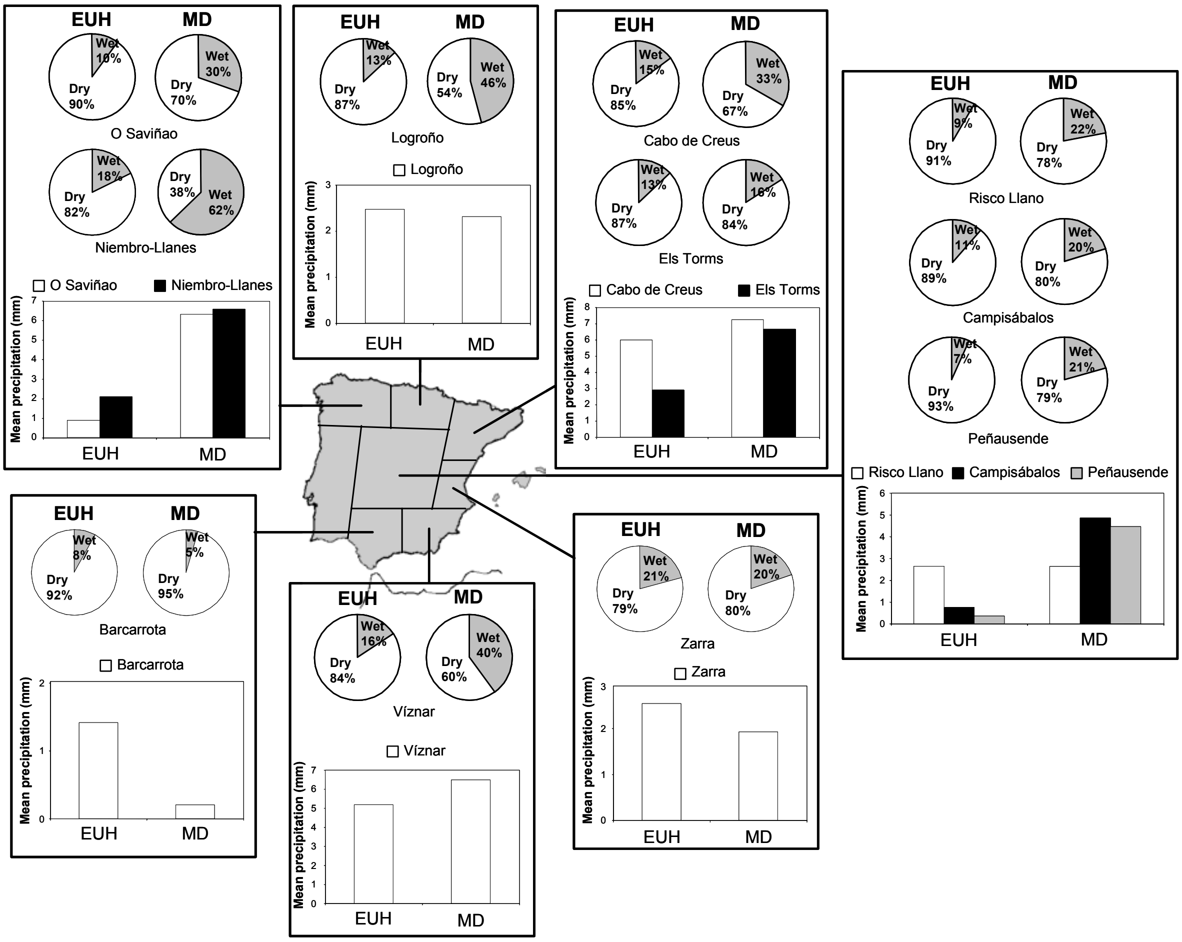


Figure 4.6. Mean daily precipitation and % of wet and dry days recorded during EUH and MD European events in EMEP stations in Spain for the period 1998-2003.

4.4. Mediterranean episodes

4.4.1. Mean pressure fields

The transport of Mediterranean air masses over the Iberian Peninsula occurs under two synoptic scenarios. The first is characterised with a depression centred over north Africa or over the Mediterranean (north African Depression-Mediterranean Depression, NAD-MD scenario). This scenario is practically the same as NAD African transport scenario with the depression slightly displaced over the north. This depression is observed at surface and at 850 and 700 hPa although in these two upper levels is slightly shifted and covers the southeastern Iberian Peninsula (Figure 4.7 (a), (b) and (c)).
The second meteorological scenario is associated an anticyclone over the European continent or over the Mediterranean (EUropean High-Mediterranean High, EUH-MH scenario). These situations resemble to NAH-S African episodes but with a slight shift of

the location of the high towards the north. This feature can only be observed in surface and 850 hPa altitude levels but not at 700 hPa level (Figure 4.7 (d), (e) and (f)).
As Mediterranean transport scenarios are very similar to a couple of African transport scenarios, it may occur that while Mediterranean air masses may affect some areas of Iberia, some others, may be affected by African air masses (generally after a transect over the Mediterranean Sea).

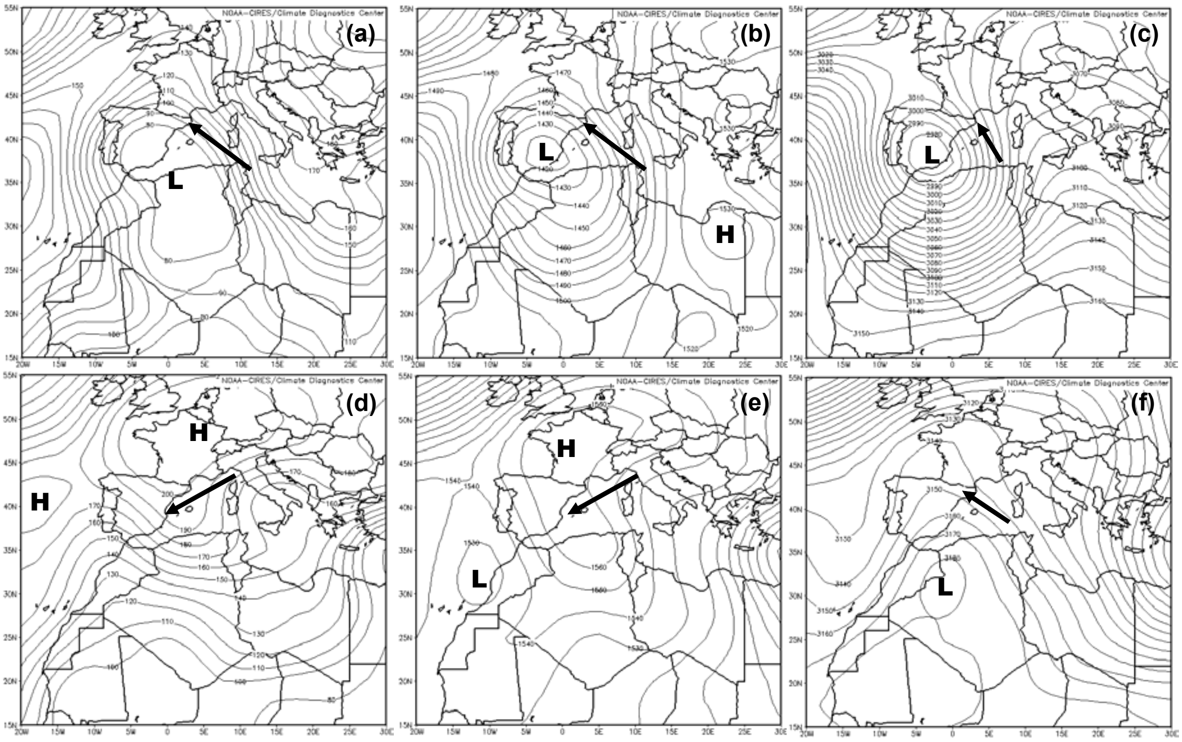


Figure 4.7. Mean geopotential height for 1000, 850 and 700 hPa calculated using data from the first day of NAD-MD (a, b and c), and EUH-MH (d, e and f) episodes in 2003.

4.4.2. Precipitation

As shown in Table 4.5, the frequency of precipitation during Mediterranean events (Below 11% in the northwest, between 24-35% in the north, in the centre, in the southwest and the southeast and between 39 and 56% in the northeast and in the east) is relatively high compared with the mean frequency in 1998-2003 (41-44% in the northwest, 28% in the north, 18-22% in the northeast, 30-34% in the centre, 19% in the east, 27% in the southwest and 22% in the southeast) for the north and the eastern regions of Iberia, but not so frequent for the centre and the western regions (the very low frequency in the northwest is not significant since Mediterranean episodes were scarce in that region in 1998-2003). The intensity of the rain events associated with Mediterranean episodes (Table 4.5) was, in general, of the same order or lower than the intensity of rainfall events in 1998-2003. However, in northeastern Iberia the intense of rainfall during Mediterranean episodes is moderately high.
It can be stated that the rain frequency was clearly more frequent during NAD-MD events (frequency of precipitation in the EMEP stations between 30 and 81%, Figure 4.8) than during EUH-MH episodes (with precipitation frequencies between 19 and 37% in the different regions of the Iberian Peninsula, Figure 4.8) in all the stations and regions (this cannot be generalised for northwestern Iberia because there was not enough precipitation data available to support this). Figure 4.8 also shows the mean daily rainfall

collected during the two Mediterranean air mass transport scenarios. For both NAD-MD and EUH-MH scenarios the volume of precipitation was relatively high.

Table 4.5. Mean daily precipitation (mm) and % of rain days recorded during episodes with Mediterranean advection in EMEP stations in Spain for the period 1998-2003.

MED EPISODES	*northwest*		*north*	*northeast*	
	O Saviñao	**Niembro-Llanes**	**Logroño**	**Cabo de Creus**	**Els Torms**
% rain days	0	11	35	39	56
Mean daily precipitation	-	3.1	3.1	6.1	7.3

MED EPISODES	*centre*			*east*	*southwest*	*southeast*
	Risco Llano	**Campisábalos**	**Peñausende**	**Zarra**	**Barcarrota**	**Víznar**
% rain days	29	33	27	42	24	25
Mean daily precipitation	5.3	5.7	2.2	3.8	4.6	5.3

Summarising, rain was more frequent during NAD-MD Mediterranean events than during EUH-MH. In the eastern regions, rain associated with NAD-MD events was more intense than during EUH-MH episodes but this does not stand for other regions where there was no general trend. The moisture of Mediterranean air masses can be the cause of this high frequencies and intensities of precipitation over the Iberian Peninsula during Mediterranean events.

4.5. Episodes without dominant advective conditions

4.5.1. Mean pressure fields

Two types of synoptic situations explaining the events with lack of prevalent advective conditions were observed. In these situations no transport of external air masses over the Iberian Peninsula so the PM load is generated completely at a local/regional scale. The first scenario is associated with the presence of an anticyclone over the Iberian Peninsula during the cold seasons of the year (Winter Iberian Anticyclone, WIA scenario). The original air mass gradually cools over Iberia until it becomes colder and drier. Under these scenarios strong episodes of pollution occur in urban and industrial locations due to the high stability leading to frequent formation of near ground inversion layers over cities (Font, 2000). It can be observed that the anticyclone over the Iberian Peninsula is only present at surface level while in the upper levels western flow occurs over the Iberian Peninsula (Figure 4.9 (a), (b) and (c)).
The second scenario occurs, by definition, in the warm season of the year. It is associated with the development of a thermal low over the central plateau and the convergence of winds from the coastal areas, through natural passes, towards the centre of the Peninsula (Iberian Thermal Low, ITL scenario). The Iberian thermal low formation is associated with the strong heating over the central plateau in summer. These processes are accompanied by a compensatory subsidence over the surrounding areas (Millán et al., 1997). As detailed by Millán et al. (1997), a complex set of mesoscale circulation cells develop over the eastern flank of the Iberian Peninsula owing to the combination of the sea breeze and the up-slope winds. These result in the aging and re-circulation of pollutants in the eastern Iberian Peninsula. Moreover, in other regions of the Iberian Peninsula up-slope breezes also develop owing to the intense convection characterising ITL episodes. As shown in Figure 4.9 (d), (e) and (f) these complex dynamics occurs only at surface level where the development of the African thermal low can be observed. The formation of this low pressure centre is the response to the strong

heating of the surface and the consequent generation of an uplift flux. The situation at 850 and 700 hPa differs completely with the presence of an anticyclone over north Africa inducing Atlantic flow above 1500 m.a.s.l.

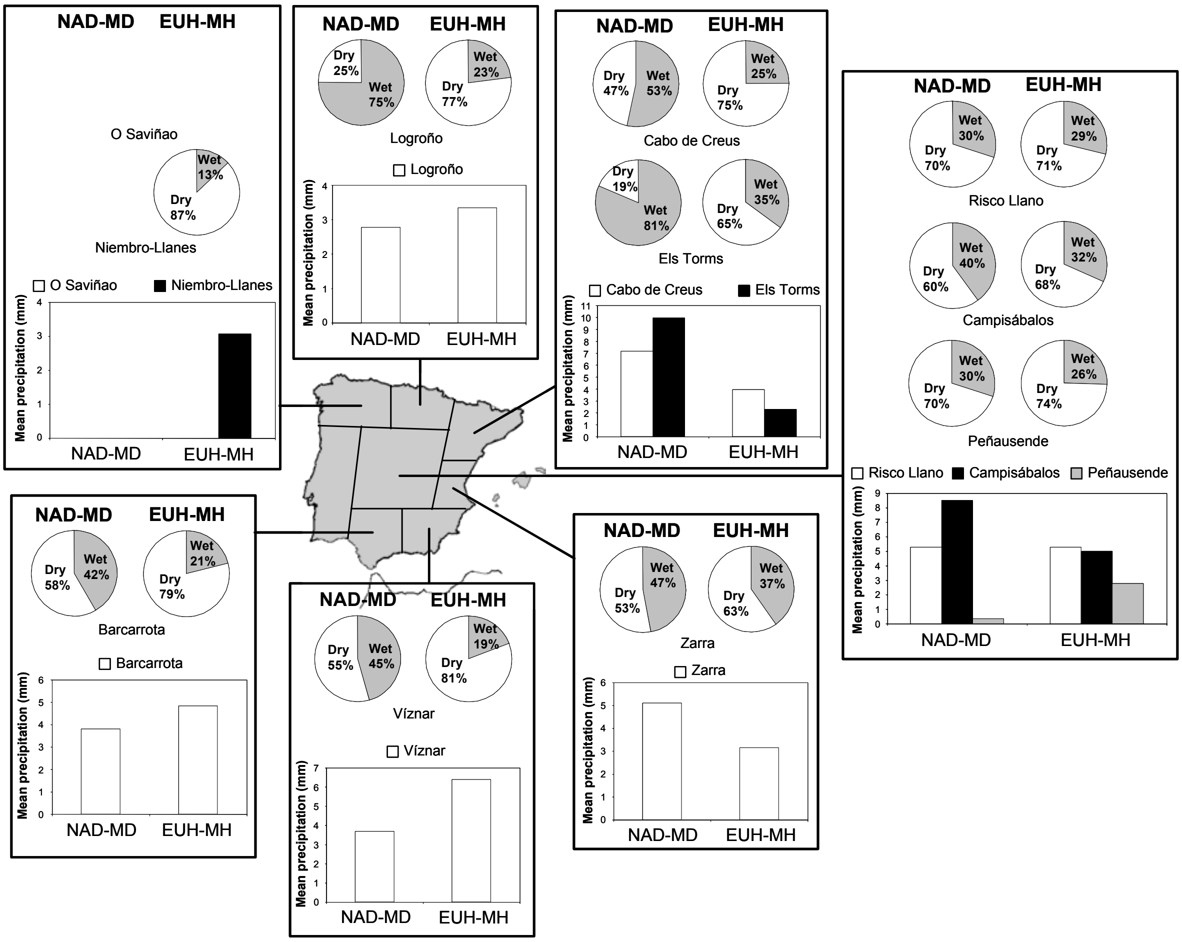


Figure 4.8. Mean daily precipitation and % of wet and dry days recorded during NAD-MD and EUH-MH Mediterranean events in EMEP stations in Spain for the period 1998-2003.

4.5.2. Precipitation

The number of rainy days during episodes without advective conditions (between 10 and 23% in the different regions of Iberia, Table 4.6) was low in all the regions of the Iberian Peninsula compared with the mean frequency of occurrence of rain in 1998-2003 (41-44% in the northwest, 28% in the north, 18-22% in the northeast, 30-34% in the centre, 19% in the east, 27% in the southwest and 22% in the southeast). The mean daily precipitation collected during the episodes without dominant advective conditions (Table 4.6) was similar or lower than the mean daily rainfall of precipitation in 1998-2003.

During WIA episodes, the frequency of rain in the EMEP sites (between 10 and 37% in the different regions of Iberia, Figure 4.10) was slightly higher than during ITL events (between 6 and 19% in the different regions of Iberia, Figure 4.10). As shown in Figure 4.10, the intensity of the rain during WIA episodes was higher than during ITL events in the stations located in the northeast, southwest and southeast and lower in the other four regions (Figure 4.10).

Thus, although precipitation was infrequent both under WIA and ITL scenarios, it was somewhat more frequent during WIA events. The intensity of these rain episodes varied depending on the region or station.

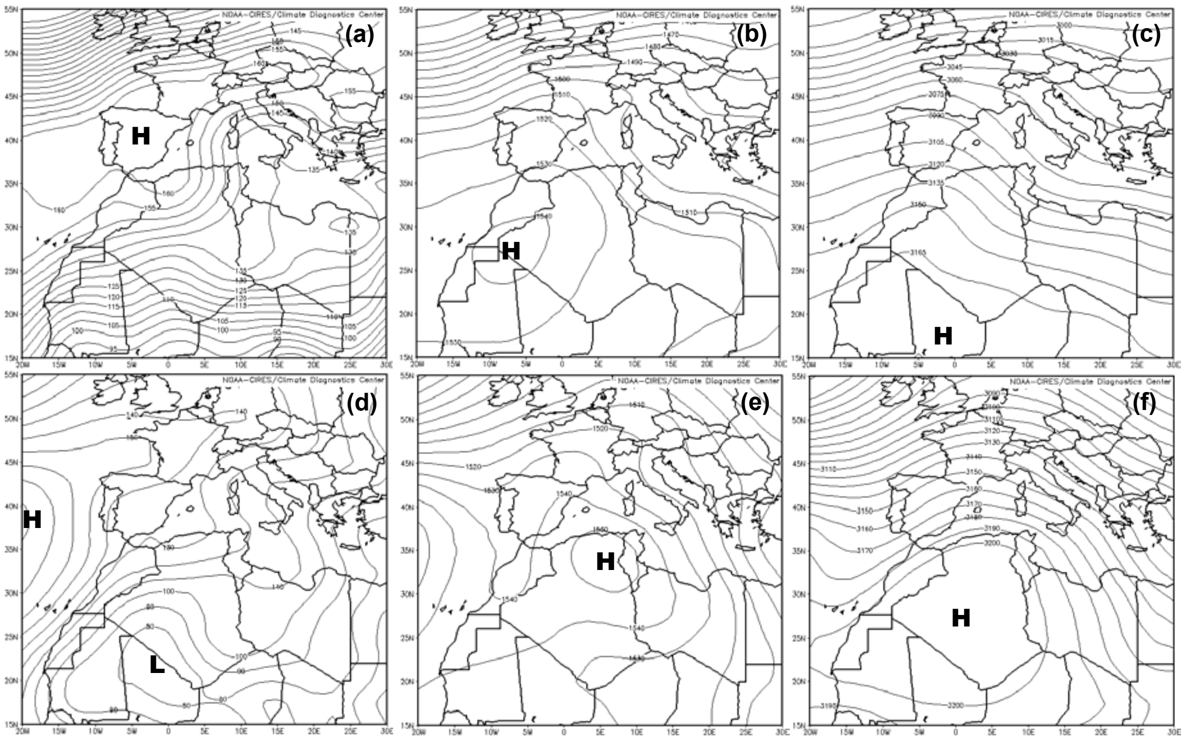


Figure 4.9. Mean geopotential height for 1000, 850 and 700 hPa calculated using data from the first day of WIA (a, b and c), and ITL (d, e and f) episodes in 2003.

Table 4.6. Mean daily precipitation (mm) and % of rain days recorded during episodes without dominant advective conditions in EMEP stations in Spain for the period 1998-2003.

NOADV EPISODES	*northwest*		*north*	*northeast*	
	O Saviñao	**Niembro-Llanes**	**Logroño**	**Cabo de Creus**	**Els Torms**
% rain days	23	23	17	10	19
Mean daily precipitation	3.6	3.3	3.6	4.0	4.3

NOADV EPISODES	*centre*			*east*	*southwest*	*southeast*
	Risco Llano	**Campisábalos**	**Peñausende**	**Zarra**	**Barcarrota**	**Víznar**
% rain days	17	22	16	13	13	10
Mean daily precipitation	4.3	2.6	3.9	3.5	5.2	5.0

4.6. Synthesis

Different air mass transport scenarios have been described in this chapter. The classification was made according to the air mass source areas, that is, Atlantic (source area in the Atlantic Ocean), African (source area in the African continent), European (source area in the European continent), Mediterranean (source area in the Mediterranean Sea) and episodes without dominant advective conditions (local or regional air masses). Each of these events may occur under different synoptic meteorological scenarios with particular precipitation regimes. This section synthesises the main meteorological characteristics of all these scenarios.

4.6.1. Atlantic episodes

These events occur when the Azores High and the Iceland low are located in their standard locations (AZH-NAtD scenario) or when a depression locates by to the Portuguese coast (AD(ATL) scenario). The origin of the Atlantic air masses is generally different in these two situations, AZH-NAtD situations generally involves air masses from the north, northwest or west regions of the Atlantic Ocean and AD(ATL) from the west or the southwest regions (Figure 4.11).

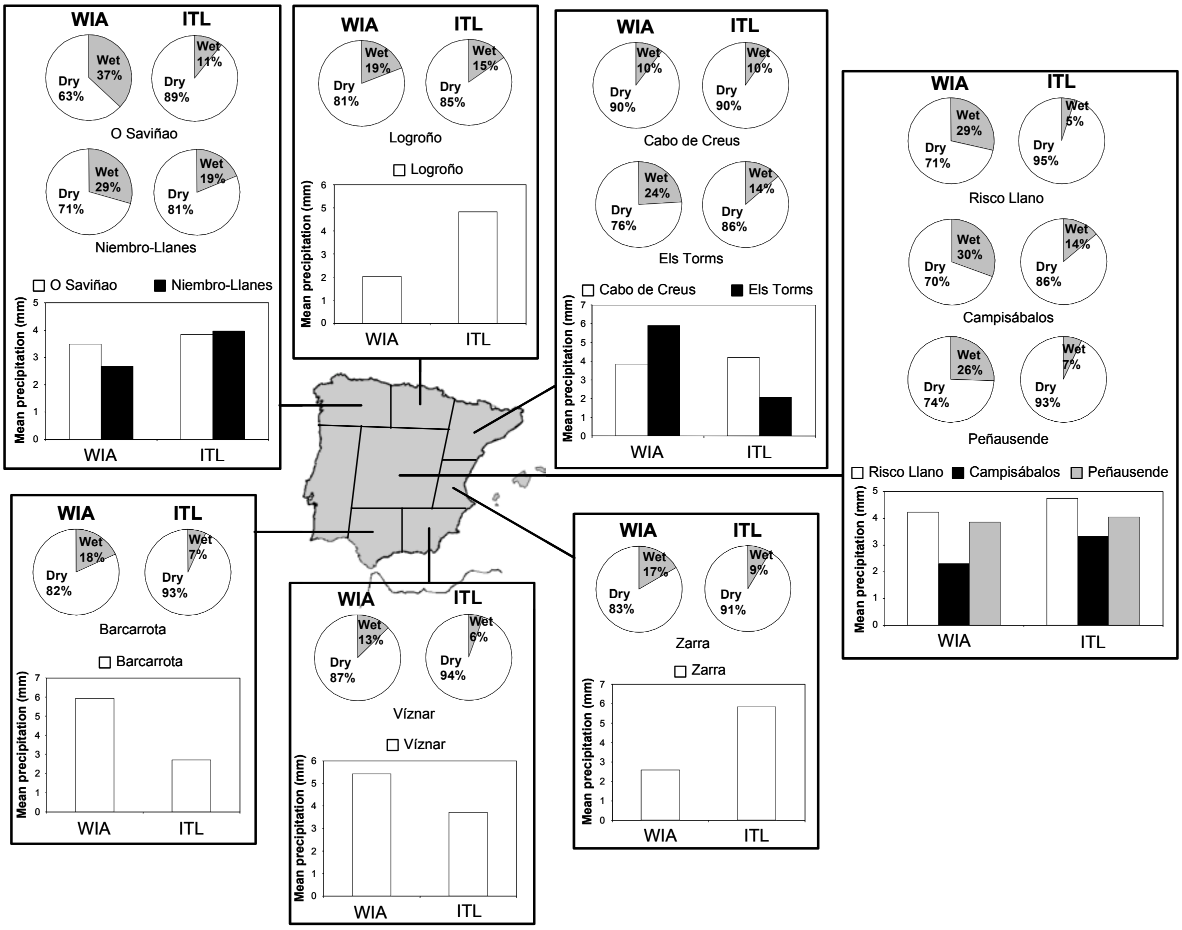


Figure 4.10. Mean daily precipitation and % of wet and dry days recorded during WIA and ITL Mediterranean events in EMEP stations in Spain for the period 1998-2003.

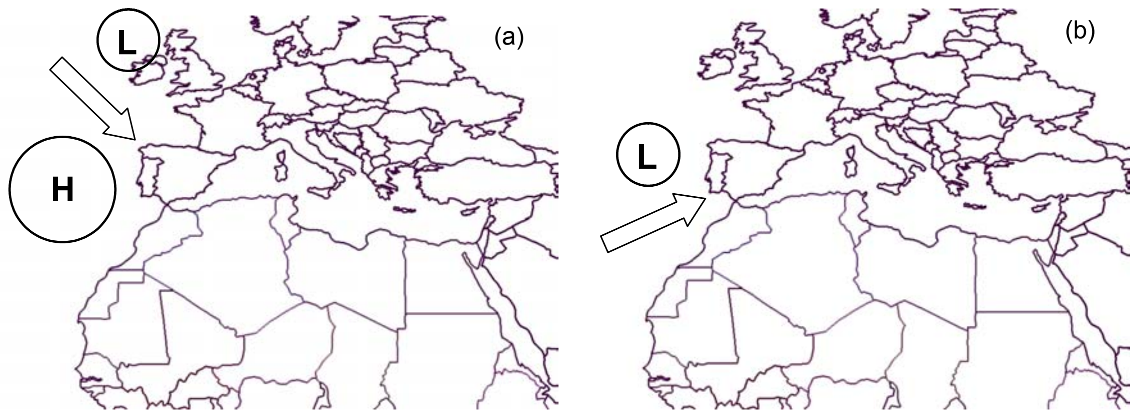


Figure 4.11. Schematic representation of the AZH-NAtD (a) and AD(ATL) (b) synoptic scenarios resulting in episodes of Atlantic air mass transport over the Iberian Peninsula.

The Atlantic episodes were generally associated with a moderately high rainfall frequency as recorded in the EMEP stations. As shown in Figure 4.12, precipitation was not as frequent during AZH-NAtD events as during AD(ATL). Moreover, for both transport scenarios, the frequency of precipitation associated to both transport scenarios decreases from west to east. In fact during AZH-NAtD episodes the stations located on the eastern flank of the Iberian Peninsula showed a rainfall frequency above the mean frequency in 1998-2003 (Figure 4.12).

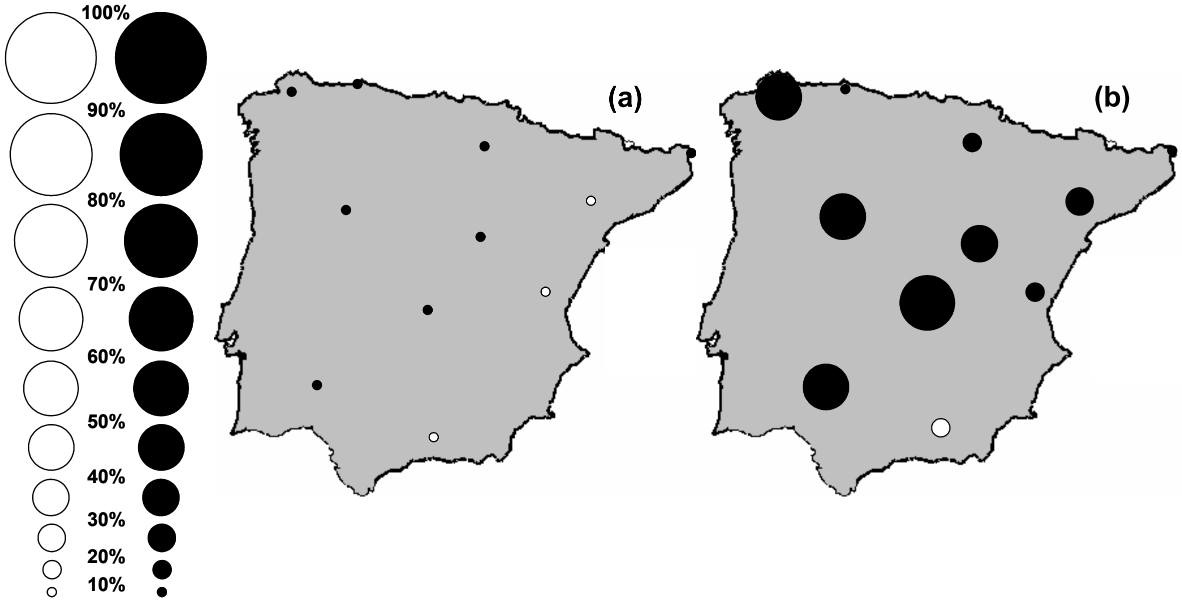


Figure 4.12. Difference between the proportion of rainy days during AZH-NAtD (a) and AD(ATL) (b) episodes and annual proportion of rainy days in the EMEP stations in 1998-2003. The black dots indicate positive differences (higher frequency of occurrence) and the white dots indicate negative differences (lower frequency of occurrence).

4.6.2. African episodes

Four different synoptic situations explain the occurrence of African dust outbreaks. The first occurs when an anticyclone is located over northern Africa or the Iberian Peninsula at surface level (NAH-S scenario) causing a narrow convex transport plume which reaches the Iberian Peninsula from its western flank. This scenario would induce the transport of African air masses from the western Sahara, Mauritania, Mali and the Sahel (Figure 4.13).

The second is characterised with the presence of a depression over the Atlantic Ocean by to the Portuguese coast (AD(NAF) scenario, Figure 4.13). The source areas involved in this type of episodes would be the western regions of north Africa (Mauritania, Mali and Morocco).

A third transport scenario is associated with the presence of a depression over northern Africa or the western Mediterranean (NAD scenario, Figure 4.13). The main emission regions in north Africa during these episodes may be Algeria. Tunisia, Libya and Chad.

Finally, the fourth transport scenario occurs mainly in summer when the intense heating yields the development of a semi-permanent thermal low over north Africa and, in many occasions, another over the Iberian Peninsula and the important injection of dust up to altitudes around 5000 m.a.s.l. An anticyclone located at high altitudes (>1500 m) drives the transport of dust over the Mediterranean basin (NAH-A scenario) forming a wide plume of dust (Figure 4.13).

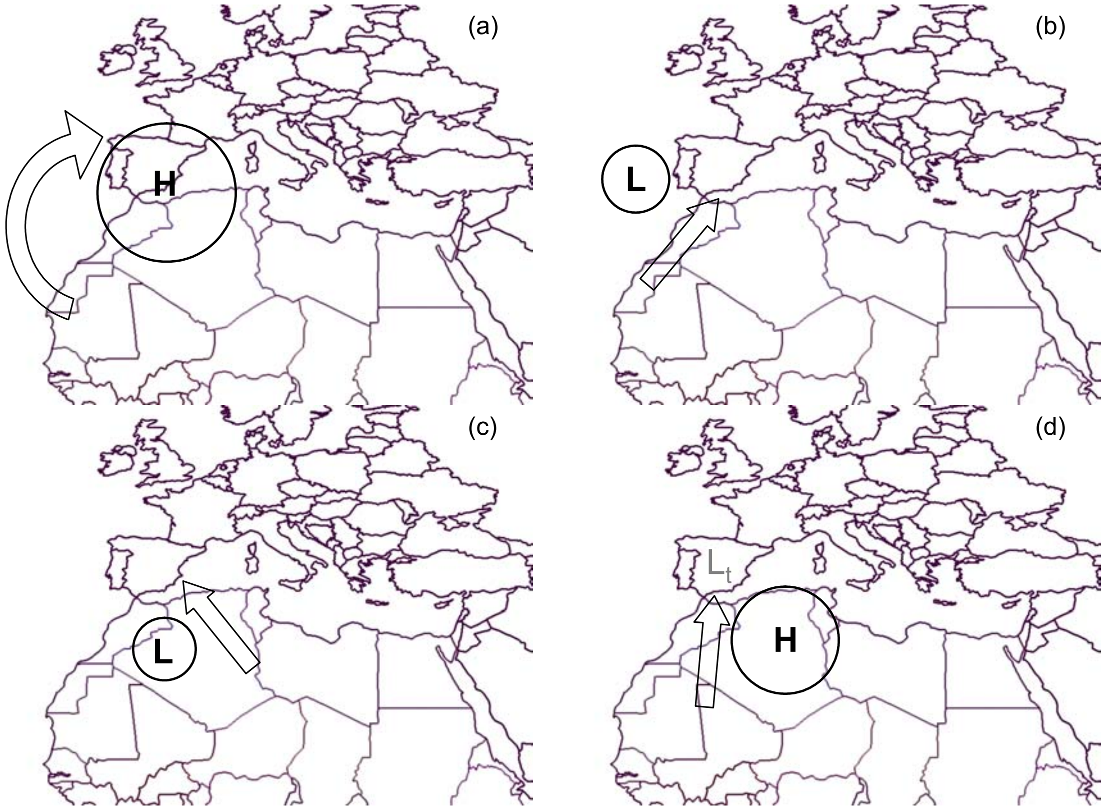


Figure 4.13. Schematic representation of the NAH-S (a), AD(NAF) (b), NAD (c) and NAH-A (d) synoptic scenarios resulting in episodes of African air mass transport over the Iberian Peninsula. L_t means Thermal low.

With respect to the frequency of occurrence of rain in the EMEP stations in 1998-2003 during the four transport scenarios, two different regimes may be distinguished. NAH-S and NAH-A scenarios were dry because the majority of the EMEP stations registered low frequency of occurrence of precipitation below the average (Figure 4.14). AD(NAF) and NAD scenarios were wet in most of the regions. However, during NAD events precipitation was frequent in the eastern flank of the Iberian Peninsula but not in the western flank (Figure 4.14).

4.6.3. European episodes

Two synoptic scenarios are proposed to explain the episodes of transport of European air masses over the Iberian Peninsula (Figure 4.15**)**. These are the presence of an anticyclone over the north Atlantic or the European continent (EUH scenario) or the presence of a depression over the western Mediterranean (MD scenario).

The frequency of occurrence of precipitation during European events is low. During EUH episodes the precipitation is less frequent than the average in most of the stations while during MD episodes the frequency of occurrence of rain is higher than the average in the east and the north and lower in the rest of the regions (Figure 4.16).

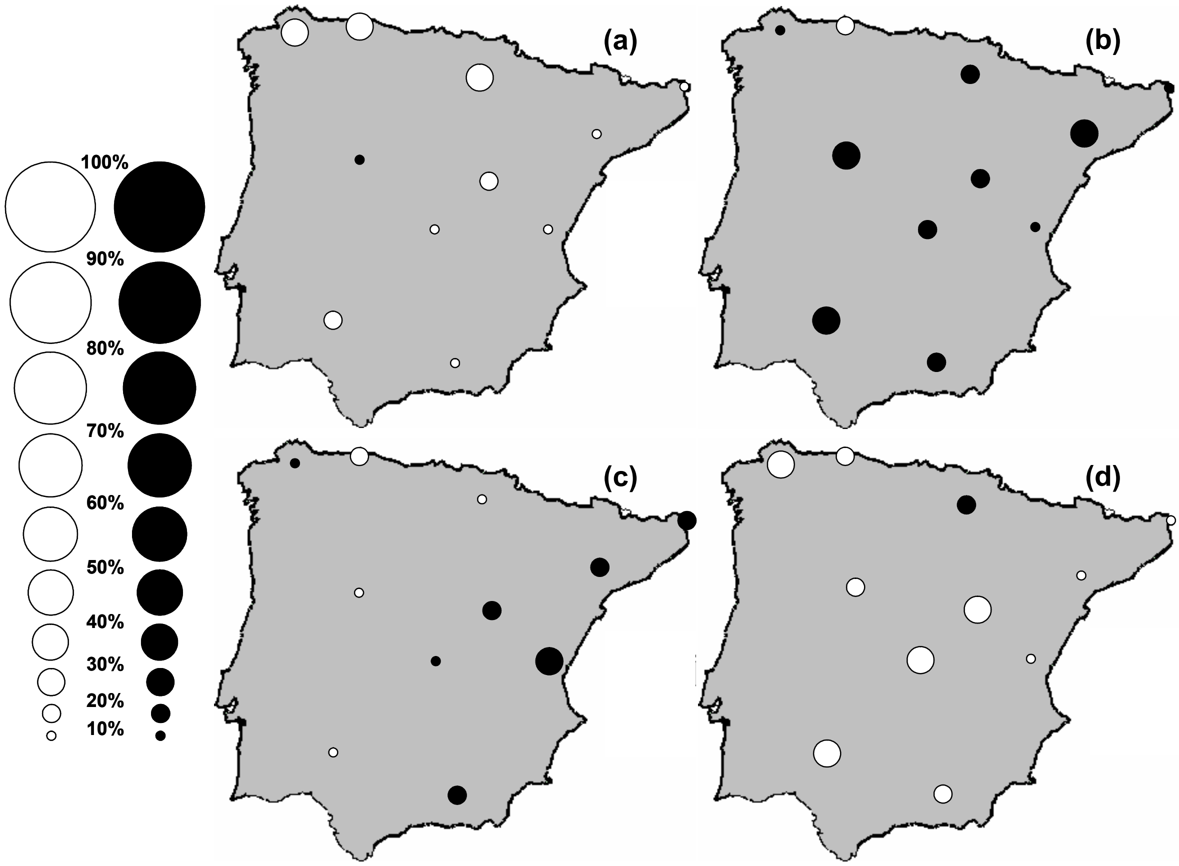


Figure 4.14. Difference between the proportion of rainy days during NAH-S (a), AD(NAF) (b), NAD (c) and NAH-A (d) episodes and the annual proportion of rainy days in the EMEP stations in 1998-2003. The black dots indicate positive differences (higher frequency of occurrence) and the white dots indicate negative differences (lower frequency of occurrence).

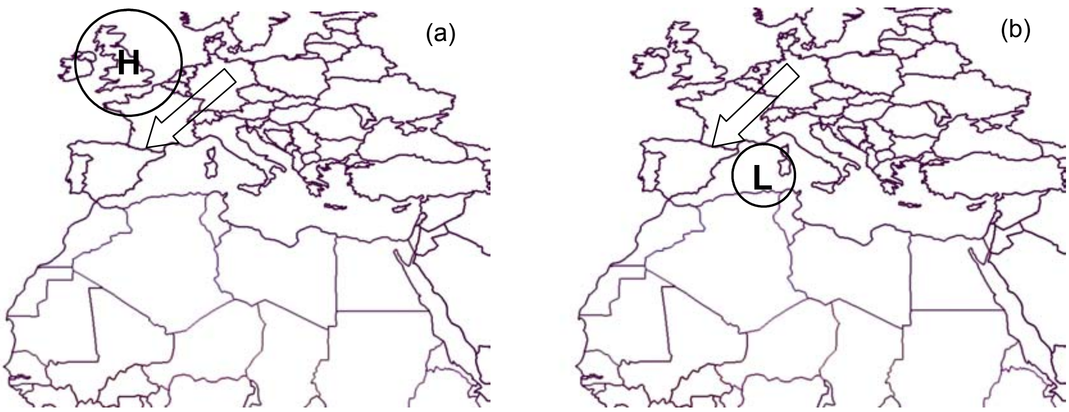


Figure 4.15. Schematic representation of the EUH (a) and MD (b) synoptic scenarios resulting in episodes of European air mass transport over the Iberian Peninsula.

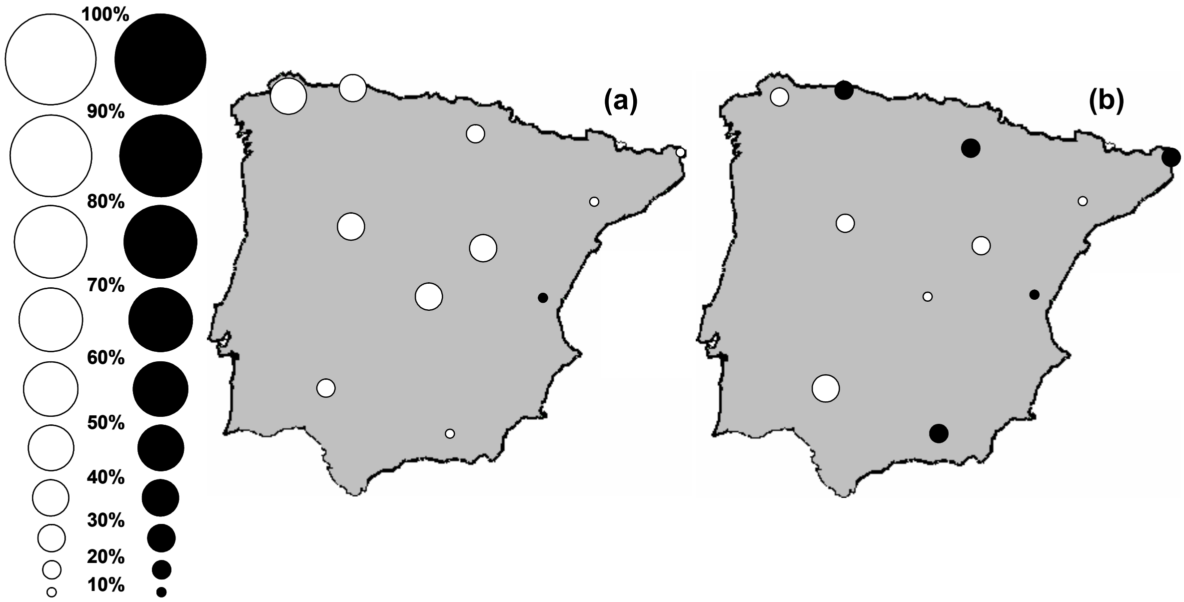


Figure 4.16. Difference between the proportion of rainy days during EUH (a) and MD (b) episodes and the mean values recorded in the EMEP stations in 1998-2003. The black dots indicate positive differences (higher frequency of occurrence) and the white dots indicate negative differences (lower frequency of occurrence).

4.6.4. Mediterranean episodes

As presented in Figure 4.17, the transport of Mediterranean air masses over the Iberian Peninsula is originated when a depression develops over northern Africa and/or the Mediterranean Sea (NAD-MD scenario) or when an anticyclone is located over the European continent or the Mediterranean Sea (EUH-MH scenario).

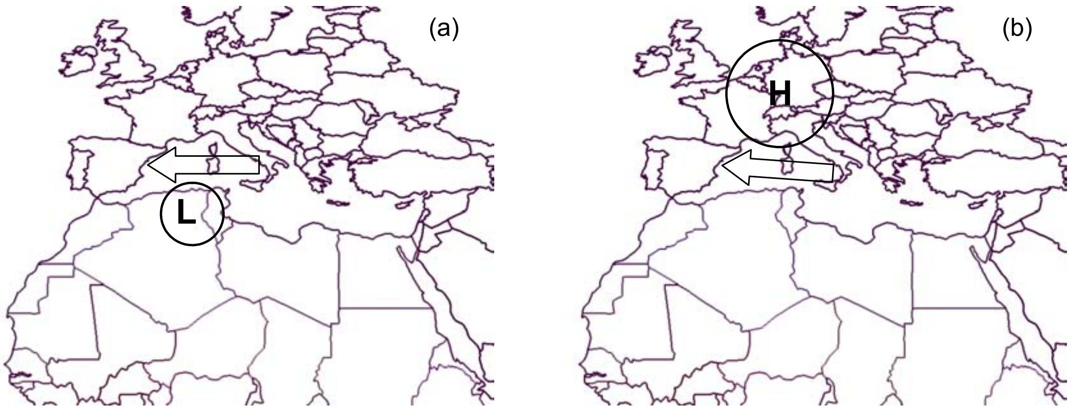


Figure 4.17. Schematic representation of the NAD-MD (a) and EUH-MH (b) synoptic scenarios resulting in episodes of Mediterranean air mass transport over the Iberian Peninsula.

The Mediterranean episodes of NAD-MD type were associated with high frequency of precipitation in the east and the north of the Iberian Peninsula and moderately high in the rest of the regions. EUH-MH events were moderately dry in all the regions with the exception of the northeast were the occurrence of precipitation was more frequent than the average (Figure 4.18).

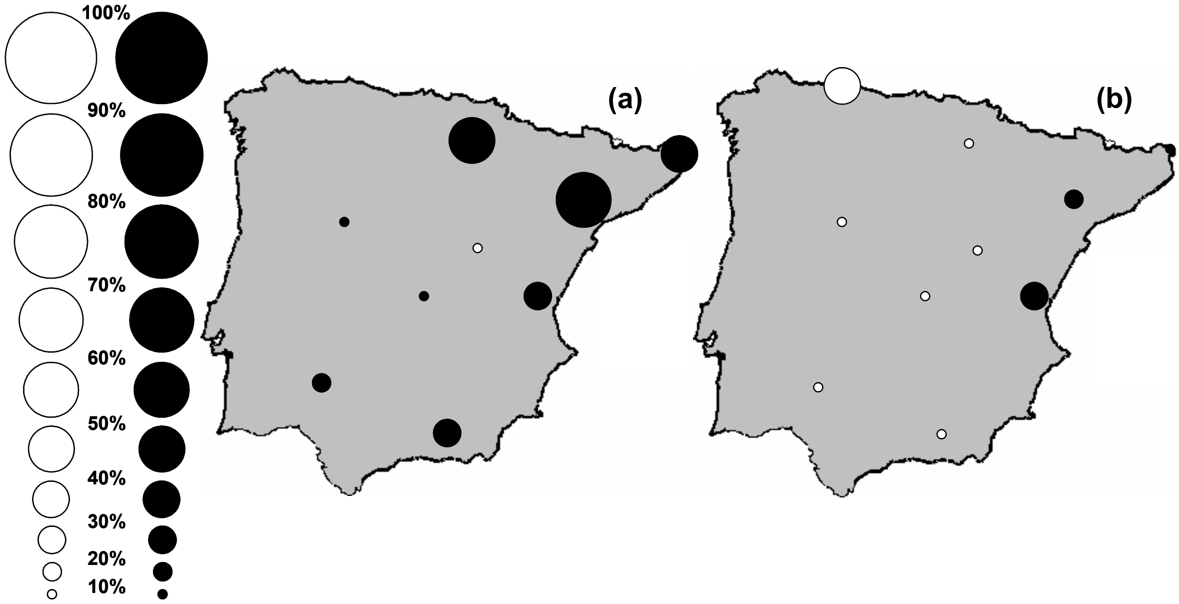


Figure 4.18. Difference between the proportion of rainy days during NAD-MD (a) and EUH-MH (b) episodes and the annual proportion in the EMEP stations in 1998-2003. The black dots indicate positive differences (higher frequency of occurrence) and the white dots indicate negative differences (lower frequency of occurrence).

4.6.5. Episodes without dominant advective conditions

As presented in Figure 4.19, the events with lack of prevailing advective conditions in the Iberian Peninsula may occur in the cold seasons of the year when an anticyclone covers the Iberian Peninsula (WIA scenario) or in the warm seasons of the year, when the Iberian thermal low is formed over the continental areas of the Iberian Peninsula owing to the strong heating of the surface (ITL scenario). In this second scenario a complex system of convective cells and breezes circulations is established over the Iberian Peninsula as detailed by Millán et al., 1997. These dynamics have been proved to have an effect in the proliferation of aged pollutants especially over the eastern Iberian Peninsula.

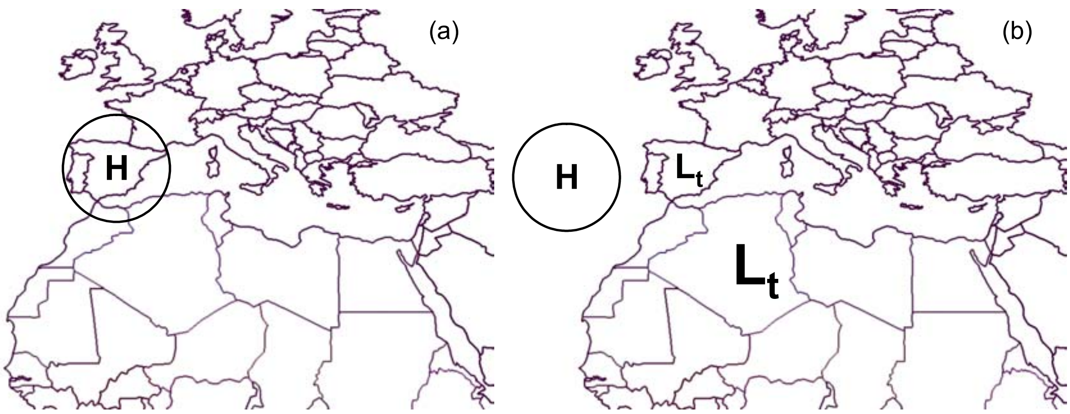


Figure 4.19. Schematic representation of the WIA (a) and ITL (b) synoptic scenarios resulting in episodes without dominant advective conditions over the Iberian Peninsula. L_t means Thermal low.

The episodes with lack of advective conditions are generally dry. WIA events are moderately drier than the average in all the areas of the Iberian Peninsula and ITL episodes are considerably dry (Figure 4.20).

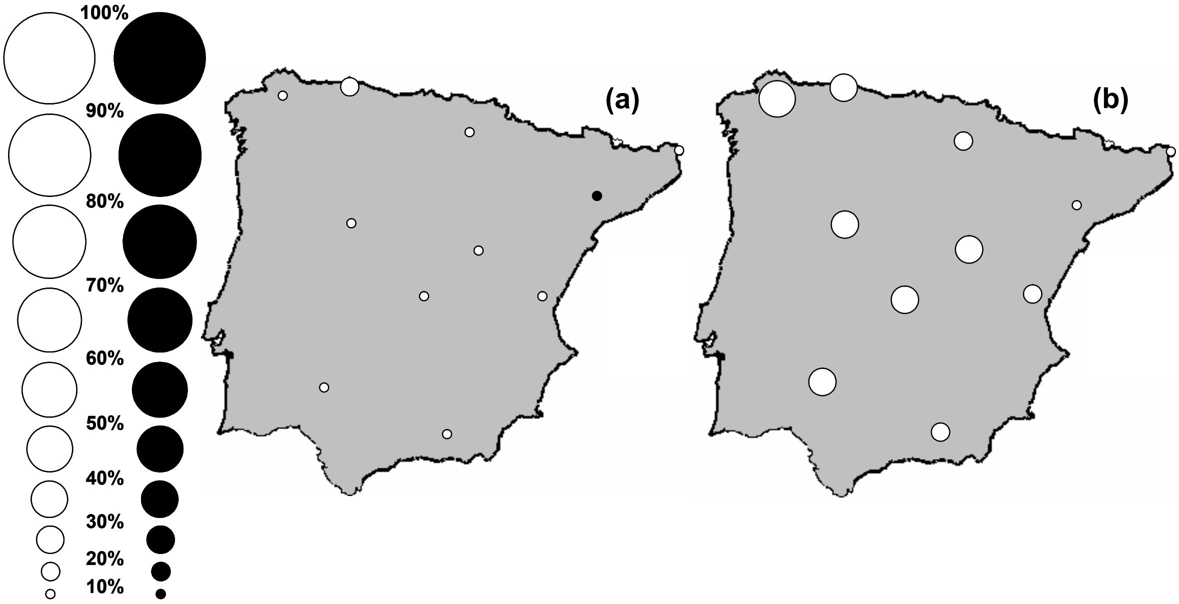


Figure 4.20. Difference between the proportion of rainy days during WIA (a) and ITL (b) episodes and the mean annual values recorded in the EMEP stations in 1998-2003. The black dots indicate positive differences (higher frequency of occurrence) and the white dots indicate negative differences (lower frequency of occurrence).

5. PM events in regional background areas of the Iberian Peninsula

5. OCCURRENCE OF PM EVENTS IN REGIONAL BACKGROUND AREAS OF THE IBERIAN PENINSULA

After the identification of the meteorological scenarios causing the different types of PM episodes in the Iberian Peninsula this chapter will focus on the following objectives: a) Description of the temporal variability of PM events, b) Evaluation of the impact of different air mass transport events on the air quality monitoring stations located in rural and natural areas (regional background) and c) Description of the geographical variability within the Iberian Peninsula.
The meteorological scenarios identified in the previous chapter of this dissertation were the following:

(a) **Atlantic episodes**

(a.1) **AZH-NAtD scenario**: When the Azores high and the Iceland low were placed on their standard locations.

(a.2) **AD(ATL) scenario**: When a relatively deep low was located over the Atlantic Ocean in front of the Portuguese coast.

(b) **African episodes**

(b.1) **NAH-S scenario**: When an anticyclone over northern Africa and the Iberian Peninsula was present at surface level.

(b.2) **AD(NAF) scenario**: When an Atlantic depression by the Portuguese coast develop.

(b.3) **NAD scenario**: When depressions were located over northern Africa and/or the western Mediterranean.

(b.4) **NAH-A scenario**: When an anticyclone shifted at high atmospheric levels was present over north Africa or the Iberian Peninsula.

(c) **European episodes**

(c.1**) EUH scenario**: When an anticyclone was located over the European continent or over the northern Atlantic Ocean.

(c.2**) MD scenario**: When depressions develop over the western Mediterranean.

(d) **Mediterranean episodes**

(d.1) **NAD-MD scenario**: When a depression was present over northern Africa and/or the Mediterranean Sea.

(d.2) **EUH-MH scenario**: When an anticyclone was located over the European continent and/or over the Mediterranean Sea.

(e) **Episodes without dominant advective conditions**

(e.1) **WIA scenario**: Caused by an anticyclone covering partly or completely the Iberian Peninsula out of summer.

(e.2) **ITL scenario**: Situations in which the thermal Iberian low developed over the Iberian plateau during summer owing to the great heating of the surface.

5.1 Northwestern Iberian Peninsula

This region is surrounded by the Atlantic Ocean on its western and northern flanks. The dominant Nothwestern winds and the common passage of frontal systems result in a humid and well ventilated area. The rainfall regime affects the levels of PM in two ways: i) the direct effect of washing out or scavenging of aerosols and ii) the reduction of re-suspension of mineral dust due to the high moisture of soils from this area.
Daily PM data series from three regional background stations belonging to the EMEP network located over northwestern Iberian Peninsula were used during this study. Noia

station (42º 44’ N, -8º 55’ E, 683 m.a.s.l.) offered data on TSP (1998-June 2000). At Niembro (43º 27’ N, -4º 51’ E, 134 m.a.s.l.), TSP (1999-January 2003) and PM10 and PM2.5 (March 2001-2003) were registered. At O Saviñao (43º 14’ N, -7º 42’ E, 506 m.a.s.l.) data on TSP, PM10 and PM2.5 (March 2001-2003) were available. All these data series were collected using the high volume gravimetric method. The PM levels recorded in these stations should represent the regional background although the station at Niembro offered mean PM levels clearly superior to those recorded at Noia and O Saviñao. This probably reflected the impact of local anthropogenic sources over Niembro station. In this case, Niembro station would not represent the regional background. For this reason attention will be preferably paid to Noia and O Saviñao data.

The advection of Atlantic air masses is the most common atmospheric transport scenario in the study region. The number of days with Atlantic advection in 1998-2003 reached 1468 days (71.5% of the number of days in 1998-2003) grouped in 223 episodes (50.8% of the number of episodes in 1998-2003, Figure 5.1). Among Atlantic episodes AZH-NAtD were the most frequent (8 times more frequent than AD(ATL)).

The frequency of occurrence of situations without dominant advective conditions and episodes with European and African advection was of the same order. Each of these three situations resulted in 8-10% of the number of days (between 182 and 227 days in 1998-2003) and around 15% (66-67 episodes in the study period) of the number of episodes in 1998-2003 (Figure 5.1). EUH scenario was the most common situation among European episodes (twice as frequent as MD) while ITL scenario among episodes with lack of advective conditions (1.3 times more frequent than WIA). With respect to the African transport scenarios only NAD scenario showed a clear lower frequency compared to the other three scenarios (NAH-A, AD(NAF) and NAH-S were 2-3 times more frequent than NAD).

The episodes of Mediterranean advection were scarce over northwestern Iberia with only 28 days (1.3% of the total number of days) grouped in 16 PM episodes (3.6% of the total number of episodes).

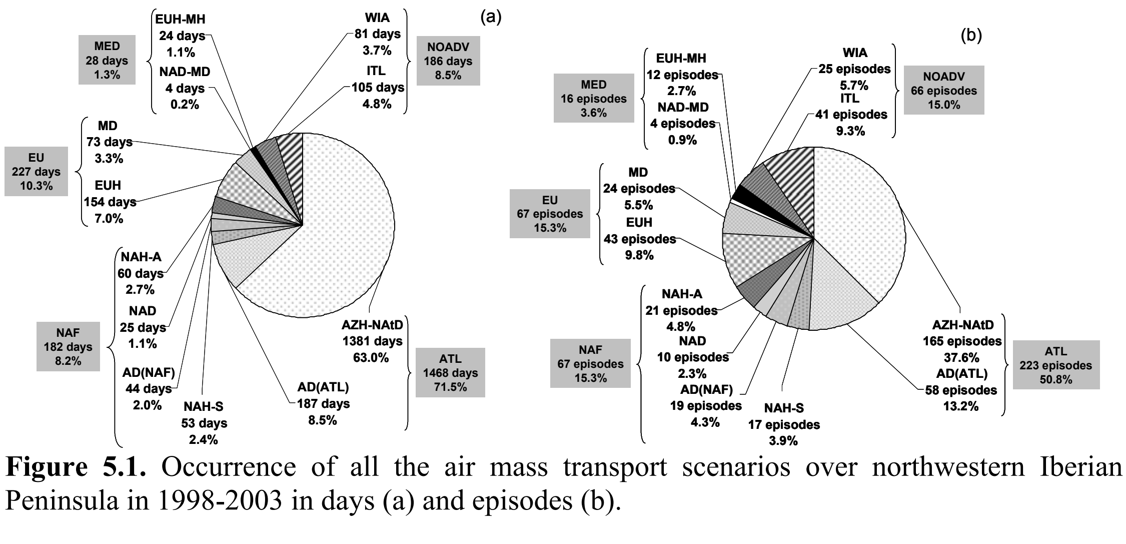


Figure 5.1. Occurrence of all the air mass transport scenarios over northwestern Iberian Peninsula in 1998-2003 in days (a) and episodes (b).

The Atlantic episodes were especially frequent in all the months of the year over northwestern Iberia. April, November (26 days as a mean on both months) and July (25 days as a mean) showed the highest frequency and March (16 days per on average) the lowest. As Figure 5.2 shows, AZH-NAtD episodes occurred all along the year with means above 12 days in all the months of the year. Concretely, July and November were months with high frequency of occurrence of AZH-NAtD episodes (more than 24 days on average on both months). AD(ATL) episodes also occurred in all the months but showed a higher frequency of occurrence in months such as December, March and April (with 5 days on average in all the months). In the period June-August the number of days associated with AD(ATL) situations were almost negligible.

The transport of African air masses over northwestern Iberia occurred in all the months but with a clear predominance of the period January-March (with 5 days as monthly mean in March) and the period May-June (with 5 days as monthly mean in June). April (only 2 days in the period 1998-2003) and July and September (3 days in 1998-2003 on each of these months) marked the minima in the monthly distribution of days with African advection. NAH-S and NAH-A episodes showed a marked seasonality. While the first scenario only occurred in the period January-March (means from 2 or 3 days in the three months) the latter, only occurred in summer with especial frequency in June (a mean of 5 days). AD(NAF) and NAD African events were distributed all throughout the year with the exception of summer months. AD(NAF) scenario reached the highest frequency of occurrence in March (2 days on average) and NAD scenario in May (2 days as monthly mean).

European events occurred all throughout the year although a higher relative frequency was registered in the period November to April and in September closely related to the high frequency of occurrence of EUH situations from January to March (with means up to 4 EUH days during March). MD events were not as frequent as EUH events and occurred mainly in April (with a monthly average of 3 days). The lowest number of days with European advection was registered in summer.

The frequency of occurrence of situations with lack of dominant advective conditions was particularly high in summer when ITL situations occurred almost exclusively. In August, a mean of 6 days without dominant advective conditions was recorded (all of them classified as ITL). WIA situations occurred in the rest of the year but especially in October and December (means of 3 days in these months) and February (2 days as a mean). The number of days with Mediterranean advection were almost negligible and no conclusions can be drawn on the seasonality of the occurrence of these episodes.

On average, the Atlantic episodes were the longest (with a mean duration of 8 days per episode). Most of the events reached a mean duration of 3 days with the exception of Mediterranean events with a mean duration of 2 days. All the transport scenarios also reached a mean duration of 2 or 3 days with the exception of AZH-NAtD with mean duration of 8 days, EUH with a mean duration of 4 days and NAD-MD episodes with 1 day (Table 5.1).

As shown in Table 5.2, the annual mean PM levels in the period 1998-2003 recorded in northwestern EMEP stations ranged between 17-27 µgTSP m^{-3}, 15-19 µgPM10 m^{-3} and 10-11 µgPM2.5 m^{-3}. The highest PM levels were recorded at Niembro. As expected, none of these stations exceeded the annual limits values established for PM10 by the 1999/30/CE Directive neither in the 2005 phase (limit annual value of 40 µg m^{-3}) nor in the 2010 phase (target annual mean of 20 µgPM10 m^{-3}) in any of the years in 2001-2003 although Niembro reached 20 µgPM10 m^{-3} as annual mean in 2001 and 2003. With respect to the PM2.5 annual cap value included in the Air Quality directive draft issued by the EU Commission in September 2005 of 25 µgPM2.5 m^{-3}, it was not surpassed neither in Niembro nor in O Saviñao.

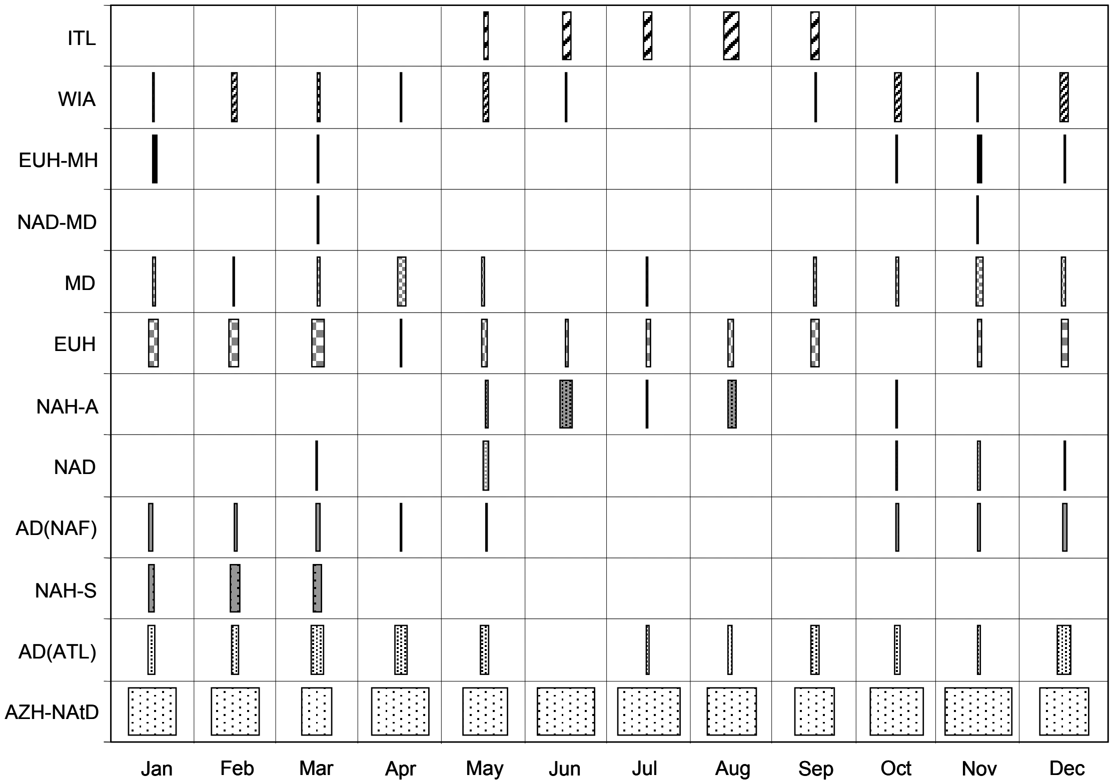


Figure 5.2. Mean number of days with each type of PM episode per month over northwestern Iberia in 1998-2003.

Table 5.1. Mean duration of PM episodes in northwestern Iberian Peninsula for 1998-2003.

	Mean duration (days/episode)		**Mean duration (days/episode)**
Atlantic episodes	**7**	**European episodes**	**3**
AZH-NAtD	8	*EUH*	4
AD(ATL)	3	*MD*	3
African episodes	**3**	**Mediterranean episodes**	**2**
NAH-S	3	NAD-MD	1
AD(NAF)	2	EUH-MH	2
NAD	2	**Episodes without dominant advection**	**3**
NAH-A	3	*WIA*	3
		ITL	3

Table 5.2. Mean levels of TSP, PM10 and PM2.5 recorded in EMEP stations in 1998-2003 in northwestern Iberian Peninsula.

MEAN LEVELS	**Noia**	**Niembro**			**O Saviñao**		
($\mu g\ m^{-3}$)	TSP	TSP	PM10	PM2.5	TSP	PM10	PM2.5
1998	17	na	na	na	na	na	na
1999	16	29	na	na	na	na	na
2000	*[1]19	28	na	na	na	na	na
2001	na	26	*[2]20	*[2]11	22	*[2]16	*[2]12
2002	na	28	19	10	20	14	9
2003	na	na	20	11	na	15	9
Mean 98-03	17	27	19	11	20	15	10

*[1]Calculated with data of 50% of the months of the year
*[2]Calculated with data of 83% of the months of the year
na: Not available

Table 5.3 shows the mean PM levels registered in the three regional background stations during each type of episode. In this discussion we will pay attention almost exclusively to Noia and O Saviñao data because we consider these stations to represent the regional background of the area while Niembro is suspected to be affected directly by local anthropogenic sources.
Episodes with advection of Atlantic air masses resulted in low PM levels (14 µgTSP m^{-3} in Noia and 16 µgTSP m^{-3}, 10 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3} in O Saviñao). These episodes were commonly associated with the passage of frontal systems over the Iberian Peninsula resulting in precipitation and, in consequence, decrease of the PM levels by scavenging. In consequence, these aerosols would have local or regional origin assuming the low concentration of particles in Atlantic air masses. The mean PM levels registered during AZH-NAtD events (14 µgTSP m^{-3} in Noia and 16 µgTSP m^{-3}, 11 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3} in O Saviñao) and during AD(ATL) (14 µgTSP m^{-3} in Noia and 11 µgTSP m^{-3}, 8 µgPM10 m^{-3} and 5 µgPM2.5 m^{-3} in O Saviñao) episodes were higher for first scenario which is generally associated with less rain frequency than AD(ATL). The decrease in PM levels by rainfall scavenging accounts for this difference.
The highest PM means registered in the regional background stations occurred during African dust outbreaks (30 µgTSP m^{-3} in Noia and 37 µgTSP m^{-3}, 28 µgPM10 m^{-3} and 18 µgPM2.5 m^{-3} in O Saviñao). Not all the transport scenarios causing African advection exerted the same impact on PM levels. PM mean levels during the episodes associated with anticyclonic conditions (NAH-S and NAH-A) reached higher values than those associated with depressions. One of the factors that could account for these differences is the low rain frequency associated with the anticyclonic scenarios. Furthermore, during NAH-A situations the African plumes travel at high altitudes (>1500 m.a.s.l.) and the dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is distributed and affects the sampling stations. Moreover, the formation of secondary particles is enhanced during NAH-A situations because of the intense insolation and the poor renovation of air masses. This results in a local/regional contribution of PM which may increase PM levels. During NAH-S, 34 µgTSP m^{-3} in Noia and 40 µgTSP m^{-3}, 29 µgPM10 m^{-3} and 16 µgPM2.5 m^{-3} in O Saviñao were registered. During NAH-A, 29 µgTSP m^{-3} in Noia and 40 µgTSP m^{-3}, 33 µgPM10 m^{-3} and 25 µgPM2.5 m^{-3} in O Saviñao were recorded. The other two transport scenarios causing African episodes (AD(NAF) and NAD) resulted in high PM mean levels (17 µgTSP m^{-3} in Noia and 26 µgTSP m^{-3}, 25 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3} in O Saviñao during AD(NAF) and 34 µgTSP m^{-3}, 21 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3} in O Saviñao during NAD) although lower than those obtained during NAH-S and NAH-A.
Mean PM levels recorded during episodes without dominant advective conditions reached high values but only for ITL events (25 µgTSP m^{-3} in Noia and 35 µgTSP m^{-3}, 25 µgPM10 m^{-3} and 20 µgPM2.5 m^{-3} in O Saviñao). Although precipitation is scarce in both WIA and ITL situations, during WIA events mean PM levels registered in regional background stations (23 µgTSP m^{-3} in Noia and 24 µgTSP m^{-3}, 17 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3} in O Saviñao) were only slightly higher than the annual mean levels. The aging of air masses, the high rate of resuspension or the enhancement of transformation of gaseous precursors into secondary aerosols due to the increased photochemistry of summer are the factors which increase PM levels during ITL episodes. Contrarily, from late autumn to early spring, when WIA events occurred, the dispersive conditions were reduced and, in consequence, the vertical development of

the boundary layer was low. This is especially relevant when thermal inversions developed over urban and/or industrial sites. In these circumstances the anthropogenic contribution of PM in regional background stations is reduced.
Mean PM levels recorded during European episodes were also elevated (24 µgTSP m^{-3} in Noia and 29 µgTSP m^{-3}, 20 µgPM10 m^{-3} and 15 µgPM2.5 m^{-3} in O Saviñao). However, MD transport scenario leaded to mean PM levels of the same order of the mean annual levels (14 µgTSP m^{-3} in Noia and 23 µgTSP m^{-3}, 15 µgPM10 m^{-3} and 11 µgPM2.5 m^{-3} in O Saviñao), and only during EUH scenario PM levels were high (29 µgTSP m^{-3} in Noia and 33 µgTSP m^{-3}, 23 µgPM10 m^{-3} and 18 µgPM2.5 m^{-3} in O Saviñao). This is explained by the lower rain frequency associated with EUH scenario with respect to MD which results in a lower relative scavenging potential of the first scenario.

Table 5.3. PM mean levels registered during different transport episodes over northwestern Iberian Peninsula in 1998-2003.

Mean PM levels	**Noia**	**Niembro**			**O Saviñao**		
(µg m^{-3})	TSP	TSP	PM10	PM2.5	TSP	PM10	PM2.5
Total 98-03	**17**	**27**	**19**	**11**	**20**	**15**	**10**
Atlantic episodes	**14**	**24**	**16**	**8**	**16**	**10**	**7**
AZH-NAtD	14	24	16	8	16	11	7
AD(ATL)	14	24	16	9	11	8	5
African episodes	**30**	**40**	**31**	**18**	**37**	**28**	**18**
NAH-S	34	43	30	17	40	29	16
AD(NAF)	17	32	27	13	26	25	12
NAD	na	50	33	17	34	21	12
NAH-A	29	41	33	20	40	33	25
European episodes	**24**	**32**	**23**	**14**	**29**	**20**	**15**
EUH	29	34	24	16	33	23	18
MD	14	27	20	12	23	15	11
Mediterranean episodes	**18**	**26**	**16**	**10**	**22**	**17**	**16**
NAD-MD	39	36	na	na	na	na	na
EUH-MH	15	24	16	10	22	17	16
Episodes without dominant advection	**24**	**38**	**25**	**16**	**32**	**21**	**17**
WIA	23	31	23	14	24	17	12
ITL	25	40	27	18	35	25	20

na: Not available

Combining information about the mean number of days and the PM mean levels into an impact index (II=mean number of days per year influenced by each type of scenario multiplied by the mean PM levels for each scenario in the whole period 1998-2003 and divided by 365 days) we can evaluate the impact of each transport scenario on PM levels for different size ranges. II gives us information about the contribution (in concentration units) of each type of transport scenario on the mean levels of PM recorded at a certain site. Moreover, II can be understood as the relative weight of each scenario with respect to the annual mean levels registered in a certain station and for a determined size range and it can be expressed as percentage.
Based on this index, the Atlantic episodes had the highest weight on PM mean levels regardless the size range. This is due to the great number of days with Atlantic air mass transport over northwestern Iberia. However, the weight of Atlantic events is lower as the size range decreases from 60-55% on TSP in Noia and O Saviñao respectively to 52% on PM2.5 (Figure 5.3). This may reflect the coarse size of the marine salts which are dominant in the Atlantic air masses. The weight of AZH-NAtD events (47-53%) is always higher than the weight of AD(ATL) episodes (4-7%).

African and European episodes had a similar weight on average. However, the influence of European events increases in the finer size ranges, from 15 and 14% for TSP in Noia and O Saviñao respectively, to 17% for PM2.5 in O Saviñao. The weight of African episodes is maximum in PM10 with 17% falling down to 15% in PM2.5 in O Saviñao (Figure 5.3). This can be explained by the size of dust particles reaching the Iberian Peninsula, with a dominant grain size mode in the PM10-PM2.5 range during African outbreaks, and a very fine grain size of PM transported from Europe, such as atmospheric ammonium sulphate. This fact explains the higher impact of European events on PM2.5 mean levels compared with TSP mean levels. The weight of NAH-A transport scenario is higher for the finer size ranges in virtue of the increased photochemistry during summer when this scenario occurred. This is the only African transport scenario with higher impact on PM2.5 than on PM10.

Episodes without a dominant air mass advection had a weight ranging from 12 or 13% on TSP in Noia and O Saviñao respectively to 15% on PM2.5 in O Saviñao (Figure 5.3). As the weight of WIA scenario is constant regardless the size range (4-5%), this general increase in the impact on fine size ranges is caused by the increase of the weight of ITL episodes on finer grain size ranges. ITL episodes mainly occur in summer so the intensity of photochemical processes results in the formation of fine particles during these events. Thus, the weight of ITL meteorological scenario ranges from 7 to 9% on TSP in Noia and O Saviñao respectively to 10% on PM2.5 in O Saviñao (Figure 5.3). Finally, owing to the low frequency of occurrence of Mediterranean PM episodes the weight of these events did not surpass 2% (Figure 5.3).

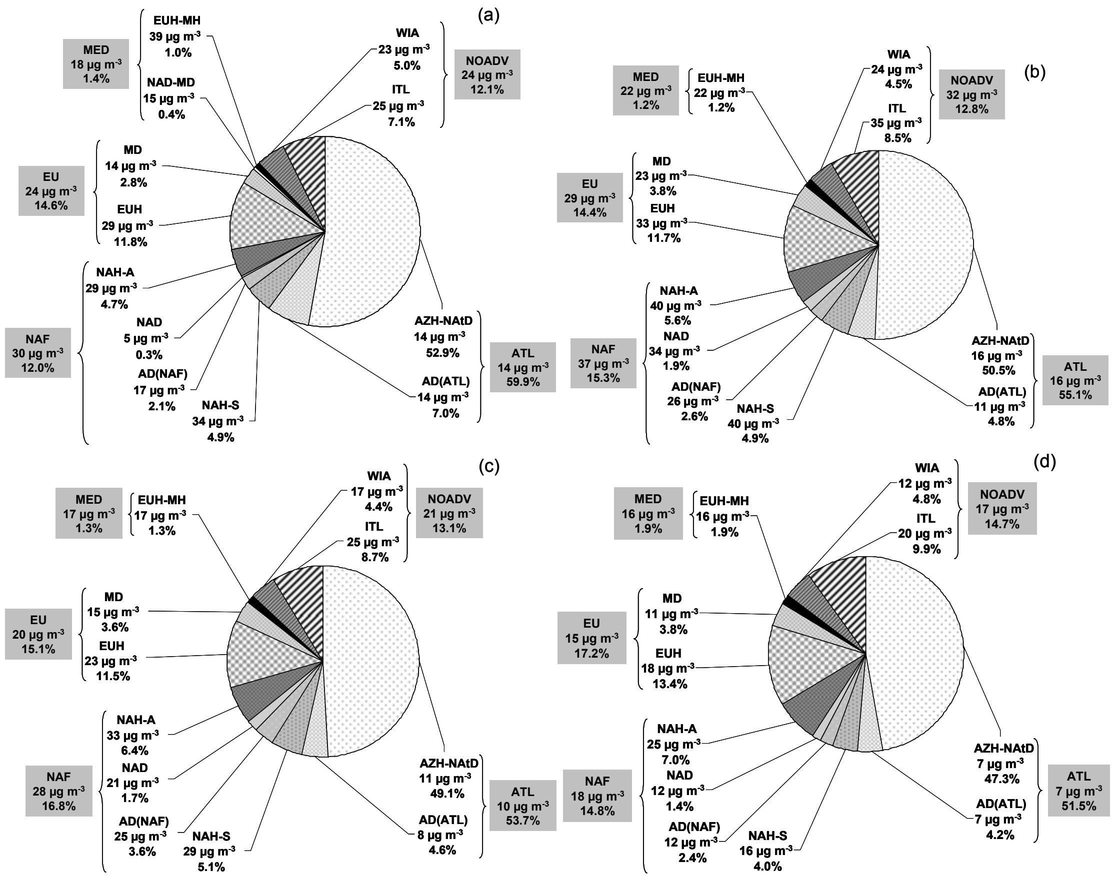


Figure 5.3. Relative impact (in %) of different PM episodes and meteorological scenarios on TSP annual mean levels in Noia (a), on TSP in O Saviñao (b), on PM10 in O Saviñao (c) and on PM2.5 in O Saviñao (d).

The 1999/30/CE Directive established a daily limit value for PM10 of 50 µg m^{-3}. The number of exceedances of this value should not be more than 35 times by 2005 and 7 times by 2010. More recently, in the II PM Position paper on particulate matter (EC, 2004), a daily limit value of 35 µg m^{-3} for PM2.5 which should not be exceeded more than 35 times in a year was proposed. Using the PM10/TSP ratio obtained from O Saviñao time series for 2001-2003 (0.7), an equivalent daily limit value of 70 µg m^{-3} was obtained and can be used for TSP. Thus, the number of exceedances in Noia was 2 in the period 1998-June 2000. The daily limit value for PM10 was exceeded in 8 occasions in O Saviñao from March 2001 to December 2003 (a mean of 2-3 times per year). In this period the recommended PM2.5 daily limit value was exceeded 5 times (a mean of 1-2 times per year, Table 5.4). Thus, as expected for this type of regional background sites, the number of exceedances was never surpassed in the whole period neither in Noia nor in O Saviñao.

The influence of African dust transport on the number of exceedances of the daily limit values of TSP, PM10 and PM2.5 is evident since most of these exceedances occurred during African dust outbreaks. From the total number of exceedances of 70 µgTSP m^{-3} in Noia (2), one (50%) occurred during a dust outbreak. From the 8 PM10 exceedances in O Saviñao 7 (88%) were associated with African intrusions and from the 5 PM2.5 exceedances 4 (80%) were attributed to African events (Figure 5.4). 20% of the PM2.5 exceedances (1) and 12% of PM10 exceedances (1) were registered during European transport events.

Table 5.4. Number of annual exceedances of the daily limit value established by the 1999/30/CE Directive (50 µgPM10 m^{-3}) and of the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) in O Saviñao. The number of annual exceedances of an equivalent TSP daily limit value (70 µg m^{-3}) in Noia is also shown. This equivalent limit value was worked out applying PM10/TSP of 0.7 and PM2.5/TSP of 0.5 ratios as obtained in O Saviñao.

NUMBER OF EXCEEDANCES	Equivalence to AQ Directive 1999/30/CE and to II PM PP suggestions for TSP: TSP > 70 µg m^{-3}	AQ Directive 1999/30/CE: PM10 > 50 µg m^{-3}	II PM position paper suggestions: PM2.5 > 35 µg m^{-3}
	Noia	O Saviñao	O Saviñao
1998	0	na	na
1999	0	na	na
2000	*[1]2	na	na
2001	na	*[2]1	*[2]2
2002	na	5	2
2003	na	2	1
Total 98-03	2	8	5
Annual mean 98-03	0.7	2.7	1.3

*[1]Calculated with data of 50% of the months of the year
*[2]Calculated with data of 83% of the months of the year
na: Not available

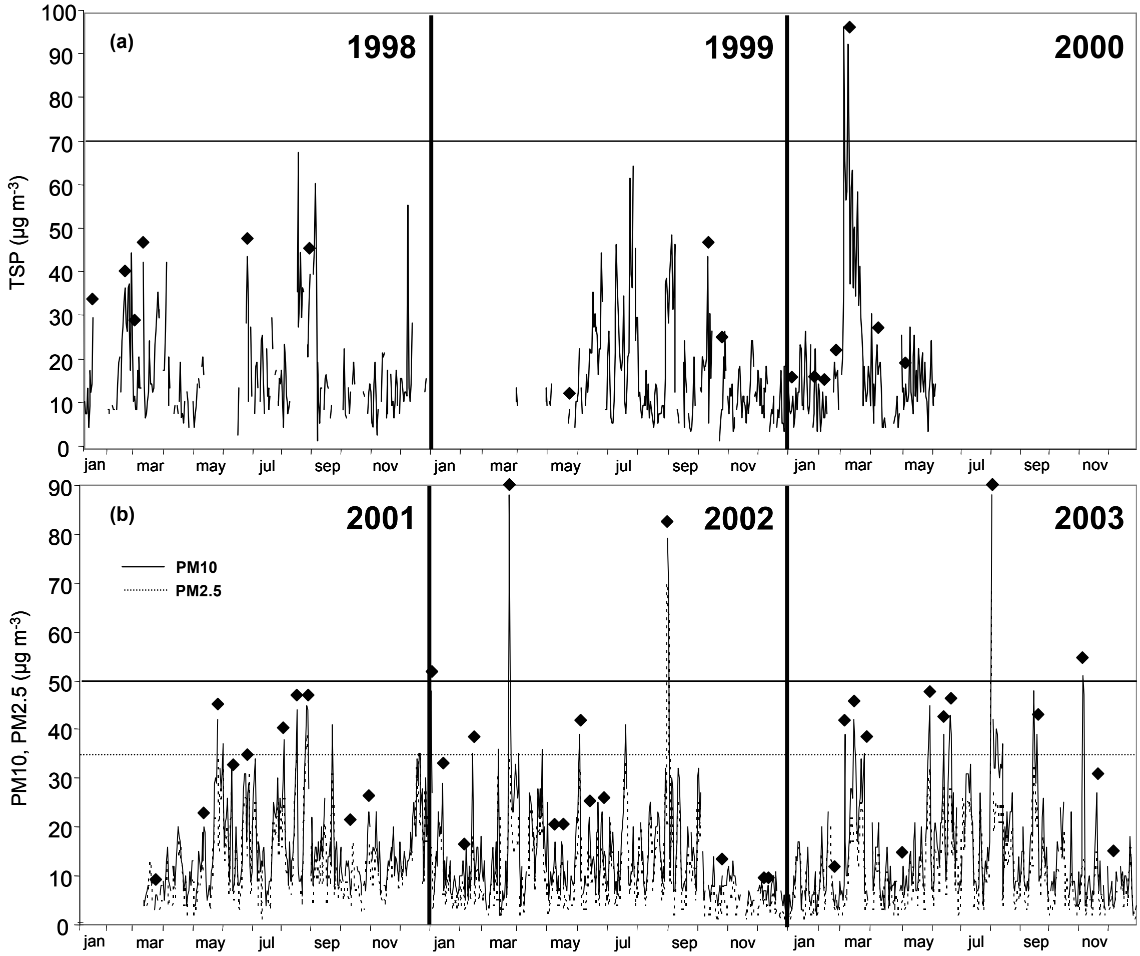


Figure 5.4. Daily TSP levels in Noia for 1998-2000 (a), and daily PM10 and PM2.5 levels in O Saviñao for 2001-2003 (b). The black dots mark the occurrence of African dust episodes. The horizontal lines mark the daily limit values established by the 1999/30/CE Directive (50 µgPM10 m^{-3}), the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) and the equivalent daily limit value for TSP (70 µgTSP m^{-3}).

On the basis of the statistical work undertaken in this section, a critical interpretation of the monthly mean levels in the EMEP stations located over northwestern Iberian Peninsula (Figure 5.5) show that:

The highest PM levels are usually registered in summer in regional background stations owing to several factors:

(a) The enhancement of photochemical formation of secondary particles due to a higher insolation during summer.
(b) The lower precipitation regime during summer (Figure 5.5) which results in the reduction of processes such as the washing out of aerosols from the atmosphere.
(c) The low renovation of air masses during episodes with lack of advection such as during ITL events characteristic of summer.
(d) The higher frequency of occurrence of African dust outbreaks over the Iberian Peninsula.

As shown by Figure 5.5, this occurred in O Saviñao in TSP, PM10 and PM2.5 with maximum monthly means in August for all size ranges. In Noia high levels of TSP in summer occurred but the maximum monthly mean was registered in March. This was caused by very intense African dust intrusions in 1998 and 2000 although contributions of local sources cannot be discarded. In Niembro, the summer maximum were not registered, thus, Niembro cannot be considered as a regional background station owing to the contribution of local sources. In general, secondary maximums were recorded in March owing to the frequent occurrence of African events in this month. These events also occurred in January and February but, in comparison to March, the precipitation in these two months is considerably higher than in March. Therefore, no such peak is observed. In December, a slight elevation was registered explained by the occurrence of European events in this month. Nevertheless, this peak was not important.

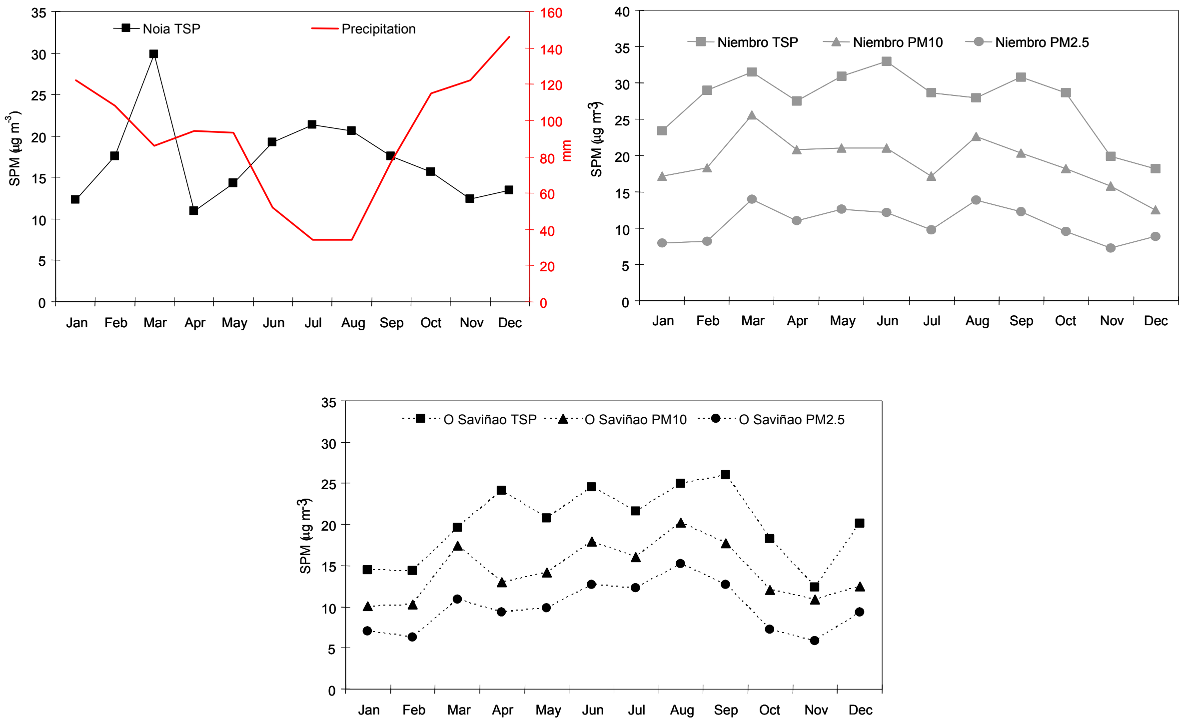


Figure 5.5. Mean monthly precipitation of Rozas Aeródromo station (Lugo, 43° 07' N, 07°27' W, 444 m.a.s.l) for 1971-2000 (INM, 2001) and TSP, PM10 and PM2.5 monthly means registered in Noia (1998-June 2000), Niembro (1999-2003) and O Saviñao (February 2001-2003).

5.2 Northern Iberian Peninsula

The climatic conditions of this area do not differ greatly from the conditions of the northwestern Iberian Peninsula. The passage of frontal systems results in a well ventilated area with a moderately high regime of precipitation with the subsequent decrease in the levels of PM. However, the situation of this area, closer to the European continent makes it more likely to be affected by the transport of air masses from the European continent. In addition, the locationt of this region, when compared with northwestern Iberia, is closer to the Mediterranean across which great quantities of north African dust are transported especially during summer.

Daily data recorded during the period 1998-2003 from three regional background stations were used to evaluate the impact of the different air mass transport scenarios on PM levels over northern Spain. Logroño station (42º 27' N, -2º 30' E, 445 m.a.s.l.) belonging to the EMEP network offered data on TSP from 1998 to January 2001 measured by the gravimetric method. Valderejo (42º 53' N, -3º 14' E, 911 m.a.s.l.) and Izki (42º 39' N, -2º 30' E, 835 m.a.s.l.) stations from the Air Quality monitoring network of the Government of the Basque Country offered TSP data from January

1999 to November 1999 in Valderejo, PM10 data from November 1999 to 2003 in Valderejo and PM10 data from May 2001 to 2003 in Izki. These data were sampled using the β-attenuation method based on monitoring the attenuation of β-radiation through a filter where the PM is continuously being deposited.

While Valderejo and Izki stations can respond to the qualification of regional background according to the mean annual PM levels, Logroño station registered mean PM levels too elevated to be considered a regional background station. In fact this station was retired from its location by January 2001 owing to its vicinity to the city of Logroño. Thus, Logroño station was influenced by anthropogenic sources. For these reasons, in this synthesis, PM data from Valderejo and Izki will preferably be used.

The advection of Atlantic air masses was the most common transport scenario in northern Iberia during the study period (1998-2003). This type of advection accounted for 56.7% of the total number of days (1243 days) and 43.1% of the total number of episodes (237 episodes out of 551 episodes). AZH-NAtD is the dominant scenario during Atlantic transport. The number of days with Atlantic advection caused by this scenario was 8 times greater than the number of days caused by AD(ATL) scenario (Figure 5.6).

The number of days in which a lack of advective conditions was observed reached 15.3% of the total number of days in 1998-2003 (337 days). These days were grouped in 101 episodes (18.3% of the episodes). The frequency of occurrence of ITL situations was superior to the frequency of occurrence of WIA situations (1.4 times as many ITL days as WIA days).

The occurrence of advection of European air masses was slightly lower than situations of lack of advective conditions (319 days resulting in 14.5% of the days and 90 episodes resulting in 16.3% of the episodes during 1998-2003). EUH scenario caused most of these European events (2-3 times more than MD scenario).

African dust outbreaks occurred over northern Iberia in 234 days (10.7% of the days) and in 92 events (16.7% of the episodes in 1998-2003 over northern Iberia) with a clear prevalence of NAH-A scenario with an occurrence around 2 times the occurrence of each the other African transport scenarios (NAH-S, AD(NAF) and NAD).

Advection of air masses from the Mediterranean was not common, this only occurred in 58 days (2.7% of the days) distributed in 31 episodes (4.6% of the episodes) in the study period. EUH-MH scenario was more than twice as frequent as NAD-MD scenario.

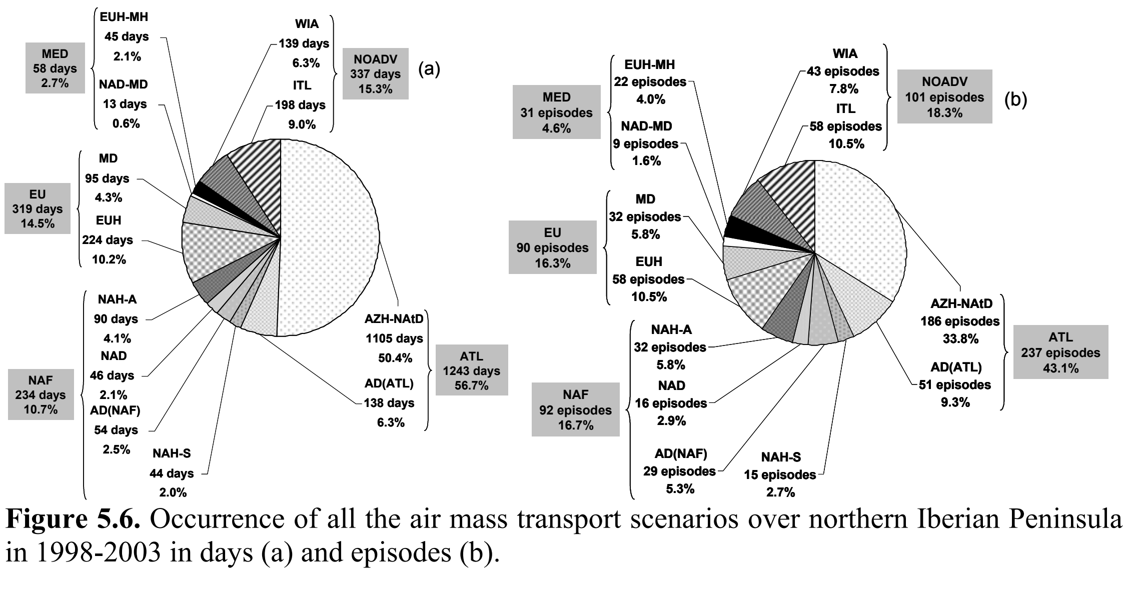


Figure 5.6. Occurrence of all the air mass transport scenarios over northern Iberian Peninsula in 1998-2003 in days (a) and episodes (b).

As Figure 5.7 shows, the advection of Atlantic air masses over northern Iberia was highly frequent. The maximum frequency of these situations registered in autumn-winter (18 to 23 days as a mean from October to January) and also in April and July (22 and 20 days on average respectively). The period with the lowest frequency of these situations was May-June with 13-11 days on average. AZH-NAtD occurred in all the months with especial frequency in November with a mean of 21 days. AZH-NAtD situations showed their lowest frequency of occurrence in March, May and June with a mean of 11 days on each of these months. Atlantic episodes associated with AD(ATL) scenario occurred in all the months with less frequency in summer (in June none of these events were registered in 1998-2003). In April and December peak frequencies of 4 AD(ATL) days on average were recorded.

African episodes were observed in all months but summer (with a frequency peak in June with a mean of 7 days) February-March (with a mean of 5 days in both months) were the periods with the highest frequency of occurrence. On the other hand, very low frequencies of African dust outbreaks were registered in April and September. The occurrence of NAH-S events was restricted to January-March (mean of 3 days in both February and March). AD(NAF) episodes were distributed all along the year exept in summer. Important frequencies of occurrence of AD(NAF) episodes were registered in March and December (mean of 2 days in both months). NAD episodes occurred mainly in May (mean of 3 days) and in November (mean of 2 days) while in summer and in December-January these events practically did not occur.

European episodes were also registered in all the seasons of the year over northern Spain. In particular, November-April (8 days as a mean in March) was the period in which European transport was favoured. EUH episodes were particularly frequent among European episodes. These events had a high frequency of occurrence during January-March (7 days as the highest mean in March) and a low frequency in April-May and in October. Precisely, April-May was the period in which MD events showed their highest frequency of occurrence (3 days on both months as average).

Episodes with advection of Mediterranean air masses occurred in all the months with the exception of July and August but the frequency was low (only reached 3 days as mean in January). NAD-MD episodes were registered only in January-April but the number of days was very scarce. EUH-MH was somewhat more frequent but only in January and May means over 1 day were registered.

The episodes with no dominant advective conditions occurred along all the year but, while ITL episodes occurred in summer (more than 8 days as mean in June, July and August) WIA events did not occur in summer and the highest frequency was registered in May (a mean of 7 days) and October (5 days as a mean).

Atlantic episodes were the longest PM events registered over northern Spain. A mean duration of 5 days per episode was recorded for these episodes. However the mean duration of AZH-NAtD (6 days per episode) was not comparable with the duration of AD(ATL) episodes (3 days per episode). The other events reached mean durations of 2 or 3 days per episodes with the exception of NAD-MD (Mediterranean transport) episodes with 1 day per episode and EUH events (European transport) with 4 days per episode (Table 5.5).

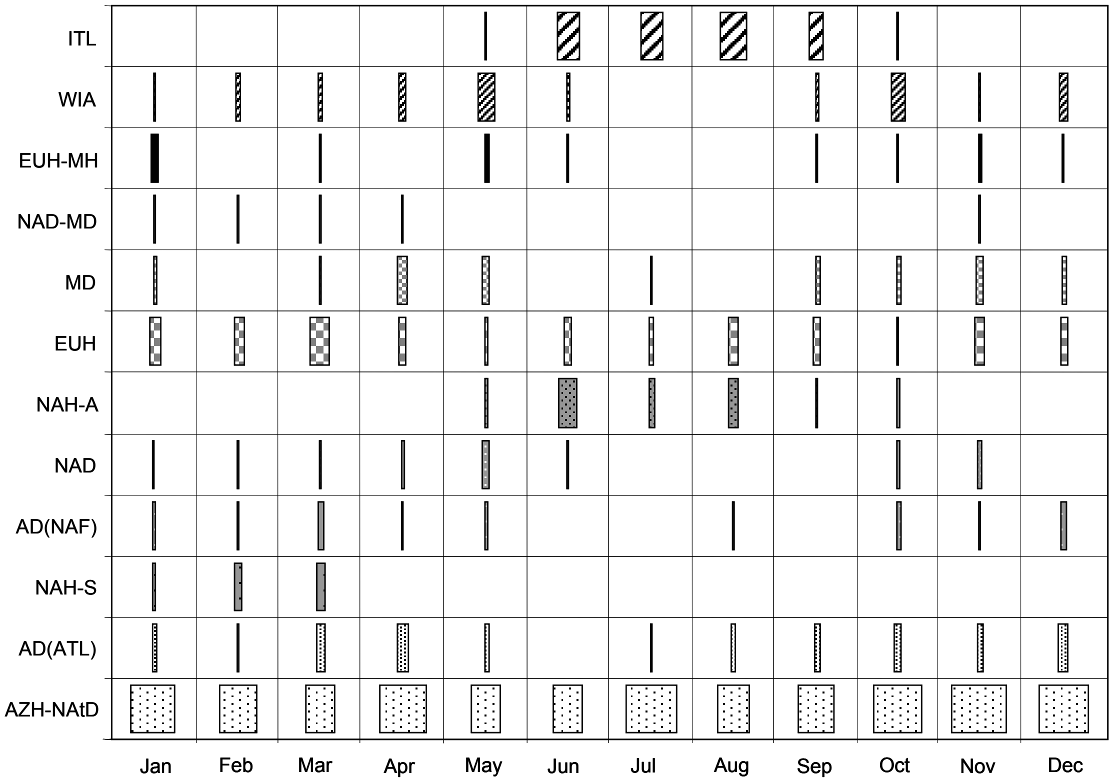


Figure 5.7. Mean number of days with each type of PM episode per month over northern Iberia in 1998-2003.

Table 5.5. Mean duration of PM episodes in northern Iberian Peninsula for 1998-2003.

	Mean duration (days/episode)		Mean duration (days/episode)
Atlantic episodes	**5**	**European episodes**	**3**
AZH-NAtD	6	*EUH*	4
AD(ATL)	3	*MD*	3
African episodes	**3**	**Mediterranean episodes**	**2**
NAH-S	3	NAD-MD	1
AD(NAF)	2	EUH-MH	2
NAD	3	**Episodes without dominant advection**	**3**
NAH-A	3	*WIA*	3
		ITL	3

As shown in Table 5.6, the mean annual PM levels in Logroño (30 µgTSP m^{-3} from 1998 to 2000) were clearly superior to the levels recorded in the other two stations (19 µgTSP m^{-3} and 14 µgPM10 m^{-3} in Valderejo and 14 µgPM10 m^{-3} in Izki). The lowest annual means were registered in 2002 owing to a very wet summer. High mean PM levels were recorded in 2000. Logroño station recorded mean PM levels too elevated to be considered a regional background station. In fact this station was retired from its location by January 2001 owing to its vicinity to the city of Logroño. In the study period, no exceedances of the annual limit value established by the 1999/30/CE Directive were then registered in Valderejo and Izki neither for the limit value established for 2005 (40 µgPM10 m^{-3}) nor for the target value established for 2010 (20 µgPM10 m^{-3}) although in Izki in 2001, a PM10 mean of 20 µg m^{-3} was recorded.

According to the data presented in Table 5.7 a number of conclusions about the impact of different transport episodes or PM levels can be drawn. Firstly the inspection of PM data from Logroño station suggests the influence of local sources owing to the high TSP levels measured. This station was taken out from the EMEP network in January

2001. Owing to this fact, the following analysis will be undertaken using data from Valderejo and Izki solely.

Table 5.6. Mean levels of TSP, PM10 and PM2.5 recorded in regional background stations in 1998-2003 in northern Iberian Peninsula.

MEAN LEVELS ($\mu g\ m^{-3}$)	Logroño	Valderejo		Izki
	TSP	TSP	PM10	PM10
1998	30	na	na	na
1999	28	*[1]19	na	na
2000	33	na	17	na
2001	na	na	13	*[2]20
2002	na	na	12	11
2003	na	na	13	12
Mean 98-03	30	19	14	14

*[1]Calculated with data of 90% of the months of the year
*[2]Calculated with data of 67% of the months of the year
na: Not available

In Valderejo, the mean TSP levels registered reached 19 $\mu g\ m^{-3}$ and the mean PM10 levels reached 14 $\mu g\ m^{-3}$ (the same PM10 mean levels were registered in Izki). The mean PM levels registered during Atlantic episodes the were lowest, with 14 μgTSP m^{-3} in Valderejo and 10 μgPM10 m^{-3} in both Valderejo and Izki. The relatively low concentration of pollutants in Atlantic air masses and the relatively high frequency of rain associated with the frontal systems crossing the Iberian Peninsula during Atlantic episodes may account for this fact. In consequence, most of the PM load recorded during the Atlantic episodes was associated with local/regional contributions. Among Atlantic scenarios, AZH-NAtD was associated with lower TSP means in Valderejo than AD(ATL) (14 $\mu g\ m^{-3}$ and 16$\mu g\ m^{-3}$ respectively), but with higher PM10 means in both Valderejo (11 and 9 $\mu g\ m^{-3}$ for AZH-NAtD and AD(ATL) respectively) and Izki (10 and 9 $\mu g\ m^{-3}$ for AZH-NAtD and AD(ATL) respectively). The mean PM levels were lower during AD(ATL) episodes owing to the higher frequency of rain associated with this scenario with respect to AZH-NAtD.

African dust outbreaks exerted an important influence on PM levels resulting in the highest mean PM levels (35 μgTSP m^{-3} and 21 μgPM10 m^{-3} in Valderejo and 22 μgPM10 m^{-3} Izki). Generally, the anticyclonic events (NAH-S and NAH-A) registered the highest PM means in virtue of the low precipitation frequency characterising these episodes when compared with NAD and AD(NAF). Furthermore, during NAH-A situations the African plumes travel at high altitudes (>1500 m.a.s.l.) and the dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is distributed and affects the sampling stations. Moreover, the formation of secondary particles is enhanced during NAH-A situations because of the intense insolation and the poor renovation of air masses. Furthermore, during NAH-A episodes, re-suspension of soil material by the intense convection is enhanced. These factors result in a local/regional contribution of PM which may increase PM levels. During NAH-A episodes mean PM levels reached 33 μgTSP m^{-3} and 26 μgPM10 m^{-3} in Valderejo and 26 μgPM10 m^{-3} in Izki and during NAH-S events mean PM levels reached 40 μgTSP m^{-3} and 20 μgPM10 m^{-3} in Valderejo and 23 μgPM10 m^{-3} in Izki. During AD(NAF) the mean PM levels were 22 μgTSP m^{-3} and 17 μgPM10 m^{-3} in Valderejo and 18 μgPM10 m^{-3} in Izki while during NAD events the mean PM levels were 43 μgTSP m^{-3} and 16 μgPM10 m^{-3} in Valderejo and 16 μgPM10 m^{-3} in Izki.

Episodes without prevalent advective conditions also registered high mean PM levels but only for ITL scenario and not for WIA scenario. Under both scenarios precipitation is reduced so the scavenging potential of the atmosphere is reduced in episodes with lack of advective conditions. During ITL episodes mean PM levels reached 29 µgTSP m^{-3} and 23 µgPM10 m^{-3} in Valderejo and 23 µgPM10 m^{-3} in Izki while during WIA events means of 18 µgTSP m^{-3} and 14 µgPM10 m^{-3} were recorded in Valderejo and 13 µgPM10 m^{-3} in Izki. ITL episodes occur in the warm season of the year when several factors result in an increase in PM levels. These are the low rainfall regime, the aging of pollutants in air masses, the high rate of re-suspension of soil material owing to convective movements or the enhancement of the transformation of gaseous precursors into secondary aerosols by the increased photochemistry and the scarce renovation of air masses. During WIA episodes stagnant atmospheric conditions prevail and the poor vertical development of the boundary layer results in a reduction of the dispersion of pollutants. This is particularly important when thermal inversions occur over urban or industrial sites reducing the transport of pollutants towards rural sites.

During European events mean PM levels were somewhat higher than the annual mean levels (21 µgTSP m^{-3} and 14 µgPM10 m^{-3} in Valderejo and 14 µgPM10 m^{-3} in Izki). Mean PM levels recorded during EUH events (21 µgTSP m^{-3} and 16 µgPM10 m^{-3} in Valderejo and 15 µgPM10 m^{-3} in Izki) were slightly higher than during MD episodes (21 µgTSP m^{-3} and 12 µgPM10 m^{-3} in Valderejo and 12 µgPM10 m^{-3} in Izki). This can be explained by the higher frequency of rain associated with MD episodes with respect to EUH events.

Mediterranean episodes had not an important impact on PM levels (16 µgTSP m^{-3} and 12 µgPM10 m^{-3} in Valderejo and 11 µgPM10 m^{-3} in Izki). This can be generalised for both NAD-MD (14 µgTSP m^{-3} and 12 µgPM10 m^{-3} in Valderejo and 11 µgPM10 m^{-3} in Izki) and EUH-MH (18 µgTSP m^{-3} and 12 µgPM10 m^{-3} in Valderejo and 11 µgPM10 m^{-3} in Izki) scenarios. Mediterranean episodes are commonly associated with rainfall which results in a decrease of PM levels by scavenging.

Table 5.7. PM mean levels registered during different transport episodes over northern Iberian Peninsula in 1998-2003.

Mean PM levels	**Logroño**	**Valderejo**		**Izki**
(µg m^{-3})	TSP	TSP	PM10	PM10
Total 98-03	**30**	**19**	**14**	**14**
Atlantic episodes	**24**	**14**	**10**	**10**
AZH-NAtD	24	14	11	10
AD(ATL)	30	16	9	9
African episodes	**52**	**35**	**21**	**22**
NAH-S	65	40	20	23
AD(NAF)	42	22	17	18
NAD	36	43	16	16
NAH-A	60	33	26	26
European episodes	**28**	**21**	**14**	**14**
EUH	32	21	16	15
MD	15	21	12	12
Mediterranean episodes	**35**	**16**	**12**	**11**
NAD-MD	27	14	12	11
EUH-MH	38	18	12	11
Episodes without dominant advection	**42**	**26**	**19**	**18**
WIA	41	18	14	13
ITL	44	29	23	23

Combining information about the mean number of days and the PM mean levels into an impact index (II=mean number of days per year influenced by each type of scenario multiplied by the mean PM levels for each scenario in the whole period 1998-2003 and divided by 365 days) we can evaluate the impact of each transport scenario on PM levels for different size ranges. II gives us information about the contribution (in concentration units) of each type of transport scenario on the mean levels of PM recorded at a certain site. Moreover, II can be understood as the relative weight of each scenario with respect to the annual mean levels registered in a certain station and for a determined size range and it can be expressed as percentage.

As Figure 5.8 shows, the great frequency of occurrence of days with advection of Atlantic air masses resulted in a high weight of Atlantic episodes in all stations and size ranges (II from 42 to 45%) regardless the low mean PM levels registered during these events. Among Atlantic episodes AZH-NAtD scenario had II in the range 37-39% depending on the size range and the station and AD(ATL) reached weights which ranged from 4 to 6%.

Episodes with lack of prevalent advective conditions had an important impact (II in the range 20-22%) mostly explained by ITL episodes which had a weight ranging from 13% in Logroño for TSP to 16% in Izki for PM10. The weight of ITL episodes on finer grain size ranges rises slightly in PM10 with respect to TSP probably due to the higher intensity of photochemical processes in summer resulting in the formation of fine particles. Unfortunately, data on PM2.5 is not available which would allow supporting this fact. Conversely, WIA episodes had a constant weight in TSP and in PM10 (II around 6%).

The II of European episodes is stable around 16% in all size ranges. This would confirm that the particles arriving with European air masses fall in the size range below 10 µm of diameter (in fact these are expected to be fine particles, PM2.5, with anthropogenic origin). The higher frequency of occurrence and the higher PM levels recorded during EUH episodes explain the difference of the II of this scenario (11-12%) with respect to MD scenario (II in the range 2-5%).

African episodes had a similar impact on TSP levels (18-19%) than on PM10 levels (16-17%). This happens because most African dust particles have sizes in the PM10-PM2.5 range. The weight of NAH-A transport scenario is higher for PM10 owing to the increased photochemistry during summer when this scenario stablishes which results in the formation of fine secondary aerosols. The IIs of the other African transport scenarios ranged in 3-5% for NAH-S, 2-5% for NAD and around 3% for AD(NAF) depending on the station and size range. Finally, the weight to Mediterranean episodes was low than 3% in all cases.

The number of exceedances of the PM10 daily limit value established by the 1999/30/CE Directive of 50 µg m^{-3} in Valderejo reached 9 for all the study period. However, all these exceedances occurred during 2000 while the rest of the years were devoid of exceedances. Similarly, in Izki, from the total number of excedances (15) of the PM10 daily limit value, 14 were registered in 2001 (Table 5.8). In this sense, 2000 and 2001 may be considered anomalous in Valderejo and in Izki respectively.

Applying a PM10/TSP ratio of 0.7 the equivalent daily limit value for TSP would be 70 µg m^{-3}. Using this equivalent limit value, no TSP exceedance was registered in Valderejo although it is important to note that in Valderejo only 11 months of daily TSP data was available during 1999 (Table 5.8). From the 9 exceedances of the daily limit value registered in Valderejo, 8 were recorded in 18 consecutive days in 2000 and from the 15 exceedances registered in Izki, 11 occurred in 12 consecutive days in

2001. These facts would suggest the influence of specific and sporadic local sources in those periods over those stations.

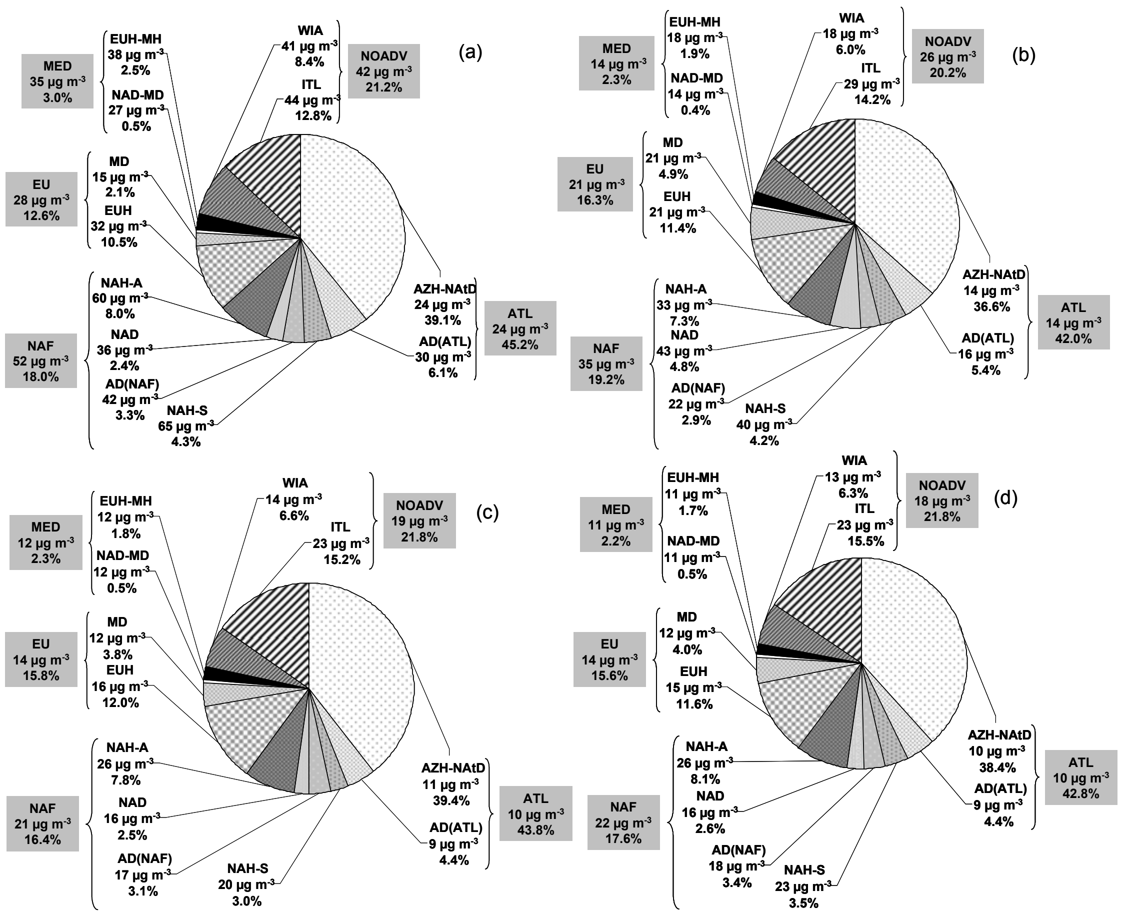


Figure 5.8. Relative impact (in %) of different PM episodes and meteorological scenarios on TSP mean levels in Logroño (a), on TSP levels in Valderejo (b), on PM10 mean levels in Valderejo (c) and on PM2.5 mean levels in Izki (d).

Table 5.8. Number of annual exceedances of the daily limit value established by the 1999/30/CE Directive (50 µgPM10 m^{-3}) and of an equivalent TSP daily limit value (70 µg m^{-3}) in Valderejo and Izki. This equivalent limit value was worked out applying PM10/TSP of 0.7.

NUMBER OF EXCEEDANCES	Equivalence to AQ Directive 1999/30/CE and to II PM PP recommendations for TSP: TSP > 70 µg m^{-3}	AQ Directive 1999/30/CE: PM10 > 50 µg m^{-3}	
	Valderejo	**Valderejo**	**Izki**
1998	na	na	na
1999	*0	na	na
2000	na	9	na
2001	na	0	14
2002	na	0	1
2003	na	0	0
Total 98-03	0	9	15
Annual mean 98-03	0.0	2.3	5.0

*Calculated with data of 90% of the months of the year
na: Not available

African episodes did not account for any of the 9 exceedances registered in Valderejo (Figure 5.9). Both Atlantic episodes and episodes without prevalent advection accounted for 4 (44%) of those exceedances respectively while European episodes accounted for 1 (12%) of the exceedances. As Izki concerns, 7 out of the 15 exceedances (46%) were registered during African events, 4 (27%) during episodes with lack of advection and 4 (27%) during Atlantic events (Figure 5.9).

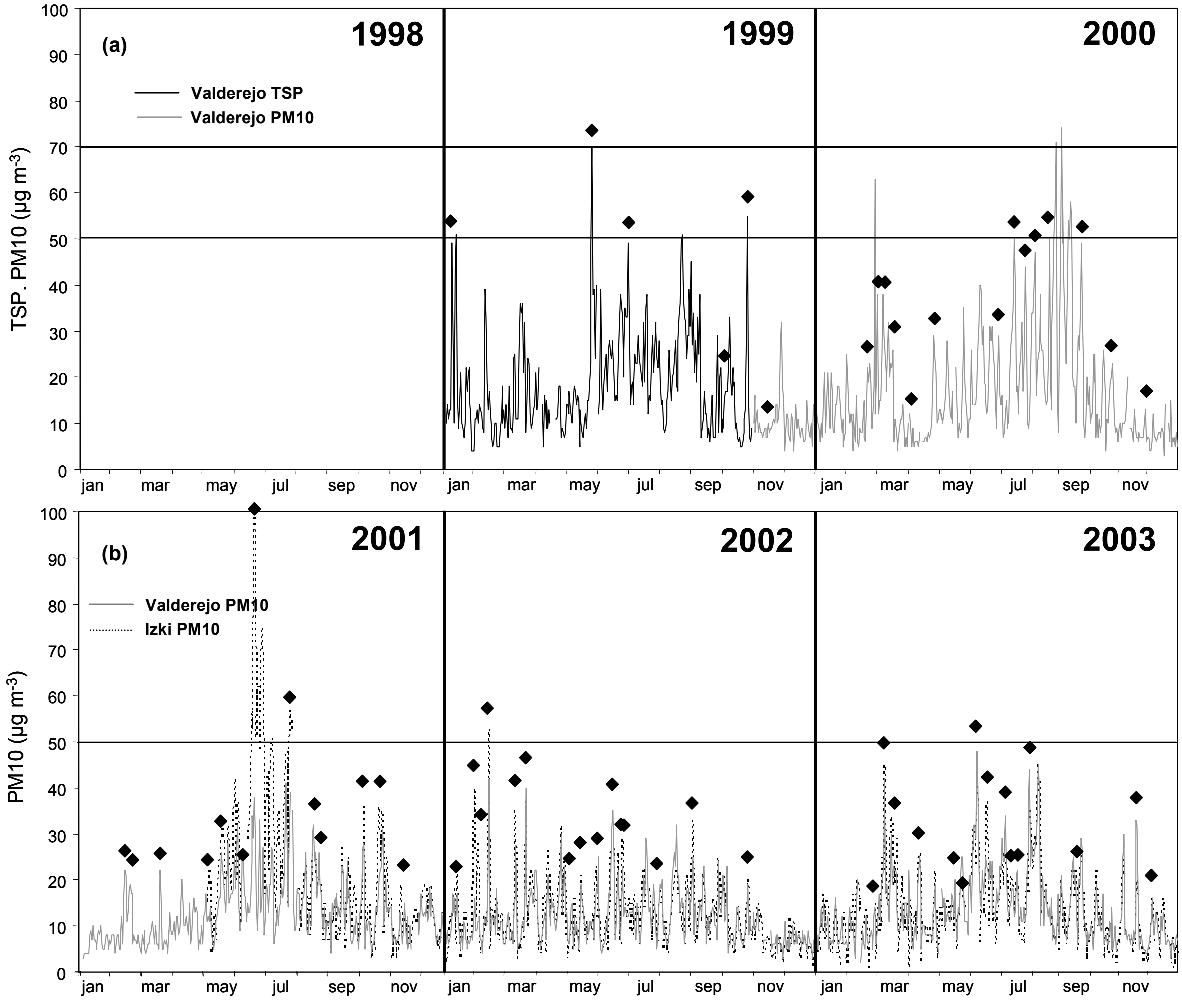


Figure 5.9. Daily TSP levels in Valderejo for 1999 (black line in (a)), daily PM10 levels in Valderejo 1999-2003 (grey line in (a) and (b)) and daily PM10 levels in Izki 2001-2003 (black dotted line in (b)). The black dots mark the occurrence of African dust episodes. The horizontal lines mark the daily limit values established by the 1999/30/CE Directive (50 µgPM10 m^{-3}) and the equivalent daily limit value for TSP (70 µgTSP m^{-3}).

The monthly mean levels registered in regional background stations over northern Iberia can be explained as follows:

The highest PM levels in regional background stations over northern Iberia were registered in summer owing to these factors:

(a) The enhancement of photochemical formation of secondary particles due to a higher insolation during summer.

(b) The lower precipitation regime during summer (Figure 5.10) which results in the reduction of processes such as the washing out of aerosols from the atmosphere.

(c) The low renovation of air masses during episodes with lack of advection such as during ITL events.

(d) The higher frequency of occurrence of African dust outbreaks over the Iberian Peninsula.

The summer maximum is registered in all the stations and in all size ranges with the exception of Logroño station with a maximum in March. As stated above, this station was suspected to be affected by local sources and taken out from the EMEP network in 2001. The summer maximum is common for TSP and PM10 in Valderejo and Izki and a secondary maximum was also found in March probably owing to African dust outbreaks occurred in this month. These events also occurred in January and February but, in comparison to March, the precipitation is higher in these two months (Figure 5.10). These typical winter African episodes do not occur with the same frequency all the years and this is the main reason why the March PM peak is not so marked.

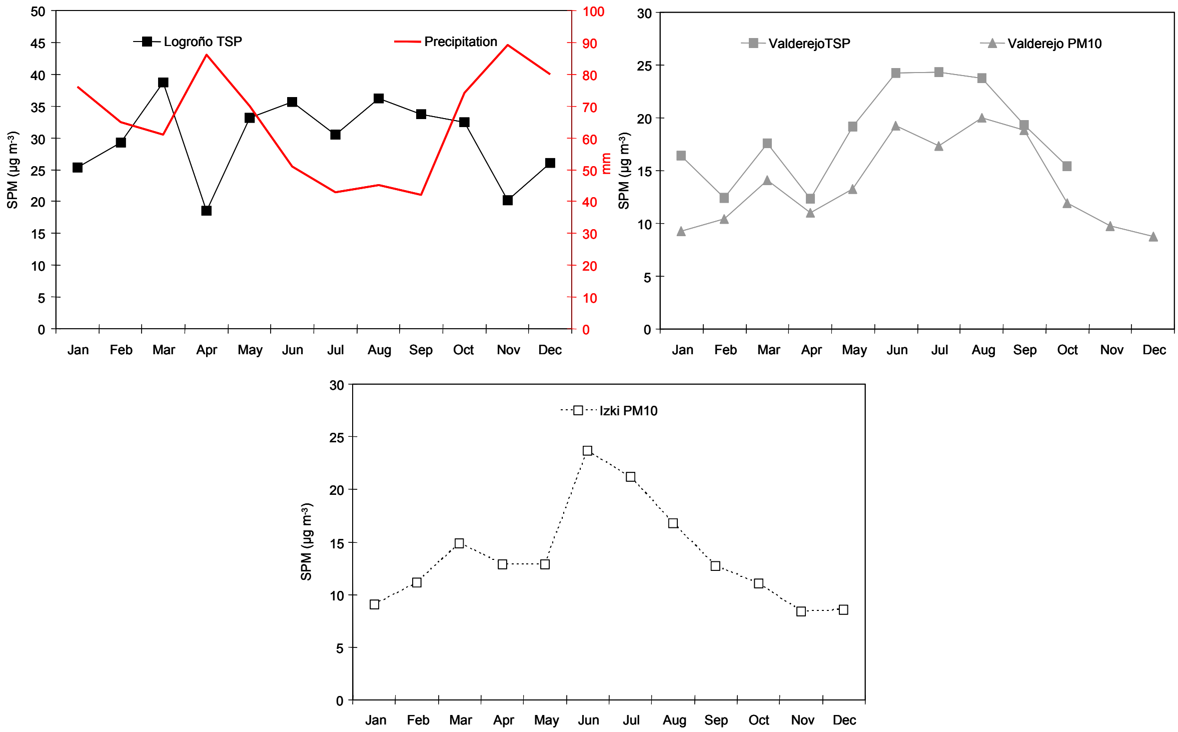


Figure 5.10. Mean monthly precipitation of Aeropuerto de Foronda station (Vitoria, 42° 53' N, 02°43' W, 508 m.a.s.l) for 1971-2000 (INM, 2001) and TSP and PM10 monthly means registered in Logroño (1998-January 2001), Valderejo (TSP from January 1999-October 1999 and PM10 from November 1999 to 2003) and Izki (May 2001-2003).

5.3 Northeastern Iberian Peninsula

This region of the Iberian Peninsula is characterised by a typical Mediterranean climate in which two rain periods can be distinguished in spring and autumn. In summer the precipitation is reduced to low levels and important drought episodes occur. This rainfall regime influences the type of vegetation cover of the area. This is less dense than in northern and northwestern Iberia so resuspension of soil material may become an important source of PM over northeastern Iberia. Owing to the location of this region (close to the European continent and the Mediterranean) the transport of European air masses and the transport of north African dust across the Mediterranean basin in summer may influence PM levels greatly (Rodriguez et al., 2001). Finally, weak baric gradient conditions are common over eastern Iberia especially during summer. Under these situations the renovation of air masses is poor and the aging and recirculation of contaminated air masses commonly occur in summer, late spring and early autumn (Millan et al., 1997). These mechanisms may influence PM levels at the regional background sites considerably (Rodríguez et al, 2003).

1998-2003 data on PM levels measured in a group of air quality monitoring stations classified as regional background sites over northeastern Iberia were used in this study. The EMEP stations were: a) Roquetas station (40º 49' N, 0º 29' E, 44 m.a.s.l.) with data on TSP from 1998 to June 2000, b) Cabo de Creus station (42º 19' N, 3º 19' E, 23 m.a.s.l.) with data on TSP from 1998 to January 2003, and data on PM10 and PM2.5 from March 2001 to the end of 2003 and c) Els Torms station (41º 24' N, 0º 43' E, 470 m.a.s.l.) with TSP data from November 2001 to January 2003 and data on PM10 and PM2.5 from March 2001 to the end of 2003. These measurements were made using the gravimetric method and high volume samplers. Furthermore, daily PM10 data for the whole period 1998-2003 from Monagrega station (40º 30' N, -0º 12' E, 600 m.a.s.l.) were used. This rural station belongs to ENDESA network and the measurements were performed continuously with TEOM (tapered element oscillating microbalance) instrumentation. These instruments incorporate an inertial balance that directly measures the mass collected on an exchangeable filter cartridge by monitoring the corresponding frequency changes of a tapered element. This technique has been proved to underestimate PM10 at Monagrega in winter by a 32% and by less than 5% in the rest of the year (Rodríguez, 2002).

Air quality measurements at Roquetas station were interrupted since 2000 owing to the direct influence of the emissions from the city of Tortosa. TSP levels recorded at this site were excessively high for a regional background site owing to this influence. Cabo de Creus station, offered also elevated PM levels for a regional background area. This site is located in a very windy area with poor soil cover and very close to the shoreline. This could influence the measurements owing to the great degree of resuspension of crustal and marine aerosols although the transport of polluted air masses from the Gulf of Lion increasing PM levels at Cabo de Creus may be a frequent scenario. Under these circumstances, data from Els Torms and Monagrega was preferably used to draw conclusions.

The Atlantic advection was the most frequent transport situation over the northeastern region. In 42.3% of the days (926 days) Atlantic air masses affected the study area in 1998-2003. This meant 33.0% (211 episodes) of the total number of episodes in 1998-2003. Among Atlantic scenarios, days associated with AZH-NAtD scenario were 8.6 times more frequent than days associated with AD(ATL) scenario.

Episodes without prevalent advection were also frequent over this region. These occurred in 146 episodes (22.9% of the total number of events) which resulted in 492 days (22.5% of the days). WIA and ITL situations were, approximately, equally frequent. European transport situations accounted up to 362 days (16.5% of the total number of days) distributed in 127 episodes (19.9% of the total number of events). EUH situations dominated over MD situations (2 or 3 times more frequent).

Transport from northern Africa was slightly less frequent than European episodes (349 days and 119 episodes which resulted in 15.9 and 18.6% of the total number of days and episodes respectively in 1998-2003). The summer scenario, NAH-A, was the most common situation among African transport episodes. This scenario was 3-4 times more frequent than NAH-S, twice as frequent as AD(NAF) and more than 1.5 times more frequent than NAD. Finally, Mediterranean air mass transport prevailed in 62 days grouped in 35 episodes (2.9 and 5.5% respectively to the total number of events and days in 1998-2003, Figure 5.11).

Episodes of Atlantic advection occurred all throughout the year, but less frequently in summer (maximum frequency in November-December, February and April with means of 16-17 days in each of those months and minimum frequencies from May to August with means in the range 7-11 days). AZH-NAtD episodes were particularly frequent in November (a mean of 16 days) and February (15 days on average), and less frequent in August (6 days on average). The highest frequency of AD(ATL) events was observed in April (3 days, Figure 5.12). These events were scarce in summer.

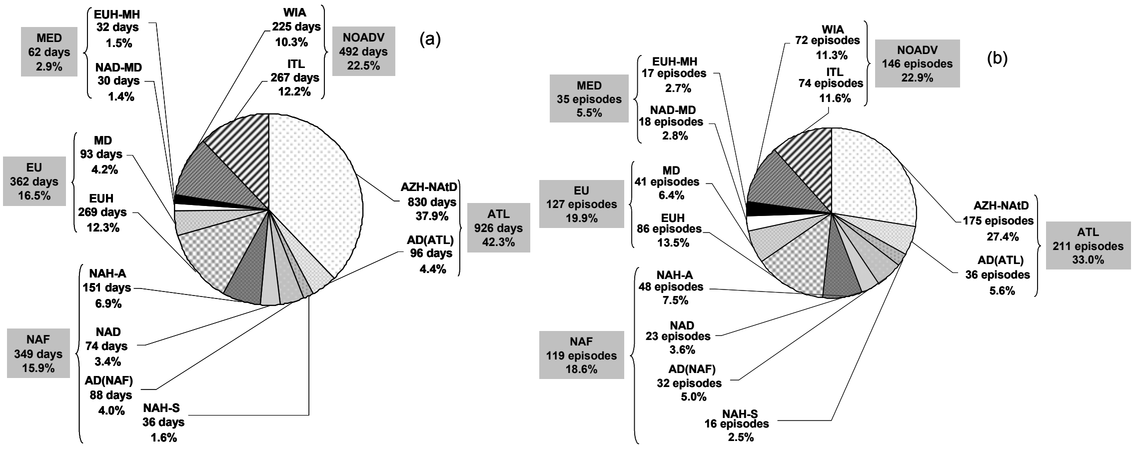


Figure 5.11. Occurrence of all the air mass transport scenarios over northeastern Iberian Peninsula in 1998-2003 in days (a) and episodes (b).

The transport of African air masses over northeastern Iberia occurred all throughout year but with especial frequency in May-August (with a frequency peak in June with 9 days on average) and January-March (6 days as a mean in March). Minima were detected in April (a mean of 2 days) and September, November and December (3 days as a mean in each of these months). With respect to the occurrence of the different African transport scenarios, NAH-S occurred only from January to March (a mean of 3 days per year in March). AD(NAF) episodes practically did not occur from June to September, with the maximum frequency of occurrence in March, May and December (3 days on average per year on each of those months). NAD situations did not occur in summer and reached the maximum occurrence (4 days as a mean) in May. Finally, summer episodes (NAH-A) were particularly frequent in June (9 days per year) but also in July (6 days on average) and August (7 days on average).

Episodes of European advection were registered in all the seasons (Figure 5.12) of the year over the study area being more frequent from autumn to spring (with the highest means in March with 8 days as average and December with 7 days as mean) than in summer (the lowest mean in July with 2 days on average). EUH episodes were particularly frequent from November to March (with a maximum monthly mean of 8 days in March) and occurred less frequently in summer. MD episodes were concentrated in spring and in autumn (3 days as monthly mean in three months: April, May and October).

The advection of Mediterranean air masses occurred all throughout the year with the exception of summer and had a low frequency of occurrence (Figure 5.12). These events occurred with the highest frequency in October-January (3 days on average in January) and spring (2 days as a mean in April). NAD-MD episodes were registered more frequently in January, April, October and November (all these months with a mean frequency of occurrence of 1 NAD-MD day). EUH-MH had a period of relatively higher frequency in November-January (2 days on average in January).

Situations with lack of advective conditions also occurred all along the year but while ITL episodes, by definition, only occurred during summer (specifically from May-October), WIA events did not occur from June to September. ITL situations reached their highest frequency of occurrence in June-August (with a mean of 3-4 days in each of those three months). The mean number of WIA days was maximum in April, May and October (2-3 days in each month on average, Figure 5.12).

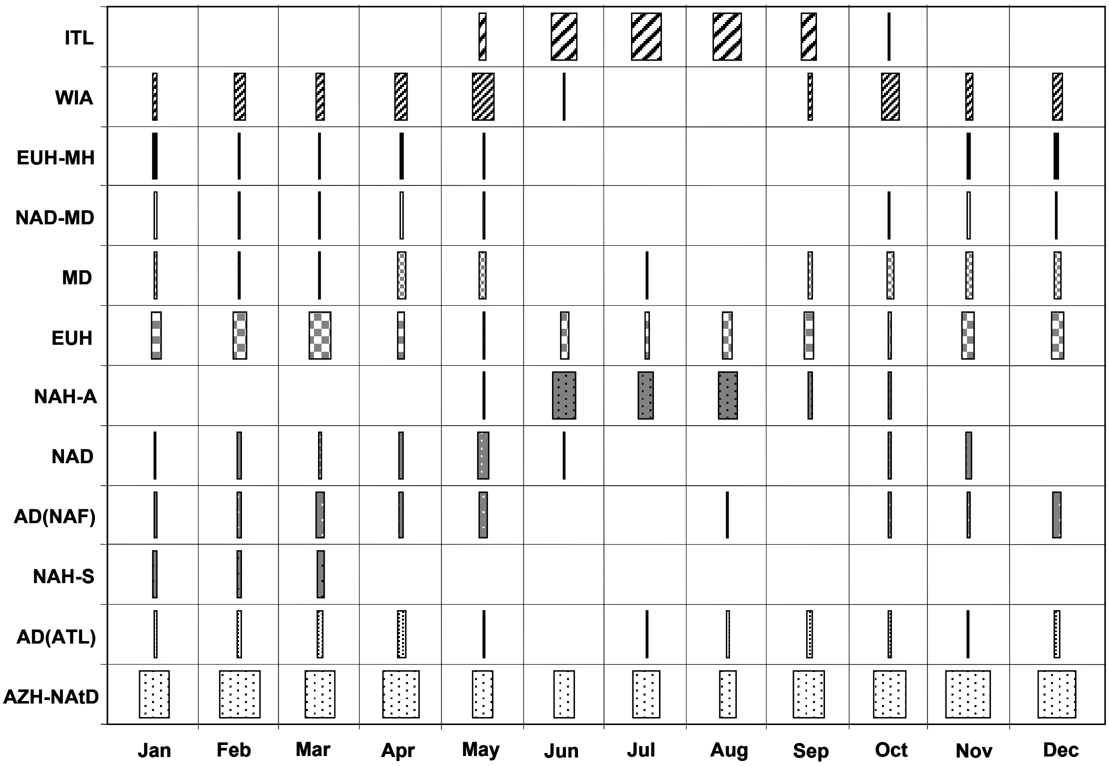


Figure 5.12. Mean number of days with each type of PM episode per month over northeastern Iberia in 1998-2003.

All types of PM episodes over northeastern Iberian Peninsula had a very similar mean duration as shown in Table 5.9. All episodes had a mean duration of 3 days with the exception of Atlantic (4 days) and Mediterranean (2 days) events. Among transport scenarios, a mean duration of 3 days per episode was also constant for all cases with the exception of the two Atlantic scenarios (AZH-NAtD with 5 days and AD(ATL) with 2 days), one African scenario (NAH-S) and the two types of Mediterranean scenarios (NAD-MD and EUH-MH) with 2 days per episode on average, and EUH events with 4 days per episode as mean duration.

Table 5.9. Mean duration of PM episodes in northeastern Iberian Peninsula for 1998-2003.

	Mean duration (days/episode)		**Mean duration (days/episode)**
Atlantic episodes	**4**	**European episodes**	**3**
AZH-NAtD	5	*EUH*	4
AD(ATL)	2	*MD*	3
African episodes	**3**	**Mediterranean episodes**	**2**
NAH-S	2	NAD-MD	2
AD(NAF)	3	EUH-MH	2
NAD	3	**Episodes without dominant advection**	**3**
NAH-A	3	*WIA*	3
		ITL	3

Mean PM levels in Roquetas and in Cabo de Creus were elevated when compared with those obtained at Els Torms and Monagrega. Annual mean PM levels for the period

1998-2003 were 39 µgTSP m^{-3} in Roquetas; 38 µgTSP m^{-3}, 21 µgPM0 m^{-3} and 14 µgPM2.5 m^{-3} in Cabo de Creus; 27 µgTSP m^{-3}, 18 µgPM0 m^{-3} and 12 µgPM2.5 m^{-3} in Els Torms and 17 µgPM0 m^{-3} in Monagrega (Table 5.10). Air quality measurements at Roquetas station were interrupted since 2000 owing to the direct influence of the emissions from the city of Tortosa. TSP levels recorded at this site were excessively high for a regional background site owing to this influence. Cabo de Creus is located in a very windy area with poor soil cover and very close to the shoreline. This could influence the measurements owing to the great degree of resuspension of crustal and marine aerosols although the transport of polluted air masses from the Gulf of Lion increasing PM levels at Cabo de Creus may be a frequent scenario.

No exceedances of the annual limit value established by the 1999/30/CE Directive were registered for the limit value of 2005 (40 µgPM10 m^{-3}), but in Cabo de Creus the target value established for 2010 (20 µgPM10 m^{-3}) was surpassed in 2003 with an annual mean of 25 µgPM10 m^{-3}. The Air Quality draft directive issued by the EU Commission in September 2005 establishes a PM2.5 annual cap value of 25 µgPM2.5 m^{-3}. This value was never reached in the period 2001-2003 neither in Els Torms nor in Cabo de Creus. A general reduction of annual PM means occurred in 2002 owing to an anomalously wet summer in the Iberian Peninsula (Table 5.10).

Table 5.10. Mean levels of TSP, PM10 and PM2.5 recorded in regional background stations in 1998-2003 in northeastern Iberian Peninsula.

MEAN LEVELS ($\mu g\ m^{-3}$)	Roquetas	Cabo de Creus			Els Torms			Monagrega
	TSP	TSP	PM10	PM2.5	TSP	PM10	PM2.5	PM10
1998	41	33	na	na	na	na	na	18
1999	35	41	na	na	na	na	na	17
2000	na	37	na	na	na	na	na	17
2001	na	40	*20	*12	32	*19	*12	19
2002	na	35	19	13	23	15	10	13
2003	na	na	25	17	na	20	13	16
Mean 98-03	39	38	21	14	27	18	12	17

*Calculated with data of 83% of the months of the year
na: Not available

Due to the large differences between mean PM levels recorded at Roquetas and Cabo de Creus when compared with those recorded at Els Torms and Monagrega, only PM data only from Els Torms and Monagrega will be discussed here (Table 5.11).

The lowest mean PM levels in regional background stations from northeastern Iberia were registered during Atlantic and Mediterranean episodes. During Atlantic events 23 µgTSP m^{-3}, 13 µgPM10 m^{-3} and 9 µgPM2.5 m^{-3} were recorded at Els Torms and 12 µgPM10 m^{-3} at Monagrega). These levels would have local or regional origin assuming the low concentration of particles in Atlantic air masses. Moreover, these episodes were commonly associated with the passage of frontal systems over the Iberian Peninsula resulting in precipitation and, in consequence, decrease of the PM levels by scavenging. These mean PM levels were similar to those obtained for Mediterranean episodes (22 µgTSP m^{-3}, 15 µgPM10 m^{-3} and 10 µgPM2.5 m^{-3} at Els Torms and 11 µgPM10 m^{-3} at Monagrega). Mediterranean episodes are commonly associated with rainfall which results in a decrease of PM levels by scavenging. Scenarios characterised by the presence of anticyclones such as AZH-NAtD (with mean PM levels of 24 µgTSP m^{-3}, 14 µgPM10 m^{-3} and 9 µgPM2.5 m^{-3} at Els Torms and 12 µgPM10 m^{-3} at Monagrega) and EUH-MH (with mean PM levels of 22 µgTSP m^{-3}, 17 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3} at Els Torms and 13 µgPM10 m^{-3} at Monagrega) resulted in higher PM mean levels than those associated with depressions such as AD(ATL) (with mean PM levels of 16 µgTSP m^{-3}, 10 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3} at Els Torms and 9 µgPM10 m^{-3} at Monagrega) and NAD-MD (with mean PM levels of 21 µgTSP m^{-3}, 13 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3} at Els Torms and 9 µgPM10 m^{-3} at Monagrega). The higher relative frequency of rain associated with AD(ATL) and MD confer these scenarios a greater scavenging potential.

African dust outbreaks exerted an important influence on PM levels as reflected in Table 5.11. In fact the highest mean PM levels were recorded during these events (35 µgTSP m^{-3}, 24 µgPM10 m^{-3} and 16 µgPM2.5 m^{-3} at Els Torms and 27 µgPM10 m^{-3} at Monagrega). From the four African transport scenarios, NAH-S (35 µgTSP m^{-3}, 27 µgPM10 m^{-3} and 20 µgPM2.5 m^{-3} at Els Torms and 29 µgPM10 m^{-3} at Monagrega) and NAH-A (36 µgTSP m^{-3}, 26 µgPM10 m^{-3} and 18 µgPM2.5 m^{-3} at Els Torms and 34 µgPM10 m^{-3} at Monagrega) offered higher mean PM levels than AD(NAF) (32 µgTSP m^{-3}, 21 µgPM10 m^{-3} and 11 µgPM2.5 m^{-3} at Els Torms and 19 µgPM10 m^{-3} at Monagrega) and NAD (35 µgTSP m^{-3}, 23 µgPM10 m^{-3} and 14 µgPM2.5 m^{-3} at Els Torms and 21 µgPM10 m^{-3} at Monagrega). The lower PM levels measured under AD(NAF) and NAD scenarios may be attributed to the higher scavenging by rainfall compared to the anticyclonic scenarios. Furthermore, during NAH-A events, the atmospheric conditions of the lowest levels of the atmosphere (weak baric conditions resulting in poor renovation of air masses together with the aging and recirculation of contaminated air masses at eastern Iberia as explained by Millan et al., 1997) resulted in an significant increase of PM levels especially by generation of secondary species from gaseous precursors. At the same time, during NAH-A situations the African plumes travel at high altitudes (>1500 m.a.s.l.) and the dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is distributed and affects the sampling stations. These two contributions increase PM levels during NAH-A events.

During situations of lack of advective conditions high mean PM levels were also registered (Table 5.11). 35 µgTSP m^{-3}, 23 µgPM10 m^{-3} and 14 µgPM2.5 m^{-3} at Els Torms and 21 µgPM10 m^{-3} at Monagrega were recorded during such events. Under these situations precipitation is reduced so the scavenging potential is reduced in episodes without lack of advective conditions. However, the impact of ITL and WIA events on PM levels was not similar. At Monagrega 16 and 26 µgPM10 m^{-3} were recorded as mean levels for WIA and ITL events, respectively. At Els Torms the difference between the mean PM levels obtained for the two scenarios was not so important. At this station, 29 µgTSP m^{-3}, 19 µgPM10 m^{-3} and 14 µgPM2.5 m^{-3} were recorded during WIA events and 31 µgTSP m^{-3}, 22 µgPM10 m^{-3} and 15 µgPM2.5 m^{-3} during ITL episodes. Providing the low vertical development of the boundary layer (where most pollutants are present) during WIA episodes, an increase of PM levels at Els Torms under these situations would suggest the influence of local/regional industrial or urban emissions. A regional background station should not be greatly influenced in its PM levels during WIA episodes.

During European episodes mean PM levels (Table 5.11) were of the same order of the mean annual PM levels (26 µgTSP m^{-3}, 18 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3} at Els Torms and 15 µgPM10 m^{-3} at Monagrega). However, these results are obtained from averaging PM levels obtained for EUH and MD days. While during EUH episodes mean PM levels were moderately high (29 µgTSP m^{-3}, 20 µgPM10 m^{-3} and 14 µgPM2.5 m^{-3} at Els Torms and 15 µgPM10 m^{-3} at Monagrega), during MD events, due to frequent rainfall associated with these episodes, mean PM levels were relatively low

(21 µgTSP m^{-3}, 14 µgPM10 m^{-3} and 9 µgPM2.5 m^{-3} at Els Torms and 13 µgPM10 m^{-3} at Monagrega).

Table 5.11. PM mean levels registered during different transport episodes over northeastern Iberian Peninsula in 1998-2003.

Mean PM levels	Roquetas	Cabo de Creus			Els Torms			Monagrega
(µg m^{-3})	TSP	TSP	PM10	PM2.5	TSP	PM10	PM2.5	PM10
Total 98-03	**39**	**38**	**21**	**14**	**27**	**18**	**12**	**17**
Atlantic episodes	**34**	**34**	**18**	**11**	**23**	**13**	**9**	**12**
AZH-NAtD	35	35	18	11	24	14	9	12
AD(ATL)	30	31	19	11	16	10	7	9
African episodes	**52**	**45**	**24**	**17**	**35**	**24**	**16**	**27**
NAH-S	77	38	23	17	35	27	20	29
AD(NAF)	46	45	24	15	32	21	11	19
NAD	46	44	24	15	35	23	14	21
NAH-A	48	48	24	19	36	26	18	34
European episodes	**39**	**43**	**25**	**16**	**26**	**18**	**12**	**15**
EUH	40	43	26	18	29	20	14	15
MD	35	44	24	14	21	14	9	13
Mediterranean episodes	**27**	**39**	**24**	**12**	**22**	**15**	**10**	**11**
NAD-MD	22	45	28	13	21	13	8	9
EUH-MH	34	35	22	11	22	17	12	13
Episodes without dominant advection	**42**	**35**	**23**	**16**	**30**	**20**	**14**	**22**
WIA	44	31	21	13	29	19	14	16
ITL	41	37	24	18	31	22	15	26

Combining information about the mean number of days and the PM mean levels into an impact index (II=mean number of days per year influenced by each type of scenario multiplied by the mean PM levels for each scenario in the whole period 1998-2003 and divided by 365 days) we can evaluate the impact of each transport scenario on PM levels for different size ranges. II gives us information about the contribution (in concentration units) of each type of transport scenario on the mean levels of PM recorded at a certain site. Moreover, II can be understood as the relative weight of each scenario with respect to the annual mean levels registered in a certain station and for a determined size range and it can be expressed as percentage.

Figure 5.13, shows that the II of Atlantic episodes (under which long range PM transport contributions are minimal, and probably most of PM load has a regional/local origin) was the highest in all size ranges and at both Els Torms and Monagrega stations. The impact index of Atlantic episodes at Els Torms ranged from 31 to 36% being higher in the coarser size ranges. This may be explained by the coarse size of marine salts, dominant particles in the relative clean Atlantic air masses. At Monagrega, the contribution reached 29% on PM10. AZH-NAtD contributes to the major part of these loads (27-33% depending on the station and size range) while AD(ATL) only reached to weights around 2-3%.

Following Atlantic events, episodes without dominant advective conditions (with a major regional/local PM load) were the events with the highest impact (Figure 5.13). These events contributed with 25-29% to the annual mean in the different size ranges. The contribution of WIA episodes (approximately constant between 11-12% at Els Torms and 9% at Monagrega) is lower than the impact of ITL episodes (14-16% at Els Torms and 19% at Monagrega). This is due to the lower PM mean levels recorded during these events when compared with ITL episodes, since the frequency of occurrence of both episodes was similar. Episodes without dominant advective conditions, in general, and, ITL episodes, in particular, increase their impact in fine size ranges. This is due to the intense photochemical processes in summer resulting in the formation of fine particles. This mechanism is enhanced by the typical aging and recirculation of contaminated air masses over eastern Iberian Peninsula influenced by the particular orography of eastern Iberian flank (Millán et al., 1997).

African episodes had an impact which ranged from 21 to 26% with their maximum influence on PM10 (in accordance with the typical African dust grain size in the range PM10-PM2.5). NAH-A episodes with contributions ranging from 9 to 14% had a higher impact on PM2.5 than on coarser size ranges at Els Torms. This occurs because during these events, similar conditions to those described for ITL episodes co-exist with the intrusions of dust on upper levels of the troposphere. NAH-S had a weight of 2-3%, with a slightly more importance on PM2.5. In this case the segregation of fine particles in the dust plume is very important owing to the long transport distance travelled by the dust in an "Atlantic arch". Along this long range transport, coarse dust particles may deposit by gravitational settling and, the proportion of fine dust particles in the plume may increase. Finally, AD with an impact of 5-4% and NAD with of an impact around 4% in all stations, yielded a higher impact index in PM10 than in PM2.5 (Figure 5.13).

European episodes had an impact on PM mean levels between 17-18% at Els Torms and 15 % at Monagrega (Figure 5.13). EUH scenario (with contributions to annual PM levels ranging from 13 to 15% at Els Torms and 11% at Monagrega) showed higher influence on PM2.5 than on coarser size ranges at Els Torms. The explanation of this feature is that, typically, particles arriving during European episodes are fine aerosols, PM2.5, with anthropogenic origin. MD events, often associated with rainfall, had a low frequency of occurrence, so they yielded low contribution (around 3% in all cases).

Mediterranean episodes had a low impact on mean PM levels (Figure 5.13). This impact ranged from 2 to 3%. Among scenarios, EUH-MH had an impact of 1-2% and NAD-MD of 1%.

The number of exceedances of the daily limit value for PM10 established by the 1999/30/CE Directive of 50 µg m^{-3} at Monagrega reached 40 days for all the study period (a mean of 6-7 exceedances per year) while at Els Torms 11 exceedances were registered from March 2001 to the end of 2003 (a mean of 3-4 per year). Recently, in the II PM Position paper on particulate matter (EC, 2004), a daily limit value of 35 µg m^{-3} for PM2.5 which should not be exceeded more than 35 times in a year was proposed. Eleven exceedances (3-4 per year) of the PM2.5 suggested limit value occurred in the period March 2001-2003 (Table 5.12).

It is important to note that 2002 had an anomalously wet summer season over the Iberian Peninsula which resulted in a low number of exceedances (1 in PM10 and PM2.5 at El Torms and 1 at Monagrega). This contrasted with 2003 with a dry and hot summer and a high number of African days. The number of exceedances in this year reached 7-8 for PM10 and PM2.5 in all the stations. The anomalously high number of exceedances at Monagrega in 2001 occurred in several consecutive days in summer. A very important increase in the background levels was detected during that year as shown in Figure 5.14. This elevation in the background levels at Monagrega station can be interpreted as an episodical local contribution from the Andorra po wer plant located near Monagrega station. Gaseous precursors emitted by this plant could have been rapidly transformed into secondary species under the enhanced photochemistry during summer.

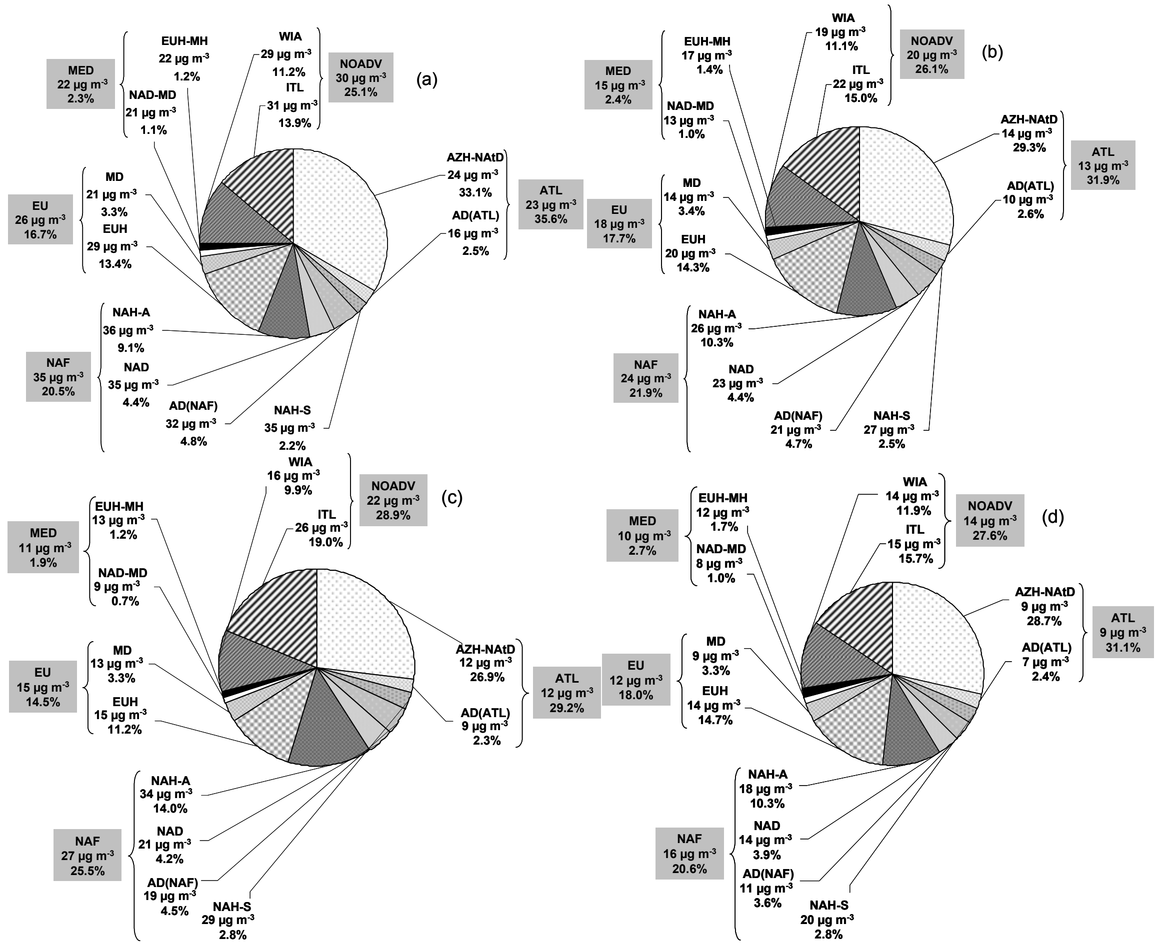


Figure 5.13. Relative impact (in %) of different PM episodes and meteorological scenarios on TSP mean levels in Els Torms (a), on PM10 mean levels in Els Torms (b), on PM10 mean levels in Monagrega (c) and on PM2.5 mean levels in Els Torms (d).

Table 5.12. Number of annual exceedances of the daily limit value established by the 1999/30/CE Directive (50 µgPM10 m^{-3}) in Els Torms and in Monagrega. The number of annual exceedances and of the PM2.5 daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) at Els Torms is also shown.

NUMBER OF EXCEEDANCES	AQ Directive 1999/30/CE : PM10 > 50 µg m^{-3}		II PM position paper suggestions: PM2.5 > 35 µg m^{-3}
	Els Torms	**Monagrega**	**Els Torms**
1998	na	7	na
1999	na	4	na
2000	na	5	na
2001	*2	16	*2
2002	1	1	1
2003	8	7	8
Total 98-03	11	40	11
Annual mean 98-03	3.7	6.7	3.7

*Calculated with data of 83% of the months of the year
na: Not available

The number of exceedances of the daily limit values of PM10 at Monagrega was affected by African dust outbreaks. In total, from the 40 exceedances of 50 µg m^{-3} of PM10 at Monagrega from 1998-2003, 25 (63%) occurred during African dust outbreaks, 5 (12%) during episodes without prevalent advective conditions and 2 (5%) during European episodes. In 8 out of the 40 exceedances (20%) the situation

consisted in Atlantic advection and the origin was attributed to local/regional causes. These 8 days, occurred in the summer of 2001 during the episode of high PM levels recorded at Monagrega probably, as stated above, by a local contributions.
In Els Torms the African episodes caused 8 excedances (73%) of the PM10 daily limit value and 6 exceedances (54%) of the PM2.5 daily limit value proposed in the II PM position paper. One exceedance of the PM10 daily limit and another of the PM2.5 limit value (9% in both cases) occurred under European episodes. During episodes without dominant advection 1 of the PM10 daily exceedances (9%) and 3 of the PM2.5 daily exceedances (27%) occurred while during Atlantic episodes only 1 of the PM10 daily exccedances (9%) and 1 of the PM2.5 daily exceedances (9%) were recorded probably owing to local/regional contributions.

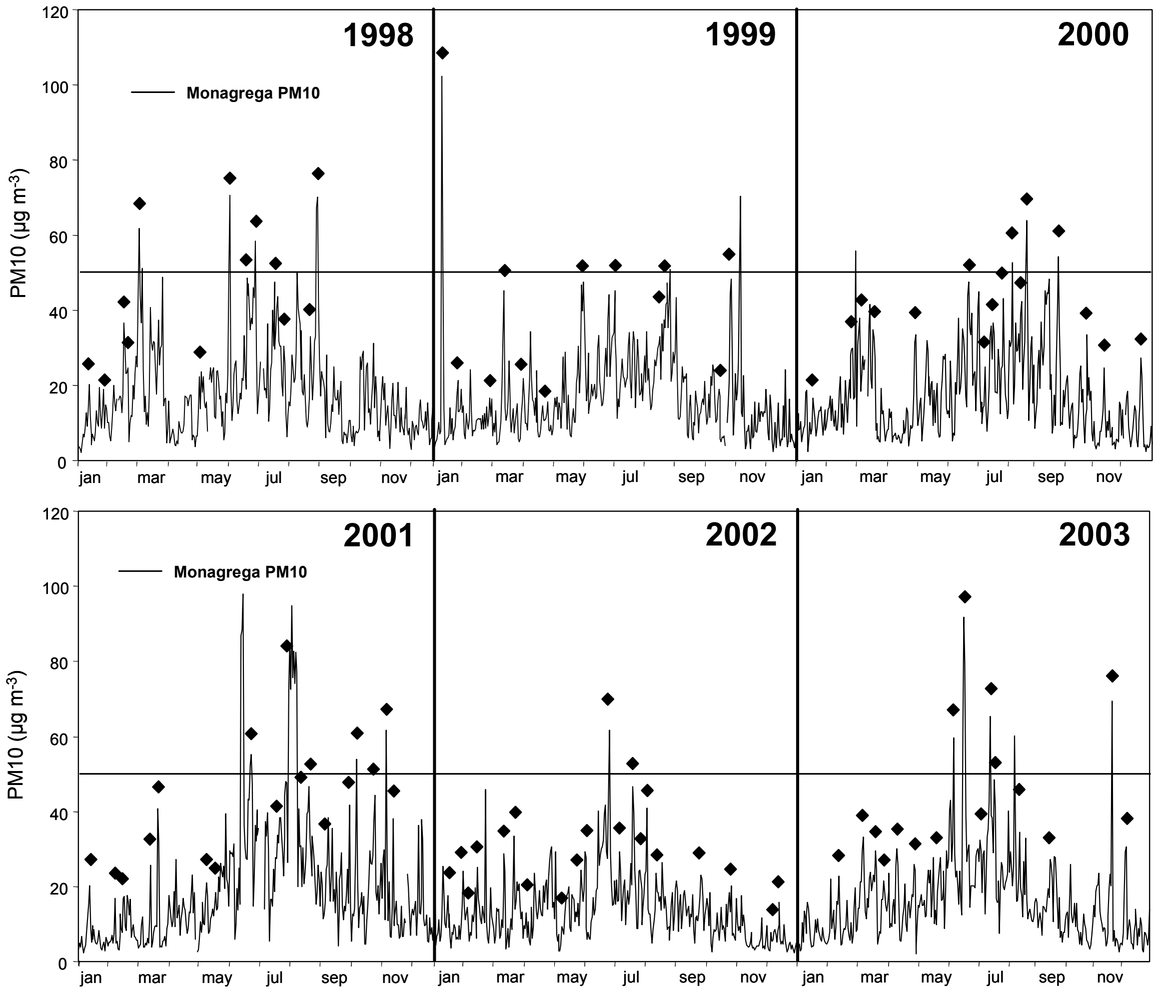


Figure 5.14. Daily PM10 levels in Monagrega for 1998-2003. The black dots mark the occurrence of African dust episodes. The horizontal lines mark the daily limit values established by the 1999/30/CE Directive (50 µgPM10 m^{-3}).

The highest PM levels in regional background stations over northeastern Iberia were registered in summer owing to these factors:

(a) The enhancement of photochemical formation of secondary particles due to a higher insolation during summer.

(b) The lower precipitation regime during summer (Figure 5.15) which results in the reduction of processes such as the washing out of aerosols from the atmosphere.

(c) The low renovation of air masses during episodes with lack of advection such as during ITL events.
(d) The higher frequency of occurrence of dry African dust outbreaks over the Iberian Peninsula.
(e) The increased rates of resuspension of crustal material owing to the poor vegetal coverage of this area and the intense atmospheric convective dynamics

The summer maximum was not registered in Roquetas which showed higher levels in February-March and November than in summer time. The influence of pollution from the nearby city of Tortosa in the low dispersive atmospheric conditions of winter resulted in these winter maxima. In Cabo de Creus the annual mean PM levels are too high to represent the regional background. This is particularly relevant in TSP monthly means distribution at this station which showed a clear summer maximum. This may be attributed to the influence of the typical high speed of wind frequently blowing over the area where the station is located causing resuspension of crustal and marine aerosols (which mainly belong to coarse size ranges). At Els Torms and Monagrega series the above mentioned summer maxima were present and a secondary maximum was present around February-March. This peak could be attributed to African dust outbreaks with important impact on PM levels occurring during these months over the region (Figure 5.15). These typical winter African episodes do not occur all the years and that is the main reason why the March PM peak is so marked.

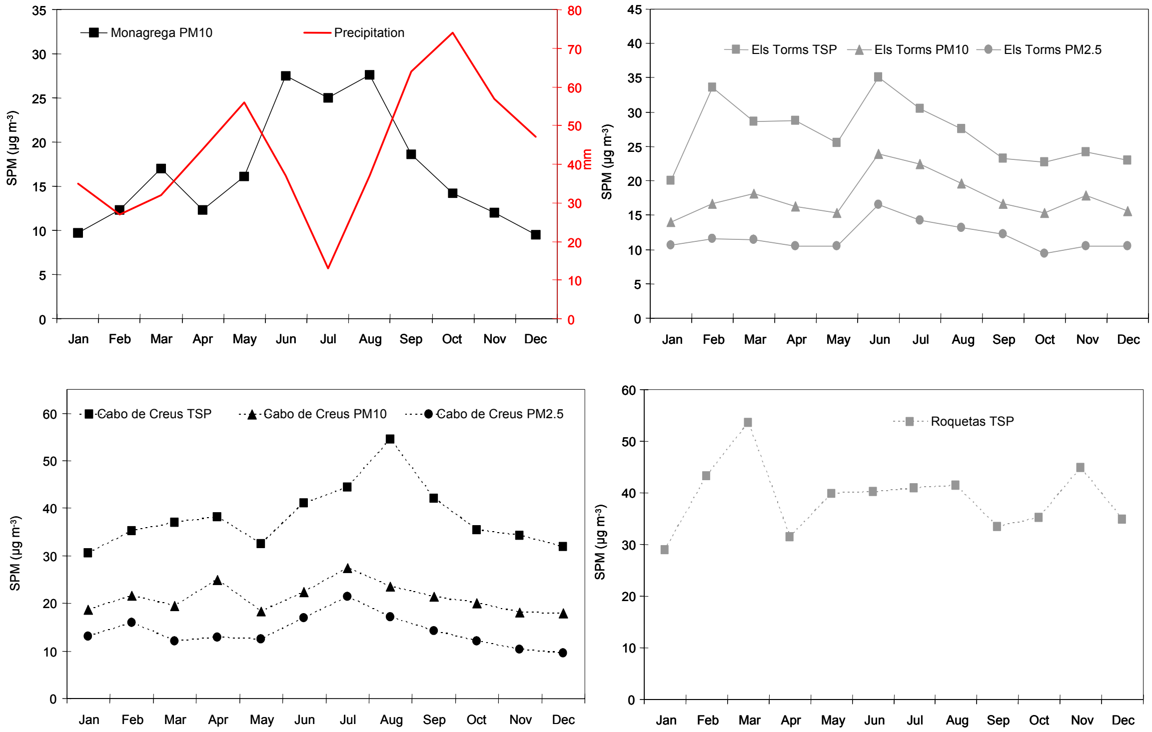


Figure 5.15. Mean monthly precipitation of Observatorio del Ebro station (Tortosa, 40° 49' N, -00°29' W, 48 m.a.s.l) for 1971-2000 (INM, 2001) and TSP monthly means registered in Roquetas (1998-June 2000), Cabo de Creus (TSP from 1998-January 2003 and PM10 and PM2.5 from March 2001 to 2003), Els Torms (from November 2000-January 2003 and PM10 and PM2.5 from March 2001 to 2003), Monagrega (PM10 from 1998 to 2003).

5.4 Central Iberian Peninsula

Two plateaus divided by the central range characterise the central region of Spain, the northern plateau with an average altitude of 800-900 m and the southern plateau with an average altitude of 600-700 m. These plateaus are surrounded by mountain ranges of higher elevation such as the Galaico-Cantabrian system to the north and northwest, the Iberian range to the east and northeast and Sierra Morena and the Penibetic range to the south. These orographic characteristics confer the Iberian plateau a considerable degree of isolation and continentality. In consequence the climate of the study region can be considered continental with cold and relatively dry winters and warm and dry summers and two wet seasons in spring and autumn.

The location of the study region makes it susceptible to be reached by African air masses, especially over its southernmost region. These air masses could easily reach central Spain from its eastern flank across the Mediterranean or across the Atlantic Ocean in the typical dust plumes called "Atlantic arches". By contrast, the influence of European air masses over central Iberia is greatly reduced with respect to the northern band of the Iberian Peninsula owing to the isolation provoked by the Pyrenees and the Iberian range and the higher distance to the European continent. During summer under situations of great insolation and lack of advective conditions the Iberian thermal low (ITL) develops together with a strong vertical development of the boundary layer owing to the strong convective movements near the surface (Millán et al., 1997). Under this situation resuspension of soil material and the enhanced formation of secondary aerosols from precursor gases from urban or industrial centres by photochemical processes could affect PM levels in regional background stations (Rodríguez et al, 2003).

For this study, data on daily levels of PM from four EMEP air quality monitoring stations available for the period 1998-2003 were used to evaluate the impact of several PM episodes on regional background levels. These stations were: a) San Pablo de los Montes station (39º 23' N, - 4º 21' E, 917 m.a.s.l.) with data on TSP from 1998 to June 2000, b) Risco Llano station (39º 31' N, - 4º 21' E, 1241 m.a.s.l.) with data on TSP from November 2000 to the end of 2003, and data on PM10 and PM2.5 from March 2001 to the end of 2003, c) Campisábalos station (41º 17' N, - 3º 09' E, 1360 m.a.s.l.) with TSP data from March 1998 to the end of 2003 and data on PM10 and PM2.5 from March 2001 to the end of 2003 and d) Peñausende station (41º 17' N, - 5º 52' E, 985 m.a.s.l.) with data on TSP available from July 2000 to the end of 2003 and data on PM10 and PM2.5 from March 2001 to the end of 2003. The sampling method at EMEP stations was the gravimetric method using filters collected from high volume samplers on a 24 hours basis.

These stations are located at elevated sites and far enough from urban or industrial emission sources and, consequently, are suitable locations for representing the regional background levels of ambient PM. Campisábalos data will be preferably used in some parts of the following synthesis because of the long data record available from this station. However, ambient PM data from the other three stations can be also considered representative of the regional background.

As shown in Figure 5.16, during 1998-2003, air mass transport from the Atlantic Ocean was the dominant situation over central Iberia concerning both the number of episodes and days. In a total of 1060 days (48.4% of the total number of days in the study period) and 237 episodes (39.4% of the total number of PM episodes in 1998-2003) this air mass transport scenario occurred. The number of days with a AZH-NAtD synoptic situation was 8 times more frequent than with AD(ATL) scenario.

Situations without prevailing advective conditions were also frequent over the study region. This scenario occurred in 528 days (24.1% of the days) grouped in 153 episodes (25.3% of the events) during 1998-2003. Among these episodes, WIA and ITL events were equally frequent.

During the study period, air mass transport from northern Africa occurred over central Iberian Peninsula in 311 days (14.1% of the days in 1998-2003) which resulted in 110 events (18.3% of the episodes registered in 1998-2003). The most frequent African transport scenario was NAH-A which corresponded, in general with summer episodes (6.6% of the days in 1998-2003). This scenario was 3 times more frequent than NAD and NAH-S scenarios and twice as frequent as the AD(NAF) scenario.
The occurrence of European and Mediterranean air mass transport events was clearly lower than the other three episodes. The transport of air masses from the European continent prevailed in 168 days (7.7% of the days in the study period) grouped in 48 events (8.0% of the PM episodes in 1998-2003) while advection from the Mediterranean was the dominant situation in 124 days (5.6% of the 1998-2003 number of days) grouped in 54 episodes (9.0% of the transport events during the study period). EUH (double number of days than MD) and EUH-MH (5 times more frequent than NAD-MD) were the dominant synoptic scenarios among European and Mediterranean episodes.

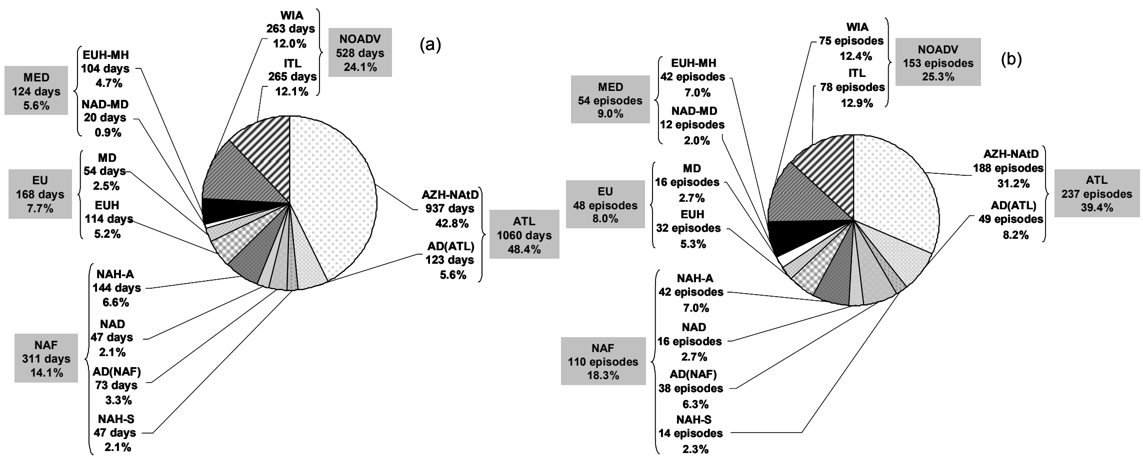


Figure 5.16. Occurrence of all the air mass transport scenarios over central Iberian Peninsula in 1998-2003 in days (a) and episodes (b).

As shown in Figure 5.17, Atlantic episodes occurred over central Iberian Peninsula in 1998-2003 in all the months of the year but with higher frequency in autumn (with a mean of 21 days in November) and spring (with a mean of 21 days in April) and lower frequency in summer (with the minimum of 8 days on average in June). November (20 days on average), January (18 days as a mean) and April (a monthly mean of 16 days) were the months in which AZH-NAtD events were highly frequent. The frequency peaks of AD(ATL) were registered in April (4 days as monthly mean), September (3 days on average) and December (3 days as a mean).
As shown in Figure 5.17, African episodes occurred over central Iberia in all seasons of the year but the seasonal variation of the occurrence of different transport scenarios is important. The maximum frequencies of occurrence of African dust outbreaks were registered in May-August (with 9 days as a mean in June) and in January-March (with 7 days on average in March). The lowest occurrences of these episodes were registered in April, September and November (with less than 2 days as a mean in those months). NAH-S episodes occurred from January to March (a mean of 3 days on February and March). AD(NAF) events did not occur in summer and in March (3 days as monthly mean) and December (3 days as a mean) the frequency of occurrence was the highest. A major proportion of NAD episodes occurred in May (2 days as monthly mean) and, practically, did not occur in summer. Finally, NAH-A events were characteristics from

late spring to early autumn (from 5 to 8 days as monthly means in the period June-August).

The advection of European air masses over central Iberian Peninsula was an uncommon process during summer (Figure 5.17). Thus, in July no European event was recorded. From November to March a mean of 4 days with European advection was registered in all the months. While EUH events were relatively more frequent in winter (3 or 4 days as monthly means in January-March), the occurrence of MD episodes only reached noticeable levels in November (3 days on average) and April (2 days as monthly mean).

Mediterranean events occurred over central Iberian Peninsula during all the months of the year (Figure 5.17) but with higher relative frequency from autumn to winter (with 4 days as a mean in January and 3 in March and November) than in summer (only 2 days with Mediterranean advection in the whole study period in August). The frequency of occurrence of NAD-MD episodes was low and only March (2 days as monthly mean) the occurrence of these situations was relatively high. The monthly distribution of days with EUH-MH situations had frequency peaks in January (4 days as a mean) and November (3 days on average) but also in June a considerable number of days were registered (2 days as monthly mean).

As shown in Figure 5.17, the situations without prevailing advective conditions were frequent over central Iberia and occurred all throughout the year. ITL episodes occurred solely from May to October (10 to 12 days as monthly means from June to September). WIA episodes, which did not occur from June to August, were especially frequent in May (10 days as monthly mean), October (8 days on average) and December (7 days as mean).

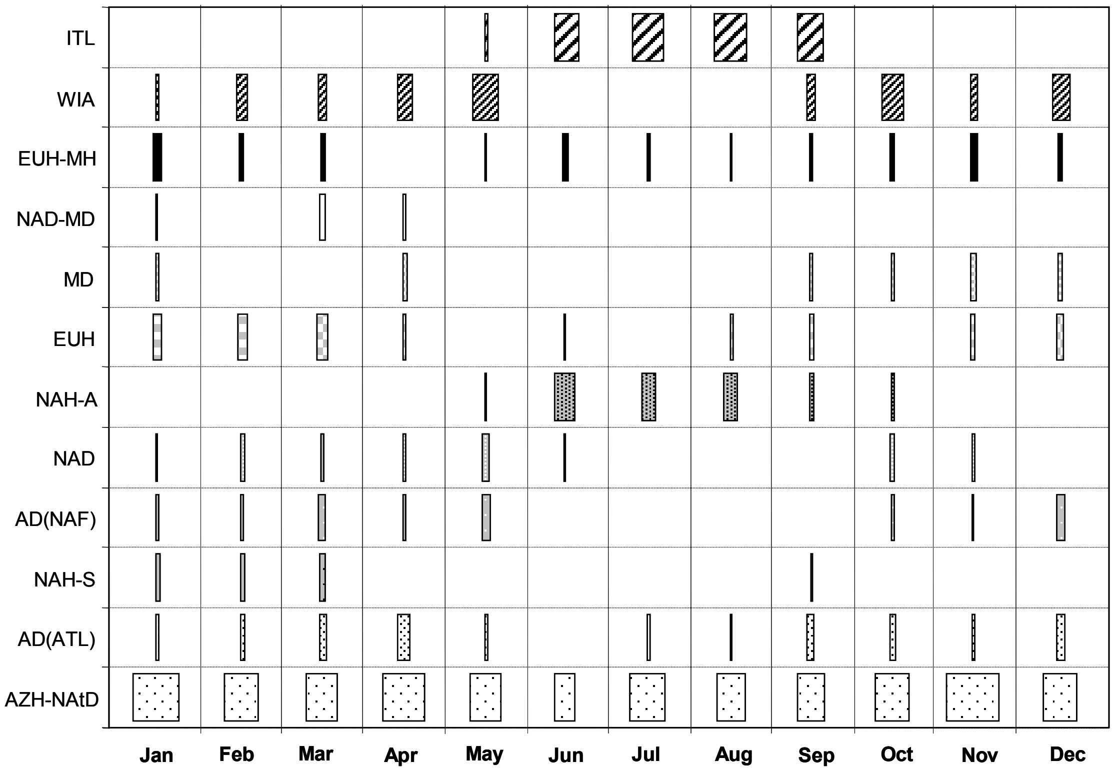


Figure 5.17. Mean number of days with each type of PM episode per month over central Iberia in 1998-2003.

As shown in Table 5.13, the Atlantic episodes over central Iberian Peninsula had a mean duration of 4 days, with AZH-NAtD episodes having a mean duration of 5 days and of 2 days for AD(ATL). As the Atlantic events, the European episodes had a mean duration of 4 days. Among these, EUH events (4 days on average) were longer than MD episodes (3 days as a mean). African events and episodes without prevailing advective conditions had 3 days as mean duration. Among African episodes, NAH-A (4 days as mean duration) were longer on average than NAH-S, NAD (3 days as mean duration in both cases) and AD(NAF) (with a mean duration of 2 days). With respect to the episodes without prevalent advective conditions, WIA had a mean duration of 4 days and ITL of 3 days. Mediterranean episodes had a mean duration of 2 days (the same mean duration of NAD-MD and EUH-MH events), the lowest mean duration among all the episodes.

Table 5.13. Mean duration of PM episodes in central Iberian Peninsula for 1998-2003.

	Mean duration (days/episode)		**Mean duration (days/episode)**
Atlantic episodes	**4**	**European episodes**	**4**
AZH-NAtD	5	*EUH*	4
AD(ATL)	2	*MD*	3
African episodes	**3**	**Mediterranean episodes**	**2**
NAH-S	3	*NAD-MD*	2
AD(NAF)	2	*EUH-MH*	2
NAD	3	**Episodes without dominant advection**	**3**
NAH-A	4	*WIA*	4
		ITL	3

All the EMEP stations in the central Iberian Peninsula were located at high altitudes (San Pablo de los Montes station at 917 m.a.s.l, Risco Llano station at 1241 m.a.s.l, Campisábalos station at 1360 m.a.s.l and Peñausende station at 985 m.a.s.l) and far from cities or industrial emission sources so the mean PM levels were reduced (Table 5.14). Mean PM levels were 22 µgTSP m^{-3} San Pablo de los Montes; 22 µgTSP m^{-3}, 14 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3} at Risco Llano; 18 µgTSP m^{-3}, 12 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3} at Campisábalos and 18 µgTSP m^{-3}, 13 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3} at Peñausende). These mean PM levels did not show a great interannual variation and in no case the annual limit values of the 1999/30/CE Directive for 2005 (40 µgPM10 m^{-3}) or for 2010 (20 µgPM10 m^{-3}) were exceeded. With respect to the mean PM2.5 levels, in no station the annual limit value established by EU Commission in September 2005 in the Air Quality directive draft of 25 µgPM2.5 m^{-3} was surpassed during the whole study period.

As shown in Table 5.15, the lowest levels of PM were recorded during Atlantic episodes (15 µgTSP m^{-3} at San Pablo de los Montes; 15 µgTSP m^{-3}, 8 µgPM10 m^{-3} and 5 µgPM2.5 m^{-3} at Risco Llano; 11 µgTSP m^{-3}, 7 µgPM10 m^{-3} and 5 µgPM2.5 m^{-3} at Campisábalos and 11 µgTSP m^{-3}, 8 µgPM10 m^{-3} and 5 µgPM2.5 m^{-3} at Peñausende). The Atlantic air masses transported towards the study area were relatively clean and these PM levels would indicate the regional background levels without major external contributions. Moreover, the common occurrence of rain associated with the passage of frontal systems during Atlantic episodes confer these events a high scavenging potential which may also explain the low mean PM levels recorded at regional background stations. The mean PM levels recorded during AZH-NAtD episodes (15 µgTSP m^{-3} at San Pablo de los Montes; 15 µgTSP m^{-3}, 8 µgPM10 m^{-3} and 5 µgPM2.5 m^{-3} at Risco Llano; 11 µgTSP m^{-3}, 7 µgPM10 m^{-3} and 5 µgPM2.5 m^{-3} at Campisábalos and 11 µgTSP m^{-3}, 8 µgPM10 m^{-3} and 5 µgPM2.5 m^{-3} at

Peñausende) were slightly higher than during AD(ATL) events (11 µgTSP m^{-3} at San Pablo de los Montes; 6 µgTSP m^{-3}, 5 µgPM10 m^{-3} and 3 µgPM2.5 m^{-3} at Risco Llano; 9 µgTSP m^{-3}, 6 µgPM10 m^{-3} and 4 µgPM2.5 m^{-3} at Campisábalos and 7 µgTSP m^{-3}, 6 µgPM10 m^{-3} and 4 µgPM2.5 m^{-3} at Peñausende). This is probably caused by the higher rainfall of the latter scenario (Table 5.15).

Table 5.14. Mean levels of TSP, PM10 and PM2.5 recorded in EMEP stations in 1998-2003 in central Iberian Peninsula.

MEAN LEVELS (µg m^{-3})	**San Pablo de los Montes**	**Risco Llano**			**Campisábalos**			**Peñausende**		
	TSP	TSP	PM10	PM2.5	TSP	PM10	PM2.5	TSP	PM10	PM2.5
1998	24	na	na	na	*[2]18	na	na	na	na	na
1999	20	na	na	na	15	na	na	na	na	na
2000	*[1]20	na	na	na	20	na	na	na	na	na
2001	na	23	*[3]15	*[3]9	22	*[3]14	*[3]9	19	*[3]15	*[3]10
2002	na	23	12	7	17	11	7	18	12	8
2003	na	na	14	7	na	12	7	na	13	8
Mean 98-03	22	22	14	7	18	12	8	18	13	8

*[1]Calculated with data of 50% of the months of the year
*[2]Calculated with data of 83% of the months of the year
*[3]Calculated with data of 83% of the months of the year
na: Not available

Also low PM levels were registered during episodes of Mediterranean advection over the study area (21 µgTSP m^{-3} at San Pablo de los Montes; 13 µgTSP m^{-3}, 10 µgPM10 m^{-3} and 6 µgPM2.5 m^{-3} at Risco Llano; 14 µgTSP m^{-3}, 9 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3} at Campisábalos and 17 µgTSP m^{-3}, 13 µgPM10 m^{-3} and 9 µgPM2.5 m^{-3} at Peñausende, Table 5.15). Precipitation was frequent during Mediterranean episodes. The mean PM levels during the two types of Mediterranean events, NAD-MD and EUH-MH, were comparable but slightly higher during EUH-MH events (in the EMEP stations, the ranges of variation of mean PM levels were 14-18 µgTSP m^{-3}, 10-11 µgPM10 m^{-3} and 5-8 µgPM2.5 m^{-3} during NAD-MD events and 13-21 µgTSP m^{-3}, 8-13 µgPM10 m^{-3} and 6-10 µgPM2.5 m^{-3} during EUH-MH events, Table 5.15).
The mean PM levels recorded during European episodes were lower than the annual PM means at all sites with the exception of Peñausende (19 µgTSP m^{-3} at San Pablo de los Montes; 19 µgTSP m^{-3}, 13 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3} at Risco Llano; 13 µgTSP m^{-3}, 10 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3} at Campisábalos and 20 µgTSP m^{-3}, 14 µgPM10 m^{-3} and 10 µgPM2.5 m^{-3} at Peñausende). The distance from the European continent to the study area (greater than to the northern regions of the Iberian Peninsula) resulted in a greater degree of dilution/dispersion of the pollutants in European air masses. The existence of National road (N-630) 11 kms to the east of Peñausende sampling station may be the cause of the relatively increased PM levels during episodes of eastern advection at this site (European and Mediterranean episodes). During EUH episodes, in virtue of their relatively low rainfall associated, with the mean PM levels recorded were higher than for MD events. The ranges of PM levels in the EMEP stations were 14-24 µgTSP m^{-3}, 11-17 µgPM10 m^{-3} and 7-12 µgPM2.5 m^{-3} during EUH events, and 9-16 µgTSP m^{-3}, 8-11 µgPM10 m^{-3} and 6-8 µgPM2.5 m^{-3} during MD events (Table 5.15).
The PM levels recorded during episodes without dominant advective conditions were above the annual PM levels for 1998-2003 (26 µgTSP m^{-3} at San Pablo de los Montes; 25 µgTSP m^{-3}, 16 µgPM10 m^{-3} and 9 µgPM2.5 m^{-3} at Risco Llano; 26 µgTSP m^{-3}, 15 µgPM10 m^{-3} and 10 µgPM2.5 m^{-3} at Campisábalos and 25 µgTSP m^{-3},

15 μgPM10 m^{-3} and 11 μgPM2.5 m^{-3} at Peñausende, Table 5.15). However, while during summer episodes, ITL, the PM levels were relatively high (31-35 μgTSP m^{-3}, 19-20 μgPM10 m^{-3} and 11-13 μgPM2.5 m^{-3}, Table 5.15) due to factors such as the low rainfall (this stands also for WIA events), the aging of air masses, the high rate of resuspension or the enhancement of transformation of gaseous precursors into secondary aerosols in virtue of the increased photochemistry. From late autumn to early spring, when WIA events occurred, the dispersive conditions were reduced and, in consequence, the vertical development of the boundary layer was low; this is especially relevant when thermal inversions developed over urban and/or industrial sites. As the EMEP stations over central Iberia are located at relatively high altitudes and far from sources of anthropogenic pollutants, the PM levels registered during WIA episodes were low (15-19 μgTSP m^{-3}, 10-12 μgPM10 m^{-3} and 7-9 μgPM2.5 m^{-3} were the levels recorded during these events in the EMEP sites, Table 5.15).

As shown in Table 5.15, the highest mean PM levels were registered during north African dust outbreaks (45 μgTSP m^{-3} at San Pablo de los Montes; 41 μgTSP m^{-3}, 25 μgPM10 m^{-3} and 12 μgPM2.5 m^{-3} at Risco Llano; 40 μgTSP m^{-3}, 23 μgPM10 m^{-3} and 12 μgPM2.5 m^{-3} at Campisábalos and 29 μgTSP m^{-3}, 22 μgPM10 m^{-3} and 12 μgPM2.5 m^{-3} at Peñausende). Among the different scenarios in which African events were classified, the summer events, NAH-A, drew to the highest mean PM levels (38-71 μgTSP m^{-3}, 24-31 μgPM10 m^{-3} and 14 μgPM2.5 m^{-3}). During NAH-A events, the atmospheric conditions of the lowest levels of the atmosphere (weak baric conditions resulting in poor renovation of air) and the intense insolation resulted in an significant increase of PM levels especially by generation of secondary species from gaseous precursors. At the same time, during NAH-A situations the African plumes travel at high altitudes (>1500 m.a.s.l.) and the dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is distributed and affects the sampling stations. These two contributions contribute to increase PM levels during NAH-A events. Also during NAH-S episodes de PM levels were high (18-41 μgTSP m^{-3}, 16-23 μgPM10 m^{-3} and 8-12 μgPM2.5 m^{-3} were the levels recorded during these events). The low rainfall probability associated with NAH-A and NAH-S events could contribute to these relatively high levels. Precipitation was more frequent during AD(NAF) and NAD which leaded to lower relative PM levels during these episodes (20-28 μgTSP m^{-3}, 16-19 μgPM10 m^{-3} and 8-9 μgPM2.5 m^{-3} were recorded during AD(ATL) and 21-32 μgTSP m^{-3}, 18-23 μgPM10 m^{-3} and 9-11 μgPM2.5 m^{-3} during NAD events).

Combining information about the mean number of days and the PM mean levels into an impact index (II=mean number of days per year influenced by each type of scenario multiplied by the mean PM levels for each scenario in the whole period 1998-2003 and divided by 365 days) we can evaluate the impact of each transport scenario on PM levels for different size ranges. II gives us information about the contribution (in concentration units) of each type of transport scenario on the mean levels of PM recorded at a certain site. Moreover, II can be understood as the relative weight of each scenario with respect to the annual mean levels registered in a certain station and for a determined size range and it can be expressed as percentage.

Table 5.15. PM mean levels registered during different transport episodes over central Iberian Peninsula in 1998-2003.

Mean PM levels ($\mu g\ m^{-3}$)	**San Pablo de los Montes**	**Risco Llano**			**Campisábalos**			**Peñausende**		
	TSP	TSP	PM10	PM2.5	TSP	PM10	PM2.5	TSP	PM10	PM2.5
Total 98-03	**22**	**22**	**14**	**7**	**18**	**12**	**8**	**18**	**13**	**8**
Atlantic episodes	**15**	**15**	**8**	**5**	**11**	**7**	**5**	**11**	**8**	**5**
AZH-NAtD	16	15	8	5	11	7	5	12	9	5
AD(ATL)	11	6	5	3	9	6	4	7	6	4
African episodes	**45**	**41**	**25**	**12**	**40**	**23**	**12**	**29**	**22**	**12**
NAH-S	41	18	17	8	27	16	9	23	23	12
AD(NAF)	22	28	16	8	21	16	9	20	19	8
NAD	30	32	23	11	28	22	9	21	18	10
NAH-A	71	59	31	14	56	27	14	38	24	14
European episodes	**19**	**19**	**13**	**7**	**13**	**10**	**7**	**20**	**14**	**10**
EUH	21	22	13	7	14	11	7	24	17	12
MD	13	15	11	7	9	8	6	16	10	8
Mediterranean episodes	**21**	**13**	**10**	**6**	**14**	**9**	**7**	**17**	**13**	**9**
NAD-MD	17	16	10	5	14	11	8	18	11	8
EUH-MH	21	13	10	6	14	8	6	16	13	10
Episodes without dominant advection	**26**	**25**	**16**	**9**	**26**	**15**	**10**	**25**	**15**	**11**
WIA	19	17	12	7	15	10	7	18	12	9
ITL	34	34	19	11	35	20	12	31	19	13

Regardless, the low PM levels recorded during Atlantic events the important frequency of occurrence of these episodes resulted in high II in all stations and size ranges. During these episodes the long range PM contribution is minimal and most of PM load had a local or regional origin. The impact of Atlantic episodes ranged from 29-33%, being AZH-NAtD the scenario contributing with most of the weight (26-31%) in response to the high occurrence of this type of events. AD(ATL) scenario only reached an impact of 2-3% (Figure 5.18). The II of Atlantic events is higher in PM2.5 than in TSP and PM10. The contribution of fine aerosols to Atlantic air masses may come from anthropogenic sources in areas in the Iberian Peninsula crossed by these air masses before reaching central Iberia.

Close to the impact of Atlantic episodes was the weight of episodes without prevailing advective conditions (Figure 5.18). The occurrence of these situations was not as frequent as Atlantic episodes but the high PM load (mainly due to ITL episodes) accounted for an elevated impact of these events (28-33%). The weight of ITL scenario is almost double of the weight of WIA scenario (18-22% for ITL and 10-12% for WIA). Episodes without dominant advective conditions, in general, and, ITL episodes, in particular, increase their impact in fine size ranges. This is due to the intense photochemical processes in summer resulting in the formation of fine particles. As the frequency of occurrence of both scenarios is similar, this difference in weight is attributed to the higher PM levels recorded during ITL episodes in virtue the low rainfall, the aging of air masses, the high rate of resuspension and the important rate of photochemical transformation of gaseous precursors into secondary aerosols during summer.

As shown in Figure 5.18, the impact of African episodes on PM annual values were also important but the frequency of these events (reduced with respect to Atlantic episodes and episodes without dominant advective conditions) resulted in a range of II from 22 to 30%. The impact of African episodes was slightly reduced in PM2.5 with respect to PM10 and TSP but still significant, with relative impacts of 22-23, 27 and 28-30% respectively. The coarse size of dust particles would explain this fact and, in particular for NAH-A events, the altitude of these stations (1241 m.a.s.l. Risco Llano and 1360 m.a.s.l. Campisábalos), makes them susceptible of receiving the direct impact of the dust plume travelling at high altitudes during NAH-A episodes. In these cases, as the size of the dust grains is coarse, the II of these episodes would be biased towards TSP and PM10. Among African episodes, NAH-A had the most important contribution on the annual PM levels with weights ranging from 12 to 20%. AD(NAF) and NAD had an impact ranging from 3 to 5% and 3 to 4% respectively. The weight of NAH-S events ranged from 2 to 4%.

The influence of European events on annual PM levels at regional background stations was low (II in the range 5-8% for all the stations, Figure 5.18). The location of the central Iberian area, far to the European continent, could explain the low PM levels recorded during these episodes. The air masses travelling from central Europe would have had a greater dispersion and dilution of PM when these reached the study area. Moreover, the frequency of occurrence of European episodes was reduced when compared with areas of northern Iberian Peninsula. From the two transport scenarios considered for European events in this study EUH had a higher weight (II ranging in 4-6%, Figure 5.18) than MD (II ranging in 1-2%, Figure 5.18) because both the frequency of occurrence and the PM levels recorded during the first episodes were higher. The PM levels were higher owing to the lower rainfall patterns associated with EUH episodes.

Also very low weights were associated with Mediterranean episodes (4-5%) as a response to both the low frequency of occurrence of these events over central Iberian Peninsula and the low PM levels recorded at regional background stations during their occurrence (rainfall, commonly associated with Mediterranean episodes, resulted in these low levels). During NAD-MD episodes the rain was even more frequent than during EUH-MH. Furthermore, the latter scenario was more frequent than NAD-MD. Under these circumstances the impact of NAD-MD was around 1% while the weight of EUH-MH ranged from 3 to 4% (Figure 5.18). As for the Atlantic episodes, the weight of Mediterranean events was maximum in PM2.5. The explanation is similar to that exposed for the episodes of Atlantic advection, the relatively clean Mediterranean air masses may be loaded with fine anthropogenic aerosols from sources located at the part of the Iberian Peninsula which the Mediterranean air masses have to cross before reaching the central Iberian Peninsula.

The 1999/30/CE Directive established a daily limit value of 50 $\mu g\ m^{-3}$ for PM10. This level must not be exceeded in more than 35 times per year by 2005 and in more than 7 times per year by 2010. As shown in Table 5.16 and Figure 5.19, from March 2001 to 2003, the number of exceedances in Risco Llano and Campisábalos were 9 (3 per year) and 6 (2 per year) respectively, below the annual number of exceedances allowed by the Directive. In the II PM Position paper on particulate matter (EC, 2004), a daily limit value of 35 $\mu g\ m^{-3}$ for PM2.5 which should not be exceeded more than 35 times in a year was proposed. Only 1 exceedance of this value occurred in Risco Llano from March 2001-2003 while no exceedance was registered at Campisábalos in that period. Using 0.7 as the PM10/TSP ratio (the average ratio recorded at Campisábalos in 2001-2003), an equivalent daily limit value for TSP (70 $\mu g\ m^{-3}$) was obtained. This level was exceeded in 36 occasions from 1998-2002 at Campisábalos (7 or 8 per year).

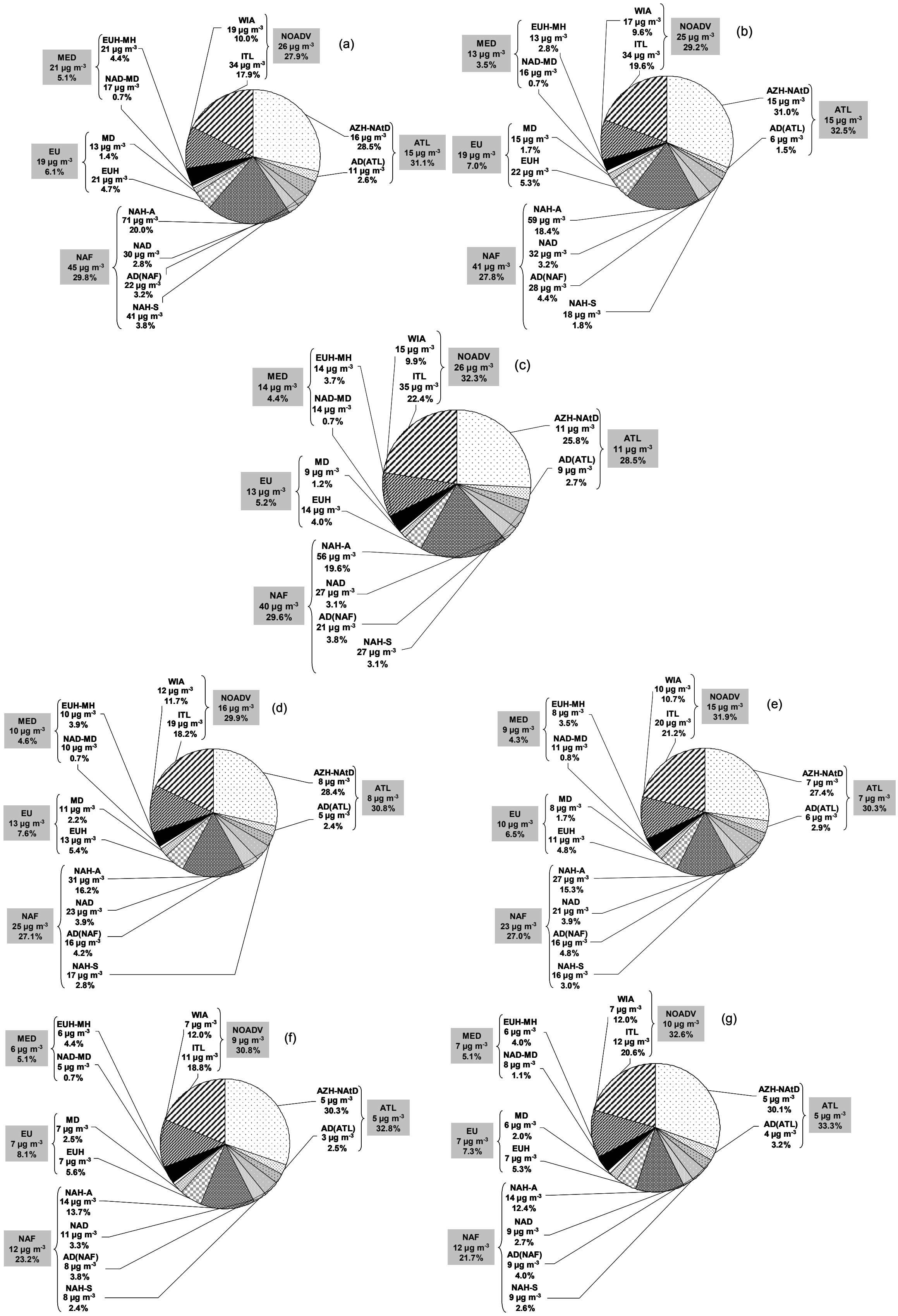


Figure 5.18. Relative impact (in %) of different PM episodes and meteorological scenarios on TSP mean levels in San Pablo de los Montes (a), on TSP levels in Risco Llano (b), on TSP mean levels in Campisábalos (c), on PM10 mean levels in Risco Llano (d), on PM10 mean levels in Campisábalos (e), on PM2.5 mean levels in Risco Llano (f) and on PM2.5 mean levels in Campisábalos (g).

From the 36 exceedances of the TSP equivalent limit value registered at Campisábalos from 1998 to 2002, 25 (69%) occurred during dust outbreaks, 8 (22%) during episodes without dominant advective conditions, only 2 (6%) during Atlantic episodes and 1 (3%) during European episodes. These last 3 exceedances can be attributed to local PM contributions. The occurrence of exceedances of the daily PM10 limit value from the 1999/30/CE Directive and the daily PM2.5 limit value suggested in the II PM position paper was completely influenced by African dust outbreaks. In fact, all the exceedances of both limit values occurred under African episodes at Campisábalos and Risco Llano. Among the exceedances of the PM10 and PM2.5 limit values, none were registered during episodes without dominant advective conditions. The existence of exceedances of the equivalent TSP limit value during those events would suggest the important amount of resuspended crustal particles (generally very coarse) in the ambient PM levels under conditions of lack of advection (especially in summer).

Table 5.16. Number of annual exceedances of the daily limit value established by the 1999/30/CE Directive (50 µgPM10 m^{-3}) and of the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) at Campisábalos and Risco Llano. The number of annual exceedances of an equivalent TSP daily limit value (70 µg m^{-3}) at Campisábalos is also shown. This equivalent limit value was worked out applying PM10/TSP ratio of 0.7.

NUMBER OF EXCEEDANCES	**Equivalence to AQ Directive 1999/30/CE and to II PM PP suggestions for TSP: TSP > 70 µg m^{-3}**	**AQ Directive 1999/30/CE: PM10 > 50 µg m^{-3}**		**II PM position paper suggestions: PM2.5 > 35 µg m^{-3}**	
	Campisábalos	**Risco Llano**	**Campisábalos**	**Risco Llano**	**Campisábalos**
1998	*[1]2	na	na	na	na
1999	3	na	na	na	na
2000	9	na	na	na	na
2001	14	*[2]2	*[2]2	*[2]1	*[2]0
2002	8	4	3	0	0
2003	na	3	1	0	0
Total 98-03	36	9	6	1	0
Annual mean 98-03	7.2	3.0	2.0	0.3	0.0

*[1]Calculated with data of 83% of the months of the year
*[2]Calculated with data of 83% of the months of the year
na: Not available

As for the other regions previously analysed, the highest PM levels in regional background stations over central Iberia were registered in summer owing to these factors:

(a) The enhancement of photochemical formation of secondary particles due to a higher insolation during summer.
(b) The lower precipitation regime during summer (Figure 5.20) which results in the reduction of processes such as the washing out of aerosols from the atmosphere.
(c) The low renovation of air masses during episodes with lack of advection such as during ITL events.
(d) The higher frequency of occurrence of dry African dust outbreaks over the Iberian Peninsula.
(e) The increased rates of resuspension of crustal material owing to the poor vegetal coverage of this area and the intense atmospheric convective dynamics

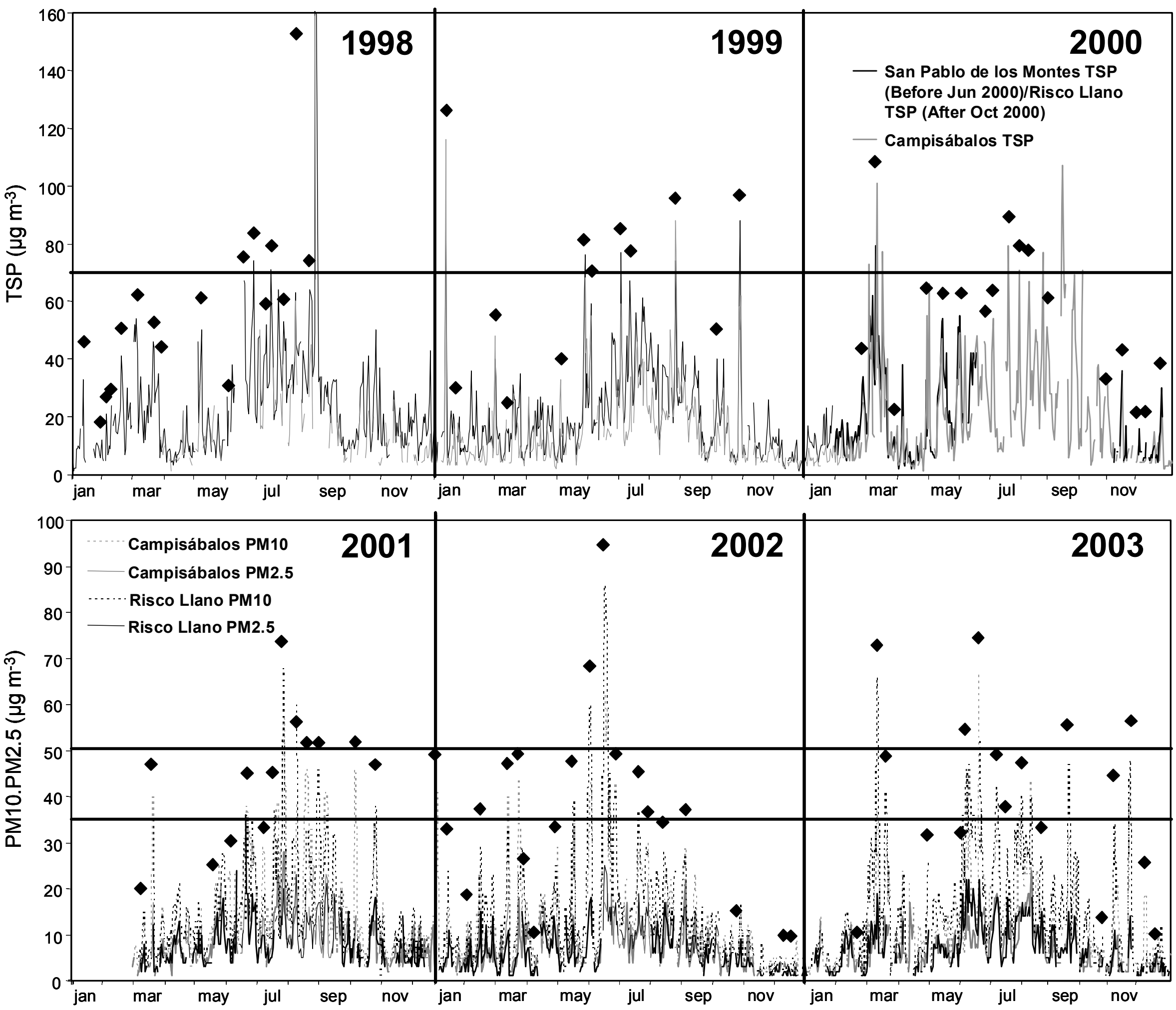


Figure 5.19. Daily TSP levels in San Pablo de los Montes, Risco Llano and Campisábalos for 1998-2000 (a), and daily PM10 and PM2.5 levels in Risco Llano and Campisábalos for 2001-2003 (b). The black dots mark the occurrence of African dust episodes. The horizontal lines mark the daily limit values established by the 1999/30/CE Directive (50 µgPM10 m^{-3}), the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) and the equivalent daily limit value for TSP (70 µgTSP m^{-3}).

The summer maximum was registered in all the stations for all size ranges (Figure 5.20). In most of the stations secondary maxima were recorded in February-March probably attributed to African dust outbreaks with important impact on PM levels occurring during these months. These typical winter African episodes do not occur all the years and that is why the March PM peak is so marked. Furthermore the relatively low values of rainfall recorded in March months (Figure 5.20) also could contribute to the relatively higher PM means.

5.5 Eastern Iberian Peninsula

This area of the Iberian Peninsula has the typical Mediterranean climate. Very dry summers and winters alternate with wet seasons in spring and autumn. The temperature in summer is high and in winter is mild. In response to this climate, the soil cover is poor so re-suspension processes are likely to occur especially in summer. Furthermore, the location of this region makes it susceptible to receive contributions of north African dust across the Mediterranean basin. This is especially important in summer (Rodriguez et al., 2001). Moreover, weak baric gradient conditions are common over eastern Iberia especially during summer. Under these situations the renovation of air masses is poor and the aging and recirculation of contaminated air masses commonly occur in summer, late spring and early autumn (Millán et al., 1997). These mechanisms may influence PM levels at the regional background sites increasing them considerably (Rodríguez et al., 2003).

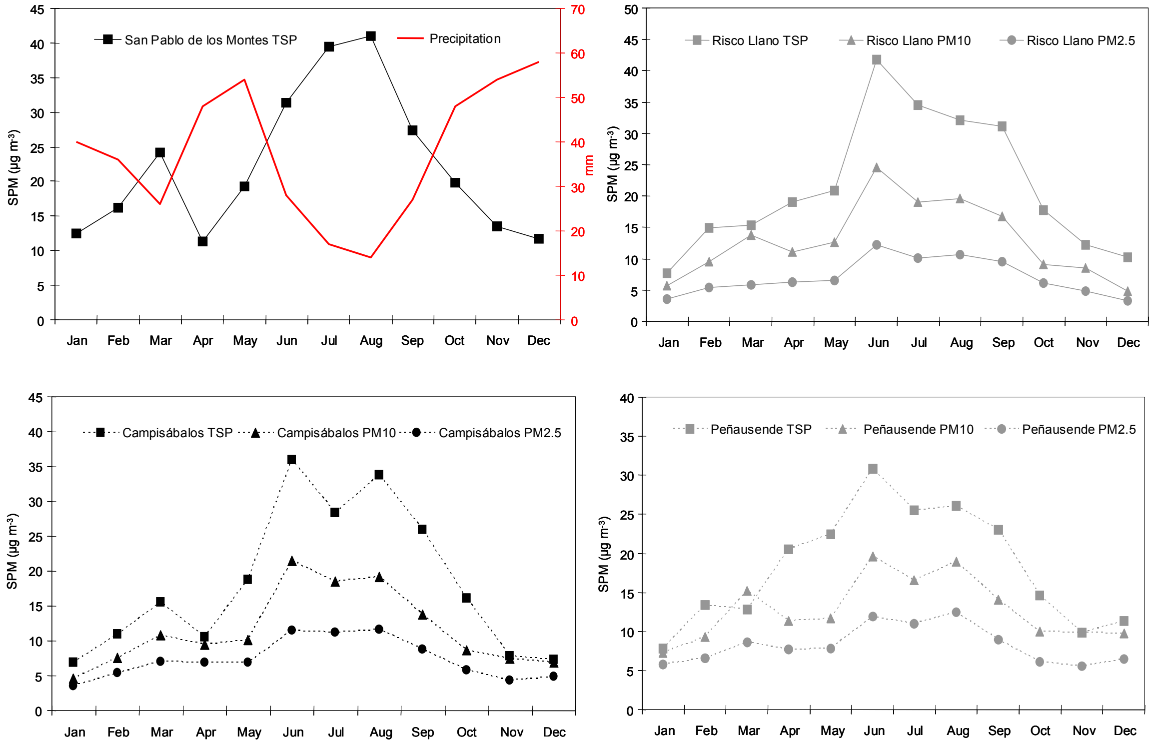


Figure 5.20. Mean monthly precipitation of Aeródromo Cuatro Vientos station (Madrid, 40° 23' N, 03° 47' W, 687 m.a.s.l) for 1971-2000 (INM, 2001) and PM monthly means registered in San Pablo de los Montes (1998-June 2000), Risco Llano (TSP from November 2000-January 2003 and PM10 and PM2.5 from March 2001 to 2003), Campisábalos (TSP from March 1998-January 2003 and PM10 and PM2.5 from March 2001 to 2003) and Peñausende (TSP from July 2000-January 2003 and PM10 and PM2.5 from March 2001 to 2003).

Data on PM levels for the period 1998-2003 from a regional background station located at Zarra (39º 05' N, -1º 06' E, 885 m.a.s.l., eastern Iberian Peninsula), were used for this study. This air quality monitoring station belongs to the EMEP network and was operational from January 1999 offering data on TSP from then to January 2003 and data on PM10 and PM2.5 from March 2001. The measurements were performed using high volume samplers and following the gravimetric method.

As shown in Figure 5.21, the most frequent transport situation over eastern Iberian Peninsula in 1998-2003 was the Atlantic advection. A total of 176 Atlantic episodes (31.8% of the total number of episodes in 1998-2003) resulting in 825 days (37.7% of the days in the study period) were registered. The dominant Atlantic transport scenario was AZH-NAtD which occurred 8 times more frequently than AD(ATL) scenario.

Situations with no advective conditions over the study area were also common. A total of 587 days (26.8% of the days in 1998-2003) grouped in 176 episodes (27.3% of the episodes registered in the study period) with these conditions were observed over the study area. Among scenarios giving rise to lack of advection, WIA scenario was slightly more frequent than ITL.

Also frequent over the eastern Iberian Peninsula were African dust outbreaks. In the study period, 141 African episodes (22.0% of the events in 1998-2003) which resulted

in 465 days (21.1% of the days in the study period) occurred over eastern Iberia. The African dust outbreaks occurred with especial frequency in summer under NAH-A transport scenario. These situations were 4-5 times more frequent than NAH-S situations and around 3 times more frequent than AD and NAD situations.
The transport of air masses from the European continent occurred less frequently. These situations accounted for 215 days (9.8% of the days in 1998-2003) distributed in 72 episodes (11.2% of the total number of episodes in 1998-2003) in 1998-2003. Distinguishing between European transport scenarios, EUH scenario was dominant over MD (more than twice as many EUH situations as MD situations).
The least frequent transport situation over the study area in 1998-2003 was the Mediterranean advection. Only 50 Mediterranean events (7.8% of the events registered from 1998 to 2003) resulting in 99 days (4.6% of the days in the study period) were registered in the study period. EUH-MH scenario caused Mediterranean transport with double frequency than MD scenario.

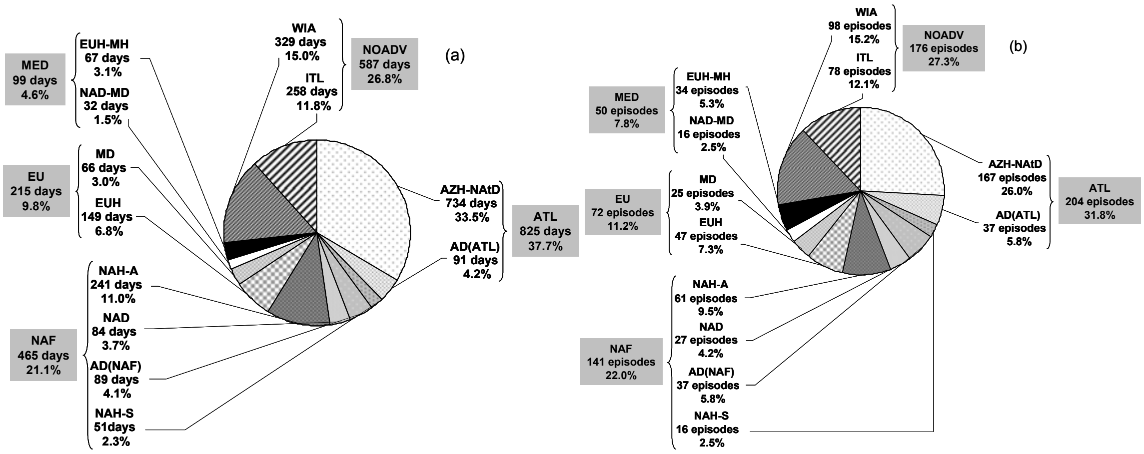


Figure 5.21. Occurrence of all the air mass transport scenarios over eastern Iberian Peninsula in 1998-2003 in days (a) and episodes (b).

The seasonal distribution of the occurrence of different transport scenarios is shown in Figure 5.22. The frequency of occurrence of Atlantic events is high all throughout the year (with frequency peaks in November with 17 days as a mean in and April with 12 days on average) but declining in summer (from May to August the frequencies of occurrence were below 8 days in all the months). AZH-NAtD situations were very common along the year but reached a frequency peak in November (monthly mean of 17 days). AD(ATL) situations were relatively frequent in April and December with a monthly mean of 3 days.
African dust outbreaks were observed over the study area in all the months of the year but distributed differently depending on the transport scenario. The maximum frequencies of occurrence were registered in May-August (12 days in both June and August) and in January-March (9 days in March), and minimum in April and December (2 days as mean in both months). NAH-S events practically only occurred in the period January-March (means of 3 days in February and March), AD(NAF) and NAD events practically did not occur from June to September (March and May with monthly means of 4 and 3 days respectively for AD(NAF), and 4 days in May for NAD situations were the frequency peaks), and NAH-A occurred only from late spring to early autumn (especially from June to August with monthly means ranging from 10 to 12 days in this period).

The occurrence of episodes of transport of European air masses over the eastern Iberian Peninsula, although scarce all along the year, was considerably less frequent during the warm seasons (only 3 days in the whole study period in July) than during the cold seasons (with the frequency peak in January with 6 days on average). However, while EUH scenario was typical from winter (in the 3 months of December-February the mean frequency reached 4 days), MD scenario was typical in autumn (3 days as monthly mean in November) and spring (2 days as monthly mean in April).
The transport of Mediterranean air masses over the study area was infrequent (only a monthly mean of 3 days in November and January). The NAD-MD scenario was relatively more common in October, January, March, April and May with means of 1 day in each of these months. The occurrence of EUH-MH was more frequent in November, January and September with monthly means of 2 days.
The episodes characterised by a lack of dominant advective conditions occurred all along the year with higher relative frequency from May to October. The occurrence of WIA scenario was very important in May and October (11 days as monthly mean in both months) while ITL situations were characteristic of summer (reaching the maximum frequency in July and August with 11 and 12 days as monthly means respectively).
None of the episodes considered in this study reached very long mean durations over eastern Iberia (2 to 4 days in all cases, Table 5.17). On average, Atlantic episodes, with 4 days, were the longest and Mediterranean events, with 2 days, were the shortest. All the rest of the events had 3 days as mean duration. The mean duration of the episodes associated with the different transport scenarios distinguished in this study only reached 4 days for AZH-NAtD (Atlantic episodes) and for NAH-A (African events). Both Mediterranean types (NAD-MD and EUH-MH), AD(ATL) and AD(NAF) had a mean extent of 2 days.
As expected for a regional background station, the mean PM levels recorded at Zarra for the study period (1998-2003) were low (23 µgTSP m^{-3}, 16 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3}). As shown in Table 5.18, no exceedance of the annual limit value established by the 1999/30/CE Directive was registered neither considering the limit value for 2005 (40 µgPM10 m^{-3}) nor the target value for 2010 (20 µgPM10 m^{-3}). The requirement about the annual mean PM2.5 cap value (not exceeding 25 µgPM2.5 m^{-3}) established in the Air Quality directive draft issued by the EU Commission in September 2005 was met in all the years from 2001 to 2003.
According to the information shown in Table 5.19, there is a great variability in the mean PM levels recorded at Zarra during the different transport episodes.
During episodes of Atlantic advection over the study area the mean PM levels were low in Zarra (16 µgTSP m^{-3}, 11 µgPM10 m^{-3} and 6 µgPM2.5 m^{-3}). These episodes were commonly associated with the passage of frontal systems over the Iberian Peninsula resulting in precipitation and, in consequence, decrease of the PM levels by scavenging. Moreover, these levels would have local or regional origin assuming the low concentration of particles in Atlantic air masses. A greater influence of rain during AD(ATL) scenario resulted in lower PM levels (13 µgTSP m^{-3}, 9 µgPM10 m^{-3} and 4 µgPM2.5 m^{-3}) than during AZH-NAtD (13 µgTSP m^{-3}, 11 µgPM10 m^{-3} and 6 µgPM2.5 m^{-3}).

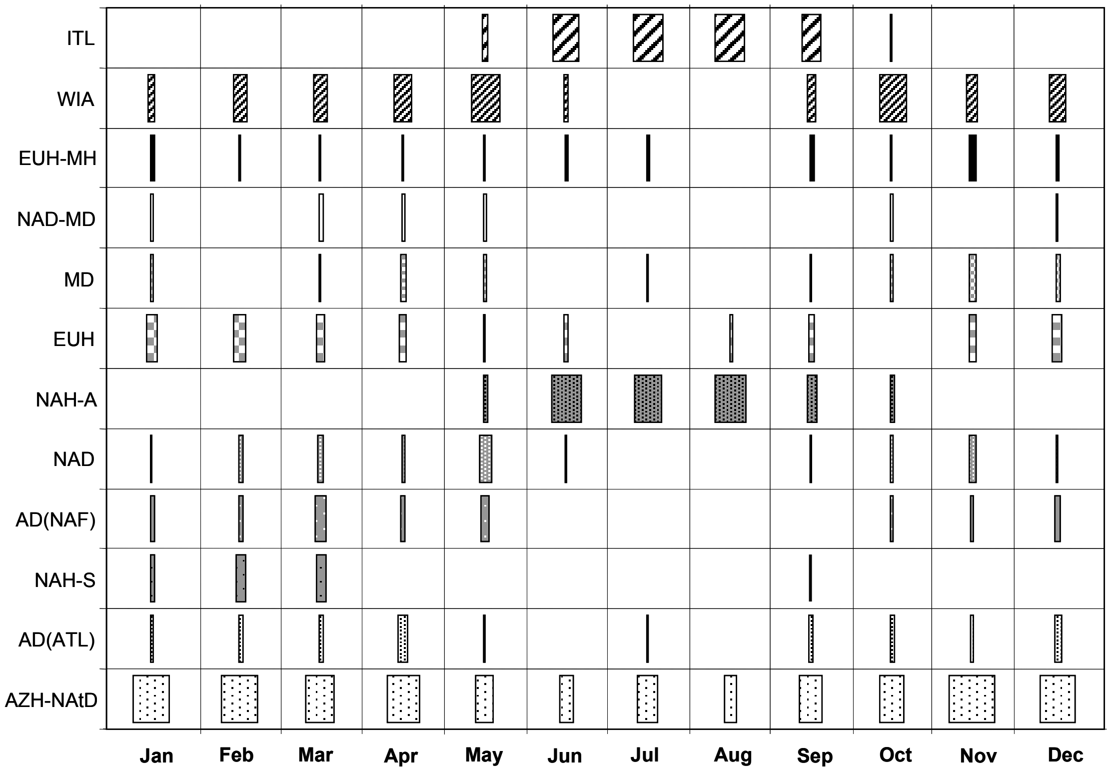


Figure 5.22. Mean number of days with each type of PM episode per month over eastern Iberia in 1998-2003.

Table 5.17. Mean duration of PM episodes in eastern Iberian Peninsula for 1998-2003.

	Mean duration (days/episode)		**Mean duration (days/episode)**
Atlantic episodes	**4**	**European episodes**	**3**
AZH-NAtD	4	*EUH*	3
AD(ATL)	2	*MD*	3
African episodes	**3**	**Mediterranean episodes**	**2**
NAH-S	3	NAD-MD	2
AD(NAF)	2	EUH-MH	2
NAD	3	**Episodes without dominant advection**	**3**
NAH-A	4	*WIA*	3
		ITL	3

Table 5.18. Mean levels of TSP, PM10 and PM2.5 recorded in Zarra in 1998-2003.

MEAN LEVELS (μg m^{-3})	**Zarra**		
	TSP	PM10	PM2.5
1998	na	na	na
1999	24	na	na
2000	26	na	na
2001	22	*16	*9
2002	21	15	8
2003	na	16	8
Mean 98-03	23	16	8

*Calculated with data of 83% of the months of the year
na: Not available

Low mean PM levels were also recorded at Zarra during European episodes (18 µgTSP m^{-3}, 13 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3}). The distance from the European continent to the study area (greater than to the northern regions of the Iberian

Peninsula) resulted in a greater degree of dilution/dispersion of the pollutants. This factor could explain those low PM levels. Rainfall was more common during MD events and this had a reflection lowering the mean PM levels recorded during these situations (16 µgTSP m^{-3}, 11 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3}) when compared with the mean PM levels recorded during EUH episodes (19 µgTSP m^{-3}, 14 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3}).

The mean PM levels at Zarra when Mediterranean air masses affected the eastern Iberian Peninsula were also low (18 µgTSP m^{-3}, 10 µgPM10 m^{-3} and 6 µgPM2.5 m^{-3}). The common rainfall events over eastern Iberia associated with Mediterranean transport and the relatively clean air masses involved in this type of transport could account for these relatively low levels. During NAD-MD the mean PM levels (12 µgTSP m^{-3}, 10 µgPM10 m^{-3} and 5 µgPM2.5 m^{-3}) were lower than during EUH-MH (20 µgTSP m^{-3}, 11 µgPM10 m^{-3} and 6 µgPM2.5 m^{-3}), probably due to the higher frequency of rainfall associated with the first scenario compared with the latter.

The African dust outbreaks had an important impact on PM levels at Zarra (36 µgTSP m^{-3}, 23 µgPM10 m^{-3} and 11 µgPM2.5 m^{-3}). However owing to the influence of rain PM scavenging, the levels recorded during the episodes associated with the presence of depressions near the Iberian Peninsula, AD(NAF) and NAD, were lower (23 µgTSP m^{-3}, 19 µgPM10 m^{-3}, 8 µgPM2.5 m^{-3} during AD(NAF) and 28 µgTSP m^{-3}, 17 µgPM10 m^{-3}, 9 µgPM2.5 m^{-3} during NAD) than during the events characterised by the presence of anticyclones (33 µgTSP m^{-3}, 21 µgPM10 m^{-3}, 11 µgPM2.5 m^{-3} during NAH-S and 45 µgTSP m^{-3}, 26 µgPM10 m^{-3}, 12 µgPM2.5 m^{-3} during NAH-A). Moreover, under the NAH-A scenario, the atmospheric conditions of the lowest levels of the atmosphere (weak baric conditions resulting in poor renovation of air masses together with the aging and recirculation of contaminated air masses at eastern Iberia as explained by Millan et al., 1997), together with the intense insolation resulted in an significant increase of PM levels especially by photochemical generation of secondary species from gaseous precursors. At the same time, during NAH-A situations the African plumes travel at high altitudes (>1500 m.a.s.l.) and the dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is distributed and affects the sampling stations. These two contributions contribute to increase PM levels during NAH-A events.

When lack of dominant advection was detected over eastern Iberia the mean PM levels recorded at Zarra were considerably high (27 µgTSP m^{-3}, 18 µgPM10 m^{-3}, 10 µgPM2.5 m^{-3}). However, the mean PM levels registered during WIA episodes were low (20 µgTSP m^{-3}, 15 µgPM10 m^{-3}, 9 µgPM2.5 m^{-3}). These events occurred in the cold part of the year when an anticyclone covered partly or completely the Iberian Peninsula (hence the precipitation is infrequent). In these circumstances the atmospheric conditions do not favour dispersion of pollutants and the vertical extent of the boundary layer is reduced. This is especially relevant when thermal inversions develop over urban and/or industrial sites. Thus, at Zarra, located at a rural site, the anthropogenic contribution to the PM load will be diminished and the PM levels reduced. During ITL episodes, factors such as low rainfall (this also stands for WIA events), the aging of air masses, the high rate of re-suspension or the enhancement of transformation of gaseous precursors into secondary aerosols (in virtue of the increased photochemistry), account for the relatively high PM levels recorded at Zarra. These, together with the recirculation of contaminated air masses typical from the eastern flank of the Iberian Peninsula in summer, late spring and early autumn (Millan et al., 1997) result in a high impact on the mean PM levels recorded at Zarra during ITL events (35 µgTSP m^{-3}, 21 µgPM10 m^{-3}, 11 µgPM2.5 m^{-3}).

Table 5.19. PM mean levels registered during different transport episodes over eastern Iberian Peninsula in 1998-2003.

Mean PM levels ($\mu g\ m^{-3}$)	**Zarra**		
	TSP	PM10	PM2.5
Total 98-03	**23**	**16**	**8**
Atlantic episodes	**16**	**11**	**6**
AZH-NAtD	16	11	6
AD(ATL)	13	9	4
African episodes	**36**	**23**	**11**
NAH-S	33	21	11
AD(NAF)	23	19	8
NAD	28	17	9
NAH-A	45	26	12
European episodes	**18**	**13**	**8**
EUH	19	14	8
MD	16	11	7
Mediterranean episodes	**18**	**10**	**6**
NAD-MD	12	10	5
EUH-MH	20	11	6
Episodes without dominant advection	**27**	**18**	**10**
WIA	20	15	9
ITL	35	21	11

Combining information about the mean number of days and the PM mean levels into an impact index (II=mean number of days per year influenced by each type of scenario multiplied by the mean PM levels for each scenario in the whole period 1998-2003 and divided by 365 days) we can evaluate the impact of each transport scenario on PM levels for different size ranges. II gives us information about the contribution (in concentration units) of each type of transport scenario on the mean levels of PM recorded at a certain site. Moreover, II can be understood as the relative weight of each scenario with respect to the annual mean levels registered in a certain station and for a determined size range and it can be expressed as percentage.

In Figure 5.23, the impact of all the episodes and transport scenarios is shown. As stated above, Atlantic episodes were the most frequent transport scenario over eastern Iberia in the study period; however, the weight of these episodes on the annual PM levels in Zarra was not the highest. As will be presented below, African events and episodes with lack of advective conditions contributed to a higher degree. The II of Atlantic episodes on mean annual PM levels at Zarra ranged from 25 to 27% with the highest relative impact on PM2.5. This is due to the minimal long range transport contributions during Atlantic events. Thus, most of the PM load had a local/regional origin and has an important proportion of fine particles. Moreover this may be due to the contribution of fine aerosols to Atlantic air masses from anthropogenic sources in areas in the Iberian Peninsula crossed by these air masses before reaching eastern Iberia. AZH-NAtD events (II ranging from 23 to 25%) contributed to a higher extent than AD(ATL) with II slightly above 2% in all cases owing to the difference in frequency of occurrence and the difference in mean PM levels recorded during these two scenarios.

Episodes without major prevalent advective conditions have also a high II on annual PM levels at Zarra. In fact, these events had the highest impact index among all for PM2.5 (II ranging from 26 to 33%). The local or regional anthropogenic origin of a major part of the particles during these events both in winter (WIA episodes) and especially in summer (ITL episodes) may account for this high load of fine particles. The weight of WIA episodes ranged from 13 to 17% with the highest impact index in PM2.5. The common development of thermal inversions over urban/industrial sites during WIA episodes reduced the influence of pollutants in rural sites. The low rainfall regime during WIA episodes accounts for a relatively high residence time of these pollutants. As the coarse particles settle more rapidly, the proportion of fine particles increases. This can explain why WIA events have higher impact on PM2.5 than in PM10 and TSP. ITL episodes had II ranging from 16 to 17% with slightly more weight on TSP. During these summer episodes the generation of secondary species from gaseous precursors is enhanced in virtue of the meteorological conditions (weak baric conditions resulting in poor renovation of air masses together with the aging and recirculation of contaminated air masses over eastern Iberia, Millan et al., 1997). These processes would result in the formation of fine particles. However, the contribution of the re-suspension of crustal particles can also be important owing to the strong convection derived from the high temperatures in summer could explain the slightly higher II for TSP.

The African dust outbreaks had a very high II especially in the coarser size ranges (II ranging from 28 to 33% with the maximum for TSP). The coarse size of the mineral dust aerosols would explain this difference. Distinguishing between transport scenarios, NAH-A reached the highest impact (II in the range 17-21% with higher weight in TSP than PM10 and PM2.5). This may be attributed to possible contribution of re-suspension of soil material (which is a source of coarse aerosols) increased by the convective dynamics. Furthermore, the altitude of Zarra station, 885 m.a.s.l., makes it susceptible of receiving the direct impact of the dust plume travelling at high altitudes during NAH-A episodes. In these cases, as the size of the dust grains is coarse, the II of these episodes would be biased towards the coarser PM fractions. AD and NAD had similar impact index (between 4 and 5% for both scenarios) and NAH-S only reached II around 3% owing to the low frequency of occurrence of these type of events.

The European events did not have high impact index (8-9%) but reached the highest II for PM2.5. This reflected the fine size of the aerosols with European origin which had anthropogenic sources. EUH scenario had II from 6 to 7% and MD scenario had an II ranging from 2 to 3%.

Mediterranean episodes had very low weight on annual PM means at Zarra (slightly above 3%). EUH-MH episodes had II ranging from 2 to 3% while NAD-MD events only reached 1% as II.

As shown in Table 5.20 and Figure 5.24, the number of exceedances of the daily limit value established by the 1999/30/CE (50 µgPM10 m^{-3}) at Zarra reached 8 from 2001 to 2003 (2-3 per year). The maximum number of exceedances allowed by the Directive would be 35 by 2005. As expected, this requirement was met for the three years. Using a PM10/TSP ratio of 0.7 (this is the mean PM10/TSP ratio at Zarra) an equivalent limit value of 70 µgTSP m^{-3} was worked out. This equivalent limit value was exceeded in 15 occasions from 1999 to 2002 (3-4 per year). In the II PM Position paper (EC, 2004) it was proposed to establish a daily limit value of 35 µg m^{-3} for PM2.5 which should not be exceeded more than 35 times in a year. This daily limit value was not exceeded during the period 2001-2003.

All the daily exceedances (8 of the 50 µgPM10 m^{-3} and 15 of the 70 µgTSP m^{-3}) occurred during African dust outbreaks, hence, this type of events control almost completely the occurrence of exceedances at Zarra.

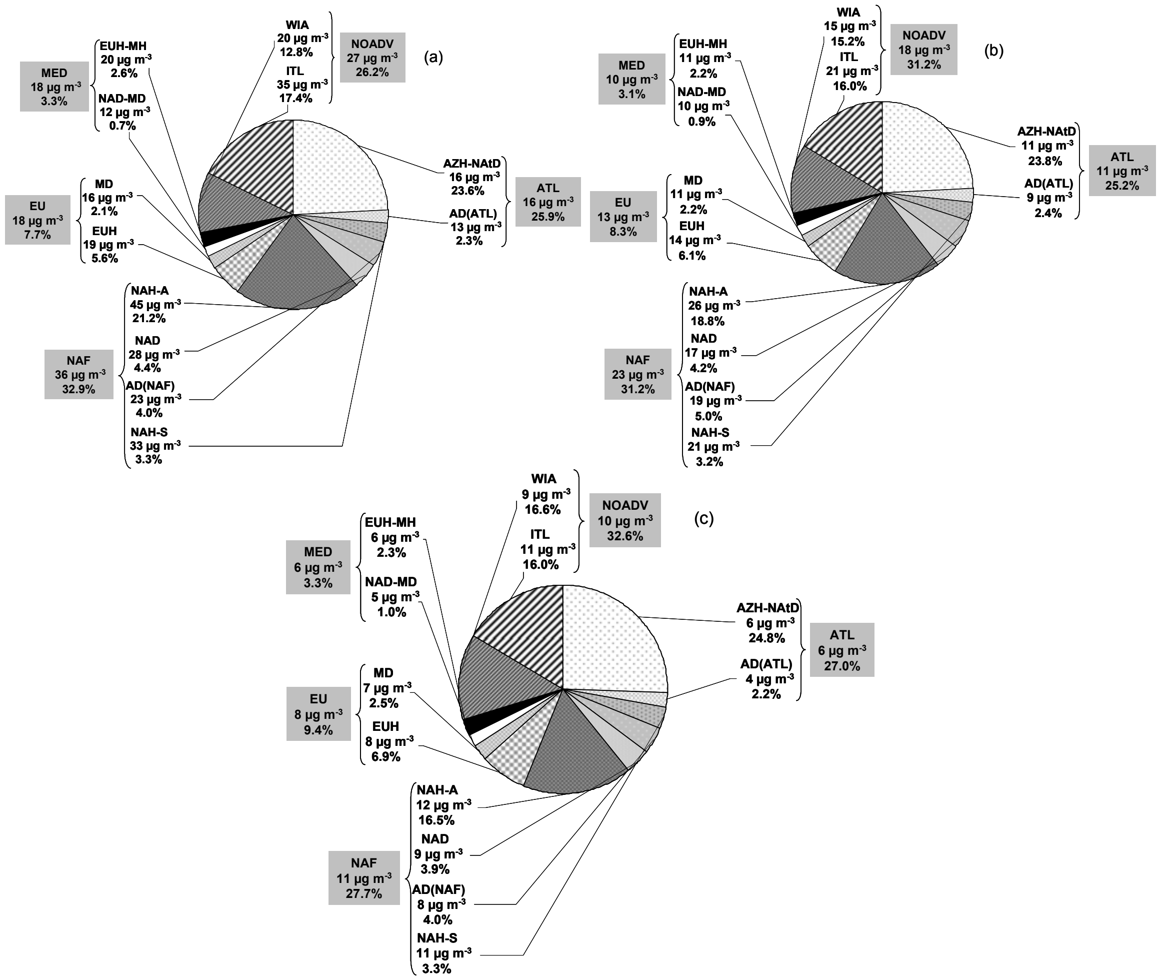


Figure 5.23. Relative impact (in %) of different PM episodes and meteorological scenarios on mean levels of TSP (a), PM10 (b) and PM2.5 (c) in Zarra.

Table 5.20. Number of annual exceedances of the daily limit value established by the 1999/30/CE Directive (50 µgPM10 m^{-3}) and of the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) at Zarra. The number of annual exceedances of an equivalent TSP daily limit value (70 µg m^{-3}) at Zarra. This equivalent limit value was worked out applying PM10/TSP ratio of 0.7.

NUMBER OF EXCEEDANCES	Equivalence to AQ Directive 1999/30/CE and to II PM PP suggestions for TSP: TSP > 70 µg m^{-3}	AQ Directive 1999/30/CE : PM10 > 50 µg m^{-3}	II PM position paper suggestions: PM2.5 > 35 µg m^{-3}
	Zarra	**Zarra**	**Zarra**
1998	na	na	na
1999	4	na	na
2000	7	na	na
2001	1	*0	*0
2002	3	1	0
2003	na	7	0
Total 98-03	15	8	0
Annual mean 98-03	3.8	2.7	0.0

*Calculated with data of 83% of the months of the year
na: Not available

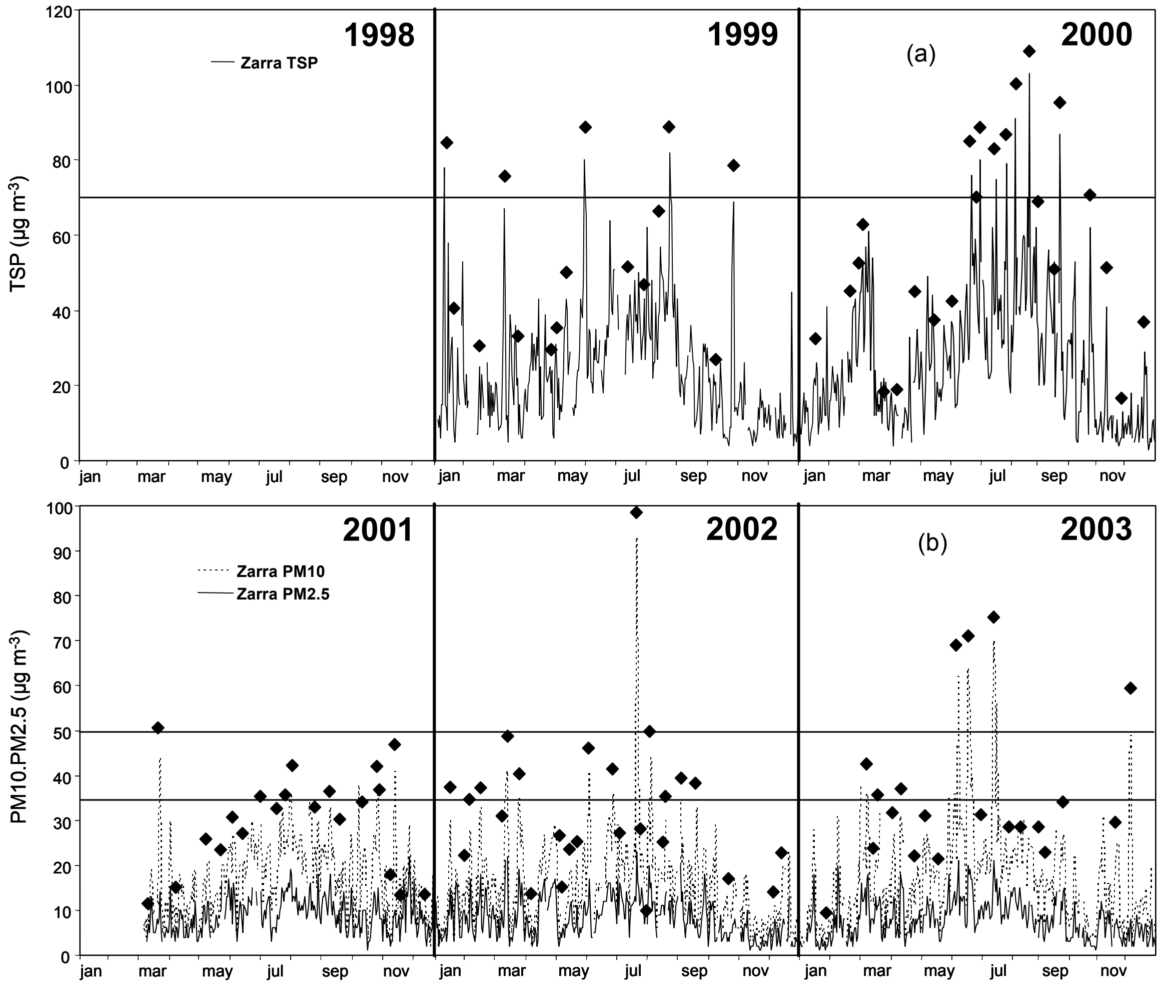


Figure 5.24. Daily TSP levels in Zarra for 1998-2000 (a), and daily PM10 and PM2.5 levels in Zarra for 2001-2003 (b). The black dots mark the occurrence of African dust episodes. The horizontal lines mark the daily limit values established by the 1999/30/CE Directive (50 µgPM10 m^{-3}), the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) and the equivalent daily limit value for TSP (70 µgTSP m^{-3}).

The highest monthly PM levels in a regional background station located over eastern Iberia were expected to be recorded during summer due to these factors:

(a) The enhancement of photochemical formation of secondary particles due to a higher insolation during summer.
(b) The lower precipitation regime during summer (Figure 5.25) which results in the reduction of processes such as the washing out of aerosols from the atmosphere.
(c) The low renovation of air masses during episodes with lack of advection such as during ITL events.
(d) The aging and breeze driving re-circulation of polluted air masses characteristic from the eastern flank of the Iberian Peninsula in summer (Millán et al., 1997).
(e) The higher frequency of occurrence of dry African dust outbreaks over the Iberian Peninsula.
(f) The increased rates of re-suspension of crustal material owing to the poor vegetal coverage of this area and the intense atmospheric convective dynamics

The summer maximum was clear at Zarra so this could be useful as regional background station. Moreover a second order maximum was recorded in March for all size ranges. This peak could be attributed to African dust outbreaks with important impact on PM levels occurring during these months over the region (Figure 5.25). These typical winter African episodes do not occur all the years and that is the main reason why the March PM peak is so marked.

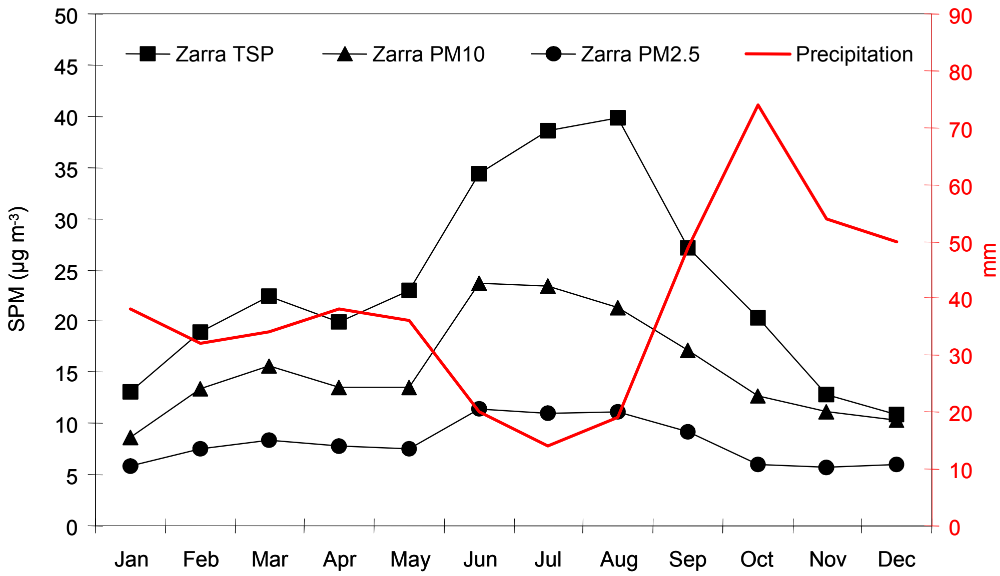


Figure 5.25. Mean monthly precipitation of Manises station (Valencia, 39° 29' N, -00°28' W, 57 m.a.s.l) for 1971-2000 (INM, 2001) and PM monthly means registered in Zarra (TSP from January 1999-January 2003 and PM10 and PM2.5 from March 2001 to 2003).

5.6 Southwestern Iberian Peninsula

The climate of the southwestern area of the Iberian Peninsula is characterised by dry and warm summers with a clear wet season in winter and another (generally with less precipitation) in spring. The location of this region (close to the African continent and to the Atlantic Ocean) makes it susceptible to receive important contributions of crustal PM from northern Africa. Also, the atmospheric ventilation may be greater than in the eastern Iberian Peninsula by the influence of Atlantic episodes. On the contrary, the influence of European air masses on PM levels would be reduced. In summer, weak baric gradient conditions may develop (probably with less frequency than in the eastern flank of the Iberian Peninsula) provoking poor renovation and aging of air masses. These mechanisms may influence PM levels at the regional background stations (Rodríguez et al, 2003).

Daily PM levels from Barcarrota (38º 29' N, 6º 55' W, 393 m.a.s.l.), air quality monitoring station belonging to the EMEP network, were used in this study to interpret the variation of PM levels in regional background sites of southwestern Iberia. This station was operational measuring TSP from March 1999 to January 2003 and PM10 and PM2.5 since March 2001. All these measurements were performed using high volume samplers and following the requirements of the gravimetric method.

As shown in Figure 5.26, the dominant transport scenario over southwestern Iberian Peninsula in 1998-2003 was the advection of Atlantic air masses with a total of 245 episodes (42.7% of the episodes registered from 1998 to 2003) gathering 1254 days (57.3% of the total number of days in the study period). The major part of these situations occurred under AZH-NAtD transport scenario (6-7 times the number of days associated with AD(ATL) scenario).

The second episodes in terms of frequency of occurrence were situations of advection of African air masses. A total of 139 African dust outbreaks (24.2% of the episodes in

1998-2003) resulting in 418 days (19.1% of the 2191 days) occurred over southwestern Iberia. Among the meteorological scenarios causing these events, NAH-A was the most frequent with approximately twice as many days as AD(NAF) scenario, three times more days than NAH-S scenario and up to 4 times the number of days associated with NAD scenario.

Also relatively frequent were the situations with lack of prevailing advective conditions. A total of 344 days (15.7% of the days in 1998-2003) distributed in 110 events (19.2% of the total number of episodes in 1998-2003) were registered over the study area in 1998-2003. The WIA scenario was 1.3 times more frequent than ITL scenario.

Owing to the location of the study area, the occurrence of European and Mediterranean transport was scarce. Only 51 Mediterranean episodes (8.9% of the episodes in the study period) and 29 European episodes (5.0% of the episodes registered in 1998-2003) resulting in 103 (4.7% of the days in 1998-2003) and 72 (3.2% of the days of 1998-2003) days respectively occurred over the study area in the study period. Among the Mediterranean transport scenarios, EUH-MH was more than 4 times more frequent than NAD-MD whereas among the European transport scenarios, EUH twice as frequent as MD.

Figure 5.27 shows the seasonal distribution of the days associated with each transport scenario in southwestern Iberia for the period 1998-2003. This shows the high frequency of occurrence of situations of transport of Atlantic air masses all throughout the year with the highest frequency of occurrence in April (27 days as monthly mean), January (with a monthly average of 22 days), November (a monthly mean of 21 days) and, secondarily, July-August (18 days as monthly mean in July). The lowest relative frequency were registered in March, June and September (less than 15 days as monthly average in all these cases). AZH-NAtD situations were especially frequent in April with a monthly mean of 22 days and in November with a monthly average of 20 days. AD(ATL) situations only reached 5 days as monthly mean in April.

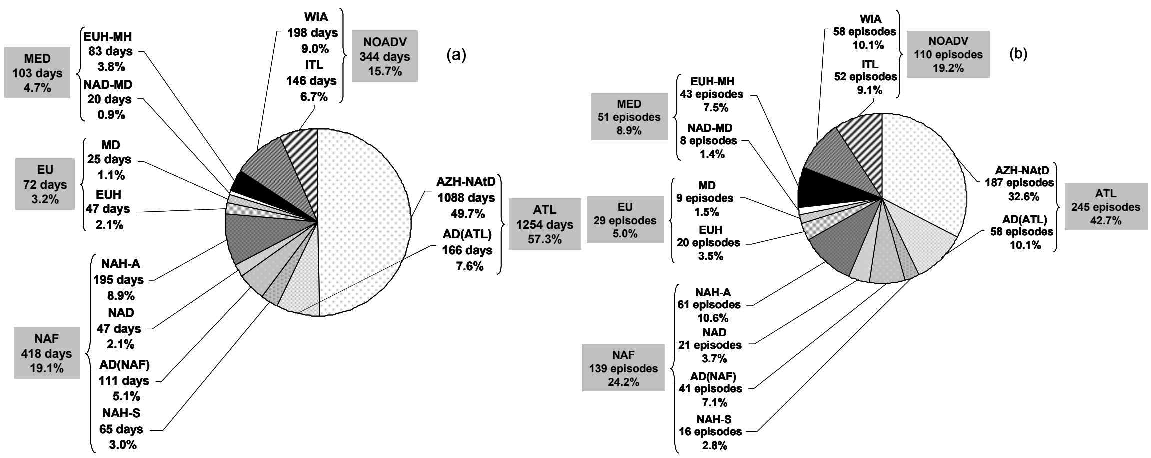


Figure 5.26. Occurrence of all the air mass transport scenarios over southwestern Iberian Peninsula in 1998-2003 in days (a) and episodes (b).

Although episodes of transport of African air masses over southwestern Iberia occurred in all the months a frequency maxima were registered in summer (with the peak in June with 11 days as monthly mean) and in March (with 9 days as monthly mean). In April the number of days with African advection was the lowest with only 2 days on average. NAH-S events were rare out of the period January-March (with monthly averages of 4 days in both February and March) although a few of these situations were detected from September to December. AD(NAF) episodes did not occur in summer and reached high frequencies of occurrence in December and March (4 days as monthly average in these two months). NAD scenario only reached 2 days as monthly average in October, and NAH-A scenario was characteristic of summer with a frequency peak of 11 days as monthly mean in June.

The transport of European air masses over the study area, in general unfrequent, was especially rare from May to October and somewhat more frequent in November to April with three maxima in February (a monthly mean of 3 days), November (2 days as monthly mean) and April (2 days as monthly average). Situations characterised by EUH scenario only reached relevant frequencies of occurrence in February (3 days as monthly average) while MD scenario in November (2 days as monthly average) and April (more than 1 day of monthly mean).

The transport of Mediterranean air masses over southwestern Iberian Peninsula was also scarce but occurred mainly in spring (in March 3 days as monthly mean was the frequency peak) and autumn (a mean of 3 days in November and December) although Mediterranean episodes occurred also in summer (with a mean of 2 days in June). NAD-MD situations, very rare in general, only reached 1 day as monthly average in November, December and March. EUH-MH scenario reached up to frequencies of 2 days on average in November, December, March and June.

The situations characterised by the lack of prevailing advection were reported all throughout the year but a frequency maximum was observed in the warm season (mainly owing to ITL situations) of the year. However, in December a significant number of these situations were also detected. WIA days did not occur in summer and reached up to frequencies of occurrence of 7 days as mean in October and 6 days on average in both December and May. ITL events only registered from May to October but the period with the highest frequency of was August-September (7 days as monthly average in these two months).

As shown in Table 5.21, Atlantic episodes were on average the longest among all types of events (5 days). All the other events had a mean duration of 3 (African events and episodes without dominant advection) or 2 (Mediterranean and European episodes) days. The mean duration of all the meteorological transport scenarios was 2 or 3 days with the exception of the Atlantic events of the type AZH-NAtD (6 days) and the African episodes of the type NAH-S (5 days).

As shown in Table 5.22, the mean PM levels recorded at Barcarrota during 1998-2003 were low (23 μgTSP m^{-3}, 16 μgPM10 m^{-3} and 8 μgPM2.5 m^{-3}). The 1999/30/CE Directive established limit value for 2005 (40 μgPM10 m^{-3}) and a target limit value for 2010 (20 μgPM10 m^{-3}). As expected, the annual means in the period 1998-2003 in Barcarrota did not exceed any of those two limit values. The Air Quality directive draft issued by the EU Commission in September 2005 established an annual mean cap value of 25 μgPM2.5 m^{-3}. This requirement was also met by Barcarrota station in the period 2001-2003.

As shown in Table 5.23, the PM levels recorded at Barcarrota during the different episodes considered in this study may vary into a large range of values. Two factors may account for the low PM levels recorded during episodes of Atlantic advection (21 μgTSP m^{-3}, 13 μgPM10 m^{-3} and 8 μgPM2.5 m^{-3}). The common passage of fronts (frequently accompanied by rain) and the relatively clean Atlantic air masses transported during these episodes. Thus, the PM load recorded at Barcarrota during Atlantic episodes would have a major local/regional origin. AD(ATL), characterised by the presence of a depression near the Portuguese coast resulted in lower relative PM levels than AZH-NAtD, in general drier events (15 μgTSP m^{-3}, 8 μgPM10 m^{-3} and 4 µgPM2.5 m^{-3} during AD(ATL) episodes and 22 µgTSP m^{-3}, 13 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3} during AZH-NAtD events).

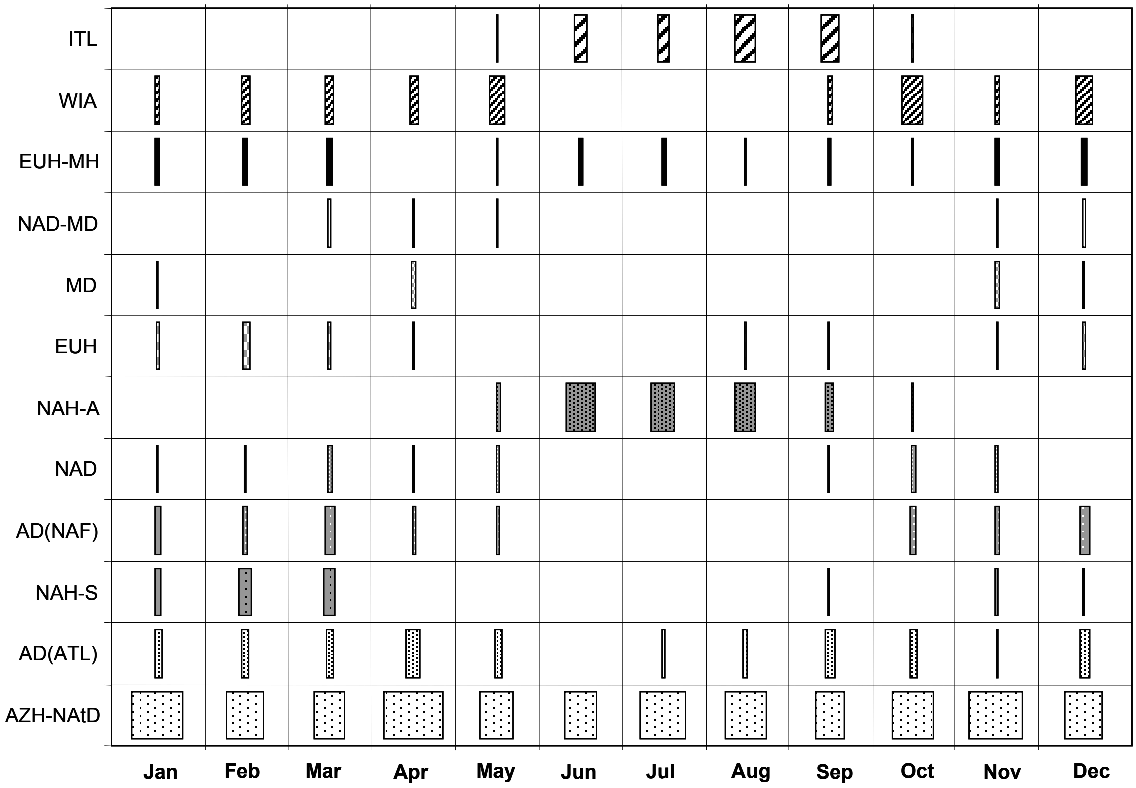


Figure 5.27. Mean number of days with each type of PM episode per month over southwestern Iberia in 1998-2003.

Table 5.21. Mean duration of PM episodes in southwestern Iberian Peninsula for 1998-2003.

	Mean duration (days/episode)		**Mean duration (days/episode)**
Atlantic episodes	**5**	**European episodes**	**2**
AZH-NAtD	6	*EUH*	2
AD(ATL)	3	*MD*	3
African episodes	**3**	**Mediterranean episodes**	**2**
NAH-S	5	NAD-MD	3
AD(NAF)	3	EUH-MH	2
NAD	2	**Episodes without dominant advection**	**3**
NAH-A	3	*WIA*	3
		ITL	3

Table 5.22. Mean levels of TSP, PM10 and PM2.5 recorded in Barcarrota in 1998-2003.

MEAN LEVELS (µg m^{-3})	**Barcarrota**		
	TSP	PM10	PM2.5
1998	na	na	na
1999	*[1]30	na	na
2000	29	na	na
2001	28	*[2]19	*[2]11
2002	25	16	12
2003	na	17	8
Mean 98-03	27	17	11

*[1]Calculated with data of 83% of the months of the year
*[2]Calculated with data of 83% of the months of the year
na: Not available

Also low mean PM levels were recorded at Barcarrota during European episodes (23 μgTSP m^{-3}, 15 μgPM10 m^{-3} and 10 μgPM2.5 m^{-3}). The long transect which European air masses have to undergo to reach the study area from central and eastern Europe, allow the pollutants to disperse and dilute so the PM levels were low. However, during the transport scenario characterised by the presence of depressions (MD scenario) the levels were lower than during that characterised by the presence of an anticyclone (EUH scenario), due to the rain commonly associated with these depressions (17 μgTSP m^{-3}, 12 μgPM10 m^{-3} and 8 μgPM2.5 m^{-3} during MD episodes and 27 μgTSP m^{-3}, 17 μgPM10 m^{-3} and 12 μgPM2.5 m^{-3} during EUH events).
The relative clean Mediterranean air masses and the high frequency of rainfall episodes characterising the Mediterranean air mass transport may account for the low mean PM levels recorded at Barcarrota during Mediterranean episodes (15 μgTSP m^{-3}, 8 μgPM10 m^{-3} and 4 μgPM2.5 m^{-3}). It was expected to record higher mean PM levels during EUH-MH episodes in virtue of the more frequent occurrence of rain associated with NAD-MD scenario. However, this was not observed (31 μgTSP m^{-3}, 15 μgPM10 m^{-3} and 11 μgPM2.5 m^{-3} during NAD-MD episodes and 26 μgTSP m^{-3}, 15 μgPM10 m^{-3} and 8 μgPM2.5 m^{-3} during EUH-MH events). The occurrence of NAD-MD episodes is very low and any conclusion drawn with PM means calculated with such low number of days should be taken with care. In fact, the mean PM levels for NAD-MD events was higher than during EUH-MH events owing to a particular NAD-MD event with high PM levels occurred in at the end of March 2002. In this episode local/regional contributions could have contributed greatly to increase the PM levels.
The episodes with lack of advective conditions over southwestern Iberian Peninsula had an important impact on PM levels at Barcarrota (PM means of 36 μgTSP m^{-3}, 20 μgPM10 m^{-3} and 13 μgPM2.5 m^{-3} were recorded during these events). Nevertheless, the impact of the two meteorological scenarios considered in this study was considerably different. ITL episodes occur in the warm season of the year when a number of factors results in an increase in the PM levels (46 μgTSP m^{-3}, 30 μgPM10 m^{-3} and 21 μgPM2.5 m^{-3}). These are the low rainfall regime, the aging of pollutants in air masses, the high rate of re-suspension of soil material owing to convective movements or the enhancement of the transformation of gaseous precursors into secondary aerosols by the increased photochemistry derived from the intense insolation and the scarce renovation of air masses. During WIA episodes the mean PM levels were low (24 μgTSP m^{-3}, 15 μgPM10 m^{-3} and 9 μgPM2.5 m^{-3}). Under low baric gradient conditions in winter when WIA episodes occur, stagnant atmospheric conditions prevail and the poor vertical development of the boundary layer results in a reduction of the dispersion of pollutants. This is particularly important when thermal inversions occur over urban or industrial sites reducing the transport of pollutants towards rural sites. However, the lack of rain associated with WIA events would tend to increase PM levels owing to the reduction of the scavenging potential of the atmosphere.
The highest mean PM levels were recorded at Barcarrota during African dust outbreaks due to the high load of crustal aerosols contained in the African air masses (41 μgTSP m^{-3}, 27 μgPM10 m^{-3} and 16 μgPM2.5 m^{-3}). During NAH-A events the mean PM levels were the highest among all types of African episodes (50 μgTSP m^{-3}, 30 μgPM10 m^{-3} and 20 μgPM2.5 m^{-3}). During these episodes, the transport of the African dust plumes occurred at high altitudes (>1500 m.a.s.l.) while, at surface levels, low gradient baric conditions stand. The dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is

distributed and affects the sampling stations. Simultanously, at surface, a low baric gradient occurred across the Iberian Peninsula. In consequence, the renovation of superficial air masses is poor and, owing to the important insolation, the generation of secondary species from gaseous precursors contributed also to regionally increase PM levels. Moreover, precipitation is reduced and re-suspension is enhanced during summer (when NAH-A scenario mainly develops). These two factors may also increase PM levels. AD(NAF) episodes gave rise to the lowest mean PM levels probably owing to the rain associated with these events (27 µgTSP m^{-3}, 22 µgPM10 m^{-3} and 9 µgPM2.5 m^{-3}). In the same manner, NAD episodes are associated with depressions that could cause frequently rain but, in this case, the rain would more likely affect the eastern part of Spain rather than the western side. That may be the cause of the higher PM levels during NAD episodes (40 µgTSP m^{-3}, 23 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3}). Finally, NAH-S episodes occur under dry anticyclonic conditions which result also in high mean PM levels at Barcarrota (36 µgTSP m^{-3}, 24 µgPM10 m^{-3} and 13 µgPM2.5 m^{-3}).

Combining information about the mean number of days and the PM mean levels into an impact index (II=mean number of days per year influenced by each type of scenario multiplied by the mean PM levels for each scenario in the whole period 1998-2003 and divided by 365 days) we can evaluate the impact of each transport scenario on PM levels for different size ranges. II gives us information about the contribution (in concentration units) of each type of transport scenario on the mean levels of PM recorded at a certain site. Moreover, II can be understood as the relative weight of each scenario with respect to the annual mean levels registered in a certain station and for a determined size range and it can be expressed as percentage. For the case of Barcarrota this is shown in Figure 5.28.

Although the mean PM levels recorded during episodes of Atlantic advection were low the high frequency of occurrence of these situations result in the highest II among all the episodes considered in this study (43-44% depending on the station and the size range). The weight of Atlantic events is lower as the size range decreases. This reflects the coarse size of the marine salts which are dominant in the Atlantic air masses. Most of these II resulted from the occurrence of AZH-NAtD events (39-40%) while AD(ATL) only reached to II of 3-4%.

African dust outbreaks also reached to important II (28-30% depending on the station and the size range) with the lowest relative weight registered for PM2.5 probably owing to the coarse size of dust particles. This stands for NAH-S (around 4% in all size ranges), AD(NAF) (5-7%) and NAD (2-3%). On the contrary NAH-A scenario (16-17%) reached to slightly higher II in PM2.5 probably as a reflection of the fine size of the secondary particles derived from the photochemical transformation of gaseous precursors as explained above.

The episodes without dominant advective conditions also had a relatively high impact on annual PM levels at Barcarrota with II in the range 19-22% with the highest relative impact in PM2.5. This also occurred for ITL events (II from 11 to 14%) owing to the photochemical generation of secondary species from gaseous precursors in virtue of the meteorological conditions (strong insolation and weak baric gradient conditions resulting in poor renovation of air masses and the aging of polluted air masses). The weight of WIA episodes in all size ranges reached II around 8%.

The episodes with advection of Mediterranean air masses did not reach to important II owing to the low frequency of occurrence of these events and also to the low mean PM levels recorded at Barcarrota for these situations (4-5%). The weights of NAD-MD and EUH-MH scenarios reached around 1% and 3-4% respectively.

Table 5.23. PM mean levels registered during different transport episodes over southwestern Iberian Peninsula in 1998-2003.

Mean PM levels	**Barcarrota**		
(µg m^{-3})	TSP	PM10	PM2.5
Total 98-03	**27**	**17**	**11**
Atlantic episodes	**21**	**13**	**8**
AZH-NAtD	22	13	8
AD(ATL)	15	8	4
African episodes	**41**	**27**	**16**
NAH-S	36	24	13
AD(NAF)	27	22	9
NAD	40	23	12
NAH-A	50	30	20
European episodes	**23**	**15**	**10**
EUH	27	17	12
MD	17	12	8
Mediterranean episodes	**27**	**15**	**9**
NAD-MD	31	15	11
EUH-MH	26	15	8
Episodes without dominant advection	**36**	**20**	**13**
WIA	24	15	9
ITL	46	30	21

European episodes were the situations with the lowest II among all the episodes considered in this study (II around 3%). EUH reached to II in the range 2-3% and the weight of MD did not reach 1% in any size range. It is important to remark that the highest II of European episodes were observed for PM2.5. This reflected the fine size of the anthropogenic aerosols with European origin. However, the contribution of anthropogenic sources emitting fine aerosols or gaseous precursors located over the Iberian Peninsula in the regions crossed by the European air masses before reaching southwestern Iberia should not be discarded.

The 1999/30/CE European directive established a daily limit value of 50 µgPM10 m^{-3} which should not be exceeded more than 35 times per year by 2005. As shown in Table 5.24 and Figure 5.29, in Barcarrota a total of 7 exceedances of that limit value were recorded from 2001 to 2003 (2-3 per year). Moreover, In the II PM Position paper (EC, 2004) it was proposed to establish a daily limit value of 35 µg m^{-3} for PM2.5 which should not be exceeded more than 35 times in a year. In Barcarrota this level was exceeded in 10 occasions from 2001 to 2003 (3-4 per year). Finally, in order to cover all the study period, an equivalent limit value for TSP of 70 µg m^{-3} using the mean 2001-2003 PM10/TSP ratio at Barcarrota (0.7) was worked out. From 1999 to 2002 a total of 32 exceedances (8 per year) of this value were registered at Barcarrota.

The influence of the African episodes on the number of exceedances of the above presented daily limit values is clear since 22 exceedances of the TSP equivalent limit value (69% of the 32 exceedances in 1999-2002), 5 exceedances of the PM10 daily limit value (71% of the 7 exceedances in 2001-2003) and 4 exceedances of the PM2.5 daily limit value (40% of the 10 exceedances in 2001-2003) were registered during events of this nature. The episodes without dominant advective conditions occurred in summer also caused a number of exceedances of the limit values. A total of 5 exceedances of the TSP equivalent limit value (16% of the 32 exceedances in 1999-2002), 2 exceedances of the PM10 daily limit value (29% of the 7 exceedances in 2001-2003) and 2 exceedances of the PM2.5 daily limit value (20% of the 10 exceedances in 2001-2003) were registered during episodes without prevailing advective conditions in summer.

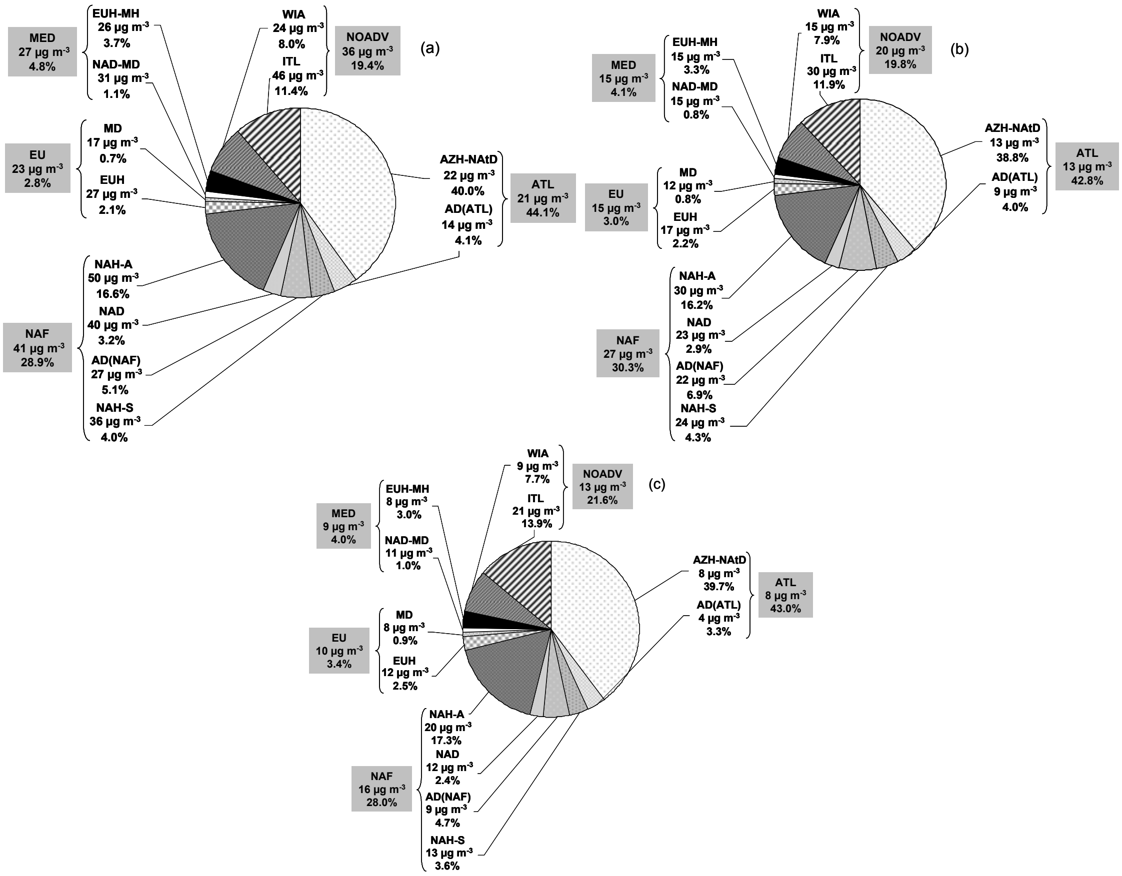


Figure 5.28. Relative impact (in %) of different PM episodes and meteorological scenarios on mean levels of TSP (a), PM10 (b) and PM2.5 (c) in Barcarrota.

Apart from these two types of episodes that were expected to result in considerably high PM levels and, consequently, in exceedances of the daily limit values, exceedances were also registered during Atlantic and Mediterranean episodes. During Atlantic episodes 4 exceedances of the equivalent TSP daily limit value (13% of the 32 exceedances in 1999-2002) and 4 exceedances of the PM2.5 suggested limit value (40% of the 10 exceedances in 2001-2003) occurred while during Mediterranean events, 1 exceedance of the TSP equivalent limit value (3% of the 32 exceedances in 1999-2002) was registered. The Mediterranean and Atlantic exceedances should be interpreted as result of local/regional contributions. Moreover, the exceedances caused by Atlantic transport may be a reflection of the contribution of anthropogenic pollutants originated over Portugal.

Table 5.24. Number of annual exceedances of the daily limit value established by the 1999/30/CE Directive (50 µgPM10 m^{-3}) and of the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) at Barcarrota. The number of annual exceedances of an equivalent TSP daily limit value (70 µg m^{-3}) at Barcarrota is also shown. This equivalent limit value was worked out applying PM10/TSP ratio of 0.7.

NUMBER OF EXCEEDANCES	Equivalence to AQ Directive 1999/30/CE and to II PM PP suggestions for TSP: TSP > 70 µg m^{-3}	AQ Directive 1999/30/CE : PM10 > 50 µg m^{-3}	II PM position paper suggestions: PM2.5 > 35 µg m^{-3}
	Barcarrota	Barcarrota	Barcarrota
1998	na	na	na
1999	*[1]7	na	na
2000	13	na	na
2001	7	*[2]3	*[2]3
2002	5	0	7
2003	na	4	0
Total 98-03	32	7	10
Annual mean 98-03	8.0	2.3	3.3

*[1]Calculated with data of 83% of the months of the year
*[2]Calculated with data of 83% of the months of the year
na: Not available

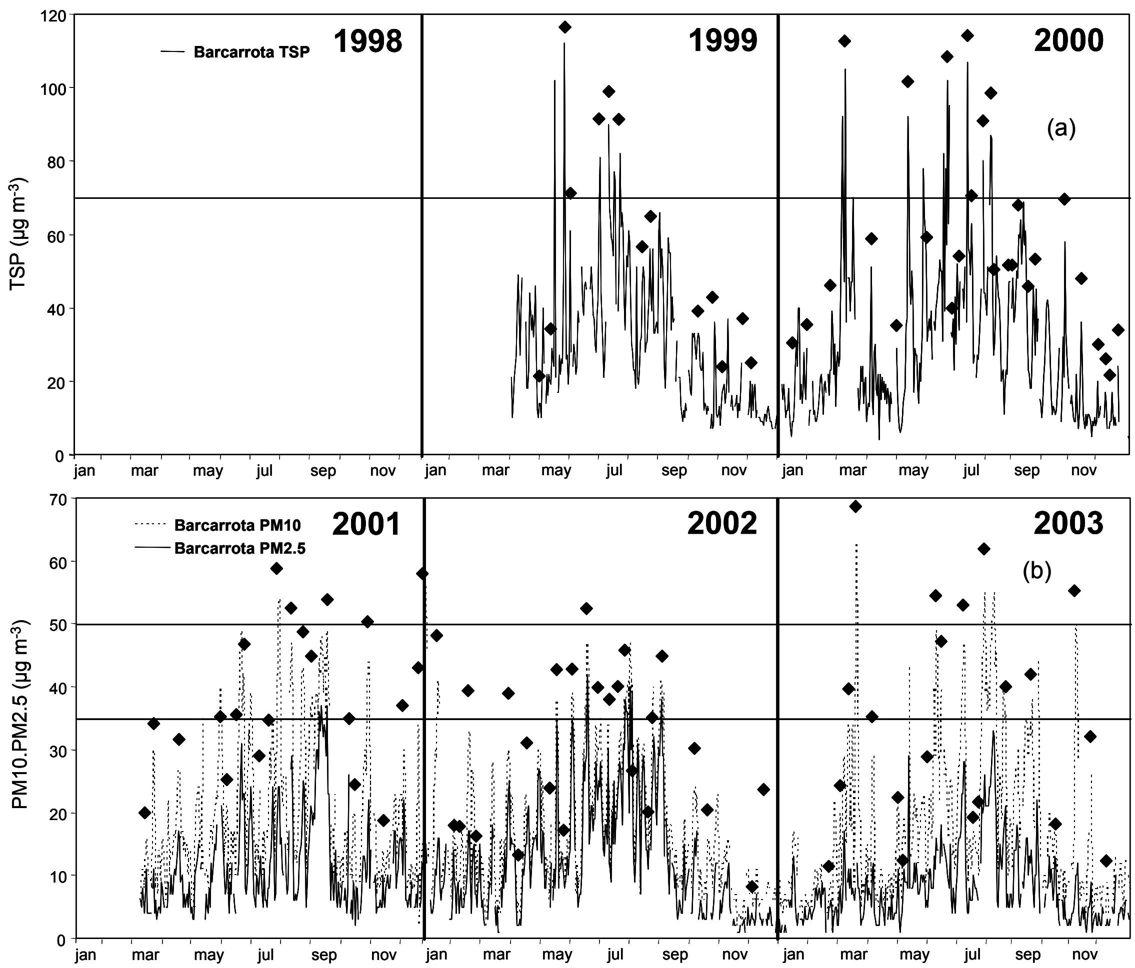


Figure 5.29. Daily TSP levels in Barcarrota for 1998-2000 (a), and daily PM10 and PM2.5 levels in Barcarrota for 2001-2003 (b). The black dots mark the occurrence of African dust episodes. The horizontal lines mark the daily limit values established by the 1999/30/CE Directive (50 µgPM10 m^{-3}), the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) and the equivalent daily limit value for TSP (70 µgTSP m^{-3}).

In a regional background station located at southwestern Iberian Peninsula (where Barcarrota is located) the highest mean PM levels are recorded in summer due to the following factors:

(a) The enhancement of photochemical formation of secondary particles due to a higher insolation during summer.
(b) The lower precipitation regime during summer (Figure 5.30) which results in the reduction of processes such as the washing out of aerosols from the atmosphere.
(c) The low renovation of air masses during episodes with lack of advection such as during ITL events.
(d) The higher frequency of occurrence of dry African dust outbreaks over the Iberian Peninsula.
(e) The increased rates of re-suspension of crustal material owing to the poor vegetal coverage of this area and the intense atmospheric convective dynamics

In Barcarrota, the highest monthly PM levels were recorded in summer so this station could be considered to represent the regional background. The second order peak recorded in March for PM10 that could reflect the effect of the African dust outbreaks with important impact on PM levels occurring in this period of the year (Figure 5.30). These typical winter African episodes do not occur all the years and that is the main reason why the March PM peak was so marked.

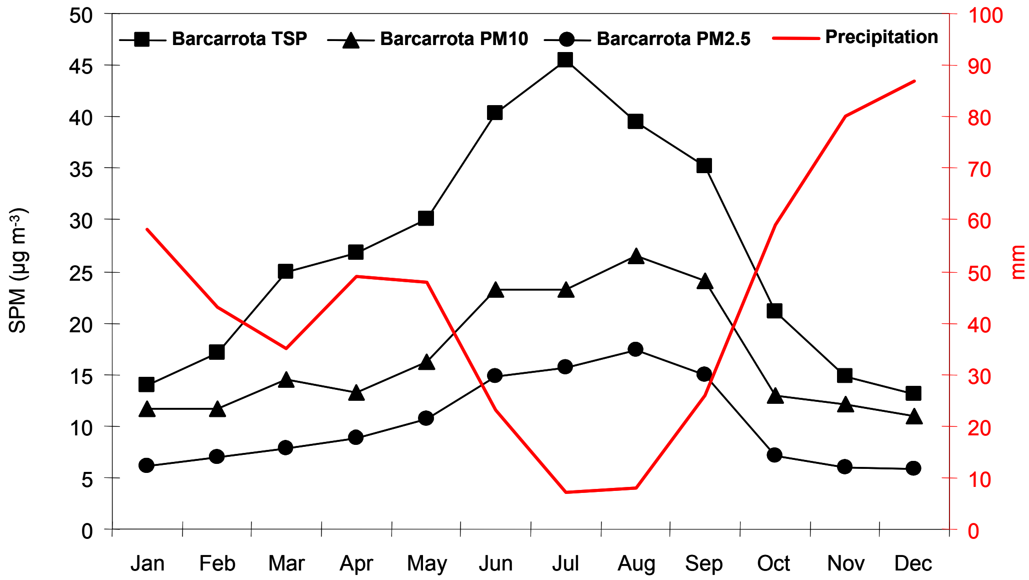


Figure 5.30. Mean monthly precipitation of Carretera de Trujillo station (Cáceres, 42º 53' N, 2º 43' W, 405 m.a.s.l) for 1971-2000 (INM, 2001) and PM monthly means registered in Barcarrota (TSP from March 1999-January 2003 and PM10 and PM2.5 from March 2001 to 2003).

5.7 Southeastern Iberian Peninsula

The climate of the southeastern region of the Iberian Peninsula is characterised by very dry and warm summers and moderately mild temperatures in the rest of the year. The annual precipitation regime is low. The vegetation cover in the area is poor in extense areas so re-suspension processes are likely to occur especially in summer owing to convective processes and the lack of precipitation. This source of crustal material may affect PM levels recorded at air quality monitoring stations. Furthermore the location of this region, very close to the African continent makes it susceptible to receive contributions of north African dust all along the year. These contributions may be very important in summer (Rodriguez et al., 2001). Moreover, weak baric gradient conditions are common over southeastern Iberia especially during summer. Under these situations the renovation of air masses is poor and the aging and recirculation of contaminated air masses commonly occur in summer, late spring and early autumn (Millán et al., 1997). These mechanisms may increase considerably PM levels at the regional background sites (Rodríguez et al, 2003).

Daily PM levels from an EMEP station located at Víznar (37º 14' N, 3º 28' W, 1230 m.a.s.l.) were used for evaluating the regional background levels. TSP was measured from before 1998 to January 2003 and PM10 and PM2.5 have been continuously measured from March 2001. These measurements were performed following the gravimetric method using high volume samplers.

Figure 5.31 shows the relative occurrence of days and episodes according to the air mass transport scenario. The advection of Atlantic air masses was the most common situation with 211 events (32.2% of the episodes registered from 1998 to 2003) resulting in 782 days (35.7% of the days in 1998-2003). The major part of these situations occurred under AZH-NAtD scenario (7-8 times as many situations as AD(ATL) situations).

The situations with lack of dominant advective conditions were also frequent. A total of 191 episodes (29.1% of the episodes registered from 1998 to 2003) with a total of 626 days (28.6% of the days in 1998-2003) occurred in 1998-2003 over the study area. The proportion of WIA events is slightly higher than ITL events (1.5 times more frequent).

The African dust outbreaks occurred also frequently accounting for 160 episodes (24.4% of the episodes registered from 1998 to 2003) and 578 days (26.4% of the days in 1998-2003) in 1998-2003. The transport scenario which accounted to the major part of the African episodes was NAH-A (5 times as frequent as NAH-S, 3-4 times as frequent as NAD and 2-3 times as frequent as AD(NAF)).

Considerably less frequent were situations of advection of European air masses. A total of 40 European episodes (6.1% of the episodes registered from 1998 to 2003) and 105 days (4.8% of the days in 1998-2003) occurred in the study period. EUH episodes were considerably more frequent than MD events (twice as many EUH situations as MD situations).

Finally, the transport of Mediterranean air masses over southeastern Iberia was also infrequent because in the whole study period only 54 Mediterranean episodes (8.2% of the episodes registered from 1998 to 2003) resulting in 100 days (4.6% of the days in 1998-2003) were observed. The most frequent Mediterranean scenario was EUH-MH (3-4 times more frequent than NAD-MD).

The seasonal distribution of the days associated with each type of transport scenario in southeastern Iberian Peninsula in 1998-2003 is shown in Figure 5.32. The high frequency of occurrence of situations of transport of Atlantic air masses is clear, but also a low summer frequency was observed (minimum frequency of occurrence in August with a monthly mean of 4 days). Autumn (frequency peak in November with 18 days), January and April (17 days as monthly mean in these two months) were the periods of maximum frequency. In the same periods the highest frequencies of occurrence of AZH-NAtD situations were recorded (monthly means of 18 days in November, 15 days in January and 13 days in April). The days associated with AD(ATL) scenario were particularly frequent in April (monthly average of 4 days) while in the rest of the months the mean occurrences of this scenario did not surpass 2 days.

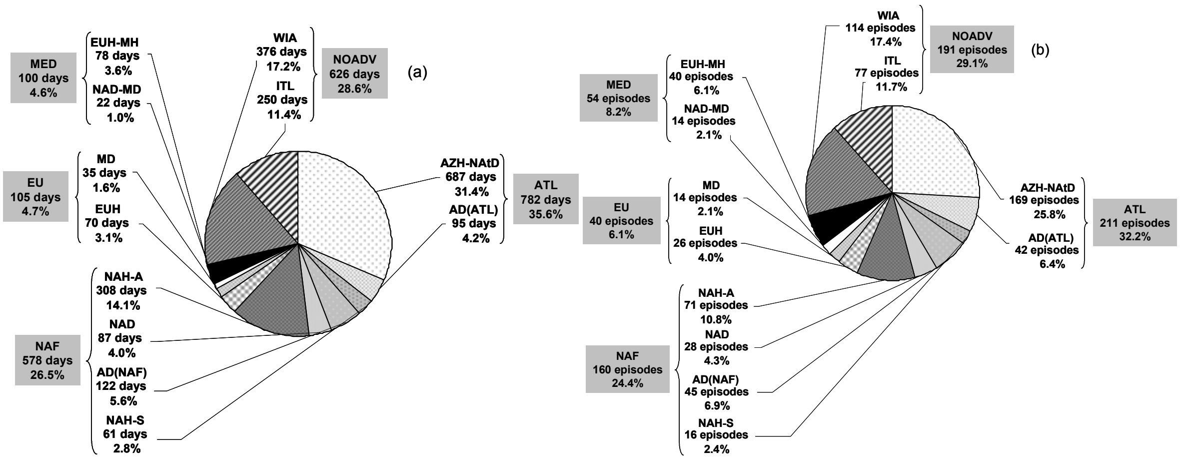


Figure 5.31. Occurrence of all the air mass transport scenarios over southeastern Iberian Peninsula in 1998-2003 in days (a) and episodes (b).

The transport of African air masses over the study area was characteristic from the warm season (reaching up to 15 days as monthly mean in July). Second order frequency maxima were observed in January-March (9 days as monthly mean in March) and October (7 days as monthly average). NAH-S scenario occurred almost uniquely from January to March (4 days as monthly mean in February). AD(NAF) scenario reached frequencies of 5 days as a monthly mean in March and 3 days in October, December and May. NAD situations were especially frequent in May (4 days as monthly average), November (3 days as monthly mean) and March (monthly mean of 2 days). Finally NAH-A scenario uniquely occurred from late spring to early autumn but with a especial frequency in summer (13-15 days as monthly means in June-August with the frequency peak in July).

The situations of transport of European air masses over southeastern Iberia were scarce. Only from November to April the occurrence of European situations were relatively important (2 or 3 days as means in all the months with the frequency peak in January). The situations associated with EUH scenario mainly occurred from December to March (with monthly means reaching up to 3 days in January) while the days associated with MD scenario commonly occurred in three periods: April, November-December and September (with monthly means of 1 day in these four months).

The transport of Mediterranean air masses was characteristic of November to January (3 days as monthly mean in December), March, June and September (all these months with means of 2 days). The days associated with NAD-MD scenario only reached frequencies of occurrence of 1 day as a monthly mean in December-January and March-April. EUH-MH situations were more frequent and reached 2 days as monthly means in November, December, June and September.

The situations of lack of prevailing advective conditions were observed all along the year but the highest relative frequencies were observed in May (with a monthly mean of 14 days) and July-October (reaching up to monthly means of 13 days in both August and September). WIA situations, characteristic from the cold seasons of the year, were particularly frequent in April-May (with a monthly mean of 11 days in May), October (10 days as monthly average) and, with slightly less frequency, in December (9 days as monthly mean). On the contrary, ITL episodes, by definition, only occurred in the warm part of the year resulting in an important number of days with lack of advective conditions in June-September (up to 13 days as monthly mean in August).

The mean duration of the different air mass transport events over southeastern Iberia in 1998-2003 are presented in Table 5.25. Atlantic and African episodes reached up to 4 days as monthly mean durations, European events and episodes with lack of dominant advective conditions lasted on average 3 days and Mediterranean episodes were the shortest with 2 days as average duration. Among transport scenarios, all lasted on average 2 or 3 days with three exceptions: AZH-NAtD Atlantic episodes, and the two types of African episodes associated with the development of anticyclones, NAH-S and NAH-A which reached 4 days as mean duration.
The mean PM levels recorded at Víznar in the study period were low (40 µgTSP m^{-3}, 22 µgPM10 m^{-3} and 11 µgPM2.5 m^{-3}, Table 5.26), although considerably high if compared with those obtained at other regional background of the Iberian Peninsula. As expected, the annual limit value established by the 1999/30/CE for 2005 (40 µgPM10 m^{-3}) is not exceeded in any of the years. On the contrary, the annual limit value proposed in the European Directive for 2010 (20 µgPM10 m^{-3}) was exceeded in 2001, 2002 and 2003. With respect to the annual cap value (25 µgPM2.5 m^{-3}) established by the EU Commission in September 2005 in the Air Quality directive draft, it was never reached in Víznar in 2001-2003.

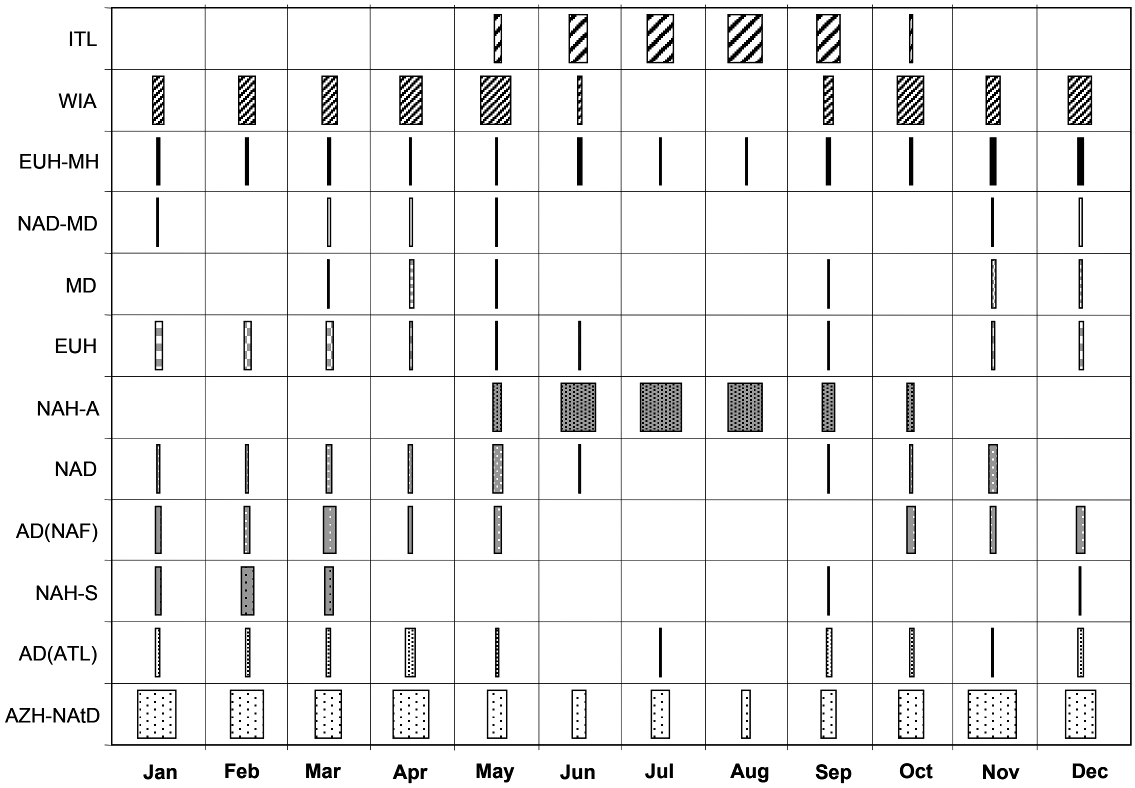


Figure 5.32. Mean number of days with each type of PM episode per month over southeastern Iberia in 1998-2003.

Table 5.27 shows the annual mean PM levels recorded under the different events considered in this study and a great variation between these levels can be observed. Low mean PM levels were recorded at Víznar during Atlantic episodes (26 µgTSP m^{-3}, 13 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3}). The relatively low concentration of pollutants in Atlantic air masses and the relatively high frequency of occurrence of rain associated with the frontal systems crossing the Iberian Peninsula during Atlantic episodes may account for this fact. In consequence, most of the PM load recorded during the Atlantic episodes was associated with local/regional contributions. The higher frequency of rain associated with the Atlantic depressions during AD(ATL) episodes resulted in very low mean PM levels during these situations compared with during AZH-NAtD events (26 µgTSP m^{-3}, 13 µgPM10 m^{-3} and 7 µgPM2.5 m^{-3} during AZH-NAtD events and 20 µgTSP m^{-3}, 9 µgPM10 m^{-3} and 4 µgPM2.5 m^{-3} during AD(ATL) episodes).

Table 5.25. Mean duration of PM episodes in southeastern Iberian Peninsula for 1998-2003.

	Mean duration (days/episode)		**Mean duration (days/episode)**
Atlantic episodes	**4**	**European episodes**	**3**
AZH-NAtD	4	*EUH*	3
AD(ATL)	2	*MD*	3
African episodes	**4**	**Mediterranean episodes**	**2**
NAH-S	4	NAD-MD	2
AD(NAF)	3	EUH-MH	2
NAD	3	**Episodes without dominant advection**	**3**
NAH-A	4	*WIA*	3
		ITL	3

Table 5.26. Mean levels of TSP, PM10 and PM2.5 recorded in Víznar in 1998-2003.

MEAN LEVELS (µg m^{-3})	**Víznar** TSP	PM10	PM2.5
1998	36	na	na
1999	42	na	na
2000	44	na	na
2001	41	*24	*12
2002	39	21	10
2003	na	21	9
Mean 98-03	40	22	11

*Calculated with data of 83% of the months of the year
na: Not available

Low mean PM levels were recorded at Víznar during situations of transport of European air masses over southeastern Iberia (23 µgTSP m^{-3}, 15 µgPM10 m^{-3} and 10 µgPM2.5 m^{-3}). The long transport which European air masses have to undergo to reach the study area, allows the pollutants to disperse and dilute so the PM levels were low. The PM levels recorded during MD episodes were lower than during EUH events (17 µgTSP m^{-3}, 12 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3} during MD episodes and 27 µgTSP m^{-3}, 17 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3} during EUH events) because the rain commonly associated with the Mediterranean depressions resulted in a high frequency of PM washing out of the atmosphere.

The Mediterranean episodes also had a low impact on PM levels at Víznar (30 µgTSP m^{-3}, 16 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3}) because the Mediterranean air masses are relative clean and the occurrence of rainfall over the eastern flank of Iberia is common during Mediterranean events, which results in the washing out of the atmosphere. Among the two transport scenarios distinguished for Mediterranean transport, EUH-MH had a slightly higher impact on PM levels than NAD-MD (32 µgTSP m^{-3}, 16 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3} during EUH-MH episodes and 24 µgTSP m^{-3}, 15 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3} during NAD-MD episodes). This may be the result of the higher frequency of rain occurred during NAD-MD episodes than during EUH-MH events.

The mean PM levels recorded at Víznar during episodes with lack of advective conditions (42 µgTSP m^{-3}, 22 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3}) were similar to the annual mean PM levels. The scarce occurrence of rain during these episodes contributes to increase PM levels because the rain scavenging of aerosols is reduced. However, the mean PM levels recorded during WIA and ITL were different (means of 54 µgTSP m^{-3}, 28 µgPM10 m^{-3} and 14 µgPM2.5 m^{-3} for ITL events and means of 24 µgTSP m^{-3}, 15 µgPM10 m^{-3} and 9 µgPM2.5 m^{-3} for WIA). The low rainfall regime, the aging and re-circulation of polluted in air masses (Millán et al., 1997), the high rate of re-suspension or the enhancement of transformation of gaseous precursors into secondary aerosols by the increased photochemistry, tend to increase PM levels regionally during ITL episodes over the eastern flank of the Iberian Peninsula (Rodríguez et al, 2003). During WIA episodes, the low vertical growth of the boundary layer especially during the typical development of thermal inversions over industrial/urban sites reduces the anthropogenic contribution of PM in regional background stations.

The highest mean PM levels in Víznar were recorded during African dust outbreaks (62 µgTSP m^{-3}, 35 µgPM10 m^{-3} and 14 µgPM2.5 m^{-3}) owing to the high load of crustal aerosols of the African air masses. Among the different types of African events distinguished in this study, NAH-A event had the highest impact on PM levels (81 µgTSP m^{-3}, 42 µgPM10 m^{-3} and 16 µgPM2.5 m^{-3}). Apart from the high loads of mineral aerosols in the African air masses, these high mean PM levels were reached owing to the regional contribution consisting in secondary aerosols provinient from the photochemical transformation of gaseous precursors. During NAH-A situations the African plumes travel at high altitudes (>1500 m.a.s.l.) and the dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is distributed and affects the sampling stations. Moreover, the formation of secondary particles is enhanced, at surface, because low pressure gradient conditions remain causing lack of advective conditions. In these circumstances, superficial air masses are hardly renovated and the aging and recirculation of contaminated air masses aided by the orographic conditions of eastern Iberian Peninsula commonly occur (Millán et al., 1997). Furthermore, during NAH-A episodes, precipitation is reduced and re-suspension of soil material by convection is enhanced. NAH-S episodes, with low frequency of rain associated, (48 µgTSP m^{-3}, 35 µgPM10 m^{-3} and 15 µgPM2.5 m^{-3}) and NAD events because of the vicinity of the active desert source areas during this type of transport (northern Algeria and Tunisia) to southeastern Iberia (45 µgTSP m^{-3}, 25 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3}), were episodes associated with high PM levels at Víznar. The lowest PM levels among African episodes were recorded during AD(NAF) events which commonly are characterised by the presence of rain (36 µgTSP m^{-3}, 21 µgPM10 m^{-3} and 8 µgPM2.5 m^{-3}).

Combining information about the mean number of days and the PM mean levels into an impact index (II=mean number of days per year influenced by each type of scenario multiplied by the mean PM levels for each scenario in the whole period 1998-2003 and divided by 365 days) we can evaluate the impact of each transport scenario on PM levels for different size ranges. II gives us information about the contribution (in concentration units) of each type of transport scenario on the mean levels of PM recorded at a certain site. Moreover, II can be understood as the relative weight of each scenario with respect to the annual mean levels registered in a certain station and for a determined size range and it can be expressed as percentage. The II in Víznar of all the episodes is presented in Figure 5.33.

Table 5.27. PM mean levels registered during different transport episodes over southeastern Iberian Peninsula in 1998-2003.

Mean PM levels ($\mu g\ m^{-3}$)	**Víznar**		
	TSP	PM10	PM2.5
Total 98-03	**40**	**22**	**11**
Atlantic episodes	**26**	**13**	**7**
AZH-NAtD	26	13	7
AD(ATL)	20	9	4
African episodes	**62**	**35**	**14**
NAH-S	48	35	15
AD(NAF)	36	21	8
NAD	45	25	12
NAH-A	81	42	16
European episodes	**28**	**15**	**9**
EUH	34	17	11
MD	14	12	8
Mediterranean episodes	**30**	**16**	**8**
NAD-MD	24	15	8
EUH-MH	32	16	8
Episodes without dominant advection	**42**	**22**	**12**
WIA	32	18	10
ITL	54	28	14

Owing to the high PM levels recorded at Víznar during African dust outbreaks together with a considerably high frequency of occurrence of these events resulted in the highest II among all types of episodes (35-42%). NAH-S, AD(NAF) and NAD episodes reached II in the ranges 3-5%, 4-5% and 4-5% respectively with the highest weight in PM10 in accordance to the common grain size of the dust in the African plumes. The II of NAH-A scenario ranged from 22 to 28% with higher weight in TSP than PM10 and PM2.5. This may be attributed to possible contribution of re-suspension of soil material (which is a source of coarse aerosols) increased by convective dynamics. Furthermore, the altitude of this station, 1230 m.a.s.l., makes it susceptible of receiving the direct impact of the dust plume travelling at high altitudes during NAH-A episodes. In these cases, as the size of the the dust grains is coarse, the II of these episodes would increase in the coarse PM fractions.

The impact index of episodes without dominant advective conditions was considerably high with II in the range 30-33%. The highest weights of these episodes were observed in PM2.5. During ITL episodes II remains constant in all grain size ranges (between 15 and 16%). During these episodes there is a marked increase of photochemical generation of secondary PM species from gaseous precursors in virtue of the meteorological conditions (strong insolation and weak baric gradient conditions resulting in poor renovation of air masses and the aging and recirculation of polluted air masses). In this way the proliferation of fine secondary aerosols should increase the II of ITL in PM2.5. The weight of WIA events ranged from 14 to 17% and the highest IIs were obtained for PM2.5. This could reflect the existence of a local/regional source of fine aerosols (like traffic or other anthropogenic sources).

As described above, the mean PM levels recorded during episodes of Atlantic advection were low. However, the frequency of occurrence of these events was high and consequently the II was high for all grain size ranges (21-24%). The highest weight of Atlantic events was observed for PM2.5 which, suggests the existence of a local/regional source of fine particles. The contribution of anthropogenic sources of fine aerosols in areas in the Iberian Peninsula crossed by the Atlantic air masses before reaching eastern Iberia may explain the highest weight if Atlantic episodes on PM2.5.

The impact of AD(ATL) was negligible compared with AZH-NAtD (around 2% for AD(ATL) and 19-22% for AZH-NAtD).
The European episodes had a low II owing to the low frequency of occurrence and the low PM levels recorded at Víznar during such situations (3-5%). The highest II of European episodes were observed for PM2.5. This reflects the fine grain size of the anthropogenic aerosols with European origin. While EUH episodes had II around 3% MD events only reached 1% approximately.
Also low IIs were obtained for Mediterranean episodes which were quite infrequent and with low PM levels associated (3-4%). The slightly higher weight in PM2.5 suggests the existence of a local source of fine particles. While NAD-MD did not reach 1% as II in any size range EUH-MH had II slightly below 3% in all size ranges.

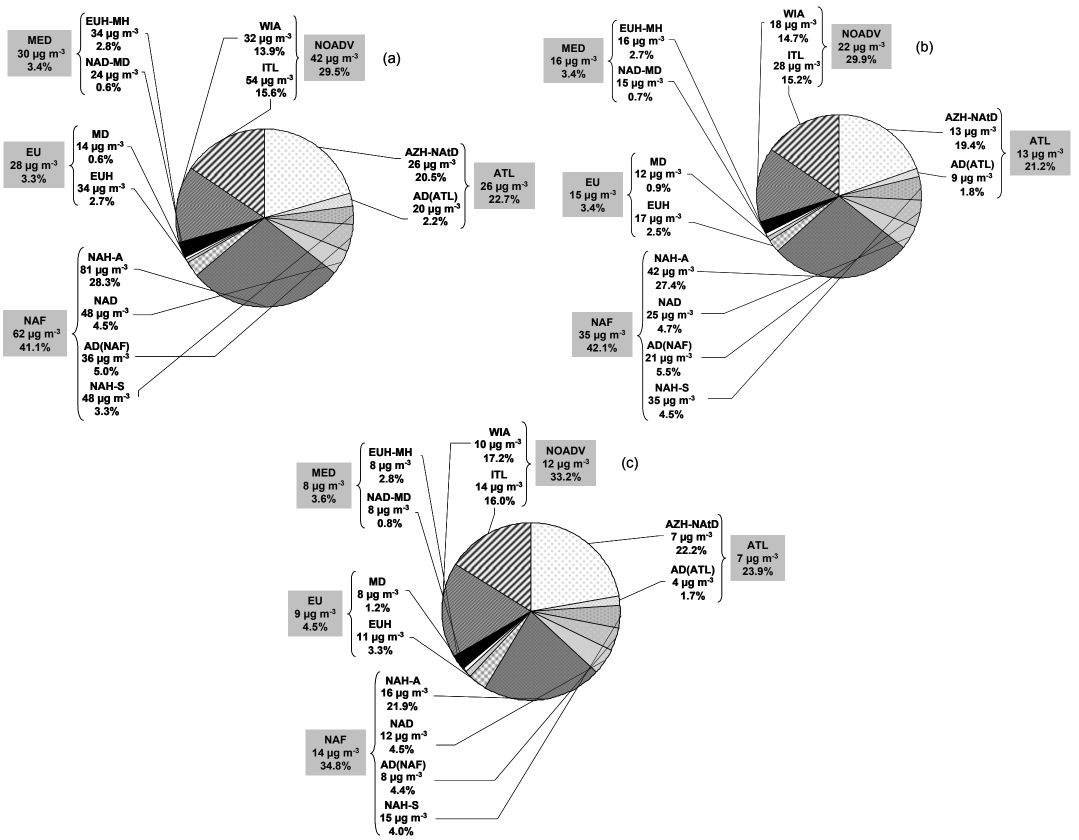


Figure 5.33. Relative impact (in %) of different PM episodes and meteorological scenarios on mean levels of TSP (a), PM10 (b) and PM2.5 (c) in Víznar.

The 1999/30/CE European directive established a daily limit value of 50 µgPM10 m^{-3} which should not be exceeded more than 35 times per year by 2005. As shown in Table 5.28 and Figure 5.34, at Viznar in a total of 41 times (13-14 days per year) this level of PM10 was excceded in 2001-2003. More recently, in the II PM position paper, a daily limit value for PM2.5 of 35 µg m^{-3} was suggested. This limit value should not be exceeded more than 35 times in a year. In Viznar only 1 exceedance of this value was registered in 2001-2003. An equivalent limit value for TSP of 83 µg m^{-3} using the mean PM10/TSP ratio at Víznar (0.6) was worked out. In 1998-2002 a total of 113 exceedances of this equivalent limit value occurred (22-23 per year) in Víznar.
The influence of African dust outbreaks in the number of exccedances recorded at Víznar of the above mentioned limit values is clear since 103 of the 113 exceedances of the equivalent TSP limit value (91% of the exccedances in 1998-2002), 40 of the 41 exceedances of the PM10 limit value (98% of the exceedances in 2001-2003) and the

unique exccedance of the suggested PM2.5 limit value occurred under the transport of African air masses over the study area. Episodes without advection provoked 4 exceedances of the TSP equivalent daily limit value (3% of the exceedances in 1998-2002) and 1 exceedance of the PM10 limit value (2% of the exceedances in 2001-2003). The remaining exccedances of the TSP limit value occurred in this manner: 3 under situations of transport of Atlantic air masses (3% of the exceedances in 1998-2002), 2 under situations of transport of Mediterranean air masses (2% of the exceedances in 1998-2002) and 1 under a situation of transport of European air masses (1% of the exceedances in 1998-2002).

Table 5.28. Number of annual exceedances of the daily limit value established by the 1999/30/CE Directive (50 µgPM10 m^{-3}) and of the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) at Víznar. The number of annual exceedances of an equivalent TSP daily limit value (83 µg m^{-3}) at Víznar is also shown. This equivalent limit value was worked out applying PM10/TSP ratio of 0.6.

NUMBER OF EXCEEDANCES	Equivalence to AQ Directive 1999/30/CE and to II PM PP suggestions for TSP: TSP > 83 µg m^{-3}	AQ Directive 1999/30/CE : PM10 > 50 µg m^{-3}	II PM position paper suggestions: PM2.5 > 35 µg m^{-3}
	Víznar	**Víznar**	**Víznar**
1998	8	na	na
1999	29	na	na
2000	33	na	na
2001	19	*12	*1
2002	24	15	0
2003	na	14	0
Total 98-03	113	41	1
Annual mean 98-03	22.6	13.6	0.3

*Calculated with data of 83% of the months of the year
na: Not available

The highest mean PM levels in a regional background station of southeastern Iberian Peninsula are expected to be maximum in summer because the following factors are common in this season over this region:

(a) The enhancement of photochemical formation of secondary particles due to a higher insolation during summer.
(b) The lower precipitation regime during summer (Figure 5.35) which results in the reduction of processes such as the washing out of aerosols from the atmosphere.
(c) The low renovation of air masses during episodes with lack of advection such as during ITL events.
(d) The aging and breeze driving re-circulation of polluted air masses characteristic from the eastern flank of the Iberian Peninsula in summer (Millán et al., 1997).
(e) The higher frequency of occurrence of dry African dust outbreaks over the Iberian Peninsula.
(f) The increased rates of re-suspension of crustal material owing to the poor vegetal coverage of this area and the intense atmospheric convective dynamics

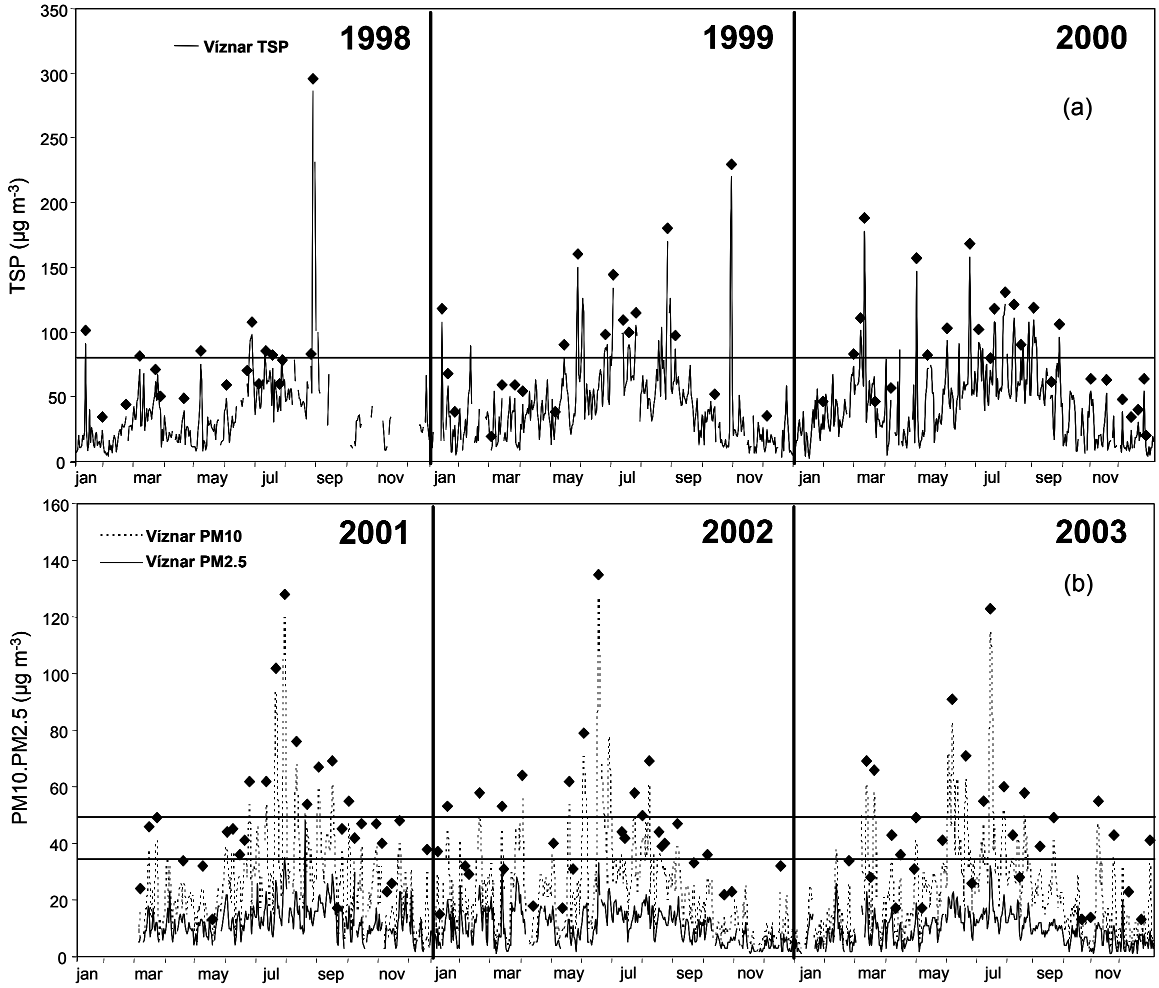


Figure 5.34. Daily TSP levels in Barcarrota for 1998-2000 (a), and daily PM10 and PM2.5 levels in Barcarrota for 2001-2003 (b). The black dots mark the occurrence of African dust episodes. The horizontal lines mark the daily limit values established by the 1999/30/CE Directive (50 µgPM10 m^{-3}), the daily limit value recommended by the II PM position paper (35 µgPM2.5 m^{-3}) and the equivalent daily limit value for TSP (83 µgTSP m^{-3}).

Víznar registered the summer maximum although the mean PM levels were very high for the regional background stations standards. However, as the mean PM levels recorded at Víznar during Atlantic events were low and, in these situations, most of the PM load corresponds to local/regional sources, it can be concluded that the local/regional contributions, although cannot be discarded, may not be so elevated and the high mean PM levels can be attributed to the influence of the African episodes. The location of Víznar, close to the African continent and at a high altitude makes it susceptible of reciving an important impact of African dust outbreaks. A second order peak was also recorded in March (Figure 5.35) owing to the occurrence of African dust outbreaks with important impact on PM levels in this month. However this peak is not so marked because, as observed in Figure 5.34 the occurrence of these episodes is not fixed every year, depending on the occurrence of African events in this period during the different study years.

5.8 Synthesis

The objectives of this chapter are to: a) Interpret the spatial and seasonal varibility of PM levels in the regional background of the Iberian Peninsula, b) Evaluate the impact of the different events of air mass transport on the PM levels in rural and natural areas (regional background), and c) Describe the spatial and temporal variability of the occurrence of different PM events.

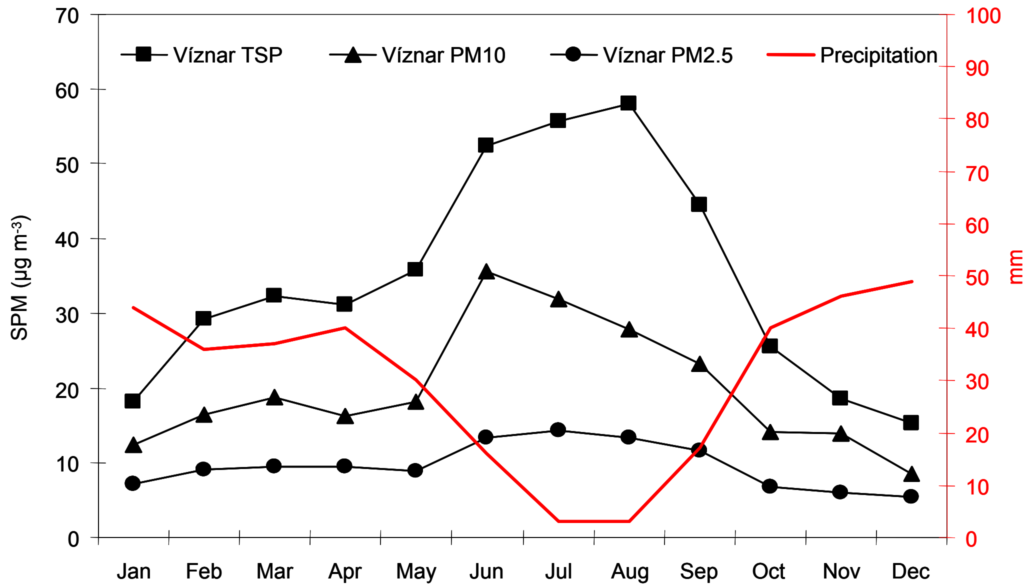


Figure 5.35. Mean monthly precipitation of Base aérea station (Granada, 37º 08' N, 3º 38' W, 685 m.a.s.l) for 1971-2000 (INM, 2001) and PM monthly means registered in Víznar (TSP from January 1998-January 2003 and PM10 and PM2.5 from March 2001 to 2003).

Daily PM data series in the period 1998-2003 from regional background stations belonging to the EMEP network in Spain were used for this study. These were located in Noia (42º 44' N, -8º 55' E, 683 m.a.s.l.), Niembro-Llanes (43º 27' N, -4º 51' E, 134 m.a.s.l.), O Saviñao (43º 14' N, -7º 42' E, 506 m.a.s.l.), Logroño (42º 27' N, -2º 30' E, 445 m.a.s.l.), Roquetas (40º 49' N, 0º 29' E, 44 m.a.s.l.), Cabo de Creus (42º 19' N, 3º 19' E, 23 m.a.s.l.), Els Torms (41º 24' N, 0º 43' E, 470 m.a.s.l.), San Pablo de los Montes (39º 23' N, -4º 20' E, 917 m.a.s.l.), Risco Llano (39º 31' N, -4º 21' E, 1241 m.a.s.l.), Campisábalos (41º 17' N, -3º 09' E, 1360 m.a.s.l.), Peñausende (41º 17' N, -5º 52' E, 985 m.a.s.l.), Zarra (39º 05' N, -1º 06' W, 885 m.a.s.l.), Barcarrota (38º 29' N, 6º 55' W, 393 m.a.s.l.) and Víznar (37º 14' N, 3º 28' W, 1230 m.a.s.l.). Measurements of atmospheric pollutants were interrupted by 2001 and 2000 at Logroño and Roquetas respectively owing to local emissions affecting these stations. Furthermore the high PM levels recorded at Niembro-Llanes station indicate a possible influence of local sources so, although the station is still operative in the EMEP network, the data from this station, as well as from Logroño and Roquetas, will not be evaluated in this synthesis. Furthermore, data from two regional background stations belonging to the air quality monitoring network of the Autonomous Government of the Bask Country were also used in this study. These were Valderejo (42º 53' N, -3º 14' E, 911 m.a.s.l.), operative measuring TSP from January 1999 to November 1999 and PM10 after that date, and Izki (42º 39' N, -2º 30' E, 835 m.a.s.l.) where PM10 is being continuously measured since May 2001. These data were obtained using β-attenuation instrumentation on an hourly basis. Finally, another regional background station belonging to ENDESA air quality monitoring network located at Monagrega (40º 59' N, -0º 12' E, 600 m.a.s.l.) was also used. In this station PM10 data is being measured since 1996 with TEOM (tapered element oscillating microbalance) instrumentation.
As shown in Figure 5.36, the mean PM levels were higher in the regional background stations located at the east of the Iberian Peninsula. Cabo de Creus and Víznar

registered the highest mean PM levels in 1998-2003 (38-40 µgTSP m^{-3}, 21-22 µgPM10 m^{-3} and 14-11 µgPM2.5 m^{-3}, Figure 5.36) followed by Barcarrota, Zarra, Els Torms and Monagrega (23-27 µgTSP m^{-3}, 16-18 µgPM10 m^{-3} and 8-12 µgPM2.5 m^{-3}, Figure 5.36). In the centre, north and northwest the mean PM levels recorded in 1998-2003 in regional background stations were lower. In Noia, O Saviñao, Valderejo, Izki, San Pablo de los Montes, Risco Llano, Campisábalos and Peñausende the mean PM levels ranged in 17-22 µgTSP m^{-3}, 12-15 µgPM10 m^{-3} and 7-10 µgPM2.5 m^{-3} (Figure 5.36).

5.8.1. Atlantic episodes

Two meteorological scenarios were observed to cause the transport of Atlantic air masses over the Iberian Peninsula. The most common (AZH-NAtD) occurred when the Azores high and the Iceland low were located at their standard locations. Another occurred when a depression was located over the Atlantic Ocean opposite to the Portuguese coast (AD(ATL)).

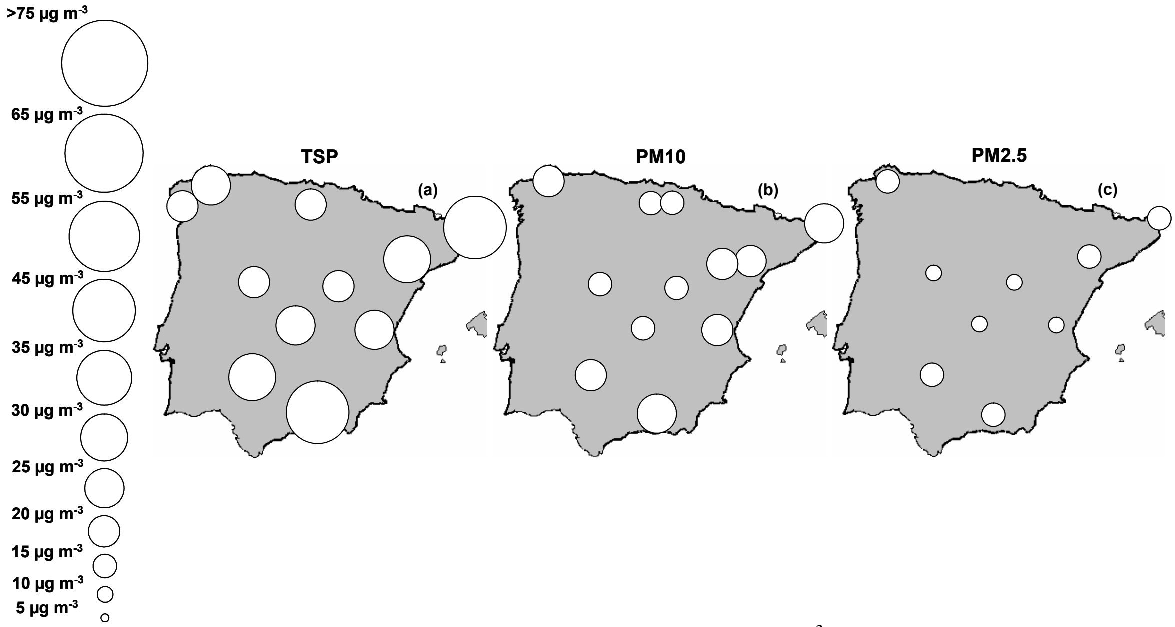


Figure 5.36. Mean TSP (a), PM10 (b) and PM2.5 (c) levels (in µg m^{-3}) in regional background stations of the Iberian Peninsula in the period 1998-2003.

The transport of Atlantic air masses over the Iberian Peninsula is the most common situation in all the regions, but the frequency of occurrence of these episodes was more abundant on the western regions of the Iberian Peninsula than on the eastern regions (Figure 5.37). This pattern is opposed to the behaviour of the mean PM levels generally higher over the eastern flank. The maximum frequency of occurrence of Atlantic situations was registered in the northwestern region (261 days per year, Figure 5.37) while the minimum in the southeastern area (115 days per year, Figure 5.37).

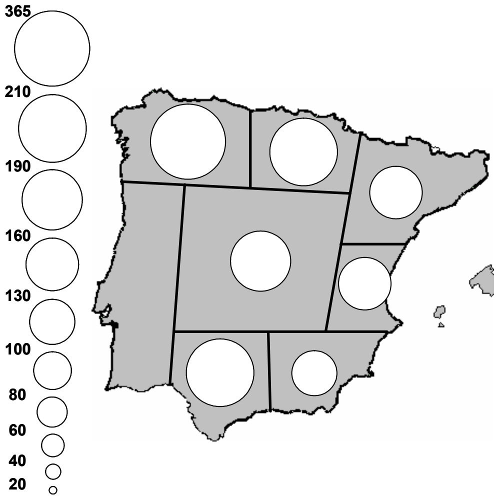


Figure 5.37. Mean annual number of days with Atlantic advection in 7 geographical regions of the Iberian Peninsula.

Although the frequency of occurrence of Atlantic episodes is high throughout all the year in all regions, a seasonal variation can be observed (Figure 5.38). In general, there was a very high incidence of Atlantic episodes in autumn. In summer, the frequency of occurrence of Atlantic events was relatively lower. This was clear in the eastern and southern regions but not as clear in the north and northwest where Atlantic episodes were also common in summer. In winter, the occurrence of Atlantic episodes is high and in spring somewhat lower.

With respect to the two transport scenarios, the seasonality of AZH-NAtD events was identical to the seasonality of Atlantic episodes. AD(ATL) episodes were scarce but more frequent in autumn, winter and spring than in summer.

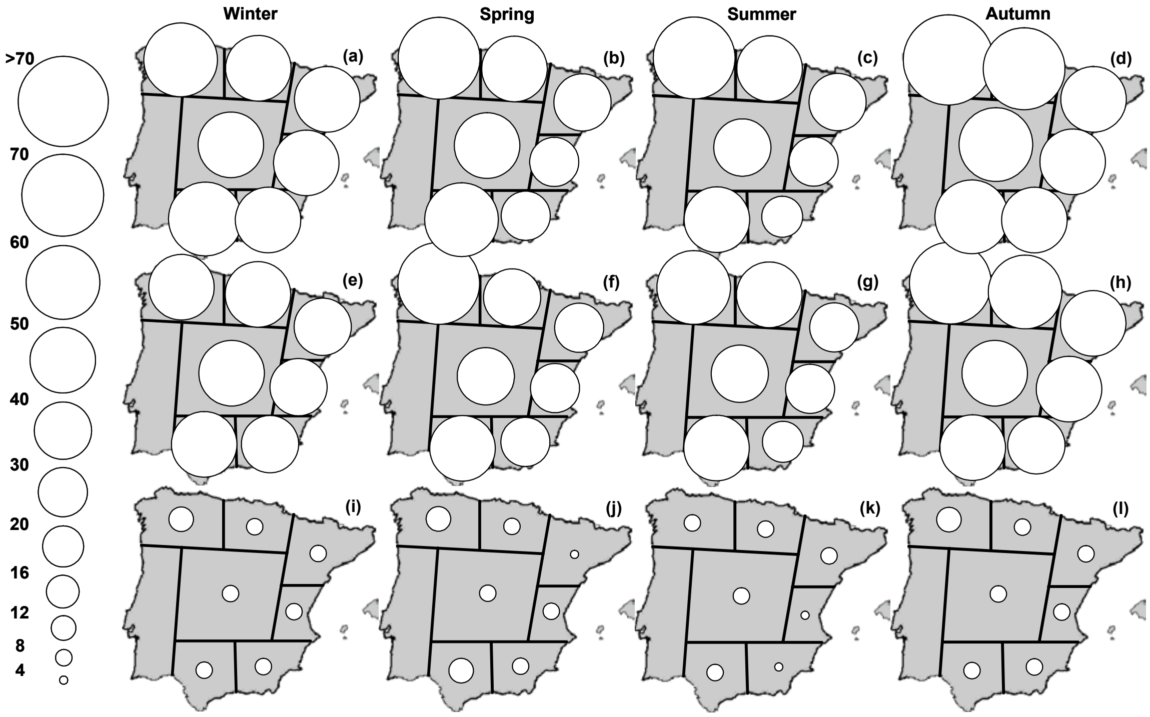


Figure 5.38. Mean seasonal number of days with Atlantic advection in 7 geographical regions of the Iberian Peninsula. The standard periods of January-March (winter), April-June (spring), July-September (summer) and October-December (autumn) were used. The Atlantic (a-d), AZH-NAtD (e-h) and AD(ATL) (i-l) scenarios are distinguished.

The persistency of the Atlantic events could be described with the mean duration of the episodes. However, the proportion of Atlantic episodes with more than 7 days can be also informative. In Figure 5.39, these two variables are presented. On average, Atlantic episodes had durations of 6 days in the northwest, 5 days in the north and the southwest and 4 days in the remaining regions. The probability for an Atlantic event to last more than a week was calculated. The proportion of long events (more than 7 days) is also clearly higher in the northwest (30% of the episodes) than in the other regions. In the north and the southwest this proportion was around 20%, in the northeast and the centre slightly above 15% and in the other two regions (the east and the southeast) slightly above 10%.
The mean PM levels recorded at the regional background stations during episodes of transport of Atlantic air masses over the Iberian Peninsula were low (Figure 5.40). The effect of the rain in washing out the atmosphere may account for this fact since precipitation is very common when air fronts cross the Iberian Peninsula during Atlantic events. Moreover, the arrival of the relatively clean Atlantic air masses results in a decrease of PM levels by the effect of renovation of air masses. In these circumstances, the mean PM levels during Atlantic events could be attributed to local or regional contributions. In this manner, the stations with the highest local/regional contributions for TSP were observed in the east and south of Iberia (means from 16 to 34 µg m^{-3}). For the rest of Iberia the mean TSP levels during Atlantic events ranged from 11 to 16 µg m^{-3}. For PM10, most of the stations registered means from 7 to 10 µg m^{-3} (in the centre of Iberia) or 10 to 15 µg m^{-3} (in the north, east and south of the Iberian Peninsula). Only in Cabo de Creus, the mean PM10 levels during Atlantic episodes reached values above these ranges (18 µg m^{-3}). The mean PM2.5 levels during Atlantic episodes were uniform in all the stations (between 5 and 9 µg m^{-3}) with the exception of Cabo de Creus where these reached 11 µg m^{-3}.

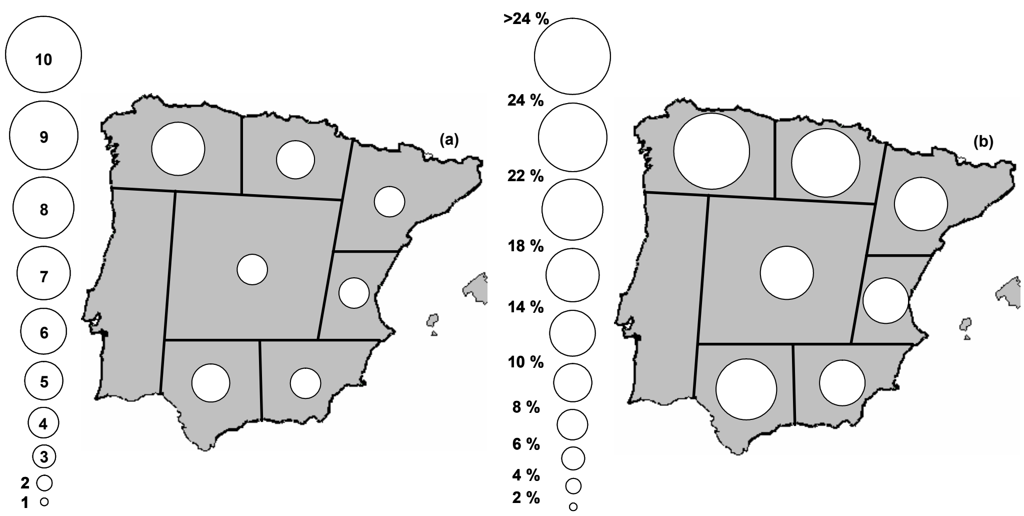


Figure 5.39. Mean duration of Atlantic episodes (a) and proportion of Atlantic episodes with more than 7 days (b) in 7 geographical regions of the Iberian Peninsula in 1998-2003.

As shown in Figure 5.40, the two transport scenarios defined for Atlantic transport had different impact on PM levels. As the majority of the Atlantic episodes corresponded to AZH-NAtD situations, the mean PM levels recorded at the regional background stations during this scenario were approximately the same described in the previous paragraph. This situation changes for AD(ATL) because the mean PM levels recorded during these episodes were lower in all the stations and size ranges. During these episodes mean TSP levels varied in the ranges 7-14 µg m^{-3} in the centre and northwest and 13-20 µg m^{-3} in the rest of the stations with the exception of Cabo de Creus (31 µg m^{-3}). In PM10 the lowest levels during AD(ATL) events were recorded in the centre (5-7 µg m^{-3}) while in the rest of the stations the mean levels ranged from 8 to 10 µg m^{-3}. Only in Cabo de Creus mean PM levels reached high levels (19 µg m^{-3}). In PM2.5 minimal levels were recorded (below 5 µg m^{-3}) with the exception of the stations in the northeast (up to 11 µg m^{-3} in Cabo de Creus).

Combining information on the mean annual occurrence and the mean PM levels recorded during a certain episode, the impact index (II) of that episode was obtained. II is then the weight of that episode on the annual mean PM levels and can it be expressed as a percentage of the annual mean PM level.

The II of the Atlantic episodes was high in all the regions but not because of the high mean PM levels recorded at the ragional background stations during these episodes but because of the high frequency of occurrence of these situations. The II of the Atlantic events were 50% in the northwest, above 40% in the north and southwest and above 30% in the northeast and the centre. In the east and southeast the weight of Atlantic episodes ranged from 20 to 30% (Figure 5.41).

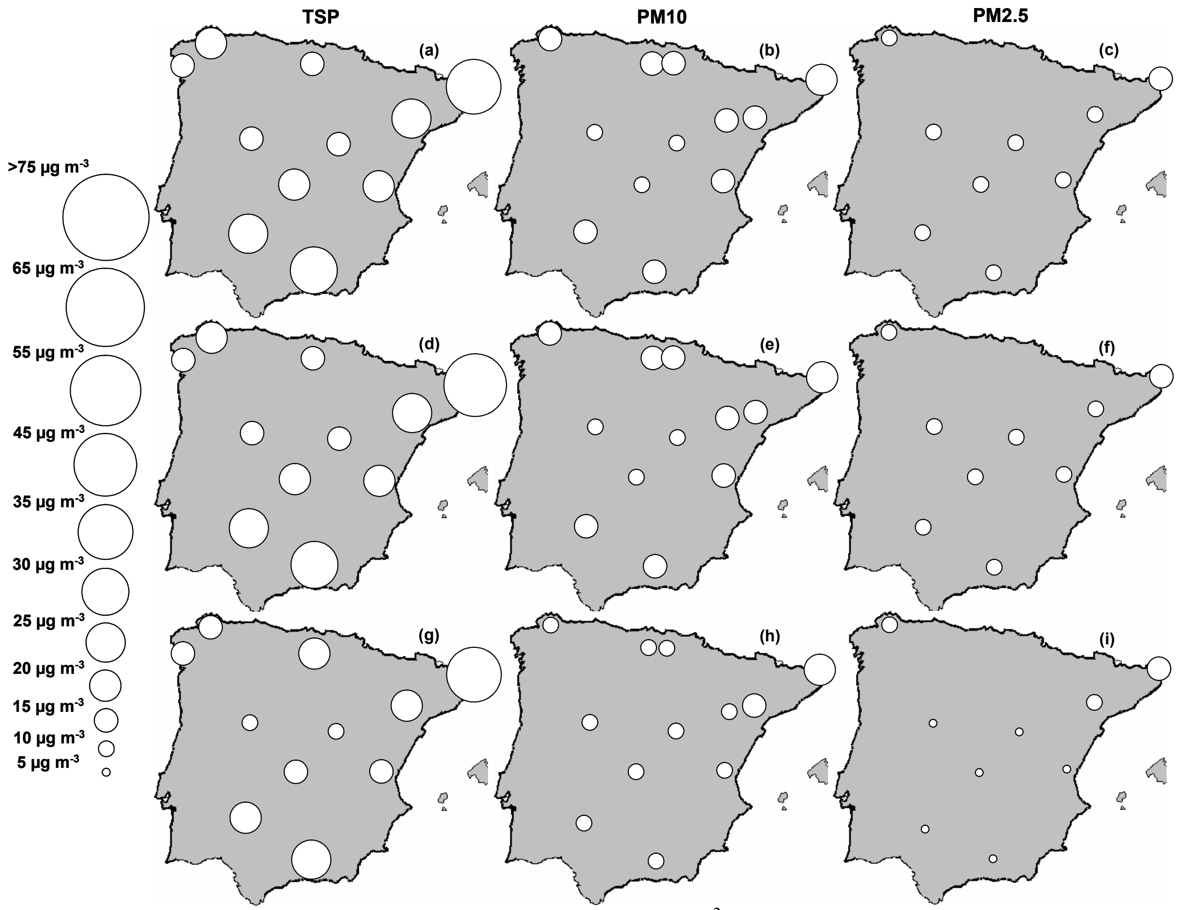


Figure 5.40. Mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations during Atlantic episodes. This figure shows the mean PM levels recorded during Atlantic (a-c), AZH-NAtD (d-f) and AD(ATL) episodes (g-h).

The frequency of occurrence of AZH-NAtD was high while the frequency of occurrence of AD(ATL) was very low. This explains the difference in weight between these two scenarios. The weight of AD(ATL) episodes only reached values slightly above 5% in TSP in the north and northeast. In general, the weight of AZH-NAtD scenario was above 20% in most regions and for all the size ranges (Figure 5.41). The impact of these events is higher in the northwest, north and southwest than in the rest of the regions.

5.8.2. African episodes

The African dust outbreaks occurred over the Iberian Peninsula under four different meteorological scenarios: a) when an anticyclone was present at surface level over northern Africa and the Iberian Peninsula (NAH-S scenario), b) when a depression developed over the Atlantic Ocean opposite the Portuguese or the Moroccan coasts (AD(NAF) scenario), c) when a depression was located over northern Africa or the Mediterranean (NAD scenario), and d) when the thermal low developed in the warm season over northern Africa and/or the Iberian Peninsula owing to the intense heating of the surface and an anticyclone located at upper levels of the troposphere (>1500 m) forced the transport of dust (NAH-A scenario).

As shown in Figure 5.42, there is a clear gradient in the frequency of occurrence of dust outbreaks from southeast to northwest. The mean PM levels recorded at regional background sites showed a similar gradient. In the northwest a mean of 30 days per year was registered while in the southeast this mean reached 96 days per year (not far from the 115 days with Atlantic advection per year).

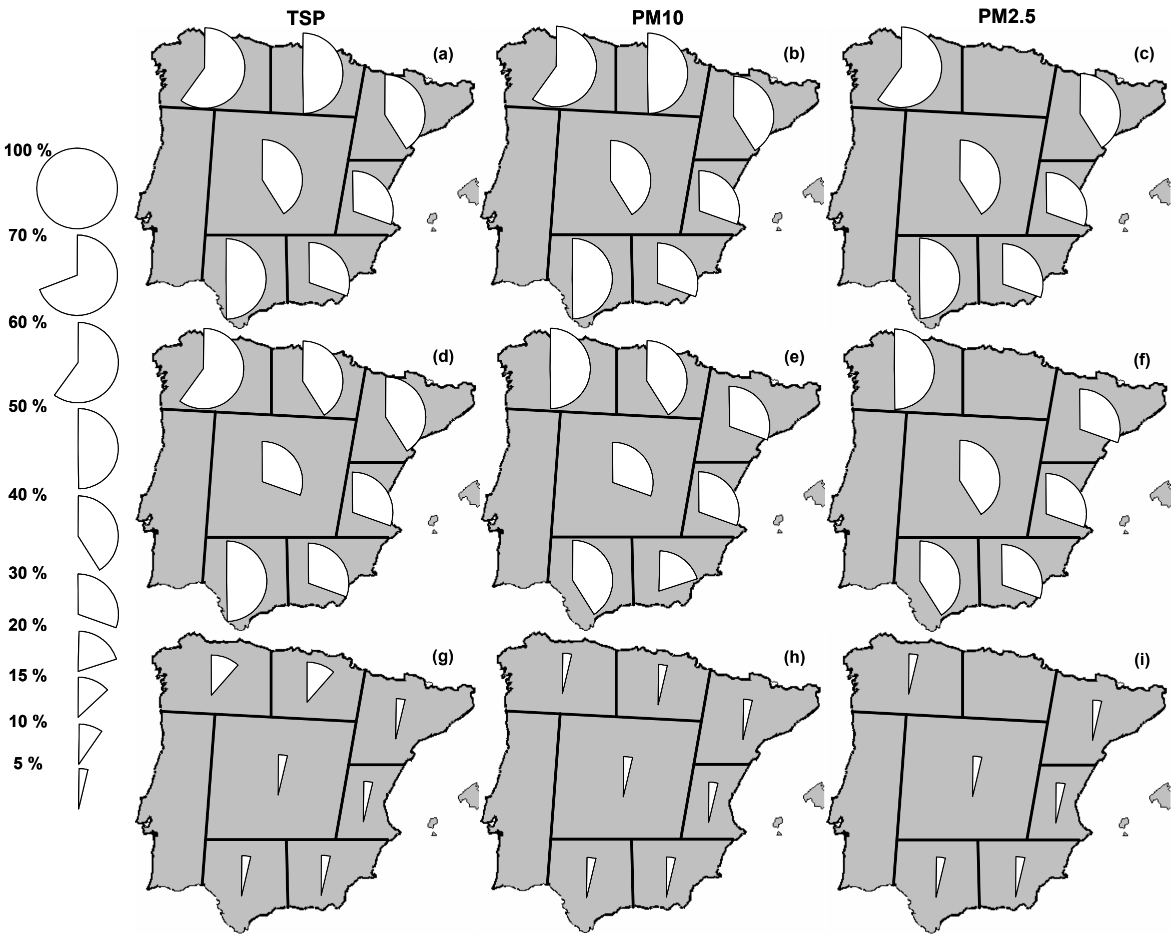


Figure 5.41. Relative impact (in %) of Atlantic (a-c), AZH-NAtD (d-f) and AD(ATL) episodes (g-i) on mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations in the Iberian Peninsula.

The African dust outbreaks occurred over the Iberian Peninsula in all the seasons of the year although in autumn, the frequency of occurrence was lower than in the other seasons. In late spring and summer the frequency was maximum (Figure 5.43).
The occurrence of the different transport scenarios followed a marked seasonality (Figure 5.43). NAH-S situations occurred almost uniquely in winter and resulted in an important proportion of the African events in the western flank of the Iberian Peninsula. AD(NAF) situations practically did not occur in summer and were relatively frequent in winter and autumn. In spring some AD(NAF) situations occurred especially over the eastern Iberian Peninsula. As AD(NAF) events, NAD episodes practically did not occur in summer. During the rest of the year these episodes occurred with a similar seasonal frequency (somewhat superior in spring) although it was slightly higher over the southeast than in the other regions. NAH-A episodes only occurred from late spring to early autumn but with a very high frequency from June to September. These were the most frequent African transport scenarios in all the regions although the proportion of these situations among the total number of African situations was considerably higher in the south and east of the Iberian Peninsula than in the northwest.

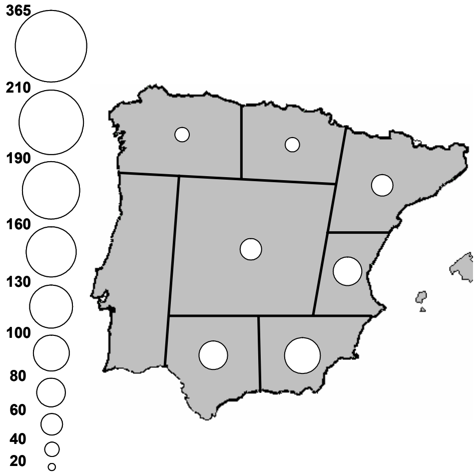


Figure 5.42. Mean annual number of days with African advection in 7 geographical regions of the Iberian Peninsula.

The mean duration of the African events was of the same order in all the regions of the Iberian Peninsula (3 days) with the exception of the southeast with 4 days (Figure 5.44). African episodes with length above 7 days were not frequent although in the southeast 9% of the African events lasted more than a week. This proportion decreased towards the north and to the west. Thus, in the north and northeast only 1 and 3% and in the rest of the regions the proportion of long African events ranged from 4 to 6%.
The mean PM levels recorded during African dust outbreaks in regional background stations of the Iberian Peninsula were considerably high for all size ranges. During African events, the mean TSP and PM10 levels ranged from 29 to 45 µgTSP m^{-3} and 22 to 28 µgPM10 m^{-3} in all the stations with the exception of Víznar (62 µgTSP m^{-3}, 35 µgPM10 m^{-3}). This station is located close to the African Continent. With respect to PM2.5, the mean levels ranged from 11 to 18 µg m^{-3} recording the highest levels in the northwest, northeast and southwest. Conversely to TSP and PM10, in PM2.5 the levels in Víznar during dust outbreaks were comparable to those recorded in the rest of stations in Iberia (Figure 5.45).

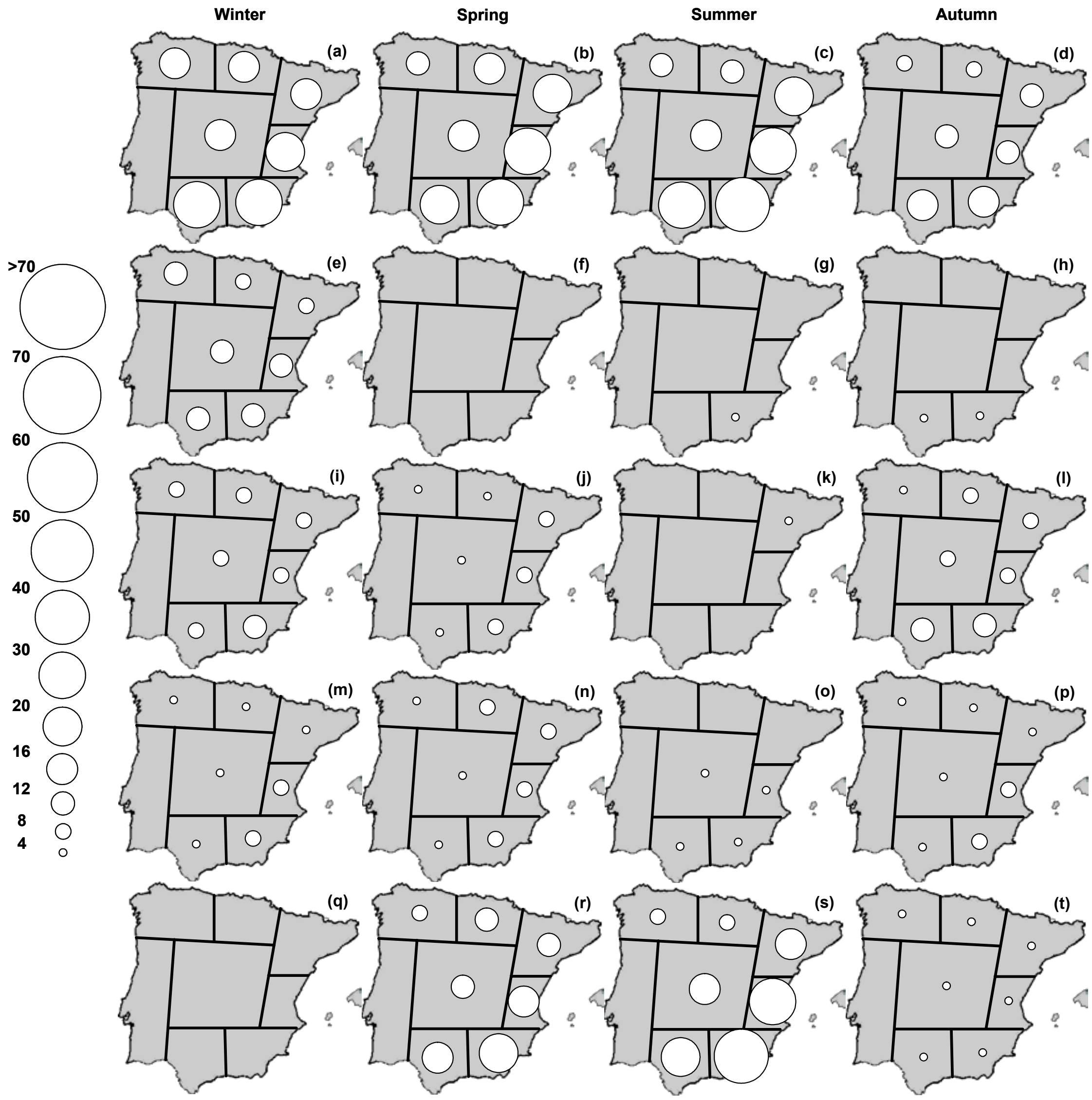


Figure 5.43. Mean seasonal number of days with African advection in 7 geographical regions of the Iberian Peninsula. The standard periods of January-March (winter), April-June (spring), July-September (summer) and October-December (autumn) were used. The African (a-d), NAH-S (e-h), AD(NAF) (i-l), NAD (m-p) and NAH-A (q-t) scenarios are distinguished.

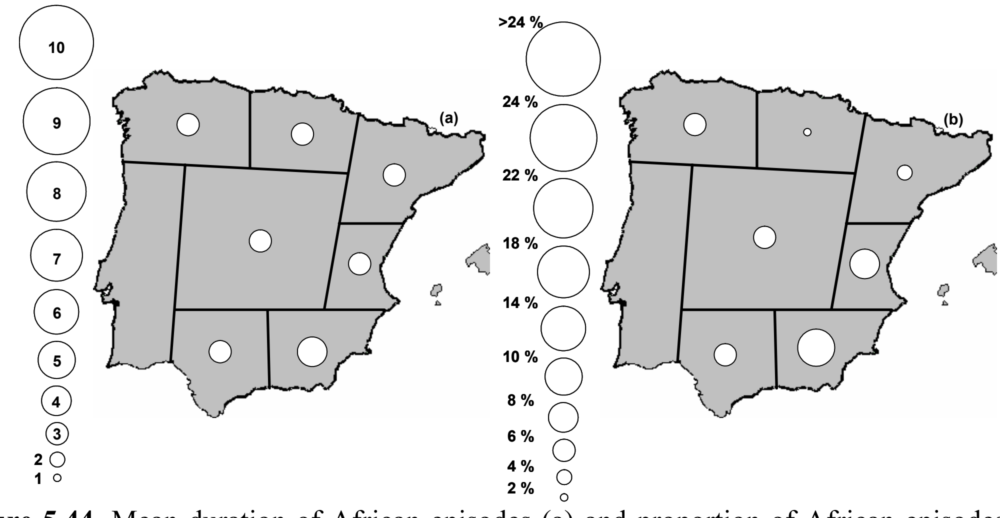


Figure 5.44. Mean duration of African episodes (a) and proportion of African episodes with more than 7 days (b) in 7 geographical regions of the Iberian Peninsula in 1998-2003.

The African transport scenario which generally gave rise to the highest mean PM levels was NAH-A (mean levels in the ranges 29-81 µgTSP m^{-3}, 24-42 µgPM10 m^{-3}, 14-25 µgPM2.5 m^{-3}, Figure 5.45) with the highest mean levels in Víznar (southeast). These episodes mainly occur from late spring to early autumn so, apart from the high loads of mineral aerosols in the African air masses, these high mean PM levels were reached owing to the regional contribution consisting in secondary aerosols arising from the photochemical transformation of gaseous precursors. During NAH-A situations the African plumes travel at high altitudes (>1500 m.a.s.l.) and the dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is distributed and affects the sampling stations. The formation of the secondary particles is enhanced during NAH-A situations because, at surface, a low pressure gradient remains causing lack of advective conditions. In these circumstances, the lower air masses are hardly renovated and the aging and recirculation of contaminated air masses commonly occur. This is particularly common over the eastern Iberian Peninsula owing to the orographic conditions (Millán et al., 1997). Furthermore, during NAH-A episodes, precipitation is reduced and re-suspension of soil material by convection is enhanced. Also during NAH-S events mean PM levels were high (mean levels in the ranges 22-48 µgTSP m^{-3}, 16-35 µgPM10 m^{-3}, 8-20 µgPM2.5 m^{-3}) with the highest TSP and PM10 mean levels in Víznar and the highest PM2.5 mean levels in Els Torms. The lowest mean PM levels during NAH-S episodes were recorded over the centre of the Iberian Peninsula. The low rainfall regime associated with these events gave rise to these high PM levels. The higher rain frequency associated with AD(NAF) and NAD scenarios resulted in lower mean PM levels when compared with NAH-A and NAH-S. During AD(NAF) mean PM levels varied in the following ranges: 17-45 µgTSP m^{-3}, 16-25 µgPM10 m^{-3}, 8-15 µgPM2.5 m^{-3}. During NAD events the mean PM levels ranged in 21-45 µgTSP m^{-3}, 16-25 µgPM10 m^{-3}, 9-15 µgPM2.5 m^{-3} (Figure 5.45).

Combining information on the mean annual occurrence and the mean PM levels recorded during a certain episode, the impact index (II) of that episode was obtained. II is then the weight of that episode on the annual mean PM levels and can it be expressed as a percentage of the annual mean PM level.

The weight of African episodes on annual mean PM levels recorded in regional background stations of the Iberian Peninsula is considerably higher in the south and east than in the north and west. Thus, the weight of African events ranged from values below 15% in TSP and PM2.5 and below 20% in PM10 in the northwest up to values above 50% in TSP and PM10 and above 40% in PM2.5 in the southeast (Figure 5.46).

Among the four transport scenarios NAH-A, owing to the important impact of this scenario on PM levels and its relatively high frequency of occurrence, had the highest weight in all regions (from below 10% in the northwest up to values above 20% in the southeast). The other three scenarios did not reach very high weights (in most regions below 5% and in no case above 15%, Figure 5.46).

5.8.3. European episodes

The transport of European air masses over the Iberian Peninsula was detected under two different synoptic situations. When an anticyclone covered the European continent or the north Atlantic Ocean (EUH scenario) and when a depression developed over the Mediterranean (MD scenario).

The frequency of occurrence of European air mass transport situations shows a clear gradient from south to north-northeast (Figure 5.47). A mean of 12 days per year was registered in the southwest and a mean of 60 days per year was registered in the northeast. The situations of transport of European air masses over the Iberian Peninsula occurred typically in the cold part of the year (in Figure 5.48). However, although European events were registered in spring and summer, the seasons with the highest frequency were autumn and winter. EUH situations were clearly more frequent in winter than in the other three seasons. MD situations, in general less frequent than EUH situations, occurred more frequently in spring and autumn.

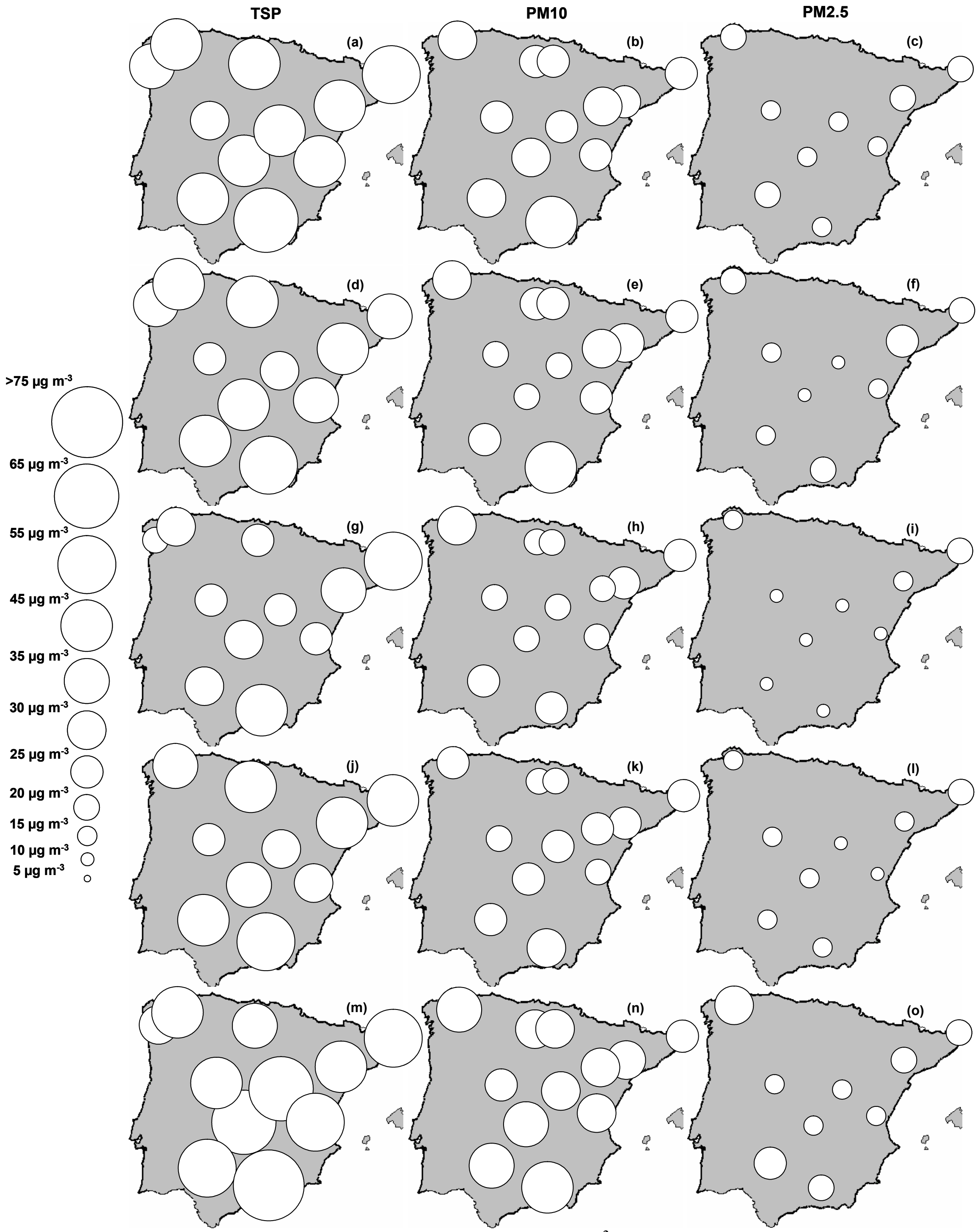


Figure 5.45. Mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations during African episodes. This figure shows the mean PM levels recorded during African (a-c), NAH-S (d-f), AD(NAF) (g-i), NAD (j-l) and NAH-A episodes (m-o).

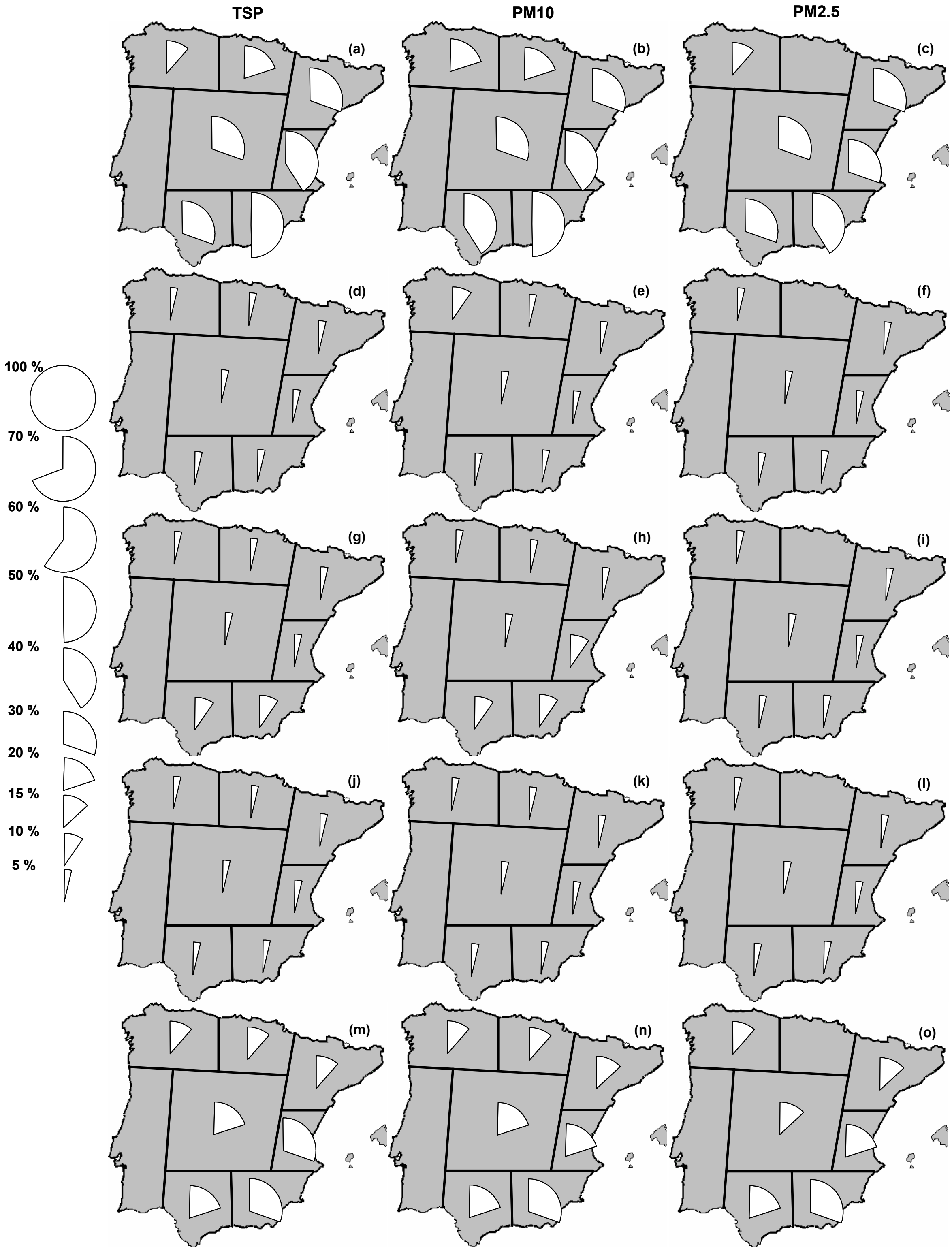


Figure 5.46. Relative impact (in %) of African (a-c), NAH-S (d-f), AD(ATL) (g-i), NAD (j-l) and NAH-A episodes (m-o) on mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations in the Iberian Peninsula.

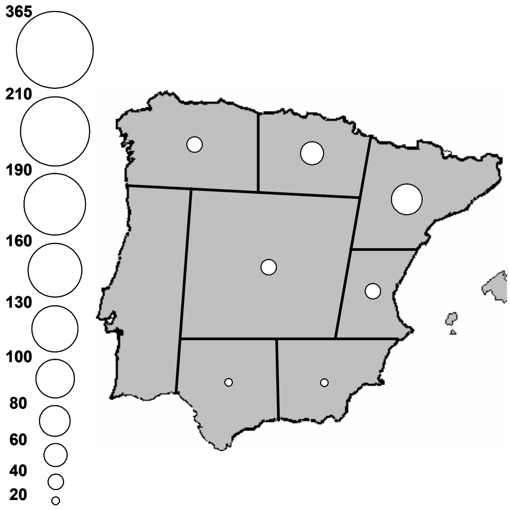


Figure 5.47. Mean annual number of days with European advection in 7 geographical regions of the Iberian Peninsula.

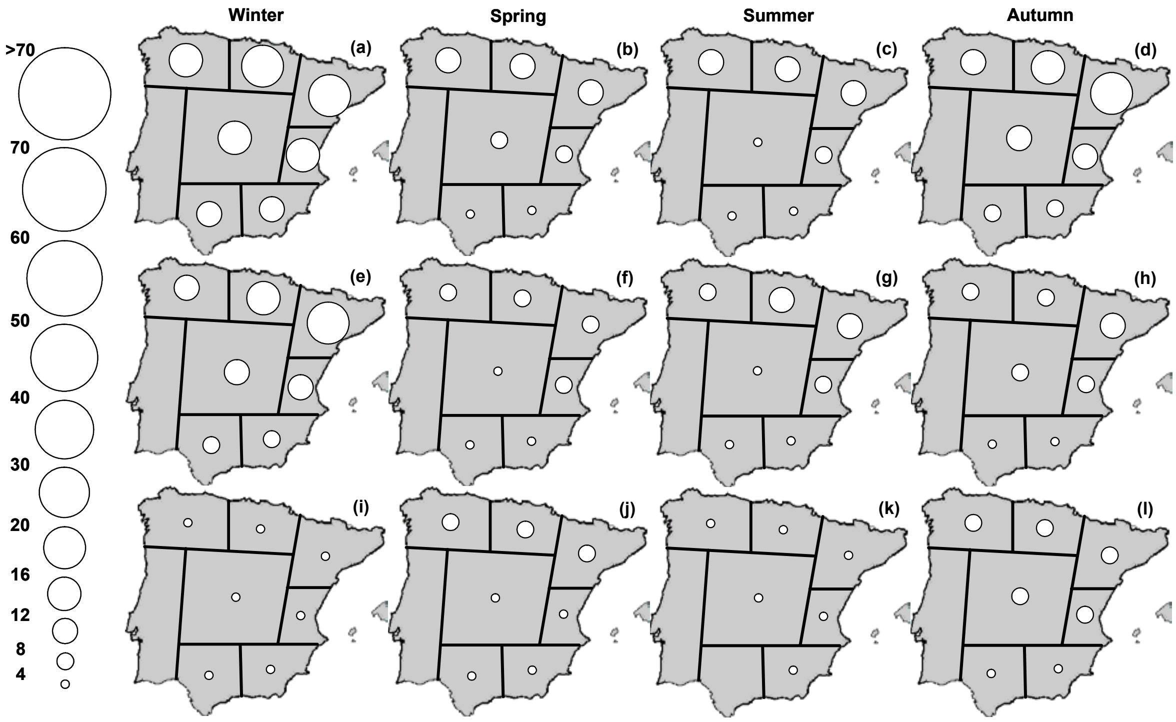


Figure 5.48. Mean seasonal number of days with European advection in 7 geographical regions of the Iberian Peninsula. The standard periods of January-March (winter), April-June (spring), July-September (summer) and October-December (autumn) were used. The European (a-d), EUH (e-h) and MD (i-l) scenarios are distinguished.

The mean duration of European events reached 4 days in the centre, 2 days in the southwest and 3 days in the rest of the regions (Figure 5.49). The proportion of European episodes with duration >7 days ranged from 4 to 8% although in the southwest and southeast of the Iberian Peninsula the proportion of "long European events" was 0%.

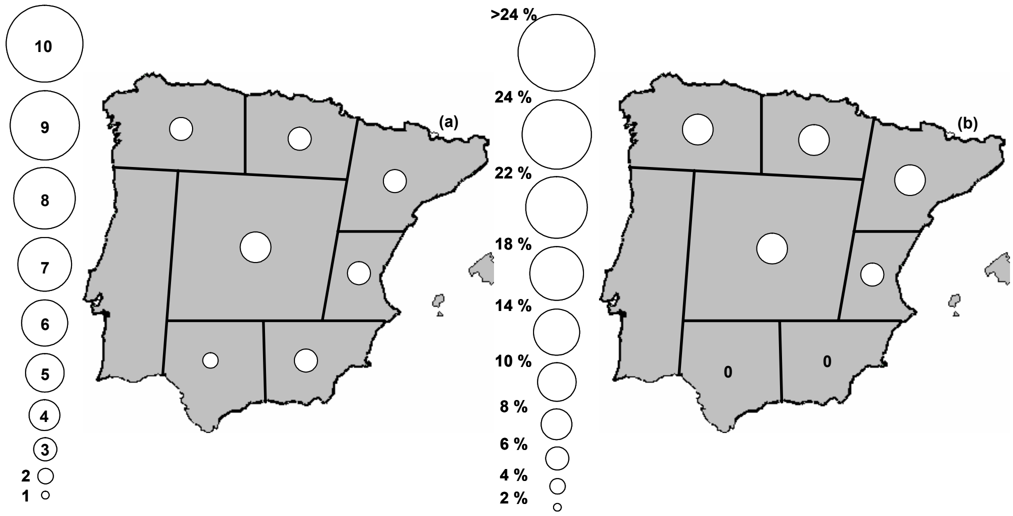


Figure 5.49. Mean duration of European episodes (a) and proportion of European episodes with more than 7 days (b) in 7 geographical regions of the Iberian Peninsula in 1998-2003.

The mean PM levels recorded at regional background stations during European episodes were moderately high in the northern regions and moderately low in the rest. The impact of these episodes on PM levels is not clear although, the majority of the European transport episodes occurred in winter and autumn when local/regional contributions in regional background sites are minimal owing to the low dispersive conditions of the atmosphere and the low rate of soil resuspension. However, at least in some particular cases an increase in background PM levels in the Iberian Peninsula during European events was evident. The mean PM levels recorded during European events were moderately higher than the annual mean PM levels in the northwest and north (21-29 µgTSP m^{-3}, 14-21 µgPM10 m^{-3} and 15 µgPM2.5 m^{-3}), of the same order of the annual mean PM levels in the northeast and centre (13-43 µgTSP m^{-3}, 10-25 µgPM10 m^{-3} and 7-16 µgPM2.5 m^{-3}), and lower than the annual mean PM levels (18-28 µgTSP m^{-3}, 13-15 µgPM10 m^{-3} and 8-10 µgPM2.5 m^{-3}) in the east, southwest and southeast (Figure 5.50). The dispersion and dilution of pollutants in European air masses may explain the lower impact of European episodes on PM levels in the south of Iberia than in the north.
The mean PM levels recorded during EUH events were higher than the annual mean PM levels in the northwest, north, northeast and centre (21-29 µgTSP m^{-3}, 14-21 µgPM10 m^{-3} and 15 µgPM2.5 m^{-3}, Figure 5.50), of the same order in the southwest, in Barcarrota (27 µgTSP m^{-3}, 17 µgPM10 m^{-3} and 12 µgPM2.5 m^{-3}, Figure 5.50) and a lower in the east and southeast (19-34 µgTSP m^{-3}, 14-17 µgPM10 m^{-3} and 8-11 µgPM2.5 m^{-3}, Figure 5.50). MD episodes are more frequently associated with rainfall than EUH. Precipitation produces the washing out of pollutants from the atmosphere and, consequently, a decrease in ambient PM levels. Consequently, the mean PM levels during MD events (ranging in 19-34 µgTSP m^{-3}, 14-17 µgPM10 m^{-3} and 8-11 µgPM2.5 m^{-3}, Figure 5.50) were lower than the annual mean PM levels in all stations.
As a summary, it can be stated that dry European events (EUH) had an impact on PM levels at regional background stations of the northern flank of the Iberian Peninsula. In the rest of the regions the low PM levels associated with European episodes may be attributed to the frequent washing out of the atmospheres during MD events and/or the dispersion and dilution suffered by the pollutants in European air masses in the transect from central Europe to the centre or south of Iberia.

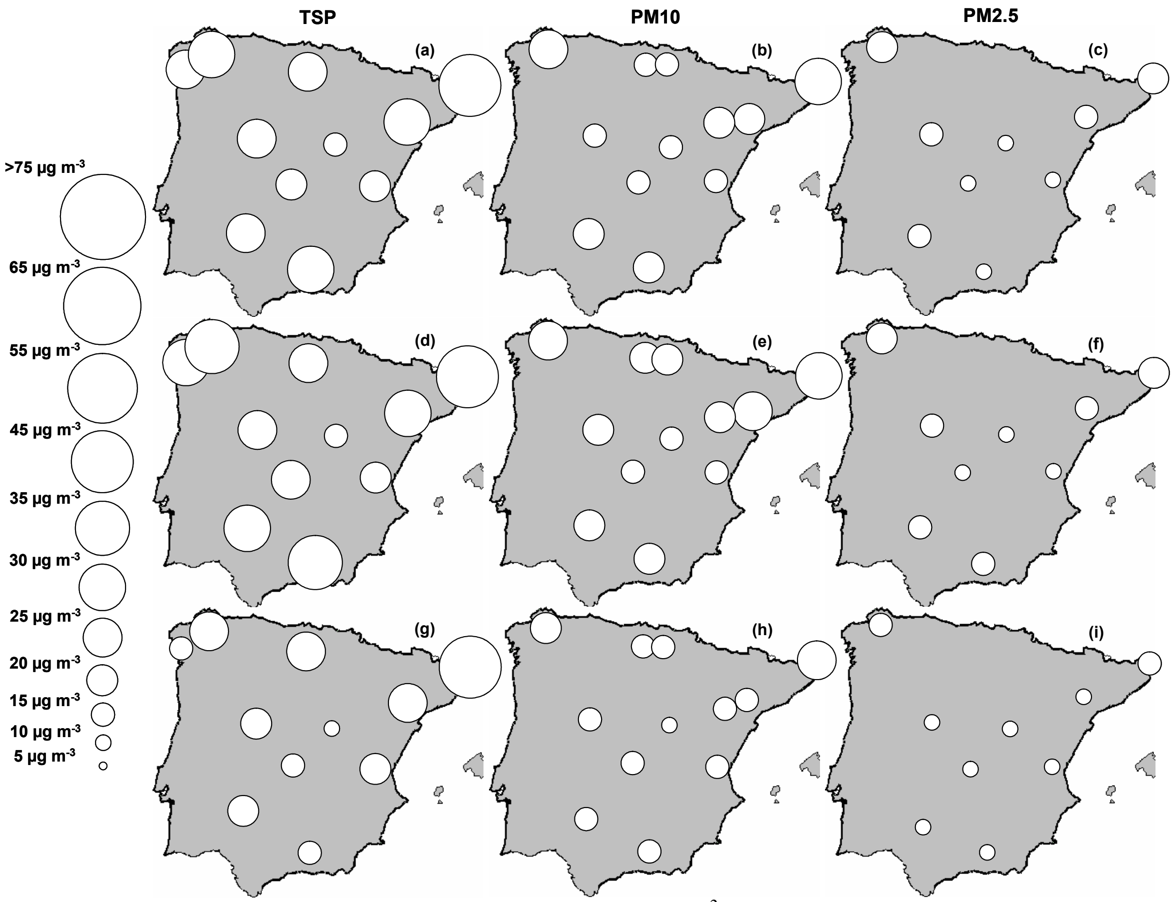


Figure 5.50. Mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations during European episodes. This figure shows the mean PM levels recorded during European (a-c), EUH (d-f) and MD episodes (g-i).

Combining information on the mean annual occurrence and the mean PM levels recorded during a certain episode, the impact index (II) of that episode was obtained. II is then the weight of that episode on the annual mean PM levels, and can it be expressed as a percentage of the annual mean PM level.

As shown in Figure 5.51, the impact of European episodes on annual mean PM levels of regional background stations was moderately high in the north of the Iberian Peninsula (between 15 and 20% in the northwest, north and northeast) and diminished towards the south (between 5 and 10% in the centre and the east and below 5% in the southwest and southeast).

The low frequency of occurrence of MD events and the low mean PM levels recorded during these episodes resulted in very low weights (below 5% in all the regions). EUH events were more frequent and gave rise to moderately high mean PM levels, thus, although the weight of this scenario in the south was below 5% in the rest of the regions the impact reached up to 10-15% in northern regions (Figure 5.51).

5.8.4. Mediterranean episodes

Two synoptic situations cause the transport of Mediterranean air masses over Iberia. Mediterranean episodes occurred when a depression developed over northern Africa or the Mediterranean Sea (NAD-MD scenario) and when an anticyclone covered the European Continent or the Mediterranean Sea (EUH-MH scenario).

The transport of Mediterranean air masses was the least frequent situation among PM events. Annual means from 5 to 17 days were registered in all the regions of Iberia with the exception of the centre where 21 days per year were registered (Figure 5.52).

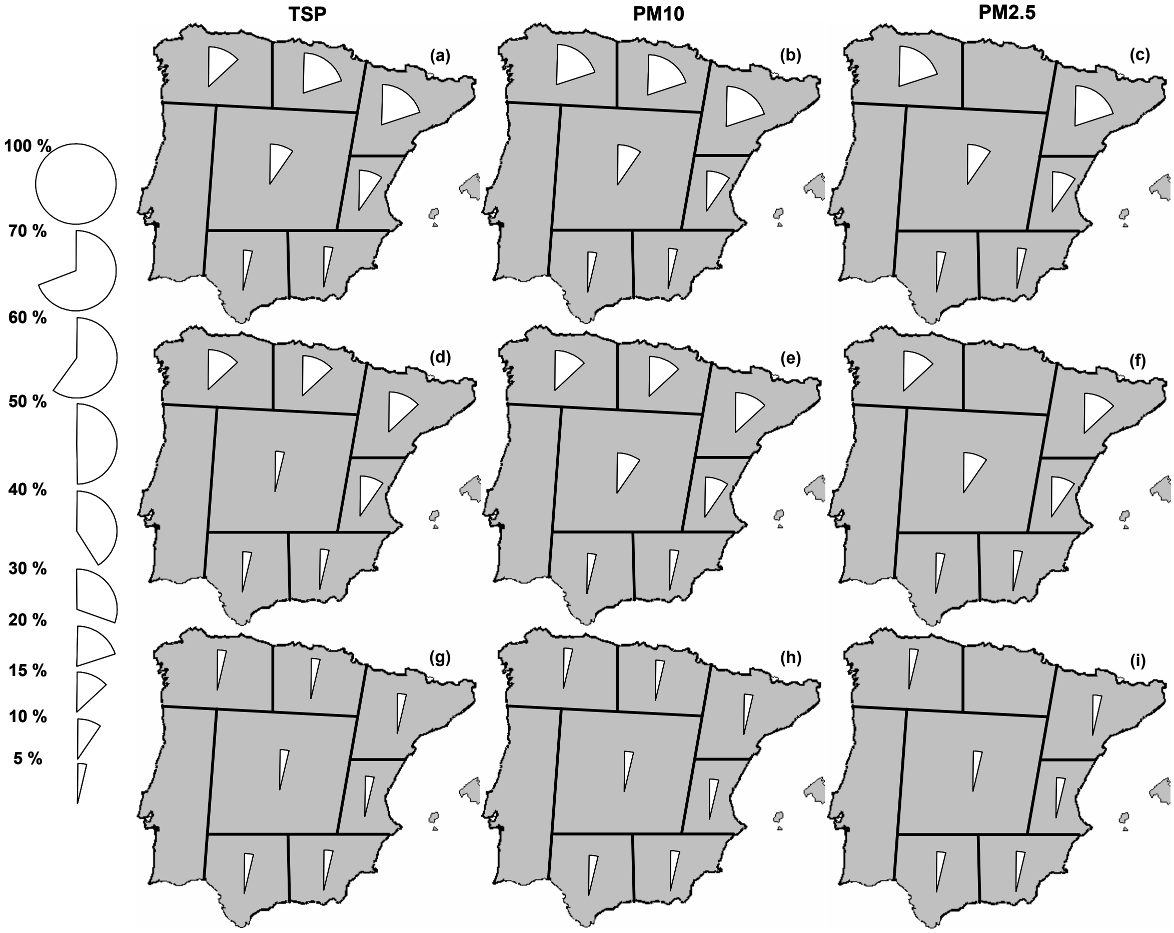


Figure 5.51. Relative impact (in %) of European (a-c), EUH (d-f) and MD episodes (g-i) on mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations in the Iberian Peninsula.

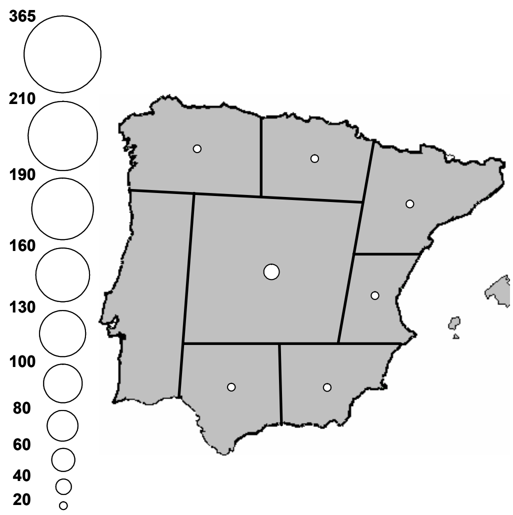


Figure 5.52. Mean annual number of days with Mediterranean advection in 7 geographical regions of the Iberian Peninsula.

The transport of Mediterranean air masses was scarce in all the seasons but especially infrequent in summer. Winter and autumn were the seasons in which Mediterranean episodes occurred with the highest frequency (Figure 5.53). NAD-MD events were rare in all the seasons and EUH-MH episodes were relatively more frequent in winter and autumn than in spring and summer (Figure 5.53).

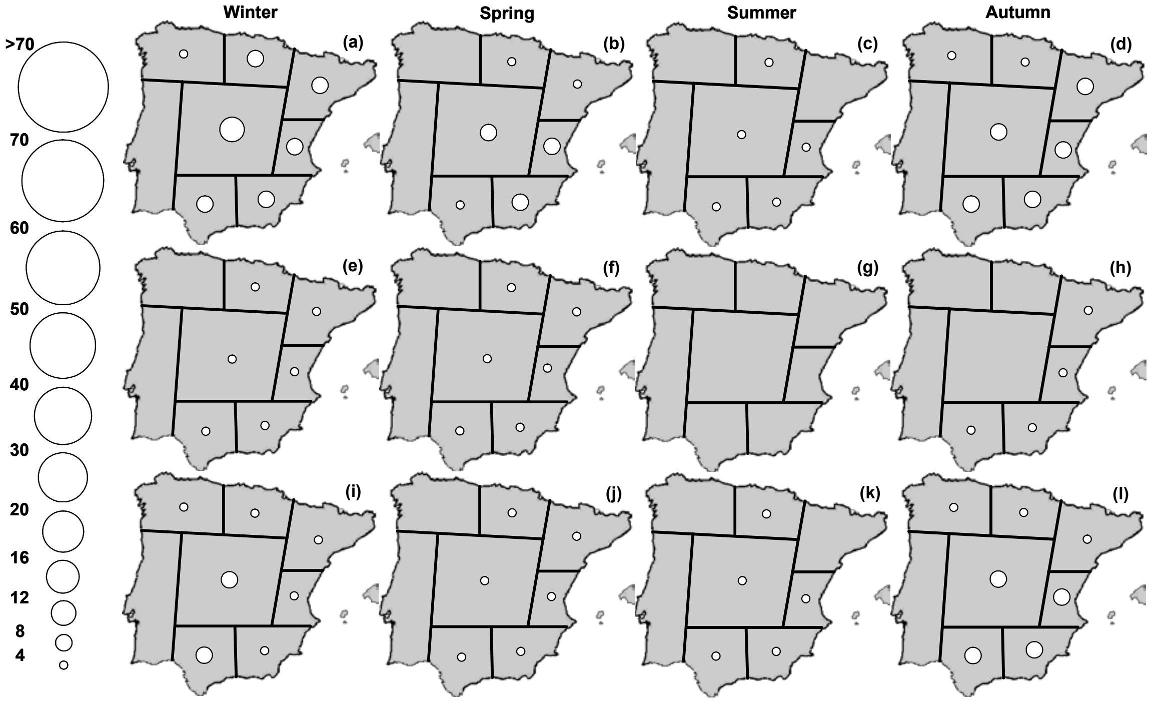


Figure 5.53. Mean seasonal number of days with Mediterranean advection in 7 geographical regions of the Iberian Peninsula. The standard periods of January-March (winter), April-June (spring), July-September (summer) and October-December (autumn) were used. The Mediterranean (a-d), NAD-MD (e-h) and EUH-MH (i-l) scenarios are distinguished.

The Mediterranean events were on average short with mean durations of 2 days per events in all the regions. This was also evident when inspecting the number of "long Mediterranean events" (those with durations above 7 days). In 1998-2003, only in the centre and the north one of these episodes was registered. In the rest of the regions no "long Mediterranean event" occurred (Figure 5.54).

The mean PM levels recorded at regional background stations of the Iberian Peninsula during Mediterranean episodes were low owing to the high frequency of occurrence of rain associated with these episodes and to the relative clean character of the marine air masses. The mean PM levels varied in the ranges: 14-39 µgTSP m^{-3}, 9-24 µgPM10 m^{-3} and 6-16 µgPM2.5 m^{-3} (Figure 5.55). In all the stations these levels were lower than the annual mean PM levels. Thus, the contribution to PM load in regional background stations during Mediterranean episodes was mainly local or regional.

The rainfall regime associated with NAD-MD events was relatively more frequent than with EUH-MH. This resulted in lower mean PM levels during the first scenario than during the latter owing to the effect of the rain scavenging (12-45 µgTSP m^{-3}, 9-28 µgPM10 m^{-3} and 5-13 µgPM2.5 m^{-3} during NAD-MD events and 14-35 µgTSP m^{-3}, 11-22 µgPM10 m^{-3} and 6-16 µgPM2.5 m^{-3} during EUH-MH, Figure 5.55). However, these mean levels were lower than the annual mean PM levels in most of the stations.

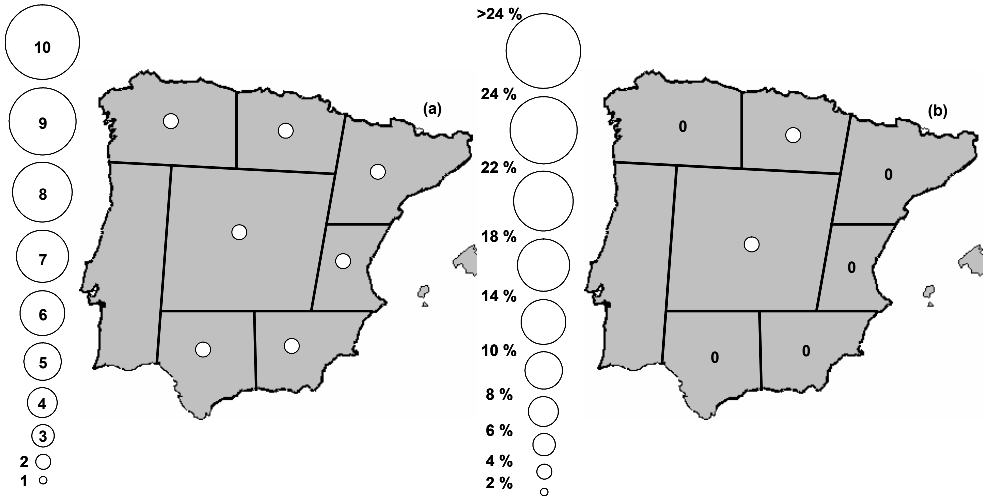


Figure 5.54. Mean duration of Mediterranean episodes (a) and proportion of Mediterranean episodes with more than 7 days (b) in 7 geographical regions of the Iberian Peninsula in 1998-2003.

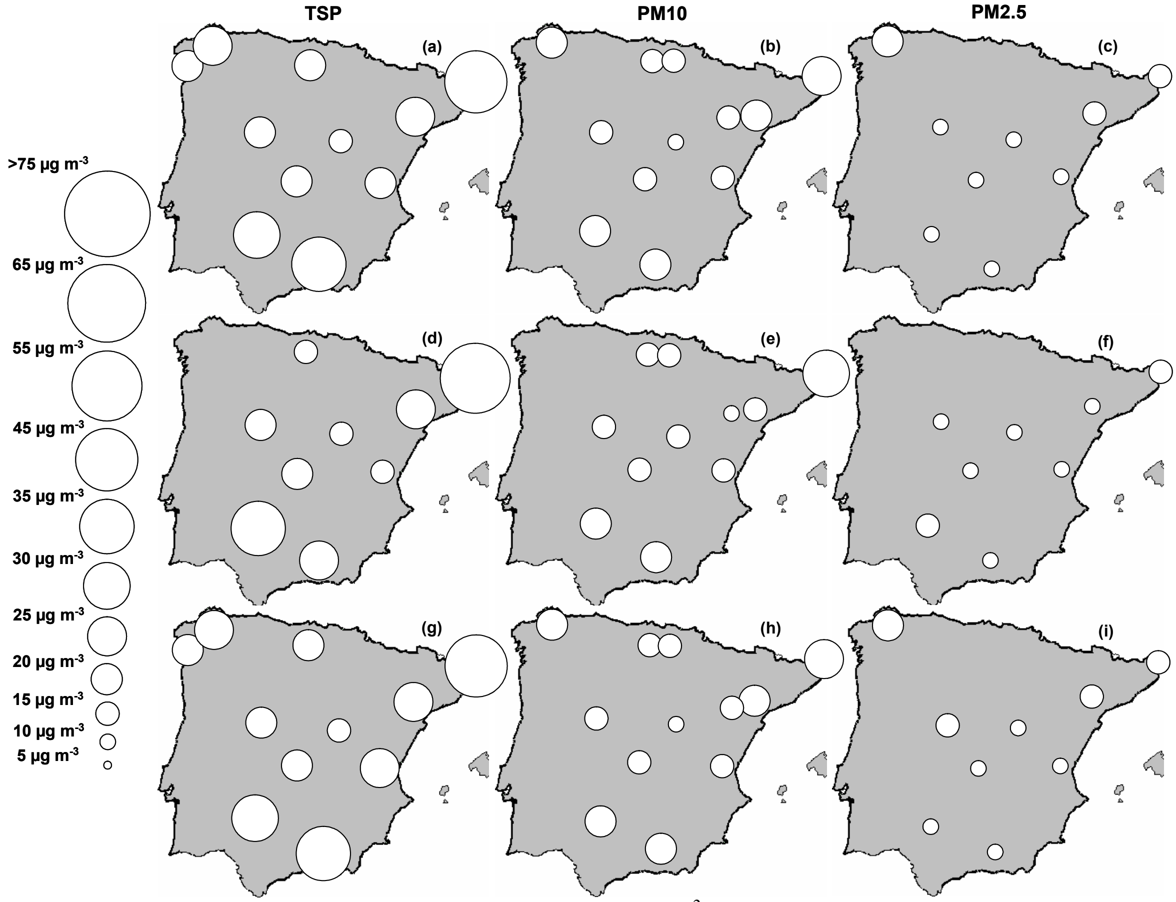


Figure 5.55. Mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations during Mediterranean episodes. This figure shows the mean PM levels recorded during Mediterranean (a-c), NAD-MD (d-f) and EUH-MH episodes (g-i).

Combining information on the mean annual occurrence and the mean PM levels recorded during a certain episode, the impact index (II) of that episode was obtained. II is then the weight of that episode on the annual mean PM levels and can it be expressed as a percentage of the annual mean PM level.

Figure 5.56 shows the very low weight of the Mediterranean episodes on the annual mean PM levels of all the stations in the Iberian Peninsula (in all regions below 6%). This occurs because both the frequency of occurrence and the mean PM levels recorded at regional background sites during these events were low. Both NAD-MD and EUH-MH scenarios had low weights in the annual mean PM levels (in all regions and size ranges below 5%).

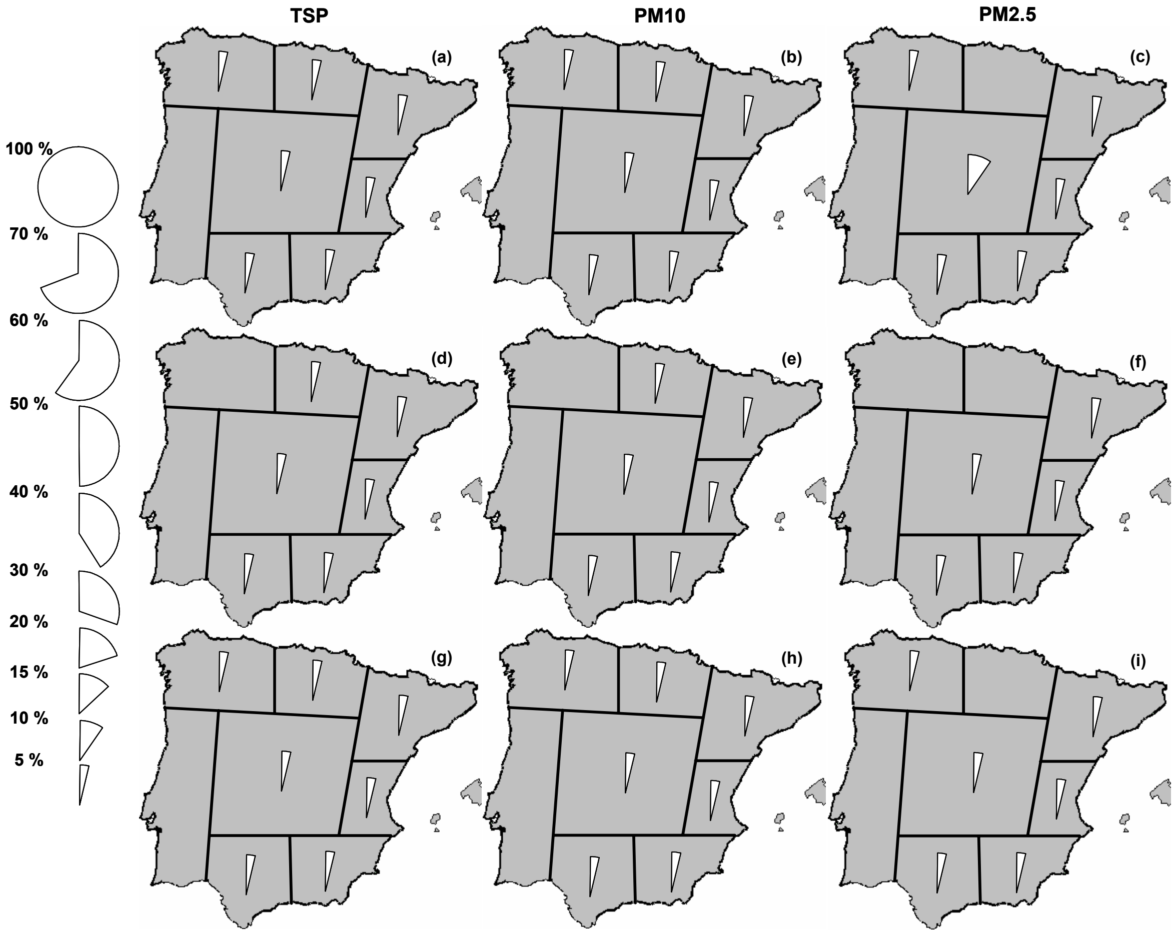


Figure 5.56. Relative impact (in %) of Mediterranean (a-c), NAD-MD (d-f) and EUH-MH episodes (g-i) on mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations in the Iberian Peninsula.

5.8.5. Episodes without dominant advective conditions

The episodes without dominant advective conditions occurred over the Iberian Peninsula in the cold seasons when an anticyclone covered the Iberian Peninsula (WIA scenario) or in the warm seasons under low pressure gradient and the development of the Iberian thermal low owing to the great heating of the surface (ITL scenario).

As shown in Figure 5.57, the situations without dominant advective conditions were less frequent in the northwest, north and southwest (with annual frequencies of 31-57 days) than in the northeast, the centre and the east (with annual means of 82-98 days) and the southeast (with annual mean of 104 days). As for the mean PM levels, there is a frequency gradient from west to east.

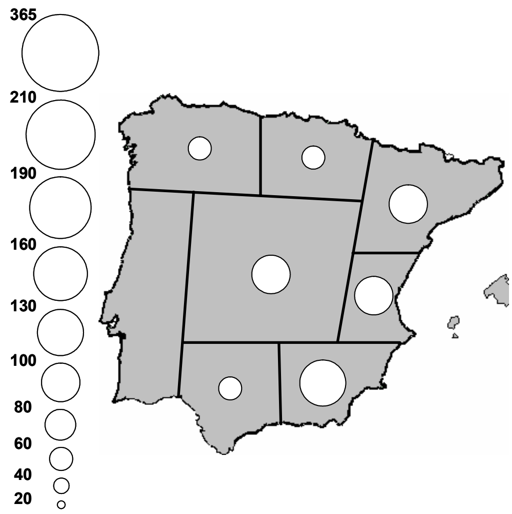


Figure 5.57. Mean annual number of days without dominant air mass advection in 7 geographical regions of the Iberian Peninsula.

The situations without dominant advective conditions occurred in all the seasons of the year. These episodes were less frequent in winter than in the other three seasons while the highest frequency of occurrence of these situations was registered in summer (Figure 5.58).

As shown in Figure 5.58, the seasonality of the two synoptic scenarios giving rise to situations without dominant advective conditions was clear owing to the definition of these scenarios. The ITL episodes were registered basically from late spring to early autumn with a clear maximum frequency in summer. The WIA events practically did not occur in summer while the maximum frequency of occurrence of this scenario was observed in spring (mostly in May) and autumn (mostly in October and December).

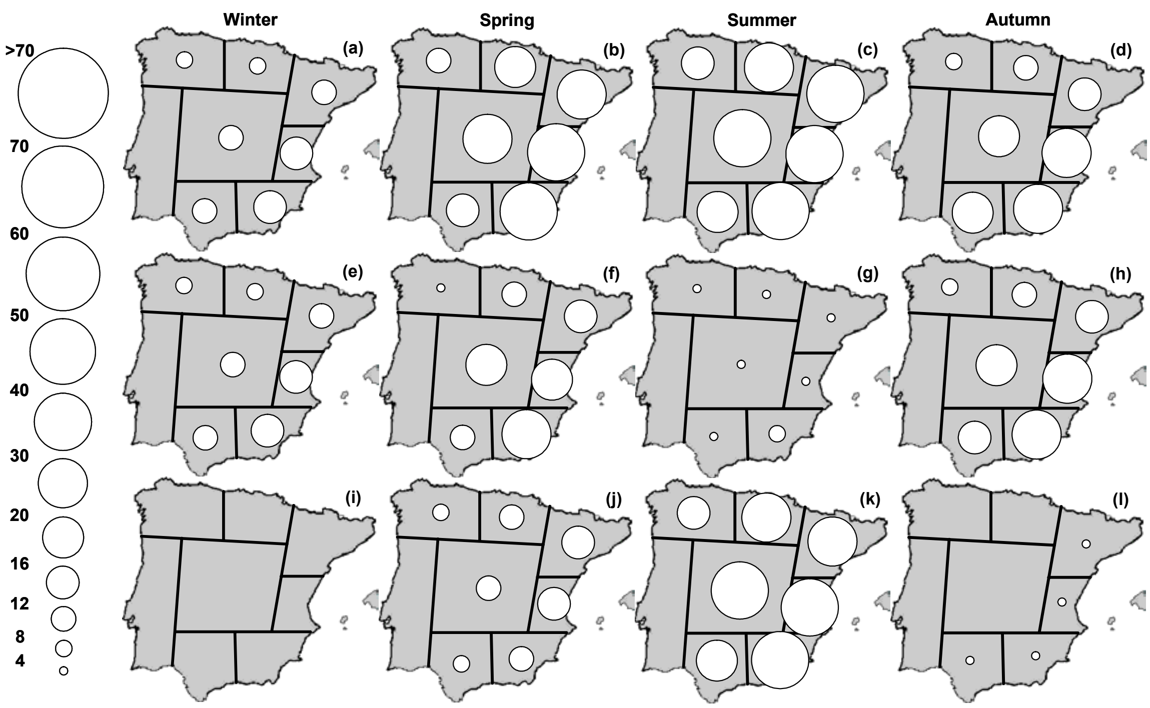


Figure 5.58. Mean seasonal number of days without dominant advective conditions in 7 geographical regions of the Iberian Peninsula. The standard periods of January-March (winter), April-June (spring), July-September (summer) and October-December (autumn) were used. The non advective (a-d), WIA (e-h) and ITL (i-l) scenarios are distinguished.

The mean duration of the episodes without advective conditions was the same in all the regions (3 days). With respect to the proportion of episodes without dominant advective conditions with more than 7 days the minimum was registered in the northwest (2%). The maximum frequency of occurrence of these long events was registered in the centre and the southeast (8-9%) while in the rest of the regions this proportion ranged from 4 to 7% (Figure 5.59).

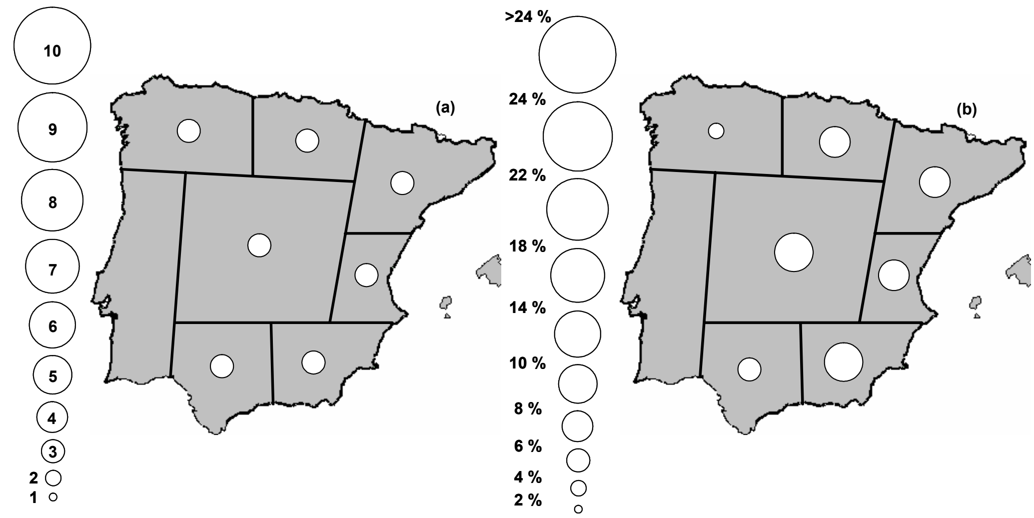


Figure 5.59. Mean duration of episodes without dominant advective conditions (a) and proportion of episodes without dominant advective conditions with more than 7 days (b) in 7 geographical regions of the Iberian Peninsula in 1998-2003.

During episodes without dominant advective conditions the mean PM levels recorded at regional background stations were higher than the annual mean PM levels in all the regions (24-42 µgTSP m^{-3}, 15-23 µgPM10 m^{-3} and 10-17 µgPM2.5 m^{-3}, Figure 5.60). A factor that may account for these high PM mean levels was the low frequency of occurrence of rain associated with episodes without dominant advective conditions.
Apart from the low rainfall regime, during ITL situations, the aging and re-circulation of polluted in air masses (Millán et al., 1997), the high rate of re-suspension or the enhancement of transformation of gaseous precursors into secondary aerosols by the increased photochemistry tend to increase PM levels in regional background stations over the eastern flank of the Iberian Peninsula (Rodríguez et al, 2003) and, as shown in this study, all over the Iberian Peninsula. During WIA episodes, the low vertical growth of the boundary layer especially during the typical development of thermal inversions over industrial/urban sites reduces the anthropogenic contribution of PM in several regional background stations (far from the large emission sources and, in many cases, out of the boundary layer). Thus, during WIA events the mean PM levels in regional background sites (18-32 µgTSP m^{-3}, 10-21 µgPM10 m^{-3} and 7-14 µgPM2.5 m^{-3}, Figure 5.60) were comparable or slightly lower than the annual mean PM levels while during ITL events the mean PM levels (25-54 µgTSP m^{-3}, 19-30 µgPM10 m^{-3} and 11-21 µgPM2.5 m^{-3}, Figure 5.60) were clearly superior to those annual mean PM levels.

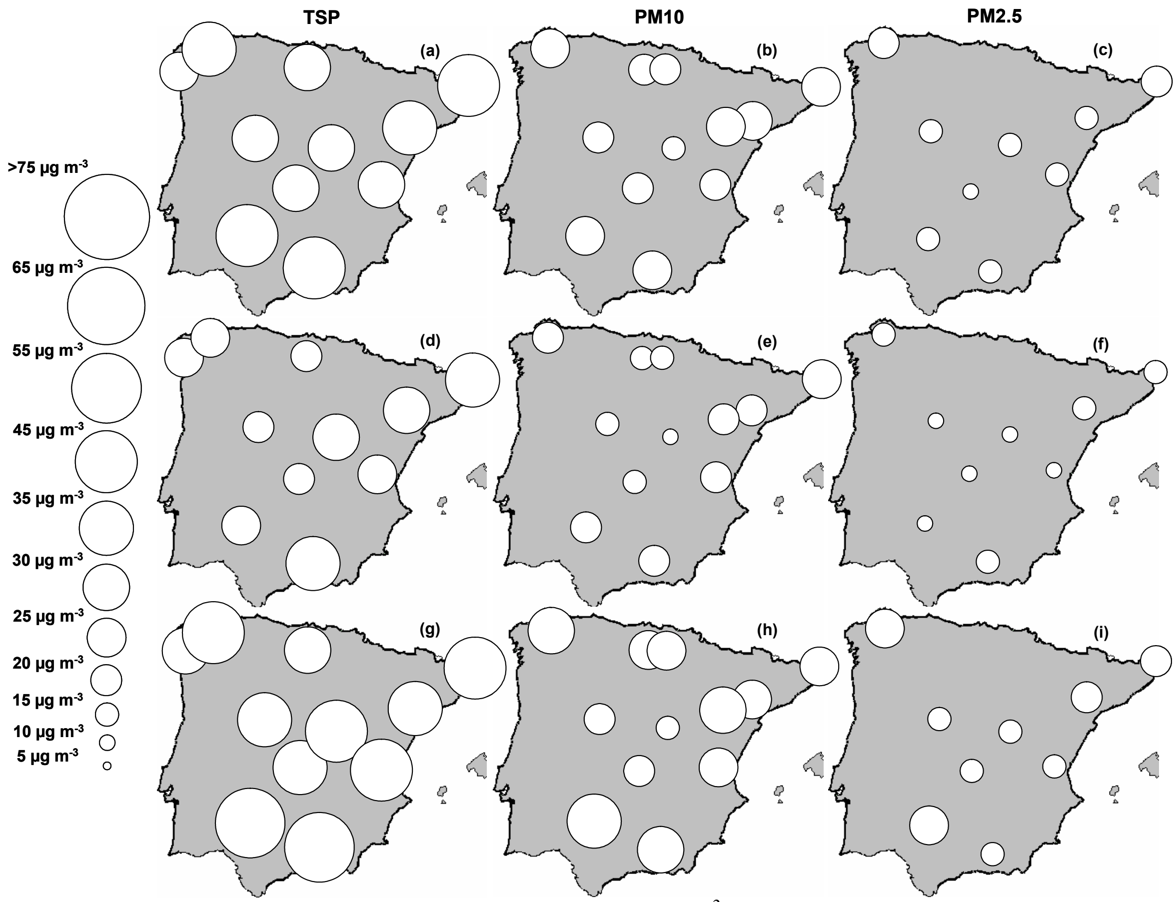


Figure 5.60. Mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations during episodes without dominant advective conditions. This figure shows the mean PM levels recorded during episodes without dominant advective conditions (a-c), WIA (d-f) and ITL episodes (g-i).

Combining information on the mean annual occurrence and the mean PM levels recorded during a certain episode, the impact index (II) of that episode was obtained. II is then the weight of that episode on the annual mean PM levels, and can it be expressed as a percentage of the annual mean PM level.

As the episodes without dominant advective conditions occurred over all regions of the Iberian Peninsula with a relatively high frequency and the mean PM levels associated with these events were moderately high, the weight of the episodes without advective conditions was important in all the regions ranging in 10-15% in the northwest, 15-30% in the southwest, 20-30% in the north and northeast and 20-40% in the centre, east and southeast (Figure 5.61).

Although the proportion of WIA and ITL situations among episodes without prevailing advective conditions was similar in most regions (around 50% each), the clearly higher mean PM levels recorded during ITL episodes resulted in a higher weight of this scenario. The weight of WIA events ranged from values below 5% in the northwest, 5-10% in the north and southwest, 5-15% in the centre and northeast and 10-20% in the east and southeast. The weight of ITL ranged in 5-10% in the northwest, 10-15% in the southwest, 10-20% in the north and northeast and 15-20% in the centre, east and southeast (Figure 5.61).

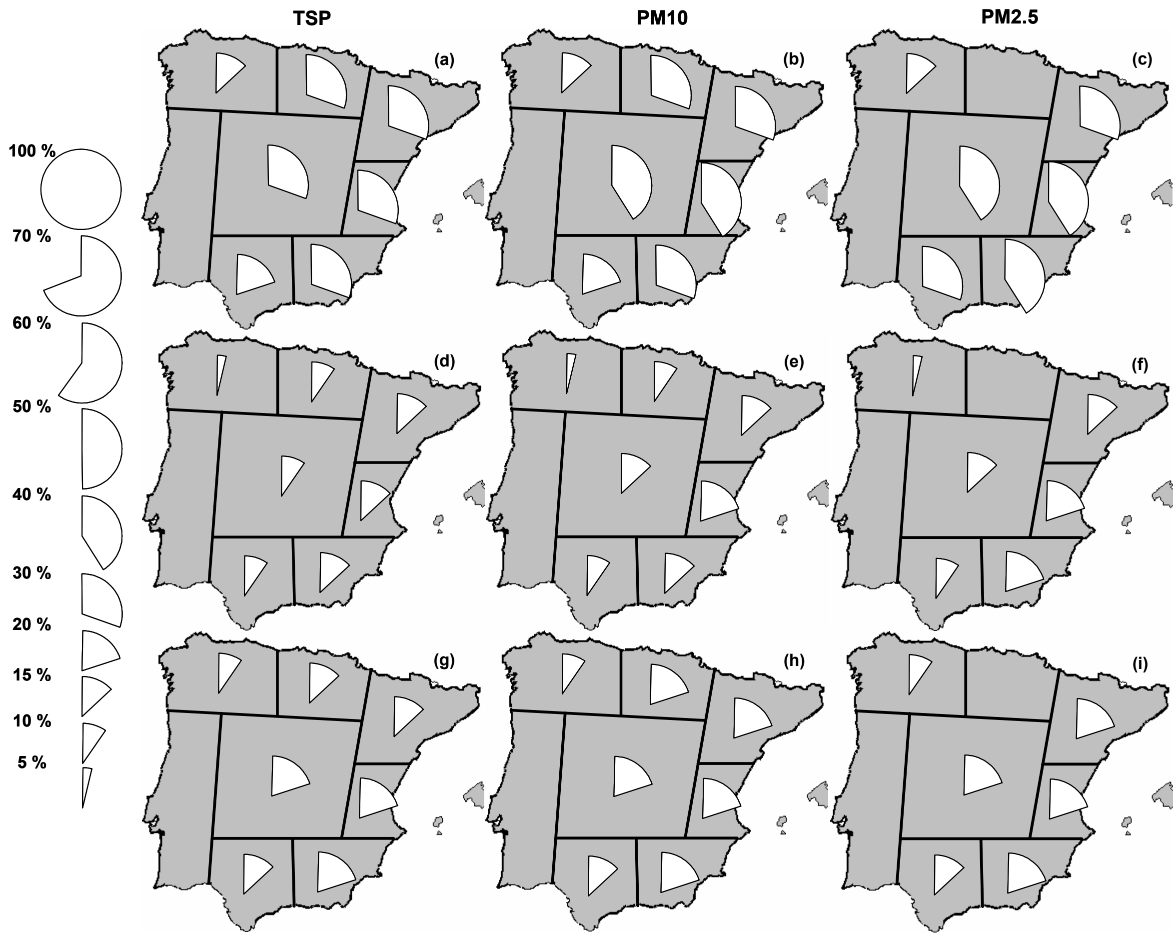


Figure 5.61. Relative impact (in %) of episodes without dominant advective conditions (a-c), WIA (d-f) and ITL (g-i) on mean TSP, PM10 and PM2.5 levels (in µg m^{-3}) in regional background stations in the Iberian Peninsula.

As a summary, Figures 5.62 and 5.63 show the frequency of occurrence of the different episodes and their impact index (II, expressed as % of the annual mean PM levels) in all the regions of the Iberian Peninsula for the study period (1998-2003). The transport of Atlantic air masses was the most common situation in all the regions although the frequency is lower over the east (35-42% of the days) than in the rest of the regions (48-73% with the highest frequency in the northwest). This had a reflection on the impact of Atlantic events on the annual mean PM levels which are generally high (23-26% for TSP, 21-26% for PM10 and 24-27% for PM2.5 in the southeast and the east; 31-36% for TSP, 31% for PM10, 31-33% for PM2.5 in the northeast and the centre, 43-44% for TSP and 43% for both PM10 and PM2.5 in the southwest and the north and 57% for TSP, 54% for PM10 and 51% for PM2.5 in the northwest).
The occurrence of the African episodes increased in frequency from north to south and from west to east, that is, 19-26% on the south and the east, 14-16% in the centre and the northeast and 8-11% in the northwest and north. The high PM levels recorded during African episodes is the reason why these events have the largest II in some regions (42% for TSP, 43% for PM10 and 35% for PM2.5 in the southeast and 33% for TSP, 32% for PM10 and 28% for PM2.5 in the east) and high II in all the rest of the regions (29% for TSP, 30% for PM10 and 28% for PM2.5 in the southwest; 29% for TSP, 27% for PM10 and 22% for PM2.5 in the centre; 20% for TSP, 24% for PM10 and 21% for PM2.5 in the northeast; 19% for TSP and 17% for PM10 in the north and 14% for TSP, 17% for PM10 and 15% for PM2.5 in the northwest). As can

be observed the II of the African events decreases with increasing distance to the African continent. One particular feature that can be generalised is that the II of African episodes in PM2.5 annual mean levels is lower than the II in TSP and PM10. This may be a reflection of the typical size of the dust in the African plumes (characterised, according to Alfaro et al. (1998), with three modes centred on 1.5, 7 and 15 µm, that is, mostly in the ranges PM10-PM2.5 and TSP-PM10).

The situations without dominant advective conditions were considerably frequent over the east and the centre (22-29% of the days in 1998-2003), and less frequent in the southwest, north and northwest (8-16% of the days in 1998-2003). The II of these episodes reached 29-30% for TSP, 30-31% for PM10 and 32-33% for PM2.5 in the southeast, east and centre; 25% for TSP, and 27% for both PM10 and PM2.5 in the northeast; 19-21% for TSP, 20-22% for PM10 and 22% for PM2.5 in the southwest and the north and 13% for TSP, 13% for PM10 and 15% for PM2.5 in the northwest. The II of the episodes without dominant advective conditions is higher in PM2.5 owing to the fine size of the secondary aerosols coming from photochemical transformation of gaseous precursors. In summer events, the formation of these fine particles is very intense.

European and Mediterranean episodes were less frequent which resulted in low II for all size ranges. In fact, the frequency of occurrence of Mediterranean ranged from 1 to 6% of the days which resulted in very low II (1-5% for all size ranges in all the regions of Iberia). The transport of European air masses was quite rare in the southwest and southeast (3-5% of the days) and in the northwest, centre and east (8-10% of the days) and moderately frequent in the northern regions (15-17% of the days). The frequency of occurrence of European events increased with the distance to the European continent. Apart from the frequency of occurrence, the PM levels recorded during European episodes only were moderately high in the northern flank of the Iberian Peninsula. The dispersion and dilution of the pollutants in European air masses reaching the Center or the southern Iberian Peninsula resulted in low mean PM levels in these regions. Therefore, the II of the European events only reached moderately high values in the northern flank (14-17% for TSP; 15-16% for PM10 and 17-18% for PM2.5) while in the rest of the region II ranged from 3 to 8% for TSP, 3 to 8% for PM10 and 3 to 9% for PM2.5. In all the regions, the II of European episodes is slightly higher in PM2.5 than in TSP and PM10. This is explained by the fact that the anthropogenic aerosols are mainly sulphate, nitrate and other species coming from the transformation of gaseous pecursors which are, in general, fine.

In consequence, the annual mean PM levels in regional background stations are influenced in a different way by the air mass transport episodes considered in this study depending on the study area. The role of the Atlantic episodes modulating background PM levels in the west and the north of the Iberian Peninsula, where this transport scenario is considerably common, is very important. Moreover, the precipitation associated with the passage of frontal systems during Atlantic episodes washes aerosols out from the atmosphere more frequently over the west and north. The influence of the Atlantic episodes on annual mean PM levels decrease over the east where African episodes and episodes without prevailing advective conditions are relatively more frequent. These two types of episodes are generally associated with high PM levels. This would explain the higher mean PM levels registered in the regional background stations over the eastern flank of the Iberian Peninsula. Local factors such as the soil type and the vicinity to the coast line may influence the background PM levels. Thus, crustal soil materials in dry regions such as the east and great regions of the south of Iberia are susceptible to be resuspended more frequently than over the northwest where the vegetation cover is well developed. The African dust outbreaks are the main type of episode in terms of the impact on regional background annual PM levels over the southeast of the Iberian Peninsula. Finally, it is important to remark that the influence of European events on annual mean PM levels in regional background stations is low with the exception of those located over the north of the Iberian Peninsula where the frequency of occurrence of these episodes is moderately high and where the pollutants in European plumes reach without having suffered strong dispersion or dilution.

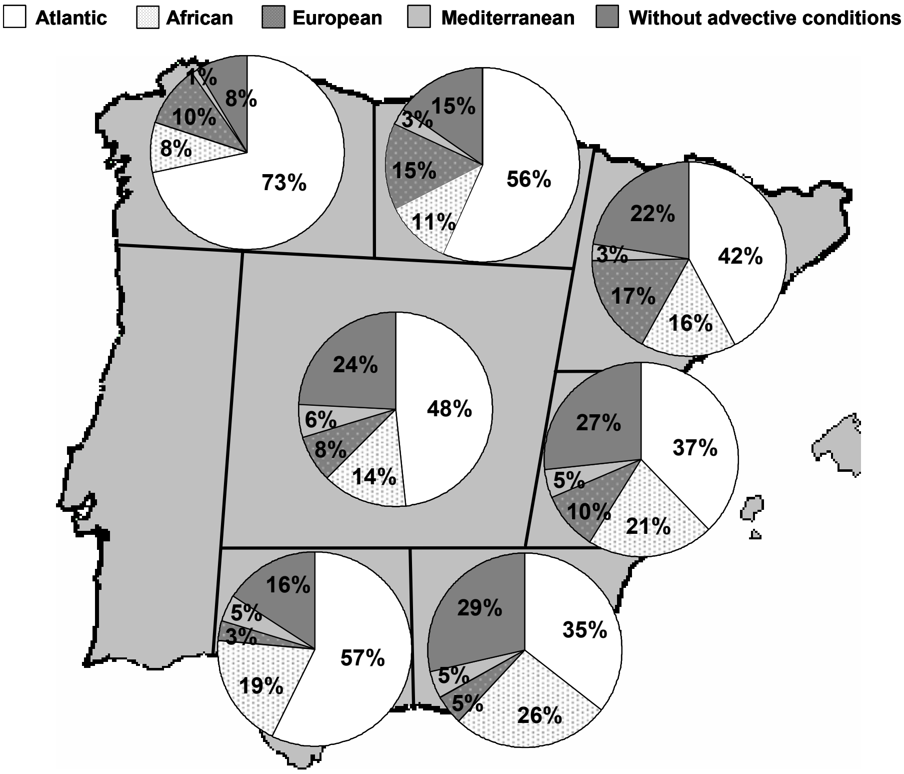


Figure 5.62. Proportion of days (in %) associated with the air mass transport episodes considered in this study (Atlantic, African, European, Mediterranean and without dominant advective conditions) in 1998-2003 over seven regions of the Iberian Peninsula.

5.8.6. Exceedances of the PM daily limit values

The 1999/30/EC Directive established a limit value for the daily mean of 50 μgPM10m^{-3} which should not be surpassed more than 35 times in a year by 2005. In 2004, the Working Group on PM part of the CAFE (Clean Air For Europe) programme issued the II PM Position paper on particulate matter (EC, 2004). The Position Paper recommended a change in the reference parameter from PM10 to PM2.5 and also suggested a daily limit value of 35 μgPM2.5 m^{-3} (that should not be exceeded more than 10% of the days of the year, that is, 35 times per year). Furthermore, an annual limit value in the range 12-20 μgPM2.5 m^{-3} was also suggested. More recently, a draft for a new air quality directive (AQD) was issued by the EC in September 2005. In this new AQD, the recommendation of the II position paper of setting a daily limit value for PM2.5 was not taken into account. The 2005 PM10 limit values fixed by the Air Quality Directive 1999/30/CE would remain, whereas the 2010 indicative limit values will be replaced by a PM2.5 annual cap value of 25 μg m^{-3} to be met by all types of stations (including hotspots) by the 1st of January 2015. Furthermore, the new AQD will stablish a PM2.5 exposure reduction target consisting in the 20% reduction of the tri-annual PM2.5 means obtained for urban background sites of a State Member between 2008-2010 and 2018-2020.

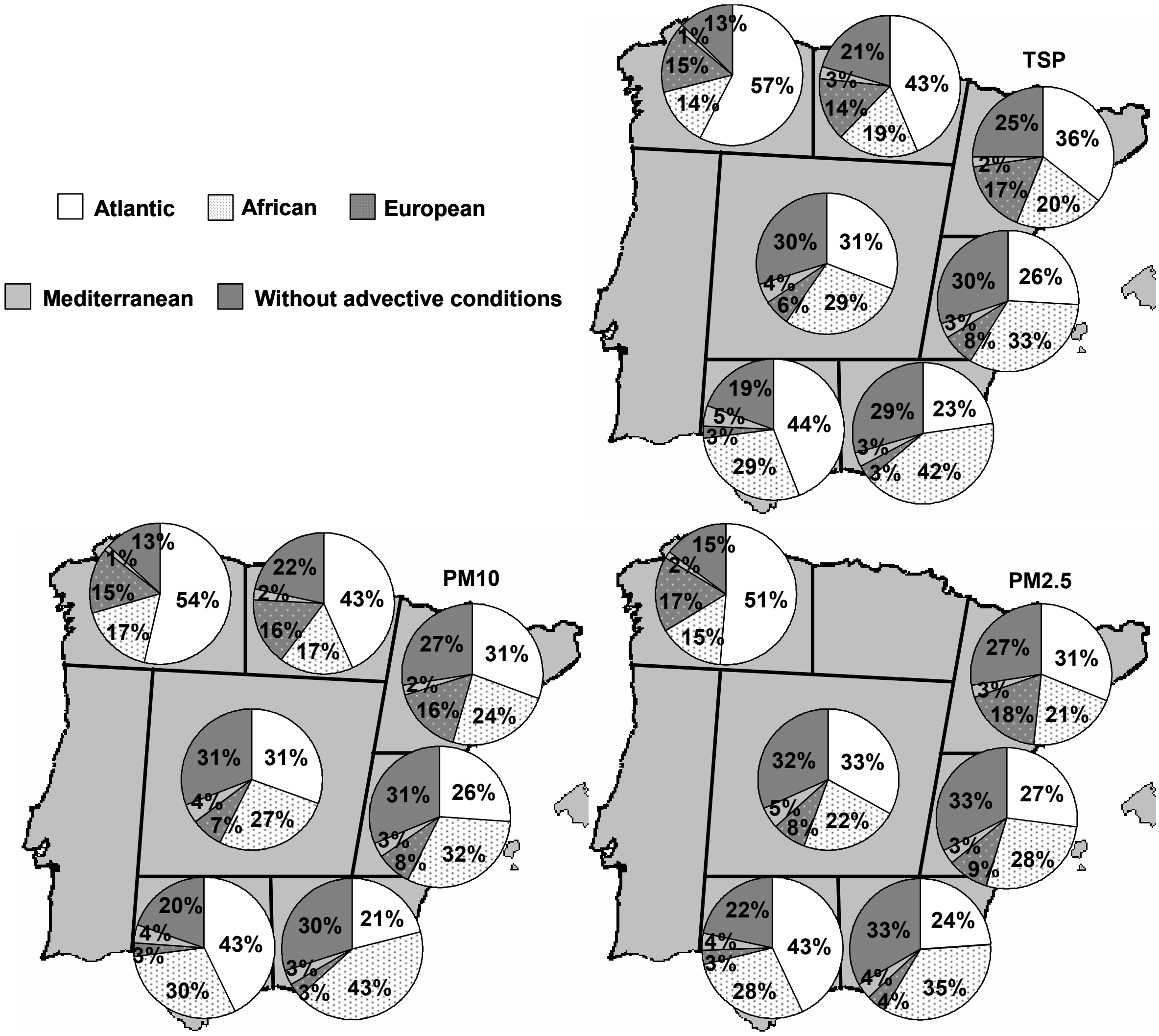


Figure 5.63. Relative impact (in %) of the air mass transport episodes considered in this study (Atlantic, African, European, Mediterranean and without dominant advective conditions) on the annual mean PM levels recorded at the regional background stations from seven regions of the Iberian Peninsula for 1998-2003.

Levels of PM10 and PM2.5 are measured at EMEP stations since March 2001, PM10 levels are measured since 1995 at Monagrega (belonging to ENDESA), and at Valderejo and Izki (both belonging to the Autonomous Government of the Bask Country) since November 1999 and May 2001 respectively. Based on these data, the number of exceedances of the daily limit value established in the 1999/30/EC Directive (50 µgPM10 m^{-3}) and of the daily limit value proposed in the II PM Position Paper (35 µgPM2.5 m^{-3}) were calculated and attributed to the different PM events established in this study.

As observed in Figure 5.64, the number of exceedances of the PM10 limit value was higher than the number of exceedances of the PM2.5 limit value. In 2001-2003 the number of PM10 exceedances was 8 in O Saviñao, 15 in Izki, 15 in Cabo de Creus, 11 in Els Torms, 24 in Monagrega, 9 in Risco Llano, 6 in Campisábalos, 8 in Peñausende, 8 in Zarra, 7 in Barcarrota and 41 in Víznar. The number of PM2.5 exceedances was 5

in O Saviñao, 18 in Cabo de Creus, 11 in Els Torms, 1 in Risco Llano, none in Campisábalos, 4 in Peñausende, none in Zarra, 10 in Barcarrota and 1 in Víznar.
The major part of the PM10 exceedances in regional background stations occurred during African dust outbreaks (100% in Zarra, Risco Llano and Campisábalos; more than 98% in Víznar, 88% in O Saviñao and in Peñausende, 73% in Els Torms, 71% in Barcarrota, 63% in Monagrega, 47% in Izki and down to 13% in Cabo de Creus). Exceedances of the PM10 daily limit value were registered as well during episodes without dominant advective conditions (accounting for 27-29% of the daily PM10 exceedances in Izki, Cabo de Creus and Barcarrota, 13% in Monagrega, 9% in Els Torms and only 2% in Víznar) and during European episodes (accounting for 40% of the daily PM10 exceedances in Cabo de Creus, 12% in O Saviñao and 9% in Els Torms). Also, during Atlantic events, exceedances of the limit value of PM10 were recorded in some stations (accounting for 27 and 33% of the daily PM10 exceedances in Izki and Monagrega respectively, 20% in Cabo de Creus, 12% in Peñausende and 9% in Els Torms).
As shown in Figure 5.64, African episodes also accounted for a high proportion of the PM2.5 daily exceedances, although in a lower extent than for PM10 (accounting for 100% of the daily PM2.5 exceedances in Víznar and Risco Llano, 80% in O Saviñao, 40-55% in Barcarrota and Els Torms and 17-25% in Cabo de Creus and Peñausende). In PM2.5, the proportion of exceedances associated with European events (accounting for 18-22% of the daily PM2.5 exceedances in Els Torms, O Saviñao and Cabo de Creus) and episodes without dominant advective conditions (accounting for 44-50% of the daily PM2.5 exceedances in Cabo de Creus and Peñausende and 20-27% in Barcarrota and Els Torms) increased with respect of what occurred for PM10 as well as those associated with Atlantic events (accounting for 40% of the daily PM2.5 exceedances in Barcarrota and 17-25% in Cabo de Creus and Peñausende).
The exceedances associated with Atlantic transport should be attributed to local or regional contributions since the oceanic air masses are relatively clean. In the case of Barcarrota a possible transboundary transport from Portugal may also be the cause of these exceedances. With respect to the exceedances in Izki, during Atlantic transport, all these occurred in a period of 21 days in June-July 2001 when a local source may have been active because 12 of the 15 PM10 daily exceedances recorded at Izki in 2001-2003 occurred in this period. Monagrega station is located near a power plant which may be an important local source of pollutants.
The vicinity of Cabo de Creus station to the highly industrialised area of the Gulf of Lion may explain the high number of exceedances of the PM10 and PM2.5 limit values. High loads of anthropogenic aerosols from this region may reach to Cabo de Creus during European transport and episodes without dominant advective conditions, in this second case, driven mainly by the breezes. These particles are fine but, during European events, the number of exceedances of the PM10 limit value is higher than the number of exceedances of the PM2.5 limit value. This suggests the presence of a local source of large aerosols which is activated during the European transport. The winds associated with the European events may increase the sea surface movement and, consequently, the production of marine aerosols which are generally large and may also contribute to increase PM10 given that this station is located by the Mediterranean coastline. These winds may also provoke soil resuspension which is another source of coarse particles.
Finally it is important to note that, during episodes without dominant advective conditions, the number of exceedances of the daily limit value increased slightly for PM2.5 with respect to PM10. The fine size of the aerosols originated from the

photochemical transformation of gaseous precursors and the aging of polluted air masses in summer may account for this fact.

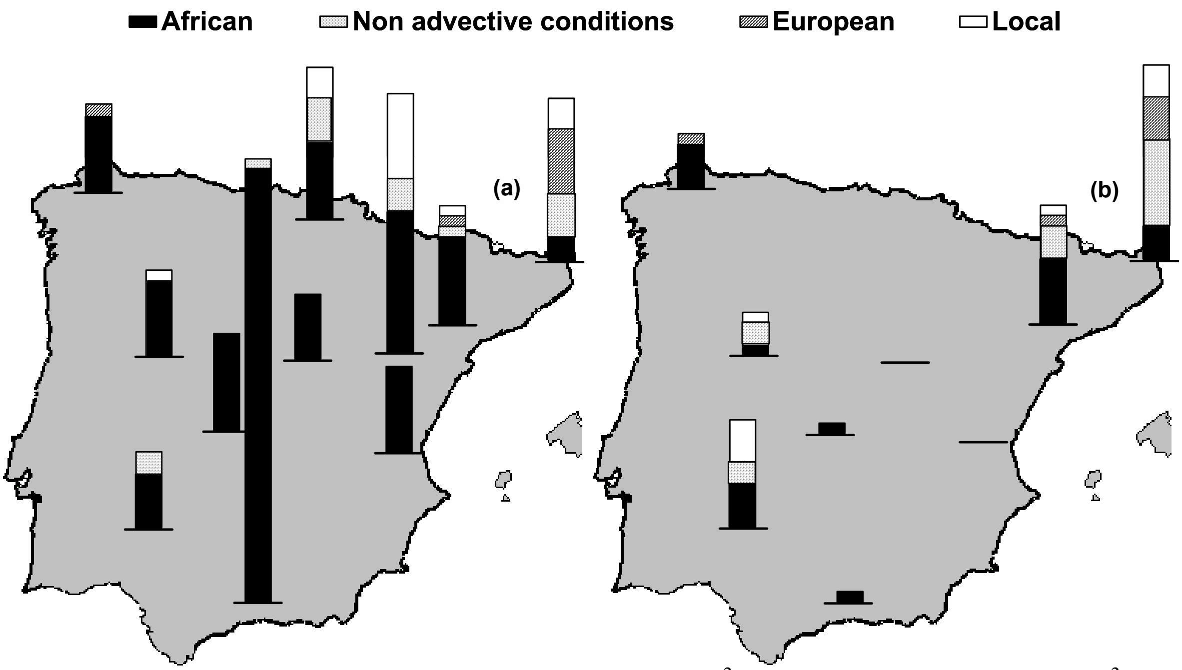


Figure 5.64. Number of exceedances of the 50 µgPM10 m^{-3} (a) and of the 35 µgPM2.5 m^{-3} (b) daily values in regional background stations of the Iberian Peninsula from 2001 to 2003 with the exception of Monagrega (1998-2003). The origin of these exceedances is shown.

Figure 5.65 shows an example of a north African dust outbreak occurred over the Iberian Peninsula from the 21st to the 29th of March 2002. The daily PM10 and PM2.5 levels recorded at regional background stations during this episode were high, causing exceedances of the PM10 daily limit value (50 µg m^{-3}) in O Saviñao (68, 88 and 51 µg m^{-3} on the 21st, 22nd and 23rd respectively) and Peñausende (62 µg m^{-3} on the 22nd). These two stations are located on the northwstern flank of Iberia which is the region first affected by the dust outbreak. During this event, exceedances of 35 µgPM2.5 m^{-3} (daily limit value proposed in the II PM position paper) were not recorded although moderate increases in the PM2.5 levels were generally recorded (clear from the 21st to the 23rd in the northwest, north and centre and more moderate from in the 24th in the south). As observed in the geopotential height maps in Figure 5.65, the synoptic scenario causing this episode was NAH-S, characterised by the presence of an anticyclone over the southern flank of the Iberian Peninsula at surface levels (1000 hPa). This situation also developed at upper levels (850 and 700 hPa). During these episodes a convex and narrow dust plume generally forms over the Atlantic Ocean (Atlantic arch). This plume firstly affects the western flank of Iberia. These features can be observed in the maps from the NAAPS model, the 5-days HYSPLIT4 backtrajectories and in the SeaWIFS satellite image shown in Figure 5.65. Moreover, the NAAPS surface dust concentration map confirms the impact at surface level.

A second example of an African episode, occurring from the 21st to the 26th June 2001, with a clear impact on PM levels in the regional background sites is presented in Figure 5.66. The impact of this event on the PM10 levels is evident causing exceedances of the limit value of the 50 µgPM10 m^{-3} in Izki (57, 53, 53, 102, 90, 51, 61 and 62 µg m^{-3} from the 22nd to the 29th respectively, although a local contribution in this station in this period cannot be discarded since these very persistent high PM10 levels were not recorded in the closeby station of Valderejo). Furthermore, in Monagrega (52 and 55 µg m^{-3} on the 26th and 27th respectively), Peñausende (52 µg m^{-3} on the 22nd) and Víznar (54 µg m^{-3} on the 25th) exceedances of the PM10 daily limit value were recorded. Exceedances of the limit value for PM2.5 of 35 µg m^{-3} suggested in the II PM position paper were recorded in Risco Llano (36 µg m^{-3} on the 23rd) and in Peñausende (37 µg m^{-3} on the 22nd). As observed in the geopotential height maps in Figure 5.66, the presence of a thermal low at 1000 hPa over northern Africa owing to the great heating of the surface in summer, displaced the north African high aloft (above 1500 m.a.s.l). This anticyclone was the feature which, in fact, caused the transport of dust over the Iberian Peninsula in the free troposphere. The anticyclone can be observed in the 850 and 700 hPa geopotential height maps. In consequence this episode can be defined as NAH-A. An elevation of the background levels of PM10 and PM2.5 was recorded owing to a regional contribution of PM consisting mainly in secondary aerosols arising from the photochemical transformation of gaseous precursors. As explained above, during NAH-A situations, the African plumes travel at high altitudes (>1500 m.a.s.l.) and the dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is distributed and affects the sampling stations. The formation of the above mentioned secondary particles is enhanced during NAH-A situations because, at surface, a low pressure gradient remains causing lack of advective conditions. In these circumstances, superficial air masses are hardly renovated and the aging and recirculation of contaminated air masses aided by the orographic characteristics of the eastern Iberian Peninsula commonly occur (Millán et al., 1997). Furthermore, during NAH-A episodes, precipitation is reduced and re-suspension of soil material by convection is enhanced so a local contribution also occurs. Thus, owing to these complex convective dynamics there is mixing of aerosols in the troposphere during NAH-A events. The dust plume can be observed in the the SeaWIFS satellite image as in the NAAPS map (confirming also the impact at surface levels). The HYSPLIT backtrajectories show an anticyclonic transport at 2500 metres and short trajectories at 500 and 1500 metres indicating low pressure gradient conditions.

The third example presented in Figure 5.66 occurred from the 19th to the 28th of June 2003. The daily PM10 and PM2.5 levels recorded at regional background stations during this episode were high, causing exceedances of the PM10 daily limit value (50 µg m^{-3}) in Cabo de Creus (78 µg m^{-3} on the 27th), Els Torms (113, 73 and 56 µg m^{-3} on the 24th, 25th and 26th respectively), Monagrega (60, 92 and 79 µg m^{-3} on the 23rd, 24th and 25th respectively), Risco Llano (52 µg m^{-3} on the 23rd), Campisábalos (67 µg m^{-3} on the 23rd), Zarra (64, 56 and 54 µg m^{-3} on the 23rd, 24th and 25th respectively) and Víznar (63 µg m^{-3} on the 23rd). The PM2.5 levels reached values surpassing 35 µg m^{-3} (daily limit value proposed in the II PM position paper) in Cabo de Creus (38 on the 27th), Els Torms (93 and 50 µg m^{-3} on the 24th and 25th respectively) although increases in PM2.5 were recorded in most of the stations. This episode is meteorologically characterised again by the presence of the north African thermal low which displaced the north African anticyclone up to high tropospheric levels. However, in this case, the presence of a low pressure centre at all altitude levels in front to Portugal, combined with the effect of the anticyclone over the Mediterranean basin triggered the transport of dust evident in the SeaWIFS image and the NAAPS surface dust concentration maps (Figure 5.67). This event can be classified as NAH-A although surface transport also occurred as can be observed in the NAAPS model map.

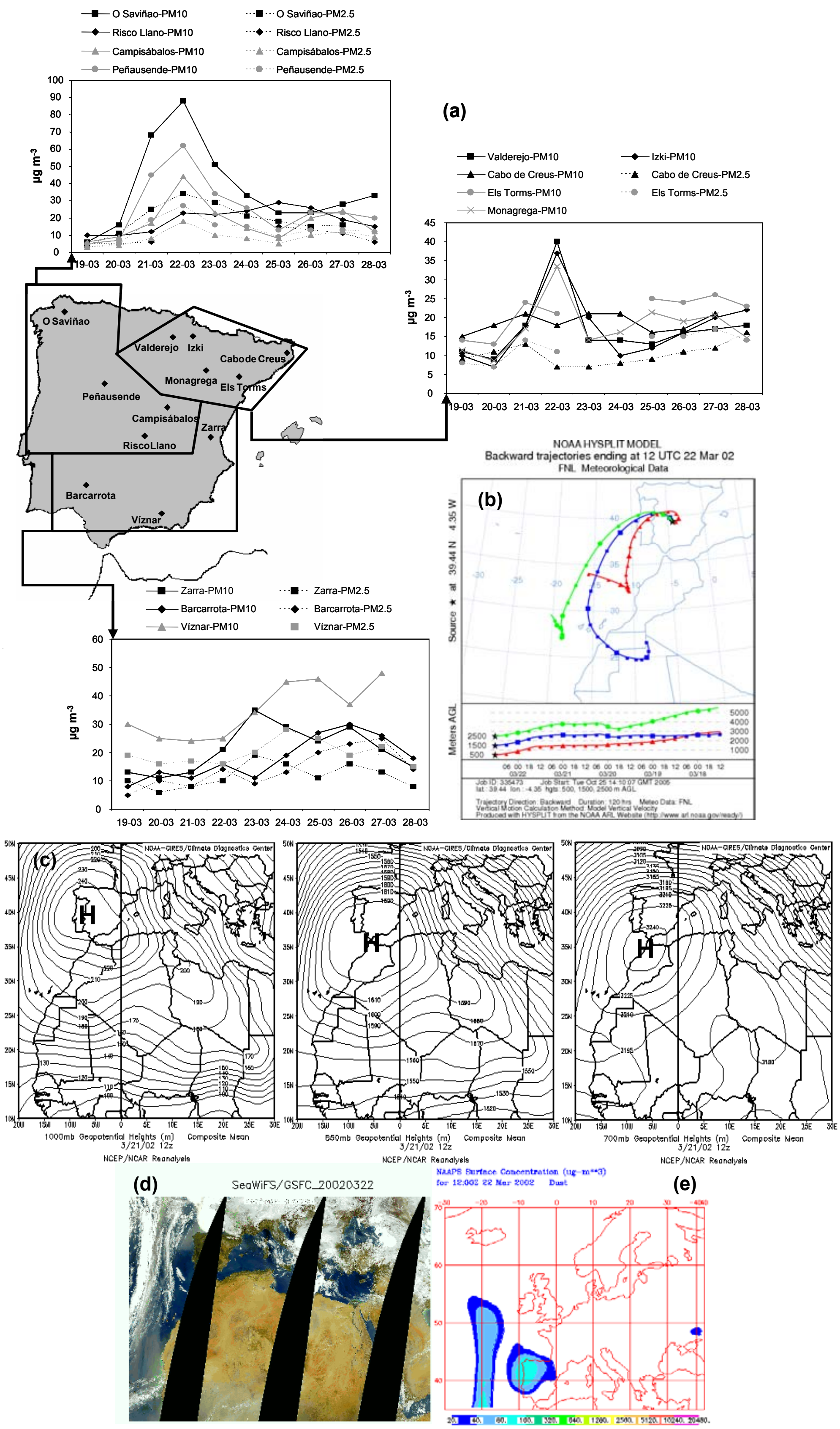


Figure 5.65. African dust outbreak occurred over the Iberian Peninsula in March 2002. This figure shows: (a) PM10 and PM2.5 daily levels (µg m^{-3}) in regional background stations during the episode, (b) 5 days HYSPLIT back-trajectories for 500, 1500 and 2500 metres above ground level, (c) Geopotential height maps at 1000, 850 and 700 hPa, (d) SeaWIFS image and (e) NAAPS surface dust concentration map.

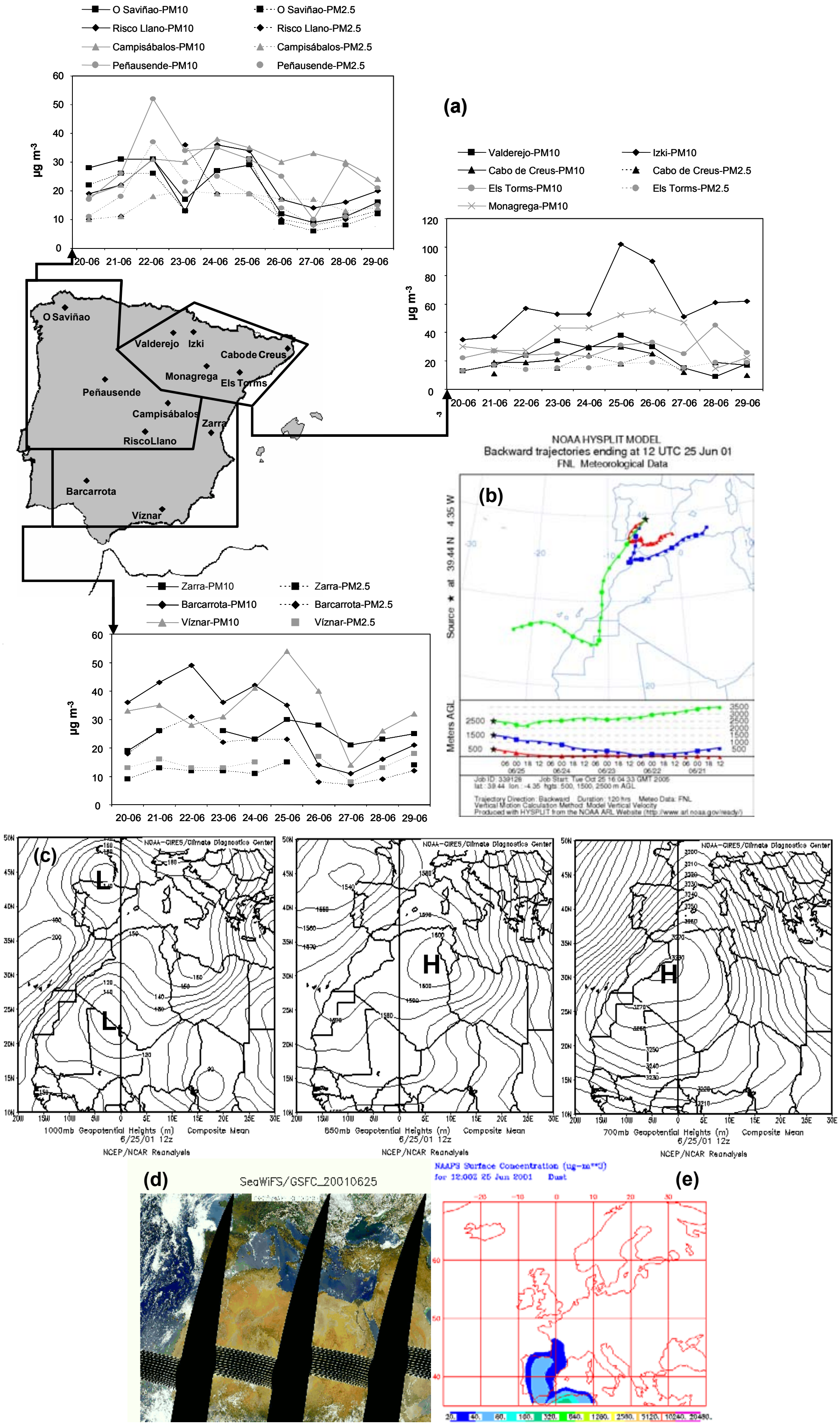


Figure 5.66. African dust outbreak occurred over the Iberian Peninsula in June 2001. This figure shows: (a) PM10 and PM2.5 daily levels (µg m^{-3}) in regional background stations during the episode, (b) 5 days HYSPLIT back-trajectories for 500, 1500 and 2500 metres above ground level, (c) Geopotential height maps at 1000, 850 and 700 hPa, (d) DREAM dust loading maps, (e) SeaWIFS image and (f) NAAPS surface dust concentration map.

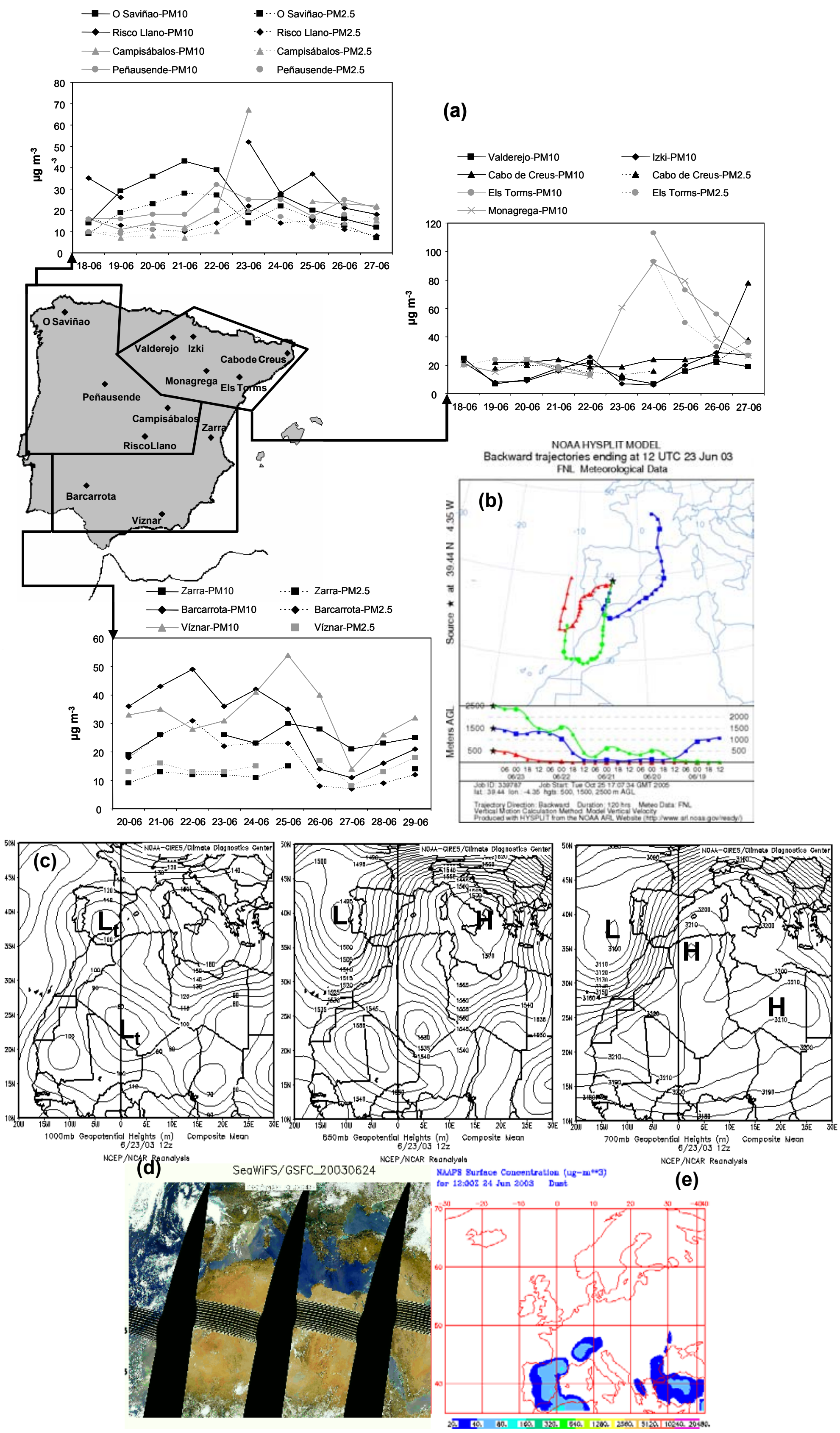


Figure 5.67. African dust outbreak occurred over the Iberian Peninsula in June 2003. This figure shows: (a) PM10 and PM2.5 daily levels (µg m^{-3}) in regional background stations during the episode, (b) 5 days HYSPLIT back-trajectories for 500, 1500 and 2500 metres above ground level, (c) Geopotential height maps at 1000, 850 and 700 hPa, (d) DREAM dust loading map, (e) SeaWIFS image and (f) NAAPS surface dust concentration map.

High PM levels were also recorded during episodes without dominant advective conditions, as occurred practically during the whole month of August 2003 over extended regions of the Iberian Peninsula. The lack of advective conditions was caused by the low pressure gradient over the Iberian Peninsula at 1000 hPa (surface) and also at 850 and 700 hPa (Figure 5.68). The lack of advective conditions is reflected in the short 5-days HYSPLIT backtrajectories shown in Figure 5.68. Furthermore at surface, a low thermal pressure centre was present caused by the strong insolation of the superficial air masses over the Iberian Peninsula and at higher levels an anticyclone can be observed. In consequence this event can be classified as ITL. Major characteristics of the ITL situations, such as the low rainfall regime, the aging and re-circulation of polluted in air masses (Millán et al., 1997), the high rate of re-suspension or the enhancement of transformation of gaseous precursors into secondary aerosols by the increased photochemistry, tend to increase PM levels in regional background stations over the eastern flank of the Iberian Peninsula (Rodríguez et al, 2003) and other regions of Iberia. Furthermore, the regional and local circulations and re-circulations in summer favour the dispersion of pollutants from urban/industrial centres and the arrival of these pollutants to rural sites increasing background PM levels. PM10 and PM2.5 levels in the regional background stations showed a common increase during this episode. The increase of PM2.5 levels was more intense than during the African episodes presented above. This probably occurred as a consequence of the high rate of formation of fine secondary aerosols from gaseous precursors. In Monagrega (60 µg m^{-3} on the 15^{th} respectively) and Barcarrota (53 and 55 µg m^{-3} on the 11^{th} and 12^{th} respectively), exceedances of the PM10 daily limit value (50 µg10 m^{-3}) were recorded and exceedances of the 35 µgPM2.5 m^{-3} were recorded in Cabo de Creus (42, 38 and 42 µg m^{-3} on the 23^{rd}, 11^{th}, 12^{th} and 13^{th} respectively).
Figure 5.69 shows the example of an European episode which occurred over north and northeastern Iberia fron the 6^{th} to the 8^{th} of November 2003. The 5-days HYSPLIT backtrajectories indicates the transport from the European continent and the NAAPS sulphate surface concentration map confirms the transport of anthropogenic sulphate from central Europe to northeastern Iberia. This transport was caused by the presence of an anticyclone over central Europe at 1000, 850 and 700 hPa (Figure 5.69). PM10 and PM2.5 levels in the regional background stations of the northeast and the north of Iberia increased resulting in an exceedance of the PM10 daily limit value (50 µg m^{-3}) and an exceedance of the PM2.5 daily limit value proposed by the II PM position paper (35 µg m^{-3}) in Els Torms on the 8^{th} of November (52 µgPM10 m^{-3} and 36 µgPM2.5 m^{-3} respectively).

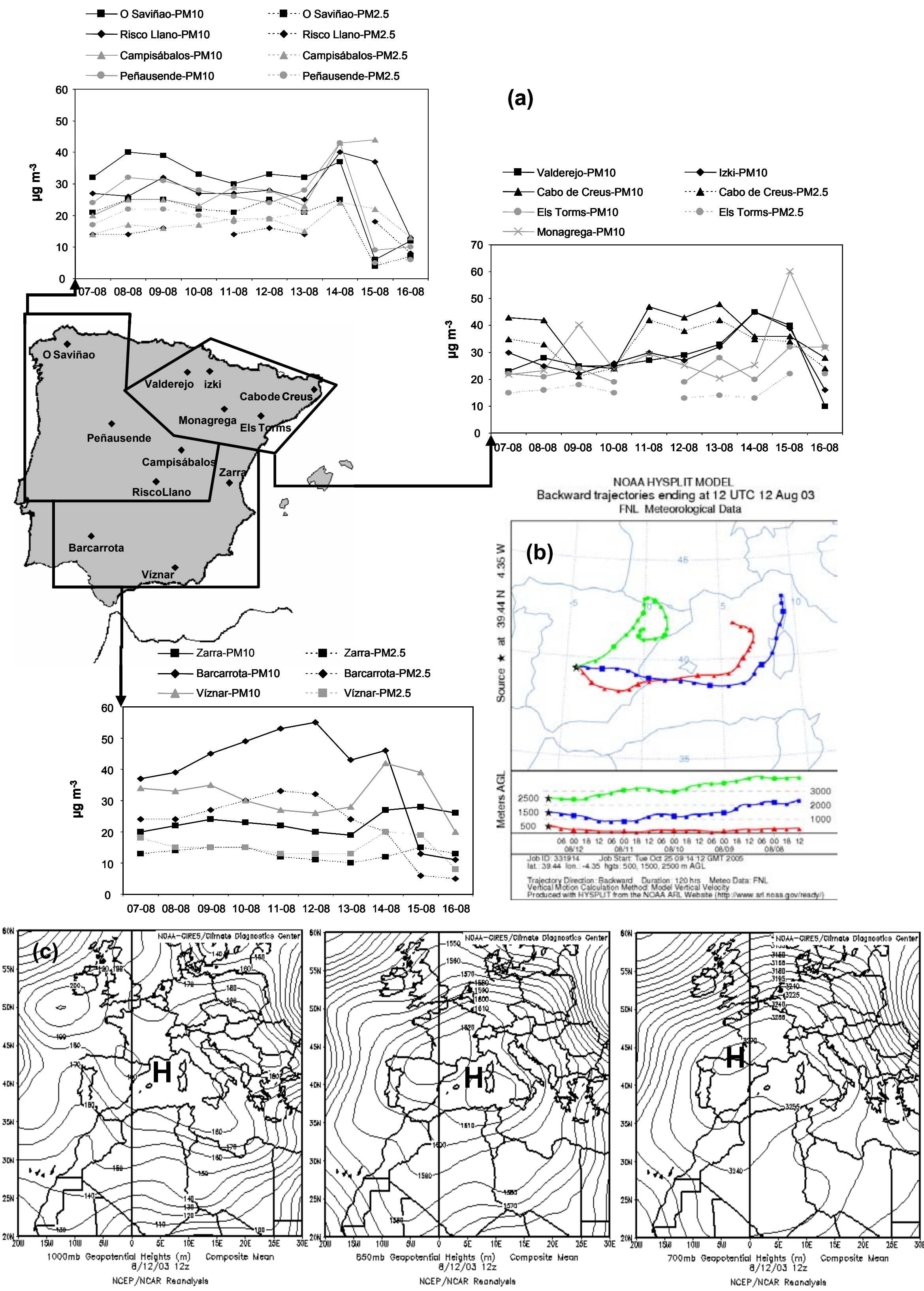


Figure 5.68. Episode without dominant advective conditions occurred over the Iberian Peninsula in August 2003. This figure shows: (a) PM10 and PM2.5 daily levels (µg m^{-3}) in regional background stations during the episode, (b) 5 days HYSPLIT back-trajectories for 500, 1500 and 2500 metres above ground level and (c) Geopotential height maps at 1000, 850 and 700 hPa.

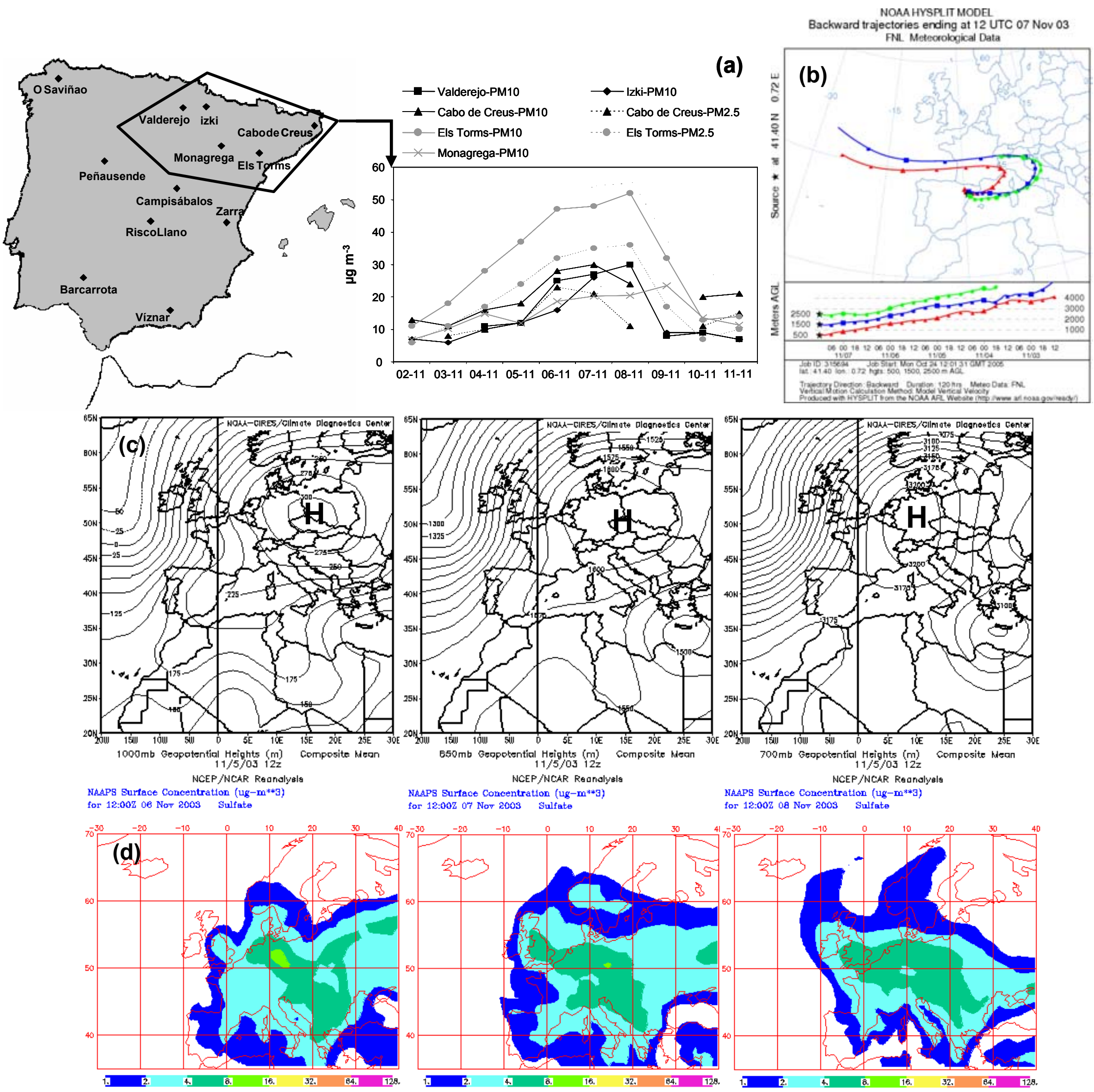


Figure 5.69. European episode occurred over the northeastern Iberian Peninsula in November 2003. This figure shows: (a) PM10 and PM2.5 daily levels (µg m^{-3}) in regional background stations of north and northeastern Iberia during the episode, (b) 5 days HYSPLIT back-trajectories for 500, 1500 and 2500 metres above ground level, (c) Geopotential height maps at 1000, 850 and 700 hPa and (d) NAAPS surface sulphate concentration maps.

6. Wet and dry African dust episodes over eastern Spain

6. WET AND DRY AFRICAN DUST EPISODES OVER EASTERN SPAIN

Although many studies have dealt independently with African episodes influencing bulk deposition and levels of ambient PM in Spain, none of them have considered simultaneously wet deposition and suspended particulate matter to investigate such dust outbreaks over Spain. In this section, we will undertake a combined study of wet and dry African episodes over eastern Spain performing the methodology detailed in chapter 3. Data on the chemical composition of bulk deposition collected at La Castanya (Barcelona, 41º 46' N, 02º 21' E, 700 m.a.s.l.) were used to identify wet African episodes while the African episodes with impact on PM levels were identified by the inter-correlation of TSP and PM10 time series from rural, urban and industrial air quality monitoring stations showing parallel increments of PM levels. Once the time series of wet deposition and high PM events influenced by African episodes were obtained, these were combined to create a time series of dust outbreaks from 1996-2002.

6.1 Occurrence of African episodes in 1996-2002 over eastern Iberian Peninsula

During the period 1996-2002, 112 African dust episodes were identified accounting for a total of 378 days, with a mean duration of 3 days per episode. This represents a mean of 16 episodes per year and that 15% of the days the African dust reached eastern Iberia. The mean monthly occurrence for the study period is 5 days.

In 93 out of the 112 episodes (330 days, with a mean of 4 days per episode) an impact on levels of PM in the air quality monitoring stations was detected. This represents a mean of 13 episodes per year and that in 13% of the days the African dust influenced the levels of PM in eastern Iberia. The mean monthly occurrence for the study period is 4 days per month.

In 49 out of 112 episodes (72 days, with a mean of 1-2 days per episode) wet deposition occurred simultaneously with African events. This represents a mean of 7 episodes per year (3% of the days). The mean monthly occurrence for the study period is slightly less than 1 day per month. It should be pointed out that the total number of episodes differs from the addition of "high PM" and wet episodes since some of the episodes included days during which PM levels were influenced by dust outbreaks and, simultaneously, wet dust deposition.

The monthly distribution of African episodes is characterised by three modes with a clear prevalence of the period May to August (Figures 6.1 to 6.3). In particular, the period May-August has the highest mean number of days per month (from 6 to 9 days), followed by March and October (with 6 and 5 days per month, respectively), whereas the lowest monthly occurrences are recorded for December, November and April (with 0.2, 2 and 2 days per month respectively). It is noticeable that in March, May, June, July and August, dust events are always present while in December only one dust invasion day was recorded in the whole study period (1996-2002). The above seasonal pattern of the African episodes is clearly dominated by the PM (non-wet) episodes given that the same trend described is shown. Wet events only showed relatively higher monthly frequency in May (with 3 days per month).

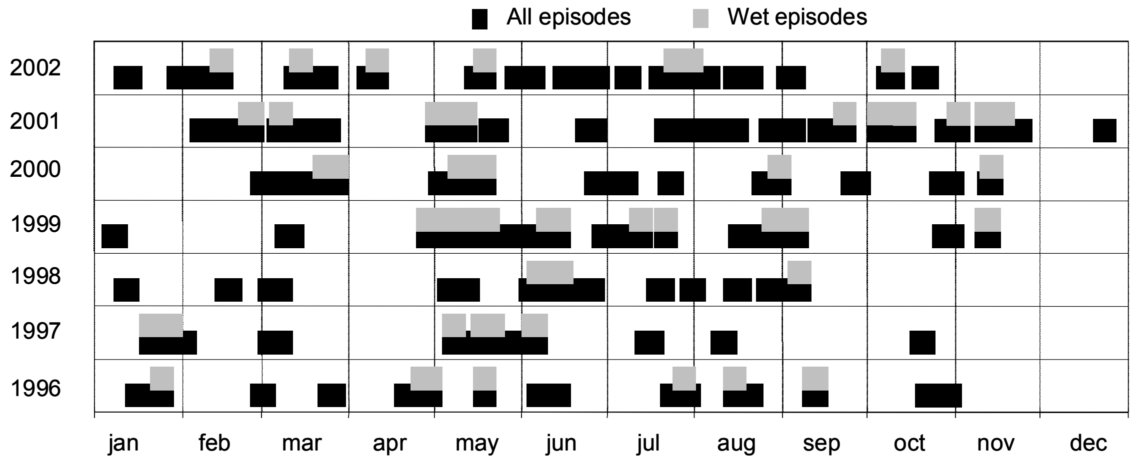


Figure 6.1. Occurrence of African dust outbreaks over eastern Iberian Peninsula for 1996-2002. Episodes occurring simultaneously with precipitation are highlighted.

Saharan dust outbreaks last longer in the period May-October than in the rest of the year with the exception of March when the duration of the episodes is similar to that of the summer events (Figure 6.4). The longest Saharan episodes take place in June with mean and maximum lengths of 6 and 13 days for all episodes and 7 and 13 days for the PM (non-wet) events. Wet episodes show the higher mean duration in April-June and November (1 to 2 days), whereas the longest wet episodes were recorded in May, June and November (3 days).

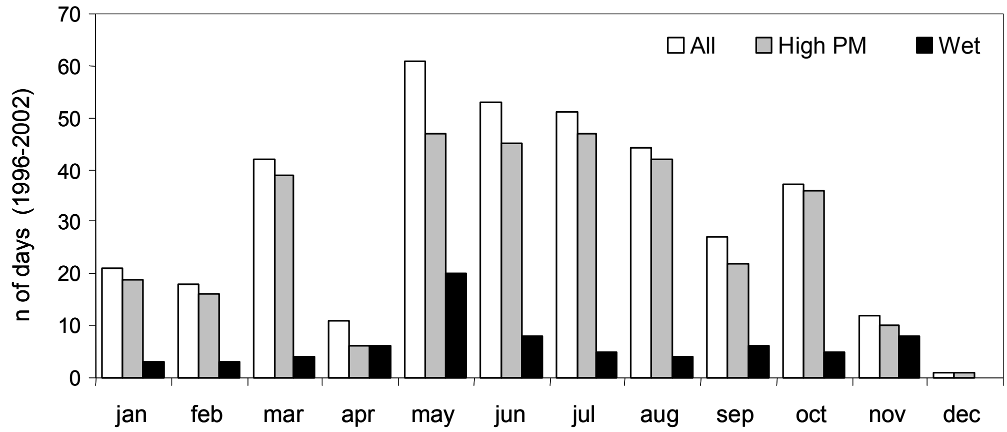


Figure 6.2 Number of days per month with African dust outbreaks over eastern Iberia for 1996-2002. High PM and wet deposition events are distinguished.

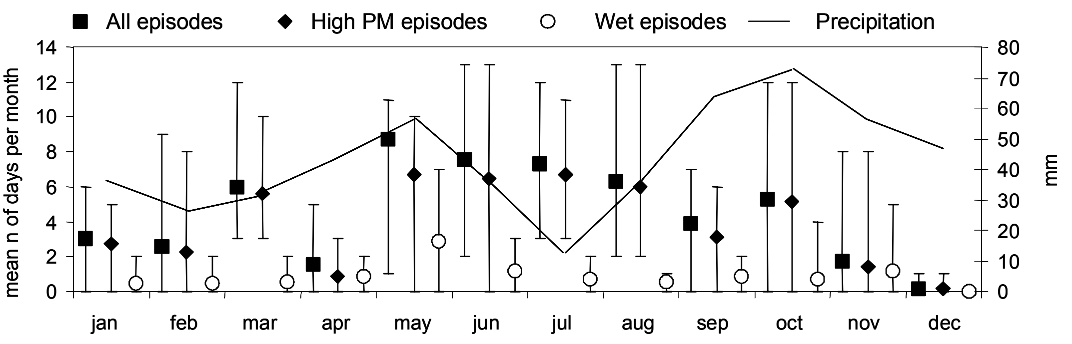


Figure 6.3 Mean monthly precipitation of Tortosa (40° 49' N, 00°29' E, 48 m.a.s.l) for 1971-2000 (INM, 2001) and mean number of days with African event per month for 1996-2002.

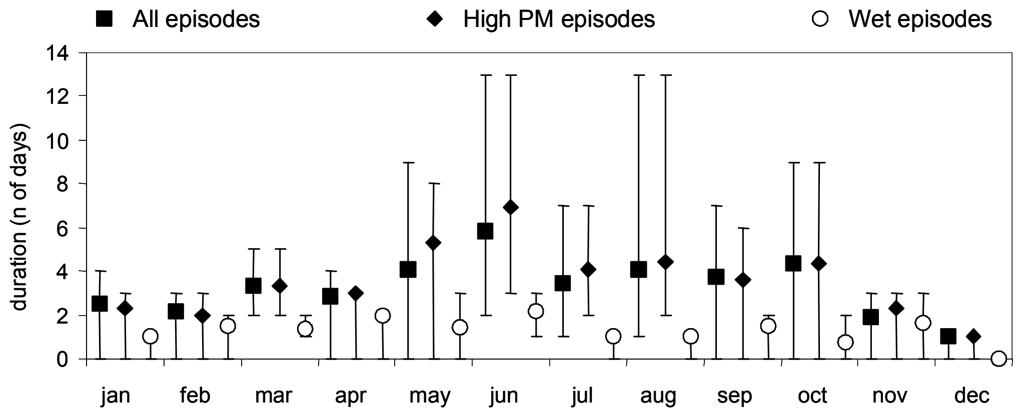


Figure 6.4. Mean duration of African dust outbreaks over eastern Iberia per month for 1996-2002.

6.2 Phenomenology of dust outbreaks over eastern Iberian Peninsula

Based on the results of the meteorological evaluation of the African episodes identified, 4 scenarios giving rise to the transport of highly dust loaded air masses from northern Africa to the Iberian Peninsula may be distinguished. These were previously presented in chapter 4 but it is worth describing them in detail here:

Scenario 1. North African high located at surface level (NAH-S). This type of scenario accounts for the occurrence of African air mass intrusions over the Iberian Peninsula from the western Atlantic via an Atlantic arch (Querol et al, 2002). As shown by the TOMS aerosol index maps, this scenario is present in most of the study period during January to March (Figure 6.5). The most outstanding feature of this scenario is the no-presence of the quasi-permanent Azores high. These convex and Atlantic long range transport plumes are caused by an anticyclone located over southern Iberia, north Africa, the western Mediterranean or off the Atlantic coast (Figure 6.6). The transport is confined at low levels and it is well detected at ground level and 850 hPa as shown in Figure 6.6. This figure also shows that the major sources of dust for this scenario are Western Sahara and Sahel, although it has to be noted that dust transport constrained to the lower atmospheric levels (<1000 m) is not detected by TOMS measurements (Torres et al., 1998, 2002). Only 3 out of the 15 NAH-S episodes identified occurred with wet deposition (20%).

Scenario 2. Atlantic depression (AD). A relatively deep low pressure (observed from sea level to 700 hPa centred off southwest the Portuguese coast with an associated high or ridge over the central Mediterranean sea may also be the cause of dust transport towards eastern Iberia. This transport scenario results in a synoptic flow coming from the south in all altitude levels (Figure 6.6). Source areas for mineral dust may vary widely but according to the transport scenario, western regions (Mauritania, Mali, Morocco) may be the main emission areas. Nine out of the 22 AD episodes identified occurred with wet deposition (41%).

Scenario 3. North-African depression (NAD). The Azores high is lightly shifted to the west of its normal position, a ground level low is centred over Morocco, Algeria, Tunisia, or even the western Mediterranean and a trough is observed over the Iberian Peninsula. This meteorological scenario favours the transport of African air masses towards Iberia across the Mediterranean (Figure 6.7). The air mass transport associated with this scenario is confined to the lower layers. Most of these episodes occur with rain events. NAD situations may commonly arise by the entry of depressions from over the Atlantic to north Africa or the western Mediterranean. According to this scenario, the dust sources may be regions from Algeria, Tunisia, Libya and Chad. Twenty out of the 23 NAD episodes identified occurred with wet deposition (87%).

Scenario 4. north-African high located at upper levels (NAH-A). The most frequent scenario causing dust outbreaks over Iberia is produced by the intense heating of the Sahara and the consequent development of the north African thermal low (Figure 6.7) and the considerable vertical growth of the boundary layer. This convective system pumps dust up to 5000 m a.s.l. Once the dust is injected into the mid-troposphere it may be transported towards Iberia by the western branch of the high present over north Africa (lifted to upper atmospheric levels, see Figure 6.7 and Rodríguez et al., 2001 for case studies). In these cases the air masses are heavily loaded with dust and are transported towards the north covering most of the western Mediterranean basin and Iberia, forming a wide plume of dust. By contrast, narrow Atlantic arches are formed in NAH-S scenarios (Figure 6.5). Given that the transport of dust is carried out at a considerable altitude, a number of studies have documented episodes of dust transport over Europe reaching altitudes of up to 6 km without impact on the low atmospheric levels (Ansmann et al., 2003). These episodes exerted considerable influence on the levels of PM over the eastern Iberia since only 17 out of 52 NAH-A (33%) were accompanied by local convective rains.

The scenario NAH-S accounted for the occurrence of 13 % (15 episodes in the period 1996-2002) of the African episodes recorded in eastern Spain, whereas the scenario NAH-A accounted for 46% (52 episodes in the study period). Scenarios AD and NAD accounted for around 20% of the episodes in each case (22 and 23 episodes). As shown in Figure 6.8, the seasonal occurrence of the four African transport scenarios is well defined. Thus, practically all the NAH-S episodes detected in the study period occurred in the period January-March. AD events occurred in winter, autumn and spring, but conversely, NAH-A episodes were detected only from May to October. Finally most of NAD episodes occurred in May and November, but none in July-August.

6.3 Regional background levels of ambient PM in eastern Iberia during African episodes

The air quality monitoring station of Monagrega (Teruel) is located in a rural area, was selected as a regional background site to evaluate the incidence of dust outbreaks in the ambient levels of PM10.

Mean annual ambient PM10 levels measured at Monagrega in 1996-2002 ranged from 17 to 19 $\mu g\ m^{-3}$, with the exception of 2002 when a very rainy summer accounted for a marked decrease in PM10 levels (13 $\mu g\ m^{-3}$).

The influence of African dust transport on the levels of PM10 measured at Monagrega is quite evident given that of the 24 peak PM10 events exceeding daily levels of 50 $\mu g\ m^{-3}$, 20 were measured under the influence of the African transport (Figure 6.9). This resulted in 27 days exceeding 50 $\mu g\ m^{-3}$ in the whole period 1996-2002 owing to dust outbreaks.

Considering only the days influenced by African dust outbreaks over eastern Spain in 1996-2002 (378 out of 2557 days), a mean PM10 level of 22 $\mu g\ m^{-3}$ was obtained, similar to that obtained for the days characterised by regional re-circulation processes (21 $\mu g\ m^{-3}$, 307 days), but much higher than for the other atmospheric scenarios (13 $\mu g\ m^{-3}$, 1361 days, with local PM contributions and an Atlantic advection prevalence, or 15 $\mu g\ m^{-3}$, 511 days, with European and Mediterranean transport).

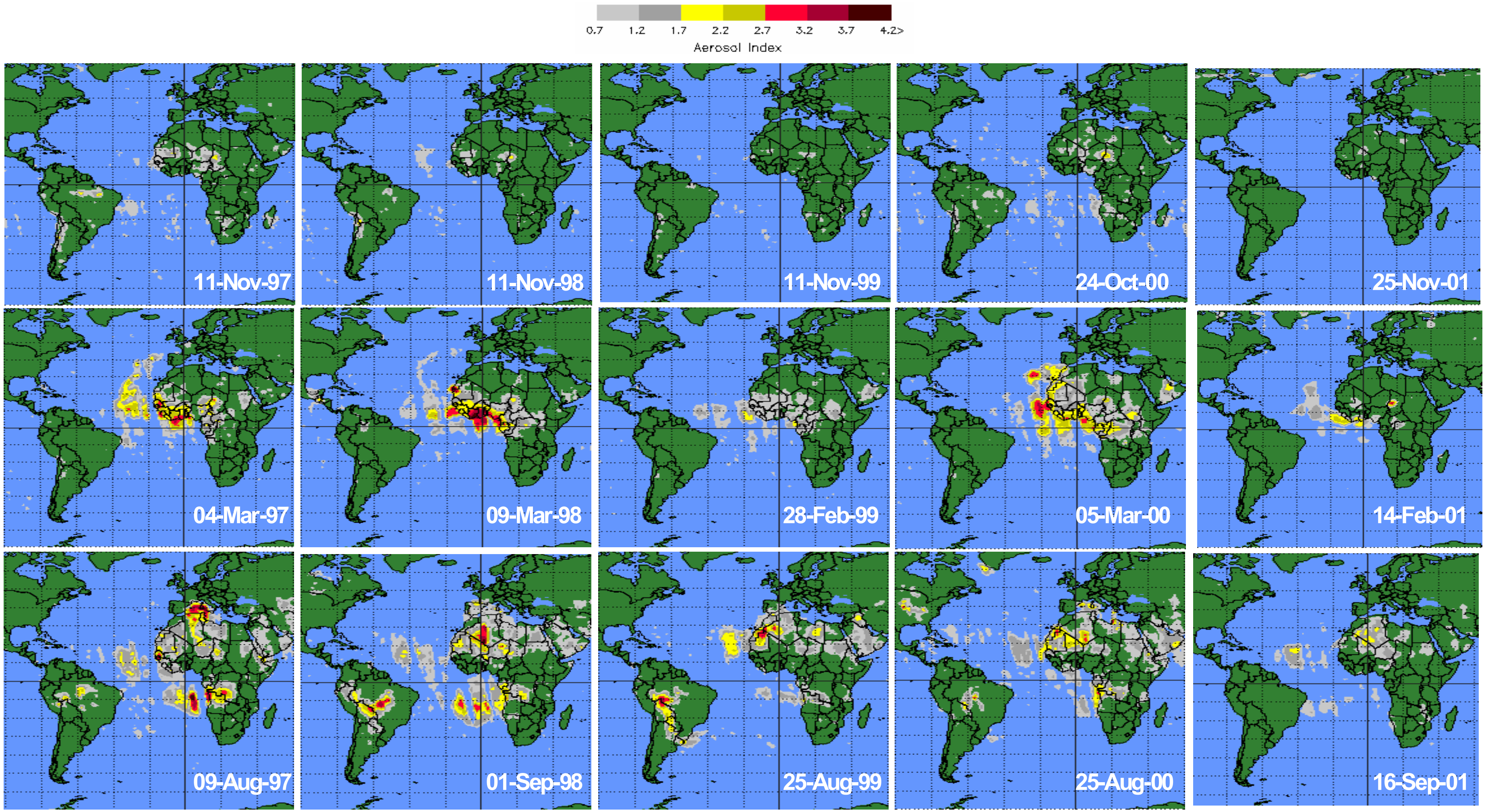


Figure 6.5. Aerosol index from TOMS-NASA for selected days in different periods of the year: autumn, late winter and summer for 1997-2001.

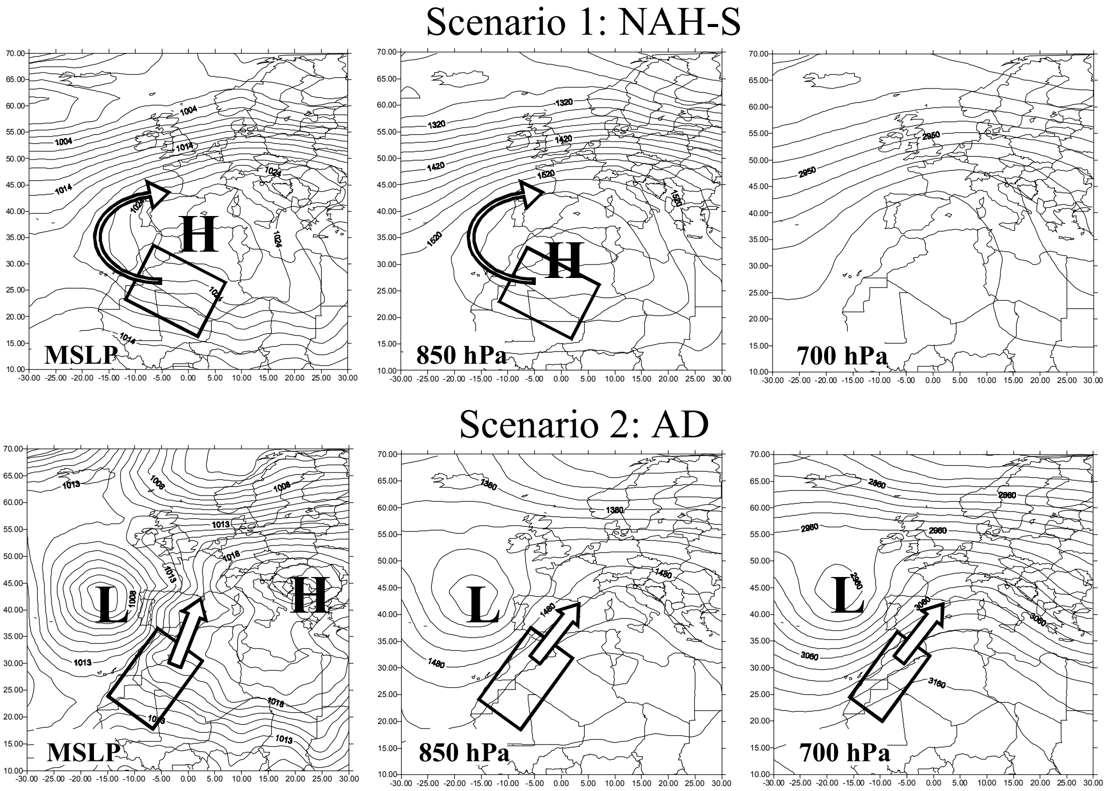


Figure 6.6. Mean geopotential height for 850 and 700 hPa and mean sea level pressure (MSLP) calculated from the NOAA meteorological daily data of the first day of each dust episode for NAH-S scenario 1 (15 episodes) and AD scenario 2 (22 episodes).

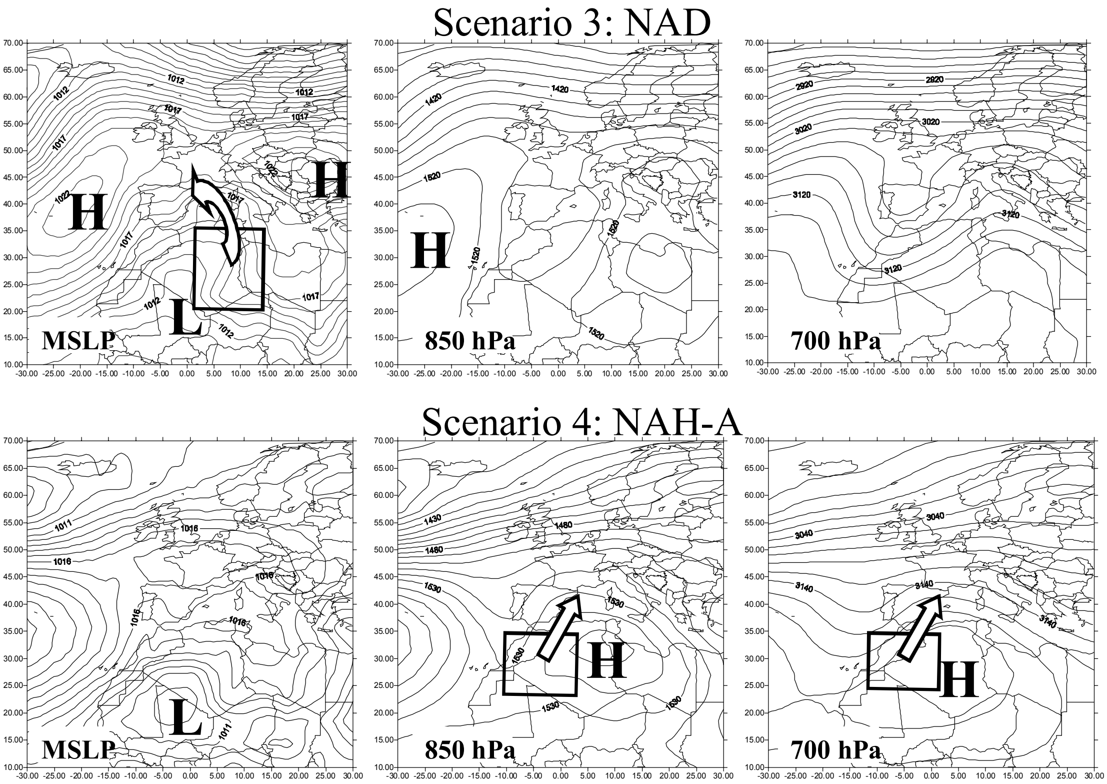


Figure 6.7. Mean geopotential height for 850 and 700 hPa and mean sea level pressure (MSLP) calculated from the NOAA meteorological daily data of the first day of each dust episode for NAD scenario 3 (23 episodes) and NAH-A scenario 4 (52 episodes).

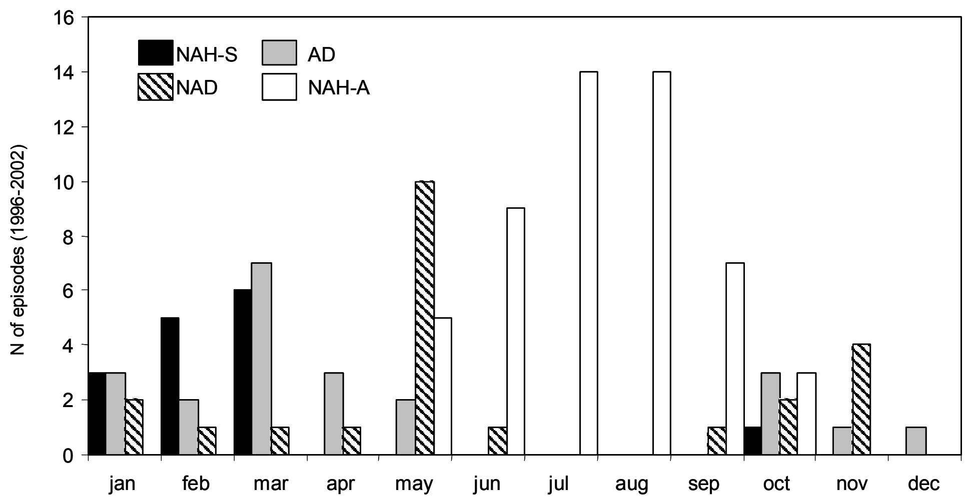


Figure 6.8. Number of dust outbreaks per month in 1996-2002 under the meteorological scenarios distinguished.

The regional re-circulation episodes are typical during summer and were reflected in PM time series by an increase of the background levels in all stations. These peaks were more extended extent but were less pronounced than the peaks due to African events. Furthermore, the elevation in PM levels was always accompanied by elevation in O_3 levels. These facts allowed the detection of these events and the differentiation of these two types of events.

Although there are wide variations in the levels of PM10 in the case of the different African transport scenarios (Table 6.1), the highest mean PM10 levels were measured for the NAH-S and NAH-A scenarios (31 and 30 μg m^{-3}, Table 6.1) whereas the lowest levels were measured for the NAD scenario (17 μg m^{-3}). However, if we combine the mean number of days and the mean levels of PM10 into an impact index (I=mean n of days per year influenced by each type of scenario multiplied by the mean PM10 levels for each scenario in the whole period 1996-2002) we can conclude that NAH-A has the highest impact on PM10 levels (I=874, Table 6.1). The other three scenarios have a very similar impact on PM10 levels in the range of I=186-228 (Table 6.1), approximately four times less than the NAH-A scenario. The lower levels recorded under low pressure scenarios result mainly from the higher rainfall rates. Under anticyclonic settings, two situations may arise. During NAH-S episodes, larger amounts of dust are injected into the troposphere than during NAH-A events because of the intensive convective processes which take place at the source regions. However, under the NAH-S scenario the dust laden air masses are transported a longer way than under the NAH-A scenario (transport over the Atlantic ocean vs. over the Mediterranean basin), and thus they are subject to higher dust segregation by transport. Consequently, the average PM levels recorded under both types of episodes are similar (31 and 30 μg m^{-3}). Although the dust transport occurs at high altitudes in the case of the NAH-A scenario, the considerable vertical development of the boundary layer over the continental areas of the Iberian Peninsula (up to 2500 m, Crespi et al., 1995) causes the dust to abate, resulting in a high impact on surface PM levels.

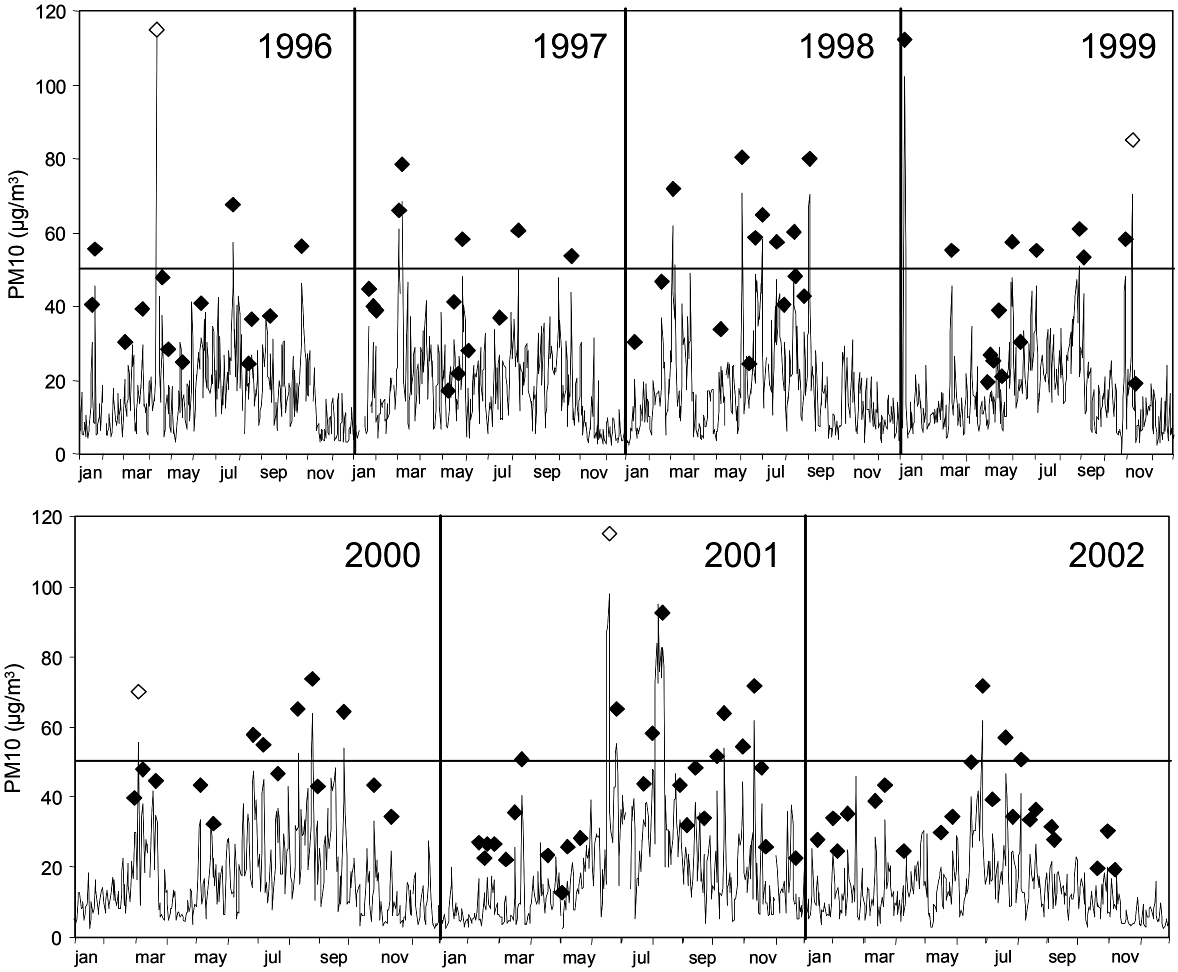


Figure 6.9. Daily PM10 levels in Monagrega for 1996-2002. The black dots mark African dust episodes and the white ones episodes exceeding 50 µgPM10 m^{-3} with non African origin.

In the period January-March, the highest monthly PM10 means are found for the scenario NAH-S (19-40 µg m^{-3}) while in the other two scenarios occurring in this period (AD and NAD) PM10 monthly means range from 12 to 23 µg m^{-3} (Table 6.2). In May a higher simultaneous occurrence of African and rain episodes results in low PM10 monthly means for the NAD and NAH-A scenarios (15 and 19 µg m^{-3}) and higher PM10 monthly means (34 µg m^{-3}) for the scenario AD, although this scenario is not common in May (0.7 days per month, Table 6.2). From June to September the monthly means of PM10 for the African episodes (NAD and NAH-A) are high (32-40 µg m^{-3}) with the exception of the NAD episode in September with a monthly mean of 18 µg m^{-3} (Table 6.2). In October similar PM10 monthly means are recorded for all scenarios (24 to 30 µg m^{-3}). Finally, in November and December few episodes occurred, with relatively low PM10 monthly means for all the scenarios (12-19 µg m^{-3}, Table 6.2).

6.4 Seasonal evolution of dust outbreaks

The following periods can be distinguished in accordance with the seasonal distribution of the different transport scenarios and the analyses of the PM time series:
January-March: Thirty episodes occurred in these months during 1996-2002. Fourteen of these African air mass intrusions may be classified as NAH-S dust outbreaks, whereas twelve events belong to the AD type. The remaining 4 episodes belong to the NAD type. Given that the rain in the first quarter of the year is scant in eastern Iberia, there is a low frequency of wet African episodes (8 events in 7 years). Furthermore, most of these

episodes take place in the lower levels of the atmosphere. Consequently, these episodes often exert considerable influence on levels of PM (Table 6.2).

Table 6.1. Number of days with dust outbreaks occurred under the 4 different meteorological scenarios differentiated and mean daily ambient air levels of PM10 ($\mu g\ m^{-3}$) recorded at Monagrega rural site (Teruel, Spain) for those days. The impact index of each type of scenario is defined as the mean number of days per year with that scenario multiplied by the mean PM10 levels recorded with that scenario.

	NAH-S	AD	NAD	NAH-A
2002				
PM10 ($\mu g\ m^{-3}$)	16	13		23
Days	14	8	0	48
2001				
PM10 ($\mu g\ m^{-3}$)	23	12	17	39
Days	4	12	30	30
2000				
PM10 ($\mu g\ m^{-3}$)	29	21	21	30
Days	3	11	7	25
1999				
PM10 ($\mu g\ m^{-3}$)	78	33	10	35
Days	2	3	10	41
1998				
PM10 ($\mu g\ m^{-3}$)	42	39	41	31
Days	7	2	4	31
1997				
PM10 ($\mu g\ m^{-3}$)	46	39	15	19
Days	6	6	16	7
1996				
PM10 ($\mu g\ m^{-3}$)	30	20		27
Days	9	20	0	22
Mean PM10 ($\mu g\ m^{-3}$)	31	21	17	30
Impact index ($\mu g\ m^{-3}\cdot year$)	199	186	228	874

April: African episodes are infrequent over the Iberian Peninsula. Only 4 episodes were recorded (3 with wet deposition), 3 of them being of the AD type and the remaining one NAD.

May: The frequency of African dust outbreaks over the Iberian Peninsula is high in this month and 17 episodes occurred during the study period. Of these episodes, 10, 5 and 2 correspond to the NAD, NAH-A and AD types, respectively. May is a very rainy month in the western Mediterranean, and as a consequence, 13 episodes were accompanied by wet deposition.

June-August: As reported for May, the summer period has also a high frequency of African events (38 events in the study period). However, this period is characterised by a lower number of wet episodes than in May (13 episodes in May and 11 episodes between June and August during the study period) owing to the antyciclonic conditions of summertime.

September-October: African events are less frequent than in the previous three months. However, 17 episodes occurred in these months, 7 of them accompanied by wet deposition. The NAH-A was the dominant scenario in 10 out of the 17 episodes, followed by NAD and AD scenarios, whereas only one NAH-S episode occurred in this period.

November: Five episodes were found in this month, 4 of them with wet events. The high rainfall rate of this month accounts for the high proportion of wet episodes (Figure 6.1 and 6.2). All these episodes are of the NAD and AD type.
December: Only 1 episode occurred during this month in the 7-year period (AD type).

Table 6.2. Number of days per month with dust outbreaks occurred under the 4 different meteorological scenarios differentiated and mean daily ambient air levels of PM10 (µg m^{-3}) recorded at Monagrega rural site (Teruel, Spain) for those days.

	NAH-S	AD	NAD	NAH-A
January				
Days per month	1.0	1.1	0.6	0.0
PM10	32	19	23	
February				
Days per month	1.4	0.6	0.4	0.0
PM10	19	12	14	
March				
Days per month	2.4	3.3	0.3	0.0
PM10	40	21	18	
April				
Days per month	0.0	1.6	0.3	0.0
PM10		16	8	
May				
Days per month	0.0	0.7	3.4	4.6
PM10		34	15	19
June				
Days per month	0.0	0.0	0.6	7.4
PM10			40	32
July				
Days per month	0.0	0.0	0.0	6.6
PM10				32
August				
Days per month	0.0	0.0	0.0	6.9
PM10				36
September				
Days per month	0.0	0.0	0.6	3.4
PM10			18	31
October				
Days per month	1.3	1.3	1.3	1.4
PM10	30	27	25	24
November				
Days per month	0.0	0.3	1.4	0.0
PM10		19	16	
December				
Days per month	0.0	0.1	0.0	0.0
PM10		12		

6.5 Examples

In this section an example of each of the four dust episodes differentiated is presented. An event of the type NAH-S is presented in Figure 4.10. This episode affected the eastern Iberian Peninsula during the 12th and the 13th of February 2002. The presence of the north African high over the Mediterranean basin at surface levels induces the transport forming the Atlantic arch. The dust reaches the Iberian Peninsula from its western flank and affects the whole Iberian Peninsula. This event had an impact on PM

levels as demonstrated by the concentration peak recorded in the time series of PM10 levels from rural air quality monitoring stations in eastern Spain.
An example of an AD episode is shown in Figure 6.11. This event affected the eastern Iberian Peninsula from the 28th October to the 1st of November 2001. The presence of a depression in front of Portugal at surface levels, reinforced by a high covering the Mediterranean induced the transport of dust that affected the entire Iberian Peninsula. The rural air quality stations in eastern Iberia recorded high levels of PM especially on the 30th and the 31st October 2001.
The example of a NAD episode presented in Figure 6.12 occurred from 11th to 12th of November 2001. An intense depression at surface levels located over Majorca induced the transport of dust which affected only the eastern Iberian Peninsula. High PM10 levels were recorded in the rural air quality stations in eastern Spain. Moreover, this episode was accompanied by rain and wet deposition of dust was recorded at La Castanya.
The summer NAH-A event which affected the eastern Iberian Peninsula from the 23rd to the 26th of June 2001 is presented in Figure 6.13. The presence of an anticyclone at high levels of the atmosphere (850 hPa and above) over north Africa and the Mediterranean favoured the southern transport creating a wide plume of dust which covered the Iberian Peninsula. High levels of PM10 were recorded in Monagrega during this event.

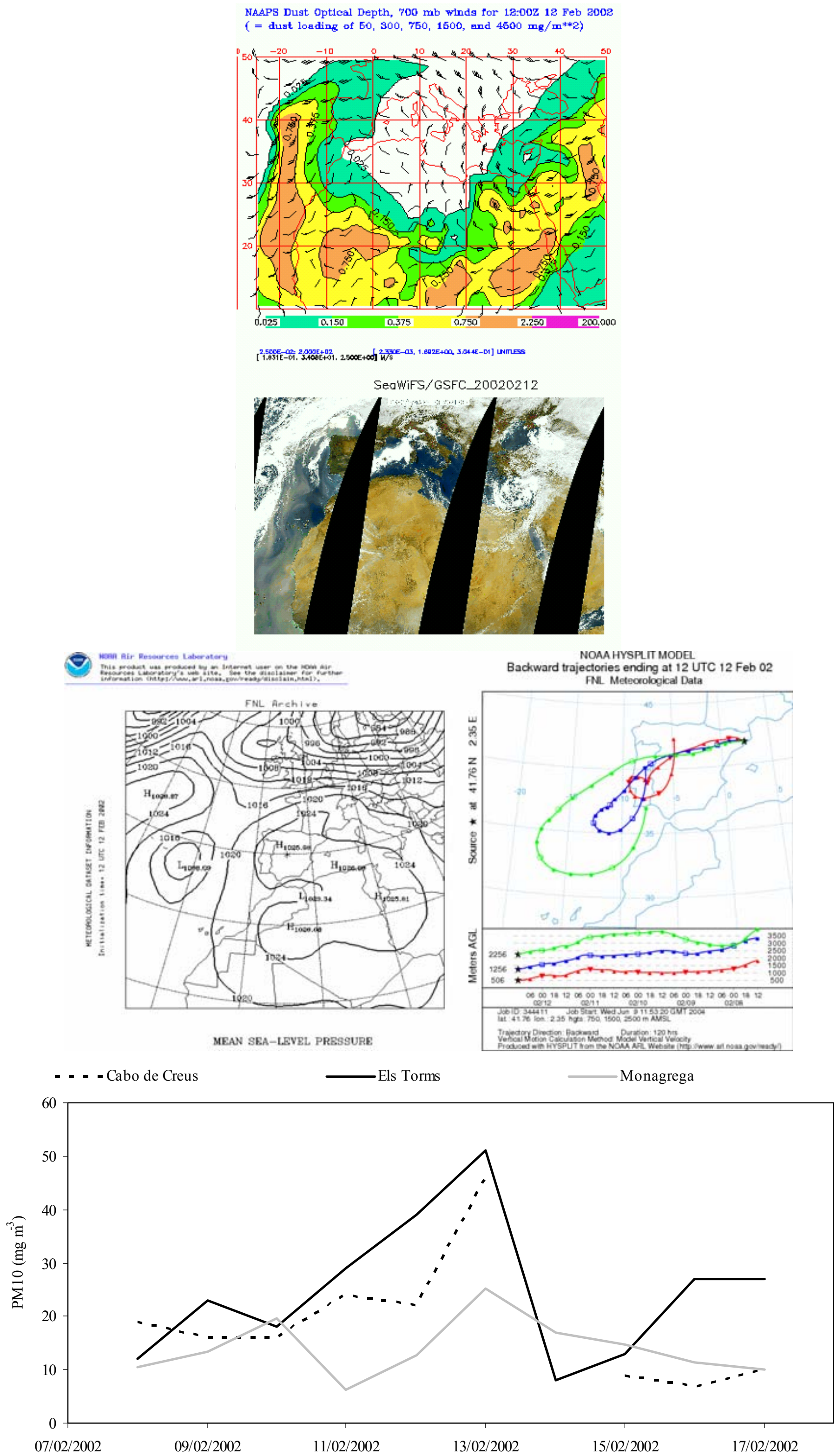


Figure 6.10. Example of an African dust episode of the type NAH-S in eastern Iberia (12-13 February 2002). This figure shows the NAAPS dust optical depth map, the SeaWIFS 'true color' image, the mean sea level pressure map, the 5-days HYSPLIT4 back trajectories for 500, 1500 and 2500 m.a.s.l. and the series of PM10 levels recorded in three regional background stations in eastern Iberia (Cabo de Creus, Els Torms and Monagrega) during the episode.

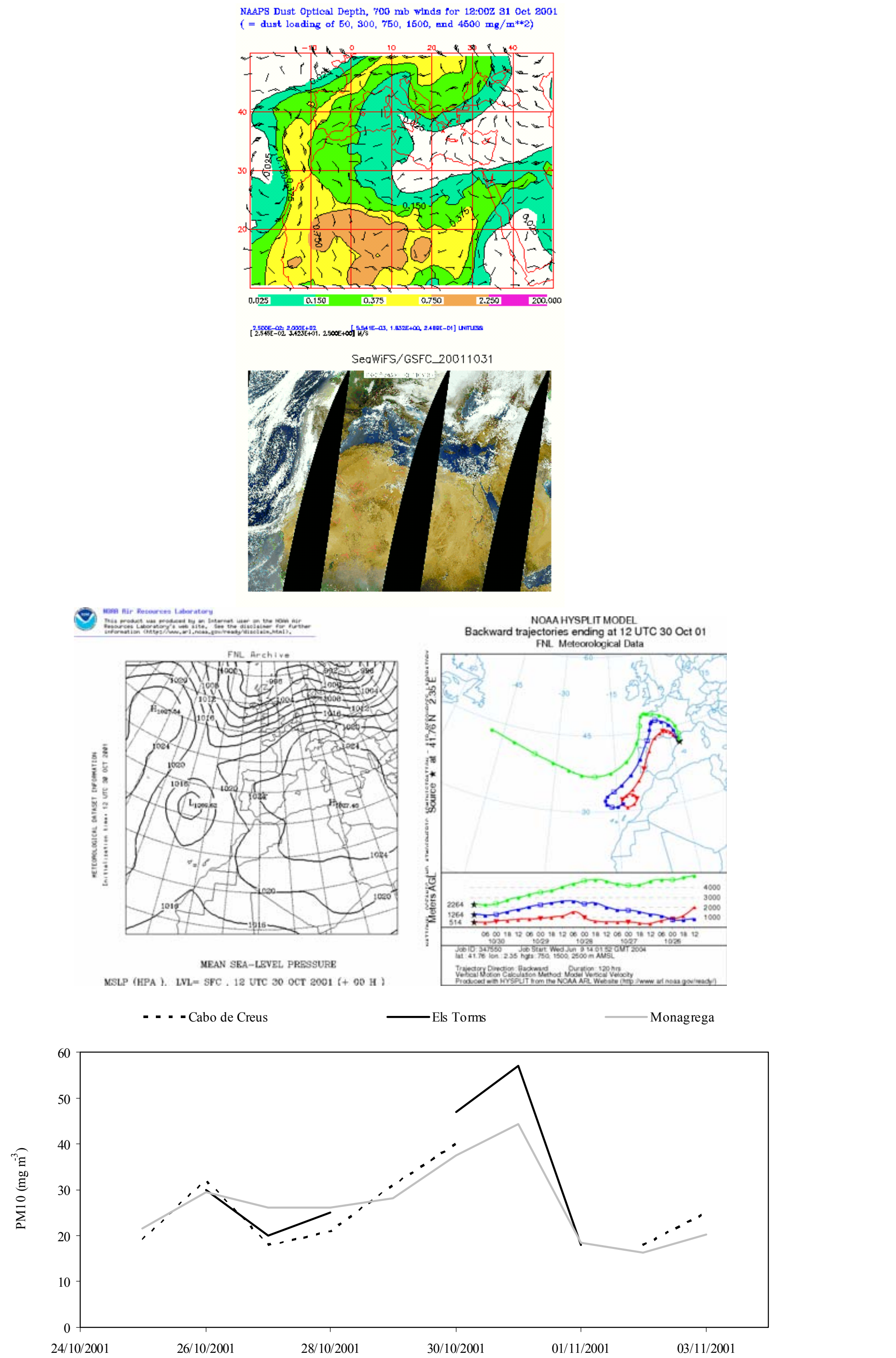


Figure 6.11. Example of an African dust episode of the type AD in eastern Iberia (28 October to 1 November 2001). This figure shows the NAAPS dust optical depth map, the SeaWIFS 'true color' image, the mean sea level pressure map, the 5-days HYSPLIT4 back trajectories for 500, 1500 and 2500 m.a.s.l. and the PM10 levels recorded in three regional background stations in eastern Iberia (Cabo de Creus, Els Torms and Monagrega) during the episode.

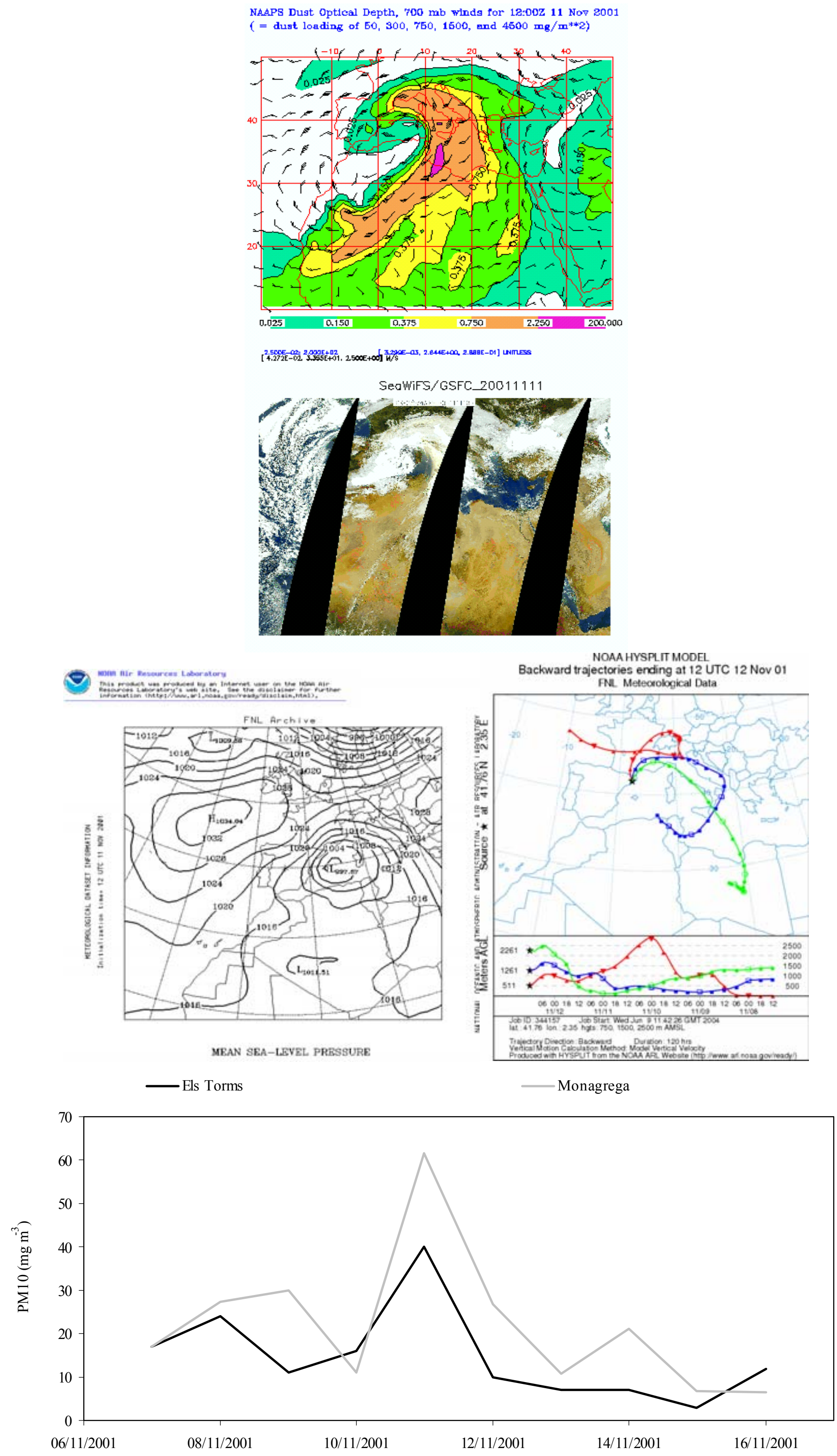


Figure 6.12. Example of an African dust episode of the type NAD in eastern Iberia (11-12 November 2001). This figure shows the NAAPS dust optical depth map, the SeaWIFS 'true color' image, the mean sea level pressure map, the 5-days HYSPLIT4 back trajectories for 500, 1500 and 2500 m.a.s.l. and the PM10 levels recorded in three regional background stations in eastern Iberia (Cabo de Creus, Els Torms and Monagrega) during the episode.

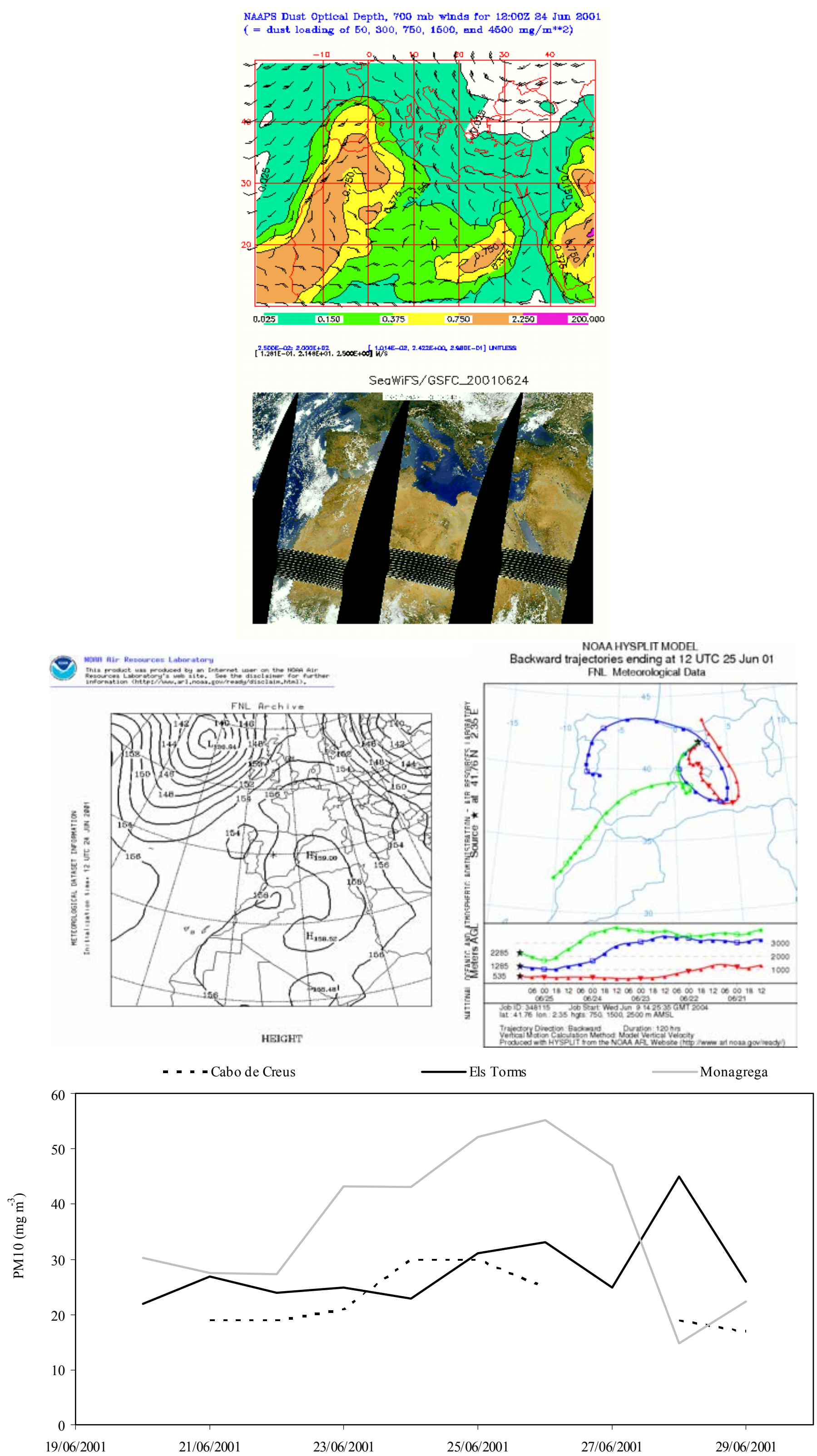


Figure 6.13. Example of an African dust episode of the type NAH-A in eastern Iberia (23-26 June 2001). This figure shows the NAAPS dust optical depth map, the SeaWIFS 'true color' image, the 850 hPa geopotential height map, the 5-days HYSPLIT4 back trajectories for 500, 1500 and 2500 m.a.s.l. and the PM10 levels recorded in three regional background stations in eastern Iberia (Cabo de Creus, Els Torms and Monagrega) during the episode.

7. Intense African “red rains” occurred in the period 1983-2003 over northeastern Spain simulated with SKIRON/Eta model

7. INTENSE AFRICAN “RED RAINS” OCCURRED IN THE PERIOD 1983-2003 OVER NORTHEASTERN SPAIN SIMULATED WITH SKIRON/ETA MODEL

A total of 543 samples of weekly precipitation were collected at the rural sampling station of La Castanya (Montseny, Barcelona, 41º 46’ N, 02º 21’ E, 700 m.a.s.l.) from January 1983 to December 2003 (with a 16 months interruption from January 2001 to June 2002). Precipitation for analysis was collected on a weekly basis, filtered and analysed. Rain events with insoluble PM deposition > 1000 mg m^{-2} were selected. This produced a series of 16 episodes.

The identification of African events was achieved by means of isentropic back trajectory computation using the HYSPLIT model (Draxler and Rolph, 2003) and synoptic chart analysis (at surface, 850 hPa and 700 hPa) and, when available, evaluation of TOMS-NASA aerosol index maps (Herman et al., 1997), SKIRON/Eta and NAAPs aerosol maps provided by Atmospheric Modeling and Weather Forecasting Group in the University of Athens (Kallos et al., 1997) and the Naval Research Laboratory (http://www.nrlmry.navy.mil/aerosol), respectively, meteorological charts by NCEP Climate Diagnostics Center (http://www.cdc.noaa.gov/Composites/Hour/) and the NOAA Air Resources Laboratory (http://www.arl.noaa.gov/ready/amet.html), and satellite imagery supplied by NASA SeaWIFS (McClain et al., 1998).

The insoluble PM deposition load from the 16 intense events reached 78280 mg m^{-2}, this accounts for more than 80% of the total amount of insoluble PM deposited in all African wet deposition events in the two study periods.

Table 7.1 shows the description of the intense events. The insoluble PM deposition load ranged from 1000 to 19435 mg m^{-2}. The “red rains” occurred in the wet periods of the Iberian Peninsula (late winter-spring and autumn). Nine of the 16 intense events occurred in late winter-spring and the rest (7 events) occurred in autumn. The insoluble PM deposition load collected during the late winter-spring intense events reached 35642 mg m^{-2} (3960 mg m^{-2} per event) clearly lower than the 42638 mg m^{-2} (4264 mg m^{-2} per event) during the autumn events (Figure 7.1).

7.1 Meteorological description of episodes

Two meteorological scenarios were suggested to be responsible for episodes of wet deposition of north African dust over northeastern Spain. Both are linked to the presence of depressions associated to frontal situations. One transport scenario is the Atlantic depression (AD): A relatively deep low pressure centre located off west the Portuguese coast with an associated high or ridge over the central Mediterranean Sea may be the cause of dust transport towards eastern Iberia. This transport scenario results in a synoptic flow coming from the south.

Inspecting the maps of various meteorological variables obtained after simulating the 16 episodes with SKIRON/Eta model, it was concluded that 6 of the 16 intense events of dust deposition corresponded to an AD scenario (Table 7.1). The total insoluble PM deposition load in the 6 events classified as AD is 26305 mg m^{-2} (34% of the total amount of dust deposition in the 16 events whole sampling period and 4384 mg m^{-2} per episode, Figure 7.1). These AD intense events occurred in autumn (4 out of the 6 episodes) and in late winter-spring (2 out of the 6 episodes).

An example of an AD intense wet deposition event is the one occurred on December 1987 (sampling date 05/12/1987). As proved by the simulation made with SKIRON/Eta, the transport and deposition of north African dust occurred over the Iberian Peninsula from the 3rd to the 5th December 1987 (Figure 7.2). The wet deposition of dust affected on the 4th the west, centre and north of the Iberian Peninsula and the east on the 5th and 6th. The strong winds registered over western Morocco and western Algeria on the 4th were caused by the combined effect of a deep depression over the Atlantic right by the Portuguese coastline and an anticyclone over Libya. The displacement of the depression to the northwest of the Iberian Peninsula on the 5th and the 6th created a western flow which resulted in the end of the dust outbreak.

Table 7.1. Intense events of dust deposition in La Castanya (Montseny, NE Spain) including the insoluble PM deposition load. The classification in terms of the meteorological scenario is also shown.

Sampling date	Rain days	Precipitation (mm)	Insoluble PM deposition load (mg m^{-2})	Synoptic scenario
12/11/1984	9-11	49.7	16356	NAD
25/04/1985	21,22,25	30.8	3631	AD
04/11/1987	28,29	42.5	1013	AD→NAD
05/12/1987	3,4,5	70.9	3989	AD
09/05/1988	6,7,8	5.3	1402	NAD
11/03/1991	5,6	26.9	2958	AD
28/03/1991	24,25	169.0	19435	NAD
16/10/1991	9,10,11	15.4	6731	AD
11/03/1992	4-6,8	22.6	2739	NAD
21/11/1996	11-17	256.0	6440	AD
03/05/1999	28,29,2,3	5.3	1000	NAD
14/06/1999	9,12,13	19.8	1001	NAD
15/11/1999	11-12	80.3	5553	NAD
27/02/2003	19-21,24-26	165.0	1435	AD→NAD
13/05/2003	6-7	27.0	2040	NAD
27/11/2003	21-24,26	56.3	2556	AD
Mean		65.2	4892	

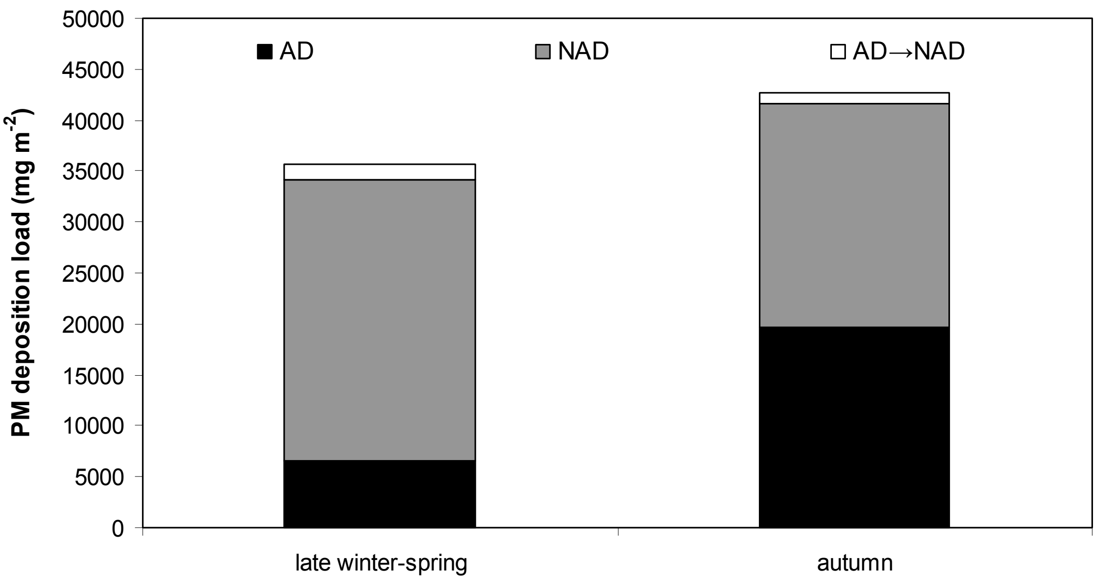


Figure 7.1. Insoluble deposition fluxes at La Castanya during the 16 most intense dust wet deposition episodes distinguishing transport scenarios (AD, NAD and AD→NAD) and seasonal occurrence (either late winter-spring or autumn).

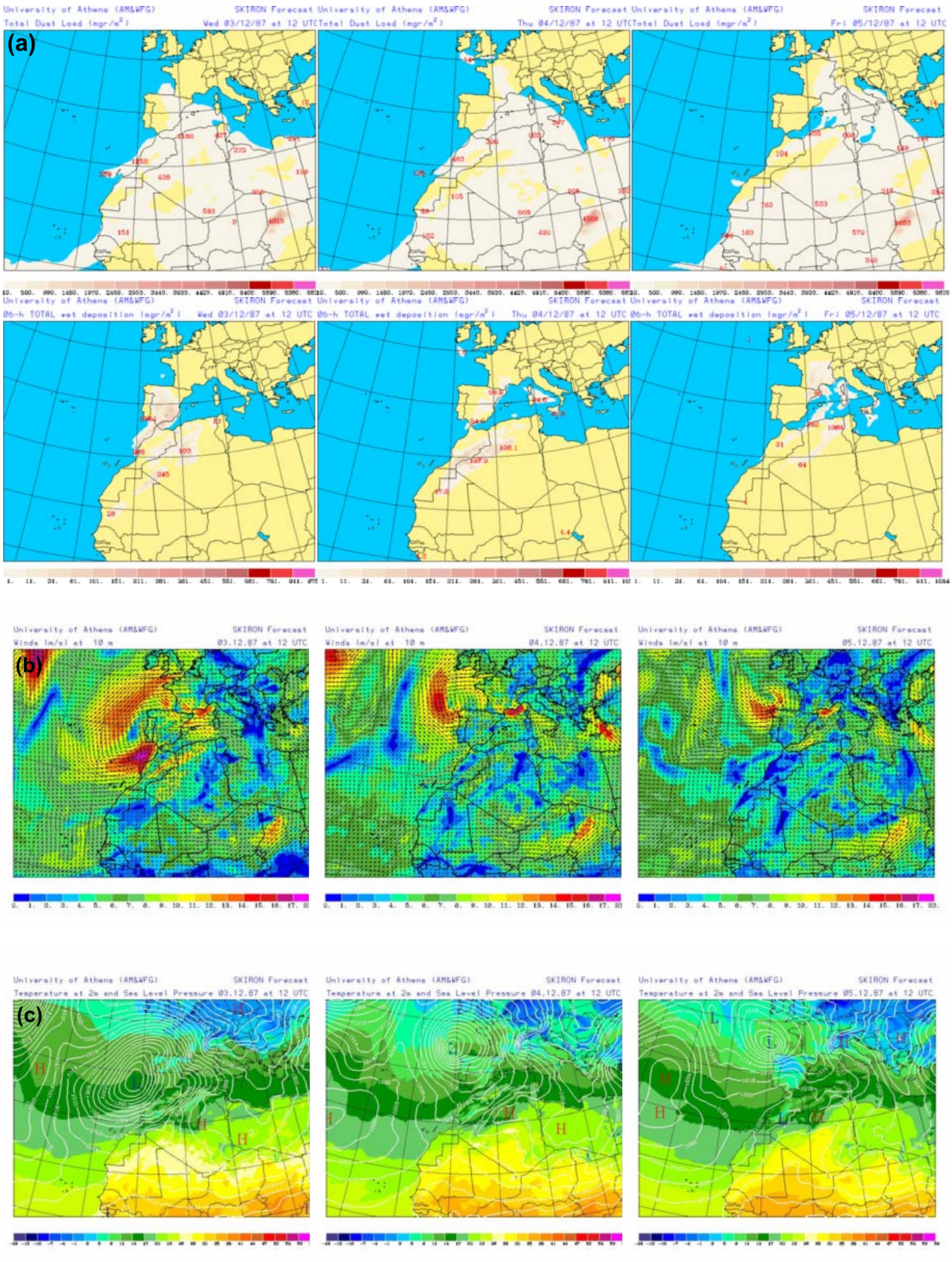


Figure 7.2. SKIRON/Eta maps of total dust load and total wet deposition (a), winds at 10 metres (b) and temperature at 2m and sea level pressure (c) for the 3rd, 4th and 5th December 1987 (AD episode).

Another second transport scenario is the north African depression (NAD): A low centre located over Morocco, Algeria, Tunisia, or even the western Mediterranean, may favour the transport of African air masses towards Iberia across the Mediterranean.
Eight of the 16 intense events occurred under the NAD meteorological scenario (Table 7.1). The insoluble fraction deposited during these events was 49526 mg m^{-2} (63% of total amount of dust deposition in the 16 intense episodes and 6191 mg m^{-2} per event). This amount is considerably higher than the total amount of insoluble dust deposited in the AD events. Intense events associated with NAD scenario occurred also in spring (6 events) and in autumn (2 events).
Among the 16 intense events, an example of a NAD episode occurred on March 1992 (sampling date 11/03/1992) is presented in Figure 7.3. As shown in the SKIRON/Eta maps, transport and wet deposition of dust occurred over the eastern Iberian Peninsula from the 4^{th} to the 5^{th} March 1992. The deposition of dust occurred over southeastern Iberia during the 4^{th} and over northeastern Iberia during the 5^{th}. The strong winds registered over central and eastern Algeria and Tunisia on the 4^{th} and 5^{th} were a reflection of the effect of a relatively deep depression centred on Algeria. The transport of African air masses over eastern Iberia was reinforced by the presence of a high pressure centre over Italy. On the 6^{th}, the Azores high shifted its location towards the east covering the west and north of the Iberian Peninsula generating a northern flow which retired the dust from the Iberian Peninsula.
The intense wet deposition episodes responded mainly to AD and NAD transport scenarios. However, hybrid situations may also cause intense wet deposition of dust over Iberia. A depression originally located over the Atlantic Ocean in front of Portugal may evolve crossing northern Africa and reaching eastern Algeria, Tunisia or the Mediterranean. This corresponds to an AD situations evolving towards a NAD situation (AD→NAD scenario).
The AD→NAD hybrid scenario was only associated with 2 of the 16 intense episodes. During these events an insoluble load of 2449 mg m^{-2} deposited (3% of total amount of dust deposition in the 16 intense episodes and 1224 mg m^{-2} per event). One of the episodes occurred in late winter-spring and the other in autumn.
An example of an AD→NAD episode is presented in Figure 7.4. This dust outbreak over the Iberian Peninsula occurred on February 2003 (sampling date 27/02/2003) running from the 24^{th} to the 26^{th}. The SKIRON/Eta maps, show that the transport and deposition of dust first occurred over the central and western Iberian Peninsula (on the 24^{th}) and in the next two days (25^{th} and 26^{th}) over the east. This is in accordance with the movement of a depression which initially was located over the Atlantic Ocean off northwest the Iberian Peninsula, on the 25^{th} the depression was located over the southeastern Iberian Peninsula and on the 26^{th} it reached eastern Algeria. As a consequence of this displacement of the depression, the strongest winds over north Africa were registered over Morocco and western Algeria on the 24^{th}, over northern Algeria on the 25^{th} and over Tunisia on the 26^{th}.

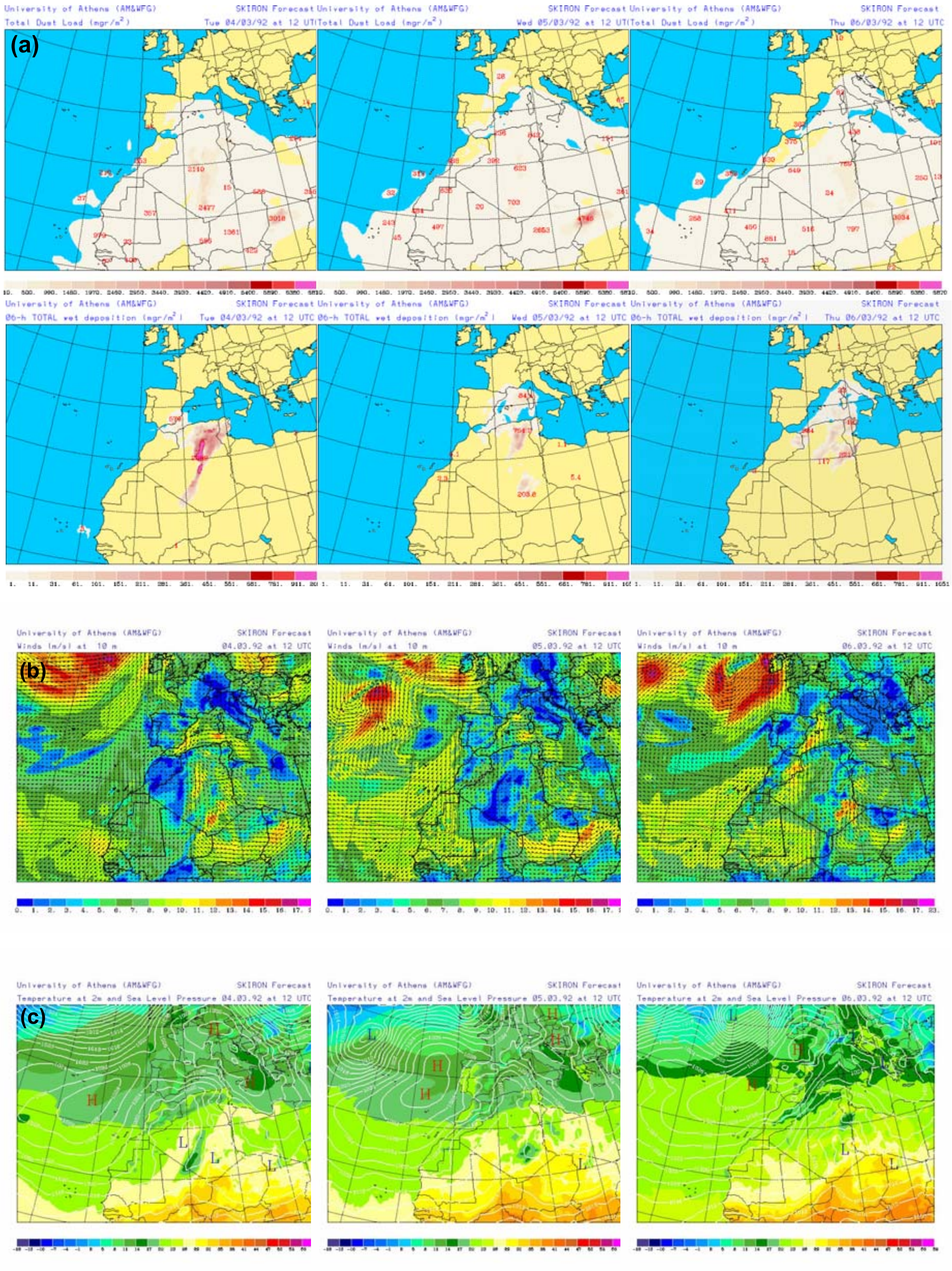


Figure 7.3. SKIRON/Eta maps of total dust load and total wet deposition (a), winds at 10 metres (b) and temperature at 2m and Sea level pressure (c) for the 4th, 5th and 6th March 1992 (NAD episode).

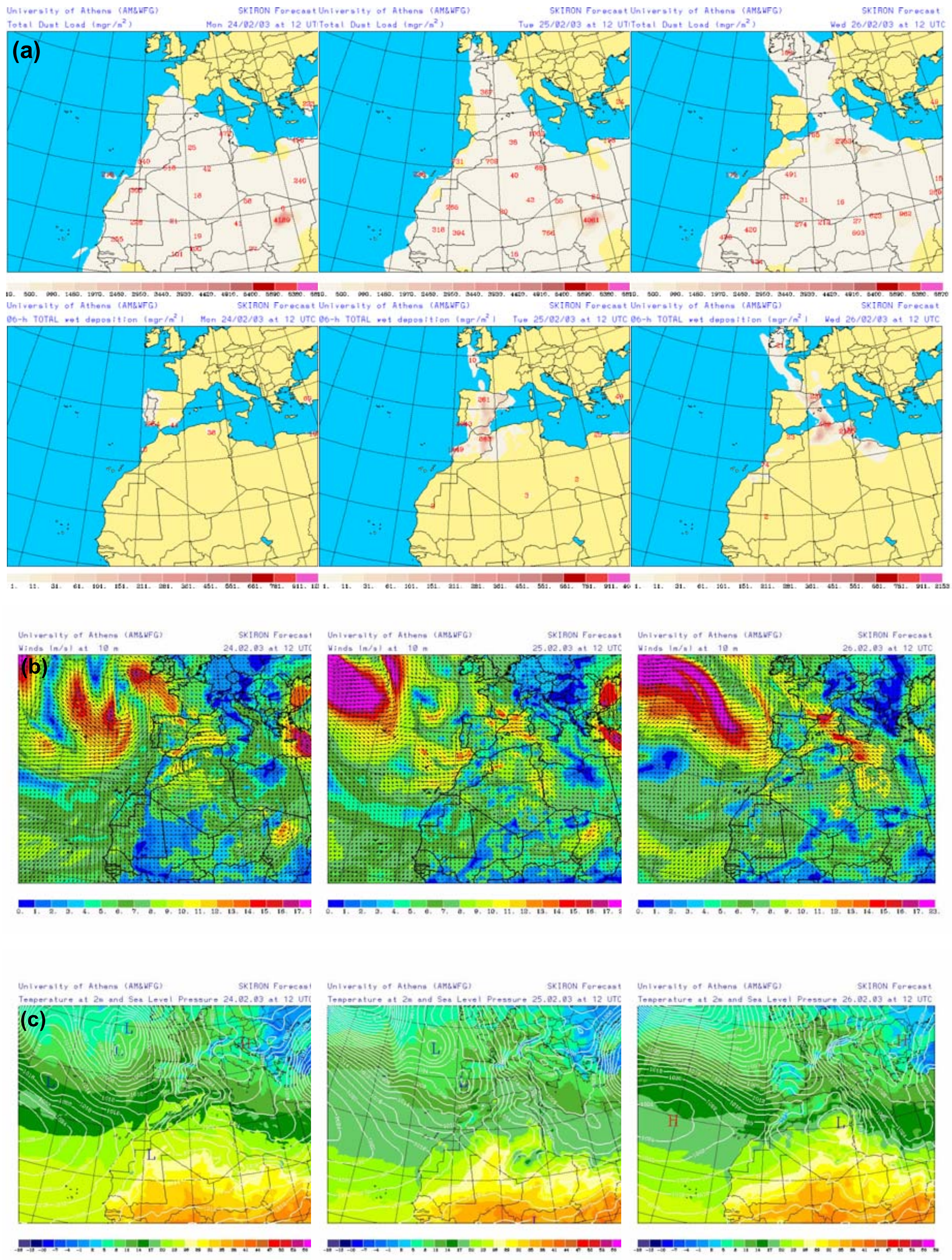


Figure 7.4. SKIRON/Eta maps of total dust load and total wet deposition (a), winds at 10 metres (b) and temperature at 2m and Sea level pressure (c) for the 24th, 25th and 26th February 2003 (AD→NAD episode).

7.2 Estimation of PM concentration and wet deposition fluxes by SKIRON/Eta

These intense wet deposition events were simulated with SKIRON/Eta and the performance of this model was firstly evaluated by means of the threat score test proposed by Wilks (1995). Making use, when available, of TOMS aerosol index maps and SeaWIFS satellite imagery, the presence of dust over 3 regions of the Iberian Peninsula (west, centre or east, Figure 7.5) was confirmed and then compared with the dust load maps of SKIRON/Eta. The model may either had predicted dust in a region were there was dust (Hits=a, Figure 7.6), predicted dust were there was not (False alarm=b, Figure 7.6) or not predicted dust in region were actually there was dust (Miss=c, Figure 7.6). The “Probability of detection” or POD, defined as a/(a+c), for the episodes simulated reached a value of 0.79. The “Bias” or B, defined as (a+b)/(a+c) gives an estimation of how close was SKIRON/Eta of predicting the exact number of cases which actually occurred in each region. If B=1 the number of forecasted and observed cases are the same, if B<1 the number of predicted cases are less than the observed and if B>1 the number of predicted cases are more than the observed. For the episodes studied B reached a value of 2.03, thus, SKIRON/Eta overestimated the number of cases. However, when using TOMS data, the detection of dust located in the first 1000 metres of the atmosphere is not possible (Torres et al., 1998 and 2002). AD and NAD transport scenarios are generally associated with low level atmospheric transport which may have been undetected by TOMS. Moreover, the dust plumes are difficult to be observed in SeaWIFS images when clouds are present. Since, the events inspected in this study were generally associated with rain, the cloud cover over the Iberian Peninsula may have confused dust detection. These two factors may have resulted in the underestimation on the number of dust events detected.

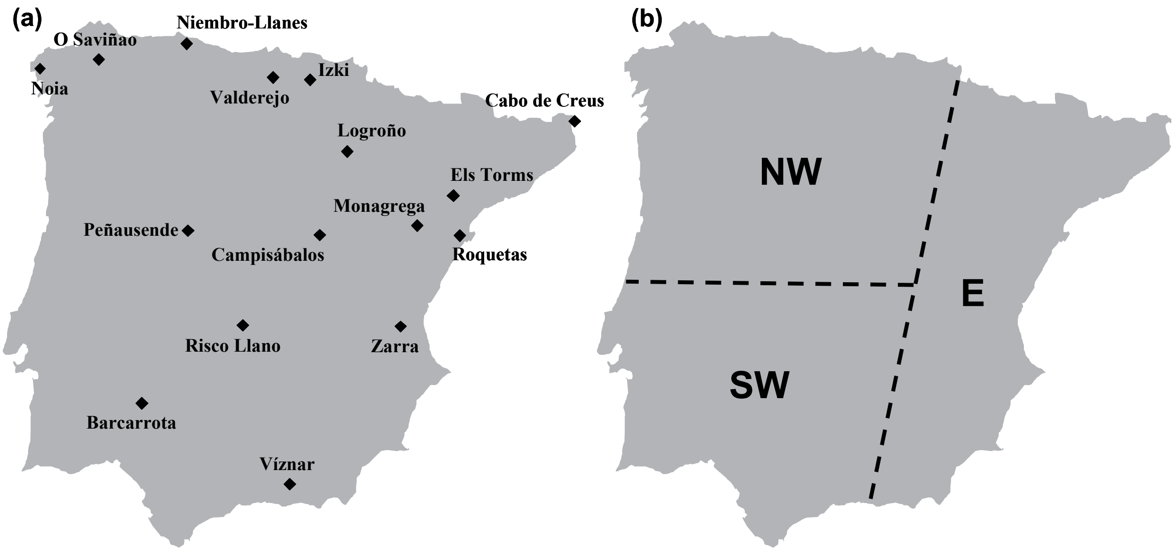


Figure 7.5. Regional background monitoring stations from which TSP and PM10 daily data was obtained (a) and three regions in which the Iberian Peninsula was divided in order to perform the qualitative validation test proposed by Wilks (1995) (b).

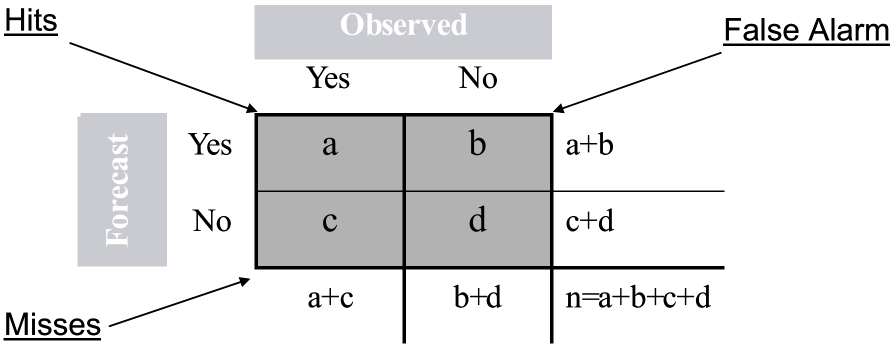


Figure 7.6. Scheme of the score thread test (Wilks, 1995) for a qualitative validation of models.

The performance of SKIRON/Eta was also validated in the quantitative stage. For this purpose, TSP and PM10 daily concentrations from regional background monitoring stations (Figure 7.5) were compared with the dust concentrations simulated by SKIRON/Eta. A number of these stations belong to the EMEP network and other regional air quality monitoring stations (see Table 7.2).

Table 7.2. Spanish air quality monitoring stations from which TSP and PM10 data was obtained for SKIRON/Eta validation.

Site	Air quality monitoring network	Location	Altitude (m.a.s.l.)
Noia	EMEP-MMA*	42º 44' N, -8º 55' E	683
Niembro-Llanes	EMEP-MMA	43º 27' N, -4º 51' E	134
O Saviñao	EMEP-MMA	43º 14' N, -7º 42' E	506
Logroño	EMEP-MMA	42º 27' N, -2º 30' E	445
Roquetas	EMEP-MMA	40º 49' N, 0º 29' E	44
Cabo de Creus	EMEP-MMA	42º 19' N, 3º 19' E	23
Els Torms	EMEP-MMA	41º 24' N, 0º 43' E	470
San Pablo de los Montes	EMEP-MMA	39º 23' N, -4º 20' E	917
Risco Llano	EMEP-MMA	39º 31' N, -4º 21' E	1241
Campisábalos	EMEP-MMA	41º 17' N, -3º 09' E	1360
Peñausende	EMEP-MMA	41º 17' N, -5º 52' E	985
Zarra	EMEP-MMA	39º 05' N, -1º 06' E	885
Bancarrota	EMEP-MMA	38º 29' N, -6º 55' E	393
Víznar	EMEP-MMA	37º 14' N, -3º 28' E	1230
Valderejo	Autonomous Government of the Bask Country	42º 53' N, -3º 14' E	911
Izki	Autonomous Government of the Bask Country	42º 39' N, -2º 30' E	835
Monagrega	ENDESA	40º 59' N, -0º 12' E	600

*MMA: Spanish Ministry of the Environment

Although the concentration of crustal elements in air samples collected during African dust outbreaks is dominant (from 50 to 80% of the PM10 concentration in rural sites) during episodes occurred over northeastern Spain according to Rodríguez et al. (2002), a considerable fraction of the TSP and PM10 concentrations would correspond to local/regional anthropogenic (mainly carbonaceous compounds, sulphate and nitrate) or other natural species different from African dust (such as bioaerosols or marine salts). Furthermore, it is not possible to separate the effects of local sources of crustal species from remote sources (African deserts). These factors may partly explain why SKIRON/Eta slightly underestimates PM10 and TSP concentrations (Figures 7.7 and

7.8). These scattering plots indicate a logical larger underestimation of TSP concentrations since PM10 levels are lower than TSP levels. This underestimation in dust concentration predictions by SKIRON/Eta system has been previously detected in the work by Kallos et al. (2005).

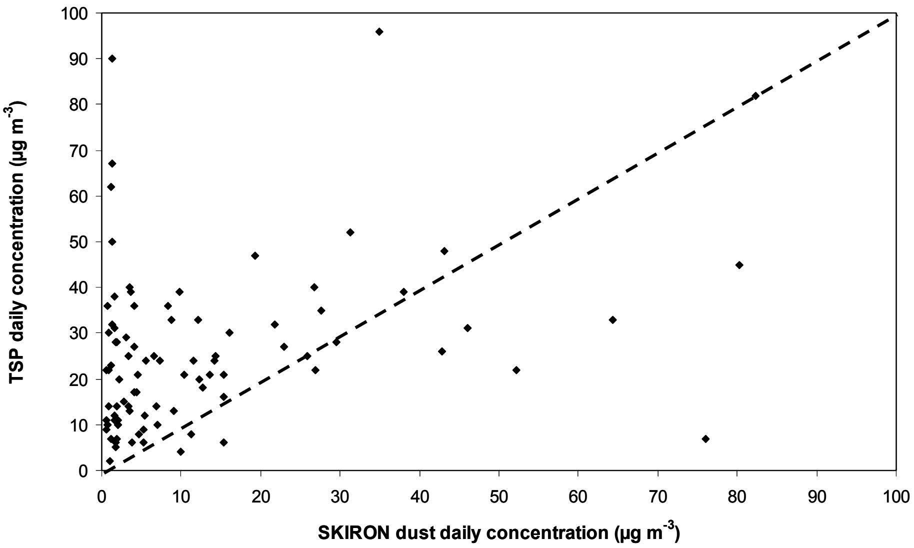


Figure 7.7. Daily TSP concentrations at regional background stations of the Iberian Peninsula versus dust concentration predicted by SKIRON/Eta for the 16 intense episodes.

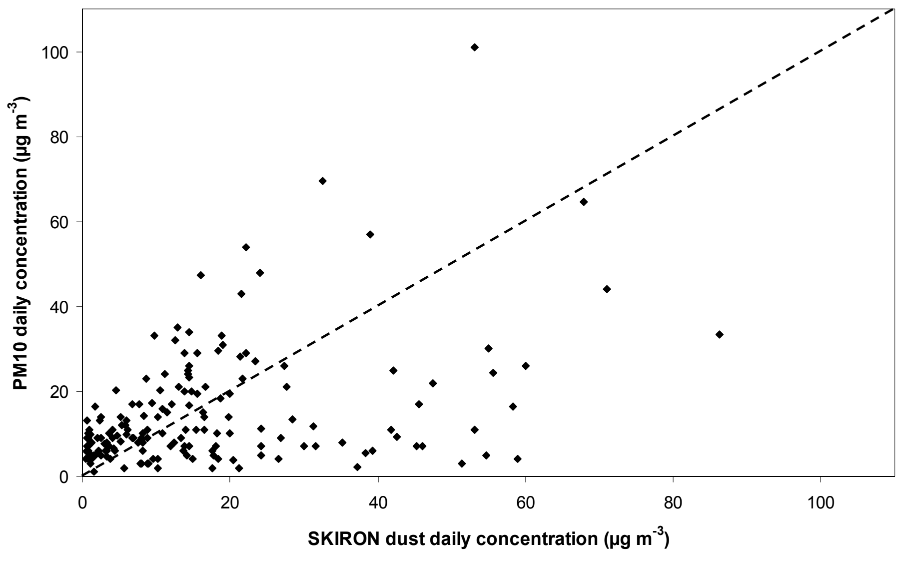


Figure 7.8. Daily PM10 concentrations at regional background stations of the Iberian Peninsula versus dust concentration predicted by SKIRON/Eta for the 16 intense episodes.

The occurrence of the 16 wet deposition episodes occurred over northeastern Spain was captured by SKIRON/Eta. However, although the qualitative performance of the model simulating “red rains” is satisfactory, the quantification of the dust fluxes is underestimated. In particular, the total annual dust wet deposition for 2003 over northeastern Iberia according to SKIRON/Eta fell in the range 500-1000 mg m^{-2} (Kallos et al., 2005) while in three intense episodes sampled at La Castanya in 2003 (sampled on 27/02/2003, 13/05/2003 and 27/11/2003) the insoluble PM load reached 1435, 2040 and 2556 mg m^{-2} respectively (Table 7.1). Various factors may contribute to this mismatch since the wet deposition of dust consists on the interaction of dust and rain. Firstly, it is difficult to compare the deposition levels measured with a sampler and extrapolate results to a 0.2°x0.2° grid; more sampling points should be available to obtain mean values that may represent wide areas to be compared with model outputs. Furthermore, the wet deposition sampled method also has limitations since it consists on an open collector. An important fraction of the amount of deposited material could correspond to resuspension of dust from the area around the collector. This secondary process cannot be captured by SKIRON/Eta. A third reason may have to do with the prediction of rain by the model. This is influenced by the relatively coarse resolution used for the experiments (0.2ºx0.2º) which is not enough to fully simulate the convective processes. In general, the quantitative prediction of rain with such coarse model resolution is a difficult task. Finally other errors may be present from the contamination of the samples from anthropogenic sources as well as the different time intervals for monitoring deposition and for modelling increments.

7.3 Source areas detection

Maps showing dust surface flux, that is, the mass of dust emitted into the atmosphere per unit time and square metre, were produced in order to identify the most active source areas involved in these episodes. Inspecting these maps the first conclusion to be drawn is that the dust influx intensity has a clear daily cycle since this variable is maximum at 12 UTC related to the highest intensity of convection at this part of the day (see example in Figure 7.9). As a result of these dynamics, practically all the desert areas of northern Africa are activated at 12 UTC emitting roughly 100 to 1000 times more dust mass into the atmosphere than at 00, 06 and 18 UTC (Figure 7.9). Thus, dust is mobilised owing to convection with roughly the same intensity depending on the time of the day. However, the moisture of certain areas of northern Africa in some periods of the year may prevent dust to be elevated even at the time of the day with the maximum convection. This convection effect overlaps with the effect of the synoptic winds which can also generate dust mobilisation over northern Africa. This second factor explains the different emissions from certain source areas. Once convective movements have lifted dust from the desert surface, synoptic winds associated with the depressions involved in the two transport scenarios described above (AD, NAD and AD→NAD), trigger the transport of this material over the Iberian Peninsula from different areas of northern Africa.

The active source areas involved in these 16 episodes were constrained to the northernmost regions of the Saharan desert (northern, western, and central Algeria and Tunisia, Table 3). Although dust mobilisation may have occurred at more southern (Mali, Niger or the Bodele depression) or eastern (Libyan Desert) areas, this material was not transported towards the Iberian Peninsula in any of the cases. This was verified with the surface winds and dust load maps. In general, during AD events the source areas located at the west of central sections of northern Africa tend to be especially active (from the Western Sahara to central Algeria) while whenever the transport was associated with a depression located over northern Africa (NAD and AD→NAD episodes) Tunisia and central and eastern Algeria showed higher relative activity. Examples of two episodes with different active source areas are shown in Figure 7.10. The first example (Figure 7.10a) is an episode of AD type (sampled on the 16/10/1991) in which western and northern Algeria were the most active source areas persistently during the event. The winds over these regions transported dust over the Iberian Peninsula from the 9th to the 11th of October. Winds favouring the transport towards the western Mediterranean can be observed over southern Algeria and Tunisia only on the 9th but, since these regions were not persistently active throughout the episode, the contribution to the transported dust plume should not be important. The second example is an NAD episode (sampling date 28/03/91) during which northern and eastern Algeria and Tunisia were the most active source areas. These regions persistently emitted dust which was injected over the Mediterranean from the 24th to the 26th of March. The emission at the Western Sahara and Mauritania was very important all throughout the episode although the northern winds over those regions transported the dust towards the south not reaching the Iberian Peninsula.

Owing to the mixing effect of the diurnal cycle explained above (dust is mobilised from all desert areas at the time of maximum heating owing to convective movements and mixed in the atmosphere) and the various source areas contributing to form the dust plumes in these events, the distinction of specific source areas for these 16 episodes is not an easy task.

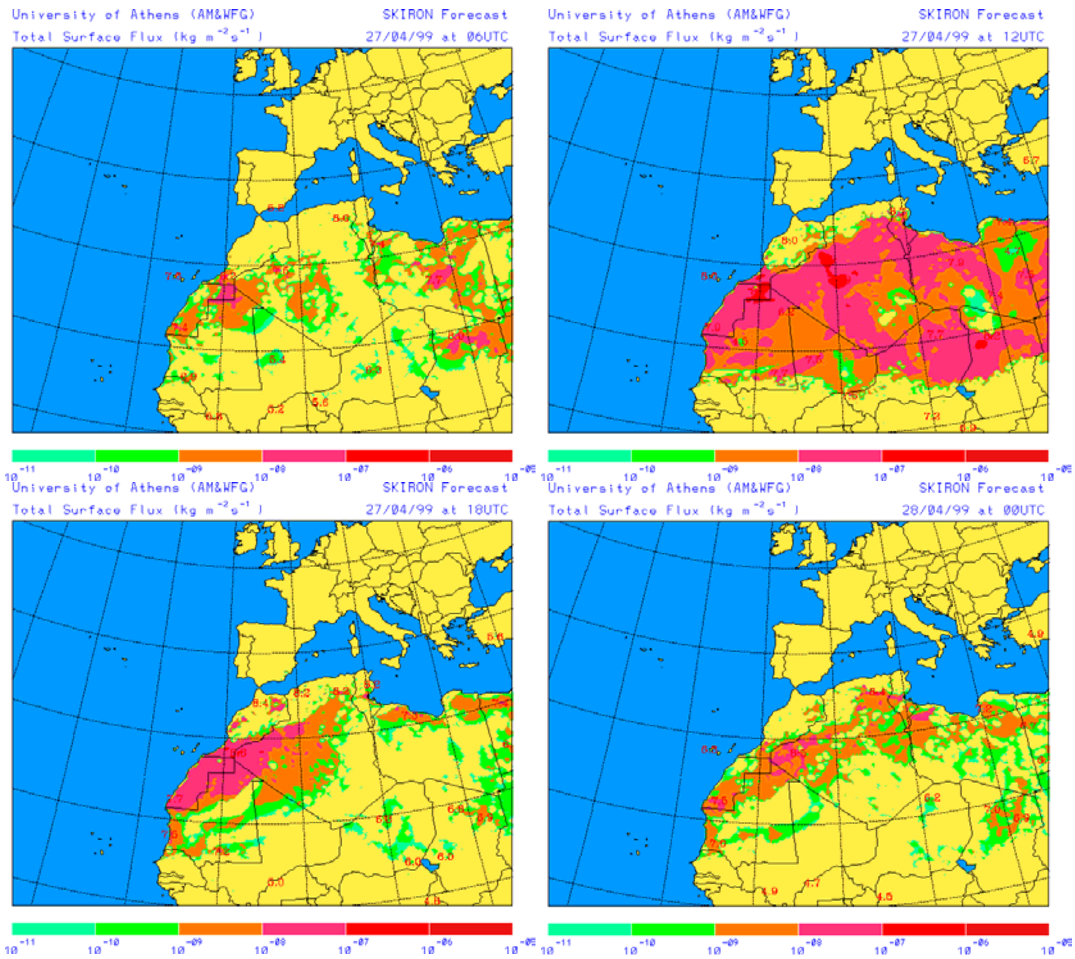


Figure 7.9. Total surface flux at 06, 12, 18 and 24 hours for 27/04/1999.

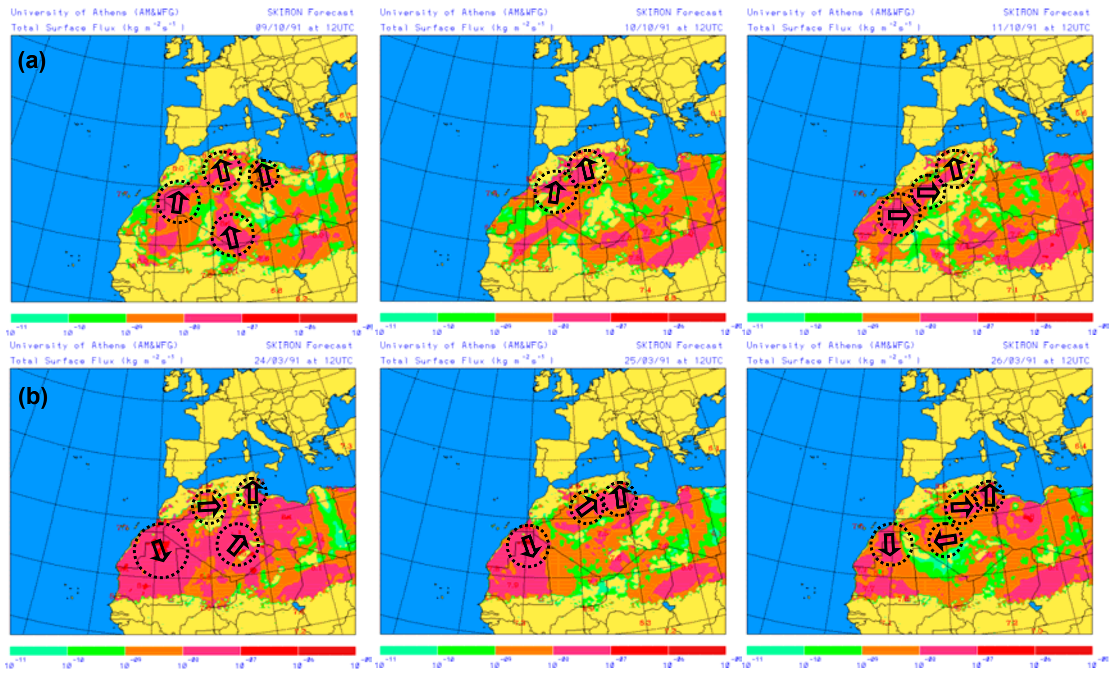


Figure 7.10. Total surface flux at 12 hours for two intense African dust deposition episodes running from the 9th to the 11th of October 1991 (a) and from the 24th to the 26th of March 1991. The dotted circles highlight the most active source areas while the arrows inside the circles denote the wind direction over that area.

Table 7.3. Active source areas involved in each of the intense African dust wet deposition events occurred over northeastern Iberian Peninsula.

Sampling date	Synoptic scenario	Active source areas (Dates)
12/11/1984	NAD	Western Sahara+western Algeria (08-09/11) central Algeria+Tunisia (10-11/11)
04/11/1987	AD→NAD	western Algeria+Tunisia (28-29/10)
05/12/1987	AD	western Algeria (03-04-05/12)
09/05/1988	NAD	central Algeria (05-06/05) Tunisia (07/05)
11/03/1991	AD	Western Sahara+western Algeria (04/03) western+central Algeria (05/03) central+eastern Algeria (06/03)
24/03/1991	NAD	northern Algeria+Tunisia (24,25/03)
16/10/1991	AD	western+northern+central Algeria (09-10-11/10)
11/03/1992	NAD	central Algeria (04-05/03)
21/11/1996	AD	western+northern Algeria (11-17/11)
03/05/1999	NAD	Western Sahara+western Algeria (27/04) western Algeria+northern Algeria+Tunisia (28-29-30/04; 01/05) central Algeria (02/05)
14/06/1999	NAD	western Algeria+northern Algeria (09-12/06)
15/11/1999	NAD	western+northern Algeria (11-12/11)
27/02/2003	AD→NAD	western+central Algeria (24/02) centralAlgeria+Tunisia (25/02) Tunisia (26/02)
13/05/2003	NAD	central Algeria+Tunisia (06-07/05)
27/11/2003	AD	Tunisia (20-21/11) central+western Algeria (22-23-24/11)

8. Determination of the contribution of northern Africa dust source areas to PM10 concentrations over the Iberian Peninsula using the HYSPLIT4 model

8. DETERMINATION OF THE CONTRIBUTION OF NORTHERN AFRICA DUST SOURCE AREAS TO PM10 CONCENTRATIONS OVER THE IBERIAN PENINSULA USING THE HYSPLIT4 MODEL

A methodology for the identification and quantification of the contribution of large dust source areas to the PM10 concentrations at distant receptors was presented in chapter 3. In this section this methodology will be firstly tested by applying it to a northern Africa dust storm outbreak. This dust outbreak took place from 12^{th} to 15^{th} March 2003 over the central Iberian Peninsula and yielded in high PM10 levels in regional background stations. Moreover, the performance of HYSPLIT4 dust module was validated qualitative and quantitatively and, finally, the methodology was applied to 7 very intense north African dust outbreaks previously characterised chemically with PM samples at La Castanya rural station (Barcelona, 41º 46' N, 02º 21' E, 700 m.a.s.l.). In this manner, we will determine the source areas of dust mainly contributing in African episodes over Spain and we will be able to assess the chemical differences of the crustal material reaching distant locations during African dust outbreaks.

8.1 Case study in March 2003

From March 12^{th} to 15^{th} 2003 a north African dust outbreak occurred over the Iberian Peninsula. In the days before March 12^{th} an anticyclone was located over the Iberian Peninsula. However, the transport over the Iberian Peninsula begins when a depression developed over the Atlantic Ocean in front of the Moroccan coast (AD scenario according to the classification presented in chapter 4). This caused the displacement of the anticyclone towards northern Algeria. This situation persisted until the 15^{th} when the effect of an anticyclone over the European continent resulted in an easterly flow (Mediterranean advection) which displaced the dust to the west affecting southwestern and northeastern Iberia (Figure 8.1). The episode was evident when inspecting other sources of information such as NAAPs dust map, SeaWIFS satellite images, and HYSPLIT4 back trajectories. Surface concentration maps of NAAPs showed the impact of this episode on surface levels (Figure 8.1). In consequence, this episode had an important impact on PM10 levels at regional background sites of the whole Peninsula (Figure 8.2). In particular, high PM10 levels were recorded at the central plateau of the Iberian Peninsula. On March 14^{th} daily PM10 means of 66 and 67 $\mu g\ m^{-3}$ were registered at Risco Llano and Campisábalos respectively. On March 15^{th}, 62 $\mu g\ m^{-3}$ of PM10 were recorded at Peñausende. Therefore, this episode was chosen as the case study to test the methodology of identification of dust source areas presented in section 3.

8.2.1 Model adjustment

The episode of March 12^{th} to 15^{th} 2003 was chosen owing to the high PM10 levels recorded at the regional background stations of the central plateau of the Iberian Peninsula (Risco Llano, Campisábalos and Peñausende). Several simulations of this African dust outbreak were performed with HYSPLIT4 to establish the adequate parameters which resulted in the best simulation of the episode. A simulation would be considered adequate if it reproduces the same order of magnitude and the temporal variation of PM10 levels recorded at Risco Llano, Campisábalos, and Peñausende stations during the dust outbreak.

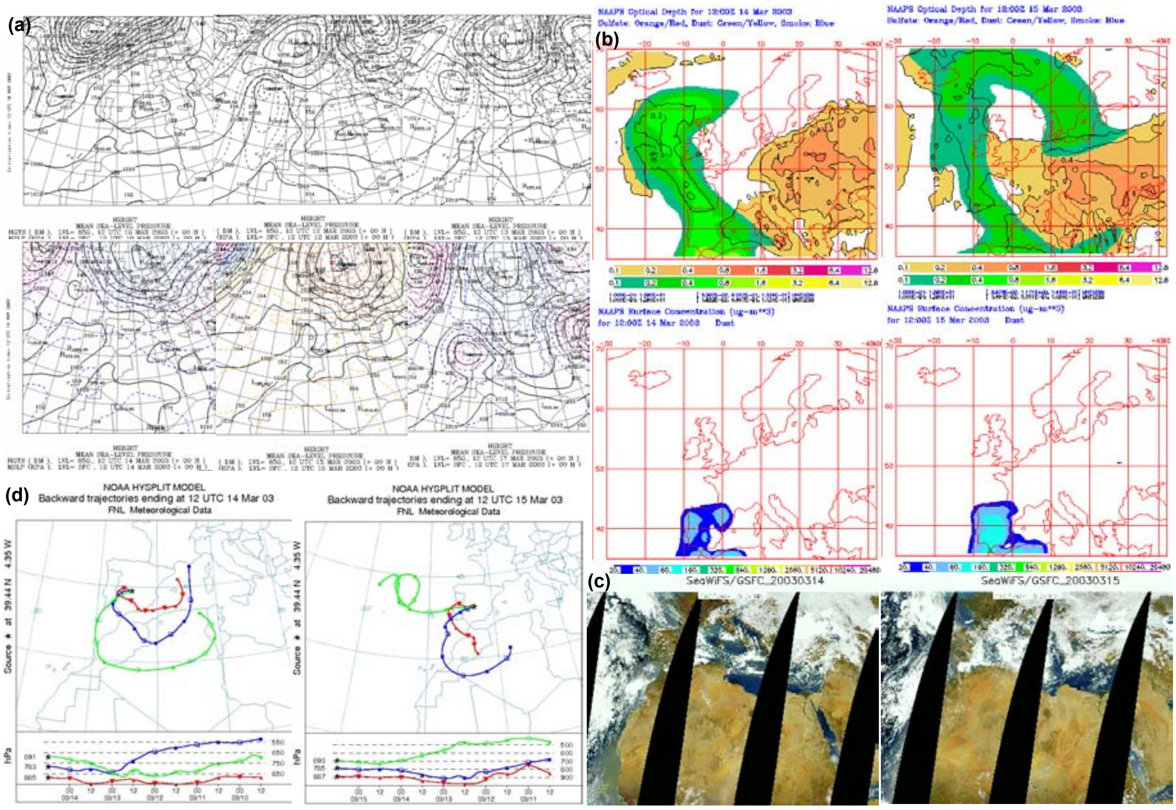


Figure 8.1. North African dust outbreak occurred in March 2003 over the Iberian Peninsula. NOAA Meteorological charts including geopotencial hight at 850 hPa and surface pressure fields for 10/03, 12/03, 13/03, 14/03, 15/03 and 17/03 (a) and NAAPs dust loading and surface concentration maps (b), SeaWIFS satellite images (c) and HYSPLIT4 5-day back trajectories for 14/03 and 15/03 (d) are shown.

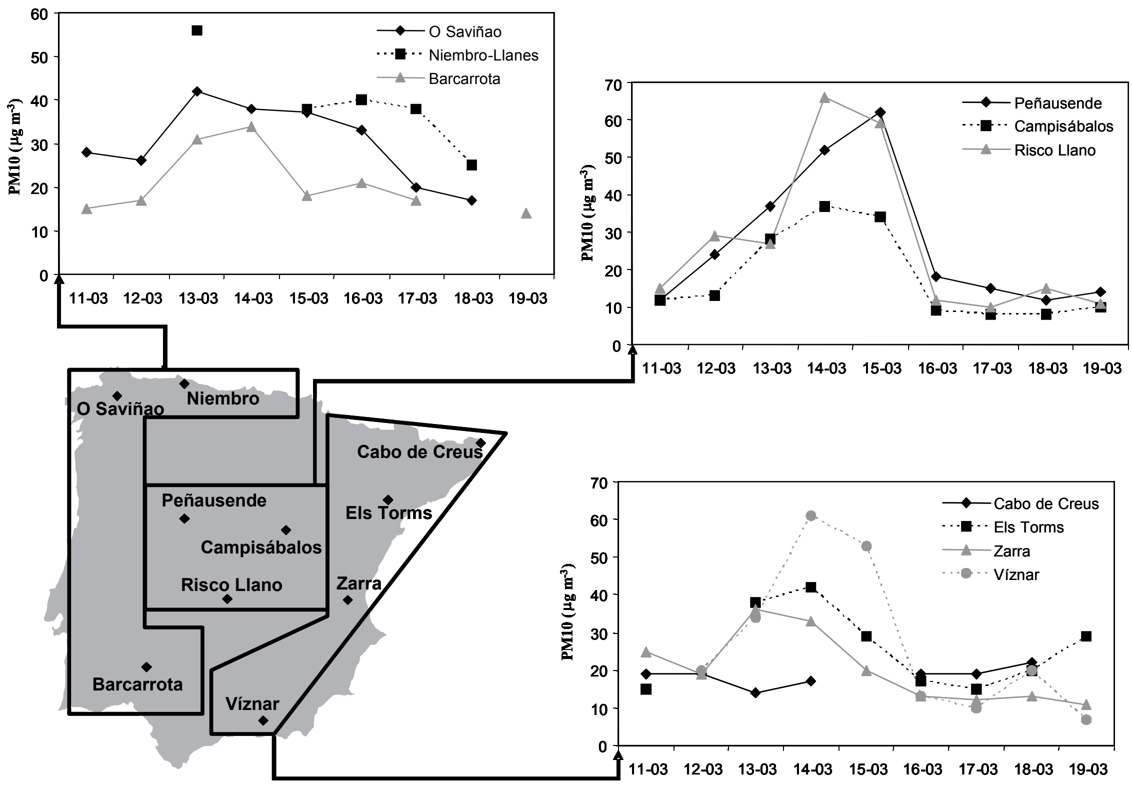


Figure 8.2. Daily mean PM10 levels registered at EMEP stations in Spain from 11/03/03 to 19/03/03: During this period a north African dust outbreak occurred over the Iberian Peninsula.

The Final Run (FNL) global meteorological fields were used as input to the HYSPLIT4 model. FNL consists of a large set of global meteorological variables grouped in a 6-hour archive with data since January 1997. These data originate from the operational series of computer analyses and forecasts undertaken by the National Centers for Environmental Prediction (NCEP). (http://www.arl.noaa.gov/ready/amet.html). The spatial resolution FNL data set is 1x1 degree latitude and uses pressure levels for vertical data.

In the simulations, the emission area was set to the whole desert areas of northern Africa, that is, continental areas within latitude 10 to 25° N and longitude -20 to 40° E. The vertical velocity used for the simulations was the one calculated by the model. To compute vertical velocities, the horizontal winds are fitted to an equation that balances the divergent flow at each grid point with the large-scale flow and then the divergence is integrated through each meteorological model layer to give a vertical velocity at the top. The maximum number of particles during the simulation was set to 1000000, thus if the model generated more particles these would not be taken into account. Moreover, the concentration grid resolution was 1.0x1.0 degrees (the same as FNL meteorological data). Changing this resolution to 0.5x0.5 degrees or to 2.0x2.0 degrees would not alter the output in a noticeable manner. In the first attempts to reproduce the episode, wet and dry deposition were not included.

The first two parameters to be modified were the number of particles emitted per cycle and the model type. Three values for number of particles emitted per cycle were used, namely 500, 5000, and 50000 particles cycle^{-1}. Also, three different model types were utilized, namely 3D particle (3D), Top-hat (TH) in the horizontal with particle in the vertical, and Gaussian (GS) in the horizontal distribution with particle in the vertical. As shown in Figure 8.3 and summarized in Table 8.1, the sensitivity of the model to the use of the different model types is important. The 3D particle approach showed the poorest performance and it was not considered adequate since the PM10 concentrations simulated were far from the measured ones. Under this approach, some stations showed big overestimations while others presented important underestimations. Generally, using 500 particles cycle^{-1} resulted in a less accurate performance than the utilization of 5000 or 50000 particles cycle^{-1}. Moreover, two cases show the best model performances: TH approach with 5000 particles cycle^{-1} and GS approach with 50000 particles cycle^{-1}. For the sake of diminishing computational time the first option was chosen. Nevertheless, none of these simulations were satisfactory since in all cases the modeled starting and the ending date of the episode have not matched the actual dates in which the PM episode occurred over central Spain. Indeed, a delay of one or two days in the simulation with respect to the actual occurrence was observed.

In order to improve the simulation, wet and dry deposition fluxes were incorporated into the next step of the model adjustment. For the application of the deposition module, particles diameter, density, and shape must be included as model inputs. Moreover, in-cloud and below-cloud parameters for wet deposition and a deposition velocity for dry deposition must be defined. Consequently, the particle diameter was set to 5 μm based on the size of dusts particles recorded over Sardinia (central Mediterranean) that showed a bimodal structure with the prevailing peak ranging 2-8 μm (Molinaroli et al., 1993 and Guerzoni et al., 1997). The in-cloud and below-cloud parameters were set to 3.2 10^5 L L^{-1} and 3.0 10^{-5} s^{-1}, respectively (based upon various experimental data as given by Hicks, 1986).

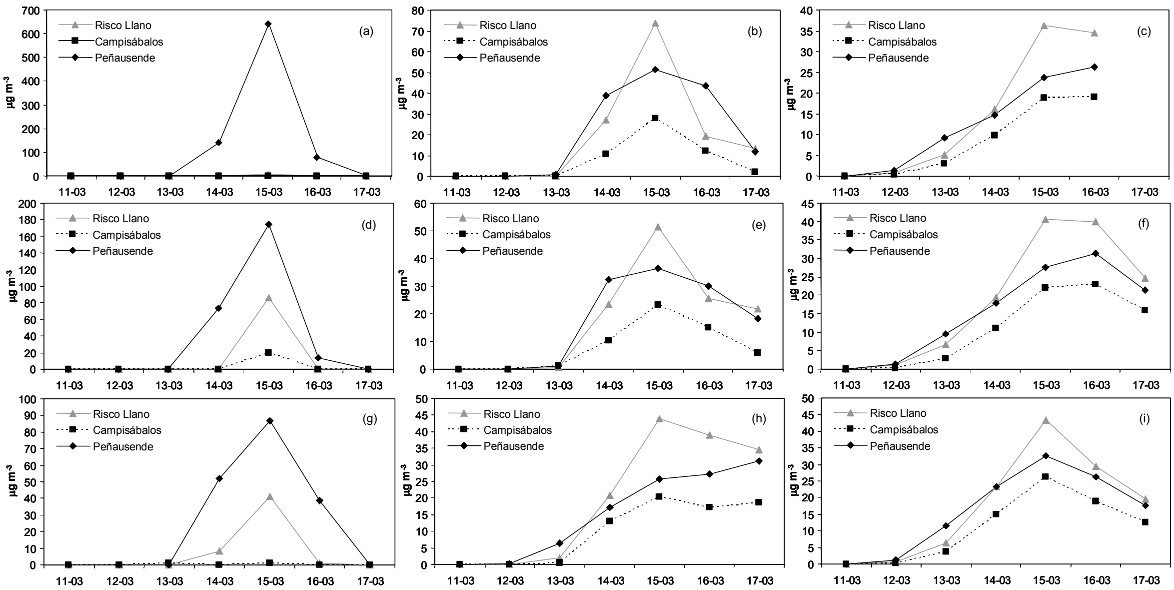


Figure 8.3. PM10 levels at Risco Llano, Campisábalos and Peñausende derived from the HYSPLIT4 simulation of the dust outbreak occurred over central Iberian Peninsula from 12-15 March 2003. These simulation were carried out varying the number of particles emitted per cycle (500, 5000 and 50000) of simulation and the particle model (3D, TH and GS): 500 particles cycle^{-1} were used for (a) 3D particle model, (b) TH particle model and (c) GS particle model; 5000 particles cycle^{-1} were used for (d) 3D particle model, (e) TH particle model and (f) GS particle model; 50000 particles cycle^{-1} were used for (g) 3D particle model, (h) TH particle model and (i) GS particle model.

Table 8.1. Summary of the performances of HYSPLIT4 simulating PM10 levels at Risco Llano, Campisábalos and Peñausende during the dust outbreak occurred in 12-15 March 2003.

	3D particles	**Top-hat particles**	**Gaussian particles**
500 particles per cycle	Overestimation of PM10 levels at Peñausende and underestimation at Risco Llano and Campisábalos. Does not match the starting date. Does not match the ending date.	Slight overestimation of PM10 levels at all stations. Does not match the starting date. Does not match the ending date.	Matches PM10 levels approximately at all stations. Slight underestimation at Peñausende. Matches the starting date. Does not match the ending date.
5000 particles per cycle	Overestimation of PM10 levels at Peñausende and Risco Llano. Does not match the starting date. Matches the ending date.	Matches PM10 levels approximately at all stations. Slight underestimation at Peñausende. Matches the starting date. Does not match the ending date.	Matches PM10 levels approximately at all stations. Slight underestimation at Peñausende. Matches the starting date. Does not match the ending date.
50000 particles per cycle	Overestimation of PM10 levels at Peñausende. Underestimation at Campisábalos. Does not match the starting date. Matches the ending date.	Matches PM10 levels approximately at all stations. Slight underestimation at Peñausende. Matches the starting date. Does not match the ending date.	Matches PM10 levels approximately at all stations. Slight underestimation at Peñausende. Matches the starting date. Does not match the ending date.

On the other hand, deposition velocity (V_d) for dust particles may vary within a wide range. Arimoto et al. (2003) suggested a range of deposition velocities for dust particles from 0.3 to 3 cm s^{-1}. Accordingly, a new series of simulations were performed varying

V_d within this range. In particular, values of 0.3, 1.0, and 3.0 cm s^{-1} were used. The simulation using V_d=0.6 cm s^{-1} resulted in the best fit (Figure 8.4). Therefore, the inclusion of dry and wet deposition resulted in an important improvement of the timing of the simulated concentration peak.

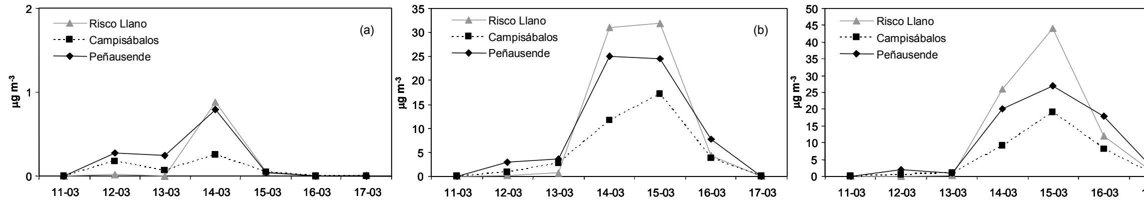


Figure 8.4. PM10 levels at Risco Llano, Campisábalos and Peñausende derived from the HYSPLIT4 simulation of the dust outbreak occurred over central Iberian Peninsula from 12-15 March 2003. These simulation were carried out incorporating wet and dry deposition and varying the deposition velocity (Vd): (a) Vd=3.0 cm s^{-1}, (b) Vd=1.0 cm s^{-1}, (c) Vd=0.3 cm s^{-1}. Moreover, for these simulations a TH model particle was used and 5000 particles $cycle^{-1}$ were released.

Using the parameters described before, the simulated daily mean PM10 levels agree reasonably well to those recorded at the EMEP stations (Figure 8.5). The background levels for 1998-2003 were subtracted at each station (14, 12 and 13 µg m^{-3} for Risco Llano, Campisábalos, and Peñausende respectively) because they can be attributed to local or regional contributions and not to the African contribution. However, in all cases the model underestimated concentrations from 12th to 14th and overestimated concentrations on the 16th. Thus, the impact of the African episodes simulated by the model is delayed by 1 day. This can be explained by the relative coarse spatial resolution of the FNL data

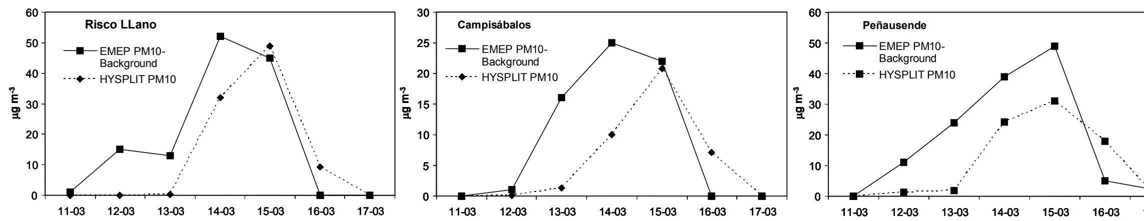


Figure 8.5. Comparison between daily mean PM10 levels (subtracting background levels) at Risco Llano, Campisábalos and Peñausende and mean daily PM10 levels obtained at those sites after the HYSPLIT4 simulation of the African dust outbreak occurred over central Iberian Peninsula from 12th to 15th March 2003.

8.2.2 Source apportionment

Once the episode was simulated with a unique source area covering the entire desert region of northern Africa (Figure 8.6), the model was run eight times considering as potential sources the areas proposed by Prospero et al. (2002) and one more time considering the rest of the desert as source area (Figure 8.7). Following this procedure, the contribution from each source area can be established. From HYSPLIT4 dust concentration maps (Figure 8.8), it can be inferred that only western source areas such as Mali, Mauritania and the western flanks of the Ahaggar Mountains, Mauritania and Western Sahara, and other regions of northwestern Africa (areas 7, 8, and 9 in Figure 8.7) contributed to the dust plume arriving to central Spain from the 12th to the 15th of

March 2003. Closer source areas such as Tunisia and northeastern Algeria (area 1 in Figure 8.7) or eastern Libyan Desert (area 2 in Figure 8.7) were not intensively active during this specific event because the anticyclone covering that area during the days under study prevented strong winds to develop. It is interesting to notice that although large amounts of dust were emitted by large source areas such as Sudan and the flanks of Ethiopian Highlands (area 4 in Figure 8.7), Lake Chad and the Bodele depression (area 5 in Figure 8.7), and Niger and the southern flanks of the Ahaggar mountains (area 6 in Figure 8.7), they barely reached the Iberian Peninsula during this specific episode (Figure 8.8).

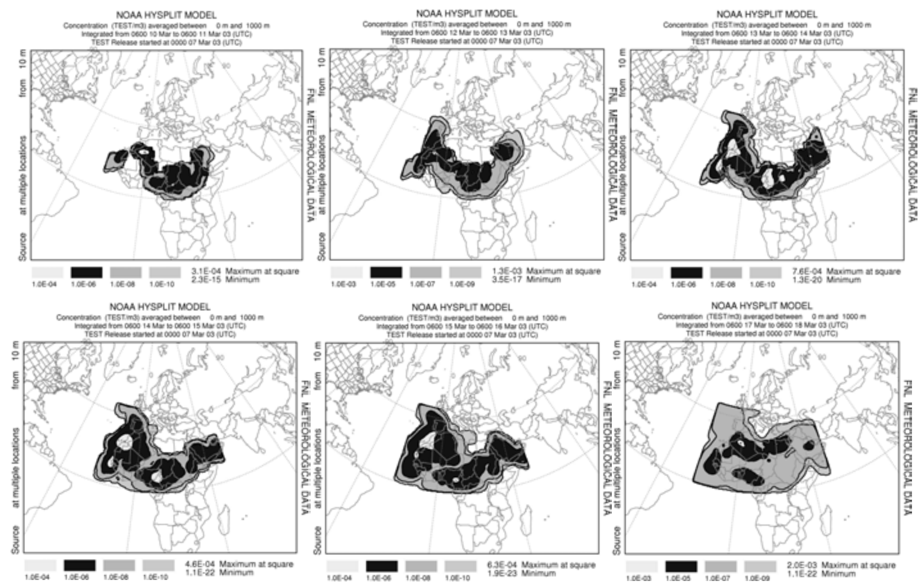


Figure 8.6. HYSPLIT4 dust concentration maps between 0 and 1000 meters AGL for the following days: 10, 12, 13, 14, 15 and 17 March 2003.

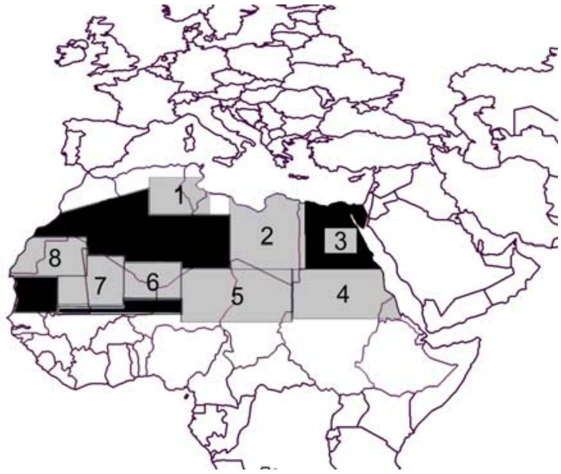


Figure 8.7. Source areas of dust over northern Africa. The source areas identified by Prospero et al. (2002) are highlighted in grey. The rest of the desert is highlighted in black.

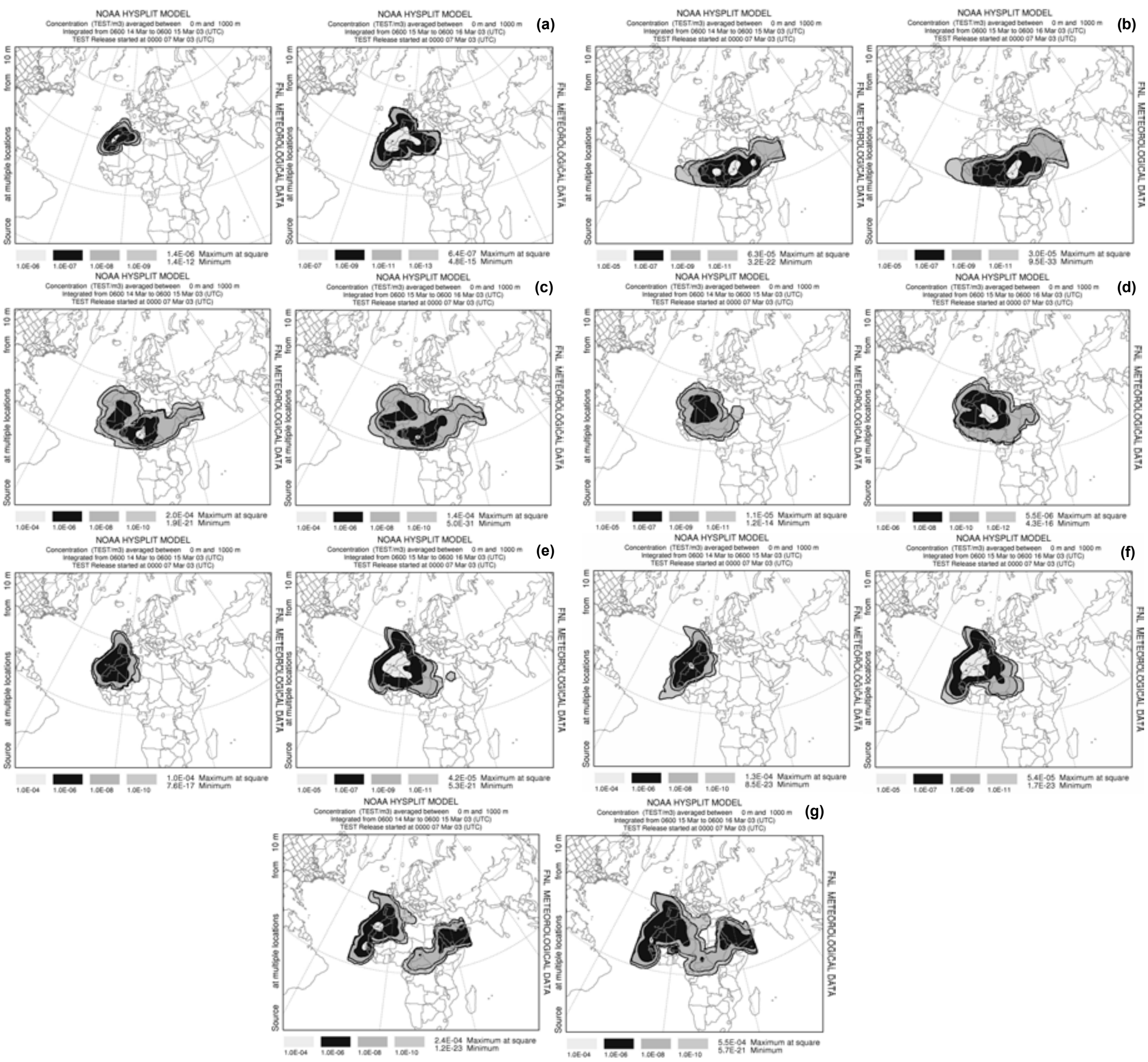


Figure 8.8. HYSPLIT4 dust concentration maps between 0 and 1000 metres AGL for 14 and 15 March 2003 restricting the emission to: (a) Tunisia and northeast Algeria, (b) Sudan and the Flanks of Ethiopian Highlands, (c) Lake Chad and the Bodele depression, (d) Niger and the southern flanks of the Ahaggar Mountains, (e) Mali, Mauritania and the western flanks of the Ahaggar Mountains, (f) Mauritania and Western Sahara and (g) Rest of the desert. Eastern Libyan desert and Egypt source areas did not contribute so dust maps for these areas are not shown.

In order to quantify the contribution of each source area, the contribution of the entire desert was first compared with the sum of contributions from all the source areas considered in this study to check for internal consistency. This was accomplished by comparing the daily mean PM10 concentrations simulated in central Spain letting the whole north African desert act as a unique source area with those PM levels obtained by summing the simulated contributions from each separate source area. As shown in Table 8.2, the simulation with the whole north African desert as source area gave very similar daily mean PM10 concentrations to those estimated by summing the contributions of all source areas separately at the three EMEP stations over central Spain. Moreover, only Mali, Mauritania and the western flanks of the Ahaggar Mountains (area 7), Mauritania and Western Sahara (area 8), and other regions of northwestern Africa included in the “Rest of the desert” area seem to have a significant contribution.

Table 8.2. PM10 contributions (μg m^{-3}) of the different source areas as simulated by HYSPLIT4 for EMEP stations over central Iberian Peninsula. The sources are: (1) Tunisia and northeast Algeria, (2) Eastern Libyan Desert, (3) Egypt, (4) Sudan and the flanks of Ethiopian Highlands, (5) Lake Chad and the Bodele depression, (6) Niger and the southern flanks of the Ahaggar Mountains, (7) Mali, Mauritania and the western flanks of the Ahaggar Mountains, (8) Mauritania and Western Sahara and (9) Rest of the desert. PM10 levels obtained after a simulation carried out with the whole north African desert as unique source.

Risco Llano											
	Src 1	**Src 2**	**Src 3**	**Src 4**	**Src 5**	**Src 6**	**Src 7**	**Src 8**	**Src 9**	**Sum Srcs 1-9**	**Src Global north African desert**
11/03	0	0	0	0	0	0	0	0	0	0	0
12/03	0	0	0	0	0	0	0	0	<1	0	0
13/03	0	0	0	0	0	0	0	0	<1	0	0
14/03	<1	0	0	0	0	0	4	7	21	32	32
15/03	<1	0	0	0	0	0	9	14	26	49	48
16/03	0	0	0	0	0	0	1	2	6	9	11
17/03	0	0	0	0	0	0	<1	<1	1	1	1

Campisábalos											
	Src 1	**Src 2**	**Src 3**	**Src 4**	**Src 5**	**Src 6**	**Src 7**	**Src 8**	**Src 9**	**Sum Srcs 1-9**	**Src Global north African desert**
11/03	0	0	0	0	0	0	0	0	0	0	0
12/03	0	0	0	0	0	0	0	0	<1	0	0
13/03	0	0	0	0	0	0	0	0	1	1	2
14/03	<1	0	0	0	0	0	1	2	7	10	11
15/03	<1	0	0	0	0	0	3	5	13	21	22
16/03	0	0	0	0	0	0	1	1	5	7	9
17/03	0	0	0	0	0	0	<1	<1	<1	0	0

Peñausende											
	Src 1	**Src 2**	**Src 3**	**Src 4**	**Src 5**	**Src 6**	**Src 7**	**Src 8**	**Src 9**	**Sum Srcs 1-9**	**Src Global north African desert**
11/03	0	0	0	0	0	0	0	0	0	0	0
12/03	0	0	0	0	0	0	0	0	1	1	1
13/03	0	0	0	0	0	0	<1	<1	1	2	2
14/03	<1	0	0	0	0	0	4	6	14	24	26
15/03	<1	0	0	0	0	0	6	8	17	31	30
16/03	<1	0	0	0	0	0	3	5	10	18	18
17/03	0	0	0	0	0	0	<1	<1	1	1	1

According to the model results, the PM10 dust load over central Iberian Peninsula originated from three areas, namely Mali, Mauritania and the western flanks of the Ahaggar Mountains (area 7 in Figure 8.7), Mauritania and Western Sahara Mauritania (area 8 in Figure 8.7), and the so-called “Rest of the desert” (black region in Figure 8.7). HYSPLIT4 model estimations showed that for March 15th the contributions of the Mauritania area ranged from 25 to 30% at Risco Llano and Peñausende and from 20 to 25% at Campisábalos. The contribution from the Mali source area was found to be approximately 20% at Risco Llano and Peñausende and from 15 to 20% at Campisábalos. The “rest of the desert” regions would contribute with 50-55% at Risco Llano and Peñausende and about 60% at Campisábalos (Figure 8.9).
The source apportionment methodology was applied to 7 African dust outbreaks occurred over the Iberian Peninsula between in 2002 and 2003 (Table 8.3).

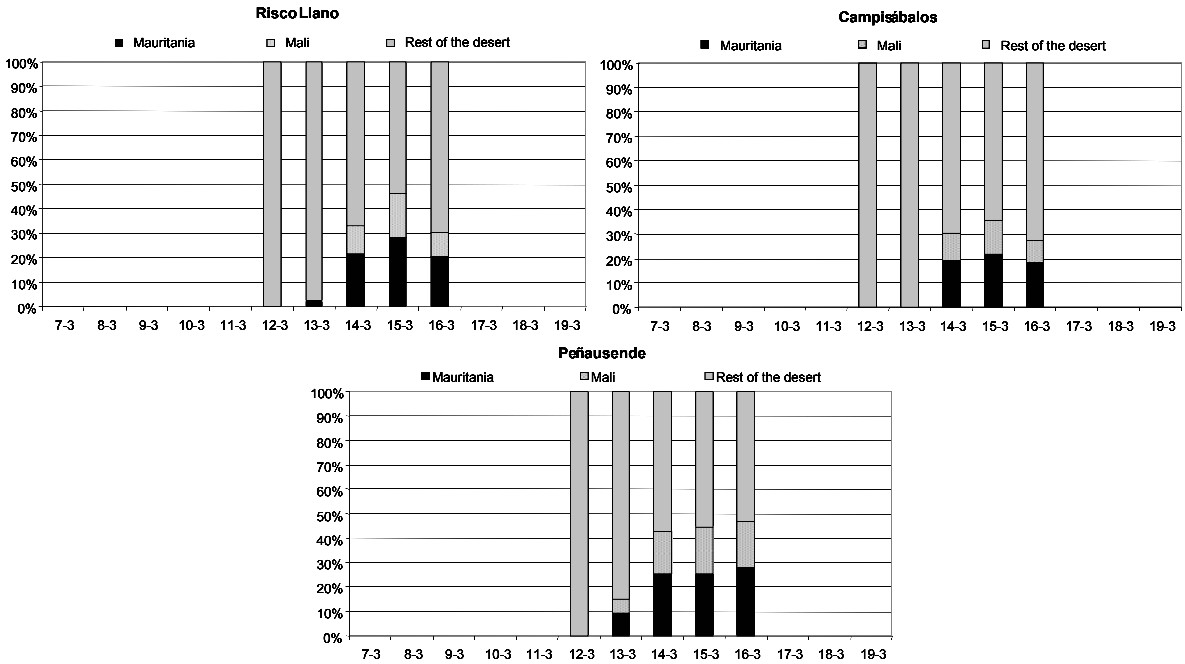


Figure 8.9. Contribution of each source area to the PM10 concentrations over central Iberian Peninsula during the dust outbreak occurred from 12th to 15th March 2003 at Risco Llano, Campisábalos and Peñausende.

Table 8.3. African dust outbreaks simulated with HYSPLIT4 for this study. Dates within these periods for which speciation of TSP was available at La Castanya are also shown.

Period of simulation	Dates with chemical analyses of TSP available at La Castanya
17-23 March 2002	22, 23
17-23 June 2002	17, 18, 21, 22, 23
22-28 June 2002	26, 27, 28
20-26 March 2003	24, 25, 26
8-14 June 2003	10, 11, 12, 13
21-27 June 2003	26
16-22 July 2003	18, 19, 20, 21

8.3 HYSPLIT4 dust module validation

The performance of the dust module included in HYSPLIT4 was firstly validated qualitatively. For this purpose, the SeaWIFS imagery for the dates simulated were compared with HYSPLIT4 concentration maps at the three levels defined for this study (0-1000, 1000-2500 and 2500-5000 metres above sea level). This was made following the thread score validation test proposed by Wilks (1995). The Iberian Peninsula was divided in three regions (south, northeast and northwest, Figure 8.10b) and the model predictions for each of those regions where compared with SeaWIFS imagery. The model may either predict dust in a region where there was dust (Hits=a, Figure 8.11), predict dust were there was not (False alarm=b, Figure 8.11) or not predict dust in region were actually there was dust (Miss=c, Figure 8.11). The "Probability of detection" or POD, defined as a/(a+c), for the episodes simulated reached a value of 0.96. The "Bias" or B, defined as (a+b)/(a+c) gives an estimation of how close was SKIRON/Eta of predicting the exact number of cases which actually occurred in each region. If B=1 the number of forecasted and observed cases are the same, if B<1 the number of predicted cases are less than the observed and if B>1 the number of predicted cases are more than the observed. For the episodes studied with HYSPLIT4, B reached a value of 1.23. The POD and B values show a good qualitative performance of HYSPLIT4 when simulating north African dust intrusions over the Iberian Peninsula.

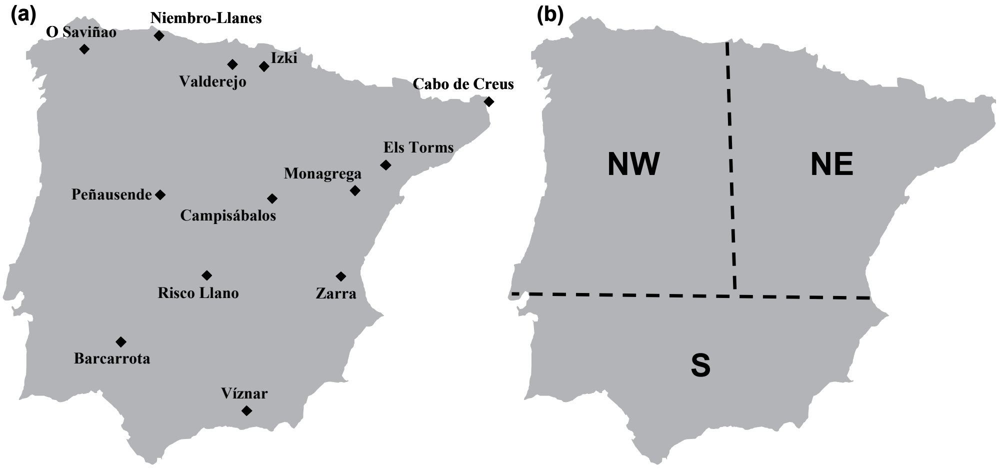


Figure 8.10. Regional background monitoring stations from which PM10 daily data was obtained for quantitative validation of HYSPLIT4 (a) and three regions in which the Iberian Peninsula was divided in order to perform the qualitative validation test proposed by Wilks (1995) (b).

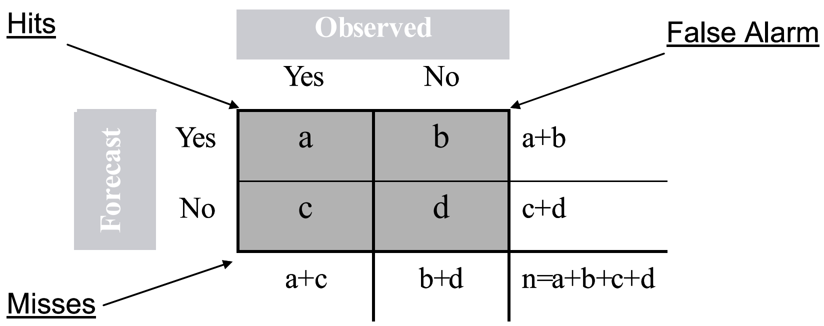


Figure 8.11. Scheme of the thread score test (Wilks, 1995) for a qualitative validation of models.

For a validation of HYSPLIT4 in the quantitative level, dust concentrations obtained from HYSPLIT4 were compared with PM10 daily concentration levels from 13 regional background monitoring stations (Figure 8.10a and Table 8.4) distributed all over the Iberian Peninsula. From the 13 stations, 10 belong to the EMEP air quality monitoring network, 2 (Valderejo and Izki) belong to the air quality monitoring network of the Autonomous Government of the Basque Country and 1 (Monagrega) to the ENDESA air quality monitoring network. All the simulations lasted 11 days although the dust concentrations were computed only for the last 7 days since the first 4 days were used as a “cold start” period needed for the generation of the semi-permanent north African dust layer. Therefore, the dust concentrations simulated by the model over Iberia for those first 4 days are not realistic since the dust available for transport is scarce yet.
As shown in Figure 8.12, PM10 levels were generally higher than dust concentrations. This is reasonable since a considerable fraction of the PM10 concentrations (20-50% according to Rodríguez et al., 2002) would correspond to local/regional anthropogenic (mainly carbonaceous compounds, sulphate and nitrate) or other natural species different from African dust (such as bioaerosols or marine salts). Furthermore, it is not

possible to separate the effects of local sources of crustal species (resuspension and regional transport of such aerosols) from remote sources (African deserts). Giving all these circumstances, even the quantitative performance of the model can be considered as correct especially taking into account that most of the events simulated occurred in summer. In this period of the year, owing to the intense insolation, in the regional background stations there are major regional contributions of PM consisting mainly in secondary aerosols arising from the photochemical transformation of gaseous precursors. During summer African episodes, the African plumes travel at high altitudes (>1500 m.a.s.l.) and the dust penetrates in the mixing layer because the vertical development of this layer can reach up to 2500 metres over continental areas in summer (Crespi et al., 1995). Once into the boundary layer the dust is distributed and affects the sampling stations. The formation of the above mentioned secondary particles is enhanced during NAH-A situations because, at surface, a low pressure gradient remains causing lack of advective conditions. In these circumstances, superficial air masses are hardly renovated and the aging and recirculation of contaminated air masses aided by the orographic conditions of eastern Iberian Peninsula commonly occur (Millán et al., 1997). Thus, owing to these complex convective dynamics there is mixing of aerosols in the troposphere during African events in summer. Furthermore, during summer, precipitation is reduced and re-suspension of soil material by convection is enhanced so a local contribution also occurs.

Table 8.4. Spanish air quality monitoring stations from which PM10 data was obtained for HYSPLIT4 validation.

Site	Air quality monitoring network	Location	Altitude (m.a.s.l.)
Niembro-Llanes	EMEP-MMA*	43º 27’ N, -4º 51’ E	134
O Saviñao	EMEP-MMA	43º 14’ N, -7º 42’ E	506
Cabo de Creus	EMEP-MMA	42º 19’ N, 3º 19’ E	23
Els Torms	EMEP-MMA	41º 24’ N, 0º 43’ E	470
Risco Llano	EMEP-MMA	39º 31’ N, -4º 21’ E	1241
Campisábalos	EMEP-MMA	41º 17’ N, -3º 09’ E	1360
Peñausende	EMEP-MMA	41º 17’ N, -5º 52’ E	985
Zarra	EMEP-MMA	39º 05’ N, -1º 06’ E	885
Bancarrota	EMEP-MMA	38º 29’ N, -6º 55’ E	393
Víznar	EMEP-MMA	37º 14’ N, -3º 28’ E	1230
Valderejo	Autonomous Government of the Bask Country	42º 53’ N, -3º 14’ E	911
Izki	Autonomous Government of the Bask Country	42º 39’ N, -2º 30’ E	835
Monagrega	ENDESA	40º 59’ N, -0º 12’ E	600

*MMA: Spanish Ministry of the Environment

However, in terms of HYSPLIT4 dust module, there can be many reasons for misprediction. The dust emission rate depends upon the low-level wind speed exceeding some threshold value and the threshold value is defined for different soil types. In the current land-use data base, only one type permits dust emissions. For instance, if the soil in those regions is less "crusted" than the previous year (perhaps because of an extended drought) then in the real-world emissions may occur at a lower threshold velocity than is assumed in the model. The opposite conditions can also occur, if for instance there was a lot of rain the previous winter, extra vegetation would inhibit dust storms and the model would over-predict. In consequence the model's threshold velocity may need to be "tuned" for each evaluation period. Another factor is that the emission rate depends upon how well the low-level wind speeds are predicted by the meteorological model.

Different meteorological models could produce different results, especially if they have different vertical resolutions.
In any case, a potential underestimation of dust concentrations by HYSPLIT4 would not change the conclusions obtained in this work since it should not affect the relative proportions of dust transported from each source area.

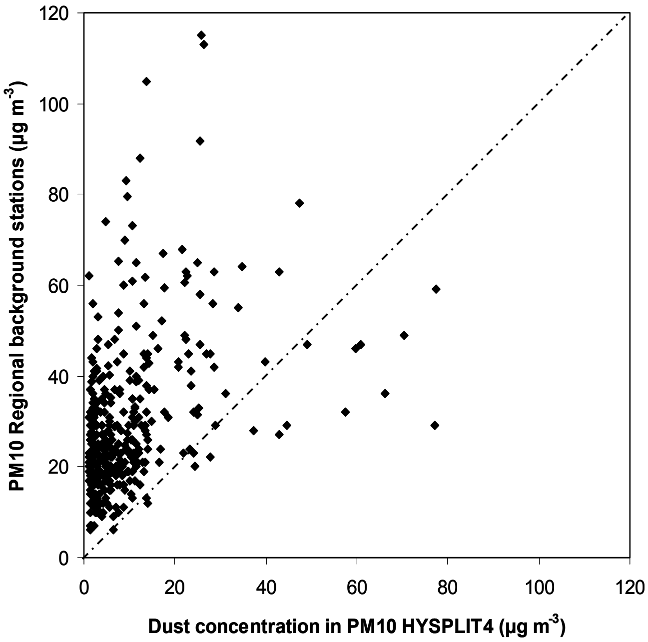


Figure 8.12. Daily PM10 concentrations at regional background stations of the Iberian Peninsula versus dust concentration predicted by HYSPLIT4 for the 7 episodes simulated.

8.4 Identification of north African dust source areas during 7 major dust outbreaks in the Iberian Peninsula

Following the methodology proposed in section 3.5 , the proportion of dust reaching La Castanya from each of the 11 source areas defined in north Africa were computed for every day of the 7 episodes simulated with HYSPLIT4. In one of the cases (from the 13^{th} to the 23^{rd} of March of 2002) the model underpredicted dust concentrations over the eastern Iberian Peninsula, in consequence the modelled PM10 levels were not high enough (very close to zero) for performing the source areas attribution. Instead, the dust concentrations obtained during this event for O Saviñao (NW Iberian Peninsula) were used assuming that the proportion of dust coming from each of the source areas would be approximately the same not change much from the northwest (O Saviñao) to the northeast (La Castanya) of Iberia.
As shown in Figure 8.13, western and eastern Algeria were the most active source areas during African dust outbreaks over Iberia (mean contributions above 30% for both regions) followed by Tunisia-northeastern Algeria and Mauritania-Western Sahara (both areas with mean contributions around 13%). In a lesser extent dust from Mali-Mauritania-western flanks of the Ahaggar Mountains and from western Mauritania was also transported towards the Iberian Peninsula (7 and 1% as mean contributions respectively). The remaining source areas considered in this study did not supply dust to the plumes transported towards the Iberian Peninsula during the simulated episodes. This even applies to the region of Lake Chad-Bodele depression which has been identified as major global dust emitter (Kalu, 1979, McTainsh and Walker, 1982,

Goudie, 1983, Brooks and Legrand, 2000, Prospero et al., 2002). The prevailing easterlies affecting semi-permanently this region transport the dust mobilised there across the Atlantic Ocean towards the American continent (Prospero and Carlson, 1981, Prospero and Nees, 1986, Swap et al., 1992, Perry et al., 1997, Prospero, 1999, Kallos et al., 2006) and not towards western Europe.

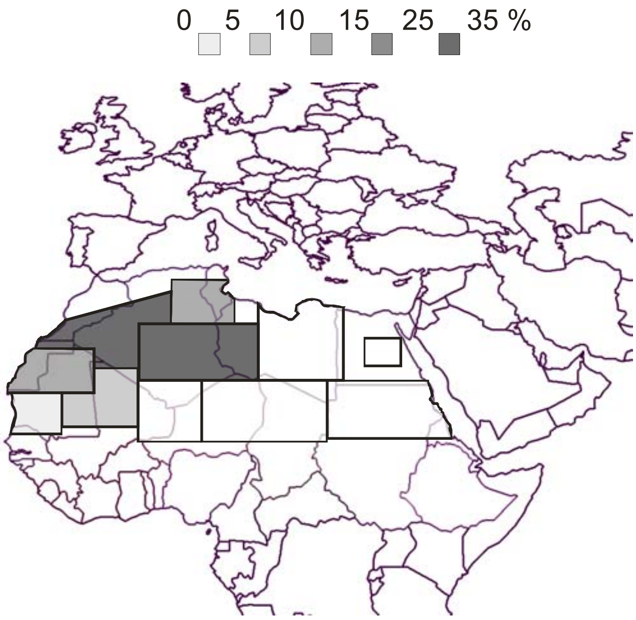


Figure 8.13. Mean relative contribution of the 11 source areas during the 7 episodes simulated.

Despite these common features, the contribution from the different source areas may differ greatly between episodes. Two examples of African dust outbreaks over the Iberian Peninsula with different source areas are presented in Figures 8.13 to 8.16. In the first example the dust was transported over the Iberian Peninsula forming a convex long range transport plume formed over the Atlantic Ocean. These convex and Atlantic plumes are caused by an anticyclone located over southern Iberia, north Africa or the western Mediterranean and occur typically from January to March with the transport mainly restricted to the lowest levels of the atmosphere (see chapter 5). This altitude effect is captured by HYSPLIT4 since dust concentrations obtained for the 0-1000 m layer are one order of magnitude higher to those obtained for the 1000-2500 m layer (Figure 8.13). As shown in Figure 8.14 large proportions of dust from western Algeria, Mauritania-Western Sahara and Mali-Mauritania-western flanks of the Ahaggar Mountains were transported over Iberia during this event and minor proportions from eastern Algeria. On the 21^{st}, when the highest dust concentration over O Saviñao (NW Iberian Peninsula) were predicted (22 µgPM10 m^{-3}), 39, 38 and 19% of the dust had its origin at western Algeria, Mauritania-Western Sahara and Mali-Mauritania-western flanks of the Ahaggar Mountains respectively and only 4% at eastern Algeria. The proportion of dust from western Algeria decreased from 52% on the 20^{th} down to 8% on the 23^{rd} this decrease was parallel to an increase in the contribution of dust from Mauritania-Western Sahara (from 30% on the 20^{th} up to 62% on the 23^{rd}) and Mali-Mauritania-western flanks of the Ahaggar Mountains (from 14% on the 20^{th} up to 28% on the 22^{nd}).

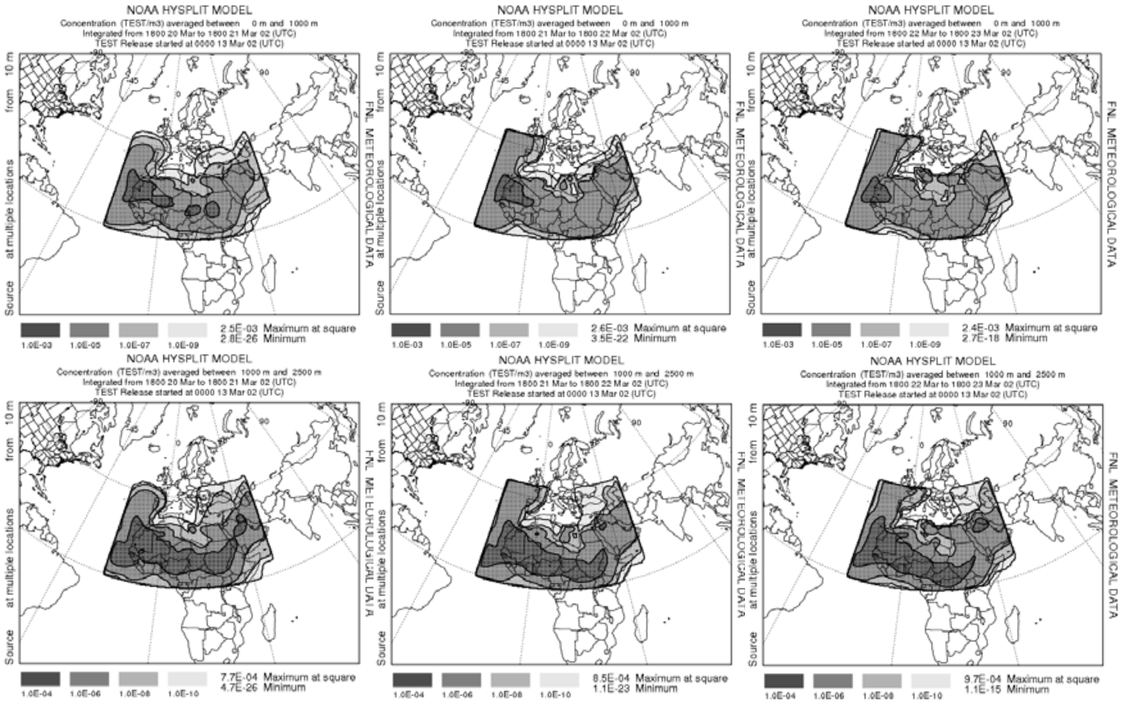


Figure 8.13. African dust outbreak over the Iberian Peninsula occurred in March 2002 simulated with HYSPLIT4. Dust concentration maps of the layers 0-1000 m.a.s.l. and 1000-2500 m.a.s.l. are shown.

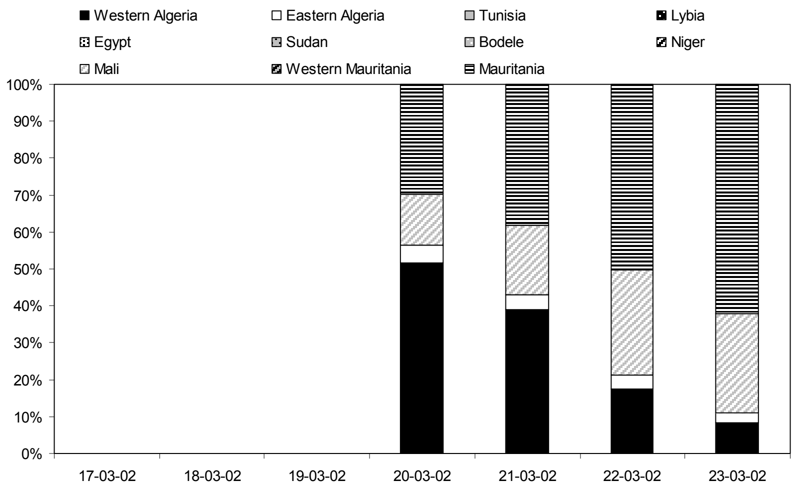


Figure 8.14. Contribution of each source area to the PM10 concentrations over La Castanya (Montseny, NE Iberian Peninsula) during the dust outbreak occurred from 20th to 23rd March 2002.

During the second example (occurred in June 2003, Figures 8.15 and 8.16) the dust was carried over the Iberian Peninsula and the western Mediterranean forming a wide plume. The typical summer transport scenario (NAH-A) triggered this episode. As defined in chapters 4 and 5, it is originated by the intense heating of the Sahara and the consequent development of the north African thermal low and the considerable vertical growth of the boundary layer. This convective system pumps dust up to high atmospheric levels. Once the dust is injected there, it is transported towards Iberia by the western branch of the high present over north Africa at high altitude (>1500 m). In consequence the dust concentrations at elevated levels are higher than at surface. HYSPLIT4 supported this feature predicting peak dust concentrations at La Castanya (on the 24th of June) at the 1000-2500 metres layer twice as high as at the 0-1000 metres layer. As observed in Figure 8.16, the source areas with major contribution to the dust plume reaching La Castanya (NE Iberian Peninsula) were western Algeria, eastern Algeria and Tunisia-northeastern Algeria, while minor contributions arrived from Mauritania (below 5% in all the cases). On the 24th (the peak concentration date) contributions of 50, 32 and 18% of the dust were estimated to come from Tunisia-northeastern Algeria, western Algeria and eastern Algeria respectively. The contribution of western Algeria to the dust plume affecting La Castanya increased from 21% on the 23rd to 53% on the 26th. Simultaneously, the contribution of Tunisia-northeastern Algeria diminished from 58% to 24%. The fraction of material coming from eastern Algeria oscillated around 20% during all the days of the event.

Once the proportion of dust coming from different African source areas during the 7 episodes was determined, data from chemical analyses of filters collected at La Castanya were used to establish differences in the composition of the dust transported to this location (Table 8.5).

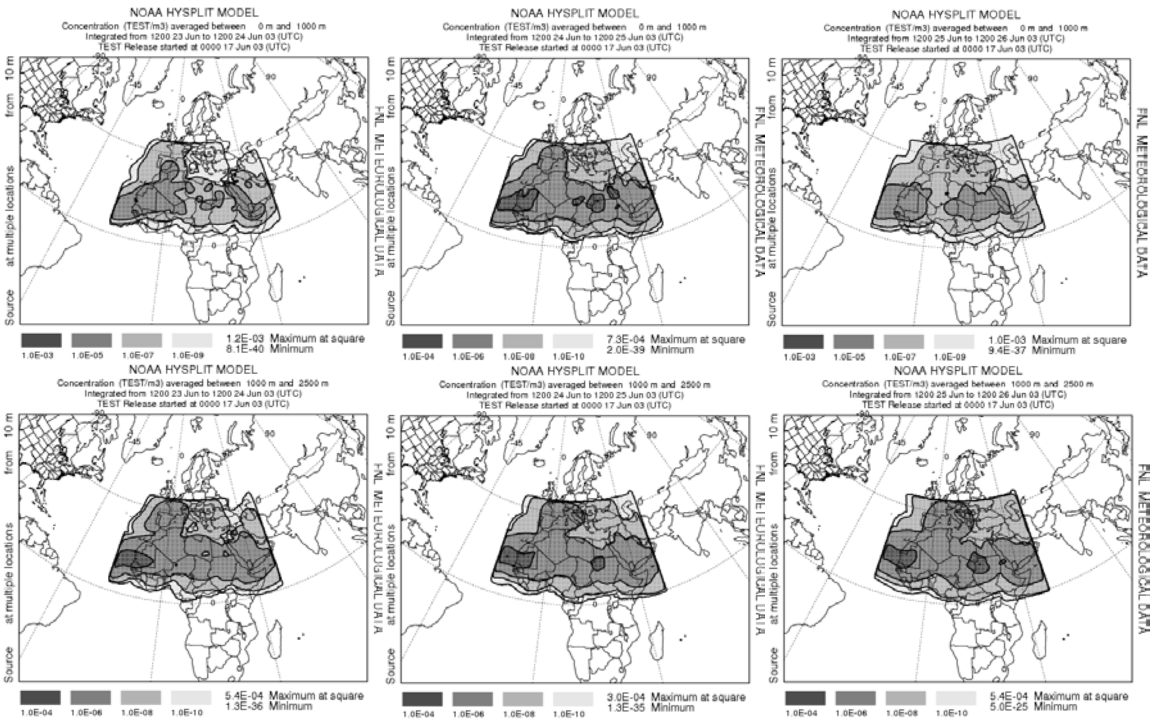


Figure 8.15. African dust outbreak over the Iberian Peninsula occurred in June 2003 simulated with HYSPLIT4. Dust concentration maps of the layers 0-1000 m.a.s.l. and 1000-2500 m.a.s.l. are shown.

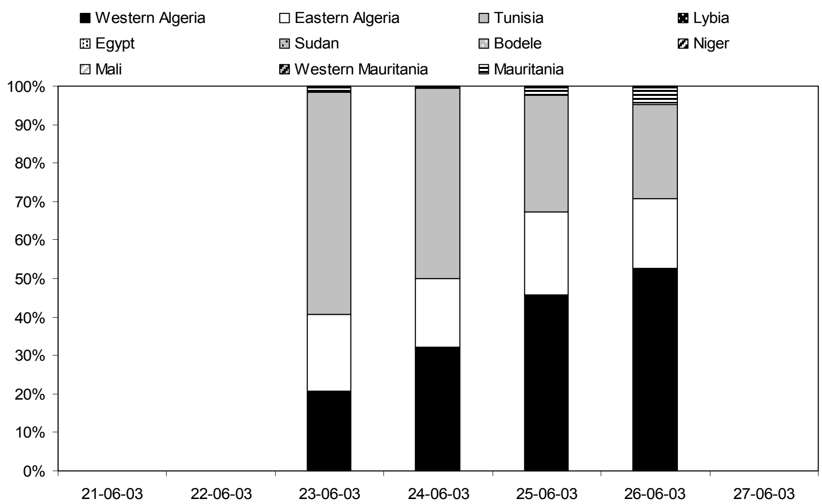


Figure 8.16. Contribution of each source area to the PM10 concentrations over La Castanya (Montseny, NE Iberian Peninsula) during the dust outbreak occurred from 23rd to 26th June 2003.

Table 8.5. TSP levels and concentration of the major species (all in µg m^{-3}) collected at La Castanya (Montseny, NE Iberian Peninsula) during the 7 north African dust outbreaks simulated in this study.

Date	TSP	SO_4^{2-}	NO_3^-	NH_4^+	OC+EC	CO_3^{2-}	SiO_2	Al_2O_3	Ca	K	Mg	Fe_2O_3
22/03/2002	50	4.6	4.6	1.0	8.6	3.0	6.1	2.4	2.0	0.6	0.4	1.1
23/03/2002	41	3.0	3.6	0.6	9.6	1.6	5.2	2.1	1.1	0.5	0.3	0.8
17/06/2002	27	3.5	0.6	1.2	6.6	1.5	4.2	1.4	1.0	0.3	0.2	0.7
18/06/2002	36	4.4	1.0	1.4	8.0	2.8	6.2	2.1	1.9	0.4	0.3	0.9
21/06/2002	46	5.5	1.2	1.7	9.0	4.9	9.8	3.3	3.2	0.6	0.4	1.4
22/06/2002	51	6.3	1.3	2.4	9.9	3.3	10.5	3.5	2.2	0.6	0.4	1.5
23/06/2002	40	5.1	0.9	1.9	7.5	2.4	8.9	3.0	1.6	0.5	0.3	1.2
26/06/2002	57	5.9	1.8	1.2	9.1	4.0	15.6	5.2	2.7	0.8	0.6	2.1
27/06/2002	56	6.0	2.5	1.5	8.5	5.0	14.1	4.7	3.3	0.8	0.6	2.0
28/06/2002	45	7.5	4.0	1.4	6.5	3.4	6.4	2.1	2.3	0.5	0.4	0.9
24/03/2003	30	2.9	4.4	1.2	8.7	1.5	3.0	1.0	1.0	0.3	0.2	0.5
25/03/2003	37	3.1	1.1	1.1	8.9	2.6	4.0	1.3	1.7	0.4	0.3	0.7
26/03/2003	38	5.1	6.4	0.8	5.4	1.8	4.0	1.3	1.2	0.4	0.3	0.7
10/06/2003	39	3.7	2.0	0.5	5.7	3.6	8.7	2.9	2.4	0.5	0.4	1.2
11/06/2003	34	4.6	1.2	1.0	5.3	2.5	6.3	2.1	1.6	0.4	0.3	0.8
12/06/2003	31	4.9	0.7	1.4	6.0	1.6	4.6	1.5	1.1	0.3	0.2	0.7
13/06/2003	43	5.4	1.2	1.4	5.5	3.2	9.5	3.2	2.1	0.6	0.4	1.2
26/06/2003	43	5.9	1.3	1.0	5.4	2.6	10.0	3.3	1.7	0.6	0.4	1.4
18/07/2003	46	4.2	1.0	0.6	5.1	3.1	7.3	2.4	2.0	0.5	0.4	1.1
19/07/2003	46	4.6	0.6	0.7	4.7	2.7	9.9	3.3	1.8	0.6	0.4	1.5
20/07/2003	55	2.9	0.6	0.4	2.6	2.7	18.1	6.0	1.8	0.8	0.6	2.4
21/07/2003	80	3.4	1.1	0.6	4.8	4.0	21.1	7.0	2.7	1.0	0.7	2.9

As shown in Figure 8.17, the differences in the chemical composition of the samples collected during the 7 simulated episodes were not important. This is normal since the closest regions to the Iberian Peninsula (eastern Algeria, western Algeria and Tunisia) had important contributions in most of the episodes. The chemical differences between the different samples are not important owing to the great mixing of dust from different Saharan source areas in the plumes reaching the Iberian Peninsula during these episodes, especially in the time of maximum convection during the day (see chapter 6).

Nevertheless, two groups of samples can be distinguished in Figure 8.17, principally owing to the Al_2O_3 content. The northern Saharan airborne dust has a higher concentration in calcium and lower concentration in aluminium than the airborne dusts from south Sahara and Sahel (Sarnthein et al., 1982, Chiapello et al., 1997, Caquineau et al., 1998). In consequence, the samples with the highest relative Ca concentrations coincide with days characterised with dust transport mainly from northern Sahara (western, eastern Algeria and Tunisia) in the lowest atmospheric levels (the black circles). The white circles denote days with transport from the northern Sahara but at high altitudes after dust has been lifted owing to convective movements. Although the concentration of Ca-carbonate in north Saharan dust is high, the segregation of these minerals in the process of elevation of dust masses up to several kilometres is important. In consequence, the proportion of finer minerals (clays) increases and results in lower Ca/Al ratios. The samples of days in which the transport occurred mainly from the Sahel or the southern Sahara (source areas of Mali, western Mauritania and Western Sahara) either at surface level (denoted by black squares in Figure 8.17) or in altitude (denoted by black squares in Figure 8.17) showed the logical relative predominance of aluminium. However, the relatively small number of samples available for this study does not allow drawing further conclusions.

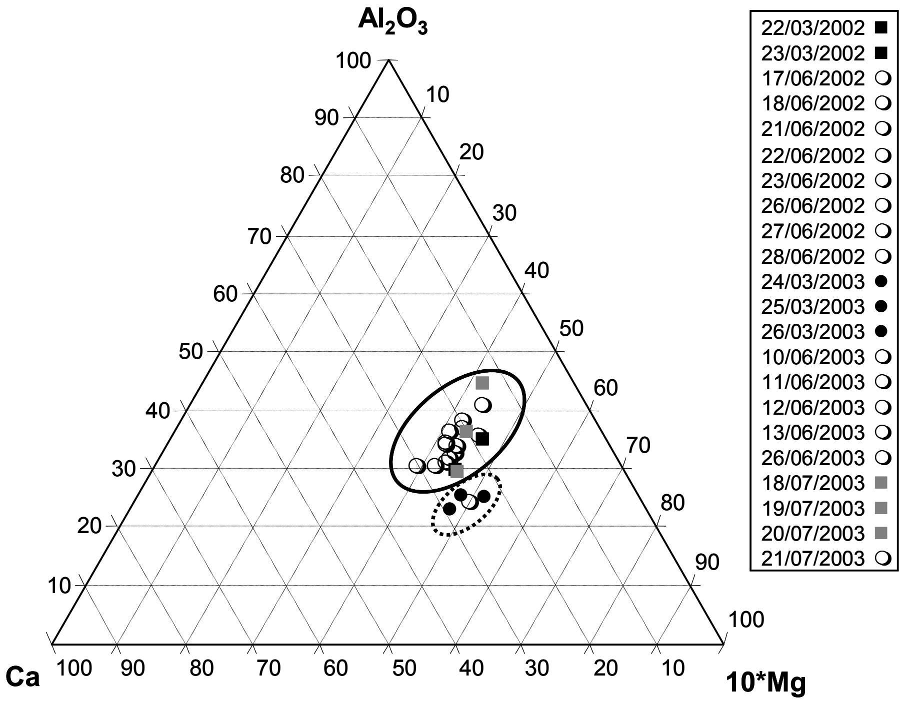


Figure 8.17. Relative concentrations of three major crustal components (Al_2O_3, Ca and Mg) of TSP for daily samples collected at La Castanya (Montseny, NE Iberian Peninsula) during the 7 north African dust outbreaks simulated in this study. The samples differentiated with squares denote major contributions of southwestern source areas (Mauritania-Western Sahara and Mali-Mauritania-western flanks of the Ahaggar Mountains) while the circles denote major contributions from northern source areas (western and eastern Algeria and Tunisia-northeastern Algeria). Furthermore, the black colour denotes low atmospheric transport while the white and grey colours denote transport at high atmospheric levels.

9. Conclusions

9. CONCLUSIONS

One of the objectives of this work was to interpret the spatial and seasonal variability of PM levels in regional background stations of the Iberian Peninsula. This was made through the identification and the subsequent evaluation of the frequency of occurrence of air transport scenarios from different source areas having a higher or lower impact in the PM levels. PM data from various regional background stations belonging to the EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe) network and to regional background stations from other air quality monitoring networks were used as a basis of this study. The quality of the data was evaluated so that data from stations influenced by local anthropogenic sources were discarded. The main conclusions obtained in this study can be summarised as follows:

1- PM levels in regional background stations ranged in 17-40 µgTSP m^{-3}, 12-22 µgPM10 m^{-3}, 7-12 µgPM2.5 m^{-3}. As expected for regional background sites PM levels were maximum in summer owing to the increase of soil re-suspension, the enhancement of the photochemical production of secondary aerosols, the increment in the transport of dust from north Africa, the poor renovation of air masses under summer conditions and the low frequency of precipitation.

2- The advection of Atlantic air masses occurred in all the regions of the Iberian Peninsula during all the year with relative higher frequency in autumn and spring. These events had a relatively long duration (4-7 days on average depending on the region). These episodes affected more frequently to the western (48-72% of the days) than to the eastern regions (36-42% of the days).

2.1- The Atlantic episodes may be caused by the presence of the Azores high and the Iceland low on their standard locations (AZH-NAtD scenario) or by the location of a depression over the Atlantic ocean near the Moroccan or Portuguese coasts (AD(ATL) scenario). These two scenarios may cause precipitation frequently associated with the passage of frontal systems. AZH-NAtD is more frequent (6-9 times more frequent depending on the area) than AD(ATL), while the second scenario is accompanied with rainfall more frequently with the consequent impact on the decrease of PM levels.

2.2- The PM levels recorded during Atlantic episodes were low (11-34 µgTSP m^{-3}, 7-18 µgPM10 m^{-3}, 5-11 µgPM2.5 m^{-3}) in virtue of the renovation of air masses, the washing out of pollutants associated with precipitation and the clean character of Atlantic air masses. In consequence, the origin of PM levels during Atlantic events is mainly local/regional. Combining information of occurrence of Atlantic episodes and the PM levels associated with these situations the impact index (II) was defined as the proportion of the annual PM mean associated with Atlantic episodes. The Atlantic events had a major impact in most regions owing to the high frequency of these episodes despite the low PM levels generally recorded during them (23-60% of TSP, 21-54% of PM10, 24-52% of PM2.5). Within these, AZH-NAtD events had more impact than AD(ATL) owing to the higher relative frequency and the impact on PM levels.

3- The occurrence of African dust outbreaks showed the highest frequency in summer with second order maxima generally in January-March. These events had a mean duration of 3-4 days. Over the east and the south of Iberia these events occurred more frequently (16-27% of the days) than in the north and west (8-14% of the days).

3.1- Four scenarios were found to be responsible of the advection of African air masses over the Iberian Peninsula. The scenarios associated with the presence of a depression over the Atlantic off west or southwest the Iberian Peninsula (AD(NAF) scenario) or over northern Africa or the western Mediterranean (NAD scenario) have a relatively high frequency of precipitation. The presence of an anticyclone covering the Iberian Peninsula or north Africa at low atmospheric levels (NAH-S scenario) or at upper atmospheric levels (NAH-A scenario) gave rise to dry episodes. During NAH-A situations, occurring mainly in summer, the north African thermal low and, sometimes, the Iberian thermal low develop at surface creating a low advective situation. NAH-A is 2-3 times more frequent than the other three scenarios in most of the regions.

3.2- The African dust outbreaks resulted in high PM levels in all regions (29-62 μgTSP m^{-3}, 21-35 μgPM10 m^{-3}, 11-18 μgPM2.5 m^{-3}) due to the high load of dust in the African air masses. Owing to their frequent association with rain episodes, PM levels were usually lower during AD(NAF) and NAD than during NAH-S and NAH-A. Moreover during NAH-A the poor renovation of air masses, the enhancement of the photochemical transformation of gaseous precursors into secondary particles and the convective re-suspension also contributed to increase PM levels. Thus, the II of African episodes was high (12-41% of TSP, 16-42% of PM10, 15-35% of PM2.5), especially for NAH-A events.

4- The advection of European air masses influenced PM levels mainly over the north of Iberia (10-17% of the days with respect to 3-10% in the rest of the regions), with higher frequency in the cold seasons of the year with an average duration of 2-4 days.

4.1- The European transport may occur under the effect of an anticyclone covering the European continent or the north Atlantic Ocean (EUH scenario), or a depression located over the Mediterranean (MD scenario). The first scenario is basically dry while the latter is frequently associated with rain; furthermore, EUH scenario is more frequent than MD (2-3 times in all the regions).

4.2- During European events the regional background PM levels were moderately high over the north of the Iberian Peninsula (21-43 μgTSP m^{-3}, 14-25 μgPM10 m^{-3}, 12-16 μgPM2.5 m^{-3}) but, owing to the dispersion/dilution of pollutants, these were low over the centre and the south (13-28 μgTSP m^{-3}, 10-15 μgPM10 m^{-3}, 7-10 μgPM2.5 m^{-3}). The II of the European episodes is low in the centre and the south (3-7% of TSP, 3-8% of PM10, 3-9% of PM2.5) and moderate in the north (14-17% of TSP, 15-18% of PM10, 17-18% of PM2.5). As the frequency and the PM levels were higher during EUH situations, their II was higher than that of MD scenario.

5- The frequency of episodes of advection of Mediterranean air masses was very low in all the regions of Iberia (below 6% of the days). The duration of these events was also low (2 days on average in all the regions).

5.1- Two transport scenarios may cause Mediterranean advection. These are the location of a depression over north Africa or the Mediterranean (NAD-MD scenario) or the presence of an anticyclone covering the European continent or the Mediterranean (EUH-MH scenario). Both situations are infrequent and are linked to episodes of precipitation especially over the eastern flank of Iberia.

5.2- PM levels in regional background sites during Mediterranean events were low since these episodes are often accompanied by rain (13-39 μgTSP m^{-3}, 9-24 μgPM10 m^{-3}, 6-16 μgPM2.5 m^{-3}). The low PM levels and frequency of Mediterranean episodes result in very low II of these events in all the regions (below 5% in all size ranges and regions).

6- The episodes characterised by the lack of advective conditions were frequent in all the regions of Iberia but especially over the east, the centre and south (16-24% of the days with respect to 9-15% in the north and northwest). These situations had a moderate mean duration (3 days in all the regions) and occurred manly in summer although a moderately high frequency was observed in the rest of the year.

6.1- The situations with lack of dominant advective conditions occur either in winter when an anticyclone covers partly or completely the Iberian Peninsula (WIA scenario) or, in summer. The latter is caused by low pressure gradient conditions prevailing over the Iberian Peninsula and the intense heating of the surface resulting in the development of the Iberian thermal low. This gives rise to a complex convective dynamics characterised by the important vertical development of the boundary layer, the poor renovation and ageing of air masses and, over the east, the re-circulation of air masses driven by the intensified sea breezes (ITL scenario). Both scenarios are dry and equally frequent in most regions although ITL events occur in a shorter period (mainly from May to September).

6.2- The regional background PM levels were very different during the two distinguished scenarios without dominant advective conditions. Thus, PM levels associated with WIA episodes were low (15-32 µgTSP m^{-3}, 10-23 µgPM10 m^{-3}, 7-14 µgPM2.5 m^{-3}) because common thermal inversions diminish dispersion of pollutants from cities and industrial centres towards rural locations. On the contrary, during ITL episodes, PM levels were high (25-54 µgTSP m^{-3}, 21-30 µgPM10 m^{-3}, 14-21 µgPM2.5 m^{-3}) owing to various factors: the increase of re-suspension by convection, the dispersion of pollutants from polluting centres towards rural areas favoured by the increase in the vertical development of the boundary layer and the proliferation of secondary aerosols by enhanced photochemical reactions under strong insolation conditions. In consequence, for a similar frequency of occurrence, the II of ITL (7-22% of TSP, 9-21% of PM10, 10-21% of PM2.5) is higher to that of WIA (5-14% of TSP, 4-15% of PM10, 5-17% of PM2.5).

7- From 2001 to 2003, the exceedances of the daily limit value of 50 µgPM10 m^{-3} recorded in regional background stations of Spain were scarce (6-41 in the 3-years period depending on the station) but mostly associated with African dust outbreaks (47-100% of the PM10 exceedances in the different monitoring stations). This also stands for the exceedances of 35 µgPM2.5 m^{-3} (17-100% of the exceedances during African events) which were less frequent in regional background sites (0-18 days in the 2001-2003 period).

The study presented in section 6 was focused on the occurrence and seasonal distribution of wet and dry African dust outbreaks over the eastern Iberian Peninsula for the period 1996-2002, combining information from the time series of: a) chemistry of wet deposition at rural station near Barcelona and b) daily PM levels from urban, industrial and rural monitoring stations from the eastern area of Iberia. With these data, a complete time series of wet (events with important influence on deposition fluxes of crustal elements but low PM levels) and dry (generally causing high PM levels) African episodes was compiled. In this manner a combined study on PM levels and deposition fluxes over the Iberian Peninsula was carried out. This is something that, to our knowledge, had never been done. The main conclusions obtained in this study were:

8- During the seven year period, 112 African dust episodes accounted for a total of 378 days, with a mean duration of 3 days per episode and a mean of 16 episodes $year^{-1}$. An impact on PM levels at the air quality monitoring stations was detected in 93 out of the 112 episodes, and wet deposition occurred simultaneously with African PM intrusions in 49.

8.1- The monthly distribution of African intrusions was characterised by three modes with a clear predominance of the period May to August, whereas the lowest monthly occurrences are recorded for December, November and April. Wet episodes occurred mainly in May.

8.2- Based on a meteorological evaluation, the four different scenarios causing transport of dust air masses from northern Africa presented above were confirmed: NAH-S, AD(NAF), NAD and NAH-A. The wet African events mostly occurred under AD(NAF) and NAD scenarios.

8.3- These meteorological patterns showed a clear seasonal trend. NAH-S occurred from January to March, AD(NAF) and NAD in late winter-spring and autumn and NAH-A in summer.

8.4- African dust outbreaks had an important impact on the regional background PM levels in eastern Iberia. Mean daily levels of PM10 at the rural station in Monagrega showed increases when a dust outbreak occurred. The mean daily levels in Monagrega for the days with African intrusion of the NAH-S and NAH-A type are 31 and 30 $\mu g\ m^{-3}$ whereas, owing to rain occurrence, when the AD(NAF) and NAD scenarios were produced, the daily means are lower (21 and 17 $\mu g\ m^{-3}$ respectively). Moreover, the days with more than 50 $\mu g\ m^{-3}$ recorded at Monagrega in 1996-2002 corresponded almost completely with African dust outbreaks.

8.5- The II of the NAH-A scenario (mainly occurring in summer) proved to be approximately four times greater than that of the other three scenarios.

The work presented in section 7 consisted on a detailed study of the most intense African wet deposition episodes occurred over northeastern Iberian Peninsula in two non consecutive periods 1983-2000 and 2002-2003. These events were identified by means of the quantification of insoluble deposition matter in weekly rainwater samples collected at a rural site. Sixteen events with more than 1000 mg m^{-2} of insoluble matter accounted for 80% of the wet deposition load of insoluble African dust in the whole study period. These 16 episodes were simulated with SKIRON/Eta regional model. The most important conclusions were:

9- Based on a meteorological evaluation, three different scenarios causing transport of dust air masses from northern Africa were distinguished. These scenarios were characterised by: (1) the presence of an Atlantic depression (AD(NAF) scenario) situated in front of Portugal, (2) a north-African depression (NAD scenario), and (3) an Atlantic depression which, during the event, evolves towards the north of Africa (AD→NAD scenario). Independently of the episode type, the occurrence of these “red rains” is maximum in late winter-spring (9 of 16) and in autumn (7 of 16).

9.1- Qualitatively, SKIRON/Eta captured the transport of dust over different regions of the Iberian Peninsula during these episodes with a probability of detection of 79% obtained after a comparison with TOMS maps and SeaWIFS images. The quantitative validation of SKIRON/Eta was carried out comparing the model dust concentration values with PM10 and TSP concentrations at regional background stations distributed all over the Iberian Peninsula. The model underestimated slightly PM10 and, to a higher extent, TSP concentrations, probably as a result of local contributions to PM levels not computed by SKIRON/Eta. Thus, even quantitatively, the performance of the model can be considered correct. Finally, the wet deposition fluxes collected at La Castanya were underestimated by SKIRON/Eta owing to the combined effect of several error sources: a) the large differences in the scale of sampling (fractions of m^2) and the model (km^2), b) the unknown proportion of resuspended crustal material in the wet deposition fluxes quantification and c) the deviations in the rainfall and dust load predictions and in the washing out ratio used in the model.

9.2- The dust source areas active during the intense wet deposition episodes were identified by means of dust flux maps provided by SKIRON/Eta. A maximum daily emission was found following the maximum heating of surface owing to convective movements. This affects the totality of north Africa. In addition to this, synoptic winds also mobilise and transport dust over the Iberian Peninsula. During the “red rains”, the most active source areas covered the northernmost regions of the Saharan desert (northern, western, and central Algeria and Tunisia). For AD events the source areas located at the west of central sections of northern Africa tended to be especially active while during whenever the transport was associated with a depression located over northern Africa (NAD or AD→NAD episodes) Tunisia and central and eastern Algeria showed higher relative activity.

A methodology for the identification and quantification of the contribution of large dust source areas to the PM10 concentrations at distant receptors is presented in section 8. This methodology was tested with a north Africa dust storm outbreak occurred from 12th to 15th March 2003 that reached the central Iberian Peninsula. Configuration parameters of HYSPLIT have been adjusted in order to obtain the closest estimation of the measured PM10 levels in this study. Following this methodology, the African dust source areas contributing to dust transport over the Iberian Peninsula were determined with HYSPLIT4 for 7 African dust outbreaks occurred in 2002 and 2003 for which chemical speciation of TSP from the rural station of La Castanya were available. These 7 simulations were also employed to carry out a validation of the dust module of HYSPLIT4 in both the qualitative and in the quantitative stage.

10- The suitable model performance was achieved using a concentration grid of 1x1 degree, Top-Hat particle type model, and an emission rate of 5000 particles cycle^{-1}. Moreover, wet deposition was incorporated using 3.2 10^5 L L^{-1} and 3.0 10^{-5} s^{-1} as in-cloud and below-cloud parameters, respectively. Dry deposition was set by defining a particle diameter of 5 µm and a vertical deposition velocity of 0.6 cm s^{-1}.

10.1- In the 7 episodes simulated, the main source areas of African dust reaching Spain were western and eastern Algeria with mean contributions 31 and 35% respectively, followed by Tunisia-northeastern Algeria and Mauritania-Western Sahara (both areas with mean contributions of 13%) and, in a lesser extent, from Mali-Mauritania-western flanks of the Ahaggar Mountains and western Mauritania (7 and 1% as mean contributions respectively).

10.2- All the samples collected at La Castanya during these 7 events had a very similar composition since most of the dust plumes were composed of north Saharan dust (with a similar chemical compositions in the desert soil) and owing to the mixing of dust particles from a various locations over northern Africa. Differences in Ca/Al ratios mostly occurred linked to the transport mechanism and to a lesser extent to chemical differences of dust mobilised over specific regions of Africa. In particular, during summer episodes north Saharan dust also reaches the Iberian Peninsula but after a process of elevation by means of the intense convection over the Saharan dust in summer which causes segregation of coarse particles (mainly Ca-Carbonates) with respect to clay minerals (where Al resides). This explains why, during summer episodes, the Ca/Al ratio is lower than during days associated with low atmospheric transport from northern Sahara. In these events the transport occurs directly over Iberia at the lowest levels of the atmosphere so the segregation of large carbonates is reduced. A more prolonged sampling with more cases would allow the characterisation of certain episodes showing chemical differences in PM.

10.3- HYSPLIT4 showed a good performance simulating qualitatively the African episodes over the Iberian Peninsula. The shape and extent of the dust plumes as observed in SeaWIFS are well reproduced by HYSPLIT4 yielding a probability of detection of 96%. The daily PM10 levels recorded during these events at regional background stations distributed all over Iberia were underestimated by HYSPLIT4 although this behaviour can be considered correct since the local/regional fraction of PM10 is not accounted by HYSPLIT4 in these simulations.

10. Future research lines

10. FUTURE RESEARCH LINES

Based on the results obtained in this thesis the following research lines on the fields of particulate matter pollution and wet deposition are proposed:

Evaluation of the quality of PM data from regional background stations: The PM data used for this study were obtained from regional background stations; however, these stations are located in locations with different characteristics of altitude, soil coverage and natural surroundings. Some questions arise: what are the minimum requirements needed for a monitoring station to be considered representative of the regional background? Do these requirements depend on factors such as climate or orography of a region? How many regional background stations are needed to optimise the design of an air quality monitoring network in Spain? The location of each Spanish regional background station should be studied with detail with especial interest on the evaluation of the nearby potential sources of atmospheric pollutants. This requires a systematic control of these stations to detect if changes in the local/regional environment such as industrialisation or urbanisation of the area, may affect the stations measurements. This would be a control mechanism of the quality of regional background sites. On the basis of these studies, a definition of a regional background monitoring stations may be established.

Measurements of organic-elemental carbon (OC+EC): The OC+EC can affect the radiative balance of the atmosphere in two ways: a) The EC, scatters, absorbs and emits radiation and has a positive forcing (warming) and b) a great part of the OC is soluble so it can act as cloud condensation nuclei resulting in a negative forcing (cooling) because clouds reflect incoming radiation. Given these climate effects, measurements of OC+EC in regional background stations should be carried out.

Measurements of the variability of number particle concentration in regional background areas: These measurements are being carried out in urban environments on the light of studies highlighting the health effects of the number of particles. To our knowledge these works are scarce in rural environments so the regional background levels of particle number are not well defined yet. The episodes considered in this thesis may have a completely different impact on the particle number density and in the mass density (which is the standard parameter to be controlled according to legislation). The impact of different transport events on the particle number density should then be studied.

Study of episodes with impact on PM levels in regional background areas caused by biomass burning: In this study we have considered different episodes with impact on PM levels on the basis of the origin of the air masses involved in the transport. Other events or processes can also have a high impact in these levels. Among them, the episodes of biomass burning in the Iberian Peninsula may be a subject of study. The occurrence of these episodes has a marked seasonality with a very high frequency in summer when extent forest fires occur in Spain and Portugal owing to the severe drought associated with Mediterranean climate. During these events the levels of OC and EC should be studied.

Validations of dust models: One of the most important needs for the scientific community working on the modelling of transport and deposition of dust is the validation of the models outputs. For these validations, using data from air quality monitoring stations located far from the direct influence of anthropogenic sources of aerosols is appropriate since it is there where the impact of dust outbreaks on PM levels and deposition fluxes is detectable. Models generally show a very good qualitative performance when simulating African dust outbreaks but the quantification of PM concentration and, especially, deposition fluxes is still subject to important errors. Sensitivity tests should be carried out for the determination of the influence of changes in meteorological data, model resolution, friction velocity, source strength, washing out ratio, etc… on the models' outputs. The validation work should begin with a prior compilation of PM and dust deposition data from the maximum number of regional background stations available at a certain area, and the study of the quality of these data. This is very important because limitations of sampling methods are known and should be taken into account for the validation. The optimum situation would be to have data from stations well distributed around the study area to avoid scale problems in the comparisons. As can be inferred, this work should involve expertises in modelling and in sampling for an appropriate interpretation of both aspects.

11. Scientific contributions

11. SCIENTIFIC CONTRIBUTIONS

In the development of this thesis the following publications and contributions to conferences have been presented:

Publications

Escudero, M., S. Castillo, X. Querol, A. Avila, M. Alarcón, M.M. Viana, A. Alastuey, E. Cuevas, and S. Rodríguez (2005), Wet and dry African dust episodes over Eastern Spain, *Journal of geophysical research*, *110* (D18S08), 10.1029.

Escudero, M., A. Stein, R.R. Draxler, X. Querol, A. Alastuey, S. Castillo, and A. Avila (2006), Determination of the contribution of Northern Africa dust source areas to PM10 concentrations over Central Iberian Peninsula using the HYSPLIT model, *Journal of geophysical research*, *111* (D06210), 10.1029.

Escudero, M., C. Spyrou, S. Castillo, G. Kallos, X. Querol, A. Alastuey, and A. Avila (Submitted to Journal of geophysical research), Intense African "red rains" occurred in the period 1983-2003 over Northeastern Spain simulated with SKIRON/Eta model.

Escudero, M., A.F. Stein, R.R. Draxler, X. Querol, A. Alastuey, S. Castillo, and A. Avila (Submitted to Atmospheric environment), African dust source apportionment at Western Mediterranean with HYSPLIT4.

Alastuey, A., X. Querol, S. Castillo, M. Escudero, A. Avila, E. Cuevas, C. Torres, P.M. Romero, F. Exposito, O. Garcia, J.P. Diaz, R.V. Dingenen, and J.P. Putaud (2005), Characterisation of TSP and PM2.5 at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan dust episode (July 2002), *Atmospheric environment*, *39* (26), 4715-4728.

Avila, A., M. Alarcón, S. Castillo, M. Escudero, J.G. Orellana, P. Masqué, and X. Querol (Submitted to Journal of geophysical research), African dust in red rains: mineralogical and chemical characteristics related to source areas and transport patterns from North Africa to Eastern Spain.

Alados-Arboledas, L., H. Horvath, G. Pavese, F. Esposito, X. Querol, L. Ramírez, A. Alcántara-Ruiz, F.J. Olmo, H. Lyamani, I. Foyo-Moreno, M. Gangl, L. Fenk, B. Jost, L. Leone, S. Castillo, M. Escudero, and B. Espinar (2004), Indalo 2003 field campaign, *Journal of aerosol science*, *35* (Supplement 2), 981-1048.

Contributions to conferences

Escudero, M., S. Castillo, M.M. Viana, X. Querol, A. Alastuey, N. Moreno, and A. Avila (2003), Statistical and Meteorological Analysis of Wet and Dry African Dust Episodes over the Eastern Iberian Peninsula for the Period 1996-2002, in *2nd workshop on Mineral dust*, Paris, France.

Avila, A., M. Alarcón, M. Escudero, and X. Querol (2004), Present-day dust deposition fluxes to northeastern Spain in red rains, in *EGU 1st General Assembly*, edited by E.G. Union, Nice, France.

Querol, X., A. Alastuey, M.M. Viana, S. Rodríguez, S. Castillo, J. Pey, M. Escudero, B. Artiñano, P. Salvador, S. Garcia do Santos, R. Fernandez Patier, C. Ruiz, J. de la Rosa, A. Sánchez de la Campa, M. Menéndez, and J.I. Gil (2004), Niveles y composición de PM10 y PM2.5 en España, in *IX Congreso de Ingeniería Ambiental - Proma 2004*, Bilbao.

Alados-Arboledas, L., H. Horvath, G. Pavese, F. Esposito, X. Querol, L. Ramírez, A. Alcántara-Ruiz, F.J. Olmo, H. Lyamani, I. Foyo-Moreno, M. Gangl, L. Fenk, B. Jost, L. Leone, S. Castillo, M. Escudero, and B. Espinar (2004), Indalo 2003 field campaign, in *European Aerosol Conference (EAC)*, Budapest, Hungary.

Alados-Arboledas, L., H. Horvath, G. Pavese, F. Esposito, X. Querol, L. Ramírez, A. Alcántara-Ruiz, F.J. Olmo, H. Lyamani, I. Foyo-Moreno, M. Gangl, L. Fenk, B. Jost, L. Leone, S. Castillo, M. Escudero, and B. Espinar (2005), Columnar properties of the atmospheric aerosol during the INDALO2003 field campaign, in *European Aerosol Conference (EAC)*, Gent, Belgium.

Alados-Arboledas, L., H. Horvath, G. Pavese, F.J. Expósito, X. Querol, L. Ramírez, A. Alcántara-Ruiz, F.J. Olmo, H. Lyamani, I. Foyo-Moreno, M. Gangl, L. Fenk, B. Jost, L. Leone, S. Castillo, M. Escudero, and B. Espinar (2004), INDALO 2003. Presentación general de la campaña, in *4ª Asamblea Hispano-Portuguesa de geofísica y geodesia*, Figueira da Foz, Portugal.

12. References

12. REFERENCES

Ackerman, S.A., and S.K. Cox (1989), Surface weather observations of atmospheric dust over the southwest summer monsoon region, *Meteorology and atmospheric physics*, *41* (1), 19-34.

Alastuey, A. (1994), Caracterización mineralógica y alterológica de morteros de revestimientos de edificios de Barcelona, University of Barcelona.

Alastuey, A., X. Querol, A. Chaves, C.R. Ruiz, A. Carratalá, and A. López-Soler (1999), Bulk deposition in a rural area located around a large coal-fired power station, Northeast Spain, *Environmental pollution*, *106* (3), 359-367.

Alastuey, A., X. Querol, S. Castillo, M. Escudero, A. Avila, E. Cuevas, C. Torres, P.M. Romero, F. Exposito, O. Garcia, J.P. Diaz, R.V. Dingenen, and J.P. Putaud (2005), Characterisation of TSP and PM2.5 at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan dust episode (July 2002), *Atmospheric environment*, *39* (26), 4715-4728.

Alfaro, S.C., A. Gaudichet, L. Gomes, and M. Maillé (1998), Mineral aerosol production by wind erosion: Aerosol particles sizes and binding energies, *Geophysical research letters*, *25* (7), 991-994.

Allen, G., C. Sioutas, P. Koutrakis, R. Reiss, F.W. Lurmann, P.T. Roberts, and R.M. Burton (1997), Evaluation of the TEOM method for measurement of ambient particulate mass in urban areas, *Journal of the air & waste management association*, *47*, 682-689.

Alonso, L., G. Gangoiti, M. Navazo, M. Millán, and E. Mantilla (2000), Transport of tropospheric ozone over the Bay of Biscay and the Eastern Cantabrian coast of Spain, *Journal of Applied Meteorology*, *39*, 475-486.

Alpert, P., and E. Ganor (1993), A jet-stream associated heavy dust storm in the Western Mediterranean, *Journal of geophysical research*, *98* (D4), 7339-7349.

Alpert, P., and E. Ganor (2001), Sahara mineral dust measurements from TOMS: comparison to surface observations over the Middle East for the extreme dust storm, March 14-17, 1998, *Journal of geophysical research*, *106* (D16), 18275-18286.

Alpert, P., B.U. Neeman, and Y. Shay-El (1990), Climatological analysis of Mediterranean cyclones using ECMWF data, *Tellus*, *42A*, 65-77.

Andreae, M.O. (1983), Soot carbon and excess fine potassium - Long-range transport of combustion-derived aerosols, *Science*, *220* (4602), 1148-1151.

Andreae, M.O., Climatic effects of changing atmospheric aerosol levels, in *World survey of climatology*, edited by A. Henderson-Sellers, Elsevier, Amsterdam, 1995.

Andreae, M.O., T.W. Andreae, H. Annegarn, F. Beer, H. Cachier, W. Elbert, G.W. Harris, W. Maenhaut, I. Salma, R. Swap, F.G. Wienhold, and T. Zenker (1998), Airborne studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical composition, *Journal of geophysical research*, *103* (D24), 32119-32128.

Andreae, M.O., R.J. Charlson, F. Bruynseels, H. Storms, R.V. Grieken, and W. Maenhaut (1986), Internal mixture of salt, silicates and excess sulphate in marine aerosols, *Science*, *232* (4758), 1620-1623.

Ansmann, A., D. Müller, I. Mattis, and U. Wandinger (2003), Raman-lidar profiling of dust optical properties at UV and visible wavelengths, in *2nd Workshop on mineral dust*, Paris.

Arimoto, R. (2001), Eolian dust and climate: relationships to sources, tropospheric chemistry, transport and deposition, *Earth science reviews*, *54*, 29-42.

Arimoto, R., R.A. Duce, B.J. Ray, W.G.E. Jr., J.D. Cullen, and J.T. Merrill (1995), Trace elements in the atmosphere over the North Atlantic, *Journal of geophysical research*, *100*, 1199-1214.

Arimoto, R., B.J. Ray, N.F. Lewis, U. Tomza, and R.A. Duce (1997), Mass-particle size distributions of atmospheric dust and the dry deposition of dust to the remote ocean, J*ournal of geophysical research*, *102*, 15867-15874.

Arimoto, R., R.A. Duce, B.J. Ray, and U. Tomza (2003), Dry deposition of trace elements to the western North Atlantic, *Global biogeochemical cycles*, *17* (1), 1010, doi:10.1029/2001GB001406.

Avila, A. (1996), Time trends in the precipitation chemistry at a mountain site in Northeastern Spain for the period 1983-1994, *Atmospheric environment*, *30*, 1363-1373.

Avila, A., I. Queralt, and M. Alarcón (1997), Mineralogical composition of African dust delivered by red rains over North-Eastern Spain, *Journal of geophysical research*, *102*, 21977-21996.

Avila, A., M. Alarcón, and I. Queralt (1998), The chemical composition of dust transported in red rains-its contribution to the biogeochemical cycle of a Holm Oak forest in Catalonia (Spain), *Atmospheric environment*, *32* (2), 179-191.

Avila, A., and M. Alarcón (1999), Relationship between precipitation chemistry and meteorological situations at rural site in NE Spain, *Atmospheric environment*, *33*, 1663-1677.

Avila, A., and F. Rodà (2002), Assessing decadal changes in rainwater alkalinity at a rural Mediterranean site in the Montseny Mountains (NE Spain), *Atmospheric environment*, *36*, 2881-2890.

Avila, A., and M. Alarcón (2003), Precipitation chemistry at a rural Mediterranean site: between anthropogenic pollution and natural emissions, *Journal of geophysical research*, *108* (D9), Art. No. 4278.

Bellot, J., and T.B. Golley (1989), Nutrient input and output of an irrigated agroecosystem in an arid Mediterranean landscape, *Agriculture ecosystems & environment*, *25* (2-3), 175-186.

Bergametti, G., L. Gomes, G. Coudé-Gaussen, P. Rognon, and M.N.L. Coustumer (1989a), African dust observed over Canary Islands: source regions identification and transport pattern for some summer situation, *Journal of geophysical research*, *94*, 14855-14864.

Bergametti, G., A.L. Dutot, P. Buat-Menard, R. Losno, and E. Remoudaki (1989b), Seasonal variability of the elemental composition of atmospheric aerosol particles over the NW Mediterranean, *Tellus*, *41B*, 353-361.

Biermann, A.H., and J.M. Ondov (1980), Application of surface-deposition models to size-fractionated coal fly-ash, *Atmospheric environment*, *14* (3), 289-295.

Blake, D.F., and K. Kato (1995), Latitudinal distribution of black carbon soot in the upper troposphere and lower stratosphere, *Journal of geophysical research*, *100* (D4), 7195-7202.

Blanchard, D.C. (1969), The oceanic production rate of cloud nuclei, *Journal de recherches atmosphériques*, *4*, 1-6.

Blanchard, D.C. (1985), The oceanic production of atmospheric sea salt, *Journal of geophysical research*, *90* (NC1), 961-963.

Braaten, D.A., and T.A. Cahill (1986), Size and composition of Asian dust transported to Hawaii, *Atmospheric environment*, *20* (6), 1105-1109.

Brimblecombe, P. (1996), *Air composition & chemistry*, Cambridge University press.

Brink, H.M.t., J.P. Veefkind, A. Waijers-Ijpelaan, and J.C.v.d. Hage (1996), Aerosol light-scattering in the Netherlands, *Atmospheric environment*, *30*, 4251-4261.

Brooks, N., and M. Legrand (2000), Dust variability over northern Africa and rainfall in the Sahel, in *Linking climate change to land surface change*, edited by S.J. McLaren, and D. Kniveton, pp. 1-25, Kluwer Academic Publishers.

Bücher, A., and G. Lucas (1984), Sédimentation éolienne intercontinentale, pussières sahariennes et géologie, *Bulletin centre researche et exploration-production Elf-Aquitaine*, *8*, 155-165.

Buishand, T.A., G.T. Kempen, A.J. Frantzen, H.F.R. Reijnders, and A.J.v.d. Eshof (1988), Trend and seasonal variation of precipitation chemistry data in the Netherlands, *Atmospheric environment*, *22*, 339-348.

Burnett, R.T., J. Brook, T. Dann, C. Delocla, O. Philips, S. Cakmak, R. Vincent, M.S. Goldberg, and D. Krewski (2000), Association between particulate- and gas-phase components of urban air pollution and daily mortality in eight Canadian cities, *Inhalation toxicology*, *12* (4), 15-39.

Bustos, J.J., E. Cuevas, C. Marrero, and S. Alonso (1998), Caracterización de las masas de aire en la troposfera libre y en la capa de mezcla en Canarias, in *IX Asamblea Geodesia y Geofísica*, pp. 9-13, Aguadulce (Almería).

Butler, T.J., and G.E. Likens (1991), The impact of changing regional emissions on precipitation chemistry in the Eastern United States, *Atmospheric environment*, *25* (2), 305-315.

Caboi, R., R. Cidu, A. Cristini, L. Fanfani, and P. Zuddas, Influence of Saharan dust and marine spray on the chemical composition of rain in Sardinia, Italy, in *Water-rock interaction*, edited by Y.K. Kharala, and A.S. Maest, Balkema, Rotterdam, 1992.

Callot, Y., B. Marticorena, and G.B. G (2000), Geomorphologic approach for modelling the surface features of arid environments in a model of dust emissions: application to the Sahara desert, *Geodinamica acta*, *13* (5), 245-270.

Camarero, L., and J. Catalán (1993), Chemistry of bulk precipitation in the Central and Eastern Pyrenees, Northeast Spain, *Atmospheric environment*, *27*, 83-94.

Camarero, L., and J. Catalán (1998), A simple model of regional acidification for high mountain lakes: application to the Pyrenean lakes (North-East Spain), *Water research*, *32* (4), 1126-1136.

Campbell, I.D., K. McDonald, M.D. Flannigan, and J. Kringayark (1999), Long-distance transport of pollen into the Arctic, *Nature*, *399* (6731), 29-30.

Capel, J.J. (2000), *El clima de la Península Ibérica*, Ariel Geografía.

Caquineau, S., A. Gaudichet, L. Gomes, M.C. Magonthier, and B. Chatenet (1998), Saharan dust: clay ratio as a relevant tracer to assess the origin of soil delivered aerosols, *Geophysical research letters*, *25*, 983-986.

Carlson, T.N., and J.M. Prospero (1972), The large scale movement of Saharan air outbreaks over the northern equatorial Atlantic, *Journal of Applied Meteorology*, *11*, 283-297.

Carratalá, A. (1993), Caracterización química de la precipitación en la Comunidad Valenciana, PhD thesis, Universidad de Alicante.

Carratalá, A., and J. Bellot (1998), Neutralization of nitrate and sulphate in precipitation on the eastern Mediterranean coast of Spain. Implications for acidification risk, *Water, air and soil pollution*, *104*, 237-257.

CEN (1998), Air Quality - Determination of the PM10 fraction of suspended particulate matter - Reference method and field test procedure to demonstrate reference equivalence of measurement methods, European Committee for Standardization (European Standard EN 12341), Brussels.

Chaves, A.L. (2001), Deposición atmosférica alrededor de la central térmica Teruel (NE España), PhD thesis, Universitat Politécnica de Catalunya, Barcelona.

Chester, R., M. Nimmo, M. Alarcón, C. Saydam, K.J.T. Murphy, G.S. Sanders, and P. Corcoran (1993), Defining the chemical character of aerosols from the atmosphere in the Mediterranean sea and surrounding regions, *Oceanologica acta*, *16*, 231-246.

Chiapello, I., G. Bergametti, L. Gomes, and B. Chatenet (1995), An additional low layer transport of Sahelian and Saharan dust over the North-Eastern Tropical Atlantic, *Geophysical research letters*, *22* (23), 3191-3194.

Chiapello, I., G. Bergametti, and B. Chatenet (1997), Origins of African dust transported over the northeastern tropical Atlantic, *Journal of Geophysical Research*, *102* (D12), 13701-13709.

Chuang, C.C., J.E. Penner, K.E. Taylor, A.S. Grossman, and J.J. Walton (1997), An assessment of the radiative effects of anthropogenic sulphate, *Journal of geophysical research*, *102*, 3761-3778.

Chuang, C.C., J.E. Penner, J.M. Prospero, K.E. Grant, G.H. Rau, and K. Kawamoto (2002), Cloud susceptibility and the first aerosol indirect forcing: sensitivity to black carbon and aerosol concentrations, *Journal of geophysical research*, *107* (D21), Art. No. 4564.

Colbeck, I., B. Atkinson, and Y. Johar (1997), The morphology and optical properties of soot produced by different fuels, *Journal of aerosol science*, *28* (5), 715-723.

Conlan, D.E., and J.W.S. Longhurst (1993), Spatial variability in urban acid deposition, 1990: results from the Greater Manchester Acid Deposition Survey network in the UK, *Science of the total environment* (128), 101-120.

Cogbill, P.M., and G.E. Likens (1974), Acid precipitation in the northeastern United States, *Water resources research*, *10*, 1133-1137.

Coudé-Gaussen, G. (1981), Etude détaillée d'un échantillon de poussières éoliennes prélevé au Tanezrouft, le 10 décembre, *Recherches géographiques à Strasbourg*, *16-17*, 121-130.

Coudé-Gaussen, G., P. Rognon, G. Bergametti, L. Gomes, B. Strauss, J.M. Gros, and M.N.L. Coustumer (1987), Saharan dust over Fuerteventura Island (Canaries), Chemical and mineralogical characteristics, air mass trajectories and probable sources, *Journal of geophysical research*, *92*, 9753-9711.

Crespi, S.N., B. Artíñano, and H. Cabal (1995), Synoptic classification of the mixed-layer evolution, *Journal of applied methods*, *34*, 1666-1676.

Crutzen, P.J., and M.O. Andreae (1990), Biomass burning in the tropics - Impact on atmospheric chemistry and biogeochemical cycles, *Science*, *250* (4988), 1669-1678.

D'Almeida, G.A. (1986), A model for Saharan dust transport, *Journal of climate and applied meteorology*, *25*, 903-916.

Dayan, U., J. Hefter, and J. Miller (1991), Dust intrusion into the Mediterranean basin, *Journal of applied meteorology*, *30*, 1185-1199.

Delany, A.C., A.C. Delany, D.W. Parkin, J.J. Griffin, E.D. Goldberg, and B.E.F. Reimann (1967), Airborne dust collected at Barbados, *Geochimica and cosmochimica*, *31* (5), 885.

Dockery, D.W., C.A. Pope, X. Xu, J.D. Spengler, J.H. Ware, M.E. Fay, B.G. Ferris, and F.E. Speizer (1993), An association between air pollution and mortality in six U.S. cities, *New England journal of medicine*, *329*, 1753-1759.

Dockery, D.W. (2001), Epidemiologic evidence of cardiovascular effects of particulate air pollution, *Environmental health prespectives*, *109* (4), 483-486.

Drablos, D., and A. Tollan (1980), *Proceedings of international conference on ecological impact of acid precipitation*, Sandefjord, Norway.

Draxler, R.R. (1995), Hybrid single-Particle Lagrangian Integrated Trajectories, NOAA-ARL.

Draxler, R.R. (2002), Forecasting dust storms using HYSPLIT, in *The Sino-US workshop on dust storms and their effects on human health*, Raleigh, North Carolina.

Draxler, R.R., and G.D. Hess (1997), Description of the HYSPLIT_4 modeling system, ERL ARL.

Draxler, R.R., and G.D. Hess (1998), An overview of the HYSPLIT_4 modelling system for trajectories, dispersion, and deposition, *Australian meteorological magazine*, *47*, 295-308.

Draxler, R.R., D.A. Gillette, J.S. Kirkpatrick, and J. Heller (2001), Estimating PM10 air concentrations from dust storms in Iraq, Kuwait, and Saudi Arabia, *Atmospheric environment*, *35*, 4315-4330.

Draxler, R.R., and G.D. Rolph (2003), HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html), NOAA Air Resources Laboratory, Silver Spring, MD.

Drees, L.R., A. Manu, and L.P. Wilding (1993), Characteristics of aeolian dusts in Niger, West Africa, *Geoderma*, *59*, 212-233.

Dubief, J., Review of the North African climate with particular emphasis on the production of eolian dust in the Sahel zone and in the Sahara, in *Saharan dust. Mobilization, transport, deposition*, edited by C. Morales, pp. 27-48, John Wiley & Sons, Chichester, 1979.

Duce, R.A., C.K. Unni, B.J. Ray, J.M. Prospero, and J.T. Merrill (1980), Long-range atmospheric transport of soil dust from Asia to the tropical north pacific - temporal variability, *Science*, *209* (4464), 1522-1524.

Duce, R.A., Sources, distributions and fluxes of mineral aerosols and their relationship to climate, in *Aerosol forcing of climate*, edited by R.J. Charlton, and J. Heintzenberg, pp. 43-72, Wiley & sons, 1995.

Dulac, F., P. Buat-Ménard, U. Ezat, S. Melki, and G. Bergametti (1989), Atmospheric input of trace metals to the western Mediterranean: uncertainties in modelling dry deposition from cascade impactor data, *Tellus*, *41B*, 362-378.

Dulac, F., D. Tanre, G. Bergametti, P.B.-d. Menard, M. Desbois, and D. Sutton (1992), Assessment of the African airborne dust mass over the Western Mediterranean using Meteosat data, *Journal of geophysical research*, *97*, 2489-2506.

Eastern, R.C., and L.K. Peter (1994), Binary homogeneous nucleation: temperature and relative humidity fluctuations, nonlinearity, and aspects of new particles production in the atmosphere, *Journal of applied meteorology*, 775-784.

EC (2004), Second position paper on particulate matter, European Commission.

EMEP (2001), EMEP manual for sampling and chemical analysis, Norwegian Institute for Air Research, Kjeller, Norway.

EPA (1996), *Air Quality Criteria for Particulate Matter*, Washington.

Ericksson, D.J., and R.A. Duce (1988), On the global flux of atmospheric sea salt, *Journal of geophysical research*, *93* (C11), 14079-14088.

Font, I. (1955), *El clima del Sahara (con especial referencia a la zona española)*, CSIC, Madrid.

Font, I. (2000), *Climatología de España y Portugal*, Ediciones Universidad de Salamanca.

Fowler, L.D., and D.A. Randall (1996), Liquid and ice cloud microphysics in the CSU general circulation model .2. Impact on cloudiness, the earth's radiation budget, and the general circulation of the atmosphere, *Journal of climate*, *9* (3), 530-560.

Gangoiti, G., M.M. Millán, R. Salvador, and E. Mantilla (2001), Long-range transport and re-circulation of pollutants in the Western Mediterranean during the project Regional Cycles of Air Pollution in the West-Central Mediterranean Area, *Atmospheric Environment*, *35*, 6267-6276.

Gangoiti, G., L. Alonso, M. Navazo, A. Albizuri, G. Pérez-Landa, M. Matabuena, V. Valdenebro, M. Maruri, J.A. García, and M. Millán (2002), Regional transport of pollutants over the Bay of Biscay: analysis of an ozone episode under a blocking anticyclone in west-central Europe., *Atmospheric Environment*, *36*, 1349-1361.

Gillette, D.A., D.W. Fryrear, T.E. Gill, T. Ley, T.A. Cahill, and E.A. Gearhart (1997), Relation of vertical flux of PM10 to total aeolian horizontal mass flux at Owens Lake, *Journal of geophysical research*, *102*, 26009-26015.

Ganor, E., and Y. Mamane (1982), Transport of Saharan dust across the Eastern Mediterranean, *Atmospheric environment*, *16* (3), 581-587.

Gao, Y., Y.J. Kaufman, D. Tanre, D. Kolber, and P.G. Falkowski (2001), Seasonal distributions of aeolian iron fluxes to the global ocean, *Geophysical research letters*, *28* (1), 29-32.

Gimeno, L., and E. Hernández (1997), Influence of latitude on rain acidity in Europe, *Toxicological and environmental chemistry*, *62*, 161-168.

Golitsyn, G., and D.A. Gillette (1993), A joint soviet-american experiment for the study of Asian desert dust and its impact on local meteorological conditions and climate - introduction, *Atmospheric environment*, *27* (16), 2467-2470.

Götz, G., Aerosols and climate, in *Atmospheric particles and nuclei*, edited by G. Götz, E. Mészáros, and G. Vali, pp. 193-241, Akadémiai Kiadó, Budapest, 1991.

Goudie, A.S. (1983), Dust storms in space and time, *Progress in physical geography*, *7* (4), 502-530.

Goudie, A.S., and N.J. Middleton (2001), Saharan dust storms: nature and consequences, *Earth-science reviews*, *56*, 179-204.

Granat, G. (1972), On the relation between pH and the chemical composition in atmospheric precipitation, *Tellus*, *24*, 550-560.

Griffin, D.W., V.H. Garrison, J.R. Herman, and E.A. Shinn (2001), African desert dust in the Caribbean atmosphere: microbiology and public health, *Aerobiologia*, *17*, 203-213.

Guerzoni, S., A. Cristini, R. Caboi, O. LeBolloch, I. Marras, and L. Rundeddu (1995a), Ionic composition of rainwater and atmospheric aerosols in Sardinia, Southern Mediterranean, *Water, air and soil pollution*, *85*, 2077-2082.

Guerzoni, S., G. Quarantotto, E. Molinaroli, and G. Rampazzo (1995b), More data on source signature and seasonal fluxes to the Central Mediterranean Sea of aerosol dust originated in desert areas, *Water pollution research reports*, *32* (267-273).

Guerzoni, S., W. Landuzzi, R. Lenaz, G. Quarantotto, G. Cesari, R. Rampazzo, and E. Molinaroli (1992), Mineral atmospheric particulate from south to southwest Mediterranean: seasonal variations and characteristics, *Water pollution research reports*, *28*, 483-493.

Guerzoni, S., E. Molinaroli, and R. Chester (1997), Saharan dust inputs to the Western Mediterranean sea: depositional patterns, geochemistry and sedimentological implications, *Deep-sea research II*, *44* (3-4), 631-654.

Hamonou, E., P. Chazette, D. Balis, F. Dulac, X. Schneider, E. Galani, G. Ancellet, and A. Papayannis (1999), Characterization of the vertical structure of Saharan dust export to the Mediterranean basin, *Journal of geophysical research*, *104* (D18), 22257-22270.

Han, Q., W.B. Rossow, J. Chou, and R.M. Welch (1998), Global survey of the relationships of cloud albedo and liquid water path with droplet size using ISCCP, *Journal of climate*, *11*, 1516-1528.

Harrison, R.M., and A.M.N. Kito (1990), Field intercomparison of filter pack and denuder sampling methods for reactive gaseous and particulate pollutants, *Atmospheric environment*, *24*, 2633-2640.

Haywood, J.M., and V. Ramaswamy (1998), Global sensitivity studies of the direct radiative forcing due to anthropogenic sulphate and black carbon aerosols, *Journal of geophysical research*, *103* (D6), 6043-6058.

Herman, J.R., P.K. Bhartia, O. Torres, O. Hsu, C. Seftor, and E. Celarier (1997), Global distribution of UV-absorbing aerosols from Nimbus 7/TOMS data, *Journal of geophysical research*, *102*, 16911-16922.

Hermann, E. (1903), Die Staubfälle vom 19 bis 23 Februar 1903 über dem Nordatlantischen Ozean, Grossbrittanien und Mittel-Europa, *Annallen hydrog.*, *31*, 425-438 and 475-483.

Herut, B., and M. Krom, Atmospheric imput of nutrients and dust to the SE Mediterranean, in *The impact of desert dust across the Mediterranean*, edited by S. Guerzoni, and R. Chester, pp. 349-358, Kluwer academic publishing, Dordrecht, 1996.

Hicks, B.B. (1986), Differences in wet and dry particle deposition parameters between North America and Europe, in *Aerosols: Research, Risk Assessment, and Control Strategies*, pp. 973-982, Lewis Publishers, Chelsea, MI.

Hidy, G.M. (1994), *Atmospheric sulphur and nitrogen oxides*, Academic Press Limited, London.

Hildemann, L.M., W.F. Rogge, G.R. Cass, M.A. Mazurek, and B.R.T. Simoneit (1996), Contribution of primary aerosol emissions from vegetation-derived sources to fine particle concentrations in Los Angeles, *Journal of geophysical research*, *101* (D14), 19541-19549.

Hobbs, P.V., Aerosol clouds interaction, in *Aerosol-clouds-climate interaction*, edited by P.V. Hobbs, pp. 33-73, 1993.

Horvath, H., Effects on visibility, weather and climate, in *Atmospheric acidity. Sources, consequences and abatement*, edited by M. Radojevic, and R.M. Harrison, pp. 435-466, Elsevier, London, 1992.

Hovmand, M.F., and K. Kemp (1996), Downward trends of sulphur deposition to Danish spruce forest, *Atmospheric environment*, *30*, 2989-2999.

Hudson, J.G., and X.Y. Da (1996), Volatility and size of cloud condensation nuclei, *Journal of geophysical research*, *101* (D2), 4435-4442.

Husar, R.B., D.M. Tratt, B.A. Schichtel, S.R. Falke, F. Li, D. Jaffe, S. Gasso, T. Gill, N.S. Laulainen, F. Lu, M.C. Reheis, Y. Chun, D. Westphal, B.N. Holben, C. Gueymard, I. McKendry, N. Kuring, G.C. Feldman, C. McClain, R.J. Frouin, J. Merrill, D. DuBois, F. Vignola, T. Murayama, S. Nickovic, W.E. Wilson, K. Sassen, N. Sugimoto, and W.C. Malm (2001), Asian dust events of April 1998, *Journal of geophysical research*, *106* (D16), 18317-18330.

Hutchinson, T.C., and M. Havas (1980), *Effects of acid precipitation on terrestrial ecosystems*, New York.

INM (2001), *Guía resumida del clima en España 1971-2000*, 257 pp., Ministerio de Medio Ambiente, Spain.

IPCC (2001), *Climate Change 2001: The Scientific Basis*, Cambridge University Press.

Irwin, J.G., G. Campbell, and K. Vincent (2002), Trends in sulphate and nitrate wet deposition over the United Kingdom: 1986–1999, *Atmospheric environment*, *36* (17), 2867-2879.

Jaenicke, R. (1978), Dynamics of atmospheric aitken particles, *Berichte der bunsen-gesellschaft-Physical chemistry chemical physics*, *82* (11), 1198-1202.

Jaenicke, R., Monitoring and critical review of the estimated source strength of mineral dust from the Sahara, in *Saharan dust: mobilisation, transport and deposition*, edited by C. Morales, pp. 233-242, Willey & Sons, Chichester, 1979.

Janjic, Z.I. (1994), The step-mountain eta coordinate model: further developments of the convection, viscous sublayer and turbulence closure schemes, *Monthly weather review*, *122*, 927-945.

Joseph, J.H., and N. Wolfson (1975), Ratio of absorption to backscatter of solar-radiation by aerosols during khamsin conditions and effects on radiation balance, *Journal of applied meteorology*, *14* (7), 1389-1396.

Kallos, G., V. Kotroni, and K. Lagouvardos (1997), The regional weather forecasting system SKIRON: an overview, in *Symposium on regional weather prediction on parallel computer environments*, pp. 109-122, University of Athens, Greece.

Kallos, G., V. Kotroni, K. Lagouvardos, and A. Papadoupoulos (1998), On the long-range transport of air pollutants from Europe to Africa, *Geophysical research letters*, *25* (5), 619-622.

Kallos, G., P. Katsafados, C. Spyrou, and A. Papadopoulos (2005), Desert dust deposition over the Mediterranean Sea estimated with the SKIRON/Eta - Model Validation, in *4th EuroGOOS Conference*, Brest, France.

Kallos, G., A. Papadopoulos, P. Katsafados, and S. Nickovic (2006), Trans-Atlantic Saharan dust transport: Model simulation and results, *Journal of geophysical research (in press)*.

Kalu, A.E., The African dust plume: its characteristics and propagation across West Africa in winter., in *Saharan dust. Mobilization, transport, deposition*, edited by C. Morales, John Wiley & Sons, 1979.

Kubilay, N., and A.C. Saydam (1995), Trace-elements in atmospheric particulates over the eastern Mediterranean - concentrations, sources, and temporal variability, *Atmospheric environment*, *29* (17), 2289-2300.

Kubilay, N., A.C. Saydam, S. Yemenicioglu, G. Kelling, S. Kapur, C. Karaman, and E. Akça (1997), Seasonal chemical and mineralogical variability of atmospheric particles in the coastal region of the Northeast Mediterranean, *Catena*, *28* (3-4), 313-328.

Lafon, S., J.L. Rajot, S.C. Alfaro, and A. Gaudichet (2004), Quantification of iron oxides in desert aerosol, *Atmospheric environment*, *38* (8), 1211-1218.

Lacis, A.A., and M.I. Mishchenko (1995), Climate forcing, climate sensitivity and climate response: A radiative modeling prespective on atmospheric aerosols, in *Aerosol forcing of climate*, edited by R.J. Charlson, and J. Heintzenberg, pp. 11-42, Wiley and sons.

Lalas, D.P., D.N. Asimakopoulos, D.G. Deligiorgi, and C.G. Helmis (1983), Sea breeze circulation and photochemical pollution in Athens, Greece, *Atmospheric environment*, *17*, 1621-1632.

Laurenzi-Tabasso, M., and M. Marabelli (1992), *Il degrado dei monumento in Roma in rapporto all'inquinamento atmosferico*, Betagamma. Viterbo, 169.

Lave, L.B., and E.P. Seskin (1970), Air pollution and human health, *Science*, *169* (3947), 723.

Lazaridis, M., A. Semb, S. Larssen, A.G. Hjellbrekke, Ø. Hov, J.E. Hanssen, J. Schaug, and K. Tørseth (2002), Measurements of particulate matter within the framework of the European Monitoring and Evaluation Programme (EMEP) I. First results, *Science of the total environment*, *285*, 209-235.

Le-Bolloch, O., S. Guerzoni, and E. Molinaroli, Atmosphere-ocean mass fluxes at two coastal sites in Sardinia 39-41 degrees N, 8-10 degrees E, in *The impact of desert dust across the Mediterranean*, edited by S. Guerzoni, and R. Chester, pp. 217-222, Kluwer academic publishing, Dordrecht, 1996.

Levin, Z., E. Ganor, and V. Gladstein (1996), The effects of desert particles coated with sulphate on rain formation in the Eastern Mediterranean, *Journal of applied meteorology*, *35*, 1511-1523.

Levine, J.S. (1990), Atmospheric trace gases-burning trees and bridges, *Nature*, *346* (6284), 511-512.

Levine, J.S. (1991), *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, MIT Press, Cambridge, Mass.

Likens, G.E., and F.H. Bormann (1974), Acid rain: a serious regional environmental problem, *Science*, *184*, 1176-1179.

Liou, K.N., and S.C. Cheng (1989), Role of cloud microphysical processes in climate: an assessment from a one-dimensional perspective, *Journal of geophysical research*, *94*, 8599-9607.

Lippmann, M., The 1997 US EPA standards for particulate matter and ozone, in *Air pollution and health*, edited by R.E. Hester, and R.M. Harrison, pp. 75-99, Royal society of chemistry, 1999.

Littmann, T. (1991), Dust storm frequency in Asia: climatic control and variability, *International journal of climatology*, *11*, 393-412.

Lohmann, U., G. Tselioudis, and C. Tyler (2000), Why is the cloud albedo-particle size relationship different in optically thick and optically thin clouds?, *Geophysical research letters*, *27*, 1099-1102.

Losno, R., G. Bergametti, P. Carlier, and G. Mouvier (1991), Major ions in marine rainwater with attention to sources of alkaline and acidic species, *Atmospheric environment*, *25A*, 763–770.

Lovett, G.M. (1994), Atmospheric deposition of nutrients and pollutants in North America: an ecological perspective, *Ecological applications*, *4*, 629-650.

Löye-Pilot, M.D., J.M. Martin, and J. Morelli (1986), Influence of Saharan dust on the rain acidity and the atmospheric input to the Mediterranean, *Nature*, *321*, 427-428.

Lu, H., and Y. Shao (1999), A new model for dust emission by saltation bombardment, *Journal of geophysical research*, *104* (D14), 16827-16841.

Marchand, G., J. Lavoie, and L. Lazure (1995), Evaluation of bioaerosols in a municipal solid-waste recycling and composting plant, *Journal of the air & waste management association*, *45* (10), 778-781.

Marticorena, B., and G. Bergametti (1996), Two-year simulations of seasonal and interannual changes of the Saharan dust emissions, *Geophysical research letters*, *23* (15), 1921-1924.

Marticorena, B., G. Bergametti, D. Gillette, and J. Belnap (1997), Factors controlling threshold friction velocity in semiarid and arid areas of the United States, *Journal of geophysical research*, *102*, 23277-23287.

Martín Vide, J., and M.C. Moreno (1985), Les pluges de fang a Barcelona, *Revista catalana de Geografía*, *1*, 60-70.

Matter, U., H.C. Siegmann, and H. Burtcher (1999), Dynamic field measurements of submicron particles from diesel engines, *Environmental science and technology*, *33* (11), 1946-1952.

Matthias-Maser, S., and R. Jaenicke (1994), Examination of atmospheric bioaerosol particles with radii > 0.2 µm, *Journal of aerosol science*, *25*, 1605-1613.

Matzner, E., and K.J. Meiwes (1994), Long-term development of element fluxes with bulk precipitation and throughfall in two forested ecosystems of the German solling area, *Journal of environmental quality*, *23*, 162-166.

McClain, C.R., M.L. Cleave, G.C. Feldman, W.W. Gregg, S.B. Hooker, and N. Kuring (1998), Science quality SeaWiFS data for global biosphere research, *Sea technology*, *39* (9), 10-15.

McGovern, F.M., M.J. Nunes, F. Raes, and H. Gonzales-Jorge (2002), Marine and anthropogenic aerosols at Punta Del Hidalgo, Tenerife, and the aerosol nitrate number paradox, *Journal of Geophysical Research*, *107 (D24)* (4766), 1-10.

McTainsh, G.H., and P.H. Walker (1982), Nature and distribution of Harmattan dust, *Zeitschrift für geomorphology*, *26*, 417–435.

Mesinger, F., Z.I. Janjic, S. Nickovic, D. Gavrilov, and D.G. Deaven (1988), The steep-mountain coordinate: Model description and performance for cases of Alpine lee cyclogenesis and for a case of an Appalachian redevelopment, *Monthly weather review*, *116*, 1493-1518.

Mészáros, A., and K. Vissy (1974), Concentration, size distribution and chemical nature of atmospheric aerosol particles in remote oceanic areas, *Journal of Aerosol Science*, *5*, 101-109.

Mészáros, E., and L. Horváth (1984), Concentration and dry deposition of atmospheric sulphur and nitrogen compounds in Hungary, *Atmospheric Environment*, *18*, 1725-1730.

Mészáros, E. (1999), *Fundamentals of atmospheric aerosol chemistry*, Akdémiai Kiadó.

Michalsky, J.J., E.W. Pearson, and B.A. LeBaron (1990), An assessment of the impact of volcanic eruptions on the Northern Hemisphere's aerosol burden during the last decade, *Journal of geophysical research*, *95* (D5), 5677-5688.

Middleton, N.J. (1986), Dust storms in the Middle East, *Journal of arid environments*, *10*, 83-96.

Middleton, N.J., Desert dust, in *Arid Zone Geomorphology*, edited by D.S.G. Thomas, pp. 411-436, John Wiley & Sons Ltd., Chichester, England, 1989.

Middleton, N.J. (1991), Dust storms in the Mongolian People's Republic, *Journal of arid environments*, *20*, 287-297.

Milford, J.B., and C.I. Davidson (1985), The sizes of particulate trace elements in the atmosphere, *Journal of the air pollution control association*, *35*, 1249-1260.

Millán, M., L. Alonso, J. Legarreta, M. Albizu, I. Ureta, and C. Egusquiaguirre (1984), A fumigation episode in an industrialized estuary: Bilbao, November 1981, *Atmospheric Environment*, *18* (3), 563-572.

Millán, M., E. Otamendi, L. Alonso, and I. Ureta (1987), Experimental characterization of atmospheric diffusion in complex terrain with land-sea interactions, *Journal of Air Pollution Control and Hazardous Waste Management*, *37* (7), 806-811.

Millán, M.M., B. Artíñano, L. Alonso, M. Navazo, and M. Castro (1991), The effect of meso-scale flows on regional and long range atmospheric transport in the western Mediterranean area, *Atmospheric environment*, *25A* (5/6), 949-963.

Millán, M.M., R. Salvador, E. Mantilla, and B. Artíñano (1996), Meteorology and photochemical air pollution in southern Europe: experimental results from EC research projects, *Atmospheric environment*, *30* (12), 1909-1924.

Millán, M., R. Salvador, E. Mantilla, and G. Kallos (1997), Photo-oxidant dynamics in the Mediterranean basin in summer: results from European research projects, *Journal of Geophysical Research*, *102*, 8811-8823.

Molinaroli, E., S. Guerzoni, and G. Rampazzo (1993), Contribution of Saharan dust to the Central Mediterranean basin, *Geological society of America*, *SP 284*, 303-312.

Möller, D., Sulphate aerosols and their atmospheric precursors, in *Aerosol forcing of climate*, edited by R.J. Charlson, and J. Heintzenberg, pp. 73-90, Wiley and sons, 1995.

Monn, C., and S. Becher (1999), Cytotoxicity and proinflamatory cytokines from human monocytes exposed to fine (PM2.5) and coarse particles (PM2.5-10) in indoor and outdoor air, *Toxicology and applied pharmacology*, *155*, 245-252.

Monn, C., O. Braendli, G. Schaeppi, C. Schindler, U. Ackermannliebrich, P. Leuenberger, and S. Team (1995), Particulate matter less than 10 μm (PM10) and total suspended particulates (TSP) in urban, rural and alpine air in Switzerland, *Atmospheric environment*, *29* (19), 2565-2573.

Moulin, C., C.E. Lambert, F. Dulac, and U. Dayan (1997), Control of atmospheric export of dust from North Africa by the North Atlantic Oscillation, *Nature*, *387*, 691-694.

Moulin, C., C.E. Lambert, U. Dayan, V. Masson, M. Ramonet, P. Bousquet, M. Legrand, Y.J. Balkanski, W. Guelle, B. Marticorena, G. Bergametti, and F. Dulac (1998), Satellite climatology of African dust transport in the Mediterranean atmosphere, *Journal of geophysical research*, *103* (D11), 13137-13144.

Murphy, D.M., J.R. Anderson, P.K. Quinn, L.M. McInnes, F.J. Bretchel, S.M. Kreidenweis, A.M. Middlebrook, M. Pósfai, D.S. Thomson, and P.R. Buseck (1998), Influence of sea-salt on aerosol radiative properties in the Southern Ocean marine boundary layer, *Nature*, *392* (6671), 62-65.

N'Tchayi, M.G., J.J. Bertrand, and S.E. Nicholson (1997), The diurnal and seasonal cycles of wind-borne dust over Africa north of the equator, *Journal of applied meteorology*, *36*, 868-882.

Nemmar, A., M.F. Hoylaerts, P.H.M. Hoet, D. Dinsdale, T. Smith, H. Xu, J. Vermylen, and B. Nemery (2002), Ultrafine particles affect experimental thrombosis in an in vivo hamster model, *American journal of respiratory and critical care medicine*, *166*, 998-1004.

Newell, R.E., and J.W. Kidson, The tropospheric circulation over Africa and its relation to the global tropospheric circulation, in *Saharan dust. Mobilization, transport, deposition*, edited by C. Morales, pp. 133-169, John Wiley & Sons, 1979.

Nickovic, S., D. Jovic, O. Kakaliagou, and G. Kallos (1997), Production and long-range transport of desert dust in the Mediterranean region: Eta model simulations, in *Air pollution modeling and its application XII*, edited by S. EGryning, and N. Chaumerliac, pp. 237-245, Plenum press.

Nickovic, S., G. Kallos, A. Papadopoulos, and O. Kakaliagou (2001), A model for prediction of desert dust cycle in the atmosphere, *Journal of geophysical research*, *106* (D16), 18113-18129.

Nihlen, T., and S. Olsson (1995), Influence of eolian dust on soil formation in the Aegean area, *Zeitsxhrift fur geomorphologie*, *39*, 341-361.

Novakov, T. (1984), The role of soot and primary oxidants in atmospheric chemistry, *Science of the total environment*, *36*, 1-10.

O'Dowd, C.D., and M.H. Smith (1993), Physico-chemical properties of aerosols over the northeast Atlantic: evidence for wind-speed-related sub-micron sea-salt aerosol production, *Journal of geophysical research*, *98*, 1137-1149.

Özkaynak, H., and G.D. Thurston (1987), Associations between 1980 U.S. mortality rates and alternative measures of airborne particle concentration, *Risk analysis*, *7*, 449-461.

Özsoy, E., N. Kubilay, S. Nickovic, and C. Moulin (2001), A hemispheric dust storm affecting the Atlantic and Mediterranean in April 1994: analyses, modelling, ground-based measurements and satellite observations, *Journal of geophysical research*, *106* (D16), 18439-18460.

Pacyna, J.M., Source inventories for atmospheric trace metals, in *Atmospheric particles*, edited by R.M. Harrison, and R.E.V. Grieken, pp. 387-423, 1998.

Pedersen, U., J. Schaug, and J. Skjelmoen (1992), EMEP data report 1990 part 1: annual summaries, Norwegian institute for air research.

Perry, K.D., T.A. Cahill, R.A. Eldred, D.D. Dutcher, and T.E. Gill (1997), Long-range transport of North African dust to the Eastern United States, *Journal of geophysical research*, *102*, 11225-11238.

Peters, A., H.E. Wichmann, T. Tuch, J. Heinrich, and J. Heyder (1997), Respiratory effects are associated with the number of ultrafine particles, *American journal of respiratory and critical care medicine*.

Peterson, J.T., and C.E. Junge, Sources of particulate matter in the atmosphere, in *Man's impact on the climate*, edited by W.H. Matthews, W.W. Kellogg, and G.D. Robinson, pp. 310-320, MIT Press, Cambridge, MA, 1971.

Pope, C.A., D.W. Dockery, R.E. Kanner, G.M. Villegas, and J. Scharwtz (1999), Daily changes in oxygen saturation and pulse rate associated with particulate air pollution and barometric pressure, *American journal of respiratory and critical care medicine*, *159*, 365-372.

Pope, C.A., R.T. Burnett, M.J. Thun, E.E. Calle, D. Krewski, K. Ito, and G.D. Thurston (2002), Lung cancer, cardiopulmonary mortality and long-term exposure to fine particulate air pollution, *JAMA*, *287*, 1132-1141.

Pósfai, M., J.R. Anderson, P.R. Buseck, T.W. Shattuck, and N.W. Tindale (1994), Constituents of a remote Pacific aerosol: A TEM study, *Atmospheric environment*, *28* (10), 1747-1756.

Pósfai, M., and A. Molnár, Aerosol particles in the troposphere: A mineralogical introduction, in *Environmental mineralogy*, edited by D.J. Vaughan, and R.A. Wogelius, pp. 197-252, Eötvös University press, 2000.

Prieditis, H., and I.Y.R. Adamson (2002), Comparative pulmonary toxicity of various soluble metals found in urban particulate dusts, *Experimental lung research*, *28*, 563-576.

Prodi, F., and G. Fea (1979), Case of transport and deposition of Saharan dust over the Italian peninsula and Southern Europe, *Journal of geophysical research*, *84* (NC11), 6951-6960.

Prospero, J.M., and T.N. Carlson (1972), Vertical and areal distribution of Saharan dust over the western equatorial North Atlantic Ocean, *Journal of Geophysical Research*, *77*, 5255-5265.

Prospero, J.M., and T.N. Carlson (1981), Saharan air outbreaks over the tropical North Atlantic, *Pure and applied geophysics*, *119*, 667-691.

Prospero, J.M., and R.T. Nees (1986), Impact of the North African drought and El Niño on mineral dust in Barbados trade winds, *Nature*, *320*, 735-738.

Prospero, J.M., R. Schmitt, E. Cuevas, D.L. Savoie, W.C. Graustein, K.K. Turekian, A. Volz-Thomas, A. Díaz, S.J. Oltmans, and H.L. II (1995), Temporal variability of summer-time ozone and aerosols in the free troposphere over the eastern North Atlantic, *Geophysical research letters*, *22* (21), 2925-2928.

Prospero, J.M., Saharan dust transport over the North Atlantic ocean and the Mediterranean: an overview, in *The impact of desert dust across the Mediterranean*, edited by S. Guerzoni, and R. Chester, pp. 133-151, Kluwer academic publishing, Dordrecht, 1996.

Prospero, J.M. (1999), Long range transport of mineral dust in the global atmosphere: impact of African dust on the environment of the south-eastern United States, *Proceedings of the National Academy of Sciences USA*, *96*, 3396-3403.

Prospero, J.M., P. Ginoux, O. Torres, S.E. Nicholson, and T.E. Gill (2002), Environmental characterization of global sources of atmospheric soil dust identified with the Nimbus 7 Total Ozone Mapping Spectrometer (TOMS) absorbing aerosol product, *Reviews of geophysics*, *40* (1), 2-1:2-31.

Pueschel, R.F., D.F. Blake, K.G. Snetsinger, A.D.A. Hansen, S. Verma, and K. Kato (1992), Black carbon (soot) aerosol in the lower stratosphere and upper troposphere, *Geophysical research letters*, *19*, 1659-1662.

Putaud, J.P., U. Baltensperger, E. Brüggemann, M. Facchini, S. Fuzzi, R. Gehrig, H.C. Hansson, R.M. Harrison, A. Jones, P. Laj, W. Maenhaut, N. Mihalopoulos, K. Müller, F. Palmgren, X. Querol, S. Rodriguez, G. Spindler, H. Brink, P. Tunved, R. Dingenen, B. Wehner, E. Weingartner, A. Wiedensohler, P. Wåhlin, and F. Raes (2002), A European aerosol phenomenology: physical and chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe., *Eurotrac* European project.

Querol, X., A. Alastuey, A.L. Soler, E. Mantilla, and F. Plana (1996), Mineral composition of atmospheric particulates around a large coal-fired power station, *Atmospheric environment*, *30* (21), 3557-3572.

Querol, X., A. Alastuey, J.A. Puicercus, E. Mantilla, J.V. Miró, A. López-Soler, F. Plana, and B. Artíñano (1998), Seasonal Evolution of Suspended Particles Around a Large Coal-Fired Power Station: Particle Levels and Sources, *Atmospheric environment*, *32* (11), 1963-1978.

Querol, X., A. Alastuey, S. Rodríguez, F. Plana, C.R. Ruiz, N. Cots, G. Massagué, and O. Puig (2001), PM10 and PM2.5 source apportionment in the Barcelona Metropolitan Area, Catalonia, Spain, *Atmospheric Environment*, *35* (36), 6407-6419.

Querol, X., A. Alastuey, S. Rodríguez, M.M. Viana, B. Artíñano, P. Salvador, E. Mantilla, S.G.D. Santos, R.F. Patier, J.D.L. Rosa, A.S.D.L. Campa, and M. Menedez (2002), Interpretación de series temporales (1996-2000) de niveles de partículas en suspensión en España, Ministerio de Medio Ambiente, Madrid.

Rahn, K.A. (1981), Relative importances of North America and Eurasia as sources of arctic aerosol, *Atmospheric environment*, *15* (8), 1447-1455.

Ramsden, A.R., and M. Shibaoka (1982), Characterization and analysis of individual fly-ash particles from coal-fired power-stations by a combination of optical microscopy, electron-microscopy and quantitative electron micro-probe analysis, *Atmospheric environment*, *16* (9), 2191.

Reiff, J., S. Forbes, F.T.M. Spieksma, and J.J. Reynders (1986), African dust reaching Northwestern Europe: a case study to verify trajectory calculations, *Journal of climate and applied meteorology*, 1543-1567.

Rodà, F., J. Bellot, A. Avila, A. Escarré, J. Piñol, and J. Terradas (1993), Saharan dust and the atmospheric inputs of elements and alkalinity to Mediterranean ecosystems, *Water, air and soil pollution*, *66*, 277-288.

Rodríguez, S. (1999), Comparación de la variaciones de ozono superficial asociadas a procesos de transporte sobre y bajo la inversión temperatura subtropical en

Tenerife, Tesis de Licenciatura thesis, Universidad de La Laguna, Tenerife, Canarias.

Rodríguez, S., X. Querol, A. Alastuey, G. Kallos, and O. Kakaliagou (2001), Saharan dust contributions to PM10 and TSP levels in Southern and E. Spain, *Atmospheric environment*, *35*, 2433-2447.

Rodríguez, S. (2002), Sources and processes affecting levels and composition of atmospheric particulate matter in the Western Mediterranean, PhD thesis, Universitat Politècnica de Catalunya.

Rodríguez, S., X. Querol, A. Alastuey, and F. Plana (2002), Sources and processes affecting levels and composition of atmospheric aerosol in the Western Mediterranean, *Journal of geophysical research*, *107* (D24), 4777.

Rodríguez, S., X. Querol, A. Alastuey, M.M. Viana, and E. Mantilla (2003), Events affecting levels and seasonal evolution of airborne particulate matter concentrations in the Western Mediterranean, *Environmental Science and Technology*, *37*, 216-222.

Rosenfeld, D. (2000), Suppression of rain and snow by urban and industrial air pollution, *Science*, *287*, 1793-1796.

Ryall, D.B., R.G. Derwent, A.J. Manning, A.L. Redington, J. Corden, W. Millington, P.G. Simmonds, S. O'Doherty, N. Carslaw, and G.W. Fuller (2002), The origin of high particulate concentrations over the United Kingdom, March 2000, *Atmospheric environment*, *36* (8), 1363-1378.

Salvador, P., B. Artíñano, D.G. Alonso, X. Querol, and A. Alastuey (2004), Identification and characterisation of sources of PM10 in Madrid (Spain) by statistical methods, *Atmospheric environment*, *38* (3), 435-447.

Salvador, R., M. Millán, E. Mantilla, and J.M. Baldasano (1997), Mesoscale modelling of atmospheric processes over the western Mediterranean area during summer, *Journal of environment and pollution*, *8* (3-6), 513-529.

Samara, C., R. Tsitouridou, and C. Balafoutis (1992), Chemical composition of rain in Thessaloniki, Greece, in relation to meteorological conditions, *Atmospheric environment*, *26* (3), 359-367.

Sánchez, J. (1993), *Situaciones atmosféricas en España*, Ministerio de obras públicas, transportes y medio ambiente.

Sarnthein, D., J. Thiede, U. Pflaumann, H. Erlenkeuser, D. Futterer, B. Koopman, H. Lange, and E. Seibold (1982), Atmospheric and Oceanic circulation patterns off northwest Africa during the past 25 million years, in *Geology of the Northwest African continental margin*, edited by U.V. Rad, K. Hinz, M. Sarthein, and E. Seibold, pp. 545-604.

Savoie, D.L., J.M. Prospero, and R.T. Ness (1987), Nitrate, non-sea-sulphate and mineral aerosol over the northwestern Indian Ocean, *Journal of geophysical research*, *92*, 933-942.

Schnell, R.C., and G. Vali (1976), Biogenic ice nuclei. Part II: bacterial sources, *Journal of atmospheric sciences*, *33*, 1565-1570.

Schütz, L. (1980), Long-range transport of desert dust with special emphasis on the Sahara, *Annals of the New York academy of sciences*, *338*, 515-532.

Schütz, L., R. Jaenicke, and H. Pietrek, Saharan dust transport over the north Atlantic ocean, in *Desert dust*, edited by T.L. Péwé, pp. 87-100, Geological society of America, 1981.

Schwartz, J., D.W. Dockery, and L.M. Neas (1996), Is daily mortality associated specifically with fine particles?, *Journal of the air & waste management association*, *46*, 927-939.

Seidl, W., G. Brunnemann, E. Kins, E. Kölher, K. Reusswig, K. Ruoss, T. Seiler, and R. Dlugi, Nitrate in the accumulation mode; data from measurement campaigns in Eastern Germany., in *Nucleation and atmospheric aerosols*, edited by M.K.a.P.E. Wagner, pp. 431-434, Pergamon Press, Oxford, UK, 1996.

Senior, C.A., and J.F.B. Mitchell (1993), Carbon-dioxide and climate - the impact of cloud parameterization, *Journal of climate*, *6* (3), 393-418.

Sequeira, R. (1982), Acid rain - An assessment based on acid-base considerations, *Journal of the air pollution control association*, *32* (3), 241-245.

Sievering, H., B. Lerner, J. Slavich, J. Anderson, M. Pósfai, and J. Cainey (1999), O3 oxidation of SO2 in sea-salt aerosol water: size distribution of non-sea-salt sulphate during the first aerosol characterization experiment (ACE1), *Journal of geophysical research*, *104* (D17), 21707-21717.

Singer, A., Y. Shamay, and M. Fried (1993), Acid-rain on Mt. Carmel, Israel, *Atmospheric environment*, *27* (15), 2287-2293.

Singer, A., E. Ganor, S. Dultz, and W. Fischer (2003), Dust deposition over the Dead Sea, *Journal of arid environments*, *53* (1), 41-59.

Sokolik, I.N., and O.B. Toon (1996), Direct radiative forcing by anthropogenic airborne mineral aerosols, *Nature*, *381*, 681-683.

Speizer, F.E. (1989), Studies of acid aerosols in 6 cities and in a new multi-city investigation - design issues, *Environmental health perspectives*, *79*, 61-67.

Swap, R., M. Garstang, S. Greco, R. Talbot, and P. Kallberg (1992), Saharan dust in the Amazon basin, *Tellus*, *44* (2), 133-149.

Swap, R., S. Ulanski, M. Cobbett, and M. Garstang (1996), Temporal and spatial characteristics of Saharan dust outbreaks, *Journal of Geophysical Research*, *101*, 4205-4220.

Talbot, R.W., Harris, R. C. Browell, E. V. Gregory, G. L. Sebacher, D. I. and Beck, S. M (1986), Distribution and geochemistry of aerosols in the tropical North Atlantic troposphere: relationship to Saharan dust, *Journal of Geophysical Research*, *91*, 5173-5182.

Tegen, I., and I. Fung (1994), Modelling of mineral dust transport in the atmosphere: sources, transport, and optical thickness, *Journal of geophysical research*, *99*, 22897-22914.

Tegen, I., and A.A. Lacis (1996), Modelling of particle size distribution and its influence on the radiative properties of mineral dust aerosol, *Journal of geophysical research*, *101*, 19237-19244.

Tindale, N.W., and P.P. Pease (1999), Aerosols over the Arabian Sea: atmospheric transport pathways and concentrations of dust and sea salt, *Deep-sea research part II*, *46* (8-9), 1577-1595.

Torres, C.J., E. Cuevas, J.C. Guerra, and V. Carreño (2001), Caracterización de las masas de aire en la región subtropical, in *V Simposio nacional de predicción*, edited by I.N.d. Meteorología, Madrid, 20-23 Noviembre, 2001.

Torres, O., P.K. Bhartia, J.R. Herman, Z. Ahmad, and J. Gleason (1998), Derivation of aerosol properties from satellite measurements of backscattered ultraviolet radiation: Theoretical basis, *Journal of geophysical research*, *103*, 17099-17110.

Torres, O., P.K. Bhartia, J.R. Herman, A. Sinyuk, P. Ginoux, and B. Holben (2002), A long-term record of aerosol optical depth from TOMS observations and comparison to AERONET measurements, *Journal of atmospheric science*, *59*, 389-413.

Tsunogai, S., and T. Kondo (1982), Sporadic transport and deposition of continental aerosols to the pacific-ocean, *Journal of geophysical research*, *87* (NC11), 8870-8874.

Tunved, P., H.C. Hansson, M. Kulmala, P. Aalto, Y. Viisanen, H. Karlsson, A. Kristensson, E. Swietlicki, M.D. Maso, J. Ström, and M. Komppula (2002), One year boundary layer aerosol size distribution data from five Nordic background stations, *Atmospheric chemistry & physics*, *3*, 2183-2205.

Turn, S.Q., B.M. Jenkins, J.C. Chow, L.C. Pritchett, D. Campbell, T. Cahill, and S.A. Whalen (1997), Elemental characterization of particulate matter emitted from biomass burning: Wind tunnel derived source profiles for herbaceous and wood fuels, *Journal of geophysical research*, *102* (D3), 3683-3699.

Turnbull, A.B., and R.M. Harrison (2000), Major component contributions to PM10 composition in the UK atmosphere, *Atmospheric environment*, *34* (19), 3129-3137.

Uematsu, M., R.A. Duce, J.M. Prospero, L. Chen, J.T. Merrill, and R.L. McDonald (1983), Transport of mineral aerosol from Asia over the North Pacific Ocean, *Journal of geophysical research*, *88* (NC9), 5343-5352.

Utell, M.J., M.W. Frampton, and P.E. Morrow (1991), Air pollution and asthma: clinical studies with sulphuric acid aerosols, *Allergy proceedings*, *12* (6), 385-388.

Viana, M., X. Querol, A. Alastuey, E. Cuevas, and S. Rodríguez (2002), Influence of African dust on the levels of atmospheric particulates in the Canary Islands air quality network, *Atmospheric environment*, *36*, 5861-5875.

Viana, M., X. Querol, A. Alastuey, G. Gangoiti, and M. Menendez (2003), PM levels in the Basque Country (Northern Spain): analysis of a 5 year data record and interpretation of seasonal variations, *Atmospheric Environment*, *37* (21), 2879-2891.

Wagenbach, D., and K. Geis, The mineral dust record in a high altitude alpine glacier (Colle Gnigetti, Swiss Alps), in *Paleoclimatology and paleometeorology: modern and past patterns of global atmospheric transport*, edited by M. Leinen, and M. Sarnthein, pp. 543-564, NATO ASI Series C, Kluwer academic publishers, Boston, 1989.

Wakamatsu, S., A. Utsunomiya, J.S. Han, A. Mori, I. Uno, and K. Uehara (1996), Seasonal variation in atmospheric aerosol concentration covering Northern Kyushu, Japan and Seoul, Korea, *Atmospheric environment*, *30* (13), 2343-2354.

Warneck, P. (1988), *Chemistry of the natural atmospheres*, Academic press, INC.

Weast, R.C. (1978), *CRC Handbook of chemistry and physics*, CRC press inc.

Westphal, D.L., O.B. Toon, and T.N. Carlson (1987), A two-dimensional numerical investigation of the dynamics and microphysics of Saharan dust storms, *Journal of geophysical research*, *92* (D3), 3027-3049.

Whitby, K.T. (1978), Physical characteristics of sulphur aerosols, *Atmospheric environment*, *12* (1-3), 135-159.

Wilks, D.S. (1995), *Statistical methods in the Atmospheric Sciences: an Introduction*, 464 pp., Academic Press.

WHO (2003), Health aspects of air pollution with particulate matter, ozone and nitrogen dioxide, World Health Organization, Bonn, Germany.

Woodcock, A.H. (1972), Smaller salt particles in oceanic air and bubble behaviour in the sea, *Journal of geophysical research*, *77*, 362-371.

Zhang, X.Y., S.L. Long, R. Arimoto, Z.X. Shen, F.M. Mei, D. Wang, and Y. Cheng (2003), Characterization and temporal variation of Asian dust aerosol from a site in the northern Chinese deserts, *Journal of atmospheric chemistry*, *44*, 241-257.

Centre de Recerca Ecològica i Aplicacions Forestals

CREAF

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

CSIC

INSTITUTO DE CIENCIAS DE LA TIERRA "JAUME ALMERA"

MINISTERIO DE MEDIO AMBIENTE

INM INSTITUTO NACIONAL DE METEOROLOGÍA

OBSERVATORIO ATMOSFÉRICO DE IZAÑA

UNIVERSITAT DE BARCELONA

DEPARTAMENT D'ASTRONOMIA I METEOROLOGIA