Chapter 1

Introduction

1.1 Characteristics of atmospheric particulate matter

Atmospheric particulate matter (PM) is made up of solid and/or liquid (except pure water) particles which enter the atmosphere by natural or anthropogenic causes. The term atmospheric aerosol (solid and/or liquid particles suspended in a gaseous medium) is often used as a synonym for atmospheric particles. In this study both atmospheric particulate matter and atmospheric aerosol are used indiscriminately.

PM is emitted by a wide variety of natural and anthropogenic sources which influence its physical properties (e.g. size, specific surface, density or number-density) and chemical composition. Particles may be classified as primary or secondary in accordance with their formation mechanism. Primary particles are directly emitted into the atmosphere, or are formed in the air by rapid condensation of emitted gas molecules. Secondary particles are formed in the air after chemical transformation of their gaseous precursors. These chemical reactions may involve exclusively the gaseous phase (gas to particle conversion by homogeneous nucleation) or include reactions with solid and/or liquid phases (gas to particle conversion by heterogeneous nucleation).

PM associated with each source emission tends to have a specific size distribution and chemical composition. PM may vary in size from a few nanometers (nm) to several tenths of microns (µm). Early (Husar and Whitby, 1973; Whitby and Cantrell, 1976; Whitby, 1978) and recent (Hoppel et al., 1994, 1996; Harrison et al., 1999a, 1999b; Raes et al., 2000) studies of PM grain size distribution have resulted in a conceptual model to understand the size distribution of atmospheric aerosol in ambient air on the basis of its formation and removal mechanisms in the atmosphere (Figure 1-1).

The <u>nucleation mode</u> (or ultrafine particle mode) expands in the range 0.005 - 0.1 µm (Figure 1-1), and presents the maximum number-density of particles around 0.01µm (other authors distinguish the nucleation and Aitken modes in the ranges <0.01µm and 0.01-0.1µm, respectively). These particles may be formed by gases emitted at high temperatures, which rapidly condense in contact with cooler ambient air (e.g. heavy metals emitted by industrial smelter activities). Processes of nucleation after the reaction of gases with OH or O_3 may also
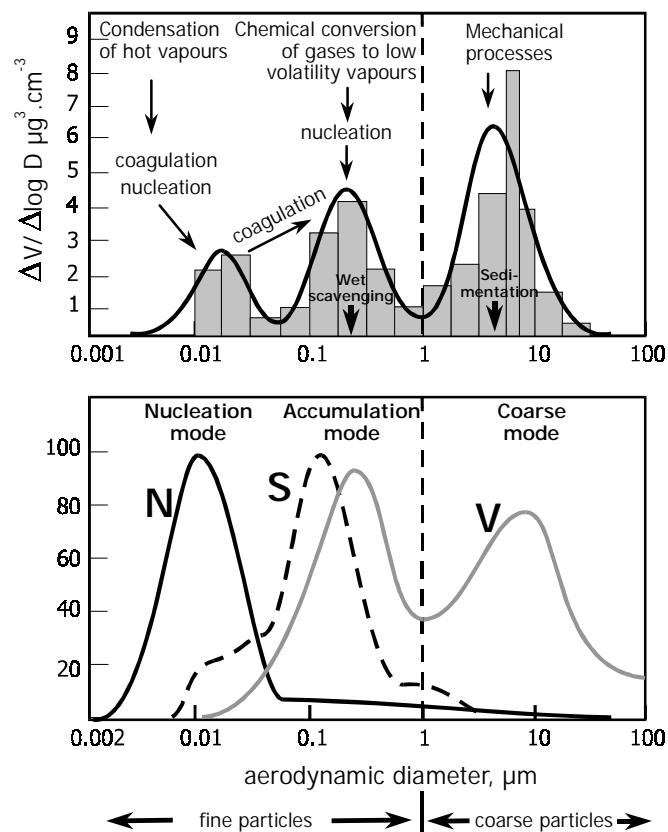
Figure 1-1. Ideal scheme of aerosol size distribution based on mechanisms of aerosol formation and extraction from the atmosphere (upper from Seinfeld and Pandis, 1998; lower from Heintzenberg, 1989). Number-density (N), surface (S) and volume (V) size distributions.

produce particles in this size range (e.g. $(NH_4)_2SO_4$ or NH_4NO_3). Thus, nucleation and condensation are the main mechanisms for the formation of new particles in the nucleation mode. Only few types of particles are directly emitted into the atmosphere in this size range. One of these is the elemental carbon particle (soot or black carbon) formed during incomplete combustion processes (pirolysis).

The accumulation mode expands in the range 0.1 – 1 µm (Figure 1-1). Particles in this range may result from two main processes: transfer of particles from the nucleation mode by coagulation processes and gas condensation. Collisions of particles due to thermal agitation induce the formation of agglomerates, which results in the formation of coarser particles. This process is known as coagulation. Low vapour pressure gas condensation on the surface of pre-existing particles in the air is the second mechanism introducing particles into the accumulation mode. These gases may be directly emitted into the atmosphere, or may be the result of a chemical reaction. The heterogeneous nucleation (which involve gaseous, liquid and/or solid phases) is especially important in the accumulation mode given the maximum surface of the atmospheric aerosol (Figure 1-1). The particle number-density here is significantly lower than in the nucleation mode due to the fact that neither coagulation nor condensation produces new particles.

The underlined coarse mode expands in the range >1μm (Figure 1-1). Most of the particles in this range (mainly in the range>2.5μm) are formed by mechanical processes, such as the erosion of the surface of the Earth (mineral dust) or other materials, or the bursting bubbles on the ocean surface (sea spray). The coarse mode is characterised by a low number-density of particles with a relatively high mass-density. Although the primary particles predominate in the coarse mode, secondary particles may also be found. These secondary particles are mainly formed by the chemical interaction of gases with primary particles of crustal or marine origin. For example, the reaction of the gaseous nitric acid with calcium-carbonate or sea salt result in the formation of calcium-nitrate or sodium-nitrate (Harrison and Pio, 1983; Mamane and Mehler, 1987; Mamane and Gottlieb, 1992; Wall et al., 1988; Wu and Okada, 1994), respectively, in the range >1μm owing to the original coarse size of the calcium-carbonate and sodium-chloride.

It is unlikely that nucleation, condensation and coagulation processes produce particles >1μm. Moreover, the mechanical process forming primary particles cannot easily reduce the size of particle to diameter <1μm. Thus, the transfer of particles from different modes of the size spectrum presents a barrier around 1μm. Particles <1μm are known as fine particles, whereas particles >1μm are term coarse particles. However, the limit between the fine and coarse modes is frequently fixed at 2.5μm in epidemiological studies (discussed below).

The residence time of the particles in the atmosphere also influences the size distribution. Owing to the effect of gravity, coarse particles (>1μm) are rapidly removed from the atmosphere by sedimentation (residence time for particles >20μm is ~ hours). On the other hand, particles <0.1μm are transformed into coarser particles by coagulation processes. Thus, the particles ranging in size from 0.1 to 1 μm (accumulation mode) present the largest residence time in the atmosphere. Particles in this range (0.1-1μm) are mainly made up of soluble material. Thus, they constitute efficient cloud condensation nuclei and are mainly extracted from the atmosphere by precipitation processes (mainly in-cloud scavenging). Thus, the residence time of these particles is similar to that of water (~10 days; Pósfai and Molnár, 2000). However, a significant proportion of carbonaceous particles have hydrophobe properties, and a period for surface oxidation is required before they can be wetted and removed from the atmosphere. This results in a longer residence time for shoot and organic particles (up to 46 days was reported by Gaffney et al., 2002) than for the soluble fraction.

The thermodynamic properties also exert a considerable influence on the processes of secondary particle formation, such as nucleation and condensation. Nucleation depends on the concentrations of gaseous precursors, relative humidity and temperature. In particular, nucleation is favoured by decreases in the temperature and/or increases in relative humidity (Eastern and Peter, 1994). On the other hand, the gas / aerosol mass partitioning of semi-volatile chemical species undergoes wide variations as a function of the temperature and relative humidity of the ambient air (Wexler and Seinfeld, 1990; Meng and Seinfeld, 1996). This is especially important for species such as ammonium-nitrate and some organic aerosols (Adams et al., 1999).

1.2 Sources of atmospheric particulate matter

Atmospheric PM is a multi-component system constituted by a large number of natural and anthropogenic species of different grain size distribution. Chemical characterisation is a technique widely used to identify the major and trace PM species, and their natural and/or anthropogenic origins. The major PM components are sulphate, nitrate, ammonium, sodium, chloride, carbon (organic and elemental), mineral dust and water. The predominance of these chemical components in PM and their size distribution are closely linked to their origin and formation mechanisms.

1.2.1 Natural particles

Mineral PM from the soil accounts for a large fraction of the natural primary fraction of PM. The chemical composition and mineralogy of these particles may undergo regional variations as a function of the geology of the source areas. In general these particles are made up of silicates [quartz (SiO_2), clay (mainly kaolinite, $Al_2Si_2O_5(OH)_4$, and illite, $K(Al,Mg)_3SiAl_{10}(OH)$) and feldspars ($KAlSi_3O_8$ and $(Na,Ca)(AlSi)_4O_8)$]], carbonates [calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$)] and minor amounts of calcium-sulphate ($CaSO_4 \cdot 2H_2O$) and iron oxides (Fe_2O_3). These natural mineral dust contributions to ambient PM may result from the local re-suspension of arid soils or from the long range transport from arid regions. Mineral particles enter the atmosphere as a result of the action of the wind on arid surfaces. In the light of experiments in wind tunnels, Alfaro et al. (1998) argue that the re-suspended dust tends to show a size distribution characterised by three modes centred in 1.5, 6.7 and 14.2 µm. The relative abundance of each population (or mode) is a function of wind speed.

Volcanic emissions are also a source of primary mineral PM. However, their contribution to bulk PM levels in ambient air is limited in time and space.

The primary fraction of sea spray is mainly constituted by sodium chlorides (NaCl) and sulphates (mainly Na_2SO_4, $MgSO_4$ or K_2SO_4). Sea spray is mainly generated by bubble processes on the ocean surface. This bubbling, which is due to surf activity caused by the wind, produces sea spray aerosols mainly in the coarse mode of PM (Warneck, 1988). Sea spray generation occurs in the white capes of waves.

Biogenic sources of primary PM give rise to the fraction known as bio-aerosol or biological residues. This fraction is mainly constituted by vegetal debris, pollen, spores, and minor amounts of micro-organisms (e.g. virus, bacteria, fungus, protozoon or alga). Virus and bacteria present sizes <2µm whereas the remains of plants and spores exhibit sizes in the coarse mode of PM (Pósfai and Molnár, 2000).

Sulphate, nitrate and organic aerosol are the main components of the natural secondary fraction of PM. Natural sulphate is formed after the oxidation of sulphured gases, such as the SO_2 emitted by volcanoes, or sulphide dimethyl (($CH_3)_2S$) of marine biogenic origin. Nitrate is the final product formed by the oxidation of nitrogen oxides (NOx= $NO+NO_2$). The main natural sources of NOx are found in soil transpiration (Roelle et al., 2001) and lightning (Price et al.,

1997a, 1997b). The main sources of secondary organic aerosol precursors occur in large forested areas (Harrison et al., 2001), where important amounts of organic vapours such as isoprene and monoprene (Yu et al., 1999) are emitted during plant transpiration. The oxidation of these organic vapours gives rise to low vapour pressure gases which form new particles by nucleation processes (Christoffersen et al., 1998; Koch et al., 2000).

1.2.2 Anthropogenic particles

The main sources of anthropogenic particles are located in urban and industrial areas. In urban environments, primary PM is made up of mineral particulate matter eroded from the pavement by road traffic (road dust) and remains resulting from the abrasion of brakes and tyres. Moreover, carbonaceous particles (mainly elemental carbon) and elements such as K, Pb, Br or Cl are vehicle exhaust products emitted as primary PM. Particles mechanically generated by road traffic (remains of brakes, tyres and pavement, and re-suspended dust) are coarse particles, whereas primary particles emitted by the vehicle exhaust are fine particles (elemental carbon and trace elements).

Industrial activities such as building, mining, manufacture of cement, ceramics and bricks, and smelters are typical sources of primary PM. Moreover, coal combustion has also been a traditional source of primary PM. Primary particles associated with smelter emissions are mostly fine PM given that most of these are formed by condensation of hot vapours. The chemical composition varies as a function of the specific smelter type, but Ni, V, Mn and Cu are frequently emitted (Pacyna, 1998). Other industrial sources (building, mining and cement, ceramics and bricks) mostly emit coarse primary PM of crustal composition. Moreover, a large fraction of these emissions of crustal PM occur as fugitive emissions linked to the manipulation of dusty materials. Coal combustion has historically been a large source of primary PM (fly ash). However, these emissions have been reduced in most industrialised countries owing to the current use of emission abatement technologies and the progressive replacement of coal by other fuels.

Anthropogenic secondary PM is mainly constituted by sulphate, nitrate and carbon contained in organic PM. A large proportion of SO_2 (gaseous precursor of sulphate) emissions is caused by coal combustion in power plants and other industrial activities. The SO_2 oxidation gives rise to the formation of sulphuric acid (H_2SO_4) which may or may not be neutralised by ammonia (NH_3), ammonium (NH_4^+), calcium carbonate ($CaCO_3$) or sodium chloride ($NaCl$), to form acid-ammonium-sulphate (NH_4HSO_4), ammonium-sulphate (($NH_4)_2SO_4$), double sulphate of calcium and ammonium ($Ca(NH_4)_2(SO_4)_2$), calcium-sulphate ($CaSO_4$) and sodium-sulphate (Na_2SO_4). Sulphuric acid and its NH_4^+ derivatives present a fine size distribution ($<1\mu m$), whereas the fractions neutralised by calcium-carbonate and sodium-chloride exhibit a size distribution in the coarse mode ($>1\mu m$) of PM (Mildford and Davidson, 1987).

Nitrogen oxides are mainly emitted by traffic in urban environments, and by some industrial processes. NOx oxidation leads to the formation of nitric acid (HNO_3 - gas), which

may be neutralised and transformed into NH_4^+ or Na^+ nitrate (particle). The size distribution of nitrate depends on the neutralising agent. Thus, ammonium-nitrate (NH_4NO_3) is present in the fine mode (<1µm), whereas calcium-nitrate (Ca_2NO_3 formed by the neutralisation of HNO_3 by crustal $CaCO_3$) and sodium-nitrate ($NaNO_3$ produced by the neutralisation of HNO_3 by marine NaCl) occur in the coarse mode (Harrison and Kito, 1990; Wakamatsu et al., 1996).

Large extensions of crop cultivation and the combustion of bio-mass and fossil fuels constitute important sources of organic vapour precursors of secondary organic aerosols. Aromatic and non methanic hydrocarbons derived from gasoline usage are significant precursors of organic aerosols (Odum et al., 1996, 1997a, 1997b). These vapours are also emitted (fugitive emission) by means of gasoline evaporation (Watson et al., 2001). Organic aerosol is formed after the oxidation of the gaseous precursor, and the size distribution ranges from <1µm to 10µm with a maximum in the fine mode particles.

Human activities may also give rise to anthropogenic bio-aerosols. Bacteria and fungi generated in solid waste recycling and composting plants constitute a potential risk to health (Marchand et al., 1995).

1.3 Environmental impact of particulate matter

Figure 1-2 shows an ideal scenario of PM emissions, dispersion and transport, showing the typical sources and sinks. Industrial and urban areas are important sources of anthropogenic aerosols and their gaseous precursors. The coarsest particles emitted in these environments are removed from the air in the proximity of the source area by sedimentation, whereas fine particles are susceptible to being transported long distances from the source area. Once gaseous pollutants are emitted, they undergo oxidation processes and gas to particle conversion. Most of the secondary particle formation processes are directly or indirectly related to photochemical processes, which involve photo-oxidants and radicals such as O_3, H_2O_2, OH or HO_2. Thus, SO_2 in the presence of NH_3 or NH_4^+ is transformed into ammonium-sulphate and NOx into ammonium-nitrate. Moreover, anthropogenic species may interact with natural ones. For example, the reaction of HNO_3 with crustal $CaCO_3$ or with marine NaCl gives rise to calcium-nitrate and sodium-nitrate, respectively. Once in the air, both anthropogenic and natural PM may undergo long range transport. Anthropogenic sulphate and nitrate from Southern Europe undergo long range transport to North Africa (Savoie et al., 1989; Kallos et al., 1998; McGovern et al., 1999; Prospero et al., 1995) and remote sites in the North Atlantic (Glaccum and Prospero, 1980; Muhs et al., 1990; Swap et al., 1996; Rajkumar et al., 2000) such as the Canaries (McGovern et al., 1999; Putaud et al., 2000) or Barbados (Savoie et al., 1989, 1992).
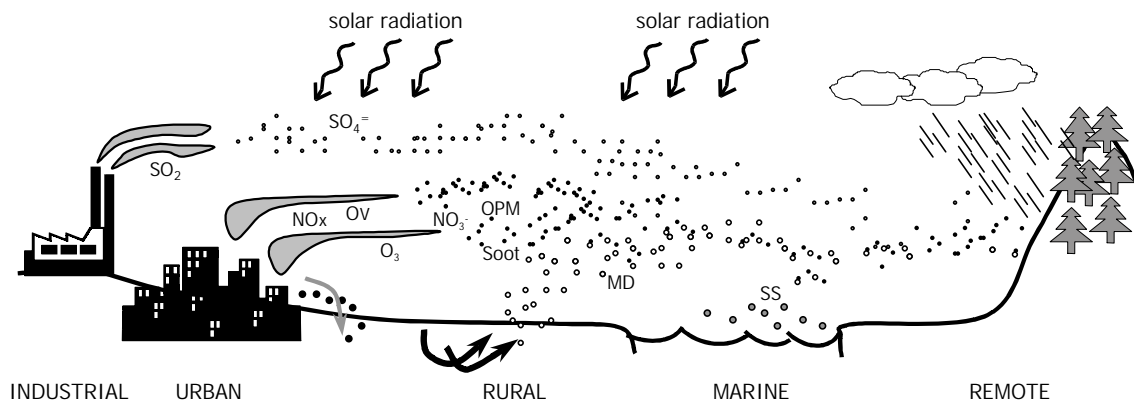
Figure 1-2. Scenario of natural and anthropogenic PM emissions, dispersion and transport (OV: organic vapours, OPM: organic PM, MD: mineral dust, SS: sea spray).

Mineral dust from North Africa undergoes long range transport toward the Mediterranean and Southern Europe (Löye-Pilot et al., 1986; Dayan et al., 1991; Dulac et al., 1992; Molinaroli et al., 1993; Guerzoni et al., 1997; Avila et al., 1997, 1998, 1999; Querol et al., 1998b; Hamonou et al., 1999), Canaries (Conde-Gaussen et al., 1989; Bergametti et al., 1989a; Prospero et al., 1995), Cape Verde (Chiapello et al., 1995; Caquineau et al., 1998), Barbados (Prospero and Ness, 1986; Savoie et al., 1992; Arimoto et al., 1997), North America (Prospero et al., 1987; Perry et al., 1997; Prospero, 1999) or South America (Prospero et al., 1981; Swap et al., 1992). Finally, wet or dry scavenging processes remove aerosols from the atmosphere.

During residence in the atmosphere and after deposition, particles interact with the environment on local, regional and synoptic scales. A brief summary of the main impacts of aerosols on the environment with a special emphasis on air quality is presented below.

1.3.1 Impact on climate, visibility and ecosystems

Atmospheric aerosol plays a role in climate owing to its influence on the radiative balance and on the processes related to cloud formation and radiative properties. Aerosols scatter and/or absorb radiation (direct effects on climate) depending on their chemical composition and size. It has been argued that the back-scattering of short wave solar radiation caused by anthropogenic sulphate may partially compensate for the warming caused by greenhouse gases (Charlson et al., 1991, 1992; Swartz et al., 1996). Despite the fact that aerosols have a much shorter residence time in the atmosphere (~ days to weeks) than greenhouse gases (~ years to decades), the compensatory effects of sulphate on the greenhouse warming occur on a regional scale around the source areas of aerosols, such as the Eastern United States, Europe or Eastern Asia (Taylor and Penner, 1994). Aerosols may also influence the cloud radiative properties and cloud lifetime (indirect effects on climate). Aerosol pollution produces an increase in the number-density of cloud condensation nuclei, which results in a decrease in the mean size of cloud drop and enhances the back-scattering capacity of clouds. Moreover, this decrease in the mean cloud drop, diminishes the possibility of rain

(Rosenfeld, 2000; Toon, 2000). In recent years, research on climate and aerosol has focused attention on the extent of aerosol pollution (from source to remote sites; e.g. ACE projects; Bates et al., 1998; Johnson et al., 2000) and on the influence of natural mineral desert dust on the radiative balance (Taylor et al., 1996; Sokolik and Toon, 1996; Tegen et al., 1996; Hansen et al., 1998).

Atmospheric aerosol produces visibility impairment given that suspended particles absorb and scatter radiation (extinction of light). Ammonium-sulphate, sulphuric acid, organic PM and elemental carbon are anthropogenic aerosols which exert considerable influence on visibility impairment (White, 1990; White et al., 1994; Horvath, 1992). Sulphate and organic PM, and elemental carbon contribute to visibility reduction because of their capacity to scatter and absorb visible radiation, respectively. Research on visibility impairment by atmospheric aerosol pollution is currently being carried out in the United States, where fine aerosol chemical composition and visibility are monitored in the IMPROVE (Interagency Monitoring of PRotected Visual Environments) network (Malm et al., 1994; Malm, 1999). In the Eastern United States, sulphate is the main aerosol component causing light extinction, whereas in the Western United States both sulphate and carbonaceous particles make a significant contribution to light extinction. Moreover, in the arid Western United States, mineral desert dust also contributes to visibility impairment. An increase in the visibility range in the last decade in the United States has been attributed to air pollutant abatement strategies (Schichtel et al., 2001). Natural mineral dust particles may also lead to marked decreases in visibility, mainly during episodes of dust storm and transport to distant regions (e.g. a North African dust transport event over the Canaries in Figure 2-1). A review of the visibility range on a global scale and its relation to natural and anthropogenic aerosols is presented by Husar et al. (2000).

PM deposition exerts a significant influence on the chemical components and nutrient dynamics in aquatic and terrestrial ecosystems. Deposition of acid pollutants such as sulphuric-acid (H_2SO_4) or acid-sulphates (e.g.NH_4HSO_4) contributes to soil acidification with adverse effects on forests and crop cultivation and on the economy (Horvath, 1992; Manson, 1992). Enhanced rates of nitrate deposition contribute to the eutrophication of the waters of lakes and reservoirs, affecting aquatic ecosystems with a negative impact on the life of aquatic animals (US NRC, 1991). On the other hand, the deposition of natural mineral desert dust transported to distant areas exerts an influence on the bio-geo-chemical cycle of some elements. This deposition influences nutrient dynamics (e.g. K, N, P or Ca) with a beneficial impact on marine and terrestrial ecosystems (Graham and Duce, 1979; Reichholf, 1986; McDowell et al.,1990; Duce, 1991; Swap et al., 1992). Nutrients supplied by Saharan dust deposition exert an influence on phytoplankton productivity in the North Atlantic ocean (Duce, 1986, 1991), and contribute to the nutrient requirements of forests in Southern Europe (Avila et al., 1997, 1998) and the Amazon (Reichholf, 1986; Swap et al., 1992). Moreover, Ca-rich alkaline desert dust neutralises the acid pollutants deposited on soils (Löye-Pilot et al., 1986; Avila et al., 1997, 1998).
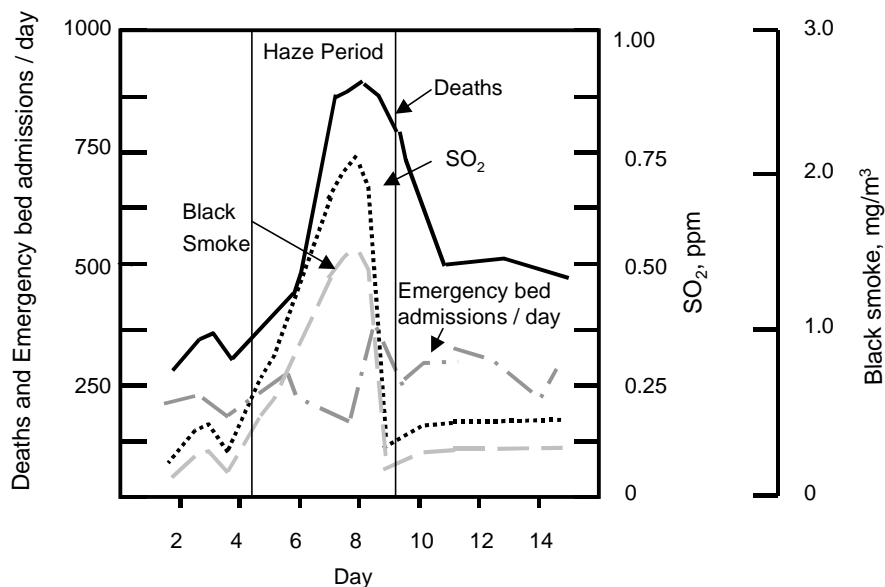
Figure 1-3. Evolution of daily number of deaths and hospitalisations, and daily levels of SO_2 and black smoke in London on 5-9 December 1952 (data compiled by Lippmann, 2001).

In urban environments, PM pollution leads to the deterioration of buildings and monument surfaces, resulting in costly reconstruction. This deterioration is caused by the reaction of acid species with the stone (BERG, 1989), and by soiling of surfaces (Beloin and Hayniec, 1975; Creighton et al., 1990; Pio et al., 1998), resulting in black spots in the areas protected from the rain.

1.3.2 Impact on urban air quality and human health

Evidence of the impact of PM air pollution on human health was first obtained during intensive winter pollution episodes in the industrialised countries of Europe and North America at the end of the XIX century and in the first half of the XX century. In the United Kingdom it was observed that the daily number of deaths and hospitalisations due to bronchitis rose during and in the days following winter haze episodes (UK Ministry of health, 1952). During the winter haze event in London on the days 5-9 December 1952, extremely high SO_2 and black smoke concentrations were registered in ambient air (Figure 1-3). According to the British authorities, exposure to air pollution resulted in 4000 deaths. Bronchitis was the main cause of death in individuals over the age of 55 (UK Ministry of health, 1952). In the Meuse valley (Belgium) 60 deaths out of a population of 6000 people were recorded during a winter pollution and haze episode (Firket, 1936). In Donora (Pennsylvania, United States), 20 deaths occurred during the winter pollution and haze event in October 1948, 43% of morbidity being registered (Schrenk et al., 1949).
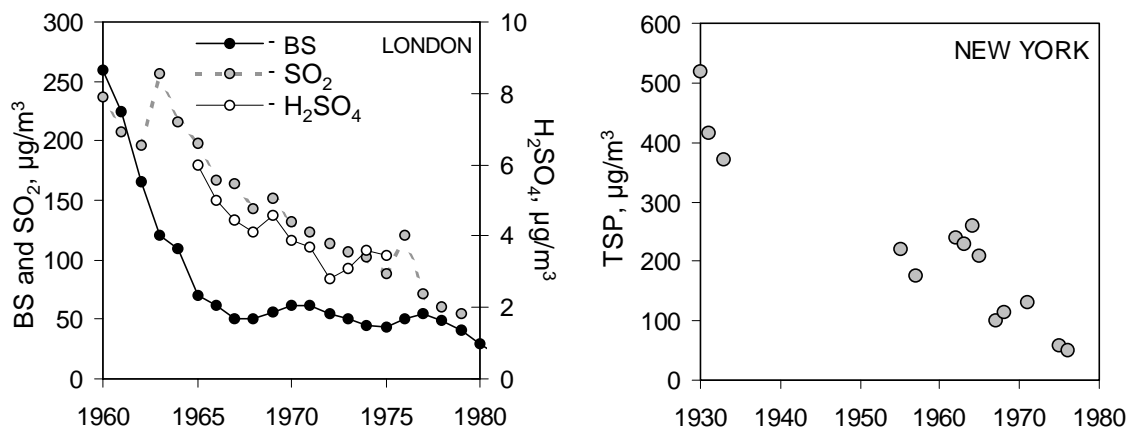
Figure 1-4. Left: Annual mean levels of black smoke (BS), SO_2 and sulphuric acid (H_2SO_4) from 1960 to 1980 in London. Right: Annual mean levels of TSP for several years in the period from 1930 to 1980 in New York. Data compiled by Lippmann (2001).

Given the adverse effects of PM pollution on the health of the population, the British authorities took measures to reduce ambient levels of black smoke and to abate pollutant emissions, e.g. the Clean Air Act. Similar measures were also taken in other industrialised countries, which included the identification of air pollution sources, the building of higher stacks and the separation of industrial from urban areas. In the last decades, a considerable effort has been made to reduce SO_2 and soot emissions derived from coal combustion, which has been the main source of air pollution in many cities. Thus, levels of PM have experienced a drastic decline in cities in Western Europe and North America (Figure 1-4). The introduction of new technologies in Western Europe has significantly changed the main sources and features of PM in ambient air. At present, the transport sector accounts for a large proportion of PM emissions (Colvile et al., 2001). Between 1950 and 2000, the number of cars in the world has increased by a factor of 10, and exhaust vehicle emissions pose a health risk because of fine PM emissions and tropospheric ozone production (Fenger, 1999; Colvile et al., 2001).

During the last decade, a number of epidemiological studies have found a relationship between current PM10 (particulate matter with diameter <10µm, inhalable fraction of PM) concentrations in ambient air and the number of hospitalisations and deaths due to respiratory and cardiovascular diseases (e.g. Pope et al., 1995; Dockery and Pope, 1996). After studying the age, race and sex of non-smokers, Schwartz (1993) found that an increase in the exposure to PM levels was associated with an increase in the risk of chronic bronchitis. Exposure of pregnant women to high TSP and PM10 levels has also been related to a decrease in the gestation period and a decrease in the weight of new-borns (Xu et al., 1995; Wang et al., 1997; Woodruft et al., 1997).
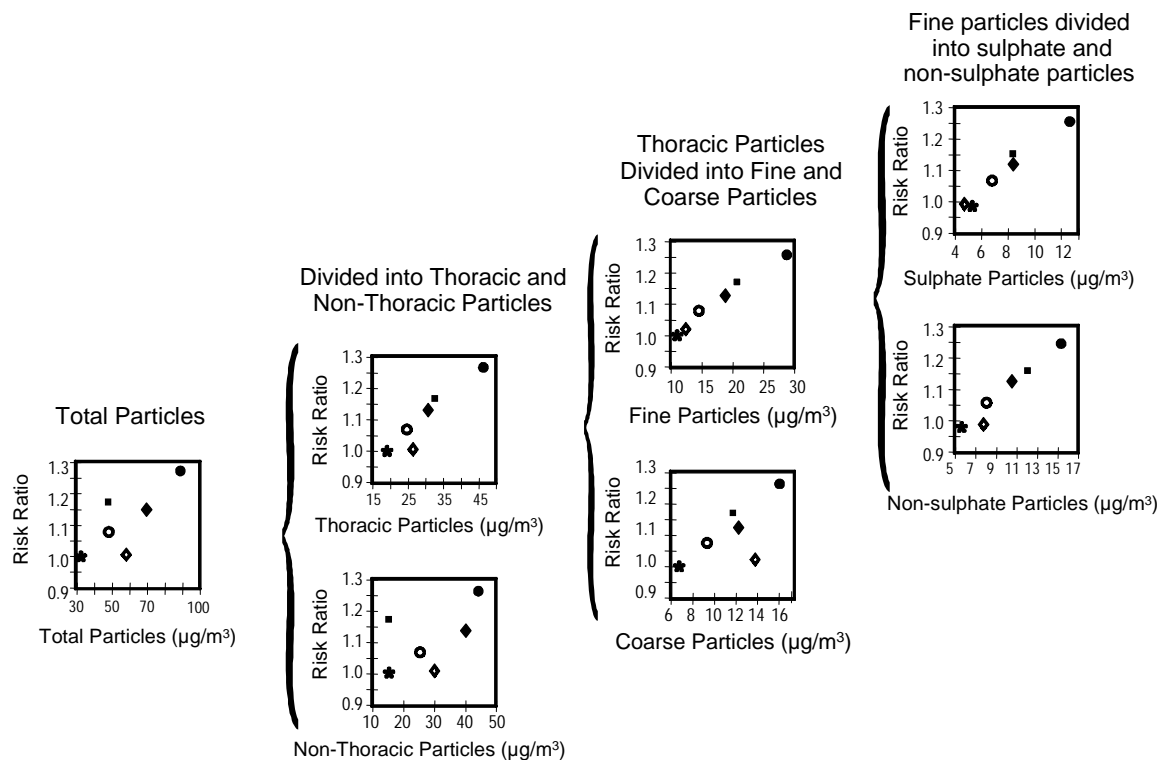
Fine particles divided into sulphate and non-sulphate particles

Thoracic Particles Divided into Fine and Coarse Particles

Divided into Thoracic and Non-Thoracic Particles

Total Particles

Risk Ratio — Sulphate Particles (µg/m³)

Risk Ratio — Fine Particles (µg/m³)

Risk Ratio — Non-sulphate Particles (µg/m³)

Risk Ratio — Thoracic Particles (µg/m³)

Risk Ratio — Coarse Particles (µg/m³)

Risk Ratio — Total Particles (µg/m³)

Risk Ratio — Non-Thoracic Particles (µg/m³)

Figure 1-5. Risk ratio of mortality versus PM levels expressed as the concentration of total suspended particles, thoracic particles (PM10), non-thoracic particles (>10µm), fine particles (<2.5µm), coarse particles (2.5-10µm), fine sulphate particles and fine non-sulphate particles. Extracted from US EPA (1996).

PM10 particles reach the lungs through the respiratory pathways, causing damage to the respiratory system, and alterations in the blood coagulation and cardiac rhythm (Donaldson and Macnee, 1999). PM10 particles increase the effects of respiratory and coronary diseases, giving rise to hospitalisations and premature deaths by asthma, bronchitis and heart attack. A number of epidemiological studies have shown that the most adverse effects associated with the exposure to PM10 are mainly caused by PM2.5 (particulate matter with an aerodynamic diameter <2.5µm: alveolar fraction of PM). Dockery et al. (1993) and Schwartz et al. (1996) found that the correlation between the risk of mortality and PM levels increased when expressing PM levels from TSP, PM10 to PM2.5 concentrations (Figure 1-5). These authors found the same degree of correlation between fine sulphate particles and the mortality risk and between fine non-sulphate particles and mortality risk.

Given the lack of knowledge of the specific causes of the adverse effects of PM on human health, some epidemiological studies have focused on the following topics (Lippmann, 2001): a) identification of the specific PM10 components or properties (physical such as number-density, mass-density or size, or chemical such as acidity) responsible for adverse health effects, b) the degree to which the health effects associated with PM10 depend on the simultaneous exposure to irritant vapours (e.g. O_3, SO_2 or NOx), c) the extent to which the

exposure to relatively low PM10 levels during long periods predispose to acute health effects during intensive PM10 episodes (known as "harvest" effect).

A recent study in the United States (Aerosol Research Inhalation Epidemiological Study: ARIES project) has shown that respiratory and cardiovascular diseases appear to be related to different pollutants (Vickery, 2002). PM2.5, the carbon-containing components of PM2.5 and CO are associated with cardiovascular effects. PM10 and the coarse fraction of PM10, are associated respiratory effects. The study also pointed out that all the components of PM are not equally toxic. The chemical composition of PM2.5 appears to be of importance. Carbonaceous particles (but not those containing sulphate and nitrate) are associated with health effects.