UNIVERSITAT ROVIRA I VIRGILI

ENVIRONMENTAL LEVELS OF PAHs AND OTHER SVOCs IN A PETROCHEMICAL AREA. COMBINING MONITORING AND MODELLING TOOLS

Noelia Domínguez Morueco

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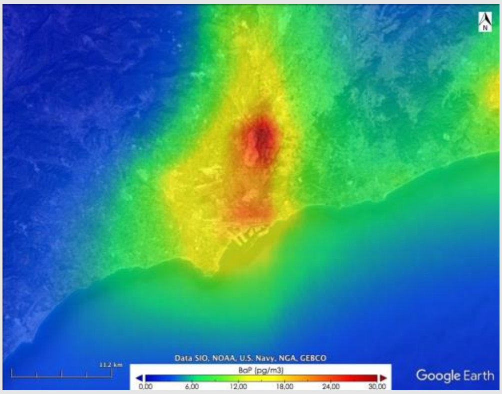
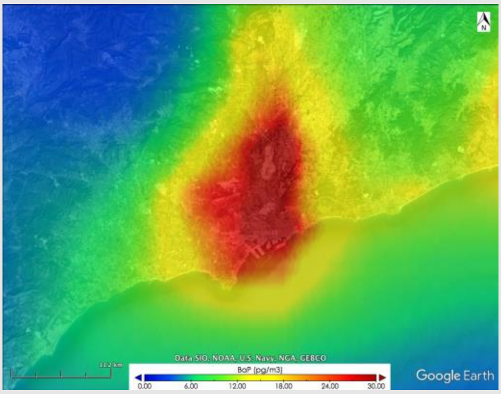
NOELIA DOMÍNGUEZ MORUECO





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Noelia Domínguez Morueco

ENVIRONMENTAL LEVELS OF PAHS AND OTHER SVOCS IN A PETROCHEMICAL AREA. COMBINING MONITORING AND MODELLING TOOLS.

DOCTORAL THESIS

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UNIVERSITAT ROVIRA i VIRGILI

Tarragona, 2018

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CERTIFY

That the present doctoral thesis, entitled “Environmental levels of PAHs and other SVOCs in a petrochemical area. Combining monitoring and modelling tools” presented by Noelia Domínguez Morueco for the award of the degree of Doctor, has been carried out under our supervision at the Department of Chemical Engineering at Universitat Rovira i Virgili, and it fulfills all the requirements to be eligible for the Distinction of International Doctor.

Tarragona, December 2017

Dr. Martí Nadal Dr. Jordi Sierra Prof. Marta Schuhmacher

A mis padres
y a mi hermana

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SUMMARY/RESUMEN

SUMMARY

Pollution is the contamination of the environment by introduction of contaminants or pollutants in concentrations that may cause damage to environment and harm organisms (humans, plants and animals). According to European Environment Agency (EEA) air pollution is the single largest environmental health risk in Europe, and can cause respiratory problems and shorten lifespans. Atmospheric transport is the primary distribution pathway of substances, moving these pollutants from atmospheric emission sources (natural or anthropogenic) via deposition to terrestrial and aquatic ecosystems. Among these substances there are the called semi-volatile organic compounds (SVOCs), characterized by their high toxicity, the recalcitrant to degradation processes character and their potential for long-range atmospheric transport (LRAT), reaching to remote and poorly accessible areas, far away from the emission sources. Besides, most of SVOCs are lipophilic and bioaccumulative, which increase the risk to human exposure. According to the United States Environmental Protection Agency (US EPA), the category of SVOCs includes a large number of compounds such as polycyclic aromatic hydrocarbons (PAHs). PAHs are by-products of incomplete combustion or pyrolysis of fossil fuels and other organic materials such as wood and biomass and they can be issued by natural (e.g., volcanoes, forests fires, and grassland combustion) or anthropogenic sources. Although PAHs can be released by both sources, the anthropogenic origin have been identified as the main responsible of the PAHs presence in the environment, being the petrochemical industries an important emission sources of PAHs to air. Among the different PAHs, benzo(*a*)pyrene (BaP) has already been classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC) and is the only PAH with a legislated average limit in the atmosphere: 1 ng m^{-3} of BaP over 1 year. Furthermore, international studies suggest that the toxicity and environmental fate and transport of PAHs can be affected by the variations in the temperature and solar radiation

associated with climate change, mainly in the most vulnerable regions, such as the Mediterranean basin.

In this thesis, atmospheric pollution due to the presence of PAHs and other SVOCs (polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) as hexachlorobenzene (HCB), brominated flame retardants (BFRs) and synthetic musk fragrances (SMs)) has been assessed in Tarragona country Spain that is home to the one of the largest chemical/petrochemical industrial complex in Southern Europe.

The chapter 1 of this thesis was focused in to determine the monitoring approaches necessary for SVOCs environmental determination by means of passive sampling techniques. Among these techniques, passive air samplers with polyurethane foam (PUF-PAS) and lichen transplants were selected, since they are cheap, easy to deploy or to collect and allows the simultaneous sampling in remote and/or poorly accessible areas without available electric current and at different locations and/or scales.

PUF-PAS are worldwide used for air monitoring at global/regional scale, since have been the devices preferred by the United Nations Environment Program for global air monitoring. However, few international studies have been conducted in order to study the suitability of PUF-PAS for SVOCs (POPs) monitoring at a local scale. This chapter has confirmed that the use of PUF-PAS is fully viable for Tarragona county (local scale) sampling, since these devices have been able to capture different groups or families of SVOCs, such as PAHs, PCBs, BFRs, SMs and HCB, even at very low air concentrations (ng/m^3), at different locations and involving low maintenance and costs. In addition, good correlations have been found between the PUF-PAS and lichens transplants when analyzing the environmental burden of PAHs, confirming the suitability of lichens as passive samplers. Regarding to SVOCs levels recorded by PUF-PAS and lichens transplants, it is observed that the area over the industrial influence (chemical and petrochemical areas) has higher concentrations of PAHs, PCBs and HCB than in urban areas and these are higher than in the background areas. On the other hand, SMs and BFR concentrations were lower than those and did not show significant differences between zones.

The chapter 2 of this thesis was aimed to improve analytical procedures for SVOCs determination using “green” alternatives. In last decades, several methods have been developed in order to detect, identify and quantify the chemicals released into the environment. Among these extraction and clean-up protocols are soxhlet, sonication, pressurized liquid extraction (PLE), microwave-assisted extraction (MAE), microextraction techniques, solid-phase extraction (SPE), among others. In general, all these methods are effective but time and solvent consuming, and requiring expensive equipment, for this reason, a multi-residue method involving QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) coupled to GC-MS (Gas Chromatography–Mass Spectrometry) was validated for the simultaneous extraction of PAHs, PCBs, BFRs, SMs and HCB in soils and vegetation samples. The results showed that the QuEChERS methodology was a valid technique to make a screening of the compounds presents in a sample, either soil or vegetation, including those collected in Tarragona county. In addition, QuEChERS technique provided a considerable reduction in the amount of solvent and operating time, without compromising the performance of the method given by the validation parameters.

When the three passive sampling techniques, PUF-PAS, vegetation and soils were evaluated together some differences arise. PUF-PAS tend to capture the most volatile SVOCs, mainly associated with the gas phase. Vegetation traps the PAHs contents in the gas phase, but it also retains some of those sorbed to the particulate phase (which has not been washed by natural processes), while soils capture the heaviest and more resistant to degradation molecules, that could be associated with particulate phase. Concerning the monitoring time, the results obtained from PUF-PAS and ruderal vegetation (*Piptatherum L.*) versus soil showed that these matrices are able to provide information regarding the levels and sources of SVOCs at short- (2-3 months) and long-term, respectively.

Finally, the chapter 3 of this thesis was aimed to use the modelling approaches as a combined tools for monitoring PAHs in the environmental. The combination of monitoring and modelling tools is of high importance, being very valuable and complementary techniques. In this sense, monitoring is critical for models implementation and modelling helps predict the contaminants behavior in the environment, since they transform the valuable datasets into a complete understanding of spatial, temporal and chemical transport patterns. Likewise, models can identify the priority areas for sampling campaigns. In this thesis two different models, MUM-Fate (Multimedia Urban Model) and WRF+CHIMERE (Weather Research and Forecasting), were used in order to predict PAHs fate, emissions and future concentrations considering actual and future climate conditions (RCP8.5 scenario, 2031-2050).

MUM-Fate model is a mass balance model based on the Level III steady-state fugacity of Mackay (1991), characterized by dividing the total study area into 7 different boxes or bulk media compartments. In the case of Tarragona county, MUM-Fate model provided a preliminary approximation of the PAHs distribution in the bulk media compartments defined for this area, by using simple approaches and calculations. Among the different compartments considered by this model, the organic film as the compartment with the highest concentrations of PAHs. However, and due the high losses in this compartment, the model positioned the soils and sediments as the greatest PAHs sinks in Tarragona County. Also this model was used to predict the emissions by backcalculations.

Regarding to WRF+CHIMERE model, is a kind of chemistry transport models (CTMs) that can complement the field data also considering the meteorology of the study area, the atmospheric chemistry processes and climate change, contributing to diminish the gaps still existing regarding SVOCs environmental behaviour. In this case, WRF+CHIMERE predictions indicate that in the future (2031-2050) concentrations of BaP will increase in air and decrease in soils in Tarragona county, resulting in an increase of $5x10^{-8}$ in the life-time risk of lung cancer, particularly in the most populated areas.

RESUMEN

La polución es la contaminación del medio ambiente por la introducción de contaminantes o compuestos en concentraciones que pueden causar daños a la salud humana y a los ecosistemas. Según la Agencia Europea del Medio Ambiente (AEMA), uno de los mayores riesgos para la salud ambiental en Europa es la contaminación del aire, que puede causar problemas respiratorios y acortar la esperanza de vida. El transporte atmosférico es la principal vía de distribución de sustancias, moviendo estos contaminantes desde las fuentes de emisión atmosférica (naturales o antropogénicas) hacia a los ecosistemas terrestres y acuáticos a través procesos de deposición. Entre estas sustancias se encuentran los llamados compuestos orgánicos semivolátiles (SVOCs), caracterizados por su alta toxicidad, carácter recalcitrante a los procesos de degradación y su potencial para el transporte atmosférico de largo alcance (LRAT), llegando a áreas remotas y poco accesibles, lejos de las fuentes de emisión. Además, la mayoría de los SVOCs son compuestos lipófilos y bioacumulativos, lo que aumenta el riesgo de exposición humana. De acuerdo con la Agencia de Protección Ambiental de los Estados Unidos (US EPA), la categoría de SVOCs incluye una gran cantidad de compuestos, tales como hidrocarburos aromáticos policíclicos (HAP o sus siglas en ingles PAHs). Los PAHs son subproductos de la combustión incompleta o pirólisis de combustibles fósiles y otros materiales orgánicos, como madera y biomasa, que pueden emitirse por fuentes naturales (por ejemplo, volcanes, incendios forestales y pastizales) o antropogénicas. Si bien ambas fuentes pueden liberar los PAHs, se ha determinado que el origen antropogénico es el principal responsable de su presencia en el medio ambiente, siendo las industrias petroquímicas fuentes importantes de emisión al aire. Entre los diferentes PAHs, el benzo(*a*)pireno (BaP) ya ha sido clasificado como cancerígeno para los humanos (Grupo 1) por la Agencia Internacional para la Investigación del Cáncer (IARC) y es el único PAHs con un límite promedio legislado en la atmósfera: 1 ng m^{-3} de BaP durante 1 año. Además, diversos estudios internacionales sugieren que la toxicidad y el transporte y destino ambiental de los PAHs pueden verse afectados por las variaciones en la temperatura y la radiación solar asociadas al cambio climático, principalmente en las regiones más vulnerables, como la cuenca mediterránea.

En esta tesis, se ha evaluado la contaminación atmosférica debida a la presencia de PAHs y otros SVOCs (bifenilos policlorados (PCB), plaguicidas organoclorados (OCP) como el hexaclorobenceno (HCB), retardantes de llama bromados (BFR) y fragancias sintéticas (SMs)) en Tarragona, España, donde se localiza el complejo industrial químico/petroquímico más grande del sur de Europa.

El capítulo 1 de esta tesis se centró, principalmente, en identificar las técnicas de monitoreo pasivo necesarias para la determinación ambiental de SVOCs. Entre estas técnicas, se seleccionaron muestreadores pasivos de aire con espuma de poliuretano (PUF-PAS) y trasplantes de liquen, ya que son baratos, fáciles de instalar o recolectar y permiten el muestreo simultáneo en áreas remotas y poco accesibles, donde no se dispone de corriente eléctrica y en diferentes ubicaciones y/o escalas.

Los PUF-PAS son dispositivos que se utilizan en todo el mundo para el monitoreo del aire a escala global/regional, siendo uno de los dispositivos preferidos dentro del Programa de las Naciones Unidas para el Medio Ambiente para el monitoreo del aire a escala global. Sin embargo, pocos estudios internacionales han estudiado la idoneidad de PUF-PAS para el monitoreo de SVOCs (o compuestos orgánicos persistentes, POPs) a escala local. Este capítulo ha confirmado que el uso de PUF-PAS es totalmente viable para el muestreo en el área de Tarragona (escala local), ya que estos dispositivos han podido capturar diferentes grupos o familias de SVOCs, como PAHs, PCB, BFR, SMs y HCB, incluso a concentraciones en aire muy bajas (ng/m^3), en diferentes ubicaciones e implicando poco mantenimiento y costes. Además, se han encontrado buenas correlaciones entre los trasplantes de líquenes y los PUF-PAS cuando se analiza la carga ambiental de los PAHs, confirmando la idoneidad de los líquenes como muestreadores pasivos. En cuanto a los niveles de SVOCs registrados por PUF-PAS y trasplantes de líquenes, se observa que el área con influencia industrial (áreas químicas y petroquímicas) tiene mayores concentraciones de PAHs, PCB y HCB que en áreas urbanas y estos niveles a su vez son más altos que en las áreas de fondo. Por otro lado, las SMs y BFR fueron los compuestos que presentaron las concentraciones más bajas y no mostraron apenas diferencias significativas entre las zonas.

El objetivo del capítulo 2 de esta tesis fue mejorar los procedimientos analíticos para la determinación de SVOCs utilizando alternativas "verdes". En las últimas décadas, se han desarrollado varios métodos para detectar, identificar y cuantificar los productos químicos liberados en el medio ambiente. Entre estos protocolos de extracción y limpieza se encuentran soxhlet, sonicación, extracción líquida presurizada (PLE), extracción asistida por microondas (MAE), técnicas de microextracción, extracción en fase sólida (SPE), entre otros. En general, todos estos métodos son efectivos pero consumen tiempo y una alta cantidad de disolventes, además de requerir equipos caros. Por este motivo, se validó un método de extracción múltiple que incluye QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) acoplado a GC-MS (Gas Cromatografía-Espectrometría de masas) para la extracción simultánea de PAHs, PCB, BFR, SM y HCB en suelos y muestras de vegetación. Los resultados mostraron que la metodología QuEChERS fue una técnica válida para realizar un cribado de los compuestos presentes en las muestras ambientales (suelos y vegetación), incluyendo las recogidas en Tarragona. Además, la técnica QuEChERS proporcionó una reducción considerable en la cantidad de disolvente y el tiempo de operación, sin comprometer el rendimiento del método de acuerdo a los parámetros de validación.

Cuando se evaluaron juntas las tres técnicas de muestreo pasivo, PUF-PAS, vegetación y suelos, surgieron algunas diferencias. PUF-PAS tienden a capturar los SVOCs más volátiles, principalmente asociados con la fase gaseosa. En cambio, la vegetación es capaz de atrapar los compuestos presentes en la fase gaseosa, además de retener algunos de los sorbidos en la fase particulada (que no haya sido lavada por procesos naturales); mientras que los suelos capturan las moléculas más pesadas y más resistentes a la degradación, que podrían estar asociados a la fase particulada. Con respecto al tiempo de monitoreo, los resultados obtenidos de PUF-PAS y vegetación rastrera (*Piptatherum L.*) versus suelo mostraron que estas matrices son capaces de proporcionar información con respecto a los niveles y fuentes de SVOCs a corto (2-3 meses) y largo plazo, respectivamente.

Finalmente, el capítulo 3 de esta tesis tuvo como objetivo utilizar los enfoques de modelado como herramientas adicionales en el monitoreo ambiental de PAHs. La combinación de herramientas de monitoreo y modelado es de gran importancia, siendo técnicas muy valiosas y complementarias. En este sentido, el monitoreo es crítico para la implementación de los modelos y el modelado ayuda a predecir el comportamiento de los contaminantes en el ambiente, ya que son capaces de transformar los conjuntos de datos de campo en patrones de transporte espacial, temporal y químico. Del mismo modo, los modelos pueden identificar las áreas prioritarias para las campañas de muestreo. En esta tesis, dos modelos diferentes, MUM-Fate (Multimedia Urban Model) y WRF+CHIMERE (Weather Research and Forecasting), fueron utilizados con el objetivo de predecir el destino final de los PAHs, así como sus emisiones asociadas y concentraciones futuras, teniendo en cuenta las condiciones climáticas actuales y de cambio climático (escenario RCP8.5, serie temporal 2031-2050).

El modelo MUM-Fate es un modelo de balance de masas basado en el concepto de fugacidad descrito por Mackay en 1991 (en este caso, Nivel III de fugacidad), que se caracteriza por dividir el área de estudio total en 7 compartimentos diferentes. En el caso de Tarragona, el modelo MUM-Fate proporcionó una aproximación preliminar de la distribución de los PAHs en los compartimentos definidos para esta área, mediante el uso de enfoques y cálculos simples. Entre los diferentes compartimentos considerados por este modelo, la película orgánica característica de las superficies impermeables fue el compartimento con mayores concentraciones de PAHs. Sin embargo, y debido a las altas pérdidas en este compartimiento, el modelo posicionó a los suelos y sedimentos como los mayores sumideros de PAHs en Tarragona. Así mismo, este modelo permitió estimar las emisiones de PAHs en Tarragona mediante retrocalculaciones. En cuanto al modelo WRF+CHIMERE, es un tipo de modelo de transporte químico que puede complementar los datos de campo considerando también la meteorología del área de estudio, los procesos químicos atmosféricos y el cambio climático, contribuyendo de esta manera a disminuir la incertidumbre en el comportamiento ambiental de los SVOCs. En este caso, las predicciones de WRF+CHIMERE indicaron que en escenarios futuros de cambio climático (RCP8.5, 2031-2050) las concentraciones de BaP aumentarán en el aire y disminuirán en los suelos de Tarragona, lo que resulta en un aumento de $5x10^{-8}$ en el riesgo de padecer cáncer de pulmón en las zonas más pobladas.

INTRODUCTION

1. Environmental pollution - Semi-volatile organic compounds (SVOCs)

Pollution is the contamination of the environment by introduction of contaminants or pollutants in concentrations that may cause damage to environment and harm organisms (humans, plants and animals). Since the start of the industrial revolution in the 19th century, environmental pollution has grown into a global transboundary problem that affects air, water, soils and ecosystems and is linked directly to human health and well-being. A key issue is the growth of the global population, from an estimated 1 billion in at the beginning of the 19th century to more than 7.5 billion today. This, combined with rapid economic development, has led to a massive increase in global production, consumption and mobility, together with increased demand for food and energy.

Pollution can be produced by natural origin (e.g. volcanic eruptions) or by anthropogenic origin and can reach the environment due to diffuse and punctual sources (Fig. 1). Diffuse pollution can be caused by a variety of activities that have no specific point of discharge. Agriculture is a key source of diffuse pollution, but urban land, forestry, atmospheric deposition and rural dwellings can also be important sources. Point sources, such as discharges from the treatment of industry, urban wastewater and fish farms are defined as stationary locations or fixed facilities from which pollutants are discharged. The anthropogenic origin is the most frequent and is linked to three main human activities: fossil-fuel combustion, primarily by industry and transport; the application of synthetic fertilisers and pesticides in agriculture; and the growing use and complexity of chemicals. For instance, the use of fossil-fuels such as coal and petroleum generated increases in the emission of different pollutants into the atmosphere, such as nitrogen oxides (NOx), sulphur oxides (SOx), carbon monoxide (CO) or organic compounds of different volatilities (VOCs) (CEC, 1997) (Fig. 1). From 1990 to 2010, annual global emissions from fossil fuels rose by 50 %, from around 6 billion tonnes to almost 9 billion tonnes (UNEP, 2012). In terms of chemicals, more than 100 million substances have been added in the CAS

REGISTRY (www.cas.org). From those, more than 100,000 substances are commercially available in Europe alone, and the number of new substances coming on to the global market is increasing rapidly.

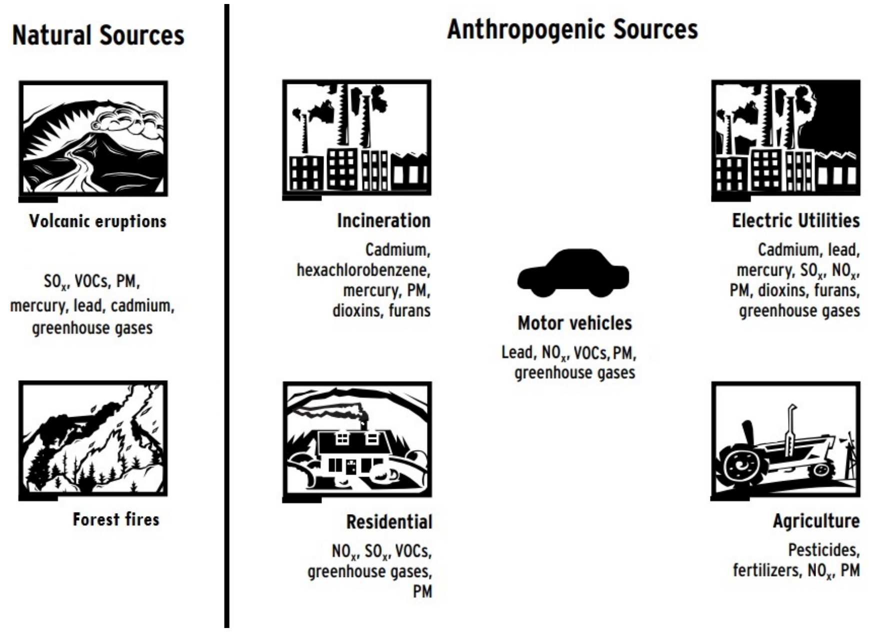


Fig. 1. Common sources of environmental pollutants. Source: modified from Commission for Environmental Cooperation (CEC), (1997).

Atmospheric transport is the primary distribution pathway of substances, moving these pollutants from atmospheric emission sources (natural or anthropogenic) via deposition to terrestrial and aquatic ecosystems (He and Balasubramanian, 2010) (Fig. 2). According to EEA (2016) air pollution is the single largest environmental health risk in Europe, and can cause respiratory problems and shorten lifespans. It also contributes vegetation and ecosystems damage, and leads to several important environmental impacts, which affect vegetation and fauna directly (e.g. causes eutrophication in sensitive habitats), as well as the quality of soil and water (e.g. acidification), and the ecosystem services they support.

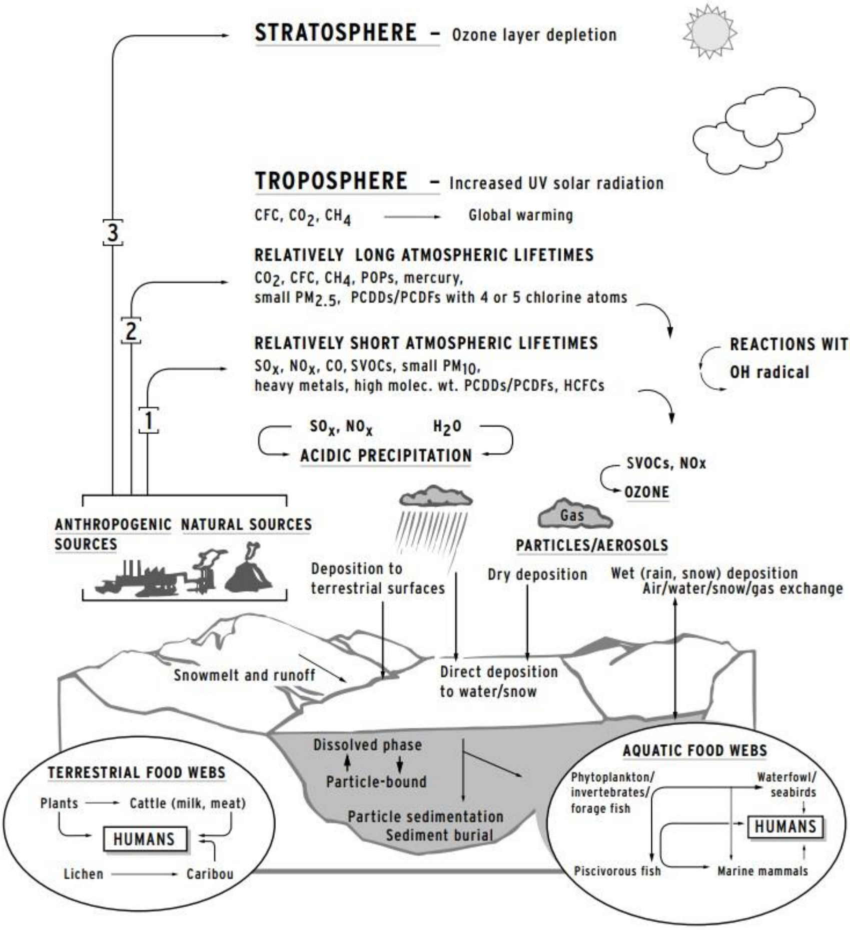


Fig. 2. Pathways of transport and accumulation of environmental pollutants. Source: modified from Commission for Environmental Cooperation (CEC), (1997).

Of particular concern are persistent, bio-accumulative and toxic substances that remain in the environment for a long time. It is recognized that potential harm should not be evaluated only on the basis of the effects on living organisms and on the ecosystems but also on the basis of possible exposure (Vighi and Calamari, 1993). Among these substances are the called semi-volatile organic compounds (SVOCs), defined by the United States Environmental Protection Agency (US EPA) Terminology Reference System such as those organic compounds that can volatilize relatively slowly at standard temperature of 20 ºC and pressure of 1 atm (boiling point range: 240-260 to 380-400 ºC). In recent years, the interest of the scientific community by SVOCs has been increasing due their high toxicity, the recalcitrant to degradation processes character and their potential for long-range atmospheric transport (LRAT), reaching to remote and poorly accessible areas, far away from the emission sources (Cai et al., 2008). Besides, most of SVOCs are lipophilic and bioaccumulative, which increase the risk to human exposure (Sun et al., 2014).

According to the US EPA, the category of SVOCs includes a large number of compounds such as:

- Polycyclic aromatic hydrocarbons (PAHs), dibenzodioxins and dibenzofurans
- Pesticides (insecticides, fungicides, herbicides, biocides etc.)
- Polychlorinated biphenyls (PCBs)
- Brominated flame retardants (BFRs)
- Perfluoroalkyl compounds (PFCs)
- SVOCs degradation products

Since SVOCs are linked to negative human health effects, these compounds are subject to national and international control strategies, such as the Stockholm Convention, the Convention of Long-Range Transboundary Air Pollution (LRTAP) or the REACH legislation (Melymuk et al., 2016). The Stockholm Convention (www.pops.int) defined in 2001 a total of 12 SVOCs as persistent organic pollutants (POPs). POPs is a group of chemical substances with highly persistence and health effects already recognized (e. g. dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disruption effects, and carcinogenicity) whose production, use, and emissions should be reduced or banned legally (UNEP, 2001). Among them were PCBs; organochlorine pesticides (OCPs), such as hexachlorobenzene (HCB) or BFRs (legacy POPs); while others SVOCs like PAHs are usually characterized as “potential POPs”.

Although the Stockholm Convention has been coming into force in 2004 and was signed by more than 150 countries worldwide -most of them developed countries- the characteristics of these compounds, together with their past extensive use around the world, has led their remain in the present environment.

2. Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic (benzene) rings made entirely from carbon and hydrogen (WHO, 2002; 2010). This kind of structure make PAHs a compounds with low solubility in water and therefore, with highly lipophilic character and soluble in most organic solvents (WHO, 2010).

Depending on the aromatic rings number, PAHs can be classified into low molecular weight PAHs (LMW PAHs), a group that includes PAHs with a number between 2 and 3 rings; intermediate molecular weight PAHs, which includes those PAHs with 4 aromatic rings; and high molecular weight PAHs (HMW PAHs), which includes those PAHs with a number of rings between 5 and 6 (WHO, 2002). Generally, LMW PAHs occur in the atmosphere predominantly in the gas phase, whereas HMW PAHs are largely bound to particulate phase. In the case of intermediate molecular weight PAHs, they are usually partitioned between the gas and particulate phases, depending on the atmospheric temperature (WHO, 2002).

The stability, persistence and hazardous potential of PAHs increase with the number of aromatic rings, this fact coupled with their hydrophobic (lipophilic) character, makes PAHs ubiquitous environmental contaminants, as well as risky compounds to ecosystem and human health (WHO, 2002; Ghosal et al., 2016; Liu et al., 2017a). Furthermore, international studies suggest that the toxicity and environmental fate and transport of PAHs can be affected by the variations in the temperature and solar radiation associated with climate change, mainly in the most vulnerable regions, such as the Mediterranean basin (Nadal et al., 2015; Marquès et al., 2016a). For this reason, PAHs have been classified as priority pollutants by US EPA and by the European Environment Agency (EEA).

The US EPA has developed a list of 16 priority PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(*1,2,3-c,d*)pyrene, dibenzo(*a,h*)anthracene, and benzo(*g,h,i*)perylene), 7 of them being classified as probable human carcinogens under the 2B classification (Leung et al. 2015) (Fig. 3).

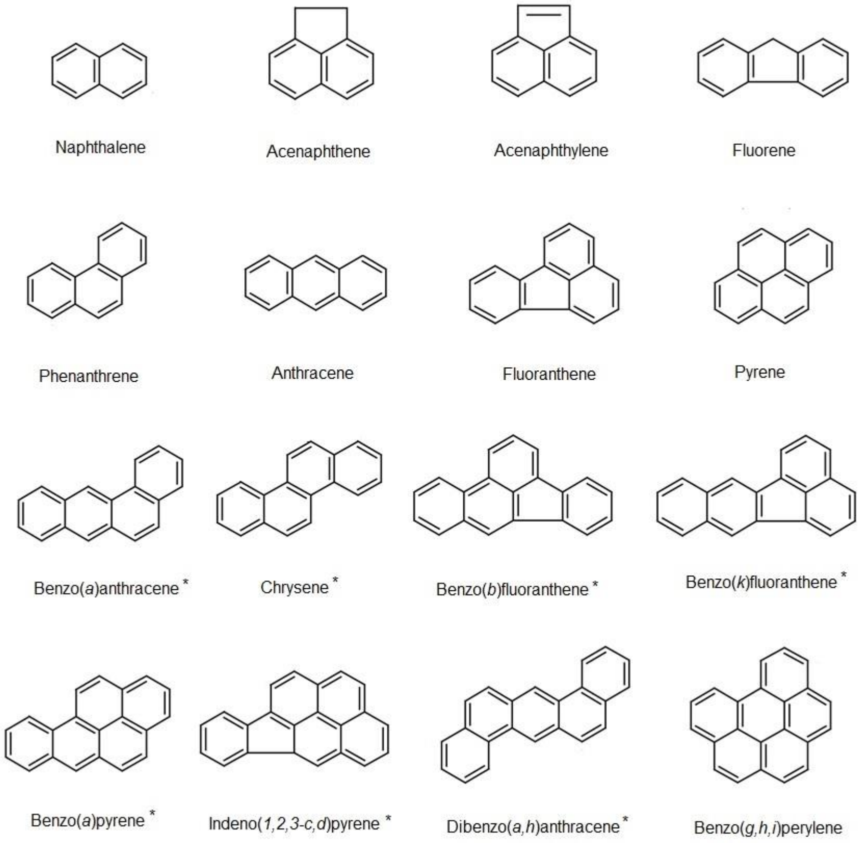


Fig. 3. List of 16 priority PAHs developed by US EPA. * 7 PAHs classified as probable human carcinogens under the 2B classification.

Other agencies, such as the International Agency for Research on Cancer (IARC), also suggest that there is an association between risk of cancer and exposure to PAHs, classifying the benzo(*a*)pyrene as carcinogenic to humans (group 1); the dibenzo(*a,h*)anthracene as probably carcinogenic (group 2A); and as possibly carcinogenic to humans (group 2B) in the case of naphthalene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene and indeno(*1,2,3-c,d*)perylene. Although the rest of the listed PAHs are not classifiable as to its carcinogenicity to humans (group 3), some of them, such as fluoranthene have mutagenic characteristics (IARC, 2013; 2017). The most important exposure route of PAHs is via inhalation, for this reason, the Air Quality Directive (EU, 2004) prescribes that benzo(*a*)pyrene concentration in air for the protection of human health is set at 1 ng/m^3 as an annual mean.

Due their potential carcinogenic and mutagenic properties, PAHs environmental exposure is being widely studied. One of the methodologies worldwide used to evaluate the PAHs exposure is the toxic equivalents (TEQs). This methodology allows to estimate the relative toxicity of certain groups of compounds in relation to the most toxic compound present in the mixture by using the toxic equivalency factors (TEFs) (Van den Berg et al., 1998; Hong et al., 2009):

$$TEQ = \sum (C \times TEF) \tag{1}$$

where *C* is the compound concentration in the mixture and *TEF* is the toxic equivalent factor for each compound.

As noted above, among the different PAHs, benzo(*a*)pyrene (BaP) is one of the most potent carcinogens, for this reason it is often used as a marker for total exposure to carcinogenic PAHs (WHO, 2010). In this sense, the carcinogenic risk associated of a PAH mixture is expressed through its benzo(*a*)pyrene equivalent concentration (BaP_{eq}); and it is calculated by multiplying the concentration of each individual PAH present in the sample (PAH_i) by its respective toxic equivalent factor (TEF_i):

$$BaP_{eq} = \sum_{i=1}^{n} PAHi \times TEFi \qquad (2)$$

In this thesis the TEF$_i$ for each PAHs were according to Nadal et al. (2004a) (adapted from Nisbet and LaGoy, 1992 and Larsen and Larsen, 1998) (Table 1).

Table 1. TEFs values for each PAHs according to Nadal et al., 2004a.

PAHs	TEFs
Naphthalene (Naph)	0.001
Acenaphthylene (Acy)	0.001
Acenaphthene (Ace)	0.001
Fluorene (Fluo)	0.001
Phenanthrene (Phen)	0.0005
Anthracene (Ant)	0.0005
Fluoranthene (Flt)	0.05
Pyrene (Pyr)	0.001
Benzo(*a*)anthracene (BaA)	0.005
Chrysene (Chry)	0.03
Benzo(*b*+*k*)fluoranthene B(b+k)F	0.1
Benzo(*a*)pyrene (BaP)	1
Indeno(*1,2,3-c,d*)pyrene (Icdp)	0.1
Dibenzo(*a,h*)anthracene (DahA)	1.1
Benzo(*g,h,i*)perylene (BghiP)	0.02

[a]Benzo(*b*)fluoranthene and benzo(*k*)fluoranthene are quantified together.

PAHs are by-products of incomplete combustion or pyrolysis of fossil fuels and other organic materials such as wood and biomass (Chen et al., 2011; Wang et al., 2012); and they can be issued by natural (e.g., volcanoes, forests fires, and grassland combustion) or anthropogenic sources. Although PAHs can be released by both sources, the anthropogenic origin have been identified as the main responsible of the PAHs presence in the environment (Jaward et al., 2004; Wang et al., 2010; Estellano et al., 2012). Major anthropogenic sources are located in urban areas and they include incineration activities, power generation, domestic heating, vehicles emissions, and industrial activities (Chen et al., 2011. Among these, petrochemical industries are particularly important emission sources of PAHs to air (Nadal et al., 2009, 2011).

Once released to the atmosphere, and as SVOCs, PAHs are compounds susceptible to suffering LRAT, reaching at other environmental matrices such as water and aquatic systems, soils and sediments (Nadal et al., 2004). For this reason, the source appointment is a crucial step in their global control. Numerous studies have developed different strategies in order to identify the PAHs sources. The molecular diagnostic ratios (MDR) for PAHs, is one of the method most applied for the different environmental matrices (Tobiszewski and Namieśnik, 2012). MDR are based on the theory that some PAHs are emitted in constant proportions from the sources and their concentrations remain constant between the source and the receptor (Katsoyiannis et al., 2011; Tobiszewski and Namieśnik, 2012). Different sources can be identified by using the MDR, for instance, ratios such as Ant/(Ant+Phe), BaA/(BaA+Chry), Flt/(Flt+Pyr) or IcdP/(IcdP+BghiP) can provide information about the pyrogenic or petrogenic origin of the emission source (Katsoyiannis et al., 2011). Likewise, Flt/(Flt+Pyr) and IcdP/(IcdP+BghiP) can also identify if the source is related with fuel combustion or grass/coal/wood combustion. In turn, the ratio BaP/BghiP can provide information about the presence of traffic or nontraffic in the matrix studied (Katsoyiannis et al., 2011).

In general, the total emissions of PAHs have been declining in developed countries since the 1970s or 1980s, and according to EEA, European PAH emissions have decreased around 89 % in the period between 1990 and 2015. However, nowadays in some European countries (Denmark, Lichtenstein and Malta) and in developing countries, such as China and India, PAH emissions have been continuously increasing (Liu et al., 2017a; EEA, 2017).

3. Other SVOCs

3.1. Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a kind of organohalogenated contaminants (OCs) consisting of a total of 209 congeners composed by molecules with 1–10 chlorine atoms attached to the two rings of biphenyl (Erickson and Kaley, 2011; IARC, 2017) (Fig. 4). Depending on the chlorine number, PCBs can be classified as tri-, tetra-, penta-, hexa-, hepta- or octa-CBs and their stability, persistence and toxicity will associated with its number and position (Devi et al., 2014; IARC, 2016).

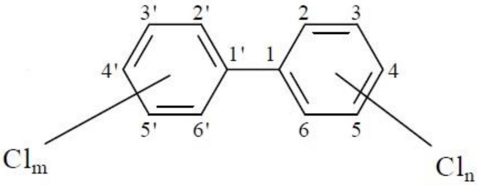


Fig. 4. General chemical structure of PCBs. Source: modified from IARC, 2016.

PCBs are compounds with high toxicity associated, and in some cases, the toxic effects are comparable to chlorinated dibenzo-*p*-dioxins, more specifically with the congener 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). For this reason, a total of 12 PCBs congeners have already defined as dioxin-like PCBs by the World Health Organization (WHO) in 2005 (Fig. 5).

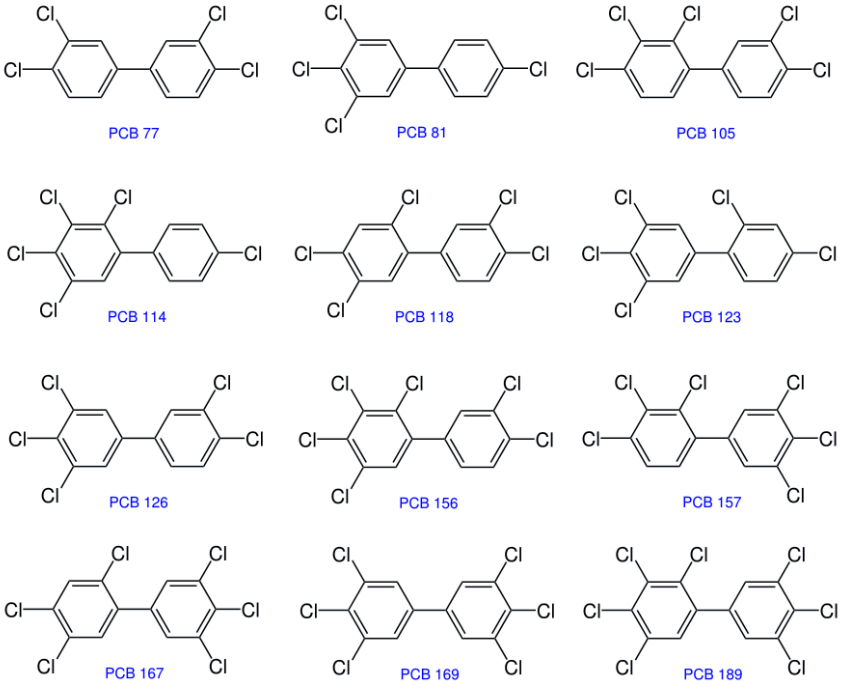


Fig. 5. Dioxin-like PCBs congeners identified by the World Health Organization.

As in the case of PAHs, the health risk associated to PCBs environmental exposure can be evaluated through the TEQs. In this sense, the risk associated at these 12 dioxin-like PCB congeners can be estimated through their 2,3,7,8-TCDD equivalent concentration (2.3.7.8-TCDDeq). Thus, 2.3.7.8-TCDDeq in environmental samples is calculated by multiplying the concentration of each individual dioxin-like PCB present in the sample (PCBj) by the respective TEFj (Drimal et al., 2016):

$$2.3.7.8\text{-}TCDDeq = \sum_{j=1}^{n} PCBj \times TEFj \quad (3)$$

The TEFj for each dioxin-like PCB were those defined by the World Health Organisation (WHO) in 2005 (Table 2).

Table 2. TEFs values for each dioxin-like PCB according to WHO, 2005.

Dioxin-like PCB	TEFs
PCB 77	0.0001
PCB 81	0.0003
PCB 105	0.00003
PCB 114	0.00003
PCB 118	0.00003
PCB 123	0.00003
PCB 126	0.1
PCB 156	0.00003
PCB 157	0.00003
PCB 167	0.00003
PCB 169	0.03
PCB 189	0.00003

Regarding PCBs carcinogenic potential, it is well known that these compounds had carcinogenic, mutagenic and teratogenic effects in experimental animals. But, recently the IARC has evidenced positive associations between PCBs exposure and non-Hodgkin lymphoma and cancer of the breast in humans (IARC, 2016). For this reason, the PCBs IARC classification has gone from group 2A or “probably carcinogenic in humans” to group 1 or “carcinogenic to humans”. In addition, and because their hydrophobic (lipophilic) character, bioaccumulative potential, environmental persistence and long range transport capability, coupled with the effects above described, PCBs were one of the firsts compounds listed as POPs in the Stockholm Convention on May 22, 2001.

Unlike PAHs, PCBs are compounds only issued by anthropogenic sources and were manufactured for the first time at the beginning of 1929 by Monsanto/USA. PCBs were commercialized as complex mixtures synthesized by direct chlorination of biphenyl with chlorine gas in the presence of $AlCl_3$ (Alawi et al., 2017). Due to their non-flammability chemical stability, high boiling point and resistance to both acids and alkalis, PCBs had been used in a wide variety of applications, including dielectric fluids in capacitors and transformers, heat transfer fluids, hydraulic fluids, lubricating oils, and as additives in paints, carbonless copy (“NCR”) paper, adhesives, sealants, and plastics (Erickson and Kaley, 2011; IARC, 2016;

Nguyen et al., 2016; Sun et al., 2016). PCBs production was ceased in most countries by the end of the 1970s or early 1980s, and aaccording to the EEA, their emissions decreased by 77 % between 1990 and 2015, mainly because of reductions in 'Industrial processes and product use' emissions (EEA, 2017). Even though PCBs are compounds worldwide banned by the Stockholm Convention, they are still present in the environment due their extensively use, LRAT potential and persistence. For instance, the primitive dismantling of electronic and electrical waste (e-waste) has been demonstrated to be a substantial emission source of PCBs (Zhu et al., 2014). Once PCBs are emitted at the atmosphere, they can reach into different media (water and sediments, vegetation, etc) being the soils an important reservoir (Ren et al., 2007).

3.2. Hexachlorobenzene (HCB)

Hexachlorobenzene (HCB) is a kind of OCs, more specifically is considered as an organochlorine pesticide (OCP), which consists of a single benzene ring with 6 chlorines attached (Fig. 6). This structure confers HCB a chemical stability, hydrophobic nature and high persistence, which allows the LRAT and its bioaccumulation, being the soils the main sinks in the environment (IARC, 2001; Wang et al., 2017).

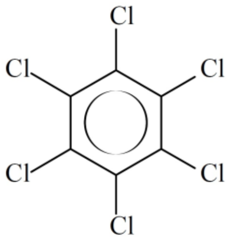


Fig. 6. Chemical structure of HCB. Source: from IARC, 2001.

HCB is an anthropogenic compound issued by the chlorination of benzene at 150–200 °C with a ferric chloride catalyst or distillation of residues from the production of tetrachloroethylene (IARC, 2001). Although HCB was commercialized and used extensively as a fungicide from the

1950s, this compound has also been used in the past for a variety of applications such as, military pyrotechnic smokes, carbon anode treatments, aluminium fluxing and degassing, synthetic rubber peptizing agent, wood preservation material or as intermediate in organic synthesis (Bailey, 2001; IACR, 2001; Breivik et al., 2004). In the 1970s, the use of HCB in these applications was discontinued in many countries owing to concerns about adverse effects on the environment and human health. Consequently, the Stockholm Convention listed the HCB as one of the 12 initial POPs, and the IARC has classified this compound in group 2B or “as possibly carcinogenic to humans”. Nevertheless, some developing countries may continue using this compound and it still occurs as a by-product of the production of a number of chlorinated solvents and other industrial chemicals (IARC, 2001).

3.3. Brominated flame retardants (BFRs)

Brominated flame retardants (BFRs) are anthropogenic compounds included into the group of halogenated organic flame retardants. BFRs comprise a variety of chemicals as polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) stereoisomers and tetrabromobisphenol-A (TBBP-A). Among those, PBDEs were one of the BFR most commonly used in the past (Covaci et al., 2007; Segev et al., 2009; Gorga et al., 2013; Katima et al., 2017) PBDEs are produced by bromination of diphenyl ether in the presence of a Friedel–Craft catalyst (e.g. $AlCl_3$) in a solvent such as dibromomethane. Diphenyl ether molecules contain 10 hydrogen atoms, which can be exchanged with bromine, resulting in 209 possible congeners with similar structure to that of PCBs (Alaee et al., 2003) (Fig. 7).

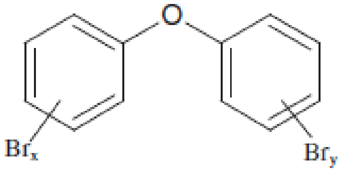


Fig. 7. Chemical structure of PBDEs. Source: modified from Gorga et al., 2013**.**

PBDEs have been manufactured since the 1970's in three major forms: penta-BDE, octa-BDE, and deca-BDE; and were mainly used in order to retard the spread of fire/flame in household products (carpets, upholstered furniture, curtains, fabrics, etc.) electronical appliances, car interiors or building materials (Gorga et al., 2013; Ding et al., 2016; Katima et al., 2017; Liu et al., 2017b; McGrath et al., 2017b). Although, PBDEs are compounds strongly associated with indoor environments, some international studies have already demonstrated their presence in outdoor matrices (Zheng et al., 2015; Ding et al., 2016; McGrath et al., 2016). In this sense, the industries involved in the manufacture or disposal of flame retarded goods are expected to be one of the key outdoor emission sources (McGrath et al., 2017a).

Recently, toxicological reports have demonstrated a range of adverse effects in humans and animals derived from PBDEs exposure, including endocrine disruption and neurodevelopmental toxicity (McGrath et al., 2016). In addition, its lipophilic character, bioacumulative potential, as well as, their high manufacture volume and widespread consumption makes them persistent in the environment and suitable for the LRAT (Covaci et al., 2007; Zheng et al., 2015; Yu et al., 2016; Katima et al., 2017). For this reason, the forms penta-BDE and octa-BDE are currently included in the list of banned POPs under the Stockholm Convention, while deca-BDE has been officially proposed (McGrath et al., 2017a).

In order to replace the legacy PBDEs, “novel” BFRs (NBFRs) such as pentabromotoluene (PBT), pentabromoethylbenzene (PBEB) or hexabromobenzene (HBB) have been commercialized (Zheng et al., 2015; Li et al., 2016; McGrath et al., 2017) (Fig. 8). The NBFRs can be released to the environment by the same mechanisms as PBDEs and have comparable physicochemical properties to PBDEs. Consequently, they have similar fate as persistent pollutants in air, soil and sediments, and also exhibit analogous bioaccumulation and toxic potential (McGrath et al., 2017a).

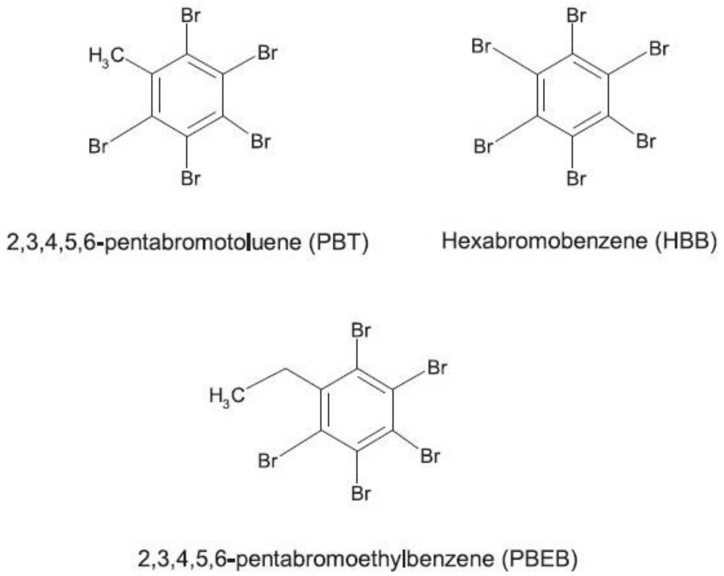
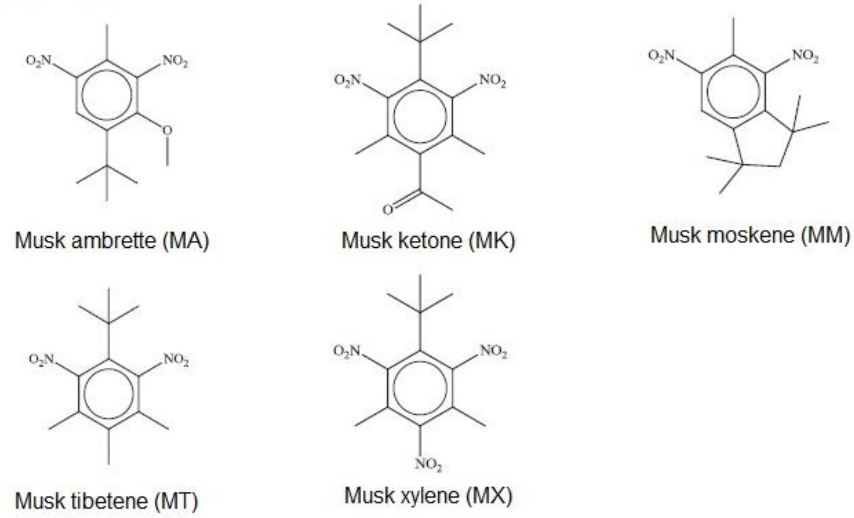


Fig. 8. Chemical structure of PBT, HBB and PBEB. Source: modified from Ezechiáš et al., 2014.

3.4. Synthetic musks (SMs)

Synthetic musks (SMs) are fragrances used as additives and fixative elements in a range of personal care and other consumer products, including perfumes, cosmetics, shampoos, lotions (sunscreen lotions), washing and cleaning agents, and fabric softeners (Lu et al., 2011; Homem et al., 2015b). Although SMs are not recognized as SVOCs, they have similar physical-chemical properties, which gives them a semivolatile character, lipophilic nature, bioacumulative potential and also appropriate for LRAT (Peck and Hornbuckle, 2004; Nakata et al., 2012; Homem et al., 2013; Villa et al., 2014). In addition, SMs have been produced in large quantities and have an intensive and widespread use, for this reason, they are considered as emerging contaminants (Lu et al., 2011; Lange et al., 2015; Homem et al., 2016).

According to their chemical structure, SMs can be divided in four groups: nitro, polycyclic, macrocyclic, and alicyclic musks (Homem et al., 2013, 2015c). Among the different SMs, nitro musk fragrances were first produced commercially in 1900s as substitutes for the natural musks fragrances. These compounds consists in two-fold or three-fold nitratebenzene derivatives with additional alkyl, keto or methoxy groups (Vallecillos et al., 2015) (Fig. 9).



Musk ambrette (MA)

Musk ketone (MK)

Musk moskene (MM)

Musk tibetene (MT)

Musk xylene (MX)

Fig. 9. Chemical structure of nitro musks. Source: modified from Homem et al., 2015b.

Nitro musks were worldwide used until 1990s, but their potential toxicity, namely phototoxic, neurotoxic, carcinogenic and oestrogenic activity made that most of them (musk ambrette, musk moskene and musk tibetene) were banned from cosmetic products in Europe, while others (musk xylene and musk ketone) were innitially restricted, due to suspected carcinogenic effects at high concentration levels (Homem et al., 2015-a,c). Nowadays, the musk xylene has been also banned by the REACH legislation, due its high persistence and bioacummulative potential.

In the last decades, and as a result of legislation, a decreasing use of nitro musks has been observed. Consequently, a second group of synthetic musks has emerged, the polycyclic musks. They are chemically acetylated and highly methylated pyran, tetralin, and indane compounds and the most representatives are cashmeran, celestolide, galaxolide, phantolide, tonalide and traseolide (Homem et al., 2016) (Fig. 10).

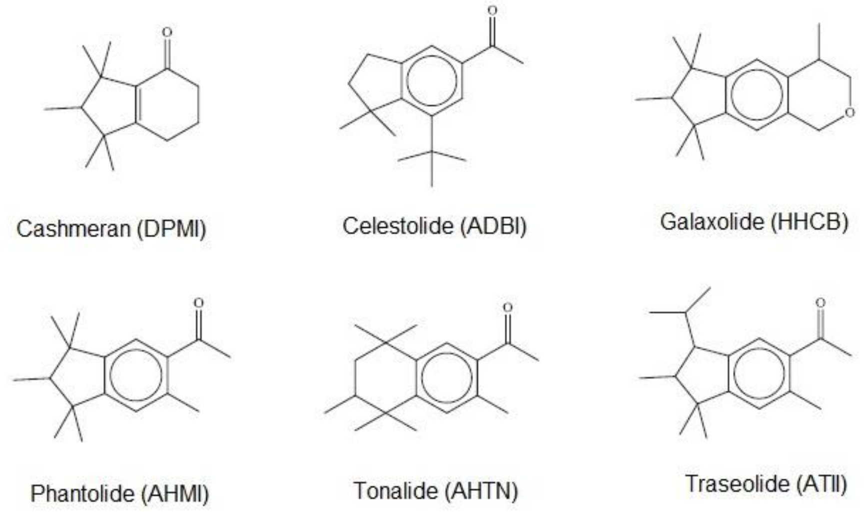


Fig. 10. Chemical structure of polycyclic musks. Source: modified from Homem et al., 2015b.

Among the different polycyclic musks, galaxolide and tonalide are the two predominant congeners, which account for 95 % of commercially used polycyclic musks (Vallecillos et al., 2015). For this reason, both have being identified in the high production list of some environmental protection agencies, such as US EPA (EPA's high production list) (Villa et al., 2014; Trabalón et al., 2015; Vallecillos et al., 2015).

Dermal absorption from personal care products applications is reported as one of the major sources of exposure of SMs (Homem et al., 2015c; Trabalón et al., 2015). Nevertheless, the volatilization process during its production and use, as well as the volatilization from landfills or sewage treatment plants, has been recognized as an important source of polycyclic musks to the environment (Villa et al., 2014). In fact, and due its high production and bioacumulative and LRAT potential, galaxolide and tonalide have aready presents in different environmental compartments such as air, fresh water, sea water, sediments, marine biota and even in human samples (Nakata et al., 2012; Lange et al., 2015; Homem et al., 2015c; 2016). As for the adverse health effects, a potential oestrogenic and anti-oestrogenic effects associated to both compounds have been observed (Homem et al., 2015a).

4. Environmental monitoring

The occurrence and behaviour of SVOCs in the environment have become a growing concern since most of them have adverse effects to humans and the ecosystem. Due to atmospheric transport is the primary distribution pathway of contaminants, air monitoring programs such as the European Monitoring and Evaluation Program (EMEP), the Arctic Monitoring and Assessment Program (AMAP) or the Integrated Atmospheric Deposition Network (IADN) have been established with the aim of provide long-term atmospheric measurements of SVOCs (POPs) Camenzuli et al., 2016.

Numerous devices and techniques have been developed to enable environmental sampling. In the case of air, two main configurations are currently in use: active or passive sampling.

Active air sampling is based in a pulling air through a trap with an electric pump. The active air samplers (AAS) are classified as either high volume or low volume samplers. High volume samplers, are devices with sampling rates between 15−80 m^3/hour yielding total sample volumes of >400 m^3, while low volume air samplers have sampling rates of <3 m^3/hour, resulting small sample volumes (e.g., <200 m^3) (Melymuk et al., 2014). Because its sampling rates are knowing, AAS can provide quantitative concentrations of SVOCs in both gas phase and particle phase (size of particles PM_{10}, $PM_{2.5}$ and PM_1), over short time intervals (several hours to 1 week) (Hung et al., 2013). However, its characteristics made AAS a power consumer, expensive to operate and more labour intensive devices, therefore it is unavailable for high latitude or altitude regions (Hung et al., 2013; Zhu et al., 2015). In this sense, passive sampling have become a viable alternative, since is cheaper, easy to deploy or collet and allows the simultaneous sampling in remote and/or poorly accessible areas and at different locations and/or scales (Harner et al., 2006; Pozo et al., 2009; Melymuk et al., 2014).

Passive sampling has diffusion-advection based to capture compounds on sorbents through a passive air flow, without the use of electricity (Bogdal et al., 2013; Hung et al., 2013). Passive air samplers (PAS) are the main devices, and different designs have been developed based on the adsorbent material, being polyurethane foam (PUF) one of the most widely used for air monitoring (including in the Global Atmospheric Passive Sampling (GAPS) Network) (Bohlin et al., 2008; Chaemfa et al., 2008; Pozo et al., 2009). The standard design of PAS is based on a double-dome chamber in which a PUF-disk is deployed in order to protect the adsorbent material from rainfall and direct light (Fig. 11. A) (Chaemfa et al., 2008; Seethapathy et al., 2008; Choi et al., 2012).

Unlike AAS, PAS do not provide the sampling rates, for this reason they only estimate semi-quantitative concentrations of SVOCs over longer periods (typically 1-3 months up to 1 year). In this case, the compounds uptake is described as equivalent to the rate of uptake minus the rate of loss (He and Balasubramanian, 2010; Melymuk et al., 2014). The uptake profiles of SVOCs in passive samplers generally go through the linear phase, curvilinear phase and equilibrium phase with the exposure time (He and Balasubramanian, 2010) (Fig. 11. B).

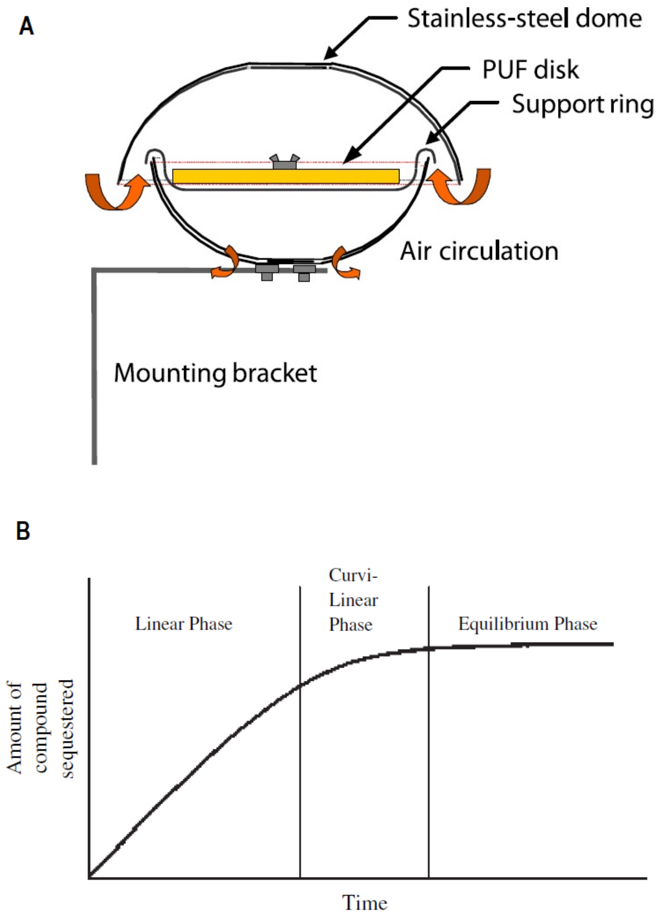


Fig. 11. A) PAS design. Source: modified from Klánová and Harner 2013; B) Idealised uptake regime of SVOCs (POPs), showing each phase of uptake. Source: from Farrar et al., 2006.

Nevertheless, it is also considered as passive sampling the collection of samples belonging to environmental matrices, such as soils or vegetation. Traditionally both matrices have been used to monitor atmospheric deposition from different sources (Augusto et al., 2009). In the case of soils, it is well recognized that they are one of the main sinks of SVOCs (POPs), due their high affinity for hydrophobic organic pollutants, reflecting therefore the long-term atmospheric pollution (Diamond et al., 2001; Kawamena et al., 2007; Cai et al., 2008; Augusto et al., 2009; Bao et al., 2015; 2016). In contrast, vegetation is mainly used to provide information on the short-term exposure due its rapid kinetic of exchange with the air (Barber et al., 2003; 2004; Augusto et al., 2007). In this case, various types of vegetation have been used as natural sampling media to evaluate atmospheric pollution of SVOCs since the 1980s, such as lichens, mosses, pine needles, tree bark, leaves, grass, vegetables, etc.,(Augusto et al., 2007; Zhu et al., 2015).

5. Environmental modelling

In the last decades, different types of models have been developed in order to predict the chemical fate and transport of contaminants, as well as estimate its future concentrations in the environmental matrices. In this sense, to combine the monitoring and modelling approaches plays complementary roles, since monitoring is critical for the continuing evaluation and improvement of the models, and modelling can help to design the sampling campaigns (Webster et al., 2005) (Fig. 12).

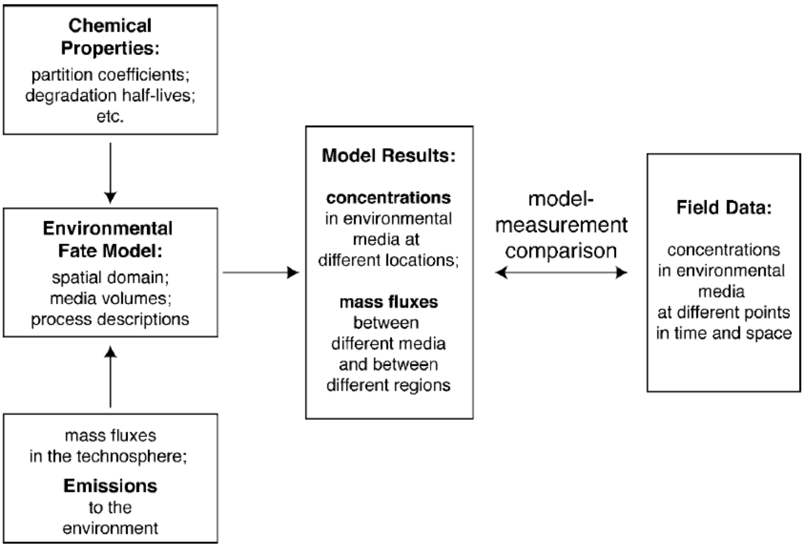


Fig. 12. Independent pieces of information needed for an environmental fate assessment of a chemical. All four components are uncertain, and the influence of the different uncertainties on the overall assessment needs to be evaluated. Source: Scheringer, 2009.

When a chemical substance is introduced into the environment (atmosphere, waters or soils) will move from their point of entry/emission to their final destination depending on the intrinsic physical-chemical properties of the contaminant (e.g. water solubility (S); octanol-water partition coefficient (K_{ow}); vapour pressure (Vp); octanol-air partition coefficient (K_{OA}); half-life time ($T_{1/2}$); etc.) and the characteristics of the environment where the contaminant has been spilled. The combination of these factors will determine the persistence, the mobility or transference and the transformation of the contaminants (Vighi and Calamari, 1993). Currently, the multimedia environmental models are one of the most used techniques for the modelling of pollutants such as SVOCs (He and Balasubramanian, 2010). This kind of models divides the environment in different boxes or bulk media compartments (e.g. air, soil, water and sediments or vegetation compartments) connected between them; and use these physical-chemical properties, reactivity data (reaction processes), and key intermedia transfer processes, to render a comprehensive treatment of contaminant dynamics (Fig. 13) (Mackay and Paterson 1991; Premier et al., 2000). Most of the multimedia environmental models are composed of mass balance equations, each one defined for each bulk media compartment. The mass balance equations are based on the fugacity concept under the different levels described by Mackay in 1991 (Fig. 14). The use of fugacity approach simplifies the model development and calculations, retaining a rigorous formulation, and allowing an extensive use of models among the scientific community (Mackay and Paterson, 1991; Csiszar et al., 2012, 2013; Domínguez-Morueco et al., 2016). In this sense, the multimedia environmental models can provide a first approximation of the SVOCs distribution in the bulk media compartments.

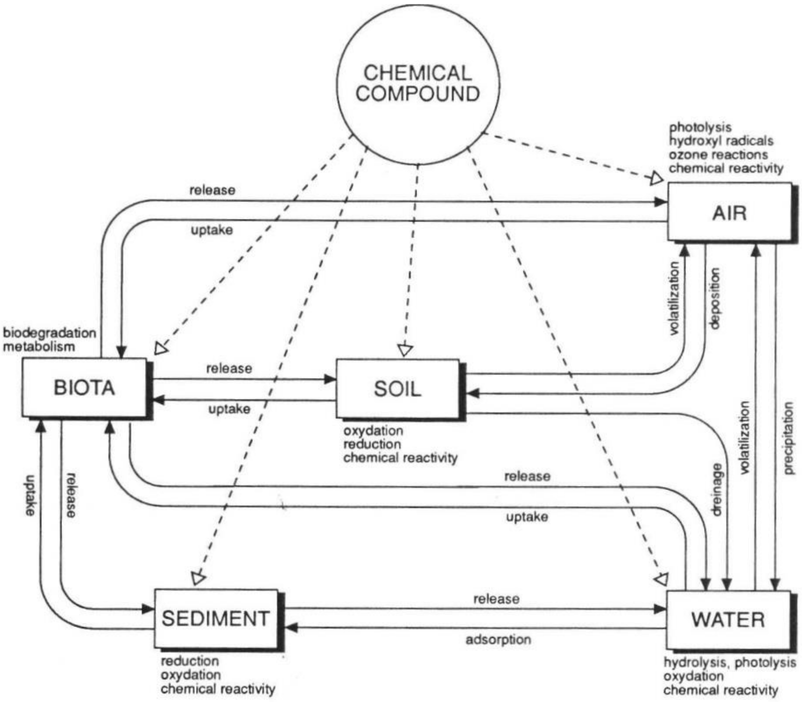
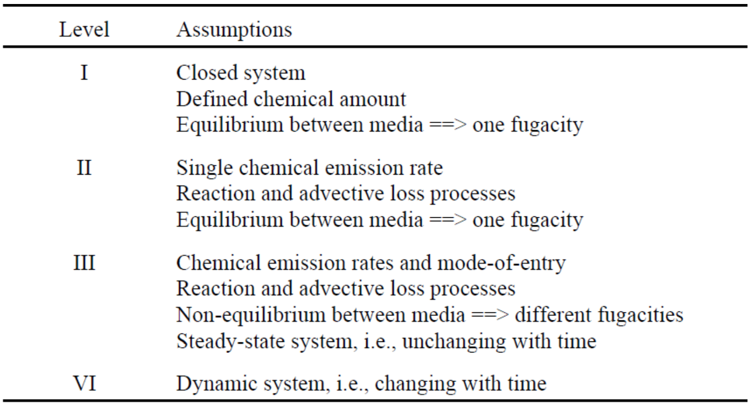


Fig. 13. Scheme of the different bulk media compartments, as well as the main transport, transformation processes and bioaccumulation for chemical compounds in the environmental matrices, and process recorded in each one. Source: Vighi and Calamari, 1993.



Level	Assumptions
I	Closed system Defined chemical amount Equilibrium between media ==> one fugacity
II	Single chemical emission rate Reaction and advective loss processes Equilibrium between media ==> one fugacity
III	Chemical emission rates and mode-of-entry Reaction and advective loss processes Non-equilibrium between media ==> different fugacities Steady-state system, i.e., unchanging with time
VI	Dynamic system, i.e., changing with time

Fig. 14. Summary of fugacity levels in multimedia models described by Mackay, 1991.

There are also other kinds of models with a higher complexity level, so called chemistry transport models (CTMs). CTMs are models capable of combine chemical processes (such as deposition, and transformations) with meteorological factors (as wind speed and direction, turbulence, radiation, clouds, and precipitation) as key elements when the environmental fate of pollutants is evaluated. CTMs assumed that the meteorology, as clouds and precipitation strongly influence chemical transformation and removal processes, and localized changes in the wind or turbulence fields continuously affect the chemical transport. Likewise, CTMs consider that chemistry can also affect the meteorology, for instance, through its effect on the radiation budget, as well as the interaction of aerosols with cloud condensation nuclei (CCN) (Grell et al., 2005). In this sense, CTMs provides a more reliable estimates of contaminants concentrations in the different environmental matrices (SVOCs concentration in air, deposition in soils or vegetation, etc.), as well as a more comprehensive insight on their behaviour, geographical and temporal distribution (simulations both short- long- temporal series) (Ratola and Jiménez-Guerrero, 2017). Furthermore, due the high computational level associated at this models, CTMs are capable to simulate the meteorological conditions associated at climate change scenarios, so they could estimate the future concentrations and distribution of SVOCs over these new conditions.

Among the diferent CTMs, the Weather Research and Forecasting (WRF) + coupled with CHIMERE (the setup used in this thesis) model is one of the most used (Fig. 15). WRF is a numerical weather prediction (NWP) and atmospheric simulation system designed as a regional model for the understanding and prediction of mesoscale weather, capable of operating at high resolutions (e.g. 50 km for Europe) (Salzmann et al., 2007; Skamarock et al., 2008). In case of CHIMERE, is an Eulerian off-line CTM that includes parameterisations to simulate reasonable pollutant concentrations over local to continental domains (from 1 km to 1 degree resolution), remaining the computationally efficient for forecast applications (Menut et al., 2013); where the key processes affecting the chemical concentrations are emissions, transport (advection and mixing), chemistry and deposition.

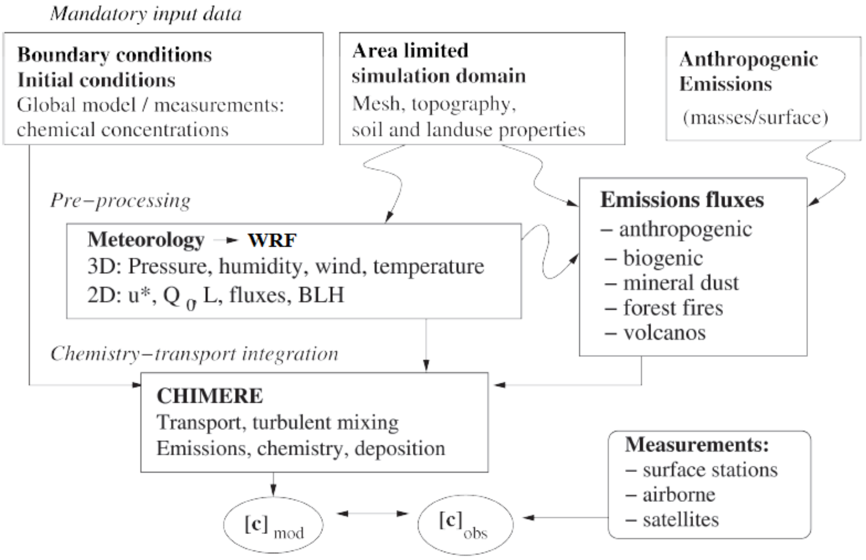


Fig. 15. General principle of a chemistry transport model such as WFR+CHIMERE. In the box "Meteorology", u* stands for the friction velocity, Q_0 the surface sensible heat flux, L the Monin–Obukhov length and BLH the boundary layer height. c_{mod} and c_{obs} are the modelled and the observed chemical concentrations fields, respectively. Source: modified from Menut et al., 2013.

HYPOTHESIS & OBJECTIVES

HYPOTHESIS AND OBJECTIVES

Located in NE of Spain, Tarragona County is home of one of the largest chemical and petrochemical complexes in Southern Europe. The industrial activities began during the 1960s and the complex is composed by a total of 33 companies, including a big oil refinery, as well as a number of chemical and petrochemical industries are currently operating. In addition, the zone is crossed by an important highway and several roads, which support an intense traffic. Furthermore, an important seasonal activity is generated, increasing their population during the summer (Nadal et al., 2004, 2007, 2011). For this reason, since 2002, a large multi-compartmental environmental monitoring program has been carried out. Although the multi-compartmental environmental monitoring program include a wide variety of compounds (toxic metals, dibenzo-*p*-dioxins (PCDD/Fs), polychlorinated naphthalenes (PCNs), PCBs, PAHs), it is necessary to continue this program expanding the range of compounds under study, e.g including emerging contaminants; considering other kind of matrices; as well as improving environmental sampling and analytical techniques. On the other hand, is also necessary to predict the future concentrations of these compounds, since the changing environmental conditions (variations in temperature, rainfall and solar radiation) can generate compounds more toxic than the parental ones or affect at their transport and final fate.

The **main objective** of this thesis is to determine the environmental levels of PAHs and other SVOCs in Tarragona County, combining monitoring and modelling tools as a crucial step in their control in this potentially high impacted area.

As **specific objectives** are:

- To determine the monitoring approaches necessary for SVOCs environmental determination by means of passive sampling techniques, such as passive air samplers with polyurethane foam (PUF-PAS) or lichen transplants.

- To improve analytical procedures for SVOCs determination using “green” alternatives such as QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) methodology.

- To use the modelling approaches (MUM-Fate model and WRF+CHIMERE model) as a combined tools of PAHs environmental monitoring.

CHAPTER 1: Environmental levels of PAHs and others SVOCs in Tarragona County, Spain: monitoring approaches.

In this chapter:

SHORT COMMUNICATION 1:

Domínguez-Morueco, N., Vilavert, L., Schuhmacher, M., Domingo, J.L., Nadal, M., 2014. **Passive air sampling of PAHs at a local scale: Preliminary results in Tarragona county, Spain.** Organohalogen Compounds. Vol. 76, 384-387.

SHORT COMMUNICATION 2:

Domínguez-Morueco, N., Ratola, N., Ramos, S., Sierra, J., Schuhmacher, M., Domingo, J.L., Nadal, M., 2016a**. Multi-component determination of semi-volatile organic compounds in Tarragona County, Spain.** Organohalogen Compounds Vol. 78, 228-232.

ARTICLE 1:

Domínguez-Morueco, N., Augusto, S., Trabalón, L., Pocurull, E., Borrull, F., Schuhmacher, M., Domingo, J.L., Nadal, M., 2017. **Monitoring PAHs in the petrochemical area of Tarragona County, Spain: comparing passive air samplers with lichen transplants.** Environ. Sci. Pollut. Res. 24(13), 11890–11900.

SHORT COMMUNICATION 1: PASSIVE AIR SAMPLING OF PAHs AT LOCAL SCALE: PRELIMINARY RESULTS IN TARRAGONA COUNTY, SPAIN.

Organohalogen Compounds (2014) 76: 384-387.

1. INTRODUCTION

The need to monitor the occurrence of contaminants in the environment has led to the development of a large range of methods and devices for sampling (Zabiegała et al., 2010). Passive air samplers (PAS) have become a viable alternative to commonly used active air sampling equipment, since those devices are cheaper, smaller, simpler to handle, and they do not require electricity and maintenance. These characteristics assist the deployment in remote areas and the simultaneous collection of samples at different locations and/or scales (Pozo et al., 2004, 2006; Bohlin et al., 2008; Zabiegala et al., 2010; Estellano et al., 2012; Vilavert et al., 2013, 2014). PAS are based on the theory of physical advection and diffusion to capture the compounds (Wang et al., 2012). Although different designs have been developed according to the adsorbent material8, polyurethane foam (PUF) is the mostly used design for air monitoring worldwide (Bohlin et al., 2008; Chaemfa et al., 2014). PAS were the preferred samplers by the United Nations Environment Program for global air monitoring (Li et al., 2011), while other initiatives such as the Global Atmospheric Passive Sampling (GAPS) (Pozo et al., 2006) are also based on the same approach. The GAPS is a worldwide ambitious monitoring program for investigating the spatial and temporal trends of persistent organic pollutants (POPs) on a global-scale (Pozo et al., 2006, 2009; Lee et al., 2007; Genualdi et a., 2010; Koblizkova et al., 2012a, b). However, few international efforts have been conducted in order to study the suitability of PUF-PAS for monitoring POPs at a local scale (Vilabert et al., 2012,2013).

POPs are transboundary chemicals with long-range atmospheric transport (LRAT), therefore capable to reach remote and sensitive regions of the planet, away from the origin source(Pozo et al., 2006; Genualdi et al., 2010; Estellano et al., 2012). According to the UNECE Protocol, POPs include a wide variety of compounds, including some polycyclic aromatic hydrocarbons (PAHs) such as benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, and indeno*(1,2,3-c,d)*pyrene. In recent years, the toxic character of these compounds has been recognized (Estellano et al., 2012), and the United States Environment Protection Agency (USEPA) has developed a list of 16 priority PAHs (Bohlin et al., 2010; Wang et al., 2010;Choi et al., 2012). Furthermore, some PAHs have been classified as carcinogens or possible carcinogens to humans by the International Agency for Research on Cancer (IARC), being benzo(*a*)pyrene and dibenzo(*a,h*)anthracene two of the most relevant (Bohlin et al., 2010; Khairy et al., 2012).

PAHs can be released by natural (e.g., volcanoes, forests fires and grassland combustion) or anthropogenic sources (e.g., oil refineries, power generation, domestic heating and traffic) (Jaward et al., 2004; Wang et al., 2010; Khairy et al., 2012). Therefore, the environmental PAH burdens are expected to be different depending on the proximity of emission sources. This preliminary investigation was aimed at studying the viability of PAS-PUF for sampling PAHs at local scale, prior to the creation of a PAH monitoring network. Air concentrations of 16 priority PAHs were determined in different areas of Tarragona County, Spain, using PAS-PUF, and resulting data were compared with international studies.

2. MATERIAL AND METHODS

PUFs (diameter: 14 cm; thickness: 1.2 cm; surface area: 360 cm2; density: 0.035g cm-3) were purchased to Newterra (Beamsville, ON, Canada). Prior to deployment, PUFs were pre-cleaned by Soxhlet extraction for 24 hours by using dichloromethane (DCM) (99.9% purity, Merck, Darmstadt, Germany) (Bohlin et al., 2008). Subsequently, they were dried in a vacuum desiccator, and stored in brown glass jars which were pre-cleaned with DCM and sealed with high density polyethylene caps (Bohlin et al., 2008). Once in the field, PUFs were inserted between two aluminum chambers to protect them from the external air, precipitation and light (Bartkow et al., 2006; Chaemfa et al., 2008; Choi et al., 2012).

PUF-PAS were deployed at three sampling points in Tarragona County for 2 months (October - December of 2013). Sampling sites were Roda de Berà, an urban/residential area, Vilallonga del Camp, a village under the potential influence of the emissions of a petrochemical complex (industrial area), and ETSQ University Campus, a presumably unpolluted or slightly polluted site (rural area). The geographical distribution of sampling sites is depicted in Figure 1.

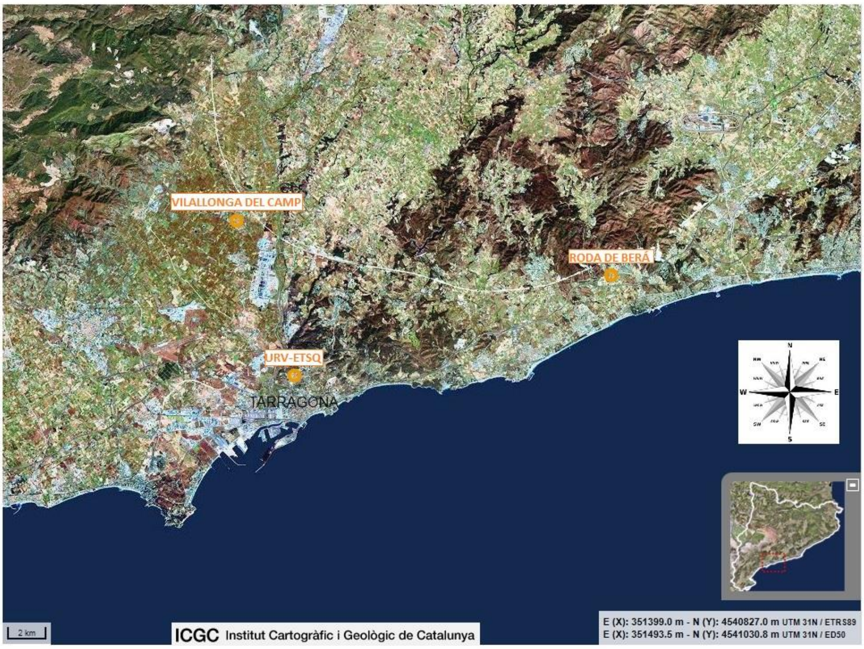


Fig. 1. Location of sampling points in Tarragona County (Spain) where PUF-PAS were deployed.

The determination of PAHs was based on the CARB Method 429. Appropriate isotope-labeled extraction standards (e.g., deuterated PAHs) were added to each sample in order to control the whole sample preparation process. The sample was extracted using dichloromethane as solvent. The extract was concentrated and analyzed by HRGC/HRMS using Agilent GCs (5890 and 6890) coupled to Waters Autospec Ultima HRMS systems with selected ion recording at resolution 8000. Samples were injected onto non-polar DB5MS-type GC columns.

The quantification was carried out by using the corresponding isotope-labeled compounds as internal standards. Additional QA/QC measures consisted on analyzing blanks and recovery standards inserted in every batch of samples. Recovery percentages differed according to individual PAHs, ranging 89-123 %, 99-134 % and 108-141 % in the urban, industrial and rural areas, respectively. For those hydrocarbons presenting levels below the limit of detection (LOD), a concentration equal to one-half of that limit was assumed.

3. RESULTS AND DISCUSSION

Airborne concentrations of PAHs as well as the sum of 16 US EPA priority PAHs (Σ_{16}PAHs) in different areas of Tarragona County (Catalonia, Spain), are summarized in Table 1. Σ_{16}PAHs concentrations ranged from 17.30 to 66.62 ng m^{-3} (or from 670 to 7530 ng/PUF, rural and industrial areas, respectively). Acenaphthylene and benzo(*a*)anthracene were not detected in any sample, while acenaphthene and anthracene only showed levels above the LOD in the industrial area. None of the 16 PAHs were detected in the rural zone, excepting naphthalene and fluorene, showing concentrations very close to their respective detection limit (4.47 and 1.08 ng m^{-3}, respectively). Therefore, if calculated in a lower-bound scenario (this is, assuming a level of zero for undetected compounds), the Σ_{16}PAHs concentration in the rural site would be only 5.55 ng m^{-3}. Anyhow, these levels are very similar to the Σ_{14}PAHs concentrations in air samples collected in winter of 2010 in different regions of Australia (Kennedy et al., 2010), where values ranged from 1.99 to 60.06 ng m^{-3}. Furthermore, they are very similar to those previously reported in a number of countries (Motelay-Massei et al., 2005; Choi et al., 2012; Estellano et al., 2014) , such as Canada (range: 8.33-18.46 ng m^{-3}), South Korea (mean: 42.6 ng m-3) and Bolivia (range: 15.67- 36.03 ng m^{-3}).

The highest Σ_{16}PAHs concentrations were detected in Vilallonga del Camp sampling point, located relatively nearly a big oil refinery and well under the potential influence of petrochemical emissions. This fact is in agreement with the results showed in other monitoring studies, where the highest values were also associated to the presence of chemical industries (Pozo et al., 2012).

Table 1. PUF-derived air concentrations (in ng m^{-3}) for PAHs in 3 areas of Tarragona County in 2013.

	Area			Sampled volume^{a}	Sampling rate^{b}
	Urban	Industrial	Rural		
Naphthalene	5.93	10.69	4.47	102.92	1.66
Acenaphthylene	<1.25	<1.25	<1.25	159.96	2.58
Acenaphthene	<2.43	3.64	<2.43	82.46	1.33
Fluorene	2.00	3.44	1.08	194.68	3.14
Phenanthrene	16.40	28.25	<9.11	109.74	1.77
Anthracene	<2.21	2.87	<2.21	90.52	1.46
Fluoranthene	3.98	9.72	<3.89	102.92	1.66
Pyrene	2.70	5.14	<2.57	155.62	2.51
Benzo[*a*]anthracene	<0.81	<0.81	<0.81	123.38	1.99
Chrysene	0.60	0.84	<0.60	166.16	2.68
Benzo[*b*]fluoranthene	0.59	0.44	<0.14	141.36	2.28
Benzo[*k*]fluoranthene	0.09	<0.07	<0.07	279.00	4.50
Benzo[*a*]pyrene	0.33	<0.13	<0.13	150.66	2.43
Indeno[123-*cd*]pyrene	0.28	0.14	<0.11	190.34	3.07
Dibenzo[*ah*]Anthracene	0.24	0.11	<0.10	203.98	3.29
Bengo[*ghi*]perylene	0.41	0.22	<0.09	229.40	3.70
Σ_{16}PAHs	36.91	66.62	17.30	-	-

^{a}In m^{3}; ^{b}Sampling rates, according to He and Balasubramanian, are given in m^{3} day^{-1}.

Air Σ_{16}PAHs concentrations showed a strong industrial>urban>rural gradient, showing the industrial area 2- and 4-times higher PAH levels than urban and rural zones, respectively. This pattern has been also found in other international studies (Motelay-Massei et al., 2005; Pozo et al., 2012).

The PAH profile was dominated by 2-4 ringed PAHs, which accounted for more than 90% of the Σ_{16}PAH concentrations (Fig. 2). Phenanthrene was the predominant hydrocarbon, with a mean percentage of 35 % of the total (range: 26-44 %), while high contributions were also noted for naphthalene and fluoranthene (21 % and 13 %, respectively). The profile observed in this study was consistent with the results reported by other authors (Bohlin et al., 2008; Choi et al., 2012; Pozo et al., 2012), who showed a predominance of 3-4 ringed PAHs. This group may reach contributions of up to 90 %, being phenanthrene the most contributive compound to the total PAH concentration. PAHs with 2-4 benzene rings are compounds with low/intermediate molecular weight and high volatility. They are predominantly present in gas phase, and maybe therefore more easily captured by the PUF-PAS (Choi et al., 2012; Estellano et al., 2012; Pozo et al., 2012). In contrast, PAHs with 5-6 benzene rings have a higher molecular weight and lower volatility, tending to remain in particulate phase (Choi et al., 2012; Estellano et al., 2012; Pozo et al., 2012). In this study, a higher concentration of higher molecular weight PAHs was observed in urban and industrial areas, more potentially affected by traffic and petrochemical emissions, respectively.

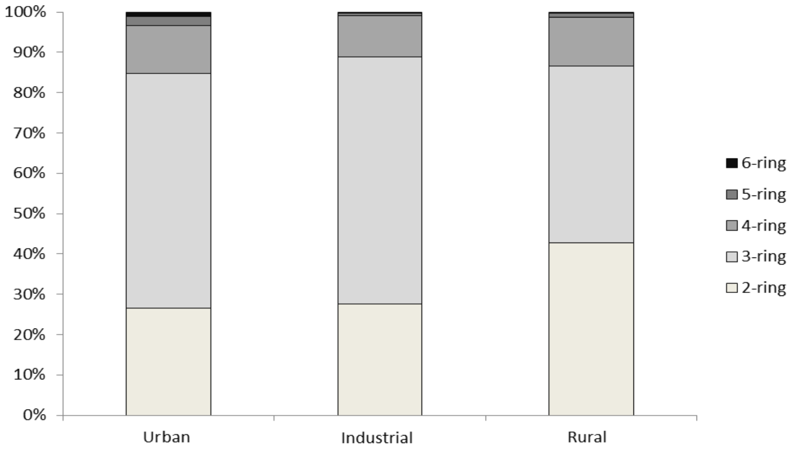


Fig. 2. PAH profile in air samples collected in Tarragona County using PUF-PAS.

Despite being this is the first approach to analyze airborne PAHs in Tarragona County by using PUF-PAS, previous research based on active air samplers has been already conducted in the same area of study. Data on PAHs in air coming from passive and active air sampling methods are very comparable, when monitoring campaigns are conducted in the same season. Nadal et al. (2011) reported that the mean Σ_{16}PAH concentration in 4 different areas of Tarragona County ranged 18.08 to 27.45 ng m^{-3}, while Ramírez et al. (2011) found Σ_{16}PAH levels ranging from 10.4 to 59.5 ng m^{-3} respectively, in the same 3 kinds of area here considered (industrial, urban, and rural). In summary, these results confirm that PUF-PAS may be a good option for PAH monitoring at local scale. The next step will be to design and deploy a PUF-PAS based monitoring network for the periodical assessment of PAHs in air of Tarragona County as a complement to existing data on PAHs in soil and vegetation (Nadal et al., 2009, 2011).

Acknowledgments

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SHORT COMMUNICATION 2: MULTI-COMPONENT DETERMINATION OF ATMOSPHERIC SEMI-VOLATILE ORGANIC COMPOUNDS IN TARRAGONA COUNTY, CATALONIA, SPAIN.

Organohalogen Compounds (2016) 78: 228–232.

1. INTRODUCTION

Semi-volatile organic compounds (SVOCs) are chemicals characterized by their bio-accumulative potential, environmental persistence and toxic effects in humans and wildlife. These properties make SVOCs transboundary chemicals via long-range atmospheric transport (LRAT), capable to reach remote and sensitive regions, away from the emission sources (Pozo et al., 2006; Genualdi et al., 2010; Zabiegala et al., 2010; Estellano et al., 2012; Vilavert et al., 2013, 2014). SVOCs include a wide variety of compounds, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and brominated flame retardants (BFRs), whose environmental analysis is a crucial step in their global control (Silva et al., 2015).

The need for SVOCs monitoring has led to the development of a wide range of sampling devices and analytical methods. However, some of these are time-consuming and/or use large amounts of organic solvents, with potential environmental problems and high economic costs (Homem et al., 2013; Silva et al., 2015). For this reason, the implementation of alternative sampling and analytical methodologies is an essential step in atmospheric monitoring. Passive sampling can provide a first approximation of SVOCs concentrations in the environment, involving low maintenance and allowing sampling in remote or poorly accessible areas (Vilavert et al., 2013, 2014 Domínguez-Morueco et al., 2017). Passive air samplers (PAS), which are based on the theory of physical advection and diffusion (Wang et al., 2012), are commonly used (Nadal et al., 2009, 2011; Ratola et al., 2006, 2016).

Moreover, it is also important to develop analytical methods covering the detection of a large number of environmental pollutants. Very recently, Silva et al.8 developed a multi-component method to simultaneously extract 5 classes of SVOCs (PAHs, PCBs, OCPs, BFRs and synthetic musk fragrances (SMs)) from one sample, being validated for the analysis of pine needles.

This study was aimed at estimating the levels SVOCs concentrations in Tarragona County (Catalonia, Spain), where one of the most important chemical/petrochemical complex in Southern Europe is located. Passive samplers, including polyurethane foam disks (PUFs) were employed. Subsequently, the multi-component protocol developed by Silva et al. (2015) was used to quantify the content of SVOCs in each sample. In this abstract, preliminary results on the analysis of PUFs are detailed.

2. MATERIAL AND METHODS

PAS with PUFs (Newterra, Beamsville, ON, Canada) were used for air monitoring. Prior to their deployment, PUF-disks were pre-cleaned by Soxhlet extraction for 24 hours with dichloromethane (DCM) (bohlin et al., 2008). Then, they were dried in a vacuum desiccator, and stored in DCM-cleaned brown glass jars(Bohlin et al., 2008).

Eight PAS containing PUF-disks were deployed for a period of 2 months (November 2014- January 2015) at several areas of Tarragona County (Fig. 1), each one characterized by the presence of different potential emission sources. The distribution of the sampling sites was as follows: two samples under the potential influence of petrochemical emissions, including a big oil refinery (Puigdelfí=P1 and Constantí=P2); two samples close to chemical industries (La Laboral=C3 and La Canonja=C4); two samples in urban areas (Tarragona=U5 and Vila-seca=U6); and two samples in background sites, at least 30 km away from the area of influence of all the suspected sources of contamination (Cambrils=B7 and Torredembarra= B8).

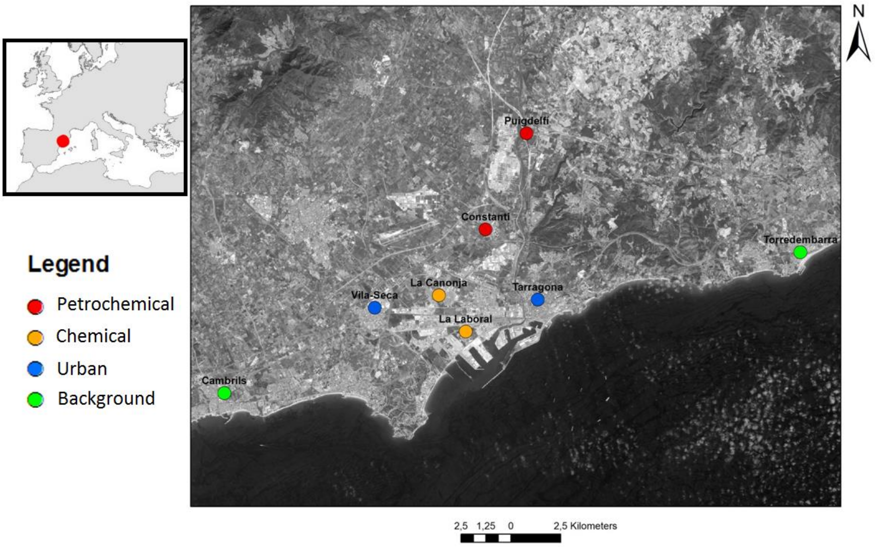

Fig. 1. Location of PUF-disks sampling points in Tarragona County (Catalonia, Spain).

Air levels of five classes of SVOCs (PAHs, PCBs, hexachlorobenzene (HCB), BFRs and SMs) were simultaneously quantified in each one of the PAS. For that purpose, the innovative multi-component protocol developed by Silva et al. (2015) was used. Air extracts were obtained by soxhlet method using 250 mL of hexane:dichloromethane (1:1) as solvent, followed by a clean-up consisted in a solid phase extraction (SPE) and gel permeation chromatography (GPC) using gravity-fed glass columns.

The analisys was carried out by gas chromatography-mass spectrometry (GC-MS), with an ion trap mass spectrometer operated in electron ionization mode (70 eV). Two Varian (Palo Alto, CA, USA) ion trap GC-MS equipments, versions 4000 and 240, were used for PAHs and SMs, and for PCBs, BFRs and HCB, respectively. Identification of target compounds was done by comparing retention times and mass spectra to those of standards and system control, data acquisition and processing was done by Varian MS workstation v. 6.9.3 software. Retention times and used target ions for both employed GC-MS equipments were similar to Silva et al. (2015).

3. RESULTS AND DISCUSSION

The total amounts of SVOCs accumulated in air samples from different areas of Tarragona County (Catalonia, Spain) are depicted in Figure 2, and in Table S1 and S2 Annex 2 . PAHs levels ranged from 2098 to 4333 ng/PUF (Fig. 2A), being in agreement with other surveys previously conducted in this area (Domínguez-Morueco et al., 2014, 2017). In 2013, PAHs amounts in PAS deployed for 2 months ranged from 670 to 7530 ng/PUF, while in 2014, minimum and maximum levels were 1363 and 7866 ng/PUF, respectively. The highest concentrations of PAHs were found in the petrochemical area (max: 4333 ng/PUF), more specifically in the point P1, corresponding to the neighborhood of Puigdelfí (village of Perafort). This finding agrees with the results of the 2014 campaign (Domínguez-Morueco et al., 2017), when Puigdelfí also showed the highest incidence of PAHs (7866 ng/PUF). In addition, the present value is relatively close to that reported in the 2013 campaign for the village of Vilallonga del Camp (7530 ng/PUF) (Domínguez-Morueco et al., 2014), a nearby town. This sampling point is located in the vicinity of a big oil refinery, thus under the potential influence of petrochemical emissions. This is confirmed by a general increase of PAHs associated to the presence of chemical industries reported by other international studies (Pozo et al., 2012).

Regarding PCBs, the values detected in Tarragona County ranged from 2.88 to 120 ng/PUF (Fig. 2B). In contrast to PAHs, the highest concentrations of PCBs were found in the chemical zone (max: 121 ng/PUF), more specifically in point C3 (La Laboral). These chemicals were extensively used worldwide in electric industries for their chemical stability (Breivik et al., 2007). Although their production was banned in most countries, the current value could be due to the presence of a chlor-alkali plant and various electrical substations in the vicinity, as well as the legacy of their use in the past.

Finally, similar concentrations of SMs (0.38 to 13.4 ng/PUF), BFRs (1.30 to 2.80 ng/PUF) and HCB (4.65 to 16.4 ng/PUF) were observed irrespective of the sampling area (Fig. 2C, D and E). This would be probably due to the fact that these compounds are mainly associated to a wide variety of products worldwide used.

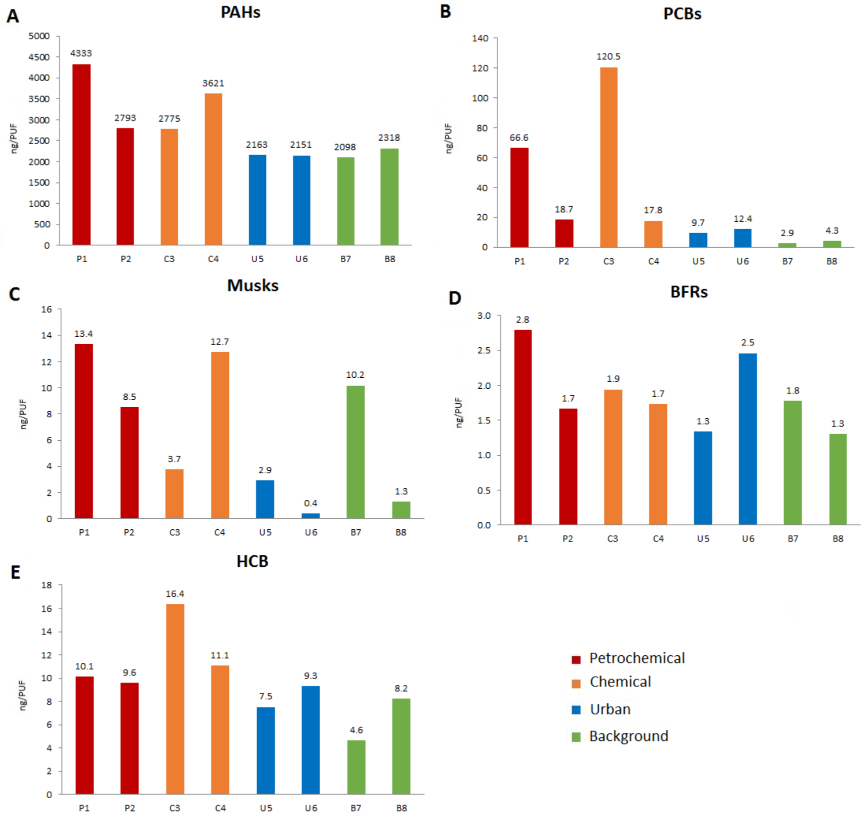

Fig. 2. SVOCs levels in air samples according to the sampling area.

In summary, the present results provide a comprehensive approach to the air levels of SVOCs in Tarragona County, by using PUF-PAS and taking advantage of multi-component protocols.

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ARTICLE 1: MONITORING PAHs IN THE PETROCHEMICAL AREA OF TARRAGONA COUNTY, SPAIN: COMPARING PASSIVE AIR SAMPLERS WITH LICHEN TRANSPLANTS.

Environmental Science and Pollution Research (2017) 24:11890–11900.

ABSTRACT

The levels of 16 polycyclic aromatic hydrocarbons (PAHs) were determined in 8 passive air samples (PAS) and 6 lichen transplants (Ramalina fastigiata) deployed for a period of 2 months in different zones of Tarragona County (Catalonia, Spain), an area with an important number of chemical and petrochemical industries. The accumulated amount of the sum of the 16 PAHs ranged between 1363 to 7866 ng/sample in air samples. The highest concentration was found in the neighborhood of Puigdelfí (village of Perafort), in the vicinity of a big oil refinery and well under the potential influence of the petrochemical emissions. In lichen samples, the sum of the 16 PAHs ranged between 247 and 841 ng/g (dry/weight), being the greatest value also observed in Puigdelfí. Data on the levels and profiles of PAHs in both passive monitoring methods were compared. A significant positive linear correlation was found between the concentrations of low molecular weight PAHs in lichens and the amounts accumulated in passive air samples (R=0.827, P<0.05), being especially significant the correlation of 4-ring PAHs (R=0.941, P<0.05). These results strongly suggest that lichens can be used to monitor gas-phase PAHs, providing data that can be quantitatively translated into equivalents for air.

Keywords: Polycyclic aromatic hydrocarbons (PAHs) · Passive air sampling (PAS) · Polyurethane foams (PUF) · Lichens samples · Biomonitoring · Tarragona, Spain.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings (Jaward et al., 2004; Nadal et al., 2004a; Wang et al., 2010; Xia et al., 2013). PAHs are products of incomplete combustion processes of natural (e.g., volcanoes, forests fires, and grassland combustion) or anthropogenic origin (e.g., incineration, power generation, domestic heating, vehicles emissions, and industrial activities) (Jaward et al., 2004; Wang et al., 2010; Estellano et al., 2012). Therefore, the environmental PAH burdens are expected to be different depending on the proximity of emission sources. In recent years, the toxic character of PAHs has been recognized (Estellano et al., 2012). Hence, the United States Environmental Protection Agency (USEPA) developed a list of 16 priority PAHs (Bohlin et al., 2010; Wang et al., 2010; Choi et al., 2012; Harner et al., 2013), 7 of them being classified as probable human carcinogens under the B2 group (Leung et al. 2015). Other agencies, such as the International Agency for Research on Cancer (IARC), have also classified some PAHs as carcinogens or possible carcinogens to humans. Among them, benzo(*a*)pyrene (BaP) has been identified as one of the most toxic (Bohlin et al., 2010; Xia et al., 2013).

Petrochemical industries have been pointed out as one of the most important anthropogenic sources of PAHs (Nadal et al., 2011). One of the largest chemical and petrochemical industrial complexes in Southern Europe is located in Tarragona County (Catalonia, Spain) (Nadal et al., 2004a, 2009). This area is composed of a total of 33 companies, including a big oil refinery, as well as a number of chemical and petrochemical industries. In addition, the presence of a highway and several roads with heavy traffic has a notable impact on the local environment (Nadal et al. 2004a, b). Since 2002, a large multicompartmental environmental monitoring program has been carried out by analyzing PAHs as well as other chemical pollutants in soil and vegetation samples from different areas of Tarragona County (Nadal et al., 2004a, b, 2007, 2009, 2011; Schuhmacher et al., 2004).

The need to monitor the occurrence of PAHs in air has led to the development of a large range of methods and devices for sampling (Zabiegała et al., 2010). Passive air samplers (PAS) with polyurethane foam (PUF) have become a viable alternative to commonly used active air sampling equipment since those devices are cheaper, smaller, simpler to handle, and they do not require electricity and maintenance (Mari et al., 2008). These characteristics assist the deployment in remote areas and the simultaneous collection of samples at different locations and/or scales (Pozo et al., 2004; Bohlin et al., 2008; Zabiegała et al., 2010; Estellano et al., 2012; Vilavert et al., 2013, 2014).

At the same time, the use of lichens (symbioses of fungi and algae) as bioindicators has proved to be very useful for the evaluation of environmental levels of PAHs (Augusto et al., 2013a; Loppi et al., 2015). Lichens are one of the most used organisms to monitor atmospheric deposition of several pollutants (Augusto et al., 2013a). They are easy to sample, while they allow monitoring of a large number of sampling sites and several pollutants within the same matrix (Augusto et al., 2010). In the past, PAHs accumulated in lichens have been compared with those measured in the particulate-phase of air by using filters from active air samplers (Augusto et al., 2013b). However, a valid comparison between PAHs in lichens and those in the air gas-phase is still missing. Very recently, Loppi et al. (2015) tried to overcome this gap, establishing a correlation between the levels of six PAHs measured in passive air samplers and those analyzed in lichen transplants of *Evernia prunastri*. The correlation between PAHs in lichens and in the gas-phase of air is crucial to optimize the use of lichens to monitor these compounds. Therefore, it is fundamental to understand whether other species of lichens are also related to airborne PAHs and lichens can be broadly applied for environmental monitoring.

The aim of this study was to determine the air levels of 16 PAHs from different areas of Tarragona County, Spain by means of passive sampling devices. Furthermore, the PAH levels and profiles in lichen transplants (*Ramalina fastigiata*) were correlated with those measured in air. Finally, the temporal trends of PAHs in air samples were determined by comparing current data with previously reported results.

2. MATERIAL AND METHODS

2.1. Sampling

A total of eight passive air samplers and eight lichen transplants were deployed for a period of 2 months (November 26, 2014–January 26, 2015) in different areas of Tarragona County, Spain. The distribution of the sampling sites was as follows: two samples were deployed under the potential influence of the petrochemical complex, which includes a big oil refinery (Puigdelfí=P1 and Constantí=P2); two samples close to a zone of chemical industries (La Laboral=C3 and La Canonja=C4); two samples in urban areas (Tarragona=U5 and Vila-Seca=U6); and two samples in background sites, 30 km away from the area of influence of all the suspected sources of contamination (Cambrils=B7 and Torredembarra= B8) (Fig. 1). Sampling sites were located at less than 2 km from the considered pollution sources.

Passive air samplers

PAS containing polyurethane foam (PUF) disks were purchased from Newterra (Beamsville, ON, Canada) (diameter 14 cm; thickness 1.2 cm; surface area 360 cm^2; density 0.035 g cm^{-3}). Prior to use, PUFs were precleaned by Soxhlet extraction for 24 h by using dichloromethane (DCM) (purity 99.5 %, Scharlab, S.L., Sentmenat, Spain). Subsequently, they were dried in a vacuum desiccator, stored in precleaned brown glass jars, and sealed with high density polyethylene caps (Bohlin et al., 2008; Pozo et al. 2009). Once in the field, PUF disks were inserted in the PAS, and those were deployed in each sampling point.

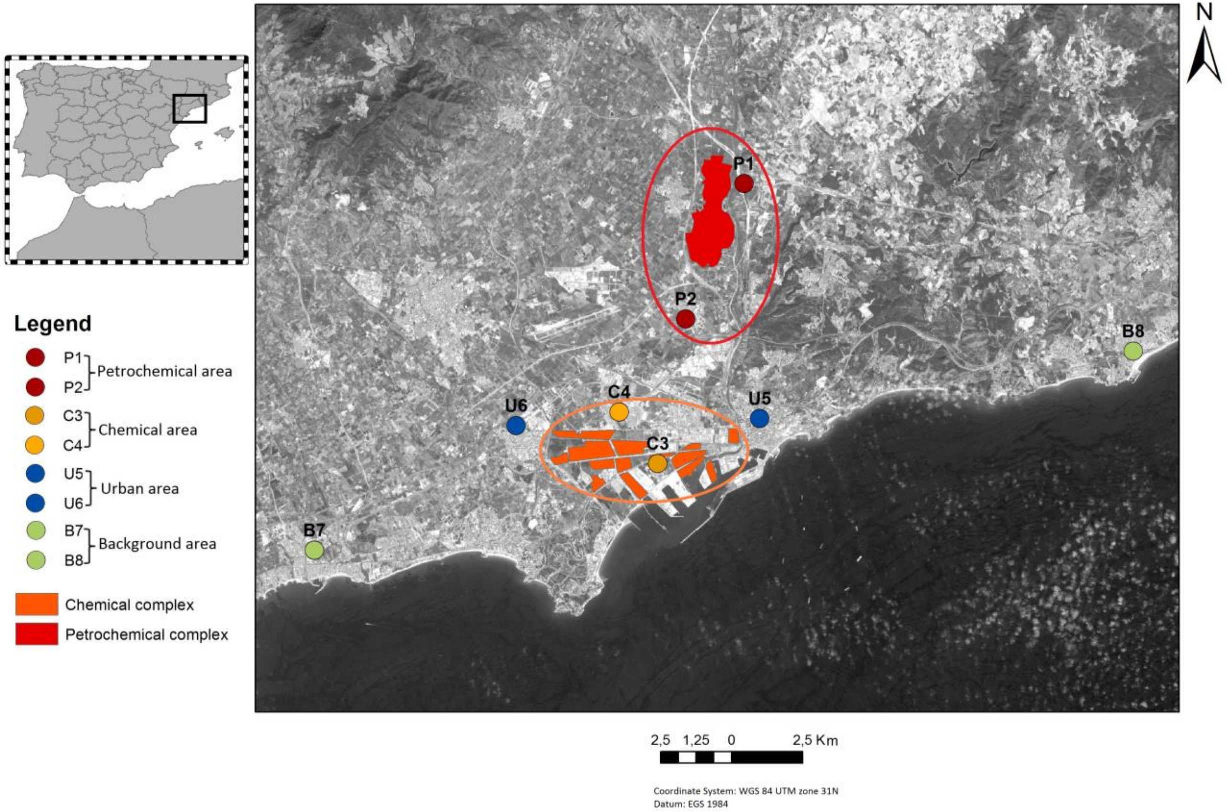

Fig. 1. Sampling area**.**

Lichen transplants

Lichens of the fruticose species *Ramalina fastigiata* (Pers. Ach.) were collected in November 2014 in mountains of L'Albiol (ca. 30 km to the north of the sampling area).

Healthy *R. fastigiata* thalli of about 2–4 cm long were collected from the available phorophytes, notably from pine and oak trees, and transplanted within 48 h to the same eight sampling sites as PAS. Transplants consisted of nylon bags of 15×15 cm filled with approximately 5 g of lichens, which were hung in handrails of monitoring stations or home balconies. After 2 months of exposure, transplants were collected, stored in brown glass bottles, protected from sunlight, and immediately stored at 4 °C. All samples (transplants after exposure and background samples) were analyzed for PAHs.

2.2. Chemical analysis

PAHs in PUFs were extracted using an accelerated solvent extraction (ASE) 200 (DIONEX, Sunnyvale, USA) through loading the sampled filters into 33 mL extraction cells. The solvent used for foams was DCM (99.9 % pure, supplied by Prolabo, VWR Spain). ASE was conducted with a 6-min preheat time, a static time of 6 min, an extraction temperature of 120 °C, an extraction pressure of 1500 psi, two subsequent cycles, a purge time of 120 s, and a flushing volume of 100 %. The extracts obtained were evaporated to about 1 mL using an R-114 rotary evaporator (Büchi, Flawil, Swiss). Before the evaporation step, 400 μL of dimethylformamide was added to prevent loss of analytes. Prior to the chromatographic analysis, internal standards (IS) (d_8-naphtalene, d_{10}-acenaphthene, d_{10}-phenanthrene, d_{12}-chrysene, and d_{12}-perylene) were added, and analytes were again dissolved in 1 mL of DCM.

The 16 USEPA priority PAHs, namely naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(*1,2,3-c,d*)pyrene, dibenzo(*a,h*)anthracene, and benzo(*g,h,i*)perylene, were determined and quantified in the extracts by gas chromatography/mass spectrometry (GC/MS) by means of a QP2010 Ultra System (Shimadzu Corporation, Tokyo, Japan). The chromatographic separation was carried out on a ZB-50 analytical column (50 % phenyldimethylpolysiloxane, 30m × 0.25mm id; 0.25 μm filmthickness) from Micron Phenomenex (Torrance, California, USA). For the analysis, a volume of 1 μL of the sample extract was injected in splitless mode, with a column rate of 1 mL/min. The compounds were quantified by a target ion using internal standard calibration and identified by retention times and qualifier ions. To calculate extraction recoveries, two PUFs were spiked with 20 μL of a 0.1 mg/L standard solution, one before and one after the extraction, being afterward analyzed. In addition, a blank PUF was also analyzed, and the peak signals were subtracted from the above. The extraction recoveries were calculated by comparing the peak area ration (analyte versus IS) of the two analysis, being ranged between 66 and 116 %, for benzo(*k*)fluoranthene and acenaphthylene, respectively (Table S1 Annex 3). The instrumental linear range was between 1, 5, 10, or 20 μg L^{-1} and 1000 or 5000 μg/L, depending on the analyte. In all cases, determination coefficients (r^2) were higher than 0.99 except for indeno(*1,2,3-c,d*) pyrene that was 0.98. The limits of detection (LODs) and the limits of quantitation (LOQs) were estimated from the instrumental signal and taking into account extraction recoveries. For LODs, a signal/noise ratio of three was considered, while LOQs were fixed to the lowest instrumental calibration point. Thus, LODs ranged from 0.3 to 5 ng/PUF, while LOQs ranged from 1 to 20 ng/PUF (Table S1 Annex 3).

PAHs in lichen samples were extracted using the Soxhlet method, as described by Augusto et al. (2010). Approximately 2 g of lichen sample was extracted in a Soxhlet for 24 h with 300 mL of acetonitrile (99.8 % pure, Optigrade supplied by Promochem, Germany). After extraction, the extracts were concentrated by rotary vacuum evaporation and cleaned up in a Florisil column (aolid phase extraction cartridges, Extrabond Florisil 2 g, 12 mL, supplied by Scharlab S.L.) with 30 mL of acetonitrile as eluting solvent.

Then, the extracts were evaporated and concentrated with a gentle stream of purified N_2 to 1 mL. The 16 USEPA priority PAHs in the lichen extracts were also quantified by GC-MS using a gas chromatograph (Hewlett-Packard G1099A) coupled with a mass spectrometer (Agilent MSD5973). An HP-5MS 5 % phenyl methyl siloxane capillary column (30 m, 0.25 mm id, 0.25 µm film thickness) (Agilent 19091S-433) was used for separating the PAHs. For the analysis, a volume of 1 µL of the sample extract was injected in splitless mode, with a column rate of 1.4 mL/min. The masses monitored by the detector were set as follows: from 40 to 600 m/z.

PAHs in lichen samples were quantified by a target ion using internal standard calibration and identified by retention times and qualifier ions. Recoveries were achieved by spiking a portion of lichen with a solution of the 16 USEPA PAHs and with d_{10}-fluorene prior to extraction. Recovery percentages differed according to individual PAHs, ranging between 56 and 151 %. The instrumental linear range was between 0.6, 1 or 5 and 500 µg/L, depending on the analyte. Determination coefficients (r^2) were higher than 0.98, except for naphthalene (r^2=0.82) and acenaphthylene (r^2=0.96). LODs ranged from 0.5 to 5 ng/g, while LOQs ranged from 1 to 20 ng/g (Table S1, Annex 3).

2.3. Data analysis

For the calculations, those PAHs presenting levels below the LOD or LOQ were assumed to have a concentration equal to one half of the LOD or LOQ. Pearson linear correlation coefficients between lichens and air passive samplers were calculated for each PAH ring group, low molecular weight (LMW), and high molecular weight (HMW) PAHs, as well as for the total of the 16 PAHs. Significant correlations were displayed in scatterplots.

3. RESULTS AND DISCUSSION

3.1. Levels of polycyclic aromatic hydrocarbons in air samples

The total amount of the 16 USEPA priority PAHs (Σ_{16}PAHs), as well as that of each individual congener, in different areas of Tarragona County (Catalonia, Spain) measured between November 2014 and January 2015 are summarized in Table 1. Most international studies using passive air samplers translate concentrations measured in PUF into equivalents for air. For that purpose, published calibrations between PAH concentrations measured by active samplers and PAS are generally used (Shoeib and Harner, 2002; Harner et al., 2013). Because calibrations tend to vary to some extent depending on the number of factors, such as wind intensity, rainfall, or temperature, this procedure may envisage results. For this reason, as well as because this study was aimed at establishing the validity of lichen transplants, amounts of PAHs accumulated in the PUFs instead of air equivalent concentrations were used.

Air PAH levels ranged from 1363 to 7866 ng/sample, with a mean value of 3414 ng/sample. These values are consistent with a preliminary survey conducted in this area in winter of 2013 (Domínguez-Morueco et al., 2014), in which PAH levels found in PAS deployed for 2 months ranged from 670 to 7530 ng/sample (Table 2). In addition, these levels are in agreement with other international studies (Table 2). Estellano et al., (2014) found an accumulation of PAHs of 2724–6222 ng/sample at four locations in urban and suburban sites of Puglia region (Italy), while Harner et al., (2013) found a range of 525–6300 ng/sample in the atmosphere of the Alberta oil sands (Canada). Similar levels were also reported by Kennedy et al. (2010) in South Australia (2169–7033 ng/sample). Contrastingly, other authors have found relatively higher amounts of PAHs in a number of countries (e.g., India, Korea, Mexico, and Sweden) (Bohlin et al., 2008; Choi et al., 2012; Cheng et al., 2013). In turn, the studies conducted by Estellano et al., (2012) in the Tuscany region, Italy, or the ones by Bohlin et al., (2008) in Lancaster, UK, reported lower values of PAH by using PAS (Table 2).

A seasonal pattern of PAHs in air was found. Airborne concentrations found in this study, performed in winter (mean temperature 9 °C; range 3–15 °C), were notably higher than PAH amounts observed in summer of 2014 (mean temperature 24 °C) in the same area under study (unpublished data) when levels ranged 2396–4743 ng/sample (Table 2). Seasonal differences have been largely reported in the scientific literature, with higher concentrations of PAHs typically found in cold seasons (Delhomme and Millet, 2012; Jyethi et al., 2014). Furthermore, this pattern also agree with data on PAH concentrations in air obtained by means of active sampling devices in Tarragona County (Ramirez et al., 2011), as well as with other international studies (Kennedy et al., 2010; Wang et al., 2010; Chen et al., 2011; Estellano et al., 2014).

The highest Σ_{16}PAH amount (7866 ng/sample) was observed in the sampling point P1, corresponding to the neighborhood of Puigdelfí (village of Perafort). This value is very similar to that found in the village of Vilallonga del Camp, a very close town, in the 2013 campaign, when a PAH amount of 7530 ng/sample was found (Domínguez-Morueco et al., 2014). Both sampling points are situated in the vicinity of a big oil refinery and well under the potential influence of petrochemical emissions. This fact agrees with the results from other international monitoring studies, in which a certain increase of PAHs have been associated to the presence of chemical industries (Pozo et al., 2012).

Phenanthrene was the predominant hydrocarbon in air, with a mean contribution of 49 % of the total (range 43–54 %). Moreover, relatively high contributions were also noted for acenaphthylene and fluoranthene (mean contribution of 16 and 10 %, respectively). The profile observed in this study was consistent with the results reported by other authors who showed a predominance of 3- and 4-ring PAHs (Bohlin et al., 2008; Choi et al., 2012; Pozo et al., 2012; Estellano et al., 2012, 2014). Since they are predominantly present in the gas-phase, LMW PAHs may be more easily captured by the PAS. In contrast, PAHs with 5–6 benzene rings have a higher molecular weight and lower volatility, tending to remain in the particulate-phase (Choi et al., 2012; Estellano et al., 2012).

Table 1. Individual and total PAH values in samples of passive air (ng/sample) and transplanted lichens (ng/g dw) in different areas of Tarragona County, Spain.

	Petrochemical area				**Chemical area**				**Urban area**				**Background area**			
	P1		**P2**		**C3**		**C4**		**U5**		**U6**		**B7**		**B8**	
	Air	Lichen	Air	Lichen	Air	Lichen	Air	Lichen	Air	Lichen	Air	Lichen	Air	Lichen	Air	Lichen
Naphthalene	117	2	77	-	102	23	205	3	231	7	62	-	63	2	67	40
Acenaphthylene	1411	<LOD	162	-	239	<LOD	1257	<LOD	276	<LOD	599	-	316	<LOD	387	<LOD
Acenaphthene	44	<LOD	28	-	26	<LOD	39	<LOD	31	<LOD	30	-	164	<LOD	30	<LOD
Fluorene	381	25	111	-	151	15	314	26	153	16	249	-	258	30	148	38
Phenanthrene	3864	114	704	-	1006	57	2485	123	900	67	2361	-	866	80	1195	113
Anthracene	117	16	22	-	38	4	98	<LOD	41	<LOD	65	-	39	<LOD	46	5
Fluoranthene	938	120	128	-	201	59	473	115	150	47	517	-	132	57	236	82
Pyrene	647	88	79	-	141	48	372	78	119	38	345	-	89	48	148	67
Benzo(*a*)anthracene	32	61	<LOQ	-	9	10	17	14	<LOQ	9	17	-	5	23	7	30
Chrysene	105	82	14	-	33	21	64	25	13	9	64	-	28	13	27	35
Benzo(*b*+*k*)fluoranthene[a]	55	79	14	-	26	22	24	28	13	19	23	-	<LOQ	49	14	73
Benzo(*a*)pyrene	15	64	<LOD	-	10	12	<LOD	16	<LOD	11	<LOD	-	<LOQ	38	<LOD	47
Indeno(*1,2,3-c,d*)pyrene	43	58	<LOQ	-	<LOQ	9	25	13	<LOD	9	<LOQ	-	11	26	<LOQ	25
Dibenzo(*a,h*)anthracene	57	64	<LOQ	-	13	9	18	13	<LOQ	9	<LOD	-	14	27	<LOQ	39
Benzo(*g,h,i*)perylene	40	67	<LOQ	-	15	9	28	8	<LOQ	6	<LOQ	-	24	7	<LOQ	42
$\sum_{16}$ **PAHs**	7866	841	1363	-	2015	297	5420	461	1947	247	4350	-	2026	402	2326	634

[a] Because of chromatographic analysis, benzo(*b*)fluoranthene and benzo(*k*)fluorantehene were reported together. LOD: Limit of detection. LOQ: Limit of quantification.

Table 2. Summary of PAH levels in PAS (in ng/sample) found in the scientific literature.

	SUM of PAHs (ng/sample)		Number of PAHs	Number of samples	Exposure period (months)	Date of exposure*	Site
	Min	Max					
Current study	1363	7866	16	8	2	Nov 2014-Jan 2015 (winter season)	Tarragona, Spain
Unpublished data	2396	4743	16	8	2	Jun-July 2014 *(summer season)*	Tarragona, Spain
Domínguez-Morueco et al., 2014	670	7530	16	3	2	Oct- Dec 2013 *(winter season)*	Tarragona, Spain
Estellano et al., 2014	2724	6222	10	4	2-5	Jan-Apr 2009 *(winter season)*	Puglia region, Italy
	919	5460				Apr-Jun 2009 *(spring season)*	
	1524	4042				Jun-Sep 2009 *(summer season)*	
	4273	14903				Sep 2009-Feb 2010 *(autumn season)*	
Harner et al., 2013	652	3784	16	18	1	Nov-Dec 2010 *(winter season)*	Alberta, Canada
	525	6300			2	Dec 2010-Feb 2011 *(winter season)*	
Cheng et al., 2013	6480	54800	15	50	1	Dec 2006-Jan 2007(winter season)	Kolkata, Mumbai and Chennai, India
Choi et al., 2012	3396	13120	13	20	≈2	Jan-Feb 20011 (winter season)	Ulsan, Korean Peninsula
Estellano et al., 2012	99	965	10	19	2-5	Apr-July 2008 (spring season)	Tuscany region, Italy
Kennedy et al., 2010	1030	2612	16	8	2	July-Aug 2007 (winter season)	Western Australia, Australia
	177	734				Jan-Feb 2007 (summer season)	
	338	4565		12		July-Aug 2007 (winter season)	Queensland, Australia
	71	2118				Jan-Feb 2007 (summer season)	
	2169	7033		12		July-Aug 2007 (winter season)	South Australia, Australia
	257	1592				Jan-Feb 2007 (summer season)	
Bohlin et al., 2008	5060	14720	13	46	2	Mar-Apr 2006 (winter season)	Mexico City, Mexico
	1242	11040					Gothenburg, Sweden
	-	1104					Lancaster, United Kingdom

*Winter and summer seasons according to the country.

3.2. Levels of polycyclic aromatic hydrocarbons in lichens transplants

Lichens were transplanted from a background site to eight different locations of Tarragona County, grouped into four areas: chemical, petrochemical, urban, and background. Unfortunately, from the eight transplants deployed in the field, two (P2 and U6) were missing at the end of the sampling period. The concentrations of individual PAHs and Σ_{16}PAHs measured in lichen transplants after 2 months of exposure are displayed in Table 1. The analysis allowed the quantitation of 14 out of the 16 USEPA PAHs.

Σ_{14}PAH concentrations in lichens after exposure varied between 247 ng/g (for the urban site U5) and 841 ng/g (for the petrochemical site P1), with an average of 480 ng/g. Preexposed lichens revealed a concentration of 307 ng/g. After being transplanted from a presumably background area to an exposed area, the lichens are expected to become enriched or depleted according to pollutant loads existent in the exposed area. In our case, four transplants became enriched for Σ_{16}PAHs, while the remaining two were depleted.

Although the first studies using lichens to measure PAHs were published some time ago (Carlberg et al., 1983), only until recently lichens have started to be used as routine monitors of PAHs. In the past, most studies were based on the use of native lichens to estimate the environmental concentrations of PAHs (Studabaker et al., 2012). In contrast, only few studies report the use of lichen transplants in areas where native lichens could not be found (Table 3).

PAH concentration ranges obtained in lichens transplanted to the area of Tarragona County are in accordance with other studies (Table 3). In order to establish a valid comparison, the obtained values were divided by the exposure period (number of months). Therefore, the cumulative effect over time is neglected, and comparisons between studies can be conducted with a high degree of reliability. The range of PAH levels in lichens sampled in Tarragona is in the high part of the range in comparison to data from Italy, the country where lichens have been more extensively used for the monitoring of PAHs. In Tarragona County, the maximum PAH concentration was 420 ng/g per month, while the greatest level in Italy was found in an Italian industrial area, reaching 344 ng/g per month (Table 3). Notwithstanding, it must be highlighted that different lichen species were used in each study, the number of quantified PAHs was different, and sampling was performed in different years and seasons. For example, concentrations of Σ_{16}PAHs measured in native lichens (*Parmotrema hypoleucinum*) collected in the southwest of Portugal in a petrochemical industrial area similar to Tarragona were found to decrease by a factor of ten during the summer season (from a maximum of 556 ng/g in winter to a minimum of 58 ng/g during summer) (Augusto et al., 2013b). This strong variation was significantly correlated with climate factors, such as temperature, relative humidity, and wind speed. These parameters, together with the use of different lichen species and the existence of different pollution sources in each study, may contribute to differences in PAH concentrations observed in lichens.

Table 3. Summary of studies using lichen transplants to monitor PAHs. Concentrations of PAHs are reported in ng/g dw per month of exposure.

	∑PAHs (ng/g per month)		**Nº PAHs**	**Nº samples**	**Lichen Species**	**Exposure period (months)**	**Date of exposure**	**Site**
	Min	**Max**						
Current study	124	420	14	6	*Ramalina fastigiata*	2	Nov 2014-Jan 2015	Tarragona, Spain
Loppi et al., 2015	6.3	227	6	7	*Evernia prunastri*	3	Apr-July 2011	Molise, Italy
Protano et al., 2014	159	344	12	11	*Pseudoevernia furfuracea*	4	Aug-Dec 2008	Latium, Italy
Guidotti et al., 2009	11	132	13	6	*Pseudoevernia furfuracea*	3	Feb-May 2005	Viterbo, Italy
Guidotti et al., 2003	5	26	5	4	*Pseudoevernia furfuracea*	5 to 20	Nov 1999-July 2001	Rieti, Italy

3.3. Comparison between passive air sampling and lichen transplants

In order to compare the accumulation of PAHs between PAS and lichens, data for the six sites, where both monitors were existent at the end of the sampling, were used. This means that P2 and U6 samples were excluded from the statistical treatment. ΣPAH values ranged between 247 and 840 ng/g in lichen transplants and between 1947 and 7866 ng/sample in PAS, both deployed at the same sampling sites during the same period (2 months). In both monitors, PAS and lichens, the highest concentration was found at site P1, located near the petrochemical complex, whereas the lowest level was found at U5 (urban area), where the traffic intensity was rather low.

The PAH ring profile found in PAS and lichens at each sampling site is displayed in Fig. 2. Air samples revealed a PAH profile dominated by LMW PAHs, especially 3-ring (accounting for more than 70% of the total concentration) and 4- ring PAHs (contributing for approximately 20 %). In lichen samples, PAH profiles seem to be also dominated by 3- and 4- ring PAHs, together accounting for 60–70 % of the profile. High molecular weight PAHs exist mainly in the particulate phase of air. Thus, they are not likely to be adsorbed by PAS. The high percentage of 3-ring PAHs (>70 %) measured in air samples from Tarragona County is in agreement with other studies performed across Europe (Jaward et al., 2004; Estellano et al., 2012, 2014; Loppi et al., 2015).

Besides intercepting PAHs existent in the gas-phase of air (mainly LMW PAHs), lichens also accumulate PAHs sorbed to the particulate matter (Fig. 2). In previous studies, PAH profiles in lichens (*P. hypoleucinum* and *Xanthoria parietina*) were compared with those found in the particulate phase of air by active air samplers (Augusto et al., 2010, 2013b). Lichens showed higher contributions of LMW PAHs when compared to air, whereas particulate phase of air presented higher contributions of 5- and 6-ring PAHs in comparison to lichens (Augusto et al., 2013b). Regardless of the difference of profiles, a significant correlation was found for PAH concentrations in lichens and in particulate-phase of air (Augusto et al., 2013b).

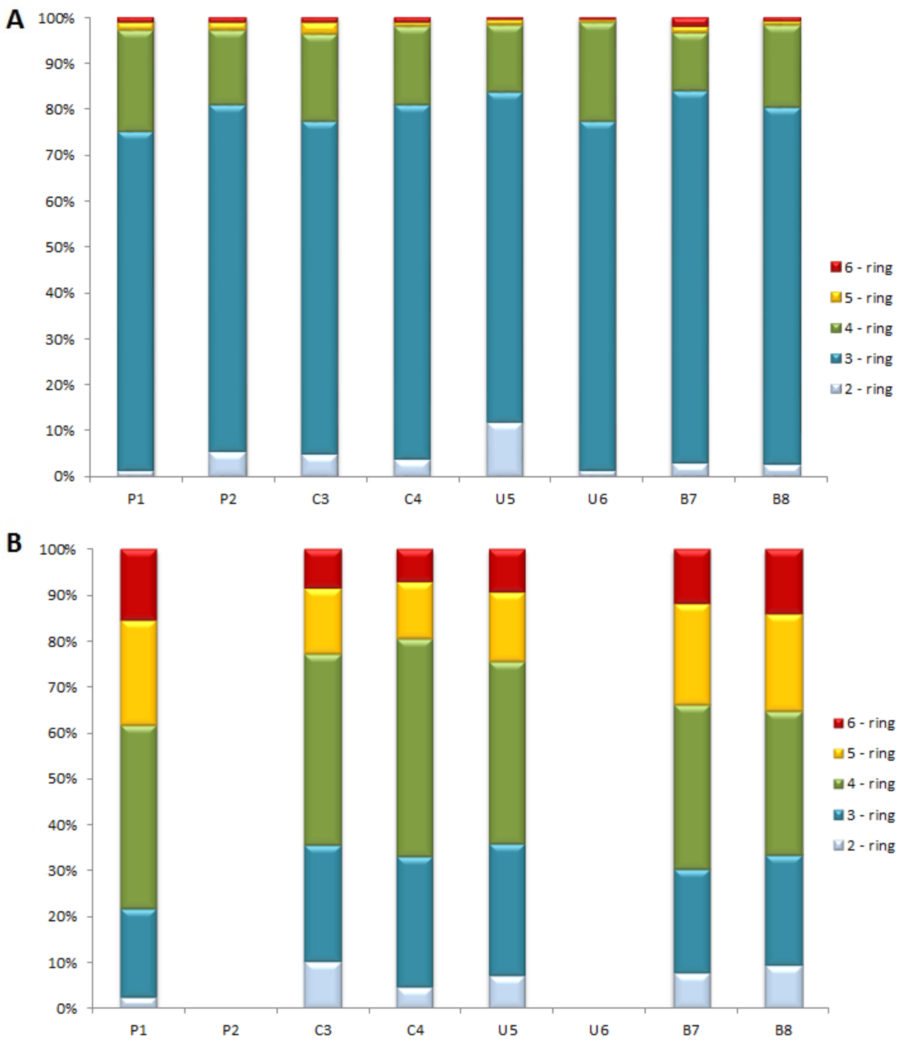

Fig. 2. PAH profiles (in percentage) according to the number of rings in a air and b lichens.

The correlations of PAH concentrations in lichens and the amount accumulated in PAS exposed at the same sampling sites for the same time span are summarized in Table 4.

Table 4. Pearson's coefficients for correlations between PAH concentrations in lichens and in passive air samples (N=6). Results are displayed for group rings (2- to 6-ring PAHs), for low molecular weight (LMW) PAHs, consisting of 2-, 3- and 4-ring PAHs; high molecular weight (HMW) PAHs, consisting of 5- and 6-ring PAHs; and for the sum of the 16 USEPA priority PAHs; Bold: significant P < 0.05.

	Air-Lichens	**p-value**
2-Rings	-0.454	0.366
3-Rings	0.687	0.131
4-Rings	**0.941**	**0.005**
5-Rings	0.622	0.187
6-Rings	0.658	0.155
Σ16PAHs	0.761	0.079
LMW-PAHs	**0.827**	**0.042**
HMW-PAHs	0.676	0.140

A significant positive linear correlation for LMW PAHs was found between PAS and lichens (*R*=0.827, *P*<0.05). This correlation was mainly supported by the significant correlation of the 4-ring PAHs (*R*=0.941, *P*<0.05). Because correlations were performed with a limited amount of data (six pairs), the respective scatterplots were also graphically represented (Fig. 3). A linear relationship of LMW PAHs, and very especially of 4-ring PAHs, between lichens and PAS, was observed.

These results are in agreement with those recently found by Loppi et al., (2015) when comparing PAHs in PAS and lichen transplants exposed for 3 months at the same sampling sites in Italy, despite the differences of the lichen species (*Evernia prunastri* vs. *R. fastigiata*) and the sampling season (spring vs. winter). The accumulation of PAHs by lichens can be influenced by the lichen species, the surface/volume ratio and algae content being important aspects (Augusto et al., 2013a). The increase of surface/volume ratio leads to a higher accumulation of PAHs as more lichen area is exposed to atmospheric pollution.

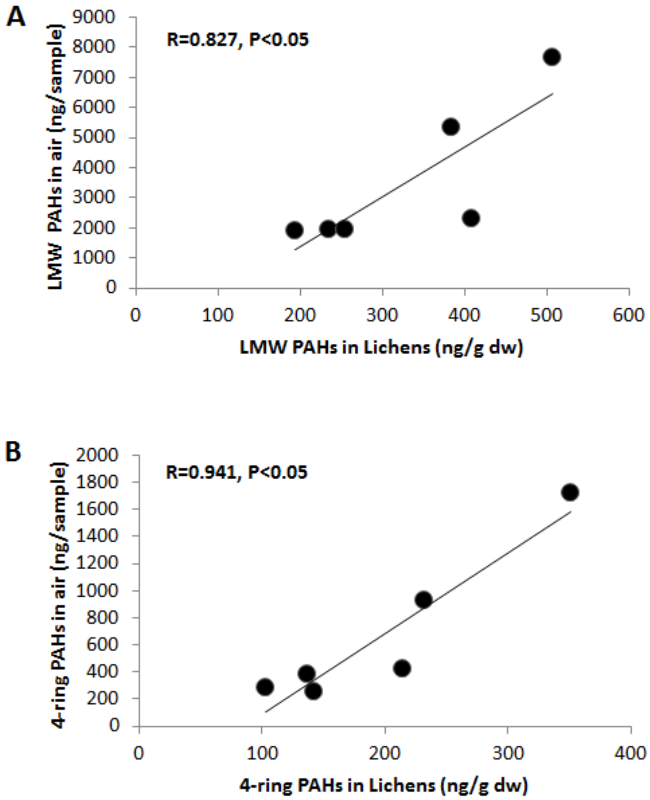

Fig. 3. Correlation between lichens and passive air samples for LMW-PAHs (A) and 4-ring PAHs (B).

The lichen *R. fastigiata* is a fruticose lichen with a branched bushy-type structure with a high surface/volume ratio. In turn, the lichen *E. prunastri* used by Loppi et al. (2015) is a foliose lichen but attached at one point and appearing fruticose. *E. prunastri* has a lower surface/volume ratio than *R. fastigiata*. Very recently, and after tracking gas-phase PAHs inside lichens, Augusto et al. (2015) observed that these compounds easily enter the lichen thallus and accumulate in the algal. Therefore, the amount of algae is likely to influence the amount of gas-phase PAHs accumulated by lichens.

Even though different lichen species were used, our results are in accordance with those reported by Loppi et al. (2015). In both investigations, a linear relationship between PAHs in lichens and PAS was established. However, the linearity of this relationship was smaller than that found by Loppi et al. (2015). It could be due to the fact that the sampling in Spain was performed during winter, where the contribution of particle-associated PAHs is bigger than in summer and spring. As lichens accumulate PAHs as both gas- and particulate phases, during winter, lichens more easily reflect the particulate-phase of PAHs. As the temperature increases, the contribution of gas-phase PAHs in air, as well as in lichens, also increases. Thus, the correlation of PAHs between PAS and lichens is expected to become stronger in summer.

Because levels of each PAH in air and lichens can be strongly influenced by climate factors, similar experimental calibrations of PAHs in PAS and in lichens, covering different seasons and lichen species, must be repeated. During summer, with high temperatures, LMW PAHs tend to exist mainly in the gas-phase of air, whereas in winter, concentrations of HMW PAHs tend to increase due to an intensification of emissions from seasonal sources. As PAS preferentially adsorb compounds in the gas-phase and lichens capture compounds existent in gas- and particulate-phase, differences should be expected when comparing both monitors over different seasons.

4. CONCLUSIONS

The levels of 16 PAHs were determined in PAS and lichen transplants (*Ramalina fastigiata*) deployed for a period of 2 months in different zones of Tarragona County (Catalonia, Spain), an area with an important number of chemical and petrochemical industries. Σ_{16}PAH concentrations in air samples ranged from 1363 to 7866 ng/sample, phenanthrene being the predominant hydrocarbon. The highest concentration was found in the neighborhood of Puigdelfí (village of Perafort) in the vicinity of a big oil refinery and well under the potential influence of petrochemical emissions. The PAH concentrations in lichen transplants varied between 247 and 841 ng/g, with the highest value also reported in the same sampling point as for the PAS. When both monitoring methods were compared, a significant positive linear correlation was found for LMW PAHs. These results strongly suggest that lichens can be used to monitor gas phase PAHs, providing data that can be quantitatively translated into equivalents for air. However, since PAHs in air may be strongly influenced by climate/meteorological factors, it is essential to perform similar experiment covering different seasons and lichen species.

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DISCUSSION CHAPTER 1

It is well known that PAS are worldwide used for air monitoring at global/regional scale, since have been the devices preferred by the United Nations Environment Program for global air monitoring (Bohlin et al., 2008; Chaemfa et al., 2008; Pozo et al., 2009). However, few international studies have been conducted in order to study the suitability of PUF-PAS for SVOCs (POPs) monitoring at a local scale. In chapter 1 of this thesis, the suitability of the use of PAS for the air pollution at a local scale was evaluated prior to the creation of a monitoring network.

The preliminary results of the first “short communication” showed that, in general terms, the devices allow the air sampling in three different areas of Tarragona County, Spain, where one of the most important chemical/petrochemical complex in Southern Europe is located. Due to this industrialized influence, the first compounds analyzed were the PAHs. A decreasing pattern of PAHs concentration was observed among the three sampling points, where the highest concentration of PAHs in air was recorded at the Vilallonga sampling point (66 ng/m^3), with great industrial influence; followed by the sampling point with the greatest urban influence (36 ng/m^3) and by the point classified as rural (17 ng/m^3). These results showed that PAS devices allow to discriminate between sampling areas with different contamination levels. Since PAHs are a large family of compounds with different characteristics, the pattern of PAHs sampled can provide insights into how these devices work. For instance, the results indicate that LMW PAHs (2-3 aromatic rings) represent more than 80% of the total PAHs sampled by the PAS, being phenanthrene (3 aromatic rings) the predominant hydrocarbon, with a mean range between 26-44 % of the total. In addition, if the 4 rings PAHs are added, they represent more than 90 % of the total contribution. This fact shows that PAS with PUF disks are particularly effective for the sampling of those contaminants presents in the gas phase air. Nevertheless, it should be noted that PUF-PAS were also capable of detecting high molecular weight PAHs.

Since PUF-PAS are devices composed by double-dome metallic chamber, the influence of environmental variables, such as temperature, over PUF-PAS ability to SVOCs capture was also investigated (short communication Annex 1). The results indicate that the environmental temperature does not affect the stability of PAHs in PUF-PAS. Once PAHs have been uptaken by the PUF-PAS, they are not easily volatilized from these devices. Consequently, PAS are good environmental monitors independently on the ambient conditions of temperature, being suitable for the comparability of data, either temporally or spatially, on the airborne concentrations of PAHs.

Given the high industrialization degree of Tarragona County, a second “short communication” was carried out in order to assess the PUF-PAS capability of capture other kind of SVOCs different of PAHs, such as PCBs, HCB, BFRs and emerging contaminants as SMs. In the same way, a greater number of sampling points were considered this time, a total of 8, divided into 4 well differentiated zones, including a two points over the influence of a big oil refinery; two samples close to chemical industries; two points in urban areas; and two samples in background sites, at least 30 km away from the area of influence of all the suspected sources of contamination.

The results showed that the major predominant compounds in the study area are the PAHs (2098-4333 ng/PUF) followed by the PCBs (2.8-120 ng/PUF). Likewise, HCB (4.65 to 16.4 ng/PUF) and SMs (0.38 to 13.4 ng/PUF) are found in similar concentrations, and BFR (1.30 to 2.80 ng/PUF) are the scarcest compounds in this area. This would be associated with the fact that many of these compounds such as nitro SMs, HCB and penta-BDE and octa-BDE are already banned and others are classified as restricted use. In addition, the lower BFRs concentrations recorded by PUF-PAS may be associated with the fact that these compounds are mostly predominant in indoor environments and their new homologs probably are more degradable than the legacy.

Regarding PAHs, the concentrations found in the study conducted in winter of 2014-2015 (PAHs levels ranged from 2098 to 4333 ng/PUF) were into the range reported in the preliminary study (winter 2013, PAHs levels ranged from 670 to 7530 ng/PUF), and a similar decreasing petrochemical>chemical>urban>background pattern was observed in this area. In addition, the highest concentrations of PAHs were also registered in the point P1, corresponding to the neighborhood of Puigdelfí (a very close town to Vilallonga), situated in the vicinity of a big oil refinery and well under the potential influence of petrochemical emissions. Concerning individual PAHs, also phenanthrene (LMW PAH) was the predominant hydrocarbon, ranging between 30 -39 % of the total contribution. Regarding, more heavier molecular weight PAHs, a greater number of them were recorded in this second study in compare with the preliminary one, and benzo(*a*)pyrene (5 aromatic rings), was also detected in all sampling points. Nevertheless, its concentration never exceeded the maximum of 1 ng/m3 admissible for air samples.

Regarding PCBs, higher concentrations were found in the chemical zone, more specifically in point C3 (La Laboral), and although these compounds are nowadays banned, the current value could be due to the presence of a chlor-alkali plant and various electrical substations in the vicinity, as well as the legacy of their use in the past.

In general terms, it is observed that the area over the industrial influence (chemical and petrochemical areas) has higher concentrations of PAHs, PCBs and HCB than in urban areas and these are higher than in the background areas. On the other hand, SMs and BFR concentrations were lower and did not show differences between zones. For this reason, this second short communication corroborated that the PUF-PAS are devices capable of capture different kinds of SVOCs, some of them present in the environment at lower concentrations, either because their use has been prohibited or restricted or because they are characteristic of indoor environments.

Finally, and in order to compare the effectiveness of PUF-PAS devices with other environmental biomonitors, a comparison between PAHs levels recorded by them and lichens transplant was conducted in Tarragona County (article 1 of this chapter). Numerous studies show that lichens can serve as passive samplers (Augusto et al., 2013a; Loppi et al., 2015). These biomonitors are characterized by being sensitive to factors such as rainfall, high levels of pollution and/or urbanization, so their presence in these areas is highly reduced. That was the case of Tarragona County, for this reason, lichen transplants from presumable unpolluted areas were used in this thesis. Lichen transplants were distributed at the same time as PUF-PAS during the same sampling period (2 months of sampling). The results indicate that the areas affected by petrochemical activity and to a lesser extent chemical have higher values of PAHs than in urban areas and background, whether considering the PAS or the transplanted lichens. It is important to note that PUFs are capable of retaining approximately 2-4 times more PAHs (expressed as ng/g) mainly contents in the gas phase than lichens transplanted from clean areas. In addition, the PAHs profile retained by each device is clearly different. The PUF-PAS retain, as we saw previously, LMW of 2, 3 and 4 rings (90 % of the total contribution), being 3 rings PAHs the most abundant. While the transplanted lichens tend to accumulate to a greater extent the HMW PAHs (4, 5 and 6 rings PAHs with a total contribution between 60-80 %). Therefore, it is clear that the profile of sampled compounds is different, being the PUF-PAS good samplers of the contaminants in the gas phase, while the transplanted lichens sample to a greater extent those compounds that are in the particulate phase.

Despite that, the good correlation between the concentration of LWM PAHs between PUFs and lichens suggests that lichens are able to sample part of the gas phase as well. However, to be able to use transplanted lichens it would be necessary to make new studies to gauge their suitability. It should also be noted that 2 of the 6 lichens have given PAHs concentration values below the initial level (of the presumable unpolluted area). The ease of use of PUF-PAS, its benefits and its price make it very suitable for the environmental sampling of numerous and different SVOCs.

CHAPTER 2: Improving analytical procedures for SVOCs determination using “green” alternatives.

In this chapter:

ARTICLE 1:

Carvalho, M.[⊥], Domínguez-Morueco, N.[‡ ⊤], Homem, V.[⊥], Sierra, J.[⊤ ┤], Nadal, M.[‡], Alves, A.[⊥], Ratola, N.[⊥], 2017. **Improving multi-component analysis of SVOCs in environmental samples using QuEChERS.** Submitted to Anal. Bioanal. Chem.

ARTICLE 2:

Domínguez-Morueco, N.[‡ ⊤], Carvalho, M.[⊥], Sierra, J.[⊤ ┤], Schuhmacher, M.[‡ ⊤], Domingo, J.L.[‡], Ratola, N.[⊥], Nadal, M.[‡], 2017. **Multi-component determination of atmospheric semi-volatile compounds in soils and vegetation samples from Tarragona County, Catalonia, Spain.** Accepted for publication in Sci. Total. Environ.

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ARTICLE 1: IMPROVING MULTI-COMPONENT ANALYSIS OF SVOCs IN ENVIRONMENTAL SAMPLES USING QUECHERS.

Submitted to Analytical and Bioanalytical Chemistry.

ABSTRACT

The aim of this study was to improve classic extraction and cleanup protocols to analyze the levels of several classes of semi-volatile organic compounds (SVOCs) in environmental matrices, observing the basic rules of green analytical chemistry. In this case, a multi-residue method involving QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) coupled to GC-MS was validated for the simultaneous extraction of PAHs, PCBs, BFRs, SMs and HCB in soils and vegetation samples. To achieve the goal, several tests were conducted throughout the procedure to optimize the main parameters to consider in the analysis: type of extraction solvent; composition of QuEChERS 1 and 2, and extract filtration and dryness. The best results overall were obtained using acetone/dichloromethane (1:1) for soils samples (mean total recovery of 101% for PAHs; 95 % for SMs; 98% for PCBs; 109% for BFRs and 94 % for HCB) and hexane/dichloromethane (2:1) for pine needles (mean recoveries of 101% for PAHs; 102 % for SMs; 87% for PCBs; 67 % for BFRs and 113 % for HCB). QuEChERS 1 composition for both matrices was better with NaCH3COO and anhydrous MgSO4 (mean total recoveries of 151 % for PAHs; 98 % for SMs; 93% for PCBs; 102 % BFRs and 78 % for HCB in soil samples; and 81 % for PAHs; 105 % for SMs; 74% for PCBs; 99 % for BFRs and 77 % for HCB in pine needles) and for QuEChERS 2, the best combination of sorbents for soils was obtained with 0.9 g of MgSO4, 150 mg of PSA and 150 mg of C18 (mean total recoveries of 93 % for PAHs; 103 % for SMs; 119 % for PCBs; 110 % BFRs and 101 % for HCB) while for pine needles the most reliable solution was given by 0.9 g of MgSO4, 0.15 g of alumina, 0.15 g of Florisil and 0.15 g of C18 (mean total recoveries of 110 % for PAHs; 101 % for SMs; 80 % for PCBs; 56 % for BFRs and 14 % for HCB). Regarding extract filtration and dryness, the sample filtration with PTFE filters of 0.2 µm and the total dryness of the sample followed by reconstitution with the injection solvent were chosen for both matrices. The optimised protocols were validated for both matrices through linearity, precision and accuracy assays. Finally, naturally contaminated samples of soils and pine needles from Porto and Aveiro (Portugal) were tested to complete the validation in field samples. The limits of detection ranged between 0.7 and 225 pg/g, which are similar to the classic approaches, as were the repeatability and mean recoveries found.

Keywords: Semi-volatile organic compounds (SVOCs) · Soil · Vegetation · QuEChERS · GC-MS

1. INTRODUCTION

Large amounts of semi volatile organic compounds (SVOCs) are continuously emitted into the atmosphere from different sources each year. Many of these SVOCs are hazardous to human health and the environment. Due to their physicochemical properties in combination with slow degradability in air, top soil, surface waters, and on vegetation surfaces, these compounds may undergo a series of volatilizations and subsequent depositions, which enhances their long-range transport potential (Trellu et al., 2016). As a consequence, more stringent regulations about environmental pollution are introduced every year (Trellu et al., 2016). Polycyclic aromatic compounds (PAHs), polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs), organochlorine pesticides (OCPs) and synthetic musks (SMs) are examples of this type of chemicals and are the focus of this work. PAHs may enter the environment from both natural (e.g. vegetation synthesis, volcanic activity and forest fires) and anthropogenic (e.g., industrial activities, power generation, incineration and traffic) sources (Lamichhane et al., 2016; Domínguez-Morueco et al., 2017; Silva et al., 2015), whereas PCBs are a large group of compounds that have been used in a wide variety of application such as microelectronic circuits, plastics, resins (Antonetti et al., 2016, Manzetti et al., 2014) and BFRs are chemicals commonly added to a wide variety of industrial and household products to improve their fire resistance (Cruz et al., 2015; Fromme et al., 2016; Manzetti et al., 2014). OCPs have also been widely employed in insect and pest control (among other uses), being hexachlorobenzene (HCB) one the most used, in fungicides, military pyrotechnic smokes, and synthetic rubber peptizing agents (Chen et al., 2016; Tong and Yuan, 2012; Wu et al., 2016). SMs are man-made chemicals of recent concern, produced in large quantities and extensively used in the fragrance industry for the production of a vast array of scented consumer products including shampoos and detergents (Homem et al., 2015).

In order to monitor these pollutants, several passive sampling methodologies and matrices have been employed to reduce the operative costs of such processes. Among others, soils or vegetation have been used to assess the levels and behaviour of several families of SVOCs (Ballesteros-Gómez and Rubio, 2011). Soil is a complex and heterogeneous matrix that plays a central role in the environment preventing the contamination of adjacent ecosystems (Correia-Sá et al., 2012; Ratola et al., 2016) and is constantly subject to an intensive exposure from a myriad of chemical compounds (Correia-Sá et al., 2012; García Pinto et al., 2011). Vegetation represents a natural fixed, relatively inexpensive mean to monitor airborne pollutants and can be therefore considered bio-samplers of atmospheric contamination (Holt et al., 2016). Pine needles, in particular, have been used as bio-monitors of atmospheric pollution because they are evergreen, and can thus be used to assess longer temporal series of pollutant exposure than deciduous species (Holt et al., 2016; Ratola et al., 2016).

In order to detect, identify and quantify chemicals released into the environment, the target analytes need to be isolated from the sample matrix. Several methods have been developed to this end and regarding SVOCs the following extraction and clean-up protocols are reported in literature: Soxhlet, sonication, pressurized liquid extraction (PLE), microwave-assisted extraction (MAE), microextraction techniques, solid-phase extraction (SPE), among others (Ribeiro et al., 2014; Zuloaga et al., 2012). In general, all these methods are effective but time and solvent consuming, and requiring expensive equipment (Silva et al., 2015). Cheaper and more environmental-friendly alternatives must be sought (Gałuszka et al., 2012), such as QuEChERS methodology.

QuEChERS is an acronym of quick, easy, cheap, effective, rugged and safe, a "green" user-friendly extraction and clean-up technique developed by Anastassiades and co-workers in 2003 (Anastassiades et al., 2003). QuEChERS are characterized by a high flexibility which allows the adaptation a wide number of applications, including the analysis of complex environmental matrices such as soil and vegetation (Bruzzoniti et al., 2014; Ribeiro et al., 2014; Socas-Rodríguez et al., 2017). The major advantages of QuEChERS are the good recoveries and reproducibility with a considerable less expensive operation than other sample preparation techniques (Rouvière et al., 2012). Moreover, this method is less time-consuming and uses very low volumes of organic solvents when compared with other extraction procedures (Ben Salem et al., 2016; Bruzzoniti et al., 2014).

Thus, the objective of this study is to improve the analytical protocols for the multi-component extraction of SVOCs from soil and pine needle and developing alternatives in line with the "green analytical chemistry" (GAC) guidelines whenever possible.

2. MATERIAL AND METHODS

2.1. Reagents and materials

Acetone (ACE), acetonitrile (ACN), dichloromethane (DCM) and n-hexane (HEX), the solvents used for extraction and clean-up tests were supplied by VWR BDH Prolabo (Leuven, Belgium). The QuEChERS were prepared in the lab using Falcon tubes from VWR and several sorbents: anhydrous magnesium sulphate ($MgSO_4$), sodium acetate ($NaCH_3COO$) and acetic acid (CH_3COOH) were from Sigma-Aldrich and PSA-bonded silica and C18 by Supelco (Bellefonte, PA, USA). Florisil (0.150 – 0.250 mm) and alumina (neutral aluminium oxide 90, 0.063 – 0.200 mm) were acquired from Merck (Darmstadt, Germany). Florisil and alumina were used after baking overnight at 450 ºC in a Nabertherm N 120/65 HA furnace (Lilienthal, Germany).

A PAHs mix solution (containing naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(*a*)anthracene (BaA), chrysene (Chry), benzo(*b*)fluoranthene and benzo(*k*)fluoranthene (B(b+k)F), benzo(*a*)pyrene (BaP), indeno(*1,2,3-c,d*)pyrene (IcdP), dibenzo(*a,h*)anthracene (DahA), and benzo(*g,h,i*)perylene (BghiP) at 2000 µg/mL in DCM/benzene 1:1), a PCB mix solution (congener numbers 28, 138, 153, 209 as 10 µg/mL in isooctane), HCB and individuals PBDE (congener numbers 28, 47, 85, 99, 100, 153, 154, 183) (as 50 µg/mL solution in isooctane), as well as musk xylene (100 µg/mL in acetonitrile) were obtained from Sigma-Aldrich (St. Louis, MI, USA). Dr. Ehrenstorfer (Augsburg, Germany) supplied another mix of PCBs (congener numbers 77, 81, 105, 114, 156, 157, 167, 189 as 10 µg/mL in isooctane), musk ketone and musk ambrette, and a mix of deuterium labelled PAHs (d-PAHs) (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}, 10 µg/mL in hexane). Individual hexabromobenzene (HBB), pentabromotoluene (PBT) and pentabromoethylbenzene (PBEB) standards (50 µg/mL each in toluene) and a mix of $^{13}C_{12}$ mass labelled PCB congeners ($^{13}C_{12}$-PCBs) (28L, 52L, 101L, 118L, 138L, 153L and 180L; 5 µg/mL in nonane) were supplied by Wellington laboratories (Guelph, ON, Canada). LGC Standards provided neat standards of cashmeran, celestolide, traseolide, phantolide, tonalide, galaxolide as well as standard solutions (10 µg/mL in cyclohexane) of musk moskene.

Helium with a purity of 99.9999 % (GC-MS carrier gas) and nitrogen with a purity of 99.995 % (for solvent reduction) were supplied by Liquide Air (Maia, Portugal).

Given that one of the analysed compound classes (synthetic musks) are present in most of the personal care products, some restriction in the use of this products had to be made for the laboratory personnel. Scented cosmetics such as perfume, lotions and hand creams were avoided. Additionally, procedural blanks were extracted and analysed in order to identify and correct eventual contamination. Apart from some PAHs, some PCBs and synthetic musks, namely galaxolide and cashmeran were detected. Consequently, the results were blank-corrected when necessary. Also, all non-calibrated glass material was baked at 400 ºC for at least 1 hour before use in the analysis.

2.2. Sample collection

During all the method development, soil samples were collected from the Faculty of Engineering premises at the University of Porto, Porto (Portugal). After collection, the samples were transported in sealed plastic bags and sieved with a 1 mm sieve, removing small rocks and root traces. Pine needles were sampled in the same area, from *Pinus pinea* species. Needles were collected as a whole, cut directly from the branches of the trees, wrapped in aluminium foil, transported to the lab in sealed plastic bags. Both soils and pine needles were stored in the freezer at -20 ºC until analysis.

The naturally contaminated samples (soils and pine needles) used for the validation of the method were collected from a residential site in Porto (the second largest city in Portugal with up to 1 million people in the metropolitan area and a background urban site near Aveiro, a 50,000 inhabitants town.

2.3. Sample extraction and clean-up

The extraction and clean-up procedures were inspired by a multi-compound method previously validated for the analysis of SVOCs (PAHs, PCBs, BFRs, HCB and SMs) in pine needles (Silva et al., 2015). The respective protocol involved ultrasound extraction (USE) followed by a classic solid-phase extraction (SPE) coupled to gel permeation chromatography (GPC). However, both these extraction and clean-up methods are time and solvent-consuming. In order to comply with the principles of green analytical chemistry (GAC) (Gałuszka et al., 2012), the QuEChERS methodology was employed and an optimisation and validation of the multi-compound protocol performed for soil and pine needles. This technique comprises three basic steps (Ribeiro et al., 2014): a microscale extraction (in this case, ultrasound) using an organic solvent; addition of anhydrous salts or buffers to promote the separation of phases and allow the extraction of the analytes into the organic phase (QuEChERS 1); and finally a dispersive SPE using appropriate sorbents as a clean-up step to remove undesired components (QuEChERS 2). To achieve the goal, several tests were conducted throughout the procedure: extraction solvent, the composition of QuEChERS 1 and 2, and extract filtration and dryness. Taking into consideration the differences between the two matrices studied (soil and vegetation), these tests were not always the same for both of them. Table 1 sums up all the main tests performed in this work.

First, 2.5 g of soil and pine needles were used, in order to reduce also the amount of sample with no loss of representativeness (Silva et al., 2015 used 5 g whereas the commercial QuEChERS developed by Anastassiades et al., 2003 contemplated 10 g). The samples were transferred into 50mL Falcon tubes and spiked with the surrogate standards (d-PAHs at 30 ng/g and $^{13}PCB_{12}$ at 12 ng/g) and, for the validation tests, with 150 µL of mix standards with the target PAHs and SMs at two different concentrations (15 and 45 ng/g) and 150 µL of mix standards with PCBs, BFRs and HCB at 6 and 18 ng/g. In the case of soils, after spiking, the Falcon tubes were shaken in a vortex for 3 min, to impregnate the soils with the standards.

The first test involved the choice of the extraction solvent. As can be seen in Table 1, in the case of soil samples, acetonitrile, acetone, and the mixtures hexane:dicloromethane (1:1), (1:2), hexane:acetone (1:1), (1:2) and acetone:dicloromethane (1:1) were selected, whereas for pine needles the choice was between acetonitrile, hexane, and the mixtures hexane:dicloromethane (1:1), (2:1) and hexane:acetone (1:2) and (2:1). To each Falcon tube 10 mL of solvent or mixtures of solvent was added (instead of the 100 mL of DCM:Hex (1:1) considered in multi-compound method by Silva et al., 2015) and the samples extracted in an ultrasound bath (J.P. Selecta, Barcelona, Spain) 10 min.

After ultrasound extraction, the QuEChERS 1 was added to the Falcon tube. In this case, three different options were considered for both matrices (see Table 1): only 6 g of $MgSO_4$, a drying agent; 6 g of $MgSO_4$ and 1.5 g of $NaCH_3COO$, salt to enhance ionic strength; and the latter with 100 µL of CH_3COOH, for buffer purposes. The tubes were then shaken in a vortex for 3 min in order to help the partitioning of the target compounds to the organic phase. Subsequently, the tubes were centrifuged in a Rotofix 32 A centrifuge from Hettich (Kirchlengern, Germany) for 10 min and the supernatant was transferred to the QuEChERS 2. In this one, several sorbents (PSA, C18, alumina and Florisil) were tested in different amounts, together with 0.9 g of $MgSO_4$ (see Table 1 for details). The tubes were then shaken for 3 min in order to conduct the dispersive SPE step. Finally, the tubes were centrifuged (10 min) and the extract was transferred to in 15 mL amber tubes and blown down to dryness under a gentle stream of nitrogen. The extract was finally reconstituted in 150 µL of hexane in 1.5 mL amber vials with insert and analysed in the GC-MS. In the meantime, two more tests were performed for both soil and vegetation: filtration and dryness. In the first, extracts with no filtration, filtered with 0.2 µm and 0.45 µm filters were tried, to assess the cleanliness of the extracts and subsequent chromatographic resolution. In the second, complete dryness of the extract before reconstitution in hexane and GC-MS analysis was compared with non-dried extracts, to evaluate the possible loss of target analytes in the process.

Table 1. Scheme of the tests performed during the optimization of the analytical protocol.

MATRIX	TEST	EXP	VARIABLES				
Soils	**Solvent**		**ACE (mL)**	**ACN (mL)**	**HEX (mL)**	**DCM (mL)**	
		1	10	-	-	-	
		2	-	10	-	-	
		3	5	-	5	-	
		4	6.66	-	3.33	-	
		5	-	-	5	5	
		6	-	-	3.33	6.66	
		7	5	-	-	5	
Vegetation	**Solvent**		**ACE (mL)**	**ACN (mL)**	**HEX (mL)**	**DCM (mL)**	
		1	-	-	10	-	
		2	-	10	-	-	
		3	5	-	5	-	
		4	3.33	-	6.66	-	
		5	-	-	5	5	
		6	-	-	6.66	3.33	
Soils and vegetation	**QuEChERS 1**		**$MgSO_4$ (g)**	**$NaCH_3COO$ (g)**	**CH_3COOH (µL)**		
		1	6	1.5	-		
		2	6	-	-		
		3	6	1.5	100		
	QuEChERS 2		**$MgSO_4$ (mg)**	**PSA (mg)**	**ALU (mg)**	**FLO (mg)**	**C18 (mg)**
		1	900	300	-	-	150
		2	900	-	300	-	150
		3	900	-	-	300	150
		4	900	-	150	150	-
		5	900	300	-	-	-
		6	900	150	-	150	300
	Filter	**1**	No filter				
		2	0.2 µm				
		3	0.45 µm				
	Dryness	**1**	Dry				
		2	Not dry				

Procedural lab and sample blanks were performed each day of analysis. Overall, the amount of target compounds found were minimal, but whenever needed the results were blank-corrected. An internal standard correction was used for the quantification of the analytes, using the deuterated and carbon-marked compounds.

2.4. GC-MS analysis

The chromatographic analysis is similar to that described by Silva et al. (2015), using one equipment for PAHs and SMs and another for HCB, PCBs and BFRs. Two Varian (Palo Alto, CA, USA) ion trap GC-MS equipments, versions 4000 and 240, were used for PAHs and SMs, and for PCBs, BFRs and HCB, respectively. In both cases, a CP-1177 split/splitless injector and CP 8410 auto-sampler were used and the ionization mode was by electron impact (EI) with ionization energy of 70 eV and filament emission current of 50 mA. Two different capillary columns were used. For PAHs and SMs a Br5-MS (30 m x 0.25 mm, 0.25 µm film thickness) was used, whereas for PCBs, BFRs and HCB the separation was carried out with an Agilent J & W (Santa Clara, CA, USA) CP-Sil 8CB capillary column (50 m x 0.25 mm I.D., 0.2 µm film thickness). Helium at 1 mL/min was the carrier gas and the injection volume was 2 µL in splitless mode for both apparatus, as well as the temperatures for the manifold, transfer line and ion trap (50 °C, 250 °C and 250 °C, respectively). In the case of injector temperatures, these were different to potentiate the proper vaporisation of the target compounds in each case: 280 °C for PAHs and SMs and 300 °C for PCBs, BFRs and HCB. Also two distinct GC oven temperature programs were employed. For PAHs and SMs, temperature ramping started at 60 °C (held for 1 min), raised to 175 °C at 6 °C/min (held for 11.11 min) and then to 300 °C at 5.5 °C/min (held for 10 min) with a total runtime of 64 min. For PCBs, BFRs and HCB, temperature was programmed from 110 °C (held for 1.5 min) to 150 °C at 20 °C/min, to 220 °C at 5 °C/min (held for 17.5 min) and finally to 300 °C at 5 °C/min (held for 9 min), with a total analysis time of 60 min. For both GC-MSs, the detection was made employing the time-scheduled selected ion storage (SIS) mode. Identification of target compounds was done by comparing retention times and mass spectra to those of standards and system control, data acquisition and processing was done by Varian MS workstation v. 6.9.3 software. Retention times and used target ions for both employed GC-MS methods were similar to Silva et al. (2015) and example chromatograms of standard solutions are presented in supporting information (Fig. S1 and S2, Annex 4).

3. RESULTS AND DISCUSSION

3.1. QuEChERS optimization

Since its first introduction by Anastassiades et al. (2003), the QuEChERS method has undergone various modifications and enhancements to improve the recovery of target compounds from different matrices beyond its original scope of application (Rejczak and Tuzimski, 2015). As mentioned previously, in this work, the effect of extraction solvents, drying and filtration of extracts and the composition of QuEChERS 1 and 2 were evaluated for the extraction of SVOCs from soils and vegetation (pine needles). The "one-factor-at-a-time" approach where each experimental parameter is optimized separately and independently of others factors was followed. To reach the best options in each case, recovery assays were performed, using spikes of 15 ng/g for PAHs and SMs and of 6 ng/g for PCBs, BFRs and HCB. Each assay comprised a lab blank, a sample blank and two replicates of the spiked samples.

Solvent tests

The extraction solvent is one of the most important parameters to optimize in multiresidue analysis since it can ensure minimal co-extraction of matrix interferents (Bragança et al. 2012). Commercial QuEChERS commonly employ acetonitrile as extraction solvent (Sadowska-Rociek et al., 2013; Bruzzoniti et al., 2014). Consequently, this and other solvents and mixtures of solvents referred by several international studies (Bragança et al., 2012; Rouvière et al., 2012; Sadowska-Rociek et al., 2013; Ben Salem et al., 2016; Berton et al., 2016) were also tested for soils and pine needles. Given the different nature of these matrices, the options suggested in literature and the expertise gathered by the authors led to some different choices of solvents to test for each one of them.

Thus, and as seen in Table 1, for soils two pure solvents, acetone (ACE) and acetonitrile (ACN), and five mixtures, HEX/ACE (1:1), HEX/ACE (1:2), HEX/DCM (1:1), HEX/DCM (1.2) and ACE/DCM (1:1) were tested. As can be seen from the results, presented in Figure 1 (a), there are not so significant differences in the mean recoveries between the different solvents for the 5 families of compounds. However, the mixture ACE/DCM (1:1) showed the best mean recoveries (mean total recovery of 101% for PAHs; 95 % for SMs; 98% for PCBs; 109% for BFRs and 94 % for HCB) overall with lowest standard deviations. This was also the option that produced cleaner final extracts and clearer chromatograms. Regarding vegetation, two pure solvents, n-hexane (HEX) and acetonitrile, and four mixtures, HEX/ACE (1:1), HEX/ACE (1:2), HEX/DCM (1:1) and HEX/DCM (2:1) were tested. The results presented in Figure 1 (b) show that ACN yielded the best overall mean recoveries and lowest standard deviations. However, a slightly lower resolution of the chromatograms was seen. Acetonitrile is a kind of solvent with low volatility, large volume expansion during vaporization into the gas chromatograph, interference in specific thermoionic flame detectors and electrolytic conductivity, and present considerable toxicity (Prestes et al., 2009). Although proven to deliver high recoveries for a wide range of pesticides in fruits and vegetables (Anastassiades et al., 2003), ACN may not be the most suitable solvent under the economic point of view or when other environmental pollutants or matrices are analyzed. Also, ACN is less volatile than other solvents, making the blow down steps more time and nitrogen consuming (Rejczak and Tuzimski, 2015). For these reasons, the mixture HEX/DCM (2:1) was selected as the most suitable for the extraction of SVOCs from vegetation (mean recoveries of 101% for PAHs; 102 % for SMs; 87% for PCBs; 67 %

for BFRs and 113 % for HCB). For the analysis of vegetation is needed a more apolar mixture of solvents (HEX/DCM (2:1)) than for the extraction of soils (ACE/DCM (1:1)), this is expectable taking into account that vegetation tissues are more lipophilic than soil components.

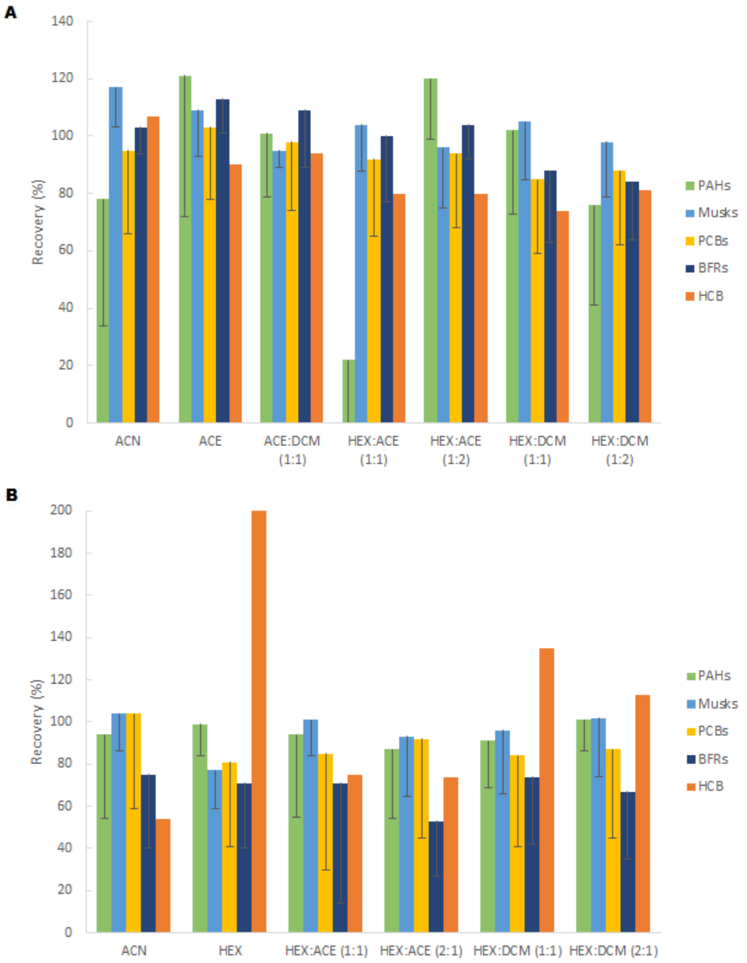

Fig. 1. Comparison of the mean recoveries for different extraction solvents of spiked soils (a) and vegetation (b) using QuEChERS method (error bars only show the below levels for simplicity).

QuEChERS 1 composition

After the solvent extraction, anhydrous salts and/or buffers (e.g. anhydrous magnesium sulphate, sodium chloride, sodium acetate, acetic acid) are added to the extract to ensure and enhance the separation between the aqueous and organic phases, with the target compounds nestling into the latter (Homem et al., 2013). In this work, magnesium sulphate ($MgSO_4$) was always used, as drying agent to help the salting-out process, and the effect of sodium acetate ($NaCH_3COO$) and acetic acid (CH_3COOH) was evaluated. Sodium acetate is a salt used to increase the ionic strength and the aqueous phase polarity and to maintain sample pH (pH 5.0–5.5) (Ribeiro et al., 2014). Acetic acid allowed a greater stability and higher recoveries of alkaline-sensitive compounds (Lehotay et al., 2005) and can also help to buffer the work extract.

As seen in Table 1, for both soils and vegetation, three different compositions were tested: only 6 g of $MgSO_4$; 6 g of $MgSO_4$ with 1.5 g of $NaCH_3COO$; and 6 g of $MgSO_4$, 1.5 g of $NaCH_3COO$ with 100 µL of CH_3COOH. For soils, the results presented in Figure 2 (a) show that the best performance overall was obtained in the presence of $NaCH_3COO$ and anhydrous $MgSO_4$ (mean total recoveries of 151 % for PAHs; 98 % for SMs; 93% for PCBs; 102 % BFRs and 78 % for HCB). In the presence of CH_3COOH a sensible decrease in the percentage of recovery of BFRs is observed. When only anhydrous $MgSO_4$ is present a higher standard deviation is perceived, together with dirtier extracts. The same trend in observed in Figure 2 (b) for vegetation, were the best performance was obtained with $NaCH_3COO$ and anhydrous $MgSO_4$ (81 % for PAHs; 105 % for SMs; 74% for PCBs; 99 % for BFRs and 77 % for HCB). Lower recoveries of PCB's are also found in the presence of CH_3COOH is also observed. Buffer methods were firstly introduced to provide pH that would help on the extraction of pesticides, which are sensitive in both acidic and basic conditions and regardless of matrix. But for some matrices and other analytes this procedure may not be recommended due to the potential negative effect on the PSA sorption ability, particularly those with a high lipidic content (Socas-Rodríguez et al., 2017). This can be the case of soils and pine needles. For all these reasons, $NaCH_3COO$ and anhydrous $MgSO_4$ were chosen as the most appropriate contents of QuEChERS 1.

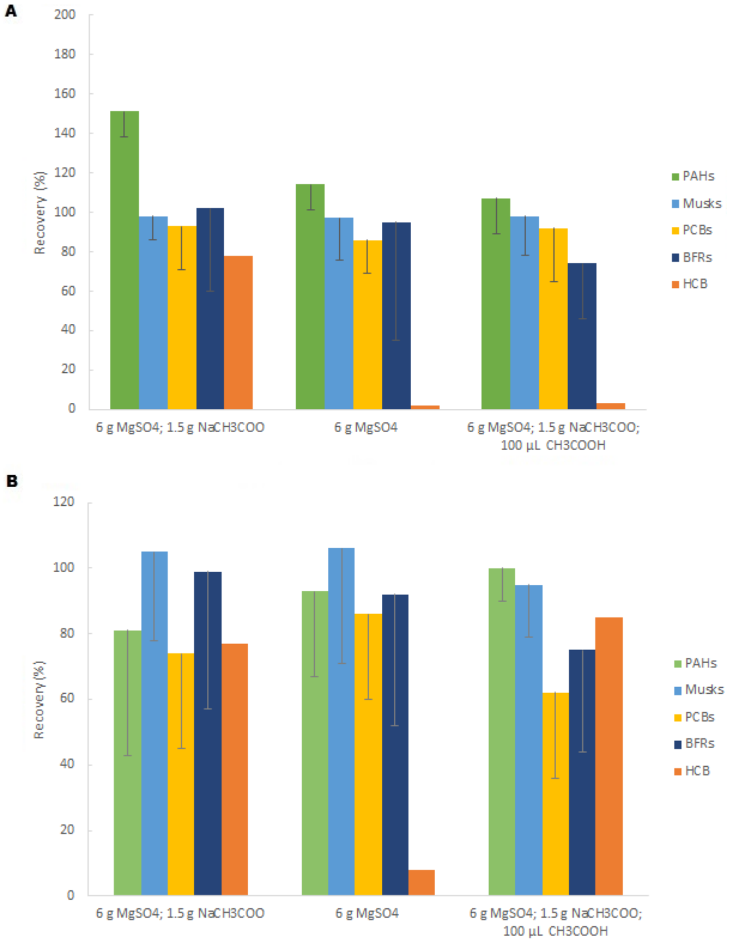

Fig. 2. Comparison of the mean recoveries of different QuEChERS 1 contents for spiked soils (a) and vegetation (b) (error bars only show the below levels for simplicity).

QuEChERS 2 composition

With the target compounds concentrated in the organic phase, an effective clean-up is required to obtain the desired chromatographic resolution. This is obtained with QuEChERS 2, through a dispersive solid phase extraction (d-SPE) step, the selectivity of which is crucial to obtain satisfactory and accurate results. Different sorbents can be used to remove co-extractives, depending on the polarity of the chemicals in study and on the type of sample analysed (Rejczak and Tuzimski, 2015). In this work, the performance of primary secondary amine (PSA), Florisil (FLO), alumina (ALU) – these three allow the removal of various polar organic acids, polar pigments, some sugars and fatty acids from the preliminary extracts (Masiá et al., 2015; Rejczak and Tuzimski, 2015), avoiding the retention of the target apolar chmicals - and octadecyl-silica (C18), a more polar material, very suitable in the removal of fats and waxes from lipidic matrices (Bruzzoniti et al., 2014; Masiá et al., 2015) were evaluated. In total, six different combinations (see Table 1) were tested, all of them having 0.9 g of $MgSO_4$ to remove any remaining water: 0.3 g of PSA and 0.15 g of C18; 0.3 g of PSA; 0.3 g of Florisil and 0.15 g of C18; 0.3 g of alumina and 0.15 g of C18; 0.15 g of alumina, 0.15 g of Florisil and 0.15 g of C18; and 0.15 g of alumina and 0.15 g of Florisil.

Figure 3 presents the comparison of the recoveries of different QuEChERS 2 content for soils and vegetation. Although again the differences between all options were sometimes negligible, for soils, the best performance was obtained with 0.9 g of $MgSO_4$, 0.15 g of PSA and 0.15 g of C18 (mean total recoveries of 93 % for PAHs; 103 % for SMs; 119 % for PCBs; 110 % BFRs and 101 % for HCB), which is the amounts and sorbents used in the commercial QuEChERS. In the clean-up step for vegetation, the best results were found for 0.9 g of $MgSO_4$, 0.15 g of alumina, 0.15 g of Florisil and 0.15 g of C18 (mean total recoveries of 110 % for PAHs; 101 % for SMs; 80 % for PCBs; 56 % for BFRs and 14 % for HCB). That is, PSA being replaced by a mix of alumina and Florisil. According to Lehotay et al. (2005) PSA, as anion exchanger, does not allow the removal of chlorophyll (non-ionic molecule) and although this substance does not interfere in the chromatographic analysis, it can build up in the injection port liner and increase the frequency of liner changes and column maintenance. PSA was also found to reduce the recoveries of compounds like pesticides in some cases (Socas-Rodríguez et al., 2017). Alumina and Florisil are sorbent known for their good performance with vegetation matrices, including pine needles (Ratola et al., 2006; Lavin and Hageman, 2012), so the combination of both is likely to be more effective that PSA for this matrix in particular. Also, with this scheme, the cleanness of extracts and the resolution of the chromatographic peaks were the best of all options. Thus, the mixture 0.9 g of $MgSO_4$, 0.15 g of alumina, 0.15 g of Florisil and 0.15 g of C18 was chosen as the most suitable for vegetation.

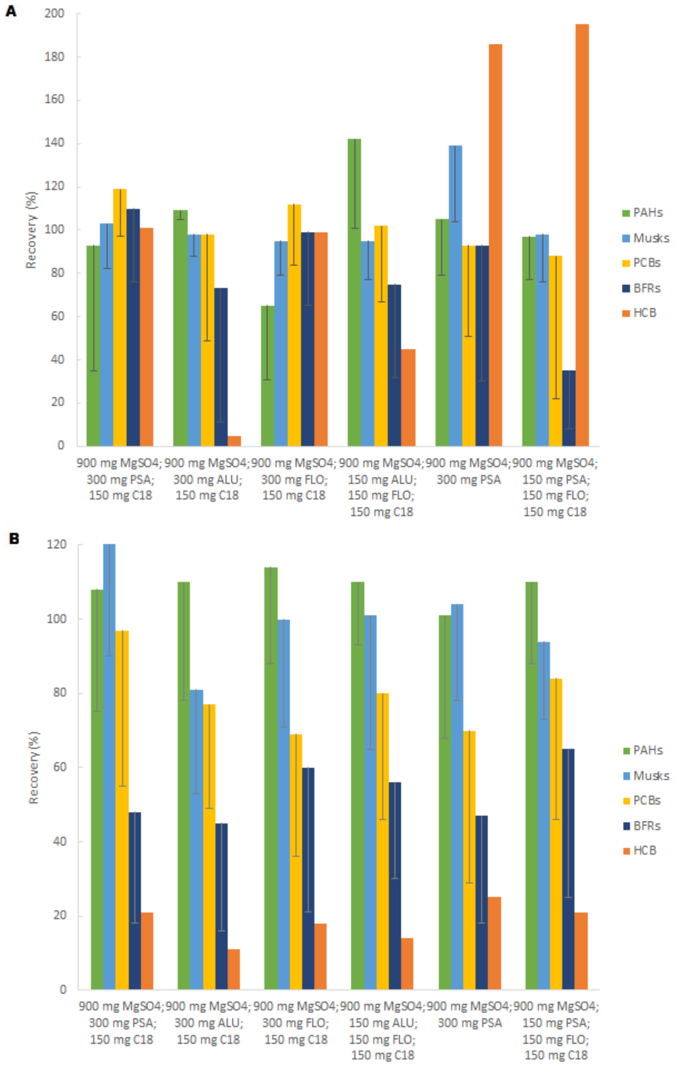

Fig. 3. Comparison of the mean recoveries of different QuEChERS 2 contents for spiked soils (a) and vegetation (b) (error bars only show the below levels for simplicity).

Filter and dryness tests

It is well known that within the wide variety of environmental matrices, some of them are easier to handle than others, which could cause interferences in the extraction process and in the subsequent chromatographic analysis. Soils and vegetation are complex and heterogeneous matrices, and as result of that they can produce complicated extracts (Bragança et al., 2012; Sadowska-Rociek et al., 2013). For example, in the case of vegetation, fats, waxes and resins can be dissolved in samples extracts, whereas in soils, numerous organic and inorganic compounds can cause problems. Therefore, the sample filtration before the GC analysis is an option that can be used to improve selectivity and extract cleanness, to protect the chromatographic system, and extend the GC column lifetime, but only if it does not compromise the overall recoveries of the target analytes. In this work, the recoveries using unfiltered extracts were compared with those after filtration with PTFE filters (0.2 and 0.45 µm). The results showed no appreciable retention of the target compounds and the internal standards in the filters, allied to an improvement of the chromatographic resolution for both filters in soils and vegetation extracts. In fact, after filtration the extracts obtained were considerably more transparent. PTFE 0.45 µm filters were chosen due to their generally better performance and easier operation.

To improve the sensitivity of the method, the samples are commonly concentrated under a nitrogen stream. In our case, two possible scenarios were tested: sample dryness and subsequent reconstitution with 150 µL of HEX and the reduction of sample volume until 150 µL without dryness. The best recoveries were obtained in the latter case. When the samples were completely dried, an important loss of the most volatile compounds was observed.

3.2. Method validation

After reaching the optimal solution, the method developed was validated for soils and pine needles, namely defining linearity ranges, coefficients of determination (R^2), limits of detection (LODs), and precision and accuracies via repeatability and recovery assays. Tables 2 and 3 present the complete results. In order to represent a broad scope of SVOCs occurrence in the environment, two spiking levels (corresponding to the low and high ranges of the calibration curve) were chosen. Since the presence of the five families of target chemicals in the environment is diverse and given that two GC-MS devices are used in the quantification, the linearity ranges were adapted to that fact. For PAHs and SMs it was from 10 to 1000 µg/L, with coefficients of determination ranging from 0.9967 to 0.9996, whereas for BFRs, PCBs and HCB linear behaviour was set from 4 to 400 µg/L, with a R^2 between 0.9912 and 0.9995. When dealing with pollutants at residual levels, low LODs are essential to take valid conclusion about their occurrence. This parameter was estimated based on the rule of signal-to-noise (S/N) ratio of 3. LODs for 2–4 ring PAHs (Naph–Chry) ranged from 4.4 to 62.1 pg/g and from 20.5 to 225 pg/g for the 5–6 ring PAHs (B(b+k)F, BaP, DahA BghiP and IcdP). In the case of SMs, LODs ranged from 10.5 to 128.6 pg/g. Regarding PCBs and BFRs, LODs ranged from 1.1 to 9.5 pg/g, and from 3.6 to 75.8 pg/g, respectively, and for HCB, LOD was 0.7 pg/g.

Regarding the precision and accuracy of the method, the repeatability and recovery assays were done in four replicates of soil and vegetation samples, spiked at two levels, as mentioned above. For the lower level, 15 ng/g of PAHs and SMs and 6 ng/g of PCBs, BFRs and HCB were considered, whereas for the higher levels, 45 ng/g of PAHs and SMs and 18 ng/g of PCBs, BFRs and HCB were assumed. As can be seen in Tables 2 and 3, for all SVOCs, the overall recoveries were rarely below 50 % for both spiking levels and both matrices. In fact, for PAHs the mean recoveries were 106 ± 12 % for soils and 86 ± 17 % for vegetation samples. In the case of SMs, 96 ± 7 % for soils and 99 ± 17 % in vegetation. The mean recoveries for PCBs ranged from 92 ± 15 % in soils and 85 ± 18 % in vegetation. Only PCB 209 shows low recoveries in the pine needles at both spiking levels, probably due to matrix effects or to a lower chromatographic response. BRFs mean recoveries were of 89 ± 15 % for soils and 87 ± 17 % for vegetation; finally, for HCB 70 ± 8 % for soils and 62 ± 11 % for vegetation were obtained in the optimized protocols. In this sense, the good recoveries confirmed that the proposed method is also a perfectly fit multi-residue approach to handle such a complicated matrix as vegetation and soils, and at several levels of occurrence of SVOCs. Regarding the repeatability (expressed as the RSD of four extractions), SVOCs showed values mostly below 20 % in all cases. The mean repeatability for PAHs was of 12 ± 7 % for soils and of 8 ± 5 % for vegetation, similar to those of SMs (4 ± 3 % for soils and 10 ± 9 % for vegetation. The mean repeatability for PCBs and BFRs were only slightly higher (8 ± 8 % in soils and 14 ± 9 % for vegetation versus 12 ± 9% for soils and 14 ± 9 % for vegetation, respectively; finally for HCB, values of 3 ± 0.3 % for soils and 8 ± 6 % for vegetation samples were obtained, confirming the very good results in general.

Table 2. Method validation parameters: linearity range, coefficient of determination (R^2), limit of detection (LOD), recovery and repeatability for PAHs and SMs.

				Soils (n=4)		**Soils (n=4)**		**Vegetation (n=4)**		**Vegetation (n=4)**	
	Linearity (µg/L)	**R^2**	**LOD** pg/g (fw)	**Recovery (%)**		**Repeatability (RSD %)**		**Recovery (%)**		**Repeatability (RSD %)**	
PAHs				15 ng/g	45 ng/g	15 ng/g	45 ng/g	15 ng/g	45 ng/g	15 ng/g	45 ng/g
Naphthalene	10-1000	0.9991	62.1	109	93	8	3	89	62	4	3
Acenaphthylene	10-1000	0.998	34.6	109	108	6	2	103	68	6	6
Acenaphthene	10-1000	0.9986	36.0	109	110	5	2	100	86	5	24
Fluorene	10-1000	0.9986	51.4	116	120	4	2	104	64	5	2
Phenanthrene	10-1000	0.9992	4.4	95	101	20	9	92	113	5	6
Anthracene	10-1000	0.9992	6.7	101	80	18	18	97	86	12	16
Fluoranthene	10-1000	0.9988	26.9	110	107	19	25	92	109	5	4
Pyrene	10-1000	0.9986	24.7	108	87	20	20	86	94	3	8
Benz(*a*)anthracene	10-1000	0.9994	21.4	99	100	13	7	91	68	13	5
Chrysene	10-1000	0.9993	25.0	108	107	18	11	114	97	7	5
Benzo(*b*+*k*)fluoranthene	10-1000	0.9996	20.5	136	126	19	12	84	59	5	12
Benzo(*a*)pyrene	10-1000	0.9996	66.7	96	93	20	10	80	55	9	9
Indeno(*1,2,3-c,d*)pyrene	10-1000	0.9994	225.0	112	111	20	9	96	94	7	3
Dibenzo(*a,h*)anthracene	10-1000	0.9994	138.5	124	120	11	3	91	66	8	6
Benzo(*g,h,i*)perylene	10-1000	0.9987	128.6	93	103	22	10	92	59	15	11

				Soils (n=4)		**Soils (n=4)**		**Vegetation (n=4)**		**Vegetation (n=4)**	
	Linearity (µg/L)	**R^2**	**LOD** pg/g (fw)	**Recovery (%)**		**Repeatability (RSD %)**		**Recovery (%)**		**Repeatability (RSD %)**	
Musks				15 ng/g	45 ng/g	15 ng/g	45 ng/g	15 ng/g	45 ng/g	15 ng/g	45 ng/g
Cashmeran	10-1000	0.9979	128.6	109	93	4	15	97	80	27	32
Celestolide	10-1000	0.999	40.0	93	100	2	1	91	115	3	6
Phantolide	10-1000	0.9991	10.5	92	96	2	1	76	103	10	6
Musk ambrette	10-1000	0.9989	40.9	95	103	4	2	96	95	2	22
Traseolide	10-1000	0.9988	69.2	84	92	2	1	81	151	4	5
Musk xylene	10-1000	0.9967	120.0	85	90	6	5	86	94	19	6
Galaxolide	10-1000	0.999	13.3	92	90	8	4	98	133	5	9
Tonalide	10-1000	0.9992	40.0	103	111	5	2	110	106	4	5
Musk moskene	10-1000	0.998	112.5	104	93	3	6	91	88	3	18
Musk tibetene	10-1000	0.9989	45.0	99	89	6	4	94	102	20	4
Musk ketone	10-1000	0.9991	78.3	91	95	6	5	93	97	5	4

Table 3. Method validation parameters: linearity range, coefficient of determination (R^2), limit of detection (LOD), repeatability and recovery for PCBs, BFRs and HCB.

				Soils (n=4)		Soils (n=4)		Vegetation (n=4)		Vegetation (n=4)	
	Linearity (µg/L)	**R^2**	**LOD** pg/g (fw)	**Recovery (%)**		**Repeatability (RSD %)**		**Recovery (%)**		**Repeatability (RSD %)**	
PCBs				6 ng/g	18 ng/g	6 ng/g	18 ng/g	6 ng/g	18 ng/g	6 ng/g	18 ng/g
PCB 28	4-400	0.9987	2.4	92	101	4	2	86	89	2	7
PCB 52	4-400	0.9991	1.1	100	98	2	2	96	105	3	3
PCB 77	4-400	0.9991	3.8	101	96	2	5	117	84	4	27
PCB 81	4-400	0.998	4.3	92	83	3	4	102	97	15	27
PCB 101	4-400	0.9985	7.5	105	96	3	4	97	90	5	17
PCB 105	4-400	0.9986	7.9	68	95	10	12	87	84	19	7
PCB 114	4-400	0.9993	7.3	97	70	15	1	79	88	17	14
PCB 118	4-400	0.998	9.5	86	108	7	6	95	93	9	11
PCB 123	4-400	0.9973	9.5	98	94	5	6	87	106	24	27
PCB 126	4-400	0.9978	7.0	100	73	32	21	104	65	23	12
PCB 138	4-400	0.9976	1.9	107	92	6	2	99	83	4	4
PCB 153	4-400	0.9993	2.1	97	104	2	4	90	83	3	7
PCB 156	4-400	0.9987	3.1	108	123	3	1	82	64	8	1
PCB 157	4-400	0.9953	3.0	93	113	10	3	83	79	17	25
PCB 167	4-400	0.9984	4.0	72	54	2	6	93	74	7	33
PCB 169	4-400	0.9988	2.6	80	87	19	28	96	76	33	18

				Soils (n=4)		**Soils (n=4)**		**Vegetation (n=4)**		**Vegetation (n=4)**	
	Linearity (µg/L)	**R^2**	**LOD** pg/g (fw)	**Recovery (%)**		**Repeatability (RSD %)**		**Recovery (%)**		**Repeatability (RSD %)**	
PCBs				6 ng/g	18 ng/g	6 ng/g	18 ng/g	6 ng/g	18 ng/g	6 ng/g	18 ng/g
PCB 180	4-400	0.9977	2.4	111	83	15	8	81	101	17	26
PCB 189	4-400	0.9991	2.7	66	69	8	23	96	46	16	12
PCB 209	4-400	0.9982	2.5	114	83	14	13	37	26	18	16
BFRs											
BDE 28	4-400	0.9986	3.6	85	96	5	4	80	83	5	7
BDE 47	4-400	0.9986	6.2	96	99	15	1	97	80	12	22
BDE 85	4-400	0.9995	75.8	86	90	29	25	87	134	27	8
BDE 99	4-400	0.9978	24.0	82	75	8	8	77	102	14	18
BDE 100	4-400	0.9986	22.2	68	93	21	9	78	52	5	9
BDE 153	4-400	0.9988	12.1	72	86	14	17	100	91	8	7
BDE 154	4-400	0.9993	7.3	88	88	14	33	113	88	12	15
BDE 183	4-400	0.996	27.2	66	74	17	13	81	79	17	35
HBB	4-400	0.9912	6.6	92	74	8	4	74	71	27	6
PBEB	4-400	0.9991	9.9	114	117	8	6	97	68	5	28
PBT	4-400	0.9953	8.1	119	99	12	2	103	81	7	13
HCB	4-400	0.9985	0.7	64	76	3	3	70	55	3	12

As mentioned above, in the last years, some classic methods developed to extract and determine the concentrations of SVOCs, although very reliable, were sometimes time- and solvent-consuming. The QuEChERS protocol developed in this study aims to imitate those performances, with a much faster and clean procedure. Comparing the present results with those reported by Silva et al. (2015) for a multi-component protocol consisting of USE followed by a classic SPE coupled to GPC, there is an agreement between the current indicators (PAHs in pine needles with recoveries of 55–114 % and LODs of 4.4–225 pg/g) and those of Silva et al. (2015) (40–121 % recoveries; LODs: 3.4–332.6 pg/g). Regarding SMs, slightly higher values of recoveries and LODs were obtained with the QuEChERS methodology for pine needles (recoveries: 76–151 %; LODs: 10.5–128.6 pg/g) in comparison with the multi-component protocol (recoveries: 48–111 %; LODs: 3.8–114.3 pg/g, respectively), but these differences are not enough to infer a generally distinct performance of the QuEChERS methodology. For PCBs again the range of recoveries achieved by QuEChERS for pine needles is was quite similar to the Silva et al. (2015) protocol (26–117 % *versus* 35–113 %, respectively). However, LODs were one order of magnitude higher (1.1 – 9.5 pg/g *versus* 0.1 – 0.5 pg/g, respectively). Regarding BFRs, better recoveries were found by using QuEChERS methodology (71–113 %) comparing with the classic multi-component protocol (8–112 %). However, as in the case of PCBs, LODs values were one order of magnitude higher (3.6–75.8 pg/g *versus* 0.4 – 3.3 pg/g). This suggests that the clean-up in QuEChERS is not as effective as in a classic SPE column for PCBs and BFRs, which is possible, particularly in complicated matrices as in this case pine needles. For HCB, the recoveries were lower for QuEChERS and LODs were similar in both methods (QuEChERS: 55–70 %; LODs: 0.7 pg/g vs Silva et al. (2015): 79–85 %; LODs: 0.4 pg/g). Again, the clean-up of the SPE columns is likely to produce better results for a pesticide like HCB.

When comparing the current LODs with other international studies, it can be seen that they are generally in line with the existing literature. Al-Alam et al. (2017) obtained LODs for PAHs in *Pinus nigra* between 10–480 pg/g, using a combined method based on accelerated solvent extraction (ASE), followed by purification by solid-phase extraction (SPE) and with the analysis performed by GC-MS/MS and LC-MS/MS. Similar LODs were also reported by Gorshkov (2008) for PAHs in *Pinus sylvestris* by using USE followed by SPE silica gel cartridges and with the analysis performed by GC-MS. In addition, the present LODs for PAHs obtained with the QuEChERS methodology were lower than those found by Navarro-Ortega et al. (2012) (300–3500 pg/g) for in three species of pines (*Pinus halepensis*, *Pinus pinea* and *Pinus nigra*) by using pressurized liquid extraction system (ASE) followed by SPE alumina cartridges and with the analysis performed by GC-MS. In the case of SMs, there are still few international studies that analyse these compounds in environmental samples. Among these studies, Ribeiro et al. (2017) found comparable LODs for SMs in different coastline plant species using QuEChERS followed by GC-MS (LODs ranged from 20 to 370 pg/g, with the exception of musk ambrette which recorded a LOD value of 1320 pg/g). Regarding PCBs, similar LODs values for pine needles were recently found by Li et al. (2016) (1.9–8.6 pg/g) using ASE coupled with SPE clean-up and GC–MS/MS; or by Al Dine et al. (2015) for PCBs and OCPs (3.5–21 pg /g) employed ASE cells followed by GC using electron capture detectors (ECD). In the case of BFRs, similar values that those present in this study were reported by Ratola et al. (2011b) in three species of pines (*Pinus halepensis*, *Pinus pinea* and *Pinus nigra*) (11–70 pg/g) using a SPE clean-up with alumina and Florisil before GC-MS in negative chemical ionization.

In the case of soils, only a few international studies have used the QuEChERS methodology in multi-component SVOCs analysis, but to our knowledge, only devoted to a single family of compounds. This is the case of Rouvière et al. (2012), to extract simultaneously 34 organochlorine pesticides in soils samples (analysis performed by GC-MS). Among these compounds, HCB was considered, obtaining a higher recovery (93.9%) than those reported in this study (64-76%; mean 70 %). Nevertheless, the LODs obtained at the present study are lower than those reported by these authors (0.7 pg/g *versus* 5.1 x 10^4 pg/g, respectively). Similar trends were found by Correia-Sá et al. (2012), where the recoveries for HCB ranged from 68 to 82 % and the LOD was 2.4 x 10^4 pg/g; or by Fernandes et al. (2013), where the recoveries ranged from 70 to 80%, and with a LOD of 6.8 x 10^3 pg/g. Recently, Cvetkovic et al. (2016) have improved the QuEChERS methodology coupled with GC-MS but only for the extraction of PAHs in soil samples. In this case, similar recoveries than those reported in the current study were registered (ranged between 81 and 110%), but, as for the HCB, Cvetkovic et al. (2016) obtained higher values for the LODs (ranged between 0.36 x 10^3 and 1.53 x 10^3 pg/g). Likewise, Homem et al. (2017) have improved the QuEChERS methodology coupled with GC-MS but only for the extraction of SMs in beach sands. In this case, similar recoveries were obtained (97% by Homem et al., 2017 and 96% at the present study). Nevertheless, the LODs obtained by Homem et al. (2017) were lower than those recorded at the present study (0.79-38 pg/g *versus* 10.5-128.6 pg/g, respectively).

When comparing the current LODs for soils with other international studies using other extraction strategies, it can be seen that they are generally in line with the existing literature. For instance, Guo and Lee (2013) obtained LODs for PAHs between 30–250 pg/g, using a combined method based on microwave assisted extraction and solvent bar microextraction (MAE–SBME) before GC-MS analysis. As in the case of vegetation, there are still international limited number of studies that analyse the presence of SMs in soils. Despite this, the LODs actually obtained are into the range determined by Aguirre et al. (2014) for amended soils (10–1100 pg/g) using stir-bar sorptive extraction (SBSE) followed by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS). Regarding PCBs and BFRs, similar LODs values were obtained by Zhu et al. (2014) (10–30 pg/g and 2–200 pg/g, respectively) using Soxhlet extraction followed by a classic SPE clean-up coupled to GC–MS.

3.3. Naturally contaminated samples

The validation of an analytical methodology is not complete before testing it with field samples. In this case, soils and pine needles from Porto and Aveiro (Portugal) were collected and the concentrations of SVOCs found in each case are summarized in Table 4.

∑PAHs levels in soils samples were of 498.3 ng/g for Porto and 171.8 ng/g for Aveiro. The samples collected in Porto showed the highest values, probably due to the fact that this city is the second most densely populated in Portugal, with a strong commercial and industrial presence, including a petroleum refinery, thermo-electrical plants and a considerable number of important factories (Ratola et al., 2015). Aveiro, in turn, is a smaller city of about 50,000 inhabitants and less urban pressure. These results are in agreement with other international studies such as the one by Nadal et al. (2009) in Tarragona County, Spain, where urban areas similar to Porto recorded the highest value for PAHs in soils (446.2 ng/g) and coastal areas showed concentrations quite similar to Aveiro (160.1 ng/g). When PAHs were individually assessed, fluoranthene was the predominant hydrocarbon in both areas, with a contribution of 17 % and 27 % of the total 16 PAHs, respectively. Likewise, pyrene was the second most predominant hydrocarbon in the soils of these areas, with a contribution of 17 % and 21 % of the total 16 PAHs, respectively. This pattern is also consistent with other studies in literature (Nadal et al., 2009; Nam et al., 2009). Regarding ∑PAHs in pine needles, 124.8 ng/g and 121.8 ng/g were detected in Porto and Aveiro, respectively. In this case, the concentrations were quite similar between sampling areas and were significantly lower than those reported by Silva et al. (2015) (ranged from 245.8 to 967.8 ng/g). However, in our case *Pinus pinea* needles were analysed whereas Silva et al. (2015) sampled *Pinus pinaster* needles, It is known that the latter species has typically a higher uptake ability towards SVOCs in comparison with *Pinus pinea*, particularly for PAHs (Ratola et al., 2011a). Consequently, the differences between site types are also not so evident for *Pinus pinea* needles. When PAHs were individually assessed, pyrene was the predominant hydrocarbon in Porto, followed by phenanthrene, with a contribution of 29 % and 25 % of the total, respectively. In turn, phenantrene was the predominant hydrocarbon in Aveiro with a total contribution of 46 %, followed by fluoranthene with a total contribution of 15 %. In this case, the patterns observed in this study are quite similar to those described by Silva et al. (2015).

Regarding ∑SMs, levels in soils were 20.1 ng/g for Porto and 5.8 ng/g for Aveiro. SMs are anthropogenic compounds mainly associated with cosmetics, personal care and household products, such as makeup, perfumes, deodorants, soaps, shampoos, etc., so it is not surprising that they can easily reach to the environment, particularly in areas of stronger human presence. This, it is not surprising that Porto registered again the highest value. Unlike other SVOCs, SMs have hardly been studied in environmental matrices. In some of those few studies, Aguirre et al. (2014) found similar values of SMs in amended soils (between 0.03 and 7.8 ng/g); as did Homem et al. (2017) in beach sand (range from 0.01 to 27 ng/g). Galaxolide was the predominant fragrance in Porto soils, followed by cashmeran, with a total contribution of 56 % and 32%, respectively. In the case of Aveiro soils, cashmeran was the predominant SM, followed by galaxolide, with a total contribution of 72 % and 18 %, respectively, but there is no apparent explanation for this shift in trend. International studies have also pointed out that galaxolide is one of the most commonly detected compounds, since it is one of the most used in these products (Ramírez et al., 2011; Homem et al., 2017; Ribeiro et al., 2017). Musks ambrette, moskene and tibetene were not detected in this study, nor were musks xylene and ketone. This could be associated to the fact that musks ambrette, moskene and tibetene are currently banned and musks xylene and ketone have a restricted use under the EU Directive 2012/21/ EU. Concerning ∑SM levels in pine needles, again similar values were recorded in Porto and Aveiro (16.8 and 16.4 ng/g, respectively). These levels were in agreement with the values reported by Silva et al. (2015) in *Pinus pinaster* needles (value for Porto: 20.7 ng/g). When the individual SM were assessed, it can be seen that galaxolide and cashmeran were again predominant in both sampling points and musks ambrette, moskene, tibetene, xylene and ketone were also not detected.

∑PCBs levels in soils confirmed the pattern: 22.6 ng/g for Porto and 8.3 ng/g for Aveiro. In this case, the concentrations are in the same order of magnitude as those found by Schuster et al. (2011) in Norwegian soils (0.21–27.1 ng/g) or by Schuhmacher et al. (2004) in Spain (0.66–12.04 ng/g). When the individual PCBs were analysed, it can be seen that PCB 180 was one of the predominant PCBs in soils samples, with a contribution of 31 % and 55 % of the total PCBs in Porto and Aveiro, respectively. PCB 180 was one of the congeners that were more extensively used in the commercial formulations and is one of the six indicators (PCBs 28, 52, 101, 138, 153, 180) proposed as markers of PCB contamination by EU legislation (EU Commission Regulation, 1259/2011). And it is the least volatile of them, hence prone to be associated with particulate matter in the atmosphere and more rapidly deposit in soils. PCBs 105, 114, 126, 156, 167 and 169 were not detected in soils samples, probability due to the fact that PCBs are banned in Europe since 1985 (Silva et al., 2015) and these congeners were not the most present in the technical mixtures. Concerning PCBs in pine needles, 9.5 ng/g were recorded in Porto and 2.0 ng/g in Aveiro, higher than those reported by Silva et al. (2015): from 0.35 to 1.01 ng/g). Regarding individual PCBs, the congener number 101 was the predominant PCB in both areas, with a total contribution of 82 % and 61 % in Porto and Aveiro, respectively. This value is unexpected, as typically the most volatile congeners of the six PCB markers (PCBs 28 and 52) are those that prevail in vegetation (Barber et al., 2003; Nadal et al., 2009), a matrix more prone to trap airborne pollutants in the gas phase.

In the case of BFRs in soils, levels were 3.0 ng/g in Porto and 1.0 ng/g in Aveiro soils, consistent with those reported recently by Liu et al. (2017) in China (0.01–3.33 ng/g). PBDE congeners 47, 99 and 100 were the predominant BFRs in soils from both sampling areas (ranging from 17 % to 45 % of the total BFRs), and the observed pattern was consistent with the predominance of these congeners in the technical mixtures of PBDEs used before the international ban of these chemicals and other international studies (Orta-García et al., 2016). Regarding BFRs in pine needles, the levels recorded for Porto (1.1 ng/g) and Aveiro (0.3 ng/g) were consistent with those reported by Silva et al. (2015) (0.45 – 0.87 ng/g). Concerning individual BFRs, PBDEs 47 and 99 were again predominant in both sampling areas, in line with the findings of Silva et al. (2015), which also reported that. On the other hand, PBDEs 85, 154, 183 and the new flame retardants HBB, PBEB and PBT were not detected in both soils and pine needles, also similarly to Silva et al. (2015), that only analysed the latter matrix.

Finally, levels between 0.011 ng/g and 0.004 ng/g were detected for HCB in soils from Porto and Aveiro, respectively. When comparing with literature, Wang et al. (2007) found higher levels (0.02–1.25 ng/g). In pine needles, the levels recorded for Porto (0.173 ng/g) and Aveiro (0.078 ng/g) were also lower than those reported by Silva et al. (2015). This could be associated with the lower recoveries found for HCB in the QuEChERS protocol.

Table 4. Levels of PAHs, SMs, PCBs, BFRs, and HCB in naturally contaminated soil and pine needle samples collected from two sites (Porto and Aveiro). Results in ng/g dry weight (mean of duplicate analysis); nd: not detected.

	Soils		Vegetation	
	Porto	Aveiro	Porto	Aveiro
PAHs	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Naph	3.306	2.426	13.556	2.860
Acy	2.871	1.088	3.264	2.108
Ace	1.024	0.197	3.410	1.108
Fluo	1.643	0.757	6.391	1.532
Phe	47.040	18.114	31.775	56.392
Ant	3.090	1.573	6.062	3.391
Flt	87.176	46.788	11.493	18.323
Pyr	85.960	35.228	35.821	16.444
BaA	23.764	4.473	1.095	1.767
Chry	54.560	17.788	7.208	15.380
B(b+k)F	34.692	12.213	1.038	1.763
BaP	45.840	9.333	1.700	0.258
IcdP	6.336	13.384	0.924	nd
DahA	64.480	1.601	0.814	0.159
BghiP	36.548	6.848	0.214	0.388
∑ PAHs	498.3	171.8	124.8	121.9
Musks				
Cashmeran	6.356	4.200	7.732	6.882
Celestolide	0.028	0.022	0.283	0.254
Phantolide	0.120	0.182	0.391	nd
M. ambrette	nd	nd	nd	nd
Traseolide	nd	0.202	nd	nd
M. xylene	2.426	nd	3.315	nd
Galaxolide	11.168	1.048	3.568	9.304
Tonalide	nd	0.143	1.519	nd
M. moskene	nd	nd	nd	nd
M. tibetene	nd	nd	nd	nd
M. ketone	nd	nd	nd	nd
∑Musks	20.1	5.8	16.8	16.4
HCB	0.011	0.004	0.173	0.078

	Soils		Vegetation	
	Porto	Aveiro	Porto	Aveiro
PCBs	(ng/g)	(ng/g)	(ng/g)	(ng/g)
PCB 28	0.238	0.035	0.322	0.371
PCB 52	0.018	0.002	0.084	0.042
PCB 77	nd	0.021	nd	nd
PCB 81	0.001	0.018	nd	nd
PCB 101	1.708	0.306	7.788	1.250
PCB 105	nd	nd	nd	nd
PCB 114	nd	nd	nd	nd
PCB 118	7.628	0.188	nd	nd
PCB 123	2.298	1.178	0.722	0.533
PCB 126	nd	nd	nd	nd
PCB 138	0.540	0.057	0.203	0.144
PCB 153	0.599	0.330	0.302	0.046
PCB 156	nd	nd	nd	nd
PCB 157	1.459	1.058	nd	nd
PCB 167	nd	nd	nd	nd
PCB 169	nd	nd	nd	nd
PCB 180	7.088	4.532	0.468	0.061
PCB 189	0.271	0.135	nd	nd
PCB 209	0.760	0.396	nd	nd
∑PCBs	22.6	8.3	9.5	2.0
BFRs				
BDE 28	0.152	0.135	0.073	nd
BDE 47	0.989	0.174	0.333	0.117
BDE 85	nd	nd	nd	nd
BDE 99	0.851	0.457	0.653	0.099
BDE 100	0.574	0.259	0.005	0.033
BDE 153	0.395	nd	nd	nd
BDE 154	nd	nd	nd	nd
BDE 183	nd	nd	nd	nd
HBB	nd	nd	nd	nd
PBEB	nd	nd	nd	nd
PBT	nd	nd	nd	nd
∑BFRs	3.0	1.0	1.1	0.3

4. CONCLUSIONS

A multi-compound protocol using QuEChERS and coupled with GC-MS quantification was optimized and validated for the simultaneously extraction of five different classes of SVOCs (PAHs, PCBs, BFRs, SMs and HCB) in soils and vegetation (pine needles) samples. After several tests involving the key parameters in QuEChERS-based protocols, two final configurations were obtained, depending on the matrix:

- Soils: extraction solvent: ACE/DCM (1:1); composition of QuEChERS 1: $NaCH_3COO$ and anhydrous $MgSO_4$; composition of QuEChERS 2: 0.9 g of $MgSO_4$, 150 mg of PSA and 150 mg of C18; and filtration with PTFE filters of 0.2 µm and sample dryness before reconstitution in the GC-MS injection solvent.
- Pine needles: extraction solvent: HEX/DCM (2:1); composition of QuEChERS 1: $NaCH_3COO$ and anhydrous $MgSO_4$; composition of QuEChERS 2: 0.9 g of $MgSO_4$, 0.15 g of alumina, 0.15 g of Florisil and 0.15 g of C18; and filtration with PTFE filters of 0.2 µm and sample dryness before reconstitution in the GC-MS injection solvent.

Successful linearity, selectivity, precision, accuracy, repeatability, and good recovery values (with RSDs below 20% in all cases) were obtained. The method LODs obtained were similar to those obtained by other worldwide standardized methods. Over all, the present results showed that the proposed method, can reduce costs (much less solvents and sorbents) and operation time, without compromising the performance of the method given by the validation parameters. It was also clear that throughout the optimization process, some of the options that were discarded in the end also produced very good results. This suggests that they could also be used after proper validation for other matrices or other operative conditions. Being able to reproduce multi-residue protocols based in classic extraction and clean-up strategies using alternatives that abode by the principles of green analytical chemistry should be an objective of analytical chemists, also to allow many more scientists to perform these kind of studies where logistic and financial frameworks are not so favorable.

Regarding real samples, pine needles tend to accumulate preferentially PAHs and PCBs of lower molecular weight that predominate in gas-phase. In turn, soils tend to accumulate pollutants present in the particulate-phase, with higher molecular weight and with greater stability or recalcitrance.

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ARTICLE 2: MULTI-COMPONENT DETERMINATION OF ATMOSPHERIC SEMI-VOLATILE ORGANIC COMPOUNDS IN SOILS AND VEGETATION FROM TARRAGONA COUNTY, CATALONIA, SPAIN.

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ABSTRACT

Tarragona County, Spain, is home to the most important chemical/petrochemical industrial complex in Southern Europe, raising concerns about the presence and effects of the numerous environmental contaminants. In order to assess the levels and patterns of five classes of semi-volatile organic compounds (SVOCs) (polycyclic aromatic hydrocarbons (PAHs), synthetic musks (SMs), polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs) and one organochlorine pesticide, hexachlorobenzene (HCB)), 27 samples of soil and vegetation from different areas (petrochemical, chemical, urban/residential, and background) of Tarragona County were analysed. To achieve this goal, an innovative multi-component analytical procedure based on the “green” extraction technique QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) and GC-MS were used. The results show that PAHs levels in soils ranged from 45.12 to 158.00 ng/g and from 42.13 to 80.08 ng/g in vegetation samples; and in general, the urban areas presented the higher levels, mainly associated with the presence of a nearby highway and several roads with heavy traffic. In the case of SMs, levels in soils and vegetation ranged from 5.42 to 10.04 ng/g and from 4.08 to 17.94 ng/g, respectively, and in both cases, background areas showed the highest levels, suggesting an influence of the personal care products derived from beach-related tourism in the coast. Regarding PCBs, the chemical area, showed the highest values of PCBs in both matrices (from 6.62 to 14.07 ng/g in soils; from 0.52 to 4.41 ng/g in vegetation) at the same sampling point, probably associated with the presence of two sub-electrical stations located in the

vicinities. In general terms, BFRs values recorded in soil and vegetation were quite similar between matrices and sampling areas, which may reflect their predominant association with indoor environments and also their banning for several years. Concerning HCB, similar values were found in both matrices and in all areas, reflecting its high volatility and strong proneness to long-range atmospheric transport (LRAT) that tends to even the levels close and more distant to the emission points.

Keywords: Semi-volatile organic compounds (SVOCs) · Passive sampling · Soil · Vegetation · Tarragona, (Spain).

1. INTRODUCTION

It is well known that chemical and petrochemical industries can potentially release a considerable number of pollutants to the environment, such as semi-volatile organic compounds (SVOCs) (Nadal et al., 2011; Alghamdi et al., 2015). SVOCs include a wide variety of chemicals, characterized by their volatility, toxic effects in humans and wildlife, bio-accumulative potential and environmental persistence (UNEP, 2008 a, b, c). These characteristics make SVOCs transboundary chemicals via long-range atmospheric transport (LRAT), capable to reach remote and sensitive regions, far away from the emission sources (UNEP, 2008 a, b, c). In this study, five families of compounds are targeted: polycyclic aromatic hydrocarbons (PAHs), mainly associated with combustion processes (Domínguez-Morueco et al., 2017); polychlorinated biphenyls (PCBs), used in transformers, capacitors, paints (Erickson and Kaley, 2011); brominated flame retardants (BFRs), present in electrical appliances and furniture (McGrath et al., 2016); organochlorine pesticides (in this case hexachlorobenzene, HCB) applied predominantly in agriculture (Zhu et al., 2014); and synthetic musks (SMs), contaminants of emerging concern widely incorporated in personal care and household products (Silva et al., 2015). Some SVOCs such as PCBs, BFRs, and OCPs were already classified as “persistent organic pollutants (POPs)” by the Stockholm

Convention (www.pops.int), while others like PAHs are usually characterized as “potential POPs” (Cai et al., 2008; Silva et al., 2015). All these compounds are emitted by anthropogenic sources only (industrial activities, agriculture, vehicle transit, etc.), except for PAHs, which can also have natural origins (forest fires, volcanic eruptions, etc.). Although the use of some of them like PCBs and OCPs has been restricted or banned in most developed countries (UNEP, 2008a), they remain in the environment due to their persistence and past extensive use.

The atmosphere is the main SVOCs recipient in the environment through direct emissions, although other pathways have been identified, for example, by spraying onto soils and vegetation (He and Balasubramanian, 2010). Once applied or released into the atmosphere, SVOCs are transported and deposited (through dry or wet deposition) over different environmental matrices such as water, soil, biota, or even in ice-cores of remote areas (Herbert et al., 2004; Schuhmacher et al., 2004; Nam et al., 2008; He and Balasubramanian, 2010; Nadal et al., 2011; Yogui et al., 2011; Ratola et al., 2014; Liu et al., 2016). Experimental observations and modeling results (Diamond et al., 2001; Kawamena et al., 2007; Cai et al., 2008; Bao et al., 2015; 2016; Domínguez-Morueco et al., 2016) demonstrate that, among all environmental matrices, soils are one of the main reservoirs of SVOCs, given their high affinity for hydrophobic organic pollutants. In this sense, soil sampling can provide current SVOCs levels, as well as long-term information on the so-called “legacy SVOCs”, already banned. This fact coupled with the natural re-volatilization processes associated with changes in seasons and climate conditions, make soils a secondary source of SVOCs (Ma et al., 2011; Komprda et al., 2013; Bao et al., 2016), reaching other environmental matrices such as water bodies and vegetation. However, plants can absorb SVOCs not only from soil via the roots, but mainly via deposition from the surrounding atmosphere (via aerial parts, especially leaves) (Barber et al., 2004; Yogui et al., 2011). Once captured, the rapid kinetic of exchange between vegetation and air causes that some SVOCs return to the atmosphere (Barber et al., 2003; 2004). This re-volatilization process is higher than in the case of soils, so vegetation plays an important role as short-term source and sink of SVOCs (Bao et al., 2016).

The need to monitor SVOCs led to the development of a wide range of sampling devices. However, some of these have a high initial cost and also require electricity and maintenance, which is a disadvantage in many sampling areas, in particular more remote ones (Mari et al., 2008; Zhu et al., 2015; Domínguez-Morueco et al., 2017). Thus, passive sampling based on soils and vegetation can provide a first approximation of SVOCs concentrations in the environment, without maintenance and reaching remote or poorly accessible areas. Furthermore, the use of soil and vegetation could be an appropriate tool to assess short and long-term SVOCs levels. Likewise, it is also important to develop expedite analytical methods that allow the quantification of a large number of environmental pollutants in these complex matrices, while reducing the use of potentially harmful inputs like organic solvents (Domínguez-Morueco et al., 2016b). In order to comply with these guidelines, and following an initial methodology developed by Silva et al. (2015), a new protocol based in the “green” alternative QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) -a user-friendly extraction and clean-up technique developed by Anastassiades et al. (2003)-, and GC-MS quantification was validated for the simultaneous analysis of the 5 target classes of SVOCs (Carvalho et al., submitted to Anal. Bioanal. Chem.).

The objective of this study is then to determine the SVOCs levels and patterns of PAHs, SMs, PCBs, BFRs, and HCB in soil and vegetation samples from different areas of Tarragona County, Spain, where the most important chemical/petrochemical industrial complex in Southern Europe is hosted. Moreover, source apportionment and human health risks derived from the exposure to those contaminants were also evaluated and here presented, in order to determine the effects of such a potential pollution “hot spot” area.

2. MATERIAL AND METHODS

2.1. Sampling

By the end of January 2016, a total of 27 soil samples and 27 vegetation samples were collected in different zones of Tarragona County, with the following distribution: 7 in a zone under the potential influence of petrochemical complex, which includes a big oil refinery; 9 in the vicinity of the chemical area and 6 in residential and urban zones of Tarragona County. These sampling sites were located less than 2 km from the considered pollution sources. In addition, 5 sampling points were selected in background areas, about 30 km away from the potentially primary sources of contamination. The geographic location of each sampling point is shown in Fig. 1.

A total of 100 g approximately of soil were collected from the soil horizon A (0-5 cm depth) in each sampling point and kept in polyethylene bags. Subsequently, the soils were dried at room temperature and sieved through a 2-mm mesh screen (Nadal et al., 2004a, 2009, 2011). Likewise, a total of 50 g of vegetation samples (*Piptatherum L.*) were obtained by cutting the plants 5 cm above ground, and dried at room temperature (Nadal et al., 2009, 2011). All samples were properly stored until the analysis.

2.2. Reagents and materials

The reagents and materials used were similar to those described previously in article 1 chapter 2 (Carvalho et al., submitted to Anal. Bioanal. Chem.).

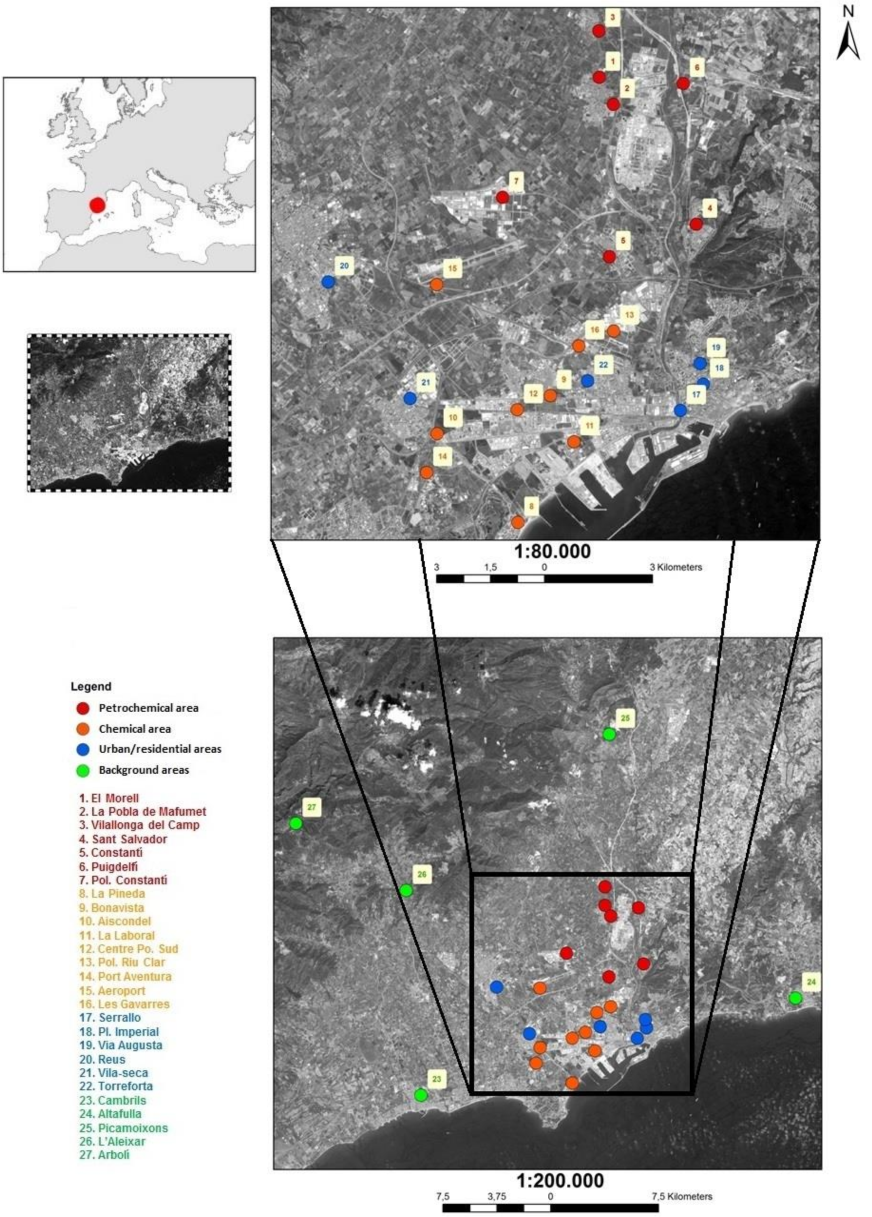

Fig. 1. Detailed map of the sampling points.

2.3. Sample extraction

As mentioned previously, a multi-component extraction protocol using the “green” technology QuEChERS was optimized to extract the target SVOCs extraction from soil and vegetation samples (Carvalho et al., submitted to Anal. Bioanal. Chem.). This methodology was similar for both matrices, except for some details explained henceforth.

A total of 2.5 g of soil and vegetation were transferred into 50mL Falcon tubes and spiked with the pertinent surrogate standards (100 µL composed by 5 µL of d-PAHs and 4 µL of mass-labelled PCBs). After spiking, the samples were shaken in a vortex for 3 min, to better impregnate the standards.

For soils, 10 mL of acetone:DCM (1:1) were then added, whereas for vegetation 20 mL of the extraction solvent (Hex:DCM 2:1) were required in order to have all the sample submerged. Subsequently, all the samples were first extracted in a sonication bath (J.P. Selecta, Barcelona, Spain) for 10 min.

After ultrasound extraction, for both matrices, the content of the QuEChERS 1 (6 g of $MgSO_4$ and 1.5 g of CH_3COONa) was added to each Falcon tube and the content vortexed for 3 min. Then, the tubes were centrifuged in a Rotofix 32A centrifuge from Hettich (Kirchlengern, Germany) for 10 min and the supernatant collected and transferred to QuEChERS 2. The QuEChERS 2 composition for soil samples was 0.9 g of $MgSO_4$, 0.3 g of primary secondary amine (PSA) and 0.15 g of C18 sorbent for polar molecules. For vegetation samples the composition of QuEChERS 2 considered was 0.9 g of $MgSO_4$, 0.15 g of alumina, 0.15 g Florisil and 0.15 g of C18. The tubes were shaken again during 3 min in order to conduct the dispersive solid-phase extraction (d-SPE). After that, the tubes were centrifuged (10 min) and the extract was collected and filtered with a conventional 0.2 µm size filter from Terumo Europe NV (Leuven, Belgium) in order to remove more unwanted compounds. The final sample extract was concentrated until dryness with nitrogen and subsequently re-dissolved with 100 µL of Hex before chromatographic analysis.

2.4. GC-MS analysis

The chromatographic analysis was similar to that described by Silva et al. (2015) and also described previously in Carvalho et al. (submitted to Anal. Bioanal. Chem.).

2.5. Quality control and quality assurance (QA/QC)

Given that SMs are present in most personal care products, some restrictions in the use of this products had to be enforced for the laboratory personnel. Scented cosmetics such as perfume, lotions and hand soap and creams were avoided. Additionally, procedural blanks were frequently done in order to identify and correct possible external contaminations. The blanks were extracted following the same protocol as the samples. In general, only some PAHs, some PCBs and SMs, namely galaxolide and cashmeran, were detected. Consequently, the results were blank-corrected when necessary. Also, all non-calibrated glass material was baked overnight at 400 ºC before use in the analysis to eliminate possible remaining compounds. The recoveries for PAHs ranged in mean from 106 % ± 12 for soils and from 86 % ± 17 vegetation samples. In the case of SMs ranged in mean from 96% ± 7 for soils and 99 % ± 17 vegetation. The recoveries for PCBs ranged in mean from 92 % ± 15 in soils samples and from 85 % ± 18 for vegetation. BRFs recoveries ranged in mean from 89 % ± 15 for soils and from 87 % ± 17 for vegetation samples; and in the case of HCB from 70 % ± 8 for soils and from 62 % ± 11 for vegetation samples. Regarding LODs, a range from 4.4 to 62.1 pg/g was obtained for 2–4 ring PAHs (Naph–Chry) and between 20.5 and 225 pg/g for the 5–6 ring PAHs (BbF + BkF, BaP, DahA BghiP and IcdP). LODs for SMs ranged from 10.5 to 128.6 pg/g, for PCBs from 1.1 to 9.5 pg/g and for BFRs from 3.6 to 75.8 pg/g. Finally, for HCB the LOD was 0.7 pg/g.

2.6. Data analysis

Data analysis was carried out using the statistical software package XLSTAT version 18.02 from Addinsoft (New York, USA). Chemicals showing concentrations under the limit of detection (LOD) were assumed to have a concentration equal to one-half of that value (ND = ½ LOD). The level of significance was set at a probability lower than 0.05 ($p < 0.05$). To evaluate significant differences between groups, the Levene test was applied to verify the equality of variances. Subsequently, ANOVA or Mann Whitney tests were applied depending on the distribution of the data (normal or not, respectively). A principal component analysis (PCA) was performed for PAH profiles (contribution of each compound, or each group of rings, for the sum of the total), for SMs profile, BFRs profile and PCBs profile in soil and vegetation samples according to the different sampling areas. The sampling sites considered were petrochemical area (n=7), chemical area (n=9), urban area (n=6) and background area (n=5).

3. RESULTS AND DISCUSSION

3.1. Soil samples

The mean total SVOCs levels from soils samples collected in different areas of Tarragona County are summarized in Table 1 and the individual values for each sampling point in Table S1 (Annex 5). With the exception of nitro musks (ambrette, xylene, moskene, tibetene and ketone), PCB 169 and some brominated flame retardants (BDE 183 and HBB), all the target SVOCs were detected.

The mean total of the 16 priority PAHs listed by the United States Environmental Protection Agency (US EPA, 1993) ranged from 45.12 to 158.00 ng/g. Regarding the $\sum_7$ PAHs classified at least as probable human carcinogens under the B2 group (benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(*1,2,3-c,d*)pyrene, dibenzo(*a,h*)anthracene) (US EPA, 1993), levels ranged from 15.75 to 82.77 ng/g. The samples collected at the urban areas showed the highest mean values (157.00 and 82.77 ng/g for $\sum_{16}$ PAHs and $\sum_{7}$ carcinogenic PAHs, respectively), followed by the chemical industry area (97.52 ng/g for $\sum_{16}$ PAHs and 47.07 ng/g for $\sum_{7}$ carcinogenic PAHs). In turn, the background areas as expected presented the lowest values of the total PAHs (45.12 ng/g), as well as of the 7 carcinogenic PAHs (16.62 ng/g). The levels in the urban area were between 3- and 4-folder higher than those found in the petrochemical and background areas, respectively. Although no statistically significant differences were found in the levels of the total 16 PAHs, significant differences ($p<0.05$) were found in the total 7 probable carcinogenic PAHs between urban and petrochemical and background areas (82.77 ng/g vs 15.75 ng/g and 16.62 ng/g, respectively). This fact denotes a notable influence of urban sources on the surrounding environment. When PAHs were individually assessed, fluoranthene was the predominant compound in urban and chemical areas, with a contribution, in both zones, of 13% of the total 16 PAHs (Table 1). In addition, statistically significant differences between both areas and background areas were found for this compound (21.14 ng/g and 12.34 ng/g, respectively, vs 3.61 ng/g: $p<0.05$) (Table 1). In the petrochemical area, pyrene was the main PAH, with a contribution of 28 % of the total 16 PAHs. No statistically significant differences were found between areas. On the other hand, naphthalene prevailed in background areas, with a contribution of 34 % of the total 16 PAHs; and statistically significant differences between these areas and petrochemical and chemical areas were found for this compound (15.42 ng/g vs 2.14 ng/g and 2.94 ng/g, respectively: $p<0.05$). The higher volatility of this compound compared to other PAHs could favour its accumulation far from the emission points. Concerning the ring patterns, a clear difference between petrochemical/chemical/urban and background areas was observed, since PAHs with 4, 5 and 6 rings were the predominant in the former areas while 2 and 4 rings PAHs prevailed in background areas (Fig. 2 A). Both facts are in agreement with the theory that the low molecular weight PAHs are ubiquitous pollutants with a high long-range transport capacity, being the naphthalene identified as one of the typical PAH markers of background pattern (Nadal et al., 2009). Among the 16 priority PAHs, benzo(*a*)pyrene was identified by the International Agency for Research on Cancer (IARC) as one of the most dangerous. In this study, a significant increase of benzo(*a*)pyrene was found in the urban area comparing to the petrochemical and background areas (20.32 ng/g vs 3.65 ng/g and 4.10 ng/g), and with the same contribution to the total 16 PAHs than fluoranthene (13%). However, the values recorded in the different sampling points did not exceed the maximum levels allowed for PAHs in soils by the Spanish legislation (Royal Decree 9/2005, setting a limit for industrial soils of 2000 ng/g, for urban soils of 200 ng/g, and for soils with other uses of 20 ng/g) (BOE, 2005).

As mentioned above, Tarragona County is potentially a high-impact region. For this reason, since 2002, a large multi-compartmental environmental monitoring program has been carried out, comprising the analysis of some organic pollutants in soil and vegetation samples (Nadal et al., 2004a, b, 2007, 2009, 2011; Schuhmacher et al., 2004). Among these pollutants, the 16 priority PAHs and, among them, the 7 carcinogenic PAHs were monitored. When comparing the mean total concentrations found in this study with those found in the previous surveys conducted in this area (112 – 1002 ng/g $\sum_{16}$ priority PAHs and 37 – 397 ng/g $\sum_{7}$ carcinogenic PAHs from Nadal et al., 2004a; 97.2 – 446.2 ng/g $\sum_{16}$ priority PAHs and 28.2 – 189.0 ng/g $\sum_{7}$ carcinogenic PAHs from Nadal et al., 2009; 133.2 – 684.7 ng/g $\sum_{16}$ priority PAHs and 34.0 – 351.6 ng/g $\sum_{7}$ carcinogenic PAHs from Nadal et al., 2011), it can be seen that the current values would be in the lowest part of the range. In general, a decreasing tendency in the PAHs concentrations is observed in Tarragona County since the beginning of the multi-compartmental environmental monitoring program in 2002. This fact could be explained by the reduction in the PAHs emissions observed between 1990 and 2010 in the majority of the European countries (Garrido et al., 2014), probably associated with changes in the legislation, enforcing the modernisation of industrials processes, fuels, etc. Likewise, the present values are lower than the values of the total PAHs found by Zhu et al. (2007) in Zhejiang Province, China (85.2 – 676.2 ng/g), by Wang et al. (2012b) in south China (127 – 10,6000 ng/g) and well below the average defined by Nam et al. (2009) for the European soils (714 ng/g). In addition, $\sum_{16}$ priority PAHs in Tarragona soils are within the range recorded in other international studies as conducted by Nam et al. (2008) in the UK and Norwegian soils (42 –11200 ng/g and 8.6 – 1050 ng/g, respectively); by Liu et al. (2016) in Eastern China (15.9 – 1,675.5 ng/g); or within the global range defined by Nam et al. (2009) (<1 - 7,840 ng/g in soils from Antarctic/Australia and mainland Europe, respectively). In turn, Chrysikou et al. (2008) recorded in soils from Northern Greece lower values than those presented in this study (11.2 – 28.1 ng/g). Regarding the spatial distribution, the present work is in agreement with the previous studies conducted in Tarragona County, since all have also identified the highest concentrations of PAHs in urban areas and fluoranthene as one of the predominant PAHs (Nadal et al., 2004a; 2007; 2009; 2011). This could be associated with the presence of highway and several roads with heavy traffic in this area, since traffic has been demonstrated to be one of the most important emission sources of PAHs (Nadal et al., 2009). As in previous studies in Tarragona County, the fact that PAHs levels recorded in petrochemical soils were not, contrary to what was expected, the highest in the study was associated to the considerable height of the stacks and torches of the oil refinery. This coupled with its Northern location and the prevailing North-Northwest annual wind direction would facilitate the deposition of PAHs far from these sources (Nadal et al., 2009). This is the case of naphthalene, which as in these studies, was also one of the predominant PAHs in Tarragona background areas (Nadal et al., 2009).

Regarding to the mean total PCBs, the levels found in soils from different Tarragona areas ranged from 6.62 to 14.07 ng/g (Table 1). The samples collected in the chemical area showed the highest mean values (14.07 ng/g), followed by urban area (10.81 ng/g). As in the case of PAHs, the background sites presented the lowest values of the total PCBs (6.62 ng/g). The levels in the chemical area were 2 times higher than those found in the petrochemical and background areas (14.07 ng/g vs 6.79 ng/g and 6.62 ng/g, respectively), being these differences statistically significant ($p<0.05$). Individually, PCB 153 was the predominant congener in chemical and petrochemical areas, with a contribution of 46 % and 24 % of the total PCBs, respectively (Table 1). PCB 153 is a non-dioxin-like congener found in high concentrations in the environment (especially in soils), in human tissue and in other biological samples (Wania, 1999; Abass et al., 2013). On the other hand, PCB 138 was the predominant PCB in urban areas, with a contribution of 40% of the total PCBs. This congener (as well as PCB 153 among others) is present in the common Aroclor formulations used frequently in the past and in the proposed lists of indicator PCB congeners (Ishikawa et al., 2007). For this compound, statistically significant differences between urban areas and petrochemical areas (4.28 ng/g vs 0.83 ng/g); and between background areas and chemical areas were found (1.09 ng/g vs 3.86 ng/g) (Table 1). Relating to background areas, the contribution was very similar between congeners (PCB 138 contributed with 16 % of the total PCBs; and PCB 101, 123, 126 and 180 with 15 %, of the total PCBs each one). In this case, statistically significant differences between urban/background areas and petrochemical/chemical areas were found only for PCB 123, whereas for PCB 138 the significant differences were mainly found between chemical and petrochemical areas and for PCB 180 between chemical and petrochemical/urban areas (Table 1). As in the case of PAHs, a molecular weight pattern was observed for tri, tetra, penta, hexa, hepta and octa CBs between sampling areas, since octa and hepta CBs were the predominant congeners in petrochemical, chemical and urban areas while penta and hexa CBs prevalence was seen in background areas (Fig. 2 B).

In the multi-compartmental environmental monitoring program conducted since 2002 in Tarragona County, some PCB congeners were also included, namely 28, 52, 101, 118, 138, 153 and 180. When comparing the current concentrations of these specific congeners (mean total of 5.27 ng/g, 12.21 ng/g, 7.64 ng/g and 3.50 ng/g in petrochemical, chemical urban and background areas, respectively) with those found in the Tarragona monitoring program (0.77 – 4.67 ng/g from Nadal et al., 2007; 0.58 – 5.09 ng/g from Nadal et al., 2009; 0.46 – 5.92 ng/g from Nadal et al., 2011; and 0.66 – 12.04 ng/g from Schuhmacher et al., 2004), it can be seen that the present values are moderately higher. In addition, the values of PCBs found in Tarragona soils were higher than the values recorded by Grimalt et al. (2004) (0.41 – 1.5 ng/g); by Wang et al. (2012) (0.6 – 1.44 ng/g) or by Cabrerizo et al. (2012) (0.005−0.14 ng/g) in soils from remote areas (European high altitude mountain and Antarctica region). Similar levels were reported by other international studies, such as the study conducted by Bogdal et al. (2017) in Swiss soils (0.5 – 10 ng/g); by Chrysikou et al. (2008) in Northern Greece (4.02 – 11.2 ng/g); by Roots et al. (2010) in Estonian soils (<LOD – 12 ng/g) or by Zhu et al. (2014) (1.46 – 19.2 ng/g) in soils from the industrialized area of Shouguang, China. Furthermore, PCBs in Tarragona soils were within the range recorded by Schuster et al. (2011) in Norwegian soils (0.21 – 27.1 ng/g); by Pérez-Vazquez et al. (2015) (0.30 ng/g – 80.5 ng/g) and Orta-García et al. (2016) (4.0 – 65.5 ng/g) in Mexico, or by Sun et al. (2016) in soils from Kenya (nd – 55.49 ng/g). Contrastingly, other authors such as Zhang et al. (2007) (70 ng/g – 990 ng/g) (Hong Kong, China), Ren et al. (2007) (140 ng/g – 184 ng/g) (across China) or Alawi and Azeez (2017) (38 – 980 ng/g) (Waset region, Iraq) have found relatively higher amounts of PCBs in soil samples than those presented in this study. On the other hand, the highest values of PCBs recorded in the chemical area and the great contribution of PCB 153 were also consistent with previous studies conducted in Tarragona County (Nadal et al., 2007; 2009; 2011; Schumacher et al., 2004). The chemical area was mainly influenced by the sampling point 11 (La Laboral), which recorded the maximum values of the total PCBs in soils (35.34 ng/g) and the maximum for the PCB 153 (22.90 ng/g) of this study (Table SI 1). PCBs were compounds widely used in the electrical industry between the 1950s-1980s in capacitors and transformers, besides being used in other industries as plasticizers in paints and joint sealants (Loizeau et al., 2014; Silva et al., 2015; Bogdal et al., 2017). Although banned in Europe in 1985, PCBs can still be found in the environment due to its presence in old

equipment and facilities. Thus, the presence of high concentrations of PCBs in sampling point 11 could be associated with the presence of two sub-electrical stations located in the vicinity. Moreover, other studies state that, among all PCBs, congeners 153, 138 and 180 are the most resistant to degradation in soils (Wong et al., 2009), which would be associated with its dominant presence in other areas such as urban or background as well.

The levels of synthetic musks (SMs), brominated flame retardants (BFRs) and HCB were analyzed for the first time in soils samples from Tarragona County (Table 1).

SMs are mainly used as fragrance additives and fixative elements in personal care and household products (Ramírez et al., 2011; Silva et al., 2015; Ribeiro et al., 2017) and are chemicals of emerging concern due to their lipophilic character, and bioaccumulative and partially biodegradable potential (Ramírez et al., 2011; Silva et al., 2015; Homem et al., 2015, 2016; Ribeiro et al., 2017), associated with their extensive use worldwide. BFRs are also employed worldwide to avoid and/or delay combustion processes in electrical appliances and furniture (Silva et al., 2015), and as in the case of SMs, are lipophilic and have bioaccumulation potential in wildlife and humans (Covaci et al., 2007). Some of them (PBDEs, for instance) are already banned in Europe and other parts of the world, following the Stockholm Convention regulation on POPs. Due to their range of applications, SMs and BFRs are compounds strongly associated with indoor environments, and although BFRs have already been monitored in outdoor environments (Zheng et al., 2015; McGrath et al., 2016) only a few international studies (Ribeiro et al., 2017) measured SMs environmental presence. However, the present study show that some of these compounds were detected in Tarragona soil samples. SMs levels in soils ranged from 5.42 to 10.04 ng/g, and without statistically significant differences between sampling areas. In this case, the concentrations found in background areas were 2 times higher than those found in the petrochemical and urban areas. Recently, Ribeiro et al. (2017) confirmed the presence of SMs and UV-filters associated with personal care products near coastal areas. These compounds could be introduced into the environment through anthropogenic activities such as swimming in the sea or sunbathing, leading to a massive transfer of pollutants from human skin to sea water, sand or air. In this case, the background areas selected in this study are in coastal zones with a significant influence of tourism, so the observed levels of SMs could be related to the use of personal care products such as sunscreen in the area. When comparing the current concentrations of SMs with those found in other international studies, it can be seen that the present values are quite similar at those reported by Aguirre et al (2014) in amended soils (0.03 – 7.8 ng/g); by Homen et al. (2017) in beach sands (0.01 – 27 ng/g) or in the chapter 3 of this thesis for real samples of soils (5.8 – 20.1 ng/g). Regarding individual SMs, galaxolide was one of the predominant musks in all sampling areas (with a contribution between 43 % and 67 % of the total) followed by cashmeran (between 23 % and 44 %, Fig. 2 C). In both cases, no statistically significant differences were found between sampling areas. This pattern is in agreement with other international studies, which corroborate that both galaxolide and cashmeran are the most used musks in personal care and household products (Ramírez et al., 2011; Carvalho et al., submitted to Anal. Bioanal. Chem.). Nitro musks ambrette, xylene, moskene, tibetene and ketones, were not detected in this study, probably reflecting the fact that some of them were already banned or restricted in some countries and replaced by polycyclic musks (Homem et al., 2015, 2016).

Among the different BFRs, polybrominated diphenylethers (PBDEs) were the most commonly used in the past in commercial mixtures. Due to their toxicity and persistence, nowadays, the use of some of these PBDEs (penta-BDE and octa-BDE) are banned and replaced by “novel” BFRs (NBFRs) (Zheng et al., 2015; Li et al., 2016; McGrath et al., 2017), such as pentabromotoluene (PBT), pentabromoethylbenzene (PBEB) or hexabromobenzene (HBB). With the exception of BDE 183 and HBB, all the BFRs were detected in Tarragona soils. BFRs levels in soils ranged from 0.25 to 1.43 ng/g, and levels in the chemical and urban areas were between 4- and 6-folder higher than those found in the petrochemical and background areas, respectively. Consequently, statistically significant differences were found between chemical/urban area and petrochemical/background areas (1.36 and 1.28 ng/g vs 0.26 and 0.16 ng/g, respectively). Concerning individual BFRs, BDE 47 was overall the predominant congener in all the sampling areas, with a contribution between 10 % and 54 % of the total BFRs (Fig. 2 D). In this case, statistically significant differences were found between the different sampling areas (Table 1). BDE 99 and BDE 153 were the second and third most prevailing compounds in all the sampling areas (ranged 13 – 49 % and 12 – 26 %, respectively), and statistically significant differences were also found between urban and petrochemical/background areas, and between urban and background areas, respectively. Likewise, the overall contribution of the NBFRs to the total levels was minimal (less than 6%). This fact could be associated with the fact that only three of the novel BFRs are analysed and that other types of flame retardants are being used to replace PBDEs. The PBDEs ranges are in line with similar international studies like those of Zheng et al. (2015) (0.003 – 6.3 ng/g) and Liu et al. (2017) (0.007 – 3.33 ng/g) in China. Likewise, Tarragona soils were within the PBDEs range recorded by Hassanin et al. (2004) in UK and Norwegian soils (0.65 – 12.0 ng/g); by Pérez-Vázquez et al. (2015), in San Luis Potosi, Mexico (0.7 – 11.6 ng/g); or by Sun et al. (2016) in Kenya (0.19 – 35.65 ng/g). In turn, other studies reported higher values of PBDEs than the values presented in this study (Zhu et al., 2014, 18.8 – 5179 ng/g in China; Li et al., 2016, 18 – 26,000 ng/g and 4.6 – 34,000 ng/g in manufacturing area in China; McGrath et al., 2016, nd – 70.5 ng/g in Melbourne soils, Australia; Orta-García et al., 2016, 1.8 – 127 ng/g in a metropolitan area of Monterey, Mexico). Regarding to individual PBDEs contribution, the present pattern is in agreement with other authors (McGrath et al., 2016; Orta-García et al., 2016), who state that congeners 47> 99> 153 have the most incidence in soil samples.

With respect to HCB, the values in Tarragona soils ranged from 0.02 ng/g to 0.04 ng/g, being similar between sampling areas and without statistically significant differences. Although, HCB is a pesticide whose production has already been banned for decades in most countries, it is frequently remain in detectable amounts in the environment due its historical use (Zhu et al., 2014). Also HCB is formed as a by-product during the manufacturing of other chemicals (manly solvents and pesticides) (Bailey, 2001). In this case, the concentrations recorded in Tarragona County were considerably below those found in numerous international studies (Grimalt et al., 2004, 0.15 – 0.91 ng/g in soils from European high altitude mountain; Roots et al., 2010, nd – 0.5 ng/g in Estonian soils; and Wang et al., 2007, 0.0156 – 1.25 ng/g; Fang et al., 2017, 20 – 4850 ng/g and Wang et al., 2017, nd – 4.5 ng/g all of them in soils from China region), which confirms that it is not currently used. Also, being more volatile than most of the other target SVOCs, it is less likely that they deposit in soils in high amounts.

Table 1. Concentrations of SVOCs in soils samples from four areas of Tarragona County (Catalonia, Spain) (ng/g).

	Petrochemical area (n = 7)		**Chemical area (n = 9)**		**Urban area (n = 6)**		**Background area (n = 5)**	
	Mean± SD	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**
Naphthalene	2.14^{b} ± 1.29	60.16	2.94^{b} ± 3.46	117.87	7.15^{ab} ± 8.62	120.52	15.42^{a} ± 13.29	86.18
Acenaphthylene	0.83 ± 0.62	74.95	3.32 ± 8.60	259.01	1.04 ± 0.96	92.35	0.23 ± 0.16	71.84
Acenaphthene	2.19^{ab} ± 4.25	193.49	0.78^{a} ± 0.57	73.37	0.56^{ab} ± 0.39	69.92	0.24^{b} ± 0.26	111.56
Fluorene	3.53^{ab} ± 8.42	238.63	1.22^{a} ± 1.60	130.67	0.82^{ab} ± 0.62	75.35	0.22^{b} ± 0.25	114.48
Phenanthrene	2.71 ± 1.90	70.41	7.16 ± 7.99	111.51	7.03 ± 8.10	115.15	1.99 ± 0.61	30.85
Anthracene	0.20^{ab} ± 0.07	35.84	0.73^{a} ± 0.82	112.36	0.41^{ab} ± 0.85	205.27	0.12^{b} ± 0.26	217.29
Fluoranthene	3.07^{bc} ± 1.08	35.13	12.34^{ab} ± 11.65	94.40	21.14^{a} ± 18.50	87.50	3.61^{c} ± 5.12	141.66
Pyrene	13.77 ± 28.31	205.55	12.20 ± 10.47	85.82	19.15 ± 14.69	76.71	3.45 ± 4.24	122.82
Benzo(*a*)anthracene	1.89^{b} ± 1.15	60.75	7.50^{ab} ± 7.35	97.95	10.83^{a} ± 11.99	110.70	1.87^{b} ± 2.65	141.28
Chrysene	3.74^{b} ± 1.82	48.63	10.46^{ab} ± 9.50	90.82	16.18^{a} ± 12.34	76.21	4.29^{b} ± 4.75	110.77
Benzo(*b*+*k*)fluoranthene	4.62^{b} ± 2.41	52.11	10.16^{ab} ± 9.00	88.58	20.16^{a} ± 9.66	47.91	4.58^{b} ± 5.00	109.12
Benzo(*a*)pyrene	3.65^{b} ± 1.44	39.60	10.71^{ab} ± 10.23	95.57	20.32^{a} ± 12.41	61.07	4.10^{b} ± 5.76	140.61
Indeno(*1,2,3-c,d*)pyrene	1.49^{bc} ± 0.75	50.82	6.35^{ab} ± 6.70	105.54	12.36^{a} ± 7.33	59.35	1.22^{c} ± 2.09	171.42
Dibenzo(*a,h*)anthracene	0.36^{b} ± 0.27	73.75	1.89^{ac} ± 1.86	98.09	2.92^{a} ± 1.78	60.95	0.56^{bc} ± 0.71	125.75
Benzo(*g,h,i*)perylene	5.46^{b} ± 5.05	92.49	9.76^{ab} ± 8.37	85.77	17.92^{a} ± 8.97	50.07	3.23^{b} ± 3.41	105.70
Σ16PAHs	**49.64 ± 50.38**	**101.49**	**97.52 ± 87.91**	**90.14**	**158.00 ± 100.29**	**63.47**	**45.12 ± 45.72**	**101.35**
Σ 7 prob. carcinogenic PAHs**	**15.75^{b} ± 6.52**	**41.41**	**47.07^{ab} ± 44.31**	**94.13**	**82.77^{a} ± 53.83**	**65.04**	**16.62^{b} ± 20.54**	**123.57**

	Petrochemical area (n = 7)		**Chemical area (n = 9)**		**Urban area (n = 6)**		**Background area (n = 5)**	
	Mean± SD	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**
Cashmeran	1.99 ± 2.17	109.07	1.79 ± 2.52	140.77	2.09 ± 1.47	70.45	4.39 ± 2.35	53.56
Celestolide	0.18 ± 0.38	205.29	0.03 ± 0.02	58.39	0.02 ± 0.01	31.82	<LOD	-
Phantolide	0.22 ± 0.46	206.19	0.10 ± 0.11	105.37	0.05 ± 0.11	207.60	0.01 ± 0.02	120.32
Galaxolide	2.53 ± 1.82	71.94	5.24 ± 3.95	75.47	2.87 ± 1.87	65.02	5.26 ± 4.45	84.69
Traseolide	0.07 ± 0.08	125.27	0.05 ± 0.06	106.64	<LOD	-	<LOD	-
Tonalide	0.77 ± 1.23	159.42	0.33 ± 0.16	48.37	0.21 ± 0.20	98.69	0.18 ± 0.08	45.43
Musk ambrette	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Musk xylene	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Musk moskene	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Musk tibetene	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Musk ketone	<LOD	-	0.18 ± 0.42	234.63	<LOD	-	<LOD	-
Σmusks	**5.91 ± 3.49**	**59.15**	**7.83 ± 4.88**	**62.38**	**5.42 ± 2.62**	**48.28**	**10.04 ± 5.61**	**55.95**
PCB 28	0.10 ± 0.12	119.81	0.04 ± 0.02	60.90	0.11 ± 0.07	65.37	0.03 ± 0.01	26.77
PCB 52	0.06 ± 0.07	119.62	0.05 ± 0.04	78.32	0.10 ± 0.13	133.58	0.02 ± 0.01	24.12
PCB 77	0.17 ± 0.32	192.83	0.18 ± 0.33	187.85	0.35 ± 0.44	125.45	<LOD	-
PCB 81	0.10 ± 0.17	173.66	0.03 ± 0.04	135.69	0.17 ± 0.26	153.25	0.02 ± 0.05	202.46
PCB 101	1.21 ± 1.20	98.98	0.24 ± 0.50	213.03	0.97 ± 1.05	107.69	1.02 ± 1.0	97.60
PCB 105	0.02 ± 0.03	201.74	<LOD	-	<LOD	-	<LOD	-
PCB 114	0.01^{c} ± 0.005	88.34	0.01^{c} ± 0.01	101.59	0.04^{b} ± 0.02	54.08	0.17^{a} ± 0.07	42.52

	Petrochemical area (n = 7)		**Chemical area (n = 9)**		**Urban area (n = 6)**		**Background area (n = 5)**	
	Mean± SD	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**
PCB 118	1.17^{a} ± 1.01	87.03	0.02^{b} ± 0.05	236.65	<LOD^{b}	-	<LOD^{b}	-
PCB 123	<LOD^{b}	-	0.19^{b} ± 0.37	191.89	1.07^{a} ± 0.19	17.36	0.96^{a} ± 0.41	42.40
PCB 126	<LOD	-	0.33 ± 0.65	197.67	0.71 ± 0.72	101.86	1.01 ± 0.68	67.46
PCB 138	0.83^{b} ± 0.84	101.11	3.86^{a} ± 3.55	91.79	4.28^{ac} ± 4.05	94.65	1.09^{bc} ± 1.00	92.52
PCB 153	1.61 ± 1.78	110.50	6.53 ± 7.65	117.27	0.76 ± 0.70	93.04	0.34 ± 0.11	32.36
PCB 156	<LOD	-	0.17 ± 0.34	196.68	0.40 ± 0.27	65.75	0.35 ± 0.25	72.30
PCB 157	0.01 ± 0.003	84.69	0.02 ± 0.03	185.93	0.04 ± 0.08	184.57	0.11 ± 0.16	137.15
PCB 167	0.01 ± 0.01	168.68	0.05 ± 0.10	192.20	0.05 ± 0.08	158.08	<LOD	-
PCB 169	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PCB 180	0.29^{b} ± 0.15	50.93	1.47^{a} ± 0.65	43.94	1.42^{b} ± 0.34	24.18	1.00^{ab} ± 0.60	60.66
PCB 189	0.22 ± 0.23	107.13	0.11 ± 0.16	141.61	0.29 ± 0.13	47.19	0.38 ± 0.24	63.74
PCB 209	1.00^{ab} ± 1.06	106.03	0.77^{a} ± 1.42	184.00	0.05^{b} ± 0.03	51.36	0.12^{ab} ± 0.08	64.91
ΣPCBs	**6.79^{b} ± 2.26**	**33.23**	**14.07^{a} ± 9.54**	**67.79**	**10.81^{ab} ± 4.63**	**42.78**	**6.62^{b} ± 0.30**	**4.54**
BDE 28	0.004 ± 0.003	78.75	0.02 ± 0.01	77.27	0.01 ± 0.01	143.16	0.004 ± 0.004	117.81
BDE 47	0.07^{bc} ± 0.07	102.19	0.78^{a} ± 0.70	90.52	0.13^{b} ± 0.06	49.14	0.04^{c} ± 0.03	91.10
BDE 85	<LOD	-	<LOD	-	<LOD	-	<LOD	-
BDE 99	0.13^{b} ± 0.14	102.68	0.29^{ab} ± 0.31	105.67	0.67^{a} ± 0.51	77.02	0.03^{b} ± 0.02	53.61
BDE 100	0.04 ± 0.05	121.76	0.06 ± 0.04	68.99	0.10 ± 0.08	80.97	0.03 ± 0.02	62.15
BDE 153	0.07^{ab} ± 0.00	135.85	0.17^{ab} ± 0.16	92.12	0.35^{a} ± 0.50	143.02	0.06^{b} ± 0.03	50.12

	Petrochemical area (n = 7)		**Chemical area (n = 9)**		**Urban area (n = 6)**		**Background area (n = 5)**	
	Mean± SD	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**
BDE 154	<LOD	-	0.04 ± 0.04	111.27	0.02 ± 0.01	66.70	0.01 ± 0.01	75.28
BDE 183	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PBT	<LOD	-	<LOD	-	0.01 ± 0.004	68.05	0.01 ± 0.02	129.69
PBEB	<LOD	-	0.02 ± 0.02	113.05	0.01 ± 0.01	107.98	<LOD	-
HBB	<LOD	-	<LOD	-	<LOD	-	<LOD	-
ΣBFRs	**0.38^{b} ± 0.17**	**45.79**	**1.43^{a} ± 0.78**	**54.67**	**1.35^{a} ± 0.51**	**37.79**	**0.25^{b} ± 0.04**	**15.64**
HCB	**0.02 ± 0.01**	**55.04**	**0.04 ± 0.02**	**56.05**	**0.03 ± 0.04**	**162.35**	**0.02 ± 0.01**	**36.74**

LOD = limit of detection. CV = coefficient variation.

*Benzo(*a*)anthracene, chrysene, benzo(*b*+*k*)fluoranthene, benzo(*a*)pyrene, indeno(*1,2,3-c,d*)pyrene, dibenzo(*a,h*)anthracene.

Different superscripts indicate significant differences between groups ($p<0.05$).

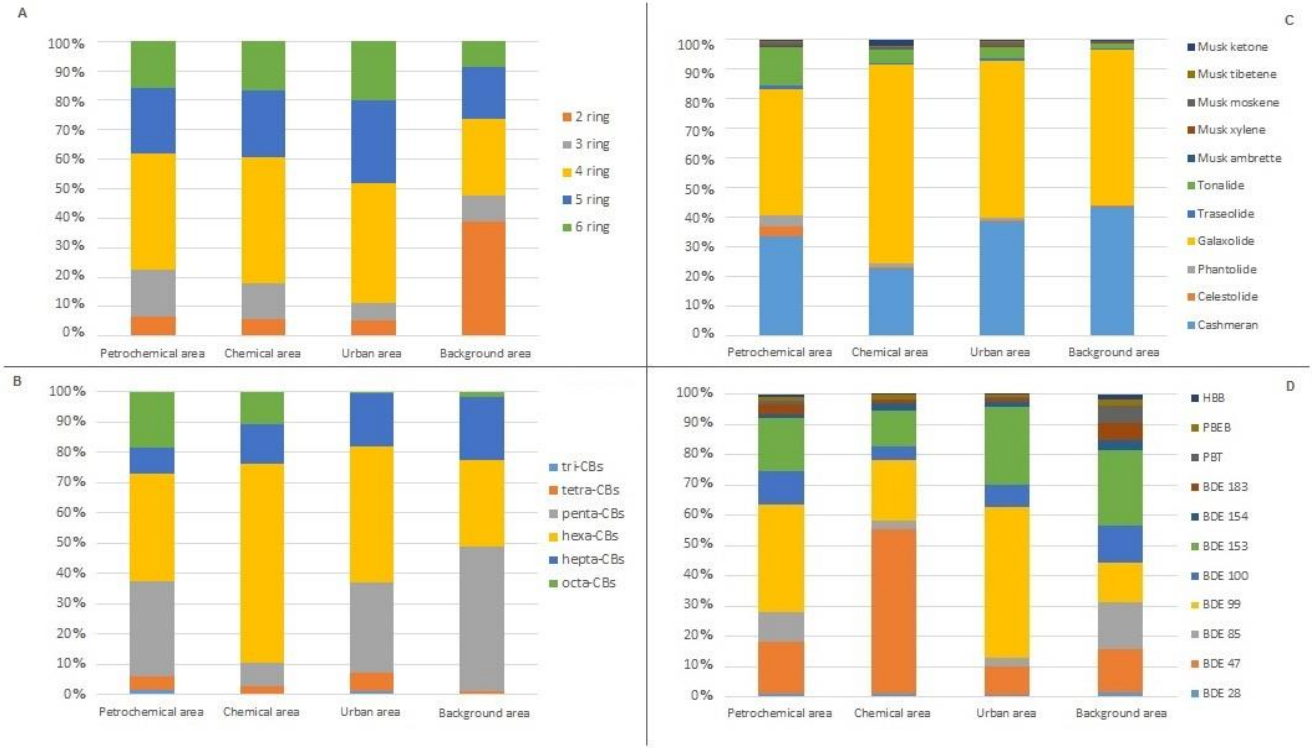

Fig. 2. Contribution (%) of each range (PAHs and PCBs) or individual compound (SMs and BFRs) to the total in soil samples from Tarragona County (Catalonia, Spain).

3.2. Vegetation samples

The mean total SVOCs levels in vegetation samples collected in different areas of Tarragona County are summarized in Table 2 and the individual compound values for each sampling point are recorded in Table S2 (Annex 5). Unlike soils, a larger number of compounds were not detected in the analysis in this matrix. Among these compounds were: traseolide and nitro musks (ambrette, xylene, moskene, tibetene and ketone); PCB 105, 114, 123, 126, 156, 157, 157, 169, 189; 209; and some brominated flame retardants such as BDE 85, 154, 183 and PBT, PBEB and HBB. Contrary to soils, vegetation is more prone to trap gas-phase atmospheric compounds (Yogui et al., 2011), although in this case, being a species of ground vegetation, also the deposition of heavier compounds is admissible.

PAHs levels in vegetation samples ranged from 42.13 to 80.08 ng/g for the $\sum_{16}$ priority PAHs and from 3.37 to 8.48 ng/g for the $\sum_{7}$ carcinogenic PAHs. The samples collected at the petrochemical and urban areas were quite similar, showed the highest values for both $\sum_{16}$ priority PAHs (80.08 ng/g petrochemical areas and 79.43 ng/g urban areas) and $\sum_{7}$ carcinogenic PAHs (7.74 ng/g petrochemical areas and 8.48 ng/g urban areas). In turn, the background areas presented the lowest values of the 7 carcinogenic PAHs (3.37 ng/g). Although no statistically significant differences were found in the levels of the total 16 PAHs, a significant difference ($p<0.05$) were found in the total 7 carcinogenic PAHs between petrochemical and background areas (7.74 ng/g vs 3.37 ng/g), which denotes a significant influence of petrochemical industries in the surrounding environment. Individually, naphthalene was the predominant hydrocarbon in all the areas a contribution, between 26 % and 57 % of the total 16 PAHs. Although for a different kind of vegetation, this patterns is consistent with that observed by Ratola et al., (2010) in pine needles, in which the younger leaves recorded naphthalene as the predominant compound. Being the most volatile, naphthalene can not only be trapped easier by the vegetation, but also be transported to more distant areas, including the background sites.

In addition, statistically significant differences between petrochemical and urban and background areas were found for this compound (38.83 ng/g vs 20.49 ng/g and 23.37 ng/g, respectively: $p < 0.05$). Phenanthrene and pyrene were the second and third prevailing PAHs in all the sampling areas, with a contribution between 8–20 % and 7–16 % of the total 16 PAHs (Table 2). In both cases, statistically significant differences between chemical areas and petrochemical, urban and background areas were found (Table 2). Regarding benzo(*a*)pyrene, no statistically significant differences were found between sampling areas. However, as in the case of soils, the urban areas recorded the highest concentration of this compound (0.75 ng/g), probably associated with heavy traffic. Regarding PAHs ring patterns (Fig. 3 A), it can be seen that, in comparison with soils, vegetation showed more affinity towards the low molecular PAHs, probably associated with rapid exchange kinetics between vegetation and the surrounding air (Yogui et al., 2011). Notwithstanding, comparing the results of Domínguez-Morueco et al (2015) in a study at the same area with lichen transplants it can bee seen that PAHs ring profile is more similar to the soil profile of the present study. When comparing the total concentrations of 16 priority PAHs and $\sum_7$ carcinogenic PAHs found in this study, with those detected in the multi-compartmental environmental monitoring program conducted in Tarragona County (28 – 179 ng/g $\sum_{16}$ priority PAHs and <2.0 ng/g $\sum_7$ carcinogenic PAHs Nadal et al., 2004a; 94.2 – 128.8 ng/g $\sum_{16}$ priority PAHs and 11 – 14.8 ng/g $\sum_7$ carcinogenic PAHs from Nadal et al., 2009; and 40.1- 211.7 ng/g $\sum_{16}$ priority PAHs and 5.6 – 13.3 ng/g $\sum_7$ carcinogenic PAHs from Nadal et al., 2011) it can be seen that, as in the soils samples, the values are in the lowest part of the range, and for hence, there would be a reduction of general levels of PAHs in Tarragona County. Comparing with other literature, such as the study conducted by Wang et al. (2012b) in ground vegetation from South China (199 – 2,420 ng/g), the present values were considerably lower. In turn, the concentrations from Tarragona County were higher than the values recorded by Chrysikou et al. (2008) in ground vegetation or Cabrerizo et al. (2012) (14.1–34.7 ng/g and 6–10 ng/g, respectively) in grass. Comparing to soils, the petrochemical area was the zone that recorded the highest values of total PAHs (80.08 ng/g), and this pattern is consistent with the last study conducted by Nadal et al., in 2011 in Tarragona, as are the similarly high detected in urban areas (79.43 ng/g), in agreement with the multi-compartmental environmental monitoring program conducted previously in Tarragona County (Nadal et al., 2004a; 2009). These results confirm traffic and industries as the main anthropogenic sources of PAHs in the area.

In Table 2, it can be seen that the mean total PCBs levels by site type ranged from 0.52 to 4.41 ng/g. Petrochemical, chemical and urban area showed similar values of PCBs (4.08 ng/g, 3.33 ng/g and 4.41 ng/g, respectively). As in soils, the background sites presented the lowest values of total PCBs, with statistically significant differences ($p<0.05$) found with the rest of zones (Table 2). Concerning individual PCBs, PCB 52 (a tetra-CB) was the predominant PCB in all sampling areas, with a contribution between 63 % and 89 % of the total PCBs (Table 2) and no statistically significant differences were found between areas. As in the case of PAHs, there is a general affinity of vegetation towards the low molecular PCBs in all sampling areas (Fig. 3 B). When comparing the current combined concentrations of PCBs 28, 52, 101, 118, 138, 153 and 180 (mean total of 4.05 ng/g, 3.28 ng/g, 4.35 ng/g and 0.49 ng/g in petrochemical, chemical urban and background areas, respectively) with those found in the Tarragona monitoring program (2.50–2.94 ng/g from Schuhmacher et al., 2004 and 1.55–3.88 ng/g) it can be seen that the present values are quite similar and also in agreement with those detected in other international studies (Tato et al. (2011), 0.32–2.05 ng/g; Cabrerizo et al. (2012), 0.39–2.40 ng/g, both in grass, and Chrysikou et al. (2008), 3.64–25.9 ng/g in ground vegetation). On the other hand, Wang et al. (2011) found PCB concentrations in grass higher than those presented in this study, in an area close to an electronic waste recycling site of South China (6.7–1500 ng/g). In terms of spatial distribution, although there was not a clear “hot spot”, site 11 (La Laboral) was again one of the points with the highest concentration of PCBs (8.84 ng/g).

In the case of SMs, levels in vegetation samples ranged from 4.08 to

17.94 ng/g and, unlike soils samples, statistically significant differences were found between background areas and petrochemical area (17.95 ng/g vs 4.08 ng/g). In this case, a decreasing pattern was observed among sampling areas (background area>urban area>chemical area>petrochemical area). This pattern would confirm the theory described above, which shows an influence of the personal care products derived from coastal tourism in these areas. As in the case of soils samples, the literature is very scarce regarding the presence of fragrances in vegetation samples. The values recorded in the present study would be within the range recently defined by Ribeiro et al. (2017), in five Portuguese coastline ground vegetation plant species (4.70 – 350 ng/g). When SMs were individually assessed, galaxolide and cashmeran were again the predominant musks in all the sampling areas, with a contribution between 29 % and 91 % and from 2 % to 57 % of the total SMs, respectively (Fig. 3 C). In the case of cashmeran, statistically significant differences were found between urban and petrochemical/chemical areas (Table 2).

Regarding BFRs, BDEs 85, 154, 183 and the currently-used PBT, PBEB and HBB were not detected in the vegetation samples. PBDEs levels ranged from 0.47 to 1.12 ng/g, and levels in the chemical areas were 2 times higher (and statistically significant) than those found in the background areas (Table 2). As in soils, BDE 47 was the prevailing BFRs in vegetation samples from all areas, with a contribution between 16% and 66 % of the total BFRs (Fig. 3 D), and with statistically significant differences between chemical and background areas. BDEs 28 and 99 followed (4 – 64 % and 3 – 31 %, respectively). In the case of BDE 99, statistically significant differences were found between petrochemical, urban and background areas (Table 2). When comparing with levels found in other studies, it can be seen that the present values are lower than those found by Wang et al. (2011a) or Yu et al., (2016) in China (1.5 – 89.4 ng/g and 2.74 – 138 ng/g, respectively) in grass samples. Regarding the individual BFRs, the current values are in agreement with these studies, which state that congeners 47 and 99 are the most abundant BFRs in vegetation. Congeners 47 and 99 were the most used PBDEs worldwide until their general ban. This coupled with their persistence may be a reason for them to remain strongly present in the environment (Zheng et al., 2015; Li et al., 2016; McGrath et al., 2017)

Finally, HCB values in vegetation varied from 0.13 ng/g to 0.17 ng/g, being again similar between sampling areas and without statistically significant differences. In this case, the concentrations recorded in Tarragona County were within the range observed in literature, such as the studies conducted in grass samples by Wang et al. (2007) in Mt. Qomolangma, China (0.0156 – 1.25 ng/g) or by Cabrerizo et al. (2012) in Antarctica (0.080 – 0.20 ng/g).

Table 2. Concentrations of SVOCs in vegetation samples from four areas of Tarragona County (Catalonia, Spain) (ng/g).

	Petrochemical area (n = 7)		**Chemical area (n = 9)**		**Urban area (n = 6)**		**Background area (n = 5)**	
	Mean± SD	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**
Naphthalene	38.83^{a} ± 14.64	37.71	23.86^{ab} ± 10.01	41.93	20.49^{b} ± 10.30	50.24	23.37^{b} ± 6.70	28.66
Acenaphthylene	0.32^{ab} ± 0.32	97.67	0.17^{b} ± 0.12	72.15	0.49^{a} ± 0.29	59.69	0.47^{a} ± 0.28	58.89
Acenaphthene	0.85 ± 0.37	43.63	0.43 ± 0.64	149.35	0.43 ± 0.22	50.36	0.47 ± 0.42	89.78
Fluorene	5.32^{ab} ± 5.58	104.96	1.06^{b} ± 0.72	68.24	1.96^{ab} ± 1.56	79.68	2.76^{a} ± 1.59	57.65
Phenanthrene	10.11^{a} ± 3.76	37.24	3.56^{b} ± 1.35	37.92	16.06^{a} ± 15.81	98.46	12.47^{a} ± 5.07	40.66
Anthracene	0.58^{b} ± 0.27	47.05	0.32^{b} ± 0.24	74.23	3.48^{a} ± 2.76	79.33	1.87^{a} ± 1.67	88.84
Fluoranthene	4.11^{ab} ± 1.90	46.15	2.87^{b} ± 1.07	37.28	12.12^{ab} ± 12.23	100.86	9.97^{a} ± 7.59	76.10
Pyrene	11.40^{a} ± 5.06	44.36	2.76^{b} ± 1.24	45.04	12.97^{a} ± 13.15	101.40	9.07^{a} ± 8.57	94.52
Benzo(*a*)anthracene	1.14^{a} ± 0.51	44.36	0.31^{b} ± 0.30	97.67	1.14^{ac} ± 1.47	128.61	0.49^{bc} ± 0.21	42.20
Chrysene	2.39 ± 1.07	44.68	1.56 ± 1.37	88.01	3.36 ± 3.32	98.86	1.75 ± 1.27	72.43
Benzo(*b*+*k*)fluoranthene	3.26 ± 2.60	79.76	2.33 ± 1.22	52.42	2.33 ± 3.09	132.54	0.47 ± 0.35	74.65
Benzo(*a*)pyrene	0.54 ± 0.19	34.26	0.44 ± 0.42	95.93	0.75 ± 0.77	102.80	0.24 ± 0.25	104.06
Indeno(*1,2,3-c,d*)pyrene	<LOD	-	0.71 ± 1.39	197.04	0.63 ± 1.26	200.97	<LOD	-
Dibenzo(*a,h*)anthracene	0.29 ± 0.31	106.73	0.39 ± 0.48	124.99	0.28 ± 0.37	133.33	0.31 ± 0.20	63.18
Benzo(*g,h,i*)perylene	0.82^{b} ± 0.78	95.27	1.36^{ab} ± 0.71	52.49	2.95^{ab} ± 2.01	67.92	2.43^{a} ± 1.81	74.50
Σ16PAHs	**80.08 ± 29.58**	**36.94**	**42.13 ± 11.19**	**26.57**	**79.43 ± 58.89**	**74.14**	**66.27 ± 21.46**	**32.39**
Σ 7 prob. carcinogenic PAHs[*]	**7.74^{a} ± 3.46**	**44.71**	**5.74^{ab} ± 2.31**	**40.26**	**8.48^{ab} ± 8.11**	**95.61**	**3.37^{b} ± 1.36**	**40.42**

	Petrochemical area (n = 7)		**Chemical area (n = 9)**		**Urban area (n = 6)**		**Background area (n = 5)**	
	Mean± SD	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**
Cashmeran	<LOD^{b}	-	1.63^{bc} ± 2.71	166.12	6.81^{a} ± 5.41	79.52	3.48^{ac} ± 4.06	116.79
Celestolide	0.03^{c} ± 0.01	48.06	0.18^{c} ± 0.28	152.43	0.48^{b} ± 0.17	36.49	1.43^{a} ± 1.21	84.48
Phantolide	<LOD	-	0.21 ± 0.29	139.42	<LOD	-	<LOD	-
Galaxolide	3.70 ± 5.51	149.17	5.19 ± 4.61	88.83	3.49 ± 7.03	201.52	12.06 ± 15.93	132.04
Traseolide	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Tonalide	0.10^{ab} ± 0.08	73.64	0.23^{a} ± 0.50	220.36	0.94^{b} ± 0.97	102.59	0.79^{ab} ± 1.00	126.87
Musk ambrette	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Musk xylene	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Musk moskene	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Musk tibetene	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Musk ketone	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Σmusks	**4.08^{b} ± 5.56**	**136.41**	**7.62^{ab} ± 5.02**	**65.83**	**11.90^{ab} ± 9.93**	**83.50**	**17.94^{a} ± 13.68**	**76.26**
PCB 28	0.25 ± 0.12	48.95	0.14 ± 0.14	97.72	0.19 ± 0.38	204.72	<LOD	-
PCB 52	3.02 ± 2.28	75.46	2.78 ± 2.53	91.13	3.91 ± 2.48	63.45	0.33 ± 0.37	112.66
PCB 77	<LOD	-	0.01 ± 0.01	182.66	0.01 ± 0.01	125.29	<LOD	-
PCB 81	<LOD	-	0.01 ± 0.02	234.92	0.02 ± 0.05	206.13	<LOD	-
PCB 101	0.10 ± 0.05	47.53	0.10 ± 0.07	62.73	0.08 ± 0.03	31.77	0.11 ± 0.03	28.12
PCB 105	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PCB 114	<LOD	-	<LOD	-	<LOD	-	<LOD	-

	Petrochemical area (n = 7)		**Chemical area (n = 9)**		**Urban area (n = 6)**		**Background area (n = 5)**	
	Mean± SD	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**
PCB 118	0.57^{a} ± 0.05	8.72	0.03^{b} ± 0.02	77.12	0.02^{bc} ± 0.02	129.18	0.01^{c} ± 0.003	52.88
PCB 123	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PCB 126	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PCB 138	0.02 ± 0.03	141.69	0.13 ± 0.21	162.07	0.08 ± 0.07	104.38	0.01 ± 0.02	201.34
PCB 153	0.08 ± 0.09	114.80	0.02 ± 0.03	114.74	0.04 ± 0.02	65.48	0.02 ± 0.01	54.35
PCB 156	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PCB 157	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PCB 167	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PCB 169	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PCB 180	0.02^{c} ± 0.02	154.93	0.06^{a} ± 0.02	37.05	0.05^{ab} ± 0.03	56.26	0.02^{bc} ± 0.01	26.45
PCB 189	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PCB 209	<LOD	-	<LOD	-	<LOD	-	<LOD	-
ΣPCBs	**4.08^{a} ± 2.22**	**54.49**	**3.33^{a} ± 2.63**	**79.12**	**4.41^{a} ± 2.83**	**64.29**	**0.52^{b} ± 0.38**	**73.39**
BDE 28	0.04 ± 0.04	90.58	0.05 ± 0.05	107.11	0.09 ± 0.20	221.23	0.30 ± 0.62	209.54
BDE 47	0.32^{ab} ± 0.25	78.91	0.70^{a} ± 0.35	50.69	0.50^{ab} ± 0.34	68.04	0.07^{b} ± 0.05	65.30
BDE 85	<LOD	-	<LOD	-	<LOD	-	<LOD	-
BDE 99	0.25^{a} ± 0.09	33.67	0.18^{ab} ± 0.12	70.36	0.06^{b} ± 0.05	96.41	<LOD^{c}	-
BDE 100	<LOD	-	0.02 ± 0.02	76.19	0.03 ± 0.03	83.45	<LOD	-
BDE 153	0.13^{a} ± 0.07	55.98	0.11^{ab} ± 0.12	115.26	0.02^{b} ± 0.02	99.46	<LOD^{c}	-

	Petrochemical area (n = 7)		**Chemical area (n = 9)**		**Urban area (n = 6)**		**Background area (n = 5)**	
	Mean± SD	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**	**Mean± SD**	**CV (%)**
BDE 154	<LOD	-	<LOD	-	<LOD	-	<LOD	-
BDE 183	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PBT	<LOD	-	<LOD	-	<LOD	-	<LOD	-
PBEB	<LOD	-	<LOD	-	<LOD	-	<LOD	-
HBB	<LOD	-	<LOD	-	<LOD	-	<LOD	-
ΣBFRs	**0.83^{ab} ± 0.28**	**34.26**	**1.12^{a} ± 0.48**	**42.93**	**0.76^{ab} ± 0.40**	**52.48**	**0.47^{b} ± 0.66**	**141.11**
HCB	**0.13 ± 0.08**	**62.14**	**0.15 ± 0.16**	**104.70**	**0.17 ± 0.10**	**57.58**	**0.14 ± 0.09**	**61.25**

LOD = limit of detection. CV = coefficient variation.

*Benzo(*a*)anthracene, chrysene, benzo(*b*+*k*)fluoranthene, benzo(*a*)pyrene, indeno(*1,2,3-c,d*)pyrene, dibenzo(*a,h*)anthracene.

Different superscripts indicate significant differences between groups (p<0.05).

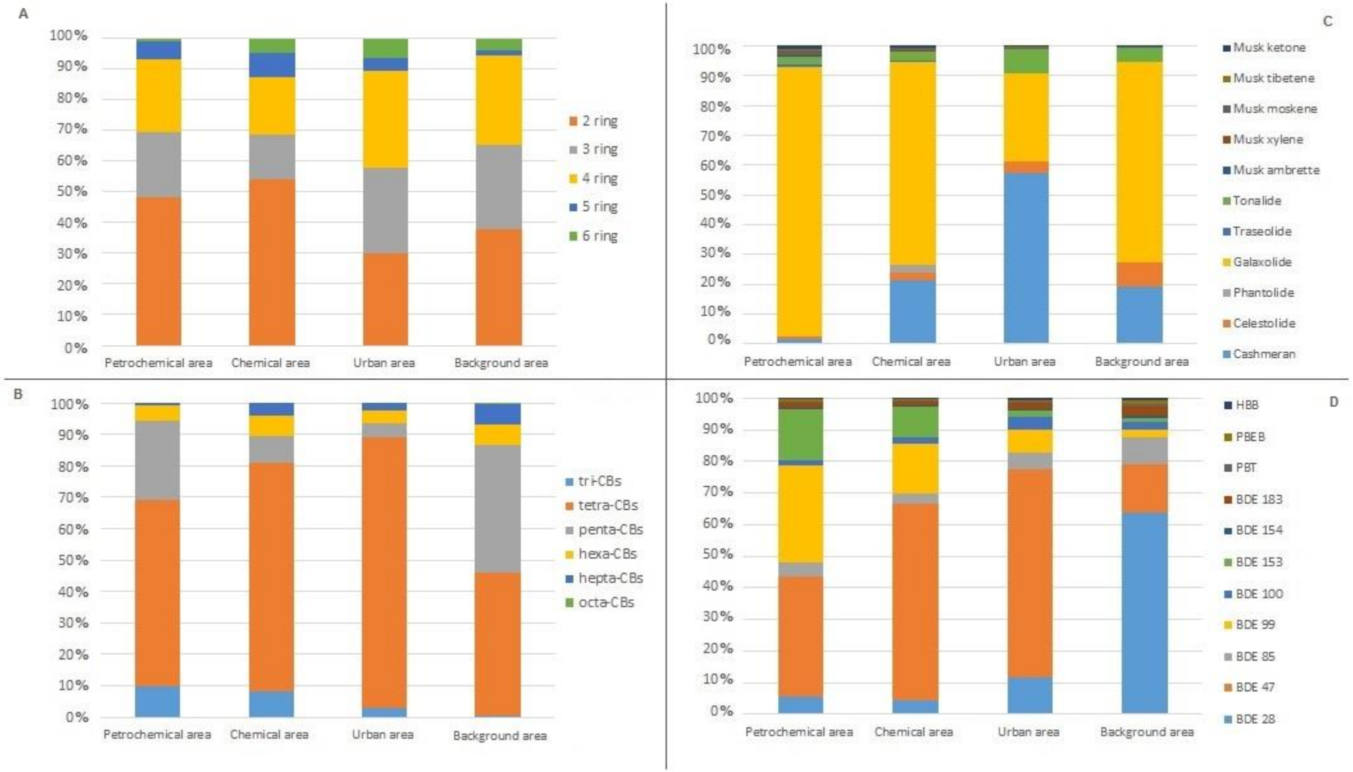

Fig. 3. Contribution (%) of each range (PAHs and PCBs) or individual compound (SMs and BFRs) in vegetation samples from Tarragona County (Catalonia, Spain).

3.3. SVOCs profiles in soil samples vs in vegetation samples

Principal component analysis (PCA) was applied to the SVOCs normalized concentrations in the 27 soil and 27 vegetation samples at each sampling area. Figure 4 represents the PCA separates by sampling matrix (soils in brown and vegetation in green) and sampling area for PAHs (A), PCBs (B), SMs (C) and BFRs (D). Regarding PAHs (Fig. 4 A), PC1 is positively weighted by PAHs ring profiles from soils samples, while is negatively weighted by PAHs ring profiles from vegetation samples. In turn, PC2 is positively weighted by 4, 5 and 6-rings PAHs and soils samples and negatively weighted by 2 and 3-rings PAHs and vegetation samples. These results show a clear difference between soil and vegetation samples, confirming that soil samples tend to accumulate the heavier PAHs (4, 5 and 6 rings PAHs), and vegetation has more affinity for the more volatile PAHs (2 and 3-rings PAHs). This pattern is consistent with the percentage of contribution of the total 16 PAHs described above where, for example, fluoranthene and benzo(*a*)pyrene were predominant in soils and naphthalene in vegetation. These results could indicate that vegetation tends to capture contaminants present predominantly in the gas-phase (Low molecular weight). Also, once captured, the rapid kinetic of exchange between vegetation and air causes that some SVOCs return to the atmosphere, while the soils and their high affinity for hydrophobic organic pollutants make it possible to retain the heavier (including the particulate phase pollutants) and less biodegradable compounds (Diamond et al., 2001; Bao et al., 2015; 2016). When representing the PCA for PAHs ring profiles in soil and vegetation separated by sampling areas (Fig. S1, Annex 5), it can be seen that for soils (Fig. S1 A, Annex 5), background areas present a different profile than petrochemical, chemical and urban sites. Also, 5 and 6-ring PAHs are mainly associated with urban and some chemical areas, while 2, 3 and 4-ring PAHs are predominant in petrochemical, chemical and background areas.

Regarding vegetation (Fig. S1 B, Annex 5), PAHs ring profiles from urban and background areas are opposite to those from petrochemical and chemical areas, being 3, 5 and 6-ring PAHs the most incident in the former and 2 and 4-ring PAHs in the latter areas. These results suggest different sources affecting the presence of PAHs in the Tarragona area. In the case of PCBs (Fig. 4 B) the PC1 is positively weighted by PCBs profiles from soils samples, while is negatively weighted by PCBs profiles from vegetation samples. Regarding, PC2 is positively weighted by the heavier PCBs (congener number 101, 138, 158 and 180) and soils samples, while is negatively weighted by the more volatile PCBs (congener number 28 and 52) and vegetation samples. This pattern is also consistent with the individual congener contribution, since in the case of soils samples the predominant PCBs were PCB 138 and 158 against PCB 52 in vegetation samples. Contrastingly, PCA for SMs and BFRs shows a great mix between the levels contents in soils and vegetation samples, not being able to differentiate between both matrices. This could be associated with the fact that both group of compounds are mainly associated with indoor environments, and for this reason their presence in outdoor environments is more diffuse.

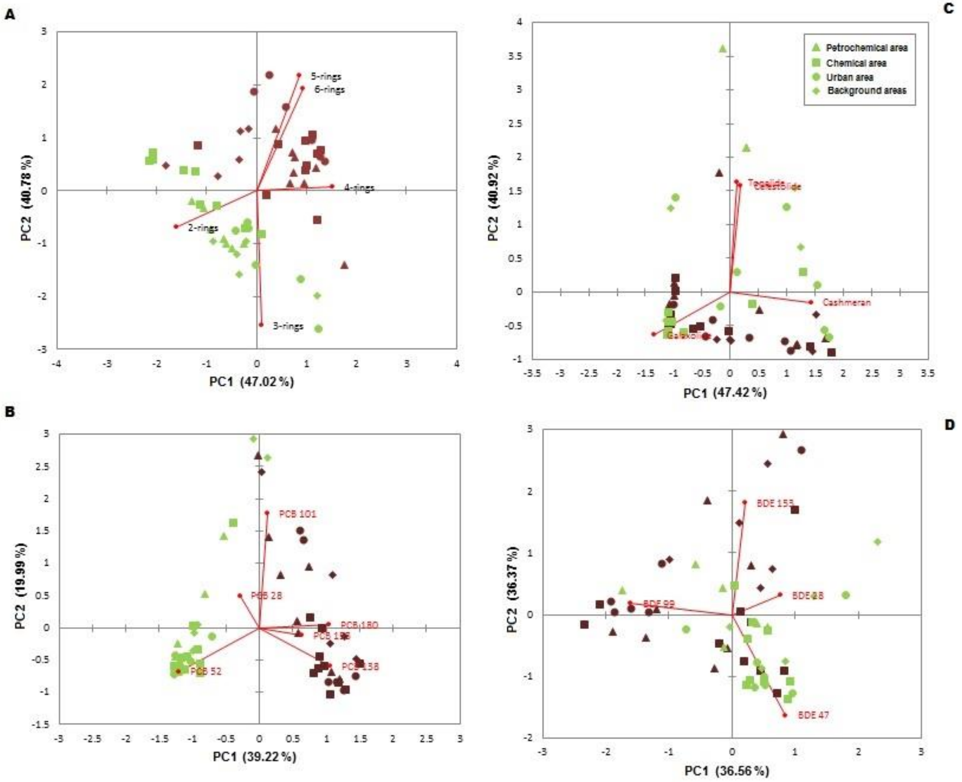

Fig. 4. Principal component analysis (PCA) for: A) PAHs ring profiles in soil (in brown) vs vegetation (in green); B) PCBs profile in soils vs vegetation; C) SMs profile in soils vs vegetation; and D) BFRs profile in soil vs vegetation from the different areas of study.

3.4. Source apportionment

In recent years, the need to identify the origin of pollutants triggered the development of a wide range of techniques that provide a first approximation of the emission sources. Among these techniques, the molecular diagnostic ratios (MDR) for PAHs, is one of the method most applied for the different environmental matrices (Tobiszewski and Namieśnik, 2012). MDR are based on the theory that some PAHs are emitted in constant proportions from the sources and their concentrations remain constant between the source and the receptor (Katsoyiannis et al., 2011; Tobiszewski and Namieśnik, 2012), although not always those remain constant, e.g. if the degradation of an individual compound is potentiated by adequate environmental conditions. Currently, there are different MDR defined for these compounds. In the present work the ratios Ant/(Ant+Phe), BaA/(BaA+Chry), Flt/(Flt+Pyr), IcdP/(IcdP+BghiP) and BaP/BghiP were used according to Katsoyiannis et al. (2011) for soil and vegetation samples from Tarragona County (Table 3). In soils, the ratios Flt/(Flt+Pyr) and IcdP/(IcdP+BghiP) showed a clear pyrogenic origin, probably associated with incomplete combustion processes. In addition, the ratio BaP/BghiP showed a predominant traffic origin for all the sampling areas. These results are in agreement with the pattern described above, where it was pointed out that the highest values were found in the urban area, probably due to the presence of heavy traffic. Contrastingly, the ratio BaA/(BaA+Chry) presented a mixed source profile (petrogenic and pyrogenic) and the ratio Ant/(Ant+Phen) showed a clear petrogenic origin, which indicates that there is also a strong influence of the petrochemical/chemical industries in Tarragona County. Concerning MDR in vegetation samples, the ratios Ant/(Ant+Phen), BaA/(BaA+Chry), Flt/(Flt+Pyr) and IcdP/(IcdP+BghiP) showed a clear mix profile between petrogenic and pyrogenic sources. In addition, the ratio BaP/BghiP only showed a traffic origin for a petrochemical sampling area. These results confirm the pattern previously described for PAHs in vegetation samples, where high concentrations were recorded in both petrochemical and urban areas. Depending on the type of matrix selected, different information about sources of contamination can be obtained. As mentioned above, and because of their high affinity for hydrophobic organic pollutants, soils can provide information on both current and long-term SVOCs concentrations. On the oder hand, also due to its limited life span, vegetation plays an important role as short-term information source. SVOC contamination in Tarragona County would be mainly associated with a mix between petrogenic and pyrogenic sources (see Table 3 for vegetation), probably due to an influence from urban and industrial areas as showed by the total concentrations in these points mentioned above. In turn, the long-term information indicates that the SVOCs contamination would have a markedly pyrogenic origin (see Table 3 for soils) mainly associated to an urban influence. This suggests that historically, the presence and influence of the pyrogenic sources is higher than the petrogenic ones in Tarragona County. This can also be seen by the BaP/BghiP ratio that reveals a evidence of strong presence of traffic (one of the most common pyrogenic sources).

Table 3. Molecular diagnostic ratios (MDR) for PAHs in soil and vegetation samples from Tarragona County (Catalonia, Spain).

	Soil samples				**Vegetation samples**					
	Petrochemical area (n = 7)	**Chemical area (n = 9)**	**Urban area (n = 6)**	**Background area (n = 5)**	**Petrochemical area (n = 7)**	**Chemical area (n = 9)**	**Urban area (n = 6)**	**Background area (n = 5)**	**Petrogenic[a]**	**Pyrogenic[a]**
Ant / (Ant+Phen)	0.08	0.09	0.03	0.04	0.06	0.10	0.23	0.14	<0.1	>0.1
BaA / (BaA+Chry)	0.34	0.38	0.36	0.27	0.33	0.16	0.25	0.29	<0.2	>0.35
Flt / (Flt+Pyr)	0.43	0.47	0.51	0.49	0.26	0.52	0.47	0.55	<0.4	>0.4
IcdP / (IcdP+BghiP)	0.25	0.34	0.40	0.21	0.26	0.22	0.15	0.06	<0.2	>0.2
									Non-Traffic[a]	**Traffic[a]**
BaP/BghiP	0.89	1.08	1.09	1.09	2.63	0.37	0.32	0.09	<0.6	>0.6

[a] Molecular diagnostic ratios according to Katsoyiannis et al. (2011).

3.5. Toxic equivalents

In order to assess the risk associated to PAHs and PCBs present in soils from Tarragona County, the concept of "toxic equivalents (TEQ)" was applied. TEQs measure the combined toxicity of certain groups of compounds in relation to the most toxic compound in the mixture through the toxic equivalency factors (TEFs) methodology (Van den Berg et al., 1998; Hong et al., 2009). In this sense, the carcinogenic risk associated of a PAH mixture is often expressed by its benzo(*a*)pyrene equivalent (BaP_{eq}) concentration, since BaP has been identified as one of the most carcinogenic hydrocarbons by the IARC. The BaP_{eq} for a soil sample is calculated by multiplying the concentration of each individual PAH in the sample by the respective toxicity equivalency factor (TEF):

$$BaP_{eq} = \sum_{i=1}^{n} PAHi \times TEFi \tag{1}$$

where TEFi is the toxic equivalence factor for each PAHi according to Nadal et al. (2004a) (adapted from Nisbet and LaGoy 1992 and Larsen and Larsen 1998). In the case of PCBs, the TEQ are based on the toxicity equivalence of each congener relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), since World Health Organization (WHO) have identified 12 PCBs with toxicological properties comparable to chlorinated dibenzo-*p*-dioxins (dioxin-like PCB congeners: PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189) (Van den Berg et al., 1998; WHO, 2005; Hong et al., 2009; Drimal et al., 2016). Hence, the health risk of these 12 dioxin-like PCB congeners or 2.3.7.8-$TCDD_{eq}$ in Tarragona soils is calculated by multiplying the concentration of each individual PCB by the respective TEF (Drimal et al., 2016):

$$2.3.7.8\text{-}TCDDeq = \sum_{j=1}^{n} PCBj \times TEFj \tag{2}$$

where TEFj is the toxic equivalence factor for each PCBj defined by the World Health Organisation (WHO) in 2005.

TEQs for the PAHs and PCBs, adjusted to the mean soil concentrations per Tarragona sampling area are summarized in Table 4. According to $\sum BaP_{eq}$ the urban and chemical areas recorded the highest values (29 ng BaP_{eq}/g and 16 ng BaP_{eq}/g, respectively). In contrast, petrochemical areas were the less contaminated zones (5 ng BaP_{eq}/g), even lower than background areas. The abovementioned aspect of the considerable height of the stacks from the refineries can be a possible explanation for this apparently unexpected result. This decreasing pattern is also in agreement with Nadal et al. (2004a) for Tarragona County soils. However, the values of BaP_{eq} calculated for the each PAH and for the total PAHs were lower than those reported by Nadal et al. (2004) (range for $\sum BaP_{eq}$: 24–124 ng/g), which would confirm the decreasing trend in the PAHs concentrations described in this study. On the other hand, although fluoranthene was the most abundant PAHs in urban and chemical areas, its contribution to the $\sum BaP_{eq}$ was extremely low (less than 1%). In contrast, benzo(*a*)pyrene, whose contribution of the total 16 PAHs in the different sampling areas was low, had the greatest impact to $\sum BaP_{eq}$ (contribution between 69% and 80%). This pattern is also consistent with Nadal et al. (2004a), and with other international studies such as the study conducted by Marquès et al. (2017) in Arctic soils.

Regarding 2.3.7.8-$TCDD_{eq}$, the highest values were calculated for background and urban areas (101.3 and 71.2 ng 2.3.7.8-$TCDD_{eq}$/kg, respectively), while petrochemical area was the area less contaminated by dioxin-like PCBs (0.5 ng 2.3.7.8-$TCDD_{eq}$/kg). This could be associated with the fact that most of dioxin-like PCBs were not detected in greatest of the Tarragona samples. Despite the PCB congeners number 153 and 138 were the most abundant PCBs in chemical/petrochemical (46 % and 24 %) and urban/background areas (40% and 16%), respectively, none of them are considered dioxin-like PCBs. For those, PCB 126 provided the greatest contribution to Σ2.3.7.8-$TCDD_{eq}$ (between 60 % and 99.9 %).

Table 4. Toxic equivalents (TEQ) for PAHs and PCBs, adjusted to the mean soil concentrations per Tarragona sampling area. (TEQ for PAHs: BaP$_{eq}$ in ng/g; TEQ for PCBs: 2.3.7.8-TCDD$_{eq}$ in ng/kg).

	TEFs[a]	**Petrochemical area (n = 7) Mean**	**Chemical area (n = 9) Mean**	**Urban area (n = 6) Mean**	**Background area (n = 5) Mean**
Naph	0.001	0.0021	0.0029	0.0072	0.0154
Acy	0.001	0.0008	0.0033	0.0010	0.0002
Ace	0.001	0.0022	0.0008	0.0006	0.0002
Fluo	0.001	0.0035	0.0012	0.0008	0.0002
Phen	0.0005	0.0014	0.0036	0.0035	0.0010
Ant	0.0005	0.0001	0.0004	0.0002	0.0001
Flt	0.05	0.15	0.62	1.06	0.18
Pyr	0.001	0.014	0.012	0.019	0.003
BaA	0.005	0.009	0.038	0.054	0.009
Chry	0.03	0.11	0.31	0.49	0.13
B(b+k)F	0.1	0.5	1.0	2.0	0.5
BaP	1	4	11	20	4
Icdp	0.1	0.1	0.6	1.2	0.1
DahA	1.1	0.4	2.1	3.2	0.6
BghiP	0.02	0.1	0.2	0.4	0.1
ΣBaP$_{eq}$		5	16	29	6
	TEFs[b]				
PCB 77	0.0001	0.0166	0.0176	0.0355	0.0002
PCB 81	0.0003	0.0286	0.0089	0.0517	0.0069
PCB 105	0.00003	0.00050	0.00012	0.00012	0.00012
PCB 114	0.00003	0.00016	0.00022	0.00110	0.00506
PCB 118	0.00003	0.03496	0.00067	0.00014	0.00014
PCB 123	0.00003	0.00014	0.00576	0.03215	0.02890
PCB 126	0.1	0.3	32.7	71.0	101.2
PCB 156	0.00003	0.00005	0.00523	0.01213	0.01038
PCB 157	0.00003	0.00009	0.00054	0.00133	0.00341
PCB 167	0.00003	0.00016	0.00159	0.00147	0.00006
PCB 169	0.03	0.04	0.04	0.04	0.04
PCB 189	0.00003	0.00656	0.00333	0.00855	0.01128
Σ2.3.7.8-TCDDeq		0.5	32.8	71.2	101.3

*Benzo(*a*)anthracene, chrysene, benzo(*b*+*k*)fluoranthene, benzo(*a*)pyrene, indeno(*1,2,3-c,d*)pyrene, dibenzo(*a,h*)anthracene.

[a] TEFs according to Nadal et al., 2004a.

[b] TEFs according to WHO 2005.

4. CONCLUSIONS

Levels of PAHs, PCBs, and for the first time in Tarragona County, synthetic musks (SMs), brominated flame retardants (BFRs) and HCB were analyzed in soils and vegetation samples, by using a multi-component analytical protocol based on the "green" extraction technique QuEChERS. Levels of PAHs and PCBs were consistent with those recorded in the multi-compartmental environment monitoring program conducted in Tarragona County since 2002. In the case of PAHs, a decreasing pattern in the concentrations were observed since 2002, probability associated with the reduction in the PAHs emission observed between 1990 and 2010 in most European countries. For PAHs, in general terms, urban areas showed the highest values for $\sum_{16}$ priority PAHs in both matrices, which according to the diagnostic ratios, could be associated with pyrogenic origin due to several roads with heavy traffic in this area. Regarding PCBs, the chemical area, showed the highest values of PCBs in both matrices in the same sampling point (point 11), probably associated with the presence of two sub-electrical stations located in the vicinities. Concerning SMs and BFRs, compounds mainly related with indoor environments, were detected in both environmental matrices considered in this study. Background areas showed the highest levels of SMs, suggesting an influence of the personal care products derived from coastal tourism in these areas. With respect to HCB, the values recorded were lower than others found in literature and similar in the patterns between sampling areas, probably due to its production being already banned for decades in most countries.

In general terms, both the SVOCs levels as well as the diagnostic ratios for PAHs showed clear differences between the two analysed matrices. Vegetation, as a short-term information source, tends to accumulate PAHs and PCBs of low molecular weight that predominate in gas-phase. In turn, due their high affinity for hydrophobic organic pollutants, soils tend to accumulate pollutants more present in the particulate-phase, with higher molecular weight and with greater stability or recalcitrance, providing information on current and long-term SVOCs concentrations. In this sense, in the short term, SVOCs contamination in Tarragona County would be mainly associated with a mix between petrogenic and pyrogenic sources, probably due to an influence from urban and industrial areas as showed by the total concentrations in these points. In turn, in the long-term, the SVOCs contamination would have a markedly pyrogenic origin mainly associated to an urban influence.

Finally, it was shown that regarding risk associated to some of the SVOCs in the Tarragona County soils, not always the compounds with the highest concentrations are those that present the most potential danger for human health. This is a reason to keep performing thorough sampling actions of these compounds as often and covering as many contaminants as possible.

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DISCUSSION CHAPTER 2

The first part of this thesis confirmed that PAS are devices capable of collecting the SVOCs present, predominantly, in the gas phase at local scale. However, it is also important to measure those heavier congeners that are associated with the particulate phase. For this reason, the second part of this thesis was aimed to select another kind of environmental matrices, also including under the passive sampling category, capable of covering the gaps left by PAS devices, such as soils and vegetation. For this reason, a more extensive sampling of soils and vegetation was designed throughout Tarragona County, which covered a total of 27 sampling points, 8 of which coincided with the passive air sampling.

When SVOCs are extracted from the PUF disks, the method worldwide used and also used in this thesis is the Soxhlet. Sometimes, other techniques such as accelerated solvent extraction (ASE) can also be used (article 1 chapter 1). However, this kind of extraction and analysis methods involve the use of large amounts of solvent (e.g. Soxhlet extraction require 250 mL of solvent for extraction plus at least 100 mL in the clean-up phase), and having associated high operating times (e.g. Soxhlet method needs 12 hours for extraction per sample). Given the large number of soil and vegetation samples (27 samples per matrix more duplicates), in this thesis it was important to adapt and validate other methods that would reduce the economic costs and the operating time. To achieve this goal, a multi-compound protocol developed by Silva et al. (2015) coupled to QuEChERS methodology initially developed by Anasstassiades et al. (2003) was optimized and validated for the simultaneously extraction of five different classes of SVOCs (PAHs, PCBs, BFRs, SMs and HCB) in soils and vegetation (pine needles) samples.

Since the QuEChERS methodology was a technique developed for the detection of pesticides in fruit and vegetable samples, it was necessary to carry out different tests in order to adapt it to soil and vegetation samples. To achieve the goal, it was necessary to optimize the main parameters to consider in the analysis: type of extraction solvent; composition of

QuEChERS 1 and 2, and extract filtration and dryness. Because both the soils and the vegetation are two matrices with different characteristics, different extraction solvents and two QuEChERS configurations were developed. Regarding the solvents, for vegetation was more suitable the utilization of a more apolar mixture (Hexane: Dichloromethane, (1:2)) than for soils (Acetone:Dichloromethane, (1:1)), this was expectable since vegetation tissues are more lipophilic than soil components. For QuEChERS 1, in both cases, the utilization of NaCH3COO, to enhance ionic strength, and anhydrous MgSO4, as drying agent, were chosen as the most appropriate reactants. Finally, with the target compounds concentrated in the organic phase, an effective clean-up was required to obtain the desired chromatographic resolution. This is obtained with QuEChERS 2, through a dispersive solid phase extraction (d-SPE). For soils the best configuration of QuEChERS 2 was: 0.9g MgSO4, 0.15g PSA and 0.15g C18 in contrast to the suitable composition for vegetation: 0.9g MgSO4, 0.15g Alumina, 0.15g Florisil and 0.15g C18. The differences between both configurations fall on that for soils it is needed and anion exchanger (PSA) to eliminate fulvic and humic acids and for vegetation Alumina and Florisil were required to eliminate polar and apolar compounds present in vegetal tissues (as sugars, chlorophylls, etc).

For both methods a successful linearity, selectivity, precision, accuracy, repeatability, and good recovery values (with RSDs below 20% in all cases) were obtained. In addition it was found that, method LODs obtained and levels found in real samples were similar to those obtained by other worldwide standardized methods.

In this sense, the QuEChERS technique provided a considerable reduction in the amount of solvent (only 10 mL per sample) as well as a reduction in the operating time (2 hours per sample), without compromising the performance of the method given by the validation parameters. Likewise, it was observed that QuEChERS methodology was a valid technique to make a screening of the compounds presents in a sample, since it allowed the simultaneous extraction of the 5 groups of compounds in both environmental matrices. However, if a higher specificity or lower detection limits are required, other kind of analysis methods should be considered.

Once the analytical method was adapted and validated, the SVOCs presents in the real samples of soil and vegetation from Tarragona were determined (article 2 of this chapter). In the case of soils samples, all the target SVOCs were detected with the exception of nitro musks, PCB 169 and some brominated flame retardants. This would be associated with the fact that many of these compounds have already been banned or have restricted use. In the case of vegetation, and in compared with soils samples, a larger number of compounds were not detected in the analysis in this matrix. This would reflect the differences between these two selected environmental matrices. In this sense, and contrary to soils, vegetation is more prone to trap gas-phase atmospheric compounds (Yogui et al., 2011), although in this case, being a species of ground vegetation, also the deposition of heavier compounds was observed.

The results show that PAHs levels in soils ranged from 45.12 to 158.00 ng/g and from 42.13 to 80.08 ng/g in vegetation samples; and in general, the urban areas presented the higher levels, mainly associated with the presence of a nearby highway and several roads with heavy traffic. Regarding PCBs, the chemical area, showed the highest values of PCBs in both matrices (from 6.62 to 14.07 ng/g in soils; from 0.52 to 4.41 ng/g in vegetation) at the same sampling point (point 11), and also is in agreement with the results provided by PUF-PAS (point 11 is C3 for PAS) (short communication 2, chapter 1 of this thesis), probably associated with the presence of two sub-electrical stations located in the vicinities. Levels of PAHs and PCBs were consistent with those recorded in previous studies since 2002. In the case of PAHs, a decreasing pattern in the total concentrations were observed since 2002, probability associated with the reduction in the PAHs emission observed between 1990 and 2010 in most European countries.

SMs levels in soils and vegetation ranged from 5.42 to 10.04 ng/g and from 4.08 to 17.94 ng/g, respectively, and in both cases, background areas showed the highest levels, suggesting an influence of the personal care products derived from beach-related tourism in the coast. In general terms, BFRs values recorded in soil and vegetation were quite similar between matrices and sampling areas, which may reflect their predominant association with indoor environments and also their banning for several years. Concerning HCB, similar values were found in both matrices and in all areas.

In general terms, both the SVOCs levels as well as the diagnostic ratios for PAHs showed that, in the short term (vegetation samples), SVOCs contamination in Tarragona County would be mainly associated with a mix between petrogenic and pyrogenic sources, probably due to an influence from urban and industrial areas. In turn, in the long-term (soil samples), the SVOCs contamination would have a markedly pyrogenic origin mainly associated to an urban influence. On the other hand, and regarding to the risk associated to some of the SVOCs in the Tarragona County soils, it was shown that not always the compounds with the highest concentrations are those that present the most potential danger for human health. This is a reason to keep performing thorough sampling actions of these compounds as often and covering as many contaminants as possible.

One of the main objectives of this thesis was to determine the main differences between the passive sampling techniques available for Tarragona County monitoring. As mentioned above, PUF-PAS, soils and vegetation were selected. Since PAHs are a family of compounds with well-differentiated physical-chemical characteristics, their analysis can provide information on the action mechanism of each passive sampling techniques with respect to other SVOCs analyzed in this thesis.

In the case of the PUF-PAS, it is observed that these devices mainly capture the low LMW PAHs, that is, the congeners with 2, 3 rings and, although to a lesser extent, some 4 rings PAHs, with a more than 90 % of the total contribution (Fig. 2 from short communication 1 and article 1, of chapter 1 of this thesis). This is so because the principle of advection-diffusion on which PUF-PAS are based, makes that congeners of 2, 3 and 4 rings, mostly associated with the gas phase, are quickly captured by the foam. Also PUF-PAS could sample the very low concentrations of 5 and 6 rings PAHs that are present in the gas phase. On the other hand, PUF-PAS are devices that allow to define the sampling period, from 1 month to 1 year, being usual 2 and 3 months sampling, which allows to establish a relationship between total concentration of PAHs captured and time.

In the case of vegetation, as in the case of PUF-PAS, it is observed that tends to accumulate PAHs with 2, 3 and 4 rings (more than 90 % of the total contribution; Fig. 3, article 2 of this chapter). However, it is detected that the percentage of total contribution associated with the 4 rings PAHs is slightly higher in comparison with PUF-PAS (more than 10 %). Likewise, in this matrix a greater percentage of contribution from 5 and 6 PAHs rings is observed, which taking into account the characteristics of this passive sampling technique, could have reached the plant through deposition process. This shows that the vegetation traps the PAHs contents in the gas phase, but also retains some of them associated to the particulate phase (which has not been washed by natural processes). Likewise, it is estimated that percentages of total contribution could vary depending on the lipophilicity associated with the selected plant. In this thesis, it was decided to use the spice of ground plant Piptatherum L. This is because Piptatherum L is a fast-growing plant (between 2 to 4 months), which allowed to make equations to the sampling period defined for the PUF-PAS (2 months sampling). However, it should be noted that, as it is a fast growing plant, there could be a possible dilution of PAHs. The pattern observed in this thesis for vegetation samples is in agreement with those found by Navarro-Ortega et al. (2012) in pine needles, where, a predominance of 3- and 4-ring PAHs, ranging from 65% to 95% of the total concentration of PAHs.

In the case of soils, a different profile of the PUF-PAS and vegetation is observed, with a clear predominance of the PAHs of 4, 5 and 6 rings (40-90 % of the total contribution), compared to the more volatile PAHs. In this sense, the soils are capturing mainly the particulate phase and to a lesser extent the gas phase. On the other hand, it must be mentioned that in the case of soils the sampling period may be longer than in the case of PUF-PAS and vegetation, since they are capable of storing compounds for a longer time. However, the soil has a high degradation capacity for this type of compounds, especially LMW PAHs, so it is important to evaluate the sink character of this matrix that is, the balance between inputs and loses. This fact has been subsequently evaluated in chapter 3 of the thesis.

In the case of PCBs, a pattern similar to PAHs has been found. PUF-PAS and vegetation trends to capture the tris- tetra- and penta-,PCBs (the most volatile), while the soils capture penta-, hexa-, hepta- PCBs, which are the heaviest and the most resistant to degradation and could be associated with particulate phase.

In this sense, this thesis confirms the importance of sampling in a complementary way with different passive sampling techniques, since depending on the characteristics of these, different information will be obtained.

CHAPTER 3: Modelling approaches as a combined tools of PAHs environmental monitoring.

In this chapter:

ARTICLE 1:

Domínguez-Morueco, N., Diamond, M.L., Sierra, S., Schuhmacher, M., Domingo, J. L., Nadal, M., 2016b. **Application of the Multimedia Urban Model to estimate the emissions and environmental fate of PAHs in Tarragona County, Catalonia, Spain.** Sci. Total Environ. 573, 1622-1629.

ARTICLE 2:

Domínguez-Morueco, N.[‡][┬], Ratola, N.[┴], Sierra, J.[┬][┤], Nadal, M [‡]., Jiménez-Guerrero, P.[┼], 2017. **Combining monitoring and modellings approaches for BaP characterization over a petrochemical area.** For submission to Sci. Total Environ.

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ARTICLE 1: APPLICATION OF THE MULTIMEDIA URBAN MODEL TO ESTIMATE THE EMISSIONS AND ENVIRONMENTAL FATE OF PAHS IN TARRAGONA COUNTY, CATALONIA, SPAIN.

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ABSTRACT

The Multimedia Urban Model (MUM-Fate) was used to estimate the emissions, fate and transport of polycyclic aromatic hydrocarbons (PAHs) in Tarragona County, Catalonia, Spain, where the largest chemical/petrochemical industrial complex of Southern Europe is located. MUM-Fate is a Level III steady-state fugacity model consisting of seven bulk media compartments (lower and upper air, surface water, sediment, soil, vegetation, and an organic film that coats impervious surfaces). The model was parameterized according to environmental conditions in Tarragona County, and used to back-calculate emissions from measured air concentrations of naphthalene, anthracene, phenanthrene, fluoranthene, pyrene, and benzo(*a*)pyrene. Modelled results in soils were within the range reported form measured concentrations. Estimated emissions of Σ_6PAH were 42 t/y, with phenanthrene having the greatest value (16 t/y). The fate and transport of Σ_6PAH were subsequently estimated by running the model an illustrative emission rate of 1mol h^{-1}. Organic film on impervious surfaces was the compartment that achieved the highest concentrations of PAHs, being up to 2×10^8 ng/m^3. However, as the film conveys chemicals to surface waters, the persistence in this compartment was <1 day. Soils and sediments were the greatest sinks for PAHs, with a persistence of 100–1000 days. The greatest loss of PAHs was due to advection from air, followed by photodegradation from air. These results provide a first approximation of the current emissions and fate of PAHs in Tarragona County.

Keywords: MUM-Fate · Polycyclic aromatic hydrocarbons (PAHs) · Urban pollution · Petrochemical area · Model evaluation

1. INTRODUCTION

Urban areas, just by virtue of dense human populations with their activities, are major sources of chemical emissions and contamination (Van Metre et al., 2000; Diamond and Hodge, 2007; Melymuk et al., 2014). Urban areas are also frequently close to industrial complexes which can contribute additional emissions and contamination. According to the United Nations, 54 % of the world's population live in urban areas, a proportion that is expected to increase to 66% by 2050 (UN, 2015).

Urban areas are dominated by impervious surfaces such as roadways and buildings (Lawand Diamond, 1998; Diamond et al., 2001). Impervious surfaces alter urban hydrographic regimes by increasing rates of surface water flow and decreasing soil infiltration (Diamond et al., 2001). Most impervious surfaces, notably surfaces of buildings, are coated with a surface film, which is the result of condensation and deposition of organic compounds, and their subsequent transformation products (Law and Diamond, 1998; Diamond et al., 2000; Gingrich et al., 2001). Organic film thickness grows with time, depending on rain events, resulting in a thickness from 2.5 to 1000 nm in temperature zones (Gill et al., 1983; Diamond et al., 2000; Gingrich et al., 2001; Wu et al., 2008; Csiszar et al., 2012). The organic film increases the capture efficiency of impervious surfaces for fine particles and facilitates the movement of compounds from impervious surfaces to receiving waters due to the wash-off process (Diamond et al., 2000, 2001; Csiszar et al., 2012).

Numerous chemicals have been identified in surface films, including a wide range of semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (Diamond et al., 2000; Gingrich et al., 2001; Lam et al., 2005; Wu et al., 2008). The film also contains biogenic organic compounds such as alkanes and alkanoic acids, metals and inorganic compounds such as sulphates and nitrates (Lam et al., 2005). PAHs are of concern not only because of their relatively high concentrations but also their potential toxicity. There is a large body of information concerning their toxicity, and particularly the carcinogenicity of some PAHs. The International Agency for Research on Cancer (IARC) has classified benzo(*a*)pyrene as carcinogenic to humans (Group 1), and dibenzo(*a,h*)anthracene, as probably carcinogenic (group 2A) (IARC, 2010). PAHs, which can be found in coal, petroleum and in tar deposits, are released by forest fires and other natural processes (Galarneau et al., 2007). However, their abundance in urban areas can be traced back to incomplete combustion of organic materials, notably vehicle emissions, domestic heating and industrial activities (Jaward et al., 2004; Wang et al., 2010; Estellano et al., 2012). Among these, petrochemical industries are particularly important emission sources of PAHs to air (Nadal et al., 2009, 2011).

Due to the notable toxicity of PAHs, it is crucial to understand how these compounds are transported throughout the environment, including their rates of removal and degradation, as well as to identify the environmental compartments where they mainly accumulate. Multimedia models are useful tools to estimate the chemical fate of organic chemicals in environmental systems. Mackay (1991) was the first to develop multimedia environmental models using fugacity as a basis. The use of fugacity simplifies model development and calculations while retaining a rigorous formulation. While the models are difficult to evaluate (e.g., Oreskes et al., 1994), they are based on fundamental principles, making possible an extensive use among the scientific community (Mackay and Paterson, 1991; Kwamena et al., 2007; Csiszar et al., 2012, 2013). An example of a fugacity model is the Multimedia Urban Model (MUM-Fate) developed by Diamond et al. (2001). This is a Level III fugacity model that assumes steady-state conditions, being specific for urban areas. This model has been applied to estimate the fate of PCBs, PAH and polybrominated diphenyl ethers (PBDEs) (Priemer and Diamond, 2002; Jones-Otazo et al., 2005; Kwamena et al., 2007; Diamond et al., 2010). As with other fugacity models, MUM-Fate considers both gas- and particle-phase chemicals.

The aim of this study was to estimate the emissions, fate and transport of PAHs in Tarragona County, Catalonia, Spain, that is home to the largest chemical/petrochemical industrial complex in Southern Europe. We achieved this aim by applying the MUM-Fate developed by Diamond et al. (2001). As noted above, the model was previously been applied in a case-study to calculate the fate of a wide range of PAHs in Toronto, Canada (Kwamena et al., 2007). The model was evaluated by comparing the model results with field data on PAH levels in soil.

2. MATERIAL AND METHODS

2.1. Description of study area

Tarragona County, located in NE of Spain and with a total population of 190,000 inhabitants (INE, 2014), is home of the largest chemical/petrochemical industrial complexes in Southern Europe. The complex includes a large oil refinery as well as large number of chemical companies. For this reason, the occurrence of PAHs in air and other environmental matrices was measured in previous monitoring studies conducted in this area (Nadal et al., 2004a, 2004b, 2007, 2009, 2011; Schuhmacher et al., 2004; Domínguez-Morueco et al., 2015).

2.2. Multimedia Urban Model

The MUM-Fate was used to investigate the dynamics of PAHs in Tarragona County, Spain. Full details of the model have been previously provided (Diamond et al., 2001; Priemer and Diamond, 2002; Jones-Otazo et al., 2005). Briefly, the model is based on the Level III steady-state fugacity model of Mackay (1991), and it consists of seven bulk media compartments: lower air (LA), upper air (UL), surface water (W), soil (S), sediment underlying the water (D), vegetation covering the soil (V), and an organic film that coats impervious surfaces (F).

In the MUM-Fate model, each bulk compartment has a specified volume where “dissolved” (e.g., gas) and particulate phases of chemicals are assumed to be in equilibrium. The entry of chemical compounds in the urban system can be through direct emission, E (mol/h), and/or by advective flow, G (m^3/h), in the air or water compartments. The model quantifies chemical transfer among compartments, chemical transformations, and advective losses from air and water using D values (mol/Pa·h). Chemical loss can also occur through burial in deep sediments and leaching from soil. The capacity of a phase for a chemical is defined by fugacity capacity (Z) values (mol/Pa·m^3). For the aerosols, soil, vegetation and film, Z values are governed by the octanol-air partition coefficient, K_{OA} and by the organic carbon fraction, f_{OC}. MUM-Fate consists of seven mass balance equations (Table. S1, Annex 6), one for each compartment, for which a steady state solution is obtained. The model is programmed in MS Visual Basic version 6.0 and runs on the PC platform in a Windows environment.

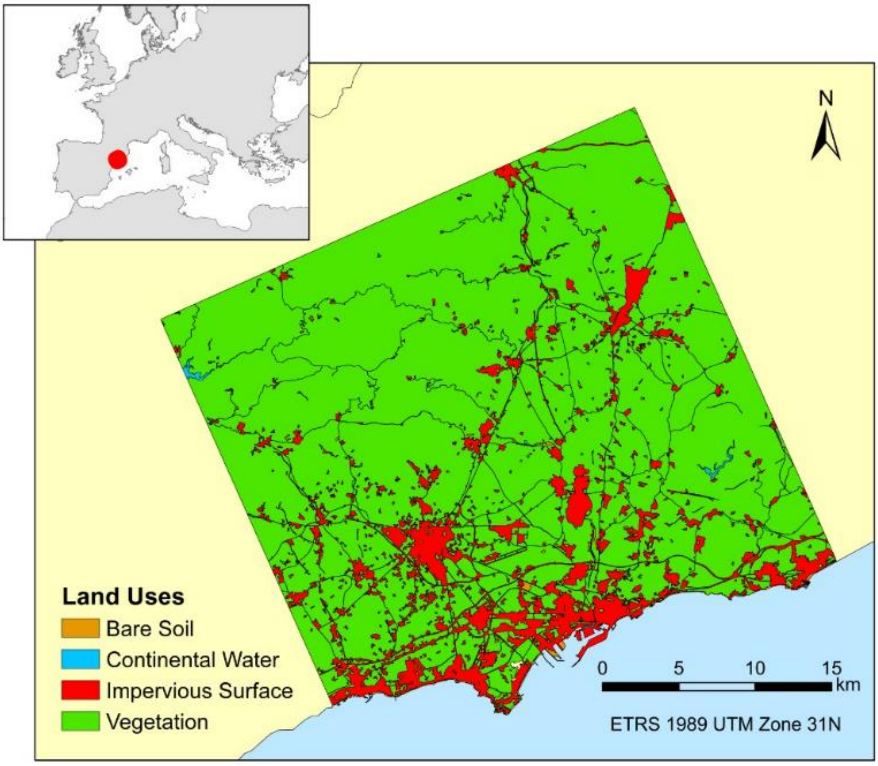

Fig. 1. Location map and land uses in Tarragona County (Catalonia, Spain).

2.3. Model parameterization to Tarragona County

The model was parameterized to simulate the environmental conditions of Tarragona County, Catalonia, Spain. A total surface area of 1000 km^2 was selected, covering the entire area sampled in previous field studies of our group (Domínguez-Morueco et al., 2015; Nadal et al., 2004a, 2004b, 2009). The land uses for the Tarragona area were provided by the Spanish Occupation Information System Land (integrated within the National Plan for Territory Observation, www.siose.es) and were extracted using the software ArcGIS version 10 (Fig. 1). Regarding the sediment compartment, the same area as that of water surface area was chosen. The film surface area was determined based on an Impervious Surface Index (ISI) of 2.8 for Tarragona City. ISI accounts for the three-dimensional nature of the urban landscape of Tarragona City. It assumes that 50% of the impervious area is two-dimensional, with an index of 1. The remaining 50% consists of three-dimensional buildings, whose average height, width and length were assumed to be 17, 20 and 18 m, respectively. A summary of surfaces that were employed in the model is presented in Table 1.

The air compartments were defined in the ranges 0–200 m and 200–2000 m for LA and UL, respectively, according to previous atmospheric boundary layer structure studies conducted in Tarragona County (Soler et al., 2011) (Table 1). The water compartment was assumed to simulate the Francolí River, which crosses the area from north to south flows into the Mediterranean Sea (Roig et al., 2013) (Table 1). The river has an average water depth of 0.5 m (Bangash et al., 2012), while a depth of 0.02 m for the sediment underlying to water was assumed (Table 1). Because of the relatively low percentage of agricultural soil, and consequently limited soil mixing, the soil thickness was assumed to be 0.05 m. Vegetation was estimated to have an overall thickness of 2×10^{-4} m, with a leaf area index (LAI) of 0.65. The LAI value was calculated averaging 46 LAI (1 × 1 km) images from Moderate Resolution Imaging Spectroradiometer (MODIS, NASA http://modis.gsfc. nasa.gov/) collected each 8 days for 2014. Due to the arid climate in the zone, wash-off is minimal (Fig. S1 Annex 6). Thus, the thickness of the film was assumed to be 0.1 μm. The film phase was assumed to consist entirely of organic matter, with an organic carbon fraction, f_{OC}, of 0.74 (Diamond et al., 2000). A value of 0.1 of organic carbon fraction was considered for air particles (Sánchez-Soberón et al., 2015). The fractions of organic carbon for the remaining compartments are shown in Table 1. The particle volume fraction in air was calculated using the annual average $PM_{2.5}$ measured in the vicinities of the oil refinery (18.4 μg/m^3). Other input variables are also summarized in Table 1.

Six different PAHs were considered in this study. They were selected as representatives of compounds with different number of aromatic rings and with physicochemical properties. In addition, the target pollutants are frequently associated with urban areas and released by petrochemical industries (Domínguez-Morueco et al., 2015; Nadal et al., 2004a, 2004b, 2009, 2011). Physicochemical properties of the selected PAHs were obtained from EpiSuite (version 4.11, US EPA, 2012) (Table 2 and Tables S2 and S3 Annex 6). Henry's law constants, octanol-water partition coefficients (K_{OW}) and octanolair partition coefficients (K_{OA}) were taken from HenryWin, KowWin and KoaWin, respectively. In addition, air-water partition coefficients (K_{AW}) were obtained from the Henry's law constant. Chemical transformation rates in all media were expressed as half-lives in that medium. For air, water, soil and sediment compartments, half-life values were obtained from AOPWin and BioWin, respectively (EpiSuite version 4.11, US EPA, 2012). Media half-life values for vegetation and organic film compartments were assumed to be 25 % and 30 %, respectively, less than that for the air compartment (Priemer and Diamond, 2002; Kwamena et al., 2007) (Table 2). The photochemical oxidation by reaction with hydroxyl radicals was assumed to be the dominant chemical transformation process for PAHs in the atmosphere (Kwamena et al., 2007). In turn, photodegradation was considered as the main degradative process in vegetation and organic film (Diamond et al., 2001). A diurnally averaged hydroxyl radical concentration of 1.5×10^6 mol/cm^3 for urban environments was adopted from AOPW in Episuite version 4.11 (US EPA, 2012).

Unless specified, default input parameters and coefficients used in MUM-Fate were taken from Diamond et al. (2001). An average steady-state scenario that spanned one year was assumed to represent the four seasons. In 2014, mean temperature (T) rain rate (U_R) and wind speed (v) were 16 °C, 638.5 mm/year and 2.4 m/s, respectively. The advective air flow (G_A) was calculated as the product of the cross-sectional area of air compartment and the annual mean wind speed for Tarragona County (Table 1). A water advection rate (G_W) was calculated using an average annual flow of 2 m^3/s for the Francolí River (Table 1). The wet deposition interception fraction (If_W) of 0.217 was calculated according to the equation described by Müller and Pröhl (1993), considering the LAI value above described, and an interception coefficient α of 1. A general value of 0.13, representing a variety of Mediterranean forest located in NE of Spain (Piqué et al., 2011), was used for the interception loss fraction (IlW) of wet deposition. The soil solids runoff rate to water (U_{SW}: 9.13×10^{-10} m/h) was calculated according to Allen and Shonnard (2002), while the soil water runoff to sediments (U_{WW}) in the Francolí River was 4.6×10^{-6} m/h (Liquete et al., 2009; Bangash et al., 2012).

Table 1. Model parameter values for Tarragona County (Catalonia, Spain).

Compartment	Lower air	Upper air	Water	Soil	Sediment	Vegetation	Film
Surface area (m^2)	1.04×10^{9}	1.04×10^{9}	1.72×10^{6}	8.51×10^{6}	1.72×10^{6}	9.03×10^{8}	1.45×10^{9}
Depth (m)	200	2000	0.5	0.05	0.02	2.00×10^{-4}	1.00×10^{-7}
Volume (m^3)	2.08×10^{11}	1.87×10^{12}	8.58×10^{5}	4.26×10^{5}	3.43×10^{4}	1.81×10^{5}	1.45×10^{2}
Fraction of organic carbon	0.1[a]	0.1[a]	0.02[b]	0.02[b]	0.04[b]	0.02[b]	0.74[c]
Density (kg/m^3)	1.175	1.175	1000	1300 [b]	1500 [b]	1000[d]	820[d]
V_a	~1.00	~1.00	-	0.20[e]	-	0.18[b]	-
V_w	-	-	~1.00	0.30[e]	0.63[e]	0.80[b]	-
V_{part}	1.57×10^{-8}	1.57×10^{-8}	3.00×10^{-5}[f]	-	-	-	0.7[b]
Advective flow (m^3/h)	5.57×10^{10}	5.01×10^{11}	7.20×10^{3}	-	-	-	-

V_a = volume fraction of air inside the compartments; V_w = volume fraction of water inside the compartments; V_{part} = volume fraction of particles inside the compartments; [a]Sánchez-Soberón et al., 2015 ; [b]Diamond et al., 2001 ; [c]Diamond et al., 2000 ; [d]Kwamena et al., 2007 ; [e]Mackay, 1991; [f]Jones-Otazo et al., 2005.

Table 2. Physical-chemical properties and transformation rates of chemicals modelled at 298ºK.

	Naphthalene	**Anthracene**	**Phenanthrene**	**Pyrene**	**Fluoranthene**	**Benzo(*a*)pyrene**
MW (g/mol)	128.12	178.24	178.24	202.26	202.26	252.32
M.P. (ºC)	80.2	215	99.2	151.2	107.8	176.5
Wsol (g/m^3)	31.7	0.041	1.29	0.135	1.29×10^{-3}	0.0038
Henry's Law constant (Pa m^{-3} mol^{-1})^a	44.6	5.63	4.29	1.21	0.89	0.046
Log (K_{ow})^b	3.3	4.46	4.46	4.88	5.16	6.13
Log (K_{oa})^c	5.19	7.55	7.57	8.80	8.88	10.86
V.P. (Pa)^d	11.3	3.50×10^{-4}	0.016	6.00×10^{-4}	1.20×10^{-3}	7.30×10^{-7}
$\tau_{1/2}$ (air) (h)^e	11.60	6.33	18.90	5.08	21.30	5.08
$\tau_{1/2}$ (water) (h)^f	318	430	430	833	833	940
$\tau_{1/2}$ (soil) (h)^f	1905	2150	2150	4164	4164	4700
$\tau_{1/2}$ (sed.) (h)^f	1910	2150	2150	4160	4160	4700
$\tau_{1/2}$ (veg.) (h)^g	8.7	4.7	14.2	3.8	16.0	3.8
$\tau_{1/2}$ (film) (h)^h	8.1	4.4	13.2	3.6	14.9	3.6

^{a}From HenryWin (EPA EpiSuite Software); ^{b}From KowWin (EPA EpiSuite Software); ^{c}From KoaWin (EPA EpiSuite Software); ^{d}From Kwamena et al., 2007; ^{e}From AOPWin (EPA EpiSuite Software); ^{f}From BioWin (EPA EpiSuite Software); ^{g}Seventy five percent of the half-lives of PAHs in the air compartment; ^{h}Seventy percent of the half-lives of PAHs in the air compartment.

2.4. Estimating emissions and model runs

Emissions into LA were only considered as total emissions from all sources including the chemical and petrochemical industries, vehicle traffic and other stationary sources located across Tarragona County. Emissions into the water compartment were assumed to be minimal. Emissions to LA were back-calculated by running the model iteratively with trial emissions of PAHs until modelled and measured air concentrations were equal. Gas- and particle-phase air concentrations of PAHs measured by the regional government in 2014 (ASP, 2015) were used for this purpose. Because of its proximity to the oil refinery and the relatively high PAH levels found in previous monitoring studies, air concentrations measured at the village of Puigdelfí adjacent to the petrochemical industry was used to back-calculate the emissions (Domínguez-Morueco et al., 2015). Air concentrations of PAHs were measured using an active air sampler deployed in Puigdelfí weekly during a 9-month period in 2014.

The model was run with an illustrative emission of 1 mol/h of PAHs into the air compartment in order to estimate the fate and transport of PAHs in Tarragona County. Finally, MUM-Fate was evaluated by comparing modelled levels using estimated air emissions with measured soil concentrations reported in that area (Nadal et al., 2004a, 2004b; Nadal et al., 2009; Nadal et al., 2011).

3. RESULTS AND DISCUSSION

3.1. MUM-Fate evaluation

One of the most important steps in modeling process is the model evaluation. Since models reproduce conditions in an open system (all natural systems are "open") and results are non-unique, models of natural systems cannot be verified or validated (Oreskes et al., 1994). Therefore, the results of MUM-Fate were evaluated, which simply involves comparing modelled and measured concentrations. Tarragona County, as an area highly impacted by industrial activities, has sustained a large multi-component environmental monitoring program since 2002. As part of this program, PAHs have been analyzed in soil and vegetation samples from different zones of Tarragona County (Nadal et al., 2004a, 2004b, 2007, 2009, 2011; Schuhmacher et al., 2004).

MUM-Fate was run with theΣ_6PAH emissions estimated for 2014. Modelled soils concentrations are summarized in Table 3.With the exception of naphthalene, PAH concentrations in soil estimated by the MUM-Fate model, were within the range reported in previous monitoring surveys (Nadal et al., 2004a, 2009, 2011). Based on the correspondence between measured and modelled soil concentrations (R^2 ranging from 0.56 to 0.92; Fig. S2 Annex 6), the current model was deemed to provide a reasonable representation of PAH dynamics in Tarragona County.

Table 3. Modelled soil concentrations by MUM-Fate model for Tarragona area in 2014 and soil concentrations (range and sampling points) reported in previous Tarragona field studies.

Compound	**MUM-Fate**	**Nadal et al., 2004**		**Nadal et al., 2009**		**Nadal et al., 2011**	
	Soil estimated concentrations (ng/g) (min-max)	**Sampling points (ng/g)**	**Range (ng/g)**	**Sampling points (ng/g)**	**Range (ng/g)**	**Sampling points (ng/g)**	**Range (ng/g)**
Naphthalene	7.4×10^{-3} (2.2×10^{-4}-3×10^{-2})	-	<2-8.3	-	9.9-71.6	-	2-55.7
Anthracene	2.6 (0.1-7.6)	3.1 (P)	<2-51	2.1 (P, C)	<2-4.7	1 (P)	1-19.9
Phenanthrene	9.1 (0.6-52.5)	16 (P); 7.9 (B)	7.9-131	7.5 (P); 9.1 (C)	7.5-34.4	7 (B)	3.6-49.8
Pyrene	20.6 (5.2-100.2)	20 (P)	2.5-180	12.8 (C); 44.4(U)	6.2-44.4	26 (B)	11-111
Fluoranthene	37.9 (1.7-192)	23 (C)	5.6-180	43 (U)	6.8-43.0	23.6 (B)	7.8-106.3
Benzo(*a*)pyrene	4.6 (4.3-9.8)	18 (P)	18-100	6.6 (C); 8.1 (P)	4.9-41.8	4.9 (P)	4.9-60.9

P= petrochemical sampling point; C= Chemical sampling point; U= Urban sampling point; and B= Background sampling point.

3.2. Estimated emissions

According to the model results, the emissions ofΣ6PAH in Tarragona County were estimated to be 42 tonnes year^{-1} (t y^{-1}) in 2014, with a minimum value of 5.2 x 10^{-2} t day^{-1} (t d^{-1}), and a maximum of 0.5 t d^{-1}. The emissions of each PAH were estimated as 5.7 t y^{-1} (range: 4.6 x 10^{-4}–6.3 x 10^{-2} t d^{-1}) for naphthalene, 7.1 t y^{-1} (8.1 x 10^{-4}–5.6 x 10^{-2} t d^{-1}) for anthracene, 16.4 t y^{-1} (2.8 x 10^{-3}–0.26 t d^{-1}) for phenanthrene, 5.8 t y^{-1} (4 x 10^{-3}–7.7 x 10^{-2} t d^{-1}) for pyrene, 6.5 t y^{-1} (7.8 x 10^{-4}–9 x 10^{-2} t d^{-1}) for fluoranthene, and 0.9 t y^{-1} (2.3 x 10^{-3}–5.3 x 10^{-3} t d^{-1}) for benzo(*a*)pyrene. These results were compared with those reported by the Spanish Register of Emissions and Pollutant Sources (PRTR-Spain). PRTR-Spain is a register that provides publicly available information on pollutant emissions to air, water and soil of major industries in Spain. In 2014, the value of total PAH emissions into air reported by PRTR-Spain for all Catalonia was 0.704 t y^{-1}, a substantially lower value than that estimated by MUM-Fate for Tarragona County. This discrepancy could be due to the fact that industries registered in the PRTR-Spain are only required to declare emissions exceeding 50 kg y^{-1}. In addition, only industrial emissions are considered by the PRTR-Spain, while those associated with urban activities, such as heating or traffic, are not included. However, emissions from these sources were included in our emission estimates.

Emissions estimated by the MUM-Fate model were also compared with those reported for the European Union (EEA, 2013), corresponding to total PAH emissions to air for the 27 EU Member Countries. The mean value estimated for Tarragona County (42 t y^{-1}) is 5-times lower than the total national reported for the year 2011 (210 t y^{-1}) in Spain, the Member State with the highest contribution to the total PAH emissions in the EU. However, considering emissions per capita, values for total emissions of PAHs were estimated in 9.9·10^{-2} kg person^{-1} y^{-1} in the modelled area, being around 20 times greater than those calculated for Spanish citizens (4.3 x 10^{-3} kg person^{-1} y^{-1}). The higher emission rate calculated here is consistent with the considerable industrial activity in Tarragona County.

Finally, air emissions of PAHs estimated by the MUM-Fate model for Tarragona County, are comparable with values reported by Jiang et al. (2013) in different districts of Taiyuan, China (Qingxu: 87 t y^{-1}, Gujiao: 54 t y^{-1}, Jinyuan: 44 t y^{-1}, and Jiancaoping: 40 t y^{-1}). Other authors reported PAH emissions at country level and thus are not readily compared with estimates presented here. Singh et al. (2013) reported that PAH emissions in India were 23.81 Gg y^{-1}, while in China, Zhang et al. (2007) estimated a total emission of 28.25 Gg y^{-1}. The total annual emission of six PAHs for US and Canada was estimated to be 18.27 Gg y^{-1}, arising mostly from US sources (Galarneau et al., 2007).

3.3. Fate and transport of PAHs in Tarragona County

The relative fate and transport of six PAH were compared using MUM-Fate with an illustrative emission of 1 mol/h into air. The same PAH concentration pattern (benzo(*a*)pyrene > fluoranthene > pyrene > phenanthrene > anthracene > naphthalene) was found in all the compartments, with concentrations increasing according to molecular weight. Lower molecular weight PAHs are predominantly present in the gas-phase, so they remain in air, where they are subject to loss by advection and photodegradation. Heavier molecular weight PAHs tend to be in the particulate-phase (Choi et al., 2012; Estellano et al., 2012; Pozo et al., 2012). In the particulate phase, they can be deposited from air to other compartments. In addition, particulate-phase PAHs are more resistant to photolytic reaction than PAHs in the gas phase. In the air compartment, PAH concentrations were quite similar, irrespective of the molecular weight, reflecting the assumption of continuous emission of 1 mol/h into air.

The results of the MUM-Fate model showed that the film compartment achieves the highest concentrations of the 6 studied PAHs, being followed by sediments and soils (Fig. 2). This pattern is consistent with results found in downtown Toronto, Ontario, Canada, after applying the same model and considering the same illustrative emission of 1 mol/h into air (Diamond et al., 2001; Priemer and Diamond, 2002).

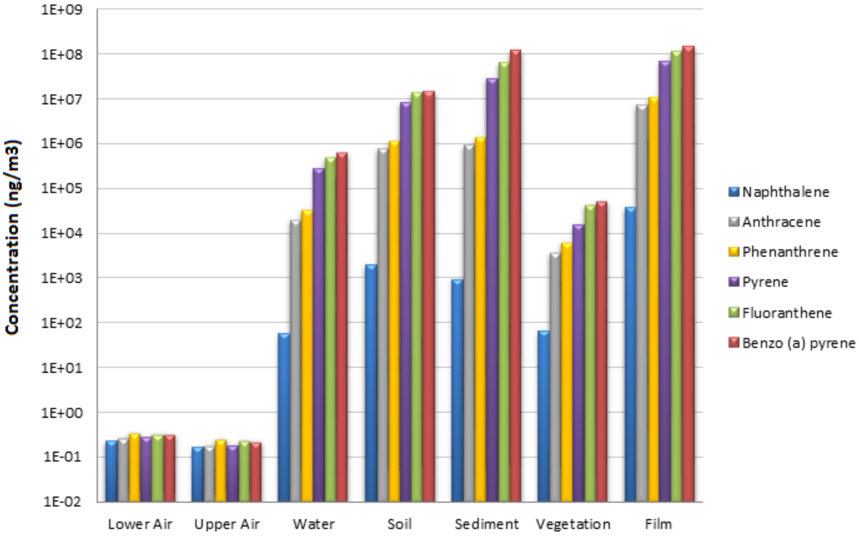

Fig. 2. MUM-Fate estimated concentrations of PAHs selected in the bulk phase (ng m^{-3}) based on an emission of 1 mol h^{-1} into air.

In contrast, soil and sediment were the greatest sinks of PAHs in Tarragona County (Fig. 3), as chemical persistence were higher in both compartments. These results also agree with those found in Toronto, Ontario, Canada (Diamond et al., 2001; Priemer and Diamond, 2002). In this case, the compartments receive PAH inputs from air, water and vegetation, while losses are relatively low (Fig. 4). As such, the persistence in soil and sediment, calculated as the ratio of chemical mass to losses from a compartment, was estimated to range from 100 to 900 days (3 years) for naphthalene and benzo(*a*)pyrene, respectively (Fig. 3). Biodegradation was the greatest loss mechanism in both soil and sediment.

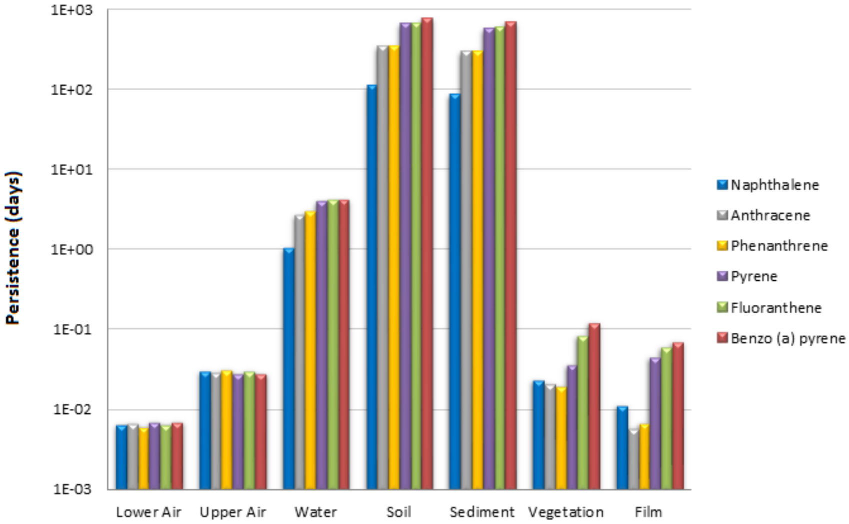

Fig. 3. MUM-Fate estimated persistence of PAHs selected in each compartment (days) based on an emission of 1 mol h^{-1} into air. Persistence is calculated as the ratio of chemical mass to inputs to that compartment.

Film on impervious surfaces receives chemical inputs from atmospheric deposition, which are balanced by high losses due to wash-off from film to water, and by photodegradation. For instance, approximately 42 % of the losses of benzo(*a*)pyrene occur by wash-off, and the remaining 58 % by photodegradation (Fig. 4). Although the film achieves the highest PAH concentrations, the rapid loss leads to a chemical persistence in film of < 1 day (Fig. 3). In this sense, the film compartment increases the mobility of PAHs (Csiszar et al., 2012).

The burdens of PAHs in vegetation were also estimated by the MUM-Fate according with the illustrative emission of 1 mol/h into air. The concentrations of PAHs were much lower than those found in downtown Toronto, Ontario, Canada (Diamond et al., 2001). It could be due to the differences in climate condition and type of vegetation for each region, which ultimately affects the deposition of these compounds. Moreover, high photodegradative reactive losses should be also playing a key role (Fig. 4).

Water concentrations ranged between 100 and 1,000,000 ng/m^3 for naphthalene and benzo(*a*)pyrene, respectively, according with the illustrative emission of 1mol/h into air. The greatest input of chemical to water was from film (0.01 to 20 mmol/h for naphthalene and benzo(*a*)pyrene, respectively) rather than from direct atmospheric deposition (< 0.1 mmol/h). Although annual precipitation is low in Tarragona County due its semi-arid climate, rainfall facilitates the transfer of PAHs accumulated on impervious surfaces to the river (Fig. 4). Chemical persistence in water is only 1–5 days due to advective loss from the Francolí River (Fig. 3), while this only exports to downstream locations < 2 % of PAHs emitted to air.

The greatest loss of PAHs from Tarragona County was due to advection from air, followed by photodegradative losses from air (Fig. 4). Due the high advective losses from air, persistence in LA and UL was < 1 day for the six PAHs. These results suggest that areas downwind of Tarragona County receive from 50 % to 70 % of emissions generated within the County (benzo(*a*)pyrene and naphthalene, respectively).

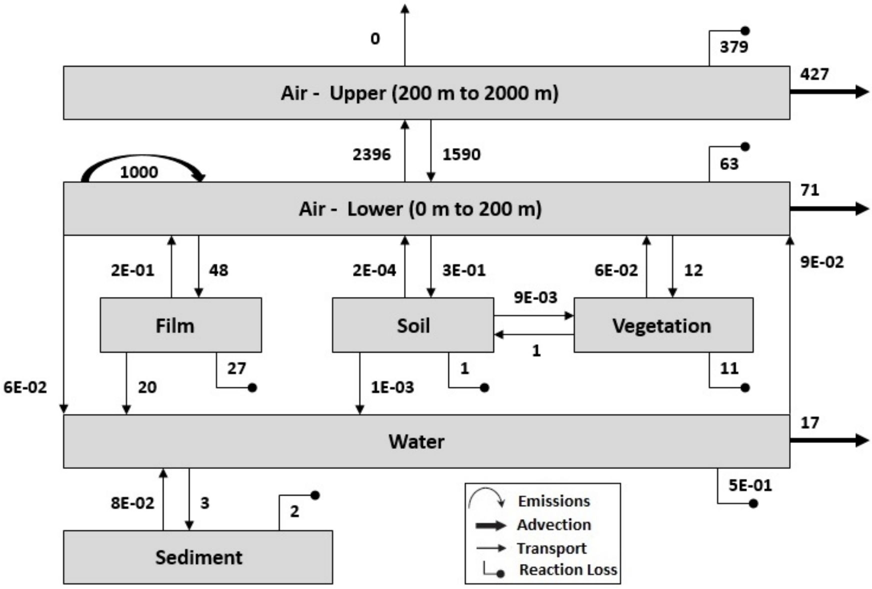

Fig. 4. MUM-Fate estimated rates of chemical movement and transformation for benzo(*a*)pyrene based on an emission of 1 mol h^{-1} into air. Transport rates are expressed in mmol h^{-1}. MUM-Fate estimated rates of chemical movement and transformation for the rest of PAHs studied are in Annex 6 (Fig. S3-S7).

4. CONCLUSIONS

The MUM-Fate was successfully applied to estimate the emissions, fate and transport of PAHs in Tarragona County, Catalonia, Spain, an area with the largest chemical and petrochemical industrial complex in Southern Europe. Total emissions of 6 PAHs of 42 t y^{-1} were estimated by back-calculation from measured air concentrations. Using the compound-specific estimated emissions, modelled soil concentrations were within the range of measured values reported for Tarragona County. The model, which was run for illustrative purposes with an emission of 1 mol/h to air for each PAH, estimated that 50–70 % of the PAHs emitted to air were lost by downwind advection. Organic film achieved the highest concentrations of PAHs. However, the high losses by wash off and photodegradation resulted in a persistence of in the film of < 1 day. Wash-off from the film delivered particle-sorbed PAHs to the river running through Tarragona County. This process, along with degradation losses, resulted in < 2 % of total air inputs being exported downriver. Soils and sediments were the greatest sinks for PAHs, as consequence of their high inputs from air, water and vegetation, relative to low losses. Persistence in soils and sediments was estimated to range 100–1000 days. The model illustrates that surface films on impervious surfaces are important in conveying PAH emitted to air to surface water, sediments and soils.

Acknowledgments

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ARTICLE 2: COMBINING MONITORING AND MODELLINGS APPROACHES FOR BaP CHARACTERIZATION OVER A PETROCHEMICAL AREA.

For submission to Science of the Total Environment.

ABSTRACT

In this study, air concentrations of BaP in two different seasons (winter 2015 and summer 2016) and ground vegetation BaP levels from Tarragona County were used as control simulations run with the chemistry transport model (CTM) WRF (Weather Research and Forecasting) + CHIMERE, in order to reproduce the incidence of that hazardous chemical in air and soils. Once the CTM was validated for the present climatology showing a good ability to represent air and soil concentrations of BaP over the target domain (petrochemical, chemical, urban and background sites), particularly in the winter, the variation of the BaP concentration in air and soils were simulated for the time series 1996-2015 and for the climate change scenario RCP8.5 (2031-2050). While for the levels in air an increase is projected, particularly in chemical and remote sites where the variation can go up to 10 %, in terms of soil deposition the findings are the opposite, with an evident decrease in soil BaP concentrations, particularly in background sites. Finally, a potential health effect of BaP for the local population (the life-time risk of lung cancer) was assessed. Although according to the projections the EU threshold for BaP atmospheric incidence (1 ng m^{-3}) will not be reached by 2050, there will be an increase in the life-time risk of lung cancer, particularly in the most populated areas.

Keywords: Benzo (*a*) pyrene · Passive sampling · WRF+CHIMERE · Human health · Tarragona (Spain).

1. INTRODUCTION

Field sampling is a crucial tool to determine the occurrence of hazardous compounds into the environment. Among the different monitoring strategies, the passive sampling of air (with appropriate uptake materials), soils or vegetation can provide information on the levels of many pollutants at different locations including remote areas, and involving low or no maintenance and reduced costs (Zabiegała et al., 2010; Cabrerizo et al., 2012; Estellano et al., 2014; Domínguez-Morueco et al., 2017). Nevertheless, to help transforming these valuable datasets into a complete understanding of spatial, temporal and chemical transport patterns it is essential to combine the field observations with modelling (Ratola and Jiménez-Guerrero, 2016).

Currently, the mass balance models or deterministic approaches are one of the most used techniques for the modelling of environmental pollutants such as semi-volatile organic compounds (SVOCs), a large group of compounds found worldwide in numerous environmental matrices (He and Balasubramanian, 2010). Mass balance techniques can provide a first approximation of the chemical fate and transport of SVOCs in environmental systems by using the fugacity concept, which simplifies the model development and calculations, allowing an extensive use among the scientific community (Mackay and Paterson, 1991; Csiszar et al., 2012, 2013; Domínguez-Morueco et al., 2016). Nevertheless, these techniques do not reflect the complexity to characterise adequately all processes involving these chemicals. In this sense, chemistry transport models (CTMs) such as the Weather Research and Forecasting (WRF) coupled with CHIMERE (the setup used in this work), can complement the field data also considering the meteorology of the study area, the atmospheric chemistry and climate change, contributing to diminish the gaps still existing regarding SVOCs environmental behaviour (Ratola and Jiménez-Guerrero, 2015, 2017). WRF is a numerical weather prediction (NWP) and atmospheric simulation system designed for the understanding and prediction of mesoscale weather (Skamarock et al., 2008), whereas CHIMERE is an Eulerian off-line CTM that includes parameterisations to simulate reasonable pollutant concentrations, but still being computationally efficient for forecast applications (Menut et al., 2013).

Among the different SVOCs, the polycyclic aromatic hydrocarbons (PAHs) have attracted the attention of the scientific community for environmental modelling due to their ubiquity in the environment, constant production/emission, long-range atmospheric transport (LRAT) capacity and relatively high toxicity (Estellano et al., 2012; Domínguez-Morueco et al., 2017). For instance, benzo(*a*)pyrene (BaP), has already been classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC), and is the only PAH with a legislated average limit in the atmosphere: 1 ng m^{-3} of BaP over 1 year (European Commission, 2009). International studies suggest that the toxicity and environmental fate and transport of PAHs can be affected by the variations in the temperature and solar radiation associated with climate change, mainly in the most vulnerable regions, such as the Mediterranean basin (Nadal et al., 2015; Marquès et al., 2016a).

PAHs are mostly emitted by anthropogenic sources, being the oil refineries a considerable emission point (Nadal et al., 2009). Located in the Mediterranean basin, Tarragona County (Catalonia, NE of Spain) is home of one of the largest chemical/petrochemical complexes in Southern Europe. For this reason, combining monitoring and modelling approaches for PAHs is very important to evaluate the impact of these contaminants in the surrounding environment, as well as to assess the risks for the local population. In this sense, associating the results provided by CTMs with the quantitative risk assessment (QRA) methods developed by the European Union, can help to unravel potentially hazardous effects to human health.

The main aim of this study was to combine monitoring data on air and ground vegetation from Tarragona County with the CTM WRF+CHIMERE in order to estimate the geographical distribution and air and soils concentrations of BaP in the time series between 1996 and 2015 and under the more extreme climate change scenario RCP 8.5 (2031-2050). To achieve this goal the modelling methodology developed by Ratola and Jiménez-Guerrero (2016) was used. Furthermore, in order to assess the potential risk of atmospheric BaP for the local population, a QRA method was conducted, concerning the risk of lung cancer associated to the presence of BaP in the atmosphere of Tarragona County.

2. MATERIAL AND METHODS

2.1. Field sampling

In this study, air and vegetation concentrations of BaP from Tarragona County were used in order to evaluate the WRF+CHIMERE modelling system.

Passive air samplers (PAS) with pre-clean polyurethane foams (PUF disks; diameter: 14 cm; thickness: 1.2 cm; surface area: 360 cm^2; density: 0.035 g cm^{-3} from Newterra, Beamsville, ON, Canada) were used to measure the atmospheric BaP levels in Tarragona County. A total of eight PAS were deployed in different areas of Tarragona County, for a period of 2 months in two different sampling campaigns: from 26/11/2014 to 26/01/2015 (winter season); and from 01/05/2016 to 01/07/2016. The distribution of the sampling sites was reported previously by Domínguez-Morueco et al., 2017 (two samples in a petrochemical area, P1 and P2; two samples close to a zone of chemical industries, C3 and C4; two samples in urban areas, U5 and U6; and two samples in background sites, B7 and B8, 30 km away from the area of influence of all the suspected sources of contamination).

Regarding vegetation samples, by end of January 2016 (25/01/2016) a total of 27 vegetation samples were collected in different zones of Tarragona County, following the distribution described by Domínguez-Morueco et al. (submitted to Sci. Total. Environ.; chapter 2) (7 in a zone in a petrochemical area; 9 in the vicinity of the chemical area; 6 in residential and urban zones of Tarragona County and 5 were selected in background areas). A total of 50 g of vegetation samples (*Piptatherum L.*) were obtained by cutting the plants 5 cm above ground, and dried at room temperature.

2.2. Field samples analysis and quantification

The analysis and quantification of BaP in environmental samples was done together with other PAHs.

In the case of air BaP was extracted from PUF samples using Soxhlet and a clean-up strategy similar to that described by Silva et al. (2015). In brief, the Soxhlet method consisted in extracting with 250 mL Hex:DCM (1:1) overnight and reduce the extracts to 1 mL in a rotary evaporator before clean-up, which consisted of two steps. First, solid phase extraction (SPE) glass columns packed with 5 g of alumina, conditionined with 50 mL of Hex:DCM (1:1) and eluted after sample loading with 50 mL of the same solvent. The extract was then reduced to 1 mL on a rotary evaporator and loaded onto gel permeation chromatography (GPC) glass columns containing 6 g of S-X3 Biobeads for the second step. Elution was done with 40 mL of Hex:DCM (1:1), from which the first 15 mL were rejected and the remaining eluate collected. The extract volume was again reduced to about 1 mL in rotavapor, followed by evaporation to dryness under a gentle stream of nitrogen. Sample reconstitution was done with 100 µL of hexane before analysis by GC-MS.

For vegetation samples, BaP was extracted by ultrasound extraction method followed by QuEChERS clean-up step according to Carvalho et al., (submitted to Anal. Bioanal. Chem.; chapter 2) and Domínguez-Morueco et al., (submitted to Sci. Total Environ.; chapter 2). A total of 2.5 g of vegetation were transferred into 50 mL Falcon tubes and extracted with 20 mL Hex:DCM (2:1) in a sonication bath for 10 min. Then, the content of the QuEChERS 1 (6 g of $MgSO_4$ and 1.5 g of CH_3COONa) was added to each Falcon tube and vortexed for 3 min. Subsequently, the tubes were centrifuged for 10 min and the supernatant collected and transferred to QuEChERS 2. The QuEChERS 2 was 0.9 g of $MgSO_4$, 0.15 g of alumina, 0.15 g Florisil and 0.15 g of C18. The tubes were shaken again during 3 min in order to conduct the dispersive solid-phase extraction (d-SPE). After that, the tubes were centrifuged (10 min) and the extract was collected and filtered with a conventional 0.2 µm size filter in order to remove more unwanted compounds. The final sample extract was concentrated until dryness with nitrogen and subsequently re-dissolved with 100 µL of hexane before the GC-MS analysis.

The details of the chromatographic analysis for both matrices can be found in Silva et al. (2015) and in chapter 2 of this thesis.

2.3. Set-up and validation of the modelling approach

The modelling methodology used follows the work developed by Ratola and Jiménez-Guerrero (2016). In this case, the WRF+CHIMERE modelling system with a resolution of 2 km for the Catalonia (Spain) domain was used, coupled to BaP emissions given by the European Monitoring and Evaluation Programme (EMEP; Vestreng et al., 2009). The main parameterisations are presented in Table 1.

Table 1. Parameterisations used in the WRF+CHIMERE modelling system.

WRF	**CHIMERE**
Microphysics → **WSM3**	Chemical mechanisms → **MELCHIOR2**
PBL → **Yonsei University**	Aerosol chemistry → Inorganic (thermodynamic equilibrium
Radiation → **CAM**	with **ISORROPIA)** and organic **(MEGAN SOA** scheme**)**
Soil → **Noah LSM**	aerosol chemistry
Cumulus → **Kain-Fritsch**	Natural aerosols → **dust, re-suspension and inert sea-salt**
	Boundary conditions → **LMDz-INCA+GOCART**

The CHIMERE version was modified to include BaP in gaseous and particulate phase. The lighter PAHs (2 or 3 aromatic rings) exist mainly in the gas phase, whereas the heavier (5 to 6 rings) consist almost entirely of the particulate phase (Srogi, 2007), and this is the case of 5-ringed BaP modelled in this work. Thus, BaP is introduced in the model as three different types at the same time: primary, semivolatile and reactive. First-order gas-phase degradation by OH radicals, which represents over 99 % of the degradation path for gas-phase BaP, was accounted for, with a $k_{OH} = 5.68 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Schwarzenbach et al., 2003). The oxidation of particulate BaP with O_3 was also included, since the respective reaction rate is one order of magnitude higher than other degradation processes, and can be considered the only effective degradation path for particulate BaP in the atmosphere (Bieser et al., 2012). In this case, the reaction constant follows the approach of Pöschl et al. (2001):

$$k = k_{max} [O_3] (1 + K_{O3} [O_3]) \tag{1}$$

being $k_{max} = 0.015$ s^{-1} and $K_{O3} = 2.8 \times 10^{-13}$ cm^3.

The model system was run and evaluated for a simulation covering a period coincident with the passive air samples; that is, for a winter (26/11/2014 to 26/01/2015) and a summer (01/05/2016 to 01/07/2016) period and in order to check the ability of the model to reproduce BaP climatologies over the target area. Moreover, the deposition in soils is assessed against the concentrations of BaP found on *Piptatherum L.* samples collected on 25/01/2016. *Piptatherum L.* is a fast-growing grass, between 2 to 4 months, beginning its growth with the first rains and when temperatures began to drop, and drying up during the warm seasons (Sulas et al., 2015). Moreover, being a ground plant with low height, the concentration accumulated during this time can be a good representation of the deposition onto the soil. Therefore, the deposition period extracted from the model was assuming to be three months until the collected samples, in line with this biomonitor.

To assess the ability of the model to reproduce current BaP air concentrations, a number of statistical parameters were tested for atmospheric levels and soil deposition. For instance, spatial correlation coefficient (*R*), mean absolute error (MAE) and mean bias (Bias) are commonly used by modellers. In addition, according to Boylan and Russell

(2006), the mean fractional bias (MFB) and the mean fractional error (MFE) were also used. These authors indicate that the model performance criterion is met when MFE ≤75 % and MFB ≤ ±60 %. As such, these criteria were chosen to supply the metrics for the evaluation of BaP by the WRF+CHIMERE system.

After the ability of the model is analysed, its accuracy for correctly reproducing the BaP climatologies was assessed, with present and future simulations run with WRF+CHIMERE. The air quality associated to the present BaP levels in this work uses simulations spanning the reference period 1996-2015 for the present, and 2031-2050 under the RCP8.5 scenario (Moss et al., 2010), as a future-enhanced forcing scenario. To date, the future-minus-present method has been the most frequent approach adopted for the evaluation of climate change impacts on projected regional air quality. This is based on the assumption that biases in simulated present-day and future climate simulations should tend to cancel each other, and thus their difference captures the signal of the concentration anomalies. This method is widely supported in most future climate-air quality interactions studies (e.g. Liao et al., 2009; Jiménez-Guerrero et al., 2013a, b, c), and therefore followed in this work. Simulations for present-day climatologies (1996-2015) were compared to a time slice covering 2031-2050. In order to isolate the possible effects of climate change on the ground concentrations of air pollution, unchanged anthropogenic emissions are assumed. Natural emissions depend on climate conditions and, consequently, are the only ones to vary between reference and future climate simulations. Therefore, the effects of climate change on air pollutants are estimated without considering possible changes on vegetation, land use, anthropogenic pollutant emission changes or any feedbacks from the chemical compounds to the meteorological fields, but allowing changes in natural emissions (e.g. Meleux et al., 2007; Jiménez-Guerrero et al., 2012). Biogenic emissions were generated dynamically using MEGAN (Model of Emissions of Gases and Aerosols from Nature) with the parameterised form of the canopy environment model. The model estimates these emissions as a function of hourly temperature and ground level shortwave radiation from WRF.

The differences between these two time slices will provide the changes in future BaP levels referring both to atmospheric concentrations and soil levels. The WRF+CHIMERE model ability to reproduce present and future climatologies over the Iberian Peninsula has been assessed in a number of previous works (e.g. Jiménez-Guerrero et al., 2012, 2013a, b, c; Jérez et al., 2013a, b). The projections over the Tarragona area (Fig. 1) indicate an increase in projected temperature around 1.0K (practically constant spatially), while precipitation decreases (increases) 5×10^{-7} kg m^{-2} s^{-1} (0.04 mm/day) in the southern (northern) part of the domain.

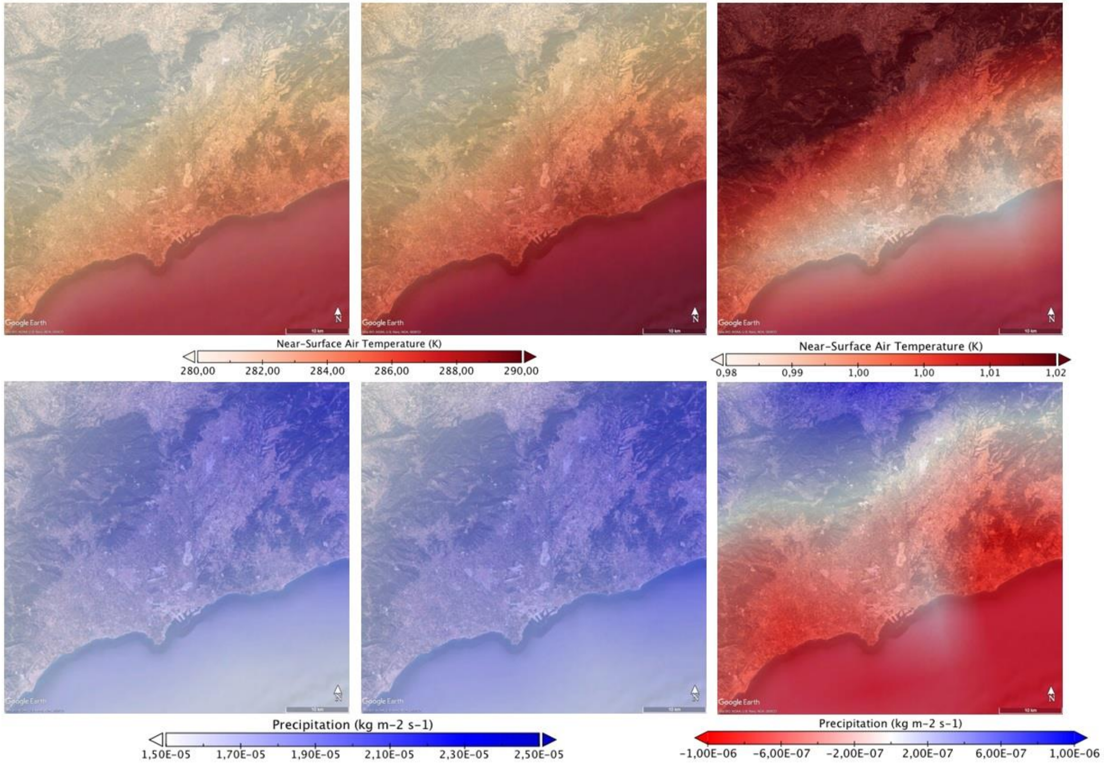

Fig. 1. Mean near-surface air temperature (top), in K, and precipitation rate (bottom), in kg m^{-2} s^{-1}, for 1996-2015 (left), 2031-2050 (center) and differences between present and future climate conditions under the RCP8.5 scenario (right) in Tarragona County, (Catalonia, Spain).

3. RESULTS AND DISCUSSION

This section presents the results of the evaluation of the model against observed BaP concentrations: atmospheric levels (section 3.1) and soil deposition (section 3.2). Section 3.3 presents the present (1996-2015) and future (2031-2050, RCP8.5 scenario) climatologies of BaP, while section 3.4 indicates possible impacts on human health for current and future BaP atmospheric levels.

3.1. Evaluation of atmospheric BaP levels.

The simulated BaP concentrations are here assessed for a winter and a summer period (26/11/2014 to 26/01/2015 and 01/05/2016 to 01/07/2016, respectively). When model simulations are evaluated against the passive air samplers (PUFs) observations, all the statistical figures estimated (see Table 2) indicate that the model tends to perform better for winter than for summer, (e.g., the mean fractional bias, MFB, is 1.2 % and 42.1 %, respectively). In general, the spatial correlation coefficient (R) indicate an accurate representation of BaP spatial patterns over the target area (R from 0.71 in summer to 0.76 in the winter, respectively). Still, the representation of the variability of the atmospheric concentrations is underestimated by the CTM in both seasons, with underpredictions around 5 pg m^{-3} of the spatial standard deviation). These are general findings applied to the whole domain, but the analysis can be done considering relevant aspect within the area of study.

Table 2. Summary for all stations of the results from the comparison of air BaP concentrations in air obtained by the chemistry transport model simulations and those estimated from stations.

ALL STATIONS	WINTER	SUMMER
SPATIAL CORR. COEF.	0.76	0.71
MFB (%)	1.2 %	42.1 %
MAE (pg m^{-3})	6.4	7.2
BIAS (pg m^{-3})	-1.9	2.3
MEAN OBSERVATIONS (pg m^{-3})	19.8	14.1
MEAN CTM (pg m^{-3})	18.0	16.4
STD OBSERVATIONS (pg m^{-3})	12.2	11.7
STD CTM (pg m^{-3})	7.9	6.7

CTM – chemistry transport model concentrations; CORR. COEF. – correlation coefficient; STD – standard deviation; MFB - mean fractional bias; MAE – mean absolute error. WINTER (26/11/2014 – 26/01/2015). SUMMER (01/05/2016 – 01/07/2016).

In fact, regarding the different site types considered (petrochemical, chemical, urban and background), the CTM can generally describe the differences seen in the BaP loads (Table 3). The distribution of the observed concentrations follow a general decreasing trend from petrochemical/chemical areas to urban and to remote sites (min 0.9 pg m^{-3} for the remote site of Cambrils, B7, in summer –with a corresponding modelled value of 5.4 pg m^{-3}– and max of 40.6 pg m^{-3} for the Puigdelfí petrochemical site, P1, in winter, with modelled concentrations of 32.5 pg m^{-3}) (Fig. 2). In this case, the typical seasonal trend observed for PAHs in the atmosphere is verified, with higher atmospheric loads of BaP in winter and lowest in summer (Srogi, 2007). This is observed in all stations except in La Laboral (C3; 23.8 vs. 30.3 pg m^{-3} in winter and summer, respectively). The modelling results observed for the mean CTM concentrations indicate a different pattern in winter and summer, with lower biases and mean fractional biases (more accurate results) in winter than in summer. Summer levels are, in general, overpredicted by the model, while winter concentrations are in general slightly underestimated. The highest errors are found in the background station of Cambrils (B7), where both wintertime and summertime BaP concentrations are overpredicted (MFB of 63.4 %

and 143.1 %, respectively). However, the low levels at this station tend to increase the percentual bias, while the absolute bias is just under 5 pg m^{-3} in both seasons. On the other hand, the lowest biases are found at La Canonja (C4) chemical site (MFB of 3.3 % and -16.5 % in summer and winter, in that order). In general, the model presents the most accurate results over the chemical/petrochemical sites. The MFEs for each individual site are below 75 % for the majority of the site types and corresponding seasons (except for U6 and B7 in summertime), complying with the model performance criterion of MFE ≤ +75 % (Boylan and Russell, 2006). These results help building confidence for the use of the CTM as a good representation for atmospheric levels of BaP, and therefore as a useful tool to assess the variations of BaP in present climate scenarios.

Table 3. Results from the comparison of air BaP concentrations in air obtained by the chemistry transport model simulations and those estimated from each individual station.

CODE/NAME/TYPE OF STATION	MEAN OBS (pg m^{-3})	MEAN CTM (pg m^{-3})	BIAS (pg m^{-3})	MFE (%)
WINTER (26/11/2014 – 26/01/2015)				
P1 / Puigdelfí / Petrochemical	40.6	32.5	-8.1	22.2
P2 / Constantí / Petrochemical	11.9	20.2	8.3	51.9
C3 / La Laboral / Chemical	23.8	18.4	-5.4	25.4
C4 / La Canonja / Chemical	21.7	18.4	-3.3	16.5
U5 / Tarragona / Urban	16.4	22.5	6.1	31.2
U6 / Vila-Seca / Urban	31.6	15.7	-15.8	67.1
B7 / Cambrils / Background	4.1	7.9	3.8	63.4
B8 / Torredembarra / Background	8.6	8.1	-0.5	5.7
SUMMER (01/05/2016 – 01/07/2016)				
P1 / Puigdelfí / Petrochemical	32.0	23.2	-8.7	31.6
P2 / Constantí / Petrochemical	8.8	18.9	10.1	73.0
C3 / La Laboral / Chemical	30.3	19.7	-10.6	42.5
C4 / La Canonja / Chemical	17.5	18.1	0.6	3.3
U5 / Tarragona / Urban	12.9	23.3	10.4	57.5
U6 / Vila-Seca / Urban	4.2	15.0	10.8	113.1
B7 / Cambrils / Background	0.9	5.4	4.5	143.1
B8 / Torredembarra / Background	6.1	7.5	1.4	21.0

CTM – chemistry transport model concentrations; OBS – observations; MFE - mean fractional error.

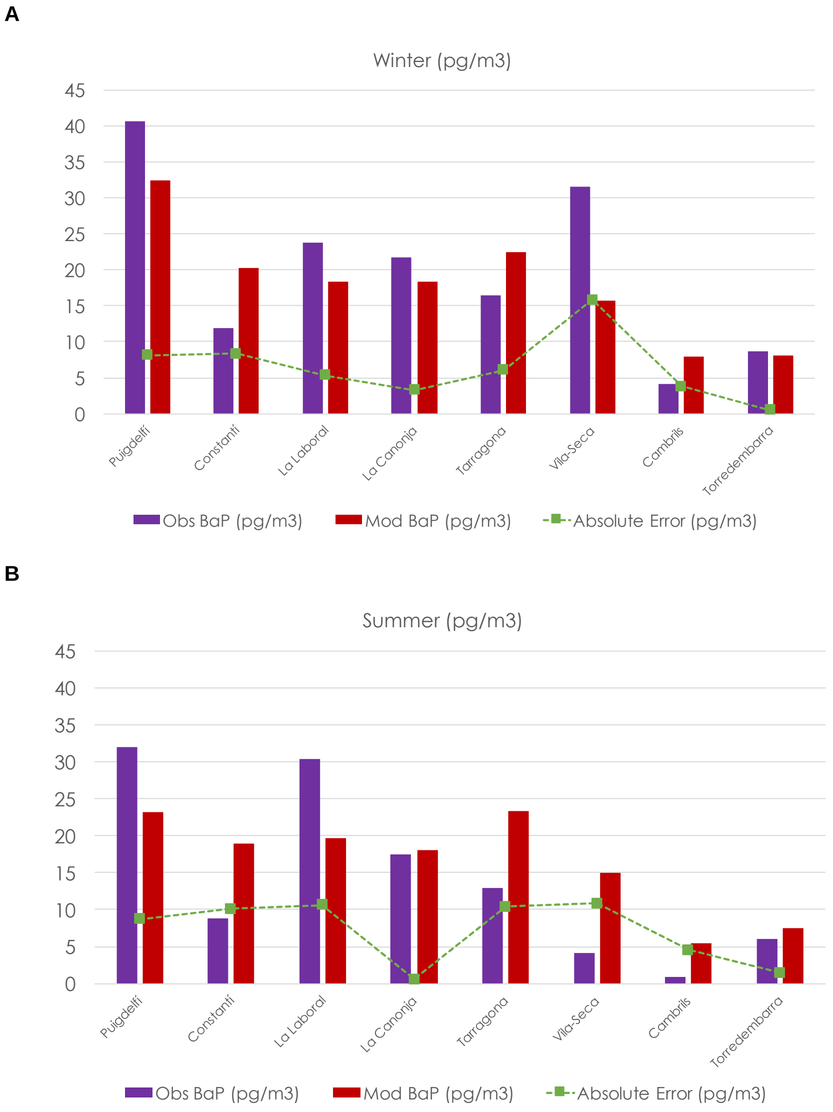

Fig. 2. A) Model evaluation for winter BaP atmospheric concentrations (pg m^{-3}) (26/11/2014 to 26/01/2015) in Tarragona County, (Catalonia, Spain). Violet: observations; Red: CTM concentrations; Green: absolute error. B) Id. for summer season (01/05/2016 to 01/07/2016).

3.2. BaP levels of soil deposition

The modelled soil deposition was compared to data from BaP levels obtained in the ground plant *Piptatherum L.* collected in field sampling campaigns in the Tarragona domain (Domínguez-Morueco et al., submitted to Sci. Total Environ.). A 3-month deposition period was selected, since it is considered to be coincident with the lifetime of this biomonitor. Table 4 summarises the main statistical validation parameters considered for all 27 sampling sites (8 of them coinciding with those of the passive air samples).

Results show a good agreement between the field monitoring and the modelling approach, which has in general an overall good capacity to describe the deposition of BaP (Table 4). The spatial coefficient of correlation (R) is even higher than for atmospheric concentrations (0.83), indicating a good performance of the model to reproduce the spatial variability of the sampling sites. Simulations tend to slightly underestimate the sampled concentrations (MFB -7.9 %, BIAS -0.03 ng g^{-1}) and the standard variation (0.47 ng g^{-1} in observations and 0.43 ng g^{-1} in the model).

Table 4. Summary of the results from the comparison of air BaP deposition in soil by the chemistry transport model simulations and those estimated from the concentrations in *Piptatherum L.* collected on 25/01/2016, for all sampling points (n=27).

ALL SAMPLING POINTS	
SPATIAL CORR. COEF. (R)	0.83
MFB (%)	-7.9%
MAE (ng g^{-1})	0.12
BIAS (ng g^{-1})	-0.03
MEAN OBSERVATIONS (ng g^{-1})	0.50
MEAN CTM (ng g^{-1})	0.47
STD OBSERVATIONS (ng g^{-1})	0.47
STD CTM (ng g^{-1})	0.43

CTM – chemistry transport model; CORR. COEF. – correlation coefficient; STD – standard deviation; MFB - mean fractional bias; MAE – mean absolute error.

There are, however, some facts worth to mention regarding the behaviour for each site (Fig. 3 and Table 5). In petrochemical areas, the model is likely to produce very accurate results, with errors generally under 10 % (average MFE of 12.05 %, and ranging from 6.21 % (El Morell) to 36.61 % (Puigdelfí, P1 site). On the other hand, background and urban areas are generally underestimated by the model, exhibiting the largest errors (MFEs of 43.45 % and 45.55 %, respectively). The maximum MFE is 74.64 % in the urban sampling site of Tarragona-Vía Augusta. The mean MFE in chemical sites is 35.46 % (ranging from 15.68 % in Bonavista, C4, to 65.55 % in Les Gavarres). Petrochemical chemical and urban and rural areas have a strong influence from local emissions, which may point towards a worse representation in BaP emissions from traffic than for industrial activities in the emission inventory.

In light of these findings, the evaluation indicates that the model presents a good ability to represent BaP atmospheric levels and soil deposition in Tarragona, especially for areas related to petrochemical and chemical industries, which are often hot spots of contamination.

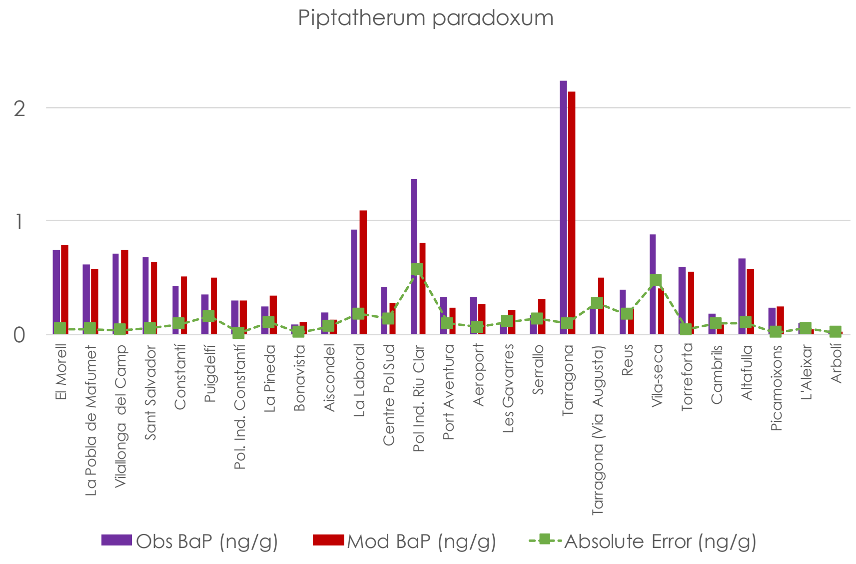

Fig. 3. Model evaluation for 3-month soil deposition of BaP (ng g^{-1}) against *Piptatherum L.* concentrations (collected on 25/01/2016). Violet: observations; Red: CTM concentrations; green: absolute error.

Table 5. Comparison of BaP deposition in soil by the CTM simulations and those estimated from the concentrations in *Piptatherum L.*, collected on 25/01/2016, for each individual station.

CODE	NAME	TYPE OF STATION	MEAN OBS (ng g^{-1})	MEAN CTM (ng g^{-1})	BIAS (ng g^{-1})	MFE (%)
1	El Morell	Petrochemical	0.74	0.79	0.05	6.21
2	La Pobla de Mafumet	Petrochemical	0.61	0.57	-0.04	7.41
3	Vilallonga del Camp	Petrochemical	0.71	0.75	0.03	4.68
4	Sant Salvador	Petrochemical	0.68	0.63	-0.05	7.99
5 (P2)	Constantí	Petrochemical	0.42	0.51	0.09	19.24
6 (P1)	Puigdelfí	Petrochemical	0.35	0.50	0.16	36.61
7	Pol. Ind. Constantí	Petrochemical	0.29	0.30	0.01	2.21
8	La Pineda	Chemical	0.24	0.34	0.10	35.23
9 (C4)	Bonavista	Chemical	0.09	0.11	0.02	15.68
10	Aiscondel	Chemical	0.19	0.13	-0.07	40.55
11 (C3)	La Laboral	Chemical	0.92	1.09	0.18	17.50
12	Centre Pol Sud	Chemical	0.41	0.28	-0.13	38.76
13	Pol Ind. Riu Clar	Chemical	1.37	0.80	-0.56	51.86
14	Port Aventura	Chemical	0.33	0.24	-0.09	32.80
15	Aeroport	Chemical	0.33	0.27	-0.06	21.25
16	Les Gavarres	Chemical	0.11	0.22	0.11	65.55
17	Serrallo	Urban	0.17	0.31	0.14	57.70
18 (U5)	Tarragona	Urban	2.23	2.14	-0.09	4.12
19	Tarragona (Via Augusta)	Urban	0.23	0.50	0.27	74.64
20	Reus	Urban	0.39	0.22	-0.17	55.71
21 (U6)	Vila-seca	Urban	0.88	0.41	-0.48	74.12
22	Torreforta	Urban	0.60	0.56	-0.04	7.04
23 (B7)	Cambrils	Background	0.18	0.09	-0.09	69.07
24 (B8)	Altafulla	Background	0.67	0.57	-0.10	16.07
25	Picamoixons	Background	0.23	0.24	0.01	5.29
26	L'Aleixar	Background	0.09	0.04	-0.05	72.47
27	Arbolí	Background	0.03	0.02	-0.01	54.78

CTM – chemistry transport model concentrations; OBS – observations; MFE - mean fractional error.

3.3. BaP climatologies and future climate scenario

3.3.1.Climatologies of atmospheric BaP concentrations

Since most of the BaP concentrations reported by the model are in the particulate phase, the response of this component to changes in future climate conditions varies as previously reported for aerosols in the Iberian Peninsula (Jiménez-Guerrero et al., 2012). As a first guess, the higher temperatures modelled by WRF+CHIMERE in the target domain (Fig. 1) favour SVOCs to remain in the gas phase. Moreover, low molecular weight PAHs are more rapidly volatilized from soils with increased temperatures, as will be discussed in section 3.3.2. On the other hand, the modelled increases in temperatures and specific humidity may also result in a faster oxidation of SVOCs, increasing the formation of condensable compounds (Liao et al., 2009). The slight increase in BaP concentrations (in the order of 0.5 pg m^{-3}, Fig. 4) may suggest that chemical production effects are outweighing volatility effects, as also stated by Dawson et al. (2009). Moreover, precipitation drives the change in the concentration of aerosols. The slight decrease in precipitation projected for the southern part of the target domain in the RCP8.5 scenario with respect to present levels (around 3%) leads to a regional increase in the levels of BaP in 2031-2050. The rise in condensable compounds is also facilitated by the decrease of precipitation, the main sink for these chemicals (Jiménez-Guerrero et al., 2012).

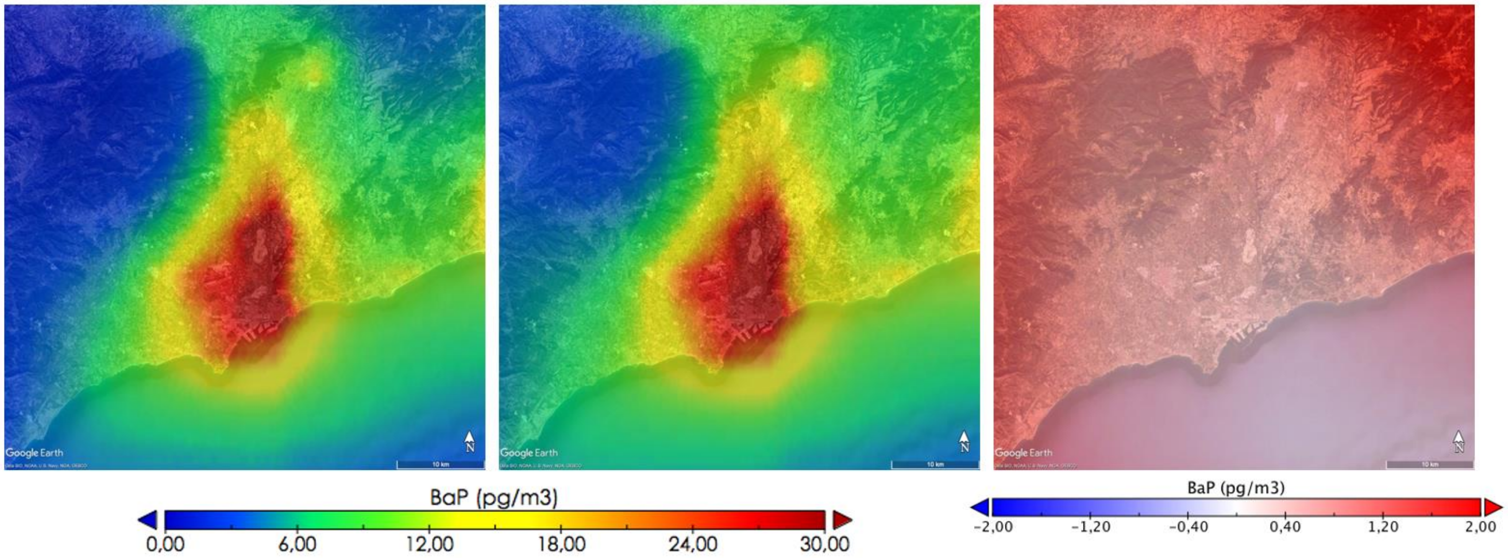

Fig. 4. BaP atmospheric concentration (pg m^{-3}) for the time periods 1996-2015 (left) and 2031-2050 (center), and differences between present and future climate conditions under the RCP8.5 scenario (right) in Tarragona County, (Catalonia, Spain).

Table 6 compares the modelled present and future BaP concentrations for each of the passive air sampling stations. It can be seen that in all cases an increase in those levels is projected, but interestingly with less extent in the urban areas. In fact, the variation is almost none, which may be an indication that the emissions of particulate matter could cancel the effect of the temperature rise and the consequent volatilisation affect. On the other hand, chemical and remote sites will suffer the strongest variations, up to 10 % in Cambrils (B7). The aforementioned decrease in precipitation could be responsible for a lower wet deposition of the particulate material, hence increasing the atmospheric loads, but also it is expected that with the rise in population, the background sites will have more urban pressure and thus more emission sources.

Table 6. Comparison of present (1996-2015) and future (2031-2050) atmospheric BaP concentrations given by the CTM simulations.

CODE/NAME/TYPE OF STATION	PRESENT (pg m^{-3})	FUTURE (pg m^{-3})	∆BaP (pg m^{-3})	∆BaP (%)
P1 / Puigdelfí / Petrochemical	26.0	27.0	0.9	3.6
P2 / Constantí / Petrochemical	19.5	20.4	0.9	4.8
C3 / La Laboral / Chemical	18.7	19.8	1.1	6.0
C4 / La Canonja / Chemical	18.2	19.9	1.7	9.1
U5 / Tarragona / Urban	22.8	22.8	0.0	0.1
U6 / Vila-Seca / Urban	15.4	15.5	0.1	0.5
B7 / Cambrils / Background	5.2	5.7	0.5	10.0
B8 / Torredembarra / Background	7.7	8.2	0.5	6.4

3.3.2. *Climatologies of BaP concentrations for soil deposition*

Climate change induces variations in some environmental factors, such as temperature, precipitation (Fig. 1) or UV-B radiation. These factors alter the fate and behaviour of a wide range of chemicals, due their influence over natural processes such as the environmental partitioning or chemical transformation (Noyes et al., 2009; EL-Saeid et al., 2015; Jia et al., 2015). In our case, future soil concentration (estimated as the average of the accumulated 3-month deposition over ground vegetation; Fig. 5) decreases up to 1.0 ng g^{-1} in the RCP8.5 scenario when 1996-2015 vs. 2031-2050 concentrations are compared. A number of studies focusing on PAHs have identified photodegradation as an important transformation pathway (Zhang et al., 2006). Our results point out that increasing the temperature and the solar radiation (as derived from the climate change projections shown in Figure 1) leads to an increase in BaP photodegradation. This agrees with a number of laboratory studies and others performed under field conditions (Marquès et al., 2016 b; 2017), indicating that low molecular weight PAHs are more rapidly volatilized from soils while medium and high molecular weight PAHs showed higher photodegradation rates.

Some PAH metabolites can be generated as photodegradation by-products, such as a variety of aldehydes, oxy-, hydroxy- and nitro-PAHs (Marquès et al., 2017) that could be even more toxic than their parental compounds (Huang et al., 1995; Mallakin et al., 1999; Ras et al., 2009). Recently, international studies have evaluated the influence of climate change over PAH photodegradation in Mediterranean soils (Marquès et al. 2016a, b; 2017) and showed that, apart from the molecular weight of each hydrocarbon, the photodegradation of PAHs in soils is highly dependent on the exposure time; the soil texture, especially in soils with a finer fraction; as well as by the presence of semiconductor minerals, such as metal oxides (Marquès et al., 2016a). This means that a reduction in the BaP soil deposition is not necessarily a reduction in the overall hazardous effects, if attributed to its metabolites.

Table 7 compares the present and future BaP levels for each sampling site. The projected decrease is clear and follows an inverse pattern as the levels in air. In fact, the decreases of BaP in the soils are higher (lower) for those sites where in the atmosphere the increase was lower (higher), namely the urban (background) sites, in this case. This trend is not surprising, since a rise in the levels in atmospheric BaP can also indicate that the deposition processes are not so effective. Emissions obviously play a very important part in this equation and it is clear that in this domain there are numerous local sources that are contributing to the BaP distribution and behaviour and that need to be continuously monitored combining field sampling strategies and modelling approaches.

Table 7. Comparison of present (1996-2015) and future (2031-2050) BaP concentration in soil given by the CTM simulations.

CODE	NAME	TYPE OF STATION	PRESENT (ng g^{-1})	FUTURE (ng g^{-1})	ΔBaP (ng g^{-1})	ΔBaP (%)
1	El Morell	Petrochemical	0.89	0.59	-0.30	-33.88
2	La Pobla de Mafumet	Petrochemical	0.75	0.53	-0.22	-29.43
3	Vilallonga del Camp	Petrochemical	0.89	0.59	-0.30	-33.88
4	Sant Salvador	Petrochemical	0.50	0.37	-0.13	-25.57
5 (P2)	Constantí	Petrochemical	1.02	0.78	-0.24	-23.53
6 (P1)	Puigdelfí	Petrochemical	1.39	1.17	-0.22	-15.51
7	Pol. Ind. Constantí	Petrochemical	0.59	0.35	-0.24	-40.30
8	La Pineda	Chemical	1.09	0.68	-0.41	-37.33
9 (C4)	Bonavista	Chemical	1.29	1.12	-0.18	-13.61
10	Aiscondel	Chemical	0.43	0.22	-0.22	-49.99
11 (C3)	La Laboral	Chemical	1.91	1.42	-0.49	-25.68
12	Centre Pol Sud	Chemical	0.77	0.50	-0.27	-34.63
13	Pol Ind. Riu Clar	Chemical	1.02	0.78	-0.24	-23.53
14	Port Aventura	Chemical	0.54	0.26	-0.28	-51.29
15	Aeroport	Chemical	0.58	0.32	-0.25	-43.88
16	Les Gavarres	Chemical	1.29	1.12	-0.18	-13.61
17	Serrallo	Urban	2.06	1.89	-0.17	-8.19
18 (U5)	Tarragona	Urban	2.06	1.91	-0.15	-7.10
19	Tarragona (Via Augusta)	Urban	0.97	0.68	-0.29	-30.27
20	Reus	Urban	0.39	0.17	-0.22	-55.52
21 (U6)	Vila-seca	Urban	0.43	0.22	-0.22	-49.99
22	Torreforta	Urban	1.29	1.12	-0.18	-13.61
23 (B7)	Cambrils	Background	0.19	0.04	-0.15	-80.70
24 (B8)	Altafulla	Background	0.32	0.08	-0.23	-74.21
25	Picamoixons	Background	0.39	0.10	-0.29	-74.66
26	L'Aleixar	Background	0.08	0.01	-0.08	-93.12
27	Arbolí	Background	0.04	0.00	-0.04	-97.88

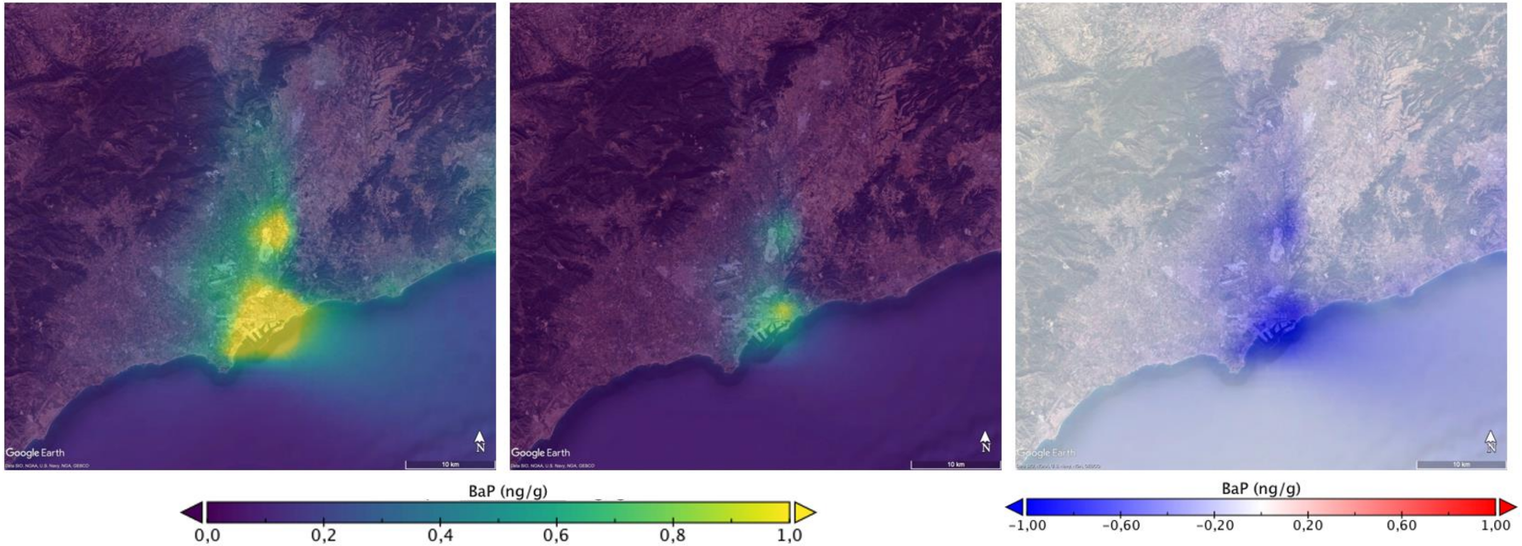

Fig. 5. BaP mean concentration in soils (ng/g) for 1996-2015 (left), 2031-2050 (center) and differences between present and future climate conditions under the RCP8.5 scenario (right) in Tarragona County, (Catalonia, Spain).

3.4. Assessment of increased health risks associated to atmospheric BaP

The benefits of the use of CTMs to describe the presence and behaviour of priority pollutants can be remarkable, even at the level of human health issues. Thus, it is also the intention of this study to provide an example of how these tools can help in the assessment (and correction) of potentially hazardous effects on humans related to atmospheric presence of BaP.

When the European Union was trying to set the target values for arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air in the Directive 2004/107/EC, a Quantitative Risk Assessment (QRA) method was based on different studies, such as Andersen et al. (1982), Lindstedt et al. (1982) or RIVM (1989) and laid out in the "Ambient air pollution by Polycyclic Aromatic Hydrocarbons (PAH)" Position Paper (European Union, 2001). These studies focused on the increased risk of lung cancer due to the industrial exposure to PAHs. Using this method and the World Health Organisation unit risk of lung cancer estimate (87 x 10^{-6} BaP m^{-3} for lifetime exposure) for PAH compounds (World Health Organisation, 2000), the European Union calculated the increased risk for three possible target values: (1) target value of 0.01 ng m^{-3} with an associated increased risk of 1 x 10^{-6}; (2) target value of 0.1 ng m^{-3} (increased life-time risk of 1 x 10^{-5}); and (3) target value of 1 ng m^{-3} with an associated increased risk of 1 x 10^{-4}.

Based on the health evidence and acceptance that the upper limit of the additional life-time risk should be less than 1 x 10^{-4}, the European Union decided on a target value for the annual mean concentration of BaP to be 1 ng m^{-3} (Butterfield and Brown, 2012), which is the one set in the Directive 2004/107/EC (European Commission, 2009).

As seen in Figure 6, and despite being a potential hot spot for atmospheric contamination, our domain stays far from the target values of 1 ng m^{-3} and even of 0.1 ng m^{-3} in both present and future simulations. In fact, while some areas downwind from the petrochemical complex of

Tarragona exceed the target value of 0.01 ng m^{-3} (10 pg m^{-3}, with an associated increased life-time risk of 1 x 10^{-6} for lung cancer), the rest of the Tarragona domain stays below it. Furthermore, the changes under RCP8.5 are not noticeable, with only an extension of the area exceeding the 0.01 ng m^{-3} target value, and an increase in the most populated areas of 5 x 10^{-8} in the life-time risk of lung cancer. This is a direct consequence of the aforementioned low changes modelled for the BaP air levels in the Tarragona domain.

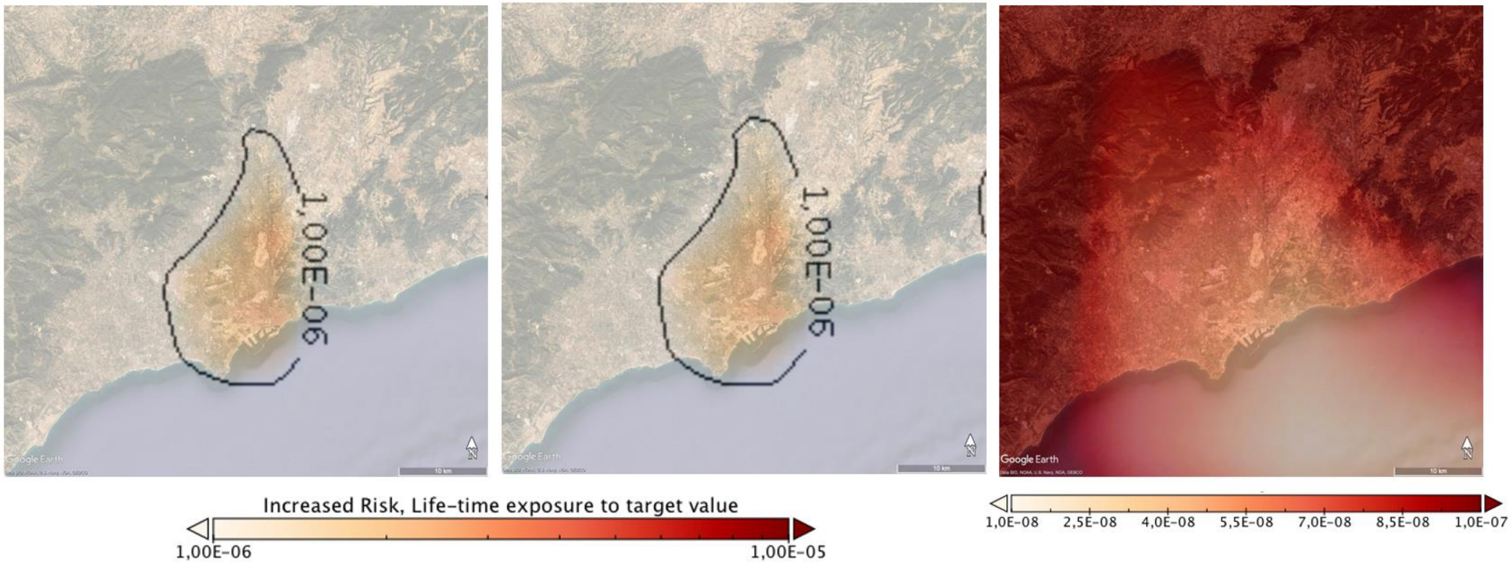

Fig. 6. Associated increased risk of lung cancer for (left) life-time exposure to the target value (contours) for the time frame 1996-2015, and (center) for the 2031-2050 climate change projection in Tarragona County, (Catalonia, Spain), as defined by the Quantitative Risk Assessment included in Butterfield and Brown (2012). (Right) Differences in the increased risk of lung cancer between present and future climate change RCP8.5 scenario.

4. CONCLUSIONS

This work intended to highlight the current presence of BaP in such a complex terrain as the Tarragona petrochemical area and how future climate change can influence its atmospheric levels for the middle 21st century. For that, a regional climate modelling system (coupling WRF and CHIMERE chemistry transport model) was validated using field-based data from passive air sampling and ground vegetation to represent soil deposition and after that, apply it to two time slices covering a present-climate condition (1995-2016) and the future RCP8.5 scenario (2031-2050) in order to obtain regional distributions of atmospheric and soil BaP levels.

Results show a good performance of the CTM to represent air and soil concentrations of BaP over the target domain (considering petrochemical, chemical, urban and background sites) with better results in the winter. It is also acceptable the plausible influence of climate change alone on the levels of gas-phase pollutants and aerosols. The findings of this study indicate that the enhanced oxidative capacity of the atmosphere together with the decrease in precipitation projected for the RCP8.5 scenario causes gas-phase emissions to turn into the particulate phase, thus slightly increasing atmospheric BaP in future climate change scenarios. On the other hand, photodegradation has a role in the variation (decrease) of future soil deposition and concentration. This photodegradation process can be very important in a region with high sunlight presence during the whole year, such as the Mediterranean basin, also pointed out as a vulnerable zone for the climate change (Marquès et al., 2016b). Nevertheless, the EU limit for BaP presence in the atmosphere of 1 ng m^{-3} will not be reached according to the projections, there will be an increase in the life-time risk of lung cancer, particularly in the most populated areas.

An important remark has to be done regarding the inherent uncertainties in the climate projections which may affect the results depicted here. Not all climatic variables are affected by the same degree of uncertainty. Future climate simulations tend to agree in a warm trend due to the increase of greenhouse gases concentrations, only differing in the intensity and spatial distribution details. However, there is not such a good agreement in the projections of precipitation changes, which strongly affect the results for BaP. This larger uncertainty is partly due to the complex mechanism that governs precipitation, which involves a wide variety of spatial scales and it is approximated by different approaches among the state-of-the-art models.

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DISCUSSION CHAPTER 3

Throughout this thesis has been corroborated the importance of field sampling as key tool to determine the environmental occurrence of pollutants. However, these kinds of tools can not provide relative information about their spatial, temporal and chemical transport patterns or final fate in the environment. For this reason, to combine the monitoring and modelling approaches plays complementary roles, since monitoring is critical for models implementation, and modelling can help to predict the contaminants behavior in the environment, as well as identify the priority areas for the sampling campaigns.

PAHs were the most predominant compounds found in all the sampling campaigns conducted through Tarragona County, for this reason, those were the compounds prioritized in the final part of this thesis.

In order to predict the emissions, fate and transport of PAHs in the study area, a multimedia environmental model was selected, since this kinds of models are one of the most used for SVOCs modelling. The multimedia environmental models are characterized by the division of the environment in different boxes or bulk media compartments (e.g. air, soil, water and sediments or vegetation) connected between them. These compartments are governed by mass balance equations based in different levels of fugacity, and the pollutants dynamics depends on its physical-chemical properties and reactivity data (reaction processes). Due to the sampling campaigns show a clear industrial and urban contamination in the study area, the Multimedia Urban Model (MUM-Fate) developed by Diamond et al. (2001) was used for Tarragona County, where the largest chemical/petrochemical industrial complex of Southern Europe is located. MUM-Fate is a Level III steady-state fugacity model of Mackay (1991), characterized by dividing the total study area into 7 different boxes or bulk media compartments (lower and upper air, surface water, sediment, soil, vegetation, and organic film), including the organic film that coats impervious surfaces, a key feature present in urban and industrialized environments. Due to MUM-Fate is a level III fugacity model the conditions are constant with time but compartments are not at equilibrium, and different fugacities apply to each medium. The model was parameterized according to actual environmental conditions in Tarragona County, and six PAHs were selected in order to represent the different rings number and molecular weight congeners (naphthalene, anthracene, phenanthrene, fluoranthene, pyrene, and benzo(*a*)pyrene).

Nowadays, one of the main problems related with the environmental pollution is quantify the emissions, since most of the main sources are diffuse. Nevertheless, mass balance models as MUM-Fate allowed estimate the total emissions in the study area through back-calculations based in measured real air concentrations of PAHs. Thus, PAHs total air emissions for Tarragona County were 42 t/y, comparable with values reported by Jiang et al. (2013) in different districts of Taiyuan, China. Regarding individual compounds, phenanthrene presented the greatest emissions value (16 t/y). This was expected pattern since phenanthrene was the predominant compound in all air sampling campaigns. Once the emissions were estimated, soils concentrations were simulated, and those compared with the real PAHs concentrations detected in this matrix in the previous multi-compartmental environment monitoring program conducted in Tarragona County since 2002. With the exception of naphthalene, PAH concentrations in soil estimated by the MUM-Fate model, were within the range reported in previous works (Nadal et al., 2004a, 2009, 2011). Based on the correspondence between measured and modelled soil concentrations (R^2 ranging from 0.56 to 0.92), the current model was deemed to provide a reasonable representation of PAH dynamics in Tarragona County.

On the other hand, MUM-Fate was run for illustrative purposes with an emission of 1 mol/h to air for each PAH; that is in order to predict the fate and transport of PAHs in the environment. The model estimated that 50–70 % of the PAHs emitted to air were lost in the boxes system by downwind advection. The same PAH concentration pattern (benzo(*a*)pyrene > fluoranthene > pyrene > phenanthrene > anthracene > naphthalene) was found in all the compartments, with concentrations increasing according to molecular weight. Among the different compartments, organic film achieved the highest concentrations of PAHs, being followed by sediments and soils. This could by associated with the hydrophobic character of PAHs, who, as SVOCs, tend to prefer organic matrices. However, the high losses by wash off and degradation in the film compartment, resulted in a persistence in these compartment of < 1 day. In this sense, the wash-off from the film delivered particle-sorbed PAHs to the river running through Tarragona County. This process, along with degradation losses, resulted in < 2 % of total air inputs being exported downriver. On the other hand, soils and sediments were the greatest sinks for PAHs, as consequence of their high inputs from air, water and vegetation, relative to low losses. Persistence in soils and sediments was estimated to range 100–1000 days, being the biodegradation the greatest loss mechanism in both matrices. In this sense MUM-Fate model provided a preliminary approximation of the PAHs distribution in the bulk media compartments defined for Tarragona County, by using simple approaches and calculations.

Although the simplicity of mass balance models allows an extensive use of models among the scientific community, they do not reflect the complexity to characterize adequately all processes involving these chemicals in the environment. The science community has pointed out that meteorological factors such as radiation, turbulence mixing, clouds presence, etc., coupled to chemical process are key elements when the spatial, temporal and chemical transport patterns of pollutants are evaluated. For this reason, in this thesis it was decided to use a higher complexity level model as chemistry transport models (CTMs). CTMs can complement the field data also considering the meteorology of the study area, the atmospheric chemistry processes and climate change, contributing to diminish the gaps still existing regarding SVOCs environmental behaviour.

The setup used in this study was the Weather Research and Forecasting (WRF) coupled with CHIMERE model. WRF is a numerical weather prediction (NWP) and atmospheric simulation system designed for the understanding and prediction of mesoscale weather (Skamarock et al., 2008), whereas CHIMERE is an Eulerian off-line CTM that includes parameterisations to simulate the pollutant concentrations in the environment (Menut et al., 2013). Due the high complexity level of this model, and for hence, high computational time, only one SVOC was modelled for Tarragona County. Among these, benzo(*a*)pyrene (BaP) was the compound selected, since its belongs to majority group of compounds presents in Tarragona County; is already classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC); and is the only PAH with a legislated average limit in the atmosphere: 1 ng m^{-3} of BaP over 1 year (European Commission, 2009).

WRF+CHIMERE is a model characterized by simulating the BaP concentrations in air; its deposition over other matrices such as soils, as well as estimate its geographical distribution over long-time temporal series. In this thesis, it was decided to use the methodology developed by Ratola and Jiménez-Guerrero (2016) for WRF+CHIMERE, since it reflects well the BaP dynamics taking into account environmental field samplings. Regarding to study domain, WRF+CHIMERE usually works with large domains (50 km), however, in this thesis a higher resolution was it was selected with the aim to equate the modeled area to field sampling campaigns. For this reason a domain for Catalonia (Spain) with a 2 km of resolution was defined and coupled to BaP emissions given by the European Monitoring and Evaluation Programme.

Once the methodology and the study domain were defined, it was decided to use the real concentrations of BaP in air in order to check the ability of the model to reproduce BaP climatologies over Tarragona County. In this case, the control simulations run covering a period coincident with the passive air sampling campaigns (PUF-PAS and 2 months sampling); that is, BaP concentrations in air recorded in winter season (26/11/2014 to 26/01/2015) (data provided in short communication 2 of chapter 1 of this thesis) and a the most recently BaP air concentrations from summer season (01/05/2016 to 01/07/2016) (data provided in the article 2, chapter 3 of this thesis). After run the control simulations, it can be seen that the model tends to perform an accurate representation of BaP spatial patterns over the target area, working a high resolution (2 km) and presenting the most accurate results over the chemical/petrochemical sites (table 2 and 3, article 2 chapter 3 of this thesis). In addition, WRF+CHIMERE showed a general decreasing trend from petrochemical/chemical areas to urban and to background areas, a pattern also observed in the field campaigns (Fig. 2 article 2 chapter 3 of this thesis). Likewise, CTM model verified the typical seasonal trend observed for PAHs in the atmosphere (article 1, chapter 1 of this thesis), where higher atmospheric loads of BaP were found in winter instead summer season.

As mentioned above, WRF+CHIMERE is a model that can also estimate the BaP deposition from air to soil. Nevertheless, the BaP soil deposition modelled by WRF+CHIMERE corresponds to the time period consider in the control simulations run for air (2 months). This fact, coupled with the long-term sink character of this matrix, made that BaP soil deposition was better assessed against the BaP concentrations found in vegetation samples (presented in chapter 2 article 2 of this thesis). This is because *Piptatherum L*. is a fast-growing grass, between 2 to 4 months, beginning its growth with the first rains and when temperatures began to drop, and drying up during the warm seasons (Sulas et al., 2015). Moreover, being a ground plant with low height, the concentration accumulated during this time can be a good representation of the deposition onto the soil. Modelled BaP deposition results show a good agreement between the field monitoring and the modelling approach, with very accurate results also in petrochemical areas.

This first evaluation of BaP dynamics modelled by WRF+CHIMERE indicates that the model presents a good ability to represent BaP atmospheric levels and soil deposition in Tarragona, especially for areas related to petrochemical and chemical industries, which are often hot spots of contamination.

International studies suggest that the toxicity and environmental response of PAHs can be affected by the variations in the temperature and solar radiation associated with the climatic change (Marquès et al., 2016). For this reason, and once the CTM was validated for the present climatology, two time slices covering a present-climate condition (1995-2016) and the future RCP8.5 scenario (2031-2050) were selected in order to obtain regional variation of the BaP concentration in air and soils.

Regarding the variations of BaP in air, an increase of concentration is projected for the future scenarios (in the order of 0.5 pg m^{-3}, Fig. 4. Article 2 chapter 3 of this thesis), particularly in chemical and remote sites where the variation can go up to 10%. This fact would be associated with the higher temperatures modelled by WRF+CHIMERE in the target domain (Fig. 1, article 2 chapter 3 of this thesis) that favour SVOCs to remain in the gas phase; promotes its soil volatilization and also result in a faster SVOCs oxidation, increasing the formation of condensable compounds. In addition, the decrease in precipitation (Fig. 1 article 2 chapter 3 of this thesis) could be responsible for a lower wet deposition of the particulate material, hence increasing the atmospheric loads, but also it is expected that with the rise in population, the background sites will have more urban pressure and thus more emission sources.

In terms of soil deposition the findings were the opposite, with an evident decrease in future soil BaP concentrations (particularly in background sites) when 1996-2015 vs. 2031-2050 concentrations are compared (a decreases up to 1.0 ng g^{-1} in the RCP8.5 scenario).

A number of studies focusing on PAHs have identified photodegradation as an important transformation pathway (Zhang et al., 2006). Our results point out that increasing the temperature and the solar radiation (as derived from the climate change projections shown in Fig. 1 article 2, chapter 3 of this thesis) leads to an increase in BaP photodegradation, among other processes. This agrees with a number of laboratory studies and others performed under field conditions (Marquès et al., 2016 b; 2017), indicating that low molecular weight PAHs are more rapidly volatilized from soils while medium and high molecular weight PAHs showed higher photodegradation rates.

Some PAH metabolites can be generated as photodegradation by-products, such as a variety of aldehydes, oxy-, hydroxy- and nitro-PAHs (Marquès et al., 2017) that could be even more toxic than their parental compounds (Huang et al., 1995; Mallakin et al., 1999; Ras et al., 2009). This means that a reduction in the BaP soil deposition is not necessarily a reduction in the overall hazardous effects, if attributed to its metabolites. For this reason, when a quantitative risk assessment (QRA) method was conducted as a final part of this thesis, it was observed that the EU limit for BaP presence in the atmosphere of 1 ng m^{-3} will not be reached according to the projections, but there will be an increase of 5 x 10^{-8} in the life-time risk of lung cancer, particularly in the most populated area.

An important remark has to be done regarding the inherent uncertainties in the climate projections which may affect the results depicted here. Not all climatic variables are affected by the same degree of uncertainty. Future climate simulations tend to agree in a warm trend due to the increase of greenhouse gases concentrations. However, there is not such a good agreement in the projections of precipitation changes, which strongly affect the results for BaP.

CONCLUSIONS

In the present thesis, the levels of PAHs and other SVOCs in environmental samples of Tarragona County (Spain), a high industrialized area, have been determined. Different passive sampling techniques and environmental prediction models, have been complementarily used. According to the results, it has been concluded that:

1. The use of PUF-PAS is fully viable at local level. In addition, these devices are capable of capturing, through advection and diffusion mechanisms, different groups or families of SVOCs, such as PAHs, PCBs, BFRs, SMs and HCB, even at very low air concentrations (ng/m^3).

2. Regarding methods optimization, QuEChERS methodology was a valid technique to make a screening of the compounds presents in a sample, either soil or vegetation, since it allowed the simultaneous extraction of different compounds in both environmental matrices (LODs range 0.7-225 pg/g). The QuEChERS technique also provided a considerable reduction in the amount of solvent and operating time, without compromising the performance of the method given by the validation parameters.

3. Good correlations have been found between the PUF-PAS and lichens transplants when analyzing the environmental burden of PAHs, confirming the suitability of lichens as passive samplers

4. When the three passive sampling techniques, PUF-PAS, vegetation and soils are evaluated together some differences arise. PUF-PAS tend to capture the most volatile SVOCs, mainly associated with the gas phase. Vegetation traps the PAHs contents in the gas phase, but it also retains some of those sorbed to the particulate phase. Finally, soils capture the heaviest and more degradation resistant molecules that could be associated with particulate phase. Concerning the monitoring time, the results

obtained from PUF-PAS and ruderal vegetation (*Piptatherum L.*) versus soil showed that these matrices are able to provide information regarding the levels and sources of SVOCs at short- (2-3 months) and long-term, respectively.

5. The environmental levels of SVOCs at Tarragona County are in agreement with other international studies. The values of PAHs and PCBs found in soil and vegetation samples are consistent with those reported a previous multi-compartmental environment monitoring program conducted in the same area of study since 2002.

6. PAHs and PCBs showed a similar concentration pattern, being higher in industrialized and urban zones with respect to those found in background areas. In turn, background areas showed the highest levels of SMs, suggesting an influence of the personal care products derived from beach-related tourism in the coast. In the case of BFRs and HCB, similar values were found in both matrices and in all areas.

7. A decreasing temporal profile of PAHs concentrations was observed, in agreement with the reduction of PAHs emissions observed between 1990 and 2010 in most European countries. In addition, PUF-PAS showed a strong seasonal variation, with higher values in winter than in summer.

8. The mass balance MUM-Fate model provided a preliminary approximation of the PAHs distribution in the bulk media compartments defined for Tarragona County, by using simple approaches and calculations. In addition, MUM-Fate model estimated the emissions of PAHs in the studied area by backcalculations.

9. MUM-Fate pointed out the organic film as the compartment with the highest concentrations of PAHs. However, and due the high losses in this compartment, the model positioned the soils and sediments as the greatest PAHs sinks in Tarragona County.

10. The WRF+CHIMERE model characterized the BaP concentrations in air and its deposition over soils for the present climatology, performing an accurate representation of BaP spatial patterns over the target area working a high resolution (2 km) and presenting the most accurate results over the chemical/petrochemical sites, which are often hot spots of contamination.

11. An increase of BaP air concentration was estimated in future climate change scenarios, particularly in chemical and remote sites, with variations of up to 10%. This fact would be associated with the high temperatures modelled by WRF+CHIMERE in the target domain. According to the model, SVOCs remain in the gas phase, soil volatilization is promoted, and SVOCs are quickly oxidized, increasing the formation of condensable compounds. In addition, the rainfall decrease could be responsible of the lower wet deposition of particulate matter, which increases the atmospheric loads.

12. Contrasting to air, an evident decrease of BaP concentrations in soils was estimated in the future. The increasing of temperature and solar radiation enhance a number of degradation processes, such as photodegradation.

13. When the quantitative risk assessment (QRA) was conducted, it was observed that the EU limit for BaP presence in the atmosphere of 1 ng m^{-3} will not be reached according to the projections, there will be a little increase of $5x10^{-8}$ in the life-time risk of lung cancer, particularly in the most populated area.

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ANNEX

ANNEX 1 – Short Communication: Assessment of PAH loss in passive air samplers by the effect of temperature.

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ABSTRACT

Passive air samplers (PAS) have become recurrent methods for environmental monitoring. However, the influence of environmental variables, such as temperature, over these devices has not been fully investigated. Since climate change is likely to induce major environmental changes, the role of the temperature needs to be studied to assure the suitability of PAS for the long-term monitoring of semivolatile organic compounds (SVOCs) and their utility to compare data from different locations. This study aimed at evaluating the potential loss of polycyclic aromatic hydrocarbons (PAHs) in PAS containing disks of polyurethane foam (PUF) at different temperatures. The gradient of temperature inside and outside the PAS was firstly determined, being noted an internal/external difference of up to 5 ºC. Secondly, a lab-controlled experiment was performed by daily analyzing PAHs in PUF-based PAS exposed to 25 ºC and 38 ºC, for a period of 7 days. A significant loss of PAHs in PUFs was not observed for any of both scenarios, remaining constant through time. Moreover, PAH levels were not significantly different according to the temperature. These findings indicate that the environmental temperature does not affect the stability of PAHs in PAS. Once PAHs have been uptaken, they are not easily volatilized from these devices. Consequently, PAS are good environmental monitors independently on the ambient conditions of temperature, being suitable for the comparability of data, either temporally or spatially, on the airborne concentrations of PAHs.

Keywords: Polycyclic aromatic hydrocarbons (PAHs) · Passive air sampling · Polyurethane foam (PUF) · Environmental temperature

1. INTRODUCTION

Passive air samplers (PAS) have become a viable alternative to traditional active air samplers (AAS) for the monitoring of semivolatile organic compounds (SVOCs). PAS are cheaper, smaller, and simpler-to-handle devices than AAS, while they do not require electricity and maintenance (Mari et al., 2008; Vilavert et al., 2013). These characteristics make them very suitable for the surveillance in remote areas of the planet, as well as for the simultaneous collection of samples at different locations and/or scales (Bohlin et al., 2008; Zabiegala et al., 2010; Estellano et al., 2012; Pozo et al., 2012; Vilavert et al., 2014).

PAS are based on the theory of physical advection and diffusion to capture organic compounds through a passive air flow (Wang et al., 2012; Bogdal et al., 2013). Different PAS designs have been developed based on the adsorbent material, being polyurethane foam (PUF) one of the most widely used for air monitoring (Bohlin et al., 2008; Chaemfa et al., 2008). The standard design of PAS is based on a double-dome chamber in which a PUF-disk is deployed in order to protect the adsorbent material from rainfall and direct light (Chaemfa et al., 2008; Seethapathy et al., 2008; Choi et al., 2012). However, the influence of environmental variables, such as wind speed and temperature, may significantly affect the accumulation capacity of these devices (Klánová et al., 2008; Seethapathy et al., 2008; Kennedy, 2010).

Temperature plays an important role on the sampling rate of SOVCs by PAS (Kennedy, 2010; Armstrong et al., 2014; Melymuk et al., 2014). High temperatures may cause an increase of molecular diffusivity, resulting in an increased sampling rate of the compounds. Furthermore, high temperatures can affect the PAS sorption capacity, shortening the linear uptake phase (Klánová et al., 2008; Seethapathy et al., 2008; Melymuk et al., 2014). These processes lead to a higher variability of PAS sampling rates when comparing different areas or seasons. Although not statistically significant, slight trends of increased sampling rates with increased temperature and relative humidity were reported when measuring airborne organophosphorus pesticides by means of PAS in the US (Armstrong et al., 2014). Temperature also controls the gas-particle partitioning of SVOCs (Klánová et al., 2008; Kennedy, 2010; Chen et al., 2011; Melymuk et al., 2014). Since the environmental temperature is also closely linked to the volatilization of organic compounds and their affinity for the gas phase (Melymuk et al., 2014), potential temperature variations may also critically affect pollutant concentrations in air. The design of the PAS is also a fundamental aspect. The double-dome recovering the PUF is generally made of stainless steel. It may generate a potentially important gradient of the temperature inside/outside the device, caused by the effect of the solar radiation over the metallic housing (Kennedy, 2010). Finally, the internal recirculation of organic compounds close to the PUF may also have a role on the uptake of chemical pollutants (Thomas et al., 2006).

Although temperature may have a critical effect on the sampling rate and the accumulation capacity of SVOCs, their potential loss by volatilization in PUF-based PAS has not been studied yet. The current short-term investigation aimed at evaluating the role of temperature over the loss of polycyclic aromatic hydrocarbons (PAHs), chosen as SVOC representatives, after they were adsorbed in PAS. A field study was firstly conducted to establish temperature differences between inside and outside the device. Subsequently, a lab controlled study in a climate chamber was carried out to analyze the progressive loss of PAHs from PAS exposed to different temperatures.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and reagents

PAS containing PUF disks (diameter: 14 cm; thickness: 1.2 cm; surface area: 360 cm2; density: 0.035 g cm^{-3}) were purchased from Newterra (Beamsville, ON, Canada). Prior to use, PUFs were precleaned with dichloromethane (DCM). Certified PAH standard mixtures, supplied by

Supelco (Bellefonte, PA, USA), were used to evaluate the loss of PAHs. The mixture contained 13 PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenzo(*a,h*)anthracene, benzo(*g,h,i*)perylene and indeno(*1,2,3-c,d*)pyrene) at a concentration of 2000 mg/mL in benzene:DCM (1:1 (v:v)). Individual standards of d_8-naphthalene, d_{10}-fluorene, and d_{12}-benzo(*a*)pyrene were purchased from Supelco (Bellefonte, PA, USA). DCM (purity 99.5%, Scharlab, S.L., Sentmenat, Barcelona, Spain) and hexane (purity 99.5%, Scharlab, S.L.) were used as solvents. Nitrogen for drying, with 99.995% of purity, was obtained from Air Liquid Group (Barcelona, Spain).

2.2. External/internal PAS temperature

The potential temperature gradient inside and outside of PAS was measured in the field. A passive sampler was deployed on the roof of the Campus Sescelades at the “Rovira i Virgili” University (Tarragona, Catalonia, Spain), from June to August 2014. The temperature inside and outside the sampler was monitored by means of a thermometer model Ebro EBI300 (Ebro Electronics, Ingolstadt, Germany). During the sampling period, temperature measurements were recorded every 5 min.

2.3. PAS exposure in a climate chamber

A climate chamber was used to evaluate the influence of the temperature over the PAH loss in the PAS. Two exposure scenarios (base, at 25 ºC; and extreme, at 38 ºC) were considered, according to the respective mean and maximum temperatures recorded inside the PAS. All the experiments were performed in darkness and at 65% relative humidity. PAHs were determined after 1 h, as well as daily for one week (1, 2, 3, 4, 5, 6 and 7 days after starting). For each exposure time, four PAS with pre-cleaned PUFs were spiked with 50 mL of a TCL PAHs mixture (100 mg/mL in DCM:hexane (1:1)). Subsequently, the four PUF-PAS were deployed inside the climate chamber, and used as replicates. Once they were retrieved from the chamber, PUFs were stored in DCM-cleaned brown glass jars and frozen at -20 ºC for subsequent analysis.

2.4. PAHs determination

Microwave-assisted extractions were performed with a microwave laboratory system for organic extraction (starT-Basic SK-12, 1200W) (Milestone S.r.l. Sorisole, BG, Italy). A microwave oven was used following an optimized 40 min program that elevates the temperature to 115 ºC at a power of 700 W (Method 3546, EPA). Before the extraction, 50 mL of d_{10}-fluorene (100 mg/mL in DCM:hexane (1:1)) were spiked to estimate the process recoveries. Afterwards, PUFs were cut into small pieces and placed in each microwave vessel along with 30 mL of DCM:hexane (1:1). Once the extraction was complete, foams were removed and samples were concentrated in a rotary evaporator to a volume of 1 mL. Subsequently, they were dried under a gentle flow of nitrogen in 1.5-mL amber glass vials. Once the solvent was evaporated, extracts were resuspended in 100 mL of a solution containing d8-naphthalene and d_{12}-benzo(*a*)pyrene (50 mg/mL in DCM:hexane (1:1 (v:v))).

The analysis was performed using a gas chromatograph (Hewlette Packard G1099A) coupled with a mass spectrometer (Agilent MSD5973). A HP-5MS 5% phenyl methyl siloxane capillary column (30 m, 0.25 mm i.d., 0.25 mm film thickness) (Agilent 19091S-433) was used for separating the PAHs. Samples (1 mL) were injected in splitless mode. For recovery percentages, four pre-cleaned PUFs were spiked with 50 mL of a PAH standard mixture (100 mg/mL in DCM:hexane (1:1)). Subsequently, these unexposed samples were extracted following the aforementioned procedure. Recovery percentages differed according to individual PAHs, ranging from 65% to 95%. Because of peak overlapping, benzo(*b*)fluoranthene and benzo(*k*)fluoranthene were quantified together.

2.5. Data treatment

Data analyses were performed by using the SPSS 19.0 statistical software package. The Levene test was applied to analyze the equality of variances. ANOVA was executed and a probability lower than 0.05 ($p < 0.05$) was considered as statistically significant. The comparison of means was performed using the Tukey's test.

3. RESULTS AND DISCUSSION

3.1. External/internal PAS temperature

The results from the monitoring of the potential differences of temperature inside and outside PUF-PAS, conducted for a period of 2 months (Summer 2014), are depicted in Fig. 1. Outside the PAS, minimum and maximum temperatures were 12.4 ºC and 33.2 ºC, respectively. In turn, the temperatures inside the device ranged from 13.1 ºC to 38.2 ºC (mean: 25 ºC). A temperature gradient ranging from 3 ºC to 5 ºC (when comparing internal and external data) was found for the first month of sampling, while in the second month, temperature was approximately 3–3.5 ºC inside the PAS. Globally, the temperature inside and outside the device was 3–4 ºC, supporting the hypothesis that the design and material of the PAS may lead to a substantial difference in the temperature inside and outside the device, as a consequence of the direct solar radiation over the metallic housing (Kennedy, 2010).

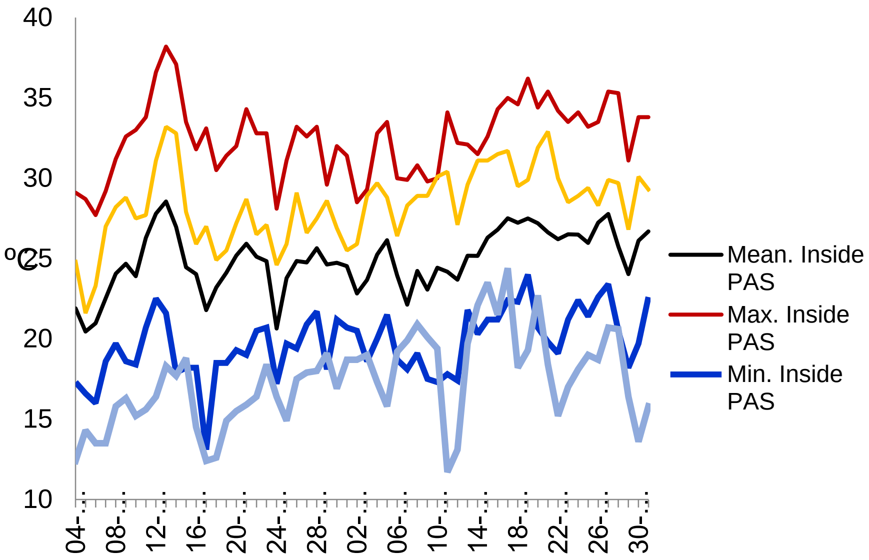

Fig. 1. Range of temperatures inside and outside the PAS for 2 months.

3.2. External/internal PAS temperature

The loss of PAHs inside the PUF-based PAS was evaluated for a period of 7 days, at 2 temperatures: 25 ºC and 38 ºC as base and extreme scenarios, respectively. The concentration loss in the base scenario (25 ºC), given in percentage, of the 13 individual PAHs in PUFs, between 1 h and 7 days after starting, is shown in Fig. 2A. Under the base scenario, PAH concentrations did not significantly change throughout the experiment ($p > 0.05$), remaining nearly constant with time. PAH levels are detailed in Table 1. Fluorene and anthracene were the only compounds showing significant differences for some of the exposure times (between 4th and 7th day for fluorene, and between 1st hour and 4th day for anthracene). It is well established that the environmental behavior of SVOCs is controlled by their psychochemical properties, playing n-octanol/air partition coefficient (K_{oa}) a key role as a key descriptor of chemical partitioning between the atmosphere and other environmental organic phases (Odabasi et al., 2006). Among the PAHs under study, fluorene and anthracene own relatively low K_{oa} values. This fact, together with their high vapor pressure, could be the reason of the higher variability in the concentrations of these 2 particular hydrocarbons.

The PAH concentrations in PUFs exposed for 1 week to an extreme temperature of 38 ºC are depicted in Fig. 2B. Similarly to the base scenario, no significant changes of the PAH levels were noted through time ($p > 0.05$). Fluorene levels were significantly lower at day-5, while those of phenanthrene were significantly reduced at day-6. Despite the similarities with the base scenario, a higher variability of the PAH concentrations was detected at 38 ºC (Table 1). It means that an increase of the temperature might lead to a greater fluctuation of PAHs in the PUF-PAS. This is related to the fact that higher temperatures make easier the volatilization of compounds, thus showing a higher affinity for the gas phase (Melymuk et al., 2014). Notwithstanding, the finding that PAH concentrations did not vary significantly proves that these devices are stable enough for air sampling irrespectively of the environmental temperature. Unlike the base scenario, some of the heaviest hydrocarbons, which are also the most hazardous (Sarigiannis et al., 2015), such as benzo(*g,h,i*)perylene, dibenzo(*a,h*)anthracene and indeno(*1,2,3-c,d*)pyrene, also showed significant differences of their concentrations 6 days after initiating the experiment.

The differences of the PAH concentrations between the two working scenarios were also evaluated. For any of the 13 PAHs, no significant differences ($p < 0.05$) were found between the extreme (38 ºC) and the base (25 ºC) scenarios, differing from the expected results. Because volatilization is directly proportional to temperature (Melymuk et al., 2014), higher temperature should lead to lower adsorption of PAHs in the foam. However, the fact that PAHs were spiked in a stock solution might have an essential influence on the final results, as the affinity of the individual compounds for the solvent would be greater, leading to a higher retention of PAHs in the PUF.

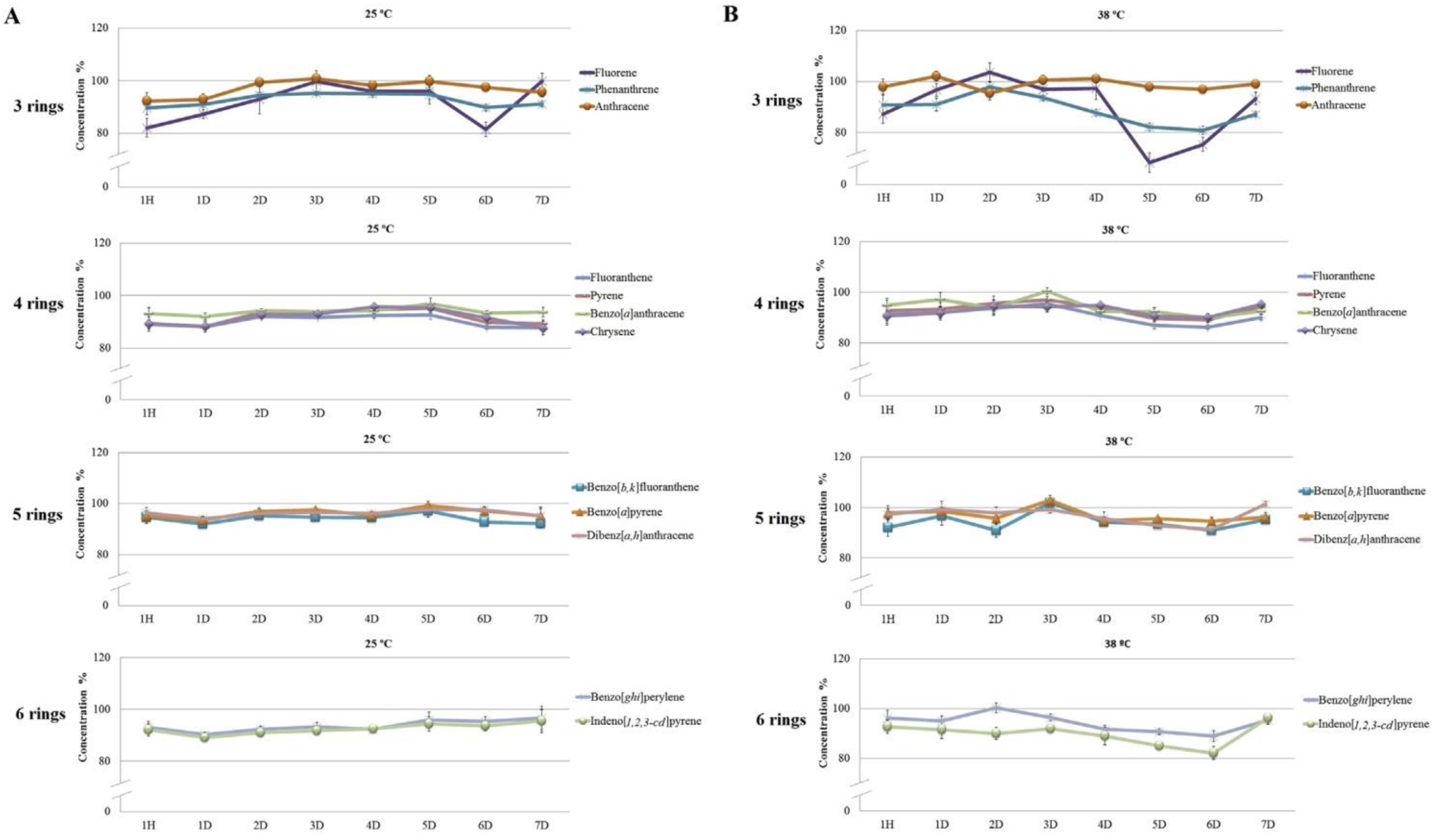

Fig. 2. Loss of PAHs (in percentage) for different molecular weight PAHs and exposure scenarios: A) 25 ºC, and B) 38ºC.

Table 1. Individual PAH concentrations (in mg/sample) in PAS exposed to 2 temperatures (25 ºC and 38 ºC) for 7 days.

		1 hour	**1 day**	**2 day**	**3 day**	**4 day**	**5 day**	**6 day**	**7 day**
25 ºC	**Fluorene**	30.8^{ab}	32.7^{ab}	33.4^{ab}	37.4^{ab}	36.0^{a}	36.0^{ab}	30.6^{ab}	37.4^{b}
	Phenanthrene	60.6	61.4	63.7	64.3	64.1	64.0	60.6	61.6
	Anthracene	66.9^{a}	67.3^{ab}	72.0^{ab}	73.1^{ab}	71.2^{b}	72.4^{ab}	70.7^{ab}	69.3^{ab}
	Fluoranthene	60.1	59.6	62.2	61.9	62.4	62.5	59.4	59.3
	Pyrene	58.2	57.3	61.0	61.1	61.5	61.9	58.4	58.1
	Benzo(a)anthracene	72.2	71.4	73.0	72.8	73.0	75.1	72.4	72.7
	Chrysene	69.1	68.4	71.9	72.1	74.2	74.0	70.9	67.9
	Benzo(*b,k*)fluoranthene	61.6	59.9	61.9	61.5	61.5	63.2	60.3	59.9
	Benzo(a)pyrene	71.5	70.1	72.8	73.1	71.6	74.5	72.9	71.5
	Benzo(g,h,i)perylene	76.7	74.4	76.2	77.0	76.0	79.0	78.6	79.7
	Dibenz(*a,h*)anthracene	89.1	87.1	89.0	89.4	89.0	90.5	90.3	88.2
	Indeno(*1,2,3-c,d*)pyrene	75.9	73.5	75.0	75.6	76.2	77.8	77.2	78.7
38 ºC	**Fluorene**	32.7^{bc}	36.3^{c}	38.9^{c}	36.3^{c}	36.5^{c}	25.6^{a}	28.2^{ab}	35.0^{c}
	Phenanthrene	61.2^{abc}	61.4^{abc}	66.1^{c}	63.2^{bc}	59.3^{abc}	55.4^{a}	54.6^{a}	58.9^{ab}
	Anthracene	71.0	74.0	69.2	72.9	73.3	70.9	70.2	71.8
	Fluoranthene	61.7	62.1	63.3	64.5	61.3	58.7	58.2	60.8
	Pyrene	60.3	60.6	62.2	63.0	61.2	58.3	57.9	61.3
	Benzo(a)anthracene	73.5	75.3	72.6	77.9	71.7	71.6	69.7	71.7
	Chrysene	70.2	71.1	73.2	73.1	73.5	70.3	69.8	73.8
	Benzo(*b+k*)fluoranthene	59.8	62.8	59.0	66.3	61.2	60.7	59.1	61.8
	Benzo(a)pyrene	73.3	73.78	71.8	76.1	71.1	71.6	70.9	72.0
	Benzo(g,h,i)perylene	79.3^{ab}	78.4^{ab}	82.8^{ab}	79.5^{b}	75.8^{ab}	74.9^{ab}	73.4^{a}	78.7^{ab}
	Dibenz(*a,h*)anthracene	90.0^{ab}	91.8^{ab}	90.6^{ab}	91.7^{ab}	88.4^{ab}	85.8^{ab}	84.4^{a}	93.8^{b}
	Indeno(*1,2,3*-c,d)pyrene	79.4^{ab}	78.3^{ab}	77.0^{ab}	78.6^{ab}	76.1^{ab}	72.8^{ab}	70.3^{a}	82.3^{b}

Different superscripts (a,b,c) indicate significant differences at $p < 0.05$.

4. CONCLUSIONS

In the current study, the effect of the environmental temperature on the loss of PAHs in PUF-PAS was evaluated. A slight temperature gradient inside and outside the PAS chamber was detected, varying from 3 to 5 ºC. However, once PAHs are adsorbed to PUFs, it seems that they are not removed irrespective of the environmental temperature. No significant changes in PAH levels were noted through time at both working scenarios (25 ºC and 38 ºC). Moreover, the loss of PAHs was not significantly different according to the temperature. In summary, we conclude that environmental temperature does not affect the stability of PAHs in PAS. Once PAHs are uptaken, they are not easily volatilized from these devices. Consequently, PAS are good environmental monitors, regardless the ambient conditions of temperature. Our findings may have an important repercussion for the comparability of data obtained at different locations worldwide, as PAH levels measured by means of passive sampling devices will not vary according to the environmental temperature. On the other hand, from a climate change perspective of increasing temperature (Teran et al., 2012), PAS are proven to be useful to investigate any potential change in the airborne concentration of PAHs, as well as other SVOCs. A correction of the baseline levels based on the temperature is not necessary. However, confirmation studies considering longer sampling periods and/or environmental temperatures are necessary to ascertain the results from this study. Moreover, complementary investigations could cover ecotoxicological analysis of the PUF and evaluation of the PAH mixtures.

Conflict of interest

The authors declare that there are no conflicts of interest.

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ANNEX 2 – Supporting information chapter 1. Short communication 2.

Table S1. Concentrations of PAHs and SMs in air samples from Tarragona, County (winter season, 26/11/2014-26/01/2015).

	P1	P2	C3	C4	U5	U6	B7	B8	LOD (ng/PUF)
PAHs									
Naph	324.2	153.5	508.9	659.7	488.7	66.5	57.7	226.8	0.053
Acy	9.9	4.7	23.8	11.5	4.5	0.3	0	0.3	0.047
Ace	164.9	164.2	112.6	114.1	165.6	149.1	199.5	97.2	0.032
Fluo	980.2	961.9	407.4	609.8	393.7	440.3	712.0	380.2	0.060
Phen	1292.1	877.3	903.0	1099.1	680.4	831.4	640.3	892.7	0.077
Ant	130.0	36.6	30.7	97.9	34.8	30.8	26.1	41.5	0.037
Flt	700.7	309.6	379.9	505.7	196.2	324.6	258.1	370.1	0.031
Pyr	542.3	205.4	284.4	375.6	161.0	223.6	171.9	248.2	0.026
BaA	92.9	39.5	60.2	73.1	15.8	37.5	15.2	34.2	0.032
Chry	47.7	14.4	18.9	32.5	5.0	14.9	4.9	13.4	0.029
B(b+k)F	16.5	8.7	13.7	15.5	1.1	4.1	0.8	2.3	0.016
BaP	9.9	2.9	5.8	5.3	4.0	7.7	1.0	2.1	0.103
Icdp	3.1	2.8	4.5	6.8	1.2	2.5	1.2	1.1	0.375
DahA	2.1	1.5	2.0	3.2	3.5	2.6	2.4	2.8	0.125
BghiP	16.3	9.8	19.0	11.0	7.5	14.9	6.6	5.1	0.231
Σ16PAHs	**4332.7**	**2792.8**	**2774.7**	**3620.7**	**2162.9**	**2150.9**	**2097.7**	**2317.9**	
SMs									**LOD (ng/PUF)**
Cashmeran	0.26	0.29	<LOD	<LOD	<LOD	<LOD	4.16	<LOD	0.214
Celestolide	0.22	0.11	0.23	0.31	0.33	0.17	0.42	0.21	0.033
Phantolide	<LOD	<LOD	<LOD	<LOD	0.26	<LOD	0.13	<LOD	0.027
Musk ambrette	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.001
Traseolide	<LOD	<LOD	0.22	<LOD	<LOD	0.21	0.42	<LOD	0.158
Galaxolide	8.48	3.06	0.62	2.84	1.35	<LOD	4.77	1.04	0.125
Musk xylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.500
Tonalide	4.28	4.93	2.67	6.57	0.93	0	0.27	<LOD	0.088
Musk moskene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.600
Musk tibetene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.600
Musk ketone	<LOD	<LOD	<LOD	2.95	<LOD	<LOD	<LOD	<LOD	0.750
Σmusks	**13.4**	**8.5**	**3.7**	**12.7**	**2.9**	**0.4**	**10.2**	**1.3**	

P = Petrochemical area; C = Chemical area; U = Urban area; B = Background area.

LOD = limit of detection. Benzo(*b*)fluoranthene and benzo(*k*)fluoranthene were quantified together.

Table S2. Concentrations of PCBs, BFRs and HCB in air samples from Tarragona, County (winter season, 26/11/2014-26/01/2015).

	P1	**P2**	**C3**	**C4**	**U5**	**U6**	**B7**	**B8**	**LOD (ng/PUF)**
PCBs									
PCB 28	54.0	7.2	9.9	5.4	3.9	5.3	1.8	1.8	0.044
PCB 52	4.8	1.6	9.3	2.8	1.6	2.2	0.5	0.9	0.001
PCB 77	0.1	0.1	1.6	0.3	0.1	0.3	<LOD	<LOD	0.013
PCB 81	0.2	<LOD	1.0	0.1	0.1	<LOD	<LOD	<LOD	0.009
PCB 101	0.4	0.9	18.8	1.5	0.8	0.1	<LOD	<LOD	0.016
PCB 105	0.3	0.4	2.6	0.6	0.3	<LOD	<LOD	<LOD	0.100
PCB 114	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.109
PCB 118	0.7	1.0	6.7	0.8	0.5	0.6	0.1	0.5	0.075
PCB 123	0.6	0.7	9.5	0.7	0.2	0.6	0.2	0.3	0.086
PCB 126	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.092
PCB 138	2.0	2.7	23.0	1.9	0.9	1.5	0.1	0.3	0.039
PCB 153	1.7	2.3	30.1	1.8	0.9	1.4	0.0	0.3	0.019
PCB 156	<LOD	0.1	1.2	<LOD	<LOD	<LOD	<LOD	<LOD	0.008
PCB 157	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.008
PCB 167	<LOD	<LOD	0.4	<LOD	<LOD	<LOD	<LOD	<LOD	0.008
PCB 169	0.6	0.2	0.1	0.8	<LOD	<LOD	<LOD	<LOD	0.005
PCB 180	1.3	1.5	6.2	1.1	0.4	0.0	0.1	0.1	0.057
PCB 189	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.018
PCB 209	<LOD	<LOD	0.1	<LOD	<LOD	0.1	<LOD	<LOD	0.003
ΣPCBs	**66.6**	**18.7**	**120.5**	**17.8**	**9.7**	**12.4**	**2.9**	**4.3**	
BFRs									**LOD (ng/PUF)**
BDE 28	0.36	0.28	0.28	0.25	0.22	0.33	0.20	0.24	0.001
BDE 47	0.55	0.77	0.58	0.21	0.44	0.29	0.19	0.33	0.022
BDE 85	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.29	<LOD	0.133
BDE 99	0.33	0.17	0.31	0.18	<LOD	0.43	0.14	0.11	0.048
BDE 100	0.000	<LOD	0.13	0.06	0.20	0.16	0.60	0.06	0.036
BDE 153	1.16	0.32	0.31	0.90	0.21	0.70	0.03	0.05	0.020
BDE 154	<LOD	<LOD	<LOD	<LOD	<LOD	0.10	0.06	0.15	0.013
BDE 183	0.26	0.08	0.08	0.03	0.08	0.27	0.10	0.21	0.092
PBT	0.09	<LOD	0.08	0.09	0.03	0.17	0.12	0.02	0.080
PBEB	<LOD	<LOD	0.17	<LOD	<LOD	<LOD	<LOD	<LOD	0.002
HBB	0.04	0.05	<LOD	<LOD	0.17	0	0.04	0.12	0.040
ΣBFRs	**2.8**	**1.7**	**1.9**	**1.7**	**1.3**	**2.5**	**1.8**	**1.3**	
HCB	**10.1**	**9.6**	**16.4**	**11.1**	**7.5**	**9.3**	**4.6**	**8.2**	0.052

P = Petrochemical area; C = Chemical area; U = Urban area; B = Background area.

LOD = limit of detection.

ANNEX 3 – Supporting information chapter 1. Article 1.

Table S1. Results for recoveries, limit of detection (LOD) and limit of quantification (LOQ) for PAHs in air samples (ng/sample) and lichen samples (ng/g dw).

	PUF-foams Recovery %	**PUF-foams**		**Lichens Recovery %**	**Lichens**	
		LOD	LOQ		LOD	LOQ
Naphthalene	110	0.3	1	124	1	5
Acenaphthylene	116	0.3	1	-	1	5
Acenaphthene	99	0.3	1	126	1	5
Fluorene	91	1.5	5	128	1	5
Phenanthrene	106	1.5	5	131	1	5
Anthracene	111	1.5	5	118	0.6	1
Fluoranthene	99	1.5	5	142	1	5
Pyrene	99	1.5	5	134	1	5
Benzo(*a*)anthracene	85	1.5	5	151	0.6	1
Chrysene	105	1.5	5	113	0.6	1
Benzo(*b*)fluoranthene	89	3	10	-	-	-
Benzo(*k*)fluoranthene	66	5	20	-	-	-
Benzo(*b*+*k*)fluoranthene*	-	-	-	56	0.6	1
Benzo(*a*)pyrene	93	3	10	66	0.6	1
Indeno(*1,2,3-c,d*)pyrene	85	3	10	101	1	5
Dibenzo(*a,h*)anthracene	86	3	10	100	1	5
Benzo(*g,h,i*)perylene	75	5	20	93	1	5

*Benzo(*b*)fluoranthene and benzo(*k*)fluoranthene were quantified together in lichens.

ANNEX 4 – Supporting information chapter 2. Article 1.

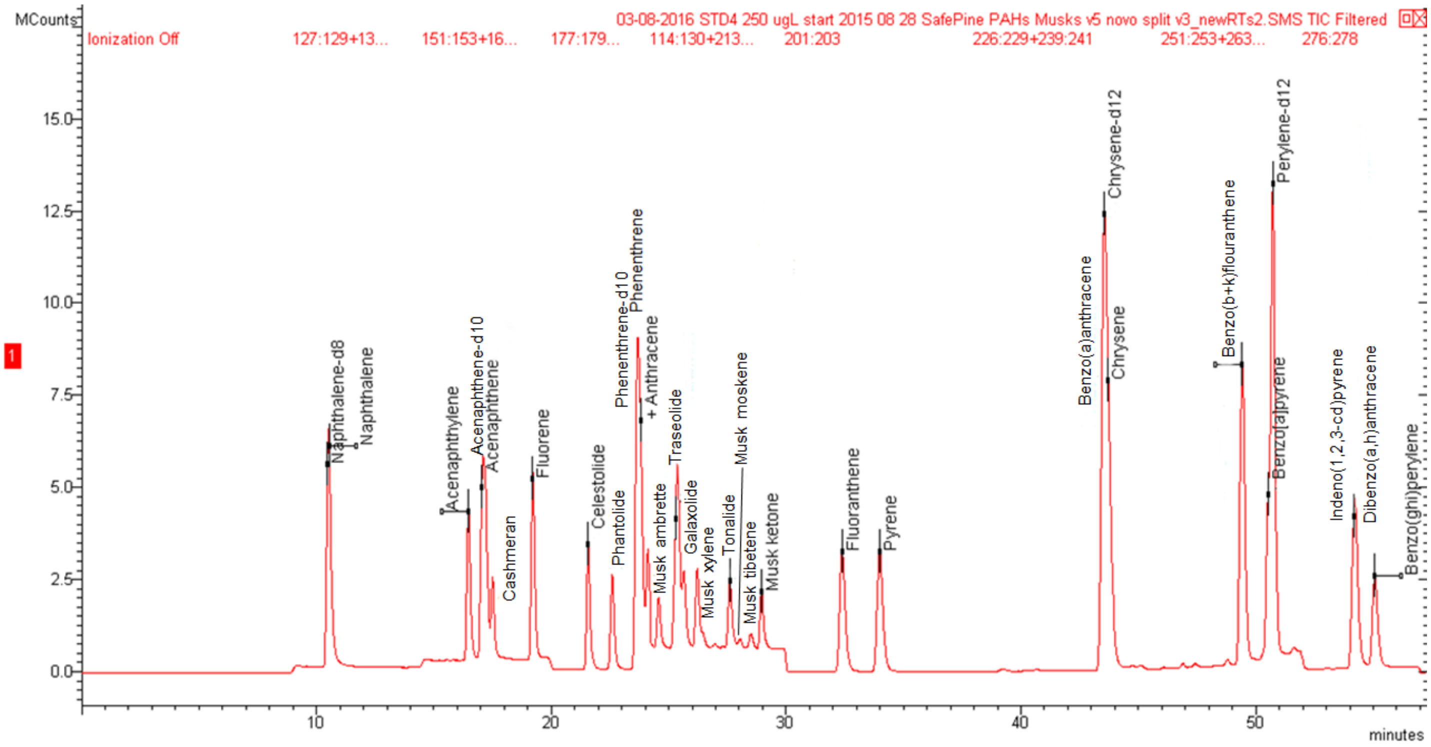

Fig. S1. Example chromatogram of standard solutions for PAHs and SMs.

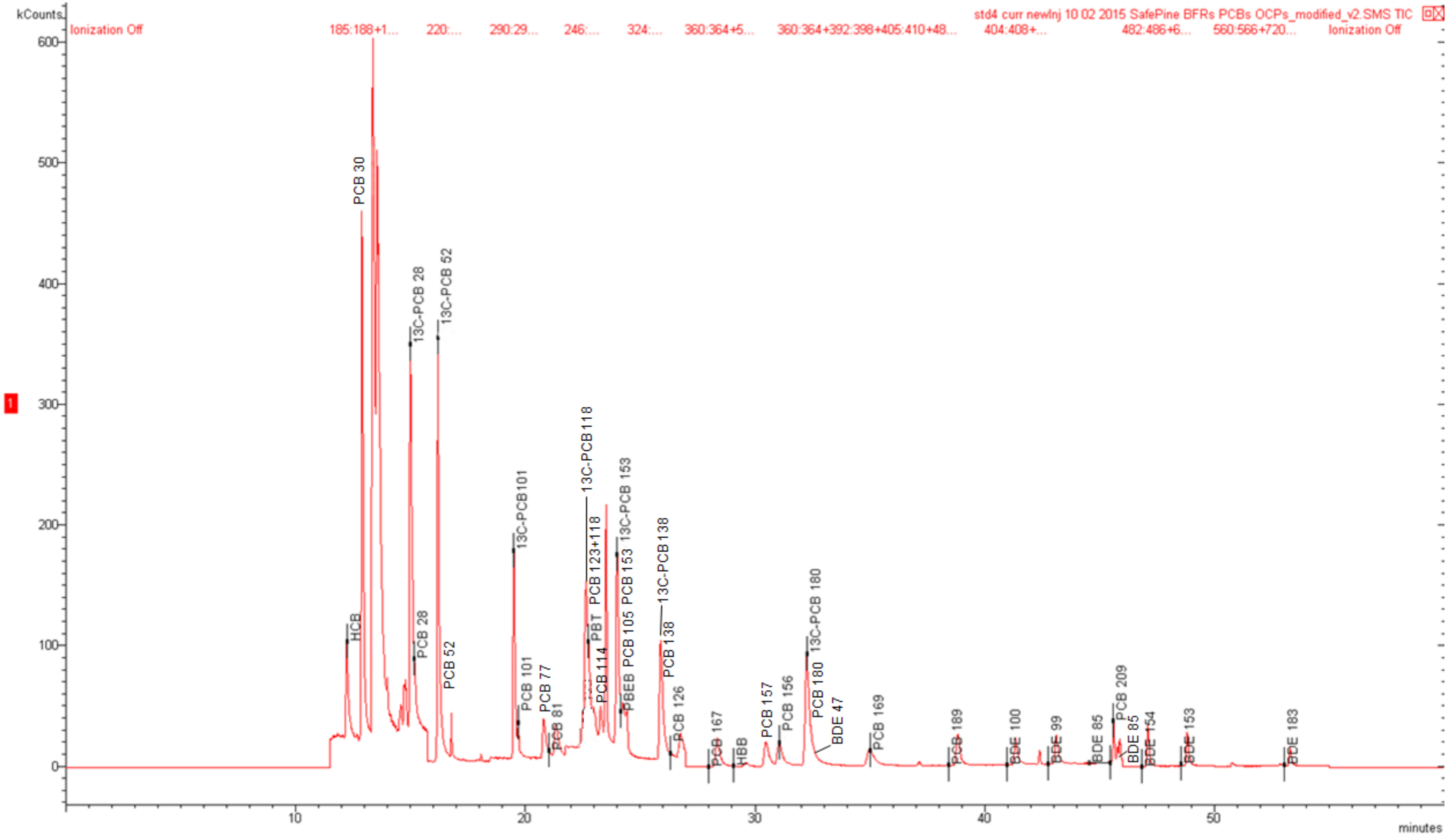

Fig. S2. Example chromatogram of standard solutions for PCBs, BFRs and HCB.

ANNEX 5 – Supporting information chapter 2. Article 2.

Table S1. Concentrations of SVOCs in soils samples of each sampling point in Tarragona County, (Catalonia, Spain) (ng/g).

Sampling Point	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
Area	**P**	**P**	**P**	**P**	**P**	**P**	**P**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**U**	**U**	**U**	**U**	**U**	**U**	**B**	**B**	**B**	**B**	**B**
Naph	0.34	1.42	3.05	4.24	2.10	2.58	1.26	1.78	0.15	<LOD	9.42	3.92	7.11	3.96	<LOD	<LOD	<LOD	<LOD	<LOD	10.12	20.90	11.80	12.06	16.74	5.02	5.70	37.57
Acy	0.86	0.66	2.16	0.79	0.56	0.47	0.29	0.51	0.32	0.46	0.57	26.25	0.51	0.32	0.71	0.23	2.20	0.45	0.36	2.36	0.52	0.36	0.17	0.51	0.13	0.11	0.21
Ace	0.21	0.37	1.83	0.25	0.33	0.64	11.74	1.19	0.37	0.17	1.04	2.04	0.51	0.51	0.63	0.51	1.17	0.76	0.57	<LOD	0.56	0.30	0.39	0.14	<LOD	<LOD	0.63
Fluo	0.15	0.24	0.39	0.32	0.32	0.66	22.63	1.12	0.41	0.12	2.51	5.03	0.52	0.44	0.55	0.30	1.35	0.99	0.50	0.03	1.67	0.40	0.26	0.10	0.06	<LOD	0.63
Phen	2.09	1.52	1.59	2.41	2.23	2.14	6.96	2.48	3.56	0.91	21.58	19.33	2.68	1.78	9.90	2.26	22.98	2.23	7.32	1.61	5.21	2.84	2.41	2.37	1.03	1.70	2.43
Ant	0.24	0.12	0.18	0.27	0.25	0.24	0.08	0.27	0.38	0.12	2.22	1.99	0.19	0.20	0.95	0.24	2.14	0.25	0.03	<LOD	0.06	<LOD	<LOD	<LOD	<LOD	<LOD	0.58
Flt	4.56	1.22	3.75	3.26	2.46	3.57	2.63	4.51	17.87	3.42	30.25	18.18	3.07	1.54	28.90	3.29	55.85	6.96	26.52	10.04	9.13	18.32	1.72	0.96	1.51	1.11	12.75
Pyr	4.03	1.35	3.91	3.28	2.33	3.58	77.94	5.11	14.51	3.07	27.00	23.56	2.89	3.39	25.37	4.93	46.86	8.59	22.51	10.01	9.02	17.89	3.09	1.03	1.30	0.96	10.86
BaA	2.50	0.67	3.83	2.23	1.16	2.20	0.66	2.69	9.99	2.09	15.28	15.52	1.47	0.31	18.68	1.52	34.52	4.19	8.40	5.23	2.10	10.55	1.74	0.16	0.69	0.30	6.47
Chry	3.56	1.04	4.73	3.36	2.44	4.23	6.82	4.08	11.25	2.12	22.53	21.08	2.57	3.41	24.05	3.01	39.77	5.55	14.50	8.69	10.73	17.87	7.57	0.70	1.37	0.77	11.06
B(b+k)F	3.48	1.42	5.81	5.63	2.52	4.84	8.68	4.15	12.40	2.82	22.19	16.76	1.85	2.06	24.37	4.84	38.16	9.61	14.95	18.37	19.34	20.53	3.88	2.08	2.06	1.50	13.37
BaP	3.95	1.25	5.53	4.90	2.41	3.73	3.76	4.17	11.35	2.86	25.03	20.00	2.29	0.73	25.81	4.13	41.32	5.12	12.17	19.03	18.72	25.57	4.74	0.53	0.65	0.68	13.90
Icdp	1.86	0.35	2.58	2.10	0.98	1.43	1.09	1.72	6.43	0.87	13.25	13.57	0.75	0.89	17.65	1.99	25.61	4.45	8.30	14.59	9.33	11.88	0.63	0.30	<LOD	<LOD	4.94
DahA	0.26	<LOD	0.59	0.80	<LOD	0.34	0.40	0.96	1.03	0.25	4.84	4.08	<LOD	1.03	4.02	0.78	5.87	0.74	1.73	2.97	2.43	3.75	1.01	<LOD	<LOD	<LOD	1.60
BghiP	2.55	2.22	5.37	5.08	2.81	3.59	16.56	4.33	7.98	2.16	21.71	17.34	1.67	6.46	22.35	3.84	32.64	6.18	12.06	18.07	21.51	17.06	7.57	0.77	0.97	0.54	6.29
Σ16PAHs	30.65	13.93	45.32	38.90	22.97	34.23	161.49	39.08	98.01	21.49	219.41	208.64	28.16	27.02	203.99	31.91	350.47	56.09	129.96	121.14	131.24	159.13	47.25	26.46	14.99	13.60	123.28
Σ 7 prob. carcinogenic PAHs*	15.60	4.80	23.08	19.01	9.58	16.77	21.40	17.77	52.45	11.03	103.10	91.01	9.00	8.43	114.57	16.26	185.25	29.65	60.06	68.88	62.66	90.15	19.57	3.84	4.94	3.43	51.34

Sampling Point	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
Area	**P**	**P**	**P**	**P**	**P**	**P**	**P**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**U**	**U**	**U**	**U**	**U**	**U**	**B**	**B**	**B**	**B**	**B**
Cashmeran	<LOD	<LOD	5.93	<LOD	2.09	3.13	2.60	6.89	2.21	<LOD	<LOD	1.78	4.87	<LOD	<LOD	<LOD	<LOD	2.34	1.63	1.06	3.47	3.95	5.19	4.68	0.65	4.31	7.11
Celestolide	<LOD	0.07	<LOD	0.10	<LOD	<LOD	1.03	<LOD	0.04	<LOD	<LOD	0.08	0.04	0.04	<LOD	<LOD	<LOD	0.04	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Phantolide	<LOD	<LOD	<LOD	0.15	0.14	<LOD	1.26	<LOD	<LOD	0.09	0.10	0.28	0.26	<LOD	0.05	0.10	<LOD	0.27	0.02	<LOD	<LOD	<LOD	<LOD	0.04	<LOD	<LOD	0.01
Galaxolide	1.79	2.37	1.61	6.11	1.36	0.81	3.64	0.97	11.49	2.18	1.52	6.78	7.88	10.20	3.66	2.43	2.37	5.91	0.64	3.45	3.50	1.37	8.25	7.26	<LOD	9.79	0.97
Traseolide	<LOD	<LOD	<LOD	0.25	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.21	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Tonalide	0.24	0.34	0.21	0.50	0.45	0.12	3.55	0.25	0.48	<LOD	0.23	0.28	0.55	0.39	0.25	0.52	0.24	0.58	<LOD	<LOD	0.24	<LOD	0.27	0.20	<LOD	0.23	0.14
Musk ambrette	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Musk xylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Musk moskene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Musk tibetene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Musk ketone	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.30	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Σmusks	2.30	3.03	7.95	7.32	4.24	4.26	12.26	8.31	14.42	2.60	2.11	10.82	13.79	10.88	4.22	3.32	2.88	9.31	2.55	4.78	7.42	5.58	13.90	12.38	0.94	14.53	8.42
PCB 52	0.01	0.04	0.05	0.06	0.04	0.01	0.23	0.08	0.04	0.01	0.13	0.04	0.04	0.03	0.02	0.03	0.07	0.06	0.04	0.03	0.03	0.36	0.03	0.02	0.02	0.02	0.02
PCB 77	0.04	0.08	0.02	0.06	0.07	0.01	0.89	0.07	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.64	0.86	1.15	0.59	<LOD	0.24	<LOD	0.15	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 81	0.04	0.06	0.03	0.02	0.03	0.01	0.47	0.02	<LOD	<LOD	0.03	0.04	0.05	0.13	<LOD	<LOD	0.54	<LOD	<LOD	<LOD	<LOD	0.49	<LOD	<LOD	<LOD	<LOD	0.11
PCB 101	2.44	0.56	1.21	3.16	<LOD	<LOD	1.13	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.50	0.53	0.08	<LOD	<LOD	2.21	2.33	0.68	0.60	<LOD	1.42	0.82	2.52	0.33
PCB 105	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.09	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 114	0.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.02	0.02	0.04	0.03	<LOD	0.03	0.06	0.06	0.10	0.17	0.14	0.29	0.14
PCB 118	2.40	1.00	1.55	2.48	<LOD	0.11	0.62	<LOD	0.16	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 123	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.05	<LOD	<LOD	0.99	0.66	1.07	0.79	1.06	1.22	0.96	1.32	1.51	0.79	0.47	0.81	1.23
PCB 126	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.61	1.31	1.94	0.25	1.08	<LOD	0.21	0.78	1.86	0.84	<LOD	1.03	1.33
PCB 138	0.32	0.63	0.24	0.36	0.71	0.89	2.65	2.29	2.27	0.60	10.42	5.18	2.91	1.14	8.81	1.15	3.70	1.68	0.99	0.69	9.81	8.83	0.42	0.76	2.84	0.47	0.94

Sampling Point	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
Area	**P**	**P**	**P**	**P**	**P**	**P**	**P**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**U**	**U**	**U**	**U**	**U**	**U**	**B**	**B**	**B**	**B**	**B**
PCB 153	4.67	3.60	0.95	0.01	0.73	0.51	0.80	0.63	0.13	7.05	22.90	13.96	7.43	4.97	1.56	0.10	0.56	0.35	0.11	0.30	1.92	1.30	0.40	0.33	0.45	0.16	0.34
PCB 156	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.77	0.79	0.65	0.11	0.69	0.58	0.17	0.21	0.38	0.02	0.17	0.53	0.63
PCB 157	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	0.01	<LOD	0.01	<LOD	<LOD	0.00	<LOD	<LOD	0.05	0.10	<LOD	<LOD	0.03	0.21	0.03	<LOD	0.32	<LOD	<LOD	<LOD	0.24
PCB 167	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.03	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.21	0.25	0.06	<LOD	0.20	0.03	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 169	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 180	0.14	0.24	0.05	0.37	0.41	0.41	0.39	0.31	0.74	1.56	1.62	2.26	2.01	1.54	2.11	1.12	1.17	1.31	1.23	1.26	2.09	1.46	0.78	1.88	1.09	0.21	1.02
PCB 189	0.17	0.01	0.12	0.27	0.69	0.27	<LOD	0.36	0.05	<LOD	<LOD	<LOD	<LOD	<LOD	0.23	0.35	0.29	0.33	0.35	0.14	0.13	0.48	0.40	0.08	0.27	0.74	0.39
PCB 209	<LOD	0.21	0.44	1.91	2.32	2.14	<LOD	2.19	4.06	0.10	0.17	0.07	0.06	0.10	0.10	0.07	0.02	0.04	0.10	0.05	0.05	0.07	0.05	0.22	0.04	0.17	0.10
ΣPCBs	10.35	6.53	4.71	8.80	5.05	4.42	7.69	6.02	7.47	9.37	35.34	21.67	12.58	9.48	17.74	6.96	11.36	5.64	8.17	7.20	16.23	16.36	6.31	6.57	6.37	6.99	6.88
BDE 28	0.01	<LOD	0.00	0.00	<LOD	<LOD	0.01	<LOD	0.01	0.03	0.02	0.04	0.03	0.02	<LOD	<LOD	<LOD	<LOD	0.01	0.03	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.01
BDE 47	0.16	<LOD	0.04	0.06	0.00	0.16	0.03	0.32	0.23	0.86	2.28	0.90	1.00	1.20	0.13	0.06	0.10	0.11	0.12	0.04	0.20	0.21	0.01	0.02	0.01	0.07	0.07
BDE 85	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BDE 99	0.36	<LOD	<LOD	0.29	0.13	0.09	<LOD	<LOD	<LOD	0.31	0.12	0.57	0.32	0.23	0.06	0.95	0.72	1.58	0.65	0.41	<LOD	0.62	<LOD	<LOD	0.06	<LOD	<LOD
BDE 100	<LOD	0.06	0.04	0.15	<LOD	<LOD	<LOD	0.15	<LOD	0.08	0.08	0.05	0.03	0.04	0.03	0.12	0.23	0.16	0.03	0.05	0.03	0.10	<LOD	0.03	0.04	0.05	<LOD
BDE 153	0.02	0.22	<LOD	<LOD	0.18	<LOD	0.03	<LOD	0.47	0.32	0.26	0.17	0.11	0.11	0.06	0.01	0.08	0.24	0.11	0.19	1.37	0.13	0.11	0.05	0.03	0.05	0.06
BDE 154	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.03	0.12	0.09	0.02	0.04	0.01	<LOD	<LOD	0.03	0.00	0.04	0.02	0.04	0.01	0.02	<LOD	<LOD	<LOD
BDE 183	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PBT	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.01	0.01	<LOD	<LOD	<LOD	0.02	<LOD	0.05	<LOD
PBEB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.05	<LOD	<LOD	0.05	<LOD	0.05	<LOD	<LOD	<LOD	0.03	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HBB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ΣBFRs	0.63	0.37	0.19	0.58	0.39	0.33	0.18	0.57	0.82	1.73	2.94	1.89	1.61	1.70	0.41	1.21	1.20	2.19	1.02	0.81	1.72	1.16	0.24	0.21	0.22	0.31	0.25

Sampling Point	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
Area	**P**	**P**	**P**	**P**	**P**	**P**	**P**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**U**	**U**	**U**	**U**	**U**	**U**	**B**	**B**	**B**	**B**	**B**
HCB	0.01	0.02	0.03	0.01	0.01	0.01	0.03	0.02	0.01	0.06	0.04	0.07	0.05	0.05	0.01	<LOD	0.00	0.01	0.00	0.01	0.11	0.02	<LOD	0.02	0.02	0.01	0.01

P = Petrochemical area; C = Chemical area; U = Urban area; B = Background area.

LOD = limit of detection. Benzo(*b*)fluoranthene and benzo(*k*)fluoranthene were quantified together.

*Benzo(*a*)anthracene, chrysene, benzo(*b*+*k*)fluoranthene, benzo(*a*)pyrene, indeno(*1,2,3-c,d*)pyrene, dibenzo(*a,h*)anthracene.

Table S2. Concentrations of SVOCs in vegetation samples of each sampling point in Tarragona County, (Catalonia, Spain) (ng/g).

Sampling Point	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
Area	**P**	**P**	**P**	**P**	**P**	**P**	**P**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**U**	**U**	**U**	**U**	**U**	**U**	**B**	**B**	**B**	**B**	**B**
Naph	50.81	58.46	47.35	38.26	31.62	30.00	15.28	31.45	16.96	27.67	29.61	33.57	32.51	25.79	6.43	10.77	16.75	37.28	11.24	14.90	29.00	13.79	26.85	26.42	30.99	16.21	16.39
Acy	0.85	0.48	0.22	0.55	0.12	<LOD	<LOD	0.10	<LOD	0.05	0.10	0.14	0.34	0.37	0.20	0.21	0.21	0.91	0.41	0.37	0.78	0.24	0.71	0.26	0.82	0.17	0.41
Ace	0.96	1.10	0.34	0.36	1.22	0.81	1.20	0.11	2.06	0.50	<LOD	<LOD	0.50	0.06	0.24	0.36	0.20	0.65	0.45	0.26	0.73	0.30	1.19	0.25	0.49	0.21	0.20
Fluo	7.26	8.69	3.79	15.51	1.13	0.47	0.38	<LOD	1.54	2.41	0.24	1.00	1.01	1.33	1.35	0.62	0.66	4.58	3.00	1.54	1.45	0.52	4.86	1.68	3.65	2.81	0.81
Phen	12.05	17.41	6.85	10.16	9.63	6.44	8.20	2.75	1.12	4.12	2.54	2.81	4.97	5.36	4.32	4.09	7.03	44.70	4.46	24.60	6.57	8.98	13.80	10.69	12.02	19.89	5.94
Ant	0.95	0.35	0.84	0.58	0.72	0.25	0.34	0.19	0.76	0.24	0.03	0.07	0.49	0.27	0.56	0.28	1.53	2.01	1.58	8.20	5.52	2.03	0.77	4.82	1.42	1.29	1.08
Flt	6.66	7.02	3.19	3.65	2.89	2.86	2.52	2.19	2.16	3.86	2.43	2.46	2.70	4.42	1.30	4.26	4.07	34.10	1.58	17.74	10.48	4.76	5.95	9.91	8.25	22.74	3.02
Pyr	18.17	19.01	9.61	10.42	7.90	7.81	6.88	2.33	1.89	3.46	2.22	1.82	3.81	3.58	0.88	4.87	4.33	36.28	3.71	20.84	8.64	4.01	5.04	7.41	6.84	23.96	2.11
BaA	1.82	1.90	0.96	1.04	0.79	0.78	0.69	0.15	0.29	0.11	0.06	<LOD	0.49	0.39	0.29	1.00	0.49	4.12	0.35	0.57	0.82	0.50	0.80	0.58	0.36	0.43	0.27
Chry	1.63	4.03	2.97	3.28	1.61	2.15	1.06	1.10	4.93	0.77	0.59	0.51	1.60	1.66	0.82	2.08	1.37	9.41	0.93	2.17	4.99	1.25	1.55	1.00	3.58	2.33	0.29
B(b+k)F	1.66	1.70	4.13	8.70	1.58	1.73	3.31	2.39	2.47	2.36	3.13	1.37	4.72	1.39	2.72	0.43	2.12	8.52	0.74	0.41	1.35	0.84	0.38	1.09	0.27	0.35	0.27
BaP	0.74	0.61	0.71	0.68	0.42	0.35	0.29	0.24	0.09	0.19	0.92	0.41	1.37	0.33	0.33	0.11	0.17	2.23	0.23	0.39	0.88	0.60	0.18	0.67	0.23	0.09	0.22
Icdp	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	4.26	<LOD	<LOD	<LOD	<LOD	<LOD	1.30	<LOD	<LOD	3.20	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DahA	0.52	<LOD	<LOD	0.87	<LOD	<LOD	0.40	<LOD	0.15	0.19	<LOD	0.15	1.49	0.46	0.85	<LOD	<LOD	<LOD	0.41	<LOD	0.98	<LOD	0.52	<LOD	0.50	0.20	0.26
BghiP	0.61	2.37	0.79	<LOD	1.03	0.80	<LOD	1.04	0.83	2.58	0.76	2.25	1.81	1.29	1.21	0.46	2.37	4.69	2.44	0.49	5.95	1.77	1.96	5.59	2.07	1.14	1.39
Σ16PAHs	104.79	123.33	81.95	94.24	60.84	54.64	40.74	44.25	35.40	52.78	42.83	46.70	57.91	46.81	21.60	30.93	41.48	189.67	34.75	92.66	78.26	39.76	64.68	70.56	71.57	91.94	32.58
Σ 7 prob. carcinogenic PAHs*	6.47	8.43	8.96	14.68	4.58	5.18	5.86	4.06	8.05	7.87	4.89	2.56	9.78	4.34	5.12	5.00	4.33	24.47	5.87	3.72	9.15	3.36	3.55	3.53	5.04	3.51	1.23
Cashmeran	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	6.63	<LOD	<LOD	<LOD	<LOD	1.67	<LOD	6.01	4.24	15.38	3.33	9.07	8.75	<LOD	1.72	<LOD	8.94	<LOD	6.59
Celestolide	<LOD	0.04	0.05	<LOD	<LOD	<LOD	<LOD	<LOD	0.90	<LOD	<LOD	<LOD	0.10	0.16	0.20	0.22	0.65	0.32	0.40	0.48	0.30	0.72	0.58	1.01	1.07	3.56	0.93
Phantolide	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.82	0.36	0.46	<LOD	0.20	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Sampling Point	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
Area	**P**	**P**	**P**	**P**	**P**	**P**	**P**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**U**	**U**	**U**	**U**	**U**	**U**	**B**	**B**	**B**	**B**	**B**
Galaxolide	<LOD	6.94	<LOD	<LOD	4.32	<LOD	14.53	9.82	5.58	<LOD	1.83	4.94	4.80	14.34	5.39	<LOD	<LOD	<LOD	<LOD	17.59	<LOD	3.26	<LOD	38.45	<LOD	14.49	7.33
Traseolide	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Tonalide	<LOD	<LOD	0.18	<LOD	<LOD	<LOD	0.24	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.55	1.60	0.88	<LOD	2.52	<LOD	0.52	<LOD	<LOD	1.78	<LOD	1.99
Musk ambrette	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Musk xylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Musk moskene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Musk tibetene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Musk ketone	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Σmusks	0.35	7.29	0.50	0.35	4.65	0.35	15.04	10.15	13.35	0.35	2.97	5.62	5.66	16.42	6.09	7.99	6.70	16.78	4.00	29.85	9.32	4.74	2.56	39.76	12.01	18.36	17.03
PCB 52	0.28	0.17	0.17	0.39	0.10	0.43	0.20	0.16	0.23	0.18	0.31	0.37	<LOD	<LOD	<LOD	0.04	0.16	0.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 77	5.27	5.86	0.23	<LOD	3.57	2.48	3.70	3.33	<LOD	0.65	8.26	4.63	2.71	1.26	1.07	3.12	2.17	7.81	0.54	4.87	3.70	4.38	0.91	<LOD	0.37	0.38	<LOD
PCB 81	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.01	0.04	<LOD	<LOD	0.03	0.01	<LOD	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 101	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.07	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.12	<LOD	<LOD	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 105	0.14	0.07	0.05	0.12	0.05	0.08	0.16	0.04	0.09	0.04	0.12	0.13	0.07	0.14	0.06	0.25	0.06	0.09	0.10	0.07	0.11	0.04	0.11	0.13	0.07	0.09	0.15
PCB 114	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 118	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 123	0.56	0.61	0.62	0.55	0.62	0.54	0.49	0.03	0.08	0.02	0.05	0.03	<LOD	0.06	<LOD	0.02	0.01	0.06	0.01	<LOD	<LOD	<LOD	<LOD	0.01	<LOD	<LOD	<LOD
PCB 126	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 138	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 153	0.06	0.02	<LOD	0.08	<LOD	<LOD	<LOD	0.67	0.06	<LOD	<LOD	0.16	0.05	0.04	0.06	0.14	0.18	0.11	0.04	0.03	0.03	<LOD	0.04	<LOD	<LOD	<LOD	<LOD
PCB 156	0.22	0.02	0.13	0.16	0.01	<LOD	<LOD	0.06	<LOD	<LOD	<LOD	<LOD	0.05	0.07	0.02	0.02	0.02	0.04	0.03	0.07	0.05	0.01	0.03	0.01	0.02	0.01	0.01
PCB 157	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 167	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Sampling Point	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
Area	**P**	**P**	**P**	**P**	**P**	**P**	**P**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**U**	**U**	**U**	**U**	**U**	**U**	**B**	**B**	**B**	**B**	**B**
PCB 169	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.03	0.01	0.03	<LOD	0.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 180	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 189	<LOD	<LOD	<LOD	<LOD	0.03	0.06	0.01	0.01	0.05	0.07	0.05	0.07	0.09	0.06	0.09	0.06	0.06	0.02	0.06	0.10	0.06	0.02	0.02	0.03	0.02	0.02	0.01
PCB 209	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ΣPCBs	6.56	6.78	1.24	1.34	4.43	3.62	4.59	4.34	0.55	1.08	8.84	5.42	3.01	1.67	1.35	3.67	2.70	9.26	0.81	5.18	3.99	4.49	1.15	0.21	0.50	0.54	0.21
BDE 28	0.12	0.04	0.02	0.01	0.04	0.01	0.07	0.14	0.09	<LOD	0.07	0.09	<LOD	0.02	0.01	0.01	<LOD	0.49	0.04	<LOD	<LOD	<LOD	1.40	0.05	0.02	<LOD	<LOD
BDE 47	0.68	0.14	0.02	0.42	0.30	0.09	0.56	0.51	1.21	1.31	0.29	0.65	0.43	0.46	0.82	0.60	0.45	0.32	0.73	1.04	0.43	0.05	0.14	0.04	0.10	0.06	0.02
BDE 85	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BDE 99	0.18	0.21	0.43	0.23	0.30	0.22	0.20	0.25	0.27	0.33	0.26	0.27	0.06	0.12	<LOD	<LOD	0.07	<LOD	<LOD	0.14	0.09	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BDE 100	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.04	<LOD	0.05	0.05	0.04	<LOD	<LOD	0.08	0.04	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BDE 153	0.18	0.02	0.08	0.07	0.23	0.16	0.18	0.06	0.35	0.02	0.22	0.21	0.02	<LOD	0.07	<LOD	0.03	<LOD	<LOD	0.04	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BDE 154	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BDE 183	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PBT	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PBEB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HBB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ΣBFRs	1.25	0.49	0.63	0.82	0.95	0.56	1.08	1.04	2.01	1.74	0.92	1.30	0.62	0.69	1.02	0.74	0.66	0.90	0.86	1.37	0.63	0.15	1.64	0.19	0.22	0.16	0.12
HCB	0.07	0.08	0.09	0.18	0.09	0.09	0.29	0.43	0.08	0.07	0.05	0.12	<LOD	<LOD	<LOD	<LOD	0.14	0.11	<LOD	<LOD	0.10	0.31	0.23	0.24	0.11	0.11	0.03

P = Petrochemical area; C = Chemical area; U = Urban area; B = Background area.

LOD = limit of detection. Benzo(*b*)fluoranthene and benzo(*k*)fluoranthene were quantified together.

*Benzo(*a*)anthracene, chrysene, benzo(*b*+*k*)fluoranthene, benzo(*a*)pyrene, indeno(*1,2,3-c,d*)pyrene, dibenzo(*a,h*)anthracene.

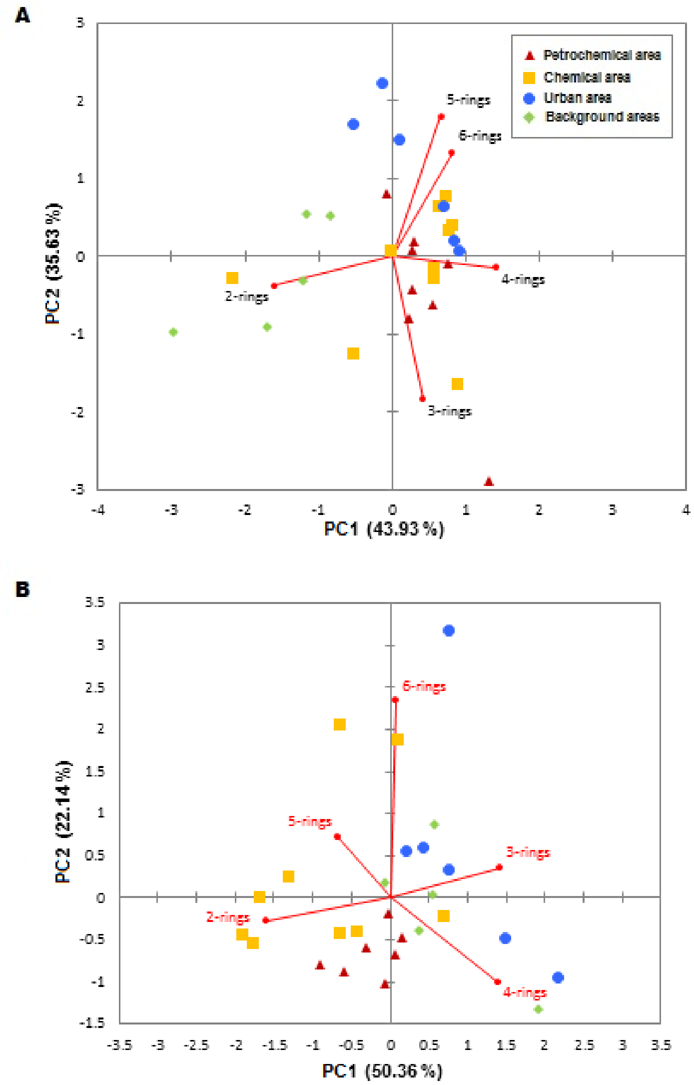

Fig. S1. Principal component analysis (PCA) for PAHs ring profiles in soil (A) and vegetation (B) collected in the different zones of study.

ANNEX 6 – Supporting information chapter 3. Article 1.

Table S1. Mass balance equation for each medium according to Diamond et al., 2001.

Medium	Mass balance equation
Air	$I_A + f_W D_{WA} + f_S D_{SA} + f_V D_{VA} + f_F D_{FA} = f_A D_{TA}$
Water	$I_W + f_A D_{AW} + f_S D_{SW} + f_D D_{DW} + f_F D_{FW} = f_W D_{TW}$
Soil	$I_S + f_A D_{AS} + f_V D_{VS} = f_S D_{TS}$
Sediment	$I_D + f_W D_{WD} = f_D D_{TD}$
Vegetation	$I_V + f_A D_{AV} + f_S D_{SV} = f_V D_{TV}$
Organic film	$I_F + f_A D_{AF} = f_F D_{TF}$

A, W, S, D, V and F represent air, water, soil, sediment, vegetation and organic film, respectively. f is fugacity. I is the contaminant input into each medium, and the subscript "T" is the total D values.

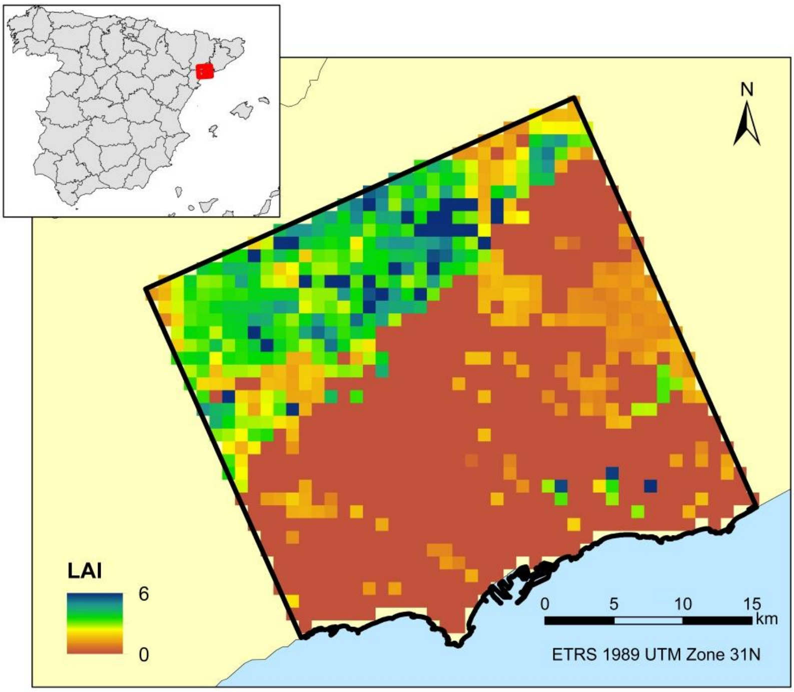

Fig. S1. Averaging 46 LAI (1x1 km) products from Moderate Resolution Imaging Spectroradiometer (MODIS. NASA http://modis.gsfc.nasa.gov/) collected each 8 days during the year 2014 in the Tarragona County, Spain.

Table S2. PAHs energies of phase transition (dUow, dUaw, dUoa).

Energies of phase transition	Naphthalene	Anthracene	Phenanthrene	Pyrene	Fluoranthene	Benzo (*a*) pyrene	Reference
dUaw (J mol^{-1})	44650	48800	53420	47630	57860	36890	Beyer et al., 2002
dUow (J mol^{-1})	-15700	-19700	-20520	-23930	-23750	-25400	Beyer et al., 2002
dUoa (J mol^{-1})	-60350	-68500	-73950	-71560	-81610	-62290	Beyer et al., 2002

Table S3. PAHs' diffusivity in air and water (Da and Dw) at 298 K.

Chemical' diffusivity in water and air (298K)	Naphthalene	Anthracene	Phenanthrene	Pyrene	Fluoranthene	Benzo (*a*) pyrene	Reference
D_a (J mol^{-1})	2.38×10^{-2}	1.92×10^{-2}	1.92×10^{-2}	1.77×10^{-2}	1.77×10^{-2}	1.53×10^{-2}	Ha and Kwon, 2010
D_w (J mol^{-1})	2.96×10^{-6}	2.09×10^{-6}	1.85×10^{-6}	1.96×10^{-6}	1.85×10^{-6}	2.05×10^{-6}	Shor et al., 2003

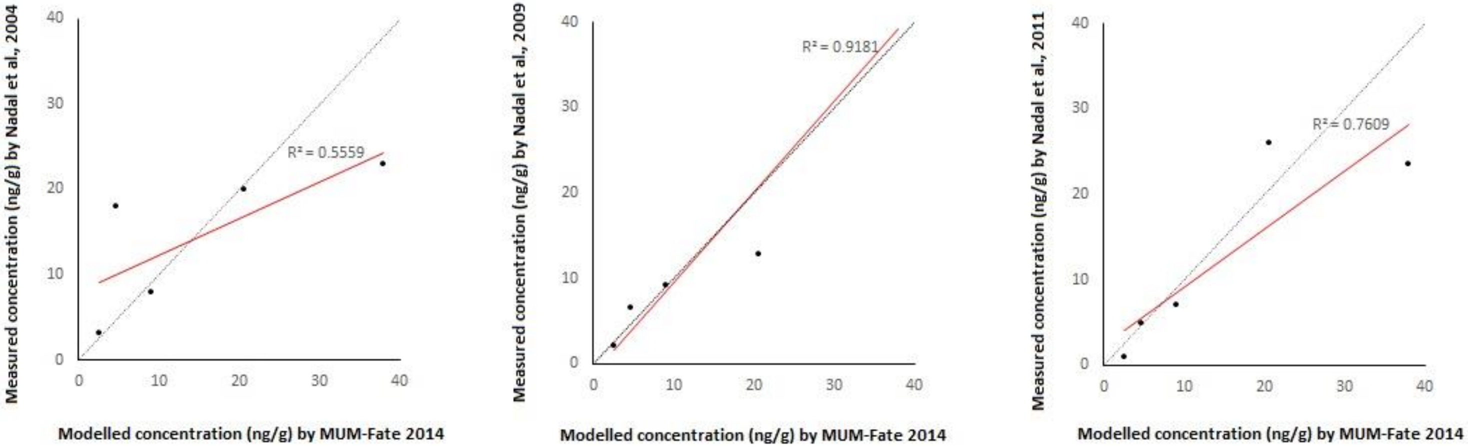

Fig. S2. Correspondence between modelled soil concentrations by MUM-Fate in 2014 and measured soil concentrations in 2004, 2009 and 2011 in Tarragona County, Spain. Red line represents the correlation between the measures and the dashed black line represents the 1:1 relationship.

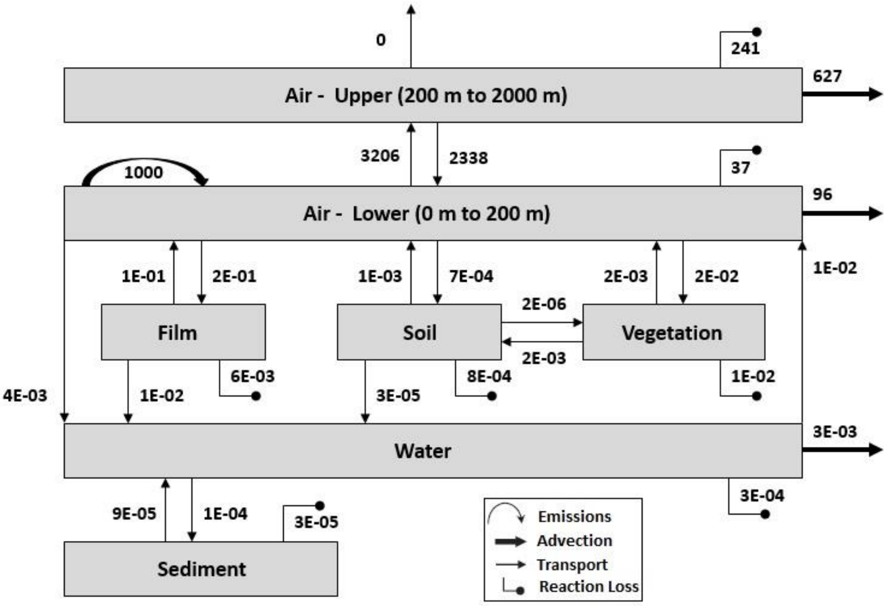

Fig. S3. MUM-Fate estimated rates of chemical movement and transformation for Naphthalene based on an emission of 1 mol h^{-1} into air. Transport rates are expressed in mmol h^{-1}.

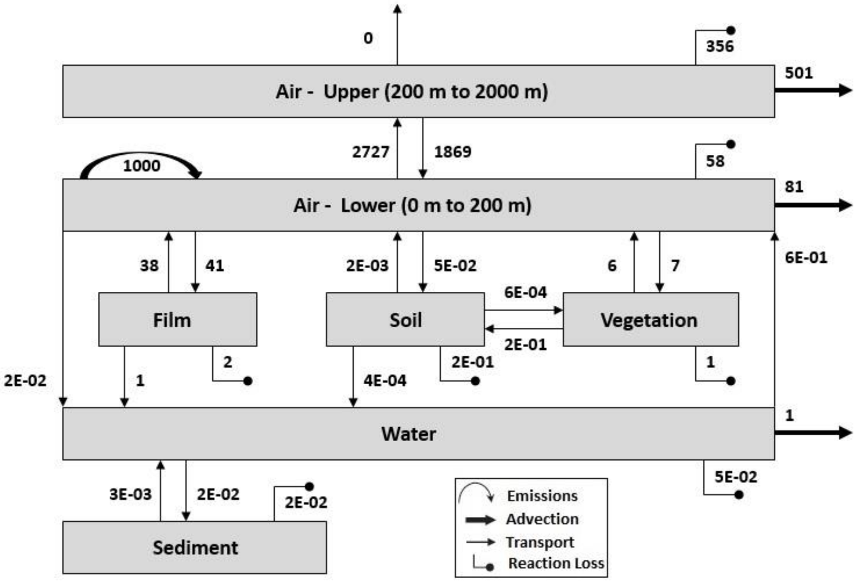

Fig. S4. MUM-Fate estimated rates of chemical movement and transformation for Anthracene based on an emission of 1 mol h^{-1} into air. Transport rates are expressed in mmol h^{-1}.

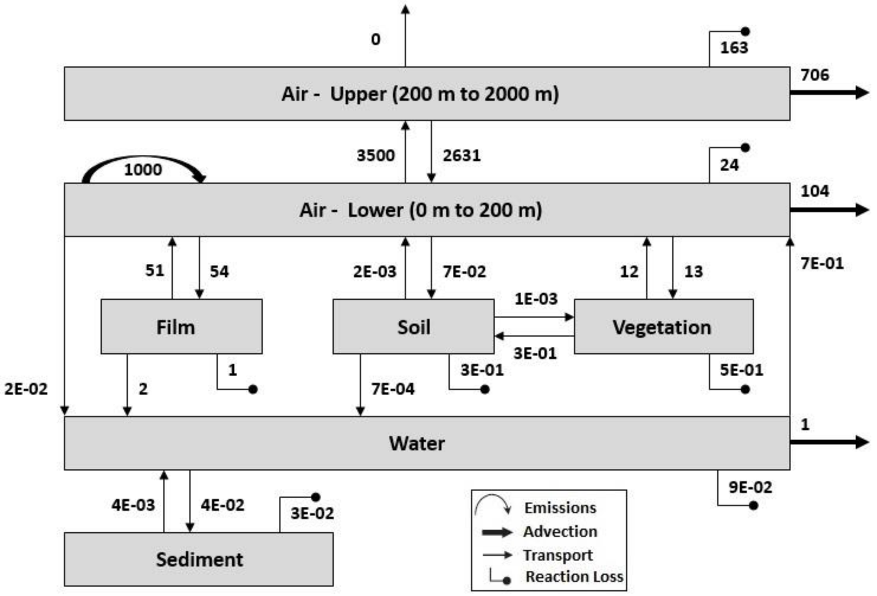

Fig. S5. MUM-Fate estimated rates of chemical movement and transformation for Phenanthrene based on an emission of 1 mol h^{-1} into air. Transport rates are expressed in mmol h^{-1}.

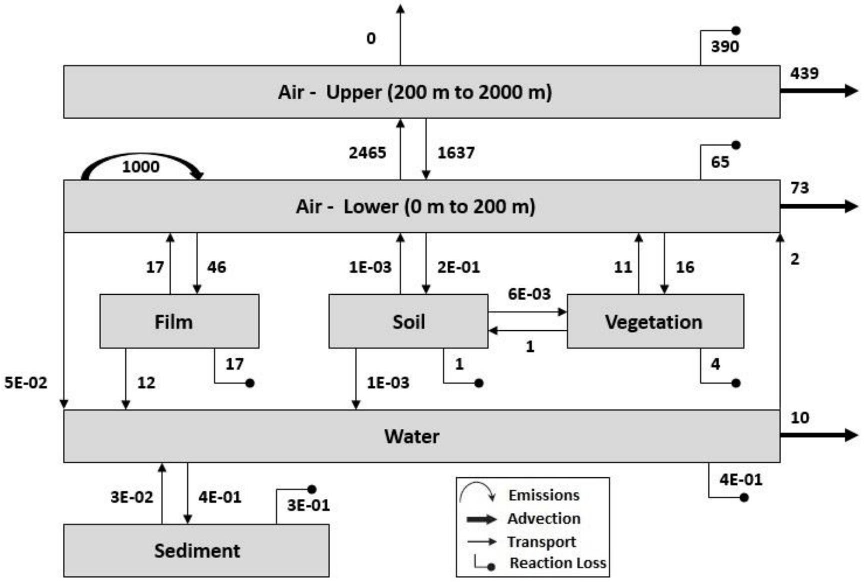

Fig. S6. MUM-Fate estimated rates of chemical movement and transformation for Pyrene based on an emission of 1 mol h^{-1} into air. Transport rates are expressed in mmol h^{-1}.

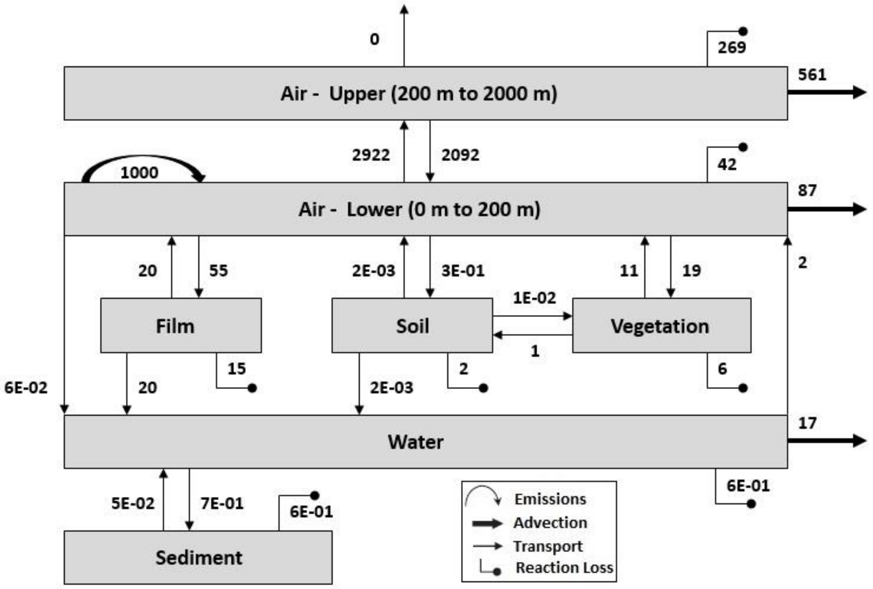

Fig. S7. MUM-Fate estimated rates of chemical movement and transformation for Fluoranthene based on an emission of 1 mol h^{-1} into air. Transport rates are expressed in mmol h^{-1}.

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