TESIS DOCTORAL

CARACTERIZACIÓN QUÍMICA Y DISTRIBUCIÓN DE IONES INORGÁNICOS E HIDROCARBUROS EN EL MATERIAL PARTICULADO ATMOSFÉRICO DEL SURESTE ESPAÑOL

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DOY MI CONFORMIDAD

Para que la presente memoria titulada “Caracterización química y distribución de iones inorgánicos e hidrocarburos en el material particulado atmosférico del sureste español”, realizada bajo la dirección de la Dra. Dña. Montserrat Varea Morcillo y el Dr. D. Juan Gil Moltó, sea presentada por Dña. Carolina Chofre Valencia para optar al grado de Doctora.

Elche, 13 de julio de 2017

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AUTORIZAN

Que la presente memoria titulada “Caracterización química y distribución de iones inorgánicos e hidrocarburos en el material particulado atmosférico del sureste español”, realizada en este departamento bajo su dirección, sea presentada por Dña. Carolina Chofre Valencia para optar al grado de Doctora.

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Los directores

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Resumen

En las últimas décadas, el material particulado ha sido y sigue siendo, objeto de estudio y control por tratarse de uno de los contaminantes que causa daños, tanto a la salud, como a los ecosistemas, el mantenimiento de las construcciones, etc.

La materia particulada es nociva, tanto por su tamaño, como por su composición, dependiendo estas características de diversos factores, como son sus fuentes de emisión o la meteorología. En la investigación realizada se estudia la composición de la PM en iones inorgánicos solubles e hidrocarburos (*n*-alcanos y PAH) en la ciudad de Elche, un escenario urbano mediterráneo, pero con la peculiaridad de presentar la mayor concentración de palmeras de toda Europa. El periodo de estudio ha resultado tener una meteorología atípica, pues se registraron elevadas tasas de precipitación y un reducido número de días bajo la influencia de periodos de estabilidad atmosférica.

Por primera vez en la ciudad, se han obtenido datos sobre la fracción submicrométrica (PM1). Este tamaño de partícula resulta ser potencialmente más nociva para la salud por penetrar a niveles más profundos del sistema respiratorio, y esto ha suscitado el interés de los investigadores en los últimos años. Los resultados obtenidos en el estudio de los iones inorgánicos solubles en agua, se compararon con datos anteriores de la misma zona, observándose una disminución de la concentración de la mayoría de estos iones, al igual que de los hidrocarburos, a causa de la meteorología acontecida durante el año de estudio, de la disminución de gases precursores y de la caída de la actividad de construcción debido a la crisis de los últimos años. Se realizaron análisis de PCA para identificar el origen de los compuestos inorgánicos asociados a la fracción submicrométrica, obteniéndose tres fuentes principales: secundario a $(NH_4)_2SO_4$ y NH_4NO_3, tráfico y resuspensión de polvo del suelo.

Con este trabajo también se pretende ampliar el conocimiento sobre los niveles de PAH y registrar los primeros datos sobre *n*-alcanos en la zona. Los resultados de los análisis de C_{max}, CPI y %WNA revelaron que, aunque la fuente predominante de *n*-alcanos sea antropogénica, en la ciudad de Elche hay una mayor influencia de los hidrocarburos biogénicos frente a otras áreas urbanas, sobre todo en verano, debido a la emisión de las numerosas palmeras repartidas por toda la ciudad.

Abstract

In the last decades, the particulate material has been, and still is, an object of study and control because it causes damages to the health, to the ecosystems, to maintenance of the constructions, etc.

Particulate matter is harmful, both because of its size and because its composition, depending on these characteristics of several factors, such as emission sources or meteorology. The studies carried out are focused on the composition of the PM in soluble inorganic ions and hydrocarbons (n-alkanes and PAH) in the city of Elche, a Mediterranean urban location, but with the peculiarity of presenting the highest concentration of palm trees in Europe. The study period had an atypical meteorology, with high precipitation rates and a reduced number of days under the influence of atmospheric stability.

For the first time in the city, information about submicron fraction (PM1) has been obtained. This particles turns out to be potentially more harmful to the health because are able to penetrate deep into the human respiratory system, and this has caused the interest of many researches in the last years. The results obtained in the study of soluble inorganic ions in water were compared with previous known data from the same area. A decrease in the concentration of most of these ions, as well as in the hydrocarbons, has been observed, due to the meteorological conditions during the study period, to the decrease of gaseous precursors and to a fall in the construction activities. PCA analyses were employed to distinguish the origin of the inorganic compounds associated with the PM1 fraction, and three main sources have been identified: secondary $(NH_4)_2SO_4$ and NH_4NO_3, local traffic, and soil dust.

This work also tries to extend the knowledge on PAH levels and to register information on *n*-alkanes, for the first time in the city of Elche. C_{max}, CPI and %WNA results revealed that, although there were a predominant contributions of anthropogenic sources to *n*-alkanes levels, in the city of Elche there was a major influence of biogenic hydrocarbons emissions, compared to other urban areas, especially in summer, due to the emission of the numerous palm tree groves distributed spread over the city.

1. Introducción

Se ha demostrado que la materia particulada atmosférica (PM) causa numerosos problemas sobre la salud humana, el clima y los ecosistemas, poniéndose de manifiesto, en los últimos años, la importancia del estudio de las partículas finas y ultrafinas. La magnitud del impacto está fuertemente ligada al tamaño y composición de las partículas, ya que estas características de la PM determinan la región del sistema respiratorio donde se depositan, así como las propiedades químicas, toxicológicas y ópticas de los aerosoles.

La materia particulada (PM) es una mezcla heterogénea y compleja, que cambia en el tiempo y en el espacio, abarcando muchos componentes químicos y características físicas diferentes. Cada componente puede tener múltiples orígenes, y cada fuente, generar varios componentes. Identificar y cuantificar la influencia de componentes específicos o mezclas, con sus fuentes de emisión, y relacionarlas con los impactos causados sobre el medioambiente, especialmente cuando las partículas interactúan con otros contaminantes, representa una de las tareas más difíciles en este área de investigación. Los conocimientos actuales no permiten una cuantificación precisa, ni una clasificación definitiva, de los efectos sobre la salud de las emisiones de la PM procedentes de diferentes fuentes o de sus componentes individuales. De hecho, dichos efectos pueden ser el resultado de múltiples componentes que actúan sobre diferentes mecanismos fisiológicos. Por todo ello, es necesario ampliar la información sobre la composición del aerosol atmosférico para modelar el forzamiento del clima, implementar medidas de mitigación orientadas a las fuentes de emisión, así como evaluar las implicaciones de la PM en la salud humana.

En este trabajo se investiga la composición inorgánica, soluble en agua, y orgánica de la PM en una zona urbana, entre octubre de 2008 y diciembre de 2009, para ampliar la información sobre los factores que determinan las concentraciones de estos contaminantes en un escenario típico del clima mediterráneo. La elección de una zona urbana radica en el hecho de que, debido a su alta densidad de población y al mayor impacto de las actividades antropogénicas, en estas zonas, la población es más susceptibles a los efectos sobre la salud asociados a la inhalación de partículas (Fotourehchi, 2016). La influencia de las variables meteorológicas sobre las variaciones temporales de los niveles de la PM durante esta campaña ha sido descrita en un trabajo anterior (Galindo et al., 2011). Así mismo, la variación en concentración másica y composición inorgánica de la PM en el área de estudio, bajo diferentes regímenes meteorológicos, han sido estudiadas en Nicolás et al., 2009. Sin embargo, solo se dispone de información preliminar sobre la composición orgánica, y ésta se limita a los hidrocarburos policíclicos aromáticos (PAH, *Polycyclic Aromatic Hydrocarbons*) (Gil-Moltó et al., 2009, Varea et al., 2011). Con el fin de ampliar dicha información, como trazadores de emisiones primarias del tráfico y otras fuentes antropogénicas, se incluyen en este trabajo, además, de los PAH, los hidrocarburos alifáticos lineales (*n*-alcanos) que aportan información no sólo sobre emisiones antropogénicas sino también sobre biogénicas.

Así mismo, se presentan los primeros datos sobre los niveles y composición de la materia particulada submicrométrica (PM1) en el área de estudio. El interés sobre el conocimiento de la PM1 ha aumentado en los últimos años debido a su impacto negativo, especialmente sobre la salud humana, la conservación de edificios históricos y la mayor eficiencia de extinción de la radiación, causando una reducción significativa de la visibilidad (Franck et al., 2011, Polichetti et al., 2009, Horemans et al., 2011, Shi et al., 2014). La PM1 se genera principalmente en procesos antropogénicos (Saarikoski et al., 2008, Pateraki et al., 2012, Vecchi et al., 2008) y, por lo tanto, está relacionada en gran medida con las actividades humanas.

Antes de exponer los resultados obtenidos en el presente trabajo, con el fin de proporcionar una base de referencia a la hora de interpretarlos, se define brevemente el concepto de PM, su clasificación por tamaños y su composición química. Igualmente, se amplía la información relativa a los compuestos objeto de estudio en este trabajo, iones inorgánicos solubles y materia orgánica (*n*-alcanos y PAH), y se describen, finalmente, las características meteorológicas y orográficas de la zona de estudio, haciendo hincapié en las condiciones ambientales registradas durante el periodo 2008-2009.

1.1. Material particulado atmosférico

La materia particulada se define como un sistema disperso, constituido por partículas sólidas y/o líquidas suspendidas en el aire (Mészáros, 1999), cuyas características físicas, como su tamaño y su composición química, están influenciadas por su origen.

Las partículas son producidas por procesos de condensación, combustión o desintegración mecánica de la superficie terrestre (Whitby, 1978). Una parte de estas partículas es emitida a la atmósfera por fuentes en la superficie (partículas primarias), mientras que otra se produce en el aire en procesos físico químicos de conversión de gas a partícula (partículas secundarias). Su origen puede ser natural (aerosol marino, producción biogénica, etc.) o antropogénico (emisión de tráfico…). Estos mecanismos de formación condicionan también su tamaño, que en función del ámbito de estudio suele adoptar distintos rangos granulométricos (Seinfeld y Pandis, 1998). Así, mientras que en el campo de las ciencias atmosféricas el límite entre las denominadas *partículas finas*, formadas por mecanismos de nucleación y de acumulación, y las *partículas gruesas* se encuentra en el diámetro de 1 µm, en otras áreas, como la epidemiológica, está distinción se hace en 2,5 µm (Figura 1).

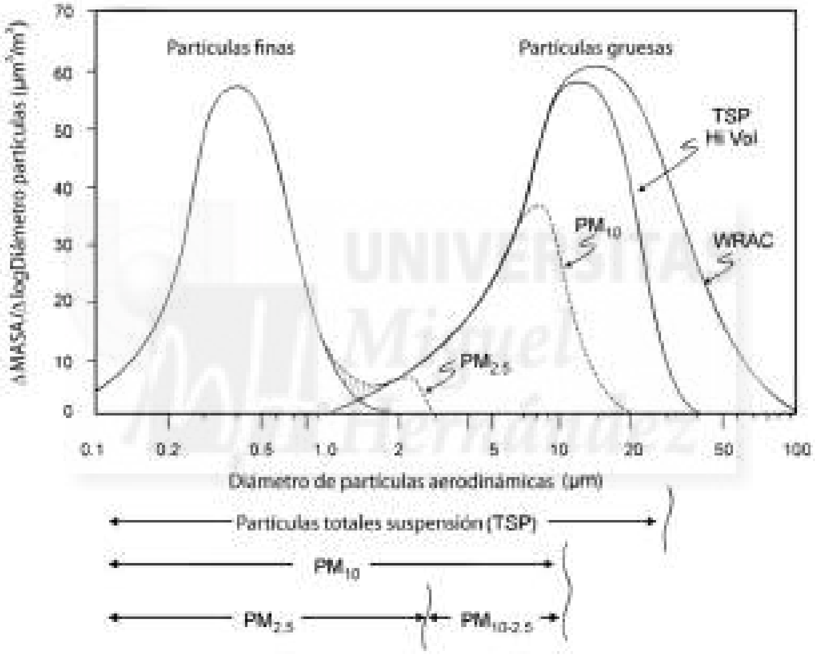

Figura 1. Distribución ideal de materia particulada atmosférica mostrando la moda fina y gruesa, y las fracciones recogidas por cabezales selectivos de tamaño. (WRAC es el “Wide Range Aerosol Clasiffier” el cual recoge el total de la moda gruesa) (Adaptado de Wilson y Suh, 1997).

Con el fin de simular el complejo proceso de penetración de las partículas atmosféricas en el sistema respiratorio humano, y haciendo referencia al tamaño de corte de los sistemas de captación, se diferencian las fracciones PM10, PM2,5 y PM1. Estas se definen como la masa de partículas que atraviesa un cabezal de diámetro aerodinámico selectivo de 10, 2,5 o 1 µm, con una eficiencia de corte del 50%. Las fracciones PM10 y PM2,5 presentan gran similitud con las denominadas fracciones torácica y respirable de alto riesgo, respectivamente, donde la torácica engloba a las partículas inhaladas que penetran en el sistema respiratorio más allá de la laringe, y la respirable de alto riesgo a las partículas inhaladas que llegan a la región alveolar. Además, en el ámbito de calidad del aire se suelen utilizar ampliamente los términos de, *fracción gruesa* de la materia particulada para la diferencia PM10-PM2,5, *fracción fina* para la PM2,5 o incluso a la diferencia PM2,5-PM1, y *fracción ultrafina* o *submicrométrica* para la PM1.

Las partículas de la fracción gruesa son generadas principalmente en procesos mecánicos naturales, pero también en procesos antropogénicos. Provienen principalmente de la corteza terrestre, del aerosol marino o de partículas orgánicas biogénicas. Por otra parte, las partículas más finas provienen principalmente de procesos de combustión o procesos de conversión de gas a partículas dentro de la atmósfera.

Entre los distintos componentes de la PM, pueden encontrarse: (a) Elementos y compuestos procedentes de la corteza terrestre (material crustal), como compuestos derivados de Si, Al, Fe, Na, K, Ca y Mg. (b) Compuestos procedentes del aerosol marino, siendo el cloruro de sodio (NaCl) el mayoritario. (c) Elementos traza de origen natural, principalmente metales, o también de origen antropogénico, como emisiones relacionadas con la producción energética y las emisiones de algunos procesos industriales, además del tráfico rodado. (d) Iones secundarios, como sulfato (SO_4^{-2}), nitrato (NO_3^-) y amonio (NH_4^+). (e) Carbono orgánico y elemental, este último es principalmente de origen antropogénico, mientras que el orgánico se emite directamente a la atmósfera o se forma por condensación de compuestos orgánicos semivolátiles, pudiendo ser de origen tanto natural como antropogénico.

1.2. Iones inorgánicos

Las especies inorgánicas solubles en agua, en las zonas urbanas, pueden representar hasta el 30% de la concentración másica de la PM10 (Putaud et al., 2010). Se sabe que refuerzan los efectos nocivos del aerosol atmosférico sobre la salud humana y el ambiente (Camargo et al., 2006, Liang et al., 2016), contribuyendo en la descomposición de los edificios de piedra y los monumentos (Nava et al., 2010) y la reducción de la visibilidad debido a los efectos de dispersión, en particular del $(NH_4)_2SO_4$ (DeBell, 2006). La contribución de cada uno de los componentes inorgánicos a los niveles de PM es altamente variable dependiendo de las características climáticas, meteorológicas y geográficas, así como del tamaño de la PM considerada.

Los iones primarios son liberados directamente a la atmósfera por diferentes fuentes naturales y antropogénicas, prevaleciendo en la fracción gruesa (Kouyoumdjian y Saliba, 2006). Entre los más abundantes se encuentran el Na^+ y el Cl^-, que proceden principalmente de la sal marina, y el Ca^{+2}, que puede ser emitido por la resuspensión del suelo o/y el polvo de la carretera, las actividades de construcción, y los procesos industriales (Chen et al., 2010, Chow et al., 2004) y que cuya parte soluble, en el área de estudio, representa más del 50% del calcio total (Yubero et al., 2011).

Sulfato, nitrato y amonio son los principales iones secundarios de la PM que, aunque pueden ser emitidos directamente a la atmósfera por procesos naturales, como por ejemplo el sulfato que está presente en el aerosol marino, la mayor parte es producida por reacciones químicas de precursores gaseosos, emitidos por fuentes antropogénicas (NO_x, SO_2) y biogénicas (NH_3). La producción antropogénica de gases precursores de sulfato se debe mayoritariamente a procesos de combustión de carburantes fósiles, mientras que el origen natural del SO_2 depende de las emisiones biogénicas y volcánicas de sulfuro de hidrogeno (H_2S) y su posterior oxidación. El dióxido de azufre es oxidado a ácido sulfúrico, principalmente en gotitas de agua, por especies como H_2O_2 u O_3, y éste, en presencia de concentraciones de amoniaco gaseoso suficientemente altas, se neutraliza completamente para producir $(NH_4)_2SO_4$, que es uno de los componentes más comunes de la fracción fina (Lin, 2002, Harrison et al., 2004). La velocidad de formación del ácido sulfúrico a partir de SO_2 depende de la intensidad de la radiación solar y de la temperatura, de ahí que las máximas concentraciones se den durante la época estival (Meszáros, 1973, Querol et al., 1999). Por otro lado, la principal fuente de óxidos de nitrógeno (NO_x) en zonas urbanas es la combustión de carburantes fósiles, principalmente emitidos por el tráfico. La oxidación homogénea de NO_x, en presencia de radical hidroxilo, conduce a la formación de HNO_3 gaseoso que, posteriormente, puede reaccionar con amoniaco para formar NH_4NO_3 en la fracción fina. Sin embargo, la constante de equilibrio de esta reacción es altamente dependiente de la temperatura, y la formación de ácido nítrico en fase gaseosa y amoníaco se favorece con el aumento de la temperatura ambiente (Mozurkewich, 1993), alcanzándose máximas concentraciones de nitrato de amonio en invierno y mínimos en verano (Querol et al., 2004). Por otro lado, el ácido nítrico tiende a reaccionar con partículas de la sal marina o partículas del suelo, dando lugar a $NaNO_3$ y $Ca(NO_3)_2$ estables en la fracción gruesa. Por esta razón, la distribución del tamaño de los nitratos depende en gran medida de la ubicación y las condiciones meteorológicas (Zhuang et al., 1999, Metzger et al., 2006, Moya et al., 2001).

Como ya se ha comentado, las variaciones espaciales y temporales de las concentraciones de los iones inorgánicos pueden ser muy significativas, ya que están controladas por numerosos factores tales como las características climáticas y orográficas, las tasas de emisión de precursores gaseosos, o el transporte a largo plazo de contaminantes. Por ejemplo, entre 2007 y 2008, en España se experimentó un descenso del 12,7, 55 y 7,7%, respectivamente, para NO_x, SO_x y NH_3, debido al descenso en el consumo de combustibles con alto contenido en azufre para la generación de electricidad, a la introducción de tecnologías de reducción y a la recesión económica mundial (Informe técnico EEA7, 2010). Además, los países mediterráneos son frecuentemente afectados por intrusiones de polvo sahariano que contribuyen a incrementar los niveles de elementos de la corteza, así como los iones secundarios (Koçak et al., 2007). Así mismos, existen estudios que han demostrado que la formación de sulfato y nitrato está favorecida por las reacciones de los óxidos presentes en partículas de polvo mineral (Usher et al., 2003, Hwang y Ro, 2006).

1.3. Materia orgánica

En los últimos años, el mayor interés se ha centrado en la fracción orgánica de la PM, que cubre miles de compuestos individuales de origen primario y secundario. Los compuestos orgánicos son componentes importantes y representan una gran parte de la masa de la PM, cuya identificación, fuentes y origen se han utilizado como trazadores para las evaluaciones de la calidad del aire (Giri et al., 2013, Medeiros y Simoneit, 2007, Schauer y Cass, 2000). Sin embargo, tanto sus efectos como sus procesos de formación o la identificación de sus fuentes de emisión, dependen en gran medida de la distribución por tamaño de partícula (Lighty et al., 2000), cuyo estudio, sobre todo en PM10 y PM2,5, se ha convertido en el objeto de varios trabajos realizados en todo el mundo, principalmente en zonas urbanas y otras zonas fuertemente industrializadas, pero el conocimiento sobre la PM1 sigue siendo limitado (Barrero y Cantón, 2007, Van Drooge et al., 2012).

En general, los distintos componentes del aerosol orgánico se distribuyen entre la fase vapor y/o sólida, dependiendo principalmente de la temperatura ambiente, su presión de vapor y su peso molecular (Simcik et al., 1998). Dentro de la PM, los diferentes compuestos orgánicos pueden encontrarse tanto en la fracción gruesa como en la fina, dependiendo principalmente de su origen, aunque las concentraciones más altas suelen asociarse con la fracción fina (Mirante et al., 2013, Tang et al., 2006).

La caracterización detallada de la materia orgánica de la PM está lejos de conseguirse, ya que varía mucho en función del entorno. Generalmente, se distinguen familias de compuestos que representan la mayor parte de la materia orgánica asociada al aerosol atmosférico. Entre las familias más habituales se encuentran los derivados carbonílicos, producidos por un gran número de fuentes diversas, en las que se incluyen procesos oxidativos, emisiones biogénicas directas, actividades antropogénicas, emisiones de automóviles, etc. También pueden destacarse los ésteres metílicos de ácidos carboxílicos, asociados frecuentemente a la quema de biomasa, los alcoholes alifáticos, los esteroles, los azúcares, los ácidos, los compuestos halogenados, los nitrados, etc., cuyos orígenes pueden ser múltiples y, por lo tanto, su uso como trazadores puede ser discutible (Alves et al., 2012). O bien, los hidrocarburos policíclicos aromáticos que, aunque representan una fracción muy pequeña de la materia orgánica total, pero debido a su carcinogenicidad, han centrado la atención principal de la mayoría de los trabajos publicados en este campo (Cancio et al., 2004, Duan et al., 2005, Wang et al., 2009).

Por otro lado, se suelen identificar ciertos compuestos orgánicos individuales (trazadores), que mediante técnicas de factorización de matriz positiva (PMF), y/o balances de masa química (CMB) proporcionan información sobre sus fuentes de emisión y su comportamiento (Aldabe et al., 2011, Richard et al., 2011, Yin et al., 2010, Zhang et al., 2009, Bi et al., 2008). Sin embargo, como estos compuestos individuales suelen ser emitidos por múltiples fuentes o formarse por diversos procesos, su utilización como trazadores directos de fuentes puede ser cuestionable. Por ello, se suelen utilizar las relaciones o ratios de diagnóstico moleculares como herramienta adicional para la conciliación de fuentes compuestas (Alves, 2008).

A continuación, se amplía brevemente la información sobre *n*-alcanos y policíclicos aromáticos (PAH), como objetos de investigación en esta memoria.

- ***n*-Alcanos**

Los *n*-alcanos son componentes mayoritarios de la fracción no polar del aerosol orgánico (Chow y Watson, 2007). Se trata de contaminantes primarios altamente resistentes a la degradación bioquímica y detectados en aerosoles a concentraciones relativamente altas (Pietrogrande et al., 2010, Young y Wang, 2002). Estos se originan mayoritariamente a partir de fuentes naturales como ceras epicuticulares vegetales, suspensión directa de pólenes, microorganismos e insectos (Simoneit, 1999), aunque también pueden ser emitidos por fuentes antropogénicas (Perrone et al., 2014, Fraser et al., 1999).

Las distribuciones porcentuales de *n*-alcanos son específicas de la naturaleza de la fuente, lo que permite extraer información sobre su origen. De hecho, las distribuciones porcentuales modales (en forma de campana) son típicas de los productos y desechos derivados del petróleo, mientras que la huella dactilar en forma de dientes de sierra, con la prevalencia de homólogos con número impar de carbonos, se asocia con las emisiones biogénicas (Bi et al., 2005). De forma similar, las relaciones entre concentraciones de compuestos con número impar y par de átomos de carbonos en la serie (CPI, *Carbon Preference Index*) puede indicar la prevalencia de unas fuentes respecto a otras (Alves, 2008). Así por ejemplo, mayor cantidad de *n*-alcanos de alto peso molecular (C_{27}-C_{33}), con un fuerte predominio de los homólogos con un número impar de carbonos, indicaría la emisión desde las hojas de árboles y muchas otras especies vegetales (CPI > 1), mientras que la emisión de vehículos se caracterizaría por el predominio de hidrocarburos con longitudes comprendidas entre C_{19} y C_{32} (CPI próximo a 1), con máximos en C_{25} para vehículos de gasolina y en C_{20} para vehículos pesados de motor diésel (Mazurek et al., 1989). También puede adaptarse el cálculo de CPI para identificar, o bien discriminar, entre algunas fuentes más concretas dentro de los orígenes más habituales de los hidrocarburos alifáticos (Bi et al., 2003, Górka et al., 2014). Además, también se utilizan otros parámetros como la contribución de los *n*-alcanos biogénicos (WNA, *Wax Normal Alkane*), o el porcentaje de la contribución de *n*-alcanos biogénicos (% WNA) (Kavouras y Stephanou, 2002).

- **Hidrocarburos policíclicos aromáticos**

Los PAH abarcan solo una pequeña fracción de la masa del aerosol atmosférico, pero representan una clase de contaminantes ambientales persistentes. La Comunidad Europea, entre otras, los incluye dentro de los contaminantes prioritarios a controlar (Figura 2), ya que algunos de ellos son conocidos por su carácter mutágeno y/o carcinógeno para todos los organismos vivos (Fang et al., 2002, Omar et al., 2006).

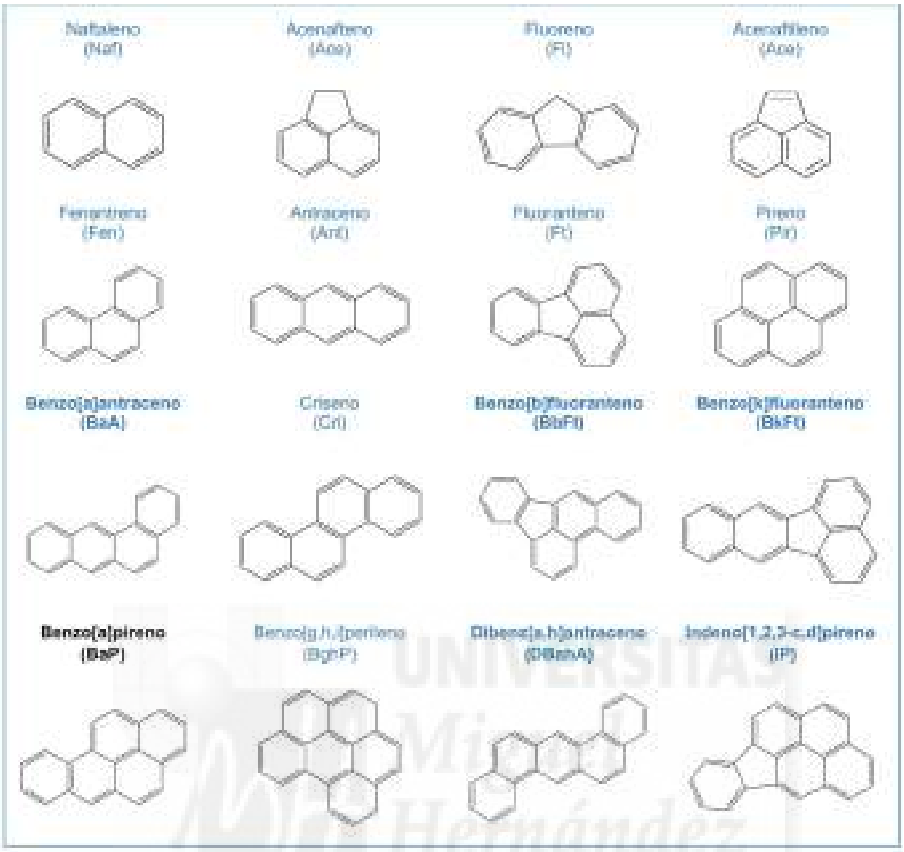

Figura 2. PAH que la Agencia de Protección Ambiental Americana (EPA, *Environmental Protection Agency*) aconseja controlar. Resaltados se muestran los PAH que la Comunidad Europea identifica como prioritarios.

La toxicidad y carcinogenicidad de estos compuestos muestran una fuerte dependencia estructural (Nisbet y LaGoy, 1992), habiendo sido demostrada de manera concluyente mediante ensayos con células bacterianas y humanas (Mukherji et al., 2002). Así, la Agencia Internacional para la Investigación del Cáncer (IARC, 1998), considera al benzo[*a*]pireno (BaP), congénere de cinco anillos, como el carcinógeno humano más potente, estableciéndose como marcador carcinógeno de los PAH, con un valor objetivo de 1 ng/m^3 de promedio anual en la fracción PM10 (Directiva 2004/107/CE). Sin embargo, para medir el riesgo que representan, en general, los PAH sobre la salud de la población se debe tener en cuenta el potencial relativo de riesgo de cada PAH individual, que habitualmente se calcula a partir de su concentración multiplicada por su factor equivalente tóxico (TEF), obteniéndose con la suma de todos ellos un índice de toxicidad más real, siendo el más utilizado el denominado benzo[a]pireno equivalente (BaPE) (Yassaa et al., 2001).

La emisión de PAH se produce siempre como una mezcla de varios congéneres y depende en gran medida de su origen. Por ello, las relaciones relativas o ratios entre las concentraciones de algunos de ellos, se consideran (a menudo solo como una suposición) como características de una fuente de emisión determinada. La mayoría de estas proporciones involucran parejas de PAH con la misma masa molecular y propiedades fisicoquímicas similares. De esta forma, para la identificación de sus principales fuentes de emisión se utilizan diferentes ratios de diagnóstico, que permiten distinguir entre la emisión desde derivados de productos petrolíferos, de combustibles fósiles y de quema de biomasa entre otros (Tabla 1).

Tabla 1. Ratios de diagnóstico (Tobiszewski y Namiésnik, 2012, Grimmer et al., 1983).

PAH ratio	Rango	Fuente
Ft / (Ft + Pir)	0,26	Combustión de biomasa
	0,4	Combustión de gasóleo
	0,6-0,7	Combustión de diésel
	>0,5	Combustión de carbón
Ant / (Ant + Fen)	<0,1	Combustión de petróleo
	>0,1	Pirogénico
Fl / (Fl + Pir)	<0,5	Combustión de gasóleo
	>0,5	Combustión de diésel
BaA / (BaA + Chry)	0,2-0,35	Combustión de carbón
	>0,35	Emisión de vehículos
	<0,2	Combustión de petróleo
BaP / (BaP + BeP)	0,5	Partículas nuevas
	<0,5	Fotolisis
BeP / (BeP + BaP)	0,6-0,8	Tráfico
	0,3	Combustión de madera
IP / (IP + BghiP)	0,22	Combustión de gasóleo
	0,35-0,7	Combustión de diésel
BbFt / BkFt	2,5-2,9	Fundiciones de aluminio
BaP / BghiP	<0,6	Emisiones que no provienen del tráfico
	>0,6	Tráfico

1.4. Características de la zona y del periodo de estudio

Las características geográficas, orográficas, climáticas y demográficas de la zona de estudio, son factores importantes que modifican no solo la concentración másica de la PM, sino también su composición, debido a que, por ejemplo, los procesos de dispersión, los mecanismos de transporte o la formación química de las partículas dependen de parámetros como la velocidad del viento, la velocidad o/y la radiación solar (Keary et al., 1998; Akpinar et al., 2008; Lin y Lee, 2004, Richmond-Bryant et al., 2009).

El clima seco mediterráneo, del que disfruta la zona de estudio, cuenta con veranos calurosos, inviernos suaves y escasas precipitaciones, concentradas principalmente en primavera. Además, entre las estaciones del año, no existen excesivos gradientes térmicos, y disfruta de un elevado número de horas de radiación solar, con valores máximos en primavera y verano. Respecto al viento, aproximadamente la mitad de los días del año se producen brisas marinas, principalmente durante las estaciones cálidas.–En cuanto a su dirección, en invierno y otoño procede principalmente del noroeste, en verano la predominante es del sureste y en primavera su tendencia es más irregular.

En general, la cuenca mediterránea occidental se caracteriza por presentar una dinámica atmosférica peculiar que genera una clara estacionalidad en los niveles registrados de la PM. Entre los principales factores se encuentran, la influencia del anticiclón de las Azores en la meteorología, la existencia de cadenas montañosas próximas a la costa, los débiles gradientes de presión sobre el Mediterráneo como consecuencia de las bajas térmicas sobre el Sahara y la Península Ibérica, las intensas brisas favorecidas por condiciones de poca advección y la escasa precipitación durante el verano y, además, el contraste estacional de temperaturas y humedad (Querol et al., 2009). De esta forma, según la zona de estudio, la PM puede estar sometida, tanto a efectos producidos por dinámicas de circulaciones de masas de aire a nivel mesoescalar (p.ej. brisas de mar y montaña), como de transporte a nivel sinóptico (p.ej. advecciones de masas de aire procedentes del Atlántico). Concretamente en Elche, durante el periodo de estudio (octubre 2008 a diciembre de 2009), se registraron condiciones climatológicas atípicas para una zona de la vertiente mediterránea como se describió en Galindo et al., 2011. Entre las características meteorológicas a destacar se encuentran:

a) Un invierno especialmente lluvioso, ya que durante los meses de enero y marzo se registraron precipitaciones mensuales acumuladas superiores a la media, lo que produjo un mayor lavado de la atmósfera y del suelo, disminuyendo la resuspensión del polvo.

b) Un reducido número de días (3,5% de los muestreados) bajo condiciones de estabilidad atmosférica de poca intensidad, que se producen de forma más habitual durante finales del otoño y durante el invierno (Jorba et al., 2013, Nicolás et al., 2011). Estos episodios, están asociados con sistemas de alta presión a gran escala, con débiles gradientes de presión superficial que producen vientos prácticamente en calma y alturas de capa de mezcla por debajo de sus espesores normales, que no solo favorecen la acumulación de los contaminantes primarios a baja altitud, sino también la formación fotoquímica de aerosoles secundarios (Mira-Salama et al., 2008, Yubero et al., 2015).

c) Un número similar de días (26%) bajo el efecto de episodios de intrusión sahariana, más frecuentes en las estaciones cálidas, y que habitualmente afectan en gran medida a toda Europa, alcanzándose cantidades anuales del orden de 100 millones de toneladas (D'Almeida, 1986), y especialmente a la zona más occidental. El transporte de masas de aire procedentes de África ocurre bajo la influencia de un centro de baja presión sobre el suroeste de la Península Ibérica y un anticiclón en el noreste de África, produciendo un aumento significativo de los niveles de la fracción gruesa, modificando las concentraciones habituales de los elementos crustales, pero también las de sulfato y nitrato, posiblemente por la adsorción de gases ácidos como el SO_2 y el HNO_3 por parte del polvo mineral (Koçak et al., 2004; Nicolás et al., 2008).

Como consecuencia de esas características durante dicho periodo se observó que:

- Las concentraciones medias de PM2,5 y PM10, registradas durante el invierno, fueron muy inferiores a las habituales, mientras que las concentraciones de PM1 no mostraron diferencias estadísticamente significativas entre verano e invierno.

- Durante el invierno, las tres fracciones, submicrométrica, fina y gruesa, fueron emitidas en su mayor parte por las mismas fuentes, con el tráfico como fuente principal. Sin embargo, durante la estación cálida predominaron otras fuentes, como la generación de partículas secundarias por reacciones fotoquímicas atmosféricas o polvo mineral sahariano, que tuvieron un impacto diferente en cada tamaño de fracción.

- La temperatura y la radiación solar mostraron una buena correlación con la fracción gruesa durante todo el período, como consecuencia de mayores tasas de emisión de fuentes naturales y de una mayor formación fotoquímica de aerosoles secundarios en verano.

- Las tres fracciones de tamaño mostraron buenas correlaciones negativas con la velocidad del viento durante el invierno, lo que indica que el principal efecto de los vientos de la estación fría fue la dispersión de los aerosoles atmosféricos.

El conocimiento de estas variaciones, así como del origen de las mismas, ayudará posteriormente al estudio y justificación de las variaciones observadas, tanto de las concentraciones de los compuestos orgánicos, como de los niveles de iones solubles en la PM.

2. Objetivos

El objetivo principal que se plantean en este trabajo es cuantificar la concentración de iones inorgánicos solubles en agua e hidrocarburos (*n*-alcanos y PAH) presentes en la PM. A partir de ellos, estudiar su distribución entre las fracciones de tamaños PM10, PM2,5 y PM1, determinar las fuentes de emisión, así como los factores que afectan a la variación estacional de sus niveles.

Este objetivo principal se desglosa en los siguientes objetivos específicos:

- Estudiar la variación interanual de las concentraciones de iones inorgánicos solubles en función de la meteorología y de factores antropogénicos.
- Determinar la contribución de los iones inorgánicos a las diferentes fracciones de la PM.
- Analizar los iones solubles asociados a la fracción PM1, determinar su variación estacional y origen.
- Estudiar la variación estacional de los hidrocarburos.
- Determinar la distribución de los hidrocarburos entre las distintas fracciones de la PM y las fuentes de emisión.
- Evaluar el índice de toxicidad de los PAH en Elche.
- Observar la influencia de fuentes biogénicas, como el palmeral, en los niveles de *n*-alcanos.

3. Área de estudio, materiales y métodos empleados

Elche es una ciudad de tamaño medio (<200.000 habitantes) que se encuentra situada en la zona centro-sur de la provincia de Alicante, a unos 12 km del mar Mediterráneo y con zonas considerablemente áridas en su parte norte (Figura 3). La ciudad es atravesada por el río Vinalopó, de escaso caudal, pero con una cuenca de gran profundidad, que divide la ciudad de norte a sur. Además, en el año 2000 la Unesco declaró como Patrimonio de la Humanidad a su palmeral, numerosos y abundantes campos de palmeras que cubren la superficie de la ciudad de manera desigual (Caballero et al., 2012). El nivel de contaminación en la zona urbana, en principio, está fundamentalmente condicionado por las emisiones del tráfico y las actividades de la construcción, ya que la industria, principalmente del calzado, actualmente se encuentra ubicada en los alrededores de la ciudad.

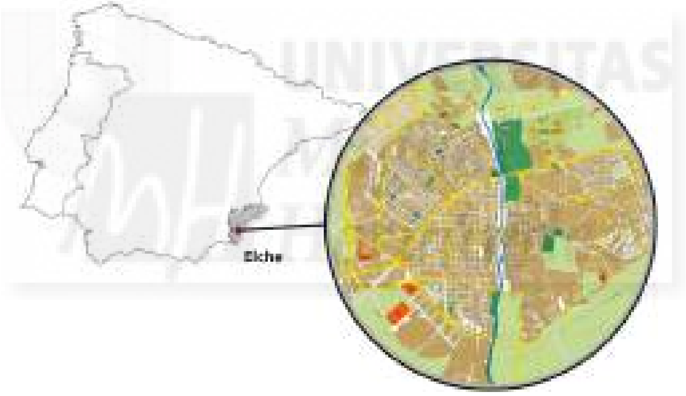

Figura 3. Elche-ubicación y entorno.

3.1. Puntos de muestreo y captación

Dado el marco de estudio, para cumplir con los objetivos propuestos, se realizó una serie de captaciones en dos puntos de muestreo, ubicándose el equipamiento en azoteas a una altura de 15 m aproximadamente. El punto principal de muestreo (UMH) se localizó en el campus de la Universidad Miguel Hernández, tratándose de un área abierta, muy ventilada y cerca de una avenida con cuatro carriles de circulación (~37.000 vehículos diarios). El segundo punto (PTG), se colocó en un jardín de palmeras del centro de la ciudad, a unos 800 m al suroeste del emplazamiento anterior (Figura 4).

Figura 4. Ubicación de los puntos de muestreo.

Los muestreos se realizaron durante 24 horas, cuatro días a la semana, durante el periodo comprendido entre octubre de 2008 y diciembre de 2009. La captación se realizó de manera simultánea en ambas localizaciones, para las fracciones PM10, PM2,5 y PM1 en el punto principal y, solo para PM10 y PM1 en PTG, utilizando filtros de fibra de vidrio recubiertos de teflón (T60A20-47 mm, Pallflex). Los muestreos comenzaron aproximadamente a las 10 AM, hora local, realizándose con captadores de bajo volumen Derenda 3.1 (2,3 m^3/h), clasificados como una unidad de referencia según las directrices europeas CEN 12341 y CEN 14907.

Los filtros, previamente a la captación, se lavaron con acetona pura en un baño de ultrasonidos, y se calentaron posteriormente a 300 ºC durante 24 horas para eliminar cualquier resto de componentes orgánicos. A continuación, los filtros se acondicionaron al menos durante 24 horas en condiciones de humedad relativa de 50 ± 5%, a una temperatura de 20 ± 1°C, antes y después de la captación. Tras el acondicionamiento, se pesaron utilizando una balanza electrónica (Ohaus, modelo AP250D) con una sensibilidad de 10 µg.

Los valores obtenidos en los puntos de muestreo se complementaron con datos de otros contaminantes atmosféricos (SO_2, NO_x y PM10) y meteorológicos (temperatura, humedad relativa y precipitación) de las estaciones de la Red de Calidad del Aire de la Comunidad Valenciana, situadas dentro de la zona de estudio. Mientras que los valores de velocidad y dirección del viento fueron obtenidos de la estación meteorológica situada en la planta municipal de tratamiento de aguas residuales.

3.2. Análisis de las muestras

Una vez realizada la captación, cada filtro se dividió en dos mitades, una se destinó al análisis de iones inorgánicos solubles en agua y la otra para los hidrocarburos.

- **Iones inorgánicos**

Para la extracción de los iones inorgánicos se cortó la porción de filtro en pequeños trozos, que se introdujeron en 20 ml de agua ultra pura y se colocaron en un baño de ultrasonidos durante 20 minutos y, finalmente, se calentaron a 60ºC durante 6 horas aproximadamente. Los análisis se llevaron a cabo mediante un cromatógrafo iónico DIONEX® DX-120 con un supresor SRS-ULTRA.

El volumen de extracción se dividió en dos partes iguales, una parte se utilizó para el análisis de aniones (Cl^-, NO_3^-, SO_4^{-2}) con una columna Dionex AS9-HC (250 x 4 mm, tamaño de partícula: 9 µm) y una disolución 9 mM de Na_2CO_3 como eluyente, a un caudal de 1,4 ml/min. Con la otra parte, se analizaron los cationes (Na^+, NH_4^+, K^+, Mg^{+2},Ca^{+2}) con una columna Dionex CS12A (250 x 4 mm, tamaño de partícula: 8,5 µm) y como eluyente una disolución de ácido metanosulfónico 20 mM, con un flujo de 0,8 ml/min (Nicolás et al., 2009).

La preparación de los patrones se llevó a cabo a partir de disoluciones estándares de cada uno de los iones con una concentración de 1000 µg/ml. Todos los reactivos empleados pertenecen a la marca comercial Merk® con calidad para análisis.

- **Hidrocarburos (*n*-alcanos y PAH)**

La concentración diaria de hidrocarburos, lineales y aromáticos, se obtuvo mediante el análisis de las muestras por cromatografía de gases y espectrometría de masas acoplada a termodesorción (TD-GC-MS) (Gil-Moltó et al., 2009).

La octava parte de cada filtro se sometió a un proceso de desorción térmica empleando un dispositivo TDS2/TDSA de Gerstel, con helio como gas portador. La muestra termodesorbida se preconcentró criogénicamente, utilizando nitrógeno líquido en un sistema de inyección de temperatura programable (Gerstel CIS4) y transfirió directamente mediante calentamiento térmico y arrastre de helio a un cromatógrafo de gases Agilent 6890N (columna capilar HP-5MSI, de 30 m), acoplado a un espectrómetro de masas Agilent 5973N en modo de monitorización de iones selectiva (SIM).

Se cuantificaron 16 hidrocarburos policíclicos aromáticos (PAH) y 27 *n*-alcanos (desde C16 hasta C40). La identificación de los analitos se realizó comparando sus tiempos de retención y sus espectros de masa con los estándares auténticos diluidos en hexano, tanto para los compuestos alifáticos (DRH-FTRPH y DRH FTRPH2 de AccuStandard), como para los aromáticos (PAH-Mix 68 de Dr. Ehrenstorfer). Las curvas de calibración se realizaron empleando filtros blancos, lavados previamente, a los que se les añadió volúmenes conocidos de las disoluciones estándar de los analitos correspondientes. Los hidrocarburos alifáticos lineales se cuantificaron por medio del ion 57, mientras que los hidrocarburos policíclicos aromáticos (PAH) se cuantificaron utilizando sus iones moleculares M+.

3.3. Tratamiento de los datos

En el estudio de iones inorgánicos se utilizaron técnicas estadísticas, con SPSS 17.0. El análisis de tendencias se realizó con el test no-paramétrico de Mann-Kendall, y la identificación de las fuentes de emisión mediante el análisis multivariante de componentes principales (PCA) con rotación ortogonal Varimax.

En el caso de los hidrocarburos, para la identificación de las principales fuentes de emisión se emplearon los siguientes índices y parámetros:

- C_{max}, que representa al *n*-alcano que muestra la concentración más elevada de la serie de hidrocarburos analizados.
- CPI, cociente entre la suma de las concentraciones de los compuestos con número impar de carbonos y la suma de los compuestos con número par.

- WNA, valor medio de la concentración de los *n*-alcanos anterior y posterior, con número par de átomos de carbono.

$$WNA = [C_n] - 0.5 \times ([C_{n-1}] + [C_{n+1}])$$

- %WNA, porcentaje de la contribución de *n*-alcanos biogénicos, representado por la relación entre la concentración total de *n*-alcanos biogénicos y la concentración total de *n*-alcanos.

$$\%WNA = (\Sigma\ WNAC_n \times 100) / \Sigma\ NA$$

- Para los PAH, se utilizan cinco ratios de diagnóstico: Ft/(Ft+Pir), BaA/(BaA+Cri), BeP/(BeP+BaP), IP/(IP+BghiP) y BaP/BghiP.
- Además de la concentración del BaP, para determinar la toxicidad de los PAH, se utilizó el índice BaPE que incluye a los seis PAH prioritarios indicados por la Comunidad Europea.

$$BaPE = 0{,}06 \times BaA + 0{,}07 \times B[b+k]Ft + BaP + 0{,}6 \times DBahA + 0{,}08 \times IP$$

4. Resultados y discusión

Los trabajos a los que se refiere esta memoria se centran en la caracterización de la PM, durante el periodo comprendido entre octubre 2008-diciembre 2009 en la ciudad de Elche, el estudio de la distribución de los contaminantes analizados en las diferentes fracciones de partículas, la variabilidad estacional que sufren las concentraciones de las especies analizadas y la identificación de sus fuentes de emisión.

Los resultados de esta investigación se presentan en los siguientes trabajos:

- Seasonal and interannual trends in PM levels and associated inorganic ions in southeastern Spain.
  Nuria Galindo, Juan Gil-Moltó, Montse Varea, Carolina Chofre, Eduardo Yubero.
  Microchemical Journal (2013), 110, 81.

- Characterization of hydrocarbons in aerosols at a Mediterranean city with a high density of palm groves.
  Carolina Chofre, Juan Gil-Moltó, Nuria Galindo, Montse Varea, Sandra Caballero.
  Environmental Monitoring and Assessment (2016), 188, 509.

El primer trabajo resume los resultados obtenidos en la caracterización de los iones inorgánicos solubles en agua (SO_4^{-2}, NH_4^+, NO_3^-, Ca^{+2}, Na^+, Mg^{2+} y Cl^-), no sólo de la PM10 y PM2,5 sino también de la fracción submicrónica.

El segundo se centra en la materia orgánica, aportándose por primera vez información sobre los niveles de *n*-alcanos, que por su relación con fuentes tanto antropogénicas como biogénicas aportan información útil sobre la influencia de los jardines de palmeras en la atmosfera de la ciudad. Además, se amplía el conocimiento y comportamiento de los PAH, sobre todo en la PM1.

A continuación, se resumen los resultados más relevantes obtenidos para cada uno de los trabajos indicados.

4.1. Seasonal and interannual trends in PM levels and associated inorganic ions in southeastern Spain

Las concentraciones medias de los principales iones solubles en agua en la ciudad de Elche fueron considerablemente más bajas en el periodo de estudio, frente a la campaña anterior, siendo esta reducción más evidente en los meses de invierno. En PM2,5, la mayor disminución se produjo para los iones SO_4^{-2} y NH_4^+, mientras que en PM10 fue para SO_4^{-2} y Ca^{+2}. Puesto que el porcentaje de días bajo intrusión sahariana fue similar en ambas campañas, la disminución en las concentraciones de dichos iones puede, en parte, explicarse por la reducción en un 7% de los eventos de acumulación local. Además, en el caso del sulfato, también contribuye la reducción de las emisiones de los precursores gaseosos (SO_2, NO_x y NH_3), observada mediante el análisis de Mann-Kendall que muestra una tendencia decreciente significativa en las concentraciones de SO_2 durante el período de estudio. Por otro lado, la concentración promedio de amonio en PM10 fue menor que en PM2,5, debido a la pérdida del NH_4^+ en el filtro de PM10 tras reaccionar con NaCl. Sin embargo, las concentraciones medias de los iones marinos (Na^+, Mg^{+2} y Cl^-), principalmente asociados al PM10, fueron muy similares durante los dos periodos, explicándose las pequeñas diferencias observadas exclusivamente por la variación de las condiciones meteorológicas interanuales.

En la PM1, los compuestos inorgánicos mayoritarios fueron los de origen secundario. Debido a su origen fotoquímico, SO_4^{-2} y NH_4^+, tuvieron una mayor contribución en verano que en invierno. Contrariamente, la contribución del NO_3^- fue mayor en invierno, debido principalmente a las menores temperaturas y a la mayor frecuencia de eventos locales de estabilidad. El resto de iones también mostraron ciclos estacionales significativos. Así, las concentraciones de K^+ se duplicaron durante la estación fría, lo que indica el predominio de las emisiones antropogénicas en invierno. Inesperadamente, Na^+ exhibió el mismo patrón estacional que K^+, descartando el origen marino y sugiriendo la existencia de Na^+ antropogénico en las partículas submicrométricas. Además, el aumento observado en las concentraciones de Ca^{+2} y Mg^{+2} en verano indica que el viento y la resuspensión de polvo del suelo, ésta última inducida por el tráfico, son las principales fuentes de estos iones. Las fuentes de todos estos iones se corroboraron mediante el estudio del PCA con rotación Varimax.

Finalmente, las variaciones en la distribución de iones en las diferentes fracciones, submicrométrica, fina y gruesa, mostraron que SO_4^{-2} tuvo un mayor aporte a la fracción submicrométrica a lo largo de todo el año, debido a la formación de $(NH_4)_2SO_4$. A diferencia del anterior, NO_3^- se vio más afectado por la estacionalidad, con máximas contribuciones en verano a la fracción gruesa, y una distribución similar entre las tres fracciones en invierno, debido principalmente a la baja estabilidad térmica del NH_4NO_3. Por su parte, los iones derivados del suelo (Ca^{+2}) y los marinos (Na^+, Mg^{+2}, Cl^-), debido a su origen mecánico, se encontraron asociados principalmente a la diferencia PM10-PM2,5. Mientras que casi el 60% del K^+ se distribuyó en PM1, lo que apunta a una la prevalencia de fuentes antropogénicas sobre las naturales. Por su parte, el NH_4^+ se asocia casi exclusivamente a las partículas menores de 1 μm, como consecuencia de su formación a partir de los ácidos sulfúrico y nítrico.

4.2. Characterization of hydrocarbons in aerosols at a mediterranean city with a high density of palm groves

Los niveles medios de *n*-alcanos registrados en Elche fueron 19,7 y 25,1 ng/m^3 para PM1 y PM10, respectivamente. Estos resultados fueron inferiores a los encontrados en ciudades con mayor densidad de población, pero superiores a los alcanzados en ciudades más pequeñas, lo que sugiere que los niveles de *n*-alcanos tienden a aumentar con la población del área de estudio.

El patrón de los *n*-alcanos, en función del número de carbonos, tanto para partículas finas como gruesas fue muy similar, apreciándose algunas diferencias estacionales. En la época cálida los hidrocarburos biogénicos C_{29} y C_{31}, se desplazaron claramente hacia las partículas gruesas, aunque sus concentraciones fueron similares en ambas estaciones. Mientras que los hidrocarburos antropogénicos experimentaron una disminución desde la estación fría a la cálida. Este comportamiento, en Elche, no puede explicarse por la densidad del tráfico ya que es constante a lo largo de todo el año. Las razones de esta variación se deben a: las menores condiciones de dispersión atmosférica que se producen durante el invierno, a cambios de las tasas de emisión que sufren los vehículos en la época fría y a las altas temperaturas del verano, que producen la evaporación de las especies más volátiles. El motivo por el que los *n*-alcanos biogénicos C_{29} y C_{31} mostraron valores similares en ambas estaciones, se debe a que, el aumento de las emisiones biogénicas durante la estación cálida compensa la disminución de la concentración debido a las inusuales características de este invierno.

El homólogo biogénico C_{31} fue el componente más abundante tanto en PM10 como en PM1 siendo más significativo en PM10, cuyo segundo componente máximo fue el C_{29}, ambos de origen natural. Mientras que en PM1, el segundo máximo se centró en los homólogos C_{23}-C_{25}. Lo que indica un mayor aporte de combustibles fósiles al PM1, y de fuentes biogénicas al PM10, resultados que fueron corroborados por los valores de CPI y %WNA calculados. Los CPI mostraron contribuciones predominantes de fuentes antropogénicas en ambas fracciones de la PM, tanto para la estación cálida como para la fría, y una concentración de los *n*-alcanos procedentes de ceras epicuticulares en PM10 mayor al de otras áreas urbanas, como indican los valores de %WNA. Esto último junto con el estudio en el segundo emplazamiento de muestreo, situado en el centro de un jardín de palmeras, corroboran la influencia de éstos sobre la atmosfera de la ciudad.

Análogamente, los niveles medios registrados de PAH (~ 1 ng/m^3) también fueron considerablemente inferiores a los observados en otras ciudades europeas, indicando una menor tasa de emisión de fuentes antropogénicas, ya que la ciudad tiene escasa actividad industrial y un bajo consumo de madera y combustibles fósiles para el calentamiento de viviendas. Además, se registraron concentraciones más elevadas, entre dos y tres veces superiores, en invierno que en verano, debido a los cambios de las tasas de emisión y las condiciones meteorológicas.

Los PAH se asociaron mayoritariamente con las partículas submicrométricas (~ 84%), lo que aumenta los efectos nocivos de estas partículas. Respecto a su abundancia, tanto en PM10 como en PM1, los PAH predominantes fueron los B[b+k]Ft durante todo el periodo. El segundo PAH predominantes fue el Cri durante la estación fría que, debido a su elevada volatilidad, fue superado en concentración por el IP durante la estación cálida. El predominio de estos compuestos individuales indica que los PAH proceden principalmente de la combustión incompleta de combustibles fósiles, siendo el tráfico su principal fuente de emisión en Elche. Estos resultados fueron corroborados con las relaciones moleculares utilizadas, descartando otras fuentes como la combustión de la madera o atribuyendo una mayor emisión de los PAH de los vehículos diésel frente a los de gasolina. Similares resultados se obtuvieron en PTG ya que, aunque se encuentre situado en un campo de palmeras, éste se encuentra ubicado entre algunas de las avenidas principales de la ciudad.

El índice de toxicidad anual de los PAH fue de 0,1 ng/m^3, contribuyendo el BaP con una media del 64%, alcanzándose el doble de concentración durante el período otoño-invierno, tanto para PM1 como para PM10. Estas concentraciones fueron muy inferiores a los niveles observados en otras áreas urbanas, y considerablemente menores que el valor límite establecido por la normativa europea.

5. Conclusiones y líneas de investigación futuras

Las concentraciones medias de la mayoría de los iones solubles, sufrieron una disminución en el periodo 2008-2009, debido a: un aumento en las precipitaciones y una menor frecuencia de eventos locales de estabilidad, una disminución en las emisiones de gases precursores y una reducción en las actividades antropogénicas.

En la PM1, los iones mayoritarios fueron los secundarios. Sulfato, amonio y calcio mostraron una mayor contribución en verano y, nitrato, sodio y potasio en invierno, debido a: su origen fotoquímico, la resuspensión, las condiciones meteorológicas y a las emisiones antropogénicas, respectivamente.

Las principales fuentes de emisión identificadas de los iones de la PM1 son las asociadas a la formación de sulfato y nitrato de amonio secundarios, a las emisiones del tráfico rodado y a la resuspensión del polvo del suelo.

Los iones primarios se encontraron principalmente en la fracción gruesa, a excepción del potasio. Éste último, junto sulfato y amonio, se asoció mayoritariamente a las partículas menores a 1 µm. Esta relación se mantuvo para amonio y sulfato, tanto en verano como en invierno, mientras que los niveles de nitrato se desplazaron hacia la fracción gruesas durante el verano, debido a la baja estabilidad térmica del nitrato de amonio.

Las concentraciones de hidrocarburos (*n*-alcanos y PAH) fueron mayores en invierno debido a las menores condiciones de dispersión atmosféricas, a cambios en las tasas de emisión que sufren los vehículos en la época fría y a las altas temperaturas del verano, que producen la evaporación de las especies más volátiles.

En la PM1, los *n*-alcanos proceden, casi exclusivamente, de combustibles fósiles, sobre todo en la estación fría, mientras que, en la PM10, la mayor contribución fue de origen biogénico. Aunque para ambas fracciones, las principales fuentes de emisión fueron antropogénicas, también se observó una mayor influencia de las fuentes biogénicas debido a su entorno.

Los hidrocarburos policíclicos aromáticos se asociaron casi exclusivamente con la PM1 durante todo el año, siendo emitidos principalmente por el tráfico. Su mayor índice de toxicidad se alcanzó durante la estación fría, pero con una concentración muy inferior a la estipulada en la normativa.

Por último, como líneas de investigación futuras se establecen:

- Relacionar los valores de contaminación atmosférica con datos hospitalarios para poder analizar una relación estadísticamente significativa entre los niveles de contaminación y los efectos adversos a la salud.
- Ampliar el estudio de contaminantes orgánicos analizando los compuestos volátiles presentes en la atmósfera.

6. Conclusions and future research directions

Mean concentrations of most soluble ions decreased in the period 2008-2009, due to: an increase in precipitation rates and a lower frequency of local pollution episodes, a decrease in gaseous precursor emissions and a reduction in anthropogenic activities.

Secondary ions were the most abundant inorganic component in PM1. Sulfate, ammonium and calcium showed higher contribution during summer, and nitrate, and potassium during winter, due to the photochemical origin, dust resuspension, meteorological conditions, and anthropogenic emissions, respectively.

Major sources associated with PM1 were identified as secondary $(NH_4)_2SO_4$ and NH_4NO_3, local traffic emissions, and soil dust.

All primary ions were mostly associated with the coarse fraction, but potassium. This one, with sulfate, and ammonium, were mainly associated to particles smaller than 1 µm. This behavior was followed by ammonium and sulfate, during both summer, and winter, meanwhile nitrate levels were shifted towards the coarse fraction during summer, due to the low thermal stability of ammonium nitrate.

The concentrations of hydrocarbons (*n*-alkanes and PAH) were higher in winter due to the lower atmospheric dispersion conditions, to changes in the emission rates suffered by vehicles in the cold season, and to the higher temperatures of the summer, which produce the evaporation of the most volatile species.

n-Alkanes associated with PM1 were mostly emitted from fossil fuel combustion, mainly during the cold season, while associated with PM10 were from biogenic origin. Both fractions have higher influences of anthropogenic sources, but biogenic emissions were also observed, due to the palm tree groves spread over the city.

PAH were almost exclusively found in PM1 during the whole period, with traffic as main emission source. Toxicity index calculated achieved the highest values in the cold season, but showing concentrations considerably lower than the limit value established by the European Community.

Finally, the study has identified the following research directions:

- To study the correlation of air pollution values with hospital data in order to analyze the possible statistically significant relationship between pollution levels and adverse health effects.
- To improve the study of organic pollutants by analyzing the volatile compounds present in the atmosphere.

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Anexo 1

Seasonal and interannual trends in PM levels and associated inorganic ions in southeastern Spain

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Seasonal and interannual trends in PM levels and associated inorganic ions in southeastern Spain

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ABSTRACT

Concentrations of PM1, PM2.5, PM10 and associated inorganic ions were measured between October 2008 and October 2009 in the city of Elche (southeastern Spain). The levels of the inorganic components in PM2.5 and PM10 were compared with those measured in the same city during the period December 2004–November 2005. A reduction of 12% and 24% in the annual concentrations of PM2.5 and PM10, respectively, was observed from 2004–05 to 2008–09. The decrease in PM2.5 was mainly attributed to a steep reduction in $(NH_4)_2SO_4$ levels caused by a significant decline in SO_2 emissions, higher precipitation rates, and a lower occurrence of winter PM episodes under high atmospheric stability conditions. In the PM10 fraction, NH_4^+, Ca^{2+} and SO_4^{2-} experienced the largest decreases. The drop in Ca^{2+} levels, higher in winter than in summer, was mainly attributed to the increase in precipitation and the reduction in construction activity. The PM1 annual average concentration in 2008–09 was only 9.2 µg/m³. Slightly higher PM1 levels were measured in summer (10.3 µg/m³) than in winter (8.8 µg/m³), due to the low frequency of local pollution episodes during winter 2009. The PCA analysis identified the contribution of three sources of ionic compounds in the submicron fraction: secondary $(NH_4)_2SO_4$ and NH_4NO_3, traffic emissions, and dust resuspension. NO_3^- size distribution exhibited a marked seasonal pattern, with a lower proportion associated with particles smaller than 2.5 µm in summer than in winter, due to the thermal decomposition of NH_4NO_3. In contrast, the SO_4^{2-} size distribution was approximately constant throughout the year.

1. Introduction

Urban aerosols are complex mixtures of liquid and solid particles directly emitted from anthropogenic as well as natural sources, or formed in the atmosphere by chemical reactions and condensation processes of gaseous precursors. The health effects of atmospheric aerosols are determined by their size and chemical composition [1,2]. As a result, many studies have focused on the study of particulate matter (PM) concentrations and physico-chemical properties worldwide [3–6]. This information is essential in order to apply effective abatement strategies. Of special concern is the submicron fraction (referred to as PM1) due to its potent relationship with cardio-respiratory diseases, as demonstrated in recent studies [7,8]. PM1 components are mostly related to anthropogenic activities and therefore, the PM1 fraction can be used to compare regions with distinct environmental characteristics [9].

Water-soluble inorganic species, especially NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}, Na^+ and Cl^-, represent a large portion of ambient PM mass concentrations and are known to strengthen the harmful effects of atmospheric aerosols on human health and the environment [10,11]. Besides, inorganic ions cause decay of stone buildings and monuments [12,13] and play a significant part in visibility reduction due to light-scattering effects, particularly $(NH_4)_2SO_4$ [14].

The contribution of each one of the inorganic components to PM levels is highly variable depending on climatic, meteorological and geographical features, as well as the PM fraction considered. Secondary inorganic ions (NO_3^-, SO_4^{2-} and NH_4^+) are formed by atmospheric chemical reactions of gaseous precursors, which can be emitted from anthropogenic (NO_x, SO_2) and biogenic (NH_3) sources. Secondary SO_4^{2-} occurs predominantly in the accumulation mode (between 0.1 and 1 µm) as $(NH_4)_2SO_4$ and NH_4HSO_4, which are formed through both heterogeneous and homogeneous oxidation of SO_2 to H_2SO_4 and subsequent reaction with gaseous NH_3. In contrast, NO_3^- usually has a bimodal size distribution, with peaks in both the accumulation and coarse (>1 µm) size ranges [15]. The homogeneous oxidation of NO_x leads to the formation of gaseous HNO_3 which can later react either with gas-phase NH_3 to form fine NH_4NO_3, or with sea-salt and soil particles to form $NaNO_3$ and $Ca(NO_3)_2$, respectively, in the coarse mode [16]. Emissions of gaseous precursors of secondary PM species fell in the member states of the European Union between 2007 and 2008. Spain was one of the countries that underwent larger decreases (12.7, 55, and 7.7%, respectively, for NO_x, SO_x and NH_3) [17]. The emission reduction was caused by the use of lower amounts of high

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sulfur fuels for electricity generation, the introduction of abatement technologies, and the global economic recession.

Primary water-soluble species (Cl^-, Na^+ and Ca^{2+}) are directly released into the atmosphere by different natural and anthropogenic sources and prevail in the coarse fraction. Na^+ and Cl^- mainly originate from sea salt while Ca^{2+} can be emitted by resuspension of soil and road dust, construction activities, and industrial processes [18–20]. It is worth mentioning that in the study area, soluble Ca^{2+} represents more than 90% of total calcium [21].

In a previous work [22], we analyzed the influence of meteorological variables on the temporal variations of aerosol levels at an urban area in southeastern Spain. In this study, we present data of the water-soluble inorganic composition of aerosols that can provide additional information about the factors that affect interannual and seasonal changes in PM levels. The first data on the PM1 ionic composition in the study area are also presented. These data have been used in a first attempt to investigate the sources of submicron particles in the study area.

2. Materials and methods

2.1. Sampling location

Elche is a medium-size city (~185,000 inhabitants) located in southeastern Spain (38°16'N; 0°41.5'W), about 12 km from the Mediterranean Sea (Fig. 1). The area has a typical dry Mediterranean climate with annual precipitation rates normally varying from 150 to 250 L/m². Rainfall is more frequent during spring and autumn. The average monthly temperatures oscillate between 12 °C in January/February and 27 °C in July/August. Two main wind regimes predominate in the region: winds blowing from the northwest prevail during autumn and winter, while in the spring and summer months the dominant wind direction is from the sea (E–S). The most important industrial activity in the city is shoe manufacturing, which does not represent a significant source of ambient PM. Therefore, local anthropogenic emissions of atmospheric particles in the urban area are mainly attributed to traffic and construction works.

The samplers were placed at a 15 m height, on top of a building on the Miguel Hernández University campus, which is located within an open area, close to a four-lane city street carrying over 37,000 vehicles per day on weekdays (Fig. 1).

2.2. Sampling and analysis

Between October 2008 and October 2009, PM10, PM2.5 and PM1 daily samples were simultaneously collected by means of three Derenda 3.1 low-volume samplers (2.3 m³/h). Sampling started at about 10 AM local time each day. The Derenda 3.1 low-volume sampler is classified as a reference unit as per the CEN 12341 and CEN 14907 European guidelines. Teflon coated glass fiber filters (T60A20-47 mm; Pallflex) were used as substrates for the collection of atmospheric aerosol samples.

PM mass concentrations were obtained by weighing the filters before and after sampling using an electronic balance (Ohaus, Model AP250D) with 10-μg sensitivity. All filters were conditioned for at least 24 h prior to weighing at a relative humidity of 50 ± 5% and a temperature of 20 ± 1 °C. The number of valid samples for PM10, PM2.5, and PM1 were 131, 114 and 130, respectively.

One-half of each filter was cut into small pieces using a stainless steel scalpel, extracted with 20 mL of ultra-pure water in an ultrasonic

Fig. 1. Location of the sampling site and the city of Elche.

bath for 20 min and warmed at 60 °C for about 6 h. A Dionex DX-120 ion chromatograph with an SRS-ULTRA suppressor was used in the analysis of major anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). Anions were separated with a Dionex AS9-HC column (250 × 4 mm, particle size: 9 μm) using Na_2CO_3 9 mM as eluent at a flow rate of 1.4 mL/min. Cations were analyzed with a Dionex CS12A column (250 × 4 mm, particle size: 8.5 μm) and 20 mM methane sulfonic acid eluent running at 0.8 mL/min.

The percentage of recovery and the analytical precision were assessed by conducting spike-recovery checks. One-half milliliter of a 40 μg/mL standard solution of inorganic ions was added separately to blank samples. Thereafter, a complete extraction procedure was followed and analyzed for water-soluble inorganic ions. The recovery results were found to be within the range of 97% to 106%. The precision estimated from the standard deviation of repeated measurements of standards and samples was in the range of 0.6% to 6% for all inorganic ions.

2.3. *Meteorological and air pollution data*

Air pollution (SO_2, NO_x and PM10), temperature, relative humidity and rainfall data were obtained from various stations of the air quality network of the regional Government of Valencia located within the study zone. Wind speed and direction were supplied by a station situated at a sewage treatment plant in the Elche surroundings.

Saharan dust outbreaks, which are a common source of atmospheric PM in the Mediterranean basin [23,24], were detected using back-trajectory analysis (HYSPLIT model) [25], the information supplied by BSC/DREAM and NAAPS dust maps, as well as satellite images of the NASA SeaWiFS Project. In the western Mediterranean, these events are more frequent and intense during summer months [24].

Autumn and winter pollution events are generally caused by the accumulation of local pollutants under intense anticyclonic, calm, and clear conditions. For the identification of these episodes, we used pressure level maps from the National Center for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) [26], as well as meteorological variables (temperature, relative humidity, wind speed and wind direction) and atmospheric pollution levels (NO_x and PM10) measured at the research area by the air quality regional network. Additionally, mixing layer depths were calculated using the data from atmospheric soundings taken at the city of Murcia (~60 km southwest of Elche).

2.4. *Trend and factor analysis*

Pollutant concentrations at the study area were analyzed for the presence of a monotonic increasing or decreasing trend with the nonparametric Mann–Kendall test. Then, the nonparametric Sen's method was used for estimating the slope of the linear trend [27]. Since the only air quality observation station of the regional network located in the urban nuclei of Elche has been repositioned twice in the last 10 years, the preceding statistical methods were applied to atmospheric pollutant data (SO_2, NO, NO_2, NO_x, and PM10) taken from the two stations nearest the city. The first one is located in a semi-rural area only 3.5 km south of the sampling site. The second station, inside the city of Alicante (~20 km northeast of Elche), is placed on a wide, busy and broad avenue, very similar to the sampling site in Elche. Time series of annual mean values from 2003 to 2011 were used.

A multivariate statistical technique, principal component analysis (PCA), was employed to identify major sources of inorganic compounds at the monitoring site (using the software package SPSS, version 17). PCA reduces the original variables of a large dataset to a smaller number of uncorrelated principal components (PC) that explain a large fraction of the total variance. In the present study, PCA with varimax rotation was applied.

3. Results and discussion

3.1. *Blank filters*

The blank concentration was measured using field blank samples. Blank filters were carried and extracted through similar procedures as followed for the extraction and preparation of the sampled filters. The overall mean concentrations of field blank samples collected over one year were in the range of 0.01 to 0.13 μg/m³ for all inorganic ions. The concentrations of all the reported PM mass and inorganic ions have been corrected for field blanks. The detection limits (determined as 3σ of blank filters) in μg/m³ were 0.11 for Cl^-, 0.07 for NO_3^-, 0.04 for SO_4^{2-}, 0.16 for Na^+, 0.01 for NH_4^+, 0.07 for K^+, 0.09 for Ca^{2+}, and 0.01 for Mg^{2+}.

3.2. *PM10 and PM2.5 concentrations: comparison with previous levels*

Table 1 shows average concentrations of PM10, PM2.5, and associated ions measured between October 2008 and October 2009. Winter (January, February, and March) and summer (June, July, and August) mean values are also presented. Since more than 50% of PM2.5 Cl^- concentrations were below the detection limit, these values were changed to the detection limit (0.11 μg/m³) for all calculations. Average values for PM2.5 and PM10 obtained between December 2004 and November 2005 have been included for comparative purposes. The details of this campaign are given in Nicolás et al. [28].

PM mass concentrations measured in Elche during 2008–09 were lower than those registered in 2004–05, especially for the PM10 fraction that experienced a 24% decrease. The decrease in PM2.5 levels was half of that observed for PM10. It is interesting to highlight the important drop in PM mass concentrations during wintertime as a result of a lower frequency of local pollution events and higher rainfall rates during the winter of 2009 [22]. This will be discussed in detail later.

The annual concentrations of the major water-soluble ions were also considerably lower in 2008–09 than in 2004–05, except for PM2.5 NO_3^- that experienced a minor decrease. During both campaigns, NH_4^+ mean concentrations in PM10 were significantly lower than in PM2.5, indicating a substantial loss of NH_4Cl by reaction of NH_4NO_3 with NaCl in the PM10 filter [29]. The components showing the most noticeable decreases in PM2.5 were SO_4^{2-} and NH_4^+. In PM10, SO_4^{2-} and Ca^{2+} experienced the highest reductions, in addition to NH_4^+ whose concentration is included in the PM2.5 fraction. Such decreases in the levels of inorganic compounds between 2004–05 and 2008–09 were quite higher in winter than in summer. The significant drop in PM2.5 NH_4^+ concentrations during winter 2009 even caused a change in its seasonal cycle. In previous works performed in the study zone [28,30], similar NH_4^+ concentrations for the two seasons were obtained. However, during 2008–09, higher concentrations were measured in summer than winter. The average levels of marine ions (Na^+, Mg^{2+}, and Cl^-), which are more abundant in PM10 than in PM2.5, were very similar for both periods considered and the observed variations could be almost exclusively attributed to year-to-year changes in meteorological conditions.

Factors that possibly influenced the reduction in PM levels and changes in ion concentrations described earlier are: (1) differences in meteorological conditions; (2) a variation in the occurrence of PM events; and, (3) a decrease in gaseous precursor emissions.

The role of local meteorology is essential in the analysis of temporal variations in PM levels [22,31,32]. A comparison between annual and seasonal averages of meteorological parameters calculated from daily values for 2004–05 and 2008–09 is presented in Table 2.

No statistically significant differences have been detected between average values of meteorological variables for the two studied periods. Nevertheless, both the accumulated rainfall and the number of days with more than 1 L/m² of total precipitation were considerably higher in 2008–09 than in 2004–05 (except for the summer season).

Table 1
Annual and seasonal mean concentrations (μg/m^3) for PM and inorganic ions in Elche for the periods December 2004–November 2005 and October 2008–October 2009.

	All data				Winter[a]				Summer[b]			
	PM10		PM2.5		PM10		PM2.5		PM10		PM2.5	
	2004/05	2008/09	2004/05	2008/09	2004/05	2008/09	2004/05	2008/09	2004/05	2008/09	2004/05	2008/09
PM	34.3	30.2	15.4	13.6	33.5	22.3	19.3	12.5	30.2	33.9	14.0	15.1
Cl^-	0.68	0.71	0.16	0.10	0.57	0.66	0.23	0.22	0.69	1.16	0.07	0.11
NO_3^-	3.78	3.00	1.37	1.22	5.28	3.13	2.53	1.77	4.83	3.01	0.48	0.08
SO_4^{2-}	4.38	3.11	3.79	2.70	2.98	1.69	2.23	1.43	6.80	4.93	5.87	4.28
NH_4^+	1.18	0.82	1.61	0.85	1.78	0.54	2.06	0.68	1.20	0.51	2.06	0.98
Na^+	0.98	1.00	0.27	0.43	0.51	0.68	0.23	0.42	1.02	1.50	0.14	0.43
Ca^{2+}	2.28	1.88	0.36	0.42	2.29	1.28	0.34	0.30	2.72	2.30	0.32	0.53
Mg^{2+}	0.16	0.16	0.03	0.04	0.11	0.12	0.02	0.01	0.25	0.25	0.03	0.06
K^+	0.29	0.29	0.21	0.24	0.33	0.33	0.28	0.29	0.30	0.21	0.29	0.16

[a] January, February, and March.
[b] June, July, and August.

This increase in rainfall was one of the reasons for the observed fall of annual and winter PM concentrations in 2008–09 and is not only due to the removal of atmospheric particles by wet deposition, but also to the washout of streets that prevents road dust resuspension. For this reason, higher relative decreases were expected for soil elements used as tracers of this source than for the other PM components [33]. Thus, increased precipitation amounts would contribute to explain the lower PM10 Ca^{2+} concentrations observed in 2008–09 regarding the values obtained in 2004–05.

Unlike $(NH_4)_2SO_4$, the gas-aerosol equilibrium of NH_4NO_3 strongly depends on temperature and relative humidity [34]. No changes in annual and seasonal average temperatures and relative humidities between 2004–05 and 2008–09 were observed. Therefore, other factors than temperature and relative humidity must have accounted for the high winter decrease in PM2.5 NO_3^- levels registered in 2008–09, as shown next.

A second important factor affecting PM concentrations and chemical composition is the frequency of specific events. Many previous studies have reported that local pollution episodes and African dust outbreaks cause a significant increase in PM levels within the Mediterranean basin [24,35–37]. The first type of event results from the accumulation of local emissions under low dispersive atmospheric conditions, while the second involves long-range transport of mineral dust from the Sahara desert. It is then important to investigate the occurrence of such episodes during the measurement period.

In the present study, one day was considered to be under the influence of a Saharan intrusion when satellite images and prediction models (ICOD/DREAM and NAAPS) indicated the presence of a high dust load over the study region, and the African origin of air masses was confirmed by means of the HYSPLIT model. Local pollution episodes are associated with the presence of stationary high pressure systems and weak surface winds that make pollutant dispersion difficult. These events, which are more frequent during late autumn and winter, were identified using pressure level maps supplied by the NOAA-CIRES Climate Diagnosis Center, as well as a series of meteorological data and contaminant levels from the Regional Environmental Surveillance Network. Table 3 shows average concentrations for PM and major inorganic ions for both types of events and for days without events during 2008–09.

The number of intrusion days represented 26% of the total sampling days, a very similar percentage to that registered in 2004–05 (23%) [38]. A significant increment in PM2.5 SO_4^{2-} and NH_4^+ concentrations during Saharan events was expected since the formation of fine $(NH_4)_2SO_4$ is enhanced by the presence of mineral dust [39]. However, fine SO_4^{2-} and NH_4^+ concentrations measured in 2008–09 under this type of episode were low compared to those obtained for the 2004–05 period. The levels of PM10 and associated Ca^{2+}, a common tracer of African outbreaks, were also inferior in 2008–09 than in 2004–05 [28]. Such results indicate that the impact of Saharan dust on PM levels in 2008–09 was smaller in absolute terms than in 2004–05. Inter-annual changes in the contribution of mineral dust have been previously reported by Querol et al. [24].

The frequency of local pollution events during 2008–09 was less than 4%, while in 2004–05 approximately 11% of the sampling days were affected by these episodes [38]. Interestingly, average levels of secondary inorganic ions measured in the PM2.5 fraction under local pollution events were almost the same for 2008–09 and 2004–05. This outcome strongly suggests that the low occurrence of this type of episodes in winter 2009 was a key factor in the reduction of PM levels from winter 2005 to winter 2009. As shown in earlier studies, fine NH_4NO_3 is a good tracer of local pollution events [40]. So, the remarkable decrease in PM2.5 NH_4^+ and NO_3^- concentrations between

Table 2
Average values and standard deviations of local meteorological variables measured in Elche for the periods December 2004–November and 2005 October 2008–October 2009.

	All data		Winter		Summer	
	2004–05	2008–09	2004–05	2008–09	2004–05	2008–09
WS (m/s)[a]	3.3 ± 1.6	3.4 ± 1.7	3.3 ± 1.5	4.1 ± 1.3	3.1 ± 0.7	3.0 ± 0.7
T (°C)	18.0 ± 6.4	18.1 ± 6.3	11.8 ± 3.4	13.0 ± 2.5	26.3 ± 1.7	26.0 ± 1.7
Rad. (W/m^2)[b]	195 ± 94	172 ± 88	144 ± 51	109 ± 50	299 ± 40	268 ± 39
RH (%)[c]	58 ± 16	61 ± 12	59 ± 17	63 ± 14	54 ± 13	60 ± 13
Rainfall (L/m^2)[d]	134	431	45	134	8	3
N (>2 L/m^2)[e]	18	37	8	13	0	0

[a] WS: wind speed.
[b] Rad.: solar radiation.
[c] RH: relative humidity.
[d] Accumulated precipitation.
[e] N represents the number of days with a precipitation higher than 2 L/m^2.

Table 3
Comparison between average concentrations (μg/m^3) on days with Saharan outbreaks or local pollution episodes and days without events in Elche during 2008–09.

	Non-event (N = 81)[a]		Intrusion (N = 34)		Local pollution events (N = 5)	
	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5
PM	21.7	11.7	41.6	17.5	60.5	28.6
NO_3^-	2.44	0.88	4.77	1.50	7.44	6.04
SO_4^{2-}	2.54	2.45	5.18	4.84	5.21	3.94
NH_4^+	0.68	0.72	0.78	1.14	1.49	3.05
Ca^{2+}	1.48	0.30	2.42	0.54	1.77	0.58

[a] Rainy days were not included.

winter 2005 and winter 2009 (see Table 1) can be mostly attributed to the low frequency of such events in winter 2009.

As mentioned before, another factor that could have contributed to the observed decrease in the concentrations of secondary inorganic ions between 2004–05 and 2008–09 is the reduction in emissions of gaseous precursors (SO_2, NO_x and NH_3). In order to assess if the decline in national emissions [17] had had an effect on atmospheric pollutant concentrations at the research area, trend analysis was conducted with the Mann–Kendall test at two stations nearby the sampling site (Table 4).

PM10 concentrations showed a monotonic reduction trend of approximately 5% per year at both sites, which is consistent with the decrease observed in Elche in the 2008–09 period with regard to the values measured in 2004–05. Both sites also exhibited a significant decreasing trend in SO_2 concentrations over the study period. Some previous works have reported a reduction in SO_4^{2-} concentrations with the decline in SO_2 concentrations, although the relationship between the two species is not always linear [41–43]. Hence, the observed fall in SO_4^{2-} atmospheric levels in Elche could have been partly caused by the reduction in SO_2 concentrations. No clear trend was observed for nitrogen oxides levels, except for NO_2 measured at the semirural location, probably because of the considerably lower reduction in NO_x emissions relative to SO_2 emissions. Anyway, changes in NO_x emissions seem to have a minor effect on NO_3^- concentration variations [44]. On the other hand, different studies have shown that NO_3^- concentrations are sensitive to NH_3 emissions, while SO_4^{2-} concentrations are not [44,45]. Unfortunately, no data on NH_3 ambient concentrations are available for the study zone.

In Spain, the current economic crisis has had a great impact on the construction industry. Between 2003 and 2007, more than 2000 new homes per year were built in the area of Elche. These figures are in stark contrast to 2008 and 2009, when only 1300 and 300 new dwellings, respectively, were built. This fall in construction activities could have accounted for a reduction in mineral matter emissions that contributes to explain the decrease in PM10 Ca^{2+} levels.

Table 4
Trends in atmospheric pollutant concentrations at a semirural site close to Elche and an urban site in the city of Alicante.

Site	Pollutant	Significance	Trend[a]	
			μg/m^3 year	%/year
Semirural—Elche	SO_2	0.05	−0.2	−5.6
	NO			
	NO_2	0.05	−0.5	−2.5
	NO_x			
	PM10	0.01	−1.6	−4.8
Urban—Alicante	SO_2	0.01	−0.5	−6.8
	NO			
	NO_2			
	NO_x			
	PM10	0.1	−2.2	−5.2

[a] The magnitude of the trend calculated by the Sen's method is only shown when the significance level is equal or below 0.1.

3.3. *PM1* concentrations: seasonal variation and sources

The annual average concentration of PM1 measured in Elche during 2008–09 (9.2 μg/m^3, Table 5) can be considered low for an urban station since values higher than 14 μg/m^3 have been reported for other Mediterranean urban locations [9,46,47]. A lower degree of industrialization of the study area could be one of the reasons why PM1 concentrations measured in Elche were rather low. Taking the findings of the preceding section into account, one could infer that the drop in SO_2 emissions and the meteorological conditions during winter 2009 (elevated precipitation amounts and low frequency of local pollution episodes) also contribute to explain the comparatively low PM1 levels in Elche during the measurement period.

Unlike previous studies [9,47], Elche registered slightly higher PM1 concentrations in summer than in winter, which can be explained by the atypical meteorology of winter 2009 as well [22].

The most abundant inorganic component of PM1 during the four seasons of the year was SO_4^{2-}, representing 24% of the PM1 annual concentration (Table 5). Nevertheless, the SO_4^{2-} contribution was much lower in winter (13%) than in summer (35%), as expected because of its photochemical origin. This behavior has also been observed at other urban environments [47], where the reduction in the contribution of SO_4^{2-} in winter was accompanied by a considerable increase in the contribution of organic matter and NO_3^-. In Elche, PM1 NO_3^- concentrations also showed a strong increase from summer to winter because of the lower temperatures and the higher frequency of local pollution events that favored the formation of particulate NH_4NO_3. However, unlike previous studies that exhibited a clear prevalence of NO_3^- over SO_4^{2-} during wintertime [47,48], SO_4^{2-} was the dominant ion in both summer and winter. This was probably due to a drop in winter NO_3^- levels caused by the low occurrence of local pollution episodes during winter 2009.

NH_4^+ was the second most abundant ionic species, accounting for almost 8% of the PM1 mass concentration. Average summer concentrations were twice those of winter possibly due to the increase in the photochemical production of $(NH_4)_2SO_4$ under strong solar radiation.

Minor ionic components also showed significant seasonal cycles. K^+ concentrations were much higher in winter than in summer, pointing to the dominance of anthropogenic emissions. Unexpectedly, Na^+ exhibited the same seasonal pattern as K^+, which rules out the marine origin and suggests the existence of anthropogenic Na^+ in submicron particles. The observed increase in Ca^{2+} and Mg^{2+} concentrations from winter to summer most likely indicates that wind and vehicle-induced resuspension of dust was the main source of these ions.

The correlation equation between the sum of SO_4^{2-} plus NO_3^- and NH_4^+ (in μeq/m^3) revealed that there was not enough NH_3 to balance both anions ($y = 0.98x + 0.02$; $r^2 = 0.97$). The value of the intercept indicates that, on average, an additional concentration of 0.02 μeq NH_4^+/m^3 (0.36 μg/m^3) would be required for the complete neutralization of SO_4^{2-} and NO_3^-. The average ammonium deficit with respect to the total amount of SO_4^{2-} and NO_3^- was 32%, which suggests that they were mainly present as $(NH_4)_2SO_4$ and NH_4NO_3. This deficit was significantly higher in winter (40%) than in summer (29%), pointing to an increase in the proportion of nitrate and/or sulfate compounds other than NH_4NO_3 and $(NH_4)_2SO_4$ during the coldest months.

To further investigate the major sources of ionic compounds associated with PM1 during the 2008–09 period, principal component analysis (PCA) with varimax rotation was applied to the whole data set (Table 6). Three components with eigenvalues higher than 1 explained 79% of the total variance.

Table 5
Statistical summary of PM1 and inorganic ions in Elche for the period October 2008–October 2009. Concentrations are given in μg/m^3.

	All data				Winter[a]				Summer[b]			
	Mean	SD	Max	Min	Mean	SD	Max	Min	Mean	SD	Max	Min
PM1	8.2	4.2	20.7	1.5	6.6	4.5	19.9	2.0	10.1	3.1	16.3	5.1
NO_3^-	0.65	0.60	4.64	0.08	1.02	0.85	3.01	0.15	0.26	0.21	1.18	0.08
SO_4^{2-}	2.22	1.56	7.47	0.20	1.13	0.68	3.06	0.20	3.51	1.58	7.47	1.41
NH_4^+	0.72	0.52	2.82	0.01	0.49	0.39	1.98	0.01	0.98	0.62	2.76	0.35
Na^+	0.31	0.13	0.80	0.10	0.31	0.15	0.65	0.10	0.25	0.05	0.36	0.16
Ca^{2+}	0.37	0.16	0.83	0.00	0.34	0.11	0.57	0.14	0.44	0.17	0.83	0.09
Mg^{2+}	0.02	0.02	0.10	0.01	0.02	0.01	0.03	0.01	0.03	0.01	0.06	0.01
K^+	0.21	0.09	0.48	0.01	0.27	0.08	0.37	0.12	0.14	0.05	0.29	0.07

[a] January, February, and March.
[b] June, July, and August.

The first component (PC1, accounting for 31% of the total variance) associates mainly with NH_4^+ and SO_4^{2-} and also shows a significant loading for NO_3^-. This component represents the secondary formation of $(NH_4)_2SO_4$ and NH_4NO_3 from their gaseous precursors. The second principal component (PC2, 28%) contains high factor loadings for K^+, Na^+, and NO_3^-. K^+ is frequently used as a tracer of biomass burning [49]; however, it also originates from other sources such as fossil fuel combustion. On the other hand, the presence of NO_3^- points to vehicle emissions [50] and, therefore, PC2 was assigned to the local traffic source. The third principal component (PC3, 19%) shows particularly high loadings for Ca^{2+} and Mg^{2+}, representing the soil source. This component also shows a significant factor loading for SO_4^{2-}, which suggests the presence of $CaSO_4$ and/or $MgSO_4$ in PM1 during the study period. The findings of the PCA analysis support that other sulfate and nitrate compounds different from ammonium salts (e.g., $NaNO_3$ and $CaSO_4$) were present in the PM1 fraction during the study period.

3.4. Distribution of inorganic components between different PM size fractions

Fig. 2 shows the distribution of PM and water-soluble ions between PM1, PM2.5–1, and PM10–2.5. NH_4^+ has been considered exclusively associated with particles smaller than 2.5 μm. For Cl^-, only the relative distribution between the fine (PM2.5) and coarse (PM10–2.5) fractions could be determined since a large number of PM1 samples were under the detection limit.

Approximately 68% of PM2.5 particles were below 1 μm, a very similar value to that obtained by Pérez et al. in Barcelona [9]. In contrast, the PM1/PM10 ratio was considerably lower (0.35 versus 0.50 in Barcelona), revealing a higher contribution of coarse particles to the PM10 mass in Elche than in Barcelona. In spite of this, the seasonal trend of the PM1/PM10 ratio was the same to that observed in Barcelona, with a decrease from winter (0.4) to summer (0.3). This is the result of a higher contribution of coarse particles to the PM10 concentration in summer than in winter probably due to: (1) lower rainfall rates enhancing dust resuspension; (2) higher occurrence of Saharan dust outbreaks; and, (3) an increment of thermal dissociation of NH_4NO_3 and subsequent reaction of the released HNO_3 with coarse NaCl and $CaCO_3$.

Table 6
PCA results for PM1 water-soluble ions measured in Elche between October 2008 and October 2009.

	PC1	PC2	PC3
NO_3^-	0.48	0.61	
SO_4^{2-}	0.80		0.38
NH_4^+	0.98		
Na^+		0.89	
Ca^{2+}			0.82
Mg^{2+}			0.89
K^+		0.85	

Factor loadings lower than 0.25 are not shown.

Crustal (Ca^{2+}) and marine (Na^+, Mg^{2+}, Cl^-) ions were mainly associated with particles larger than 2.5 μm, since they originate from mechanical processes giving rise primarily to coarse particles. Almost 60% of K^+ was distributed in PM1, suggesting the prevalence of anthropogenic over natural sources. The seasonal variations of K^+ associated with PM2.5 and PM1 particles, with higher concentrations in winter than in summer (see Tables 1 and 5), are consistent with the preceding statement.

NO_3^- was evenly distributed between the fine (<2.5 μm) and coarse (>2.5 μm) fractions: 50% of NO_3^- was found in PM10–2.5, 23% in PM2.5–1, and 27% in PM1. However, and although PM10 NO_3^- levels were similar in winter and summer, important seasonal variations in its size distribution were observed (Fig. 3).

In summer, approximately 79% of NO_3^- was associated with particles larger than 2.5 μm, 12% with particles between 2.5 and 1 μm, and 9% with particles smaller than 1 μm. As already stated, fine NH_4NO_3 thermally dissociates, releasing HNO_3, which then reacts with $CaCO_3$ and NaCl to form $Ca(NO_3)_2$ and $NaNO_3$ with a peak in the size range above 2.5 μm. In contrast, during winter, more than 60% of NO_3^- accumulated in particles smaller than 2.5 μm (40% in particles smaller than 1 μm) principally as NH_4NO_3.

SO_4^{2-} distribution between the three size fractions was practically independent of the season of the year (Figs. 2 and 3): around 68, 20, and 12% of SO_4^{2-} was found associated with PM1, PM2.5–1, and PM10–2.5, respectively, both in the summer and winter periods. As previously described, particulate SO_4^{2-} is mostly generated by atmospheric reactions of gaseous precursors (SO_2 and NH_3) giving rise to $(NH_4)_2SO_4$, mainly in the submicron fraction. The PM1/PM2.5 ratios

Fig. 2. Relative distribution of PM and inorganic ions between different size fractions in Elche during the period October 2008–October 2009.

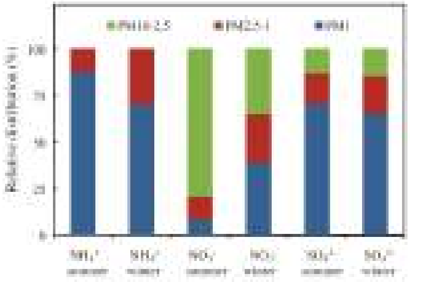

Fig. 3. Size distribution of secondary inorganic ions in summer and winter.

for NO_3^- (0.54) and SO_4^{2-} (0.77) suggest that NH_4NO_3 particles are larger than $(NH_4)_2SO_4$ particles.

NH_4^+ originates from ammonia vapor, which in the atmosphere reacts with acidic gases such as H_2SO_4 and HNO_3, accumulating in particles smaller than 1 μm. At our sampling site, the NH_4^+ proportion in the submicron fraction increased from ~70% in winter to nearly 90% in summer (Fig. 3). This is likely due to the clear predominance during summer of $(NH_4)_2SO_4$ particles that, as just mentioned, are smaller than NH_4NO_3 particles.

4. Conclusions

The annual average mass concentrations of PM2.5 and PM10 measured in an urban background station in southeastern Spain from October 2008 to October 2009 were 12% and 24% lower, respectively, than those measured in the same city between December 2004 and November 2005. The main reasons for such a decrease were identified due to a study of the variations of water-soluble ion concentrations between both periods. The three main reasons identified are as follows:

(1) During winter 2009 there were higher rates of precipitation and a lower frequency of local pollution events caused by atmospheric stagnation conditions compared to winter 2005. Consequently, the decrease in PM concentrations from 2004–05 to 2008–09 was much more significant in winter than in summer.
(2) A decrease in $(NH_4)_2SO_4$ concentrations partly due to a drop in SO_2 emissions caused by the application of emission control measures and the current economic crisis.
(3) A decrease in the emissions of coarse particles due to a fall in construction activities, which affected mainly the PM10 fraction.

PM1 concentrations during 2008–09, which were lower than those measured at other urban stations within the Mediterranean basin, were influenced by the specific meteorological and socioeconomic conditions of the study period. The PCA analysis helped to distinguish three major PM1 sources in Elche, which were identified as secondary $(NH_4)_2SO_4$ and NH_4NO_3, local traffic emissions, and soil dust.

SO_4^{2-} and NO_3^- size distributions showed marked differences due to the different thermal stabilities of $(NH_4)_2SO_4$ and NH_4NO_3.

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Anexo 2

Characterization of hydrocarbons in aerosols at a mediterranean city with a high density of palm groves

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Characterization of hydrocarbons in aerosols at a Mediterranean city with a high density of palm groves

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Abstract Samples of PM$_1$ and PM$_{10}$ were collected for 1 year at an urban background station in the city of Elche (southeastern Spain) and analyzed to determine the content of *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs). A few samples were also gathered at a second sampling point established at one of the several palm tree gardens of the city in order to evaluate the influence of biogenic emissions on the urban levels of *n*-alkanes. Diagnostic parameters obtained for aliphatic hydrocarbons (carbon maximum number (C_{max}), carbon preference index (CPI), and wax *n*-alkane content (%WNA)) revealed a higher contribution of biogenic *n*-alkanes in PM$_{10}$ than in PM$_1$. Moreover, the values of %WNA indicated that the levels of *n*-alkanes in Elche were more affected by emissions from terrestrial vegetation than in other urban areas, particularly in the palm tree grove location (%WNA = 29 for PM$_{10}$). PAH diagnostic ratios pointed to traffic as the main anthropogenic source of hydrocarbons in Elche, with predominance of diesel versus gasoline vehicle emissions. The average levels of total PAHs (~1 ng m^{-3}) were noticeably lower than the values registered at other urban areas in Europe, most likely because emissions from other sources are scarce. Both aliphatic and aromatic hydrocarbons showed higher levels in the cold season due to the lower atmospheric dispersion conditions, the increase in traffic exhaust emissions, and the lower ambient temperatures that reduce the evaporation of semivolatile species.

Keywords PAH · *n*-alkanes · PM$_1$ · PM$_{10}$ · Biogenic emissions

Introduction

The study of aerosol size distribution and chemical composition in urban areas has attracted increased attention in recent years since epidemiological and toxicological studies have found evidences of the relationship between these parameters and health effects (Kelly and Fussel 2012; Fox et al. 2015). Exposure to particulate matter (PM) is liable to cause cardiovascular and respiratory diseases, especially among the elderly and people with previous respiratory and cardiovascular disorders, as well as cancer (O'Connor et al. 2008; Hoek et al. 2013; Burkart et al. 2013).

The organic fraction of ambient PM is formed by hundreds of individual compounds that can be directly emitted from different sources or formed in the atmosphere by physico-chemical processes (Gogou et al. 1996; Kavouras et al. 2001). The greatest interest has been focused on two groups of organic compounds: *n*-alkanes and polycyclic aromatic hydrocarbons (PAH). *n*-Alkanes are dominant components of the non-polar fraction of organic aerosols (Chow and Watson 2007; Pietrogrande et al. 2011; Moussaoui et al. 2013), while PAHs are well-known due to their environmental

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persistence and carcinogenic properties. PAH toxicity and carcinogenicity show a strong structural dependence (Nisbet and LaGoy 1992). Among the commum studied PAH, benzo[*a*]pyrene, a five member ring congener, is considered the most potent human carcinogen by the International Agency for Research on Cancer (IARC 1998). For this reason, the European Community established the use of this compound as a carcinogenic marker of PAHs and fixed a target value of 1 ng m^{-3} annual average in the PM_{10} fraction (Directive 2004/107/EC). On the other hand, both aliphatic and aromatic hydrocarbons have been extensively used as tracers of pollutant emission sources.

n-Alkanes and PAHs are distributed between both the gas and particulate phases mainly depending on the ambient temperature, their vapor pressure, and molecular weight (Bi et al. 2003; Callén et al. 2008). Particulate organics can be found in both the coarse (>2.5 μm) and fine (<2.5 μm) fractions of atmospheric PM depending on their origins, although higher concentrations are usually associated to the fine PM fraction (Mirante et al. 2013; Tang et al. 2006).

PAHs are primarily emitted by anthropogenic activities such as coal and wood burning, petrol and diesel oil combustion, and industrial processes (Tobiszewski and Namieśnik 2012). Because of this, they are mostly emitted into the atmosphere in the form of gases and ultrafine or submicron particles. However, PAHs can be transferred to coarse-mode particles through volatilization and condensation processes (Richter and Howard 2000; Salwa and Khoder 2012). The sources of *n*-alkanes can be either natural or anthropogenic. Gasoline and diesel vehicles, coal, biomass and natural gas burning, cigarette smoke and unburnt heating oils are the most important anthropogenic sources of aliphatic hydrocarbons. But nature, in the form of contemporary epicuticular plant wax emissions and direct suspension of pollens, microorganisms and insects is also a major contributor to the atmospheric concentrations of these compounds (Simoneit 1999; Alves et al. 2012; Perrone et al. 2014). For instance, leaf surfaces of palms and many other plant species emit high molecular weight *n*-alkanes (C_{27}–C_{33}) with a strong odd carbon number predominance (Rogge et al. 1993).

Although organic compounds associated to different PM fractions have become the object of several works carried out worldwide, only a few recent studies have been focused on hydrocarbons associated to PM_1 in Europe (e.g., Barrero and Cantón 2007; Alves et al. 2012; Van Drooge et al. 2012). Thus, knowledge of the behavior of *n*-alkanes and PAHs in the submicron fraction is still limited.

This work is aimed at investigating the seasonal variation, sources and size distributions of *n*-alkanes and PAHs in an urban area of the eastern coast of the Iberian Peninsula with a high density of palm tree gardens. Particular attention has been given to the PM_1 fraction due to the special negative impacts on human health. Consequently, PM_1 and PM_{10} samples were collected at two sites in the study area for hydrocarbon quantification during 1 year.

Experimental

Study area and sampling sites

The sampling campaign was done at two sites in the urban area of Elche (Fig. 1), located in southeastern Spain. Elche is a medium-size city (~185,000 inhabitants), about 12 km from the Mediterranean Sea, with no significant industrial activity. Therefore, local anthropogenic emissions of atmospheric particles in the city are mainly attributed to traffic and construction works. An important part of the urban surface is unevenly covered by palm-tree gardens (Caballero et al. 2012). The Elche Palm Grove (The Palmeral of Elche) was declared a World Heritage Site by UNESCO in the year 2000.

Elche has a dry Mediterranean climate with annual precipitation rates varying between 150 and 200 mm, mainly concentrated in the fall and spring months, hot summers and mild winters. In the present study, the spring-summer season was considered from April to September of 2009. The temperature and solar radiation averaged for this period were 24 °C and 241 W m^{-2}, respectively. The fall-winter period comprised October 2008 to March 2009, with average values of temperature and solar radiation of 14 °C and 98 W m^{-2}, respectively.

The main sampling site (UMH) was located on the roof of a 15 m hight building at the Miguel Hernández University campus (38° 16′ 23″ N; 0° 41′ 27″ W), adjacent to a major city avenue (~37,000 vehicles per day on weekdays), in a highly ventilated area. A second sampling site (PTG) was placed at one of the palm tree gardens existing in the city center (38° 16′ 12″ N; 0° 41′ 56″ W), around 800 m southwest of the first site. This point was selected to evaluate the biogenic contribution to the levels of *n*-alkanes in the urban area.

Fig. 1 Location of the city of Elche and the sampling sites

Sampling and analysis

The campaign was carried out from October 2008 until September 2009. Twenty-four-hour samples of PM_1 and PM_{10} were collected on teflon-impregnated glass-fiber filters (T60A20-47 mm; Pallflex) by means of Derenda 3.1 low volume samplers (2.3 m^3 h^{-1}). Filters were previously washed with ultrapure acetone in an ultrasonic bath and heated to 300 °C for 24 h to remove organic contaminants.

PM concentrations were determined by weighing the filters before and after exposure in an electronic microbalance (Ohaus, Model AP250D) with a precision of ± 10 μg. The filters were conditioned for at least 24 h prior to weighting at a relative humidity of 50 ± 5 % and temperature of 20 ± 1 °C, and stored at −18 °C until further analysis.

During the study period, 30 and 32 representative samples of PM_1 and PM_{10}, respectively, collected at the UMH sampling point were analyzed by thermal desorption coupled with gas chromatography-mass spectrometry (TD-GC-MS). At the palm tree garden location, the number of samples analyzed was 8 and 15 for PM_1 and PM_{10}, respectively. Seventeen PAHs and 25 *n*-alkanes, from C_{16} to C_{40}, were quantified. Analyses were performed following the method described elsewhere (Gil-Moltó et al. 2009). A one-eighth portion of each filter was thermally extracted at 300 °C for 8 min with a helium flow rate of 150 mL min^{-1} using a Gerstel TDS2/TDSA thermal desorption device. Analytes were trapped at −40 °C in a cryogenically cooled programmable temperature injection system (Gerstel CIS4). The cold trap was subsequently heated to 325 °C and maintained at this temperature for 5 min. The extracted compounds were then injected in an Agilent 6890N gas chromatograph (HP-5MSI capillary column, 30 m, 0.25 mm I.D., 0.25 μm film thickness) coupled with an Agilent 5973N mass spectrometer operating in selective ion monitoring (SIM) mode. Regarding the chromatographic process, the column oven temperature started at 70 °C for 2 min, increased to 200 °C at 25 °C min^{-1} and then to 285 °C at 45 °C min^{-1}, maintaining this temperature for 40 min. The helium flow rate at the analytical column was 1 mL min^{-1} during 19 min and then increased to 1.5 mL min^{-1} until the end of the analysis. Identification of target analytes was accomplished by comparing their retention times and mass spectra with that of authentic standards diluted in hexane, both for aliphatic (DRH-FTRPH and DRH-FTRPH2 supplied from AccuStandard, New Haven, CT, USA) and aromatic compounds (PAH-Mix 68, from Dr. Ehrenstorfer, GmbH, Augsburg, Germany). Calibration curves were performed using pre-cleaned blank filters spiked with standard solutions. Linear aliphatic hydrocarbons were quantified by means of ion 57, while polycyclic aromatic hydrocarbons (PAH) were quantified using their M^+ ions.

Source assignment

Different diagnostic parameters are frequently used to identify sources of hydrocarbons. In the case of *n*-alkanes, the following molecular markers and diagnostic ratios were used:

- The carbon number maximum (C_{max}), i.e., the *n*-alkanes showing the highest concentration in the homologous series, provides information of the relative importance of organic matter from biogenic and anthropogenic sources. The odd homologues C_{27}, C_{29} and C_{31} predominate in higher plant waxes, while distributions with C_{max} at lower carbon numbers indicate a major input from fossil fuel combustion.
- The carbon preference index (CPI) has also been suggested as an indicator of the relative contribution to atmospheric *n*-alkanes from biogenic and anthropogenic sources. CPI values were calculated as the sum of the odd carbon number homologues divided by the sum of the even carbon number homologues. The CPI typically ranges from values around 1 in environments with petroleum-derived emissions, whereas a CPI higher than 3 is characteristic of rural areas, where the biogenic influence is more important (Mazurek et al. 1989).
- The contribution of wax *n*-alkanes can be calculated, as shown in Eq. (1), by subtraction of the average of the next higher and lower even carbon numbered homologues (Kavouras and Stephanou 2002).

$$\mathrm{WNAC}_n = [C_n - (C_{n+1} + C_{n-1})/2] \tag{1}$$

Negative values of C_n were taken as zero.

The percentage of wax *n*-alkanes (%WNA) can be calculated, using the Eq. (2), from the total concentration of wax *n*-alkanes (ΣWNA C_n) and the sum of the concentrations of all *n*-alkanes (Σ NA).

$$\%\mathrm{WNA} = \left(\sum \mathrm{WNAC}_n \times 100\right) / \sum \mathrm{NA} \tag{2}$$

The identification of the most probable pollution sources of PAHs is commonly performed using different diagnostic ratios available in the literature. These ratios can distinguish between PAH emitted from petroleum products, fossil fuel combustion and biomass burning (Kavouras et al. 2001; Tobiszewski and Namieśnik 2012; and references cited therein). In the present study, the following parent PAHs ratios were employed:

- Fluoranthene divided by the sum of fluoranthene plus pyrene [Ft/(Ft + Pyr)]
- Benz[*a*]anthracene divided by the sum of benz[*a*]anthracene plus chrysene [BaA/(BaA + Chry)]
- Benzo[*e*]pyrene divided by the sum of benzo[*e*]pyrene plus benzo[*a*]pyrene [BeP/(BeP + BaP)]
- Indeno(1,2,3-*cd*)pyrene divided by the sum of indeno(1,2,3-*cd*)pyrene plus benzo[*g,h,i*]perylene [IP/(IP + BghiP)]
- Benzo[*a*]pyrene divided by benzo[*g,h,i*]perylene (BaP/BghiP)

Results and discussion

n-Alkanes

Levels, size distribution and seasonal variation

Factors affecting levels and seasonal variations of PM_1 and PM_{10} at the UMH site were described in previous works (Galindo et al. 2011; Galindo et al. 2013). Thus, the present paper is exclusively focused on *n*-alkanes and PAH.

Average levels of the sum of *n*-alkanes during the study period at the UMH site were 19.7 ± 10.3 and 25.1 ± 9.0 ng m^{-3} for PM_1 and PM_{10}, respectively. The values found in this study were significantly lower than those observed in several other European urban stations located in Barcelona (140.8 ng m^{-3} in PM_1), Zurich (37.3 ng m^{-3} in PM_1) (Alves et al. 2012), Athens (77 ng m^{-3} in PM_{10}) (Karanasiou et al. 2007) or Oporto (34 ng m^{-3} in $PM_{2.5}$) (Alves et al. 2014). However, total *n*-alkane concentrations were higher than the value of 16.5 ng m^{-3} reported for $PM_{2.5}$ in Coimbra, a less populated city than those previously mentioned (Alves et al. 2014). These results suggest that the levels of *n*-alkanes tend to increase with the population of the study area.

Although very similar, the patterns of *n*-alkanes as a function of carbon number showed some variations among the fall-winter and spring-summer periods (Fig. 2). The most remarkable difference was the size distribution of biogenic hydrocarbons C_{29} and C_{31}. During the warm season, these distributions were clearly shifted towards the course fraction of PM_{10}. On the other hand, although the homologues C_{29} and C_{31} showed similar concentrations during both periods, a substantial decrease in the levels of anthropogenic hydrocarbons was observed from the cold to the warm season. This was particularly evident for hydrocarbons C_{16} to C_{21} probably due to their greater volatility. Higher winter concentrations of *n*-alkanes have also been observed in previous studies (Barrero and Cantón 2007; Pietrogrande et al. 2011; Yadav et al. 2013). In Elche, this seasonal cycle cannot be ascribed to changes in vehicle density since daily traffic within the urban area is quite constant throughout the year (Caballero et al. 2012). However, colder ambient temperatures lead to higher emissions of *n*-alkanes due to a delay in catalyst light-off time that produces an inefficient removal of hydrocarbons from the exhaust (Schauer et al. 2008; Chan et al. 2013). Additionally, during fall and winter, mixing layer heights are lower and the frequency of stable atmospheric conditions is higher than in spring and summer, favoring the accumulation of pollutants emitted by local sources. In the case of biogenic *n*-alkanes C_{29} and C_{31}, this increment is partially made up for the growth of emissions by terrestrial vegetation during spring and summer (Schnelle-Kreis et al. 2005; Górka et al. 2014).

Source assignment

Figure 3 shows the *n*-alkane concentration profile versus carbon number at the UMH site for PM_1 and PM_{10}. The biogenic homologue C_{31} was the dominant compound (C_{max}) in both PM fractions. However, as expected from its natural origin, the predominance of this alkane was significantly higher in PM_{10} than in PM_1. Actually, the second most abundant component in PM_{10} was C_{29}, of biogenic origin also, while the PM_1 profile showed a secondary maximum centered at C_{22}–C_{23}. This indicates a greater contribution of *n*-alkanes derived from fossil fuel combustion in the submicron fraction (Rogge et al. 1993). C_{29} and C_{31} were also dominant hydrocarbons in other urban background stations of the Iberian Peninsula such as Oporto and Coimbra, reflecting a significant contribution of epicuticular wax alkanes from leaf surfaces (Alves et al. 2014).

Average values of CPI and %WNA calculated for the UMH site during the cold and warm seasons are shown in Table 1. CPI_1 values reveal the importance of

Fig. 2 Distribution of *n*-alkanes between the submicron and coarse fractions during the cold and warm seasons at the UMH sampling site

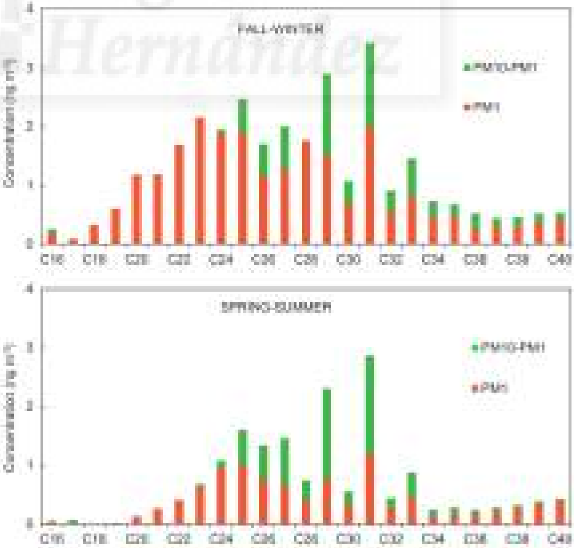
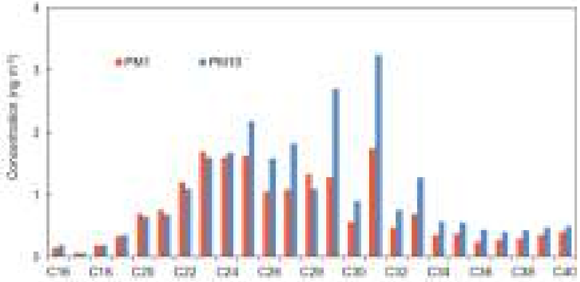


Fig. 3 Average concentrations of *n*-alkanes at the UMH site between October 2008 and September 2009



anthropogenic emissions of *n*-alkanes associated with PM_1, including vehicle emissions and unburned fuels, during both seasons. Similar values have been reported for other urban areas (van Drooge et al. 2012; Alves et al. 2014; Ladji et al. 2014). The greater CPI_1 values obtained for PM_{10} indicate a higher influence of biogenic sources, especially in the warm season when higher plant wax emissions are maxima. These values are higher than those found in other urban areas (Moussaoui et al. 2013; Górka et al. 2014), pointing to a larger input from biogenic sources in Elche. The clear predominance in PM_{10} of odd carbon number *n*-alkanes for the high molecular weight homologues during the warm season (CPI_3 = 2.64) confirms the important contribution to the coarse fraction of PM_{10} of emissions from terrestrial vegetation. On the other hand, the CPI_2 value near unity for PM_1 during the fall-winter period indicates that this *n*-alkane range was almost exclusively emitted from fossil fuel combustion during the cold season. These results were supported by %WNA values. The highest %WNA obtained for the PM_{10} fraction during the warm season (31 %) was significantly greater than those calculated for other metropolitan areas (11–17 %) (Moussaoui et al. 2013; Górka et al. 2014). As expected, the wax *n*-alkane content in PM_1 was lower than in PM_{10}.

Table 1 Diagnostic ratios for *n*-alkanes at the UMH site during fall-winter and spring-summer

	Cold season		Warm season	
	PM_1	PM_{10}	PM_1	PM_{10}
CPI_1	1.18	1.50	1.36	1.89
CPI_2	1.12	1.26	1.25	1.61
CPI_3	1.61	2.09	2.07	2.64
%WNA	15	24	18	31

$CPI_1 = \Sigma(C_{17}–C_{39})/\Sigma(C_{16}–C_{40})$, CPI for the whole range

$CPI_2 = \Sigma(C_{17}–C_{25})/\Sigma(C_{16}–C_{24})$, CPI for petrogenic *n*-alkanes

$CPI_3 = \Sigma(C_{25}–C_{35})/\Sigma(C_{26}–C_{36})$, CPI for biogenic *n*-alkanes (Bi et al. 2003; Górka et al. 2014)

Linear relationships between daily values of CPI and %WNA for the entire range of *n*-alkanes were studied in order to determine the reliability of these two indexes for source identification. Excellent positive correlations were observed for both size fractions ($r > 0.95$), indicating that the CPI and %WNA can be used for source assignment of *n*-alkanes (He et al. 2010).

As described in the Experimental section, a second sampling site (PTG) was placed at one of the city center palm tree gardens in order to evaluate the biogenic contribution to the levels of *n*-alkanes in the urban area. Despite the high density of biogenic sources at this location, *n*-alkane profiles were very similar to those described for the UMH sampling site, reaching total *n*-alkane concentrations in PM_1 and PM_{10} of 15.9 ± 5.9 and 23.2 ± 8.3 ng m^{-3}, respectively. Diagnostic parameters obtained for both sites are presented in Table 2. It is important to mention that only those samples simultaneously collected at the UMH and PTG locations have been used for calculations. For this reason, some results obtained for the UMH site may differ slightly from those previously presented.

The results shown in Table 2 point to a higher influence of biogenic emissions of *n*-alkanes at the palm tree garden than at the urban background site. The biogenic homologue C_{31} was the predominant hydrocarbon in both fractions at PTG. Moreover, CPI and %WNA values obtained at the PTG location were greater than those calculated for the UMH site, although the differences were small since traffic in the streets nearby the park, especially during rush hours, is dense.

Table 2 Diagnostic parameters for *n*-alkanes at the two sampling sites

	UMH		PTG	
	PM_1	PM_{10}	PM_1	PM_{10}
C_{max}	C_{29}	C_{31}	C_{31}	C_{31}
CPI_1	1.30	1.62	1.34	1.70
CPI_2	1.32	1.32	1.18	1.44
CPI_3	2.13	2.45	2.09	2.58
%WNA	15	26	18	29

$CPI_1 = \Sigma(C_{17}–C_{39})/\Sigma(C_{16}–C_{40})$, CPI for the whole range

$CPI_2 = \Sigma(C_{17}–C_{25})/\Sigma(C_{16}–C_{24})$, CPI for petrogenic *n*-alkanes

$CPI_3 = \Sigma(C_{25}–C_{33})/\Sigma(C_{26}–C_{34})$, CPI for biogenic *n*-alkanes (Bi et al. 2003; Górka et al. 2014)

Polycyclic aromatic hydrocarbons

Levels, size distribution and seasonal variation

Table 3 shows average mass concentrations of particle-bound PAHs for both size fractions at the UMH site. Benzo[*b* + *k*]fluoranthene represents the sum of the two five-ring homologues. Average concentrations of total PAHs measured in Elche (~1 ng m^{-3}) were considerably lower than those reported for other urban areas (>10 ng m^{-3}) (Barrero and Cantón 2007; Alves et al. 2014; Górka et al. 2014). The absence of industrial activity and the low consumption of wood and fossil fuel for house heating may be some of the causes for the low PAH levels in Elche. In fact, benzo[*b* + *k*]fluoranthene and chrysene, which are strongly associated to vehicular emissions, were the dominant PAHs in both PM fractions, pointing to traffic as the main source of these compounds.

Total PAH concentrations were between two and three times higher in the cold than in the warm season. Factors influencing the seasonal cycle of PAHs were studied in detail elsewhere (Varea et al. 2011) and will only be briefly discussed here. During summer, the higher temperatures and solar radiation favor PAH evaporation and photochemical decomposition, reducing their concentrations. Additionally, the low dispersion conditions during winter and the increase in vehicle emissions due to colder ambient temperatures promote the accumulation of PAHs and other pollutants. The most abundant PAHs during the cold season were B[b + k]Ft

Table 3 *Average concentrations* (ng m^{-3}) of PAHs in PM_1 and PM_{10} at the UMH site

Compound	Abbreviation	Cold season		Warm season	
		PM_1	PM_{10}	PM_1	PM_{10}
Total PAHs	TPAH	1.01	1.23	0.37	0.50
Acenaphthylene	Acy	0.01	0.01	<QL[a]	0.01
Acenaphthene	Ace	0.01	0.01	<QL[a]	0.01
Fluorene	Fl	0.01	0.01	<QL[a]	<QL[a]
Phenanthrene	Phen	0.02	0.04	0.02	0.03
Anthracene	Ant	0.01	0.01	<QL[a]	<QL[a]
Fluoranthene	Ft	0.06	0.09	0.02	0.04
Pyrene	Pyr	0.07	0.10	0.02	0.03
Benzo[*a*]anthracene	BaA	0.07	0.09	0.02	0.03
Chrysene	Chry	0.13	0.16	0.02	0.04
Benzo[*b* + *k*]fluoranthene	B[b + k]Ft	0.27	0.29	0.07	0.08
Benzo[*e*]pyrene	BeP	0.10	0.12	0.03	0.04
Benzo[*a*]pyrene	BaP	0.08	0.08	0.03	0.04
Benzo[*g,h,i*]perylene	BghiP	0.08	0.09	0.04	0.05
Dibenzo[*a,h*]anthracene	DBahA	0.02	0.03	0.02	0.03
Indeno(1,2,3-*cd*)pyrene	IP	0.08	0.09	0.06	0.06
Anthantrene	Ant	0.02	0.03	0.02	0.03

[a] Concentrations below the quantification limit

and Chry. However, during the spring-summer period Chry was replaced by IP as one of the major pollutants, probably because of a more pronounced shift of the gas-particle partitioning equilibrium of Chry to the gas phase due to its higher volatility.

As expected, PAHs were predominantly found in PM_1 (~84 %), with ~16 % associated with particles between 1 and 10 μm. This makes the submicron fraction more toxic for human health.

Total PAH concentrations observed at the palm tree garden were similar than those reported for the UMH site. Additionally, PAH levels had the same temporal variability at both locations, as demonstrated by the good correlations between daily total PAH concentrations measured concurrently at the two sampling sites ($r > 0.9$).

Sources and toxicity

The BaA/(BaA + Chry) ratio found in this study was 0.37 for both PM_1 and PM_{10} (Table 4), indicating that PAHs were primarily emitted by vehicle exhaust. Equivalently, the BeP/(BeP + BaP) ratios (~0.6) confirmed road traffic as the main source of PAHs, ruling out other sources such as wood combustion. The values for the ratio BaP to BghiP (>0.6) were also consistent with traffic emissions. The Ft/(Ft + Pyr) ratio was selected to distinguish between emissions from petrol and diesel engines. The ratios in Elche, between 0.47 and 0.49, point to mixed emissions from gasoline and diesel vehicles. Finally, the values calculated for the IP/(IP + BghiP) ratio, around 0.5, suggest a predominance of diesel versus gasoline exhaust emissions. This can be mainly attributed to higher PAH emissions from diesel cars compared to gasoline vehicles (Perrone et al. 2014).

Benzo[*a*]pyrene has been regarded for a long time as an index for the whole carcinogenicity of PAHs. In fact, the European Community established a target value for this compound of 1 ng m^{-3} annual average in PM_{10} (Directive 2004/107/EC). Nevertheless, the use of toxic equivalent factors provides a more accurate risk assessment for environmental PAH exposure than considering each individual PAH as an individual mutagenic agent (Nisbet and LaGoy 1992). These factors are calculated by multiplying the concentrations of the carcinogenic congeners for their relative potencies. In the present study, the PAH carcinogenicity was calculated as the benzo[*a*]pyrene equivalent concentration (BaPE) using Eq. (3) (Yassaa et al. 2001).

$$\mathrm{BaPE} = 0.06 \times \mathrm{BaA} + 0.07 \times \mathrm{B[b+k]Ft} + \mathrm{BaP} + 0.6 \times \mathrm{DBahA} + 0.08 \times \mathrm{IP} \quad (3)$$

The average BaPE values calculated for the UMH site were 0.1 ng m^{-3} for both PM_1 and PM_{10}. BaP was the highest carcinogenic contributor with ~64 % of the total BaPE concentration in both PM fractions, followed by B[b + k]Ft with around 16 %. BaPE concentrations found in Elche were much lower than those observed in many urban areas around the world (Delgado-Saborit et al. 2011; Alves et al. 2012; Ladji et al. 2014) and considerably lower than the limit value of 1 ng m^{-3} established by the European Community. As expected,

Table 4 PAH diagnostic ratios calculated for the UMH site. Reference values from the literature are also depicted

Ratio	PM_1	PM_{10}	Value	Source
BaA/(BaA + Chry)	0.37	0.37	<0.2	Petrogenic
			0.2–0.35	Coal combustion
			>0.35	Vehicular emissions
BeP/(BeP + BaP)	0.56	0.57	0.6–0.8	Traffic
			0.5	Wood combustion
BaP/BghiP	0.95	0.87	<0.6	Non-traffic emissions
			>0.6	Traffic emissions
Ft/(Ft + Pyr)	0.47	0.49	0.26	Biomass burning
			0.4	Gasoline vehicles
			0.6–0.7	Diesel vehicles
			>0.5	Coal burning
IP/(IP + BghiP)	0.51	0.50	0.22	Gasoline vehicles
			0.35–0.70	Diesel vehicles

BaPE concentrations during the fall-winter period were more than double those calculated for the spring-summer period, indicating a higher health risk during the cold season.

Conclusions

The average levels of *n*-alkanes measured at an urban background station in Elche were lower than the values found in bigger cities, but higher than those reported for less populated urban regions. The size distributions of *n*-alkanes showed that anthropogenic hydrocarbons were mainly associated to submicron particles, especially in winter. For the biogenic homologues C_{29} and C_{31} a clear shift towards the course fraction of PM_{10} during the warm season was observed. Although hydrocarbon C_{31} was the most abundant component in both fractions, PM_1 showed a second maximum at C_{23}–C_{25}, while the second contributor in PM_{10} was C_{29}. These results indicate a higher input of *n*-alkanes from biogenic sources in the course fraction of PM_{10}, which was confirmed by CPI and %WNA values calculated for both size fractions. Even though CPI and %WNA values showed predominant contributions of anthropogenic sources in both studied fractions, the wax *n*-alkane content in PM_{10} was found to be higher than those of other urban areas, pointing to significant biogenic emissions of hydrocarbons from the palm tree groves spread over the city. The slightly greater contribution of plant wax *n*-alkanes at the palm tree garden compared with the urban background site is consistent with this assumption.

The average levels of PAHs measured in Elche were at least one order of magnitude lower than those reported for many other cities in Europe, indicating lower emission rates from anthropogenic sources. Diagnostic ratios calculated for parent PAHs pointed to traffic as the main source of this class of compounds, excluding significant emissions from other sources such as wood burning.

The seasonal pattern of *n*-alkanes and PAHs was similar to that found in other urban areas, displaying a decrease in the levels of hydrocarbons from winter to summer. This behavior was due to changes in emissions rates and meteorological conditions. Only biogenic *n*-alkanes showed similar values in both seasons since the increase in biogenic emissions during the warm season would balance out the concentration decrease favored by the predominant meteorology.

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