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Evaluation of the urban/rural particle-bound PAH and PCB levels in the northern Spain (Cantabria region)

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Abstract The aim of the present study was to evaluate the polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) levels in PM_{10} and $PM_{2.5}$, at one rural and three urban sites in the Cantabria region (northern Spain). From all of these pollutants, benzo(*a*)pyrene is regulated by the EU air quality directives; its target value (1 ng/m^3) was not exceeded. The concentration values of the studied organic pollutants at the studied sites are in the range of those obtained at other European sites. A comparison between the rural–urban stations was developed: (a) PAH concentration values were lower in the rural site (except for fluorene). Therefore, the contribution of local sources to the urban levels of PAHs seems relevant. Results from the coefficient of divergence show that the urban PAH levels are influenced by different local emission sources. (b) PCB rural concentration values were higher than those found at urban sites. Because no local sources of PCBs were identified in the rural site, the contribution of more distant emission sources (about 40 km) to the PCB levels is considered to be the most important; the long-range transport of PCBs does not seem to be significant. Additionally, local PAH tracers were identified by a triangular diagram: higher molecular weight PAHs in Reinosa, naphthalene in Santander and anthracene/pyrene in Castro Urdiales. A preliminary PAH source apportionment study in the urban sites was conducted by means of diagnostic ratios. The ratios are similar to those reported in areas affected by traffic emissions; they also suggest an industrial emission source at Reinosa.

Keywords PAHs · PCBs · PM_{10} and $PM_{2.5}$

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are persistent and ubiquitous compounds in the environment. PAHs are emitted primarily during incomplete combustion of organic materials such as fossil fuels, coke, or wood (Vardar and Noll 2003); although hundreds of PAH compounds exist, according to their carcinogenic and mutagenic properties, only 16 of them are classified as priority pollutants by the US EPA (Ravindra et al. 2008). PCBs are a class of 209 chemical compounds, widely used as di-electric fluid in many applications such as transformers and capacitors or hydraulic fluids (Gambaro et al. 2004). The convention on long-range transboundary air pollution targets PAHs and PCBs as persistent organic pollutants (POPs). POPs are a group of compounds with specific properties: persistency, high bioaccumulative coefficient and ability for

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transmission to large distances (Biterma and Voutsa 2005).

Under this framework, the European Commission has developed Directive 2004/107/EC about PAH and metal levels in air, which establishes a target value for benzo(*a*)pyrene (BaP) in PM_{10}, 1 ng/m^3; additionally, this directive also proposes that each Member State shall monitor other relevant PAHs such as benzo(*a*) anthracene (BaA), benzo(*b*)fluoranthene (BbF), dibenzo(*a*,*h*)anthracene (DahA), benzo(*k*)fluoranthene (BkF), benzo(*j*)fluoranthene and indene (1,2,3-*c*,*d*) pyrene. PCBs are targeted by the Stockholm convention on persistent organic pollutants as industrial chemicals and by-products that have been recognized as causing adverse effects on humans and the ecosystem. Parties of the Stockholm convention are obligated to identify and reduce or eliminate the emission sources of PCBs to the environment.

Because of the POP low vapour pressure, these compounds exist in the atmosphere as vapour phase chemicals and in condensed form adsorbed on atmospheric particles (Ravindra et al. 2008). Gas to particle partition of POPs depends on the molecular weight, temperature, humidity and precipitation; in general, low-volatile PAHs (four or more rings) and PCBs (eight to nine Cl) are adsorbed on airborne particulate. The mobility of the particle-bound POPs is low; they are characterized by a rapid deposition and retention close to the emission source (Wania and Mackay 1996; Maliszewska-Kordybach 1999). Only the PAHs and PCBs associated with the particulate fraction are studied in the present work.

The work aims to study the levels of (a) the 16 US EPA priority PAHs—naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluoranthene (Flua), phenantrene (Phe), anthracene (Ant), fluorene (Flu), pyrene (Pyr), BaA, chrysene (Chr), BbF, BkF, BaP, DahA, benzo(*g*,*h*,*i*)perylene (BghiP) and indene(1,2,3*c*-*d*) pyrene (IcdP)—and (b) 10 PCBs—indicator PCBs (28, 52, 101, 118, 153 and 180) and PCB-8, PCB-194, PCB-206 and PCB-209—in three selected urban sites and one rural site in the Cantabria region (northern Spain). The particle-bound POP values are compared with those obtained at other urban and rural European sites; a regional inter-site comparison is also conducted using a health risk assessment tool. The identification of PAH local pollution sources and their potential carcinogenic impact were also performed.

Materials and methods

Sampling sites

Cantabria is a small region located in the north of Spain; it covers an area of 5,321 km^2 between the mountains of the Cordillera Cantábrica and the Cantabrian Sea. Some sampling sites were selected to determine the organic compounds levels in particulate matter and their distribution across the region. The studied sampling sites are located at urban (Santander (SANT), Castro Urdiales (CAST) and Reinosa (REIN)) and rural areas (Los Tojos, TOJ), Fig. 1; the studied urban areas are influenced by different industrial activities.

Santander (182,700 inhabitants, 2009) is the most populated city in the Cantabria region; Santander and some surrounding towns are considered as an agglomeration area with about 250,000 inhabitants (almost the half of the population of Cantabria). The agglomeration area includes an industrial area mostly related to steel and ferroalloy manufacturing plants which are located in the Santander suburbs, 5–10 km SW. In the SANT sampling site (43°28′26″ N, 3°47′ 47″ W, 23 m a.s.l.), PAH and PCB analyses were conducted in PM_{10} and $PM_{2.5}$.

Castro Urdiales (31,670 inhabitants, 2009) is a coastal town in the eastern area of Cantabria. This town is in the vicinity of a national highway. Furthermore, it is also located at 10–30 km NW from a highly industrial area, which is close to the Bilbao agglomeration (refinery, steel manufacturing plants) and at 4–5 km N from a limestone calcination plant burning petroleum coke. In the CAST sampling site (43°22′56″ N, 3°13′14″ W, 20 m a.s.l), only PAHs were determined in PM_{10} to compare the concentration values with other urban sites within the region.

Reinosa (10,307 inhabitants, 2009) is located in the interior of the Cantabria region; this town is in the close vicinity of a steel manufacturing plant (1–2 km). In the REIN sampling site (43°04′03″ N, 4°08′08″ W, 850 m a.s.l), only PAHs were determined in PM_{10} samples.

Los Tojos (434 inhabitants, 2009) is a small village in the centre of Cantabria region in the nature reserve of Saja-Besaya. The sampling site is located in a woodland area at 30 km SW from the industrial area of Torrelavega (energy, chemical and pulp and paper industries), at 60–65 km NE from a coal-fired power station and at 30–35 km N from a cement plant. In the

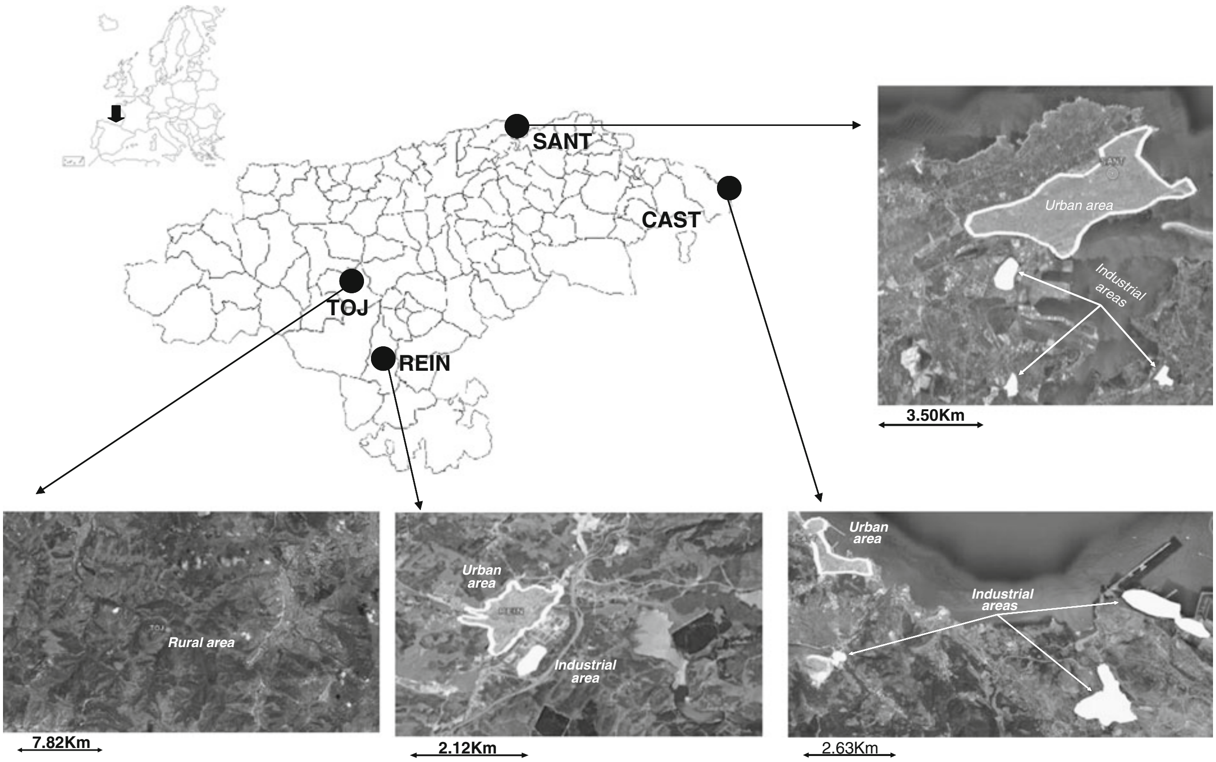

Fig. 1 Selected sampling sites in the Cantabria region. Urban sites: Santander (*SANT*), Reinosa (*REIN*) and Castro Urdiales (*CAST*). Rural site: Los Tojos (*TOJ*)

TOJ sampling site (43°09′16″ N, 4°15′14″ W, 622 m a.s.l), PAH and PCB characterization was conducted in PM_{10} samples.

At SANT site, three daily samples per week of PM_{10} and $PM_{2.5}$ were collected during the years 2008–2009; PM_{10} and $PM_{2.5}$ were sampled on glass fibre filters (sampling volume 720 m^3). However, at TOJ, CAST and REIN sites, two 48-h samples of PM_{10} per week were collected during 2008; at these sites, PM_{10} was always sampled on quartz fibre filters (sampling volume 110 m^3). Since the sampling periodicity is not the same at the four studied sites—daily and 48-h samples—the organic compounds measurements are not always simultaneous. Further details of the PM samplers can be found in Arruti et al. (2010).

At the four selected sampling sites, a minimum of 14% of the annual sampling period was selected for the PAH analysis in order to fulfil the requirements of Directive 2008/50/EC for indicative measurements: (a) At SANT sampling site, 66 and 52 daily samples were analysed in PM_{10} and $PM_{2.5}$, respectively, whereas (b) at REIN, CAST and TOJ, 24, 32 and 24, 48-h samples of PM_{10} were analysed, respectively. The time coverage of PCBs was lower because the present paper is only a preliminary study; the analysed samples were 10 and 12 at SANT and TOJ sites, respectively.

Additional data from the EMEP/VAG/CAMP station of Niembro (NIEM; 43°26′33″ N, 4°51′01″ W, 134 m a.s.l.) were also used in order to study the rural background levels of PAHs in the area (Ministerio de Medio Ambiente y Medio Rural y Marino (MARM) 2010); NIEM is a rural background monitoring station that is close to the Cantabria region.

Wind patterns at the studied sampling sites

Figure 2 shows the wind roses (2008) at the four sampling sites; the meteorological data were obtained from monitoring stations of the Cantabria air pollution network. In Santander city, the predominant wind direction is SW. However, SANT sampling site is influenced by the sea breezes, which is a characteristics wind pattern in the Santander bay; light winds blow predominantly from the SW during the morning

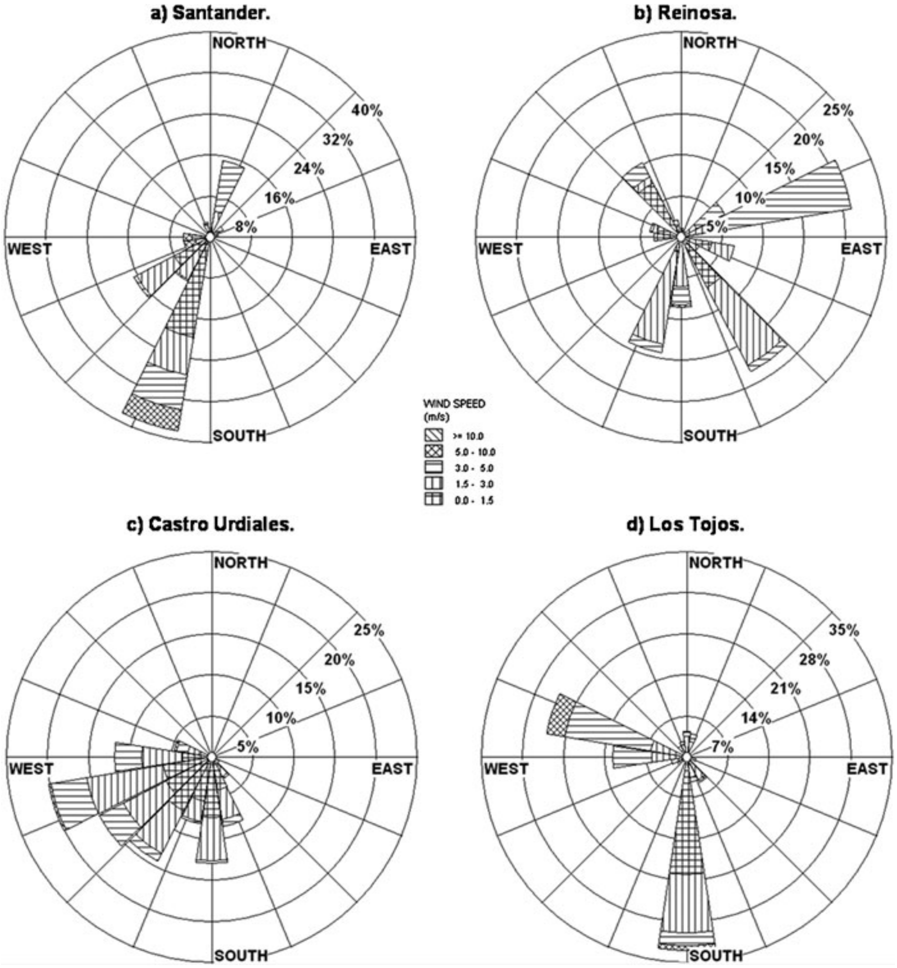

Fig. 2 Wind roses at selected sampling sites: **a** Santander, **b** Reinosa, **c** Castro Urdiales and **d** Los Tojos. Year 2008

but at night, the wind direction is the inverse NE-ENE (Ruiz et al. 2011).

In Castro Urdiales town, the predominant wind direction is also SW. The highest wind speed episodes are associated to the predominant direction; in the region, the lowest annual mean wind speed is measured in Castro Urdiales.

In Reinosa town, the predominant wind directions are NE and SE; however, there are other wind directions with a high frequency during 2008, SW and NW. According to the wind direction distribution, it is supposed that in Reinosa city, the wind directions are dominated by local patterns. The highest wind speed episodes are associated to NE direction.

In Los Tojos village, the predominant wind directions are S and E. Los Tojos is a mountainous area so the wind direction is dominated by the land contour. The highest wind speed episodes are associated to E direction probably because of the wind canalization; in the region, the highest annual wind speed is measured in Los Tojos.

Sample treatment and chemical analysis

PM_{10} and $PM_{2.5}$ concentrations were determined by the gravimetric method; before and after the weighting process, the filters were equilibrated under the same temperature and humidity conditions.

PAH analysis

The sample treatment for PAH analysis is in accordance with ISO-UNE 16362-2006 "Determination of particle-phase polycyclic aromatic hydrocarbons by high performance liquid chromatography", which is proposed by the Spanish regulation (Real Decreto

812/2007) as analytical method to determine the PAH levels in PM_{10}. Prior to the PAH extraction, all samples were spiked with an internal deuterated standard (anthracene D^{12}) in order to determine the analytical recovery efficiencies. The samples were extracted from particulate matter by Soxhlet using toluene as solvent for 9 h (10 cycles/h). The filtered extract (about 90 mL) was reduced to 1 mL under a gentle nitrogen flow (Turbovap LV, Zimark); because the extract must be dissolved in a suitable solvent, the extract volume was adjusted to 10 mL with *n*-hexane and another concentration step was conducted. A clean-up treatment was performed using an automatic system (Power Prep, Fluid Management System Inc.); samples were added to 10 g neutral silica columns and eluted with a *n*-hexane/dichloromethane mixture (60:40 *v*/*v*); the final volume was 30 mL. The eluted volume was reduced nearly to dryness under a gentle nitrogen flow; the reduced sample was re-dissolved in acetonitrile and the final volume was 100 μL. Sixteen US EPA PAHs were determined by high-performance liquid chromatography coupled to diode array and mass detectors (HPLC–DAD–MS) (1100 series, Agilent Technologies); the HPLC detector selection for each PAH was based on the detection limits and recoveries found during the development of the analytical method. The PAH separation was performed on a C18 column, 250×2.1 mm (Vydac 201-TP52); the flow rate was 0.4 mL/min and the injection volume was 20 μL. The elution was performed with a gradient starting from an eluent composition of 60% methanol in water; the methanol concentration was increased up to 100%. Liquid chromatography–atmospheric pressure chemical ionisation–mass spectrometry analyses were performed in the positive ion mode being the operation parameters optimised.

The proposed analytical method was checked by recovery tests with (a) Standard Reference Material (SRM)1649a "urban dust" and (b) doped filters. The results of the recovery tests for PAHs were in the range recommended by ISO-UNE 16632-2006, from 50% to 150%. The internal deuterated standard mean recovery was 66%; this recovery value was used to correct the amount of each PAH.

The limit of detection (l.d) was defined as the mean blank+3 standard deviations of the blanks. The values of the l.d vary from 0.23 ng/m^3 (Acy) to 0.002 ng/m^3 (BkF) and 0.16 ng/m^3 (Acy) to 0.001 ng/m^3 (Flu) in the glass fibre filter and quartz fibre filter cases, respectively; the l.d values are comparable with those reported in the literature (Lee and Jones 1999; Gambaro et al. 2007).

Taking into account the detection limits and some preliminary analyses to determine the typical PAH levels, PAH monthly values are only available. Following the Directive 2004/107/EC recommendations, the monthly value is determined using four individual samples that are analysed together.

PCB analysis

The PCB analysis in PM_{10} was performed according to the US EPA method 1668 "Chlorinated biphenyl congeners in water, soil, sediment, biosolids and tissue by HRGC/HRMS". As in the PAH case, PCB monthly values are only available; the monthly value is determined using individual samples that are analysed together.

Prior to the PCB analysis, the samples were spiked with labelled PCB standards (28-C^{13}, 52-C^{13}, 101-C^{13}, 118-C^{13}, 138-C^{13}, 153-C^{13}, and 180-C^{13}). The samples were Soxhlet-extracted with toluene for 24 h (4 cycles/h); the filtered extract (about 300 mL) was rotary evaporated (Laborota 4000, Heidolph) to 1 mL, and then the solvent was exchanged by adding 10 mL of *n*-hexane. The *n*-hexane extract was cleaned up using the same automatic multicolumn system used for PAH analysis; the clean-up system was equipped with a multilayer silica column, a basic alumina column and a carbon column. PCBs were eluted with a *n*-hexane/dichloromethane mixture; the eluate volume (about 180 mL) was reduced to 1 mL by rotary evaporation. The final volume was reduced to dryness under a gentle nitrogen flow; after the final volume reduction, the samples were wrapped in aluminium foil and stored at −20°C until the determination by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). The quantification of PCBs (8, 28, 52, 101, 118, 138, 153, 180, 194, 206 and 209) by HRGC/HRMS was conducted externally by "Servicio de Cromatografía" of the University of Cantabria.

The SRM1649a recovery tests showed that the entire method recoveries varied from 79% to 140%; similar recoveries are reported in the literature (Gambaro et al. 2004). The recoveries for the labelled standards ranged from 45% to 75%; these recoveries were in the range recommended by US EPA Method 1668. The labelled standard recoveries were used to correct the amount of each PCB.

The values of the detection limit were calculated by “Servicio de Cromatografía” of the University of Cantabria. The detection limit varies from 0.004 pg/m^3 (PCB-153) to 0.001 ng/m^3 (PCB-8) and 0.0005 pg/m^3 (PCB-138) to 0.00011 pg/m^3 (PCB-8) in the quartz fibre filter and glass fibre filter cases, respectively; the l.d values are in the same range as those reported in the literature (Gambaro et al. 2004; Lohmann et al. 2000).

Results and discussion

Particulate matter: PM$_{10}$ and PM$_{2.5}$

The PM$_{10}$ mean concentrations at the studied urban sites are 29, 22 and 20 μg/m^3 at SANT, CAST and REIN, respectively. The PM$_{2.5}$ mean concentration at SANT site is 13 μg/m^3; the PM$_{2.5}$/PM$_{10}$ ratio is 45%. At NIEM rural sampling site, the 2008 annual mean values of PM$_{10}$ and PM$_{2.5}$ are 17.0 and 9.0 μg/m^3, respectively (Ministerio de Medio Ambiente y Medio Rural y Marino (MARM) 2010); the PM$_{2.5}$/PM$_{10}$ ratio is low, 53%, but it is similar than the ratio obtained at SANT site, 45%, showing the influence of the marine aerosol contribution to PM$_{10}$ values at coastal areas. The PM$_{10}$ levels in the Cantabria region are in the range of the levels reported in other European cities (Putaud et al. 2010). Taking into account the EU regulation, the PM$_{10}$ annual limit was not exceeded and neither did the maximum number of 24-h limit value exceedances (Arruti et al. 2011).

PAHs

Table 1 shows the average concentrations of the studied particle-bound PAHs at the selected urban (SANT, REIN, CAST), rural (TOJ) and the EMEP site of Niembro. Taking into account that BaP is the only regulated PAH, the urban levels of BaP were compared with the proposed annual target value (1 ng/m^3, Directive 2004/107/EC); the urban values measured in the Cantabria region are in the range of 0.04–0.13 ng/m^3, which are much lower than the target value. Table 2 shows some values of particle-bound BaP from different European sites; a similar BaP value was found at other urban sites such as

Table 1 Mean concentrations (nanograms per cubic metre) of PM-bound PAHs at different sampling sites across the Cantabria region

PAH	Urban						Rural	
	SANT				CAST	REIN	TOJ	NIEM
	HPLC detector	PM$_{10}$	PM$_{2.5}$	Ratio PM$_{2.5}$/PM$_{10}$ (%)	PM$_{10}$	PM$_{10}$	PM$_{10}$	PM$_{10}$
Nap	DAD	0.05	<0.003		0.02	<0.01	<0.01	0.00
Acy	MS	<0.23	<0.23		<0.15	<0.15	<0.15	0.01
Ace	MS	<0.12	<0.12		0.02	0.08	0.07	0.03
Flu	DAD	0.08	0.06	73	0.01	0.57	0.29	0.00
Phe	DAD	0.11	<0.05		0.14	0.25	0.06	0.01
Ant	MS	0.04	0.01	22	0.14	0.11	0.10	0.00
Flua	DAD	<0.15	<0.15		<0.15	<0.15	<0.15	0.07
Pyr	DAD	<0.15	<0.15		0.17	<0.16	<0.16	0.03
BaA	MS	<0.09	<0.09		0.16	0.31	<0.13	0.04
Chr	DAD	0.05	0.04	69	0.05	0.19	<0.05	0.04
BbF	DAD	0.11	0.07	85	0.04	0.24	<0.04	0.04
BkF	DAD	0.03	0.02	81	0.07	0.15	<0.07	0.07
BaP	DAD	0.04	0.02	54	0.07	0.13	<0.02	0.15*
BghiP	MS	0.10	0.10	~100	<0.16	0.17	<0.16	0.07
IcdP	DAD	<0.05	<0.05	~100	<0.08	<0.08	<0.08	0.06
DahA	DAD	0.07	0.04	67	0.12	0.12	<0.10	0.03

Concentration mean values are calculated considering values under d.l as ½d.l. The PAH values at Niembro sampling site are extracted from (Ministerio de Medio Ambiente y Medio Rural y Marino (MARM) 2010)

[a]The BaP mean value at NIEM rural sampling site is high due to some outliers. The median value is only 0.014 ng/m^3

Table 2 Comparison of PM-bound BaP concentrations (nanograms per cubic metre) with previous studies

		Particle size	Sampling type		Reference
			Urban	Rural	
Spain	Cantabria—REIN	PM_{10}	0.13		Present study
	Cantabria—CAST	PM_{10}	0.07		
	Cantabria—SANT	PM_{10}	0.04		
		$PM_{2.5}$	0.02		
	Canarias (traffic)	TSP	0.3		López et al. 2002
	País Vasco	PM_{10}	0.5		Barrero and Cantón 2007
	Madrid	PM_{10}	0.2		Viana et al. 2008
	Madrid (traffic)	PM_{10}	0.1		
	Zaragoza	PM_{10}	0.5		Callén et al. 2008
Italy	Rome	PM_{10}	1.1		Menichini et al. 2007
Greece	Athens	TSP	0.2		Mandalakis et al. 2002
UK	London	PM_{10}	1.4		Kendall et al. 2001
Croatia	Zagreb	PM_{10}	1.2		Sisovic et al. 2008
Spain	Cantabria—TOJ	PM_{10}		<0.02	Present study
	Niembro (EMEP)	PM_{10}		0.15[a]	Ministerio de Medio Ambiente y Medio Rural y Marino (MARM) 2010
Italy	Latium	PM_{10}		0.02	Menichini et al. 2007
Greece	Athens (coastal)	TSP		0.02	Mandalakis et al. 2002

[a] The BaP mean value at NIEM rural sampling site is high due to some outliers. The median value is only 0.014 ng/m^3

Madrid (Viana et al. 2008). Nevertheless, Table 2 shows that the typical BaP urban values are higher than those measured at the Cantabria region. The rural BaP concentration values in the Cantabria region were in the range of other European rural sites. Finally, Table 2 also shows the large variability of BaP levels found at sampling sites of different European regions.

At the SANT site, the PAH levels in PM_{10} and $PM_{2.5}$ are measured simultaneously (Table 1). The $PM_{2.5}$-bound ∑PAH/PM_{10}-bound ∑PAH ratio is 61%. The mean ratio could be used for identifying potential emission sources of $PM_{2.5}$ and PM_{10}; higher ratios (larger than 60%) are generally linked to relatively high contributions from secondary particles and combustion sources (Akyüz and Cabuk 2009).

At the three studied urban sites, there are large differences between the winter and summer periods. ∑PAH (sum of 16 US EPA priority PAHs), and BaP concentrations are higher during the cold seasons. The winter/summer ratio for ∑PAHs ranges from 1.3 to 2.1; these ratios agree well with those presented in the literature (Vera et al. 2003). The highest PAH levels associated to the winter period are explained as a consequence of reduced vertical dispersion, lower mixing layer, enhanced sorption to particles at lower temperature and increased emissions from domestic heating (Dejean et al. 2009; Ravindra et al. 2008).

PAH source analysis

Table 1 shows that the mean values for PAHs at the studied urban sampling sites are quite different; the highest values are obtained in the REIN site. In order to determine the spatial variability of PAHs at the different urban sites across the Cantabria region, a coefficient of divergence (COD) study is conducted; the COD provides information about the degree of uniformity between sampling sites, Eq. 1 (Wongphatarakul et al. 1998).

$$\mathrm{COD}_{jk} = \sqrt{1/n \sum_{i=1}^{n} \left((x_{ij} - x_{ik})/(x_{ij} + x_{ik}) \right)^2} \qquad (1)$$

where x_{ij} and x_{ik} represent the average concentration for a chemical component i at sites j and k and n is the number of chemical components. According to previous analysis, COD values greater than 0.2 are defined as a relatively heterogeneous spatial distribution (Wilson et al. 2005). The values of COD calculated at the three studied urban sites range from 0.4 to 0.5, suggesting that different local emission sources of PAHs affect their levels in PM_{10}.

Ternary diagrams, such as that plotted in Fig. 3, may be used to compare the concentrations of the PAHs measured at three sampling sites. PAH compounds with mean values lower than the detection limit at the three sampling sites are not considered in Fig. 3; however, when the level of a single PAH is lower than the detection limit at one of the sampling site, it is considered as ½ of the detection limit for comparison purposes.

The triangular plot shown in Fig. 3 represents the spatial variation of the annual mean PAH concentration at the three studied urban sites (SANT, REIN and CAST) identifying potential local tracers; this type of diagram has been used by Louie et al. (2005) for identifying sources of metals in particulate matter. Figure 3 shows that PAHs with higher molecular weights are associated with the REIN sampling site; the PAHs with four and five rings are good tracers of industrial emissions, except for cement plants (Baramiecka et al. 2010; Yang et al. 1998). Naphthalene (low molecular weight PAH) is the most important tracer in the SANT site; the indicatory PAHs of mobile emission sources are mainly PAHs with low molecular weight (Yang et al. 1998). Pyrene and anthracene could be considered as local tracers in the CAST site; pyrene and anthracene have been used as tracers for coal combustion (Ravindra et al. 2006). Additionally to the ternary plot, Student's *t* tests are conducted to check if the differences in the average concentrations are statistically significant; the results from these tests show that mean value differences are only statistically significant in the case of PAHs which are not located in the central triangle—local PAHs in Fig. 3—with the exception of chrysene and naphthalene; in these cases, PAH mean values could be associated to some local outliers at REIN and SANT sites, respectively.

Table 1 also shows that the PAH concentration values found in the TOJ and NIEM sites are quite similar, except for fluorene and anthracene, which are higher at the TOJ site. These are typical tracers of coal combustion (Liu et al. 2010; Wenborn et al. 1999); anthracene is also a good fingerprint of cement plant emissions (Yang et al. 1998). Despite the TOJ rural site is located in a woodland area, it could be influenced by some PAH emission sources that are located in the same direction as the predominant winds (Fig. 2): a cement plant (30–35 km S) and a coal-fired power station (60–65 km SW).

The diagnostic ratios are binary ratios that can help for PAH source identification, which involve the comparison of frequently found PAH emissions (Ravindra et al. 2008). However, the diagnostic ratios should be used with caution because there are often some difficulties to discriminate between the different sources (Galarneau 2008). The diagnostic ratios used for the studied urban sites are summarized in Table 3;

Fig. 3 PAH levels in the three studied urban sites of the Cantabria region. Year 2008. Values under d.l are considered as ½ of the d.l

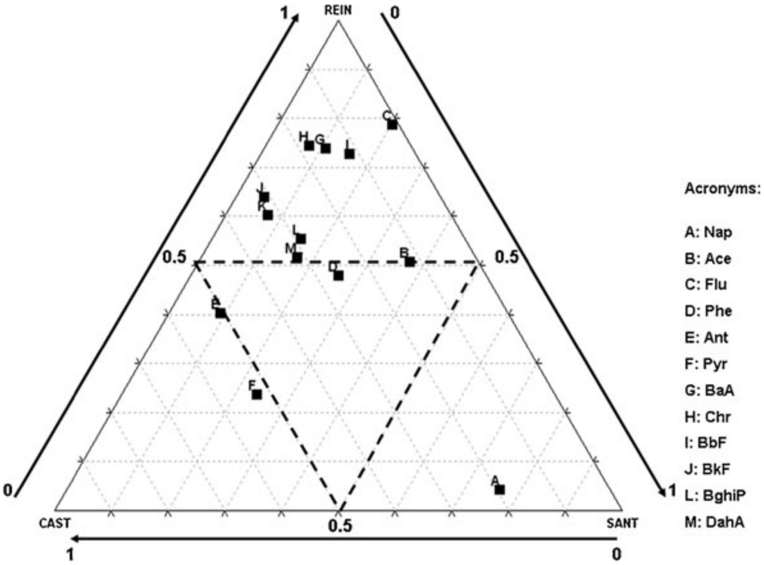

Table 3 PAH diagnostic ratios at urban sites

	Typical values of PAH ratios							
	SANT	CAST	REIN	Traffic				Industry
				Diesel	Gasoline	Road dust	Catalyst equipped cars	
BaP/(BaP + Chr)	0.36	0.42	0.44	0.5^{a}; 0.5^{b}; 0.7^{b}	0.7^{a}		0.3^{b}; 0.5^{b}; 0.4^{b}	
BbF/BkF	3.02	1.58	2.56	>0.5^{a}				
BaA/(BaA +Chr)	0.67		0.67	0.4–0.6^{b}	0.2–0.6^{d}	0.4^{b}	0.5^{b}	Industrial furnaces 0.2–0.9^{e}
								Cement plant 0.58^{e}
BFs/BghiP	0.90			0.3^{b}	1.6^{b}	4.7^{e}		Industrial furnaces 7.1–11.2^{e}
				0.2–1.7^{c} (general range for vehicles)				Cement plant 7.8^{e}
BaP/BkF	1.93	0.78	0.72					Mixed source with metallurgy influence 0.7^{f}

[a] Ravindra et al. 2008

[b] Quiteiro et al. 2007

[c] Allen et al. 2008

[d] Rajput and Lakhani 2008

[e] Manoli et al. 2004

[f] Cazier et al. 2007

the concentration ratios of PAHs in particulate matter from traffic (diesel and gasoline engines, road dust and catalyst equipped cars) and industry (industrial furnaces, cement plant and metallurgy) are also summarized in Table 3. In the SANT and CAST sampling sites, the studied ratios values are similar to those reported for traffic emissions; nevertheless, in the REIN site, the ratios determine two possible emission sources: traffic and industrial. In the REIN site, BaP/BkF ratio is similar to ratios reported for industrial emissions. BaP/BkF value is quite similar to those obtained at areas with metallurgy influence (Cazier et al. 2007); thus, the steel manufacturing plant located close to the REIN sampling site, 1 km S, could be an important local emission source of PAHs. The studied diagnostic ratios are also calculated during the winter and summer periods, in order to analyse the seasonal variations; since the diagnostic ratio values are very similar, it is suggested that the emission sources are quite similar during the two periods.

The BaA/Chr diagnostic ratio shows the photochemical degradation of air masses; BaA degrades more easily than does its isomer, Chr; then, a low BaA/Chr ratio would indicate aged air masses from long-range transport, while a high ratio value is correlated with relatively fresh air masses, probably coming from local pollution sources (Callén et al. 2008). The photochemical ratio mean values at the studied urban sites is higher than 2. Therefore, the BaA/Chr values indicate that particle-bound PAHs are mainly emitted by local sources. These results agree well with the COD conclusions.

Benzo(a)pyrene-equivalent carcinogenic power

BaP is considered the PAH with the highest carcinogenic character; nevertheless, other PAHs are also associated with carcinogenic characteristics. In order to estimate the total carcinogenic risks for humans, the benzo(*a*)pyrene-equivalent ($\mathrm{BaP_e}$) carcinogenicity is evaluated. $\mathrm{BaP_e}$ is an index that is calculated by multiplying the concentrations of each PAH with their toxic equivalent factors, Eq. 2 (Yassaa et al. 2001; Mastral et al. 2003)

$$\begin{aligned}\mathrm{BaP_e} &= \mathrm{BaA} \times 0.06 + (\mathrm{BkF} + \mathrm{BbF}) \times 0.07 \\ &\quad + \mathrm{BaP} + \mathrm{DahA} \times 0.6 + \mathrm{IcdP} \times 0.08. \end{aligned} \tag{2}$$

Table 4 Mean concentrations (picograms per cubic metre) of PM_{10}-bound PCBs in the agglomeration area (SANT) and the rural site (TOJ)

PCB	Urban SANT	Rural TOJ
PCB-8	0.03	0.08
PCB-28	0.06	0.33
PCB-52	0.06	0.23
PCB-101	0.11	0.35
PCB-118	0.06	0.32
PCB-138	0.13	0.37
PCB-153	0.16	0.47
PCB-180	0.17	0.47
PCB-194	0.007	0.07
PCB-206	0.004	0.008
PCB-209	<0.002	0.02

Concentration mean values are calculated considering values under d.l as ½d.l

The calculated mean BaP_e for the studied urban sites are 0.11, 0.23 and 0.14 ng/m^3 in the SANT, REIN and CAST sites, respectively; since the highest levels of BaP and DahA occur in the REIN site (see Table 1), it is obvious that the highest BaP_e index is also obtained in the REIN site. The BaPe values in the Cantabria region are lower than those found in other Spanish cities, such as Zaragoza, 0.54 ng/m^3 (Callén et al. 2010) or Las Palmas de Gran Canaria, 0.71 ng/m^3 (Vera et al. 2003).

PCBs

Table 4 shows the average concentrations of the studied particle-bound PCBs in the SANT and TOJ sites. Surprisingly, the PCB mean values at the rural site are greater than those obtained at the urban site, Table 4; the Student *t* test shows that these differences are statistically significant. Table 4 also shows that the congeners PCB-180 and PCB-153 are the most concentrated in the urban and rural sites; PCB-180 congener is normally predominant in particles from combustion processes such as incinerators or residential heating (Mari et al. 2008; Biterma and Voutsa 2005), and PCB-153 is an important congener in the collected PM_{10} samples from steel industry (Cetin et al. 2007). At the studied sites, there are not large differences between the PCB concentrations measured during the winter and summer periods.

Some of the PCB concentration data reported in the literature are not directly comparable with the values found at the SANT and TOJ sites because more PCB congeners are sometimes analysed in the literature. However, in an attempt of a rough comparison, literature data concerning the levels of particle-phase PCBs are given in Table 5 together with the values found in the SANT and TOJ sites for the sum of indicator PCBs (28, 52, 101, 118, 138, 153, and 180): 0.8 and 2.5 pg/m^3 for the SANT and TOJ sites, respectively. The typical concentrations of

Table 5 Comparison of PM_{10}-bound PCB concentrations (picograms per cubic metre) with previous studies

		Particle size	Sampling type		Reference
			Urban	Rural	
Spain	Cantabria—SANT	$PM_{10}/\sum$ 7ind.	0.8		Present study
	Barcelona	TSP/$\sum$ 7ind.	21		García-Flor et al. 2009
	Madrid	TSP/$\sum$ 11 PCBs	129		García-Alonso et al. 1999
Italy	Roma	$PM_{10}/\sum$ 7ind	163		Menichini et al. 2007
	Venice (coastal)	TSP/$\sum$ 54PCBs	1		Gambaro et al. 2004
	Venice (urban—industrial)	TSP/$\sum$ 54 PCBs	11		
Greece	Athens	TSP/$\sum$ 9 PCBs	1.2		Mandalakis et al. 2002
France	Banyuls-sur-Mer (coastal)	TSP/$\sum$ 7ind.	6.1		García-Flor et al. 2009
Spain	Cantabria—TOJ	$PM_{10}/\sum$ 7ind.		2.5	Present study
Italy	Latium	$PM_{10}/\sum$ 7ind		26	Menichini et al. 2007
	Ispra	TSP/$\sum$ 7ind		3.1	Castro-Jiménez et al. 2009
Greece	Finokalia	TSP/$\sum$ 39 PCBs		5	Iacividou et al. 2009
	Athens (coastal)	TSP/$\sum$ 9 PCBs		0.7	Mandalakis et al. 2002

particle-phase PCBs in various European cities range from 1 to 163 pg/m^3, showing a large variability of PCB levels. The urban PCB concentration in Santander and Venice is similar, 0.8 and 1 pg/m^3, respectively. The concentration of $\sum$PCBs in the TOJ rural site is in the range of other European sampling rural sites, from 0.7 to 26 pg/m^3.

Typical PCB emission sources are incineration, combustion of different type of fuels, industrial/metallurgical activities or power generation processes (Biterma and Voutsa 2005). As it is said above, the comparison between the urban and rural PCB values shown in Table 4 suggests that the rural site could be influenced by some PCB emission sources. Some of the typical PCB emission sources are located at about 40 km from the rural sampling site: a cement plant with a co-incineration process, a steel manufacturing plant or a coal-fired power station. A study with the Hysplit dispersion model (Draxler and Rolph 2010) is conducted in order to determine the contribution of the main local emission sources to the pollutant levels at TOJ and SANT sites; the dispersion model results show that the TOJ site is under the influence of some PCB emission sources. However, SANT site is not usually affected by these emission sources because of the specific atmospheric circulation patterns; nevertheless, further research is necessary to confirm this hypothesis.

Regional inter-site comparison

A regional comparison between the studied particle-bound POPs is conducted; a health risk assessment tool is used in order to carry out the inter-site comparison. The risk assessment is conducted by combining the exposure data with inhalation cancer potency factors, Eq. 3 (Bartoš et al. 2009; Aries et al. 2008). By this cancer risk assessment tool, the studied particle-bound PAHs and PCBs are considered together in order to compare the sampling sites.

$$\text{Risk} = \text{LADD} \times \text{CP} \tag{3}$$

where LADD is the life averaged daily dose (milligrams per kilogram day) and CP is the cancer potency (kilogram day per milligrams). The CP values used in the risk assessment are presented in Table 6. LADD is calculated from Eq. 4.

$$\text{LADD} = (\text{CA} \times \text{IR} \times \text{EF} \times \text{ED} \times \text{ET})/(\text{BW} \times \text{AT}) \tag{4}$$

Table 6 Cancer potency (kilograms day per milligram) for 16 EPA PAHs and PCBs (values extracted from Bartoš et al. 2009)

Compound	CP
Nap	3.4e−5
Acy	1.1e−6
Ace	1.1e−6
Flu	1.1e−6
Phe	1.1e−6
Ant	1.1e−5
Flua	1.1e−6
Pyr	1.1e−6
BaA	1.1e−4
Chr	1.1e−5
BbF	1.1e−4
BkF	1.1e−4
BaP	1.1e−3
BghiP	1.1e−5
IcdP	1.1e−4
DahA	1.2e−3
PCB28	1.0e−4
PCB52	1.0e−4
PCB101	1.0e−4
PCB118	1.0e−4
PCB138	1.0e−4
PCB153	1.0e−4
PCB180	1.0e−4

CP cancer potency

where CA is the concentration of each PAH or PCB (milligrams per cubic metre), IR is the breathing rate (cubic metres per hour), EF is the number of exposures per year, ED is the duration of exposures in years, ET is the number of hours per exposure, BW is a default weight of the receptor body (kilograms)

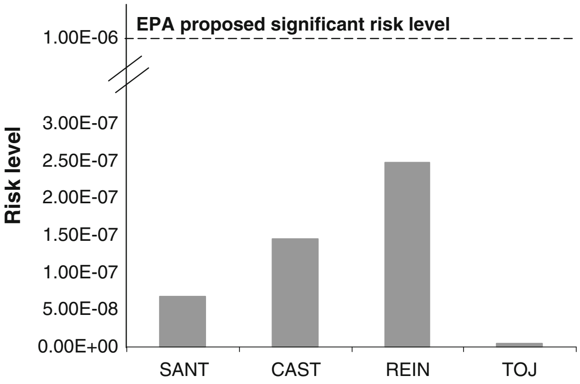

Fig. 4 Risk distribution associated to PAHs and PCBs in the Cantabria region

and AT is an average exposure extent over a lifetime. Default exposure parameters are obtained from Bartoš et al. (2009): IR=20 m^3 day^{-1}, EF=365 days, ED=70 years, ET=24 hday^{-1}, BW=70 kg and AT=35,500 days.

The calculated individual risks are shown in Fig. 4. The highest risk value takes place in the REIN sampling site, 2.48e−7, because of the levels of BaP and DahA, which exhibit the highest carcinogenic character. At the TOJ site, the risk value is the lowest, 2.2e−9; however, as it is said above, the PCB concentration values are the highest at this site. The lowest risk value is due to the fact that BaP and DahA levels at the rural site are low and that the cancer potency of PCBs is lower than those reported for BaP and DahA, as shown in Table 6. The calculated risk values are lower than the EPA proposed significant risk level, 1.0e−6 (one occurrence over one million people (Environmental Protection Agency EPA 1990)).

Conclusions

The objective of the present study is to evaluate the levels of some POPs (PAHs and PCBs) in the particulate matter at rural and urban environments in the Cantabria region (northern Spain). BaP levels at the studied sites are in the range of those obtained at different European regions; moreover, BaP levels found in the Cantabria region were below the current EU target value, 1 ng/m^3. Total PAHs and BaP highest concentration values take place during the winter period.

The comparison between rural and urban PAH concentration values shows that the highest values take place at the urban sites (except for fluorene); the rural PAH concentrations from TOJ and NIEM sites are quite similar, except for fluorene and anthracene. At the studied urban sites, COD results show that different local emission sources affect the PAH levels; the triangular diagram indicates that (a) higher molecular weight PAHs are local tracers in the REIN site, (b) naphthalene is the most important PAH tracer in the SANT site and (c) pyrene and anthracene are local tracers in the CAT site. Some diagnostic ratios are also studied in the urban sites in order to determine potential local emission sources. The diagnostic ratios values calculated in the SANT and CAST sites are similar to those reported in areas affected by traffic emissions; however, the ratios calculated in the REIN site indicate that industrial sources are also important.

The urban and rural PCB concentrations are in the range of other European sampling sites. The inter-site PCBs comparison between rural and urban site shows that the highest PCB value take place at the rural site; thus, TOJ site could be influenced by PCB emission sources located at about 40 km of the sampling site. The dispersion study of the PCB emissions concludes that TOJ site is under their potential influence; SANT site is not usually affected by these sources. Nevertheless, further research is necessary to confirm this hypothesis.

An inter-site POPs (PAHs + PCBs) values comparison is conducted using a health risk assessment tool. The highest risk value takes place in the REIN site, 2.5e−7; in the rural site (TOJ), the risk value is the lowest, 2.2e−9. The risk values calculated in all the studied sites are lower than the EPA proposed significant risk level, 1.0e−6.

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