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ProScience 3 (2016) 44-49

ProScience

Conference Proceedings

2nd International Conference on Atmospheric Dust - DUST2016

Levels and sources of polycyclic aromatic hydrocarbons in the soluble fraction of the atmospheric deposition in Cantabria (northern Spain)

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Abstract

The aim of this work is to assess the levels of polycyclic aromatic hydrocarbons (PAHs) in the soluble fraction of the bulk atmospheric deposition in four sites of a small region located in northern Spain (Cantabria). Samples were collected monthly for two years at an urban site (Santander), and for one year at an industrial (Maliaño), rural (Bárcena Mayor) and traffic (Cabezón de la Sal) sites. Samples were filtered and the filtrate was extracted, concentrated, purified and analysed for 15 PAHs: acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), and benzo[ghi]perylene (BghiP). The highest deposition fluxes of PAHs were found at the industrial site (Maliaño); the total PAH fluxes at the other sites were similar. Box plots of the PAH levels found in the literature in wet and bulk deposition samples were used to compare the values observed in this work. FLA, BaA, PHE and PYR were the most abundant PAHs at the industrial site. At the urban and rural site, the profile found in the deposition samples was similar: PHE>FLA>BaA>PYR. The traffic site showed a different profile: PYR>ANT>FLU>FLA. A preliminary source identification study was made by calculating diagnostic ratios of some PAH isomers (FLA/(FLA+PYR) and BaA/(BaA+CHR)); these ratios were compared with those found for the main PAH industrial and non-industrial sources in the region.

Keywords: Polycyclic aromatic hydrocarbons; Bulk atmospheric deposition; Diagnostic ratio

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ISSN: 2283-5954
Selection and peer-review under responsibility of DUST2016 Scientific Committee
DOI:10.14644/dust.2016.007

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are harmful semivolatile organic compounds; some of them are classified as priority pollutants due to their carcinogenic character. PAHs are emitted in particulate and gaseous phases to the atmosphere. Gaseous PAHs are mainly emitted by volatilization of petroleum-derived fuels (petrogenic origin) while gaseous and particulate PAHs are mainly derived from the incomplete combustion of solid, liquid and gaseous fuels (pyrogenic origin) (Ravindra et al., 2008). Traffic, and domestic and industrial combustion are usually the main sources of atmospheric PAHs (US EPA, 1998). However, some industrial activities such as iron foundries, ferroalloy manufacturing or carbon black production may have a significant contribution to PAHs emissions in local industrial areas (e.g., US EPA, 1998; Yang et al., 1998; Tsai et al., 2001; Yang et al., 2002).

Both the particle matter bound and the gaseous PAHs may reach the terrestrial and aquatic systems through wet and dry deposition. Thus, gaseous PAHs are scavenged by precipitation, and particulate PAHs are removed by precipitation and dry particle deposition (Galarneau, 2008). The analysis of the water soluble fraction of the bulk atmospheric deposition may indicate the potential risk of such pollutants toward the ecosystems. The sources of PAHs that are analysed at different receptor points may be preliminarily assessed by comparing the diagnostic ratios of PAH isomers (e.g., Yunker at el., 2002; Tobiszewski and Namiesnik, 2012) calculated at these sites with literature ratios corresponding to emission sources. This technique is widely used in the source apportionment of PM-bound PAHs (Mantis et al., 2005; Galarneau, 2008), but is also applied to atmospheric deposition samples (Motelay-Massei et al., 2007; Ponce de León, 2014).

The aim of this work is to assess the levels and sources of PAHs in the soluble fraction of the bulk atmospheric deposition in urban, industrial, rural and traffic sites of Cantabria, a small region located in northern Spain.

2. Methodology

2.1 Area of study

This study was performed in the Cantabria region (5300 km^2 and 593,121 inhabitants, 2011) located in northern Spain. The heterogeneity of this small region allows the comparison of the deposition rates of PAHs based on different land uses. Four sampling sites representing urban, industrial, traffic and rural environments were selected for this study:

(i) The first site was located in Santander (SANT, 43°28'22.33"N, 3°47'52.67"W, 23 m a.s.l.) on the rooftop of the building "E.T.S. de Ingenieros Industriales y de Telecomunicación" at the campus of the University of Cantabria. Santander is a medium-sized coastal city (179,921 inhabitants, 2011), which is mainly commercial and residential in nature with a low-middle pollution level. Some industrial estates (with mostly iron, steel and ferroalloy manufacturing plants) are located in the Santander suburbs (5-10 km SW) upwind of the city. The sampling point is representative of an urban background site.

(ii) Maliaño (MAL) (9,609 inhabitants, 2011) is a small town located in the southern part of Santander Bay. Maliaño is highly influenced by close industrial areas, mainly by a ferro-manganese alloy plant located 0.66 Km SSE of the monitoring station. The MAL sampling site (43º25'12.35"N, 3º50'30.13"W, 5 m a.s.l.) is situated on the rooftop of a municipal building "Casa El Botiquín". Although MAL is also influenced by urban and traffic activities, this site is considered an industrial site.

(iii) Bárcena Mayor (BAR) (434 inhabitants, 2011) is a small village at the heart of Cantabria located in the Nature Reserve of Saja-Besaya. The BAR sampling site (43°09′25.86″ N, 4°14′21.44″ W, 431 m a.s.l.) is situated between Bárcena Mayor and Los Tojos villages in a plot surrounded by woodland area and close to a cottage and a low traffic road, 50 km SW of Santander. This site is considered to be rural.

(iv) The fourth site was located in a place very close to the main motorway that crosses the Cantabria region (A8), so it was considered a road traffic site. This site (43°19′13.46″N, 4°13′53.03″W, 201 m a.s.l.) was located 1.3 km NNW of Cabezón de la Sal (CAB).

2.2 Sampling and analysis

Bulk atmospheric deposition sampling was performed using the surrogate surface approach, with a funnel-bottle bulk collector device made of brown glass. The sampling was based on the standard UNE-EN 15980:2011 (Air quality - Determination of the atmospheric deposition of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene). The funnel was 1.7 m above the ground to avoid the collection of re-suspended soil particles. The sampling was carried out monthly. At the end of each sampling period, the funnel was rinsed with 250 ml of Milli-Q water and all equipment was replaced by a clean one. At the SANT site, sampling was performed from January 2011 to February 2013 (25 samples). At the MAL and CAB sites, the sampling period was from January 2012 to February 2013 (13 samples). At the BAR site, sampling was conducted from November 2011 to February 2013 (16 samples).

Samples were filtered using glass microfiber filters (Whatman®, diam. 47 mm). The filtrate was shaken 3 times and for 20 minutes, in a glass bottle, using 200 ml of methylene chloride for each liter of sample. Extracts were combined and reduced to about 3 ml on a rotary evaporator. Because of 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). The eluted was reduced nearly to dryness under a nitrogen flow and the reduced sample was re-dissolved in n-hexane (100 μl). The following PAHs were analyzed by gas chromatography/mass spectrometry: acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), and benzo[ghi]perylene (BghiP). All results were expressed as deposition fluxes (ng m^{-2} day^{-1}).

3. Results and discussion

3.1. Levels of PAHs: comparison between the urban, industrial, rural and traffic sites in the Cantabria region and the literature values

The mean values of the deposition fluxes of the individual PAHs measured at the SANT, MAL, BAR and CAB sites are displayed in Figure 1. The values found in a literature review are also represented in the box plots (mean, median, minimum, outliers and extreme outliers).

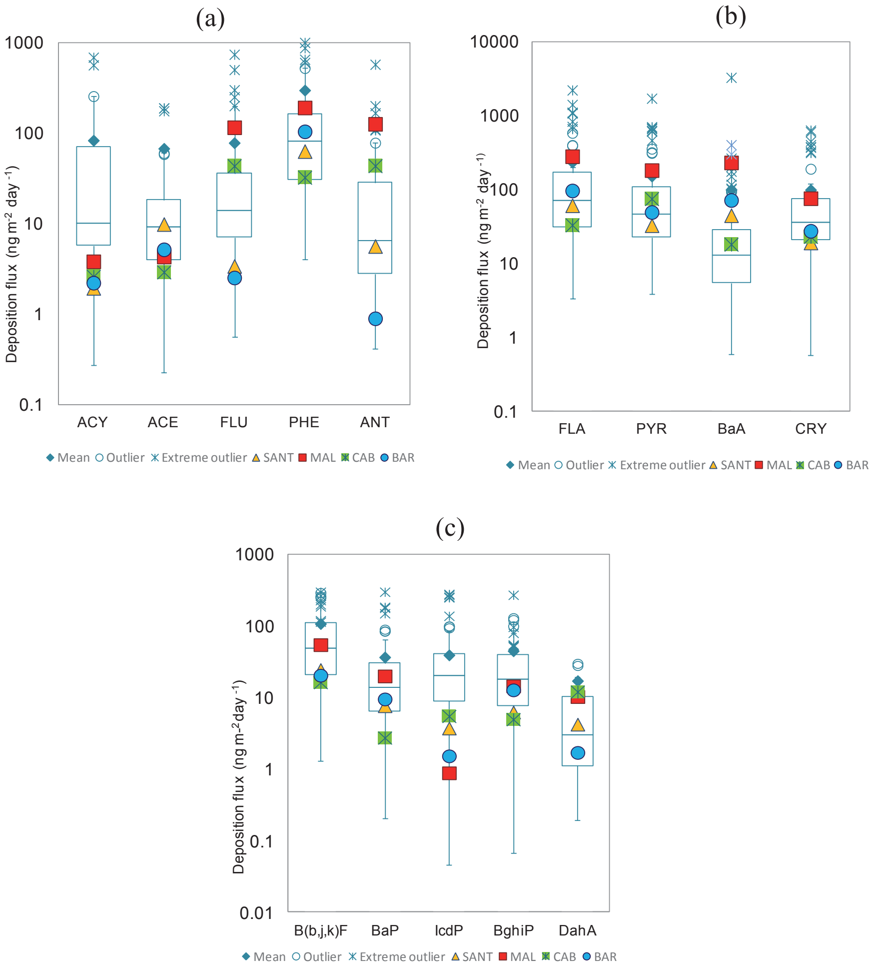

Fig. 1. Boxplot of the deposition fluxes of the studied PAHs: comparison between the measured with the literature values: (a) 3 rings; (b) 4 rings; (c) 5 and 6 rings

The highest deposition fluxes of PAHs in Cantabria were found at the industrial site (Maliaño). With the exception of the most volatile (ACY and ACE) and the heaviest compounds (IcdP, BghiP and DahA), the deposition fluxes measured at the industrial site are higher than the median and in some cases the mean of the literature values. The PAHs deposition fluxes at the other sites were similar, and in general terms lower than the mean of the literature values. Some exceptions are the levels of FLU and ANT at the traffic site (CAB), and the levels of BaA at the rural (BAR) and urban sites (SANT).

With respect to the relative abundance of the studied PAHs, FLA, BaA, PHE and PYR were the most important PAHs at the industrial site. In the urban and rural site the profile found in the deposition samples was similar: PHE>FLA>BaA>PYR. The traffic site showed a different profile: PYR>ANT>FLU>FLA.

3.2. Preliminary study on PAHs sources in the Cantabria region

The main PAHs sources in Cantabria were identified from the regional emission inventory: road traffic, residential combustion, forest fires, ferroalloys manufacturing, steel production, iron foundries and carbon black production. Ratios of some PAH isomers (FLA/(FLA+PYR) and BaA/(BaA+CHR)) for these emission sources were obtained from the literature and compared with those calculated at the studied sites. Figure 2 shows the box plots of the FLA/(FLA+PYR) ratio obtained at the studied sites together with the ratios found for potential PAHs sources in Cantabria.

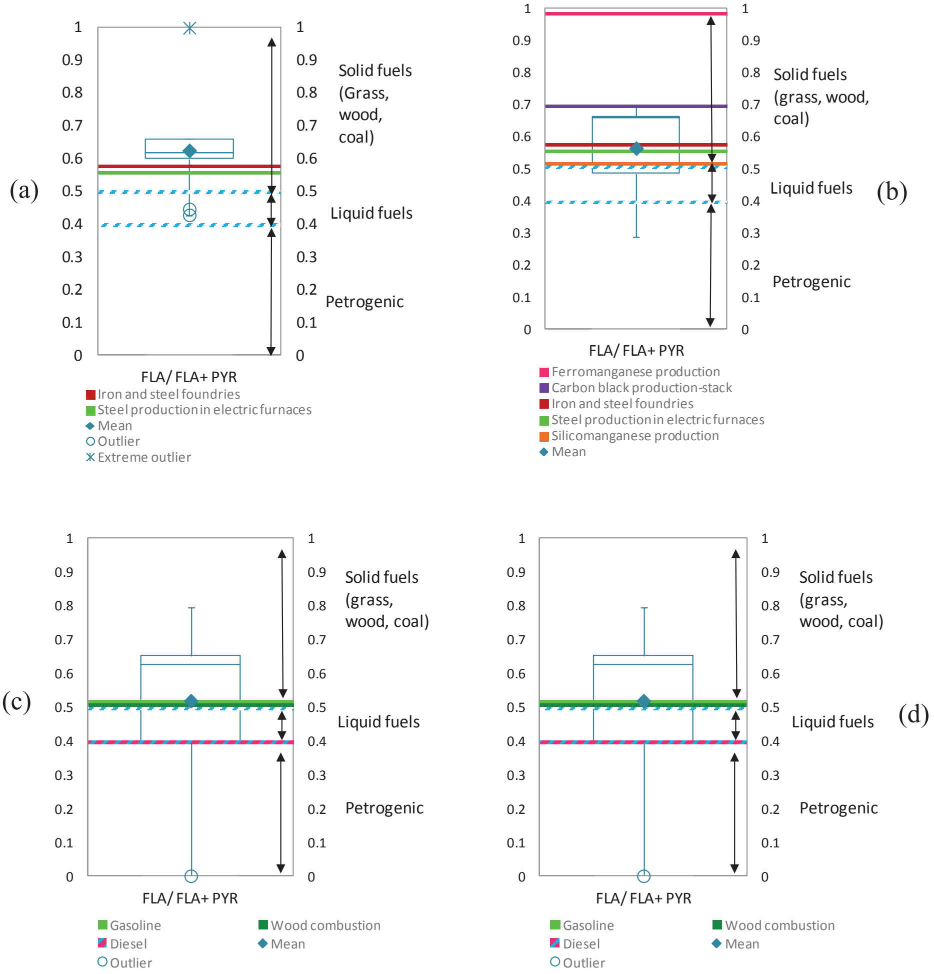

Fig. 2. FLA/(FLA+PYR) ratios at the studied sites: (a) urban; (b) industrial; (c) traffic; (d) rural

In the urban sector, the diagnostic ratios indicate that the combustion of liquid fuels (gasoline and diesel) and solids (coal and coke) caused by the city road traffic and the proximity of industrial activities such as iron foundries and steel production on electric furnaces, are the main sources. For the industrial sector the steel production in electric furnaces, iron foundries, and silicomanganese production are identified as the main sources. For the traffic sector, liquid fuels combustion is the main source, in particular gasoline. Lastly, in the rural sector the wood combustion is identified as the main emission source.

4. Conclusions

The comparison of the FLA/(FLA+PYR) and BaA/(BaA+CHR) ratios for the main PAHs potential sources identified in Cantabria obtained from the literature with the experimental ratios calculated in the atmospheric deposition samples at the studied sites shows that the combustion of liquid fuels (gasoline and diesel) from road traffic and solid fuels (coal and coke) from local industrial activities (iron foundries and non-integrated steel production) at the urban site, iron foundries and the production of silicomanganese and steel in electric furnaces at the industrial site, liquid fuels from road traffic (mainly gasoline) at the traffic site, and wood combustion at the rural site are the main PAHs sources in the studied area.

Acknowledgements

This work was supported by the Spanish Ministry of Economy and Competitiveness (MINECO) through the Projects CTM2010-16068 and CTM2013-43904R.

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