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# Evaluation of the degree of compliance of the eu target values for as, pb, cd, ni and polycyclic aromatic hydrocarbons in pm10 at four urban sites of the northwest of spain

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Trace elements and polycyclic aromatic hydrocarbons are released into the atmosphere by human activities, such as combustion of fossil fuels and wood, industrial activities and waste incinerations.
The objective of this study was to evaluate the degree of compliance with current legislation about trace metal concentrations and polycyclic aromatic hydrocarbons in PM10 in the urban atmosphere of four urban sites of the Northwest of Spain. Also, it is intended to evaluate the geographical variability and to identify the main sources by principal component analysis (PCA) and analysis of meteorological conditions effects. The results could be used as the baseline data for analysis of health risks due to inhalation of suspended aerosols, and to provide scientific evidence for setting up an air pollution control strategy.
PM10 samples were taken at 4 locations throughout the North of Galicia during 2008 and first months of 2009 in warm and cold seasons. The monitoring sites includes: heavy traffic (A Coruña), moderate traffic (Santiago de Compostela and Lugo) and urban background (Ferrol). Filters were digested according to EN 14902 and microwave assisted extracted for metal and PAH analysis, respectively.
Seasonal and spatial variations of metals and PAH concentrations and different predominant compounds in PAH profile can be linked to patterns of different anthropogenic emissions. Both types of pollutants do not exceed the annual target values or limit value, in the case of Pb, according to Directives 1999/30 and 2004/107, in three sites but the annual mean of BaP in the heavy traffic site (A Coruña) (1,10 $ngm^{-3}$) is slightly higher than the target value.

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## 1. Introduction

Airborne particulate matters, especially PM10 fraction have been recognized with greater environmental significance. As the carrier of many harmful trace metals (such as As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Sb, Se, V and Zn), they can be deposited into the human respiratory system. In general, a source of particulate matter in the air can be divided into both natural and anthropogenic sources. The trace metals with various origins affect not only the local environment but also a wide area by long range transportation (Lim et al, 2010). During the past decades, government efforts to control air pollution have achieved some positive effects, and, as a result, atmospheric pollutants have been reduced significantly.

Organic compounds associated with airborne particles have been chemically characterized in a number of studies and comprise: n-alkanes, carboxylic acids, carbonyls, steroids, aromatic compounds and alkanols. Among the minor components, polycyclic aromatic hydrocarbons (PAHs) are important in assessments of air quality, because they include potent carcinogenic and/or mutagenic species (Ladji, 2009).

The approval and publication of Council Directive 1996/62/EC (Council Directive, 1996) on ambient air quality assessment and management and its daughter directives, 1999/30/EC (Council Directive, 1999), 2000/69/EC (Directive, 2000), 2002/3/EC (Directive, 2002) and 2004/107/EC (Directive, 2004), gave rise to an important change in air quality monitoring systems in Europe.

In the present work, metals and PAHs associated with PM10 were investigated over a year with the object to evaluate the degree of compliance of the EU target and limit values. The requirements for minimum data capture and time coverage were achieved (212 samples per site).

## 2. Experimental

### 2.1 Sampling

The filters used are made of quartz fiber (Munktell) and subjected to pre-treatment at 400 ºC for 12h. Before and after sampling, they are maintained and kept in a conditioned room at 20 °C and 50% relative humidity as described in the standard EN 12341 (1998) for measuring gravimetric PM10. The samples were stored at -18 °C until analysis. We collected a total of 222 samples of PM10 in the period from June 2008 to March 2009 for 24 hours (on a weekly basis) in four cities of Galicia (A Coruña, Santiago, Lugo and Ferrol) (figure 1) using two high-volume samplers Digitel DHA-80 with a sampling volume of approximately 750 $m^3$. Heavy traffic stations are A Coruña (Provincial Delegation of the Ministry of Health), moderate traffic Fingoi (Lugo) and San Caetano (Santiago), and urban background Ferrol. All of them belong to the urban subnet of the Galician Network Monitoring Air Quality.


*Figure 1. General view of Galicia (Northwest Spain) indicating the four sampling locations*

**2.2 Metal analysis**

Due to the large variety of matrix components of atmospheric particles (organic compounds, oxides and silicates), it is necessary the use of mixtures of acid and a great time of digestion. The filters were digested following the EN 14902 (2005), and metals measured by ICP-MS. Samples were digested in closed vessels fluorocarbon polymer reinforced, with 8 mL of concentrated nitric acid ($HNO_3$ (c)) and 2 mL hydrogen peroxide ($H_2O_2$) at 220ºC. Once the microwave program has been finished, they are removed and allowed to cool to room temperature. Then, they are filtered through Whatman filter No. 40 and carried a volume of 25 mL with ultrapure deionized water. The acid extracts were frozen until analyzed by ICP-MS. Recoveries of As, Pb, Cd, Ni, V and Se ranged from 90% to 100%.

**2.3 PAHs analysis**

The filters were extracted using a microwave assisted solvent extraction with 15 ml of a mixture of hexane and acetone (1:1) at 105ºC. The extracts filtered were concentrated to dryness, redisolved in hexane and fractionated in silica gel column (activated with 5% milliQ water). After an initial washing with hexane, PAHs were eluted with 10 ml of a mixture of DCM/hexane (30:70). This extracts, concentrated with rotary vacuum evaporator and to dryness with nitrogen, were identified by gas chromatograph coupled to a mass spectrometry detector (GC-MS/MS) using isotopic dilution with perylene-d12 to quantify the PAHs. Recoveries of PAHs ranged from 70% to 109%, while recoveries of naphthalene were very low (<60%) in the warm season; so, concentrations of this PAH in this period were no taken into consideration in this study.

## 3. Results and discussion

Table 1 shows the mean, minimum and maximum concentrations of metals and PAHs found in the PM10 samples collected from over a year at four urban sites of Galicia. Average annual As, Cd, Ni and Pb do not exceed limit and target values in neither of the sites and are lower than the concentrations found in other cities in Europe. However, the mean concentration of benzo(a)pyrene is slightly higher than the target value in the heavy traffic site (A Coruña).

As shown in table 1, there are not many differences in the concentrations of the metals between the sites, only the case of Lugo which presents the lower concentrations.

Figure 2 shows the differences between the concentrations of the legislated pollutants during the warm and the cold period.

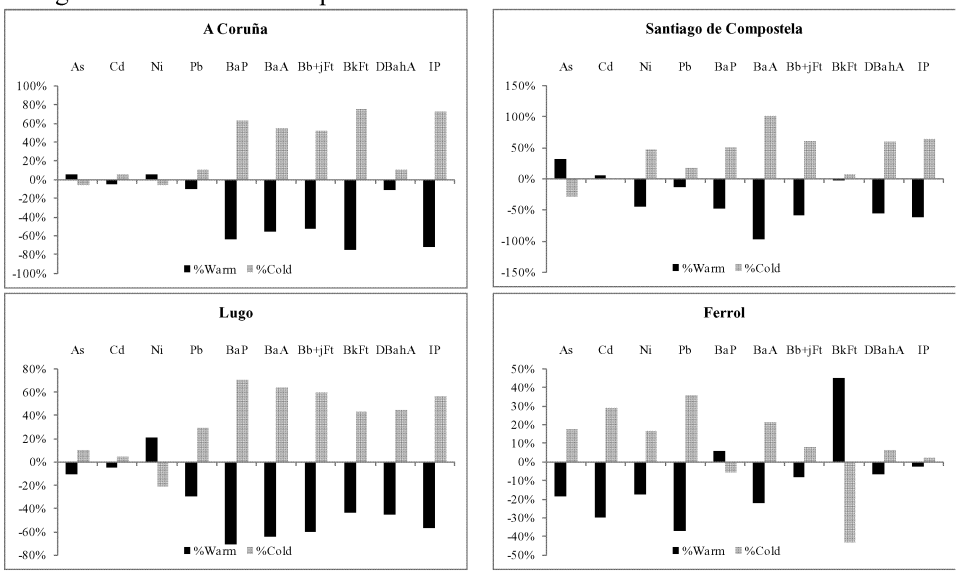


*Figure 2. Percentage increase of legislated metals and PAH mean concentrations registered during warm and cold seasons compared to mean concentrations registered during the whole period*

Regarding the PAH, we observe and increase in the cold season in all the sites. PAHs tend to show low levels in warm season (high temperatures, thermal and photochemical decompositions of PAHs) in opposition to high concentration levels in the cold season (low temperatures, higher traffic and increased fuel consumption). Only there is an increase of BkFt in Ferrol due to a punctual episode. With respect to metals, the differences are no significant.

*Table 1. Mean, minimum and maximum concentrations (ng $m^{-3}$) of metals and PAHs in PM10 from the four monitoring stations*

| | A CORUÑA | | | SANTIAGO | | | LUGO | | | FERROL | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | MEAN | MAXIMUM | MINIMUM | MEAN | MAXIMUM | MINIMUM | MEAN | MAXIMUM | MINIMUM | MEAN | MAXIMUM | MINIMUM |
| **Cd** | 0,113 | 0,642 | 0,019 | 0,067 | 0,227 | 0,016 | 0,081 | 0,250 | 0,015 | 0,155 | 1,09 | 0,013 |
| **Pb** | 5,77 | 20,0 | 2,28 | 5,73 | 42,2 | 1,11 | 3,42 | 12,3 | 0,884 | 11,25 | 45,5 | 0,914 |
| **V** | 4,77 | 15,1 | 0,547 | 5,05 | 16,2 | 0,937 | 1,18 | 3,08 | 0,211 | 5,19 | 15,3 | 0,546 |
| **Ni** | 3,00 | 9,15 | 2,67 | 6,70 | 40,3 | 1,94 | 3,46 | 22,3 | 1,56 | 4,25 | 12,5 | 2,49 |
| **As** | 0,291 | 1,33 | 0,047 | 0,295 | 1,43 | 0,047 | 0,320 | 0,936 | 0,054 | 0,292 | 0,945 | 0,047 |
| **Se** | 0,286 | 0,795 | 0,471 | 0,240 | 0,485 | 0,471 | 0,292 | 1,27 | 0,471 | 0,330 | 1,58 | 0,471 |
| **Naphthalene** | 0,149 | 4,43 | 0,068 | 1,20 | 19,1 | 0,068 | 0,335 | 3,59 | 0,068 | 0,069 | 0,213 | 0,068 |
| **Acenaphtylene** | 0,014 | 0,080 | 0,002 | 0,007 | 0,060 | 0,002 | 0,127 | 6,73 | 0,002 | 0,002 | 0,002 | 0,002 |
| **Acenaphtene** | 0,024 | 0,160 | 0,007 | 0,011 | 0,055 | 0,007 | 0,007 | 0,041 | 0,002 | 0,007 | 0,007 | 0,007 |
| **Fluorene** | 0,046 | 1,03 | 0,002 | 0,016 | 0,040 | 0,002 | 0,017 | 0,183 | 0,002 | 0,002 | 0,008 | 0,002 |
| **Phenanthrene** | 0,884 | 6,20 | 0,001 | 0,110 | 1,01 | 0,001 | 0,151 | 1,39 | 0,070 | 0,040 | 0,217 | 0,001 |
| **Anthracene** | 0,041 | 0,472 | 0,001 | 0,011 | 0,051 | 0,001 | 0,020 | 0,107 | 0,001 | 0,002 | 0,008 | 0,001 |
| **Fluoranthene** | 1,61 | 10,9 | 0,095 | 0,391 | 3,23 | 0,027 | 0,366 | 1,40 | 0,001 | 0,190 | 0,746 | 0,022 |
| **Pyrene** | 1,60 | 11,1 | 0,104 | 0,318 | 2,21 | 0,001 | 0,458 | 2,06 | 0,001 | 0,198 | 0,760 | 0,014 |
| **Benz(a)anthracene** | 0,396 | 2,02 | 0,001 | 0,665 | 1,83 | 0,001 | 0,514 | 2,53 | 0,001 | 0,823 | 9,56 | 0,200 |
| **Chrysene** | 2,38 | 18,5 | 0,001 | 0,489 | 2,69 | 0,015 | 0,668 | 2,59 | 0,001 | 0,270 | 1,56 | 0,001 |
| **Benzo(b)fluoranthene+Benzo(j)fluoranthene** | 2,06 | 19,9 | 0,001 | 0,719 | 3,31 | 0,001 | 0,537 | 2,70 | 0,001 | 0,772 | 3,14 | 0,247 |
| **Benzo(k)fluoranthene** | 1,43 | 15,5 | 0,001 | 0,379 | 9,28 | 0,001 | 0,245 | 1,40 | 0,001 | 0,414 | 2,95 | 0,001 |
| **Benzo(a)pyrene** | 1,10 | 10,9 | 0,001 | 0,279 | 1,36 | 0,001 | 0,488 | 3,06 | 0,001 | 0,087 | 0,881 | 0,001 |
| **Benzo(ghi)perylene** | 1,25 | 22,6 | 0,001 | 0,504 | 2,57 | 0,001 | 0,369 | 4,01 | 0,001 | 0,140 | 2,83 | 0,001 |
| **Dibenz(a,h)anthracene** | 0,647 | 4,49 | 0,001 | 0,264 | 0,619 | 0,001 | 0,274 | 0,737 | 0,001 | 0,142 | 0,450 | 0,001 |
| **Indeno(c,d)pyrene** | 2,12 | 28,8 | 0,088 | 0,561 | 5,16 | 0,044 | 0,581 | 3,40 | 0,001 | 0,220 | 0,764 | 0,001 |

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