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Additional Information

Trends of arsenic levels in PM10 and PM2.5 aerosol in an industrialized area

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Abstract

Arsenic is a toxic element that affects human health and it is widely distributed in the environment. In the area of study, the main Spanish and second European industrial ceramic cluster, the main source of arsenic aerosol is related to the impurities in some boracic minerals used in the ceramic process. Epidemiological studies on the cancer occurrence in Spain points out the study region as one with the greater risk of cancer. Concentrations of particulate matter and arsenic content in PM₁₀ and PM_{2.5} have been measured and characterised by ICP-MS in the area of study during the years 2005-2010. Concentrations of PM₁₀ and arsenic range 27-46 µg/m³ and 0.7-6 ng/m³ respectively in the industrial area, and 25-40 µg/m³ and 0.7-2.8 ng/m³ in the urban area. Concentrations of PM_{2.5} in the urban are range 12 to 14 µg/m³ and 0.5 to 1.4 ng/m³ in the urban background area. Most of the arsenic content is present in the fine fraction, with ratios of PM_{2.5}/PM₁₀ in the range 0.65 to 0.87. The PM₁₀, PM_{2.5} and its arsenic content show a sharp decrease in recent years associated with the economic downturn, which hit severely the production of ceramic materials in the area under study. The production decrease due to the economic crisis combined with several technological improvements in recent years such as substitution of boron, which contains As impurities as raw material, have reduced the concentrations of PM₁₀, PM_{2.5} and As in air to a extent that currently met the existing European regulations.

1. Introduction

Arsenic is a toxic element that affects human health (Jomova et al 2011) and hence, the study of arsenic in environmental media (i.e., groundwater, soil, and air) and the associated human health risks has been an active area of research for many decades (Lewis et al 2012). Arsenic is widely distributed in the environment. Its abundance ranks twentieth in the Earth's crust, with mean concentration of $1.6 \mu\text{g}\cdot\text{g}^{-1}$ (Holmes and Miller 2004); fourteenth in seawater and twelfth in the human body (Mandal and Suzuki 2002; Jomova et al 2011).

Plenty of studies have studied human exposures to arsenic in drinking water and its adverse health effects due to the relatively high concentrations of naturally occurring arsenic in drinking water in some parts of the world. Similarly, the exposure of arsenic arising from soils nearby mining and smelting activities has also been paid attention (Lewis et al 2012). On the other hand, exposures associated with arsenic in ambient air are more scarce. Nonetheless, high concentrations of arsenic and other potentially toxic elements of environmental interest may be present in the atmospheric aerosol (Sanchez de la Campa et al 2011). Anthropogenic sources are often related with combustion of fossil fuels as burning coal, copper smelting and incineration of municipal waste (Pacyna et al 2007; Fernandez-Camacho et al 2010). Arsenic is also released to the atmosphere from other smelting metals, use of some pesticides and some glass raw materials (Sanchez de la Campa et al 2011). Arsenic aerosol has also been associated with terrestrial crustal, volcanoes and groundwater origin (Sanchez de la Campa et al 2011). Nevertheless, anthropogenic emissions of arsenic to the atmosphere are about three times higher than natural ones (WHO 2000).

In the area of study, which is the main Spanish and second European industrial ceramic cluster (Delgado-Saborit and Esteve-Cano 2007), the main source of arsenic aerosol is related to the ceramic industry. Arsenic is present as an impurity in some boracic minerals,

namely colemanite, hydroboracite and ulexite, which are widely used for reducing melting point of the ceramic frits (Esteve and Ramos 1999). Vickery et al (1998) calculated that volatile losses of arsenic trioxide during the ceramic process were in the range of 0.15-0.21 mg g⁻¹ of frit for colemanite and 0.03-0.07 mg g⁻¹ of frit for hydroboracite (Vickery et al 1998). These very high values highlight the importance of the use of boracic minerals in the ceramic industry as an important source of airborne arsenic in the study area and the possible impact in the exposure to arsenic for the local population.

Arsenic is considered as one of the most toxic elements for human health (Chappell et al 2003). Continued exposure to a high concentration of arsenic may produce acute toxic effects on humans, which can be quickly diagnosed. However, chronic exposure to low doses of arsenic may give rise to cancer (Hayes 1997; Roy and Saha 2002; IARC 2009). Arsenic is recognised as a carcinogenic element producing skin, lung and urinary bladder cancer (Englyst et al 2001; Cantor and Lubin 2007). In 2000, the World Health Organization (WHO 2000) Air Quality Guidelines for Europe calculated 1.5×10^{-3} cancer risk for a lifetime exposure to a concentration of $1 \mu\text{g m}^{-3}$ (WHO 2000). Several epidemiological studies and the Ariadna Data Base show that the region of Castellón, where the study area is located, holds the 5th and 9th position in incidence of urinary bladder cancer and lung cancer respectively in Spain (Centro Nacional de Epidemiología (CNE) 2011). Both cancers are related with arsenic exposure (Englyst et al 2001; Cantor and Lubin 2007). The map of cancer occurrence in Spain points out the study region as one with the greater risk of cancer of all Spain (Benach et al 2003). On the other hand, besides promoting various types of cancer, arsenic produces other adverse effects on human health, such as hypertension, cardiorespiratory disease (Navas-Acien et al 2005), immunological system disease (Duker et al 2005), diabetes (Diaz-Villasenor et al 2007), neurological disorders (Vahidnia et al 2007) and dermal effects (Cohen et al 2006).

Given the health effects and its ubiquity in the atmosphere, airborne arsenic

aerosol is nowadays a pollutant of major interest in EU. Arsenic and its ambient air concentration in PM₁₀ are regulated by the EU Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. This Directive proposed a target value for arsenic in PM₁₀ of 6 ng·m⁻³ as an annual mean to be met from December 2012. No limits are established for arsenic on PM_{2.5}. On the other hand, the WHO guidelines on arsenic exposure state that a safe level for inhalation exposure cannot be recommended (WHO 2000).

The present work builds on previous studies by Querol and coworkers that characterized the quality of the air in the ceramic cluster area of Castellón (Querol et al 2001) and compared it with other Spanish cities (Querol et al 2004a; Querol et al 2004b; Querol et al 2008). Those studies showed the occurrence of relatively high ambient air concentrations of arsenic in PM₁₀ in the area of study. However no data on arsenic content in PM_{2.5} was reported, which has a higher potential of penetration in the respiratory system. The cited Querol studies were performed in the early part of the noughties. Since then several technical actions have been implemented by the ceramic industry to reduce the content of arsenic in the air. Considering a) the outlined health effects in the area of study, b) the technological actions implemented c) the higher potential of penetration of PM_{2.5} in the respiratory system and d) the recent economic downturn on the ceramic industry undergoing a period of severe reduction in its manufacturing output; there is the need of reassessing the levels and trends of arsenic in PM₁₀ and characterising the content of arsenic in PM_{2.5} in the ceramic area of interest.

The aim of this work focuses on characterising the levels and trends from 2006 to 2010 of arsenic on PM₁₀ and PM_{2.5} and to assess the compliance with the 2004/107/EC Directive in the ceramic industry study area.

2. Materials and Methods

2.1. Area of study

Samples were collected in two sites located in L'Alcora (Easter Spain), a city which is located within the ceramic industry cluster. The cluster is a geographical triangle of 300 km² containing more than 200 ceramic industries producing 94% and 43% of the Spanish and the European tiles respectively (Querol-Balaguer et al 2004; Delgado-Saborit and Esteve-Cano 2007). Further details of the area of study can be found in Delgado-Saborit and Esteve-Cano (2007).

2.2. Aerosol sampling and sample preparation

PM₁₀ and PM_{2.5} samples were collected in two sampling sites at L'Alcora. The first site (Site 1- Industrial) was located near a municipal sports center within an industrial area (0°12'24" W, 40°4'05" N, 240m asl). The second site (Site 2-Urban Background) was located in a retirement home (0°12'44" W, 40°4'25" N, 260m asl), considered as urban background. At the first station, PM₁₀ sampling was carried out by means of a medium volume Partisol sampler model 2000-H (Rupprecht and Patashnick, USA) furnished with a PM₁₀ inlet, operating at 2.3 m³·h⁻¹. At the second station, PM₁₀ samples were collected using a high volume sampler model MCV-AV model (MCV, Spain), operating at 30 m³·h⁻¹ furnished with a Digitel PM₁₀ inlet. PM_{2.5} samples were collected using a medium volume sampler (Derenda Medium Volume Sampler Model MV 56.1 LV53.1, Germany) furnished with a PM_{2.5} inlet. All sampling equipment was made of non-contaminating materials such as anodised aluminium, stainless steel, polyethylene and polypropylene.

Wahntman GF/A 150 mm (for MCV sampler) and Whatman QMA 47 mm (R&P and Derenda samplers) quartz glass microfiber filters were used as media collection. During a 5

year period from 01/03/2006 to 31/12/2010 a total of 3,272 24-h samples were collected, in which 1,241 were PM₁₀ samples collected at site 1 (industrial); whilst 1,310 PM₁₀ and 721 PM_{2.5} samples at site 2 (urban background). At the end of every 24-h sampling period, the aerosol samples were sealed in plastic bags and were brought back to the laboratory for chemical analysis. In the laboratory, samples were conditioned (20±1°C; 50±5% humidity) for 24 hours in a dessicator before weighting. For chemical analysis, one sample corresponding with a day per week was selected randomly for every sampler, therefore a total of three samples per day were selected. A total of 275 PM₁₀ and 99 PM_{2.5} samples were analysed.

2.3. Elemental analysis

Elemental analysis of PM₁₀ and PM_{2.5} was performed. After gravimetric determination of PM levels, filters were digested in an acid media (HNO₃, 65%, J. T. Baker and H₂O₂, 33%, PA-ACS-ISO). Extractions were carried out with 10 mL of acid and 10 mL of MQ ultrapure water, using Teflon jars and a Merck microwave oven (Esteve and Peris 2000). Once samples were digested, arsenic levels were analysed with an Inductively Coupled Plasma-Mass Spectrometrer, (ICP-MS Agilent 7500 CX with collision cell). The Limit of Detection for arsenic was 0.0073 µg·g⁻¹.

The QA/QC protocol consisted in analysing a blank filter in each batch of samples. For determine possible arsenic traces in reagents and quartz glass filters, blank filters were analysed simultaneously in the batch of their respective samples. Extraction efficiency was assessed by analysing a sample of the certified reference material SRM 1648 (urban particulate matter standard) (NIST, Gaithersburg, MD, USA).

3. Results and discussion

3.1. PM_{10} and $PM_{2.5}$ concentrations

Table 1 shows the annual averages of PM_{10} (industrial and urban sites) and $PM_{2.5}$ (urban site) and the number of exceedances of the current regulation per year. The values of PM_{10} measured in the urban background site during the period 2006-2010 are similar, albeit decreasing, to those reported previously by Querol et al for the same area for the period 2002-2005 (Querol et al 2007). The values measured at the industrial station are higher than those measured at the urban background site (Table 1), which reflects the influence of the ceramic industry emissions on the site. The levels measured at the background and industrial site are consistent with values reported for other areas in Spain, with levels ranging 30-40 $\mu\text{g}\cdot\text{m}^{-3}$ in urban background sites, and levels in the range of 46-50 $\mu\text{g}\cdot\text{m}^{-3}$ in industrial areas (Querol et al 2008).

Levels of $PM_{2.5}$ measured at the area of interest (Table 1) are lower than those measured at other urban background areas in Spain, which range 20 to 30 $\mu\text{g}/\text{m}^3$, whilst they are similar to those measured at rural background areas ($\mu\text{g}/\text{m}^3$) in Spain (Querol et al 2008), Puerto Rico (Figueroa et al., 2006), but lower than $PM_{2.5}$ levels in Italy (Marcazzan et al 2001), China (Ho et al 2002) or Taiwan (Fang et al 1999).

The decreasing pattern of PM_{10} and $PM_{2.5}$ measured during the study period reflect the effect of the combination of measures that the ceramic manufactures had already set in place in previous years (Celades et al 2012). Nonetheless, this decreasing trend might also be attributed to the fact that the economic crisis hit considerably the ceramic sector with a strong reduction in manufacturing, which has halved the production to levels similar to those experienced in 1995 (Celades et al 2012). This is consistent with a recent study which documented that levels of PM_{10} followed a similar trend of economic indicators (Arruti et al

2011).

To assess the degree of compliance in the area of study for the period 2006-2010, the concentrations measured of PM₁₀ and PM_{2.5} were compared with the guidelines given in the European Directive 2004/107/CE of the European Parliament on ambient air quality; the Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on cleaner air for Europe and the Spanish R.D. 102/2011.

Annual PM₁₀ levels in the industrial site were higher than the limit value proposed by the European Directive 1999/30/EC (i.e. annual average below 20 µg/m³ and a maximum of 7 exceedances of the level of 50 µg/m³ per year). However, the PM₁₀ levels measured in 2009 and 2010 at the urban background site would meet the new European Directive 2008/50/EC and Spanish regulation R.D. 102/2011, which sets a limit value for PM₁₀ of 40 µg/m³ with a maximum of 35 exceedances per year of the value 50 µg/m³. The same regulation established a limit annual value for PM_{2.5} of 25 µg/m³, which has been met in the area of study. It is likely that if the values of PM_{2.5} remain similar in the area of study, the PM_{2.5} values will continue to be within the values established in the current regulation.

3.2 Arsenic content in PM₁₀ and PM_{2.5}

Levels of arsenic in the atmosphere are varied. In remote and rural areas, the mean arsenic airborne concentrations range from 0.02 to 4 ng·m⁻³ (WHO 2000), whilst in urban areas arsenic concentrations range from 3 to about 200 ng·m⁻³ (Querol et al 2007; Halek et al 2010; von Schneidmesser et al 2010). Typical PM₁₀ arsenic levels in European Union countries are currently between 0.2 and 1.5 ng·m⁻³ in rural areas, 0.5 and 3 ng·m⁻³ in urban areas and lower than 50 ng·m⁻³ in industrial areas (Putaud et al 2004). Querol et al (2004b) reported arsenic PM₁₀ levels for rural, urban and some industrial sites in Spain in the range of 0.3, 0.3-1.8 and 5 ng·m⁻³, respectively. Table 2 presents the arithmetic mean, maximum and minimum concentration of arsenic found in 275 PM₁₀ samples and 99 PM_{2.5} samples

randomly selected to represent the entire sampling period 2005-2010 at both sampling sites.

The mean arsenic content of the 181 PM₁₀ samples analysed representative of the period 2005-2007 in both sampling sites (3.33 ng·m⁻³ at industrial site and 2.25 ng·m⁻³ at urban background site), is above the usual range of levels (0.3-1.8 ng·m⁻³) found in urban background in other Spanish cities (Querol et al 2004b), with the exception of Huelva industrial area, that shows larger values. On the other hand, arsenic levels representative of the period 2008-2010, are below the Spanish average arsenic content (0.99 ng·m⁻³ at industrial site and 0.93 ng·m⁻³ at urban background site) coinciding with the economic crisis.

For comparison, concentration of arsenic in PM₁₀ measured at two rural background monitoring stations are 0.05-0.35 ng·m⁻³ in San Jorge and 0.35-0.7 ng·m⁻³ in Cirat. These villages are located at 90 km and 40 km from L'Alcora, respectively. The PM₁₀ concentrations at these locations, which are not influenced by the emissions of the ceramic smelter industries, are lower than those found at L'Alcora in the present study and those found at other Spanish urban monitoring stations (Querol et al 2004b).

Previous studies of arsenic content in PM₁₀ in the area of study showed higher levels than actual with 16 ng·m⁻³ in 2002 (Pallares et al., 2007), 9.9 ng·m⁻³ in 2003, 6 ng·m⁻³ in 2004 and 2.5 ng·m⁻³ in 2005 (Minguillón et al 2009). The lower concentration of airborne arsenic in PM₁₀ measured since 2004 are associated with the introduction of several technical actions, such as the substitution of colemanite used as additive by the local frit industry (Esteve and Ramos, 1999), which was the main source of arsenic as an impurity (Arslan et al 1999). Actual measured levels are within the same range of concentration than those measured in another similar industrial area in Greece (1.9 ng·m⁻³ in PM_{2.5} and 1.1 ng·m⁻³ in PM₁₀ in 2006) (Tsopelas et al 2008). On the other hand, arsenic content of PM₁₀ and PM_{2.5} are lower than those measured in industrial zones in Murano (Italy) with values as high as 60 ng·m⁻³ in PM₁₀ in 2003 (Rampazzo et al 2008). The levels measured in the area of study are also lower than those reported in another urban-industrial area in Huelva (Spain) with average arsenic

levels in PM₁₀ and PM_{2.5} ranging between 4.7-11 and 3.0-9.2 ng m⁻³ respectively and maximum arsenic content in PM₁₀ and PM_{2.5} in the range of 22-62 and 19-60 ng m⁻³ during the period 2004-2005 (Fernandez Camacho et al 2010).

The European Directive 2004/107/EC establishes a target value for arsenic of 6 ng/m³ to be met by 2013. If the concentrations of airborne arsenic remain similar to those measured during the study period (2006-2010), it is very likely that the arsenic target value will be met in 2013.

3.3 Ratios of As in PM: As-PM_{2,5}; As-PM₁₀ and As-PM(10-2,5)

The ratios of PM_{2.5} to PM₁₀ and to coarse fraction (i.e. PM₁₀-PM_{2.5}) at the urban site for the years 2007-2010 are presented in Table 3. The arsenic PM_{2.5}/PM₁₀ ratio ranges between 0.65 and 0.87 for the urban site (Table 3), whilst the PM_{2.5}/(PM₁₀-PM_{2.5}) ratio varies between 1.9 and 6.8, for the urban site, which also indicates the accumulation of arsenic in the fine size particles. This values shows that most of the arsenic content of the aerosol is be found in the finer fraction PM_{2.5}. This represents a risk for human health, since the smaller the diameter of the particle, the greater capacity to enter the organism through the respiratory system (Sanchez-Rodas et al 2012). Heatland et al (2000) suggested that metal particles could play a role in the induction of inflammation and cytotoxicity in the human epithelial cells (Hetland et al 2000).

Table 3 shows an enrichment of the content of arsenic on the fine fraction during years 2009 and 2010 similar to the enrichment of fine particulate matter in PM₁₀. It can also be observed that the ratios from 2007-2008, prior to the economic downturn are significantly different ($p < 0.005$) than the ratios from 2009-2010. The concentration of arsenic in the fine size fraction of the PM is consequence of the combustion processes in the frit process (Vickery et al 1998). Therefore the evolution of the fine fraction will be mainly linked to the

evolution of the frit production. The ceramic tile production in 2007-2008 was 550 M m²/year, whilst during 2009 and 2010, this figure decreased to circa 350 M m²/year (Celades et al 2012). Nonetheless, the impact of the decay of manufacturing, is expected to affect similarly the content of PM₁₀ and PM_{2.5} as observed in Table 1 and Table 2. Eventually, the enrichment of the fine fraction and the arsenic content of the fine fraction is related with a decreased of the emission of PM₁₀. The main source of PM₁₀ in the ceramic industry is linked with fugitive emissions from storage and handling of raw materials (Minguillon et al 2009). From 2001 to 2007, abatement technologies were implemented and the situation changed from 2001 where practically all companies stored the raw materials outdoors, to 2007 where over 50% stored their raw materials in closed compartments. In recent years the handling and storage of raw materials has continued to increase and many companies have installed corrective measures as well. As a result the concentrations of fugitive emissions of PM₁₀ have decreased significantly.

3.4. Seasonal pattern

In order to identify possible seasonal variations of arsenic in PM₁₀ and PM_{2.5} at the two sampling sites, the seasonal levels of arsenic in PM₁₀ and PM_{2.5} for the period (2006-2010) has been plotted in Figure 1.

Figure 1 does not show a clear seasonal pattern. This may indicate that the arsenic airborne concentrations are mainly related with the industrial production of ceramic products. This suggestion is supported by the fact that the maximum arsenic values occur at random order across all the months during the period of study (Table 4). The lack of a seasonal pattern and the randomness on the maxima values suggests a prevalence of the industrial origin of airborne arsenic levels in the area of study.

3.5 Evolution in levels of arsenic in the period 2006-2010

Figure 2 shows the monthly evolution of arsenic content in PM₁₀ and PM_{2.5} during the period 2006-2010 at an industrial and urban background site within the ceramic industrial cluster.

Figure 2 shows a zigzag pattern, which may be due to the batch mode operation of smelters that operate with different quantities of raw material containing variable contents of arsenic. This zigzag pattern has been previously related with a clear industrial origin (Sanchez de la Campa et al 2008).

Figure 2 also shows a gradual decrease in the levels of arsenic across the period of study, albeit the major reductions can be observed prior to 2008. This sharper decrease can be attributed to the introduction of cleaner raw materials in the frit fusion kilns, which used colematines with lower content of arsenic (Arslan et al 1999; Karagolge et al 2002).

The second sharpest decline occurred in 2008 when the economic crisis first struck Spain and the ceramic production decreased significantly. A steady decrease is observed in the years 2009 and 2010 in which the economic crisis in Spain hit very strongly the construction sector, which was the main customer of ceramic materials, affecting considerably the production of ceramic industries settled in the study area. The concentrations of arsenic in PM levels measured during the economic crisis years are significantly lower ($p < 0.001$) than concentrations measured before the economic crisis.

Figure 3 shows the evolution between 2006-2010 of annual average levels of arsenic (ng m^{-3}) in other locations belonging to the ceramic cluster of Castellón, which spans an area of 300 km² with a population of 400,000 inhabitants. Data was obtained from the regional air quality monitoring network (i.e *Conselleria de Medio Ambiente de la Generalitat Valenciana*) in the sites located in L'Alcora, Onda, Vila-real, Burriana and Castellón. Onda and Vila-real are industrial cities like L'Alcora, Burriana is a coastal town

mainly agricultural and Castellón is a major urban and coastal city (165,000 inhabitants).

Figure 3 follows a similar trend than that shown in Figure 2, with arsenic levels declining in all cities within the ceramic cluster area. This suggests that the decline in arsenic emissions is generalised in all the ceramic manufacturing area, and that this reduction is benefiting also population located in nearby non-industrial cities such as Burriana and Castellon. The fact that Burriana shows the highest levels of arsenic in aerosol might be attributed to the use of lead arsenates as pesticides (He et al 2005) in the orange tree orchards, the main economic resource of that city and in the fact that Burriana is located downwind of the ceramic emissions (Querol et al 2007).

If we compare the reduction of arsenic levels with the decrease in sales of ceramic materials such as tiles and flooring (Figure 4), we can observe a strong correlation between both variables that clearly indicates the dependence on arsenic levels in the production industry in the area under study. Similar to the downward trend observed for the As content in PM, Table 1 shows a decrease in PM_{10} and $PM_{2.5}$ levels that mirrors the reduction in ceramic sales.

The combination of a) the zig-zag pattern in arsenic content levels; b) the relationship between particulate matter and arsenic content in air with ceramic sales; and c) the use of boron compounds (such as colemanite, hydroboracite and ulexite) in the production of frits (a raw material in tile manufacturing) reinforces the suggestion that the ceramic industry is the main source of airborne arsenic in the area of study.

4. Conclusions

The local ceramic manufacturing activity, specially that related to the smelters using boron compounds as raw materials, is suggested to be responsible for the arsenic airborne levels found in PM_{10} and $PM_{2.5}$ in the study area (L'Alcora) and surrounding cities within the

ceramic cluster area.

The PM_{10} , $PM_{2.5}$ and its arsenic content have shown a sharp decrease in recent years associated with the economic downturn, which hit severely the production of ceramic materials in the area under study. The production decrease due to the economic crisis combined with several technological improvements in recent years (e.g. substitution of boron which contains As impurities as raw material) have reduced the concentrations of PM_{10} , $PM_{2.5}$ and As in air to a extent that currently met the existing European regulations. When ceramic production boost again, it is advisable that technological improvements are considered to ensure that the the particulate matter and arsenic concentrations continue to met the regulations.

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