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RESEARCH ARTICLE

Trends in arsenic levels in PM_{10} and $PM_{2.5}$ aerosol fractions in an industrialized area

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Abstract Arsenic is a toxic element that affects human health and is widely distributed in the environment. In the area of study, the main Spanish and second largest 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 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 PM_{10} and $PM_{2.5}$ were measured and characterized by ICP-MS in the area of study during the years 2005–2010. Concentrations of PM_{10} and its arsenic content range from 27 to 46 $\mu g/m^3$ and from 0.7 to 6 ng/m^3 in the industrial area, respectively, and from 25 to 40 $\mu g/m^3$ and from 0.7 to 2.8 ng/m^3 in the urban area, respectively. Concentrations of $PM_{2.5}$ and its arsenic content range from 12 to 14 $\mu g/m^3$ and from 0.5 to 1.4 ng/m^3 in the urban background area, respectively. Most of the arsenic content is present in the fine fraction, with ratios of $PM_{2.5}/PM_{10}$ in the range of 0.65–0.87. PM_{10}, $PM_{2.5}$, and its arsenic content show a sharp decrease in recent years associated with the economic downturn, which severely hit the production of ceramic materials in the area under study. The sharp 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 PM_{10}, $PM_{2.5}$, and As in air to an extent that currently meets the existing European regulations.

Keywords Arsenic · Atmospheric particles · $PM_{2.5}$ · PM_{10} · Ceramic industry

Introduction

Arsenic (As) 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 20th in the Earth's crust, with a mean concentration of 1.6 μg/g (Holmes and Miller 2004), 14th in seawater, and 12th 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 (Chappell et al. 2003). 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, information regarding exposures associated with arsenic in ambient air is scarcer. Nonetheless, high concentrations of arsenic and other potentially toxic elements of environmental interest may be

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present in atmospheric aerosol (Sanchez de la Campa et al. 2011). Anthropogenic sources of arsenic are often related with combustion of fossil fuels such as coal, with copper smelting, and with 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, volcanic, and groundwater origins (Sanchez de la Campa et al. 2011). Nevertheless, anthropogenic emissions of arsenic to the atmosphere are about three times higher than natural ones (World Health Organization (WHO) 2000).

In the area of study, which is the main Spanish and second most important 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 the 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 of frit for colemanite and 0.03–0.07 mg/g of frit for hydroboracite. 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, all the same for the occupationally exposed workers (Chen et al. 2007).

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 recognized as a carcinogenic element producing skin, lung, and urinary bladder cancers (Englyst et al. 2001; Cantor and Lubin 2007). In 2000, the WHO Air Quality Guidelines for Europe calculated 1.5×10^{-3} cancer risks for a lifetime exposure to a concentration of 1 μg/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 fifth and ninth positions 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 the European Union (EU). Arsenic and its ambient air concentration in PM_{10} 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 PM_{10} of 6 ng/m^3 as an annual mean to be met from December 2012. No limits are established for arsenic in $PM_{2.5}$. On the other hand, the WHO guidelines on arsenic exposure state that a safe level for inhalation exposure cannot be recommended (WHO 2000) due to its carcinogenic potential.

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, b, 2008).Those studies showed the occurrence of relatively high ambient air concentrations of arsenic in PM_{10} in the area of study (8–25 ng/m^3). 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 studies of Querol et al. (2001, 2004a, b, 2008) were performed in the late 1990s and early part of the 2000s. Since then, several technical actions have been implemented by the ceramic industry to reduce the content of arsenic in the air. Considering several factors listed hereunder, there is the need of reassessing the levels and trends of arsenic in PM_{10} and characterizing the content of arsenic in $PM_{2.5}$ in the ceramic area of interest. These factors are (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.

The aim of this work focuses on characterizing the levels and trends from 2006 to 2010 of arsenic on PM_{10} and $PM_{2.5}$ and to assess the compliance with the Directive 2004/107/EC in the ceramic industry study area.

Materials and methods

Area of study

Samples were collected in two sites located in L'Alcora (Eastern Spain), a city which is located within the ceramic industry cluster. The cluster is a geographical triangle of 300 km^2 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).

Aerosol sampling and sample preparation

PM_{10} and $PM_{2.5}$ samples were collected at 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, 240 m a.s.l.). The second site (site 2—urban background) was located at a retirement home (0°12′44″ W, 40°4′25″ N, 260 m a.s.l.), considered as urban background. At the first station, PM_{10} sampling was carried out by means of a medium volume Partisol sampler model 2000-H (Rupprecht and Patashnick, USA) furnished with a PM_{10} inlet operating at 2.3 m^3/h. At the second station, PM_{10} samples were collected using a high-volume sampler (model MCV-AV; MCV, Spain) operating at 30 m^3/h furnished with a Digitel PM_{10} 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 noncontaminating materials such as anodized aluminum, stainless steel, polyethylene, and polypropylene.

Whatman GF/A 150 mm (for MCV sampler) and Whatman QMA 47 mm (R&P and Derenda samplers) quartz glass microfiber filters were used in media collection. During a 5-year period from 1 March 2006 to 31 December 2010, a total of 3,272 24-h samples were collected, in which 1,241 were PM_{10} samples collected at site 1 (industrial), while 1,310 were PM_{10} and 721 were $PM_{2.5}$ samples collected 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 h in a desiccator before weighing. For chemical analysis, one sample corresponding to a day per week was selected randomly for every sampler; therefore, a total of three samples per day were selected. A total of 275 PM_{10} and 99 $PM_{2.5}$ samples were analyzed.

Elemental analysis

Elemental analysis of PM_{10} and $PM_{2.5}$ was performed. After gravimetric determination of PM levels, filters were digested in an acid media (HNO_3, 65 %, J.T. Baker and H_2O_2, 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 and filtered with a 0.45-μm polypropylene membrane syringe filter and diluted to 25 ml using MQ ultrapure water, arsenic levels were analyzed with an inductively coupled plasma–mass spectrometer (ICP-MS) at the Technical–Scientific Services of the Universitat Jaume I. The ICP-MS (Agilent 7500 CX) contains a collision cell that removes any polyatomic interference, especially those derived from Ar and Cl. The limit of detection for arsenic was 0.073 ng/ml, which, when converted to atmospheric concentration, represents 0.05 ng/m^3 for a sampling volume of 36 m^3.

A QA/QC protocol was enforced to account for possible arsenic traces in reagents and quartz glass filters analyzing blank filters and to control the performance of the analytical technique by analyzing a certified reference material and a standard control check. Extraction efficiency was assessed by analyzing a sample of the certified reference material SRM 1648 (urban particulate matter standard) (NIST, Gaithersburg, MD, USA), using a half filter loaded with about 5 mg of SRM 1648 and digested with the other samples in every batch. Recovery rates ranged between 85 and 91 %. In each batch of samples, a blank filter, a sample of the standard reference material, and a 10-ppb standard alongside the samples (N=12) were analyzed. The analyst was blinded in the knowledge of which vials were samples, blanks, reference materials, or standard check.

Results and discussion

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

Figure 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. (2007) for the same area for the period 2002–2005. The values measured at the industrial station are higher than those measured at the urban background site (Fig. 1), which reflects the influence of the ceramic industry emissions on the site. The PM_{10} levels measured at the background and industrial sites are consistent with values reported for other areas in Spain, with levels ranging from 30 to 40 μg/m^3 in urban background sites and levels ranging from 46 to 50 μg/m^3 in industrial areas (Querol et al. 2008).

Levels of $PM_{2.5}$ measured at the area of interest (Fig. 1) are lower than those measured at other urban background areas in Spain, the latter ranging from 20 to 30 μg/m^3, while they are similar to those measured at rural background areas (in micrograms per cubic meter) in Spain (Querol et al. 2008) and 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 ceramic manufacture had already set in place in the previous years (Celades et al. 2012). Nonetheless, this decreasing trend might also be attributed to the fact that the economic crisis considerably hit the ceramic sector with a strong

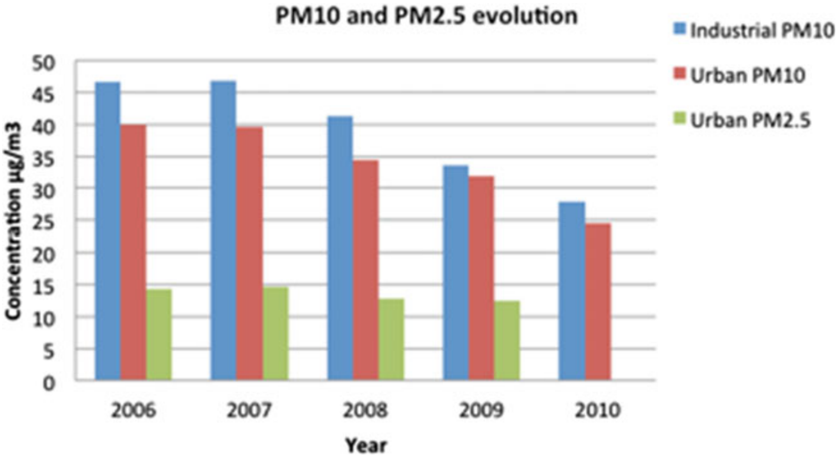


Fig. 1 Evolution of annual mean concentrations PM_{10}–$PM_{2.5}$ from years 2006 to 2010

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 PM_{10} and $PM_{2.5}$ concentrations measured 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 PM_{10} 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/m^3 and a maximum of seven exceedances of the level of 50 µg/m^3/year). However, the PM_{10} 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 PM_{10} of 40 µg/m^3, with a maximum of 35 exceedances per year of the value 50 µg/m^3. The same regulation established a limit annual value for $PM_{2.5}$ of 25 µg/m^3, which has been met in the area of study. It is likely that values of PM_{10} and $PM_{2.5}$ will continue to be within the values established in the current regulation under the following two circumstances. The first one is associated with current low ceramic production, which reduces direct emissions of PM to the atmosphere. The second one is due to recent changes in storage conditions of raw materials that limit fugitive emissions. Therefore, in the event that there is a boost in ceramic production again, further emission reduction measures should be considered, as discussed in detail in the "Evolution in levels of arsenic in the period 2006–2010" section.

Arsenic content in PM_{10} 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), while in urban areas, arsenic concentrations range from 3 to about 200 ng/m^3 (Querol et al. 2007; Halek et al. 2010; von Schneidemesser et al. 2010). Typical PM_{10} arsenic levels in EU countries are currently between 0.2 and 1.5 ng/m^3 in rural areas, between 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 PM_{10} 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 1 presents the arithmetic mean, maximum, and minimum concentrations of arsenic found in 275 PM_{10} 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 PM_{10} samples analyzed representative of the period 2005–2007 in both sampling sites (3.33 ng/m^3 at the industrial site and 2.25 ng/m^3 at the urban background site) is above the usual range of levels (0.3–1.8 ng/m^3) found in urban background areas in other Spanish cities (Querol et al. 2004b), with the exception of Huelva industrial area, that show higher 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 the industrial site and 0.93 ng/m^3 at the urban background site), coinciding with the economic crisis.

For comparison, concentrations of arsenic in PM_{10} obtained from the regional air quality network representative of the period 2005–2007 measured at two rural background monitoring stations are 0.42 ng/m^3 in San Jorge and 0.76 ng/m^3 in Cirat. Arsenic levels representative of the period 2008–2010, coinciding with the economic crisis, are 0.34 ng/m^3 at San Jorge and 0.38 ng/m^3 at Cirat. These villages are located 90 and 40 km from L'Alcora, respectively. A similar behavior was observed in the rural background sites of Morella and Zorita (Santacatalina et al. 2011) The PM_{10} concentrations at these locations, which are not directly 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

Table 1 Minimum, mean, and maximum levels of arsenic (in nanograms per cubic meter) in PM

Year	As-PM_{10} industrial site			Month of highest average	As-PM_{10} urban site			Month of highest average	As-$PM_{2.5}$ urban site			Month of highest average
	Mean	Max	Min		Mean	Max	Min		Mean	Max	Min	
2005	5.79	15.6	1.2	August	2.83	6.6	0.5	October				
2006	2.25	5.6	0.5	June	1.76	4.0	0.4	May				
2007	1.95	4.4	0.4	June	2.17	5.6	0.6	June	1.42	3.2	0.3	July
2008	1.34	3.1	0.3	October	1.37	2.9	0.3	October	0.94	1.9	0.1	November
2009	0.87	2.9	0.1	February	0.76	1.7	0.2	November	0.67	1.5	0.1	October
2010	0.75	1.6	0.1	November	0.65	1.5	0.1	January	0.54	1.2	0.1	June

(Querol et al. 2004b). However, the reduction in arsenic levels measured during the period of the economic downturn shows that the ceramic industry not only impacts the local concentrations but also impacts on the background concentrations in the larger area. The impact of local emissions in areas far from the ceramic cluster might be consequence of the regional transport inland of local emissions associated with the regional meteorology, as described in detail by Querol et al. (2007) and Millán et al. (1997).

Previous studies of arsenic content in PM_{10} in the area of study showed higher levels than current ones with 25 ng/m^3 in 1999 (Querol et al. 2001), 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 (Minguillon et al. 2009). The lower concentrations of airborne arsenic in PM_{10} 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 compared to 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 PM_{10} in 2006) (Tsopelas et al. 2008). On the other hand, arsenic content of PM_{10} 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 PM_{10} 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). During the period 2004–2005, the area of Huelva presented average arsenic levels in PM_{10} and $PM_{2.5}$ ranging from 4.7 to 11 ng/m^3 and from 3.0 to 9.2 ng/m^3, respectively, and maximum arsenic content in PM_{10} and $PM_{2.5}$ ranging from 22 to 62 ng/m^3 and from 19 to 60 ng/m^3, respectively (Fernandez-Camacho et al. 2010).

The European Directive 2004/107/EC establishes a target value for arsenic of 6 ng/m^3 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.

Ratios of As in PM: As-$PM_{2.5}$, As-PM_{10}, and As-$PM_{(10–2.5)}$

The ratios of $PM_{2.5}$ to PM_{10} and to coarse fraction (i.e., PM_{10}–$PM_{2.5}$) at the urban site for the years 2007–2010 are presented in Table 2. The arsenic $PM_{2.5}$/PM_{10} ratio ranges between 0.65 and 0.87 for the urban site (Table 2), while the $PM_{2.5}$/(PM_{10}–$PM_{2.5}$) 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 show that most of the arsenic content of the aerosol is 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 the capacity to enter the organism through the respiratory system and penetrate deep into the alveolar region of the lung (Sanchez-Rodas et al. 2012). Hetland et al. (2000) suggested that metallic particles could play a role in the induction of inflammation and cytotoxicity in the human epithelial cells.

Table 2 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 PM_{10}. It can also be observed that the ratios from 2007 to 2008, prior to the economic downturn, are significantly different ($p<0.05$) from the ratios from 2009 to 2010. The concentration of arsenic in the fine size fraction of the PM is a consequence of the combustion processes in frit production (Vickery et al. 1998). Therefore, the evolution of the fine fraction will be mainly linked to the evolution of frit production. The ceramic tile production in 2007–2008 was 550 M/m^2/year, while during 2009 and 2010, this figure decreased to approximately

Table 2 Annual average ratios at the urban site

Year	Urban site	
	$PM_{2.5}$/PM_{10}	$PM_{2.5}$/(PM_{10}–$PM_{2.5}$)
2007	0.65	1.89
2008	0.69	2.2
2009	0.87	6.77
2010	0.82	4.64

350 M/m^2/year (Celades et al. 2012). Nonetheless, the impact of the decline of manufacturing is expected to similarly affect the content of PM$_{10}$ and PM$_{2.5}$, as observed in Table 1 and Fig. 1. The enrichment of the fine fraction and the arsenic content of the fine fraction are related with a decrease of the emission of PM$_{10}$. The main source of PM$_{10}$ 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. Therefore, while practically all companies stored the raw materials outdoors in 2001, a reassessment of the situation showed that over 50 % of companies stored their raw materials in closed compartments in 2007. In recent years, the handling and storage of raw materials in closed compartments continued to increase and many more companies have installed corrective measures. As a result of the implementation of storage of raw material indoors, the concentrations of fugitive emissions of PM$_{10}$ have decreased significantly.

Arsenic seasonal pattern

In order to identify possible seasonal variations of arsenic in PM$_{10}$ and PM$_{2.5}$, an ANOVA and a Kruskal–Wallis test have been performed to the concentrations measured in spring, summer, autumn, and winter at the two sampling sites. The statistical analysis shows that there is no difference ($p>0.10$) between concentrations measured at different seasons for none of the sites, indicating that a seasonal pattern does not exist in the area of study. The lack of a seasonal pattern in the area of study differs from the common trend of higher concentrations measured in winter in comparison with summer, as widely reported in the literature (e.g., Gao et al. 2002).

In addition to the statistical analysis, the seasonal levels of arsenic in PM$_{10}$ and PM$_{2.5}$ for the period (2006–2010)—plotted in Fig. 2—neither 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 maximum arsenic values occur at random order across all the months during the period of study (Table 1). Other causes that could lead to high concentrations in the levels of arsenic in PM$_{10}$ and PM$_{2.5}$ might be associated with lack of dispersion process associated with meteorology (Millán et al. 1997; Querol et al. 2007) and stagnant atmospheric conditions, which would not facilitate the dispersion of locally emitted arsenic. Nonetheless, stagnant conditions are generally more frequent in winter than in summer, and hence, this alone would not explain fully the spikes of concentrations observed during the warmer months (Fig. 2 and Table 1). Saharan intrusions would have an effect in spikes of particulate matter concentrations (see Table S1, supporting information), but it is not expected to substantially increase the concentrations of arsenic. Therefore, the lack of a seasonal pattern, the negligible influence of stagnant condition in warmer months, and the randomness across the year on the observed maxima values of arsenic in particulate matter suggest a prevalence of the industrial origin of airborne arsenic levels in the area of study associated with the batch operating production of frits and enamels.

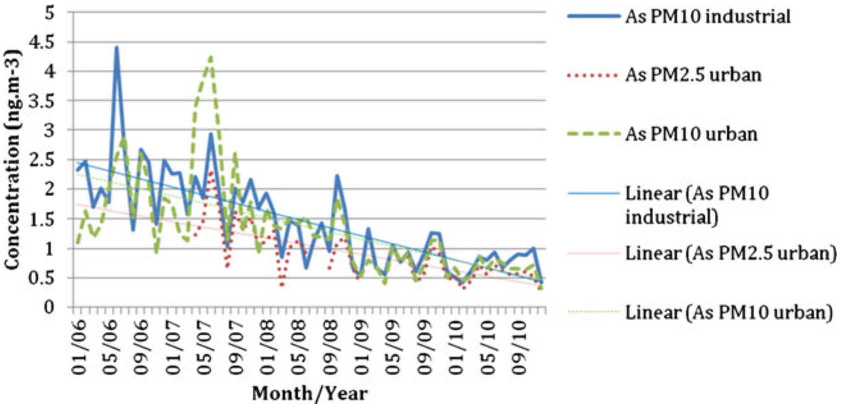
Evolution in levels of arsenic in the period 2006–2010

Figure 2 shows the monthly evolution of arsenic content in PM$_{10}$ 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 colemanites 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 ceramic production

Fig. 2 Evolution of monthly average levels of arsenic in PM for the period 2006–2010 at two sampling sites, namely, site 1—industrial (PM$_{10}$, *solid line*) and site 2—urban background (PM$_{10}$, *dotted line*; PM$_{2.5}$, *dashed line*)



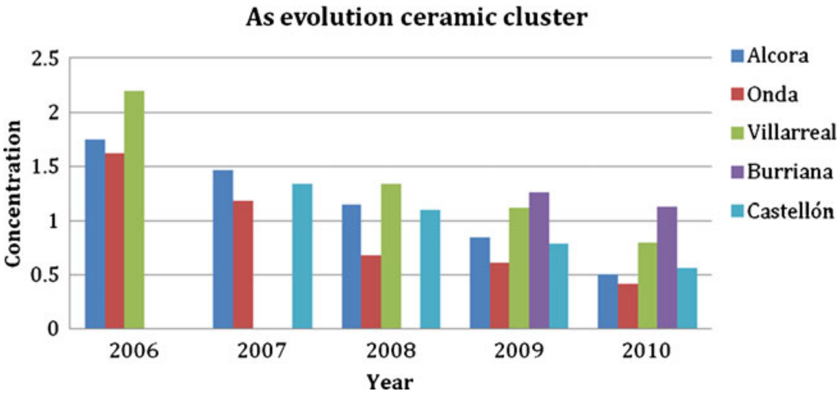


Fig. 3 Evolution during the years 2006–2010 of annual average concentrations of arsenic (in nanograms per cubic meter) measured in five sites within the ceramic cluster area

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 and 2010 of annual average levels of arsenic (in nanograms per cubic meter) in other locations belonging to the ceramic cluster of Castellón, which spans an area of 300 km^2, with a population of 400,000 inhabitants. Data were 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 and mainly agricultural, and Castellón is a major urban and coastal city (165,000 inhabitants).

Figure 3 follows a similar trend as that shown in Fig. 2, with arsenic levels declining in all cities within the ceramic cluster area. This suggests that the decline in arsenic emissions is generalized in all the ceramic manufacturing areas and not restricted to the local area of L'Alcora itself. The reduction of arsenic levels in the atmosphere is also benefiting the population located in nearby nonindustrial cities such as Burriana and Castellon or rural areas such as Zorita and San Jorge, as discussed previously. 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 orange tree orchards, which is the main economic resource of that city. It might also be attributed to 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 (Fig. 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, Fig. 1 shows a decrease in PM$_{10}$ and PM$_{2.5}$ levels that mirrors the reduction in ceramic sales.

The combination of (a) the reduction of arsenic levels both locally and at rural background areas associated with the period of the economic downturn, (b) the zigzag pattern in arsenic content levels, (c) the relationship between

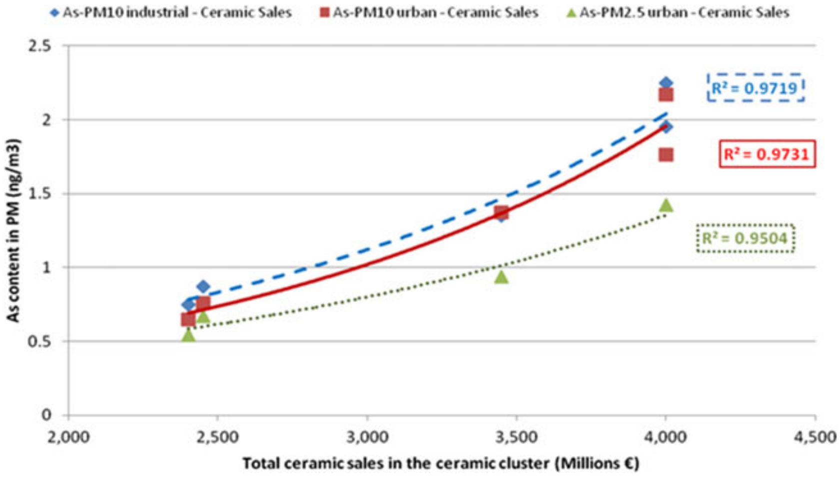


Fig. 4 Relationship between total ceramic sales in the ceramic cluster (in millions of euros considering CPI, source ASCER Spanish Association of Manufacturers of Tiles) and the arsenic content in PM for the period 2006–2010

particulate matter and arsenic content in air with ceramic sales, and (d) the use of boron compounds (such as colemanite, hydroboracite, and ulexite) in the production of frits (a raw material in tile manufacturing) provides evidence that the ceramic industry is the main source of airborne arsenic in the area of study.

Conclusions

The local ceramic manufacturing activity, especially that related to the smelters using boron compounds as raw materials, appears 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.

PM_{10}, $PM_{2.5}$, and its arsenic content have shown a sharp decrease in recent years associated with the economic downturn, which severely hit 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) has reduced the concentrations of PM_{10}, $PM_{2.5}$, and As in air to an extent that currently met the existing European regulations. However, due to the association shown in this study between levels of PM and As in ambient air with ceramic production, when there is boost in ceramic production again, it is advisable that technological improvements are considered to ensure that the particulate matter and arsenic concentrations continue to meet the regulations.

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