Study of the Levels of Concentration of As, Cd and Ni in a Ceramic Cluster

S. Pallarés · A. B. Vicente · M. M. Jordán · T. Sanfeliu

Abstract The main objective of this paper is to check the fulfilment of the European Directive 2004/107/CE, which refers to the limit values of arsenic, cadmium and nickel that will have to be carried out the first of January 2010. Three sampling points have been chosen (Alcora, Vila-real and Castellón), forming a triangle that comprise most of the ceramic cluster of the province of Castellón (Spain). This is a problematic area in relation to the fulfilment of the directive, due to its high industrial development. Apart from this main objective, the following are raised: a) The analysis of the temporal evolution of the levels of As, Cd, Ni and PM10 in the atmosphere during the year 2002; b) The identification of similar behaviour patterns and of the possible common origins in the studied pollutants; c) To show the existence of differences in the behaviour and evolution of As, Cd, Ni and PM10 in the atmospheric medium depending on the location of the sampling point; d) To check whether the levels of As, Cd, Ni and PM10 are influenced by the environmental temperature. The concentration levels of arsenic, cadmium and nickel in Alcora, Vila-real and Castellón have been determined during the year 2002, in order to check whether they are below the limits established in the future directive on these elements. The following conclusions are reached from the results obtained after the chemical analysis (using ICP–MS) of the samples collected in the three locations.

Keywords air pollution · As · Cd · Ni · ICP–MS · Directive 2004/107/CE · tile companies · ceramic cluster

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1 Introduction

During the past years, the European tile companies have been environmentally studied. The reason is that they are the origin of atmospheric pollutants, and their emission mechanism during the process of atomization and firing. The environmental legislation has simultaneously imposed stronger restrictions in the pollutant emission levels to the atmosphere and in the emissions of the tile factories. This fact is an answer to the possible harmful effects that such emissions have on plants, animals (KolKmeier, 1986; Müller, 1991), and human beings present in the surroundings.

The concentration and the physical and chemical features of the pollutants emitted during certain production cycle, are certainly influenced by the type of raw material used in each step of the process, the type of transformation that they can be submitted, and by the installation functioning conditions.

Among the different pollutant substances that can be emitted to the atmosphere, the metallic elements constitute a large group. The atmosphere is the main vehicle for the movement and redistribution of such pollutants, and the medium where almost them all are associated to particles (Schröeder, Dobson, Kane, & Johnson, 1987). The residence times in the atmosphere since metals are associated to particles, are usually short (less than 40 days). Despite this fact, there are long-distance transportations which cause perturbations in ecosystems at a global scale (Nriagu & Pacyna, 1988).

In this research, As, Cd and Ni have been studied as part of this group of polluting substances, whose concentration in the atmospheric medium is to be controlled by a European Directive 2004/107/CE. In the previous studies developed on this task, Gómez (2002), Sanfeliu, Jordán, Gómez, Álvarez, and Montero (2002), have determined the values of As in the local atmosphere, while the concentrations of Cd and Ni have shown low concentrations in relation to other national and European areas.

From these general aspects, and before deepening more in the study of such polluting substances in the sampling area, a short analysis on the possible origin sources and their toxicological effects is to be done.

Not only arsenic, but also cadmium and nickel may have a natural origin in biological processes, resuspension of the soil particles, volcanic activities, forest fires and marine breeze (Pacyna, 1998). However, the industrialization makes that most of their concentration in the atmosphere is due to the human activity.

The As is related to the combustion of fossil combustibles during the production of electricity and heating. It is associated to the inorganic or mineral fraction of such type of combustibles. It is also present in the emissions of pyrometallurgical processes used in the production of non-ferric metals (Pacyna, 1998) and in the emissions that the rubbish incineration in the municipal rubbish dumps produces. Nevertheless, the main source of As contribution in the study area is related to industrial processes based on nonmetallic materials, such as the ceramic industry.

This element is found as an impurity in boracic compounds (colemanite and hydroboracite), used in the formulation of frits and enamels, which means a possible arsenic origin, from its volatilization and/or vaporization during the firing and fusion processes. In a study made by Vickery, Moreno, and Monfort (1998) the loss due to volatilization of this element in the melting of two types of frits was calculated. The measure temperature was 1,400°C. The volatile losses of As_2O_3 was 0.15–0.21 mg/g of frit for colemanite and 0.03–0.07 mg/g of frit for hydroboracite. These data confirm the importance of this source in the study area, as the arsenic losses are high.

The main human activities related to the Cd emission refer to pyrometallurgical processes in the treatment of non-ferric metals, municipal rubbish dumps, processes of waste treatments and to their use in the colouring matter manufacture: pigments, paints, colouring of plastics, printing link, leather, glass and enamels (Fernández Espinosa, 2001; Pacyna, 1998).

Ni is found as a trace element in petroleum. This fact shows that its content in the atmosphere is mainly related to carburant combustion to produce electricity and heat (associated to the inorganic part of the coal), and to the emissions coming from traffic. As in the case of arsenic and cadmium, it is also emitted in pyrometallurgical processes used in the production of non-ferric metals and in the rubbish incineration in municipal rubbish dumps (Fernández Espinosa, 2001; Pacyna, 1998).

With regard to its toxicological effects, it is necessary to enhance the narrow relationship between the metallic elements and the particles of the atmospheric medium. Recent epidemiological studies have provided a solid evidence of the relationship between the concentration of the particulate matter in the air and the harmful effects on the respiratory system (Dockery & Pope, 1994; Schwartz, Dockery, & Neas, 1996). The particle size and shape are factors that control their own penetration capacity. Therefore, the particles of among 2.5 and 10 μm tend to settle at the upper part of the respiratory system, while the fractions of a lower size enter right to the lungs and the alveolar regions. However, the effects on health produced by inhaling particulate matter depend on a series of factors apart from the mentioned above. Such factors are: physicochemical features of the particles, their content in toxic substances, their solubility in biological fluids, the total exposition to

which the human being is submitted, and the health status of the population (Gavett et al., 1997; Smith, Veranth, Lighty, & Aust, 1998; Kodavanti et al., 1998; Bérubé et al., 1999; Laden, Neas, Dockery, & Schwartz, 2000; Baldauf, Lane, & Marote, 2001).

Some recent studies developed throughout environmental simulations of the respiration *in vivo* or *in vitro* with animal models, suggest that the metallic compounds of the particulate matter in the air are correlated to the lung toxicity observed (Pritchard et al., 1996; Gavett et al., 1997; Costa & Dreher, 1997; Kodavanti et al., 1998; Dye et al., 2001). Due to its harmful effect on the human health, atmospheric lead is nowadays being monitored, and its limit value is being more and more restricted (500 ng/m^3, in the Directive 1999/30/CE, transposed in the Spanish law in the Real Decreto 1073/2002). Atmospheric arsenic, cadmium, nickel and mercury have been proposed to be monitored (Directive 2004/107/CE).

2 Description of the Study Area

The general study zone is placed in an important industrial area of ceramics, located in the province of Castellón (Spain). This area produces approximately 93% of the Spanish pavement and the coating, and 95% of frits, enamels and colours. It is at the E-SE part of the province, and has approximately 1,000 km^2. Three places have been chosen in this ceramic cluster:

Alcora, Vila-real and Castellón, which show a high industrial density. The map (Figure 1) shows the location of the three study areas.

The main emission sources of the area are the traffic (mobile sources), the manufacturers of ceramic pavements and coats and the manufacturers of frits, enamels and ceramic colours (both fixed sources).

Alcora, Vila-real and Castellón have been chosen as the values of concentration in the ceramic cluster of the province of Castellón are to be studied, and each presents different features that represent correctly the zones of the area.

Alcora, population of around 10,000 inhabitants, is an area with a high industrial density, with topographic borders which might influence the dispersion of pollutants. In the area enclosed within the city limits a tracking station has been placed. It is particularly located in a building belonging to the town council.

As in the case of Alcora, Vila-real has a high industrial density. However, this city has no important topographic borders, as it is located in a plain (Figure 1). Vila-real has a population of around 50,000 inhabitants. A tracking station has been placed in the municipal store of Vila-real, at the SW part of the city.

The city of Castellón (166,201 inhabitants) has certain industrial density, but less than Alcora and Vila-real, and as in the case of Vila-real, it is located in a plain (Figure 1). The tracking station is right at the

Figure 1 Geographical situation of the three sampling spots (scale 1:400,000).

inner city, which will combine the industrial and urban factors. It is placed in the city Public Record Office.

3 Experimental

3.1 Sampling and determination of the concentration levels

This is a very important stage in the process, as obtaining reliable data depends on it. On the one hand, the three locations have been chosen for this study following the guidelines imposed by the Directive 2004/107/CE, not only in the case of the place, but also the number of stations in a location. On the other, a reference set and filters have been used, in order to obtain PM10 samples. This is the fraction from which arsenic, cadmium and nickel are to be analysed.

The samples have been measured during the year 2002, sampling 121 quartz fibre filters in Alcora, 97 in Vila-real and 74 in Castellón.

In the three sampling stations, the same data capture set has been used; it is a Kleinfiltergerät minivol air sampler type IND-LVS3. This device is considered as a reference according to the European regulations (EN 12341:1998) on the particle sampling PM10 and it allows the daily collection of the PM10 particle concentration present in the local atmospheric medium.

This set provides data on the aspirate volume and on the temperature, pressure and average relative humidity of those measured during the 24 h of the sampling. The aspirate air (2.3 m^3/h) by using a pump, goes through a cutting head which allows under 10 μm particles passing through. The particulate remains in quartz fibre filters with a diameter of 47 mm. Such filters are made of pure quartz microfibres (SiO_2), with a complete absence of ligands or additives, and have an important chemical and thermal stability. Before the sampling and after being collected, the filters must be kept under conditions of a temperature of 20 ± 1°C and controlled humidity (50 ± 5) percent for 48 h, before being weighted.

The levels of concentration of pollutants are determined throughout gravimetry at controlled temperature and humidity. The results are shown in micrograms (μg) of pollutant per cubic meter of aspirate air.

4 Chemical Analysis

The samples are separated for their subsequent chemical analysis with acid digestion. The extraction methods by using heavy acids, facilitates the disintegration of the crystalline structure. This fact makes it easy to determine the total quantity of certain elements present in the samples. When developing these processes in atmospheric samples collected on the filter, this permeable medium is simultaneously decomposed together with the particles. Later on, it is necessary to determine its elemental contribution in the chemical analysis.

There are several methods for acid extraction, but in this study there has been an attempt to follow the recommendations exposed in EN 14902:2005 on determination of heavy metals in samples of particle pollutants. HNO_3 (69%, hiperpur) and H_2O_2 (33%, PA-ACS-ISO) have been used as reactants.

To determine the possible As, Cd and Ni traces that the reagents and quartz fibre filters might contain, giving rise to sample contamination, digestions with only reagents (blank reagents) and filters without sample (blank filters) are performed. In the validation of the results the SRM 1648 'urban particulate matter' pattern was used, whose composition is particulate matter of anthropogenic origin collected in an industrialized urban atmosphere and adequate for use as a reference standard.

The mass spectrometry with a source of inductively coupled plasma (ICP–MS) has allowed the determinations. This is one of the methods specified in the Directive 2004/107/CE. For this purpose, a Hewlett Packard set, model 4500, has been used.

4.1 Data treatment

In the description of some results, a statistical test of variance analysis (one-way ANOVA) has been used. It is a statistical tool which allows the simultaneous comparison of measures of several groups of results, in order to know if them all are equal or if at least one of them shows differences. The STATGRAFICS Plus 4.1 Windows version has been used to develop this test.

Afterwards, Scheffé's method has been used to identify in which groups the differences have taken place. It allows to make simultaneous comparisons and confidence statements even for a class of com-

Table I Concentrations of As, Cd and Ni in nanograms per cubic meter (ng/m)³

Element	Alcora (n = 121)	Vila–real (n = 97)	Castellón (n = 74)	Limit Value
As	16.0 (0.8)	14.2 (0.6)	7.6 (0.7)	6.0
Cd	2.3 (1.2)	2.4 (0.7)	1.4 (0.7)	5.0
Ni	7.5 (1.0)	5.7 (0.9)	4.4 (0.9)	20.0

n Number of samples analysed. The variation coefficient (S_x/X_{ave}) of the data obtained is shown in the brackets.

parisons large enough to allow arbitrary post-hoc contrasts (Finkelstein & Levin, 2001).

5 Results and Discussion

5.1 Values obtained for the arsenic, cadmium and nickel in the three study areas

The mean values of concentration of the three chemical elements obtained in Alcora, Vila-real and Castellón are shown in Table I. Attached are the limit values that the future regulation will establish for each of them.

Together with the mean value, the variation coefficient of the data obtained is shown, in order to compare their relative dispersion in the different areas. The limit values to be required for the arsenic are observed to be exceeded in the three sampling areas. The highest concentration value corresponds to Alcora (10 µg/m³ higher than the value to be required in the future regulations), and the lowest one corresponds to Castellón, which is near the value to be required. According to the variation coefficient, the most significant data dispersion corresponds to Alcora.

With regard to cadmium and nickel, in none of the three areas is the limit value reached, which means

that they will likely obey the Directive 2004/107/CE. The highest nickel concentration if found in Alcora, and in cadmium the highest one is found in Vila-real. In both cases, the lowest value corresponds to Castellón. Alcora has the highest variation coefficient with regard to cadmium and nickel, which means the highest data dispersion.

The highest values obtained in Alcora (except in the case of cadmium, which is similar to that in Vila-real), are also due to the so high industrial concentration, to the existence of topographic borders that do not allow the effective pollutant dispersion.

5.2 Monthly and weekly evolution

The evolution of the concentrations of As, Cd and Ni, including PM10 because of being the granulometric fraction from which such elements are extracted, has been studied.

5.2.1 Monthly Variation

The monthly means of Ad, Cd, Ni and PM10 have been calculated in each of the locations, and are shown in the diagrams in Figures 2, 3 and 4.

5.2.1.1 Alcora Monthly differences are observed in Alcora in the four pollutants studied. The concentrations of PM10, As and Cd are higher in winter (January, February and March), and lower in summer (July, August and September). Ni shows higher values during the first six months of the year, and during the remaining months the concentration is approximately constant, although it slightly increases in November. The four analysed pollutants show a concentration peak in the month of May.

5.2.1.2 Vila-real In Vila-real the PM10 does not show significant variations in its concentration, although
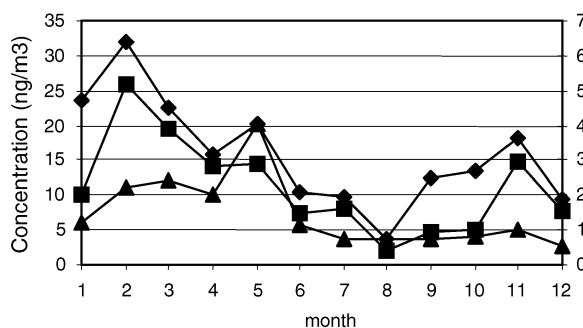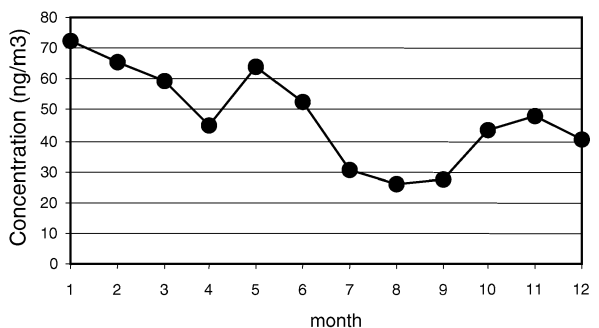

Figure 2 Annual evolution of As, Cd, Ni and PM10 in Alcora. The series are: ◆ As, ■ Cd, ▲ Ni and ● PM10. *Secondary axis*: Cd.
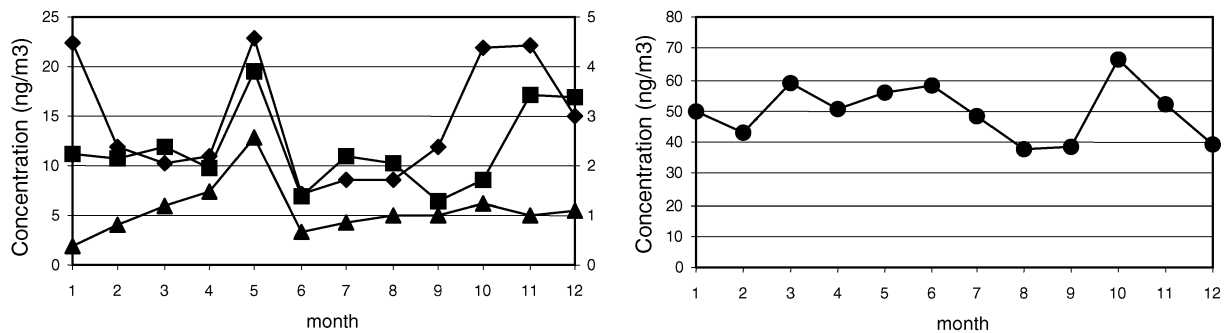
Figure 3 Annual evolution of As, Cd, Ni and PM10 in Vila-real. The series are: ♦ As, ■ Cd, ▲ Ni and ●PM10. *Secondary axis:* Cd.

high levels in the temperate months (July and October) are detected. Such values decrease in August and September (summer months). The highest levels of arsenic and cadmium appear in the last three months of the year and in January, although there is a concentration peak in May. Regarding the Ni, its concentration progressively increases since January until April, and it shows a concentration peak in May (as in the case of the other elements). In the seven remaining months, the levels stay approximately constant.

5.2.1.3 Castellón In Castellón the values of PM10 and Cd are in general higher in December, January and February, and lower in July and August (summer). The arsenic shows lower concentrations also in these months, and the *maxima* concentrations are slightly shown in November, December and January. Ni shows differences; its higher concentrations correspond to the six midmonths of the year (April–September). As in the case of Alcora and Vila-real, a maximum concentration peak of As in May has been measured, however in

the evolution of PM10 and Cd, it appears in April in Castellón.

Figure 4 shows that the evolution of arsenic and cadmium is similar, while nickel presents a different tendency. In general, the concentrations of As and Cd are lower in July, August and September. Although the maximum values of PM10 correspond to different months depending on the location, there is a general reduction of the levels during the summer months (July, August and September). This fact is associated mostly to the decrease of the industrial activity in the summer period (holiday period). Thus, a high percentage of this concentration is deduced to be coming from the industrial activities of the area (anthropogenic origin).

5.2.2 Weekly variation

Days have been classified into two groups, in order to determine the weekly variation of the concentrations: type 1 or working days (Monday to Friday) and type 2 or weekends (Saturday, Sunday and holidays). Likewise, with the aim of knowing whether there are
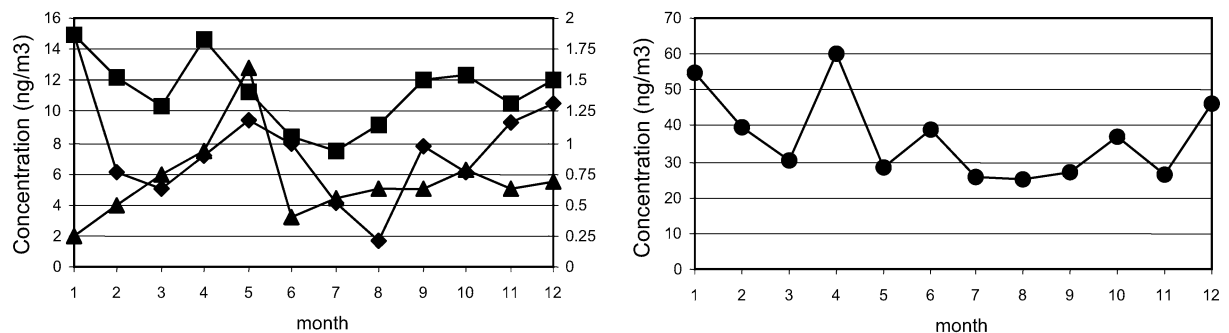

Figure 4 Annual evolution of As, Cd, Ni and PM10 in Castellón. The series are: ♦ As, ■ Cd, ▲ Ni and ●PM10. *Secondary axis:* Cd.

Table II Levels of significance for each element in every sampling area

	Level of Significance (P)		
	Alcora (WD = 103, WE = 19)	Vila-real (WD = 78, WE = 19)	Castellón (WD = 63, WE = 11)
Arsenic	0.0558	0.5674	0.7324
Cadmium	0.1434	0.9182	0.2400
Nickel	0.0030	0.0001	0.9240
PM10	0.0002	0.0344	0.0141

WD Number of working days, WE number of weekend days

differences among them, a one-way ANOVA variance test has been used for each location. The results obtained are shown in Table II.

The PM10 shows significant differences ($P > 0.05$) related to the day type in the three locations. Ni only shows differences in Alcora and Vila-real, and As and Cd do not have significant differences in any location.

Once the existence of the significant differences in some pollutants has been checked, such cases have been studied in order to know whether there is an increase or a decrease during the weekends.

Ni shows an important decrease during the non-working days (Alcora 42% and Vila-real 45%) in both stations that showed significant differences. With regard to the PM10, the mean reduction in weekends is 48% in Alcora, 18% in Vila-real and 33% in Castellón. The PM10 is a pollutant considerably linked to emissions of the ceramic industry and to the treatment and transport of its raw materials, whose activity decreases during the weekends.

5.3 Correlations between arsenic, cadmium, nickel and PM10

In order to identify the similar behaviours between the metals and the PM10, a study on the correlations between them has been made. If the coefficient

between two metals or between one metal and the PM10 is high, it means that the emission source is the same in both cases (Múgica, Maubert, Torres, Muñoz, & Rico, 2002). The results obtained are collected in Table III.

The correlations are not high in any case or in any study site. The highest correlations correspond to Alcora, where the pairs As–Cd, As–PM10 and Ni–PM10 go beyond 0.5. In Vila-real and Castellón, the correlations are very low, and only the pairs As–Cd present a relatively high index. The nickel is more related to the PM10 in Alcora than in the other locations. The correlations of this toxic element with As and Cd are usually the lowest obtained.

The study area can be said not to show high correlations between elements, or between them and the PM10. However, the three locations point out the relation As–Cd, which means that part of the concentration of these elements comes from a common emission source. On the other hand, the toxic elements and the particles can be deduced to be coming from different activities. As, Cd and Ni generally come from combustions, cooking and fusion processes, while the particulate matter, although can be generated by these processes, is mainly due to mechanical processes such as transport and preparation of raw material.

5.4 Influence of the sampling location in the concentrations

This section tries to clear out if there are significant differences between the three locations for each pollutant. In order to do it, a statistical evaluation using a variance test (one-way ANOVA) has been made, as Borai and Soliman (2001) carried out. The results obtained are collected in the Table IV.

There are important and significant differences in the four pollutants ($P < 0.05$). This shows that there

Table III Correlations between As, Cd, Ni and PM10 during the sampling period

	Alcora				Vila-real				Castellón			
	As	Cd	Ni	PM10	As	Cd	Ni	PM10	As	Cd	Ni	PM10
As	1.00	0.59	0.31	0.60	1.00	0.47	0.15	0.23	1.00	0.60	0.13	0.33
Cd		1.00	0.40	0.42		1.00	0.14	0.23		1.00	0.14	0.24
Ni			1.00	0.52			1.00	0.26			1.00	0.12
PM10				1.00				1.00				1.00

are differences among locations for each of them. Once the existence of such differences has been pointed out, a Scheffé's method has been made. This test allows to observe how the locations are gathered in As, Cd, Ni and PM10.

5.4.1 Arsenic

In relation to the arsenic behaviour, there are two different groups; Alcora and Vila-real on the one hand, and Castellón on the other. Taking into account the fact that the arsenic of this area comes mainly from boracic compounds used in the production of ceramic frits, colemanite and hydroboracite (Vickery et al. 1998), it is obvious to think that there are significant differences among the locations that hold a large quantity of such type of companies. Other important contribution of this element is the combustion of fossil combustibles in the heating and energy; in this case, it is reasonable to think that a city like Castellón has a higher proportion of this source than the other two sites.

5.4.2 Cadmium

As in the case of the arsenic, the cadmium behaves similarly in Alcora and Vila-real, which show significant differences with Castellón. In this case, and in order to find the reason for such differences, the possible sources must be taken into account. Its concentration in the atmospheric medium in the study area can be associated to emissions coming from industries which manufacture colours and enamels, as it is used to achieve an intense red colour (Fernández

Espinosa, 2001). In Vila-real and Alcora there is a bigger quantity of such companies than in Castellón, and this might be the reason why there are differences among the locations.

5.4.3 Nickel

In this case, there are also significant differences among sampling sites. However, unlike the other pollutants, such differences are identified among Vila-real and Castellón, and Alcora. Thus, in these points of similar behaviour, the majority contribution of Ni seems to be related to the emissions of the petro-chemical complex and the thermal central located in the areas nearby. In the case of Alcora, Ni mainly comes from another source of emission, and this is the reason why it shows differences with the other locations.

5.4.4 PM10

It has been previously checked that the location has an influence in the behaviour of the PM10. On the one hand, it gathers Vila-real and Alcora, which have a high industrial density, and Castellón on the other. Due to its location, Castellón can be considered as an urban station, although it has some ceramic companies and other type of industries in its surroundings. The conditions that enclose the sampling points influence much on the values obtained for each pollutant. The Castellón station is placed right at its urban centre, in a way that the traffic and other activities (such as heating, constructions, etc.) will bring more particles to the atmospheric medium than in the case

Table IV One-way variance analysis (ANOVA) for As, Cd, Ni and PM10 in different locations

Variation source refers to whether it is within groups of inside one group;

SS Square sum, df degrees of freedom, MS mean squares, F calculated, P significance level

Variation sources	SS	df	MS	F	P
Arsenic					
Among Groups	4.21626	2	2.10808	22.42	0.0000
Within the Same Group	27.1688	289	0.0940098		
Cadmium					
Among Groups	0.795376	2	0.397688	7.94	0.0004
Within the Same Group	14.4769	289	0.050093		
Nickel					
Among Groups	1.24121	2	0.620605	7.98	0.0004
Within the Same Group	22.4694	289	0.0777486		
PM10					
Among Groups	0.756175	2	0.378088	6.32	0.0021
Within the Same Group	17.2903	289	0.0598282		

of Vila-real and Alcora. These two sites will have a high contribution of PM10 coming from the different process which take place when manufacturing pavements and coatings, and in the treatment and transport of raw materials.

5.5 Influence of the environmental temperature

In this section, the possible influence of the environmental temperature on the concentration of arsenic, cadmium, nickel and PM10 has been studied. In previous studies (Sanfeliu et al., 2002) it was concluded that in certain locations the concentration of arsenic generally tended to decrease when the temperature increased. This is the reason why a study to check out if this dependence is shown in the case of the pollutants analysed and in the different sampling sites has been made.

Figures 5, 6 and 7 show the mean concentrations of the different pollutants for each temperature, when it increases. None of them shows a good line adjustment, $C = f(T)$. This is due to the fact that their concentration does not depend exclusively on the temperature, but also on other meteorological factors, such as the wind speed and direction, the relative

humidity and the atmospheric pressure. Nevertheless, a line has been drawn in each figure, in order to observe the general tendency of the concentration (C) when the temperature (T) increases.

5.5.1 Alcora

Although there are no big differences in small temperature intervals (1 or 2 °C), with bigger variations (5–10 °C) or compared to concentration values obtained for extreme temperatures, an important decrease with this meteorological parameter is observed (Figure 5).

The cadmium does not present any determined tendency with the temperature. Although according to the line drawn it could be said that it could slightly decrease with a temperature increment, this fact is due to the existence of data that get off the general tendency.

In the case of the nickel, it can be said that in this location its concentration does not show significant variations with temperature. The data do not present a clear tendency, as the Figure 5 corresponding to this element shows.

The PM10, as in the case of As, tends to decrease with a temperature increment. In this case, the tendency
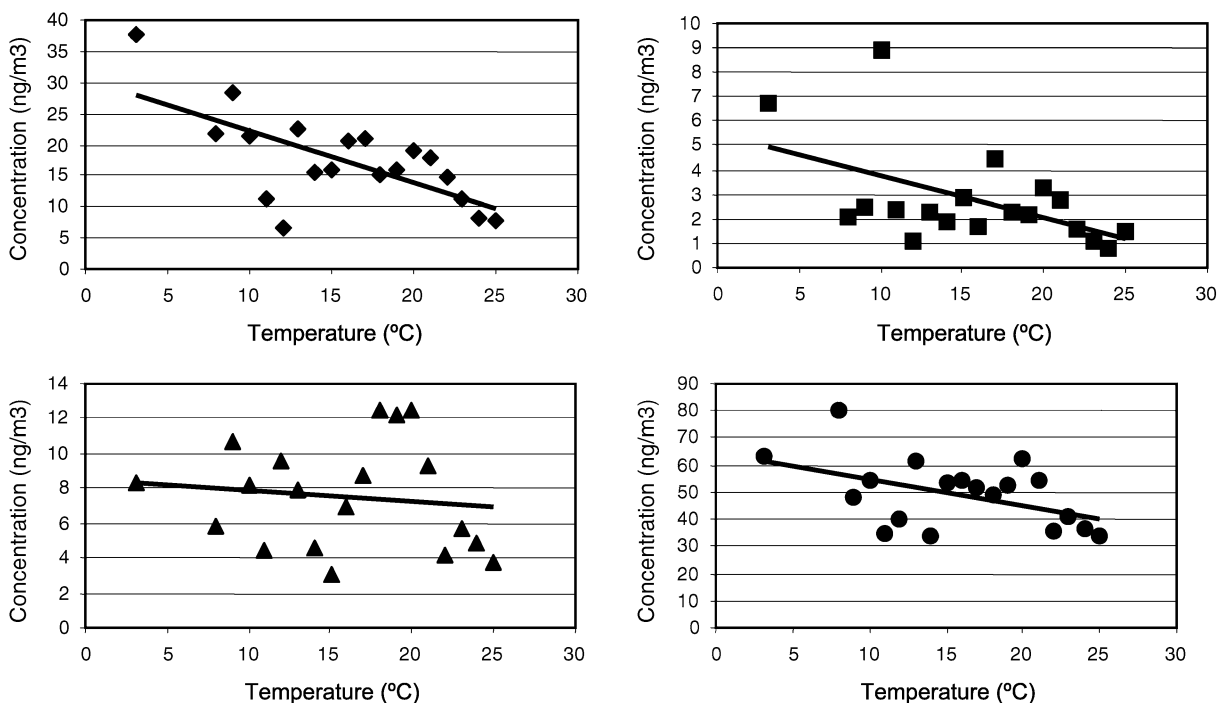

Figure 5 Variation of the elements and of the PM10 with the environmental temperature in Alcora ♦ As, ■ Cd, ▲ Ni and ●PM10.

is also more obvious when the interval of the temperatures that are shown increases.

5.5.2 Vila-real

In Vila-real the concentration of arsenic tends to decrease when the temperature increases. As in the case of Alcora, no significant differences when increasing 1–2 °C is observed. However, if the intervals higher than 5 °C are compared to the extreme temperatures, this relationship is more evident (Figure 6).

The diagram corresponding to the cadmium in Figure 6, shows that the concentrations of cadmium remain constant, and so it does not present any clear tendency when the temperature increases.

Nevertheless, the nickel tends to increase with the temperature in this location. Although it has oscillations, the general tendency is to increase its concentration with an increment of this meteorological parameter, which is more evident the larger the interval compared is.

Opposite to the situation in Alcora, the PM10 tends to increase slightly with the temperature. The data do not show a large dispersion regarding the line drawn to observe the tendency.
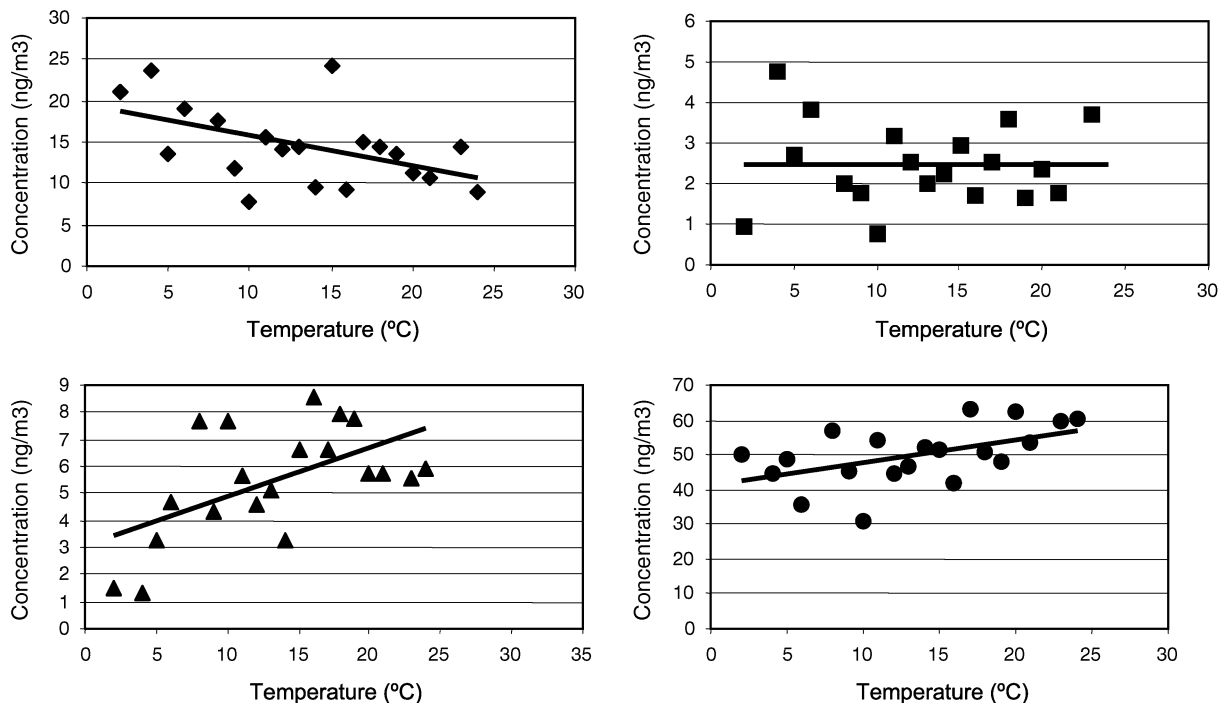
5.5.3 Castellón

In Castellón (Figure 7), the arsenic shows the same tendency than in the other locations, the concentration has an inversely proportional relationship with the temperature. However, in this case it shows a higher data oscillation than in Alcora and Vila-real. The relationship with the temperature as in the other cases, is more evident when increasing the comparison interval.

When observing the tendency line of the cadmium, its concentration could be said to decrease slightly with a temperature increment in this location. Nevertheless, the dispersion of the data regarding the drawn line is so high and the difference of the values is so small between the high and low temperature, that it might be pointed out that in this case it does not show any tendency with regard to an increment of this meteorological parameter.

The nickel in Castellón, as in the case of Vila-real, tends to increase its concentration when increasing the temperature (Figure 7). Although it shows no data oscillation, the increment of the concentration when the extreme temperatures are compared is lower than in the case of Vila-real.
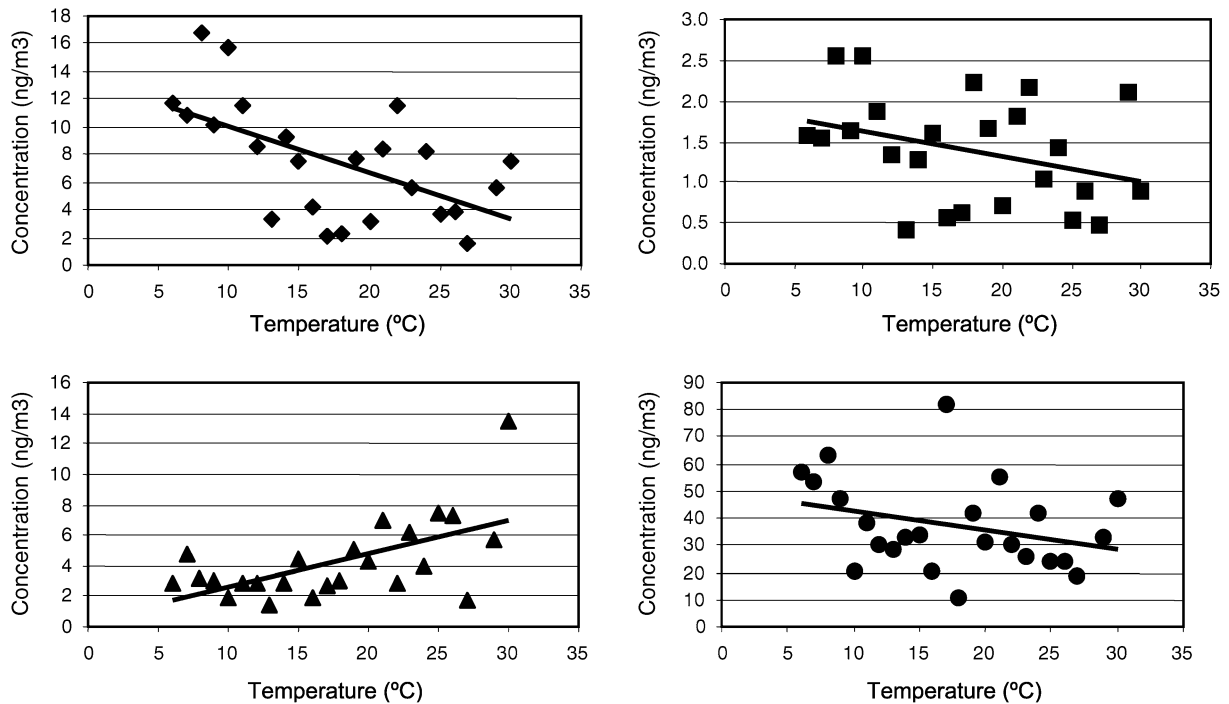

Figure 6 Variation of the elements and of the PM10 with the environmental temperature in Vila-real ♦ As, ■ Cd, ▲ Ni and ●PM10.

Figure 7 Variation of the elements and of the PM10 with the environmental temperature in Castellón. ♦ As, ■ Cd, ▲ Ni and ●PM10.

The concentration of the PM10 in this location, tends to decrease slightly when the temperature increases. However, the dispersion of the values regarding the drawn line is high, which represents a low correlation among the concentration of this fraction and the atmospheric particulate and the temperature.

There is an inversely proportional relationship between the concentration of arsenic and the temperature in the three study sites, in a way that the results obtained by Gómez, 2002 in other conditions are checked out. As in the case of other elements like B, the extra contribution of arsenic is related to volatilizations and vaporizations of these elements during the pavement cooking and frit and ceramic enamel firing processes. The highest concentrations in cold periods are related to a condensation of these elements after going through the chimney in the particles present in the atmosphere; the low temperatures favour this fact. On the contrary, during the warm months, the arsenic emitted in continuous gas phase remains for longer in this state, increasing its capacity of transport to areas away from the source. In Hrsak, Sisovic, Skrbec, & Sega (2001) found the direct relationship between the concentrations of Hg

and the air temperature due to the fact that an increment of it favours the mercury evaporation. In this way, Anderson, Kitto, McCarthy, and Zoller (1994) obtained higher concentrations of B in winter. However, when analysing the boron in its gas and particulate phase, this author pointed out that the gas phase increases in summer, while the particulate one does so in winter. A fact similar to the one detected by these authors is obtained in this study of the As. An increment of the temperature moves the aerosol–vapour balance (Wexler & Potukuchi, 1999) towards the vapour phase. It makes the particle arsenic content decrease, and so lower concentrations of this element in the PM10 are measured.

The cadmium does not show any clear tendency with the temperature in any of these locations. As a consequence, it can be said that its concentration is not linked to this meteorological parameter.

In the case of the other analysed element (Ni), two of the locations show similar behaviours with regard to the temperature (Vila-real and Castellón). Due to the fact that one of the main emission sources of the nickel is the fossil carburant combustion, this could be related to the existence of a petrochemical complex

and a thermal central placed 7.5 km away from both locations. The increment of the concentration when the temperature increases might be explained if this element is considered to be emitted in these processes mostly in flying ashes and not in its gas phase. Boix, Jordán, Querol, & Sanfeliu (2001) detected high Ni contents in particles with a perfect spherical morphology, gathered in emission filters of the chemical companies named above nearby the study site. These data agree with those obtained by Miller & Srivastava (2000), who observed that the concentrations of Ni and V in the emissions of SK Power Asnaes in Denmark (orimulsion combustion from the petroleum), were below the detection limit in the gas phase, and were relatively high in flying ashes. The very fine particles coming from combustion processes behave as a gas pollutant in the atmosphere, in a way that their dispersion is very influenced by external factors such as the temperature (Monn et al., 1995; Chan & Kwok, 2000; Gómez, 2002). The increment of fine particles, and as a consequence, the increments in the concentration of elements associated to them such as nickel in Castellón and Vila-real, is related to their dispersion when the temperature increases.

The relationship between the values of PM10 and the temperature does not follow the same tendency in the three sampling sites. In Alcora the concentration of this pollutant decreases when the temperature increases; however, in Vila-real the contrary behaviour is observed. The decrease of the concentrations of PM10 in Alcora with this parameter can be related to a lower industrial activity in the summer months (July, August and September), which is the period with higher mean temperatures. An increment in the temperature in this area without important topographic borders, favours the additional contribution of fine particles coming from other sources which are far away from the urban centre. This fact makes the levels of the particles collected in these cases increase. The values obtained in Castellón tend to decrease slightly when the studied meteorological parameter increases; the data dispersion with regard to the drawn line represents a low correlation between the PM10 and the temperature. The traffic represents a high contribution of the PM10 particles in the city of Castellón, as it is an urban station. The decrease of the vehicle circulation in this location during the summer period (periods with higher temperatures), makes a decrease in the concentration of such particles possible.

6 Conclusions

The arsenic concentrations in the three study sites exceed the values to be legislated, and so it can be said that the locations placed in the ceramic cluster of Castellón will not fulfil the Directive 2004/107/CE if no corrective measure is to be taken. Taking into account that the main sources in the arsenic study site are the colemanite and the hydroboracite, which are compounds used in the manufacture of frits and ceramic enamels, it is recommended to substitute this raw material by some with less proportion of arsenic compounds in their composition, in order to decrease its levels. Some of the companies manufacturing frits have nowadays began to use those boracic compounds with less content of arsenic.

The cadmium and nickel show mean annual concentrations below the limit values to be legislated, so they will predictably fulfil this Directive. These elements do not have the problems that the arsenic has, and in principle it will not be necessary to propose corrective measures. However, it is recommended to follow the control of cadmium and nickel concentration, together with the arsenic of the area.

The annual evolution of the arsenic and the cadmium is similar, while the nickel has a different tendency. In general, the concentrations of As and Cd are slightly lower in July, August and September. The evolution of the PM10 values along the year 2002, is different depending on the sampling spot, although in general a reduction of the levels during the summer months (July, August and September) is observed. This fact is mostly related to the decrease of the industrial activity during the summer period. Thus, it is deduced that a high percentage of the concentration is due to the industrial activities of the area (anthropogenic origin).

The nickel shows an important reduction in holidays in Alcora (42%) and Vila-real (45%). With regard to the PM10, the decrease of the concentration levels shows differences in the three locations. The PM10 is a pollutant very linked to the emissions of the ceramic companies and to the treatment and transport of their raw materials, whose activity decreases during the weekends. The arsenic and cadmium do not show any clear week evolution, since their origin is associated to continuous processes.

The correlations obtained between the concentrations of As, Cd and Ni, and between them with the

PM10, are not high in any of the study sites. In the three locations the relationship As–Cd show up, and so it can be said that they must have some common emission source. The lack of correlations between the PM10 and the chemical elements involves that they come from different activities. The chemical elements come mainly from combustions, cooking and fusion processes, while the main origin of the PM10 are the mechanical processes and the traffic as well as the contribution of the construction activities.

An inversely proportional relationship between the concentration of arsenic and the temperature is observed in the three locations. This fact is due to the movement of the aerosol–vapour balance towards the vapour phase, when the temperature increases. This fact leads to the decrease of the arsenic content in the particle and lower concentrations of this element in the PM10 are measured. The cadmium does not present a clear tendency with the temperature in any of the three locations. Its concentration can be said not to be linked to this meteorological parameter. The levels of nickel tend to increase with the temperature in Vila-real and Castellón, while in Alcora they do not show any clear tendency. In the petrochemical complex and in the thermal central, which are the main sources of nickel in both locations, this element is preponderantly associated to flying ashes. The dispersion of these ashes increases when the temperature does so, in a way that higher concentrations will be found far away from the emission source. The PM10 does not follow a clear tendency with the temperature similar in the three sampling sites. In Alcora and in Castellón, the concentration of this type of particles decreases when this meteorological parameter increases. This fact is related to the decrease of the anthropogenic activities during the summer period, and not to a dependence of the behaviour of the PM10 levels on the temperature.

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