



Metal pollution of soils and vegetation in an area with petrochemical industry

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Abstract

The aim of this study was to determine the concentrations of arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), manganese (Mn), lead (Pb), and vanadium (V) in soil and chard samples collected in various industrial sites of Tarragona County (Spain), an area with an important number of petrochemical industries. Samples were also collected in urban (Tarragona downtown) and presumably unpolluted (blank samples) sites. Human health risks derived from metal inhalation and ingestion of soils were also assessed. With the exception of an increase in the levels of Cd and V, significant differences in soil samples from the industrial and the unpolluted zone were not found. In chard samples, significant differences between collection sites were only noted for V concentrations. For non-carcinogenic risks, the current levels of metals in the industrial area were lower than those considered as safe for the general population. In relation to carcinogenic risks, only As ingestion and Cr inhalation in the industrial zone might potentially cause an increase of the cases of cancer. A Kohonen self-organized map (an Artificial Neural Network) showed differences in metal concentrations according to the zone of origin of the samples. The current results suggest that although in general terms the petrochemical complex is not a relevant metal pollution source for the area, attention should be paid to As, Cr and V.

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1. Introduction

It is well known that a large number of chemicals involved in petroleum refining and petrochemical manufacturing are toxic in various ways (Mehlman, 1992). Among those, many polyaromatic hydrocarbons, halogenated hydrocarbons,

aromatic amines and nitrosamines, and organometallic compounds are mutagens, carcinogens, or both (Kaldor et al., 1984). Some of these toxic substances are released into the atmosphere. Consequently, communities surrounding petroleum and petrochemical plants can be at increased risk of cancer and other adverse health effects (Kaldor et al., 1984; Pan et al., 1994; Bhopal et al., 1998; Lin et al., 2001). Moreover, petrochemical waste contains also inorganic contaminants that can pol-

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lute soils and pose ecological and human risks. Therefore, the disposal of petrochemical waste can result in the contamination of soils with Cd, Cr, Cu, Ni, Pb, V and Zn among other potentially toxic elements (Schroder et al., 2000).

Although current environmental levels of metals rarely produce morbidity or death in the general population, the continued exposure to low levels of toxic elements such as As, Cd, Hg, or Pb has been associated with a wide range of adverse effects (Christensen, 1995; Chang, 1996). In addition, some elements are also carcinogenic (Cd, Cr(VI), Ni) and teratogenic (As, Cd, Hg, Pb) in mammals (Domingo, 1994; Chang, 1996). Moreover, although metals such as Co, Cu, Mn, Zn, etc. are essential for humans, they can be also dangerous at high exposure levels (Domingo, 1994; Chang, 1996).

In addition to natural processes, soils can be contaminated by metals released into the environment from a number of anthropogenic sources. These elements can bioaccumulate in plants and animals eventually making their way to humans through the food chain (Frink, 1996; Abrahams, 2002). Ingestion, inhalation and skin contact are the main routes of human exposure to soil metals. Taking into account that soils and vegetation is the major sink for airborne metals, the measurement of metal levels in these media is useful to establish trends in abundance and their consequences as a result of natural and anthropogenic changes.

Since approximately 30 years ago, one of the largest petrochemical complexes in Southern Europe is located in Tarragona County (Catalonia, Spain). A big petroleum refinery, together with a number of important chemical and petrochemical industries are placed in the zone. In recent years, public concern over possible adverse health effects for the population living near this industrial complex has increased. Because of it, we recently initiated a wide survey focused on determining the current levels of various inorganic and organic pollutants in the area, and on establishing the health risks for the population living in the neighborhood of the petrochemical complex. The results concerning metals are presented in this paper. These data are also compared with metal levels

from other residential and unpolluted soils of Tarragona County.

2. Material and methods

2.1. Sampling

In winter 2002, 24 soil and 12 wild chard (*Beta vulgaris*) samples were collected in Tarragona County. This is an area which has approximately 300 000 inhabitants. A considerable number of chemical and petrochemical industries are located at the South and North–East of the study area (130 km²). Moreover, the presence of a highway and several roads with an important traffic density influences the environment of the zone (Fig. 1). Soil and vegetation (chard) samples were selected for representing long- and short-term monitors where pollutants are accumulated. Soil sampling points were chosen as follows: 15 in the industrial complex (8 in the vicinity of chemical industries and 7 near petroleum refineries), 5 in urban (Tarragona downtown) and residential (several suburbs of Tarragona City) areas, and 4 outside the study area in presumably unpolluted zones.

Every sampling point was selected depending on the location of potentially important focuses of contamination, according to the possibility of getting meteorological data in the zone (in order to get a better understanding of the process of contaminants dispersion), and finally bearing in mind the vicinity of the petrochemical complex to residential zones in which human health risks had not been previously assessed. Unpolluted sampling sites showed no visible evidence of previous chemical or petrochemical contamination. These samples were collected in rural uncultivated zones (pesticides free), which were outside the potential influence of industrial activities and traffic. Duplicate soil samples were taken from the upper 3 cm of soil and kept in polyethylene bags. All soil samples were collected at the same time as bulk samples within approximately 1 m² in each sampling site. Stones and interfering materials were removed by hand prior to collection. To avoid possible contamination, special care was taken during the sampling and subsequent handling. Soil samples were dried at room temperature until

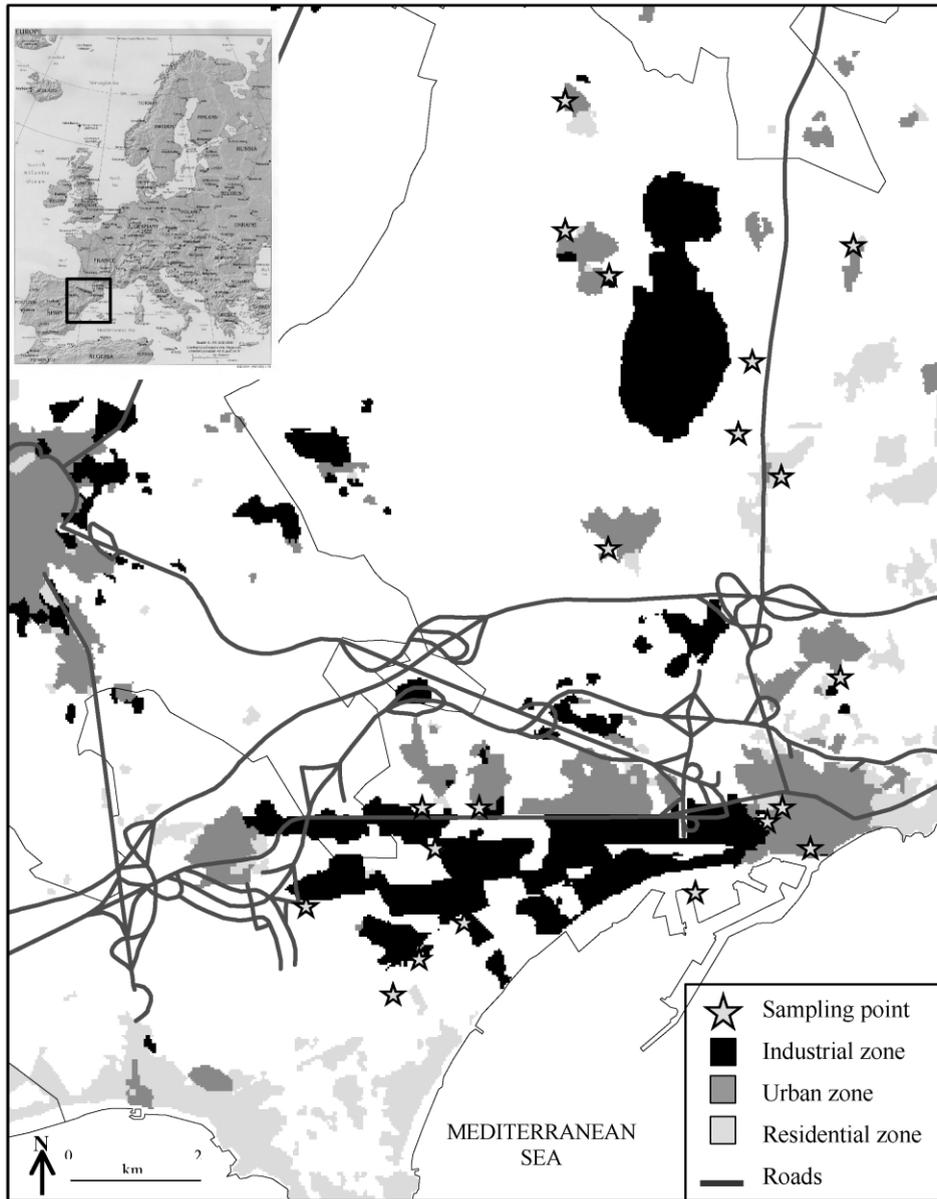


Fig. 1. Sampling points in the area of study.

constant weight and sieved through a 2-mm mesh screen to obtain a more homogenous grain distribution.

Chard samples were collected in 12 of the 24 sites in which soil samples were taken. Six samples were collected in the industrial area, 3 in the

residential zone, and 3 in unpolluted sampling points. Chard was approximately 20 cm high at the collection time. When samples were collected the weather was sunny. There was no precipitation at least during the 10 days previous to collection. Chard samples were obtained by cutting the aerial

part of the plant and subsequently packed in aluminium foils. Samples were dried at room temperature and shredded with a domestic shredder. They were kept in a double aluminium foil, packed in labeled plastic bags, and stored at room temperature until analysis.

2.2. Analytical procedure

Approximately 0.5 g of dried samples of soil or chard were treated with 5 ml of nitric acid (65% Suprapur, E. Merck, Darmstadt, Germany) in Teflon vessels for 8 h at room temperature. Subsequently, they were heated at 80 °C in a stove for 8 h. After cooling, solutions were filtered and made up to 25 ml with deionized water. Concentrations of As, Cd, Cr, Hg, Mn, Pb and V in soils were determined by inductively coupled mass spectrometry (ICP-MS, Perkin Elmer Elan 6000). In chard samples, the levels of As, Cd, Hg, Mn and Pb were measured using ICP-MS, while Cr and V concentrations were determined by atomic absorption spectrometry with graphite furnace atomization (Varian spectrophotometer, Spectra A-30) (Meneses et al., 1999). The accuracy of the instrumental methods and the analytical procedures was checked by duplication of the samples, as well as by using a reference material (Lobster hepatopancreas, NRC Canada, TORT 2), which was run up every 10 samples. The mean recovery rates were between 80 and 95%. Detection limits for soils and chards were: 0.025 µg/g for Mn, Pb and Cd; 0.05 µg/g for Hg, and 0.1 µg/g for As. Detection limit for Cr and V was 0.25 µg/g in soils and 0.01 µg/g in chards. For the statistical analysis, in those samples where an element was not detected, its concentration was assumed to be one-half of the respective limits of detection ($ND = \frac{1}{2} LOD$).

pH and organic matter content of the soil samples were also determined. Fifteen grams of sample were dissolved in 15 ml of deionized water and after mixing for 24 h the measurement of pH was done with a pH-meter. Organic matter content was evaluated according to the Loss of Ignition (LOI) method. Samples were dried in order to eliminate water content. Subsequently, they were heated for

2 h at 600 °C and the weight loss was assessed. The mean pH value of soils was 7.66 (7.03–8.22), while the mean content of organic matter in the 24 soil samples was 5.84% (2.61–9.47%).

2.3. Data analysis

Statistical significance was determined by one-way analysis of variance (ANOVA). A probability of 0.05 or lower was considered as significant. All analyses were carried out with the statistical package SPSS 11.0. In order to establish the behavior of the different elements analyzed, as well as which were the most metal-impacted sites in the area under study, a Kohonen Self-Organizing Map (SOM) was executed. It is an Artificial Neural Network (ANN) model that works with unsupervised learning algorithms.

3. Results and discussion

Table 1 summarizes metal concentrations in soil and chard samples of the 3 zones under study. In 9 soil samples Hg levels were under the limit of detection, while in chards As and Hg were not detected in 9 and 2 samples, respectively. Significant differences between collection areas were not found for As, Cd, Hg and Mn concentrations in soils. However, Cr and V levels were significantly higher in the industrial than in the unpolluted sampling sites. For these elements, no differences between the residential zone and the other two areas were seen. Lead levels differed significantly on comparing residential and unpolluted soils.

In chard samples, significant differences between areas were only found for V. Vanadium levels were higher in the industrial area than in the unpolluted zones. The most important source of atmospheric vanadium (approx. 2/3 of the total amount) is the combustion of residual fuels and coals, which according to their biological origins frequently contain this metal (ATSDR, 1992). This could be the cause of the differences between zones observed in V concentrations in soil and chard samples. Other V sources such as domestic heating and vehicle traffic can be also important, especially during winter (Soldi et al., 1996). Vanadium concentrations in soils and chards collected

Table 1
Concentrations of a number of elements in soil and chard samples

	Industrial	Residential	Unpolluted	<i>P</i>
Soil				
Arsenic	5.50 ± 1.34	4.15 ± 1.66	5.30 ± 1.42	NS
Cadmium	0.21 ± 0.10	0.19 ± 0.07	0.15 ± 0.05	NS
Chromium	13.8 ± 3.9 ^a	10.2 ± 3.2 ^{ab}	8.6 ± 0.9 ^b	< 0.01
Mercury	0.08 ± 0.08	0.08 ± 0.07	0.04 ± 0.02	NS
Manganese	212.5 ± 71.5	191.5 ± 71.8	188.9 ± 13.2	NS
Lead	36.3 ± 30.5 ^{ab}	66.1 ± 49.2 ^a	14.6 ± 3.1 ^b	< 0.05
Vanadium	19.3 ± 6.9 ^a	13.6 ± 3.3 ^{ab}	12.2 ± 2.5 ^b	< 0.05
Chard				
Arsenic	0.03 ± 0.02	0.05 ± 0.00	0.06 ± 0.06	NS
Cadmium	0.09 ± 0.09	0.10 ± 0.08	0.04 ± 0.04	NS
Chromium	0.48 ± 0.23	0.19 ± 0.13	0.23 ± 0.13	NS
Mercury	0.11 ± 0.14	0.07 ± 0.01	0.04 ± 0.01	NS
Manganese	81.7 ± 39.7	87.6 ± 38.5	47.0 ± 22.3	NS
Lead	0.71 ± 0.27	0.50 ± 0.18	0.96 ± 0.45	NS
Vanadium	1.70 ± 0.54 ^a	0.98 ± 0.41 ^{ab}	0.87 ± 0.40 ^b	< 0.05

Results are presented as mean values ± S.D. (in µg/g). For the indicated elements, those values not showing a common superscript (a,b) are significantly different at the level shown. NS = Differences are not statistically significant (*P* > 0.05).

near the petrochemical complex were, in general terms, lower than the levels previously found in areas affected by petrochemical industries (Soldi et al., 1996). The current concentrations were also similar to the levels recently found in other industrial and urban zones of Tarragona County (Llobet et al., 2000, 2002).

In recent years, numerous studies have assessed the influence of traffic on the levels of Pb in atmospheric air, soils, and vegetation of urban areas, showing that the combustion of leaded gasoline was the primary source of atmospheric releases of this metal (Sánka et al., 1995; ATSDR, 1999a; Sheets et al., 2001; Figueira et al., 2002; Parekh et al., 2002). This positive influence would explain that the current Pb levels in residential soils were significantly higher than the background concentrations. However, this difference was not observed in chards. Although in recent years the environmental levels of Pb decreased notably coinciding with the ban on the use of leaded gasoline, soils reflect much better than vegetation a long-term exposure to most pollutants. The current Pb levels in the industrial area of Tarragona were similar or lower than those recently reported for a number of industrial and urban sites (Mikula and Indeka, 1997; Meneses et al., 1999; Sánchez-

Martín et al., 2000; Mielke et al., 2001; Granero and Domingo, 2002; Schuhmacher et al., 2002).

In relation to Mn, although releases of this element include combustion of fossil fuels, incineration of wastes and cement production (ATSDR, 2000a), a great amount of Mn has its origin in the same soils (Figueira et al., 2002). Generally, the current Mn levels in soils and chards were notably lower than those previously found in other industrial zones, road-soils, and even in rural samples (Davies, 1997; Fernández and Carballeira, 2001; Adamo et al., 2002; Kozanecka et al., 2002). Although something similar occurred with Cr, in the present survey the levels of this element in industrial soils were significantly higher than those corresponding to unpolluted zones. However, no significant differences between collection zones were observed in chard, which was probably due to the relatively small number of samples. Chromium occurs naturally in the Earth's crust. Therefore, the total amount of this metal in the environment comes from both, natural (continental dust) and anthropogenic sources (mainly gas, oil and coal combustion) (ATSDR, 2000b).

With regard to As, some quantity of the total As found in soils has a natural origin, averaging a concentration of 2–5 mg/kg. Nevertheless, anthro-

Table 2
Catalan soil quality guidelines for a number of elements ($\mu\text{g/g}$)

	Catalonia	
	Non-industrial	Industrial
As	30	140
Cd	3.5	70
Cr	200	700
Hg	10	25
Mn	–	–
Pb	300	1000
V	–	–

pogenic sources can be also important, especially pesticide applications, coal combustion and waste incineration (ATSDR, 2000c). With respect to Hg, releases to the environment include natural and anthropogenic sources. Application of fertilizers, mining and smelting, combustion of fossil fuels and waste incineration are important anthropogenic sources (ATSDR, 1999b). In the present survey, soils showed a very low Hg concentration, which in some samples was even under the limit of detection ($0.05 \mu\text{g/g}$).

Cadmium enters the environment specially through application of phosphate fertilizers in agricultural soils. However, waste incineration and combustion of several materials can be also other notable contributors (ATSDR, 1999c). In general terms, As, Hg and Cd levels in Tarragona County soils were lower than those previously found in other industrial and urban areas (Shallari et al., 1998; Meneses et al., 1999; Maíz et al., 2000). Chard levels were similar to those observed in herbage analyzed in previous investigations also performed in Catalonia (Meneses et al., 1999; Llobet et al., 2000; Schuhmacher et al., 2002).

Table 2 shows the soil quality guidelines dictated by the regional government of Catalonia (Busquet, 1997), which correspond to the maximum concentration that soils may contain depending on the kind of activity. Comparing these values with the metal levels found in the present study, all soils show lower concentrations than the most restrictive guideline (soils destined to non-industrial activities).

To assess non-carcinogenic risks, the current metal concentrations were compared with the levels of metals considered as safe for people living in residential areas (Preliminary Remediation Goals) (US EPA, 2000) (Fig. 2). Although the present concentrations in industrial and residential soils are inside the safety interval, because of the most restrictive Preliminary Remediation Goals in the last case, the percentage of soil screening level seems to be higher for residential soils. Arsenic and Pb, and Pb and Cr were the elements showing the highest concentrations in residential and industrial soils, respectively. However, when comparing the current concentrations of the carcinogenic metals with the levels included in the Preliminary Remediation Goals (Fig. 3), it can be seen that Cd and Cr are within the safety interval. In contrast, As levels found in residential and industrial soils were approximately 3–10 times higher than the reference limits ($0.39 \mu\text{g/g}$ and $1.6 \mu\text{g/g}$, respectively).

Tables 3 and 4 show the predicted oral exposure in industrial (for adults) and residential (for adults and children) areas. The criteria used for calculations were also taken from US EPA (2000): a soil intake of 50 mg/day and 200 mg/day for adults and children, respectively, an average body weight of 70 kg for adults and 15 kg for children, and 250 days/year of adult exposure to industrial soils. The most conservative scenario was assumed for children exposure; that is to say, not using any

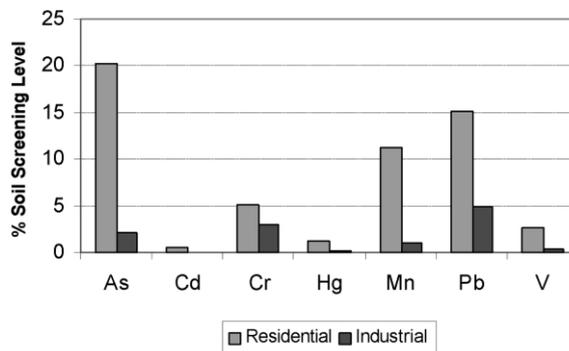


Fig. 2. Non-carcinogenic risks: comparison between metal levels in residential and industrial soils collected in Tarragona County with Preliminary Remediation Goals.

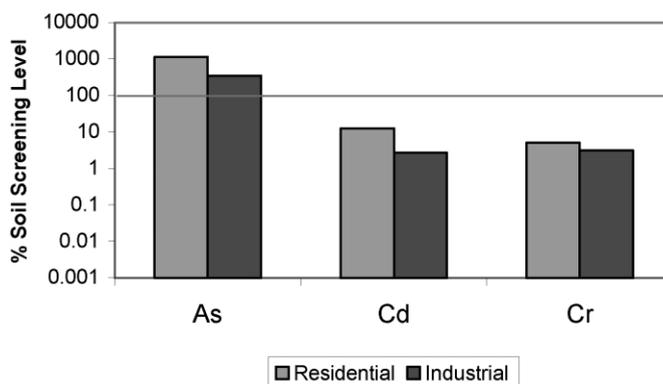


Fig. 3. Carcinogenic risks: comparison between metal levels in residential and industrial soils collected in Tarragona County with Preliminary Remediation Goals.

Table 3
Predicted oral daily exposure to metals from industrial soil for adults and hazard quotient

	RfD ₀ (mg kg ⁻¹¹ day ⁻¹¹)	Adults	
		Predicted exposure (mg kg ⁻¹ day ⁻¹)	Hazard quotient
As	3.00E-04	2.69E-06	8.97E-03
Cd	5.00E-04	9.78E-08	1.96E-04
Cr	3.00E-03	6.74E-06	2.25E-03
Hg	3.00E-04	3.91E-08	1.30E-04
Mn	2.40E-02	1.03E-04	4.31E-03
Pb	3.50E-03	1.78E-05	5.08E-03
V	7.00E-03	9.47E-06	1.35E-03

Table 4
Predicted oral daily exposure to metals from residential soil for adults and children, and hazard quotient

	RfD ₀ (mg kg ⁻¹¹ day ⁻¹¹)	Adults		Children	
		Predicted exposure (mg kg ⁻¹ day ⁻¹)	Hazard quotient	Predicted exposure (mg kg ⁻¹ day ⁻¹)	Hazard quotient
As	3.00E-04	3.14E-06	1.05E-02	5.85E-05	1.95E-01
Cd	5.00E-04	1.50E-07	3.00E-04	2.80E-06	5.60E-03
Cr	3.00E-03	7.64E-06	2.55E-03	1.43E-04	4.76E-02
Hg	3.00E-04	5.71E-08	1.90E-04	1.07E-06	3.56E-03
Mn	2.40E-02	1.41E-04	5.88E-03	2.63E-03	1.10E-01
Pb	3.50E-03	4.35E-05	1.24E-02	8.12E-04	2.32E-01
V	7.00E-03	1.03E-05	1.48E-03	1.93E-04	2.76E-02

age-adjusted factor for non-carcinogenic effects. Hazard quotients, defined as the relation between the predicted exposure and the oral reference dose (RfD₀), are also shown. A value of the hazard quotient under 1 was considered as safe.

Table 5 summarizes inhalation exposure to metals from soils. For calculations, concentrations of particulate matter in air of 68 µg/m³ and 86 µg/m³ in industrial and residential areas, respectively, (Departament de Medi Ambient, 2001), an inha-

Table 5

Inhalation exposure to metals from residential and industrial soils

	Predicated exposure ($\text{mg kg}^{-1} \text{ day}^{-1}$)		
	Residential		Industrial
	Adults	Children	Adults
As	5.39E-08	1.26E-07	4.63E-08
Cd	2.58E-09	6.02E-09	1.68E-09
Cr	1.31E-07	3.07E-07	1.16E-07
Hg	9.83E-10	2.29E-09	6.73E-10
Mn	2.43E-06	5.66E-06	1.78E-06
Pb	7.48E-07	1.75E-06	3.06E-07
V	1.78E-07	4.15E-07	1.63E-07

lation rate of $20 \text{ m}^3/\text{day}$ for adults and $10 \text{ m}^3/\text{day}$ for children and, finally, an average body weight of 70 kg and 15 kg for adults and children, respectively, were used (US EPA, 2000).

US EPA (2000) has established a cancer slope factor for ingestion (SF_0) only for As, and for inhalation (SF_i) for As, Cd and Cr. Consequently, we only assessed cancer risks for these elements and ways of exposure (Table 6). Taking into account the carcinogenic behavior of these elements (bearing in mind an exposure duration of 30 years and 6 years for adults and children, respectively), predicted exposure was recalculated. Assuming a level of 10^{-6} or lower as safe for cancer risk in adults, only As ingestion and Cr inhalation might produce an increase in the number of cases of cancer. However, As ingestion should not be of especial concern taking into account that As concentrations in soils are usually higher than the amount marked by the US EPA as the threshold value. Notwithstanding, the results of various stud-

Table 6

Risk of cancer due to oral exposure to arsenic from soils and inhalation exposure to arsenic, cadmium and chromium from soils

		Adults			Children	
		SF_0/SF_i (kg day mg^{-1})	Residential	Industrial	SF_0/SF_i (kg day mg^{-1})	Residential
Ingestion	As	1.5E+00	2.0E-06	1.7E-06	1.5E+00	7.5E-06
	As	1.5E+01	3.5E-07	2.4E-07	6.5E+00	7.0E-08
Inhalation	Cd	6.3E+00	7.0E-09	4.8E-09	2.7E+00	1.4E-09
	Cr	4.2E+01	2.4E-06	1.6E-06	1.8E+01	4.7E-07

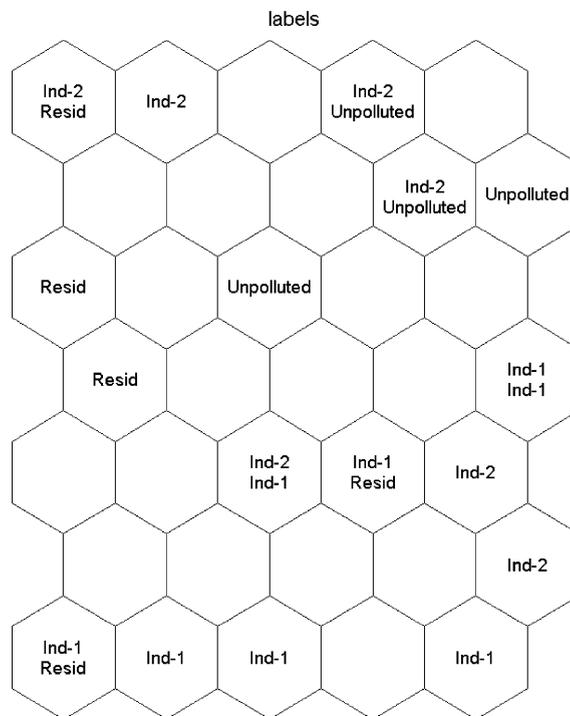


Fig. 4. SOM application to metal levels in soils. Differences between sampling points according to the metal concentrations in the specific zones.

ies exceed these levels. Therefore, a serious effort should be done to reduce As levels in soil. With respect to Cr, only Cr^{6+} is considered as carcinogenic. In the present study, no speciation was done, being assumed that Cr^{6+} meant 1/6 of the total chromium in soil (US EPA, 2000).

In order to establish if the zones close to the petrochemical refineries (marked as Industrial 2)

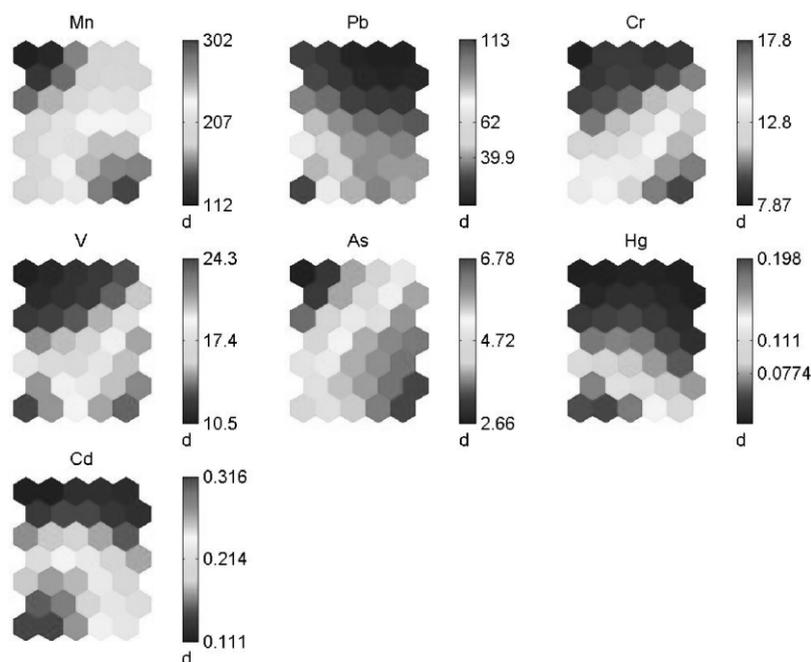


Fig. 5. SOM application to metal levels in soils. Environmental behaviour of the different elements.

and those near the chemical industries (Industrial 1) were affected by different kinds of metal pollution, a chemometric classification method (SOM) was applied on soil samples. This is a powerful tool to classify a great amount of data allowing to obtain a friendly visualization system. It allows easily to establish a diagnostic of the more polluted areas, as well as the most important contaminants. Kohonen's map was a rectangular grid of 7×5 hexagons. The learning phase was broken down with 10 000 steps and the tuning phase with 10 000 steps. The learning process gave a 35 virtual units grid (Fig. 4). The soils collected near the chemical industries (down side of the grid) appear to be more contaminated than those collected in the vicinity of the oil refineries (upper side). The results are solid taking into account several facts. Firstly, the presence of a chlorine-alkali plant in the zone marked as Industrial 1 provokes an increase of the Hg levels in the soils near the chemical complex. Secondly, the concentrations of metals in soils close to an oil refinery are, in general terms, similar or lower

than the levels found in samples of unpolluted soils (blank samples). The stacks and torches of these facilities are at least 110 m high. Thus, wind, which blows predominantly from North to West at an average of 2 m/s, weeps along the contaminants far away. However, three samples catalogued as Industrial 2 seem to be more polluted. It could be due to the fact that these sampling sites are located on the opposite side of the predominant wind, and being the wind not so strong it would place the metals emitted to air closer to the refineries.

Fig. 5 shows the component planes of the SOM in which the metal composition of each virtual unit is displayed. The most concentrated samples are those located in the down-right corner. It suggests that Mn, Cr and As have a similar behavior. Lead, Cd and Hg would represent a second group of elements located closer to the down-left corner, while V behavior would be different from the remaining elements.

In spite of the magnitude of the industrialization in the area under study, the current results suggest that chemical and petrochemical industries would

not mean a relevant metal pollution source, with the exception of As, Cr and V. Dispersion of contaminants due to the characteristics of the stacks and torches, as well as the meteorological conditions in the area play an important role in metal accumulation. It, together with the relatively limited number of samples collected in the current study, does not allow that the present results can be extrapolated to other areas with similar industrial characteristics and contamination sources. Finally, the above results indicate that ANN can be an interesting chemometric tool to be used as a classification method.

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