



Heavy metal pollution in topsoils near a cement plant: The role of organic matter and distance to the source to predict total and HCl-extracted heavy metal concentrations

Gonzalo M.A. Bermudez^{a,b}, Mónica Moreno^c, Rodrigo Invernizzi^c, Rita Plá^c, María Luisa Pignata^{a,b,*}

^a Instituto Multidisciplinario de Biología Vegetal (IMBIV), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina

^b Cátedra de Química General, Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Avda. Vélez Sársfield 1611, Ciudad Universitaria (X5016 GCA) Córdoba, Argentina

^c Técnicas Analíticas Nucleares, Comisión Nacional de Energía Atómica (CAE), Av. Del Libertador 8250 (1429) Buenos Aires, Argentina

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ABSTRACT

Heavy metal and trace element concentrations were examined in topsoils to evaluate a cement plant and an industrial waste incinerator as pollution sources. As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb and Zn were measured by Neutron Activation Analysis (NAA), and Co, Cu, Fe, Ni, Pb and Zn by a 0.5 M-hydrochloric extraction technique using an Atomic Absorption Spectrophotometer (AAS). The Cr total concentration and HCl-extracted Co and Mn were possibly related to wind transportation from an industrial area in the north of Córdoba city (Argentina). Cu, Pb and Zn in partial HCl extraction were influenced by the cement plant and the industrial area in the north of Córdoba city. The mean total Ba concentration was above the residential and agricultural land use limits stated in national and international legislation and was related to the distance to the cement plant. The concentrations of HCl-extracted heavy metals could be predicted by the organic matter percentage and the distance to the cement plant (with R^2 values of 0.50–0.74). The Ca total concentration was seen to have little influence whereas the organic matter percentage strongly affected HCl-extracted heavy metals according to the correlation analysis and multiple regression models. According to soil quality guidelines for environmental health, the human and wildlife populations in Yocsina might be experiencing toxic Ba and Cr effects.

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1. Introduction

When considering different kinds of contaminants, heavy metals are especially dangerous because of their persistence and toxicity (Adriano, 2001). Heavy metal accumulation in soils can result in a loss of soil functions leading to concerns about environmental quality protection, maintenance of human health and productivity. Soil pollution can have implications in phytotoxicity at high concentrations and result in the transfer of heavy metals to the human diet from crop uptake or soil ingestion by grazing livestock (Kabata-Pendias and Pendias, 2001; Nicholson et al., 2003; CCME, 2007; Kabata-Pendias and Mukherjee, 2007). Soil is a very specific component of the biosphere because it is not only a geochemical sink

for contaminants, but also acts as a natural buffer by controlling the transport of chemical elements and substances to the atmosphere, hydrosphere and biota (Kabata-Pendias and Pendias, 2001). Soil can behave as a sink for heavy metals resulting from the aerial deposition of particles emitted by urban and industrial activities (Al-Khashman and Shawabkeh, 2006), vehicle exhausts (Hernandez et al., 2003) and agricultural practices (Franco-Uría et al., 2008).

Cement plants are important emission sources of pollution of both organic and inorganic chemicals, and produce an input of metals and metalloids such as As, Cd, Ca, Co, Cr, Cu, Ni, Pb and Zn (Adejumo et al., 1994; Lee and Pacyna, 1999; İşikli et al., 2003, 2006; Schuhmacher et al., 2004; Al-Khashman and Shawabkeh, 2006), with industrial waste incinerators also being sources of heavy metal and organic compound pollution (Hu et al., 2003; Chang et al., 2009). Some of the heavy metals emitted by these industries are known to be toxic for human and plants, even at low concentrations (Kabata-Pendias and Mukherjee, 2007). Carreras and Pignata (2002) and Schuhmacher et al. (2009) demonstrated that cement dust and associated chemicals can spread

* Corresponding author. Address: Cátedra de Química General, Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Avda. Vélez Sársfield 1611, Ciudad Universitaria (X5016 GCA) Córdoba, Argentina. Tel.: +54 351 4344983; fax: +54 351 4332097.

E-mail addresses: pignata@com.uncor.edu, marialuisa@arnet.com.ar (M.L. Pignata).

over a large area through wind and rain, becoming accumulated in lichens, plants, animals and soils, and thus negatively affecting human health. In addition, limestone dust poses a unique set of problems to plants due to its alkaline properties (Grantz et al., 2003). The importance of pH in metal solubility is well-known as it influences heavy metal adsorption, retention and movement (Sauvé et al., 1997a, 2000). Related to this, de Matos et al. (2001) have demonstrated that pH and Ca concentration affect Cd, Cu, Pb and Zn mobility in soils by competition of adsorbing sites.

Organic matter is another important soil component that influences metal availability. It has a nutritional function by serving as a source of N, P and S, and has a high binding capacity for cations and organic contaminants (Oste et al., 2002). Hernandez et al. (2003), Micó et al. (2006) and Dragović et al. (2008) found that heavy metals are accumulated in surface organic layers in agricultural and urban soils. However, the extent to which topsoil heavy metals can be mobilized to labile forms near a cement plant remains uncertain.

The main objectives of this paper were: (a) to evaluate a cement plant and industrial waste incinerator as a point source of heavy and trace metal pollution in topsoil, (b) to predict heavy metal contents by means of soil properties and distance to the source of pollution, and (c) to elucidate possible associations between HCl-partially extracted heavy metals and total Ca concentration.

2. Materials and methods

2.1. Study area

The study area is situated in Yocsina (Fig. 1), Córdoba Province (Argentina). Yocsina is 18 km SW from Córdoba city, the second

largest city in Argentina (1 500 000 inhabitants), and has a population of 5000 inhabitants and a well-developed cement industry. Currently, its industrial processes include all the stages of manufacture in order to obtain clinker and cement, i.e. from the extraction of raw material (limestone) at the quarries (Malagueño Quarries) to packaging and cement commercialization. The cement plant uses 75% gas and 25% alternative fuels. Industrial solid wastes (hazardous and non-hazardous) are also frequently used, although no official reports are available on this issue.

Taking into account the prevalent winds (NE and NNE), two quadrants (NE and SW) were designated with the cement plant in the center. The NE quadrant was situated in a vast homogenous agricultural area where soybean and wheat are sequentially grown. Eleven topsoil samples were taken after the harvest every 350 m along the sampling transect, from 3.5 to 7.0 km from the cement plant. The SW quadrant had a heterogeneous landscape, and was characterized by the presence of agricultural activities, non-urbanized inhabited areas (individual households and gated communities) and natural vegetation patches. Therefore, the topsoil samples were taken preferentially in agricultural areas where soybean and wheat are cultivated (after harvest), or in the surroundings of individual households where vegetation grows naturally (but not closer than 15 m to walls, garden fences or unpaved streets). In the SW quadrant, a total of twelve topsoil samples were taken 4.0–7.5 km from the cement plant.

2.2. Sampling procedure

Twenty-three topsoil composite samples were collected in the study area at a depth of 0–10 cm, with stones and foreign objects being removed by hand. At each site, nine subsamples were ran-

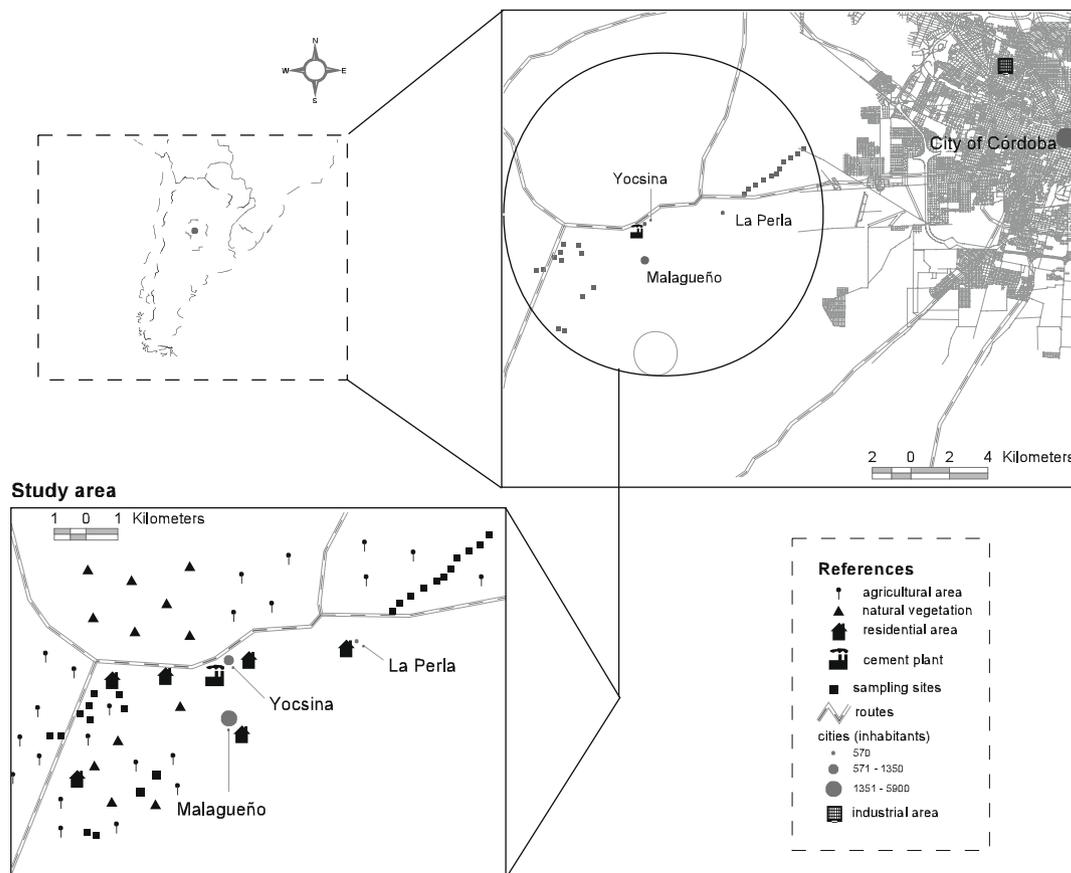


Fig. 1. Topsoil sampling area in Córdoba (Argentina) from the surroundings of a cement plant located in Yocsina. The transect determines two quadrants according to prevalent winds (NE).

domly collected within a 25 m² square with a stainless steel spatula. To avoid effects due to the differential uptake of metals by vegetation, sampling in the SW area (non-agricultural sites) was carried out at locations where plants with superficial roots were not present. Topsoils were kept in plastic bags, and once in the laboratory, they were oven-dried at 40 °C for 24 h. All subsamples were sieved to <2 mm (polyethylene sieve) and stored in darkness until analytical procedures were carried out (Bäckström et al., 2004). Each composite sample was made by mixing and homogenizing 50 g of each of the nine topsoil subsamples.

2.3. Physico-chemical analysis

2.3.1. Electrical conductivity, pH and percentage of organic matter

Soil pH and electrical conductivity (EC) were measured in 1:5 soil:water suspension triplicates (Bäckström et al., 2004). In order to calculate the dry weight, samples were oven-dried for four hours at 105 °C to constant weight (Al-Khashman and Shawabkeh, 2006). The percentage of organic matter (%OM) was determined according to Peltola and Åström (2003) by the combustion of the samples at 500 °C for 4 h.

2.3.2. 0.5 M HCl-extractable heavy metals

With the aim of analyzing labile metals in topsoils, a 0.5 M-hydrochloric acid extraction was performed. This technique has been successfully used to assess total non-residual or non-lattice-held heavy metal concentrations in streams, road sediments and soils (Sutherland and Tolosa, 2001; Sutherland, 2002; Sutherland et al., 2004). In this method, 0.5 M HCl is used to release relevant (labile) fractions of elements, as dilute HCl leach liberates adsorbed detrital and non-detrital carbonate-bound metals and much of the Fe/Mn oxide and organic-associated metals, while minimizing the loss of residual silicate-bound metals (Sutherland and Tolosa, 2001). First, topsoils were sieved with a 63 µm stainless steel mesh (Sutherland et al., 2004). Then, the extraction solution was prepared by mixing 7 g DW of topsoil with 25 mL, 0.5 M HCl and shaking it at room temperature for 30 min. After 24 h, the solution was filtered and analyzed using a Perkin-Elmer AA3110 spectrophotometer to measure Co_{HCl}, Cu_{HCl}, Fe_{HCl}, Ni_{HCl}, Mn_{HCl}, Pb_{HCl} and Zn_{HCl} (Sutherland, 2002).

2.3.3. Total metal concentration in topsoils

Topsoils (<63 µm) were analyzed by Neutron Activation Analysis (NAA) for As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb and Zn. NAA is currently a method of choice in trace analysis in environmental matrices and has been proven to be a sensitive, accurate, multi-elemental method capable of determining most lanthanides (Orvini et al., 2000). Being purely instrumental, NAA allows one to overcome problems related to sample dissolution in matrices naturally enriched with silicon and silicates. Briefly, samples were irradiated for 4 h in the RA-3 reactor (thermal flux $3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, 8 Mw) of the Ezeiza Atomic Center (CNEA – Argentine National Atomic Energy Commission). Element concentrations were calculated using software developed at the NAA laboratory, with IAEA SL-1 Lake Sediment and NIST – SRM 2709 San Joaquin Soil being used as calibration standards and GBW07405 (soil) for control purposes.

2.4. Quality control

Table 1 summarizes the analyzed concentrations in CRM GBW07405 Soil (NRCCRM, China) as determined by NAA. The overall picture can be considered satisfactory, especially if we take into account the complexity of the matrix analyzed. However, the only measurement precision was able to be evaluated for the dilute HCl digests because there were no CRMs for this leach. Estimates of

Table 1

Quality control results ($\mu\text{g g}^{-1}\text{DW}$) obtained from the analysis of GBW07405 (soil) by Neutron Activation Analysis (NAA).

| Element | Certified | Experimental |
|---------|-------------------|-------------------|
| As | 412 ± 24 | 407 ± 12 |
| Ba | 296 ± 40 | 316 ± 100 |
| Ce | 91 ± 15 | 97.9 ± 4.5 |
| Co | 12 ± 2 | 12.40 ± 0.39 |
| Cr | 118 ± 10 | 117 ± 6 |
| Cs | 15 ± 2 | 15.0 ± 0.8 |
| Eu | 0.82 ± 0.06 | 0.86 ± 0.16 |
| Fe | 9.0E+04 ± 2.0E+03 | 8.6E+04 ± 1.1E+03 |
| Hf | 8.1 ± 1.7 | 7.71 ± 0.98 |
| La | 36 ± 6 | 37.4 ± 0.5 |
| Lu | 0.42 ± 0.07 | 0.423 ± 0.047 |
| Na | 890 ± 30 | 886 ± 96 |
| Rb | 117 ± 9 | 121 ± 9 |
| Sb | 35 ± 7 | 34.7 ± 0.4 |
| Sc | 17 ± 2 | 17.4 ± 0.1 |
| Sm | 4.0 ± 0.6 | 4.54 ± 0.22 |
| Ta | 1.8 ± 0.3 | 2.03 ± 0.45 |
| Tb | 0.7 ± 0.2 | 0.755 ± 0.071 |
| Th | 23 ± 2 | 23.4 ± 0.6 |
| U | 6.5 ± 1.1 | 7.07 ± 0.97 |
| Yb | 2.8 ± 0.5 | 2.60 ± 0.55 |
| Zn | 494 ± 39 | 493 ± 35 |

precision were determined by the coefficient of variation percentage (CV%) of duplicates for the twenty-three composite topsoil samples. The mean CV% for Co_{HCl}, Cu_{HCl}, Fe_{HCl}, Mn_{HCl}, Ni_{HCl}, Pb_{HCl} and Zn_{HCl} duplicates were 6.6, 4.1, 15.9, 5.3, 11.3, 2.9 and 12.2, respectively, with the data indicating good precision of typically <15%. Laboratory blanks were routinely prepared and analyzed (one blank for every ten samples) in order to monitor the possibility of sample contamination during analysis.

2.5. Statistical methods

The Shapiro–Wilks test for normality was applied, and non-normal distributed elements were log-transformed before parametric statistics were performed. An Analysis of Covariance (ANCOVA) was used to determine the treatment effects on the elemental concentration (arbitrary category), with the distance to the cement plant, pH and %OM as covariates (quantitative factors). ANCOVA was performed for each element according to the following proposed model:

$$Y_{ij} = \mu + \alpha_i + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + e_{ij}$$

where $i = 1, 2, \dots, 12$;

With the purpose of predicting heavy metal concentrations in topsoils, multiple linear regressions were performed using the distance to the cement plant, %OM and pH as the independent variables. Pearson's correlation matrix was used to identify relationships between HCl-extracted heavy metals and Ca. The level of statistical significance was represented using * for $p < 0.05$, ** for $p < 0.01$ and *** for $p < 0.001$.

3. Results and discussion

3.1. Descriptive statistics

Descriptive statistics of elemental concentrations and soil properties, including minimum, maximums, means, standard errors of means, coefficients of variation percentage (CV%), skewness, and kurtosis are given in Table 2. According to Argentinean and Canadian soil quality guidelines (SQG, Table 3), the mean total As, Co, Cr, Sb and Zn concentrations in the study area were within the limits for agricultural, residential and industrial land use. However,

Table 2
Descriptive statistics for trace elements and heavy metal concentrations (mg kg⁻¹DW), and soil properties measured in topsoils from the surroundings of a cement plant in Córdoba, Argentina.

| Variable | n | Mean | SE | CV% | Min | Max | Skewness | Kurtosis |
|---------------------------|----|---------|-------|------|---------|---------|----------|----------|
| pH | 69 | 6.93 | 0.03 | 3.72 | 6.32 | 7.64 | 0.14 | -0.02 |
| EC (μs cm ⁻¹) | 69 | 151 | 8 | 44.4 | 79 | 332 | 1.32 | 0.93 |
| %OM | 69 | 7.75 | 0.32 | 34.6 | 1.25 | 14.8 | 0.25 | 0.58 |
| As | 23 | 7.6 | 0.2 | 14.8 | 5.0 | 9.7 | 0.14 | 0.27 |
| Ba | 23 | 580 | 20 | 17.0 | 390 | 803 | 0.43 | 0.06 |
| Ca | 23 | 1.9E+04 | 5E+02 | 12.8 | 1.5E+04 | 2.6E+04 | 1.37 | 2.86 |
| Ce | 23 | 65 | 7 | 46.5 | 4 | 113 | -1.29 | 0.77 |
| Co | 23 | 12.1 | 0.6 | 25.5 | 9.4 | 20.1 | 1.94 | 3.07 |
| Co _{HCl} | 45 | 3.82 | 0.09 | 15.1 | 2.91 | 5.49 | 0.91 | 0.59 |
| Cr | 23 | 50.2 | 2.9 | 28.1 | 37.7 | 91.5 | -0.08 | -0.64 |
| Cs | 23 | 6.8 | 0.2 | 10.4 | 5.6 | 8.1 | 1.37 | 1.14 |
| Cu _{HCl} | 45 | 3.74 | 0.13 | 24.2 | 0.59 | 6.10 | -0.39 | 2.82 |
| Eu | 23 | 1.17 | 0.04 | 18.5 | 0.93 | 1.75 | 1.80 | 2.90 |
| Fe | 23 | 3.5E+04 | 1E+03 | 17.0 | 3.0E+04 | 5.2E+04 | 1.20 | 1.20 |
| Fe _{HCl} | 45 | 726 | 28 | 26.4 | 393 | 1.2E+03 | 0.55 | -0.04 |
| Hf | 23 | 8.5 | 0.5 | 30.1 | 5.2 | 15.6 | 1.20 | 1.20 |
| La | 23 | 41.4 | 2.9 | 33.6 | 31.7 | 84.2 | 2.25 | 4.47 |
| Lu | 23 | 0.55 | 0.03 | 23.3 | 0.43 | 0.90 | 1.63 | 2.03 |
| Mn _{HCl} | 45 | 281 | 9 | 20.8 | 173 | 399 | 0.01 | -0.69 |
| Na | 23 | 1.7E+04 | 5E+02 | 13.0 | 1.2E+04 | 2.0E+04 | -0.96 | -0.08 |
| Ni _{HCl} | 45 | 3.19 | 0.14 | 30.6 | 1.43 | 7.17 | 1.64 | 5.05 |
| Pb _{HCl} | 45 | 7.70 | 0.10 | 8.44 | 6.41 | 9.50 | 0.61 | 0.68 |
| Rb | 23 | 104 | 3 | 14.3 | 77 | 142 | 1.21 | 1.70 |
| Sb | 23 | 0.798 | 0.027 | 16.3 | 0.562 | 1.07 | -0.09 | -0.60 |
| Sc | 23 | 12.2 | 0.4 | 15.3 | 10.5 | 17.2 | 1.81 | 2.60 |
| Sm | 23 | 7.63 | 0.58 | 36.2 | 4.80 | 15.7 | 1.98 | 3.65 |
| Ta | 23 | 1.27 | 0.03 | 12.0 | 1.00 | 1.54 | 0.12 | -0.59 |
| Tb | 23 | 1.24 | 0.07 | 27.9 | 0.73 | 1.81 | 0.08 | -1.50 |
| Th | 23 | 14.7 | 1.0 | 31.9 | 9.92 | 29.8 | 2.18 | 5.02 |
| U | 21 | 3.1 | 0.1 | 19.6 | 1.7 | 4.4 | 0.16 | 0.84 |
| Yb | 23 | 3.36 | 0.18 | 25.9 | 2.64 | 5.78 | 2.06 | 3.91 |
| Zn | 23 | 92.5 | 5.1 | 26.2 | 64.6 | 156 | 1.53 | 1.41 |
| Zn _{HCl} | 45 | 10.11 | 0.74 | 48.0 | 5.39 | 26.9 | 1.72 | 3.11 |

Elements without sub-index indicate total concentration determined by Neutron Activation Analysis (NAA). Sub-index_{HCl} indicates heavy metals extracted by 0.5 M HCl and measured by Atomic Absorption Spectrophotometer (AAS). CV% = coefficient of variation percentage; %OM = percentage of soil organic matter; EC = electrical conductivity.

Table 3
Soil quality guidelines for total metal concentrations (mg kg⁻¹ DW) and different land uses.

| Element | Land use | | | | | |
|---------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| | Agricultural | | Residential | | Industrial | |
| | SQG ^{a,b} | SQGEH ^c | SQG ^{a,b} | SQGEH ^c | SQG ^{a,b} | SQGEH ^c |
| As | 20 | 12 | 30 | 12 | 50 | 12 |
| Ba | 750 | 750 | 500 | 500 | 2000 | 2000 |
| Co | 40 | - | 50 | - | 300 | - |
| Cu | 150 | 63 | 100 | 63 | 500 | 91 |
| Cr | 750 | 64 | 250 | 64 | 800 | 87 |
| Ni | 150 | 50 | 100 | 50 | 500 | 50 |
| Pb | 375 | 70 | 500 | 140 | 1000 | 600 |
| Sb | 20 | - | 20 | - | 40 | - |
| U | - | 23 | - | 33 | - | 300 |
| Ta | 1 | 1 | - | 1 | - | 1 |
| Zn | 600 | 200 | 500 | 200 | 1500 | 360 |

SQG = soil quality guidelines; SQGEH = soil quality guidelines for environmental health.

^a Argentinean legislation (Law 24051).

^b CCME (Canadian Council of Ministers of the Environment) (1991).

^c CCME (2007).

the maximum total Cr concentration was above the SQG for environmental health for agricultural, residential and industrial land use (CCME, 2007). Although chromium is an essential micronutrient for the normal energy metabolism of humans and animals (Kabata-Pendias and Mukherjee, 2007), individuals exposed to chromium at high doses can suffer from dermatitis and many allergic and eczematous reactions (Işikli et al., 2003).

The Ba mean and maximum total concentrations were also above the residential and agricultural land use limits, respectively (Table 3). Mean Ba concentrations are in agreement with Guvenç et al. (2003) and Yay et al. (2008) findings in urban, industrial and rural areas in Turkey, and represent an environmental health risk according to the CCME (2007) guidelines (Table 3). However, there are only a few reports in the literature on Ba toxicity in plants and human beings. Suwa et al. (2008), for instance, found yield reductions in soybean plants after applications of high Ba concentrations.

The total As, Co, Cr and Sb median concentrations were similar to those found in urban soils of Serbia and Turkey (Guvenç et al., 2003; Popovic et al., 2008), but higher than those from rural areas in the same countries. Arsenic is a typical element of the Argentinean Pampa plains, and it has been associated with volcanic glass and other primary minerals that contribute to As-release. Pore waters and groundwater in this region are severely polluted with As (Cabrera et al., 2001; Farías et al., 2003), with concentrations being above recommended limits stated in national and international legislation for drinking waters.

The total Ca concentration was higher than those reported by Popovic et al. (2008) for Serbian soils. Although Ca is not phytotoxic and has even been cited as a protector against Pb, Ni and Cu soil pollution (de Matos et al., 2001), it was also demonstrated that under alkaline growth conditions, the fresh and dry weight of conifers correlated negatively with Ca concentrations in the organs (Mandre et al., 1999). Moreover, calcium could also compete for adsorption sites, thus effectively increasing the solubility of certain metals (Escrig and Morell, 1998). Future studies on the bioavailability of Ca cations should be performed to discover if Ca affects

dissolved organic matter and to determine the concentration of heavy metals on the labile fraction (Oste et al., 2002). In this way, it would then be possible to see if crops in Yocsina are subject to ionic Ca effects.

Regarding labile heavy metals, there are no soil standards to compare 0.5 M HCl-extracted elements. However, in our study, Cu_{HCl} , Fe_{HCl} , Mn_{HCl} , Ni_{HCl} and Zn_{HCl} concentrations were much lower than the findings of Sutherland and Tolosa (2001), who studied topsoil heavy metal concentrations in a partial HCl digestion in Hawaii, although the Pb_{HCl} concentrations were very similar. These results might be explained by the evaluation of different pollution sources, since Sutherland and Tolosa (2001) surveyed topsoil metal composition along a 100 m transect from roads.

3.2. Ancova

Table 4 shows that Ba, Co_{HCl} , Co, Cr, Cs, Cu_{HCl} , Eu, Fe, La, Lu, Na, Ni, Pb_{HCl} , Rb, Sc, Sm, Tb, Th, Yb, Zn and Zn_{HCl} were distributed according to the prevalence of the NNE and NE wind directions, i.e. with higher concentrations in the SW area. This finding provides evidence that the cement plant and the industrial waste incinerator are metal sources that influence the elemental composition of topsoil. In the SW area, higher concentrations of the elements Cs, Eu, La, Lu, Rb, Sc, Sm, Tb, Th and Yb may be explained by rock crushing during cement production. Cement is made by the reaction of crushed and ground calcareous rocks (limestone or chalk) and argillaceous rocks (clay or shale) at high tempera-

tures. Consequently, it is possible that trace elements associated with parent materials, such as Sc (Hernandez et al., 2003), were liberated into the environment by an anthropogenic activity.

The distance to the point source of pollution was also significant for Ba, Cu_{HCl} , Eu and Pb_{HCl} , with concentrations rising with increasing distance, with the exception of Pb_{HCl} , Fe_{HCl} , Sb and Mn_{HCl} . However, the fact that no differences with wind direction were found allow us to infer, at least in these cases, that Fe_{HCl} , Sb and Mn_{HCl} concentrations were not principally dependent on the cement plant.

On the other hand, %OM was a significant co-variable of Ca, Co_{HCl} , Cu_{HCl} , Hf, La, Lu, Mn_{HCl} , Ni_{HCl} , Ta, Th and Yb concentrations. This finding could be ascribed to the fact that oxides, clay minerals and organic matter have been shown to have large sorption capacities for metals (Sauvé et al., 1997b, 2000; Oste et al., 2002). Although Ca, Mn and Ta did not show an association with the predominant wind direction, these elements seemed to be related to organic matter.

3.3. Multiple regressions

Table 5 shows the linear regression models for Ba, Co_{HCl} , Cr, Cu_{HCl} , Mn_{HCl} , Pb_{HCl} and Zn_{HCl} for each quadrant (NE and SW). In the NE area, low concentrations of Cr, Cu_{HCl} and Mn_{HCl} were found in sampling sites far away from the cement plant. However, due to the NE and NNE predominant winds, it might be possible that Cr, Cu_{HCl} and Mn_{HCl} were coming from a different source in the NE

Table 4

Analysis of covariance with wind direction as the classification criterion, and distance to the cement plant, percentage of organic matter (%OM) and pH of soil as co-variables.

| Element | Classification criterion | | Co-variables | | | Mean SW (mg kg ⁻¹ DW) | Mean NE (mg kg ⁻¹ DW) |
|------------------------------|--------------------------|----------------|--------------|-----|----|----------------------------------|----------------------------------|
| | Model | Wind direction | Distance | %OM | pH | | |
| As | ns | ns | ns | ns | ns | 7.5 ± 0.4 | 7.4 ± 0.2 |
| Ba | *** | *** | ns | ns | ns | 637 ± 24 | 518 ± 18 |
| Ca | * | ns | ns | ** | ns | 1.9E+04 ± 6E+02 | 1.8E+04 ± 9E+02 |
| Ce | ns | ns | ns | ns | ns | 54 ± 12 | 77 ± 2 |
| Co | * | * | ns | ns | ns | 13.1 ± 1.0 | 10.2 ± 0.2 |
| Co_{HCl} | *** | * | ns | ns | ns | 4.10 ± 0.14 | 3.61 ± 0.08 |
| Cr | * | ** | ns | ns | ns | 55.1 ± 4.7 | 42.3 ± 1.2 |
| Cs | * | ** | ns | ns | ns | 6.4 ± 0.2 | 7.2 ± 0.2 |
| Cu_{HCl} | *** | *** | ** | * | ns | 4.12 ± 0.15 | 3.21 ± 0.17 |
| Eu | *** | *** | *** | ns | ns | 1.27 ± 0.07 | 1.06 ± 0.04 |
| Fe | * | * | ns | ns | ns | 3.9E+04 ± 2E+03 | 3.2E+04 ± 7E+02 |
| Fe_{HCl} | ** | ns | * | ns | ns | 777 ± 39 | 670 ± 38 |
| Hf | *** | ns | ns | *** | * | 8.7 ± 1.0 | 8.3 ± 0.4 |
| La | ** | ** | ns | * | ns | 48.4 ± 4.9 | 34.2 ± 0.5 |
| Lu | *** | * | ns | * | * | 0.61 ± 0.04 | 0.47 ± 0.01 |
| Mn_{HCl} | *** | ns | * | *** | * | 288 ± 14 | 271 ± 10 |
| Na | * | * | ns | ns | ns | 1.6E+04 ± 7E+02 | 1.8E+04 ± 4E+02 |
| Ni_{HCl} | ** | * | ns | ** | ns | 3.50 ± 0.24 | 2.86 ± 0.11 |
| Pb_{HCl} | *** | * | ** | ns | ns | 7.84 ± 0.16 | 7.46 ± 0.34 |
| Rb | * | * | ns | ns | ns | 110 ± 5 | 97 ± 3 |
| Sb | ns | ns | * | ns | ns | 0.821 ± 0.043 | 0.773 ± 0.041 |
| Sc | * | * | ns | ns | ns | 13.0 ± 0.7 | 11.3 ± 0.2 |
| Sm | ** | ** | ns | ns | ns | 9.17 ± 0.89 | 5.95 ± 0.18 |
| Ta | * | ns | ns | ns | ns | 1.28 ± 0.05 | 1.26 ± 0.04 |
| Tb | ** | ** | ns | ns | ns | 1.03 ± 0.09 | 1.46 ± 0.07 |
| Th | * | ** | ns | * | ns | 16.7 ± 1.6 | 12.4 ± 0.6 |
| U | ns | ns | ns | ns | ns | 3.0 ± 0.2 | 3.1 ± 0.2 |
| Yb | *** | ** | ns | ns | ns | 3.77 ± 0.30 | 2.91 ± 0.07 |
| Zn | * | ** | ns | ns | ns | 107 ± 8 | 78 ± 2 |
| Zn_{HCl} | *** | *** | ns | ns | ns | 12.9 ± 1.2 | 7.4 ± 0.3 |
| pH | – | – | – | – | – | 7.04 ± 0.03 | 6.82 ± 0.05 |
| EC ($\mu\text{S cm}^{-1}$) | – | – | – | – | – | 162 ± 14 | 140 ± 8 |
| %OM | – | – | – | – | – | 7.85 ± 0.56 | 7.74 ± 0.56 |

Elements without sub-index indicate total concentration determined by Neutron Activation Analysis (NAA). Sub-index_{HCl} indicates heavy metals extracted by 0.5 M HCl and measured by an Atomic Absorption Spectrophotometer (AAS). ns = not significant.

* Significant at 0.05 probability level.

** Significant at 0.01 probability level.

*** Significant at 0.001 probability level.

Table 5
Multiple linear regressions for some total and 0.5 M HCl-extracted metal concentrations.

| Element | Wind direction | Constant | Parameters ^a | R ² |
|-------------------|----------------|-------------------------|---|----------------|
| Ba | SW | 373(±81)*** | +0.051(±0.010) × distance** | 0.54** |
| Co _{HCl} | NE | 7.2(±1.7)*** | +0.090(±0.043) × %OM* - 1.9E-03(±7.1E-04) × distance ⁺ + 1.9E-07(±6.6E-08) × distance ^{2**} | 0.66*** |
| | SW | 3.23(±0.24)*** | -0.011(±1.6E-03) × EC*** + 0.21(±0.04) × %OM*** | 0.58*** |
| Cr | NE | 59(±4)*** | -2.0E-03(±6.8E-04) × distance ⁺ - 0.89(±0.33) × %OM | 0.72** |
| Cu _{HCl} | NE | 0.57(±0.62)ns | +5.0E-04(±1.1E-04) × distance*** | 0.50*** |
| | SW | -6.6(±3.3)ns | -0.013(±1.8E-03) × EC*** + 0.28(±0.06) × %OM*** + 3.2E-03(±0.20E-03) × distance ⁺ - 2.5E-07(±1.1E-07) × distance ^{2*} | 0.60*** |
| Mn _{HCl} | NE | 46(±35)ns | +7.2(±2.9) × %OM* + 0.031(±0.010) × distance*** | 0.73*** |
| | SW | 1041(±375) [†] | +11(±3.2) × %OM** - 120(±52) × pH [†] | 0.56*** |
| Pb _{HCl} | NE | 19(±2)*** | -0.56(±0.20) × pH [†] + 0.012(±1.5E-03) × EC*** - 3.1E-03(±6.0E-04) × distance*** + 2.8E-07(±5.6E-08) × distance ^{2***} | 0.74*** |
| | SW | 15(±4)*** | +1.4(±0.6) × pH [†] - 0.014(±1.2E-03) × distance*** + 4.3E-07(±1.0E-07) × distance ^{2***} | 0.70*** |
| Zn _{HCl} | NE | 296(±86)** | +0.62(±0.12) × %OM*** - 82(±25) × pH [†] + 5.7(±1.8) × pH ^{2**} | 0.67*** |

^a Distance = distance to the cement plant; %OM = percentage of organic matter; EC = electrical conductivity.

area. Carreras and Pignata (2002) surveyed the same area using the lichen *Usnea amblyoclada* and found that Co, Cu, Mn and Pb were associated not only with cement production, but also with metal-mechanical industries in the north of Córdoba city (Los Boulevares neighborhood).

In the NE and SW areas, Pb_{HCl} showed a negative linear relationship with distance to the cement plant. Moreover, it is worth noting that Pb was explained by the pH values in both areas. These findings are in accordance with Sauvé et al. (1997a), who found that Pb²⁺ in a soil solution could be significantly predicted by the pH.

In the SW area, Ba and Cu_{HCl} concentrations were predicted by a positive association with distance to the cement plant. Taking into account the mean and maximum Ba concentrations discussed in Section 3.1, it is of interest that this cement plant reduces barium input into the environment. Mn_{HCl} in the SW area was predicted by %OM and pH, thus strengthening the hypothesis that the cement plant has little influence on Mn topsoil concentration. Zn_{HCl} could only be predicted with R² > 0.50 in the NE area, and only by soil properties. This finding suggests that Zn_{HCl} could have diffuse and punctual sources, i.e. via long transportation from urban and industrial areas in Córdoba city, the cement plant, traffic, etc.

Organic matter was a significant independent variable for the distribution of HCl-extracted heavy metals with the exception of Pb. This result might be explained by the large sorption capacity of organic matter for metals (Sauvé et al., 1997b, 2000; Oste et al., 2002).

3.4. Correlations

The Pearson coefficients are shown in Table 6 for HCl-extracted metals and calcium. Co_{HCl} correlated positively with Cu_{HCl}, Mn_{HCl}, Ni_{HCl} and Zn_{HCl}, which agrees with Franco-Uría et al. (2008). Lower

Table 6
Pearson Correlation coefficients between 0.5 M HCl-extracted heavy metals and total Ca concentration.

| | Ca | Co _{HCl} | Cu _{HCl} | Fe _{HCl} | Mn _{HCl} | Ni _{HCl} | Pb _{HCl} |
|-------------------|--------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Co _{HCl} | -0.24 | 1 | | | | | |
| Cu _{HCl} | 0.06 | 0.76*** | 1 | | | | |
| Fe _{HCl} | 0.22 | 0.57*** | 0.59*** | 1 | | | |
| Mn _{HCl} | -0.49* | 0.73*** | 0.39* | 0.03 | 1 | | |
| Ni _{HCl} | -0.06 | 0.76*** | 0.51** | 0.59*** | 0.41** | 1 | |
| Pb _{HCl} | 0.12 | 0.30 | 0.23 | 0.06 | 0.34* | 0.33* | 1 |
| Zn _{HCl} | 0.12 | 0.58*** | 0.58*** | 0.41** | 0.34* | 0.62*** | 0.29 |

* Significant at 0.05 probability level.

** Significant at 0.01 probability level.

*** Significant at 0.001 probability level.

positive correlation coefficients were found for Cu_{HCl}, Mn_{HCl}, Ni_{HCl} and Zn_{HCl} pairs of metals, which is in agreement with Al-Khashman and Shawabkeh (2006). Although Pb_{HCl} was only correlated with Mn_{HCl} and Ni_{HCl}, Dragović et al. (2008) found high correlation coefficients between Pb and other heavy metals when Pb was ascribed to a lithogenic input. Our finding highlights the presence of an anthropogenic source of Pb in Yocsina. The total Ca concentration was only correlated with Mn_{HCl} (r = -0.49), suggesting that total Ca exerts little influence on the HCl-extractable heavy metals.

4. Conclusions

The lithogenic-related elements Cs, Eu, La, Lu, Rb, Sc, Sm, Tb, Th and Yb were associated with cement production, as higher concentrations were found downwind (predominant NE and NNE winds) to the cement plant. The total Cr and HCl-extracted Co and Mn in Yocsina were possibly related to wind transportation from an industrial area in the north of Córdoba city (Los Boulevares neighborhood). HCl-extracted Cu, Pb and Zn were shown to be influenced by the cement plant and the industrial area in NE Córdoba. The mean total Ba concentration was above the residential and agricultural land use limit stated in national and international legislation, and was related to the distance to the cement plant. The percentage of organic matter strongly influenced HCl-extracted heavy metal concentrations. According to SQG for environmental health, the human and wildlife populations in Yocsina might be experiencing toxic Ba and Cr effects.

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References

- Adejumo, J.A., Obioh, I.B., Ogunsola, O.J., Akeredolu, F.A., Olaniyi, H.B., Asubiojo, O.I., Oluwole, A.F., Akanle, O.A., Spyrou, N.M., 1994. The atmospheric deposition of major, minor and trace elements within and around three cement factories. J. Radioanal. Nucl. Chem. 179, 195–204.
- Adriano, D.C., 2001. Trace Elements in Terrestrial Environments. Biogeochemistry, Bioavailability and Risks of Metals. Springer-Verlag, New York.
- Al-Khashman, O.A., Shawabkeh, R.A., 2006. Metals distribution in soils around the cement factory in southern Jordan. Environ. Pollut. 140, 387–394.
- Bäckström, M., Karlsson, S., Allard, B., 2004. Metal leachability and anthropogenic signal in roadside soils estimated from sequential extraction and stable lead isotopes. Environ. Monit. Assess. 90, 135–160.

