



Assessment of metals behaviour in industrial soil using sequential extraction, multivariable analysis and a geostatistical approach



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ABSTRACT

The main objectives of this study were to evaluate the degree of Pb, Cu, Zn, Cd, Cr and Ni pollution using pollution indexes and geostatistical approach, and to assess metals dynamic using sequential extraction procedure and multivariable statistical analysis in surface soils and soil profiles from an industrial complex as a base for a correct management in order to avoid health and environmental problems. Results showed that the industrial activity increases both Pb (103 mg kg^{-1}), Zn (526 mg kg^{-1}) and Cu (39 mg kg^{-1}) concentrations and salinity in soil. Pollution indexes showed that industrial soils were moderately contaminated by Zn, Pb, Cu, Cr and Ni as well as a moderate ecological risk was reported. Two main areas were identified: southeast area with the highest metal concentrations, and northwest area with the lowest levels. Chemical speciation of metals showed that the residual phase was the dominant phase for all metals. However, Pb and Zn were highly associated to the reducible phase (25–30% and 35–40% respectively) and a significant concentration was associated to carbonates (5% for both metals). In contrast, Cu, Cr and Ni were mainly bound to the residual phase (>80% for all metals) with low concentrations retained to reducible phase, and very low concentrations bound to the most labile phases. Cd was the most mobile metal with high concentration associated to exchangeable (5%) and carbonates (15–20%) phases. Therefore, Pb, Zn and Cd represent the greatest risk for human health and the environment.

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1. Introduction

The development of industrialization has caused an increase of soil pollution by metals in the last decades, whose effects are not only limited to industrial soils but also affect to the adjacent lands, which is especially intense when soils are used for discharge poorly treated liquid effluents and disposal of solid waste as well as deposition of exhaust gas from the industries (Fakayode and Onianwa, 2002; Wu et al., 2011). However the persistence and distribution of metals in industrial areas is mainly affected by factors such as the nature of parental material, properties of soil or climatic condition (Krishna and Govil, 2008). Metals in soil can remain for a long period of time acting as source and sink of contamination (Acosta et al., 2015) and therefore they are potentially hazard to ecosystems and human health (Yaylali-Abanuz, 2011). Human exposure to metal pollutants may cause nervous, renal, cardiovascular and reproductive systems (Christoforidis and Stamatis, 2009). Therefore, in order to develop policies on pollution control and environmental management, as well as, to make decisions on soil remediation procedures, it is necessary to carefully evaluate the behaviour and distribution of metals in soils.

The contribution of metals to environmental pollution from industrial emissions has been the main subject of many studies in the recent years (Ordoñez et al., 2003; Al-Khashman and Shawabkeh, 2006; Sekhar et al., 2006; Govil et al., 2008; Krishna and Govil, 2008; Wu et al., 2011), where different indexes, such as contamination factor, enrichment factor or ecological risk index, have been used for determining the degree of soil pollution (Loska et al., 2004; Yaylali-abanuz, 2011; Yuan et al., 2014). However, although the total metal content in soil is useful to estimate the degree of soil pollution, the mobility of metal does not necessarily depend directly on its total metal content (Kumar et al., 2013). Chemical speciation is usually used to understand the geochemical processes governing metal mobilization (Yuan et al., 2004) because provide knowledge about the identification and quantification of different species, forms or phases of metals present in a material, such as soil, sediment or waste (Naji et al., 2010), and its availability on the environment.

In addition, the identification of pollution sources, the risk areas, and the evaluation of metals behaviour in soil have been identified as key points to reach effective soil reclamations (Chen et al., 2009; Acosta et al., 2011). The use of multivariate statistical analysis combined with geostatistical techniques have been successfully applied in the identification of sources, evaluation of metal behaviour in soil and mapping of metal spatial distribution (Rodríguez-Martín et al., 2006; Saby et al., 2009; Maas et al., 2010; Lu et al., 2012; Li et al., 2013b; Shao et al., 2014), being useful tools for developing future reclamation plans in

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industrial areas and its surrounding. However, the use of advanced analytical and statistical methods combined with spatial distribution analysis for evaluating the risk posed at the specific site has been little studied.

The main objective of this study was to demonstrate that the combination of different techniques and methods (sequential extraction procedure, multivariable statistical analysis and geostatistical approach) is a powerful tool for an integral evaluation of the environmental risk in areas affected by metals. To reach this objective, the degree of metals pollution (Pb, Cu, Zn, Cd, Cr and Ni) and the delimitation of risk areas using pollution indexes and a geostatistical approach were carried out. Otherwise, the identification of sources of metals and their behaviour were evaluated using a sequential extraction procedure and a multivariable statistical analysis.

2. Material and methods

2.1. Study area and sampling

In order to evaluate the combination of analytical, statistical and geostatistical techniques for assessing contaminated sites, the most important industrial complex of Murcia city was selected (southeast of Spain), which is located in the southwest of the city. About 841 companies are situated in this industrial area, such as manufacturing paints,

steel product, chemicals, electrical materials, etc. The climate of the area is semiarid Mediterranean with an annual average temperature of 18 °C and annual precipitation of 350 mm. The geology of the area is dominated by Quaternary alluvial deposits from the Segura and Guadalentín rivers (IGME, 1976). In the last decades, the soils where the industrial area is currently located were subjected to intense agricultural cultivation of lemon, oranges, cereals and vegetables. Currently, the industrial soil is classified as Calcaric regosol (W.R.B., 2014), characterized by low differentiation among horizons, a low organic matter content and high carbonates content. The study area also includes a natural area, without any influence of the industrial activities and with the same geological material. According with W.R.B. (2014) the natural soil is classified as Haplic calcisol, characterized by the presence of calcic horizon, with low organic matter content. This area was used as control site to determine the pollution degree of the industrial soils.

The industrial area has a surface of 3 km² where 10 surface soil samples (0–5 cm) were collected (Fig. 1). In addition, another 10 soil samples from the natural area were also sampled. At each sampling point, three sub-samples were collected 1 m apart from the vertices of a triangle to form a composite sample. Soil samples were taken using a soil spade. Two soil profiles were identified in the north-west and south-east of the industrial area corresponding to low and high pollution respectively (Fig. 1); four samples were collected from different depths (0–5 cm, 5–10 cm, 10–15 cm and 15–30 cm). All samples were taken

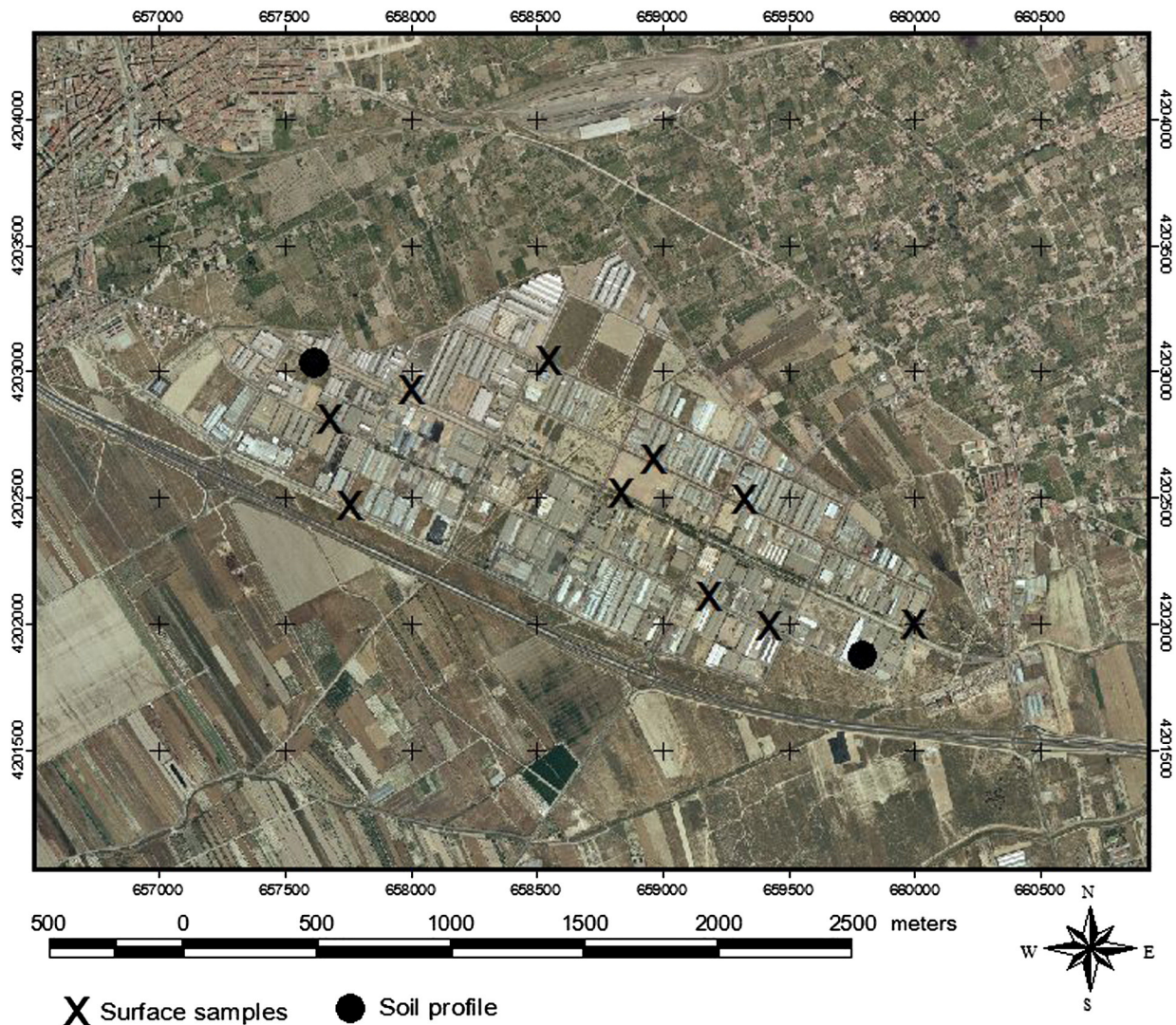


Fig. 1. Sampling location.

to the laboratory, and then they were air dried at room temperature during 72 h and sieved to <2 mm prior to physicochemical analyses.

2.2. Analytical methods

The following properties were analysed: soil organic carbon (OC) contents by the dichromate method (Soil Survey Staff, 2004); soil pH in H₂O using a glass electrode in a 1:1 soil/water suspension (Soil Survey Staff, 2004); electrical conductivity (EC) in a 1:5 soil/water suspension (Andrades, 1996); equivalent calcium carbonate by the volumetric method using Bernard's calcimeter, and cation exchange capacity (CEC) using sodium chloride and ammonium acetate (Soil Survey Staff, 2004).

For total metal content, 1 g of ground sample was digested in 10 mL nitric acid and 10 mL perchloric acid at 210 °C during 90 min. After cooling, 0.1 N HCl was added to fill a 100 mL volumetric flask (Risser and Baker, 1990). For soil extractable metals, DTPA (diethylene triamine pentaacetic) was used (Linsay and Norvell, 1978). Water soluble metals were determined according to Ernst (1996). Total, DTPA extractable and water soluble metals (Pb, Cu, Zn, Cd, Cr, Co and Ni) were measured by atomic absorption spectrometry (AAS).

Sequential extraction procedure by Tessier et al. (1979), modified by Li et al. (1995), was used for the identification of the main binding sites, the strength of metal binding to particulates and the phase associations of metals in soils (Rauret, 1998). This provides information of mobility, bioavailability and toxicity of metals bound to different soil phases. The extraction was carried out in order to obtain the following fractions: 1: exchangeable; 2: carbonate bound and specifically adsorbed; 3: bound to Fe–Mn-oxides; 4: bound to organic matter and sulfide and 5: residual.

Certified reference material (BAM-U110) from the Federal Institute for Materials Research and Testing (F.I.M.R.T., 2010) and reagent blanks were used as quality control samples during the analyses. We obtained recoveries (the sum of the five fractions from sequential extraction analysis to the total element concentration of BAM-U110) of 92–109% for Cd, 91–98% for Cu, 94–105% for Pb, 91–99% for Zn, 92–107% for Cr and 96–108% for Ni.

2.3. Enrichment factor

Enrichment factor (EF) was calculated using the modified formula (1) from Loska et al. (2004). The EF is based on the standardization of a tested element against a reference one. In this study cobalt was used as reference element due to its low occurrence. The reference environment adopted was the average concentration of elements in the natural area.

$$EF = (C_n(\text{sample})/C_{\text{ref}}(\text{sample})) / (B_n(\text{background})/B_{\text{ref}}(\text{background})) \quad (1)$$

where $C_n(\text{sample})$ is the content of the examined element in the industrial soils, $C_{\text{ref}}(\text{sample})$ is the content of the reference element in the industrial soils, $B_n(\text{background})$ is the content of examined element in the natural soils and $B_{\text{ref}}(\text{background})$ is the content of the reference element in the natural soils. According with Saeedi et al. (2012), EF was divided into five groups: $EF < 2$: deficiency to minimal enrichment; $2 \leq EF < 5$: moderate enrichment; $5 \leq EF < 20$: significant enrichment; $20 \leq EF < 40$: very high enrichment; $EF \geq 40$: extremely high enrichment.

2.4. Concentration factor

Concentration factors (CF) were calculated as the ratio of the content of a given metal (C_{metal}) to the background value ($C_{\text{background}}$):

$$CF = C_{\text{metal}}/C_{\text{background}} \quad (2)$$

The background concentration adopted was the average concentration of elements in the natural area. According to Buihyan et al. (2010) and Varol (2011), CF was divided into six groups: $CF \leq 0$: non contaminated; $0 < CF \leq 1$: slightly contaminated; $1 < CF \leq 3$: moderately contaminated; $3 < CF \leq 5$: considerably contaminated; $5 < CF \leq 6$: strongly contaminated; $CF > 6$: very strongly contaminated.

2.5. Ecological risk

This index comprises a single contamination coefficient, a comprehensive contamination measure, the toxic response factor for each metal, and a potential ecological risk index. The specific formulas are:

The single contamination coefficient : $C_{fi} = C_i/C_b$

where C_{fi} is the contamination coefficient of a particular metal, C is the measured data of soil metals, and C_b is the background value.

The comprehensive contamination measure : $E_i = C_{fi} \times T_i$

where T_i is the toxic response factor. According to Hakanson (1980) the toxicity values (T_i) are: Pb, Ni and Cu (5), Cd (30), Cr (2), Zn (1) and Ni (5).

The potential ecological risk index is : $RI = \sum E_i$

According to Sun et al. (2010), CF was divided into four groups: $RI \leq 50$ low risk; $50 \leq RI < 100$ moderate risk; $100 \leq RI \leq 200$ considerable risk and $RI > 200$ very strong risk.

2.6. Statistical treatment and spatial distribution of metals

The fitting of the data to a normal distribution for all properties and metal concentrations was checked with the Kolmogorov–Smirnov test at $P < 0.05$. We carried out a one-way ANOVA to investigate the differences among industrial and natural soils. Principal Component Analysis (PCA) was used to study the relationships among metals fractions and physicochemical properties and their grouping into a few factors. Varimax rotation was applied because it minimizes the number of variables with a high loading on each component and facilitates the interpretation of results (Micó et al., 2006). These analyses were carried out using SPSS 19.0 for Windows (Norusis, 1993).

The total concentrations of metals were used as the input data to produce distribution maps using Arcview 3.1. An Inverse Distanced Weighted (IDW) method was adopted to generate the distribution maps (Burrough and McDonnell, 1998; Lee et al., 2006).

3. Results and discussion

3.1. Geochemical characterization of soil

Geochemical characterization is essential to evaluate the environmental risk by metals in soil, since the processes and mechanisms involved on metals behaviour are affected by soil constituents and its properties (Acosta et al., 2011; Xiao et al., 2015). In this study, soils were slightly alkaline, with high amount of carbonates and moderate levels of OC, with no significant differences for pH, OC and carbonate contents between industrial and natural areas (Table 1), therefore it is expected a low metals mobility. Similar OC content in both areas is due to the former land use of the industrial soils where the application of organic fertilizers took place for crop production. In contrast, electrical conductivity was higher in the industrial soils than natural areas, which indicated that industrial activities increase soil salinity through spill or dump of industrial waste.

In addition, the comparison of the metals concentrations between affected areas by human activities and natural areas can be used to identify potential sources. Concentrations of total and DTPA extractable

Table 1
Geochemical characterization of soil surface samples.

	Industrial area				Natural area			
	Mean	Stand. dev. ^a	Minimum	Maximum	Mean	Stand. dev. ^a	Minimum	Maximum
pH	8.0	0.2	7.8	8.3	8.4	0.3	8.2	9.2
E.C. (dS m ⁻¹) ^a	0.4a ^b	0.3	0.1	1.3	0.1b	0.0	0.1	0.1
Carbonates (%)	37	5.7	28	45	39	2.8	36	46
Organic carbon (%)	1.7	0.8	0.6	3.0	1.3	0.3	1.1	1.8
Total Pb (mg kg ⁻¹)	85a	11	71	103	67b	4.4	57	71
Total Zn (mg kg ⁻¹)	176a	167	53	526	34b	6.2	25	43
Total Cu (mg kg ⁻¹)	39a	39	19	149	29b	3.6	22	35
Total Cd (mg kg ⁻¹)	1.2b	0.4	0.3	1.7	1.8a	0.6	0.6	2.5
Total Cr (mg kg ⁻¹)	43a	20	25	96	30b	9.7	18	47
Total Ni (mg kg ⁻¹)	66a	46	46	196	24b	1.3	22	27
DTPA extr. ^a Pb (mg kg ⁻¹)	3.9a	2.0	1.25	6.8	0.42b	0.12	0.28	0.67
DTPA extr. Zn (mg kg ⁻¹)	30a	60	0.76	187	2.11b	0.30	1.50	2.59
DTPA extr. Cu (mg kg ⁻¹)	3.5a	3.7	0.77	13	1.33b	0.06	1.22	1.40
DTPA extr. Cd (mg kg ⁻¹)	0.05b	0.03	0.00	0.09	0.08a	0.04	0.01	0.12
DTPA extr. Cr (mg kg ⁻¹)	0.29a	0.10	0.08	0.45	0.19b	0.05	0.13	0.29
DTPA extr. Ni (mg kg ⁻¹)	0.78a	0.16	0.63	1.16	0.29b	0.07	0.20	0.45
Water sol. ^a Pb (mg kg ⁻¹)	BDL ^c	–	–	–	0.13	0.03	0.09	0.19
Water sol. Zn (mg kg ⁻¹)	0.58a	0.62	0.00	1.89	0.10b	0.03	0.05	0.15
Water sol. Cu (mg kg ⁻¹)	0.17b	0.11	0.08	0.42	0.33a	0.12	0.11	0.46
Water sol. Cd (mg kg ⁻¹)	0.01b	0.01	0.00	0.02	0.06a	0.03	0.01	0.09
Water sol. Cr (mg kg ⁻¹)	0.20a	0.10	0.08	0.37	0.10b	0.03	0.06	0.15
Water sol. Ni (mg kg ⁻¹)	0.44a	0.13	0.26	0.65	0.09b	0.04	0.04	0.17

^a E.C.: electrical conductivity; extr.: extractable; sol.: soluble; stand. dev.: standard deviation.

^b Means followed by different letters are significantly different ($P < 0.05$).

^c BDL: below detection limit.

metals, except for Cd, were higher in industrial soils than in natural soils, showing the influence of industrial activities on metals accumulation in soils. This trend for Pb suggests the influence of traffic as main source of this metal, where Pb can be released from brake, tyres and exhaust fumes. Our results are consistent with other studies where the highest Pb concentrations occurred in areas near to industrial activities and main highways and roads (Han et al., 2009; Aelion et al., 2009).

The high variability of Zn concentrations (53–526 mg kg⁻¹) in the industrial soils indicated that this metal came from a variability of industrial activities, due to the presence of many types of factories in this area (e.g., metals recycling, steel products, plastic plants, electrical materials, etc.). Although the highest concentration of Zn reached was 526 mg kg⁻¹, the mean value (176 mg kg⁻¹) was lower than those reported by Fakayode and Onianwa (2002) and Abollino et al. (2002), in industrial areas where the main activities were the production of plastic materials, paints and pharmaceutical products, 282 and 361 mg kg⁻¹, respectively.

Mean concentration of Cu in the industrial area was low (39 mg kg⁻¹), although higher than the concentration found in the natural area. This value was lower than those reported in other industrial sites (Ravera et al., 2006; Pen-Mouratov et al., 2008), which suggests a low industrial influences on soil Cu concentrations.

Mean Ni and Cr concentrations in industrial soils were higher than in natural soils, but lower than those reported in other industrial areas (Jean et al., 2007; McNear et al., 2007). So, the concentrations of these metals are likely associated to the geological material, and came from the materials used in the construction of this industrial complex, and not from the industrial activities themselves.

The DTPA extractable concentrations of Pb, Zn, Cu, Cr and Ni were higher in industrial soils (Table 1). Therefore, high concentrations of these metals can be absorbed by plants causing a potential risk for the food chain (Pastor et al., 2007). Among all metals, Zn showed the highest water soluble fraction. With regard to Pb, despite the high total and DTPA extractable concentration, the soluble fraction was below the detection limit. This highlights the low solubility of this metal, also reported by other authors (Burgos et al., 2006), and indicates that Pb is not highly mobilized in the environment.

3.2. Soil pollution and spatial distribution of metals

In order to determine the degree of pollution in contaminated soils, concentration factors (CF), enrichment factors (EF) and ecological risk indices (ERI) has been widely used (Zhang et al., 2009; Guillén et al., 2012; Saeedi et al., 2012; Lu et al., 2014; Yuan et al., 2014; Lin et al., 2016) and they were calculated in this study (Table 2). Results showed that industrial soils had high concentrations of Pb and Zn, followed by Cr, Ni and Cu exceeding the limits proposed by Varol (2011) for considering a moderately contaminated soil ($1 < CF < 3$). Some samples of the industrial soil was classified as very strongly contaminated by Zn ($CF = 7.8$). Mean values obtained from the enrichment factors showed that industrial soils were moderately enriched by Zn ($2 < EF < 5$) (Saeedi et al., 2012). However, some samples exceeded this value for Pb, Cu, Cr and Ni. The highest EF value for industrial soil was classified as significantly enriched by Zn ($EF = 5.98$). Results obtained from ERI showed that industrial soils exceeded the values proposed by Sun et al. (2010) to consider a moderate risk ($50 \leq RI < 100$), with the highest values near to 90.

According to these results some remediation actions should be carried out in order to reduce the risk for human health and the environment. However, the selection of the best available technology for soil remediation must be based on an exhaustive knowledge on metals behaviour. In addition, the only use of these indices is not enough to develop the remediation plans or monitoring strategies since it is necessary to identify the main impacted areas to focus the major and more intense actions. In this way, spatial distribution maps are useful to visualize the spatial pattern of metals in soils (Li et al., 2013a). These maps must be used to identify metal-enriched areas for applying the remediation strategies or the placement of stations for monitoring metals concentrations. Based on the spatial distribution of Zn and Cd concentrations (Fig. 2a and c), the study area can be divided into two zones: i) southeast, with the highest Zn and Cd concentrations, located in the main entrance to the industrial complex with high traffic density take place; and ii) northwest, with moderate levels of Zn and Cd. Some authors have reported that high levels of Cd come from atmospheric deposition from highways or main roads in urban and industrial areas (Manta et al., 2002; Imperato et al., 2003).

Table 2
Concentration, enrichment and ecological risk indexes from industrial soils.

	Concentration factor			Enrichment factor			Ecological risk		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Lead	2.47	2.05	2.98	1.98	1.52	2.63	52	29	88
Zinc	2.63	0.79	7.85	2.10	0.61	5.98			
Copper	1.35	0.68	5.17	1.07	0.52	3.94			
Cadmium	0.69	0.16	0.96	0.54	0.14	0.73			
Chromium	1.44	0.82	3.21	1.12	0.63	2.07			
Nickel	1.42	0.99	4.21	1.08	0.78	2.72			

The spatial distribution map of Pb (Fig. 2b) showed that the higher concentrations were located in the southern section of the study area with a narrower range than the previous metals; therefore, the differences between north and south are not so evident

with regard to Pb concentration. Lead is mainly released from smelting, motor-vehicle exhaust fumes and from corrosion of lead pipe work (Gowd et al., 2010); in this study the main source of Pb was likely the heavy traffic.

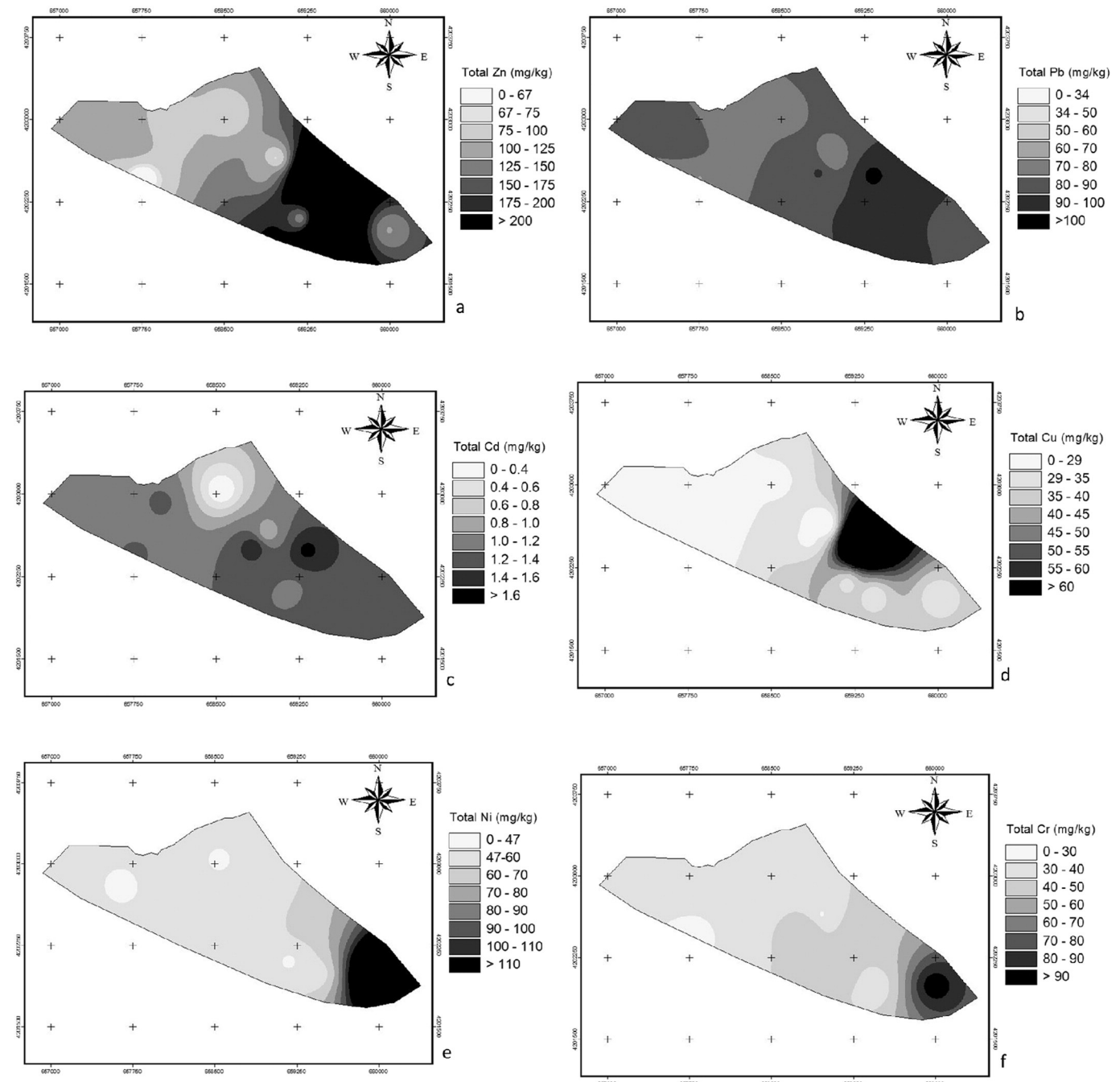


Fig. 2. Spatial distribution of total metals in the industrial area.

were not high, being only slightly higher than those found natural soils, the origin of Ni and Cr can be associated with the materials used during the construction of the industrial complex (building, roads etc.).

It was found from the concentration pattern of seven metals that the importance of identify the more impacted areas is crucial to develop remediation or monitoring strategies, since some metals, such as Cu, Ni and Cr, affected mainly small areas easily delimited where specific action can be carried out, e.g. waste discharge control. In contrast, the impact of other metals such as Pb, Zn and Cd is distributed in a wider area and therefore other strategies must be carried out, such as the implementation of phytotechnologies.

3.3. Behaviour of metals in industrial soils

For an appropriate assessment of contaminated areas is necessary to know the behaviour of metals which helps to design sustainable actions

for reducing the environmental and human health risks. In addition, it has been demonstrated that metals behaviour in soils depends of many factors, such as soil properties and characteristics, source of metals, metal distribution in soil constituents, anthropogenic activities, etc. (Abollino et al., 2002; Micó et al., 2006; Wu et al., 2011). Because of the complex mechanisms and processes occurring in the soil and in order to reach a thorough knowledge on metal behaviour is necessary to use advanced analytical and statistical methods, such as metals sequential extraction and multivariable analysis (Nogueirol et al., 2010; Acosta et al., 2014; Hossain et al., 2015; Gasparatos et al., 2015; Schneider et al., 2016).

Table 3 shows the geochemical characterization of samples collected from soil profiles. Physicochemical properties such as pH, EC and carbonates were similar between both profiles and among depths, being alkaline, saline and with high percentage of carbonates. In contrast, organic carbon contents and CEC showed differences among profiles and

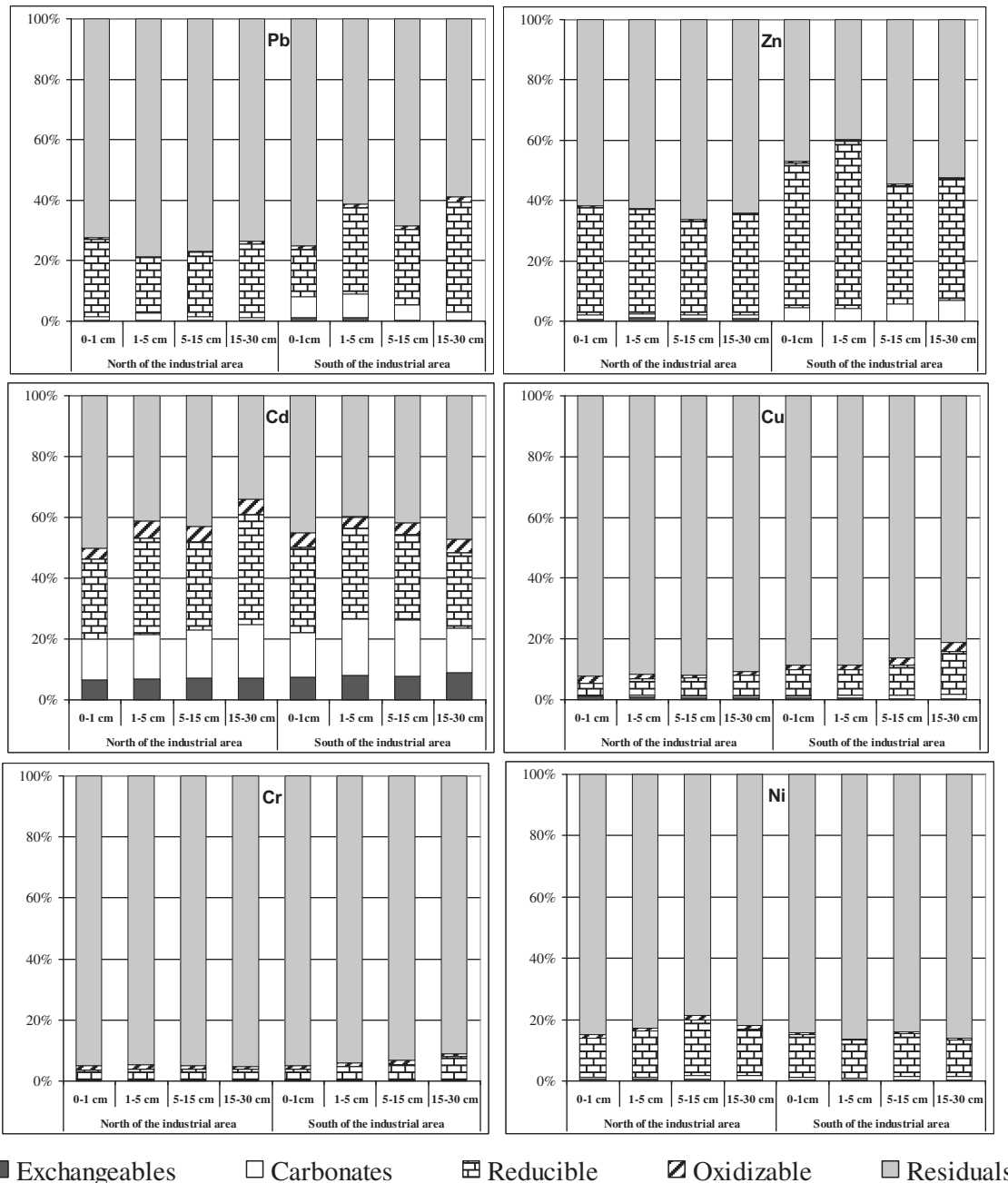


Fig. 3. Chemical partitioning of metals in soil profiles.

depths being higher in surface soil, in addition, the profile located in the northwest area had higher organic carbon content and CEC than the profile located in the southwest. Total concentrations of Pb, Zn, Cu, Cr and Ni were higher in the southwest profile, while total Cd was similar in both profiles. The DTPA concentrations of Pb and Zn were higher in the southwest profile, while Cu, Cd, Cr and Ni concentrations were similar between both profiles. However, the DTPA concentrations for all metals were similar between depths.

Concentration of each metal in each fraction from chemical speciation is reported in Table 4, while the percentage of contribution of each fraction to the total concentration for a specific metal is shown in Fig. 3. The results from principal component analysis are showed in Table 5. The highest concentration of Pb in the industrial soils was observed in the residual phase for both profiles and for the different depths. However, when the total Pb concentration increased (northwest profile), Pb was more associated to labile phases, mainly bound to Fe-Mn oxides and carbonate. This is supported by the results from PCA (Table 5) where Pb total concentration and all phases, except for exchangeable Pb, were associated to Factor 1. These results suggest that an increase in the anthropogenic Pb is proportional to Pb associated to the reducible and carbonates phases, especially observed in the northwest profile, and therefore a higher risk of mobility occurs in this area.

Zn concentration was mainly associated to the residual phase in all samples, although the fraction bound to the reducible phase was high (Table 4, Fig. 3), even higher than the value reported for Pb which had

higher total concentration. In addition, and similarly to Pb, the profile collected from the southwest area, with higher Zn concentrations, showed an important fraction of Zn bound to carbonates. PCA showed that all phases of Zn, except for Zn bound to Fe and Mn oxides, were associated to its total concentration in Factor 1 (Table 5). This indicates that Zn total concentration controls the behaviour of this element in soils, and it can be more easily mobilized from soils affected by anthropogenic pollution, since an increase of total concentration will likely promote higher concentrations of exchangeable Zn and Zn bound to carbonate.

Chemical partitioning of Cd was dominated by the residual and reducible phases, although a significant percentage of Cd was bound to the carbonate and exchangeable phases (Fig. 3). PCA showed that the concentration of Cd from the most labile fractions (exchangeable and bound to carbonates) were mainly affected by EC and carbonates content (Factor 2), while the other fractions were affected by pH, OC, CEC and its total concentration (Factor 3) (Table 5). These results suggest that Cd can become easily mobilized under pH and salinity variations, and therefore a higher environmental risk is expected for this metal than for the previous ones (Osakwe, 2013).

Cu was mainly associated to the residual phase, although a low but significant content was bound to the reducible and oxidizable phases (Table 4 and Fig. 3). The behaviour of Cu is mainly dominated by the carbonate content, EC and its total concentration, as reported in Factor 2 (Table 5) where all phases, except for soluble Cu, were included. However, soluble Cu was correlated to OC and pH in Factor 3. These observations indicate that Cu can be mobilized after organic matter mineralization, as reported by Ma and Rao (1997). However, a high environmental risk is not expected due to the low organic matter content and the low concentration of this metal in the studied soils.

Cr and Ni were mainly bound to the residual phase in all samples, with very low concentration in the rest of the chemical phases (Table 4 and Fig. 3). These results suggest that Cr and Ni came from other sources different to current industrial activities, such as lithological materials (Shi et al., 2008; Li et al., 2013a) or other materials used for constructing the industrial complex as they are incorporated in the lattice of minerals. PCA showed that the concentration of Cr from exchangeable, bound to carbonates and bound to Fe and Mn oxides were mainly affected by EC and carbonates content (Factor 2), while the other fractions were associated in Factor 1 (Table 5). In contrast, most labile fractions of Ni (exchangeable and bound to carbonates) were mainly affected by variation of pH, OC and CEC (Factor 3), while Ni bound to Fe and Mn oxides and residual fraction are associated to its total concentration.

These results suggest that the sources of metals and the soil properties (pH, CEC and EC) are important in the speciation of the studied metals in contaminated soils. Additionally, the soil composition (organic carbon and carbonates content) will determine the form of metals that dominates in the soil fractions.

4. Conclusions

The studied industrial soils were moderately contaminated by Zn, Pb, Cr, Cu and Ni, with a moderate ecological risk, and therefore some remediation actions should be carried out in order to reduce the risk for human health and the environment, techniques as phytoremediation or physical-chemical metal extraction could be used to reduce total metal content in soils, although further studies are necessary for an adequate selection. Spatial distribution maps showed two different areas, the southeast area with the highest concentration of metals and the northwest area where moderate levels of metals were found. Metals associated to industrial activity, such as Pb and Zn, showed a more disperse distribution into the industrial complex.

Results suggested that when Pb and Zn come from anthropogenic sources, they are mainly associated to the most labile phases; in contrast, when these metals come from geological sources, they are mainly bound to the most immobile phases. Cu, Cr and Ni were mainly

Table 5
Varimax-rotated factor matrix for industrial soils.

	1	2	3	Communalities
pH	0.00	-0.09	-0.52	0.58
Electrical conductivity	-0.53	0.80	0.14	0.93
Carbonates	-0.22	-0.93	0.11	0.93
Organic carbon	-0.19	-0.32	0.87	0.89
Cation exchangeable cationic	-0.23	-0.39	0.83	0.90
Pb - exchangeable	-0.20	-0.92	-0.07	0.90
Pb - bound to carbonates	0.85	0.50	0.00	0.97
Pb - bound to Fe and Mn oxides	0.97	0.21	0.04	0.99
Pb - bound to organic matter	0.92	0.28	0.09	0.93
Pb - residual	0.91	0.33	0.03	0.94
Pb - total	0.97	0.24	0.00	1.00
Zn - exchangeable	0.98	-0.11	0.01	0.98
Zn - bound to carbonates	0.99	0.11	0.03	0.99
Zn - bound to Fe and Mn oxides	0.65	0.70	0.03	0.92
Zn - bound to organic matter	0.76	0.60	-0.06	0.95
Zn - residual	0.92	-0.02	0.01	0.85
Zn - total	0.91	0.24	0.06	0.89
Cu - exchangeable	0.38	-0.12	0.65	0.58
Cu - bound to carbonates	0.11	0.96	-0.17	0.96
Cu - bound to Fe and Mn oxides	0.23	0.93	-0.25	0.98
Cu - bound to organic matter	0.10	0.97	0.05	0.95
Cu - residual	0.47	0.85	-0.05	0.95
Cu - total	0.44	0.86	-0.04	0.92
Cd - exchangeable	0.17	0.87	0.42	0.96
Cd - bound to carbonates	0.23	-0.56	0.38	0.61
Cd - bound to Fe and Mn oxides	-0.06	-0.07	0.60	0.66
Cd - bound to organic matter	-0.10	-0.27	-0.62	0.59
Cd - residual	0.01	0.35	0.80	0.77
Cd - total	0.11	0.40	0.77	0.77
Cr - exchangeable	-0.43	0.81	-0.30	0.93
Cr - bound to carbonates	0.47	0.56	-0.45	0.73
Cr - bound to Fe and Mn oxides	0.14	0.89	-0.26	0.87
Cr - bound to organic matter	0.81	-0.17	0.23	0.74
Cr - residual	0.75	0.38	-0.31	0.81
Cr - total	0.82	0.45	-0.27	0.94
Ni - exchangeable	0.26	-0.19	0.93	0.97
Ni - bound to carbonates	0.45	0.39	-0.72	0.87
Ni - bound to Fe and Mn oxides	0.97	0.01	-0.20	0.98
Ni - bound to organic matter	-0.43	-0.72	-0.11	0.72
Ni - residual	0.91	0.27	0.01	0.90
Ni - total	0.97	0.16	0.15	0.98
% of variance	38.0	30.9	15.5	

associated to the residual phase, with very low concentrations bound to Fe-Mn oxides, and with insignificant levels bound to the most labile phases. Cd was the most mobile metal since a high percentage of its concentration was associated to the exchangeable and carbonates phases. Therefore, Pb, Zn and Cd pose higher health and environmental risk because of their mobilization capacity, and should be monitored.

The optimal remediation techniques for dealing with metals contaminated soil will depend on the metal speciation, since this will influence the efficiency of these techniques. Therefore, a comprehensive and detailed understanding of the metals behaviour is critical for developing and evaluating remediation strategies at a site, which can be carried out through advances analytical, statistical and geostatistical methods such as sequential extraction, multivariable analysis and mapping.

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