Journal of Geochemical Exploration 184 (2018) 345–357

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

An assessment of the potentially hazardous element contamination in urban soils of Arica, Chile

Pedro Tume [a,c,*], Nuria Roca [b], Rodrigo Rubio [a], Robert King [a], Jaume Bech [b]

[a] Facultad de Ingeniería, Universidad Católica de la Santísima Concepción, Casilla 297, Concepción, Chile
[b] Dept. Biologia Vegetal, Facultat de Biologia, Universitat de Barcelona, Av. Diagonal 643, 08028 Barcelona, Spain
[c] Centro de Investigación en Biodiversidad y Ambientes Sustentables (CIBAS), Universidad Católica de la Santísima Concepción, Casilla 297, Concepción, Chile

ARTICLE INFO

Article history:
Received 31 May 2016
Revised 14 September 2016
Accepted 26 September 2016
Available online 28 September 2016

Keywords:
Land use factors
Topsoil contamination
Anthropogenic contamination sources

ABSTRACT

As a common component of urban ecosystems, urban soils generally have elevated concentrations of potentially hazardous elements originating from both point and diffuse sources of pollution in cities. This study focuses on the port city of Arica in northern Chile, where anthropogenic activities may have led to contamination of the uppermost topsoil layer. The purpose of this study is to (1) establish background content levels of potentially hazardous elements in topsoils of different land uses using different statistical approaches and (2) assess the degree of topsoil pollution and identify the local sources of pollution using multivariate statistical and geostatistical methods. Data from a Chilean Government CONAMA report were analyzed. Geostatistical methods such as kriging were applied to identify the spatial distribution of potential hazards elements. Potentially hazardous elements' background values were determined by median + 2MAD, inflection points within cumulative frequency plots and upper whisker of a Tukey's boxplot. Multivariate statistical methods were applied in the identification of trace metal sources (anthropogenic vs natural origin). Soil pollution assessment was performed using the geoaccumulation index (I_{geo}), enrichment factor (EF), contamination factor (C_f) and integrated pollution index (IPI). The maps obtained show high baseline values for some elements (As, Cu, Pb and Zn), which denote a clear anthropogenic contribution due to the long period of constant human activities in the study area. Therefore, background values are estimated with the median + 2 × MAD procedure and yielded As (17.4 mg kg^{-1}), Ba (23.3 mg kg^{-1}), Cr (13.6 mg kg^{-1}), Cu (37.4 mg kg^{-1}), Ni (8.3 mg kg^{-1}), Pb (313 mg kg^{-1}), V (101 mg kg^{-1}) and Zn (235 mg kg^{-1}). The calculated soil pollution indexes I_{geo}, EF, C_f and IPI revealed significant ecological impacts. Copper and As are the two trace elements with the highest contaminated soil values; however, Cu, Pb and Zn have greater numbers of soil sample sites in the moderately to heavily contaminated range. The IPI showed extremely high pollution index in ten soil sites in Arica. Moreover, significant differences were observed with different land uses, where soils along the railway line and industrial area are the most polluted.

1. Introduction

Urban soil, which is strongly influenced by anthropogenic activities, differs greatly from natural soils and receives a major proportion of potentially hazardous elements from industrial, commercial, and domestic activities. The urban area possesses a wide range of different land uses, such as traffic, industry, business, residential uses, gardens and public green spaces, which differ in their patterns of human activity and their possible impacts on soil quality (Tiller, 1992). Land use and cover may serve as an indicator of disturbance, site history, management, and the urban environment; these factors result in a mosaic of soil patches (Pouyat et al., 2007). Areas consisting predominantly of man-made soils or isolated sites with an industrial history may exhibit the highest pollutant values of urban land.

The relationship between land use and soil pollution has received limited attention and requires further study (Li et al., 2013). Heavy metals and the other harmful elements such as As have attracted much attention, as they represent a serious risk to the environment and human health because of their non-biodegradable nature, long-biological half-lives for elimination from the body and their accumulation in the food chain (Bini and Bech, 2014). Moreover, in the last several decades, the natural input of several heavy metals to soils due to pedogenesis has been exceeded by human input, even on global and regional scales (Nriagu and Pacyna, 1988).

Over the past two decades, heavy metal pollution in urban soils and urban road dust have become environmental issues with the rapid industrialization and urbanization of developing countries in the world (Acosta et al., 2009; Argyraki and Kelepertzis, 2014; Guagliardi et al.,

* Corresponding author at: Facultad de Ingeniería, Universidad Católica de la Santísima Concepción, Casilla 297, Concepción, Chile.
E-mail addresses: ptume@ucsc.cl, pedro.tume@daad-alumni.de (P. Tume).

http://dx.doi.org/10.1016/j.gexplo.2016.09.011
0375-6742/

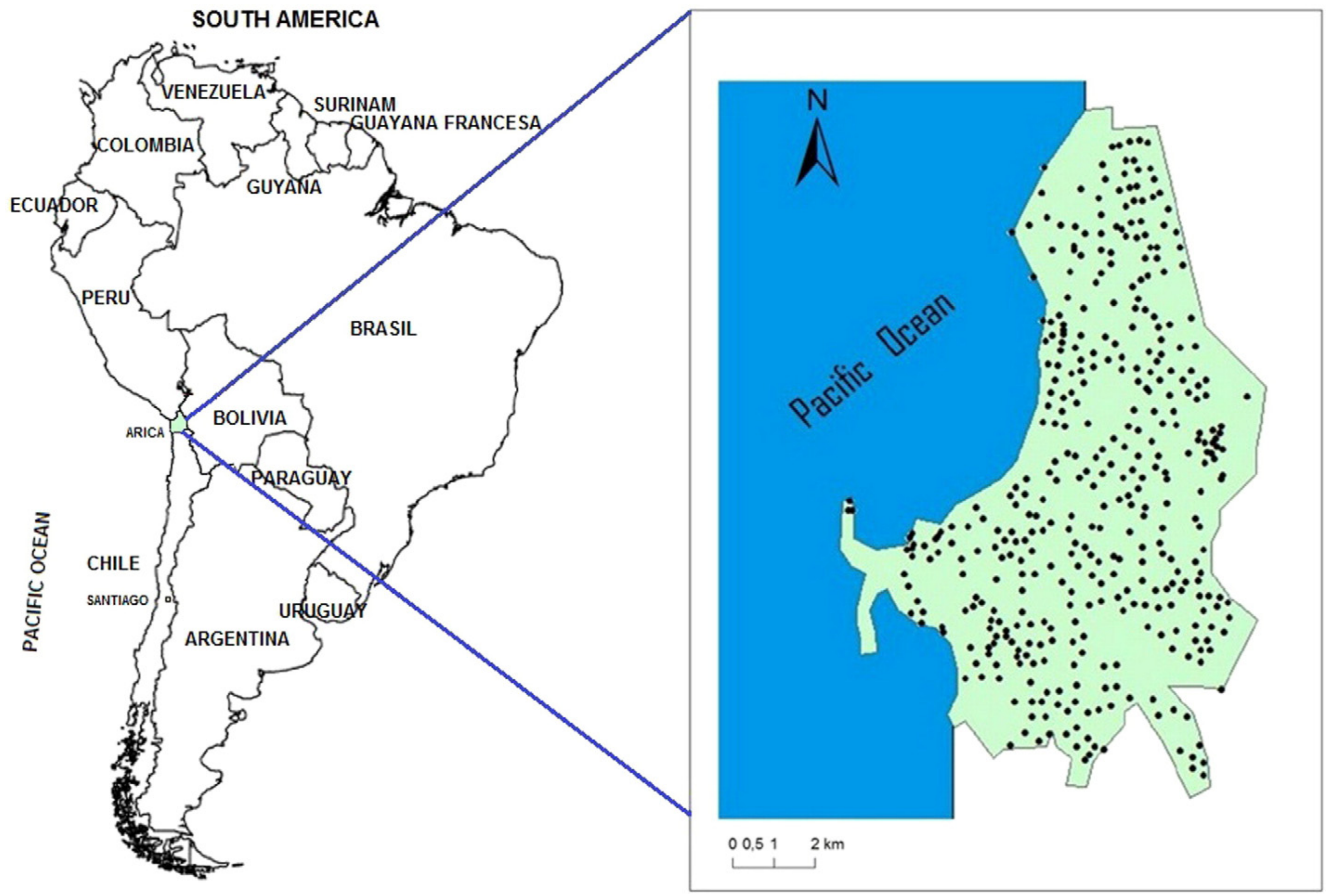

Fig. 1. Map of the study area showing the sampling sites in port city Arica.

2015; Jarva et al., 2010; Madrid et al., 2002; Massas et al., 2010; Ng et al., 2003; Presley et al., 2010). Wei and Yang (2010) reviewed studies of heavy metal contamination in several Chinese cities over the past 10 years and found that contamination of Cr, Ni, Cu, Pb, Zn and Cd is widespread in urban soils and in urban road dust (Wei and Yang, 2010). Cicchella et al. (2005, 2008) identified baseline values with an evident anthropogenic control for Cr, Co, Cu, Hg, Pb, Sb, V and Zn in the soils of the metropolitan areas of the city of Napoli or in areas characterized by industrial activities, which were clearly different from background values (Cicchella et al., 2005; Cicchella et al., 2008).

In Chile, research on trace elements concentrations in soils has been conducted in the northern and central zones of the country and on the Antarctic Peninsula (Ahumada et al., 2004; Badilla-Ohlbaum et al., 2001; De Gregori et al., 2003; Flynn et al., 2002; Higueras et al., 2004; Schalscha and Ahumada Torres, 1998). In contrast, very limited published data are available on soil contamination in urban areas of Chile (Parra et al., 2014; Salmanighabeshi et al., 2015; Tume et al., 2008; Tume et al., 2014). To date, no information has been published related to the heavy metal content of urban soils in the port city of Arica. The uppermost topsoil layer of urban soils of Arica is of particular interest as degradation may occur due to atmospheric aerosol deposition from several anthropogenic activities, including ore bulk transport or storage, industrial and vehicular emissions, fossil fuel combustion and residual disposal. The principal commodity moving through the port of Arica is the transfer of mineral concentrate from numerous mining activities onto shipping vessels for international distribution. The manipulation and movement of the ore concentrate, in conjunction with the constant coastal winds, increases the dispersion of mineral particulate in the city of Arica. Approximately 80% of Bolivia's exportation passes through the port of Arica. Furthermore, during 1984 and 1985, the company Promel transported, via the port of Arica, approximately 20,000 tons of dangerous residues with high contents of Pb, As, Cd, Hg, Cu and Zn. These residues were stored where there were no nearby homes or urban development that could be exposed to the waste in an area called the Barrio Industrial of Arica, designated as Site F. However, as the years passed, houses were built around Site F, which was originally intended for industrial activities because of its location outside the urban radius.

The geochemical baseline in an area of heavy anthropogenic impact, such as the urban area of Arica, includes the geogenic natural content (background) and the anthropogenic contribution in the soils (Cicchella et al., 2005). In recent years, environmental geochemical mapping has become increasingly relevant as it is an important indicator of the spatial distribution of potentially harmful elements that can determine contamination in an area and identify the influence of possible pollution sources (Zuzolo et al., 2016). Moreover, the degree of contamination in soil could be evaluated with a traditional pollution index such as the geoaccumulation index, enrichment factor, contamination factor and integral pollution index, all of which are based on the relative ratio of the actual concentration of each trace metal in a soil sample compared to a local reference or background value.

To better distinguish and evaluate geogenic from anthropogenic contribution in the distribution of baseline values, it was necessary to calculate background values. Knowledge of background values of potentially harmful elements in soils is necessary before a soil can be declared contaminated. The definition and distinction of background values are very important in environmental studies because legislation typically fixes the intervention limits for potentially harmful elements in soils as a function of local background values (Cicchella et al., 2005). Therefore, these background values can be defined as the natural content of

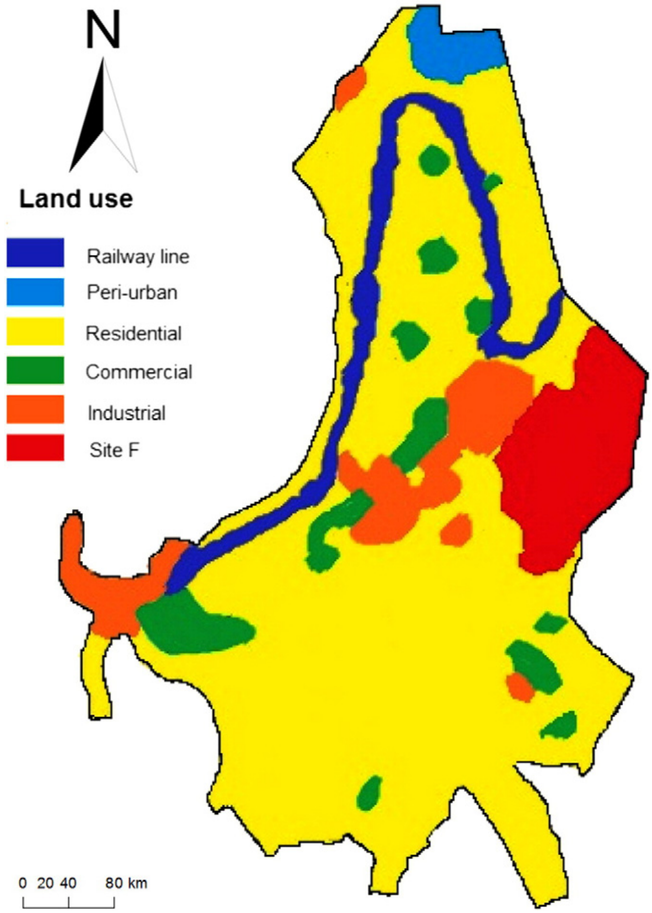

Fig. 2. Land use types in port city Arica.

potentially harmful elements in soils without human influence (Salminen and Gregorauskiene, 2000).

Different approaches have been used to establish background levels in soils. The various methods are usually classified as direct (empirical or geochemical) or indirect (statistical), and both can be combined, leading to integrated methods (Tran Thi Thu et al., 2013). Naturally and anthropogenically induced processes contribute not only to a widening of the range of the data collection (i.e., larger standard deviations) but also to a multi-modal distribution. Ideally, each mode corresponds to a relevant process with its underlying normal distribution (Matschullat et al., 2000). The objective of the methods applied in this study is the elimination of potential outliers from the data set. These outliers must be detected and eliminated as fingerprints for processes disturbing the normal data distribution (Matschullat et al., 2000).

Table 2
Spearman's correlation coefficient between trace element content (mg kg^{-1}) in the studied soils.

	As	Ba	Cr	Cu	Ni	Pb	V	Zn
As	1	0.157[a]	0.162[a]	0.326[a]	0.104[b]	0.142[a]	−0.125[b]	0.344[a]
Ba		1	0.739[a]	0.417[a]	0.030	−0.213[a]	0.062	0.094
Cr			1	0.451[a]	0.343[a]	−0.135[a]	0.348[a]	0.234[a]
Cu				1	0.181[a]	0.319[a]	−0.102	0.634[a]
Ni					1	0.426[a]	0.469[a]	0.403[a]
Pb						1	0.164[a]	0.540[a]
V							1	0.033
Zn								1

[a] Correlation is significant at the 0.01 level.
[b] Correlation is significant at the 0.05 level.

Therefore, the resulting sub-collective (free from outliers) is defined as reflecting background conditions.

This study aims to (1) establish background content levels of potentially hazardous elements in topsoils of different land uses using different statistical approaches and (2) assess the degree of topsoil pollution and identify the local sources of pollution using multivariate statistical and geostatistical methods.

2. Materials and methods

2.1. Study area

The area of study for this work was the port city of Arica, Chile (18°28′44″S–70°19′14″W), located approximately 2000 km north of the capital, Santiago (Fig. 1). The municipal district of Arica has a population of 185,268 and a surface area of 41.89 km^2.

The geological setting of the area consists predominantly of various sequences of marine and continental sediments which vary in age from the Pleistocene to Recent. The majority of the sedimentary beds are formed of gravel, sand or clay-size clastic, semiconsolidated material. On the eastern edge of the city, the sector is underlain by a Pliocene-Pleistocene unit of mass wasting/landslide debris material consisting of polymictic brechas with variable proportions of sand to clay-size matrix. Numerous slide-type and flow-type mass movement features can be discerned within the unit. Along the coastal sector, within the southern limits of the city, occurrences of the Jurassic-age El Morro Formation can be discerned. In this area, mantos of volcanic lavas alternating with beds of limestone, sandstone and siltstone can be observed and constitute the oldest rock sequence in the study area.

According to meteorological data from *Dirección Meteorológica de Chile*, the mean annual precipitation in the city is approximately 1.4 mm per year. The maximum temperature recorded in summer reached 24 °C, and the coolest temperature recorded was 14 °C. The prevailing winds are from the south-southwest, which is from the sea to the land.

The majority of the area is intensely populated, and as a consequence, a total transformation of the natural landscape has occurred

Table 1
Statistical summary of trace metal concentrations (mg kg^{-1}) in soils from city port of Arica.

	Mean	SD[a]	CV(%)[b]	Skewness	Kurtosis	Min	Percentile					Max	MAD[c]
							5	25	50	75	95		
As	22.8	90.7	397	9.8	97.8	0.1	4.3	8.3	11	14.5	32.1	1036	3.1
Ba	13.5	10.2	75.2	1.3	2.9	0.1	2.1	5.8	11.3	19.1	33.6	73.8	6
Cr	7.5	7.5	99.7	2.9	17.6	0.01	0.49	2.07	5.6	11.1	19.6	73.2	4
Cu	123	1433	1161	19.6	388	1	3.1	8.05	17	31.6	187	28,450	10.2
Ni	5.3	4.52	85	7.8	91.5	0.01	0.59	3.8	4.7	5.9	9.7	66.3	1
Pb	267	728	272	7.1	58.3	0.7	48.9	76.5	112	211	473	6289	52.6
V	54.3	31.6	58.3	1.9	6.3	0.01	22.5	33.1	42	70.6	116	254	13
Zn	221	258	117	2.6	7.6	0.5	42.3	84.4	130	226	904	1557	52.8

[a] Standard deviation.
[b] Coefficient of variation.
[c] Median absolute deviation.

Table 3
Factor matrix trace elements in soils from port city Arica.

Trace element	Principal component			
	PC1	PC2	PC3	PC4
As	0.46	0.21	0.04	0.11
Ba	−0.37	0.45	0.27	−0.37
Cr	−0.33	0.53	0.32	0.01
Cu	0.38	0.35	0.17	−0.10
Ni	0.06	-0.34	0.62	0.02
Pb	0.59	0.32	0.11	0.07
V	−0.21	0.18	0.07	0.91
Zn	0.07	−0.31	0.63	0.04
Percentage of variance(%)	25.81	19.31	16.66	12.15
Percentage of cumulative variance %	25.81	45.11	61.77	73.92

(Fig. 2). Arica is influenced by ore deposit and transportation and also has a stockpiling rail yard next to the railway station (Site F). The railway station receives ore concentrate from mines around the Arica and Visviri mining area in Bolivia, which is located 181 km away. From the stockpiling station, the ore concentrate is transported by road to the port and dock facilities of Arica.

2.2. Soil analysis

Results from a CONAMA report were statistically analyzed in this study. Soil sampling and chemical analysis were performed by AGQ América S.A. as a consulting project for the Comisión Nacional del Medio Ambiente Arica y Parinacota (CONAMA, 2009). Soils were sampled from 400 sites throughout the city of Arica (Fig. 1). At each site, subsamples were collected based on a 0.8- to 1.0-m-radius circle. Subsamples were collected at the center of the circle, and 5 subsamples were taken along the radius at an equidistance of 36° intervals. Each subsample was collected from a depth of between 0 and 30 cm, and then, each of the six subsamples was mixed to form a compound sample representative of the site. In addition, a total of 40 duplicates were collected to evaluate sampling and laboratory precision. A standard soil treatment was performed on each compound sample prior to acid digestion. Concentrations of As, Ba, Cr, Cu, Ni, Pb, V and Zn were determined following USEPA SW 846 Method 3051. Extracts were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) according to the USEPA SW 846 Method 6010B (USEPA, 1996). Duplicates of the 40 samples showed that sampling and analytical errors are marginal and that there is a considerably larger data variance than error variance. The analytical precision was estimated graphically with scatter plots and with Spearman correlations. Correlations (all 40 duplicates) were between 0.6 and 0.97 (median = 0.81), and correlations of ≥0.91 were recorded for Cu (0.97), Ba (0.93), Cr (0.92) and ≤0.9 for Zn (0.81), Pb (0.77), V (0.68) and Ni (0.66).

2.3. Data analysis

Statistical data treatments were performed using the program SPSS 19.0. The exploratory data analysis (EDA) technique was applied to

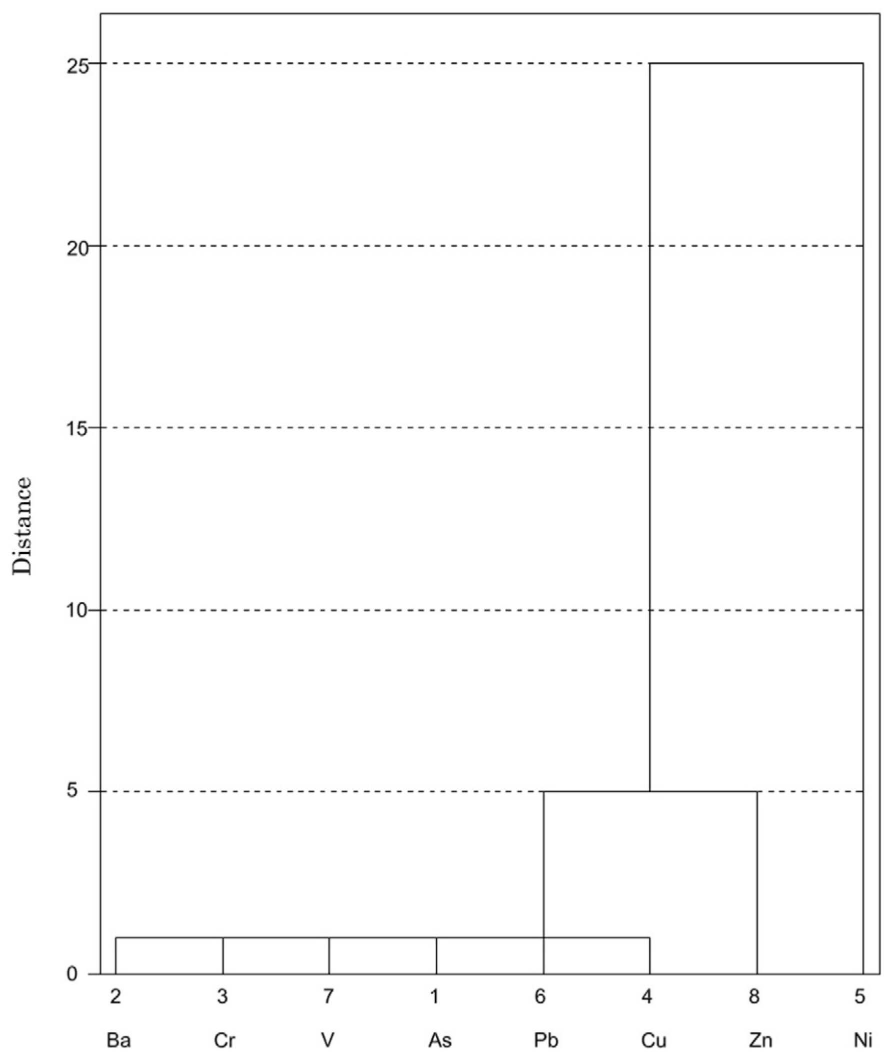

Fig. 3. Dendogram of cluster analysis (nearest neighbor, square Euclidean) for all trace elements.

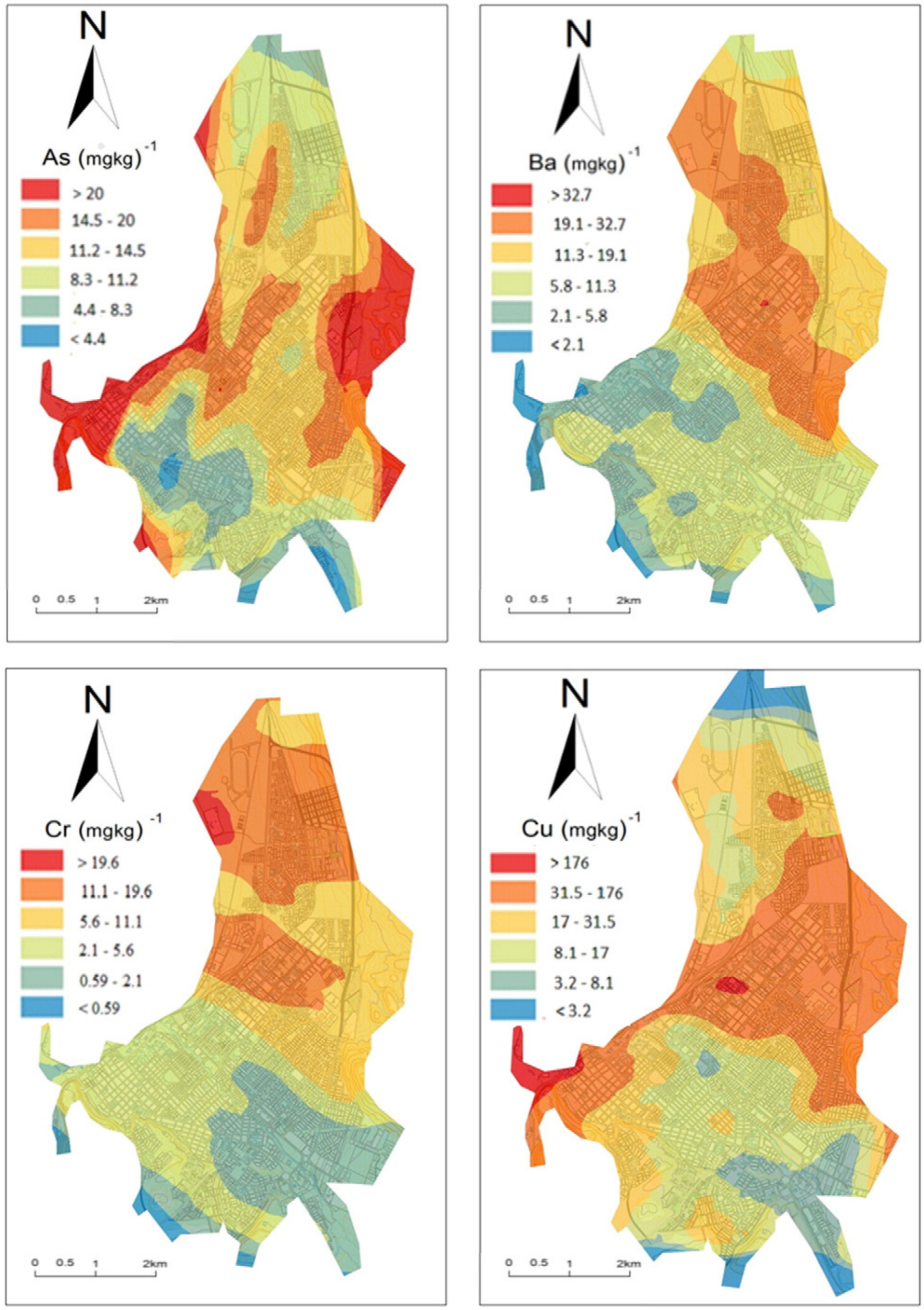

Fig. 4a. Distribution spatial of As, Ba, Cr and Cu.

statistically describe the data (Tukey, 1977). Furthermore, for each element, three different EDA graphs were presented: a histogram, box-plot and cumulative probability plot (CDF diagram). Correlation analysis was used, including principal component analysis (PCA) and cluster analysis (CA) of the classic multivariate statistical method, to process the data and identify sources of trace element contamination.

2.4. Baseline geochemical map generated

The use of geographical information systems (GIS) greatly enhances the ability of managing and representing large amounts of geochemical data. The kriging interpolation method was employed to reveal the geochemical baselines of As, Ba, Cr, Cu, Ni, Pb, V and Zn in Arica soils, as it is considered the best linear unbiased estimator (BLUE) (Isaaks and Srivastava, 1989). All maps and spatial interpolation were produced using ArcGIS (version 10.2). The data set did not show a normal distribution; thus, logarithmic and normal score transformation was performed. After visual inspection of the semivariogram and cross-validation, the best fit model for the prediction of As, Ba, Cr, Cu, Ni, Pb, V and Zn was spherical. The maps legends consist of seven classes based on the boxplot analysis chosen on the 5th, 25th, 50th, 75th, 90th, and 98th percentiles of the data distribution.

2.5. Background values

Reimann et al., 2005, reviewed and tested various calculation methods to calculate background values and proposed three alternative methods: "MAD" method using the median $\pm$ 2MAD (median absolute deviation); "upper whisker" of a Tukey's boxplot as calculated by 3rd quartile $+$ 1.5IQR (interquartile range) following a log-transformed of

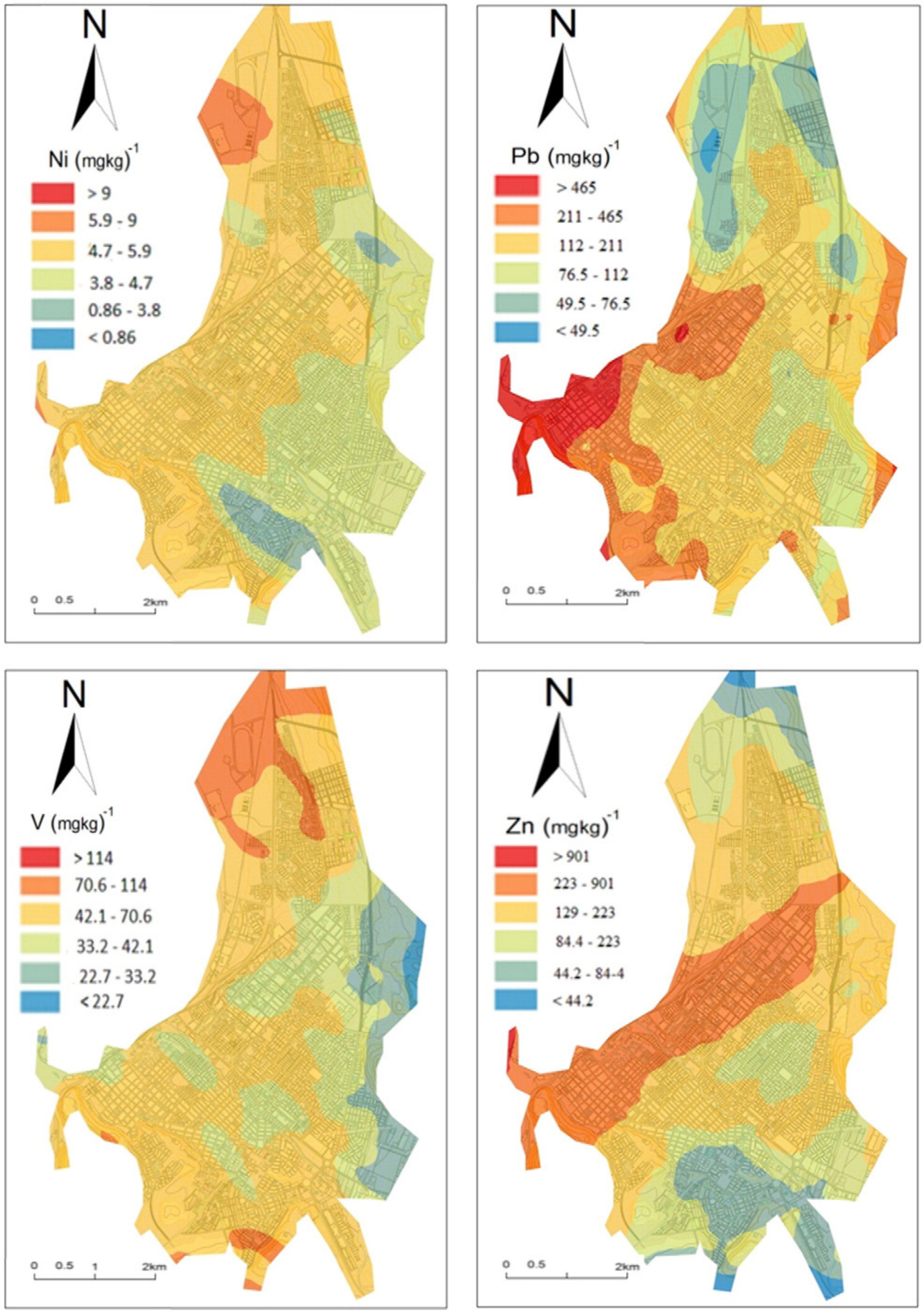

Fig. 4b. Distribution spatial of Ni, Pb, V and Zn.

the data and subsequent back-transformation; and inflection points within cumulative frequency plots (Reimann et al., 2005).

Following Jarva et al., 2010, a box and whisker plot without any logarithmic transformation led to the highest number of upper outliers and was chosen for the calculation of the upper limit of background variation for the elements following the precautionary principle (Rothwell and Cooke, 2015).

2.6. Assessment of trace metal pollution

To determine the contamination status of soil in the present study, various indices for potentially toxic elements were produced: i) geoaccumulation index (I_{geo}), ii) enrichment factor (EF), iii) contamination factor (C_f) and iv) IPI.

The geoaccumulation index is computed using the following equation:

$$I_{geo} = log_2(C_i/1.5C_b) \quad (1)$$

where C_i is the measured concentration of the particular element in soil and C_b is the background value in the soil. According to Müller, 1969, the I_{geo} for each element is calculated and classified as uncontaminated ($I_{geo} \leq 0$), slightly contaminated ($0 < I_{geo} \leq 1$), moderately contaminated ($1 < I_{geo} \leq 2$), moderately to heavily contaminated ($2 < I_{geo} \leq 3$), heavily contaminated ($3 < I_{geo} \leq 4$), heavily to extremely contaminated ($4 < I_{geo} \leq 5$), or extremely contaminated ($I_{geo} > 5$) (Müller, 1969; Sutherland, 2000).

ii) Enrichment factor (EF)

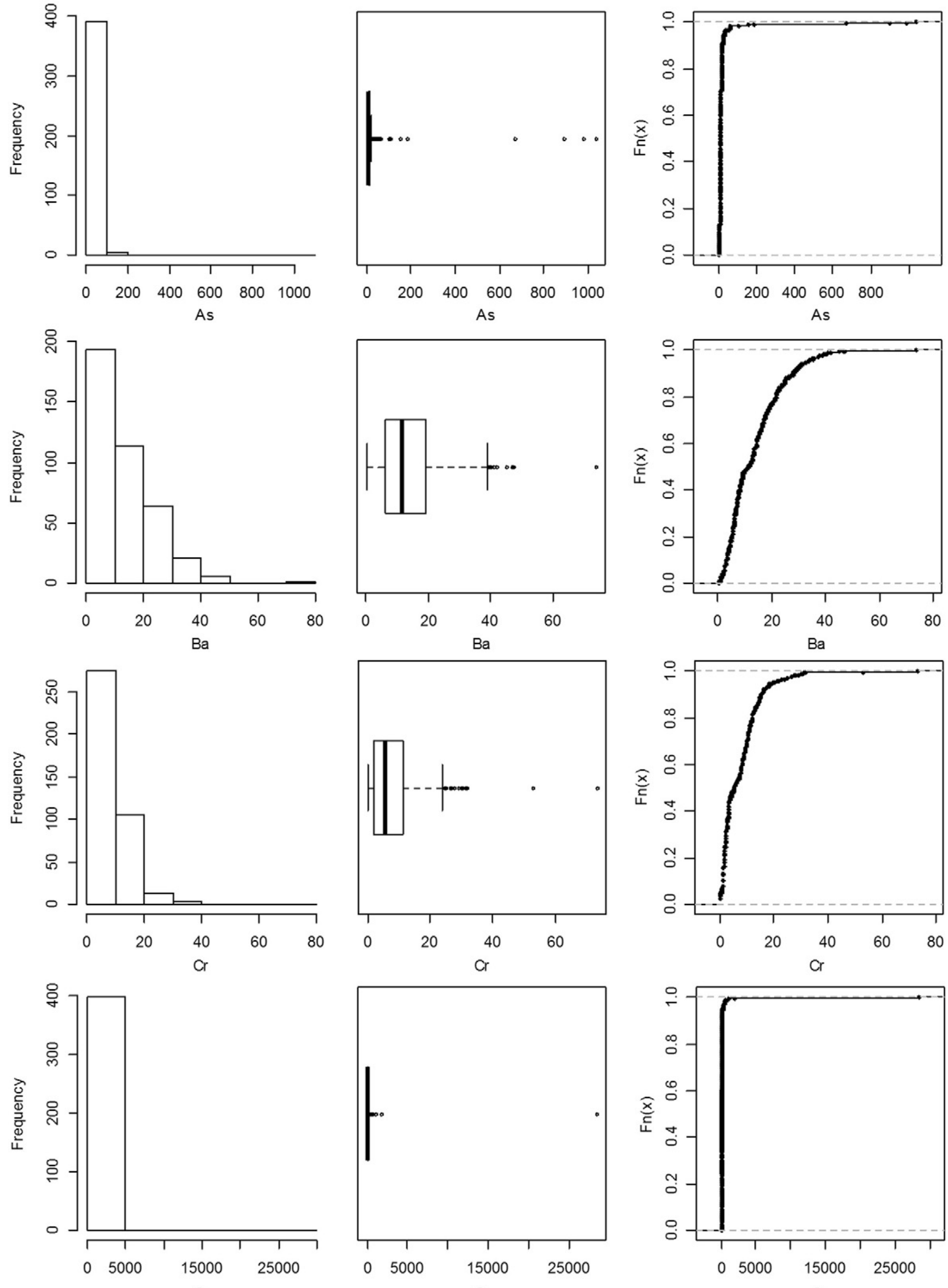

Fig. 5a. Graphical description of As, Ba, Cr and Cu contents (mg kg^{-1}) through EDA diagrams: histogram, box plot and CDF diagram.

The EF is based on the standardization of a tested element against a chosen reference element. A reference element is one characterized by low occurrence variability. The most common reference elements are Sc, Mn, Ti, Al and Fe (Loska et al., 2004). This study uses Fe as a reference element, as it is one of the main components of the Earth's crust, and its concentration in soils is related mainly with the matrix (Ağca and Özdel, 2014). The EF was calculated according to equation:

$$EF = [C_i/CFe_i/\ C_b/CFe_b] \tag{2}$$

where C_i is the concentration of the element, CFe_i is the content of Fe as the reference element, C_b is the reference content or background

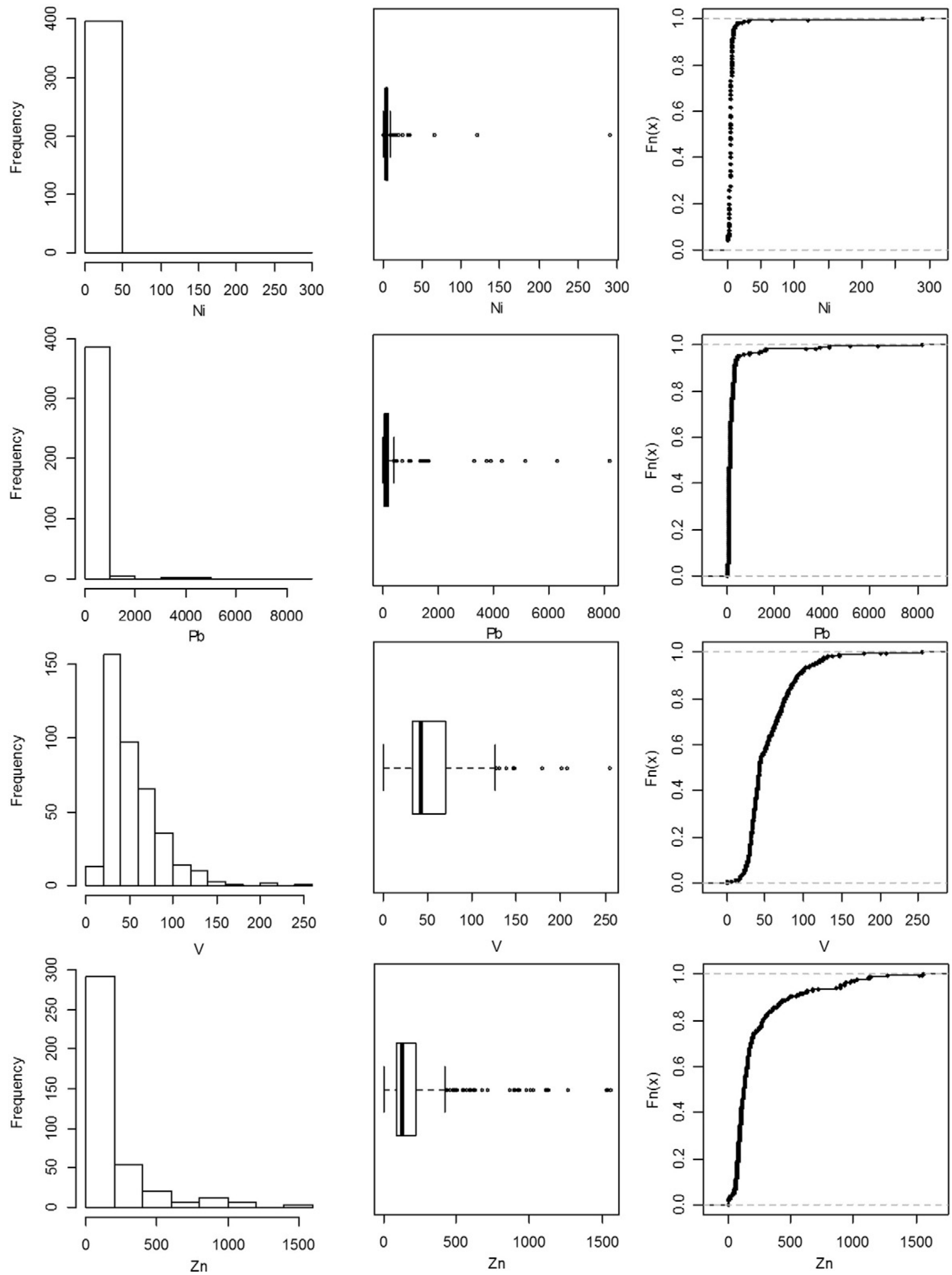

Fig. 5b. Graphical description of Ni, Pb, V and Zn contents (mg kg^{-1}) through EDA diagrams: histogram, box plot and CDF diagram.

content of the element obtained by MAD" method and CFe_b is the reference content or background of Fe, for all values referenced for this study. EF is divided into five groups: deficient to minimal enrichment (EF < 2), moderate enrichment (2 < EF < 5), significant enrichment (5 < EF < 20), very high enrichment (20 < EF < 40), and extremely high enrichment (EF > 40).

iii) Contamination factor (Cf)

The contamination factor is calculated based on the following equation:

$$C_f = C_i/Cb \tag{3}$$

where C_i is the concentration of the particular element in the soil and C_b is the content of background values obtained by MAD method.

Table 4
Statistical parameters for the soil heavy metal data set (mg kg^{-1}) from the Arica port city and their alteration through three statistical tests to derive a natural background.

		As	Ba	Cr	Cu	Ni	Pb	V	Zn
Original data set	Mean	22.8	13.5	7.5	123	5.3	267	54.3	221
	Median	11	11.3	5.6	17	4.7	112	42	130
	SD	90.7	10.2	7.5	1433	4.5	728	31.6	258
	Number n	400	400	400	400	400	400	400	400
Median + 2MAD	Upper limit	17.4	23.3	13.6	37.4	8.3	313	101	235
	Number n	336	336	340	315	328	303	291	301
	Loss (%)	16	16	14.8	21.1	17.8	24.1	27.1	24.6
Upper whisker method	Upper limit	23.8	38.8	24.6	66.7	9.1	414	127	431
	Number n	364	390	386	346	380	376	388	352
	Loss (%)	9.0	2.3	3.3	13.5	5.0	6.0	3	12.0
Cumulative frequency plots	Upper limit	20	40	17.3	62.7	9.8	363	130	376
	Number n	360	392	372	344	380	372	388	340
	Loss (%)	10	2	7	14	5	7	3	15

Hakanson, 1980, defines the following categories for C_f:: low contamination ($C_f < 1$), moderate contamination ($1 < C_f < 3$), considerable contamination ($3 < C_f < 6$) and very high contamination factor ($C_f > 6$).

Afterwards, the degree of contamination (C_{deg}) is defined as the sum of the individual contamination factors as expressed in the following equation:

$$C_{deg} = \sum C_f \tag{4}$$

Similar to Cf, the C_{deg} is divided into four groups (Hakanson, 1980): low contamination ($C_{deg} < 8$), moderate contamination ($8 < C_{deg} < 16$), considerable contamination ($16 < C_{deg} < 32$) and very high contamination factor ($C_{deg} > 32$).

iv) Integrated pollution index (IPI)

Another method used for the determination of trace element contamination is the IPI, which is defined as the average of the contamination factors computed for each trace element. The IPI is divided into four categories: low pollution level ($IPI < 1$), moderate pollution level ($1 < IPI < 2$), high pollution level ($2 < IPI < 5$) and extremely high pollution index ($IPI > 5$) (Salmanighabeshi et al., 2015).

3. Results and discussion

3.1. Content and distribution of trace elements

A statistical summary of the elements As, Ba, Cr, Cu, Ni, Pb, V and Zn is presented in Table 1. The dispersion of the concentrations is rather large indicating that in addition to diffused contamination of these

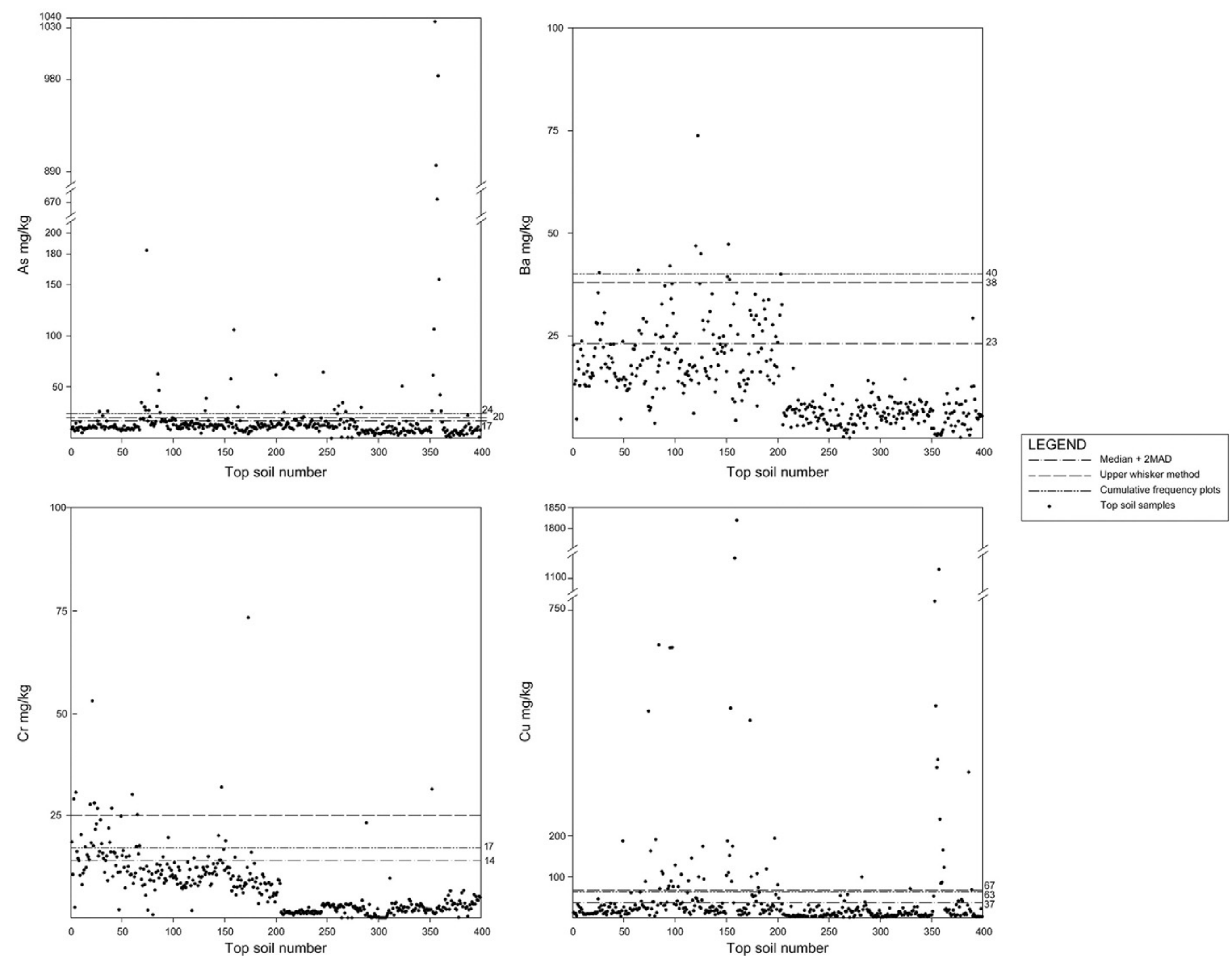

Fig. 6a. Background upper limit and topsoil horizon distribution for As, Ba, Cr and Cu.

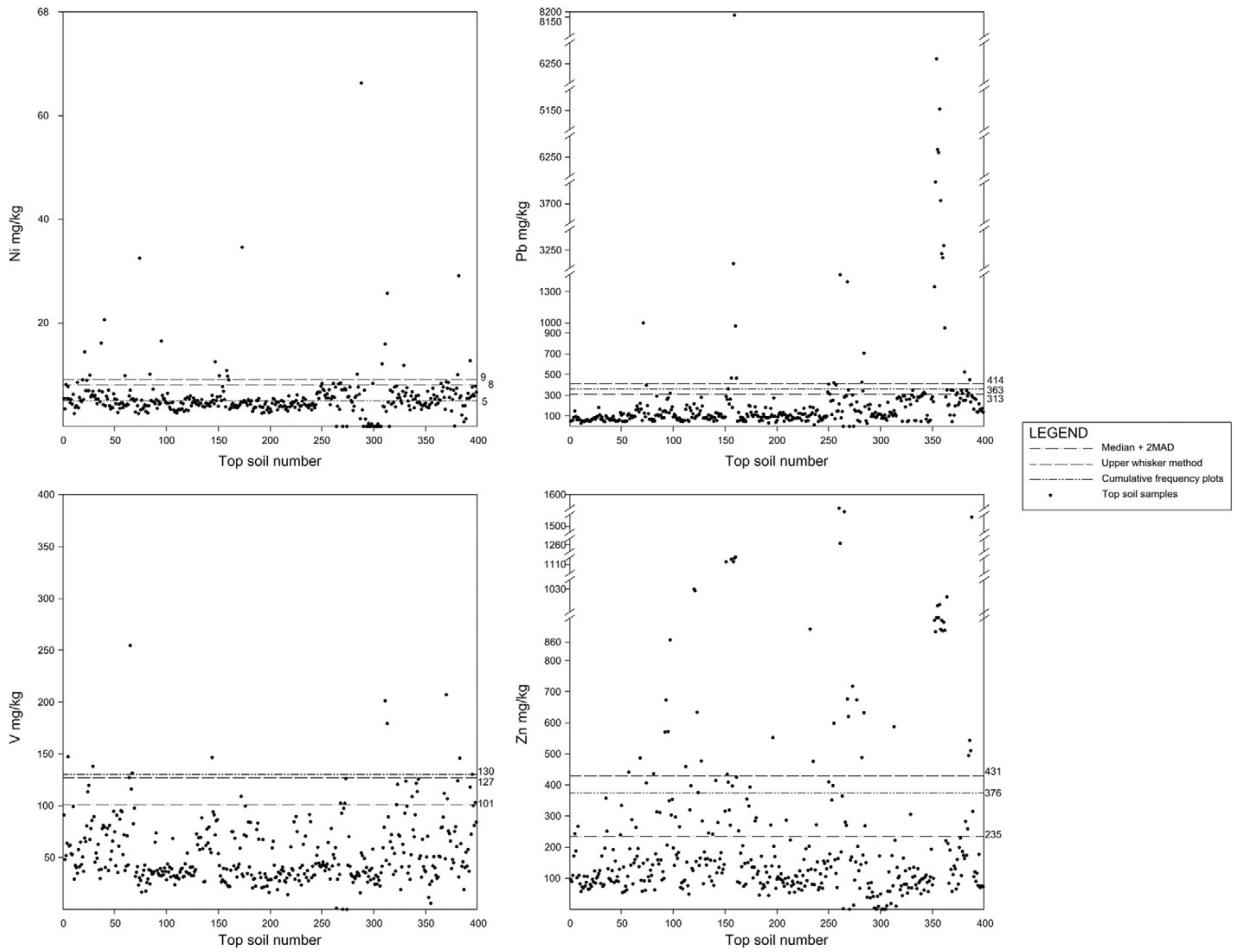

Fig. 6b. Background upper limit and topsoil horizon distribution for Ni, Pb, V and Zn.

elements within the urban environment, distinct point sources also contribute to the large concentrations. The coefficient of variation is defined as the ratio between the standard deviation and the average. When elements are derived mainly from natural sources, the coefficients of variations are small, whereas when they are controlled by anthropogenic sources, the coefficients of variations are large (Guan et al., 2014; Tume et al., 2008; Yongming et al., 2006). In the studied dataset, the coefficient of variation decreases in the order of Cu > As > Pb > Zn > Cr > Ni > Ba > V, suggesting that there is significant spatial variation in the distribution of these elements across the study area and that these elements may be strongly affected by human activities. From the perspective of skewness, the values of these eight trace element vary in order from Cu > As > Ni > Pb > Cr > Zn > V > Ba. This is consistent with the coefficient of variation classification of trace elements, indicating that the trace elements may be affected by human activity, resulting in a significant positive skewness.

Spearman's correlation matrices are presented in Table 2. Strong positive correlations at $p > 0.01$ were obtained for the pairs Zn/Cu, Zn/Pb and Ba/Cr, indicating that these elements may be derived from the same sources. Ni shows a slight correlation with Pb, V and Zn. Both the principal component analysis and CA are effective methods for identifying sources of trace elements (Cai et al., 2010; Davis et al., 2009; Nanos and Rodríguez Martín, 2012). Principal component analysis was performed for the dataset of urban soils of Arica in order to explore the relationship between the eight trace elements as variables and to assign related variables into principal components. Our analysis identified four principal components (PC1 to PC4) for the eight trace elements (Table 3) and cumulatively explains 73.9% of the total variance. The variance contribution rate of PC1 was 25.8%, and Pb, As and Cu had the larger loads. In this study, the variance contribution rate of PC2 was 19.3%, and Cr, Ba and Cu had the larger loads. The analysis shows that the contribution of PC3 was 16.7%, and Zn and Ni had large loads, while in PC4, only V has a larger load. In this study, Cu has high loads in PC1 and PC2, indicating that this trace element originated from mixed sources. CA was used to check the results of PCA. CA was performed according to the furthest neighbor method (Schucknecht et al., 2012). The results are shown in Fig. 3 as a dendogram created using clustering, and values of the distances between clusters (the squared Euclidean distance) are presented. In general, the results of the CA agreed well with those of the principal components analysis.

Maps created in the subject study (Figs. 4a and 4b) show high baseline values for some potentially harmful elements (As, Cu, Pb and Zn), which denote a clear anthropogenic contribution due to the long period of constant human activities in the study area. As seen from the maps, the spatial distribution of Ba, Cr, Ni and V is distinctly different from the spatial distribution of As, Cu, Pb and Zn. Variations in the levels of As, Cu, Pb and Zn demonstrate patterns very similar to those of the areas with the highest concentrations appearing in the vicinity of the port of Arica. In agreement with Spearman's correlations, CA and PCA, the spatial analysis suggests that the increase of As, Cu, Pb and Zn

Table 5
Literature data on published trace elements mean concentrations (mg kg^{-1}) in urban soil from various port cities around the world.

City	As	Ba	Cr	Cu	Ni	Pb	V	Zn	Reference
Aberdeen(Scotland)	ND	ND	23.9	27	14.9	94.4	ND	58.4	Paterson et al. (1996)
Annaba (Algeria)	ND	ND	30.9	39	ND	52.1	ND	67.5	Maas et al. (2010)
Atenas (Grecia)	29	ND	163	48	111	77	ND	122	Argyraki and Kelepertzis (2014)
Baltimore (USA)	ND	ND	72	45	27	231	37	141	Yesilonis et al. (2008)
Stockholm (Sweden)	ND	ND	34	71	ND	101	ND	171	Linde (2005)
Hong Kong (China)	ND	ND	17.8	16.2	4.08	88.1	ND	103	Lee et al. (2006)
Lisbon (Portugal)	5.3	107	38	37	43	89	48	97	Cachada et al. (2013)
Montreal(Canada)	ND	ND	ND	217	75.3	497	ND	489	Ge et al. (2000)
Napoli (Italy)	12.4	429	12.5	163	11.8	100	71	142	Cicchella et al. (2005)
Oslo (Norway)	5.5	ND	32.5	31.7	28.4	55.6	ND	160	Tijhuis et al. (2002)
Palermo(Italy)	ND	ND	39	77	19.1	253	58	151	Manta et al. (2002)
Paraná (Brazil)	2.1	311	92.6	163.8	39.9	20.6	576.5	128	Licht et al. (2006)
Talcahuano (Chile)	8.1	ND	39.1	50.5	31.9	49.2	ND	246	Tume et al. (2014)
Tallin (Estonia)	23	254	40	45	16	75	32	156	Bityukova et al. (2000)
Trondheim (Norway)	3	77.4	73.3	42.3	47.8	51.2	55.6	ND	Ottensen and Langedal (2001)
Galway (Ireland)	8.6	273	33.3	33.2	20.7	78.4	52.5	99.3	Zhang (2006)
Arica (Chile)	22.8	13.5	7.5	123	5.3	267	54.3	220.5	This study

came from a common anthropogenic source related to the transport of ore concentrate activities.

3.2. Background values

To better distinguish and evaluate geogenic from anthropogenic contributions in the distribution of baseline values, the background values were calculated. Both the box-plot and the cumulative probability plot diagrams show a separation between the core data and anomalous values (outliers and extreme outliers) (Figs. 5a and 5b). In general, anthropogenic influences lead to an enrichment in individual compartments or parts of natural systems, and the distributions are disturbed and skewed towards higher values. Lower values should therefore be free from anthropogenic influences. The background values of all of the studied potentially harmful elements were tested using different statistical techniques. Table 4 shows the mean and median values of the original data set, the results from the fitting Median + "MAD distribution, the upper whisker method and the cumulative frequency plots distribution. The standard deviation (σ) is given, as is the number "n" of single values within the collective/sub-collective and the relative loss of individual data points after respective fitting (data representation). Finally, the calculated upper limit (mean + 2σ) of the natural background content is given. Distributions are disturbed and skewed towards higher values. Lower values should therefore be free from anthropic influences.

The upper limit of the background content differs mainly between the cumulative frequency plots with respect to the median + 2 × MAD method and the upper whisker methods. Similar results were found by Rothwell and Cooke, 2015. The values from the median + 2 × MAD method are better at reducing the background upper limit than the upper whisker method, with the exception for Ba, Cr and Ni (Figs. 6a and 6b). Our recommendation is to use the median + 2 × MAD method as the most appropriate according to the precautionary principle, as it consistently provided the most conservative background values (Rothwell and Cooke, 2015). Therefore, the ranges obtained by the median + 2 × MAD method are chosen as background values. The upper limit of background values, expressed in mg kg^{-1}, for the studied elements are as follows: As = 17.4, Ba = 23.3, Cr = 13.6, Cu = 37.4, Ni = 8.3, Pb = 313 and Zn = 235. It can be noted that the upper limit for the Pb background range appears somewhat high, although it is lower than the value reported by Bowen (1979). This is probably due to some anomalous values that overlap with the background population (Bowen, 1979).

The median concentrations of Cr, Cu, Ni and Zn in the soils of Arica are lower than median concentrations reported for the urban soils of the port city of Talcahuano (29 mg kg^{-1}, 40 mg kg^{-1}, 30 mg kg^{-1} and 172 mg kg^{-1}, respectively, Tume et al., 2014). In contrast, the median concentrations of As, Pb are greater than the median concentrations in Talcahuano (6 mg kg^{-1}, 26.5 mg kg^{-1}, Tume et al., 2014). More elevated concentrations of As were reported for Athens, Greece (Argyraki and Kelepertzis, 2014). Other cities such as Tallin in Estonia have reported similar As concentrations (Bityukova et al., 2000). For the element Pb, Ge et al., 2000, reported more elevated concentrations in Montreal, Canada. In Hong Kong, China, Lee et al., 2006 reported lower Cu, Ni, Pb and Zn contents, but in the case of Cr, the contents were larger. Comparative trace element concentrations in urban soils from other port cities in the world are tabulated in Table 5 (Cachada et al., 2013; Cicchella et al., 2005; Ge et al., 2000; Lee et al., 2006; Licht et al., 2006; Linde, 2005; Maas et al., 2010; Manta et al., 2002; Ottesen and Langedal, 2001; Paterson et al., 1996; Tijhuis et al., 2002; Yesilonis et al., 2008; Zhang, 2006).

Once the background upper limits were established, sites with signs of anthropic concentrations were distinguished (Figs. 6a, 6b).

3.3. Ecological risk assessment

An ecological risk assessment derived from the investigated elements in urban soils of Arica was estimated using four contamination indicators. All of these soil contamination indicators were calculated with respect to established background values determined in the Arica soils. The results of the geoaccumulation index are presented in Table 6. Only Cu indicates I_{geo} values above 5 (extreme contamination). Copper and As are the two trace elements with the greatest contaminated soil values; however, Cu, Pb and Zn have greater numbers of soil sample sites in the moderately to heavily contaminated range. Both Ba and V show slightly contaminated values ($0 < I_{geo} \leq 1$).

Enrichment factor values reveal that the soils are extremely highly enriched with As, Cu, Ni and Zn. Again, Cu shows an extremely high

Table 6
Number of soil sample in each category of ecological risk assessment in Arica soils.

		As	Ba	Cr	Cu	Ni	Pb	V	Zn
Igeo	$0 < Igeo < 1$	23	16	17	36	9	5	4	39
	$1 < Igeo < 2$	4		1	12	2	7		23
	$2 < Igeo < 3$	0			9		7		
	$3 < Igeo < 4$	4			2				
	$4 < geo < 5$				0				
	$5 < Igeo$				1				
EF	$2 < EF < 5$	30	18	11	39	13	17	6	57
	$5 < EF < 20$	9	1	2	21	4	13	1	18
	$20 < EF < 40$	1			5		2		0
	$EF > 40$	3			2				1
Cf	$1 < Cf < 3$	53	63	58	54	28	27	30	72
	$3 < Cf < 6$	5	1	2	14	4	9		23
	$Cf > 6$	8			16	1	8		3

Table 7
Range, mean, standard deviation and median concentrations of trace elements in different land use types.

		As (mg kg^{-1})	Ba (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	V (mg kg^{-1})	Zn (mg kg^{-1})
Peri-urban	Range	0,1–19,2	4.7–6.7	3.4–5.7	2.8–3.8	5.8–12.7	138.5–218.7	72.6–130.4	71.1–177.4
(n:6)	Mean	8.7	5.5	4.7	3.1	7.5	159	97.8	98.7
	SD	1.4	0.71	0.81	0.39	2.6	30.8	22.7	42.2
	Median	8.1	5.4	4.7	3.0	6.4	148	92.3	76.5
Commercial	Range	0,1–19,2	2.1–41	1.1–18.8	4.7–187.7	1.5–9.8	74.25–421.8	26.4–127.3	57.8–1529
(n:23)	Mean	11.3	14.6	5.4	31.9	4.9	178	51.2	323
	SD	4.3	12.3	5.4	46.7	1.7	108	23.7	352
	Median	11.9	10.2	3.0	16.9	5.0	125	43.8	195
Industrial	Range	4,3–1036,4	0.7–73.8	1–73.2	8.1–1123	2.9–34.6	52.4–6298.4	6–70.6	46–1126.5
(n:30)	Mean	142	20.2	10.5	234	6.6	1174	35.3	548
	SD	307	17.1	13.4	283	5.8	1830	12.8	326
	Median	16.8	21.7	9.4	89.5	5.3	240	34.7	452
Residential	Range	0,6–64,5	0.2–47.3	0.0125–52.9	1.1–355.4	0.0125–66.3	1–1395.9	0.0125–254.8	0.625–1546.5
(n:283)	Mean	11.6	12.3	6.7	22	5.1	150	56.7	163
	SD	7.3	8.9	6.8	30.9	4.5	134	33	175
	Median	10.6	8.8	3.6	13.7	4.6	107	43.6	114
Site F	Range	11,9–183,3	3.7–32.7	0.8–13.5	4.5–665.8	2.5–32.5	50.5–998.9	16.7–97.8	58.3–436.4
(n:23)	Mean	30.3	17.9	9.5	104	5.7	163	36.3	165
	SD	35.4	8.0	3.3	162	6.1	199	16.7	105
	Median	19	19.2	9.8	35.9	4.4	107	34.3	144
Railway	Range	0,7–105,8	0.1–46.9	0.0125–30.6	1–28,450	0.0125–20.6	0.7–8169.7	0.1–147.4	0.5–1557.7
(n:34)	Mean	15.4	16.2	12.9	960	5.9	583	59.5	401
	SD	17.8	10	7.8	4871	3.3	1503	31.7	434
	Median	11	15.6	12	24.9	5.3	96.9	56.4	195

index value. In the case of Pb, 2 sample sites fall within the very high enrichment category ($20 < EF < 40$). The lowest C_f for the analyzed urban soil elements was for V and the highest for Cu. The sequence from lowest to highest C_f is as follows: V < Ba < Cr < Zn < Pb < Ni < As < Cu. The sums of contamination factors for all the metals examined shows that the degree of contamination in the urban soils within the study area is ranked as low contamination for 339 soil sample sites. However, 37 soil sample sites show C_{deg} values $8 < C_{deg} < 16$ and 9 sites indicate considerable contamination. Ten soil sample sites in the port city of Arica have C_{deg} values higher than 32 (= very high degree of contamination). The integrated pollution index (IPI, mean of C_f) shows values >5, indicating an extremely high pollution index in ten soil samples in Arica.

In addition to the above warning signs, significant differences were also observed in all trace element contents, except for Pb, when based on the different types of land use in the city of Arica: peri-urban (PU = 6 topsoil samples); commercial (CO = 23); industrial, IN (30); residential RE (283), residual stored "F" site (SF = 23), railway (VF = 34). The trace elements results of the Kruskal-Wallis test show significant differences based on land use types.

Larger concentrations of As and Ba were observed in soils related to industrial area and Site F soils (Table 7). However, the highest elevated concentrations of Cr, Cu and Pb were observed in soils next to railway and industrial sites. In the peri-urban soils, greater concentrations of Ni and V were observed. However, the largest content of V was detected in site C-29M29.6, which is classified for residential use. Samples collected along the railway line yield the maximum values for Cu, Pb and Zn. The large amounts of Cu and Pb in site C-17M17.8 with 28,450 and 8170 mg kg^{-1}, respectively, can be attributed to mineral particles falling during train transport. The concentrations of Pb and Cu varied significantly ($p < 0.05$) among types of land use. In the industrial area, the mean concentration of Pb, Zn, Cu, greatly exceeded the values from the other land use types, suggesting that the transport, storage and handling of bulk ore concentrate had a strong influence on the soil. The elevated concentrations of Cr were related to truck depots and automobile mechanic workshops.

The correlation values indicate that land use types have a significant influence on the amount of As, Cu, Pb and Zn (data not show). This statistical analysis suggests that the differences in the relationship of peri-urban and urban soils indicates that the urban area has been disturbed by human activities.

4. Conclusions

The background values of the studied trace elements in urban soils of Arica in mg kg^{-1} are as follows: As 17.4, Ba 23.3, Cr 13.6, Cu 37.4, Ni 8.3, Pb 313, V 101 and Zn 235. The sum of the contamination factors for all trace elements examined indicates a considerable degree of contamination in the urban soils. In general, Ba, Ni and V display the lowest level of contamination. In contrast, the greatest soil pollution was Cu detected near the railway line due to mineral particles falling during ore concentrate transport by train. The industrial soils are the most polluted as a result of the transport, storage and handling of bulk ore concentrate, although much of the urban soils demonstrate evidence of having been disturbed by human activities.

Acknowledgments

The authors gratefully acknowledge the Ministerio de Medio Ambiente of Chile for supplying the data used in this study.

References

Acosta, J.A., Cano, A.F., Arocena, J.M., Debela, F., Martínez-Martínez, S., 2009. Distribution of metals in soil particle size fractions and its implication to risk assessment of playgrounds in Murcia City (Spain). Geoderma 149, 101–109.

Ağca, N., Özdel, E., 2014. Assessment of spatial distribution and possible sources of heavy metals in the soils of Sariseki-Dörtyol District in Hatay Province (Turkey). Environ. Earth Sci. 71, 1033–1047.

Ahumada, I., Escudero, P., Ascar, L., Mendoza, J., Richter, P., 2004. Extractability of arsenic, copper, and lead in soils of a mining and agricultural zone in central Chile. Commun. Soil Sci. Plant Anal. 35, 1615–1634.

Argyraki, A., Kelepertzis, E., 2014. Urban soil geochemistry in Athens, Greece: the importance of local geology in controlling the distribution of potentially harmful trace elements. Sci. Total Environ. 482–483, 366–377.

Badilla-Ohlbaum, R., Ginocchio, R., Rodríguez, P.H., Céspedes, A., González, S., Allen, H.E., Lagos, G.E., 2001. Relationship between soil copper content and copper content of selected crop plants in central Chile. Environ. Toxicol. Chem. 20, 2749–2757.

Bini, C., Bech, J., 2014. PHEs, Environment and Human Health. Springer, Netherlands.

Bityukova, L., Shogenova, A., Birke, M., 2000. Urban geochemistry: a study of element distributions in the soils of Tallinn (Estonia). Environ. Geochem. Health 22, 173–193.

Bowen, H.J.M., 1979. Environmental Chemistry of the Elements. Academic Press, London.

Cachada, A., Dias, A.C., Pato, P., Mieiro, C., Rocha-Santos, T., Pereira, M.E., Ferreira da Silva, E., Duarte, A.C., 2013. Major inputs and mobility of potentially toxic elements contamination in urban areas. Environ. Monit. Assess. 185, 279–294.

Cai, L., Huang, L., Zhou, Y., Xu, Z., Peng, X., Yao, L.a., Zhou, Y., Peng, P.a., 2010. Heavy metal concentrations of agricultural soils and vegetables from Dongguan, Guangdong. J. Geogr. Sci. 20, 121–134.

Cicchella, D., De Vivo, B., Lima, A., 2005. Background and baseline concentration values of elements harmful to human health in the volcanic soils of the metropolitan and provincial areas of Napoli (Italy). Geochem. Explor. Environ. Anal. 5, 29–40.

Cicchella, D., De Vivo, B., Lima, A., Albanese, S., McGill, R., Parrish, R.R., 2008. Heavy metal pollution and Pb isotopes in urban soils of Napoli, Italy. Geochem. Explor. Environ. Anal. 8, 103–112.

CONAMA, 2009. Análisis Químico de Suelos de la Ciudad de Arica. Comisión Nacional del Medio Ambiente. p. 179.

Davis, H.T., Marjorie Aelion, C., McDermott, S., Lawson, A.B., 2009. Identifying natural and anthropogenic sources of metals in urban and rural soils using GIS-based data, PCA, and spatial interpolation. Environ. Pollut. 157, 2378–2385.

De Gregori, I., Fuentes, E., Rojas, M., Pinochet, H., Potin-Gautier, M., 2003. Monitoring of copper, arsenic and antimony levels in agricultural soils impacted and non-impacted by mining activities, from three regions in Chile. J. Environ. Monit. 5, 287–295.

Flynn, H.C., Mc Mahon, V., Diaz, G.C., Demergasso, C.S., Corbisier, P., Meharg, A.A., Paton, G.I., 2002. Assessment of bioavailable arsenic and copper in soils and sediments from the Antofagasta region of northern Chile. Sci. Total Environ. 286, 51–59.

Ge, Y., Murray, P., Hendershot, W.H., 2000. Trace metal speciation and bioavailability in urban soils. Environ. Pollut. 107, 137–144.

Guagliardi, I., Cicchella, D., De Rosa, R., Buttafuoco, G., 2015. Assessment of lead pollution in topsoils of a southern Italy area: analysis of urban and peri-urban environment. J. Environ. Sci. 33, 179–187.

Guan, Q., Wang, L., Wang, L., Pan, B., Zhao, S., Zheng, Y., 2014. Analysis of trace elements (heavy metal based) in the surface soils of a desert–loess transitional zone in the south of the Tengger Desert. Environ. Earth Sci. 72, 3015–3023.

Hakanson, L., 1980. An ecological risk index for aquatic pollution -control - a sedimentological approach. Water Res. 14, 975–1001.

Higueras, P., Oyarzun, R., Oyarzún, J., Maturana, H., Lillo, J., Morata, D., 2004. Environmental assessment of copper–gold–mercury mining in the Andacollo and Punitaqui districts, northern Chile. Appl. Geochem. 19, 1855–1864.

Isaaks, E.H., Srivastava, R.M., 1989. An Introduction to Applied Geostatistics. Oxford University Press, New York.

Jarva, J., Tarvainen, T., Reinikainen, J., Eklund, M., 2010. TAPIR — Finnish national geochemical baseline database. Sci. Total Environ. 408, 4385–4395.

Lee, C.S., Li, X., Shi, W., Cheung, S.C., Thornton, I., 2006. Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. Sci. Total Environ. 356, 45–61.

Li, X., Liu, L., Wang, Y., Luo, G., Chen, X., Yang, X., Hall, M.H.P., Guo, R., Wang, H., Cui, J., He, X., 2013. Heavy metal contamination of urban soil in an old industrial city (Shenyang) in Northeast China. Geoderma 192, 50–58.

Licht, O.A.B., Xuejing, X., Qin, Z., Miyazawa, M., Ferreira, F.J.F., Plawiak, R.A.B., 2006. Valores médios de referência de variáveis geoquímicas e geofísicas em sedimentos de drenagem e solos, estado do Paraná, Brasil. Bol. Paranaen. Geociências 58.

Linde, M., 2005. Trace Metals in Urban Soils -Stockholm as a Case Study, Department of Soil Sciences. Swedish University of Agricultural Sciences, Uppsala, p. 50.

Loska, K., Wiechuła, D., Korus, I., 2004. Metal contamination of farming soils affected by industry. Environ. Int. 30, 159–165.

Maas, S., Scheifler, R., Benslama, M., Crini, N., Lucot, E., Brahmia, Z., Benyacoub, S., Giraudoux, P., 2010. Spatial distribution of heavy metal concentrations in urban, suburban and agricultural soils in a Mediterranean city of Algeria. Environ. Pollut. 158, 2294–2301.

Madrid, L., Díaz-Barrientos, E., Madrid, F., 2002. Distribution of heavy metal contents of urban soils in parks of Seville. Chemosphere 49, 1301–1308.

Manta, D.S., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M., 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Sci. Total Environ. 300, 229–243.

Massas, I., Ehaliotis, C., Kalivas, D., Panagopoulou, G., 2010. Concentrations and availability indicators of soil heavy metals; the case of Children's playgrounds in the City of Athens (Greece). Water Air Soil Pollut. 212, 51–63.

Matschullat, J., Ottenstein, R., Reimann, C., 2000. Geochemical background – can we calculate it? Environ. Geol. 39, 990–1000.

Müller, G., 1969. Index of geoaccumulation in sediments of the Rhine River. GeoJournal 108–118.

Nanos, N., Rodríguez Martín, J.A., 2012. Multiscale analysis of heavy metal contents in soils: Spatial variability in the Duero river basin (Spain). Geoderma 189–190, 554–562.

Ng, S.L., Chan, L.S., Lam, K.C., Chan, W.K., 2003. Heavy metal contents and magnetic properties of playground dust in Hong Kong. Environ. Monit. Assess. 89, 221–232.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134–139.

Ottesen, R.T., Langedal, M., 2001. Urban geochemistry in Trondheim, Norway. Nor. Geol. Unders. 438, 63–69.

Parra, S., Bravo, M.A., Quiroz, W., Moreno, T., Karanasiou, A., Font, O., Vidal, V., Cereceda, F., 2014. Distribution of trace elements in particle size fractions for contaminated soils by a copper smelting from different zones of the Puchuncaví Valley (Chile). Chemosphere 111, 513–521.

Paterson, E., Sanka, M., Clark, L., 1996. Urban soils as pollutant sinks — a case study from Aberdeen, Scotland. Appl. Geochem. 11, 129–131.

Pouyat, R.V., Yesilonis, I.D., Russell-Anelli, J., Neerchal, N.K., 2007. Soil chemical and physical properties that differentiate urban land-use and cover types. Soil Sci. Soc. Am. J. 71, 1010–1019.

Presley, S.M., Abel, M.T., Austin, G.P., Rainwater, T.R., Brown, R.W., McDaniel, L.N., Marsland, E.J., Fornerette, A.M., Dillard, M.L., Rigdon, R.W., Kendall, R.J., Cobb, G.P., 2010. Metal concentrations in schoolyard soils from New Orleans, Louisiana before and after hurricanes Katrina and Rita. Chemosphere 80, 67–73.

Reimann, C., Filzmoser, P., Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. Sci. Total Environ. 346, 1–16.

Rothwell, K.A., Cooke, M.P., 2015. A comparison of methods used to calculate normal background concentrations of potentially toxic elements for urban soil. Sci. Total Environ. 532, 625–634.

Salmanighabeshi, S., Palomo-Marín, M.R., Bernalte, E., Rueda-Holgado, F., Miró-Rodríguez, C., Fadic-Ruiz, X., Vidal-Cortez, V., Cereceda-Balic, F., Pinilla-Gil, E., 2015. Long-term assessment of ecological risk from deposition of elemental pollutants in the vicinity of the industrial area of Puchuncaví-Ventanas, central Chile. Sci. Total Environ. 527–528, 335–343.

Salminen, R., Gregorauskiene, V., 2000. Considerations regarding the definition of a geochemical baseline of elements in the surficial materials in areas differing in basic geology. Appl. Geochem. 15, 647–653.

Schalscha, E., Ahumada Torres, A.I.d.L., 1998. Heavy Metals in Rivers and Soils of Central Chile.

Schucknecht, A., Matschullat, J., de Caritat, P., da Silva, J., Melo Jr., G., Pleßow, A., Mello, J.W.V., 2012. Pedogeochemistry in NE-Brazil — compared to Australia and Europe. Sci. Total Environ. 438, 342–356.

Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ. Geol. 39, 611–627.

Tijhuis, L., Brattli, B., Sæther, O.M., 2002. A geochemical survey of topsoil in the city of Oslo, Norway. Environ. Geochem. Health 24, 67–94.

Tiller, K., 1992. Urban soil contamination in Australia. Soil Res. 30, 937–957.

Tran Thi Thu, D., Cappuyns, V., Swennen, R., Nguyen Ky, P., 2013. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. Rev. Environ. Sci. Biotechnol. 12, 335–353.

Tukey, J.W., 1977. Exploratory Data Analysis. Addison-Wesley Publishing Company.

Tume, P., Bech, J., Sepulveda, B., Tume, L., Bech, J., 2008. Concentrations of heavy metals in urban soils of Talcahuano (Chile): a preliminary study. Environ. Monit. Assess. 140, 91–98.

Tume, P., King, R., González, E., Bustamante, G., Reverter, F., Roca, N., Bech, J., 2014. Trace element concentrations in schoolyard soils from the port city of Talcahuano, Chile. J. Geochem. Explor. 147, 229–236.

USEPA, 1996. Test Methods for Evaluating Solid Waste, SW-846. Method 61010B. 3rd ed. p. 24.

Wei, B., Yang, L., 2010. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchem. J. 94, 99–107.

Yesilonis, I.D., Pouyat, R.V., Neerchal, N.K., 2008. Spatial distribution of metals in soils in Baltimore, Maryland: role of native parent material, proximity to major roads, housing age and screening guidelines. Environ. Pollut. 156, 723–731.

Yongming, H., Peixuan, D., Junji, C., Posmentier, E.S., 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci. Total Environ. 355, 176–186.

Zhang, C.S., 2006. Using multivariate analyses and GIS to identify pollutants and their spatial patterns in urban soils in Galway, Ireland. Environ. Pollut. 142, 501–511.

Zuzolo, D., Cicchella, D., Catani, V., Giaccio, L., Guagliardi, I., Esposito, L., De Vivo, B., 2016. Assessment of potentially harmful elements pollution in the Calore River basin (Southern Italy). Environ. Geochem. Health 1–18.