Journal of Geochemical Exploration 184 (2018) 333–344

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

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

Spatial distribution of potentially harmful elements in urban soils, city of Talcahuano, Chile

Pedro Tume [a,d,*], Elizabeth González [b], Robert W. King [a], Victor Monsalve [a], Núria Roca [c], Jaume Bech [c]

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

ARTICLE INFO

Article history:
Received 29 February 2016
Revised 30 November 2016
Accepted 6 December 2016
Available online 8 December 2016

Keywords:
Trace metals
Soil monitoring
Soil pollution
Pollution index
Chile

ABSTRACT

The objective of this study is to ascertain the spatial distribution of Cu, Pb and Zn in order to determine the degree of contamination in urban soils from Talcahuano (Chile) and to identify the influence of possible contamination sources. A total of 420 samples were collected from the study area based on the following criteria: 140 topsoil samples (TS) (0–10 cm), 140 subsoil samples (SS) (10–20 cm) and 140 deep soil samples (DS) (150 cm). The soils were characterized for their physical characteristics such as grain size distribution, pH, organic matter content etc. and the concentrations of Cu, Pb and Zn were analyzed by Atomic Absorption Photospectrometry following Aqua Regia digestion. Correlations combined with spatial analysis were implemented in order to distinguish the sources of the trace metals and whether they are geogenic or anthropogenic of origin. Several simple and robust statistical methods were applied to the data sets in order to evaluate useful and robust background values. The degree of contamination along with the geoaccumulation index, enrichment factors and contamination factors were also evaluated. The median concentrations obtained for the studied trace metals includes: Cu 23.1 mg kg^{-1}, Pb 10.2 mg kg^{-1} and Zn 56.7 mg kg^{-1}. In general, the concentrations of Cu, Pb and Zn decrease with depth however, in certain sites the subsoil samples (SS) levels show higher concentrations than topsoil samples (TS). A possible explanation could be related to the uncontrolled clandestine landfill sites using both construction material debris and/or industrial solid wastes. Correlation analysis suggests that Cu, Pb and Zn are contributed by external sources. The spatial distribution of Cu, Pb and Zn in topsoil samples (TS) displays a spatial pattern extending along major roadway environments and emission sources. Estimated background values determined with the iterative 2σ-technique yields 43.7 mg kg^{-1} for Cu, 17.5 mg kg^{-1} for Pb and 91.7 mg kg^{-1} for Zn respectively. The geochemical index, enrichment factor and the contamination factor all register a moderate to high contamination level in some of the soil samples.

1. Introduction

Globally, more people live in urban areas than in rural areas. In 2014, 54% of the world's population resided in urban areas compared to 1950 were only 30% of the world's population was urban (Burghardt et al., 2015). It is projected that by 2050, 66% of the world's population will be urban (United Nations, 2014). Urban soils are an essential element of a city's environment (Ajmone-Marsan and Biasioli, 2010). Urban soil science is a relatively young field compared to the traditional soil sciences which focused primarily on agriculture and forest environments (Horváth et al., 2015). Urban soils are strongly influenced by anthropogenic activities, differs greatly from natural soils and receives a major proportion of trace metal emissions from industrial activities, traffic vehicle emissions, municipal waste as well as commercial and domestic activities (Cheng et al., 2014). Urban soil contamination can be divided into three broad categories based on the source of the pollution: a) point sources, such as direct discharge points and industrial sites; b) line sources (road traffic emissions), and c) non-point sources usually due to dispersed atmospheric deposition throughout urban areas (Luo et al., 2012). The prolonged presence of contaminants in urban soils and their close proximity to the human population can significantly amplify the exposure of the urban population to trace metals via inhalation, ingestion, and dermal contact (Guney et al., 2010; Laidlaw and Taylor, 2011; Wong et al., 2006). A human health concern is usually associated with excessive exposure to trace metals that causes toxic effects to biological organisms. These may include non-essential metals, such as Cd and Pb that can be toxic even at trace levels, and biologically essential

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[*] 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.2016.12.007
0375-6742/

metals, such as Cu and Zn, which may cause toxic effects at elevated concentrations (Wong et al., 2006). Numerous studies have revealed that the two principal sources of trace metal contamination, especially Cd, Cu, Pb and Zn in urban soils can be attributed to industrial discharges and traffic emissions (Luo et al., 2012; Sun et al., 2010). Ajmone-Marsan et al., 2008 reported that Cu, Pb and Zn, have a similar origin and behavior, regardless of differences is soils and environmental characteristics of the studied cities (Aveiro, Glasgow, Ljubljana, Sevilla and Torino). Currently, Cd, Cu, Pb and Zn are regarded as typical urban metals (Cachada et al., 2013; Lu and Bai, 2010; Luo et al., 2014).

Urban environment pollution has received significant attention during the last few decades and several studies were conducted on urban trace metal contamination in the USA (Burt et al., 2014; Kaminski and Landsberger, 2000; Yesilonis et al., 2008), China (Cheng et al., 2014; Lu and Bai, 2010; Luo et al., 2012), Latin America (Figueiredo et al., 2011; Rodríguez-Salazar et al., 2011; Tume et al., 2014), Europe (Ajmone-Marsan et al., 2008; Andersson et al., 2010; Buttafuoco et al., 2016; Cachada et al., 2013; Cicchella et al., 2008; De Miguel et al., 2007; Guagliardi et al., 2013; Guagliardi et al., 2015; Johnson and Ander, 2008; Ljung et al., 2006; Zacháry et al., 2015; Zuzolo et al., 2016) and Asia (Iqbal and Shah, 2011; Karimi Nezhad et al., 2015; Yaylalı-Abanuz, 2011). In Chile, the scientific literature on trace metal concentrations in soils has focused primarily in mining and agriculture areas (Ahumada et al., 2004; Badilla-Ohlbaum et al., 2001; De Gregori et al., 2003) and studies on urban soils are limited (Parra et al., 2014; Salmanighabeshi et al., 2015; Tume et al., 2008). Tume and colleagues performed a preliminary study on schoolyard soil samples (Tume et al., 2008; Tume et al., 2014; Tume et al., 2006) but a city-wide investigation was not undertaken. The urban soils of Talcahuano are of particular interest since degradation may occur due to atmospheric aerosol deposition from several anthropogenic activities, including landfill, industrial and vehicular emissions, fossil fuel combustion and solid waste residual disposal. Industrial activity in Talcahuano started in 1950 and with the rapid growth of the city, most of the residential areas are located near industries (Ahumada and Vargas, 2005).

The geochemical baseline in an area of heavy anthropogenic impact, such as the urban area of Talcahuano, includes the geogenic natural content (background) and the anthropogenic contributions to the soils (Albanese et al., 2013; Cicchella et al., 2005). In recent years, urban geochemical mapping projects have provided methods for identifying, describing and evaluating urban contamination and its sources (Buttafuoco et al., 2016).

Correctly distinguishing between natural (background) and anthropogenic trace metal contents in soils is crucial for assessing soil contamination. There are several methods available including direct (empirical or geochemical) or indirect (statistical) and both can be combined, leading to integrated methods (Desaules, 2012; Matschullat et al., 2000; Reimann et al., 2005; Tran Thi Thu et al., 2013). Geostatistics is extensively used to assess the level of soil contamination and estimating risk factors in contaminated sites by preserving the spatial distribution and uncertainty of the estimates. In addition, geostatistics and GIS provide useful tools to study the spatial uncertainty and hazard assessment (Goovaerts, 2001; Reza et al., 2015). Furthermore, the degree of contamination of the soils could be evaluated with 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 baseline value.

In this study, we aim to: (1) study the concentrations of Cu, Pb and Zn in the urban soils from Talcahuano (Chile); (2) determine the background concentrations of Cu, Pb and Zn within the study area; (3) assess the level of contamination in the urban soils based on different pollution indexes and (4) to identify natural or anthropogenic sources in order to obtain a spatial distribution of the pollutants.

2. Material and methods

2.1. Study area

The study area is located in the port city of Talcahuano approximately 600 km south of Chile's capital, Santiago (Fig. 1). The Municipal District of Talcahuano has a population of 163,628 and a surface area of 94.6 km^2 (Fig. 1). Major industries within the city boundaries include: an oil refining plant, a steel producing complex, various fish processing and petrochemical industries, a soft drink bottling plant, shipyards including a naval shipyard, and a cement factory. Many of these activities require a great amount of energy, which is produced mainly from oil derivatives and coal combustion (Pedrero et al., 2009). Based on data provided by the Direccion Meteorologica de Chile, (Meteorológica de Chile, 2016), the mean annual precipitation in the region is on the order of 1130 mm per year. The warmest month is January with an average high of 22.1 °C and the coolest is July with an average low of 5.9 °C. The summer maximum recorded is 33.2 °C and the coldest temperature measured was −3.0 °C. The cool waters of the Pacific Ocean combined with the Humboldt Current help to maintain mild temperatures throughout the year. In the six-month period between May and October, the area receives approximately 83% of its total annual precipitation, while the months from November to April have been rainless on occasions. During the winter, the prevailing winds are from the north; while as of September, the prevailing winds are from the southwest.

2.2. Geology

The current geological and geomorphological features of the study area are a result of both endogenous and exogenous factors which have shaped the area from as far back as the Paleozoic to the recent. The oldest rocks in the area correspond to a package of metamorphic (~320 Ma.) and intrusive igneous (~305 Ma.) rocks grouped within a unit denominated the "Basamento Cristalino" (crystalline basement). Disconformably overlying the crystalline basement are sequences of variable thicknesses of siliciclastic sedimentary rocks (Quiriquina, Pilpico, Cosmito, and Curanilahue Formations) deposited in marine and continental environments associated with coastal subsidence tectonics and oceanic transgressions and regressions. The Pliocene is characterized as an epoch of grand transformation in the geography of the fore-arc region with an intense stage of faulting accompanied by the rapid uplift of the topography, forming the graben of the "Fosa Complejo de Concepción" (Quezada, 1996). During the course of the Pliocene and Quaternary, rivers such as the BioBio and Andalien became more pronounced as the regional uplift advanced. Within the sunken block of the graben, various events of surfacing and submergence of the delta led to the meandering form variations of the BioBio River and the constant modification of its causeway. Mardones (1976) states that in the past, the BioBio River emptied into the ocean in the Bahia de Concepcion to the north of the study area, then into the Bahia de San Vincente to the west before evolving to its current position to the south of the study area. Most of the present day urban Talcahuano and much of Concepción are underlain by a thick sequence of unconsolidated sediments of the paleochannels of the BioBio River (Mardones, 1976). The thickness of the sediments in Talcahuano is unknown; however thicknesses of up to 150 m have been observed in drill holes in Concepción (Galli, 1967). The intense human occupation of much of the physical space that covers the majority of the lowlands in Talcahuano and Concepcion has brought as a consequence, the total transformation of the original natural landscape.

2.3. Soil sampling and analysis

Two soil sampling campaigns were conducted during March–April 2013 and March–April 2014. Sampling points within the study area were randomly distributed based on a regular grid of 1 × 1 km with

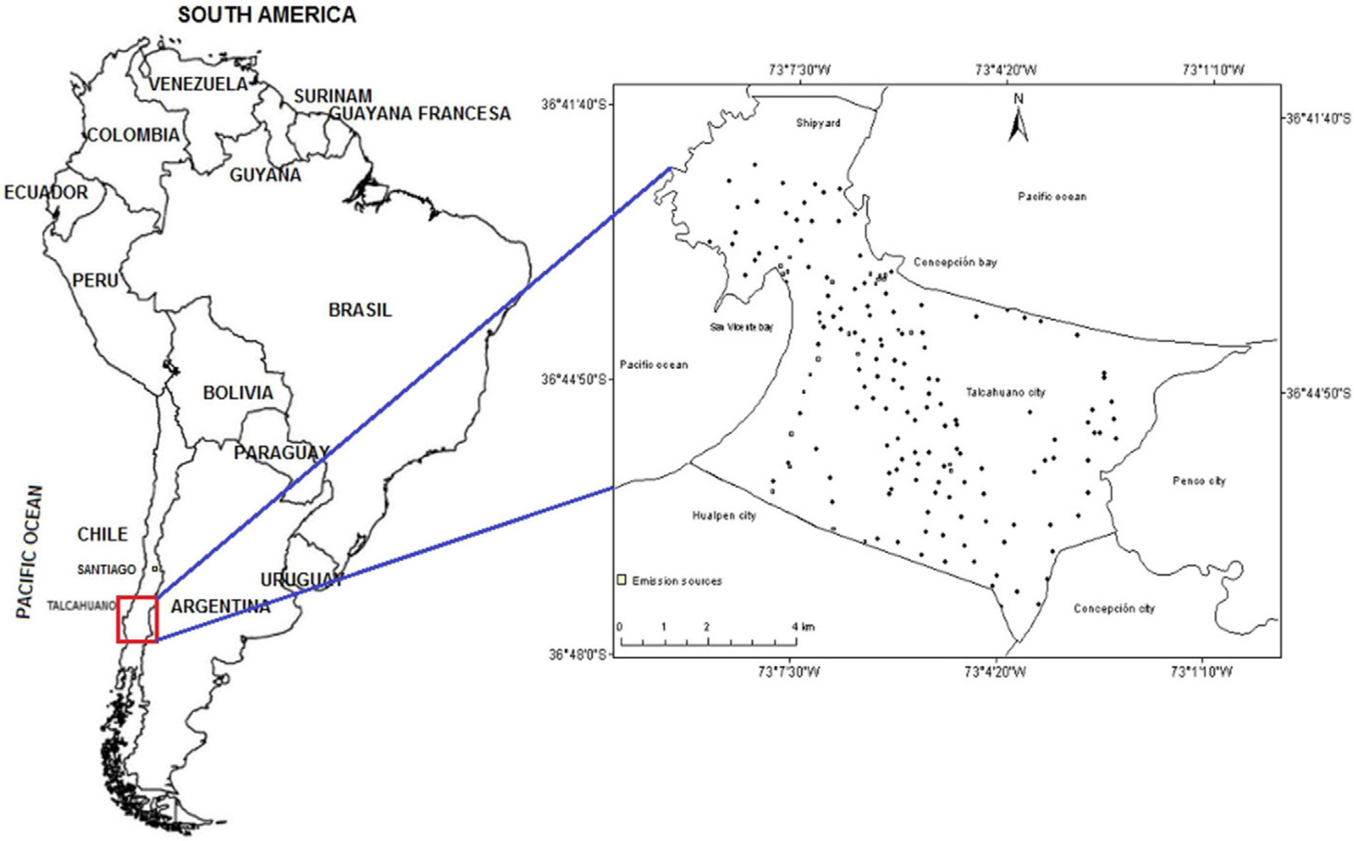

Fig. 1. Sampling locations of soils in Talcahuano city.

each grid square cell having at least one sampling point. The distribution of samples sites based on different land use includes 55 for commercial use (CO), 62 for residential use (RE) and 23 for industrial use (IN). A total number of 420 samples were collected from the study area based on the following criteria: 140 topsoil samples (TS) (0–10 cm), 140 subsoil samples (SS) (10–20 cm) and 140 deep soil samples (DS) (150 cm). At every sampling site, five subsamples of topsoils (TS) within a 1 m radius were collected and mixed to obtain a composite sample. The same procedure was repeated for the subsoil (SS) samples. The deep soil samples (DS) were collected using Dutch auger (150 cm). The initial quantity of each composite sample was approximately 2 kg. All the collected soil samples were stored in polyethylene bags for transportation and storage. Geographic coordinates of all samples were recorded using a global position system (GPS) and a sampling location map (Fig. 1) was produced by means of ArcGIS Software (version 10.2). The soil samples were promptly oven dried for at least 24 h at 35 °C, sieved through a 2 mm nylon sieve and, then stored in sealed polythene bags until instrumental analysis.

The texture was determined using the hydrometer method. The pH soil was measured in an 1:2.5 soil to water ratio. The organic carbon (OC) was determined using the humid oxidation method of Walkley and Black (Burt, 2004). The cation exchange capacity (CEC) was determined using the saturation method with 1 M sodium acetate at pH 7.0, and percolation.

The samples were digested by Aqua Regia (ISO 11466.2002). The concentrations of Cu, Pb and Zn were determined by Atomic Absorption Photospectrometry housed in the Faculty of Sciences of the Universidad Católica de Santísima Concepción. The detection limit for Cu, Pb and Zn were 2, 0.65, 1.5 mg kg^{-1} respectively. Analytical quality control procedures undertaken to assess the precision and accuracy of laboratory determinations of the concentration of the trace metals were performed using certified standard material (Trace metals clay 2 of Sigma-Aldrich) and numerous analysis duplicates. The errors of the estimate for the measured were determined by the relative standard deviation based on three replicates of one sample randomly chosen.

2.4. Data analysis

Soil geochemistry can be affected by various factors such as geology, climate, vegetation, weathering, natural mineralization and human activities (Jordan et al., 2007). Due to these factors, it is expected that mixed populations exist in urban soils, indicating geochemical variables belonging to different processes and/or sources (Dao et al., 2010). An exploratory data analysis (EDA) can serve as a diagnostic tool for issues such as multi-modality. Figs. 2, 3 and 4 show three different EDA graphs (histogram, box-plot and cumulative probability plot (CDF diagram)) for the trace metals Cu, Pb and Zn. Descriptive statistical analysis were performed on the trace metal concentration data of each topsoil (TS), subsoil (SS) and deep soil (DS) samples. Samples below the limit of detection (LD) were assigned a value 1/2 LD. A Spearman correlation analysis was used to process the data and identify sources of potentially harmful trace metal contamination. The statistical analyses were carried out using the computer program R (Team, 2015). In this study, ordinary Kriging was used for interpolating Cu, Pb and Zn concentrations, using ESRI ArcMap 10.2 and its extension Geostatistical Analyst. Cross-validation was used to compare the measured and predicted values for each potentially harmful trace metal concentration. Three types of semivariogram models (circular, spherical and exponential) were tested. The Gaussian model was not tested as it yields implausible results from its use (Oliver and Webster, 2014).

2.4.1. Background values

Natural or pedo-geochemical background concentrations were defined using data taken from the deep soil (DS) samples at 150 cm depth (Cheng et al., 2014; ISO, 2005; Ungaro et al., 2008) and used to provide a local data reference against which to compare surface soil

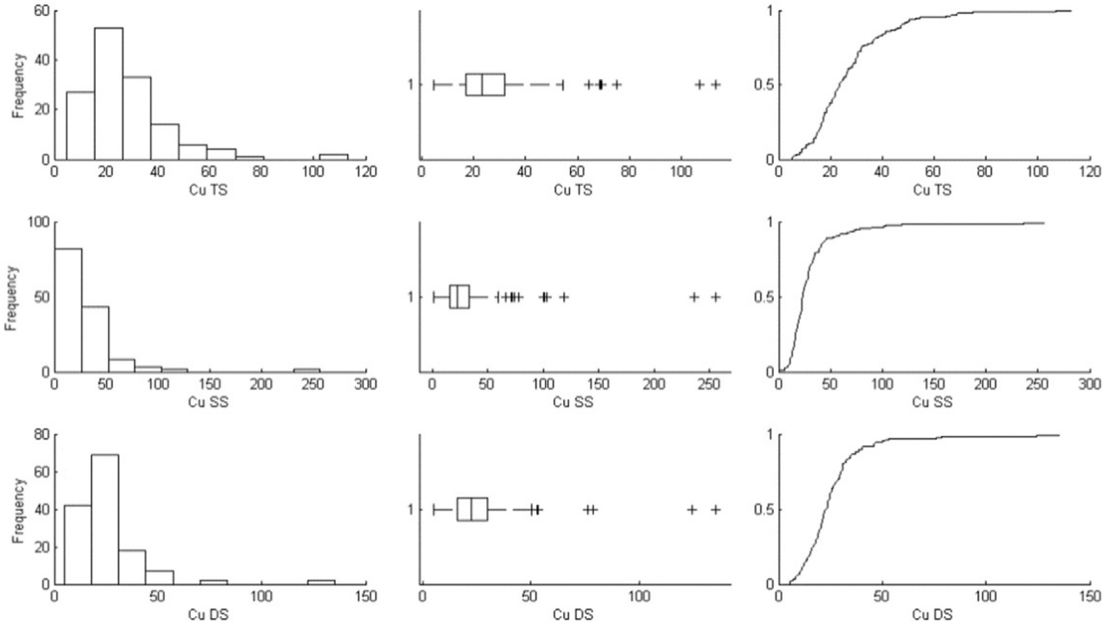

Fig. 2. Graphical description of Cu concentrations (mg kg^{-1}) through EDA diagrams: histogram, box plot and CDF diagram in TS, SS and DS.

trace metal concentrations (Rouillon et al., 2013). Several simple and robust statistical methods were applied to the different data sets in order to explore their potential in the evaluation of a useful and robust background (Matschullat et al., 2000). In this study, three different methods were used to calculate background values. In the first method (´MAD´ method), the median ± 2MAD (median absolute deviation) was used. The second method (‘upper whisker’ method), consisted in using the upper whisker of a Tukey's box plot as calculated by the 3rd quartile + 1.5IQR (interquartile range). In the third method, the iterative 2σ-technique was used based on the assumption that all values beyond the mean ± 2σ are omitted from the dataset and the new mean ± 2σ range is calculated using the reduced data. This procedure is repeated until all the values of the dataset lie within the range approaching a normal distribution (Matschullat et al., 2000; Reimann et al., 2005).

2.4.2. Assessment of potential pollution

Different environmental quality indicators are commonly used to assess the potential pollution in soils (Rodríguez-Seijo et al., 2015). The pollution levels of trace metals in the soils of Talcahuano were evaluated using 1) the geoaccumulation index (I_{geo}), 2) the enrichment factor (EF) and 3) the contamination factor (C_f).

The geoaccumulation index is calculated using the following equation:

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

where C_i is the measured content of the element in the soil, and C_b is the estimated background value in the soil. According to Müller (1969), the I_{geo} for a particular element is calculated and classified as:

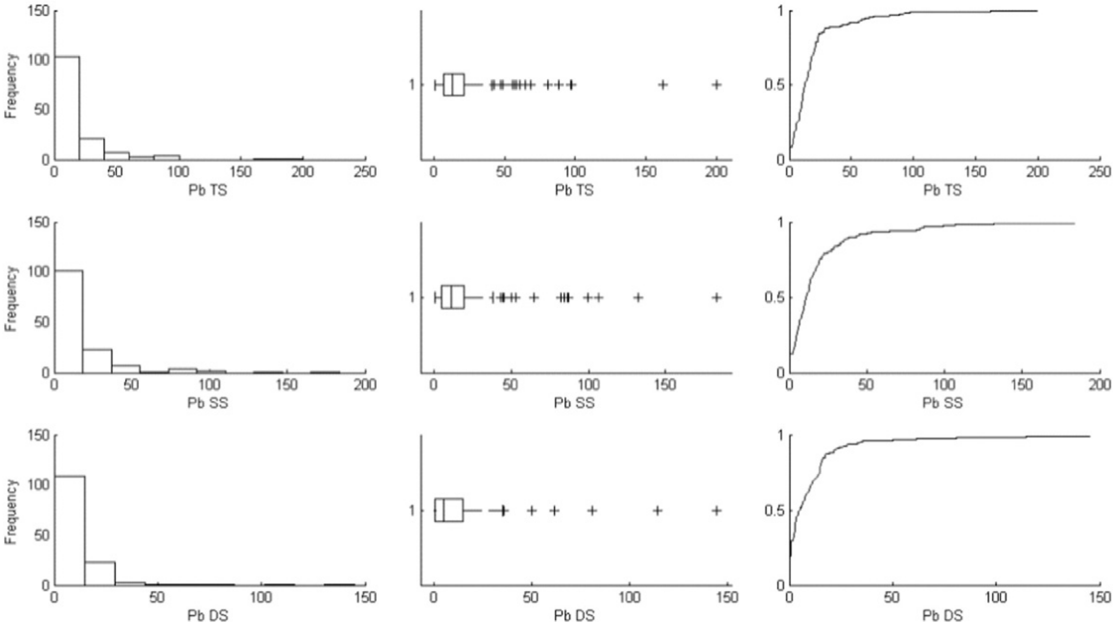

Fig. 3. Graphical description of Pb concentrations (mg kg^{-1}) through EDA diagrams: histogram, box plot and CDF diagram in TS, SS and DS.

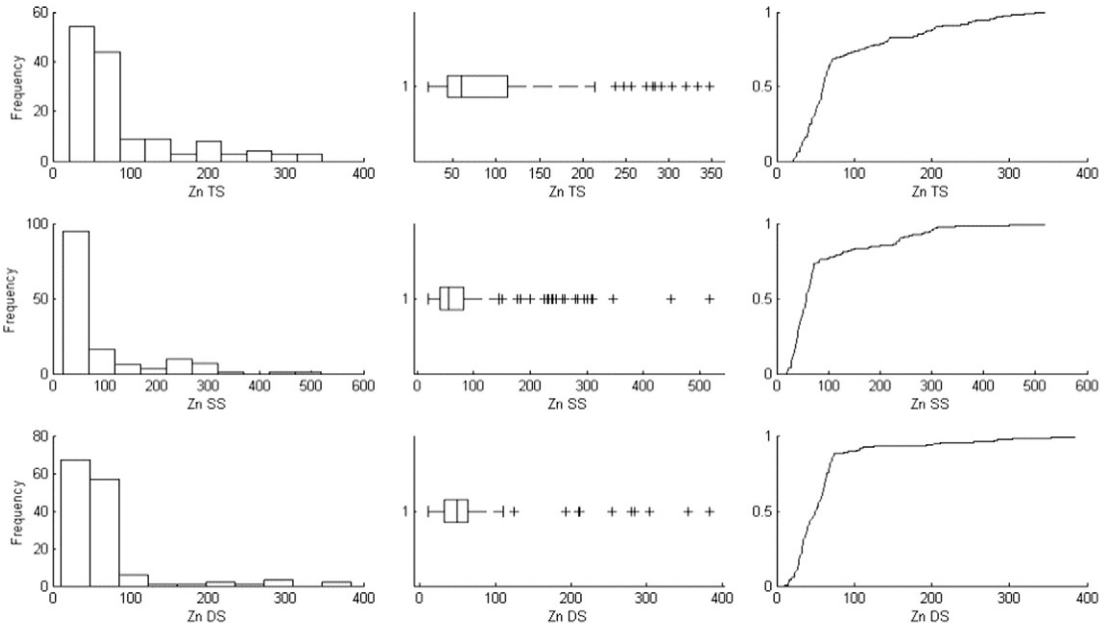

Fig. 4. Graphical description of Zn concentrations (mg kg^{-1}) through EDA diagrams: histogram, box plot and CDF diagram in TS, SS and DS.

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 ($4 < I_{geo} \leq 5$); extremely contaminated ($I_{geo} > 5$) (Müller, 1969; Sutherland, 2000).

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

$$EF = [C_i/CFe_i]/[C_b/CFe_b] \quad (2)$$

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 content of the element obtained by the iterative 2σ method and CFe_b is reference content or background of Fe. Enrichment Factor values can be subdivided into five categories: deficiency to minimal enrichment (EF < 2), moderate enrichment (2 < EF < 5), significant enrichment (5 < EF < 20), very high enrichment (20 < EF < 40), extremely high enrichment (EF > 40).

The contamination factor (CF) is calculated using the equation:

$$C_f = C_i/C_b \quad (3)$$

where C_i is the concentration of the examinated element in the soil and C_b is the content of background values obtained by the iterative-2σ method. Hakanson (1980), defines the categories for C_f as follow: low contamination ($C_f < 1$), moderate contamination ($1 < C_f < 3$),

Table 1
Statistical summary of selected physico-chemical properties for the soil samples of Talcahuano and three depths.

		Sand ($g\ kg^{-1}$)	Silt ($g\ kg^{-1}$)	Clay ($g\ kg^{-1}$)	pH	TC (%)	CEC (cmol kg^{-1})	OC ($g\ kg^{-1}$)
Top soil	Range	338–998	1.9–555	0.03–106	3.95–9.69	0.48–28.3	1.2–70.9	0.37–5.83
TS	AM ± SD	840 ± 120	146 ± 106	13.3 ± 19.6	6.9 ± 0.85	4.57 ± 3.8	13.9 ± 11.8	1.5 ± 1.1
	Median	875	117	4.2	7.0	3.7	10.3	1.5
	CV (%)	14.2	72.0	147	12.3	83.2	84.5	73.3
Sub soil	Range	366–999	0.4–557	0.01–102	3.43–8.53	0.41–26.4	0.92–76.3	0.37–4.61
SS	AM ± SD	840 ± 123	147 ± 111	13.6 ± 18.9	6.9 ± 0.87	4.39 ± 3.81	13.6 ± 11.8	1.27 ± 0.96
	Median	877	119	4.14	7.04	3.26	9.37	0.99
	CV (%)	14.6	75.1	139	12.6	86.8	86.6	75.6
Deep soil	Range	218–996	3.23–771	0.07–71.1	3.22–9.3	0.4–54.24	1.49–48.8	0.37–5.73
DS	AM ± SD	844 ± 143	143 ± 134	13.1 ± 17.3	6.7 ± 1.14	4.02 ± 6.29	11.4 ± 9.67	0.84 ± 0.85
	Median	891	98	4.4	7.0	2.3	7.9	0.5
	CV (%)	17.0	93.8	132	16.9	156.5	84.2	101.2
All samples	Range	218–999	0.4–771	0.01–106	3.22–9.7	0.4–54.2	0.92–76.3	0.37–5.83
	AM ± SD	841 ± 129	146 ± 117	13.4 ± 18.6	6.85 ± 0.96	4.33 ± 4.77	13 ± 0.96	1.2 ± 1.01
	Median	881	110	4.35	7.02	3.12	9.24	0.88
	CV (%)	15.3	80.4	139	14.0	110.2	7.4	84.2

AM = arithmetic mean.
SD = standard deviation.
CV = coefficient of variation.
TC = total carbon.
CEC = cation exchange capacity.
OC = organic carbon.

Table 2
Matrix of Spearman's correlation coefficient for TS, SS and DP in soils of Talcahuano.

		Cu	Pb	Zn	Sand	Silt	Clay	TC	pH	CEC	OC
Topsoil TS	Cu	1									
	Pb	0.280^{**}	1								
	Zn	0.467^{**}	0.424^{**}	1							
	Sand	0.027	-0.204^{*}	0.11	1						
	Silt	−0.005	0.206^{*}	−0.067	-0.992^{**}	1					
	Clay	−0.098	0.139	-0.334^{**}	-0.667^{**}	0.588^{**}	1				
	TC	0.077	0.400^{**}	−0.078	-0.642^{**}	0.636^{**}	0.470^{**}	1			
	pH	0.115	0.1	0.298^{**}	0.351^{**}	-0.318^{**}	-0.416^{**}	-0.249^{**}	1		
	CEC	0.16	0.213^{*}	0.186^{*}	-0.255^{**}	0.278^{**}	0.053	0.305^{**}	0.14	1	
	OC	0.12	0.273^{**}	0.02	-0.385^{**}	0.390^{**}	0.268^{**}	0.689^{**}	-0.167^{*}	0.246^{**}	1
Subsoil SS	Cu	1									
	Pb	0.440^{**}	1								
	Zn	0.537^{**}	0.555^{**}	1							
	Sand	-0.256^{**}	-0.179^{*}	0.01	1						
	Silt	0.273^{**}	0.188^{*}	0.017	-0.996^{**}	1					
	Clay	0.041	0.04	-0.254^{**}	-0.718^{**}	0.662^{**}	1				
	TC	0.210^{*}	0.372^{**}	0.026	-0.702^{**}	0.701^{**}	0.528^{**}	1			
	pH	0.016	0.159	0.262^{**}	0.293^{**}	-0.271^{**}	-0.388^{**}	-0.293^{**}	1		
	CEC	0.156	0.177^{*}	0.158	-0.187^{*}	0.196^{*}	0.08	0.257^{**}	0.152	1	
	OC	0.215^{*}	0.261^{**}	0.019	-0.450^{**}	0.451^{**}	0.345^{**}	0.692^{**}	-0.249^{**}	0.240^{**}	1
Deep soil DS	Cu	1									
	Pb	0.297^{**}	1								
	Zn	0.474^{**}	0.421^{**}	1							
	Sand	-0.342^{**}	-0.340^{**}	−0.052	1						
	Silt	0.362^{**}	0.350^{**}	0.086	-0.997^{**}	1					
	Clay	0.047	0.202^{*}	-0.291^{**}	-0.709^{**}	0.665^{**}	1				
	TC	0.264^{**}	0.585^{**}	0.058	-0.678^{**}	0.666^{**}	0.587^{**}	1			
	pH	0.184^{*}	0.028	0.296^{**}	0.112	−0.085	-0.294^{**}	-0.234^{**}	1		
	CEC	0.324^{**}	0.329^{**}	0.177^{*}	-0.514^{**}	0.527^{**}	0.213^{*}	0.427^{**}	0.05	1	
	OC	0.357^{**}	0.474^{**}	0.158	-0.559^{**}	0.562^{**}	0.425^{**}	0.670^{**}	−0.105	0.467^{**}	1

** Correlation is significant at the level 0.01.

* Correlation is significant at level 0.05.

considerable contamination ($3 < C_f < 6$) and very high contamination factor ($C_f > 6$) (Hakanson, 1980).

One other method used for the determination of trace metal contamination in soils is the Integrated Pollution Index (IPI) and is defined as the average of the contamination factors computed for each. The IPI is divided in 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. Soil properties

A statistical summary of selected physico-chemical properties of the soil samples of Talcahuano at the three sampling depths is presented in Table 1. Spearman rank correlation coefficient results between the analyzed trace metals and selected soil properties also at the three sampling depths are outlined in Table 2.

Table 3
Literature data on published trace elements median concentrations (mg kg^{-1}) in urban soil from various port cities around the world.

City	Cu	Pb	Zn	Reference
Annaba (Algeria)	23.8	42.3	64.7	Maas et al., 2010
Atenas (Grecia)	39	45	98	Argyraki and Kelepertzis, 2014
Baltimore (USA)	35.2	89.3	80.7	Yesilonis et al., 2008
Hong Kong (China)	10.4	70.6	78.1	Lee et al., 2006
Lisbon (Portugal)	29	62	88	Cachada et al., 2013
Naples (Italy)	97	61	99	Albanese et al., 2011
Oslo (Norway)	23.5	33.9	130	Tijhuis et al., 2002
Palermo(Italy)	63	202	138	Manta et al., 2002
Tallin (Estonia)	35	50	114	Bityukova et al., 2000
Galway (Ireland)	27	58	85	Zhang, 2006
Talcahuano (Chile)	23.4	12.5	60.1	This study

The grain size of a particular soil has been commonly accepted as an important factor to evaluate trace metal concentrations in soils (Kabata-Pendias, 2011). Close relationships between soil clay contents and many potentially harmful trace metals have been found in many studies (Kabata-Pendias, 2011). In the studied soils of Talcahuano, the clay size fraction is low and the soils are predominantly composed of sand size fraction (Table 1). Negligible differences were observed between the three sampling depths TS (0–10 cm), SS (10–20 cm) and DS (150 cm). The silt size fraction, characterized with particles with a relatively small grain size and large surface area, was found to be positively correlated with Pb ($p < 0.05$) only in topsoil (TS) depths. However, the silt fraction in subsoil (SS) samples shows significant positive correlation with Cu ($p < 0.01$) and Pb ($p < 0.05$). The deeper soil (DS) samples show a significant correlation with Cu and Pb.

Studies have shown that organic matter, pH and cation exchange capacity (CEC) also have a marked affinity to trace elements controlling the sorption and desorption processes (Kabata-Pendias, 2011). Between 44% and 48% of the Talcahuano soil samples are moderately alkaline (pH between 7.9 and 8.4) at all depths; however more acidic samples were detected. The lowest value was observed in a deep soil (DS) sample associated with a recently constructed highway, and a possible hypothesis is that solid industrial waste material was used as the underlying filler for the base. The large variability of soil pH in the studied urban area is significant. The highest value that was observed in TS is very strongly alkaline. For topsoil (TS) to deep soil (DS) the average pH values generally show a slight decrease. The data distribution of pH of the analyzed soil have a normal distribution fit in topsoil (TS) and subsoil (SS) and shows a significant positively correlation with Zn in topsoil (TS) and Cu and Zn in deepsoil (DS) samples. This is generally expected for urban soils, which usually fall in the alkaline range (Horváth et al., 2015; Lehmann and Stahr, 2007).

The low organic matter contents, greater in the topsoil (TS) fraction, could have an influence in the retention of trace metals, mainly Pb and Zn (Kabata-Pendias, 2011) and also in the low cation exchange capacity

Table 4
Statistical description of Cu, Pb and Zn concentrations (mg kg^{-1}) in soils of Talcahuano.

		AM	SD	CV (%)	Skewness	Min	LQ	Median	UQ	Max	MAD
Top soil	Cu	27.6	17.2	62.2	2.1	4.6	17.1	23.4	32.2	113	7.2
TS	Pb	19.8	26.9	136	3.9	0.3	6.9	12.5	21.0	201	7.2
	Zn	91.7	76.9	83.8	1.6	20.8	44.5	60.1	113	347	19.6
Sub soil	Cu	31.4	32.5	103	4.6	1.0	16.3	23.0	33.7	256	7.5
SS	Pb	18.8	26.2	140	3.4	0.3	5.0	10.8	19.5	184	6.8
	Zn	91.9	91.1	99.0	2.2	19.1	40.1	56.6	82.4	518	17.1
Deep soil	Cu	25.6	17.3	67.6	3.6	5.0	16.1	22.7	30.1	135	6.9
DS	Pb	10.6	18.6	175	4.6	0.3	0.7	4.9	14.6	145	4.5
	Zn	63.1	61.5	97.4	3.3	10.8	32.3	50.0	64.4	384	17.3

AM = arithmetic mean.
SD = standard deviation.
CV = coefficient of variation.
Min = minimum.
LQ = lower quartile.
UQ = upper quartile.
Max = maximum.
MAD = median absolute deviation.

of the soils. A significant positive correlation between Pb and the organic carbon content was found in the three sampling depths. The limited mobility of Pb and strong complexing with organic matter results in the bioaccumulation of this element in humus-rich soil horizons. In general, the soil properties showed a poorly significant correlation with harmful elements, associated with a poor degree of profile development of these soils.

Copper, Pb and Zn show significant positive correlation between them ($p < 0.01$). Copper, Pb and Zn have a significant positive correlation between them ($p < 0.01$) but higher than in TS. Copper, Pb and Zn demonstrate a significant positive correlation between each other ($p < 0.01$) and similar to TS.

Coefficient correlations between Cu, Pb and soil properties are higher in topsoil (TS) and subsoil (SS) samples, suggesting that Cu and Pb may have the same geochemical behavior or a common source.

3.2. Concentration and distribution of potential harmful in typical urban soils

The concentrations of Cu, Pb and Zn in urban soils have been reported for many other port cities in the world including; (Albanese et al., 2011; Argyraki and Kelepertzis, 2014; Bityukova et al., 2000; Cachada et al., 2013; Imperato et al., 2003; Lee et al., 2006; Maas et al., 2010; Manta et al., 2002; Tijhuis et al., 2002; Yesilonis et al., 2008; Zhang, 2006). The wide range of trace metal concentrations reflects different sources, intensity of anthropogenic inputs, and the history of urban development (Cachada et al., 2013; Luo et al., 2012). Differences in analytical and sampling methods, makes it difficult to make any direct comparison between these studies. In comparison with other port cities around the world (Table 3), surface soils (TS) from Talcahuano have comparable and somewhat lower concentrations of Cu, Pb and Zn than most port cities. The low concentrations of these typical anthropogenic elements may reflect the relatively short historical presence of industrial activity in Talcahuano in comparison with other port cities around the world.

Table 5
Statistical summary of Cu, Pb and Zn for each land use category sampled.

		AM	SD	CV (%)	Skew	Min	LQ	Median	UQ	Max
Commercial	Cu	29.6	18.2	61.4	0.8	4.6	15.7	26.7	41.0	74.9
n = 55	Pb	21.8	33.0	151	3.6	0.3	4.4	13.2	20.8	201
	Zn	91.2	77.4	84.8	1.3	21.4	35.2	60.0	127	303
Residential	Cu	25.0	10.0	39.8	0.7	8.9	17.7	23.1	30.4	48.7
n = 62	Pb	18.4	23.5	128	4.4	0.3	8.7	12.3	17.7	162
	Zn	89.2	72.5	81.2	2.0	22.3	46.1	60.2	99.6	333
Industrial	Cu	29.9	27.3	91.3	2.5	8.3	15.9	20.4	29.0	113
n = 23	Pb	19.0	18.8	98.8	2.0	0.3	5.8	16.1	23.6	80.8
	Zn	99.7	89.6	89.9	1.8	20.8	45.8	61.1	106	347

AM = arithmetic mean.
SD = standard deviation.
CV = coefficient of variation.
Min = minimum.
LQ = lower quartile.
UQ = upper quartile.
Max = maximum.

Statistical tendencies of the concentrations of Cu, Pb and Zn determined in topsoil (TS), subsoil (SS) and deep soil (DS) samples are summarized in Table 4. The mean values of the three trace metals were much higher than the median values, indicating the general tendency of a distribution dominated by the outliers. The coefficient of variation (CV%) reflects the degree of variability with respect to the concentrations of a metal in the soil. If the CV ≤ 20%, it shows low variability; 21% ≤ CV ≤ 50% is regarded as a moderate variability; 51% ≤ CV ≤ 100% indicates a high variability; while a CV above 100% is considered as an exceptionally high variability (Karimi Nezhad et al., 2015; Qing et al., 2015). The CV of measured trace metals in the Talcahuano urban topsoils (TS) decrease in the following order Pb > Zn > Cu. In sub soil (SS) samples, the order of the CV was Pb > Cu > Zn, while in deep soil (DS) samples, the order of the CV was similar to topsoil (TS) samples. It is generally regarded that the elements with a smaller CV are dominated by natural sources, while those with a larger CV are more likely to be affected by anthropogenic sources (Manta et al., 2002). From the results of this study, it can be observed that the concentrations of Cu, Pb and Zn decrease with depth. Histograms, box plots and cumulative probability plots are useful tools for estimating the approximate distribution of elements (Bech et al., 2011; Mrvić et al., 2011; Reimann et al., 2005). In the TS, SS, and DS Talcahuano soil samples, the distributions of Cu, Pb and Zn are both asymmetrical and right-skewed, with longer tails at higher concentrations due to the presence of a relatively small fraction of high values. As shown in the boxplots (Figs. 2, 3 and 4), there are a number of outliers in the higher concentration tails, which indicates that the natural concentrations are severely affected by external sources such as controlled and uncontrolled landfills, soil excavation, vehicular traffic

Table 6
Statistical parameters for the soil potentially harmful elements data set (n = 420 samples, mg kg^{-1}) from the Talcahuano port city and the upper limits of "MAD", "upper whisker" and "iterative 2σ-technique" methods.

		Cu	Pb	Zn
Original data set	Mean	28.2	16.4	82.3
	Median	23.1	10.2	56.7
	SD	23.5	24.5	78.4
Median + 2MAD	Upper limit	36.5	13.9	84.6
Upper whisker method	Upper limit	51	35.4	113
Iterative 2σ-technique	Upper limit	43.7	17.5	91.7

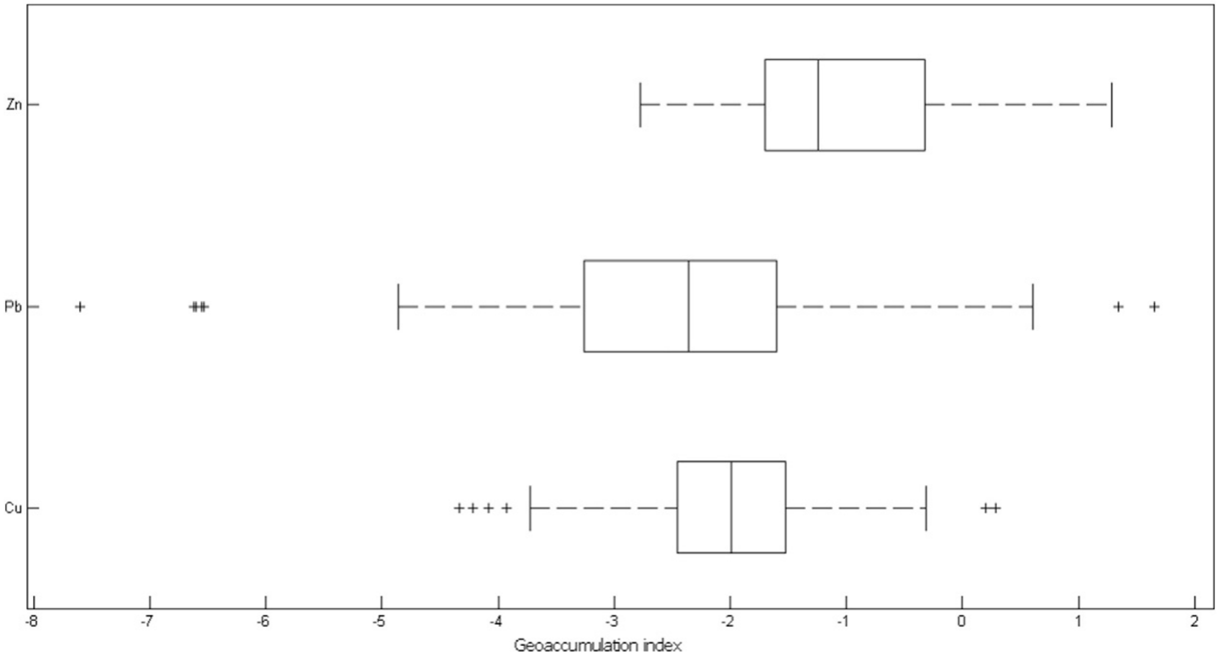

Fig. 5. Indexes of geoaccumulation for Cu, Pb and Zn in soils of Talcahuano City.

emissions, transport and redistribution. Frequently, the upper soils are directly influenced by human activities and contain most input of anthropogenic contaminants, and their concentrations decrease with depth. A paired Wilcoxon test was conducted on the soils from different sampling depths such as TS/SS and SS/DS, and assuming that the two depths belong to the same population as the null hypothesis. The test was conducted using a 95% confidence interval. Results obtained were as follows: Cu TS/SS (0.6), SS/DS (0.23); Pb TS/SS (0.07) and Zn TS/SS (0.08). The null hypothesis could not be rejected, implying that the trace metal concentrations from the two sample layers can be considered as belonging to the same population or, in other terms, the trace metal concentrations do not appear to accumulate in the surface layer and thus the nature of the underlying material (i.e. uncontrolled landfill site residue) may have a greater influence. For the trace metals Pb, SS/DS (0.00) and Zn SS/DS (0.00), differences were found in the two layers and are observed to decrease with depth.

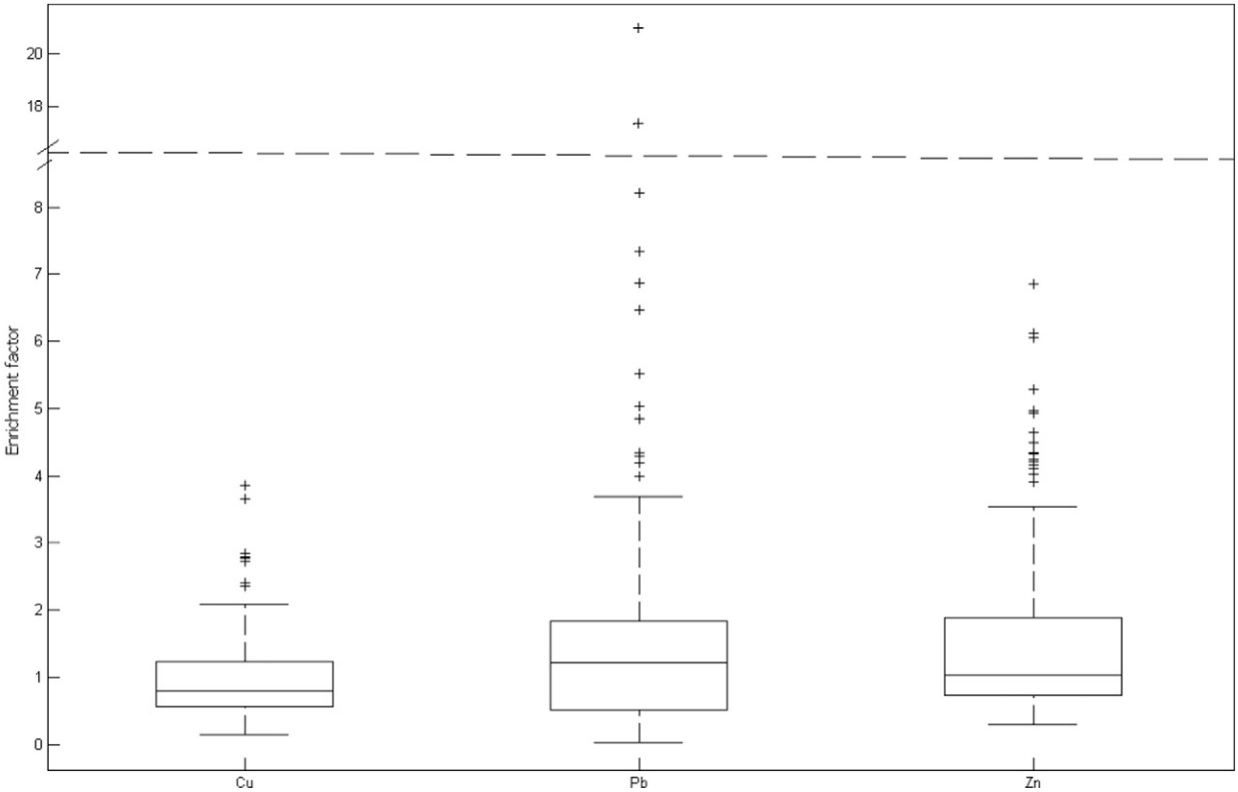

Fig. 6. Enrichment factors for Cu, Pb and Zn in soils of Talcahuano City.

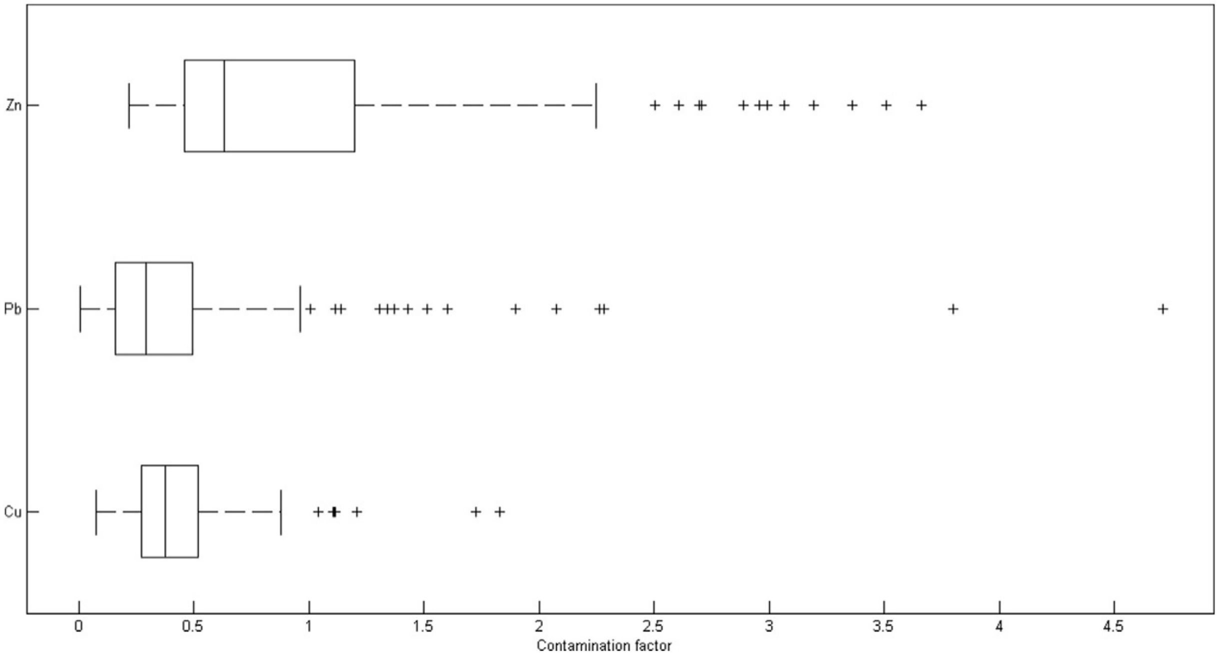

Fig. 7. Contamination factors of Cu, Pb and Zn in soils of Talcahuano City.

3.3. Relationship with different land uses

Differences in land use patterns, the intensity of human activities, the contamination history, and the distance to emission sources all may affect soil contamination to a different degree. In this study, the sampling site of each sample was cataloged into one of three possible land use including commercial, CO, residential, RE and industrial, IN. The selection of these land uses was based on the assumption that each might be differently influenced by urban activities.

In terms of trace metal concentrations, Cu and Zn decrease in the order of IN > CO > RE and Pb decreased in the order of CO > IN > RE (Table 5). These trends reflect the strong influence of industrial activities and traffic emission on trace metal concentrations in urban soils, suggesting that deposition of airborne dust particles, the waste from various industrial activities and vehicle emissions may be the main source for of trace metal contamination in urban soils of Talcahuano. For the soil samples cataloged under commercial use, the infilling of the area prior to construction may have increased the concentration of trace metals in these areas. The use of industrial solid waste residue as landfill material or as a base for the construction of roadways, increases trace metal contamination.

These results clearly show that anthropogenic activities associated with various land uses contribute to the accumulation of potentially harmful elements in the soils of Talcahuano (Acosta et al., 2011). Similar results were found in Hangzhou (Lu and Bai, 2010), Pakistan (Ali and Malik, 2011), Sevilla (Ruiz-Cortes et al., 2005),

3.4. Background values and assessment of potential pollution

The upper limits of the 'MAD', 'upper whisker' and 'iterative-2σ technique' method values are tabulated in Table 6. Values from median + 2MAD procedure gave the lowest background limit; followed by the iterative 2σ-technique, while the upper whisker method produced the highest background limits. In this study, it was decided to use the iterative 2σ-technique because in other published studies where different statistical techniques were used to evaluate the geochemical background ranges (Matschullat et al., 2000; Reimann et al., 2005), the iterative 2σ-technique was found to be the most plausible and realistic (Galuszka et al., 2015; Matschullat et al., 2000).

The extend of trace metal pollution was assessed using the geoaccumulation index (I_{geo}), the enrichment factor (EF), the contamination factor (C_f), and the integrated pollution index (IPI). All of these soil contamination indicators were calculated with respect to local background values established by the iterative 2σ-technique.

The results of the geoaccumulation index (I_{geo}) in topsoils (TS) of Talcahuano are represented in Fig. 5. The I_{geo} ranges from −4.3 to 0.3 for Cu with a mean value of −1.8; Pb ranges from −7.6 to 1.7 with a mean value of −2.6 and for Zn the range is between −2.8 and 1.3 with a mean value of −1.0. Pb. Moderately contaminated ($1 < I_{geo} \leq 2$) values were observed for Pb (2 samples) and Zn (5 samples). For Cu, Pb and Zn, no samples has an I_{geo} higher than 2.

Enrichment factor (EF) values for the topsoils (TS) of Talcahuano are plotted in Fig. 6. The EF ranges from 0.15 to 3.9 for Cu with a mean value of 1.0; 0.02 to 20.8 for Pb with a mean value of 1.8 and 0.29 to 6.9 with a mean value of 1.6 for Zn. One sample of Pb yield a very high enrichment ($20 < EF < 40$); meanwhile 7 Pb samples and 5 Zn samples show significant enrichment ($5 < EF < 20$). Copper (10 samples), Pb (21 samples) and Zn (28 samples) show moderate enrichment ($2 < EF < 5$).

Contamination factor (C_f) values in topsoils (TS) of Talcahuano are shown in Fig. 7. The C_f for Pb exhibited the highest variation, ranging from 0.01 to 4.7, with an average of 0.49 and a median of 0.28. For Cu, the C_f ranges from 0.07 to 1.8 with a mean value of 0.45, while Zn has a range of 0.2 to 3.7 with a mean value of 0.97 for Zn. Lead (2 samples) and Zn (5 samples) show considerable contamination ($3 < C_f < 6$). A moderate contamination ($1 < C_f < 3$) can be found in Cu (7 samples), Pb (13 samples) and Zn (34 samples). These data indicate that Cu, Pb and Zn contamination is extended in some TS samples of Talcahuano.

The integrated pollution index (IPI, mean of C_f) of the database show 2 samples with values ranked as high pollution level ($2 < IPI < 5$), and 19 samples with moderate pollution levels ($1 < IPI < 2$).

Of the various methods analyzed, the EF index shows the most samples with enrichment. Reimann and de Caritat, 2005, demonstrated that this index cannot be used as rigorous, objective, or sensitive tool to detect or prove anthropogenic impact on the environment. Case studies from regional geochemical surveys demonstrate that EFs can be high or low due to a multitude of reasons, of which contamination is but one (Galán et al., 2014; Reimann and de Caritat, 2005; Reimann et al., 2005).

3.5. Spatial distribution of Cu, Pb and Zn in soils of Talcahuano

All the available and generated information was integrated in a geographical information system (GIS) using ArcMap v.10.2 (ArcGIS). Geochemical maps were plotted to visualize the spatial distribution of Cu, Pb and Zn in soils of Talcahuano (Fig. 8a, b and c). The legend of the maps consists of the six classes based in the boxplot analysis and represent the 5th, 25th, 50th, 75th, and 95th percentiles of the data distribution. The distribution of Cu in topsoils (TS) displays a spatial pattern extending along the major roadway environments and emission sources. The spatial distribution of Cu in subsoil (SS) samples displays a similar pattern to topsoil (TS) samples but in certain locations shows

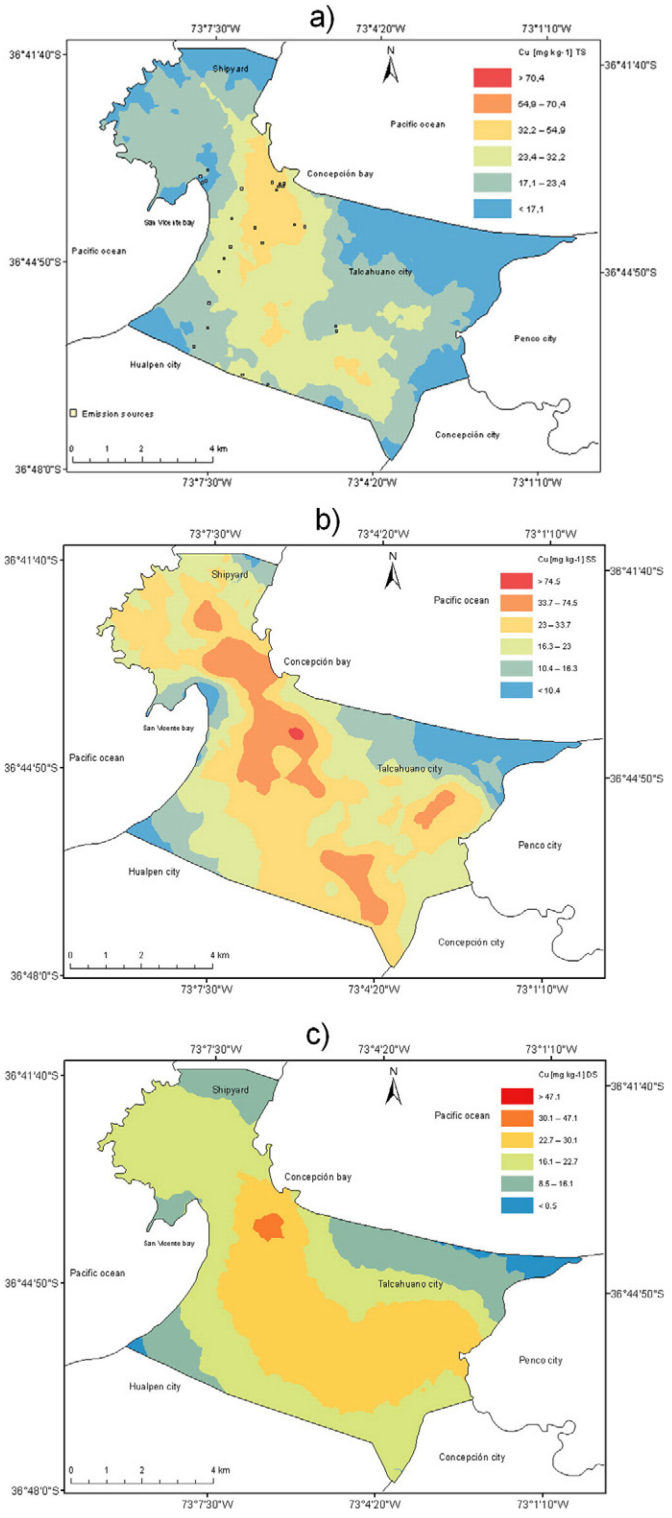

Fig. 8. a. Geochemical maps showing the spatial distribution of Cu in a) TS, b) SS y c) DS of Talcahuano. b. Geochemical maps showing the spatial distribution of Pb in a) TS, b) SS and c) DS of Talcahuano. c. Geochemical maps showing the spatial distribution of Zn in a) TS, b) SS and c) DS in soils of Talcahuano.

B

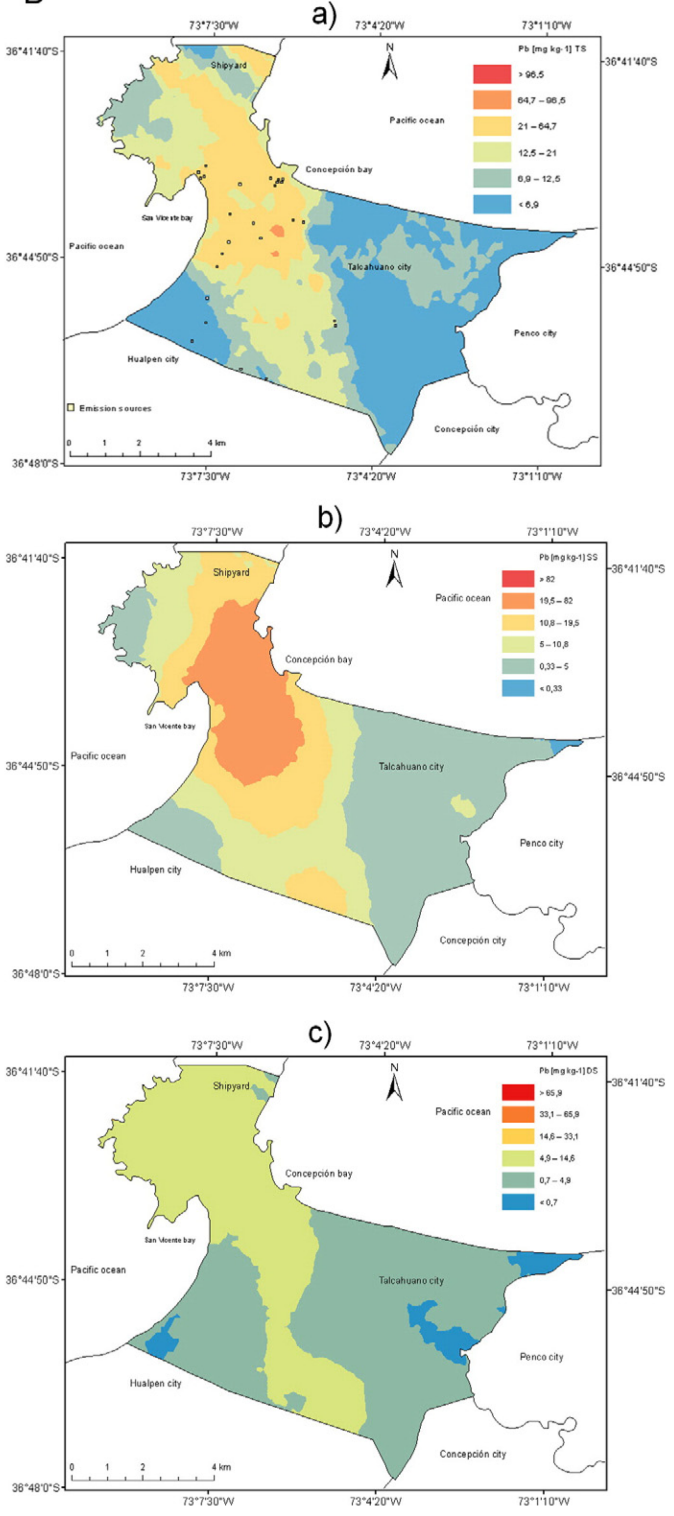

Fig. 8 (*continued*).

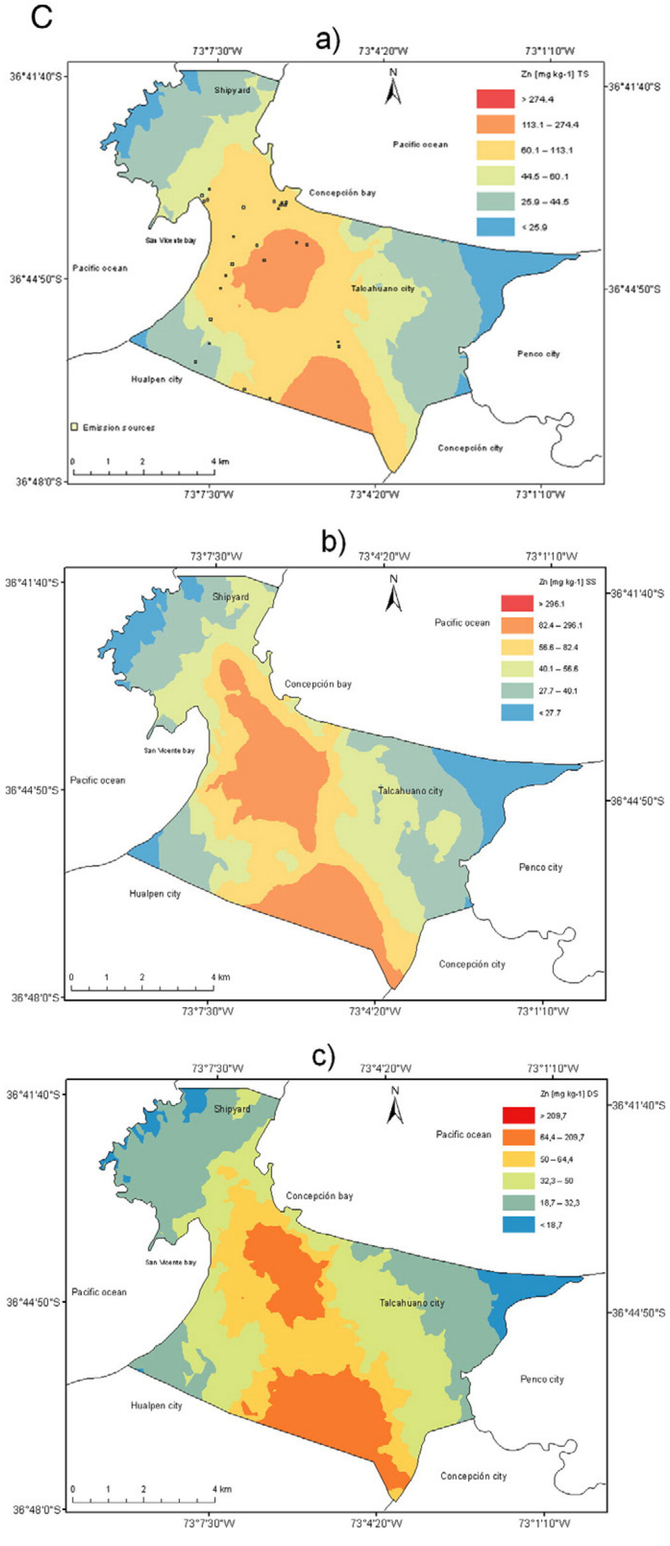

Fig. 8 (*continued*).

higher concentrations than topsoil (TS) samples. Over the years, many sectors within the city of Talcahuano have been subjected to uncontrolled landfill with both construction debris (e.g. concrete) and/or industrial solid waste which are represented by the orange/red colored areas on the map. Because of the uncontrolled nature of many of these landfill sites there are no records of the location, size, contents and distribution of these clandestine sites. The spatial distribution of Cu in deep soil (DS) samples displays a homogeneous pattern, however in some places, high concentrations have been noted. The spatial distribution of Pb in topsoil (TS) samples displays a spatial relationship extending along the principal roadways and emission sources. The spatial distribution of Pb in subsoil (SS) samples and deep soil (DS) samples displays a homogeneous pattern with lower concentrations than topsoil (TS) samples. The spatial distribution of Zn in TS, SS and DS displays a similar pattern to Cu in the three depths.

4. Conclusions

It was determined that the major factors controlling the variability of Cu, Pb and Zn concentrations in surface soils was the proximity of major roadways, emission sources and uncontrolled landfill sites. The background values estimated with the iterative 2σ-technique was 43.7, 17.5 and 91.7 mg kg^{-1} for Cu, Pb and Zn respectively. The geochemical index, enrichment factor and the contamination factor calculations registered a moderate to high contamination in some of the soil samples within the study area.

Acknowledgments

This research was supported by a FONDECYT grant 1130366.

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