

# Metal concentrations and source identification in Chilean public children's playgrounds

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**Abstract** This study is focused on four Biobio region cities, Concepción, Talcahuano, Los Ángeles, and Tomé; these cities flourished very close to different industrial activities. We determined a pseudo total concentration of seven heavy metals (Cr, Ni, Cu, Zn, As, Cd, and Pb) in playground soils through inductively coupled plasma-mass spectrometry (ICP-MS). Principal components

analysis (PCA) revealed that contamination in soils comes from three principal sources. Firstly, industrial and burning activities; secondly, the use of phytosanitary and chemical products; and thirdly, vehicular traffic emissions. Zn and Cu are the most abundant analyzed elements in all the playground's soils. Concepción reflected the lowest values of pollutants and Talcahuano the highest, reflecting the industrial effects. The average values of the analyzed elements were Cr = 32.90 mg kg<sup>-1</sup>; Ni = 23.76 mg kg<sup>-1</sup>; Cu = 31.51 mg kg<sup>-1</sup>; Zn = 63.69 mg kg<sup>-1</sup>; As = 19.51 mg kg<sup>-1</sup>; Cd = 0.50 mg kg<sup>-1</sup>; and Pb = 17.59 mg kg<sup>-1</sup>. Anomalously high values of some elements were found Cu = 462.73 mg kg<sup>-1</sup>, Zn = 364.39 mg kg<sup>-1</sup>, As = 34.7 mg kg<sup>-1</sup> in Talcahuano, Cd = 1.6 mg kg<sup>-1</sup> in Tome, and Pb = 55.59 mg kg<sup>-1</sup> in Los Ángeles. Nevertheless, according to international guideline values of pollutants (VROM 2000 and ADEC 2010) there is no risk for children in any playground studied but all playgrounds are a potential risk for the environment. It points out the necessity to continue studying and monitoring Chilean urban playground to prevent health problems in the population.

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## Introduction

Soil metal content originates from three primary sources: bedrock lithology, pedogenic soil processes, and anthropogenic sources (Kabata-Pendias 2001; Tume et al. 2008,

2014). The latter is well connected with the rapid industrial development in urban areas where soil acts as a long-time receiver and source of pollution.

The United Nations (2014) in the World Urbanization Prospect stated “The continuing urbanization and overall growth of the world’s population is projected to add 2.5 billion people to the urban population by 2050” so sustainable development challenges will be increasingly concentrated in cities, particularly in the lower-middle-income countries where the pace of urbanization is fastest. In the last 50 years in Chile, and specifically in the Concepción region, the total population grew by 33%. The urban population grew by 15%, which implies a massive urbanization close to industrial areas where people moved.

The main sources of anthropogenic metals in urban playground soils are industry, domestic heating, vehicular traffic, treated wood structures, and weed-killers (Guney et al. 2010; Cookson 2008; Szolnoki et al. 2013). The impact of anthropogenic metal enrichment in rural, periurban, and urban populations has been widely studied all around the world, particularly in 14 countries in Latin America (Bundschuh et al. 2012), urban areas in Europe (Birke and Rauch 2000; Guney et al. 2010; Szolnoki et al. 2013; Li et al. 2014), Asia (Wang et al. 2012; Chen et al. 2005; Li et al. 2001), and Oceania (Gulson et al. 2006; Taylor et al. 2013). Thus, the emission of airborne metals and their deposition and accumulation in urban soils are considered a public health risk, specially in playground areas and parks.

Children are more vulnerable to the toxic effects of metals than adults and also are more likely to unintentionally ingest soil matter by putting dirty hands and objects in their mouths or by deliberately eating earth (Moya et al. 2004; Ljung et al. 2006a, 2007; De Miguel et al. 2007; Guney et al. 2010; U.S. EPA 2011; Morrison et al. 2012). A large number of studies has focused on the study of children exposure during games in public and schools playgrounds, evaluating potential health effects and assessing risks (De Miguel et al. 2007; Guney et al. 2010; Figueiredo et al. 2011; Mostert et al. 2012; Taylor et al. 2013; Reis et al. 2014). In Chile, soil pollution studies are concentrated in the northern mining regions (Oyarzún et al. 2004 and 2006; De Gregori et al. 2003), and the central area of Chile (Romero et al. 2003; Ginocchio et al. 2004; Narváez et al. 2007; Aguilar et al. 2011; Parra et al. 2014). To date, only two urban soil studies from southern Chile have been published (Tume et al. 2008, 2014).

The Biobio region in southern Chile suffers from heavy pollution in and around the main cities (Díaz et al. 2018):

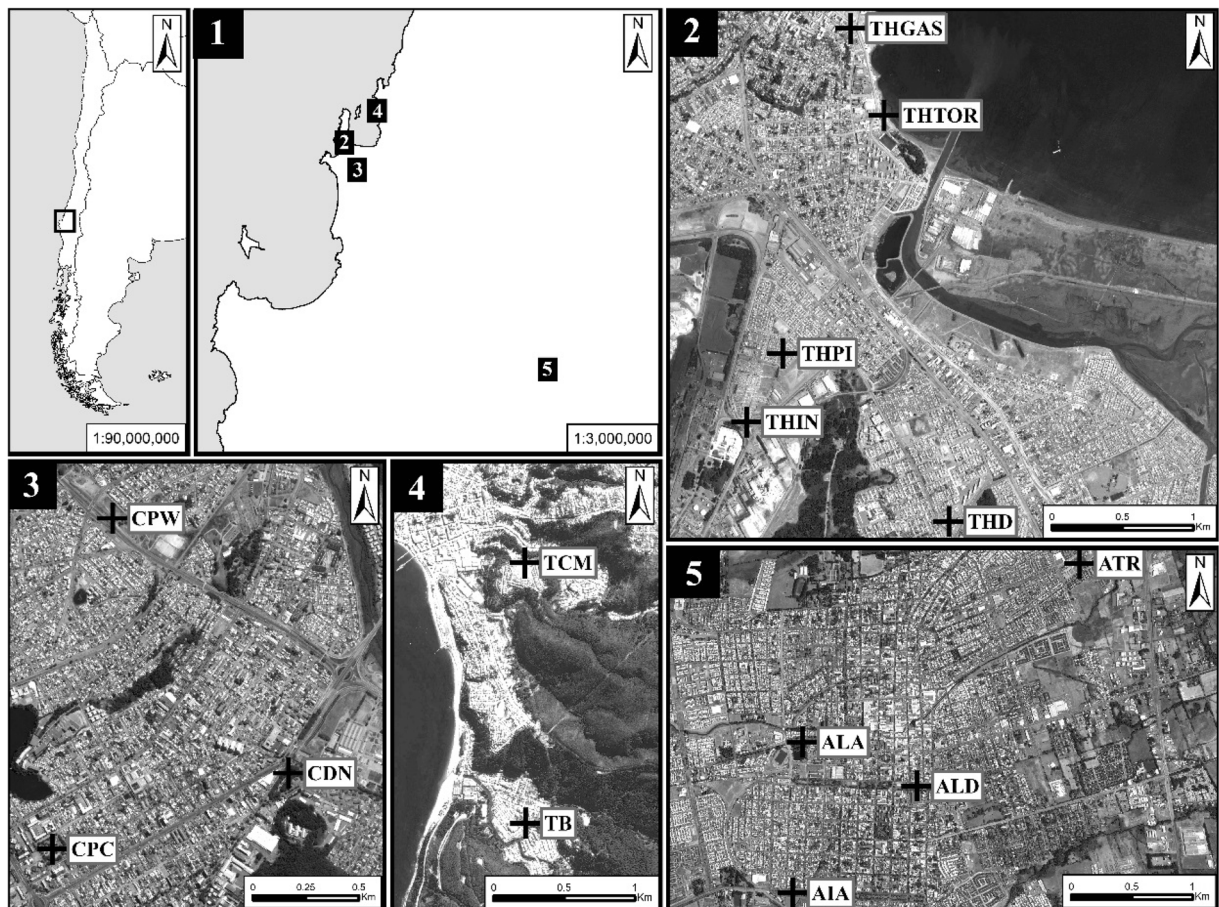
Talcahuano is surrounded by a steel factory, industries linked to steel production, metalworking industry, a cement factory, and a petrochemical complex. In the city of Los Angeles, there are large furniture and industrial complexes as well as agriculture and food processing industries. Tomé hosts a historical textile industry within the city, whereas Concepción is a university and residential city that acts as a leisure and services center for the Biobio region.

## Material and methods

### Study area

The study was conducted in the Biobio region (VIII Region) mainly in the so-called “Greater Concepcion” (pop. 1.083.043) which includes, among other cities, Concepción (population 217,322), Talcahuano (pop. 163,628), and Tomé (pop. 54,770) area and Los Ángeles city (pop. 166,556) (Fig. 1). Research was focused on four cities: Concepción (population 217,322), Los Ángeles (pop. 166,556), Talcahuano (pop. 163,628), and Tomé (pop. 54,770). Research was focused on 13 public parks located in different areas of the towns (downtown, residential, and industrial areas) were studied (Table 1). These parks and playground areas were selected according to the high possibility for children to come into contact with soil and for the presence of playing structures made of metal or plastic.

The study focused on towns that are close to important industrial areas. Since the late XIX century, the Biobio urban area has gone through a growing industrial development and human occupation, which led to a considerable loss of green areas. The Great Concepción area is one of the most important industrial centers of the country, featuring fisheries, forestry, iron and steel industries, a refinery, textile, and cement manufacturing. These industries emit an important amount of polluting metals (e.g., Cd, Hg, Zn, Pb, Cu, Cr, Ni, and Co. (Pacyna and Pacyna 2001)), which are deposited onto the soil. Furthermore, many sectors of the studied towns have been subjected to uncontrolled landfilling including urban and industrial waste (Tume et al. 2014). These landfills are a potential source of contamination and must be taken into account, even though there may be no official record of these sites due to their uncontrolled nature. The natural soil types of the area have been transformed to different degrees. Technosols (FAO 2006) are predominant in city centers, while natural soils prevail around the city. However,



**Fig. 1** Sampling point distribution in four urban areas of Biobío Region. (1) View location; (2) Talcahuano; (3) Concepción; (4) Tomé; (5) Los Ángeles

**Table 1** Code and geographic coordinate of the sampled packs from Tomé, Concepción, Los Ángeles, and Talcahuano cities

City	Code	Latitude	Longitude
Tomé	TB	36° 38' 13" S	72° 57' 05" W
Tomé	TCM	36° 37' 07" S	72° 57' 08" W
Concepción	CPW	36° 48' 14" S	73° 02' 22" W
Concepción	CPC	36° 49' 03" S	73° 02' 27" W
Concepción	CDN	36° 48' 6" S	73° 01' 53" W
Los Ángeles	AIA	37° 28' 51" S	72° 21' 39" W
Los Ángeles	ALA	37° 28' 09" S	72° 21' 32" W
Los Ángeles	ALD	37° 2' 21" S	72° 20' 57" W
Los Ángeles	ATR	37° 27' 22" S	72° 20' 03" W
Talcahuano	THD	36° 44' 49" S	73° 06' 13" W
Talcahuano	THPI	36° 44' 09" S	73° 06' 9" W
Talcahuano	THTOR	36° 43' 15" S	73° 06' 27" W
Talcahuano	THGAS	36° 42' 55" S	73° 06' 36" W

because of the lack of soil edaphologic cartography of the area, there is no information about natural soil type.

The climate of the studied area is Mediterranean with a dry season from September to May (Meteorological Service of Chile). Due to the proximity of the sea, daily and annual temperature variability is dampened. The mean annual temperature is 12.7 °C. The warmest month is January with 22.8 °C and the coolest is July with 10.5 °C. Mean annual precipitation is 1.100 mm with June and July being the rainiest months (218.2 mm and 222.1 mm, respectively). The prevailing winds come from the north during winter and from the southwest during the rest of the year (Meteorological Service of Chile).

### Soil samples

To assess contamination levels and soil properties, soil samples were manually collected with a flat

**Table 2** Analytical results of certified reference material (Sandy Loam Soil, 710375067 VHG Labs)

Elements	Certified values and uncertainty (mg/kg)	Measured concentration (mg/kg)	Mean recovery (%)
Cr	10.7 ± 1.03	9.8 ± 0.6	91.5
Ni	12.6 ± 0.893	10.6 ± 0.4	84.1
Cu	4790 ± 216	4407.1 ± 835	92.0
Zn	546 ± 16.8	481.0 ± 17.8	88.1
As	24.8 ± 2.46	24.7 ± 7.6	99.6
Cd	1.2 ± 0.0893	1.3 ± 0.13	109.1

polyethylene instrument. Sampling instruments were cleaned with deionized water after each operation to avoid possible cross-contamination between samples. Surface soils were collected at a depth of 0–5 cm. Each sample consisted of 500 g of soil. The samples were placed in plastic zip-lock bags after sampling.

Superficial soil samples from ten playgrounds in Concepcion, Talcahuano, Los Ángeles, and Tomé were collected. Five sampling sites with different degrees of contamination were chosen according to the following selection criteria: exposed soil, availability of equipment such as swing and slides, and distance to road traffic.

#### Soil analysis

The collected samples were air dried at room temperature, sieved in a nylon sieve (<2 mm), and then stored in a cupboard and preserved until analysis. Samples were homogenized and quartered and then grinded using an agate mortar in order to obtain a fine homogeneous powder (< 0.25 mm). Soil pH was measured in soil water according to a standard method (ASTM D 4972-01) with a 1:2.5 soil/water suspension using a PL-700PC, Lab-Tec with a glass electrode. Organic matter content (OM) was determined using the Walkley-Black dichromate acid oxidation method, and the pipette method was used to determine the particle size distribution (MAPA 1994). The pseudo total of metals in soils were established by inductively coupled plasma-mass spectrometry (ICP-MS) in a Bruker Aurora M90 using Aqua regia extracts (3 HCl: 1 HNO<sub>3</sub>) in soil samples < 0.25 mm fraction size because it represents the fraction more likely to adhere to children's hands (U.S EPA 2011). All the laboratory apparatuses used were cleaned with 5% (v/v) HNO<sub>3</sub> and then rinsed with deionized water. All reagents used were of analytical grade or equivalent and free from any contaminants that may have interfered with the analysis. The digestion of samples (0.25 g) was carried out in closed vessels in a microwave

oven (Mars Express, CEM Corporation, Program US EPA 3051). Stock standard solution (Multi-element Calibration Standard 2. Bruker) was used to obtain calibration curves. Blank samples were also analyzed to ensure that there was no contamination from sample collection, transportation, storage, and analytical procedures. Selected samples were duplicated in order to test the precision of the analyzing techniques. Also, accuracy and precision of the results were verified by the analysis of the reference materials Soil (CRM Sandy Loam Soil, VHG).

#### Analytical quality control

Certified standard reference samples (Sandy Loam Soil, 710375067 VHG Labs) were digested and assayed using the analytical protocol for the real samples in order to ensure the reliability of the results; the results obtained are presented in Table 2. Because Pb is not included in the reference material, we included in our analysis an internal standard solution sample (Custom Standards, NIST SRMs, VHG Labs) to control Pb results. The percentage of recovery was between 84 and 109% for all the elements, showing that the analytical methodology is operating properly for the analysis of real soil samples. Blank samples were also analyzed to ensure that there was no contamination derived from the analytical procedure. Finally, 20% of samples were duplicated in order to test the precision of the analytical technique (RSD < 10%). Calibration standards were prepared from multielemental stock solutions (Custom Standards, NIST SRMs, VHG Labs).

#### Identification of contaminated samples

Two extreme values of Cu and Zn were removed both from the AIA playground (Cu = 1274 ppm and Zn = 418.3 ppm) because they are extreme outliers from a statistical point of view. The rest of the data was

approximately log-normally distributed ([Supplementary material](#), sample AIA003).

To understand heavy metal contamination and the corresponding risk to human health, it is crucial to compare the content of heavy metal in soil and guideline values. However, in Chile, there are no soil guideline values of pollutants and different land use types. We used the Dutch soil Guidelines (VROM 2000) and the Australian Department of Environmental Conservation (ADEC 2010) to establish reference values and intervention values.

In VROM guidelines, the target values (TV) indicate the level at which there is a sustainable soil quality and that gives an indication of the benchmark for environmental quality in the long term on the assumption of negligible risks to the ecosystem. The soil remediation intervention values (IV) indicate when the functional properties of the soil for humans, plant, and animal life, are seriously impaired or threatened. They are representative of the level of contamination above in which there is a serious case of soil contamination. The TV and IV for soil metals depend on the concentration of organic substances and clay. To assess the soil quality, the standard soil values were converted for the studied soil based on the measured organic matter and clay content using the following soil type correction formula (Eq. 1) (VROM 2000).

$$\begin{aligned}
 (SW, IW)_b &= (SW, IW)_{sb} \times (A + (B \times \text{clay}\%)) \\
 &+ \left( C \times (OM\%) / A + (B \times 25) \right) \\
 &+ (C \times 10) \tag{1}
 \end{aligned}$$

in which:

- (SW,IW)<sub>b</sub> target value or intervention value for standard soil to be assessed.
- (SW,IW)<sub>sb</sub> target value or intervention value for standard soil.
- Clay % measured percentage clay (grain size < 2 μm) in the soil to be assessed.
- OM % measured percentage organic matter (OM) in the soil to be assessed.
- A, B, C substance dependent constants for trace elements.

In the case of ADEC, the Ecological Intervention Level (EILs) are only intended to be used in the context of an initial screening risk assessment to determine

whether concentrations of substances in soil at a site pose a potential risk to the environment or relevant environmental values. The health investigation levels (HILs) are primarily based on the health-based soil investigation levels.

## Results and discussion

### Soil properties

Sandy soils were the rule in this study but there are significant differences between playground park soils. The Median (Me) and median Absolute Deviation (MAD) as a measure of dispersion of the texture, pH and organic matter are reported in Table 3 (for more information, see [supplementary material](#)). Sandy soils were the rule in this study but there are significant differences between playground park soils. Based on the pH, soil samples can be classified as neutral-alkaline to moderately alkaline (pH between 6.8 and 8.4, with a mean of 7.3). THD and THPI playgrounds had a higher pH due to the influence of carbonate dust produced in the concrete factory in Talcahuano. Organic matter contents are very low. The mean value is 1.35% and the range between 0.39 and 2.9%, so the possible retention of trace elements and metals should be very low in most of the soils. The organic matter content in Talcahuano soils was the lowest, in relation to the absence of grass and trees in and around the playgrounds, while the remaining categories had closer organic matter contents.

Different soil properties such as clay composition, OM content, and pH may have an effect on the natural element concentrations in soils (Amorosi et al. 2014; Benedetti et al. 1996; Kabata-Pendias and Pendias 1999). However, the analysis of correlation between the soil characteristics and the abundance of the analyzed metals (Table 4) indicated no relationship between these values with the exception of Zn, which has a significant correlation with pH probably due to the proximity of some soils to the industrial area of Talcahuano. Correlation results agree with the lack of a common geochemical background of the soils due to the artificial origin of most of the playgrounds in the cities. Therefore, main trace metal contents ought to be independent of the heritage from the rock and edaphogenetic processes and we assumed an anthropogenic trace element origin for these elements.

**Table 3** Mean standard deviation and ranges for the analyzed properties of the playground soil

	Tomé (T) <i>n</i> = 10		Talcahuano (TH) <i>n</i> = 12		Concepción (C) <i>n</i> = 15		Los Ángeles (A) <i>n</i> = 15		Median <i>n</i> = 52
	Median	MAD	Median	MAD	Median	MAD	Median	MAD	
OM %	2.2	0.9	0.7	0.2	1.6	0.4	1.7	0.7	1.17
pH	7.1	0.4	7.8	0.5	7.1	0.3	7.2	0.5	7.29
Clay %	2.9	2.7	13.8	18.1	9.6	5.1	5.7	2.5	7.61
Lime %	4.8	5.4	13.9	15.9	12.9	5.0	9.0	3.0	9.42
Sand %	92.4	8.1	72.7	33.9	76.1	10.1	82.5	5.4	83.83

T, Tomé; TH, Talcahuano; C, Concepción; A, Los Ángeles

The high significant correlation between Cu-Zn (0.499), Cu-Cd (0.592), Cu-Cr (0.749), and Cr-Cd (0.501) suggests that these metals may originate from a common fossil fuel combustion source like industry and traffic. This relationship between traffic and/or industrial activities and trace heavy metal concentrations is consistent with previous studies (Buekers et al. 2015; Tume et al. 2014; Kumpiene et al. 2011; Li et al. 2001; Pacyna and Pacyna 2001).

#### Metal concentrations and comparison with published data

Univariate descriptive statistics for the total concentrations of Cr, Ni, Cu, Zn, As, Cd, and Pb are presented in Table 5. The analyzed data were close to bibliographic data in global and Chilean soils (Adriano 1986; Alloway 1993; Kabata-Pendias 1995; INIA 1990). The total content of metals does not allow determining its origin, but it is possible to identify the normal concentration ranges of those that are anomalous due to geochemical or anthropogenic causes. Anomalously high values of some elements were found in certain sites: Cu = 462.73 mg kg<sup>-1</sup>, Zn = 364.39 mg kg<sup>-1</sup>, As = 34.7 mg kg<sup>-1</sup> in Talcahuano, Cd = 1.6 mg kg<sup>-1</sup> in Tome, and Pb = 55.59 mg kg<sup>-1</sup> in Los Ángeles (supplementary material). For these values, an anthropogenic origin is unambiguous, but as reflected, the difference between mean and median and the variability of MAD for Pb in all cities, Cu, Zn in Talcahuano, and Cd in Tome, the existence of sources for these elements in this study are ruled out due to certain anthropogenic local additions.

We compared soil concentration of the elements with previously reported values (Massas et al. 2010; De Miguel et al. 2007; Ljung et al. 2006b; Kumpiene et al. 2011; Tume et al. 2014, 2008; Figueiredo et al.

2011; Guney et al. 2010) found specifically in playground around the world (Table 6). The mean concentrations measured in different soils from Biobio were higher than the values reported in other world cities (62 mg kg<sup>-1</sup> Cu > Massas et al. 2010; De Miguel et al. 2007; Ljung et al. 2006b; Kumpiene et al. 2011; Guney et al. 2010), (23.5 mg kg<sup>-1</sup> As > De Miguel et al. 2007; Ljung et al. 2006b; Figueiredo et al. 2011, Guney et al. 2010), (0.4 mg kg<sup>-1</sup> Cd > De Miguel et al. 2007; Ljung et al. 2006b). This suggests the impact produced in Biobio cities by their proximity to important industrial areas and by the widespread local custom to burn wood and coal in residential stoves (Pacyna and Pacyna 2001; Albanese et al. 2007; Akinola et al. 2008; Tchounwou et al. 2012; Salmanighabeshi et al. 2015., Maenhaut et al. 2016). Also, another important natural source of As in Chile are the large volcanic eruptions (Ajmone-Marsan and Biasioli 2010; Hong et al. 2012).

In this study, Talcahuano reflected the highest values of pollutants and Concepción the lowest ones. Unlike the other cities, Concepción is an academic and service city without an industrial area. The source of anthropic trace metals in Concepción playgrounds should be the vehicular emissions, stove combustion, and treatments for structures and herbicides. Nevertheless, taking into account the proximity between them and the dominant northwesterly winds in winter from Talcahuano to Concepción industrial pollutants could also reach Concepción.

Nothing has been reported to date on the concentration of heavy metals in Tomé, Concepción and Los Ángeles soils. Only previous studies in Talcahuano were found which are consistent with data obtained in this study (Tume et al. 2008, 2014). These studies in schoolyard soils from Talcahuano showed higher concentrations of Cr, Ni, Zn, Pb (mean = 26, 26.8, 227, 25.7 mg kg<sup>-1</sup> respectively) (Tume et al. 2008), and

**Table 4** Spearman correlation coefficients between soil characteristics and trace metals concentration

	Cr	Ni	Cu	Zn	As	Cd	Pb
OM %	0.346	0.093	0.275	-0.346	0.176	0.231	0.280
pH	-0.115	0.269	0.066	<i>0.500</i>	-0.440	-0.066	-0.022
Clay %	-0.379	-0.115	-0.346	0.412	0.049	-0.418	-0.198
Silt %	-0.308	-0.033	-0.215	<i>0.615</i>	0.104	-0.291	0.011
Sand %	0.335	0.093	0.308	-0.473	-0.060	0.390	0.176
Cr	1.000	0.367	<i>0.749</i>	<i>0.485</i>	0.122	<i>0.501</i>	0.186
Ni		1.000	<i>0.639</i>	0.280	-0.007	0.434	0.247
Cu			1.000	<i>0.499</i>	0.220	<i>0.592</i>	0.415
Zn				1.000	0.136	0.300	0.371
As					1.000	0.147	-0.003
Cd						1.000	0.312
Pb							1.000

Italic numbers indicate significant correlation

lower for Cu and As (mean = 40, 6 mg kg<sup>-1</sup> respectively) (Tume et al. 2014).

Guideline values

The VROM (TV, EILs) and ADEC (IV, HILs) regulation levels have been selected here and compared with the studied soil value in order to assess the environmental and health risk of trace elements in the playground of four cities of Biobio Region (Table 7).

According to the VROM, the most demanding screening assessment levels, all studied playgrounds were considered a potential risk to the environment for most of the

studied metals and risky for some of them, markedly in case of As and Cd. Playground THPI and THGAS resulted potentially risked to the health (especially for Cr, Ni, and Zn) may be evidence of the closeness to the industrial area and gas station respectively. These values are considered the threshold for attention, and further investigation should be carried out to determine whether the present levels are likely to pose an actual risk in the site-specific settings; this may lead to the need to apply minor restrictions on their use.

With the exception of THPI which has higher values of Cu and Zn, the comparison with ADEC regulation values showed soils with light environmental risk for all

**Table 5** Descriptive statistics for the dry weight total concentrations of the studied metals in the playground soils of Biobio Region

Location		Cr	Ni	Cu	Zn	As	Cd	Pb
Talcahuano (n = 12)	Median	17.76	16.01	25.03	92.15	25.12	0.42	10.95
	Mean	18.46	19.11	62.04	134.40	23.52	0.39	14.67
	MAD	6.37	7.50	126.31	93.72	7.47	0.11	9.90
Concepción (n = 15)	Median	17.02	24.09	26.49	49.99	20.86	0.34	12.45
	Mean	17.24	21.68	26.73	59.46	18.82	0.36	16.39
	MAD	6.84	7.66	7.65	20.74	5.63	0.16	11.99
Tomé (n = 10)	Median	24.10	10.87	31.62	65.08	20.96	0.35	18.38
	Mean	24.93	11.53	32.43	75.17	19.77	0.63	20.31
	MAD	9.86	3.00	11.95	35.22	7.64	0.56	11.82
Los Ángeles (n = 20)	Median	23.56	32.19	35.26	61.80	22.36	0.57	11.63
	Mean	23.90	31.44	34.81	60.99	19.86	0.54	17.12
	MAD	10.76	12.57	10.60	25.25	6.75	0.21	15.40

**Table 6** Mean trace element dry weight concentrations ( $\text{mg kg}^{-1}$ ) in playground and school soils from different cities in the world

Sites	Cr	Ni	Cu	Zn	As	Cd	Pb
Talcahuano (TH)	18.5	19.1	62.0	134.4	23.5	0.4	14.7
Concepción (C)	17.2	21.7	26.7	59.5	18.8	0.4	16.4
Tomé (T)	24.9	11.5	32.4	75.2	19.8	0.6	20.3
Los Ángeles (A)	23.9	31.4	96.8	78.9	19.9	0.5	17.1
Atenas <sup>a</sup>	84.3	77.8	42	145.6	--	--	101.3
Madrid <sup>b</sup>	18	6.5	19	74	7.1	0.165	35
Uppsala <sup>c</sup>	31.6	18.5	24.9	84	3.4	0.214	25.5
Vilnius <sup>d</sup>	36	12.1	14.4	195	--	--	54.7
Talcahuano <sup>e</sup>	26	26.8	--	227	--	--	25.7
Talcahuano <sup>f</sup>	29	30	40	172	6	--	26.5
Sao Paulo <sup>g</sup>	49.0	--	--	81.5	9.6	--	--
Estambul <sup>h</sup>	45.8	11.6	59.8	53.0	5.0	--	7.1

--, Data not available

<sup>a</sup>Massas et al. (2010), playground topsoils. <sup>b</sup>De Miguel et al. (2007), playground topsoils. <sup>c</sup>Ljung et al. (2006b), playground soils.

<sup>d</sup>Kumpiene et al. (2011), school soils. <sup>e</sup>Tume et al. (2008), urban area. <sup>f</sup>Tume et al. (2014). <sup>g</sup>Figueiredo et al. (2011), playground topsoil.

<sup>h</sup>Guney et al. (2010), playground topsoil

the studied metals and moderately contaminated in case of As. No value over HILs were found; however, As levels were over the trigger value of  $4.5 \text{ mg kg}^{-1}$  that may cause cancer risk (EPA 2004), so it will be recommendable to carry out further investigations and monitoring to determine potential risk of contamination in the playgrounds of Biobio.

#### Statistical analysis

In order to reveal relationships among the elements to identify pollution sources, cluster and PCA multivariate statistical techniques were applied to the results. The results of the PCA analysis are presented in Table 8 and the results of the cluster analysis are shown in Fig. 2.

**Table 7** Median dry weight concentration values in playground soil of Biobio and reference values ( $\text{mg kg}^{-1}$ )

Sites		Cr	Ni	Cu	Zn	As	Cd	Pb
Talcahuano	Me	17.8	16.0	25.0	92.2	25.1	0.4	10.9
Concepción	Me	17.0	24.1	26.5	50.0	20.9	0.3	12.4
Tomé	Me	24.1	10.9	31.6	65.1	21.0	0.3	18.4
Los Ángeles	Me	23.6	32.2	35.3	61.8	22.4	0.6	11.6
Transformed VROM values								
Talcahuano	IV	568.3	502.5	146.6	722.9	13.1	6.9	457.2
Concepción	IV	212.9	212.3	66.5	320.0	9.3	3.3	182.8
Tomé	IV	211.7	77.1	95.2	318.3	21.2	7.1	343.4
Los Ángeles	IV	229.8	91.5	101.4	351.7	20.5	7.2	355.5
VROM 2000								
	TV	100	35	36	140	29	0.8	85
	IV	327.3	243.6	106.3	453.4	15.7	6.2	345.1
ADEC 2010								
	EILs	400 (1 Cr <sup>VI</sup> )	60	100	200	20	3	600
	HILs	200	600	2000	14,000	200	40	600

**Table 8** Results of factor analysis in the rotated component loading matrix. Italic numbers indicate the most important components of each principal component (PC)

Rotated component matrix			
Elements	PC1	PC2	PC3
Cr	-0.015	<i>0.830</i>	0.109
Ni	0.154	0.251	<i>0.739</i>
Cu	<i>0.777</i>	0.038	-0.024
Zn	<i>0.813</i>	0.035	0.172
As	0.372	0.436	-0.580
Cd	0.094	<i>0.817</i>	0.088
Pb	0.456	0.129	<i>0.511</i>

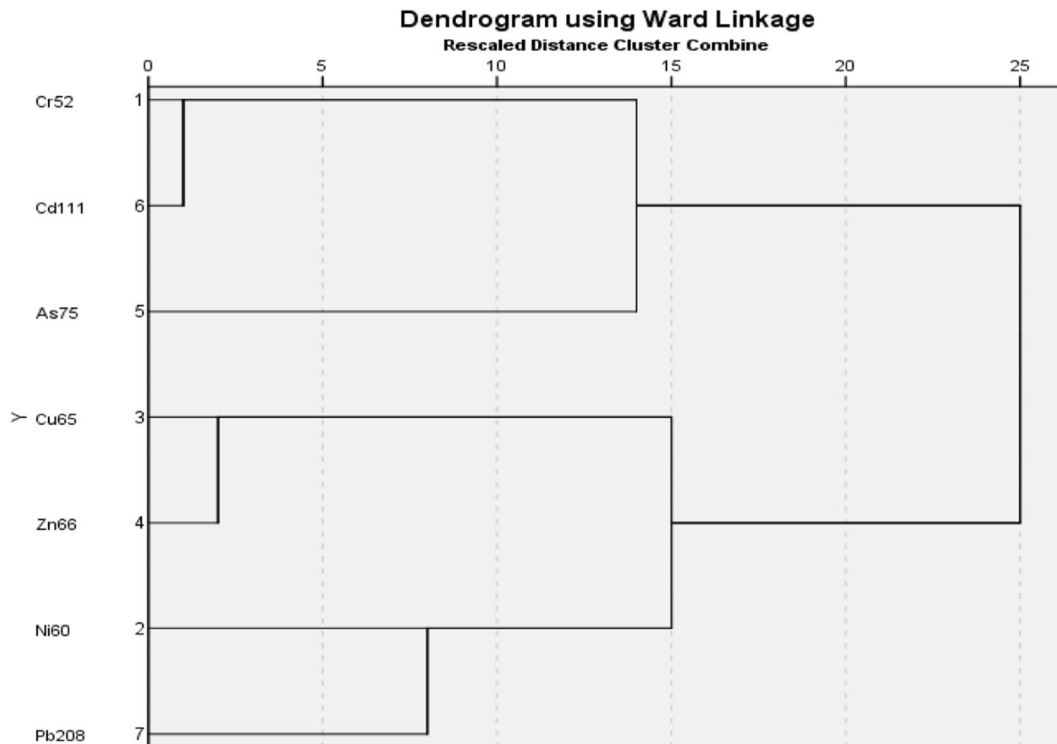
PCA components of the elemental composition of the playgrounds were plotted in Fig. 3.

The PCA classified three different factors that explained 64% of the total variance. PCA factor 1, with 24% of variance, comprises Cu and Zn (Table 8). Elements in this factor are also grouped in the cluster analysis (Fig. 2). Oil and coal combustion from ferric metallurgical industries and harbor activities should be considered the main source for these metals (Pacyna and

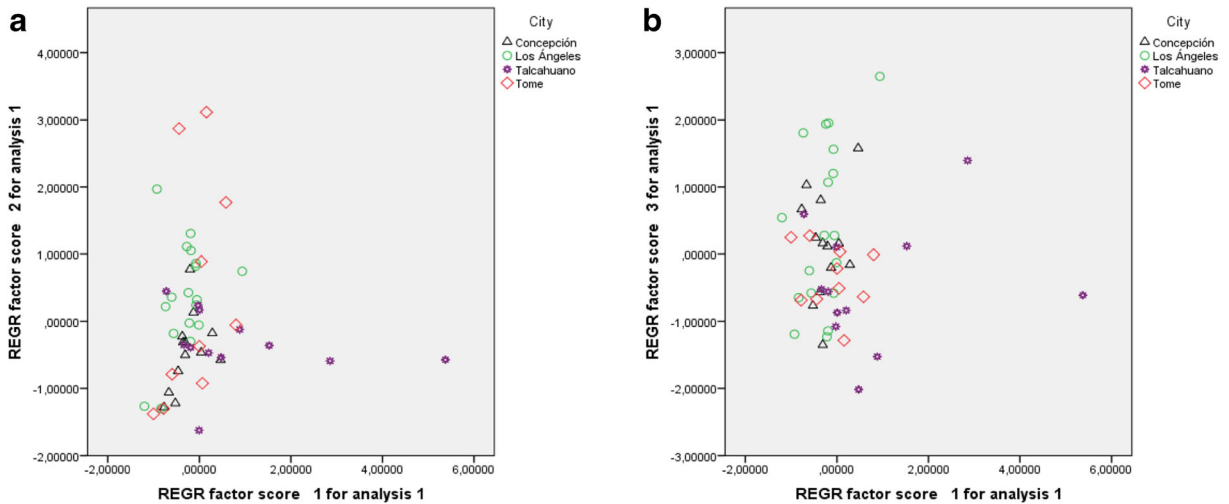
Pacyna 2001; Shalat et al. 2006; Ajmone-Marsan and Biasiolo 2010). The Talcahuano playgrounds closer to the ferric industrial area (THPI PC1 = 82.3%, THD = 61.4%) and the harbor sector (THGAS = 75.4%) have the mayor percentage of elements in PC1 factor (Fig. 4). In Tomé, the playgrounds placed in the industrial area and closer to the port also present higher values in PC1 (TCM = 59.4). The rest of playgrounds have a similar percentage in this factor around 50%.

From Fig. 3a, it can be observed that Talcahuano is closely associated with PC1 that has greatly been influenced by the metallurgical industry. Values of plot points THPI00, THPI002, and THPI003 are above 1 indicating a different source of these elements, which ought to be associated to the strong ferric metallurgic industries of this city. Most of the rest of the soils distribution of PC1 are between -1 and 1; this is probably associated with a common source related to wood stove combustion (van Lith et al. 2008; Ryu et al. 2007; Sippula et al. 2007). Also, this component reflects the heavy industrial source for the high values of Cu and Zn found in Talcahuano (Tables 5 and 6).

PCA factor 2, with 23% of variance, comprises Cr and Cd (Table 8). These elements are also grouped by cluster



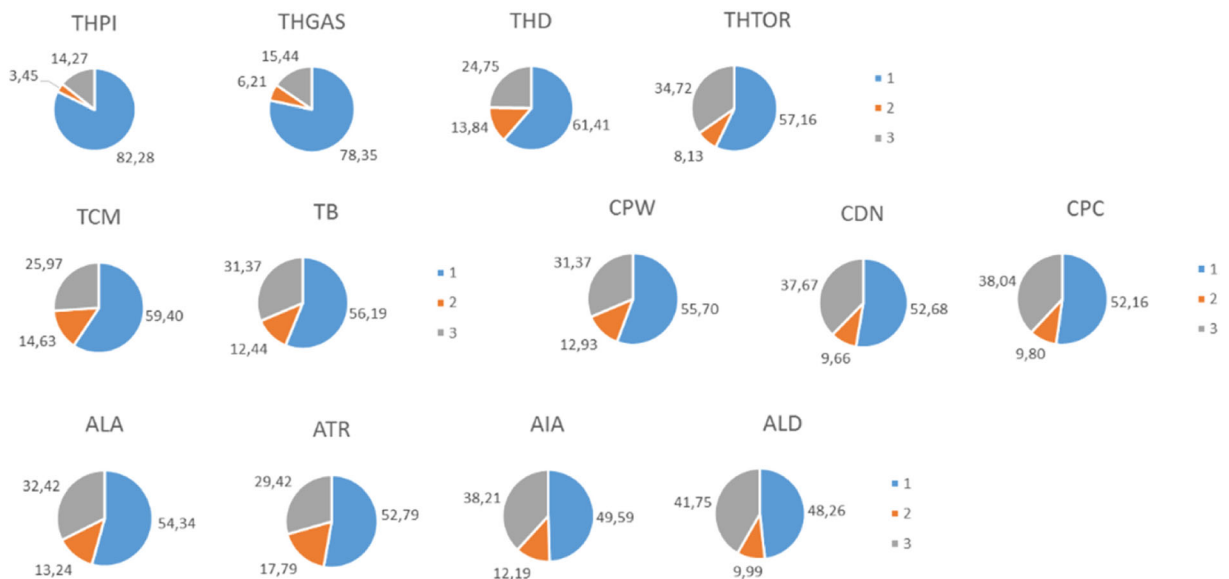
**Fig. 2** Hierarchical clustering results of the trace metal concentration in playground soils



**Fig. 3** **a** PCA components plot of the elemental composition of the playgrounds: PC1 vs PC2. **b** Components plot of the elemental composition of the playgrounds: PC1 vs PC3

(Fig. 2). The components in this factor are potentially derived from anthropogenic sources mainly associated with agricultural products and treatments applied in playgrounds like pigments and paints and/or a wide range of biocide products and herbicides with high Cr and Cd baseline values (Albanese et al. 2007; Biney et al. 1994). The wide distribution for PCA 2 in Fig. 3 might be due to the irregular application of these treatments in different playgrounds. Another diffuse source could be coming from traffic emissions in the city (Pacyna and Pacyna 2001; Shalat et al. 2006; Ajmone-Marsan and

Biasioli 2010) as reflected in the Pearson correlation (Table 4). Cr and Cd have another relationship related to this cluster because of dyes and the wool treatment industry (Akinola et al. 2008; Baral et al. 2006). This can be seen in Fig. 3 where TCM samples are distinguished from a cluster in PC2, suggesting similarities in textile industry source of metals. This observation is consistent with the fact that the TCM samples were collected close to the textile factory plant operations and influenced by metal surface deposition. Accordingly, high values of Cd for Tomé were obtained in Tables 5 and 6.



**Fig. 4** Percentage of metals present in each PCA factor for playground soils

PCA factor 3, with 17% of variance, comprises positive values for Ni, Pb, and negative values for As (Table 8). Ni and Pb elements are grouped by the cluster analysis (Fig. 2). These elements have commonly been attributed to smokestack emissions and fuel oil combustion of both gasoline and diesel engines (Lin et al. 2015). In Fig. 3b, except for Los Angeles, we cannot find different heavy metal PC3 plot distribution patterns so it makes sense to suggest road traffic as a common source of metals in the playgrounds studied. Nevertheless, road traffic influence is more accurate in Los Angeles which is located near a major transport route (Chilean Highway 5). Also, the high Pb concentration in Los Angeles could come from road traffic emissions in the city and from the nearby highway (Tables 5 and 6). In Fig. 4, it is remarkable that playgrounds close to mayor and busy transport routes (ALD = 41.8; AIA = 38.2%) or in the town (CPC = 38.1%; CDN = 37.7%) or both (THTR = 34.7%; TB = 32.4%) concentrate a mayor percentage of elements in this factor.

Due to the negative relation between As and Ni-Pb as shown in the cluster (Fig. 2) shows, As could be connected to a different source. The volcanic activity of Chile would be a common natural source of As in all playgrounds (Ajmone-Marsan and Biasioli 2010; Hong et al. 2012). Moreover, due to the extremely mobility of As, this element could also be transported by atmospheric air pathways from the copper mining areas in the north (Schwanck et al. 2016). The homogeneous distribution of As values (Table 5) in this study supports this hypothesis.

## Conclusions

In general, the concentration of As, Cd, Ni, Cu, and Zn in the studied playgrounds of Biobio is greater than in some other cities around the world (Massas et al. 2010; De Miguel et al. 2007; Ljung et al. 2006b; Kumpiene et al. 2011; Figueiredo et al. 2011; Guney et al. 2010) but with some exceptions; it is not considered to be particularly high. According to most regulatory agencies, permissible levels were found, and except for two specific samples, there is no health risk for children in any Biobio playground studied. However, more than 50% of the playground sites have high probability of contamination in at least two elements.

The results obtained in this study indicated that soils in playgrounds in the Biobio Region present local sources of trace metals. Playground soils are highly affected mainly

by a recent growth in urban population and industrial development. These outcomes are the consequence of the current proximity between industrial activities and urban areas and the city's mass transport plan.

Three different sources have been identified through the use of PCA: firstly, fuel and coal burning in the metallurgic industry, harbor activities, and home heating; secondly, the use of chemical products for the preservation of parks and facilities and for textile manufacturing industry; and lastly, road traffic-related sources and volcanic activity. However, the amount of trace elements in the top soils of almost every playground suggests an anthropogenic origin rather than geogenic.

Although the work presented here is limited to describe the influence of anthropogenic sources of heavy metals in soils of the Biobio Region, the results can contribute in providing an assessment and database of soil contamination and sources in playgrounds of Chile. There is no doubt and further studies in different settings and monitoring are needed to verify the soil pollution and to determine sources and potential contamination risk in playgrounds of Biobio cities.

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