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Concentrations of heavy metals in urban soils of Talcahuano (Chile): a preliminary study

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Abstract Concentrations of Cd, Cr, Ni, Pb, and Zn in the top-(0–10 cm) and sub-surface (10–20 cm) soils of the Talcahuano urban area were measured. The main soil properties (organic matter, $CaCO_3$, pH, particle sizes) were determined for a network of representative sampling sites. The mean Cr, Ni, Pb, and Zn contents in the urban topsoil samples from Talcahuano (37.8, 22.6, 35.2, 333 mg kg^{-1}, respectively) were compared with mean concentrations for other cities around the world. The results revealed higher concentrations of heavy metals in topsoil samples than in sub-surface samples. The samples from IS1, IS2, and IS3, located in the Talcahuano industrial park, had higher Cr, Ni, Pb, and Zn contents than did samples from the other sites. This was probably due to local pollution by industrial (metallurgical) dust, although other diffuse pollution throughout the entire port region (shipyards, metallurgy, the dismantling of old ships), and contributions from the wind from adjacent industrial, storage, and vessel areas clearly played a role. Heavy metals were lowest in the sample taken on school grounds (SG).

Keywords Urban soils · Heavy metals · Soil contamination · Talcahuano · Chile

Introduction

In densely populated urban areas, soil environmental quality is closely related to human health. Humans, particularly small children, are adversely affected by high concentrations of many heavy metals. Due to their active digestive systems, children have high heavy metal absorption rates that, given the connection between this system and the circulatory system, can lead to imbalances in the blood composition. Heavy metals can accumulate in the body, affect the central nervous system, cause poisoning, and act as co-factors in many other illnesses (Hammond 1982; Nriagu 1988; Thacker et al. 1992; Diawara et al. 2006).

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Urban soils are known to have peculiar characteristics such as horizontal and vertical variability, degradation, or even an absence of soil structure leading to compaction, modified soil reaction (in most cases, higher pH values), low organic matter content (OM), restricted aeration and water drainage, high content of anthropogenic materials, and modified soil organism populations and activities. These characteristics affect and modify the ecological functions of urban soils (Imperato et al. 2003; Ljung et al. 2006).

Heavy metal contents in the urban soil tend to increase with vehicular emissions (Harrison et al. 1981; Lau and Wong 1982; Yassoglou et al. 1987; Surthland et al. 2000), industrial residues (Schumacher et al. 1997), the atmospheric deposition of dust and aerosols (Simonson 1995), and other industrial sources such as acid rain, including SO_2 from cupola furnaces, metallurgical industries, and thermoelectric centers (Thornton 1991).

Environmental and health concerns have resulted in studies of the heavy metals in the urban soils of many cities: Madrid (De Miguel et al. 1998), Hamburg (Lux 1986), London (Thornton 1991), Hong Kong (Li et al. 2001), Berlin (Birke and Rauch 2000), Sevilla (Madrid et al. 2004), Palermo (Manta et al. 2003), Naples (Imperato et al. 2003), Belgrade (Crnkovic et al. 2006), and Galway (Zhang 2006).

In Chile, research has been done on heavy metals in agricultural soils and mining areas in the central part of the country (Schalscha and Ahumada 1998; Badilla-Ohlbaum et al. 2001; Flynn et al. 2002; Pizarro et al. 2003; Ahumada et al. 2004; Richter et al. 2004); in the north (De Gregori et al. 2003; Higueras et al. 2004); and on the Antarctic Peninsula (Carrasco and Prendez 1991). No similar studies are known for urban areas.

The industrial park in Talcahuano houses metallurgical, fishery, petrochemical, and cement manufacturing industries, amongst others. With the growth of the Municipal District, most of these industries are now located near residential areas. This situation motivated emissions monitoring of sulfur dioxide, breathable particulate material (PM-10), organic compounds, and heavy metals in the marine sediments (CONAMA 1995; Ahumada and Vargas 2005). However, trace concentrations in the Talcahuano soils have never been studied systematically, and the extent of soil contamination in the city remains unknown.

The objectives of this preliminary study were to investigate the concentrations of cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), and zinc (Zn) in the surface soils throughout Talcahuano (Chile) and to evaluate the soil environment quality in terms of metal contamination. The study's results contribute to the very limited data available on heavy metals in Latin American cities, as compared to the records for North America or Europe.

Materials and methods

Site description

The study area is located in the city of Talcahuano (36° 43′S–73° 07′W), 600 km south of Chile's capital, Santiago. Talcahuano Municipal District is a port city with a population of 163,628 and a surface of 94.6 km^2. It is one of Chile's most densely populated cities. Talcahuano has residential, industrial, and commercial areas. It is the most industrialized city in Chile and is presently considered to be the country's principal military, industrial, fishery, and commercial port. The explosive growth of industry, population, and service in recent decades has caused a serious decline in the environment of Talcahuano Municipal District and local authorities are very interested in attaining a balance between industrial development and quality of life (Municipalidad de Talcahuano 2000). In 1994, the National Environmental Commission (Comisión Nacional de Medio Ambiente, CONAMA 1995) headed up the Plan for the Environmental Recovery of Talcahuano, a local environmental management initiative for solving urban-environmental conflicts within the present paradigm of sustainable development.

Talcahuano Municipal District borders Hualpen Municipal District and the city of Concepción (regional capital) and is bound on the west by the Pacific Ocean. Talcahuano, Hualpen, and Concepción townships constitute a vehicular park of 61,765 registered vehicles (Municipalidad de Talcahuano 2000). These vehicles potentially circulate through the three townships, along with vehicles from other nearby townships.

Geologically, the study area is located in the Talcahuano depression. This depression was created by intense tectonic activity that produced several faults during the transition from the Upper Pliocene to the Lower Pleistocene. Said tectonic activity configured three morphostructural units: (1) to the east, the Coastal Range, mostly adamellitic granite from the Paleozoic (intensely weathered, intrusive rock); (2) to the west, along the Pacific coast, a chain of monoclinal faulted platforms made up of sedimentary Mesozoic and Cenozoic rocks (i.e., Cretacic, from Quiriquina Island); and (3) in the center, a deltaic fluvial plain of blackish grey basaltic sand transported as sediment by the Bio-Bio River. These sandy sediments come mostly from the high valley of the Laja River, in the Andes Mountains, where fluvial terraces from the Pleistocene and Holocene and flood plains are abundant; in the latter, smooth topography and deficient drainage have created lacustrine areas. Dunes from the Quaternary are also plentiful. Tectonic activity, responsible for the faults from the Pliocene, has persisted to date. Evidence of this activity (along with historic earthquakes) is found in the changing ocean base level caused by sediments entering from the Bio-Bio River and later regressing; this occurred from the Neolithic through the first years of the first millennium (Galli 1967). Marine terraces of different levels and ages attest to these changes along the coastline.

The nature and mineralogy of the study area's soils are controlled by the geology of the bedrock and surficial and fluvial deposits (Galli 1967). The soils in Talcahuano Municipal District are largely arenosols and anthrosols.

The climate of the study area is temperate-warm with a short dry season, a mean annual temperature of 13°C, and mean annual rainfall of 1,200 mm. The rainfall is concentrated in autumn/winter, with 70% falling between May and August; only 5% falls in summer, between December and February.

Soil samples

Surface soils were sampled at representative sites around Talcahuano at two depths: topsoil (TS: 0–10 cm) and sub-surface (SS: 10–20 cm). Composite samples, consisting of four soil cores, were collected at each site (approximately 1×1 m). This sampling strategy was adopted in order to reduce the possibility of random influences from urban waste. All the samples were collected with a spatula and kept in PVC packages. The sampling was designed to investigate trace metal concentrations in representative soils: industrial (three sites: IS1, IS2, IS3), residential and commercial (one site: RC), roadside fields (one site: RS), school grounds (one site: SG), and a city park (one site: CP).

Soil analysis

Soil samples were air dried and sieved through a 2-mm sieve prior to analysis. Particle size distribution was determined by the pipette method and soil pH was measured in water using a soil-to-water dispersion ratio of 1:2.5 (MAPA 1994). Organic matter (OM) content in the soil was determined with the Walkley–Black method of dichromate acid oxidation of C (Black 1967). Carbonates were estimated by acid-neutralization through the dissolution of $CaCO_3$ with hydrochloric acid and the subsequent titration of excess HCl with NaOH (Allisson and Moodie 1965). Table 1 shows the statistical summary of some soil properties.

Soil samples were ground in a tungsten carbide mill prior to trace element analysis. The tungsten carbide material increases the contents of W, C, Co, Ta, Ti, and Nb in soil samples but has no effect on Ba, Cr, Cu, Ni, Pb, Sr, V, Cd, or Zn concentrations.

According to ISO 11466 (2002), soil samples were digested in aqua regia in order to analyze the trace elements. The samples (3 g) were deposited in a digester and made to react with 21 ml of HCl and 7 ml of HNO_3 for 16 h at room temperature and for 2 h at 130°C. To avoid the loss of volatile elements during the extraction process, reaction containers with reflux condensers were used. The samples were then cooled at room temperature and filtered with filtering paper without ashes (Whatman 42, Whatman pic, Middlesex, UK) before being diluted to a volume of 100 ml with HNO_3 0.5 N. Heavy metal concentrations (Al, Cd, Cr, Fe, Ni, Pb, Zn) were determined in the extracts

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

Trace element	0–10 cm	10–20 cm	All samples	
	AM ± SD[a]	AM ± SD[a]	AM ± SD[a]	Range
Sand (%)	99.2±1.5	94.5±7.1	96.9±5.5	81.5–100
Silt (%)	0.5±1.1	1.7±2.7	1.1±2.1	0.0–6.5
Clay (%)	0.2±0.3	1.7±2.1	0.9±1.6	0.0–4.5
Organic matter (%)	6.7±3.8	2.5±2.4	4.6±3.8	0.0–13.2
$CaCO_3$ (%)	11.8±7.0	18.1±7.2	14.9±7.6	0.0–28.0
PH	6.6±0.7	7.0±1.0	6.8±0.9	5.6–8.4

[a] Arithmetic mean ± standard deviation

by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Each sample was analyzed in duplicate. Reagent blanks, standard reference soil samples, and internal control samples were also analyzed in order to monitor analytical accuracy and precision (Bech et al 2005; Tume et al. 2006a,b).

Data processing

All element concentrations are presented in terms of dry matter.

A simple statistical analysis of the results was done, considering all the samples studied and samples by horizon, in order to extract the most information from the data obtained in the analyses.

Results and discussion

Physico-chemical parameters

The basic physical and chemical characteristics of the composite soil samples from the investigated sites are given in Table 1. The soil texture was sandy, with grain sizes that were 96.9% sand, 1.1% silt, and 0.9% clay. The relatively high sand content observed in the top layer at most sites indicated that the soil material was probably allocthonous. A clear aeolic influence related to the dunes, adjacent beaches, and the fluvial sediments from the Bio-Bio and Andalien rivers was observed. The lithologic surroundings of granites and sandstones also influenced the sandy texture of the studied soils. Organic matter in the samples ranged from 0.0–13.2%, averaging 4.6%. The organic matter distribution pattern reflected the variable cover by plants, grasses, and vegetation in the study area. $CaCO_3$ contents varied from 0.0–28%, with an average of 14.9%. With two exceptions, the pH was around 6.8.

Distribution of trace elements

Table 2 shows the heavy metal contents in the soil samples. The industrial sites (IS1, IS2, IS3) had higher Cr, Ni, Pb, and Zn contents than the other samples, whereas the school ground (SG) sample had the lowest concentrations.

Descriptive statistics for the soil samples at both depths are presented in Table 3.

Increased Cr levels in surface soils can be caused by pollution from a variety of sources, most importantly, industrial waste and municipal sewage sludge (Kabata-Pendias 2001). In Talcahuano, the observed Cr could originate in the weathering of magnetite, pyroxene, and amphiboles from volcanic rocks. However, it was clear that this heavy metal is predominately technogenic in origin (smelting factories, shipyards, etc.) given its greater concentration in topsoils as opposed to bottom soils. Topsoil Cr varied from 13.7–52.2 mg kg^{-1} (mean: 37.8 mg kg^{-1}) and sub-surface soil Cr from 10.2–21.3 mg kg^{-1} (mean: 14.2 mg kg^{-1}). The highest chromium concentration was recorded in the industrial area. This metal could be input into the soils through the wear and friction of chromium-containing linings used with the rotaries of local industries (Banat et al. 2005; Al-Khashman and Shawabkeh 2006). The highest Cr value (52.2 mg kg^{-1}) exceeded the target value (47.1 mg kg^{-1}) determined by the Dutch Authorities.

As long as the pollutants in the soil remain below the established target values, the soil is considered to be multifunctional, i.e., fit for any land use, bearing in mind any limitations due to the natural composition of the soil. Once the soil reaches the intervention values, indicating the need for soil remediation, its functionality for humans, plants, and/or animals is jeopardized or limited; when these values are exceeded, contamination is said to be serious (VROM 2000). These levels have been selected here as references, given the lack of an official Chilean guideline for soils. The target values, intervention values, and detection levels for metals and arsenic (with the exception of antimony, molybdenum, selenium, tellurium, thallium, and silver) depend on the soil's clay and/or organic matter content. To assess the soil quality, the standard soil values were converted to standard values for the studied soil based on the measured organic matter (percentage weight lost by volatilization of the total soil dry weight) and clay content (percentage by weight of the total dry material comprising mineral particle matter with a diameter of less than 2 im). The converted values were then compared with the concentrations measured in the soil. We used the soil type correction formula to convert the metals from the Talcahuano soils (Table 3).

Depending on the soil type, the distribution of Ni is either related to organic matter or amorphous oxides and clay fractions. Worldwide, soils contain a wide variety

Table 2 The heavy metal contents (mg kg^{-1}) in soil samples from Talcahuano

	IS1[c]		IS2[d]		IS3[e]		RC[f]		RS[g]		SG[h]		CP[i]	
	TS[a]	SS[b]	TS	SS	TS	SS	TS	SS	TS	SS	TS	SS	TS	SS
Cr	43.2	21.3	13.7	14.2	52.2	10.2	38.0	12.0	42.0	11.1	22.0	10.0	39.0	18.0
Ni	21.0	27.4	31.5	38.9	21.5	28.4	23.0	27.0	16.2	29.5	18.0	26.0	22.0	28.0
Pb	129	62.1	12.5	2.7	30.3	2.0	8.0	6.0	42.2	2.0	10.0	8.3	14	30
Zn	1,016	461	280	58.5	238	41.6	60.0	67.3	632	92.5	49.3	42.3	56.7	91.7

[a] TS topsoil: 0–10 cm

[b] SS sub-surface: 0–20 cm

[c] IS1 = industrial site 1

[d] IS2 = industrial site 2

[e] IS3 = industrial site 3

[f] RC residential and commercial site

[g] RS road field site

[h] SG school ground site

[i] CP city park

(0.2–450 ppm) of Ni concentrations (Kabata-Pendias 2001). In Talcahuano, Ni was mainly geogenic and its source could be olivines and pyroxenes from weathered basalts in the upper Bio-Bio valley. The mean concentration of nickel in the topsoil was 22.6 mg kg^{-1} and in the sub-surface soil was 31.1 mg kg^{-1}, likely due to a greater quantity of clay, higher pH, and more $CaCO_3$ in the lower horizon. The highest Ni value (38.9 mg kg^{-1}, IS2) far exceeded the Dutch target value (8.5 mg kg^{-1}), although it did not reach the Dutch intervention value (51 mg kg^{-1}).

Lead concentrations in topsoil (0–10 cm) ranged from 8.0–129 mg kg^{-1} and averaged 35.2 mg kg^{-1}. The highest value (129 mg kg^{-1}) was found in the topsoil samples of the industrial area and the lowest (8.0 mg kg^{-1}, RC) in a residential and commercial area. The concentration in the sub-surface soil (10–20 cm) ranged from 1.9–61.9 mg kg^{-1}, with a mean concentration of 16.1 mg kg^{-1}. One factor contributing to the greater concentration of Pb in the topsoil, along with the probable pollution, was the metal's affinity for organic matter and its limited mobility (Tume et al. 2006a,b). The highest lead concentrations were recorded in the industrial area (IS1). This was probably due to local pollution by industrial (metallurgical) dust, without denying the contributions of diffuse pollution throughout the entire port region (shipyards, metallurgy, the dismantling of old ships), and contributions from the wind from adjacent areas with industries, storage, and vessels. All these industrial activities require a substantial amount of energy for their processes and production, involving

Table 3 Mean, standard deviation and ranges for the trace elements contents (mg kg^{-1}) for the soil samples and two depths

Trace element	0–10 cm	10–20 cm	All samples			Target	Intervention
	AM ± SD[a]	AM ± SD[a]	AM ± SD[a]	GM ± SD[b]	Range	Value[c]	Value[c]
Cr	37.8±16.7	14.3±5.1	26.0±16.9	21.5±1.9	10.2–52.2	47.1	179
Ni	22.6±6.4	31.1±5.3	26.8±7.1	25.7±1.3	16.2–38.9	8.5	51
Pb	35.2±43.3	16.1±22.5	25.7±34.6	12.6±3.6	1.9–129.2	65.3	248
Zn	333±364	122±150	227±289	123.0±3.0	41.6–1,015	61.8	318

[a] Arithmetic mean ± standard deviation

[b] Geometric mean

[c] VROM 2000, with soil type correction formula

traffic activity and the burning of fossil fuels (Alloway 1995). Direct comparisons of this study with other research were hindered by the different methodologies employed (sampling, digestion); however, the mean values of lead in the Talcahuano soils were much lower than those reported for samples from some large and/or industrialized cities (i.e., Madrid, Hamburg, London, Hong Kong, Berlin, Sevilla, Palermo, Naples, Belgrade) (Table 4) (Lux 1986; Thornton 1991; De Miguel et al. 1998; Birke and Rauch 2000; Li et al. 2001; Manta et al. 2003; Imperato et al. 2003; Madrid et al. 2004; Crnkovic et al. 2006). The highest value (129 mg kg^{-1}) surpassed the Dutch target value, but did not reach the intervention value.

Zinc had the highest concentrations of all the heavy metals studied at the Talcahuano sample sites. Here, the weathering of volcanic rocks released magnetite, pyroxene, and amphiboles, which could supply Zn to the area. However, it was readily apparent that the origins of this heavy metal were predominately technogenic (smelting factories, shipyards, etc.) as the topsoil concentrations were greater than the bottom soil concentrations. Zinc in the topsoil (0–10 cm) ranged from 49.3–1015 mg kg^{-1} (mean: 333 mg kg^{-1}) and the highest value (1015 mg kg^{-1}) was found at an industrial site (IS1), whereas the lowest concentration (49.3 mg kg^{-1}) was found on school grounds (SG). The sub-surface concentrations (10–20 cm) were 41.6–461.1 mg kg^{-1} (mean: 122.1 mg kg^{-1}). The high Zn levels were associated mainly with industrial sources and traffic emissions in the Talcahuano area. The mean Zn value in the analyzed soils was generally higher than the values reported for samples from other large and/or industrialized cities (i.e., Madrid, London, Hong Kong, Berlin, Sevilla, Palermo, Naples, Belgrade), but lower than those measured in Hamburg.

Pb and Zn concentrations ranged widely, likely reflecting the effects of various intermittent or long-term human activities on the urban environment. Such activities may result in highly localized variations of trace element concentrations (Madrid et al. 2006).

In a study on variability in concentrations of potentially toxic elements in the urban parks of six European cities, Madrid et al. (2006) observed a marked difference between the behavior of Cr and Ni and that of Cu, Pb, and Zn. Copper, lead, and zinc are amongst the metals referred to as common urban pollutants in the literature (Birke and Rauch 2000; De Miguel et al. 2007).

Cadmium was below the 0.25 mg kg^{-1} detection limit in all the samples. Therefore, these samples were not useful for this study. However, these results suggested that the concentration was probably below 0.25 mg kg^{-1} and, therefore, Cd was not included in Tables 2 and 3, the Results, or the Discussion.

Ecological Soil Screening Levels (Eco-SSLs) are concentrations of soil contaminants that are protective of ecological receptors that commonly come into contact with soil or ingest biota that live on soil. The Pb

Table 4 Mean concentration (mg kg^{-1}) in urban soils from different cities in the world

Trace element	Madrid[a]	Hamburg[b]	London[c]	Hong Kong[d]	Berlin[e]	Sevilla[f]	Palermo[g]	Naples[h]	Belgrade[i]	This study (0–10 cm)
Cr	74.7	95.4	NA	NA	35.0	42.8	39	74	32.1	37.8±16.7
Ni	14.1	62.5	NA	NA	10.7	23.5	19.1	NA	68	22.6±6.4
Pb	161.0	218.2	294.0	93.4	119.0	161	253	262	55.5	35.2±43.3
Zn	210.0	516.0	183.0	168	243.0	107	151	251	118	333±364

NA not available

[a] De Miguel et al. 1998

[b] Lux 1986

[c] Thornton 1991

[d] Li et al. 2001

[e] Birke and Rauch 2000

[f] Madrid et al. 2004

[g] Manta et al. 2003

[h] Imperato et al. 2003

[i] Crnkovic et al. 2006

concentrations in two topsoil samples from Talcahuano exceeded the Eco-SSL established by the EPA (2003) for avian wildlife (16 ppm) and mammalian wildlife (59 ppm).

Conclusions

In general, the concentrations of trace elements in the topsoil samples (0–10 cm) were greater than the concentrations in the sub-surface horizon (10–20 cm).

Some topsoil samples presented Ni, Pb, and Zn concentrations higher than the target concentrations used by the Dutch Authorities.

Although this study was clearly limited in its descriptions of the processes and factors influencing trace element concentrations in the soils of Talcahuano Municipal District, it contributed to the database of trace elements in urban soils of Latin American cities.

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