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

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### 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<sup>-1</sup>, Pb 10.2 mg kg<sup>-1</sup> and Zn 56.7 mg kg<sup>-1</sup>. 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<sup>-1</sup> for Cu, 17.5 mg kg<sup>-1</sup> for Pb and 91.7 mg kg<sup>-1</sup> 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.

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### 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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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 in 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<sup>2</sup> (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 Dirección Meteorológica 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 Bahía de Concepción to the north of the study area, then into the Bahía de San Vicente 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 Concepción 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

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