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A comparative study of soil metal concentrations in Chilean urban parks using four pollution indexes

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ABSTRACT

Toxic metal enrichment in urban soils from natural and anthropogenic sources is a public health concern that challenges sustainable urban development. Active and legacy mining is likely a major contributor of localized metal pollution in resource-based economies, although other sources associated with industrial and transportation activities may also contribute in urban settings. In mining countries, such as Chile, with no soil quality regulation, public policies that seek to protect human health should assess metal distribution and pollution indexes to guide interventions, especially in urban green spaces. To assess the role of active and legacy mining waste sites within the urban and peri-urban areas, metal concentrations in the soils of urban parks were measured in this study, and four pollution indexes were calculated for four cities of Chile. Copiapó and Andacollo in northern Chile represented the cities with several active and legacy mining waste sites located within the urban and peri-urban areas, while conurbation La Serena-Coquimbo and Gran Santiago represented the cities in mining districts that lacked major mining waste sites within their urban perimeters. A total of 82 (Copiapó), 30 (Andacollo), 26 (La Serena-Coquimbo), and 59 (Gran Santiago) composite surface soil samples were collected from the urban parks. Considering Canadian guidelines for residential/parkland soils, the value for Cu (63 mg/kg) was found to be exceeded in 99%, 50%, 100%, and 97% of samples collected from Copiapó, La Serena-Coquimbo, Andacollo, and Gran Santiago, respectively. The guidelines for lead (140 mg/kg) and zinc (250 mg/kg) were exceeded in less than 12% of samples collected from Copiapó and Gran Santiago. Arsenic was not mainly quantified (<10% quantification frequency, quantification limit = 36 mg/kg). The calculated modified pollution load, Nemerow, and soil quality indexes indicated that soils in the urban parks were more polluted in cities with urban mine wastes, however, the pollution load index ranked higher metal pollution in Gran Santiago. This study presented the first comparative study of metals in urban parks of Chile, highlighting a large proportion of parks with soil copper concentrations above the international guidelines, while showing higher median values in cities containing urban mine waste disposal sites.

1. Introduction

Urban areas are the dominant form of human habitat. Since 2007, more than 50% of global population has been living in urban areas, with an expected increase to 68.4% by 2050 (United Nations Population Division, 2018). Thus, the quality and geochemistry of urban environments should be properly understood as it is crucial for sustainable development, and environmental health concerns must be addressed (Burghardt et al., 2015; Wong et al., 2006). In particular, urban geochemical data are needed to identify contaminated areas and guide subsequent health risk assessments in urban environments, which is also demanded because of the absence of soil legislations worldwide (Johnson and Ander, 2008).

The rapid increase in urbanization, combined with the overall

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growth of population and industrialization, has harmfully affected ecosystems because of an increase in resource consumption and waste generation (Li et al., 2018; Wong et al., 2006). Urban areas concentrate anthropogenic pollution sources, such as industrial, commercial, traffic-related activities, and municipal waste. These pollution sources, combined with other anthropogenic activities in rural or peri-urban areas (such as agriculture and mining) and geogenic sources (such as parent material enriched in metals), have impacted soil quality in terms of metal concentration (Li et al., 2018; Wong et al., 2006). Metals, as environmental stressors, pose a challenge for sustainable urban development and public health, which must be addressed through multidisciplinary approaches.

Soil is an essential pathway for human exposure to contaminants through direct (ingestion, dermal contact, and inhalation) or indirect interactions (transfer from soil to air, water, or food chain). The contamination of urban soils can be an indicator of human exposure to metals (Wong et al., 2006).

Metals in soils are of particular interest because of their potential toxicity, accumulation, and persistence (Luo et al., 2012; Wong et al., 2006) and can pose potential risk to the population (Chen et al., 2016; Luo et al., 2012), with children and elderly persons being more vulnerable than adults (Landrigan and Goldman, 2011; Risher et al., 2010). Children are more likely to be exposed through soil ingestion and hand-to-mouth or object-to-mouth activities (Abrahams, 2002; Tulve et al., 2002; Watt et al., 1993).

An important source of metals in soils is active and legacy mining (Carkovic et al., 2016; Li et al., 2014; Schillereff et al., 2016), predominantly in resource-based economies, such as Chile. Several studies have reported notably Cu, As, Zn, and Pb accumulations, mainly in agricultural lands and sediments near mining activity areas across northern and central Chile (Aguilar et al., 2011; Ahumada et al., 2004; Badilla-Ohlbaum et al., 2001; Corradini et al., 2017; De Gregori et al., 2003; Ginocchio et al., 2004; Higueras et al., 2004; Narváez et al., 2007; Oyarzun et al., 2006; Romero et al., 2003). These metal accumulations have been associated with the presence of tailings, which are exposed to erosion by wind and water or acid drainage and release metals to the environment. In some cases, tailings have been found in residential areas or in their surroundings (Aragón and Alarcón Herrera, 2013; Carkovic et al., 2016; Moya et al., 2019) because of the rapid population growth and a lack of proper urban planning. Furthermore, due to increasing urbanization, traffic-related and industrial activities other than mining, have become an important source of metal concentration (Nriagu, 1992; Wang et al., 2018; Wong et al., 2006).

Urban population interacts with soil mainly in open spaces, such as parks and recreational facilities. Thus, understanding the geochemistry and quality of urban soils, particularly in parks (Li et al., 2018; Luo et al., 2012), which are frequently visited by the most vulnerable populations (children and elderly persons), is key for avoiding risks associated with human health (De Miguel et al., 2007; Han et al., 2020).

Several studies have shown contaminations by metals (As, Cu, Pb, and Zn) in urban soils in parks, sports areas, schools, and playgrounds (Dao et al., 2013; Guney et al., 2010; Han et al., 2020; Marjanovic et al., 2009; Rodríguez-Oroz et al., 2018; Valskys et al., 2016). This contamination has been associated with multiple sources, mainly from anthropogenic activities (Albanese et al., 2008; Luo et al., 2012), although in some sites, contribution by natural (geogenic and pedogenic) metals (Barbieri et al., 2018; Li et al., 2015) or a mixture of both sources (Hiller et al., 2017; Mostert et al., 2012) has been found to be important.

Total concentration of metals is the most used indicator of soil pollution, despite not considering bioavailability or mobility (Weissmannová and Pavlovský, 2017). Bioavailability is relevant for risk assessment (Bradham et al., 2014), but metal concentration is commonly used to compare anthropogenic pollution.

Pollution indexes have been widely used for natural and urban soils to evaluate metal accumulations and their anthropogenic contributions (Dong et al., 2018; Karim et al., 2015; Mazurek et al., 2017; Qingjie et al., 2008). Some indexes incorporate a specific metal, such as concentration factor (C_f) and accumulation index (I_{geo}), where both are calculated based on a pre-industrial reference value or background reference level. Therefore, using an index for urban soils can be questionable because of the near impossibility of determining the geochemical background (geogenic contribution) as soils may have originated from more than one source and/or be exogenous, and be affected by diffuse contamination (Albanese et al., 2008; Wong et al., 2006). Advantageously, C_f can be extended to be used with guidelines or standards values (Qingjie et al., 2008). On the other hand, integrated indexes that include different elements (from a single pollution index), such as pollution load index (PLI) and Nemerow pollution index ($PI_{Nemerow}$), are available (Weissmannová and Pavlovský, 2017). PLI is based on the geometric mean of a single pollution index for each metal (Karim et al., 2015), whereas $PI_{Nemerow}$ is a more complex expression that considers the maximum single pollution index (Gąsiorek et al., 2017; Mazurek et al., 2017).

Another way to evaluate the anthropogenic contribution to soil pollution is the source apportionment approach (Mostert et al., 2012; Qu et al., 2013, Qu et al., 2018). However, this approach requires vast knowledge about the pollution sources to obtain precise results or the use of a robust and local spatial receptor model (Qu et al., 2018), which is complicated to achieve because of multiple pollution sources, such as tailings and industrial activities. Another approach could be comparing equivalent background areas, with and without a particular activity (Jung and Thornton, 1996; Oladipo et al., 2014), the latter being used as a control area.

Integrated indexes are commonly used for environmental assessment in large areas with planning purposes (Cai et al., 2015). Generally, the choice of integrated pollution index has been arbitrary. The most frequently used indexes are the geoaccumulation index, the average pollution index, and the ecological risk factor (Cai et al., 2015). Selecting a proper index is key for understanding the degree of contamination (Kowalska et al., 2018), considering both soil use and purpose of the index. According to Cai et al. (2015), the ecological risk index and $PI_{Nemerow}$ were a good general-use index considering different criterions of comparison (like sensitivity and accuracy) using empirical and real data. Integrated pollution indexes are useful tools to prioritize remediation and action plans to improve soil quality and avoid human exposure, potentially providing a ranking of cities or parks. These tools are further important in states with no soil quality regulations or recommendations for metal concentrations in residential soils.

In recent years, there have been comparative studies of different soil pollution indexes (Abowaly et al., 2021; Cai et al., 2015; Kowalska et al., 2018). These studies showed that the performance of each index will depend on each specific case study. Therefore, the use of different indexes according to the condition of a mining country such as Chile is crucial and is a tool for evaluating contamination in urban soil.

Several studies have focused on the occurrence and health impacts of metals in parks or playgrounds (as mentioned above). However, only a few studies have focused on these areas in mining-affected places (Reis et al., 2014; Taylor et al., 2014) despite the potential metal accumulation in these parks and its consequent human exposure. Although pollution indexes have been used for the comprehensive evaluation of the degree of contamination in soils with different uses, such as farmland, forest, and urban (Kowalska et al., 2018), few studies have used them in urban settings near mining areas. Thus, there is a need to evaluate metal concentration in urban soils, such as parks, near mining areas using pollution index to guide policymakers, decision-makers, and stakeholders to reduce human exposure to metals.

This study focused on comparing cities with and without tailings in their urban and peri-urban areas using four pollution indexes. The aims of this research were: (1) to quantify the concentration of metals in the urban soils of parks in four cities of Chile, (2) to compare metal concentration in cities with and without mining waste in their urban area, and (3) to explore the use of pollution indexes for prioritization and public policy formulation in mining areas. The evaluation of metals in public spaces is an essential first stage for health risk assessment which will allow us to identify and, in future, take concrete actions to reduce the risk to the population.

2. Materials and methods

Metal concentrations in soils of urban parks were screened using pXRF (portable X-ray Fluorescence) in four Chilean cities. From north to south, these cities were Copiapó, La Serena-Coquimbo, Andacollo, and Gran Santiago (Fig. 1). Urban parks were chosen as public green spaces used by children and elders (Han et al., 2020; Shan, 2020). Copiapó and Andacollo were selected as urban areas where several active and legacy mine tailings were located within the urban and peri-urban areas. La Serena-Coquimbo was selected as a comparison area because of its proximity to Copiapó and Andacollo and the lower number of mine waste sites within its urban area. Finally, Gran Santiago was selected as a comparison area in terms of contamination from the tailings (absent). However, as this city is the main urbanized area of the country (contains 39% of the total population of the country) with heavy traffic, it was also considered a comparison area for the influence of urban anthropogenic sources of metals.

In Andacollo and Copiapó, the presence of abandoned mining waste combined with a dry climate facilitates wind erosion and it enhances atmospheric transport of pollutants, which could expose population to risks from potential ingestion or inhalation. The deposited dust could be remobilized depending on weather conditions, which might also expose local population (Laidlaw et al., 2005). Thus, the importance of analyzing and comparing metal concentration in dust and soils in these urban areas using pollution indexes can bridge the gap between research and policymaking. Additionally, non-adjacent cities without major tailings in their urban areas (Santiago and La Serena - Coquimbo), have been added as a guide for pollution indexes comparisons.

2.1. Site descriptions

Chile is a long and narrow country, which goes from Andean Mountains in the east to Pacific Ocean in the west. Fig. 1 shows the locations of the four selected Chilean cities. Fig. 2 shows the number of inhabitants of each city (Censo 2017) and the location of tailings is shown according to the National Mine Tailings Cadaster (SERNAGEOMIN, 2018). It can be seen that mine tailings were concentrated in Copiapó and Andacollo.

Copiapó is located in the Atacama region at an average of 291 m.a.s.l. and is characterized by a desert climate, with an annual precipitation of 12.0 mm and an average annual temperature of 15.2 °C. The main economic activity of the region and municipality is mining (27.7% of the regional GDP (Gross Domestic Product) in 2016 (INE, 2018); 44.9% to 2009 (Canales, 2015), respectively).

La Serena-Coquimbo is a conurbation of both cities of the Coquimbo region at an average of 85 m.a.s.l. This area is characterized by a desert climate, with an annual precipitation of 78.5 mm and an average annual temperature of 13.6 °C. The main economic activity of this region is mining (22.2% of the regional GDP) (INE, 2018). Mining is also the main

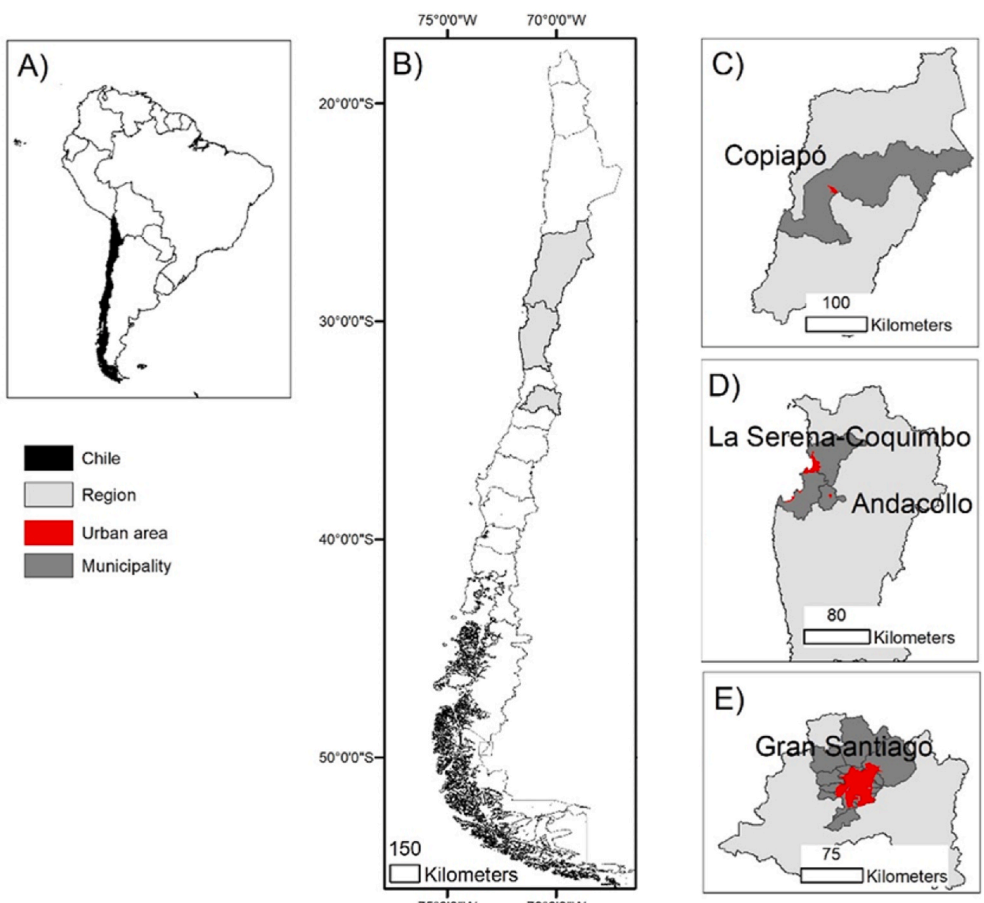

Fig. 1. Study site. A) South America, B) Chile, C) Atacama region (Copiapó), D) Coquimbo region (La Serena-Coquimbo and Andacollo), and E) Metropolitana region (Gran Santiago). The urban area of each city is depicted in red (for interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article).

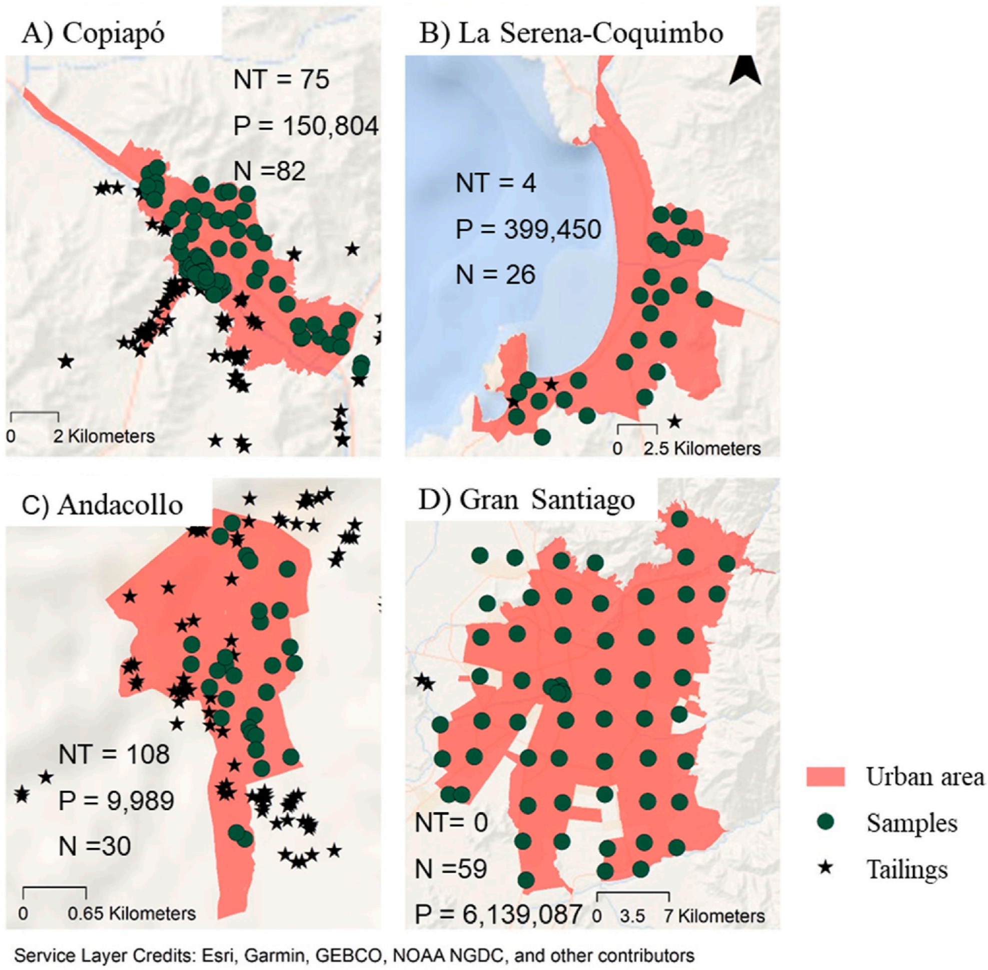

Fig. 2. Sampling distribution of soils in the parks: A) Copiapó, B) La Serena-Coquimbo, C) Andacollo, and D) Gran Santiago. The number of tailings (NT) within 2 km of urban area, as defined by the local government, the number (N) of soil samples collected, and population (P) of each city are presented here.

economic activity of La Serena and Coquimbo municipalities (26.0% for both), followed by personal services (25.6% and 24.9%, respectively) (Canales, 2015). However, these cities are not considered mining cities because of their distance from the tailings in the municipalities.

Andacollo is located in the Coquimbo region at an average of 1,017 m.a.s.l. This area also has a desert climate, with an annual precipitation of approximately 135 mm and an average annual temperature of 17 °C. The main economic activity of the municipality is mining (82.4%) (Canales, 2015).

Gran Santiago city is located in the Metropolitana region and is the capital of the region as well as the country at an average of 567 m.a.s.l. This area has a warm and temperate climate, with an annual precipitation of 312.5 mm and an average annual temperature of 14.4 °C. The economy of the region is based on financial and business services (23.3%), while mining accounts for less than 2% of the regional GDP (INE, 2018).

2.2. Sampling and analysis

Soil samples were collected from the parks of the four cities. A total of 82, 26, 30, and 59 topsoil (0–15 cm depth) samples were randomly collected from Copiapó, La Serena-Coquimbo, Andacollo, and Gran Santiago, respectively. The locations of the parks sampled in the cities are presented in Fig. 2. In each park, four random points at a distance of ~2 m from each other were sampled with a stainless steel auger and combined to obtain one composite sample per park similar as described in Carkovic et al. (2016) following standardized protocols. Sampling tools were washed with deionized water before and after sampling to avoid cross-contamination. Prior to analysis, all samples were oven-dried at 40 °C and sieved to <2 mm in the laboratory. The pH and metal contents of the samples were analyzed.

2.2.1. Analytical methods

Soil pH was determined with a pH meter (Thermo, Orion 420A+) using a soil to water ratio of 1:2.5 (w/v) (Pansu and Gautheyrou, 2006). The total metal content in the soil was determined using a portable X-ray fluorescence spectrometer (portable Innov-X Delta DS6000) following the same methodology used in Carkovic et al. (2016). Each element was validated, with its limit of quantification (LQ) being previously estimated for the same study area (Carkovic et al., 2016). The validated elements were As, Ca, Co, Cu, Fe, Mn, Pb, and Zn. Additionally, replicate samples, blanks, and reference materials were included in the routine analysis for quality assurance and control.

2.2.2. Statistical analysis

Descriptive statistics, Pearson correlation analyses, principal component analysis (PCA) based on the correlation matrix and non-parametric Mann-Whitney tests were performed for raw data using XLSTAT (Addinsoft Inc., NY, USA). These analyses were performed to identify metal enrichment and correlations between cities and elements. For statistical analyses and calculation of different indexes, values below the estimated LQ were replaced by half of the LQ (LQ/2).

The Bartlett's test of sphericity (p-value < 2.2 e-16, which is lower than the defined significance level) and Kaiser-Meyer-Olkin criterion

(0.61, which is above the suggested minimum of 0.6) showed that raw data of all cities are likely suitable for PCA.

Concentrations are compositional data, which carry exclusively relative information and require different treatment in statistical analysis (Kynčlová et al., 2017). Moreover, experiences show that use raw data can reveal interesting features (but it can be considered an incomplete and biased analysis) (Fačevicová et al., 2016). Combination with logratio alternatives of the standard statistical methods present considerable improvements (Boente et al., 2018), with centered logratio (clr) transformation most used in geochemical studies. For these reasons, Pearson correlation and PCA was developed in raw and transformed (clr) data. The clr transformation was performed using the CoDaPack software (Comas-Cufí and Thió-Henestrosa, 2011), considering As, Ca, Co, Cu, Fe, Mn, Pb and Zn.

2.2.3. Pollution index

Concentration factor, also called the contamination factor, was used to identify contamination by a single element. Equation (1) was used to calculate this for As, Co, Cu, Pb, and Zn as guidelines are available for these metals.

$$C_f^i = \frac{C_i}{C_{ri}} \tag{1}$$

where C_f^i is the concentration of metal i, and C_{ri} is the baseline, reference value, or national criteria for metal i (Qingjie et al., 2008). Owing to the impossibility of determining the background values and the lack of guidelines for soil quality for any land use in Chile, the concentration factor was calculated using the reference values for Co, Cu, Pb, and Zn provided by the Canadian guidelines for residential/parkland soils (CCME, 2020). For As, Brazilian guidelines for residential soil were used (CETESB, 2016) because values provided in the Canadian guidelines were below the LQ estimated in this study.

Contamination in each park was determined using PLI and $PI_{Nemerow}$. PLI was calculated as the geometric mean of the single factor pollution index for each metal (Karim et al., 2015), which included As, Co, Cu, Pb, and Zn (concentration factor was used). A modified PLI was calculated using the arithmetic mean of the concentration factor for each metal (PLI mod), similar to average pollution index (Qingjie et al., 2008). The geometric mean is always less than the arithmetic mean, therefore the use of the arithmetic mean is more conservative, with greater differences in locations that have both high and low concentration factors.

$PI_{Nemerow}$ (Gąsiorek et al., 2017; Mazurek et al., 2017) was calculated using Equation (2) as follows:

$$PI_{Nemerow} = \sqrt{\frac{\left(\frac{1}{m}\sum_{i=1}^{m} C_f^i\right)^2 + {C_{f\max}^i}^2}{m}} \tag{2}$$

where C_f^i is the single pollution index of a particular metal (concentration factor was used), $C_{f_{\max}}^i$ is the maximum value of the single pollution index for all measured metals, and m is the number of metals considered (five in this study).

These indexes were selected considering: (i) their easy applicability by scientifics or policy makers, (ii) simplicity of formulas that make their interpretation easier, and (iii) their common use.

Finally, a city index was calculated as the arithmetic or geometric mean of PLI or $PI_{Nemerow}$ for all parks in each city. Additionally, soil quality index (SoQI) was obtained for each city for all samples using Soil Quality Index 1.0 spreadsheet model (CCME, 2007). The guidelines were updated according to the standards mentioned above.

3. Results and discussion

3.1. Metal occurrence

The measurements of central tendencies (arithmetic mean, geometric mean, and median) of the metals (Cu, Mn, Pb, and Zn) in the park soils of the four cities of Chile are presented in Table 1. Other statistics (standard deviation, frequency of quantification, and comparison with guidelines), elements (As, Ca, Co, and Fe), and pH can be found in the appendix (Appendix Tables SM1–4).

The arithmetic mean concentrations ± standard deviations (mg/kg) of Cu and Pb were 361 ± 1,490 and 31 ± 47; 80 ± 68 and 24 ± 21; 833 ± 666 and <22; and 191 ± 127 and 48 ± 65 in Copiapó, La Serena-Coquimbo, Andacollo, and Gran Santiago, respectively (Table 1 and Appendix Table SM1–4), while the arithmetic mean concentrations ± standard deviations (mg/kg) of Mn and Zn were 947 ± 168 and 114 ± 125; 660 ± 128 and <103; 1,210 ± 397 and <103; and 1,119 ± 129 and 179 ± 119 in Copiapó, La Serena-Coquimbo, Andacollo, and Gran Santiago, respectively (Table 1 and Appendix Table SM1–4).

The decreasing order of the cities for the concentration of Cu was: Andacollo > Copiapó > Gran Santiago > La Serena-Coquimbo; for Pb: Gran Santiago > Copiapó > or = La Serena-Coquimbo > or = Andacollo; for Mn: Andacollo > Gran Santiago > Copiapó > La Serena-Coquimbo; and for Zn: Gran Santiago > Copiapó > or = Andacollo = La Serena-Coquimbo, based on all the calculated central tendencies (arithmetic mean, geometric mean, and median). It was not possible to identify a pattern for most contaminated cities based on these central tendencies, such as high values being found only in the mining cities or a single city having the highest concentration for all metals. The results only showed higher central tendency values for Cu in the cities containing urban mine waste disposal sites.

Cu concentrations ranged from <12 to 13,520 mg/kg. The highest overall value was reported in Copiapó, while the lowest was found in La Serena-Coquimbo. Copiapó showed the broadest range of Cu among all cities, with the concentrations ranging from 54 to 13,520 mg/kg.

The ranges for Pb, Mn, and Zn were narrower than those for Cu, between <22 and 432, 463–2,455, and <103–935 mg/kg, respectively. The highest overall values for Pb, Mn, and Zn were reported in Gran Santiago, Andacollo, and Copiapó, respectively. Simultaneously, the lowest values for Mn were found in La Serena-Coquimbo, whereas all cities reported <22 and <103 mg/kg values for Pb and Zn, respectively.

Arsenic was quantified a few times (<10% quantification frequency, quantification limit = 36 mg/kg, only quantified in Copiapó) (Appendix Tables SM1–4), with its highest overall value found to be 159 mg/kg. The high value of As found in Copiapó contrasted with other

Table 1
Three central tendencies for metal concentrations in the parks of different cities of Chile.

		mg/kg			
		Cu	Mn	Pb	Zn
Copiapó (mining city)	Arithmetic mean	361	947	31	114
	Geometric mean	172	933	<22	<103
	Median	154	922	23	114
La Serena-Coquimbo	Arithmetic mean	80	660	24	<103
	Geometric mean	58	649	<22	<103
	Median	62	627	<22	<103
Andacollo (mining city)	Arithmetic mean	833	1,210	<22	<103
	Geometric mean	683	1,148	<22	<103
	Median	610	1,250	<22	<103
Gran Santiago	Arithmetic mean	191	1,119	48	179
	Geometric mean	156	1,112	31	152
	Median	137	1,100	29	155
Guideline	Canadian- Residential/ parkland	63	–	140	250
	Brazilian-Residential	2,100	–	240	7,000

cities of Chile (De Gregori et al., 2003; Rodríguez-Oroz et al., 2018; Tume et al., 2014), but was similar to the values reported in the studies conducted in northern Chile (De Gregori et al., 2003) or lower than the values found in industrial areas (Tume et al., 2018b). This value was similar to other previously reported values for Copiapó (Carkovic et al., 2016). This might be explained by the natural background of the area and mining activity in Copiapó. Previous studies by this group in Copiapó showed the As concentration ranged between 9 and 182 mg/kg in peri-urban geomaterials (not published), with a calculated background of 30 mg/kg (Moya et al., 2019).

Mining cities (Copiapó and Andacollo) did not show consistently higher mean concentrations compared to non-mining cities (La Serena-Coquimbo and Gran Santiago), suggesting that pollution sources, in addition to mining, such as traffic and industrial emissions, coexisted in Chilean cities (Carkovic et al., 2016; Massas et al., 2010; Wong et al., 2006). Additionally, this result could be explained by the high variability of metal contents in the tailings due to the geochemistry of the processed ore-body (SERNAGEOMIN, 2020). However, the highest overall values for Cu, Zn, As, and Mn were also found in the mining cities, suggesting that these metals were specifically related to active and legacy mining, and the geology in these areas.

3.2. Comparison with the guidelines and reported values mainly in urban soils or parks

The average concentrations of As, Co, Cu, Mn, Pb, and Zn were found to be in the range of the values observed in the cities of other countries and Chile, except for the average concentration of Cu in Copiapó and Andacollo, which were extreme values (above the 3rd quartile plus three times the interquartile range) (Appendix Table SM5). However, these concentrations were similar to that reported in Kaňk, a village in Czech Republic with tailings in its urban area similar to Copiapó (Drahota et al., 2018) (Appendix Table SM5). Mn in Andacollo and Gran Santiago reported similar values as that in Copiapó (Carkovic et al., 2016), while the mean value of As in Copiapó was lower than that reported for Kaňk in Czech Republic (Drahota et al., 2018).

In the urban soils of Chile, some studies have reported the presence of metals, mainly focusing on As, Cu, Pb, and Zn (Rodríguez-Oroz et al., 2018; Salmanighabeshi et al., 2015; Tume et al., 2014, 2018a, 2018b, 2019). The mean values for As in the parks were within the range, as reported in previous studies (Appendix Table SM5). The mean Cu concentration in Andacollo was greater than those reported in previous studies. Gran Santiago and Copiapó also showed higher mean values for Cu than those found in the cities of Talcahuano, Hualpén (south of Chile), and Arica (north of Chile) (non-mining cities) (Appendix Table SM5). Pb has been reported to have higher concentrations in Puchuncaví-Ventanas (soil surrounding small villages), Talcahuano, and Arica cities, as reported by Salmanighabeshi et al. (2015), Tume et al. (2014), and Tume et al. (2018b), respectively, than those found for all the cities selected in this study. Among the cities selected in this study, Gran Santiago exhibited a higher mean value for Zn, which was lower than the values reported for Talcahuano in Tume et al. (2014) and Arica in Tume et al. (2018b).

Furthermore, values in each park were compared with international guidelines prescribed for residential soils. Canadian guidelines were used for all elements, except As, for which Brazilian guidelines were used. The values for Cu were found to exceed guidelines in all cities (99%, 50%, 100%, and 97% of samples of Copiapó, La Serena-Coquimbo, Andacollo, and Gran Santiago, respectively). The Canadian guidelines for Pb and Zn were exceeded in a few samples, only in Copiapó and Gran Santiago (2% and 5% for Pb and 4% and 12% for Zn, respectively). For As, Brazilian guidelines was exceeded in three samples of Copiapó (4%) (Appendix Tables SM1–4). Our research found parks that exceeded the soil guidelines for the protection of environment and human health, implying a potential health risk to the surrounding population or people who use these parks for recreational purposes.

3.3. Statistical analysis

3.3.1. Raw data

For all samples of all cities, As (metalloid) concentrations showed positive correlations with Cu, Pb, and Zn ($r = 0.7$, 0.6, and 0.6, respectively, all significant, note As had low quantification frequency (<10%)). The presence of Cu, Pb, and Zn has been linked to anthropogenic sources (Massas et al., 2010; Möller et al., 2005). Additionally, positive correlations were found between Co and Fe ($r = 0.8$) and Zn and Pb ($r = 0.9$). Co and Fe have been considered to be predominantly derived from geogenic sources, whereas Zn and Pb are commonly associated with traffic emissions and the wearing of vehicle components (Li et al., 2001; Massas et al., 2010).

Due to their different geological conditions and anthropogenic pressures, a correlation test between the metals for each city was performed. In Copiapó, all correlations (mentioned above) were found to be higher, mainly for As with Pb and Zn. Additional correlations were also found (Cu with Pb and Zn). Previous studies in this area have shown high Zn and Pb concentrations in street dust in industrial (related to industrial emissions) and downtown areas (Carkovic et al., 2016). In La Serena-Coquimbo, no strong correlation was found, except for Pb and Zn ($r = 0.7$) which showed less strength than the trend observed for all cities together (note that Fe and As were not quantified in this city). In Andacollo, only the correlation between Co and Fe was found to be high ($r = 0.9$), while Pb and Zn showed a significantly weak relationship, probably because of low population and traffic in the city, and As was not quantified. Finally, in Gran Santiago, correlations between Co-Fe and Zn-Pb were similar to that of all cities together, and two new correlations were found between Fe-Mn and Co-Mn (not strong). Arsenic was not quantified in any of the parks of Gran Santiago. Additional information and details are provided in Appendix Tables SM6–10.

PCA showed two main components F1 and F2 with eigenvalues >1, which represented 65% of the cumulative total variance of all samples. The first component (F1; 37% of the total variance) showed a high correlation with As, Cu, Pb and Zn (>0.7). The second component (F2; 28% of the total variance) showed a high correlation with Co and Fe (>0.7) and moderate with Mn (>0.55). Mn was grouped with Fe and Co (see Appendix Fig. SM1), related to a geogenic origin (Massas et al., 2010). The PCA results for each city varied each other (results not shown), suggesting different sources of metals in each case.

Differences between Co, Fe, Mn, and pH in mining and non-mining cities were not statistically significant ($p > 0.05$), suggesting similar concentrations likely from geogenic origins in the study area. Mann-Whitney test carried out for paired cities did not show statistically significant ($p > 0.05$) differences in the concentrations of: (1) As between Copiapó-Andacollo, Copiapó-La Serena-Coquimbo, and Copiapó-Gran Santiago, which was probably due to the high quantification limit set in the pXRF method; (2) Cu between Copiapó-Gran Santiago; (3) Mn between Andacollo-Gran Santiago; and (4) Pb and Zn between Copiapó-La Serena-Coquimbo. These results suggested other sources of contamination, besides mining, such as industrial and traffic activities.

3.3.2. Transformed clr data

Correlations based on compositional transformed data set showed differences compared to raw data. Unlike As in raw data, transformed clr.As not showed high correlations with any element. Positive correlations were found between clr.Co and clr.Fe ($r = 0.7$) and clr.Zn and clr.Pb ($r = 0.7$), slightly lower than with raw data. Additionally, new negative correlations were found between clr.Co and clr.Pb ($r = -0.6$) and clr.Fe and clr.Pb ($r = -0.6$). Additional information and details are provided in Appendix Tables SM11–15.

PCA showed three main components F1, F2 and F3 with eigenvalues >1, which represented 79% of the cumulative total variance of all samples transformed. The first component (F1; 38% of the total variance) showed a high correlation with clr.Co and clr.Fe (<-0.8) and with clr. Pb and clr.Zn (>0.8). The second component (F2; 27% of the total

Table 2
Park classification using PLI.

Class	N° of parks	Cities
Low level of pollution	192	All cities
Moderate level of pollution	4	Copiapó, Gran Santiago
High level of pollution	1	Copiapó
Extreme high level of pollution	0	–

Table 3
PLI mod classification of the parks (arithmetic mean).

Pollution level	N° of parks	Cities
Low	129	Copiapó, La Serena-Coquimbo, Gran Santiago
Moderate	45	All cities
High	19	Copiapó, Andacollo, Gran Santiago
Extremely	4	Copiapó, Andacollo

Table 4
Park classification using $PI_{Nemerow}$.

Pollution level	N° of parks	Cities
Clean	0	–
Warning	38	Copiapó, La Serena-Coquimbo, Gran Santiago
Slight	58	Copiapó, La Serena-Coquimbo, Gran Santiago
Moderate	25	Copiapó, Andacollo, Gran Santiago
Heavy	32	Copiapó, Andacollo, Gran Santiago

variance) showed a high correlation with clr.As and clr.Ca (>0.7) and with clr.Cu (<-0.65) and moderate with clr.Mn (>0.55). And the third component (F3; 13% of the total variance) showed a high correlation with clr.Cu (>0.65) (see Appendix Fig. SM2). clr.Zn and clr.Pb were more clearly separated from other anthropogenic elements in the compositional transformed plot, which are related with traffic activities. Although the objective of the study is not to identify emission sources, this preliminary PCA analysis provides information on the potential source of pollution and relation of elements.

3.4. Pollution index

In this study, threshold pollution values, instead of background values, were used because of the difficulty of obtaining these values for urban soils (Albanese et al., 2008; Wong et al., 2006) and the focus of the study being health risk. For the threshold values selected in this study, soil quality standards prescribed in the Canadian guidelines for the protection of environmental and human health for residential/parkland soils were used (CCME, 2020), while Brazilian guidelines (São Paulo) for residential soil were used for As values (CETESB, 2016).

Selecting a proper index is key for understanding the degree of contamination (Kowalska et al., 2018), considering both soil use and purpose of the index. In this study, both aspects were reflected in the selection of the threshold pollution value. An advantage of the selected indexes was that they were easily applicable, however, they lacked information about metal availability in soils for risk assessment, and their aggregation does not consider weighting factors (Kowalska et al., 2018). According to Cai et al. (2015), $PI_{Nemerow}$ is a good general-use index

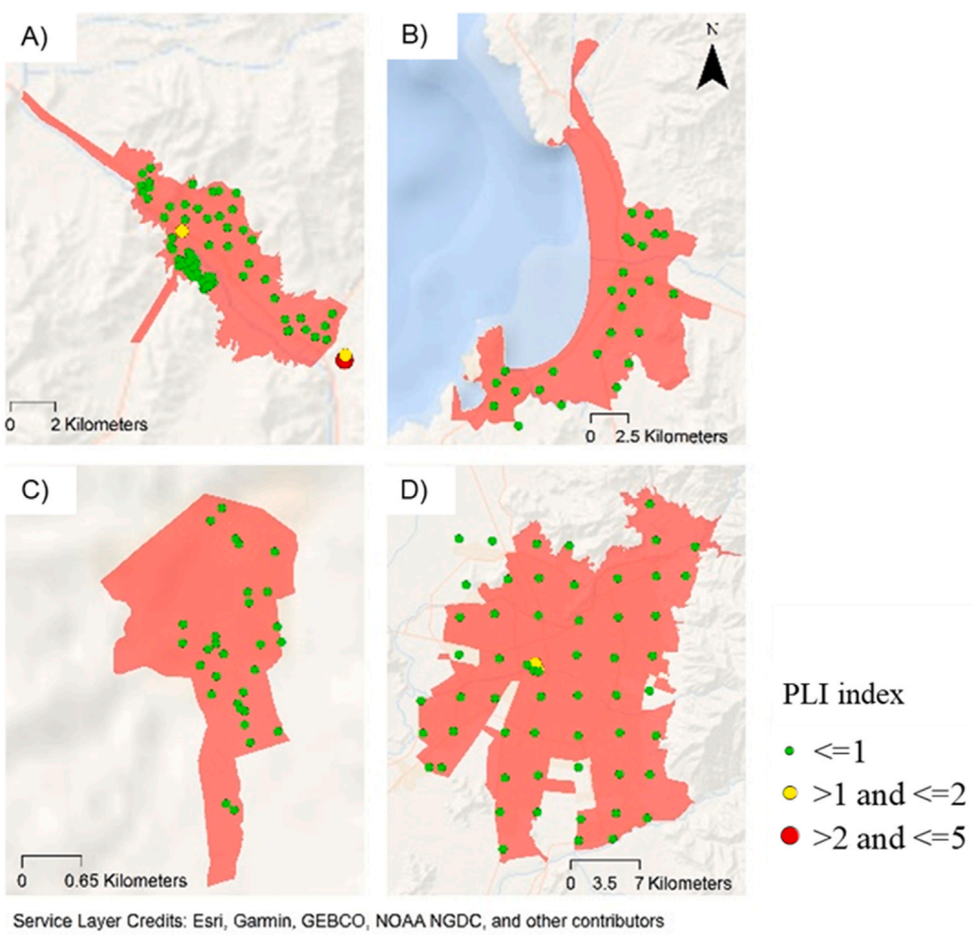

Fig. 3. PLI distribution: A) Copiapó, B) La Serena-Coquimbo, C) Andacollo, and D) Gran Santiago. Only one sample is shown in red (for interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article).

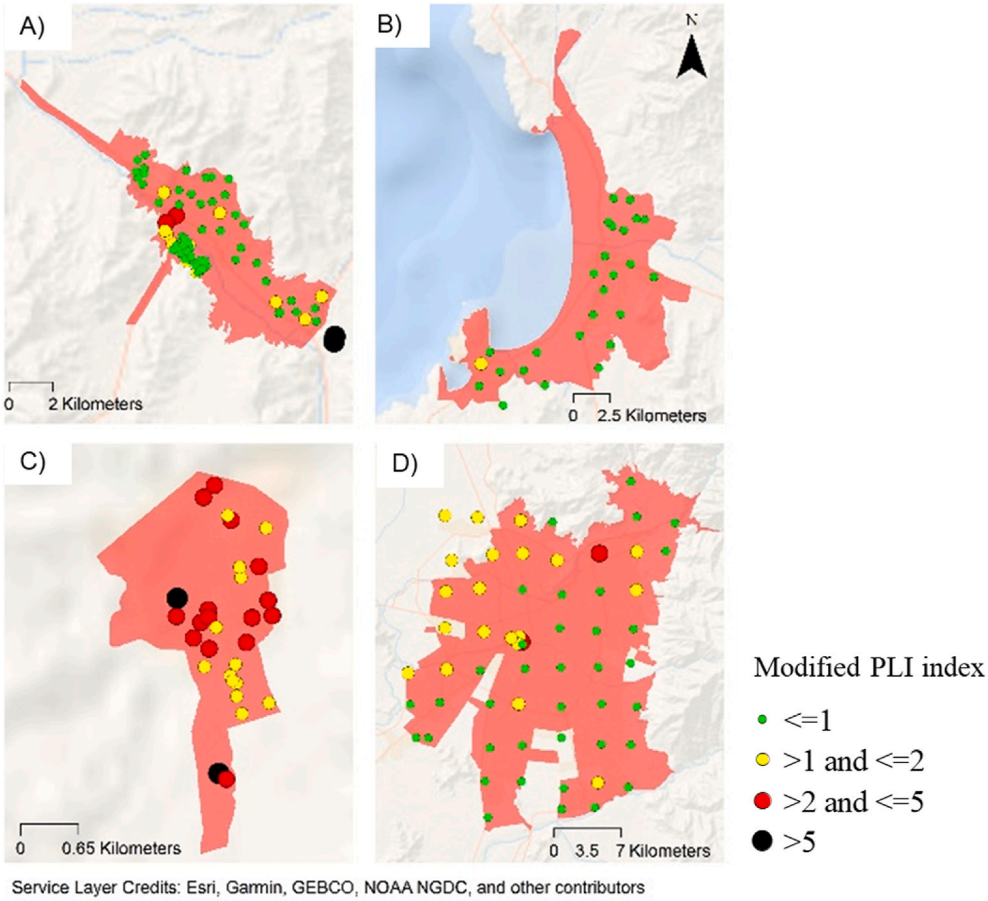

Fig. 4. PLI mod distribution: A) Copiapó, B) La Serena-Coquimbo, C) Andacollo, and D) Gran Santiago.

which meets the objectives of this study.

PLIs are shown in Tables 2 and 3. Classifications based on Wei and Yang (2010) study are as follows (for mean value, similar PLI mod; the same scale for PLI and PLI mod was used for simplicity and comparability): low level pollution if PLI $\leq$1, moderate level pollution if 1 $<$ PLI $\leq$2, high level pollution if 2 $<$ PLI $\leq$5, and extremely high level pollution if PLI $>$5. According to this classification, 97.5%, 2%, and 0.5% parks showed low, moderate, and high level pollution, respectively, with no park exhibiting an extremely high level pollution when the geometric mean was used for the calculation of the PLI (Table 2). However, when the arithmetic mean was used (PLI mod), this classification changed to 11.7% parks showing high or extreme level pollution (Table 3). In the first case where geometric mean was used, only one park in Copiapó showed high level pollution, which was concordant with the high contamination found in the mining areas. In the second case where arithmetic mean was used, parks in Copiapó, Andacollo, and Gran Santiago showed high or extremely high levels of pollution (23 in total). Moreover, parks showing extremely high-level pollution were situated in Andacollo and Copiapó, with both being mining areas (four in total and equally distributed).

$PI_{Nemerow}$ is shown in Table 4, with the pollution classes being: $\leq$ 0.1, clean; 0.7–1, warning limit; 1–2: slight pollution; 2–3, moderate pollution; and $\geq$3, heavy pollution (Gąsiorek et al., 2017; Mazurek et al., 2017). According to this index, no parks classified as clean, and 19%, 13%, and 16% fell in the warning limit, moderate, and heavy pollution classes, respectively (Table 4). Parks classified under moderate and heavy pollution classes were located in Copiapó, Andacollo (both mining cities), and Gran Santiago.

The park-wise distributions of the integrated indexes in the cities are presented in Figs. 3–5.

Indexes integrated by city are listed in Table 5. Two of the indexes ranked the cities as: Andacollo $>$ Copiapó $>$ Gran Santiago $>$ La Serena-Coquimbo (PLI mod and $PI_{Nemerow}$), and only one ranked as: Andacollo $>$ Gran Santiago $>$ Copiapó $>$ La Serena-Coquimbo (PLI) (Table 6). La Serena-Coquimbo was always categorized as the city with the lowest pollution level (independent of the index used), which was concordant with its condition as a low-density comparison city without major tailings. Andacollo and Copiapó are mining cities, where tailing without proper chemical and physical stabilization are located near the population, while Gran Santiago is a densely populated city compared to the other Chilean cities (with high atmospheric pollution (Jorquera, 2002)). All integrated indexes did not always classify mining cities as more contaminated than non-mining cities, contrary to the expectations.

SoQI scores obtained are shown in Table 7. SoQI index considers three factors for its calculations: (1) scope (percentage of parameters with no compliance to their respective guidelines), (2) frequency (percentage of individual concentrations with no compliance to their respective guidelines), and (3) amplitude (quantity by which the contaminants exceed their respective guidelines) (CCME, 2007). According to the developers of the index, it can be used to compare contaminated sites. SoQI is classified as very low (90–100), low (70–90), medium (50–70), high (30–50), and very high (0–30) (CCME, 2007). The ranking of contaminated cities using this score was Copiapó $>$ Andacollo $>$ Gran Santiago $>$ La Serena-Coquimbo.

Finally, the three integrated indexes (PLI mod, $PI_{Nemerow}$, and SoQI) showed that mining areas were more polluted than non-mining areas. However, one integrated index (PLI) showed that pollution level at Gran Santiago (non-mining city) was slightly higher than Copiapó (mining city), with all cities being classified under low level class. This highlighted the importance of selecting the index judiciously, and also that

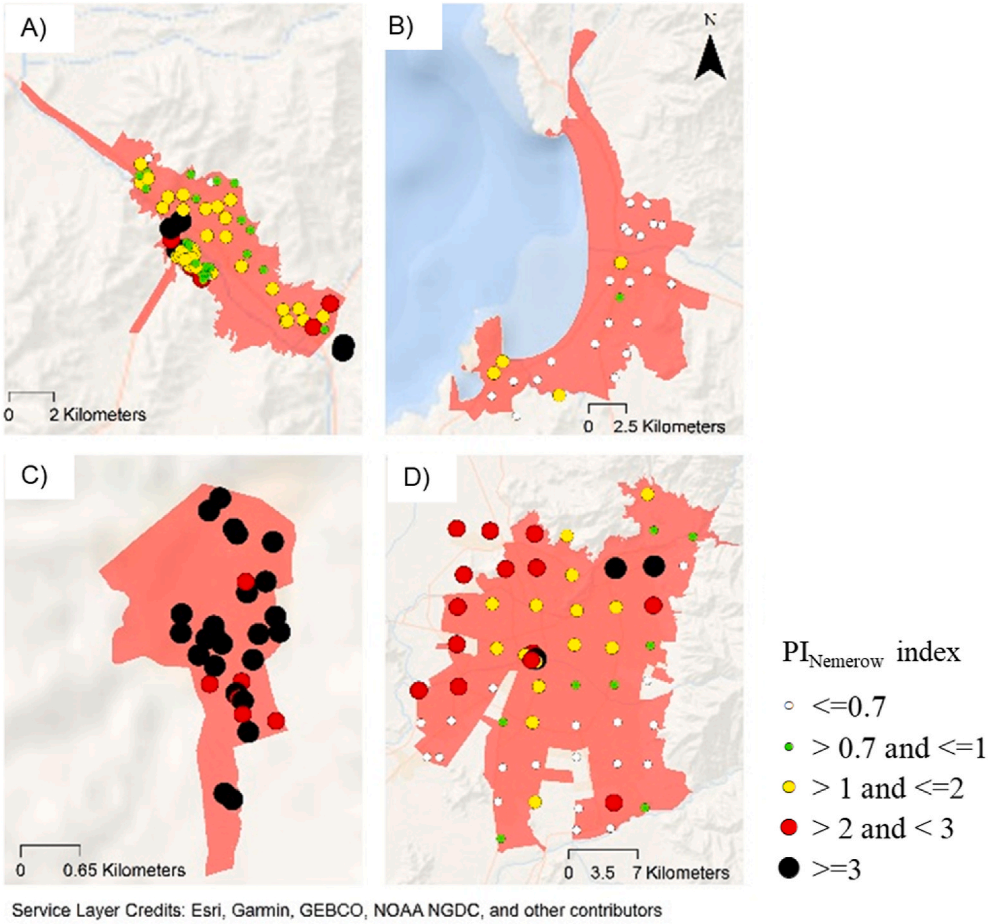

Fig. 5. $PI_{Nemerow}$ distribution: A) Copiapó, B) La Serena-Coquimbo, C) Andacollo, and D) Gran Santiago.

Table 5
City-wise pollution index.

	PLI[a]		PLI mod[b]		$PI_{Nemerow}$[b]	
	value	Pollution level	value	Pollution level	value	Pollution level
Copiapó	0.39	Low	1.4	Moderate	2.6	Moderate
La Serena-Coquimbo	0.26	Low	0.4	Low	0.6	–
Andacollo	0.47	Low	2.8	High	6.0	Heavy
Gran Santiago	0.46	Low	0.9	Low	1.4	Slight

a = geometric mean and b = arithmetic mean of the respective index by park in each city.

Table 6
City ranking based on pollution index (from 1 to 4, where 1 is more contaminated and 4 is less contaminated).

	PLI by city[a]	PLI mod by city[b]	$PI_{Nemerow}$ by city[b]
Copiapó	3	2	2
La Serena-Coquimbo	4	4	4
Andacollo	1	1	1
Gran Santiago	2	3	3

a = geometric mean and b = arithmetic mean of the respective index by park in each city.

industry and traffic activities contribute significantly to metal concentrations in densely populated cities, such as Gran Santiago. In Gran Santiago high concentrations of Cu, Zn and Pb have been reported in the particulate material (Sax et al., 2007).

Table 7
City-wise SoQI index and ranking.

	SoQI	Rank of concern	Ranking
Copiapó	24	Very high	1
La Serena-Coquimbo	69	Medium	4
Andacollo	44	High	2
Gran Santiago	47	High	3

4. Conclusions

This study was the first to perform geochemical screening using pXRF for four Chilean cities, which were compared as the representatives of mining activities. This screening focused on soils in parks as these areas were considered pollution indicators (metals deposited from traffic and industrial emissions accumulate in soil) and primary sources of exposure to metals for the most vulnerable population (children and elderly persons visiting this open space).

The ranking of the contaminated cities did not always show mining cities to be more contaminated. PLI mod, $PI_{Nemerow}$, and SoQI showed that mining areas were more contaminated than non-mining areas. However, PLI showed that non-mining cities (for example Gran Santiago) were more contaminated than Copiapó, a city with many mine waste disposal sites located in the urban area. This inconsistency highlighted the importance of judiciously selecting the appropriate index to be used.

PLI did not show any differences in the pollution classification between mining and non-mining cities as all cities were classified under the low-level pollution class. In contrast, PLI mod classified the two non-mining cities under the low-level pollution class, and the two mining cities under moderate and high-level pollution classes.

Contrary to the expectations, the findings of this study showed that the contamination in non-mining cities, such as Gran Santiago, with different pollution sources can be similar to that of a city exposed to mining activity. This finding should be considered in the action plans prepared for environmental remediation and avoiding population exposure.

Owing to lack of national guidelines or standards for soil quality, indexes used in this study were selected based on the inputs required for them and their utility to rank cities or parks (at a disaggregated level) for potential remediation and action plans. These indexes provide the first step toward better understanding the occurrence of contaminants in urban areas, enhancing health studies, and providing a tool for policy-makers, decision-makers, and stakeholders to develop remediation plans for areas with potential presence of pollutants. Further research is needed to improve our knowledge about metal concentrations in urban public areas near mining and industrial zones for protecting environment and human health, including bioavailability of metals and population exposure.

The raw and transformed clr data analysis showed principal features and correlations of metals concentrations, nevertheless, future work is needed to characterize the geochemical and anthropogenic sources in each city.

Moreover, our results highlight the need to evaluate the use of different indexes and their suitability depending on the additive effects of anthropic activities and the metal backgrounds.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix. Supplementary data

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