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Short Communication

Screening Level Carcinogenic Risk Assessment of Trace Elements in Urban Soils of a Middle-Sized City of the Central Valley of Chile

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Abstract

Recently, the increasing concentration of people in urban areas has raised concerns about the geochemistry of trace and toxic elements in urban soil. Surface soil plays an important role in human exposure through ingestion, dermal contact, and inhalation. However, studies on urban soils associated with trace and toxic elements are quite limited in South America. This work presents the first geochemical approach to urban soil in the city of Chillán, Chile. The levels of As, Cu, Sr, and Zn were measured in topsoil (0-10 cm depth) samples (n = 174) collected across a 500-m grid, chosen to be representative of the entire urban area within the city. The hazard index (HI) and carcinogenic risk (CR) were used to assess the human health risk of trace and toxic elements. The mean concentrations for Cu, Zn, As, and Sr were 71.8, 229.8, 11.2, and 234.6 µg/g dw, respectively. The values of HI for children and adults present a descending order of Cu>Sr>Zn>As. The CR values of As, Cu, Sr, and Zn were within an acceptable range for both age groups. This information will be useful to implement plans to prevent possible human exposure to toxic compounds in urban environments in future landscapes.

Keywords: health risk, heavy metals, urban soil, cancer, soil contamination, human health

Introduction

People around the world actually inhabit mainly urban areas instead of rural areas, a situation based on the fact that 54% of the world's population resided in urban areas in 2014, as compared to 30% of the urban world's population in 1950 [1]. It is estimated that around 65% of the world's population will reside in urban environments by 2050 [2]. In Chile, nearly 89% of people live in cities or towns and 11% in rural areas [3]. Therefore, the bioavailability of potentially toxic elements in urban soils is an issue of great interest lately among scientists and policymakers worldwide [4-6].

Some anthropogenic activities are increasing metal(loid) contamination, which is strongly related to mining, industrial emissions, agricultural activities, and vehicular emissions [7]. Consequently, metal(loids), which were previously stable in the Earth's crust,

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are now being dispersed into the environment and accumulated in water, sediments, soil, snow, and biota, thus affecting the health of animals and even humans [8]. Copper (Cu) is a metal that is widely used in industry because it is durable, malleable, versatile, and recyclable, and above all, because it is a great conductor. Zinc (Zn) is a metal that is a good complement to create alloys with a high degree of resistance and anti-corrosion. Arsenic (As) is a metalloid used industrially in the processing of glass, pigments, textiles, paper, metal adhesives, wood preservatives, and ammunition; it is also used in leather tanning processes and the manufacture of pesticides (organic compounds), feed additives, and pharmaceuticals [9]. Strontium (Sr) is a metal widely used in the manufacture of ceramics, glass products, pigments for paints, fireworks, fluorescent lamps, and medical supplies [10].

Urban soils are the principal compartments of any city's environment. Human activities can strongly impact soil, as urban soil contamination is the result of industrial emissions, discharge points, road traffic emissions, municipal waste, commercial and domestic activities, and dispersed atmospheric deposition across urban areas. For that reason, urban soil pollution has had an increasing impact on human health, which has been evidenced by studies carried out around the world [11-13].

In recent decades, the level of metal(loids) in the soil has increased due to human activities, such as the distribution of fertilizers, pesticides, industries, waste disposal, and air pollution [14]. In urban soils near humans, the presence of contaminants such as metals and/or metalloids can exacerbate the exposure to those chemicals [15]. Because metal(loids) produce toxic effects on biological organisms, human health is usually linked to exposure to those chemicals [13]. While the exposure of Sr is linked to skeletal disorders [16], essential metals (e.g., Cu, Zn, Fe) may cause toxic effects at high levels, whereas non-essential metalloids (e.g., As, Sr) are toxic even at very low levels [9]. Non-essential metals are known to be carcinogenic chemicals, which are absorbed from the digestive system [17, 18]. The exposure of potentially toxic elements in humans can occur through ingestion, dermal contact, and inhalation. Thus, the huge quantities of metals and metalloids entering urban environments can deteriorate the life and health of people [3].

The potentially toxic metal health risk in humans is generally estimated according to the hazard that the chemical pollutant can exert in the body, which is directly related to the levels of cancer risk (i.e., cancerous or non-cancerous), a tool recommended by the Environmental Protection Agency [19] and frequently used in other studies [20-23]. In recent years, the biogeochemistry of metal(loids) has been under research around the world [24-26], but their potential health risk in Latin American urban soils is almost non-existent [7]. Consequently, the present work aimed to determine the concentrations of As, Cu, Sr, and Zn in the urban soil of the city focus of this study, which are required to better understand the potential human health risks derived from exposure to those chemicals.

Materials and Methods

Study Area and Sampling

This study was performed in the urban area of the city of Chillán, Chile, during the summer months of January and February of 2023. Chillán is a mid-sized city in Chile, South America (Fig. 1). It is located in the central valley of Chile, a semi-industrial conurbation having a population of 184,739 people living in an urbanized area of 511 km^2 (density of ~390 inhabitants/km^2). The city is located at 36º34′S latitude and 72ºW longitude, 124 m above sea level, and 400 km south of the capital of Chile, Santiago. The region where the city of Chillán is situated is Mediterranean with a prolonged dry season (6 months) followed by a humid period and 1,100 mm of annual average precipitation [27]. The geological structure of the area is characterized by sedimentation processes and tectonic development dating back to the Pliocene. In more recent times, and based on a new climatic change, the vertical erosion of the rivers has caused deep cuts in the recent fluvioglacial materials. Important deposits of volcanic ash cover these sectors, which have been deposited mainly by the rivers that flow throughout the area, especially when dragging volcanic materials. The surrounding lands are the result of fluvial and volcanic deposits, characterized by a flat topography with smooth slopes. These deposits were transported from the Andes Mountains by the rivers because of huge volcanic and torrential events.

Topsoil samples (0-10 cm depth) were systematically collected across a 500-m grid, chosen to be representative of each urban area within the city of Chillán. For this purpose, the city was separated into four areas representative of its main activities: i) downtown; ii) industrial; iii) residential; and iv) recreational. At each sampling point, 300 g of soil was collected using a hand shovel and then carefully placed into Kraft paper bags for storage. An unsystematic method (random points) was used for sampling, giving flexibility when defining the sampling points. The least disturbed topsoil, as well as that free of plastic or garbage, was selected for sampling.

Soil Chemical Analysis

Once in the laboratory, the soil samples collected were dried until the dry mass was constant. Before the analytical analysis, all the samples were heated for 12 h (in an oven at 100ºC) to remove any adsorbed water. The samples were analyzed at the Applied Biogeochemistry Laboratory of the Faculty of Agronomy, Universidad de Concepción (Chile),

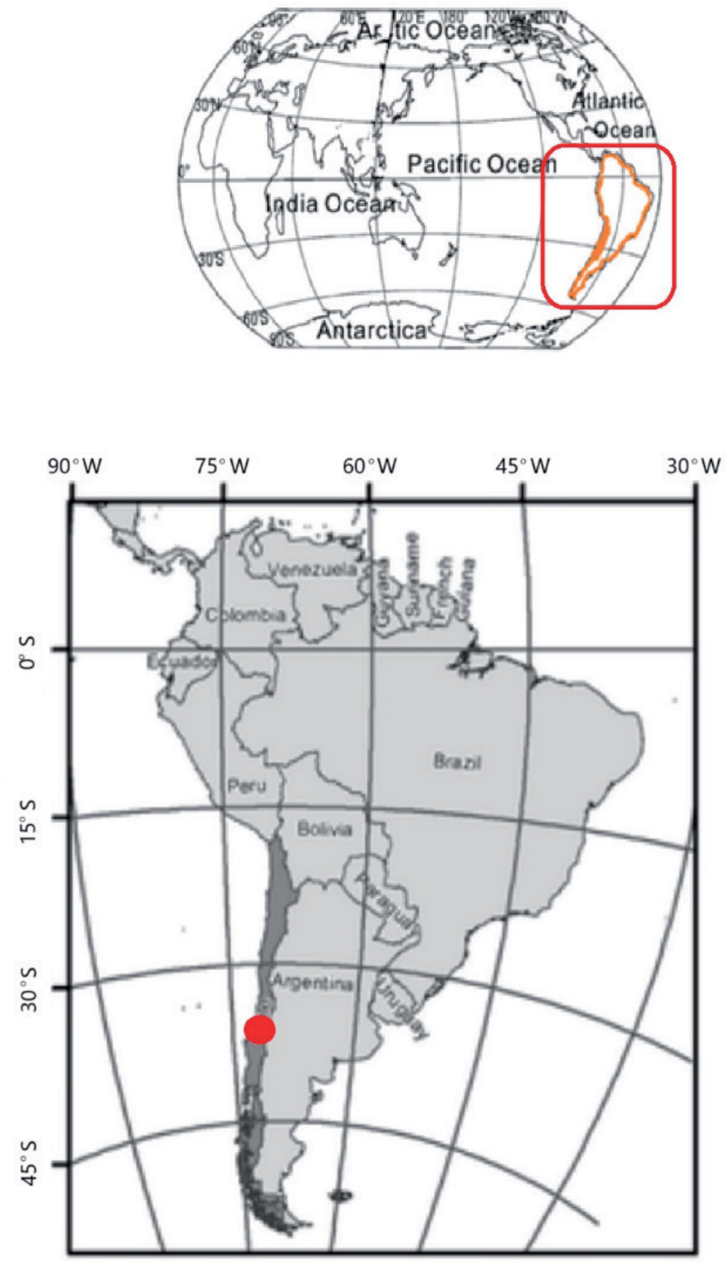

Fig. 1. Geographical location of the city of Chillán, Chile (36°36′24″S, 72°06′12″W).

using a portable battery-operated energy dispersive X-ray fluorescence spectrometer (Thermo Scientific Niton XL3t 950 He GOLDD+), following the method stated by the EPA method 6200 (Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment). A certified 99.99% silicon dioxide was used as a blank for every 20 samples analyzed. The universal reference standard "CGL 124" (USZ-42 Mongolia Central Geological Laboratory) was used to verify the accuracy and precision, with values within 95-99% and >98%, respectively. The QA/QC detection limits (μg/g) were as follows: 7.00 for Cu, 7.72 for Zn, 3.27 for As, and 3.52 for Sr.

Data Analysis

The average daily intakes through direct ingestion (ADI_{ing}), inhalation (ADI_{inh}), and dermal absorption (ADI_{dermal}) of trace and toxic elements can be calculated by the following Equations, which were adopted from the U.S. Environmental Protection Agency [19].

$$\mathrm{ADI_{ing}} = \mathrm{C} \times \frac{\mathrm{IngR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \times 10^{-6} \quad (1)$$

$$\mathrm{ADI_{inh}} = \mathrm{C} \times \frac{\mathrm{InhR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{FEP} \times \mathrm{BW} \times \mathrm{AT}} \quad (2)$$

$$\mathrm{ADI_{dermal}} = \mathrm{C} \times \frac{\mathrm{SL} \times \mathrm{SA} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \times 10^{-6} \quad (3)$$

where C is the concentration of the metal(loid) in the soil (mg/kg), IngR and InhR are the ingestion and inhalation rates, respectively (mg/day), EF is the exposure frequency (days/year), ED is the exposure duration (years), Bw is the individual's body weight (kg), AT is the average time period (days), PEF is the particle emission factor (mg^3/kg), SA is the exposed skin area (cm^2), AF is the soil adherent factor (mg/cm^2), and ABS is the fraction of applied dose absorbed through the skin. The parameters and default values used in the dose and health risk assessment are shown in Table S1 (Supplementary material).

The non-carcinogenic risk was calculated through the hazard quotient (HQ), which was assessed according to Equation (4), as suggested by [28]:

$$HQ = \frac{ADI}{RfD} \tag{4}$$

where RfD is the reference dose from Table 1 (mg/kg/day), which represents the highest daily dose of a specific metal in a particular exposure pathway that does not produce noticeable effects in an individual over their lifetime. On the other hand, the hazard index (HI) is the result of summing up all the hazard quotients obtained for individual elements, which indicates the non-carcinogenic effect in the population. It is calculated using Equation (5), according to USEPA [28]. When HI <1, it means that the non-carcinogenic risk to human health is negligible. If the HI >1, it indicates the presence of a non-carcinogenic risk to health, and this risk increases as the HI increases [17].

$$HI = \sum_{k=1}^{n} HQ_k = \sum_{k=1}^{n} \frac{ADI_k}{RfD_k} \tag{5}$$

The following dimensionless index was used to estimate the carcinogenic risk (CR) through Equation (6), as suggested by [28]:

$$CR = \sum_{k=1}^{n} ADI_k SF_K \tag{6}$$

where ADI is the average daily intake of trace and toxic elements in children and adults (both men and women), and SF represents the slope factor $(mg/kg/day)^{-1}$. When the value of $CR<10^{-6}$, the carcinogenic risk can be ignored; if the value is within the range $10^{-6}<CR<10^{-4}$, the carcinogenic risk is considered acceptable; if $CR>10^{-4}$, then the carcinogenic risk is deemed unacceptable, being a dimensionless index [28].

Descriptive and univariate statistical parameters, such as maximum, minimum, mean, median, first (Q1) and third (Q3) quartiles, and mean absolute deviation (MAD) for individual elements, were calculated using InfoStat. It was used to plot the spatial distribution of the MPs using QGIS (3.28 Firenze), an open-source geographic information system licensed under the GNU (General Public License). To interpolate the data and improve the visualization of spatial distribution, inverse distance weighted (IDW) interpolation was used, which determines cell values by a linearly weighted combination of a set of sample points.

Results and Discussion

Trace element concentrations at all sampling points are indicated in Table S2 (Supplementary material). The minimum, maximum, mean, and median contents of trace and toxic elements in urban soils of Chillán are shown in Table 1. The mean values of Cu and Zn were much higher than the median values, thus showing a distribution strongly forced by the outliers for these two elements [13]. The mean values of Cu and Zn are 2.3 and 3.4 times higher than those corresponding to background values at regional levels, respectively [29]. The maximum As, Cu, and Zn concentrations found herein are higher than those levels found in urban soil in the city of Valdivia, located 450 km south of Chillán (23, 280, and 549 µg/g, respectively [3]). On the other hand, our As, Cu, and Sr levels are lower, whereas the Sr contents are higher than those levels reported in Rancagua, a central city located 100 km south of Santiago (the capital city) and 300 km north of Chillán [7]. Some cities in central Chile, particularly Hualpén (located 100 km southwest of Chillán), present Cu, As, and Zn distributions highly dependent on industries and vehicular traffic emissions [30]. However, Chillán shows higher As, Cu, and Zn concentrations than Hualpén, even though it has less industrial development.

Geochemical maps for As, Cu, Zn, and Sr in topsoil samples from the city of Chillán are indicated in Fig. 2. The metals Cu and Zn present similar patterns, with the highest concentrations (red spots) noted in the city

Table 1. Minimum, maximum, mean, standard deviation, first (Q1) and third (Q3) quartiles, and median absolute deviation (MAD) of the trace and toxic element concentrations in the topsoil of the urban area of Chillán city.

Elements	Mean (µg/g)	Min (µg/g)	Max (µg/g)	Standard deviation	Median	Q1	Q3	MAD
Cu	71.78	7.10	1,451.4	147.98	50.8	40.81	60.10	10.03
Zn	229.53	28.56	4,072.1	380.18	156.3	104.85	230.92	54.70
As	11.54	3.42	57.83	7.11	10.15	8.93	11.59	1.28
Sr	234.99	67.11	348.24	40.76	236.9	218.51	261.41	22.49

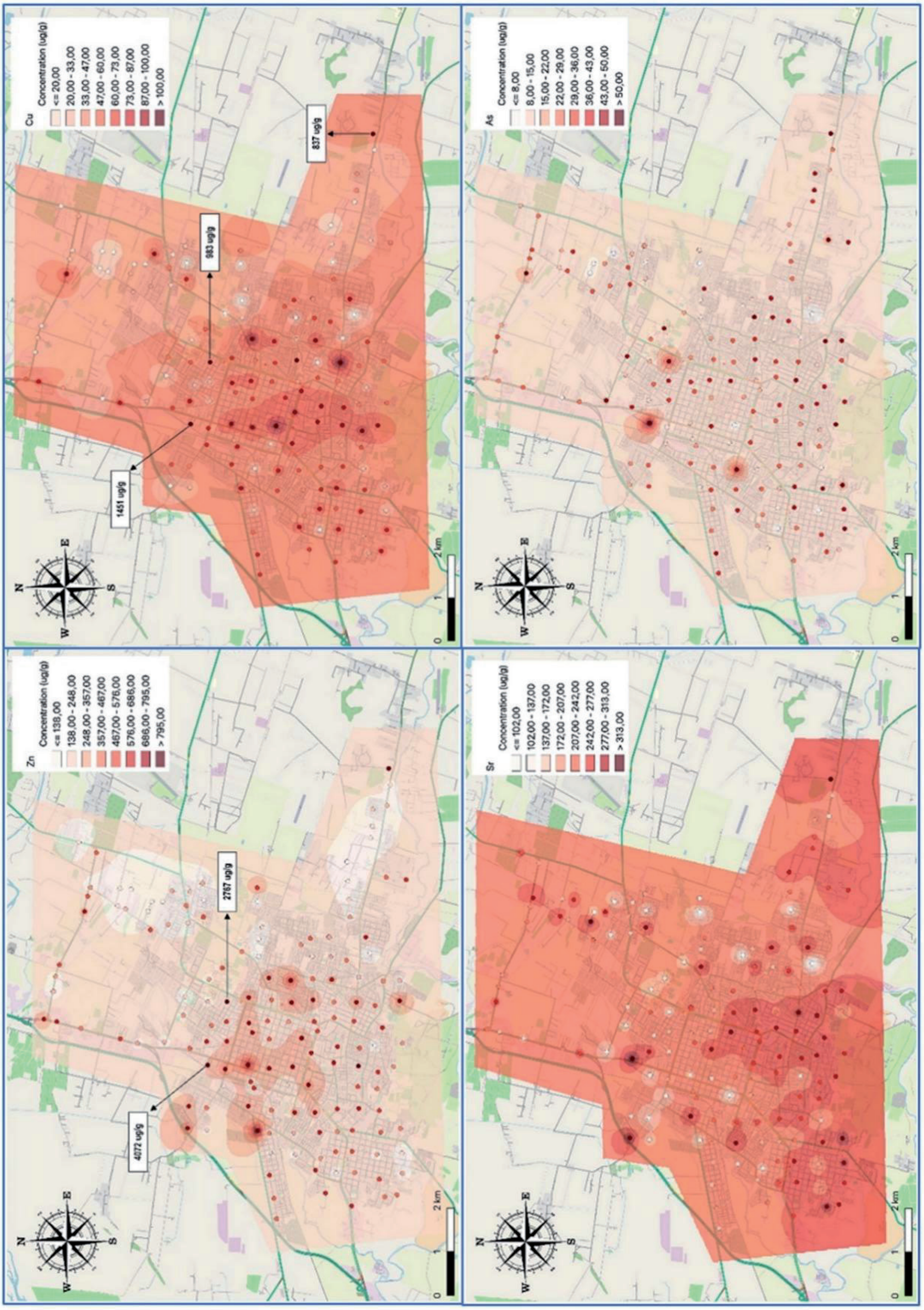

Fig. 2. Concentrations of Cu, As, Zn, and Sr in the soil of the urban area of Chillán city (μg/g dw).

center, where local commerce and public transportation converge; moderate concentrations are detected in the city's periphery and the northwestern and southeastern parts of the city; the lowest values are found in the northern part of the city. The metalloid As and the metal Sr exhibit similar patterns, with the highest concentrations in northern and southern parts of the city, where some industries are located. In Chillán, wood combustion is widely used for heating, which is directly linked to trace element contamination [27]. The major presence of Zn and Cu may be due to heavy vehicular traffic in the downtown area of Chillán. The highest As contents in topsoil samples may be related to the lower terraces along the southern part of Chillán, with fluvial sediments composed mainly of volcanic rocks and organic matter, as reported by Tardani et al. [3]. The soils where the city of Chillán is located are of volcanic origin, and volcanism is an important source of metal(loids) [31]. Copper, As, and Zn show a left-skewed distribution (Fig. 3), while Sr exhibits a distribution close to a bell shape. In comparison, Zn, Cu, and As presented a similar distribution when evaluating natural and anthropogenic inputs on the distribution of potentially toxic elements in urban soil of Valdivia, Chile [3].

The presence of heavy metals such as As, Zn, Cu, and Sr in urban soils is a pressing environmental and public health concern [20, 21]. These metals can accumulate due to various anthropogenic activities, leading to potential human exposure through multiple pathways, including ingestion, inhalation, and dermal contact. Recent studies

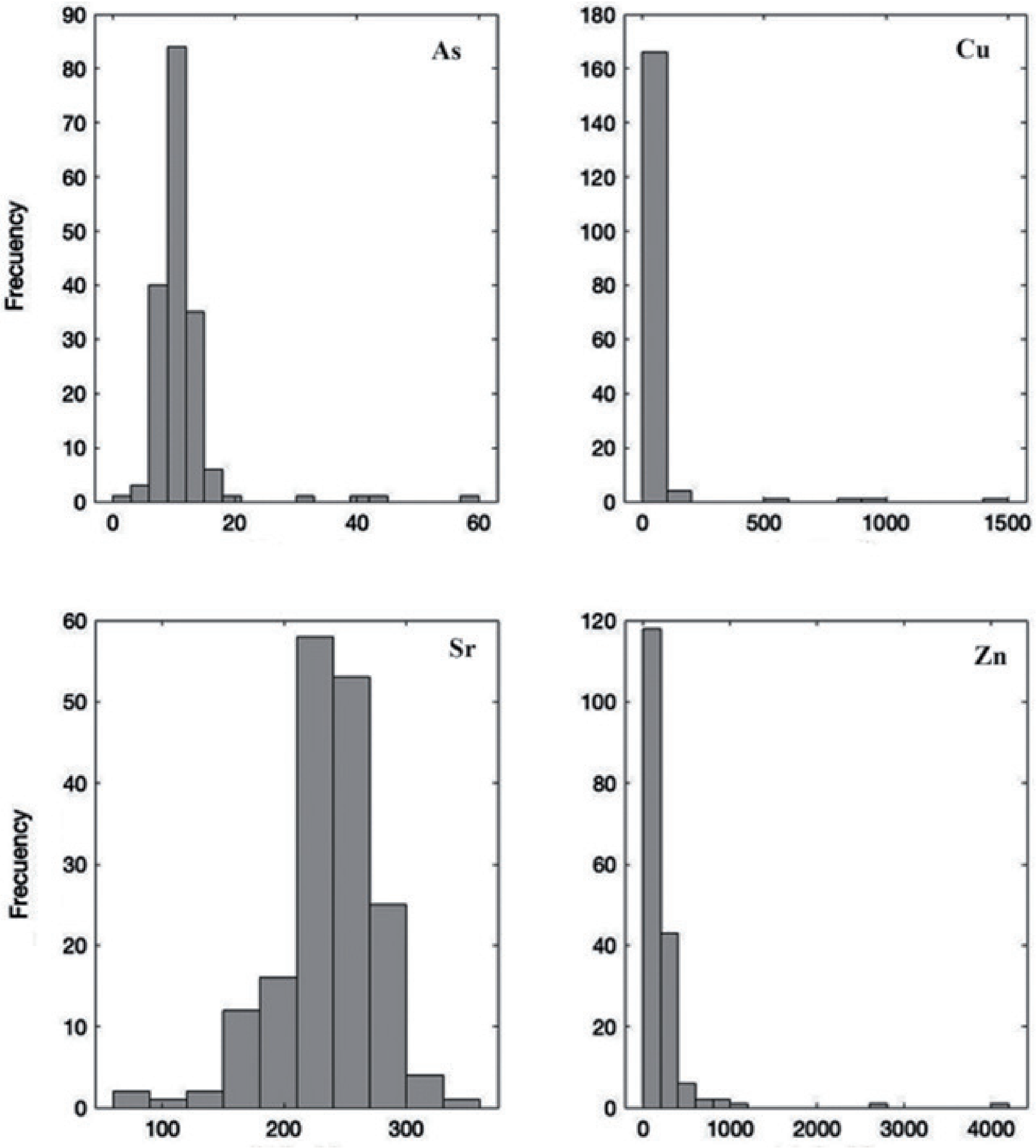

Fig. 3. Frequency histograms showing the distribution of trace and toxic element concentrations in topsoil samples (n = 174) from the city of Chillán, Chile.

emphasize the need for comprehensive assessments of these contaminants to better understand their risks to human health. Arsenic, commonly found in urban soils, poses significant health risks. Some evidence indicates elevated levels of As in urban parks and gardens, which can lead to human exposure through direct contact or food consumption [22]. In urban soils, As concentrations can vary substantially, with studies reporting values ranging from 5.2 to 30 μg/g in contaminated zones, particularly near historical mining sites and industrial activities [23]. In a recent work conducted in a Chinese city, researchers documented As levels ranging from 3.7 to 56.1 μg/g, highlighting an urgent need for monitoring and risk assessment due to the associated cancer risks, especially for populations relying on urban agriculture [32]. Similarly, in urban parks and community gardens, significant accumulation of As has been noted, emphasizing concerns over food safety in these areas [22]. Zn concentrations in urban soils typically exceed natural background levels, with studies showing ranges from 50 to over 300 μg/g in urban environments [33]. The source of this elevated Zn concentration is primarily attributed to vehicular traffic and urban runoff, leading to its accumulation in street dust and surface soils [34]. In terms of health impacts, while Zn is an essential trace metal, excessive concentrations can lead to potential toxicity, thus necessitating a careful balance in urban soil management practices. The metal Cu is another heavy metal commonly found in urban soils, often due to its extensive use in electrical wiring and plumbing materials. Urban soil Cu concentrations have been reported as high as 900 μg/g in areas proximal to industrial zones and high-traffic routes [33]. The potential for Cu to induce carcinogenic effects is less direct compared to As; however, chronic exposure through contaminated soil, particularly via food crops cultivated in these soils, remains a concern [35]. The metal Sr is not traditionally regarded as a significant health risk when compared with As or Pb, but its presence in urban soils can indicate broader contamination issues. Concentrations of Sr in urban soils have been reported to range from 20 to upwards of 300 μg/g, depending on local geological factors and anthropogenic influences [36]. While Sr is essential for bone health, excessive exposure can disrupt calcium metabolism, potentially posing long-term health risks.

In Chile, there is no national legislation specifically regulating soil metal(loids). The data found in the present study were compared with international standards in accordance with the provisions of Chilean law (Reglamento del Sistema de Evaluación de Impacto Ambiental, Ley 19300, Título II, Art. 11). However, it should be taken with caution due to the geochemical differences that exist among countries, excepting some areas of Italy that pose similar Mediterranean climatic conditions to those of Chillán. Thus, comparing the mean values of the soil geochemistry found in the present study (Table 1), we observed that Cu exceeded the threshold values stated by Canada but is below the limits of Germany, Italy, Holland, and Brazil (Table 2). Similarly, the mean Zn levels exceed the 200 μg/g established in those countries. On the contrary, our mean As and Sr concentrations are below the international threshold values. The findings obtained in the urban soil of Chillán (Table 1) show that 28% of the samples found for Cu are above the norm from Italy (120 μg/g), Canada

Table 2. Threshold values (μg/g) of metals in soils established by some countries around the world.

Elements	[a]Canada	[a]Germany	[b]Italy	[c]Holland	[c]Brazil	[d]EU	[e]USEPA
Cu	63	100	120	190	200	-	-
Zn	200	200	200	200	200	-	-
As	12	20	-	-	-	20	-
Sr	-	-	-	-	-	-	240

[a] Tardani et al. [3]; [b] Neaman [38]; [c] Valdés et al. [7]; [d] European Union (Bhattacharya et al., [39]); [e] Moghal et al. [40].

Table 3. Values of non-carcinogenic human health risks for adults and children posed by trace and toxic elements in the soil of the study area by ingestion (ing), inhalation (inh), and dermal routes.

Elements	HQ_{ing} Adults	HQ_{ing} Children	HQ_{inh} Adults	HQ_{inh} Children	HQ_{dermal} Adults	HQ_{dermal} Children	HQ_{total} Adults	HQ_{total} Children
Cu	1.26E-03	1.18E-02	1.86E-07	3.30E-07	5.04E-05	3.30E-04	1.31E-03	1.21E-02
Zn	5.39E-04	5.03E-03	7.93E-08	1.41E-07	2.15E-05	1.41E-04	5.61E-04	5.17E-03
As	5.63E-04	5.6E-03	8.28E-08	1.47E-07	2.25E-05	1.47E-04	5.86E-04	5.41E-03
Sr	2.6E-04	2.58E-03	4.06E-08	7.20E-08	1.10E-05	3.44E-06	2.87E-04	2.58E-03
HI	2.62E-03	2.47E-02	3.89E-07	6.89E-07	1.05E-04	6.22E-04	2.75E-03	2.53E-02

Table 4. Values of cancer risk (CR) in adults and children posed by trace and toxic elements in the soil of the study area by ingestion (ing), inhalation (inh), and dermal routes.

Elements	CR_{ing} Adults	CR_{ing} Children	CR_{inh} Adults	CR_{inh} Children	CR_{dermal} Adults	CR_{dermal} Children	CR_{total} Adults	CR_{total} Children
Cu	7.59E-05	7.08E-04	1.12E-08	1.98E-08	3.03E-06	1.98E-05	7.89E-05	7.28E-04
Zn	2.43E-04	2.26E-03	3.57E-08	6.33E-08	9.68E-06	6.34E-05	2.52E-04	2.33E-03
As	1.18E-05	1.10E-04	1.74E-09	3.09E-09	4.72E-07	3.09E-06	1.23E-05	1.14E-04
Sr	2.48E-04	2.32E-03	3.65E-08	6.48E-08	9.91E-06	3.09E-06	2.58E-04	2.32E-03
CR	5.79E-04	5.40E-03	8.51E-08	1.51E-07	2.31E-05	8.94E-05	6.02E-04	5.49E-03

(63 µg/g), Holland (190 µg/g), Germany (100 µg/g), and Brazil (200 µg/g). For Zn, about 22% of the values found in Chillán are above the norms of 200 µg/g established in some countries, such as Canada, Germany, and Brazil, among others. Seventy-four percent of the As concentrations in the present study area exceed the norm used in Canada (12 µg/g), Holland (55 µg/g), Germany (20 µg/g), and Brazil (35 µg/g).

The impact of the non-cancer risk presented by multiple heavy metals can be calculated through the index HQ. The non-carcinogenic risks of the elements investigated herein for adults and children are indicated in Table 3, which was obtained for the routes of ingestion, inhalation, and dermal contact for adults and children. According to USEPA [37], As, Cu, Zn, and Sr exhibited a value of HQ<1 for the two population groups, indicating that the non-carcinogenic risk to human health is negligible among the population in the city of Chillán. For the total HQ obtained, the elements showed the following trend: Cu>Sr>Zn>As, both for adults and children. The values of the HQ in the three exposure pathways for both population age groups showed the following decreasing tendency: HQing>HQder>HQinh, as similarly observed in a study conducted by Tardani et al. [3] in the city of Valdivia.

Table 4 shows the cancer risk among the population of Chillán due to oral, inhalation, or dermal exposure to As, Cu, Sr, and Zn. The total CR values for adults and children ranged between 10^{-6} and 10^{-4}, which means an acceptable risk for the urban area of Chillán, as also observed by Tardani et al. [3] in the city of Valdivia, who found the same range (10^{-6} and 10^{-4}). However, although these findings indicate an acceptable cancer risk, this situation might worsen under a climate change scenario, and therefore, more attention is required in future studies in this regard.

Conclusions

This is the first work in an urban topsoil risk assessment in the city of Chillán. Some anthropogenic activities (e.g., vehicular traffic, industries) and natural events (e.g., floods from the rivers surrounding the city) are probably the main sources of As, Cu, and Zn, and to a lesser extent, Sr. Although we found generally lower concentrations than overseas norms, some efforts must be made to avoid a real health risk in the future, so that this city will not reproduce the environmental problems of the metropolitan areas. Considering that the city of Chillán is growing in population, local and regional policies should be established focusing on thresholds for trace and toxic elements based on land use, along with controlling vehicular and industrial emissions and urbanization.

Acknowledgments

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Conflicts of interest

The authors declare that they do not have either financial or personal conflicts of interest that could have influenced this paper.

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Supplementary Material

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