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Advanced determination of the spatial gradient of human health risk and ecological risk from exposure to As, Cu, Pb, and Zn in soils near the Ventanas Industrial Complex (Puchuncaví, Chile)☆

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ABSTRACT

The townships of Puchuncaví and Quintero, on the coast of central Chile, have soils contaminated by atmospheric deposition of sulfur dioxide and trace elements from the nearby Ventanas Industrial Complex. The purpose of this study was to evaluate potential human health and ecological risks, by determining the spatial distribution of soil total concentrations arsenic (As), copper (Cu), lead (Pb), and zinc (Zn) in these townships. Total concentrations of these elements were determined in 245 topsoil samples, used to generate continuous distribution maps. The background concentrations of Cu, As, Pb, and Zn in the studied soils were 100, 16, 35, and 122 mg kg^{-1}, respectively. The concentrations of Cu, As, and Pb were positively correlated with each other, suggesting that their source is the Ventanas copper smelter. On the other hand, correlations for Zn were weaker than for other trace elements, suggesting low impact of the Ventanas copper smelter on spatial distribution of Zn. Indeed, only 6% of the study area exhibited Zn concentrations above the background level. In contrast, 77, 32 and 35% of the study area presented Cu, As, and Pb concentrations, respectively, above the background level. The carcinogenic risk due to exposure to As was above the threshold value of 10^{-04} in the population of young children (1–5 years old) on 27% of the study area. These risk values are classified as unacceptable, which require specific intervention by the Chilean government. Based on the estimated concentrations of exchangeable Cu, 10, 15, and 75% of the study area exhibited high, medium, and low phytotoxicity risk, respectively.

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1. Introduction

In recent decades, contamination of soils by trace elements (TE) has become a serious threat to human health and the environment (Liu et al., 2016). Areas such as Puchuncaví and Quintero townships, located along the coast in central Chile, are of particular concern, as for almost 3 decades, from 1964 to 1992, they received atmospheric depositions from the Ventanas Industrial Complex, containing copper smelter and thermoelectric power plant, among other industries (Folchi, 2006). New Chilean environmental regulations were established after 1992, and atmospheric emissions of SO2 and particles rich in TE were reduced using a range of technologies to comply with the new maximum permitted values (Ministerio de Minería, 1992).

The effects of these historical depositions remain latent in the soils of these townships despite the current environmental regulations. At present, the land immediately surrounding the Ventanas Industrial Complex is characterized by sparse vegetation and by severely eroded, acidic soils that contain elevated levels of TE (Ginocchio et al., 2004; Córdova et al., 2011; Ulriksen et al., 2012; Pardo et al., 2018). Such soil contamination by TE can represent a hidden danger to human health (Yousaf et al., 2016; Xie et al., 2017; Ding et al., 2018).

There are few studies that determine the potential human health risk and ecological risk associated with TE in soils of the Puchuncaví and Quintero townships (Salmanighabeshi et al., 2015; Salmani-Ghabeshi et al., 2016). Although these studies contain valuable information, they lack, in our opinion, some elements that are fundamental

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to provide complete information on the potential human health risk and ecological risk. In particular, Salmanighabeshi et al. (2015) overestimated the soil contamination indexes by using worldwide background element values of Hans Wedepohl (1995) for the upper Earth's crust, while the uncontaminated soils in central Chile tend to have elevated concentrations of TE due to high geological background (Aguilar et al., 2011). In addition, studies of Salmanighabeshi et al. (2015) and Salmani-Ghabeshi et al. (2016) considered 121 soil samples concentrated on 5 sites, which limits determination of the spatial patterns on the scale of Puchuncaví and Quintero townships. Furthermore, Salmani-Ghabeshi et al. (2016) overestimated the human health risk by considering the ingestion rate 4 times higher than the recommended by US EPA (2011).

Based on the above-mentioned arguments, this study aimed to provide more advanced determination of the spatial gradient of human health risk and ecological risk from exposure to As, Cu, Pb and Zn in soils near the Ventanas Industrial Complex (Puchuncaví, Chile). The specific objectives of this study were as following: (1) estimate the background concentrations of As, Cu, Pb, and Zn in the soils of the Puchuncaví and Quintero townships, (2) determine the spatial distribution of TE in the soils on the scale of Puchuncaví and Quintero townships, (3) assess the potential human health risk and ecological risk from exposure to As, Cu, Pb, and Zn in soils. The present study represents the first systematic study in the Puchuncaví valley on these matters.

2. Materials and methods

2.1. Study area

The area of this study included the Puchuncaví and Quintero townships (Fig. 1), with a total area of 44,800 ha (448 km^2) in irregular form, approximately 20 km wide and 33 km long. The population of these two townships is ~50,500 people (www.ine.cl), with a population density of 113 persons km-2. Located in between these two townships, is the Ventanas Industrial Complex. Control soil samples (25 in total) were also taken from other central Chilean townships, including Zapallar, Nogales, La Cruz, Limache, Quillota and Concón (Fig. 1). These samples were used to estimate the background concentrations (95th percentile) of As, Cu, Pb, and Zn in the soils of the Puchuncaví and Quintero townships.

2.2. Sampling and soil analysis

A total of 245 topsoil (0–15 cm) samples of approximately 500 g were collected in the study. All soil samples were dried for 48 h, at a constant temperature of 40 °C, and then sieved through a 2 mm mesh. Total concentrations of As, Cu, Pb and Zn were determined through sample digestion during 12 h in boiling nitric acid, followed by perchloric acid addition. Acids used in this procedure include 65% nitric acid, Merck, analytical-grade, EMSURE® ISO, and 70% perchloric acid, Winkler, analytical-grade, ACS. In order to prevent volatilization of As during the digestion process, a Teflon stopper with 30 cm-long glass reflux tube was used (Verlinden, 1982). Total concentrations of Cu, Pb and Zn in soil were determined by atomic absorption spectroscopy (AAS; GBC, SensAA, Braeside, Victoria, Australia). Total concentrations of As was determined by an atomic absorption spectrophotometer (AAS, Thermo iCE 3000 series AA Spectrometer, USA) coupled with a hydride vapour generator (model VP100). Certified reference samples were also digested in duplicate, in order to assure quality. The certified reference samples were: PACS-2, obtained from the National Research Council of Canada, and GRX-2, obtained from the United States Geological Survey. Values obtained were within 10% of the certified values, while recovery was 100% ± 7%, with spikes performed on every 10th sample. The detection limits of As, Cu, Pb, and Zn were 0.01, 0.20, 0.10, and 0.20 mg kg^{-1}, respectively. Blanks were measured and they were always under limit of detection. Pearson correlations between the TE were carried out using Minitab software (version 18).

2.3. Geostatistical interpolation method

Territorial data was managed using the ArcGIS 10.5 software program. First, a layer of sampled points was created, then this layer was joined with another layer of information including localities available in the public databases, and the limits of the townships (Biblioteca del Congreso Nacional de Chile, 2011) (Fig. 1). Then an exploratory data analysis was done using the "Explore Data" option from the "Geostatistical Analyst" extension of ArcMap. For all of the mapped variables, the distributions had positive asymmetry, of the log-normal type (Supplementary Table 1). The trends revealed by the 3D graphs that showed second order trends on the north-south axis and the east-west axis. The semivariograms revealed micro-spatial variations in the metal concentrations in the soil and the derived indicators, given the wide range of values that were observed at very close points. The semivariograms also revealed directional trends in the data.

Analysis and interpolation of spatial information was done using the procedure called Universal Kriging, a geostatistical tool found in the ArcGIS software (ESRI Inc, 2003). The Universal Kriging procedure takes into consideration both the distribution of the data, as well as the spatial trends in the data in any direction, which can then be validated (FAO, 2003). Considering the log-normal distribution of the data, we applied logarithmic transformation to the values. Then, considering the existence of spatial tendencies of the second order, a tool for removing these tendencies was applied. For each mapped variable (As and associated cancer risk, Zn, Cu, Pb, ecological risk, and phytotoxicity), different models were tested varying the interpolation parameters (variogram theoretical model, nugget, anisotropy, number of neighbors, number and size of lag, etc.). The models, which were finally selected, were those with cartography that generated less estimated error. This was evaluated using a final cross-validation that allowed a calculation of the mean squared error of the prediction (MSE, that should tend to 0) and the quadratic error method (RMS, that should tend to 1). In general terms, a spherical model was applied to predict the values. In addition, all models incorporated anisotropy and the nugget effect.

2.4. Human health risk assessment

Soil ingestion was considered as the characteristic route of exposure in this study. Following the procedure to estimate chronic daily intake (CDI) established by the US EPA (1989), the average daily intake of TE in soil ingested for adults (70 years) and children (1–5 years) was estimated using Equation (1):

$$CDI = \frac{C \ x \ IR \ x \ EF \ x \ ED}{BW \ x \ AT} \tag{1}$$

with CDI being the chronic daily intake of soil (mg kg^{-1} day^{-1}); C being equal to the TE concentration in soil (mg kg^{-1}); IR being the soil ingestion rate (20 mg day^{-1} for adults or 50 mg day^{-1} for children); EF being the frequency of exposure (350 days $year^{-1}$); ED being the duration of exposure (30 years for adults or 6 years for children); BW being the body weight average of the exposed person (70 kg for adults or 15 kg for children); and AT being the average time (10,950 days for adults or 2190 days for children).

This health risk assessment was done in order to estimate the extent to which the health of the population could be at risk from exposure to these TE-rich soil particles. The hazard quotient (HQ), defined as the ratio of the potential exposure to a substance and the level at which no adverse effects are expected, was used to evaluate the health risk of non-carcinogenic exposure. Chronic daily intake (CDI) was divided by

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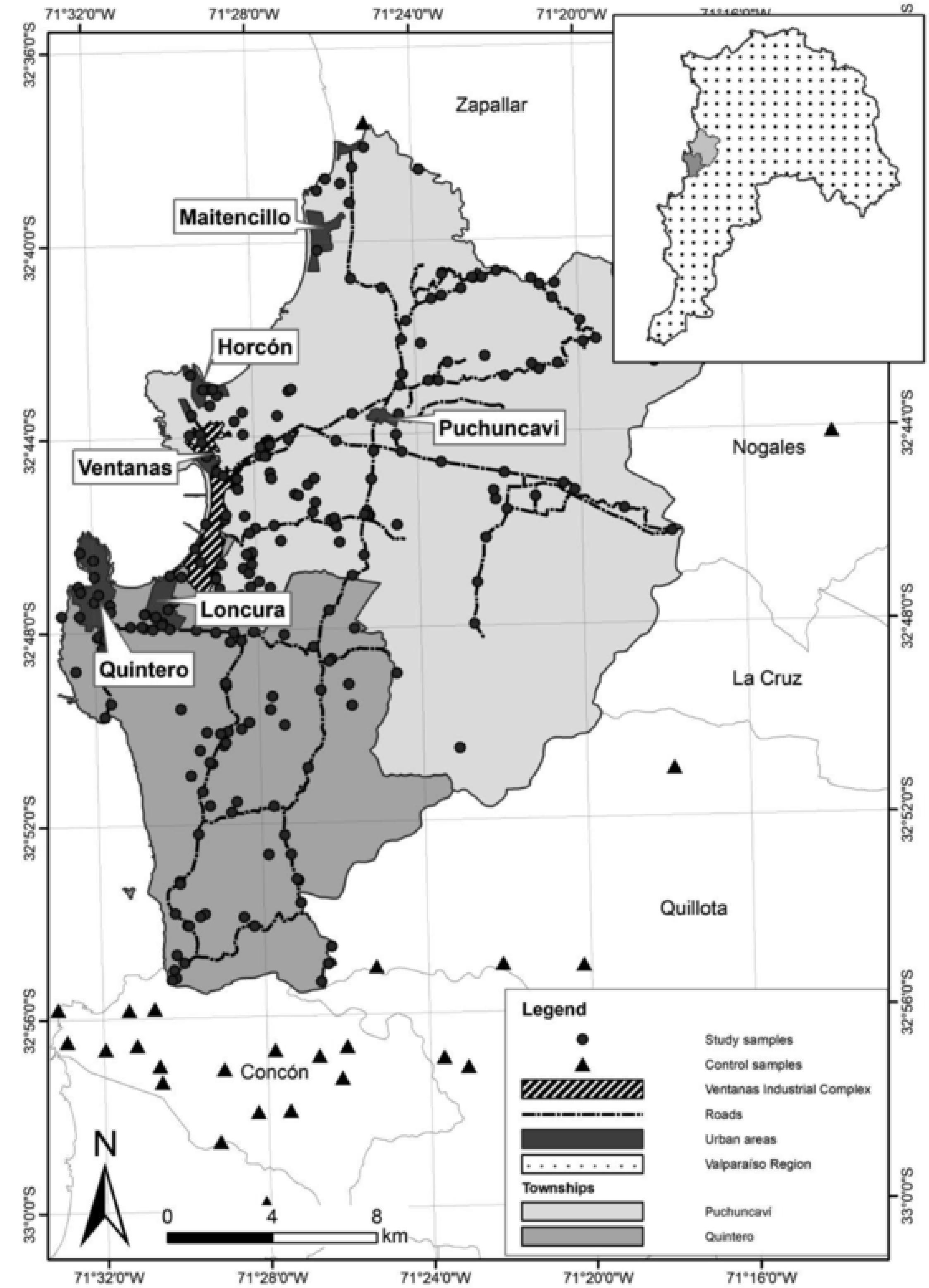

Fig. 1. Geographical location of the studied area and the controls.

the reference dose (RfD) to obtain the HQ values (Equation (2)). If the calculation yields an HQ value greater than 1, an adverse non-carcinogenic effect is considered possible. Calculation of the risk ratio (HQ) was done using Equation (2):

$$HQ = \frac{CDI}{RfD} \tag{2}$$

Calculation of carcinogenic risk assessment for As was done using Equation (3). In order to show the incremental probability of an individual developing cancer over a lifetime as a result of chronic exposure to this potential carcinogen, the CDI for As ingestion was multiplied by the slope factor (SF) of 1.5 per mg kg^{-1} day^{-1} (US EPA, 1989).

$$\text{Carcinogenic } Risk = CDI \; x \; SF \tag{3}$$

2.5. Ecological risk assessment

The potential ecological risk (Hakanson, 1980) considers the overall level of contamination in topsoil. Ecological risk was calculated as follows:

$$RI = \sum_{i=1}^{n} E_r^i \tag{4}$$

$$E_r^i = T_r^i \left(\frac{C_s^i}{C_n^i} \right) \tag{5}$$

with RI being the sum of individual potential ecological risks from all trace metals, E_r^i being the potential ecological risk index of a single element, T_r^i being equal to the toxic response factor for an individual trace metal, C_s^i being the present concentration of the trace metals in the topsoil, and C_n^i being the background concentrations of the metals in the soils found around Puchuncaví and Quintero. The toxic response factor were 10, 5, 5, and 1 for As, Cu, Pb, and Zn, respectively (Hakanson, 1980). The RI values were classified following ranking criterion of Hakanson (1980), modified by Nkansah et al. (2017): low level pollution ($RI < 50$); medium level pollution ($50 < RI < 100$); and high level pollution ($RI > 100$).

3. Results and discussions

3.1. Background concentrations of As, Cu, Pb, and Zn

The background concentrations of As, Cu, Pb, and Zn in the Puchuncaví and Quintero townships are shown in Table 1. The obtained values were similar to those reported by PGS (2015), except for Zn. The obtained value for this element was lower than that obtained by PGS (2015). However, our background value for Zn agrees with the median value of 85 mg kg^{-1} reported in our previous study in an uncontaminated area of the Puchuncaví township (Muena et al., 2010). Thus, more studies are required to explain this difference.

3.2. Distribution and health effects of As, Pb, Cu, and Zn in the study area

The concentrations of Cu, As, and Pb were positively correlated with each other (Table 2). This implies that Cu, As, and Pb were supplied by the same contamination source. Parra et al. (2014) determined that highest concentrations of Cu, As, and Pb were present in the finer particle size fractions of soils. In addition, researchers identified tenorite and calcium oxide in the fine soil particles, which are both mostly associated with smelting operations, confirming the copper smelter as the emission source for the TE-enriched particulate matter.

On the other hand, correlations for Zn were weaker than for other TE, suggesting low impact of the Ventanas copper smelter on spatial distribution of Zn. Indeed, only 6% of the study area exhibited Zn concentrations above the background level (Table 3, Supplementary Fig. 1). In contrast, 77, 32 and 35% of the study area presented Cu, As, and Pb concentrations, respectively, above the background level (Table 3).

The observed spatial distributions of As and Pb are shown in Figs. 2 and 3, respectively. The spatial distributions of Cu and pH in topsoils of the Puchuncaví and Quintero townships were presented in our previous study (González et al., 2014), however the spatial distributions of As and Pb in the topsoils in the current study also showed trends similar to those of Cu and pH. This trend, to the east of the complex, was clearly determined by the prevailing wind direction (González et al., 2014).

Even though Pb concentration was below the US EPA threshold of 400 mg kg^{-1} for children play areas (US EPA, 2001a), it can still cause children's Pb poisoning. According to Mielke et al. (1999), in order to prevent children's Pb exposure the median soil lead must be below 80 mg kg^{-1}. In the studied soils, 19 samples reached a concentration above 80 mg kg^{-1}. Indeed, soil is a reservoir of Pb that can get to children through ingestion and inhalation (Mielke, 2016). Our recent study (Berasaluce et al., 2019) demonstrated a positive correlation between Pb concentration in hair/toenails and chronic daily intake of Pb confirming that soil and indoor dust are the environmental media of human exposure to TE in the population of the Puchuncaví valley. However, Skröder et al. (2017) reported that hair is a biomarker especially useful for As exposure, but not useful enough for Cu, Cd, and Pb. Moreover, the study of Berasaluce et al. (2019) considered the population of all ages for the above-mentioned correlation analysis due to a small number of children in this study. Thus, a future study is required to study the association between soil Pb and children's blood Pb in the study area in order to provide the most reliable information about human exposure to Pb.

Researchers have shown that children consume varying amounts of soil, e.g. about 10% of children eat around 200 mg soils per day, whereas only very few children eat significant amounts of soil (Calabrese et al., 1989). The child's acceptable weekly intake will not be exceeded even with a relatively high intake of soil containing 20 mg kg^{-1}

Table 1
The 95th percentile of concentrations of As, Cu, Pb, and Zn in the soils of the Zapallar, Nogales, La Cruz, Limache, Quillota and Concón townships. These values are estimates of the background concentrations of these trace elements in the soils of the Puchuncaví and Quintero townships.

Study		Total content, mg kg $^{-1}$			
		Cu	As	Pb	Zn
Present study	(n = 15)	100	16	35	122
PGS (2015) [a]	(n = 15)	115	19	27	211

[a] Personal communication with Carlos Rodríguez, based on PGS (2015).

Table 2
Pearson correlations between Cu, As, Pb and Zn concentrations in the studied soils.

	Cu	As	Pb	Zn
Cu	–			
As	0.77 *	–		
Pb	0.71 *	0.76 *	–	
Zn	0.50 *	0.48 *	0.50 *	–

* Statistically significant ($p \leq 0.05$).

Table 3
Percentage of area affected by trace elements in soils of the Puchuncaví and Quintero townships.

	Category 1 (high)	Category 2 (medium)	Category 3 (low)	Category 4 (background)
Cu [a]	12	25	40	23
As	11	11	10	68
Pb	11	11	13	65
Zn	2	2	2	94

[a] Based on González et al. (2014).

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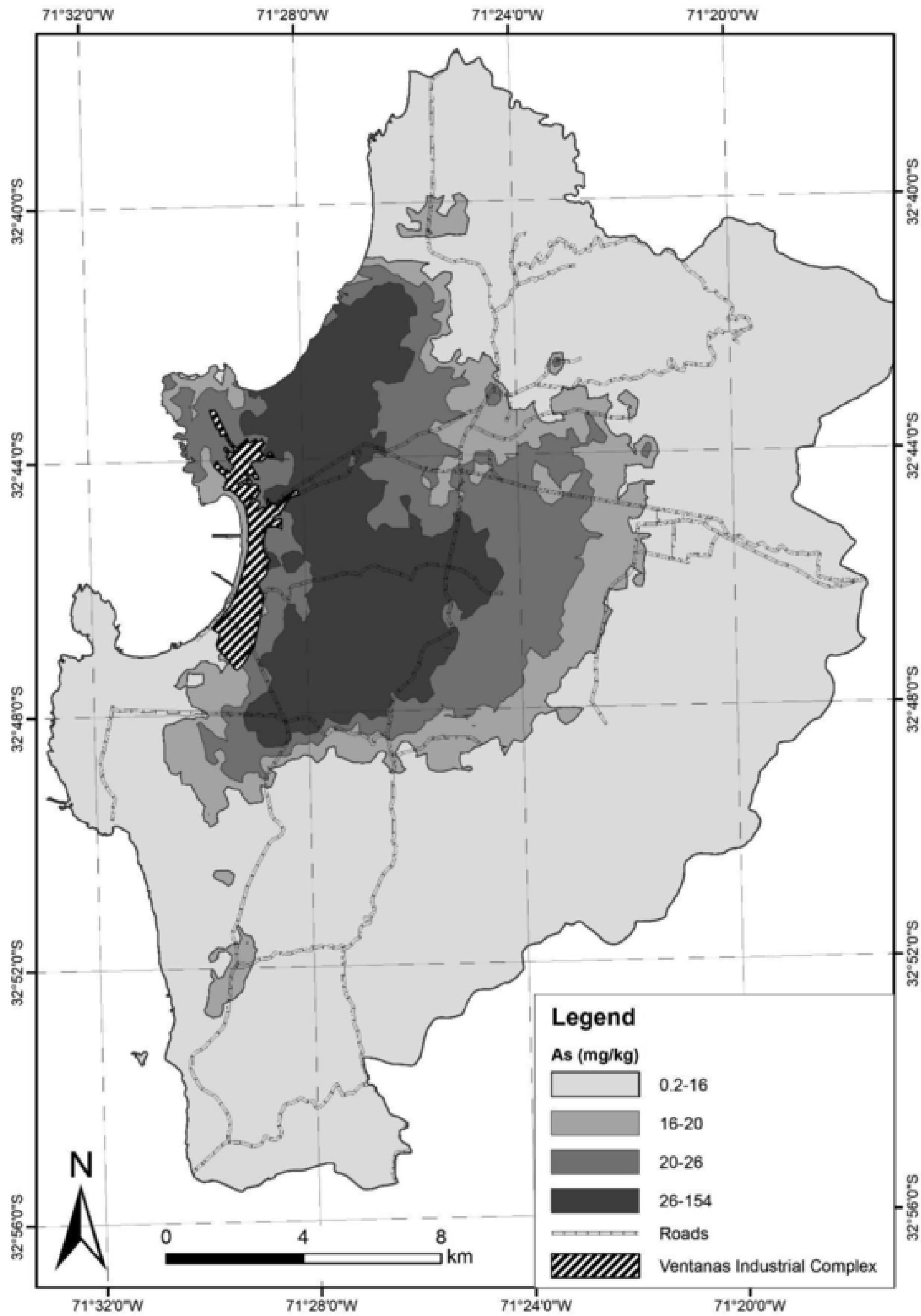

Fig. 2. Distribution of total As in the soils in the Puchuncaví and Quintero townships. The first category was defined based on the background concentration.

of As on average (Mielke et al., 2011). The area exceeding 20 mg kg^{-1} concentration of soil As reaches ~9.900 ha, that is, 22% of the total study area. Indeed, Berasaluce et al. (2019) demonstrated a positive correlation between As concentration in hair/toenails and chronic daily intake of As, confirming an unacceptable level of exposure.

Regarding the carcinogenic risk due to the intake of soil with high concentrations of As, its value exceeded the threshold of 10^{-04} for the population of young children (1–5 years) on 27% of the study area (Supplementary Fig. 2). These risk values are classified as unacceptable (US EPA, 2001b) which require specific intervention by the Chilean Government. On the other hand, there was no carcinogenic risk for adult population. These results agree with previous studies that indicate carcinogenic risk in children (1–5 years) in areas adjacent to Ventanas Industrial Complex, decreasing with distance to the industrial source (Salmani-Ghabeshi et al., 2016). As indicated above, however, the latter study overestimated the risk by considering the ingestion rate 4 times higher than the recommended by US EPA (2011).

3.3. Ecological risk and phytotoxicity

Values of the ecological risk of trace elements in the studied soils ranged from 4.2 to 234 (Fig. 4), being Cu and As the dominant ecological risk contributors. This finding is consistent with previous reports that Cu determines phytotoxicity in the study area (Ginocchio et al., 2004; Córdova et al., 2011; Ulriksen et al., 2012; Pardo et al., 2018), whereas As determines toxicity to soil invertebrates in the study area (Neaman et al., 2012; Bustos et al., 2015).

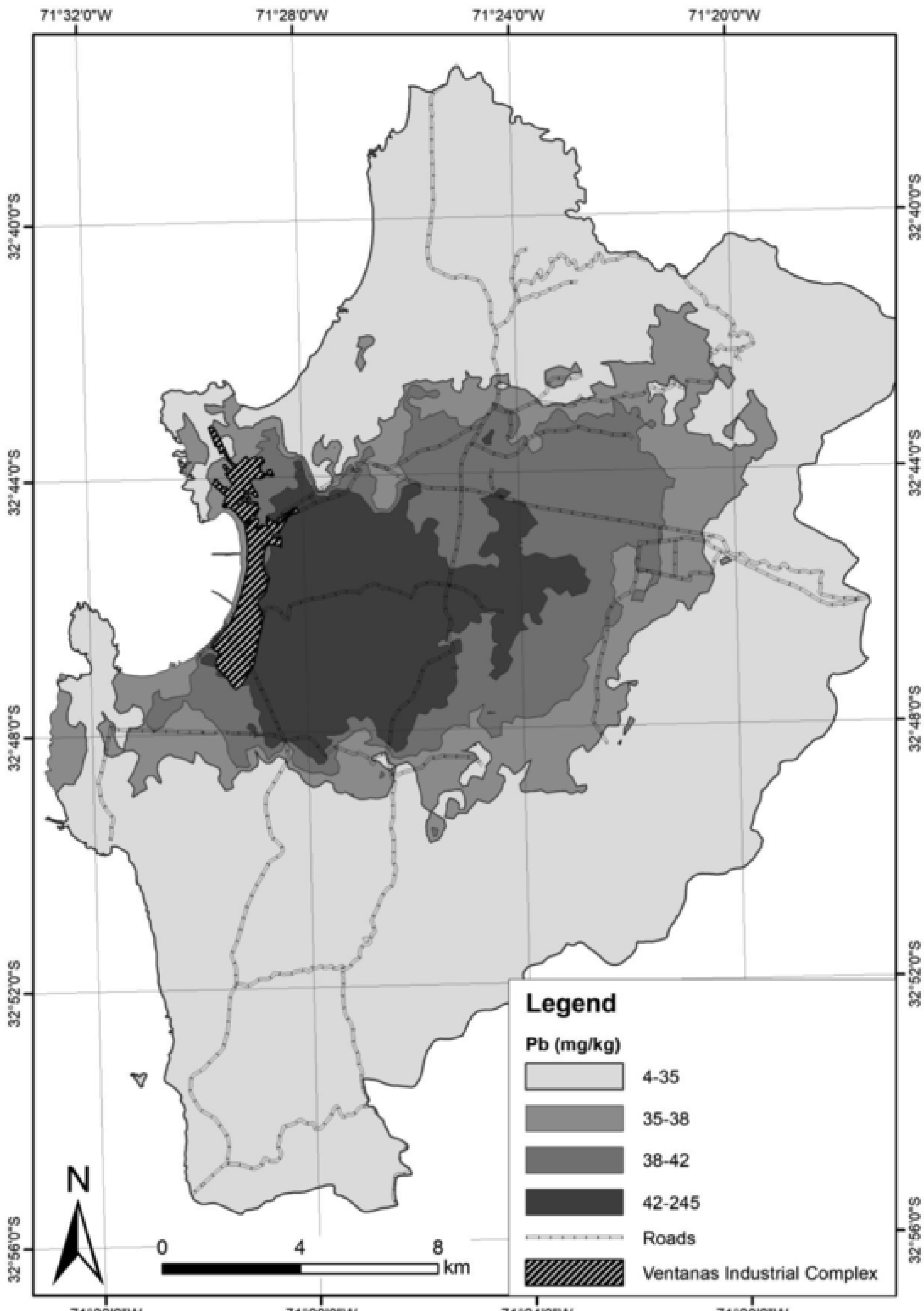

Fig. 3. Distribution of total Pb in the soils in Puchuncaví and Quintero townships. The first category was defined based on the background concentration.

Based on RI ranking criterion of Hakanson (1980), modified by Nkansah et al. (2017), 3% of the sampling sites exhibited high ecological risk, whereas 15% of the sampling sites showed medium ecological risk. However, it is well known that total metal concentration in soil is not sufficient to predict its potential phytotoxicity (McBride, 1994; Sauvé et al., 1998; Ginocchio et al., 2002; ISO 17402, 2008). It is generally considered that metal soluble fractions, extracted by chemically nonaggressive neutral salts, are more useful for assessing metal phytotoxicity in contaminated soils (Ginocchio et al., 2002; Kabata-Pendias, 2004; McBride et al., 2009). Indeed, our recent study (Lillo, 2019) demonstrated that exchangeable Cu was a good indicator of phytotoxicity, whereas the effect of total Cu was not significant, in the soils of the Puchuncaví valley. This study derived EC_{10}, EC_{25} and EC_{50} values of soil exchangeable Cu using plant response variables.

Our previous study (González et al., 2008) demonstrated that concentrations of exchangeable Cu in the soils of the Puchuncaví valley can be well predicted (R2 = 0.84) by concentrations of total soil Cu and soil pH. Considering that the areas of high and medium ecological risk overlapped with areas of low pH (range 4.3–6.2), we calculated concentrations of exchangeable Cu in our studied soils. Based on these estimated concentrations of exchangeable Cu, 10, 15, and 75% of the study area exhibited high, medium, and low phytotoxicity risk, respectively (Fig. 5), i.e., exhibiting exchangeable Cu values above the EC50, between EC10 and EC50, and below EC10 using plant biomass as a response variable (Lillo, 2019). This approach is more accurate to provide information on the degree of potential phytotoxicity in the study

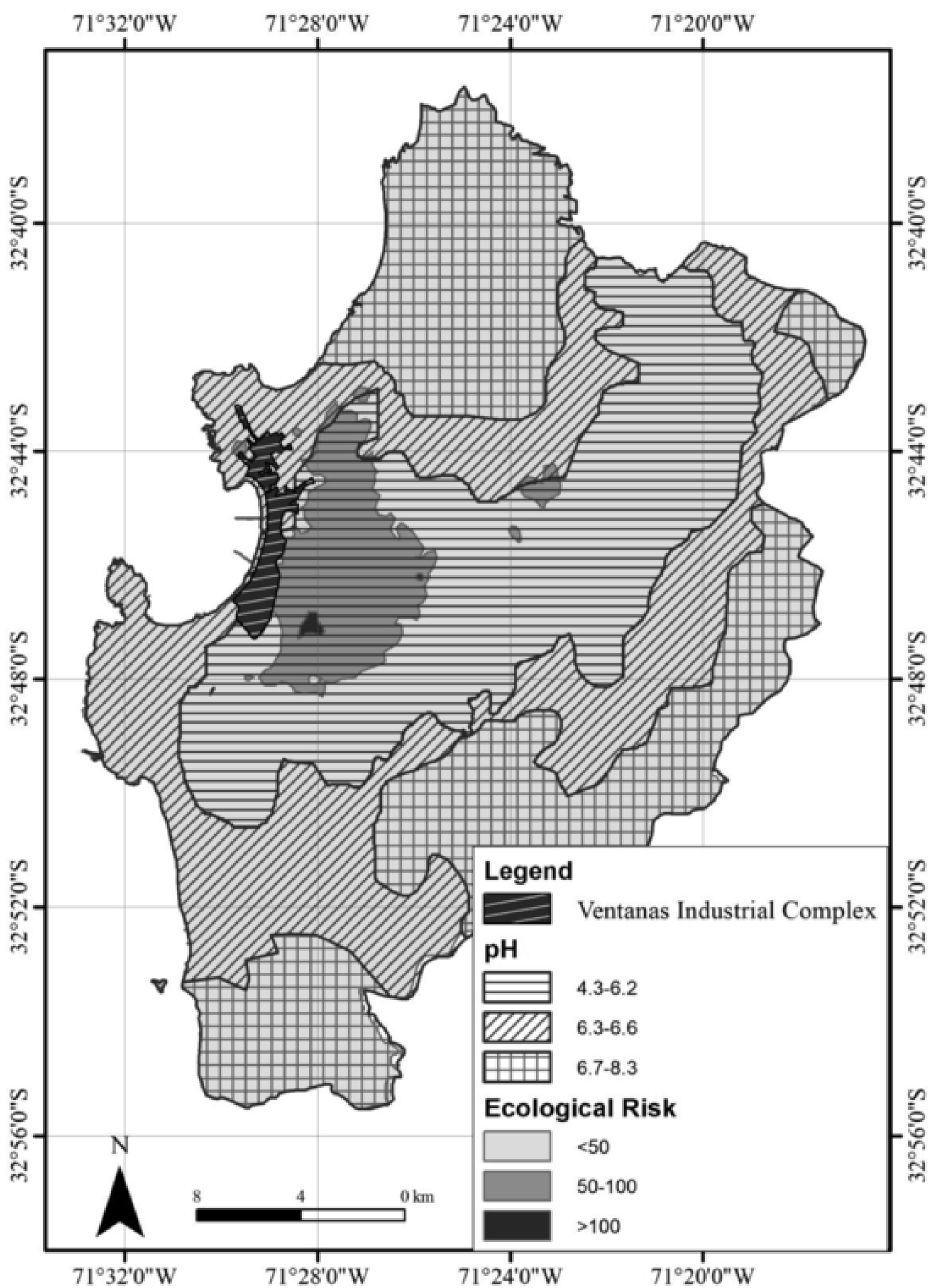

Fig. 4. The spatial distribution of the accumulated ecological risk of trace elements in the topsoil and the pH values observed in the study area.

area, in comparison to RI values, which are based on total metal concentrations. The obtained trends of spatial distribution of phytotoxicity risk is in agreement with patterns of plant species richness and abundance observed in the field conditions along the pollution gradient (Ginocchio, 2000).

4. Conclusions

The background concentrations of Cu, As, Pb, and Zn in the studied soils were 100, 16, 35, and 122 $mg\,kg^{-1}$, respectively. The concentrations of Cu, As, and Pb were positively correlated with each other, suggesting that their source is the Ventanas copper smelter. The concentrations of As and Pb in the studied soils were higher in the vicinity of the Ventanas Industrial Complex and in the direction of the predominant winds, that is, to the east of the complex. On the other hand, correlations for Zn were weaker than for other TE, suggesting low impact of the Ventanas copper smelter on spatial distribution of Zn. Indeed, only 6% of the study area exhibited Zn concentrations above the background level. In contrast, 77, 32 and 35% of the study area presented Cu, As, and Pb concentrations, respectively, above the background level.

The carcinogenic risk due to exposure to arsenic was above the threshold value of 10^{-04} in the population of young children (1–5 years old) on 27% of the study area. These risk values are classified as unacceptable, which require specific intervention by the Chilean government. Based on the estimated concentrations of exchangeable Cu, 10, 15, and 75% of the study area exhibited high, medium, and low phytotoxicity risk, respectively.

Declaration of competing interest

We declare to have conflict of interest with the following scientists due to our critics on their previous study on the subject of human

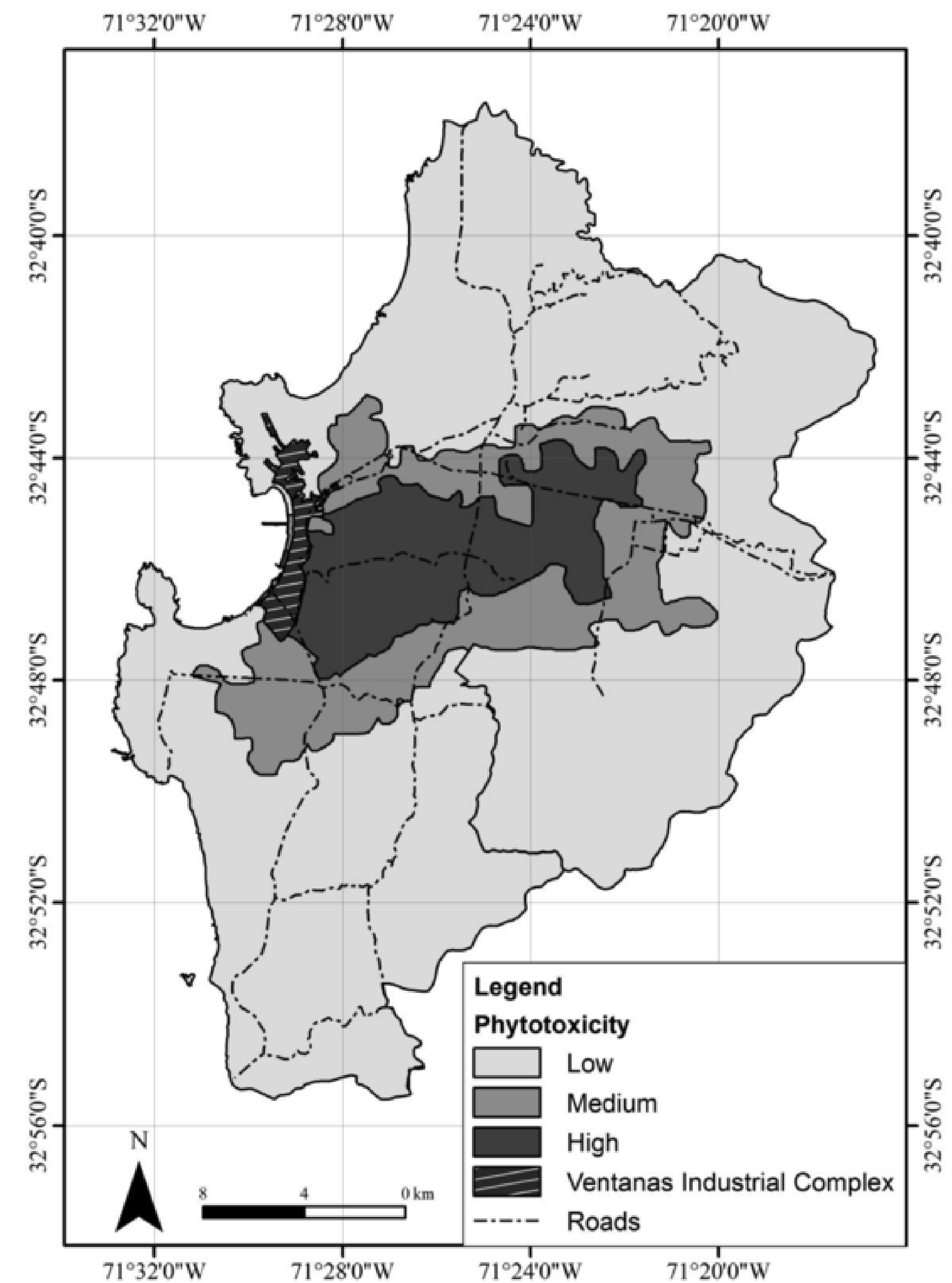

Fig. 5. The spatial distribution of potential phytotoxicity in the soils in Puchuncaví and Quintero townships.

health risk and ecological risk from exposure to As, Cu, Pb and Zn in soils near the Ventanas Industrial Complex (Puchuncaví, Chile): Soroush Salmanighabeshi, M. Rosario Palomo-Marín, Elena Bernalte, Fernando Rueda-Holgado, Conrado Miró-Rodríguez, Ximena Fadic-Ruiz, Víctor Vidal-Cortez, Mario Funes, Francisco Cereceda-Balic, Eduardo Pinilla-Gil.

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Appendix A. Supplementary data

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