Toxicology

Soil and indoor dust as environmental media of human exposure to As, Cd, Cu, and Pb near a copper smelter in central Chile

Maite Berasaluce[a], Pedro Mondaca[a], Marta Schuhmacher[b], Manuel Bravo[c], Sébastien Sauvé[d], Claudia Navarro-Villarroel[e], Elvira A. Dovletyarova[f], Alexander Neaman[a],*

[a] Escuela de Agronomía, Pontificia Universidad Católica de Valparaíso, Quillota, Chile
[b] Laboratory, Department d'Enginyeria Química, Universitat Rovira i Virgili, Tarragona, Spain
[c] Instituto de Química, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile
[d] Department of Chemistry, University of Montreal, Quebec, Canada
[e] Instituto de Estadística, Universidad de Valparaíso, Valparaíso, Chile
[f] Department of Landscape Design and Sustainable Ecosystems, RUDN University, Moscow, Russia

ARTICLE INFO

ABSTRACT

In the present study, we assessed the non-carcinogenic and carcinogenic human health risk due to exposure to trace elements in soil and indoor dust in Puchuncaví valley. We also determined the associations between trace element concentration in hair/toenails and the estimated chronic daily intake of trace elements in soil and indoor dust. We found statistically significant association between the trace element concentration in hair/toenails and the estimated chronic daily intake of soil and indoor dust. Indoor dust was more important than soil in terms of human exposure to trace elements in Puchuncaví, due to the high concentration of trace elements on this environmental media and long periods of time that the population spends at their households. With regards to non-carcinogenic risk, we found that there was no health risk associated to soil and indoor dust exposure in the Puchuncaví valley, because none of the hazard quotient values surpassed 1.0. However, carcinogenic risk due to arsenic exposure was above the threshold value of 1.0E-04 in the population of young children (from 1 to 5 years old) in all studied areas, including the control, and in the population of children (from 6 to < 18 years old) in the exposed area. Such risk values are classified as unacceptable (US EPA, 2001), requiring some target intervention from the Chilean government.

1. Introduction

1.1. Characterization of human health risk due to exposure to trace elements

The Puchuncaví valley in the coastal area of central Chile has been exposed to massive atmospheric contamination with sulfur dioxide and trace elements-rich particulate matter due to emissions from the Ventanas copper smelter. Since its opening in 1964 and until appearance of the first environmental regulations in 1991, no measures were taken in order to mitigate these emissions [1]. Despite the current environmental regulations, the cumulative environmental effects of historical emissions are still latent in the surrounding soils. Specifically, the areas immediately surrounding the Ventanas smelter are now characterized by bare and sparsely vegetated land and by soils that are severely eroded, acidic and contaminated with elevated levels of trace elements (Cu, Zn, Pb, Cd, and As) [2].

The above-mentioned soil conditions may contribute to human exposure to trace elements through inhalation of wind-blown dust or direct ingestion of soil [3]. Several other authors also highlighted the importance of incidental ingestion of soil and house dust as an exposure route to trace elements by adults and children [4–6]. Based on these evidences, soil and house dust seem to be important environmental media of human exposure to trace elements in Puchuncaví. Likewise, there are many evidences, from several countries, that trace element contamination in mining areas can cause health damage to the local inhabitants [e.g. in Ref. 7]. Based on these arguments, we hypothesized that, in the population of Puchuncaví valley, exposure to trace elements would represent a risk to human health.

For exposure assessment, we need to establish a method to estimate the "chronic daily intake" index, which refers to the average quantity of trace element intake by multiple pathways, in a certain population,
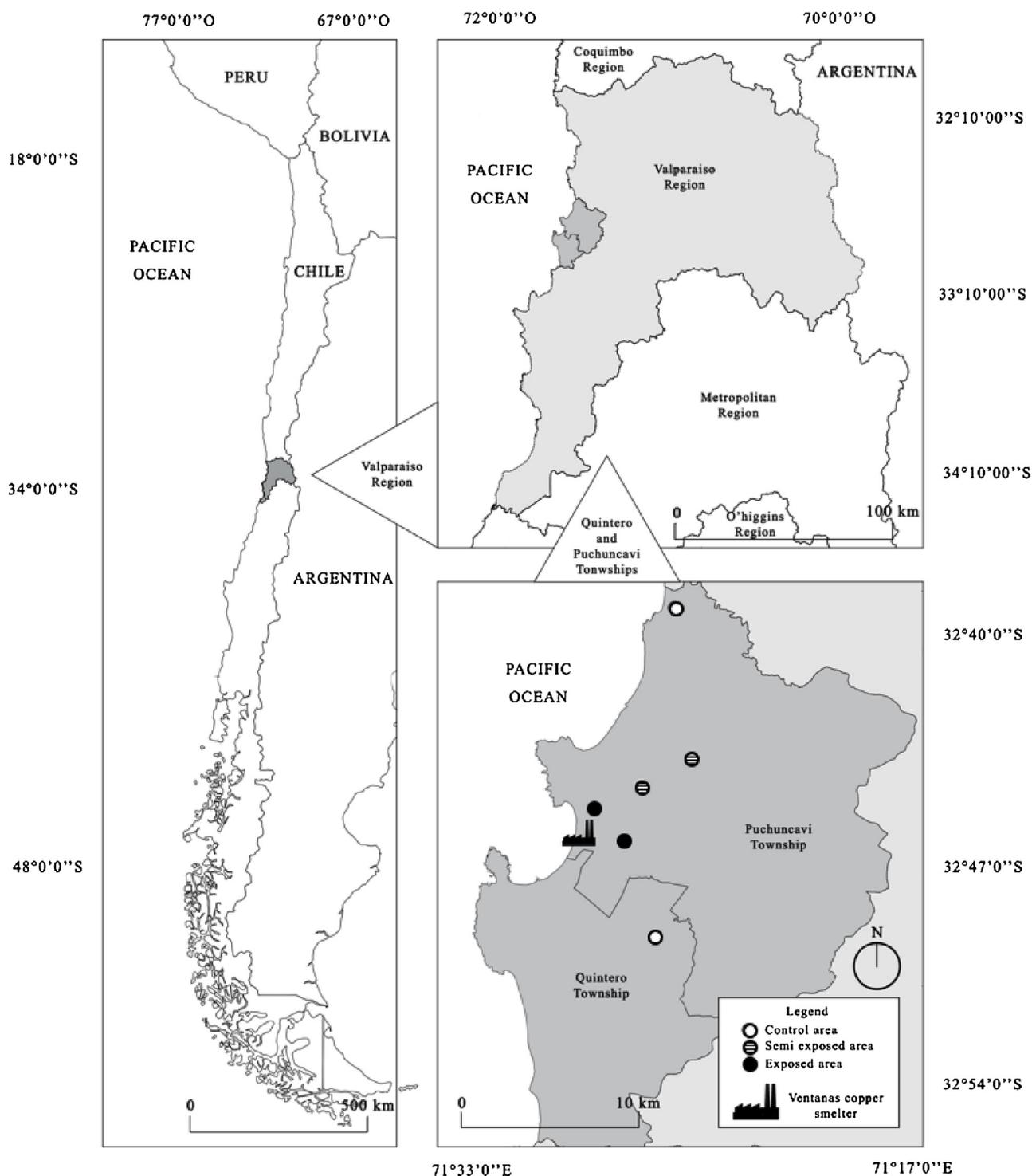

Fig. 1. Geographical location of the studied sites.

during a certain period. Estimation of the chronic daily intake is based on trace element concentration in the environmental media (soil, dust, etc.) and the exposure scenarios. The exposure scenario is a function of the age group, the exposure time and the activity factors. Chronic daily intake is the basis for non-carcinogenic and carcinogenic risk characterization through comparison with established intake permissible limits for the trace elements of interest [8,9]. This approach is based on the evidence from epidemiologic studies to support an association between exposure to trace elements and health risk. Toxicity assessment for non-carcinogenic effects is gathered regarding the potential of a substance to cause adverse effects in a developing organism as a result

of exposure [10]. While for carcinogens, risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen [11].

Therefore, the first objective of the present study was to characterize non-carcinogenic and carcinogenic human health risk due to exposure to trace elements in soil and indoor dust in Puchuncaví valley.

1.2. Biomarkers of human exposure to trace elements

Human biological samples (blood, urine, hair, and nails) could serve as biomarkers of human exposure to chemicals, demonstrating that

exposure to and absorption of the chemical has actually taken place [12]. In this sense, several authors have found significant correlation between trace element concentration in human biological sample with trace element concentration in soil and house dust [13–16]. Many studies used hair and nails for biomonitoring of long-term exposure to trace elements [17–21]. Based on these arguments, we hypothesized that trace element concentrations in hair and toenails of the population of Puchuncaví valley would be a function of estimated chronic daily intake of trace elements in soil and indoor dust. Therefore, the second objective of the present study was to determine associations between trace element concentration in hair/toenails and the estimated chronic daily intake of trace elements in soil and indoor dust.

1.3. Scientific novelty

Studies on human exposure to trace elements in Puchuncaví valley are scarce. The first available study, from the Institute of the Public Health of Chile [22], was conducted as a consequence of an emergency of high concentration of SO_2, causing acute respiratory symptoms and fainting among children from a local primary school. The study included 394 individuals from this exposed area and 361 from the control area, using blood and urine as biomarkers. The study concluded that the population of Puchuncaví valley had higher concentrations of trace elements in blood and/or urine, in comparison to a control area.

Urinary and blood levels of trace elements are reliable biomarkers of recent exposure; they are not useful for the biomonitoring of long-term exposure to trace elements because blood and urine trace element concentrations come down to a minimum level within a few hours or days of exposure [17 and references therein, [23]]. To this end, in the study of Institute of the Public Health of Chile [22], there is an uncertainty with regards to chronic exposure to trace elements in Puchuncaví valley. Arsenicals bind to reduced cysteines in peptides and proteins; keratin is a protein rich in cystein residues. For that reason, keratin-rich biological derivatives of ectoderm, such as hair and nails, provide a valuable indication of exposure that occurred several months earlier [24]. Although hair and nails are metabolically dead materials in the epidermis, the roots are highly influenced by the health status of the living organisms. The present study is the first to use hair and toenails as biomarkers to demonstrate chronic exposure of inhabitants in Puchuncaví valley.

There are some studies that determined trace element concentration in soils of Puchuncaví valley [25–27] and characterized the human health risk due to soil ingestion in Puchuncaví valley [28]. However, the present study is the first to consider indoor dust as a relevant environmental media of human exposure to trace elements.

2. Materials and methods

2.1. Ethics statement

All necessary permits were obtained for the described study. All participants were informed about the objectives and methods of the study before the investigation. Written consent was obtained from all participants. Data will be made available upon request. The privacy rights of all participants were observed.

2.2. Sampling area

The study took place in the Puchuncaví valley that has a population of 18.000 inhabitants and is located in the Valparaíso Region, 141 km NW from Santiago de Chile. Based on the spatial distribution of As, Cd, Cu, and Pb in the study area [29,30], we selected two contaminated sites (near the Ventanas copper smelter), two semi-contaminated sites, and two uncontaminated sites (8 and 17 km of distance from the Ventanas copper smelter) (Fig. 1). Specifically, the exposed area was located in Los Maitenes and La Greda, the semi exposed area was located

in Puchuncaví town and Campiche, while the control area was located in Valle Alegre and Maitencillo.

2.3. Sample collection

A total of 100 households from the three areas (exposed, semi exposed and control) were sampled. Adult homeowners were recruited and were asked to provide written consent for themselves and their children. In total, 205 persons (134 adults and 71 children) participated in the study. Smokers (past or present) were excluded from the study, as smoking is known to increase trace element contents in human biological samples [e.g., 31]. For the same reason, individuals that worked (past or present) in the mining industry were also excluded.

In each household, soil composite samples were obtained from 5 locations at the household's yard by scraping the upper 2 cm of soil with a 5 cm plastic spatula; the samples were then homogenized. Indoor dust was obtained from the top surfaces of furniture or windowsills by gently sweeping with a brush onto a plastic dustpan. The samples were collected using a different spatula, brush and dustpan in each household to avoid cross-contamination between sampling locations.

Total hair samples were cut from the occipital region using ceramic scissors [32]. Toenail clippings were also obtained. Additionally, the height and weight of each individual was measured. Each person answered a survey about his/her behavior and personal information relevant for construction of the exposure scenarios.

2.4. Soil and indoor dust analysis

Soil and indoor dust samples were air dried at 40 °C for 48 h and sieved through a < 250 μm stainless steel mesh. Total concentrations of Cu, As, Pb and Cd were determined through sample digestion (1 g) during 12 h in boiling nitric acid (16.25%), followed by perchloric acid (3.5%) addition [33]. Acids used in this procedure include 70% nitric acid, Winkler, analytical-grade, ACS and 65% perchloric acid, Merck, analytical-grade, EMSURE® ISO. In order to prevent volatilization of As during the digestion process, a Teflon stopper with 30 cm-long glass reflux tube was used [adapted from Ref. 34]. Total trace element (TE) concentrations in soil and indoor dust were determined by atomic absorption spectroscopy (AAS) (GBC, model 902, Dandenong, Australia). Quality was assured by similarly digesting two certified soil reference samples: ISE 859 (Wageningen University) and 2711A (NIST). Recovery of the certified values was 100% ± 20%. The detection limits of As, Cu, Cd, and Pb were 0.005, 0.009, 0.004, and 0.005 mg L^{-1}, respectively. Blanks were measured and they were always under limit of detection.

2.5. Hair and toenail analysis

Hair and toenail samples were washed with deionized water and acetone, procedure recommended by the International Atomic Energy Agency [32]. The washed samples were dried at 50 °C for 4–5 h and later stored in sealed polyethylene bags. An accelerated microwave digestion system (Milestone, model Start D, Sorisole, Italy) was used for the digestion of the samples. Approximately 0.15–0.20 g of hair was weighed into a Teflon digestion tube. Ultra trace concentrated nitric acid (4 mL, 65%, Merck, analytical-grade, EMSURE® ISO) and hydrogen peroxide (1 mL, 30%, Merck, analytical-grade, EMSURE® ISO) were added. Then, the tubes were closed, introduced in the microwave rotor and treated. The digestion consisted of two stages: first at a power of 1000 W (~180 °C) for 10 min and the second also at 1000 W (~180 °C) for 15 min. After cooling for 10 min, the tubes were carefully opened; each digested solution was quantitatively transferred into a 25 mL volumetric flask and then analyzed. The reference standards were digested in the same way.

The digested samples were analyzed by ICP-MS (Perkin Elmer NexION 300x) at the Department of Chemistry, University of Montreal.

The operating parameters were set as RF power 1600 W, 3 measurement replicates and integration time 1000 ms. Internal standards (indium and bismuth) were used to compensate for any variation and/or matrix effect during sample analysis. Response ratio (signal of analyte divides to signal of internal standard) was used to build calibration curves and calculate concentrations of analytes instead of absolute signal of analytes. High purity ICP-MS quality control standard 27 were purchased from Inorganic Ventures and prepared in 1% ultratrace HNO_3 (65%, Aristar Ultra, DBH) that was diluted in ultrapure (Milli-Q) water (R > 18.2 MΩ cm; total organic carbon < 2 µg L^{-1}). Quality was assured by similarly digesting in duplicate the certified reference sample GBW 07601 human hair (IGGE, China). Recovery of the certified values was 100% ± 5%. The detection limits of As, Cu, Cd, and Pb were 0.049, 0.0012, 0.012, and 0.0005 µg L^{-1}, respectively. Blanks were measured and they were always under limit of detection.

2.6. Data analysis

Data were not normally distributed and differed in the number of samples between the three areas. Therefore, TE concentrations in soil and indoor dust of the different exposure areas were compared by the Mann-Whitney's test (p < 0.05) using Minitab 17.

In this study, the ingestion of soil and indoor dust particles was considered as the route of exposure to be characterized. To model the exposure of residents, we established 4 age groups based on life stages and activity patterns: (1) young children from 1 to 5 years old, (2) children from 6 to < 18 years old, (3) adults from 18 to < 60 years old and (4) elderly adults of ≥60 years old.

The average daily intake of TE in soil and indoor dust ingested by the population was estimated using chronic daily intake (Supplementary Eq. 1) according to standardized procedures by the US EPA [35] The information collected in surveys during the sample campaign was used to model site-specific average values of exposure frequency (days year^{-1}), exposure duration (years), body weight (kg) and averaging time (days), for each age group.

For non-carcinogenic health risk, the hazard quotient (HQ) was used by dividing the chronic daily intake (CDI) by the reference dose (RfD) (Eq. 1) for each TE in soil and indoor dust, for each exposure scenario. There were 12 exposure scenarios, corresponding to 4 age groups and 3 exposure areas (Exposed, semi exposed and control). Supplementary Table 1 summarizes the RfD values used for calculations in the presents study.

$$HQ = \frac{CDI}{RfD}$$
(1)

Carcinogenic risk assessment of As was calculated by Eq. (2). The estimated As CDI was multiplied by the slope factor (SF) of As ingestion to represent the incremental probability of an individual of developing cancer over a lifetime as a result of exposure to the potential carcinogenic [35]. The SF value used was 1.5 per mg kg^{-1} day^{-1}.

Risk = CDI x SF
(2)

To determine associations between trace element concentration in hair/toenails and the estimated CDI of trace elements in soil and indoor dust, Spearman correlations were performed using Minitab 17.

3. Results and discussion

3.1. Concentrations of TE in soil and indoor dust

The TE concentrations in soil and indoor dust compared by area of exposure are summarized in Table 1. In general, there was a statistically significant increase in TE concentration in soil and indoor dust in the exposed area, in comparison to the control area (Table 1). In some cases, TE concentration in soil and indoor dust were also significantly higher in the semi exposed area, in comparison to the control area,

Table 1

Trace element concentration in soil and indoor dust compared by area of exposure. Median values, ranges (in parenthesis) and number of samples are shown.

Media, element	Trace element concentration, mg kg^{-1}		
	Control	Semi exposed	Exposed
Soil As	13	13	22*
	(5.7–34)	(8.2–28)	(6.4–137)
	n = 16	n = 44	n = 34
Indoor dust As	47	43	76
	(0.3–196)	(1.5–162)	(8.7–761)
	n = 18	n = 36	n = 29
Soil Pb	33	46**	48**
	(13-75)	(14–198)	(18–362)
	n = 19	n = 44	n = 33
Indoor dust Pb	76	82	160***
	(25–175)	(31–260)	(22–1884)
	n = 18	n = 36	n = 29
Soil Cu	105	259***	474***
	(29–301)	(22–1570)	(29–4341)
	n = 19	n = 44	n = 34
Indoor dust Cu	530	1214***	3096***
	(246–2296)	(188–3556)	(443–8358)
	n = 18	n = 36	n = 29
Soil Cd	1.9	2,1*	2.2**
	(0.60–2.6)	(1.2–5.0)	(1.4–7.7)
	n = 19	n = 44	n = 34
Indoor dust Cd	1.2	1.2	3.9**
	(0.25–9.7)	(0.08–50)	(0.1–404)
	n = 18	n = 36	n = 28

Statistically significant difference between the exposed/semi exposed area and the control area according to Mann-Whitney test (*p ≤ 0.05; **p ≤ 0.01; *** p ≤ 0.001).

showing the influence of the Ventanas copper smelter. Since smelter opening in 1964 and until appearance of the first environmental regulations in 1991, no measures have been taken in order to mitigate these emissions [1]. Although Gener thermoelectric plant was also installed in Puchuncaví in the early 1960's, it has been demonstrated that atmospheric emissions are mainly due to Ventanas copper smelter [26].

In most cases, concentrations of TE were considerably higher in indoor dust, in comparison to soil, even in the control area. In other words, TE get concentrated in the particles of indoor dust, most probably because of their small size. The distribution of TE in different particle size of soils from the Puchuncaví Valley was recently studied by Parra, Bravo, Quiroz, Moreno, Karanasiou, Font, Vidal and Cereceda [25]. This study determined that highest concentrations of Cu, Zn, As, and Pb were present in the finer fractions. Moreover, the researchers identified tenorite and calcium oxide in the fine particles, which are most likely associated with smelting activities, confirming emission of enriched particulate matter from the copper smelter. Thereby, the higher concentration of TE in indoor dust compared to soil and the statistical similarity of As and Pb in indoor dust among the studied areas suggest that control area is also affected by emissions from the copper smelter.

Background concentration of arsenic in soils in the studied area has been reported as 13 mg kg^{-1} in a previous study [30]. Therefore, the measured concentration of arsenic in soils is considered high only in case of the exposed area, while measured concentration of arsenic in indoor dust is considered high in all the studied areas (also in case of control). These results infer a larger impact zone for indoor dust. Indeed, particle size decreases with increased distance from the source, due to higher gravitational settling velocities of coarse particles in the atmosphere [36].

3.2. Characterization of human health risk due to exposure to trace elements

Chronic daily intake through non-dietary ingestion of trace elements for each age group compared by area of exposure is shown in Supplementary Table 2. Indoor dust ingestion was the main exposure pathway to trace elements because of the time individuals spent daily inside their household (as they reported in the surveys). Specifically, this time was: 75% for adults and 66% for children. This behavior is well documented; for instance, US EPA [37] indicated that adults usually spend ˜88% of the time indoors and children 71–79%. Likewise, the concentrations of TE in indoor dust were considerably higher than those in soil, contributing to higher CDI values for indoor dust, in comparison to CDI values for soil.

In relation to age groups, young children (1–5 years old) showed the highest total CDI, followed by the children age group (6 to < 18 years old). These values are the result of their lower body-weight in relation to the adults and their hand-to-mouth activities [38].

On the other hand, the hazard quotient of each age group compared by area of exposure is shown in Supplementary Table 2. A value of HQ greater than 1.0 would indicate that there is a chance of occurrence of non-carcinogenic health effects. In the case of the present study, we found that there was no health risk associated to soil and indoor dust exposure in the Puchuncaví valley, because none of the hazard quotient values surpassed 1.0 (Fig. 2).

Regarding carcinogenic risk, its value exceeded the threshold of 1.0E-04, in the case of the population of young children (1 to 5 years old) in all studied areas, including the control, and in the population of children (6 to < 18 years old) in the exposure area (Fig. 3). Such risk values (above 1.0E-04) are classified as unacceptable [39], requiring some target intervention from the Chilean government (discussed below). As mentioned above, this is due to high concentration of arsenic in indoor dust and large amount of time individuals spend inside their households. On the other hand, as a limiting factor of the present study, we highlight that arsenic reference doses used for health risk assessment have been established only for adults [40], hence they are not necessarily good estimators of health risk in infants or children.

In addition, it is important to emphasize that in spite of food chain is generally considered the main pathway for transfer of trace elements to humans [41], local-food only represents a 0.14% of the total consumed food by the population of the Puchuncaví valley [42]. Nevertheless, in another study, we assessed the potential health risk due to consumption of vegetables grown near the studied copper smelter [43].

With regards to drinking water, its quality is regulated in Chile by law [44] and periodically monitored by the authorities. Indeed, drinking water was also assessed in some households but all arsenic concentrations were under limit of detection. In accordance with these findings, in our previous studies [45,46], we demonstrated that the anthropogenic impacts of the Ventanas smelter, with respect to trace element concentrations and acidification, are restricted to the topsoil while the subsoil remains unaffected. We argued that leaching of trace elements from contaminated topsoil to groundwater is unlikely in Puchuncaví. Thus, human exposure to trace elements through consumption of drinking water is unlikely in the case of Puchuncaví.

3.2.1. Biomarkers of human exposure to trace elements

Trace element concentrations in hair and toenail compared by area of exposure are shown in Table 2. We found a high variability in hair and toenail for all the analyzed TE. In a few cases, there was a statistically significant increase in TE concentrations in hair/toenails in the exposed/semi-exposed area, in comparison to the control area. Contradictory results were found for Cu in hair showing higher levels in the control area, in comparison to exposed/semi-exposed area. As it is well known, Cu toxicity in humans occurs rarely due to effective defense homeostatic mechanisms against its toxicity [47]. These defense homeostatic mechanisms could be possibly responsible for elimination of excess of Cu from human bodies of individuals in the exposed and semi-exposed areas.

We obtained a positive Spearman correlation between trace element concentration in hair/toenails and CDI of each trace element (Table 3). Arsenic in hair/toenails showed better correlation to CDI in contrast to other TE. Similarly, Skröder, Kippler, Nermell, Tofail, Levi, Rahman, Raqib and Vahter [48] reported that hair is a biomarker especially useful for As exposure, but not useful enough for Cu, Cd, and Pb. Even though the correlations in Table 3 were weak, they confirm that soil and indoor dust are the environmental media of human exposure to TE in the population of the Puchuncaví valley. According to our results, toenails are preferable to hair as biomarkers of TE exposure.

4. Conclusions

In the present study, we assessed the non-carcinogenic and carcinogenic human health risk due to exposure to trace elements in soil and indoor dust in Puchuncaví valley. We also determined the associations between trace element concentration in hair/toenails and the estimated chronic daily intake of trace elements in soil and indoor dust. In accordance with the hypothesis, the conclusions of the present study are as follows:

1) Indoor dust was more important than soil in terms of human exposure to trace elements in Puchuncaví, due to the high concentration of trace elements on this environmental media and long periods of time that the population spends at their households. With regards to non-carcinogenic risk, we found that there was no health
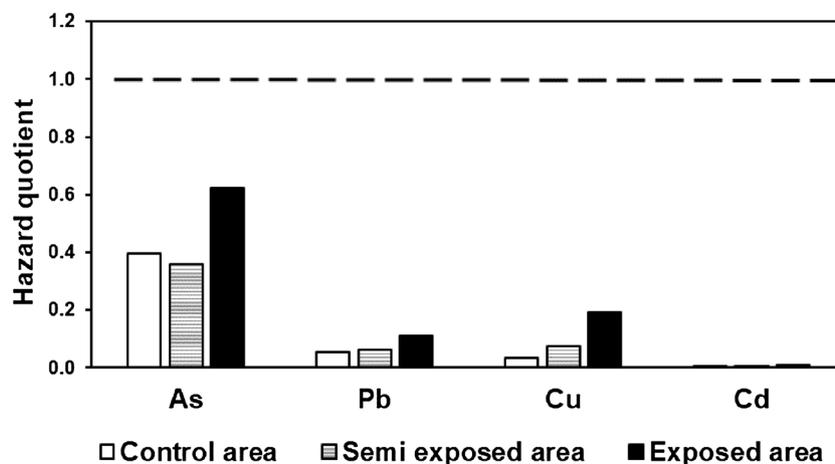

Fig. 2. Hazard quotient of age group 1–5 years old compared by area of exposure. Hazard quotient higher than 1.0 may represent health risk [1].
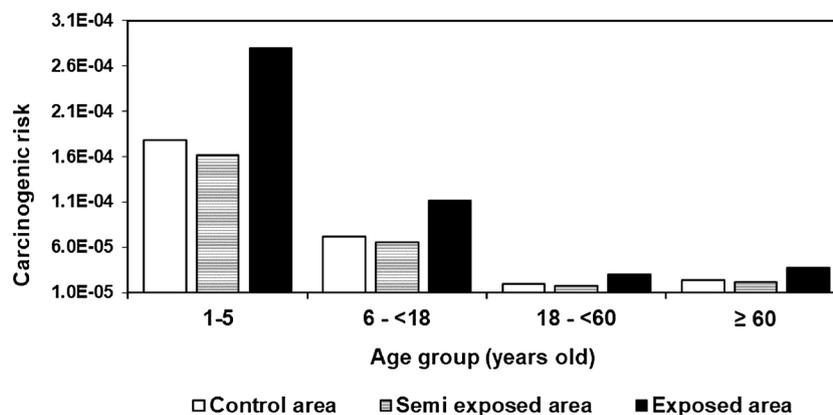
Fig. 3. Arsenic carcinogenic risk of each age group by area of exposure. According to US EPA [2], risk values above 1.0E-04 are classified as unacceptable.

Table 2
Trace element concentration in hair and toenail compared by area of exposure. Median values, ranges (in parenthesis) and number of samples are shown.

Trace element	Hair trace element concentration, mg kg^{-1}			Toenail trace element concentration, mg kg^{-1}		
	Control area	Semi exposed area	Exposed area	Control area	Semi exposed area	Exposed area
As	0.065 (0.0033–0.50) n = 25	0.14*** (0.0051–1.9) n = 88	0.13** (0.020–0.67) n = 49	0.39 (0.084–1.9) n = 28	0.41 (0.098-6.4) n = 65	0.51 (0.099–3.5) n = 47
Pb	1.3 (0.17–22) n = 25	0.81 (0.14–9.2) n = 71	0.95 (0.28–4.8) n = 44	0.60 (0.26–4.1) n = 18	0.84 (0.092–41) n = 50	0.87 (0.10–12) n = 35
Cu	39 (12.1–473) n = 25	24** (4.8–504) n = 71	23** (11–98) n = 44	8.9 (5.9–17) n = 18	11* (3.7–127) n = 50	15** (2.1–75) n = 35
Cd	0.032 (0.0034–0.17) n = 25	0.028 (0.0057–0.15) n = 66	0.033 (0.0032–0.17) n = 43	0.020 (0.0046–0.061) n = 16	0.049*** (0.0048–0.23) n = 47	0.034* (0.0058–0.19) n = 32

Statistically significant difference between the exposed/semi exposed area and the control area according to Mann-Whitney test (*p ≤ 0.05; **p ≤ 0.01; *** p ≤ 0.001).

Table 3
Spearman correlation between trace element concentration in hair/toenails and chronic daily intake (CDI) of each trace element. The ingestion of soil and indoor dust particles (or both, referred to as total) was considered as the route of exposure.

Response variable	Predictor variable	r	Response variable	Predictor variable	r
As hair	CDI As soil	0.43	As toenail	CDI As soil	0.57
	CDI As dust	0.46		CDI As dust	0.46
	CDI As total	0.46		CDI As total	0.47
Pb hair	CDI Pb soil	n.s.	Pb toenail	CDI Pb soil	0.39
	CDI Pb dust	0.27		CDI Pb dust	0.41
	CDI Pb total	0.26		CDI Pb total	0.43
Cu hair	CDI Cu soil	n.s.	Cu toenail	CDI Cu soil	0.39
	CDI Cu dust	n.s.		CDI Cu dust	0.51
	CDI Cu total	n.s.		CDI Cu total	0.52
Cd hair	CDI Cd soil	n.s.	Cd toenail	CDI Cd soil	0.59
	CDI Cd dust	n.s.		CDI Cd dust	n.s.
	CDI Cd total	n.s.		CDI Cd total	0.29

n.s. = correlation is not statistically significant (p > 0.05). All other correlations were significant (p ≤ 0.05).

risk associated to soil and indoor dust exposure in the Puchuncaví valley, because none of the hazard quotient values surpassed 1.0. However, carcinogenic risk due to arsenic exposure was above the threshold value of 1.0E-04 in the population of young children (from 1 to 5 years old) in all studied areas, including the control, and in the population of children (from 6 to < 18 years old) in the exposed area. Such risk values are classified as unacceptable [39], requiring some target intervention from the Chilean government

2) We found statistically significant association between the trace element concentration in hair/toenails and the estimated chronic daily intake of soil and indoor dust.

5. Recommendations to Chilean authorities and the population

In Chile, environmental remediation programs are difficult to establish due to economic limitations. Considering that uncertainties should be reduced as much as possible, a remediation program should be based on demonstrated human health risk and accurately described exposure pathways of human exposure to trace elements. In this study we demonstrated that indoor dust was an important environmental media of human exposure to trace elements in Puchuncaví. Thus, we recommend authorities to perform a target intervention, based on experiences with the population of a residential area in Arica (northern Chile) that was exposed to trace elements. In Arica, hundreds of houses were cleaned off trace element-containing dust, hundreds of houses were demolished, and hundreds of families received new housing [49]. We recommend authorities performing a similar target intervention in the case of the population of Puchuncaví. Likewise, we recommend the population to perform frequent wet cleaning in their houses to decrease exposure to indoor dust.

Additionally, large-scale soil revegetation programs should be carried out. In our previous studies, we demonstrated that such an option is feasible by applying lime and compost to the soils of Puchuncaví, which would allow a spontaneous re-colonization of plants from the existing soil seed bank, under a rain-fed water regime [46,50]. We recommend the population to apply lime and homemade compost to the soil in their yards.

Conflict of interest

The authors declare that they do NOT have conflict of interest.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jtemb.2019.04.006.

References

[1] M. Folchi, Historia ambiental de las labores de beneficio en la minería de cobre en Chile, siglos XIX y XX, Tesis de doctorado, Departamento de Economía y de Historia Económica, Universidad Autónoma de Barcelona, (2006) p. 727.

[2] J. Pardo, P. Mondaca, J.L. Celis-Diez, R. Ginocchio, C. Navarro-Villarroel, A. Neaman, Assessment of revegetation of an acidic metal(loid)-polluted soils six years after the incorporation of lime with and without compost, Geoderma 331 (2018) 81–86.

[3] G.M. Pierzynski, Strategies for remediating trace-element contaminated sites, in: I.K. Iskandar, D.C. Adriano (Eds.), Remediation of Soils Contaminated with Metals, Science Reviews, Northwood, UK, 1997.

[4] L. Carrizales, I. Razo, J.I. Téllez-Hernández, R. Torres-Nerio, A. Torres, L.E. Batres, A.C. Cubillas, F. Díaz-Barriga, Exposure to arsenic and lead of children living near a copper-smelter in San Luis Potosi, Mexico: Importance of soil contamination for exposure of children, Environ. Res. 101 (1) (2006) 1–10.

[5] J. Hogervorst, M. Plusquin, J. Vangronsveld, T. Nawrot, A. Cuypers, E. Van Hecke, H.A. Roels, R. Carleer, J.A. Staessen, House dust as possible route of environmental exposure to cadmium and lead in the adult general population, Environ. Res. 103 (2007) 30–37.

[6] C.S. Qu, Z.W. Ma, J. Yang, Y. Liu, J. Bi, L. Huang, Human exposure pathways of heavy metals in a lead-zinc mining area, Jiangsu Province, China, PLoS One 7 (11) (2012).

[7] G. Plumlee, S. Morman, Mine wastes and human health, Elements 7 (6) (2011) 399–404.

[8] US EPA, Exposure Factors Handbook. 2011, Washington, DC (2011).

[9] US EPA, Reference dose (RfD): description and use in health risk assessments, Background Document 1A, (1993) https://http://www.epa.gov/iris/reference-dose-rfd-description-and-use-health-risk-assessments.

[10] US EPA, Toxicity assessment, in: US EPA (Ed.), Risk Assessment Guidance for Superfund, Human Health Evaluation Manual (Part A), 1989Washington, DC.

[11] US EPA, Risk characterization, in: US EPA (Ed.), Risk Assessment Guidance for Superfund, Human Health Evaluation Manual (Part A), Washington, DC, 1989.

[12] US EPA, Guidelines for Exposure Assessment, Washington, DC (1992).

[13] H.W. Mielke, P.L. Reagan, Soil is an important pathway of human lead exposure, Environ. Health Perspect. 106 (1998) 217–229.

[14] B. Lanphear, P. Succop, S. Roda, G. Henningsen, The effect of soil abatement on blood lead levels in children living near a former smelting and milling operation, Public Health Rep. 18 (2003) 83–91.

[15] P.J. Berny, L.M. Coté, W.B. Buck, Relationship between soil lead, dust lead, and blood lead concentrations in pets and their owners: evaluation of soil lead threshold values, Environ. Res. 67 (1994) 84–97.

[16] Y. Cho, S. Seo, S.H. Choi, S. Lee, K. Kim, H.J. Kim, J.W. Choi, Association of arsenic levels in soil and water with urinary arsenic concentration of residents in the vicinity of closed metal mines, Int. J. Hyg. Environ. Health 216 (2013) 255–262.

[17] B.K. Mandal, Y. Ogra, K.T. Suzuki, Speciation of arsenic in human nail and hair from arsenic-affected area by HPLC-inductively coupled argon plasma mass spectrometry, Toxicol. Appl. Pharmacol. 189 (2) (2003) 73–83.

[18] I. Mansilla-Rivera, C.M. Nazario, F.A. Ramirez-Marrero, C.J. Crespo, C.J. Rodriguez-Sierra, Assessing arsenic exposure from consumption of seafood from Vieques-Puerto Rico: a pilot biomonitoring study using different biomarkers, Arch. Environ. Contam. Toxicol. 66 (2) (2014) 162–175.

[19] Y. Xue, L.S. Yang, Z. Ouyang, B.G. Wei, J.P. Yu, Relationships between metal concentrations in human hair and in soil, road dust, and rice, Hum. Ecol. Risk Assess. 21 (4) (2015) 1007–1019.

[20] N. Marchiset-Ferlay, C. Savanovitch, M.P. Sauvant-Rochat, What is the best

[21] M.J. Slotnick, J.O. Nriagu, Validity of human nails as a biomarker of arsenic and selenium exposure: a review, Environ. Res. 102 (1) (2006) 125–139.

[22] ISP, Evaluación de exposición a metales en la comuna de Puchuncaví y su comparación con la zona control, Instituto de Salud Pública, Available at: (2011) http://www.ispch.cl/noticia/15300.

[23] J.P. Goullé, E. Saussereau, L. Mahieu, D. Bouige, S. Groenwont, M. Guerbet, C. Lacroix, Application of inductively coupled plasma mass spectrometry multi-element analysis in fingernail and toenail as a biomarker of metal exposure, J. Anal. Toxicol. 33 (2009) 92–98.

[24] ATSDR, Toxicological profile for arsenic, agency for toxic substances and disease registry Atlanta, Georgia, (2007) p. 359.

[25] S. Parra, M.A. Bravo, W. Quiroz, T. Moreno, A. Karanasiou, O. Font, V. Vidal, F. Cereceda, Distribution of trace elements in particle size fractions for contaminated soils by a copper smelting from different zones of the Puchuncaví Valley (Chile), Chemosphere 111 (0) (2014) 513–521.

[26] S. Parra, M.A. Bravo, W. Quiroz, T. Moreno, A. Karanasiou, O. Font, V. Vidal, F. Cereceda-Balic, Source apportionment for contaminated soils using multivariate statistical methods, Chemom. Intell. Lab. Syst. 138 (2014) 127–132.

[27] S. Salmanighabeshi, M.R. Palomo-Marín, E. Bernalte, F. Rueda-Holgado, C. Miró-Rodríguez, X. Fadic-Ruiz, V. Vidal-Cortez, F. Cereceda-Balic, E. Pinilla-Gil, Long-term assessment of ecological risk from deposition of elemental pollutants in the vicinity of the industrial area of Puchuncaví-Ventanas, central Chile, Sci. Total Environ. 527–528 (2015) 335–343.

[28] S. Salmani-Ghabeshi, M.R. Palomo-Marín, E. Bernalte, F. Rueda-Holgado, C. Miró-Rodríguez, F. Cereceda-Balic, X. Fadic, V. Vidal, M. Funes, E. Pinilla-Gil, Spatial gradient of human health risk from exposure to trace elements and radioactive pollutants in soils at the Puchuncaví-Ventanas industrial complex, Chile, Environ. Pollut. 218 (Suppl. C) (2016) 322–330.

[29] I. González, A. Neaman, P. Rubio, A. Cortés, Spatial distribution of copper and pH in soils affected by intensive industrial activities in Puchuncaví and Quintero, central Chile, J Soil Sci Plant Nutr 14 (4) (2014) 943–953.

[30] PGS, Muestreo de suelos para las comunas de Quintero y Puchuncaví, Región de Valparaíso, Santiago, Chile (2015).

[31] M. Wolfsperger, G. Hauser, W. Gößler, C. Schlagenhaufen, Heavy metals in human hair samples from Austria and Italy: influence of sex and smoking habits, ScTEn 56 (1994) 235–242.

[32] T. Wang, J.J. Fu, Y.W. Wang, C.Y. Liao, Y.Q. Tao, G.B. Jiang, Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area, Environ. Pollut. 157 (8-9) (2009) 2445–2451.

[33] J.A. Maxwell, Rock and Mineral Analysis, Interscience Publishers, New York, 1968.

[34] M. Verlinden, On the acid decomposition of human blood and plasma for the determination of selenium, Talanta 29 (10) (1982) 875–882.

[35] US EPA, Risk Assessment Guidance for Superfund. Volume I: Human Health Evaluation Manual (Part A). Chapter 8: Risk Characterization, Office of Emergency and Remedial Response, Available at: U.S. Environmental Protection Agency, 1989 p. 31 http://www.epa.gov/oswer/riskassessment/ragsa/pdf/rags_ch8.pdf.

[36] M. van der Does, L.F. Korte, C.I. Munday, G.-J.A. Brummer, J.-B.W. Stuut, Particle size traces modern Saharan dust transport and deposition across the equatorial North Atlantic, Atmos. Chem. Phys. 16 (21) (2016) 13697–13710.

[37] US EPA, Exposure Factors Handbook, Washington, DC (1997).

[38] P.B. Kurt-Karakus, Determination of heavy metals in indoor dust from Istanbul, Turkey: estimation of the health risk, Environ. Int. 50 (2012) 47–55.

[39] US EPA, Process for conducting probabilistic risk assessment, in: US EPA (Ed.), Risk Assessment Guidance for Superfund: Volume III (Part A), 2001 Washington, DC.

[40] W.P. Tseng, Effects and dose - response relationships of skin cancer and blackfoot disease with arsenic, Environ. Health Perspect. 19 (1977).

[41] A. Kabata-Pendias, A.B. Mukherjee, Trace Elements from Soil to Humans, (2007).

[42] PUCV, UV, Evaluación de riesgos para la salud de las personas y biota terrestre por la presencia de contaminantes, en el área de influencia industrial y energética de las comunas de Concón, Quintero y Puchuncaví (2014).

[43] N. Lizardi, P. Mondaca, M. Aguilar, M. Valdenegro, M. Bravo, A. Neaman, Assessment of potential health risk due to consumption of vegetables grown near a copper smelter in central Chile, Ciencia e Investigación Agraria (under review) (2019).

[44] Norma Chilena Oficial N° 409/1, Norma calidad del agua potable Diario Oficial de la República de Chile, 27 de junio de 2006, 2006.

[45] A. Neaman, L. Reyes, F. Trolard, G. Bourrie, S. Sauvé, Copper mobility in contaminated soils of the Puchuncavi valley, central Chile, Geoderma 150 (3–4) (2009) 359–366.

[46] C. Ulriksen, R. Ginocchio, M. Mench, A. Neaman, Lime and compost promote plant re-colonization of metal-polluted, acidic soils, Int. J. Phytoremed. 14 (2012) 820–833.

[47] I.H. Scheinberg, Human health effects of copper, in: J.O. Nriagu (Ed.), Copper in the Environment. Part II: Health Effects. John Wiley & Sons, New York, NY, 1979, pp. 17–31.

[48] H. Skröder, M. Kippler, B. Nermell, F. Tofail, M. Levi, S.M. Rahman, R. Raqib, M. Vahter, Major limitations in using element concentrations in hair as biomarkers of exposure to toxic and essential trace elements in children, Environ. Health Perspect. 125 (6) (2017) 067021.

[49] Biblioteca del Congreso Nacional de Chile, Ley N° 20.590, establece un programa de intervención en zonas con presencia de polimetales en la comuna de Arica., 2012.

[50] S. Córdova, A. Neaman, I. González, R. Ginocchio, P. Fine, The effect of lime and compost amendments on the potential for the revegetation of metal-polluted, Acidic Soils Geoderma 166 (2011) 135–144.