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Commentary

Chilean regulations on metal-polluted soils: The need to advance from adapting foreign laws towards developing sovereign legislation

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ABSTRACT

Chile as a major international Cu producer faces serious soil contamination issues in mining areas. Currently Chile does not have any specific law governing the maximum permissible concentrations of metals in soils to protect ecosystems and human health. Chile heavily relies on the use of environmental laws of 14 foreign countries; the choice of the country depends on the similarity of its environmental conditions with those in Chile. In this study, we used an online database to compare the similarity of Chilean rocks to those in foreign countries. Likewise, we performed soil sampling and determined the background concentrations of Cu, As, Pb, and Zn in soils of the Aconcagua basin, the largest river basin in the Valparaiso Region of central Chile. The results showed that geochemical patterns in Chile have the greatest resemblance to New Zealand, Mexico, and Italy. The background Cu concentration in the Aconcagua basin (134 mg kg^{-1}) exceeded the legislated limits of New Zealand (100 mg kg^{-1}) and Italy (120 mg kg^{-1}), whereas the background Zn concentration (200 mg kg^{-1}) exceeded the legislated limit of Italy (150 mg kg^{-1}). Due to the elevated natural abundance of Cu and Zn in Chile, international laws should not be applied in Chile for the assessment of soil contamination. In addition, we assessed ecological risk using the results of our previous studies obtained by analyzing native field-contaminated soils of the Valparaiso region. In the Aconcagua basin, Cu posed high risk for plants in 11% of the samples, whereas As posed high risk for earthworms in 48% of the samples. We suggest that future studies are required to search for other organisms that can serve as biomarkers of metal toxicity because our previous studies were limited to plants and earthworms. Importantly, As posed high risk to human health in 25% of the samples in our study. There is a need for future studies to demonstrate empirically an association between soil As and children's blood As in order to establish the national threshold values of soil As to protect human health. We conclude that there is an urgent need in Chile to advance from the current approach of adapting foreign laws to developing Chilean sovereign environmental legislation.

1. Introduction

In recent decades, soil contamination with trace elements has become a serious threat to human health and the environment (Teh et al., 2016; Antoniadis et al., 2019). In particular, Chile—as a major international copper (Cu) producer (Nishiyama, 2005)—faces problems of soil contamination with several metals and metalloids (e.g., Cu, arsenic (As), lead (Pb), zinc (Zn), etc.) in mining areas (Neaman et al., 2017a,

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Table 1
Trace element concentration groups based on threshold values. Trace element background concentrations in agricultural soils of the Aconcagua and river basin were calculated as 95th percentiles using data from areas with no mining activity (see text for details). Background concentrations for the Casablanca basin, and Chilean and foreign legislation limits are also shown for comparison.

Threshold value (mg kg^{-1})	As	Cu	Pb	Zn
Ecotoxicity	14[a]	513[b]	n.a.	n.a.
Human toxicity	20[c]	n.a.	80[d]	n.a.
Background, Aconcagua	13	134	34	200
Background, Casablanca	11	55	30	88
Chilean legislation limit[e]	20	150	75	175
New Zealand legislation limit[f]	20	100	300	300
Mexican legislation limit[g]	22	n.s.	400	n.s.
Italian legislation limit[h]	20	120	100	150

n.a. = data not available.
n.s. = not specifie
[a] Effective concentration producing 25% of decrease in biological response (EC_{25}) of *Eisenia fetida* (Bustos et al., 2015).
[b] Effective concentration producing 25% of decrease in biological response (EC_{25}) of *Avena sativa* L. and *Brassica rapa* CrGC syn. Rbr in long-term bioassay (Mondaca et al., 2017).
[c] Mielke et al. (2011).
[d] Mielke et al. (1999).
[e] Thresholds for the safe application of sewage sludge, for soils with pH > 6.5 (Secretaría General de la Presidencia, 2009).
[f] Thresholds for the safe application of sewage sludge (New Zealand Water and Wastes Association, 2003).
[g] Thresholds for soil remediation on agricultural, residential or commercial lands (Secretaría de Medio Ambiente y Recursos Naturales, 2007).
[h] Thresholds for soils on public, private, and residential green spaces (Ministry for Environment and Territory and Sea, 2014).

b). Although currently there is evidence of improving environmental health in the mining industries in Chile (Newbold, 2006), a number of legacy issues still need to be resolved.

Currently, Chile does not have any specific law governing the maximum permissible concentrations of metals in soils to protect ecosystems and human health. The only law that is somewhat relevant deals with the maximum permissible concentrations of metals in soils to which sewage sludge may be applied (Table 1) (Secretaría General de la Presidencia, 2009). Regarding all other environmental issues, Chile relies on the use of environmental laws of the following 14 foreign countries: Germany, Argentina, Australia, Brazil, Canada, Spain, Mexico, the USA, New Zealand, Holland, Italy, Japan, Sweden, and Switzerland. The choice of the country depends on the similarity of its environmental conditions with those in Chile (Ministerio del Medio Ambiente, 2012).

In our previous study (Aguilar et al., 2011), we determined the Cu background soil concentration in the Aconcagua basin, the largest river basin in the Valparaiso Region of central Chile (Fig. 1). We demonstrated that the soils in this area are naturally abundant in Cu; however, there is no information available on the background soil concentrations of other metals and metalloids. Further, we determined the toxicity responses of plants and earthworms to various trace elements in soils polluted by Cu mining activities in the Valparaiso Region. Despite some confounding effects observed in these studies, we established thresholds of Cu toxicity to plants (Verdejo et al., 2015; Mondaca et al., 2017) and thresholds of As toxicity to *Eisenia fetida* (Bustos et al., 2015). Although these studies represent significant progress in soil ecotoxicology, they are not sufficient for the purposes of developing sovereign Chilean environmental legislation. However, it is difficult to undertake an extensive environmental research program in Chile due to economic limitations. Should it be demonstrated that ecological risk arising from exposure to trace elements in soils is a significant problem, it would be much easier to raise research funding.

We are unaware of any studies in Chile reporting thresholds of trace element toxicity to human health. In the absence of such data, it is necessary to understand the scope of the problem, which can be achieved by using thresholds from other countries. If the problem of human health risk in mining areas in Chile is deemed to be significant, future national studies would be justified.

Given the above-mentioned arguments, the following research questions arise: (1) Which of the aforementioned foreign countries have similar geochemical settings to Chile? (2) Should ecological risk arising from exposure to trace elements in soils be evaluated based on a suitable international legislation? (3) What is the magnitude of the ecological risk arising from exposure to trace elements in soils affected by Cu mining in Chile? (4) What is the magnitude of human health risk arising from exposure to trace elements in these soils? (5) What are the future research needs for developing sovereign legislation that would specify the maximum permissible concentrations of metals in soils and protect human health and ecosystems? In accordance with research questions posed, the main goal of the study is to evaluate the necessity to advance from the current approach of adapting foreign laws towards developing Chilean sovereign environmental legislation.

2. Materials and methods

2.1. Study area

Due to the geographical diversity of Chile, our research must focus on a specific area to best address these questions. We have chosen the Aconcagua river basin (Fig. 1) as the target area due to the following three reasons. First, it is the largest river basin in the Valparaiso Region of central Chile, with a total area of ~7300 km^2 (Hormazábal et al., 2013) and a population of ~732,000 people (Instituto Nacional de Estadísticas, 2019). Second, the Aconcagua basin has historically suffered from large-scale mining operations (El Soldado mine, Andina mine, and Chagres smelter) (Folchi, 2006; Villavicencio et al., 2014). Third, there is a significant amount of knowledge on the spatial distribution of Cu concentrations in agricultural soils of the Aconcagua basin (Aguilar et al., 2011).

Additionally, we included the Casablanca basin of Valparaiso Region (Fig. 1) in the scope of our study, which does not have any mining activities (Lara and Romo, 2002; SERNAGEOMIN, 2012), making it the appropriate area to be used as a reference point (De Gregori et al., 2003). In both river basins, the study was limited to soils located on landforms with slopes less than 15% (Fig. 1) because these are the areas of traditional human settlements on agricultural soils that have received gravity-fed irrigation.

2.2. Soil analysis

In order to determine the background concentrations of trace elements in soil of the Aconcagua basin, we sampled 20 agricultural topsoils (0–20 cm) in areas with the absence of mining activities (Lara and Romo, 2002; SERNAGEOMIN, 2012) (Supplementary Table 1). In addition, 127 topsoil composite samples (0–20 cm) of 1 kg each were collected at different locations of the Aconcagua basin (Supplementary Table 2). Soil sampling was guided by previous knowledge on Cu spatial distribution in the soils of the Aconcagua river basin (Aguilar et al., 2011), i.e., we used a judgment sampling approach (Petersen and Calvin, 1996; Pennock et al., 2008). We paid special attention to areas with mining activities, in order to account for high heterogeneity of spatial distribution of Cu in these areas (Aguilar et al., 2011). This sampling scheme has been proven to adequately account for the impact of Cu mining activities on total soil Cu concentrations (Hormazábal et al., 2013).

Likewise, we sampled 35 topsoils (0–20 cm) at different locations of the Casablanca basin (Supplementary Table 3). In this river basin, we paid special attention to sample soils used by different types of crops (fruit and vegetable crops). Variance analysis (ANOVA) was used to

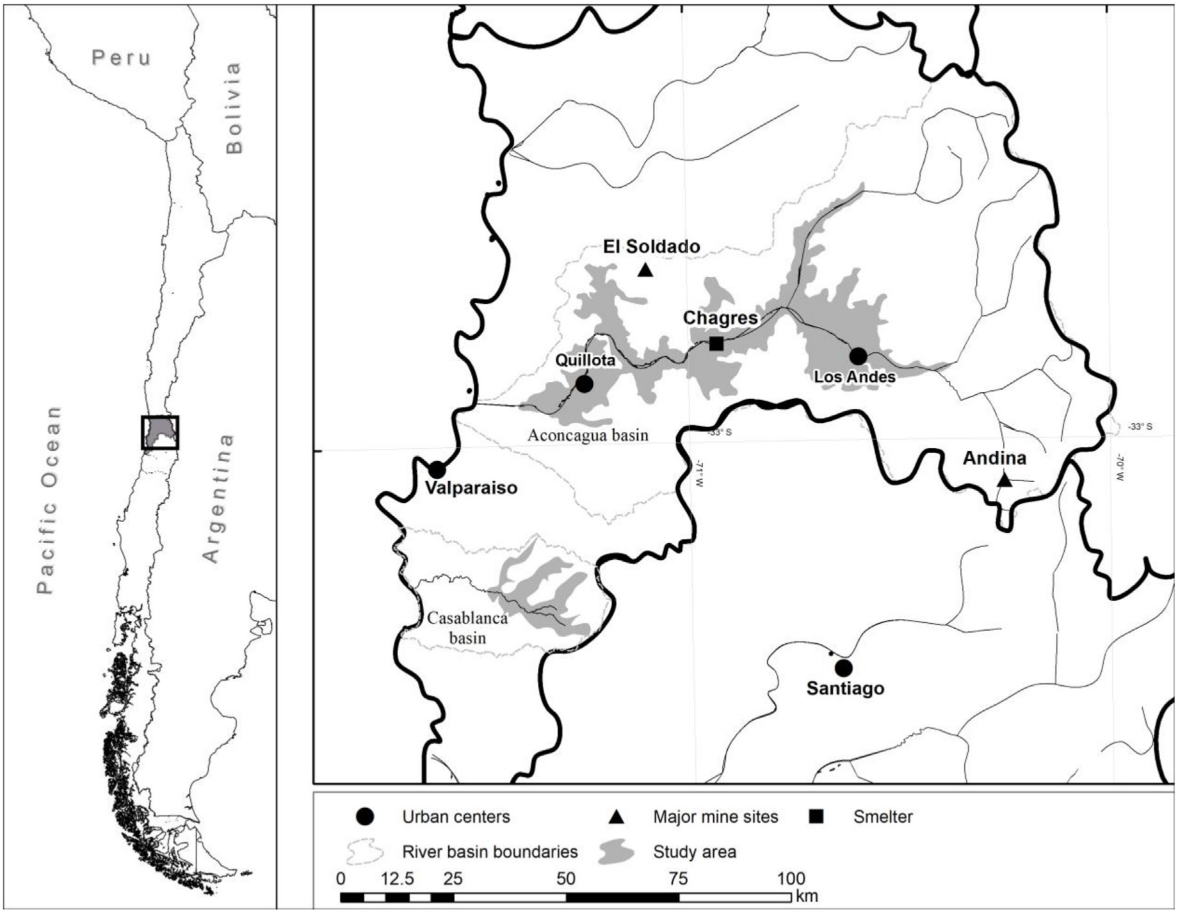

Fig. 1. Location of the Aconcagua and Casablanca river basins. The study area was limited to arable soils located on landforms with slopes < 15%.

compare the element concentrations in soils used for fruit and vegetable crops using R software (R Core Team, 2017).

The soil samples were processed by drying at 40 °C, grinding aggregates in a granite mortar, and sieving them to obtain a fraction of < 2 mm. To determine total metal concentrations, subsamples were digested for 12 h in boiling nitric acid, followed by perchloric acid addition (Maxwell, 1968). 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 were determined using 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, whereas recovery was 100% ± 7%, with spikes performed on every 10th sample.

2.3. Rock analysis

The areas occupied by different rock types in the Aconcagua and Casablanca basins were estimated using geological maps (Gana et al., 1996; SERNAGEOMIN, 2003) and software QGIS 3.4 (www.qgis.org). We used an online database (GEOROC, 2019) to obtain data on the content of Cu, As, Pb, and Zn in volcanic rocks (andesitic rocks, dacitic rocks, rhyolitic rocks, tholeiite), plutonic rocks (diorite, gabbroic rocks, granitic rocks, granodiorite), and sedimentary rocks (arenite, chert, greywacke, limestone, sandstone, shale, soil, travertine) worldwide.

The GEOROCK database was used to obtain data on the content of Cu, As, Pb, and Zn in rocks in Chile and 14 foreign countries listed in the environmental regulations in Chile (Ministerio del Medio Ambiente, 2012): Germany, Argentina, Australia, Brazil, Canada, Spain, Mexico, the USA, New Zealand, Holland, Italy, Japan, Sweden, Switzerland. The abundances of As, Pb, Cu and Zn in the upper continental crust were taken from Rudnick and Gao (2014).

In order to compare the similarity of Chilean rocks to distinct rock species, we calculated the Kullback-Leibler (KLD) divergence (Kullback and Leibler, 1951). The KLD values are measures of the difference between two datasets. The KLD value close to 0 demonstrates similar distributions for two datasets; as the dissimilarity between datasets increases, the KLD value increases. We coded a repetitive procedure ($n = 1000$) generating equal samplings for KLD analysis, which required equal sample sizes. The computations were implemented in R 3.6.1 (R Core Team, 2017) with use of LaplacesDemon library.

Likewise, we used KLD divergence to compare the similarity of Chilean rocks to rocks in foreign countries. In this case, we coded a repetitive procedure with $n = 10,000$ generating equal samplings and computing KLD values. The number of rock samples in the GEOROCK database was insufficient for Holland, Sweden, and Switzerland. The data for these countries are shown, but KLD values were not computed. Further, there were no As data available for Holland, Sweden, and Switzerland.

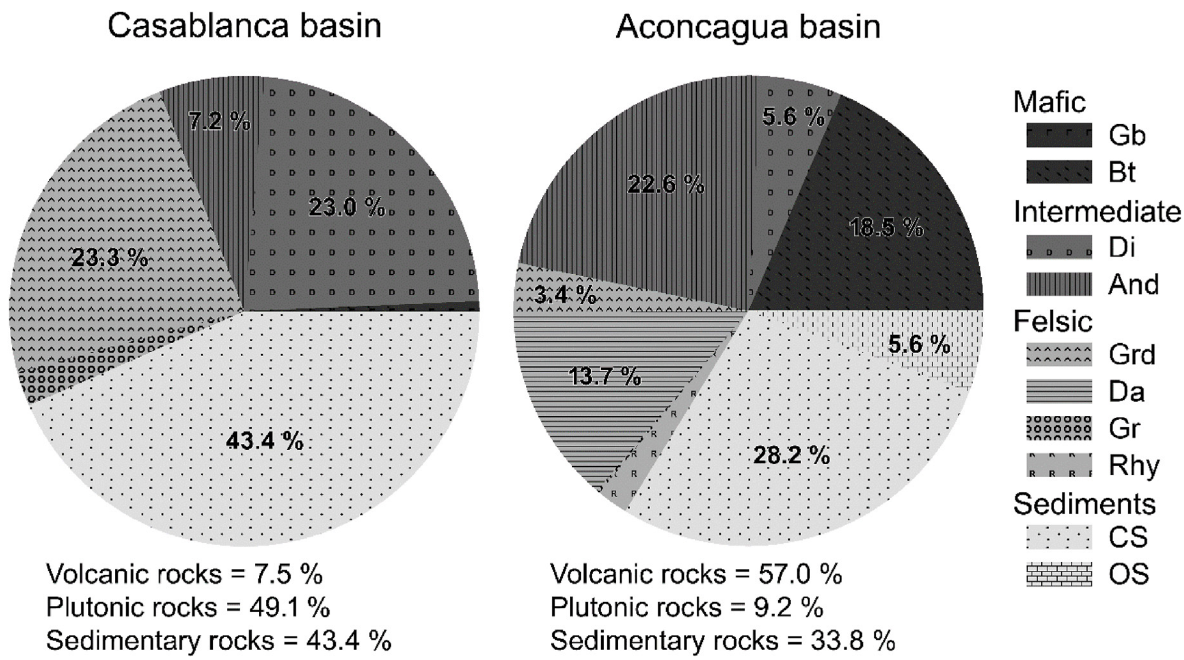

Fig. 2. Distribution of rock types in the Casablanca and Aconcagua basins. The data correspond to the area of each rock type from the total area of the basin. Volcanic rocks are Bt – basalt, And – andesite, Da – dacite, Rhy – rhyolite; plutonic rocks are Gb - gabbro, Di - diorite, Grd - granodiorite, Gr – granite; sedimentary rocks are CS – continental sediments and OS – oceanic sediments.

3. Results and discussion

3.1. Background concentrations of Cu, As, Pb, and Zn in the studied river basins

The background concentrations of As and Pb were similar in the Aconcagua and Casablanca river basins. However, background concentrations of Cu and Zn were about two times higher in the Aconcagua basin than in the Casablanca basin (Table 1). This difference in soil element concentrations can be explained by difference in rock types in these two river basins. Specifically, the basin of Casablanca comprises predominantly plutonic (intrusive) rocks (49%) and sedimentary rocks (43%), whereas the Aconcagua river runs through lands mostly covered by volcanic (effusive) rocks (57%) and sedimentary rocks (34%) (Fig. 2).

The comparison of As, Pb, Cu, and Zn abundances in Chilean rocks with main petrologic types (Fig. 3) reveals a similarity of Chilean rocks to andesites (KLD_{As} = 1.37, KLD_{Pb} = 1.48, KLD_{Cu} = 1.49, KLD_{Zn} = 0.94). Sediments also resemble the rocks sampled in Chile (KLD_{As} = 1.75, KLD_{Pb} = 0.99, KLD_{Cu} = 1.50, KLD_{Zn} = 1.27). From this perspective and considering rock types of the studied basins (Fig. 2), the Aconcagua basin is geochemically more typical for the country. This observation can be explained by the fact that young rocks associated with volcanic eruptions are abundant near the Andes, where the headwaters of Aconcagua occur (Fig. 1), whereas older eroded plutonic bedrocks are exposed at the surface near the Pacific coast, where the Casablanca river flows (Gana et al., 1996; SERNAGEOMIN, 2003).

On the other hand, comparison of different rock types worldwide reveals distinct abundances of As, Pb, Cu, and Zn (Fig. 4). Despite high variability in trace element contents, volcanic rocks (basalts, andesites, and dacites) tend to be enriched in Cu and Zn, in comparison to plutonic rocks (gabbro, diorites, and granodiorites). Thus, the difference in the predominant rock types (volcanic and plutonic) defines the Cu and Zn contents in soils of the Aconcagua basin (volcanic rocks) and Casablanca basin (plutonic rocks).

Total soil Cu concentrations may be affected by applications of Cu-containing fungicides (Schoffer et al., 2020). Nonetheless, the contribution of Cu-containing fungicides to the soil Cu concentrations is expected to be similar at all sampling locations, in both river basins, because fungicide application is not attributed to a specific crop or crop type. Rather, fungicide application is a common practice for several vegetable and fruit crops in Chile (AFIPA, 2002–2003). Indeed, our results for the Casablanca basin demonstrate that there were no statistically significant differences between soils used for vegetable crops and fruit crops with respect to concentrations of Cu and other trace elements (Supplementary Table 3). For this reason, we propose that, independent of the sources of Cu in the studied soils, background concentrations of trace elements can be used for estimating the effect of Cu mining on spatial distribution of trace elements in the Aconcagua basin.

3.2. Applicability of international laws and current Chilean regulations

Geochemical patterns observed in Chile have the greatest resemblance to the following countries, based on mean Kullback-Leibler divergence values of Cu, As, Pb, and Zn (in parentheses): New Zealand (1.16), Mexico (1.19), and Italy (1.23). The countries in which geochemical patterns differ the most from the Chilean ones are Canada (1.65), Brazil (2.02), and Australia (2.30) (Fig. 5). Other countries fall in between, such as Germany (1.24), Japan (1.39), Argentina (1.51), USA (1.59), and Spain (1.61) (Supplementary Table 4). Effectively, based on these divergencies, the countries can be grouped into two distinct categories: (1) those with active volcanism and predominance of young volcanic rocks (Chile, New Zealand, Mexico, Italy) and (2) those with ancient cratons built of plutonic rocks (Canada, Brazil, Australia).

As mentioned above, Chile heavily relies on the use of environmental laws of 14 foreign countries; the choice of the country depends on the similarity of its environmental conditions with those in Chile (Ministerio del Medio Ambiente, 2012). Since Chile geochemically resembles New Zealand, Mexico, and Italy (Fig. 5), we used the laws of these countries that deal with metal-polluted soils (Table 1). It appears that New Zealand does not have any specific law governing the maximum permissible concentrations of metals in soils to protect ecosystems and human health. As in Chile, the only law in New Zealand that is

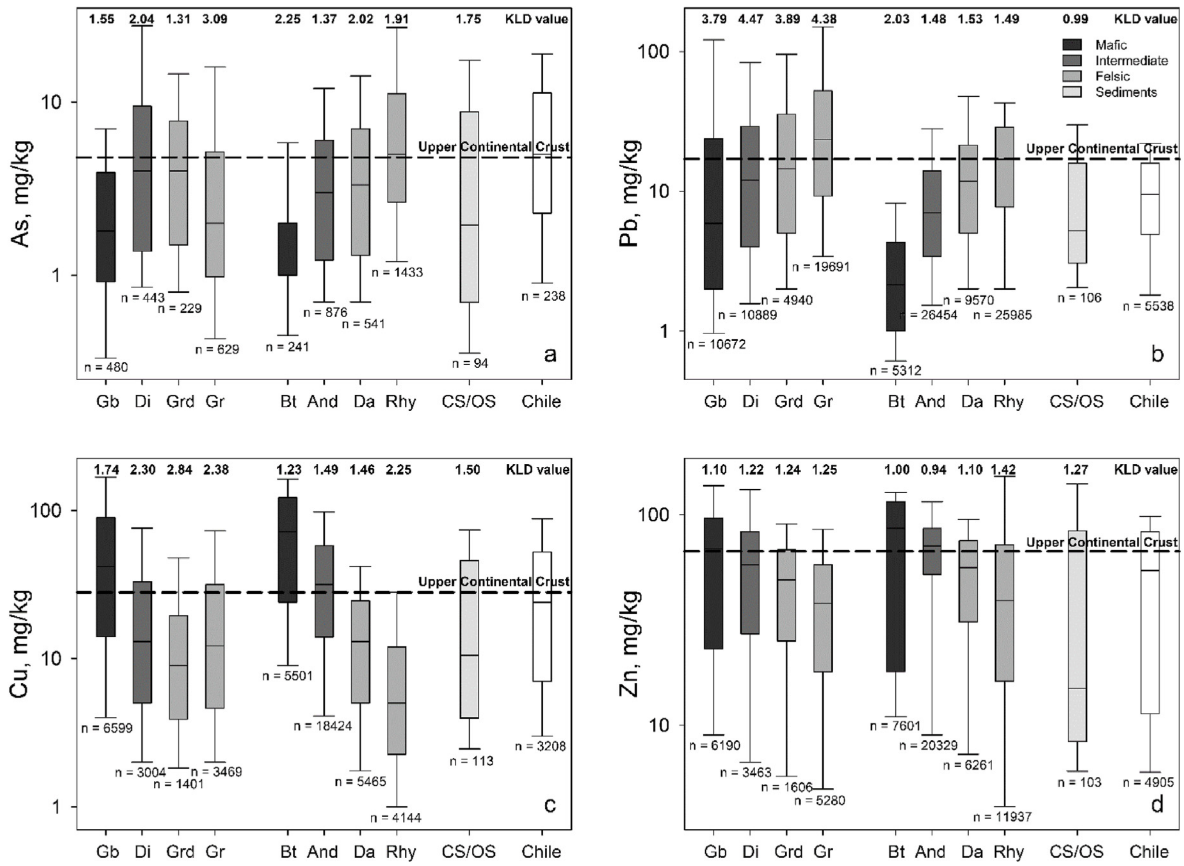

Fig. 3. Abundances of trace elements in plutonic, volcanic, and sedimentary rocks worldwide and rocks sampled in Chile. The Kullback-Leibler divergence (KLD) reveals the affinity of Chilean rocks to distinct rock types. The lower values indicate the closer similarity. Volcanic rocks are Bt – basalt, And – andesite, Da – dacite, Rhy – rhyolite; plutonic rocks are Gb - gabbro, Di - diorite, Grd - granodiorite, Gr – granite; sedimentary rocks are CS – continental sediments and OS – oceanic sediments.

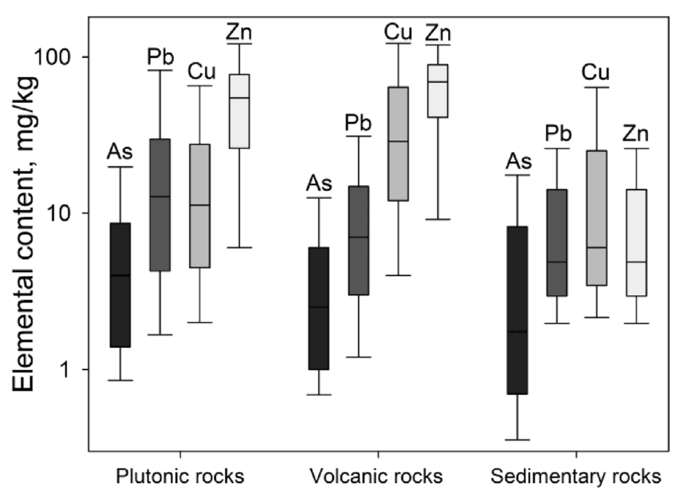

Fig. 4. Elemental content in plutonic, volcanic, and sedimentary rocks worldwide.

somewhat relevant deals with the maximum permissible concentrations of metals in soils to which sewage sludge may be applied (New Zealand Water and Wastes Association, 2003). New Zealand is currently striving to develop soil guideline values for the protection of ecological receptors (Cavanagh and Munir, 2016). Interestingly, these countries attempt to use the laws of foreign countries, such as Australia and Canada, as a reference. However, in terms of geochemical settings these countries are very distinct from New Zealand, according to our analysis (Fig. 5). Thus, the tendency to rubber-stamp foreign laws also exists in countries apart from Chile.

Mexican legislation (Secretaría de Medio Ambiente y Recursos Naturales, 2007) does not specify threshold values for Cu and Zn. Italian legislation (Ministry for Environment and Territory and Sea, 2014), on the other hand, specifies threshold values for all four elements under analysis (Table 1). Importantly, the background Cu concentration in the Aconcagua basin exceeds the legislated limits of New Zealand and Italy, whereas the background Zn concentration in the Aconcagua basin exceeds the legislated limit of Italy. Due to natural abundance of Cu and Zn in soils in the area under study, we argue that international laws for the assessment of the degree of soil contamination are not applicable to Chile. In our opinion, it is preferable to recognize the specific geochemical conditions in Chile and encourage the development of suitable national laws.

Moreover, there is a conceptual problem with all the existing international legislations because they are based on results from metal-spiked soils (Baderna et al., 2015; Cavanagh and Munir, 2016) rather than on actual field-contaminated soils. Such an approach has been repeatedly and rightly criticized due to the difficulty in extrapolating the results directly onto real field situations because metal toxicity is greater in metal-spiked soils than in field-contaminated soils where pollution may have occurred decades ago (Spurgeon and Hopkin, 1995; Davies et al., 2003; Smolders et al., 2009; Hamels et al., 2014). Such disparity is attributed to the fact that metal toxicity depends on metal residence time in soils, among other factors. This process of metal transformation over time is called "aging" and is poorly defined (Lock and Janssen, 2003; Martínez et al., 2003; Stewart et al., 2003; Ma et al., 2006; Smolders et al., 2009; McBride and Cai, 2016). For this reason,

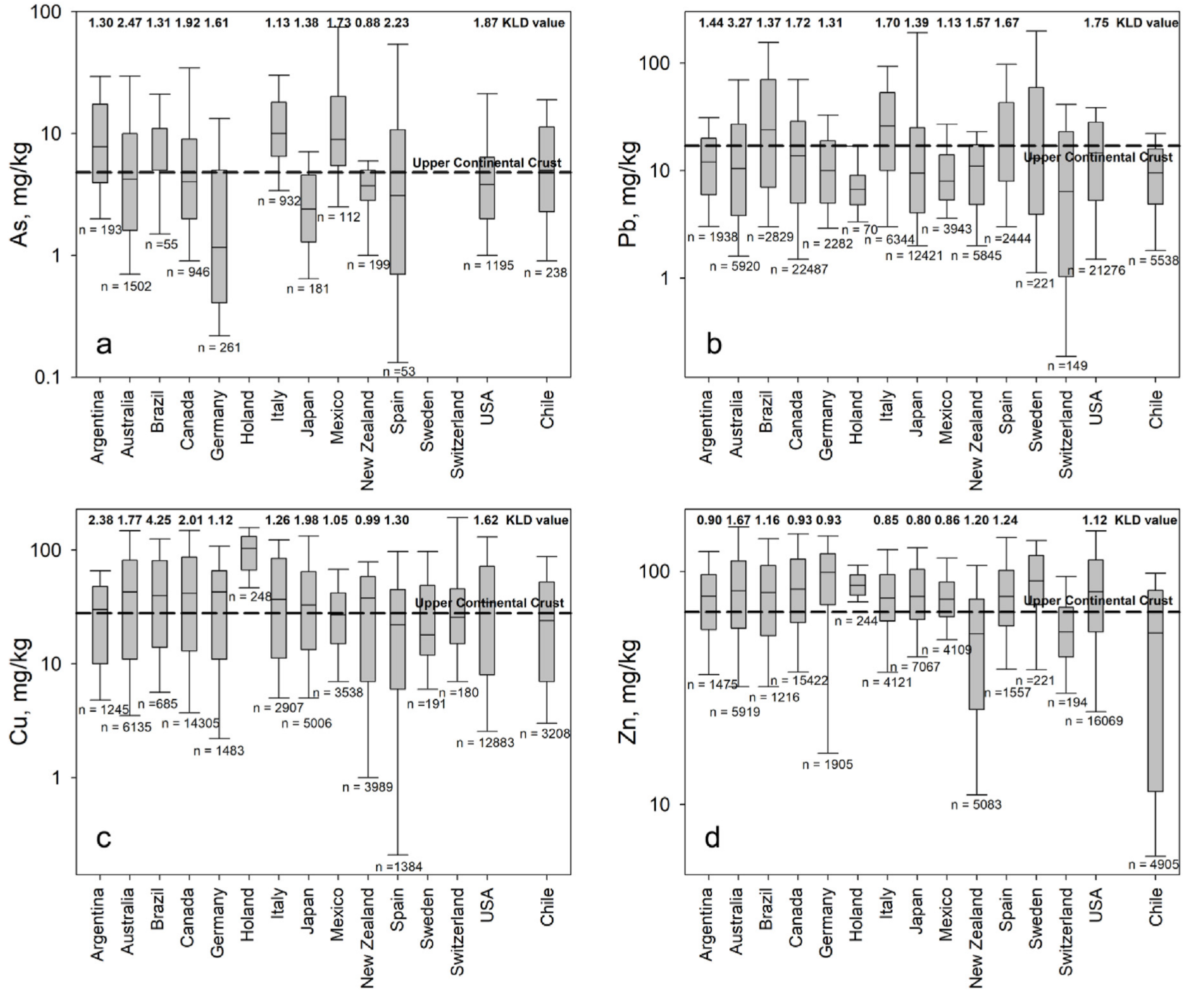

Fig. 5. Abundances of trace elements in rocks worldwide and rocks sampled in Chile. The Kullback-Leibler divergence (KLD) reveals the affinity of Chilean rocks to rocks in other countries. The lower values indicate the closer similarity.

many studies argue that metal-spiked soils are of limited use for environmental assessment and soil quality decision-making, and emphasize the importance of using field-contaminated soils for toxicity assays.

Despite this demonstrated body of knowledge, few studies with field-contaminated soils have actually been performed. For instance, the number of studies in which Cu phytotoxicity thresholds have been determined using field-contaminated soils can be counted on one hand (Mondaca et al., 2017 and references therein). Likewise, we are aware of only one study on As toxicity threshold for *Eisenia fetida* in field-contaminated soils (Bustos et al., 2015). In these studies, we demonstrate that detailed characterization of soil properties as well as metal concentrations in plant and earthworm tissues makes it possible to discern between the confounding factors and metal-toxicity factors, permitting estimation of metal toxicity thresholds.

The current Chilean regulation that establishes the maximum concentrations of metals in soils on which sewage sludge is applied (Secretaría General de la Presidencia, 2009) is unfortunately an adaptation of foreign laws due to the absence of Chilean soil ecotoxicological studies at the moment. As a consequence, in the Aconcagua basin, the background Cu concentration approaches the Chilean legislated limit, whereas the background Zn concentration exceeds this limit (Table 1). Therefore, there is a need to advance from adapting foreign laws towards developing sovereign legislation.

Finally, background metal concentrations in the Casablanca basin are below the legislated Chilean limits (Table 1). Due to the substantial discrepancy in background levels of Cu and Zn for the Aconcagua and Casablanca basins, it is necessary to investigate the impact of geological parent material on the ecotoxicity of soil Cu and Zn. The current Chilean legislation may need to be revised in order to account for the natural abundance of Cu and Zn in soils in the country. From the regulatory point of view, an absolute "one-limit-fits-all" total metal concentration may be inadequate to address actual toxicity to organisms.

3.3. Ecological risk and future research needs

We assessed ecological risk using the results of our previous studies (Table 1). These results were obtained by analyzing native field-contaminated soils of the Aconcagua river basin, i.e., they are well-suited for the ecological risk assessment of the soils of the same river basin in the present study. Specifically, the tested organisms were *Eisenia fetida* (Bustos et al., 2015), *Avena sativa* L. and *Brassica rapa* CrGC syn. Rbr (Mondaca et al., 2017). These studies report effective concentrations as total soil contents of Cu and As. It could be argued that total metal concentration in a contaminated soil is not sufficient to predict potential metal toxicity. The authors are well aware of this issue (Lillo et al., 2020). Nevertheless, in the soils of the Aconcagua basin, total soil concentrations of Cu and As were better indicators of metal ecotoxicity than either exchangeable Cu and As or free Cu^{2+} in the soil solution (Bustos et al., 2015; Verdejo et al., 2015; Delgadillo et al., 2017; Mondaca et al., 2017).

In this study, we based our ecological risk assessment on EC_{25} (effective concentration 25%) values of Cu and As (Table 1). One could

Table 2
Percentage of samples by concentration group in the Aconcagua basin.

Element	Below background value	Between background and toxicity threshold	Above toxicity threshold
As (ecotoxicity)	51	1	48
As (human toxicity)	51	24	25
Cu (ecotoxicity)	51	38	11
Pb (human toxicity)	35	63	2
Zn (ecotoxicity)	72	28	n.a.

n.a. = not applicable.

argue that ecological risk assessment should be based on the use of a metal pollution index, such as in the Spanish legislation on metal-polluted soils (Ministerio de la Presidencia, 2005). However, the validity of this legislation was questioned (Recatalá et al., 2012). These authors suggested that soil quality standards should correspond to a value between EC_{10} and EC_{50} (effective concentration 10% and 50%, respectively). In our opinion, however, the 50% inhibition represents a drastic impact (Stark et al., 2004) that might be considered acceptable for an industrial site, but would be unacceptable from an ecological perspective where even 10% reductions in organism responses may generate serious ecological dysfunctions. Nevertheless, EC_{10} values often produce nil-to-marginal effects and usually fall within the "noise level" of the control response (Checkai et al., 2014). Accordingly, we considered ecological risk to be low for concentrations below the background values, medium for concentrations between the background and EC_{25} values, and high for concentrations above the EC_{25} value (Tables 1 and 2, Figs. 6 and 7).

Although there are some ecotoxicological studies using actual field-contaminated soils polluted with Pb (e.g., Leveque et al., 2013), they do not report effective concentration values. Likewise, there are some ecotoxicological studies reporting EC_{50} values for Zn in actual field-contaminated soils (Beyer et al., 2011, 2013; Hamels et al., 2014), but they do not report EC_{25} values. For this reason, we were unable to estimate ecological risk of Pb and Zn in the soils under study. Moreover, our previous study revealed an alleviating effect of Zn on Cu toxicity to plants and soil microorganisms in agricultural soils affected by Cu mining in central Chile (Mondaca et al., 2017; Stowhas et al., 2018). For this reason, we do not expect that there would be any Zn toxicity to plants and soil organisms in the soils of the Aconcagua basin (Supplementary Fig. 1).

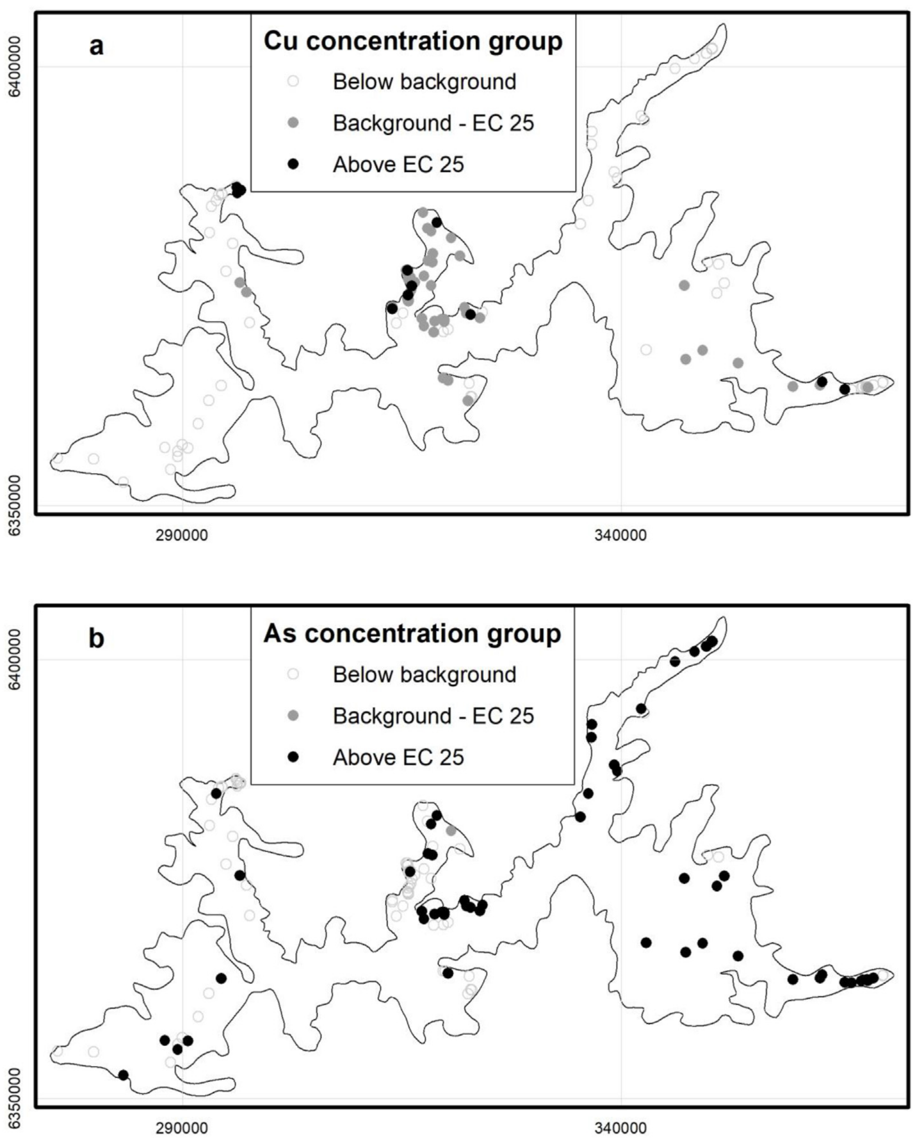

Fig. 6. Spatial distribution of ecological risk in agricultural soils of the Aconcagua river basin due to exposure to (a) copper and (b) arsenic. EC_{25} = effective concentration 25%. Threshold values are shown in Table 1.

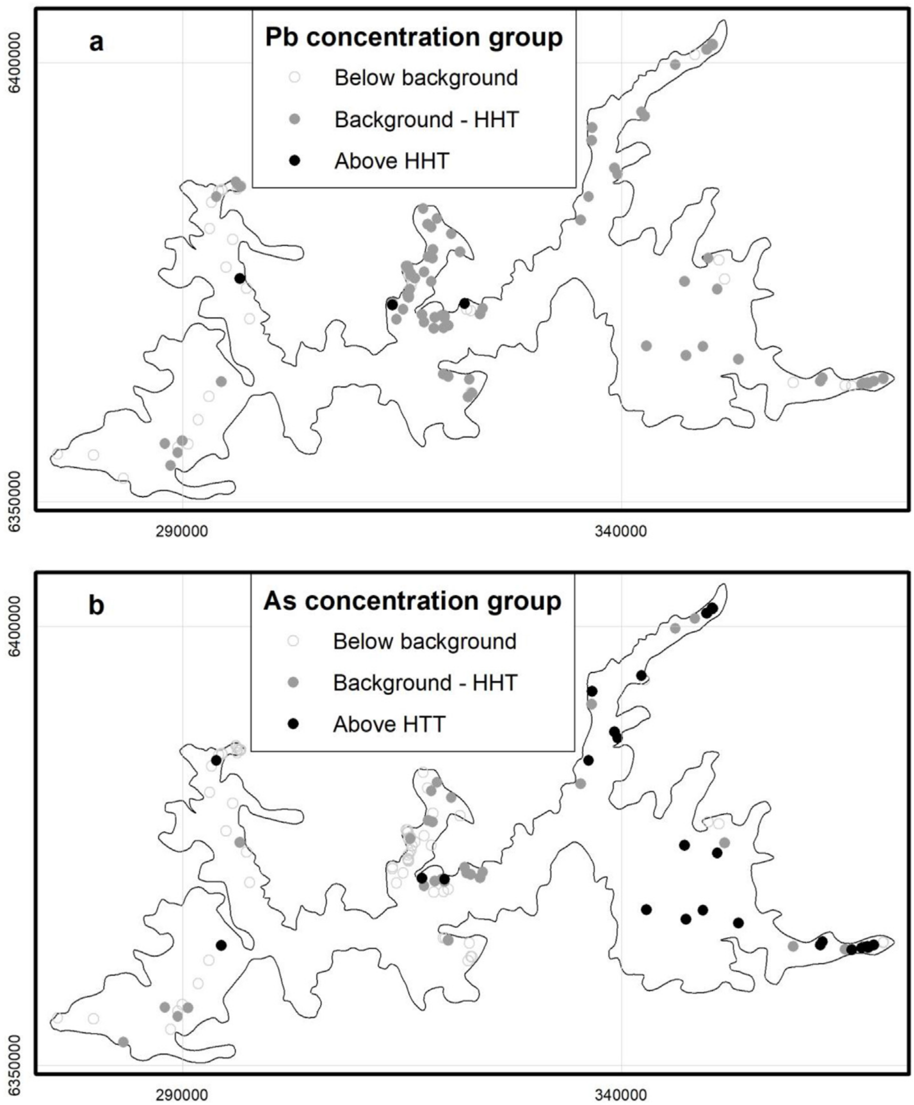

Fig. 7. Spatial distribution of human health risk in agricultural soils of the Aconcagua river basin due to exposure to (a) lead and (b) arsenic. HTT = human toxicity threshold. Threshold values are shown in Table 1.

Based on the above-mentioned threshold values, Cu represented high ecological risk for plants in 11% of the samples under study (Table 2). These findings are consistent with previous reports, which demonstrated high total soil Cu concentrations in some areas of the Aconcagua basin (Aguilar et al., 2011), thus validating a spatial association between the locations of large-scale mining projects and high total soil Cu concentrations (Hormazábal et al., 2013). Therefore, Cu phytotoxicity limits plant growth in areas affected by historical operations of large-scale mining projects (El Soldado mine, Andina mine, and Chagres smelter) (Figs. 1 and 6a). Arsenic represented high ecological risk for earthworms in 48% of the samples in this study (Table 2 and Fig. 6b). In summary, in the soils affected by Cu mining activities in the Aconcagua basin, ecological risk is mostly associated with Cu and As.

As mentioned above, our soil ecotoxicological studies are not yet sufficient for developing sovereign Chilean environmental legislation. To undertake such an ambitious project it would be important to determine background concentrations of trace elements of other river basins in central Chile, as well as to recognize the specific geochemical settings in Chile. Likewise, there is a need to expand the magnitude of our ecotoxicity analysis because our previous ecotoxicological studies were performed with a limited number of soils (n ~ 30). Finally, it is necessary to search for other organisms that can serve as biomarkers of metal toxicity because our previous studies were limited to plants and *Eisenia fetida*.

3.4. Human health risk and future research needs

Copper toxicity is generally not a concern for human health because of homeostatic mechanisms controlling Cu excretion (Scheinberg, 1979; Turnlund et al., 2005). This is the reason why we did not assess human Cu exposure in the present study. However, Bost et al. (2016) argued that there are still unresolved issues with regard to our understanding of the effects of Cu exposure on human health. With regard to Zn, the risk of human Zn exposure in the Aconcagua basin is negligible because its maximum total soil concentration is 579 mg kg^{-1}, which is far below the proposed human toxicity threshold of 2200 mg kg^{-1} for residential areas (Shayler et al., 2009).

Children playing outdoors may incidently ingest metal-polluted soil (Mielke, 2016). For instance, a positive nonlinear relationship between soil Pb concentration and blood Pb concentration is well documented in children in Indianapolis (Indiana), Syracuse (New York), and New Orleans (Louisiana) (Laidlaw et al., 2005; Mielke et al., 2007; Zahran et al., 2011). Mielke et al. (1999) reported that children exhibited a steep rise in blood Pb concentration at soil Pb concentration below 100 mg kg^{-1}. These authors thus argued that a safe soil Pb concentration for most children is ~80 mg kg^{-1}. In the studied soils, only 2% of samples reached a concentration above 80 mg kg^{-1}, suggesting the near absence of children's Pb exposure risk in the Aconcagua basin (Table 2 and Fig. 7a). However, children's exposure to Pb might be a problem in urban environments (e.g., Cheng et al., 2015; Dovletyarova et al., 2017; Dovletyarova et al., 2018; Paltseva et al., 2018) and this would require future studies to be undertaken in big cities in Chile, such as Santiago.

Concerning As, the total As threshold in soils at child-care centers, playgrounds and residential areas is established at 20 mg kg^{-1} (Mielke et al., 2011). These authors argued that at this concentration of total As, children's acceptable weekly intake would not be exceeded even when high incidental intake of soil occurs. In this study, 25% of samples reached a concentration above 20 mg kg^{-1}, suggesting a potential risk of children's As exposure (Table 2 and Fig. 7b). Thus, in the studied soils affected by Cu mining activities, As is an important factor to consider when dealing with human health (Berasaluce et al., 2019; Lizardi et al., 2020). However, only empirical data on the association between soil As and children's blood As can provide the most reliable information about human exposure to As (e.g., Rahbar et al., 2012). Therefore, future studies are required in Chile in order to establish the national threshold values of soil As in order to protect human health. In particular, these studies should consider activity factors in health risk assessment. Likewise, there is a need to determine bioaccessible As in the soils under study, in order to obtain more reliable information about children exposure to soil As.

4. Conclusion

Chile does not have any specific law governing the maximum permissible concentrations of metals in soils to protect ecosystems and human health. Chile currently uses laws from 14 different countries to address environmental concerns. We show that Chile has a higher natural abundance of Cu and Zn in soils than countries with similar geologic parent materials. Thus internationally legislated limits of soil Cu and Zn concentrations for ecosystem protection are inadequate for Chile. Further, we show that Pb and As may pose human health risks, especially in more urban areas. There is an urgent need to perform research assessing metal toxicity to ecosystems and humans in Chile in order to develop Chilean sovereign environmental legislation. These future studies should consider other metals and metalloids, besides of four elements used in this study.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

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