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De: Raul Calderon Araya [REDACTED]
Enviado el: jueves, 25 de mayo de 2023 9:51
Para: npcasuelos
Asunto: Antecedentes científicos (Norma Primaria de Calidad Ambiental para suelos de Chile)
Datos adjuntos: Occurrence, distribution and dynamics of perchlorate in Chile..pdf; Sources and fates of perchlorate in soils in Chile..pdf; Exploring the destiny and distribution of thiocyanate in the water-soil-plant.pdf; Occurrence and human exposure to bromate via drinking water, fruits.pdf; Trace element content in soil after a sediment-laden flood.pdf; Perchlorate Levels in Soil and Waters from the Atacama Desert.pdf

Estimadas (os)

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Quedo atento a comentarios y muchas gracias,
 Saludos cordiales

Dr. Raúl Calderón Araya

Profesor Asociado

CENTRO DE INVESTIGACIÓN EN RECURSOS NATURALES Y SUSTENTABILIDAD (CIRENYS)
 VICERRECTORÍA DE VINCULACIÓN CON EL MEDIO E INVESTIGACIÓN



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Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Exploring the destiny and distribution of thiocyanate in the water-soil-plant system and the potential impacts on human health



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HIGHLIGHTS

- We evaluated thiocyanate capture and accumulation in chard and spinach.
- Thiocyanate accumulation depended on the treatment and culture time.
- Chard accumulates more thiocyanate than spinach (T2 > T1): leaves > total aerial fraction
- EDI values (0–12 months) for spinach exceeded chronic and subchronic reference doses.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jay Gan

Keywords:

Chard
Spinach
Uptake
Thiocyanate
Food safety
Intake
Rhodanide

ABSTRACT

Endocrine disruptors like thiocyanate are some of the principal causes of chronic disorders worldwide. Prenatal and postnatal exposure to thiocyanate can interfere with normal neurological development in both fetuses and newborns. Currently, little information regarding thiocyanate levels and potential sources of exposure is available. In this study, we evaluated thiocyanate uptake and accumulation in chard and spinach grown under greenhouse conditions. Both chard and spinach are commonly used to produce baby foods. Three thiocyanate concentrations were compared: Control, T1 (30 ng mL⁻¹), and T2 (70 ng mL⁻¹). Thiocyanate accumulation depended on the concentration and exposure time. Chard was found to accumulate more thiocyanate than spinach, with leaf accumulation > stem accumulation ($p < 0.0194$) and maximum concentrations of 76 ng g⁻¹ (control), 112 ng g⁻¹ (T1), and 134 ng g⁻¹ (T2). The estimated daily intake (EDI) of thiocyanate for chard and spinach (fresh) exceeded the subchronic reference dose of 200 ng⁻¹ kg⁻¹ day⁻¹ and the chronic reference dose of 600 ng⁻¹ kg⁻¹ day⁻¹. In addition, the EDI of thiocyanate for spinach in baby food exceeded twice the chronic reference dose in the vulnerable newborn–1 year age group.

Abbreviations: BAF, bioaccumulation factor; ESI-MS/MS, electrospray ionization tandem mass spectrometry; EDI, estimated daily intake; FCID, Food Commodity Intake Database; LOD, limits of detection; LOAEL, lowest observed adverse effect level; NO₃⁻, nitrate; ND, not detected; ClO₄⁻, perchlorate; HSCN, thiocyanic acid; SCN⁻, thiocyanate; TF, translocation factor.

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<http://dx.doi.org/10.1016/j.scitotenv.2022.155502>

Received 10 February 2022; Received in revised form 19 April 2022; Accepted 20 April 2022

Available online 28 April 2022

However, all EDIs were lower than the lowest observed adverse effect level (LOAEL) of $1.9 \times 10^5 \text{ ng kg}^{-1} \text{ day}^{-1}$. Further studies are needed that increase our knowledge of thiocyanate levels and potential environmental sources to reduce opportunities for exposure, especially in vulnerable groups.

1. Introduction

In recent decades, the rapid expansion of industrial development, agricultural production, and human activities has intensified pollutant inputs into the environment, elevating the risks to human health (Yilmaz et al., 2019). Endocrine disruptors are pollutants of great interest to the international scientific community due to their ability to interfere with the human endocrine system and metabolism (Metcalf et al., 2022). The World Health Organization (WHO) has estimated that ~750 million people worldwide have some type of thyroid pathology, with 60% of this population being unaware of the problem.

Endocrine disruptors, such as perchlorate (ClO_4^-), nitrate (NO_3^-), and thiocyanate (SCN^-), are pollutants that competitively inhibit the transport of sodium iodide to the thyroid gland, resulting in a reduction in hormone (e.g., T3 and T4) production, particularly in people with low levels of iodide consumption (Zhu et al., 2019; Lee et al., 2017; Qin et al., 2014). Thus, pregnant women, newborns, and infants are also particularly at risk of the effects of endocrine disruptors (Zhu et al., 2019; Qin et al., 2014). Currently, one of the main problems associated with child nutrition is estimating the risks associated with the consumption of contaminated foods leading to disease generation (Pivovarov et al., 2016; Mielech et al., 2021).

The dietary intake of vegetables, such as those of the Brassica genus like broccoli, kale, Chinese cabbage, and cauliflower, has been associated with various health promoting effects (Wagner et al., 2013). However, some glucosinolates in Brassica vegetables produce indolylic isothiocyanates with anticarcinogenic activity. In contrast, progoitrin and indolylic glucosinolates degrade to goitrin and thiocyanate, respectively, and may decrease thyroid hormone production (Felker et al., 2016). Thus, it is important to identify potential environmental sources of harmful substances to reduce opportunities for exposure, especially in vulnerable groups.

Thiocyanate is the anion derived from thiocyanic acid (HSCN) and is widely used when manufacturing electronic products and furniture (Laurberg et al., 2009; Jain, 2016). Thiocyanate salts are characterized by high water solubility (KSCN : $>1000 \text{ g L}^{-1}$) that is lower than those of other endocrine disruptors, such as perchlorate salts (2090 g L^{-1}). Although the dynamics of perchlorate in the environment have been investigated, those of thiocyanate have not yet been elucidated (Calderon et al., 2020, 2021). The main route of human exposure to thiocyanate is the metabolization of cyanide from cigarette smoke into thiocyanate in the liver (Willemin and Lumen, 2017; Knight et al., 2018). However, other potential sources of thiocyanate exposure, such as drinking water and agricultural products, remain understudied despite being considered primary sources of exposure to other contaminants (Blount et al., 2008; Leung et al., 2012; Qin et al., 2014; Jain, 2016; Zhu et al., 2019). Soil fumigation is used to control soil-borne pathogens, nematodes, and weeds (Dungan et al., 2003; Zheng et al., 2004), and metam-sodium, a soil fumigant, is in use in several countries for this purpose in quantities ranging from 50 to 80 g ha^{-1} . Methyl isothiocyanate (MITC) is the primary breakdown product of metam-sodium (Dungan et al., 2003; Zhang et al., 2005). MITC is a highly volatile compound with broad, non-selective biocidal activity (DPR, 2016). The hydrolysis rate of MITC is low in water but increases significantly upon the addition of sediments similar to those found in bodies of water (DPR, 2002). Due to the relatively low leaching potential and fast degradation of MITC in the presence of water with sediments, the risk of groundwater contamination is low (Tomlin, 2000).

Once absorbed, thiocyanate has a mean half-life of 1–2 weeks and is excreted in the urine (Scherer, 2006). Studies have shown that thiocyanate and perchlorate levels in urine and serum have negative additive effects on normal thyroid gland functioning in pregnant women, newborns, and infants, which constitutes a health risk for these groups (Blount et al., 2009;

Pearce et al., 2012; Leung et al., 2012; Charatcharoenwitthaya et al., 2014; Horton et al., 2015; Lee et al., 2017; Knight et al., 2018). During the transition between the newborn (newborn–1 year) and infant (2–3 years) stages, babies are mainly fed breast milk and processed baby foods that are often made with vegetables, such as spinach, chard, and carrots. Previous studies have shown that spinach and chard accumulate soluble contaminants like perchlorate that can form part of the final food product (Calderon et al., 2021). Currently, no regulations exist for thiocyanate in either baby foods or other processed foods, although regulations are in place for perchlorate (EFSA, 2017). Our previous research (unpublished results) shows that thiocyanate is a common contaminant in various matrices 107 in Chile, such as drinking water ($1.4\text{--}15.2 \text{ ng mL}^{-1}$), irrigation water ($7.2\text{--}13.7 \text{ ng mL}^{-1}$), fruits ($0.11\text{--}0.56 \text{ ng g}^{-1}$), vegetables ($0.25\text{--}0.74 \text{ ng g}^{-1}$), agricultural soils ($7.2\text{--}125 \text{ ng g}^{-1}$), 109 and, fertilizers ($142\text{--}1132 \text{ ng g}^{-1}$). Depending on the characteristics of the soil, irrigation water, and agronomic management at regional levels, a potential risk of the continual incorporation of thiocyanate into the food chain through contaminated crops is present when considering global agricultural production (Zhang et al., 2020). Given this scenario, it is vitally important to study thiocyanate dynamics in the water-soil-plant system in controlled production systems, such as those of greenhouses, in which the conditions (e.g., soil, substrate, or water treatment system characteristics) can be modified to limit pollutant accumulation (Valloton et al., 2017; Calderon et al., 2021; Calderón et al., 2022).

Thus, the objectives of the study were to 1) estimate the uptake, accumulation, and translocation of thiocyanate in the different organs of chard and spinach grown in greenhouses under three treatments and 2) estimate the risk associated with thiocyanate intake in different age groups due to the consumption of chard and spinach. The results of our research may be used by the international scientific community to propose regulations for thiocyanate in food products, particularly baby food, and are thus much needed.

2. Materials and methods

2.1. Study site

The study was conducted during summer–autumn 2019 at the Faculty of Agronomy and Forestry Engineering of the Pontificia Universidad Católica de Chile in Santiago, Chile.

2.2. Greenhouse experiment

The experimental design followed that of Calderon et al. (2020). Briefly, spinach and chard seeds were germinated in seedling trays that had been previously filled with a moist substrate mixture composed of peat and perlite and irrigated daily for 21 days. Subsequently, the seedlings were transplanted into 4-L pots filled with the same substrate mixture. In total, 108 pots were established (54 with chard and 54 with spinach) and assigned to one of three treatments: Control, T1 (30 ng mL^{-1} of thiocyanate), and T2 (70 ng mL^{-1} of thiocyanate). The thiocyanate concentrations were prepared from a standard thiocyanate solution. All experimental treatments were carried out in triplicate, and the pots were distributed in the greenhouse in a completely random design. Each treatment was applied through a drip irrigation system. Each container was supplied daily with 270 mL, administered via four irrigations (2 min) with one dripper (2 L h^{-1}). The nutrient solution for each treatment was individually mixed in a 120-L container and completely replaced every two weeks. During the first two weeks of the experiment, the nutrient solution was composed of potassium nitrate (120 mg L^{-1}), calcium nitrate (240 mg L^{-1}),

monoammonium phosphate (30 mg L⁻¹), magnesium sulfate (120 mg L⁻¹), and Fe-EDDHA (5 mg L⁻¹; Basafer Plus; Compo Expert, Münster, Germany). The pH range of the solution was adjusted to remain between 5.5 and 6.0. At the start of the third week of growth, the fertilizer concentration in the nutrient solution was doubled.

To evaluate the thiocyanate dynamics of the water-soil-plant system, the bottoms of the experimental pots were perforated to collect leachate on a daily basis. Each week, substrate, root, stem, leaf, total aerial fraction (stem + root), and leachate samples were collected and stored at 4 °C until further analysis. The harvest periods corresponded to weeks 1–2 (groups 1–4), 3–4 (groups 2–5), and 5–6 (groups 3–6). Additionally, the thiocyanate levels in the nutrient solution and fertilizer samples were determined.

2.3. Sample preparation, extraction, and analysis

Briefly, spinach and chard samples consisting of approximately 0.20 ± 0.02 g of the root, stem, and total aerial fraction were placed in propylene tubes that had been previously fortified with 100 ng mL⁻¹ of potassium thiocyanate (¹³C, 95–99%). Acetonitrile and acetic acid were added to a final volume of 10 mL. The samples were shaken, centrifuged, and extracted using Envi-Carb cartridges (500 mg, 6 mL; Waters Corporation; Milford, MA, USA). The collected extracts were stored at 4 °C until analysis. Substrate samples (0.15 ± 0.05 g) were combined with Milli-Q water and liquid chromatography grade ethanol, fortified with 100 ng mL⁻¹ potassium thiocyanate (¹³C, 95–99%), extracted with Envi-Carb cartridges (500 mg, 6 mL; Waters Corporation), and stored at 4 °C. The leachate samples (0.2 mL) were diluted 1000-fold, fortified with 100 ng mL⁻¹ of potassium thiocyanate (¹³C, 95–99%), shaken, filtered (0.2-µm mesh), and stored at 4 °C. The nutrient solution and fertilizer samples were subjected to the same procedure as the leachate samples.

The thiocyanate concentration was determined using an Agilent 1100 series LC liquid chromatography system (Agilent Technologies, Santa Clara, CA, USA) coupled to an API 2000 electrospray ionization tandem mass spectrometry (ESI-MS/MS) triple quadrupole mass spectrometer (Applied Biosystem, Foster City, CA, USA) in negative ionization mode. The mobile phase was composed of methylamine (40 mM) in isocratic mode at a flow rate of 0.3 mL min⁻¹ using an IonPac AS-21 anion exchange column (250 mm × 2 mm; Dionex, Sunnyvale, CA, USA). Thiocyanate quantification was conducted with an 8-point calibration curve (0–2500 ng mL⁻¹) with a linear regression coefficient of 0.99. Blank, duplicate, and spiked samples (100 ng mL⁻¹) were included to evaluate the performance of the chromatography system. Thiocyanate was not detected in any of the quality controls. The limits of detection (LOD) were 1 ng mL⁻¹ for the leachate and nutrient solutions and 6 ng g⁻¹ for the substrate and plant tissue samples.

2.4. Bioaccumulation factor (BAF) and translocation factor (TF)

The bioaccumulation factor (BAF) is used to estimate the capacity of a plant species to accumulate contaminants in its tissues. A BAF > 1 indicates contaminant accumulation, whereas a BAF < 1 indicates the opposite. The translocation factor (TF) is used to describe the ability of a plant species to translocate contaminants from its roots to leaves. A TF > 1 indicates contaminant accumulation in the leaves, whereas a TF < 1 indicates that accumulation occurs in the roots (Calderón et al., 2022).

2.5. Risk estimation

The estimated daily intake (EDI) for each age group (newborn–1 year, 2–3 years, 4–10 years, 11–21 years, 22–45 years, and 46–70 years) was determined based on the average thiocyanate concentration (ng g⁻¹) in chard and spinach at the harvest stage in each treatment multiplied by the average daily vegetable intake (g) for each age group and divided by the average body mass (kg) for each age group. Information on vegetable consumption rates was obtained from the Food Commodity Intake Database (FCID 2005–2010) of the United States.

3. Results and discussion

3.1. General characterization

The first evidence of the presence of thiocyanate in fertilizers to date is presented in Table 1. Concentrations from not detected (ND)–397 ng g⁻¹ were quantified in the nitrogenous, potassic, phosphoric, and magnesium fertilizers used in the study. Interestingly, Chilean fertilizers (i.e., nitrogenous and potassic) are characterized by containing trace amounts of chemical species with no nutritional value, such as perchlorate (Calderón et al., 2022). Both perchlorate and thiocyanate are highly soluble, and the co-existence of these compounds in fertilizers (e.g., magnesium sulfate, potassium nitrate, and calcium nitrate) presents a potential human health risk due to the ingestion of contaminated foods. Monoammonium phosphate, a fertilizer imported into Chile, contained the highest concentration of thiocyanate (397 ng g⁻¹).

Our results allow us to hypothesize that agricultural soils worldwide may be potentially contaminated with traces of thiocyanate. Thus, it is necessary to understand thiocyanate dynamics in the water-soil-plant system. In our study, thiocyanate was not detected in substrate, irrigation water, or seedling samples during initial germination. However, in the Control treatment, the nutrient solution contained 10 ng mL⁻¹ of thiocyanate, which was only due to fertilizer addition.

3.2. Uptake and accumulation in tissues

3.2.1. Roots and stems

Soluble contaminant accumulation in leaves is a function of evapotranspiration and the genotype of the plant (Seyfferth and Parker, 2007). In our study, thiocyanate accumulation in the roots increased as a function of time and treatment (T2 > T1 > Control; Fig. 1). The thiocyanate concentration applied in the T2 treatment was 10-fold higher than the concentrations in water samples in Chile (7.2–13.7 ng mL⁻¹; median: 7.5 ng mL⁻¹). Thiocyanate was not detected in the leachate and substrate samples of either chard or spinach, indicating that thiocyanate was taken up by the roots and translocated to higher organs. As such, a microbial degradation process may be at work within the system, although further research is needed to confirm this hypothesis. A similar tendency to that observed in the roots (Control) was present in the stems. However, an inverse effect was observed in chard (T1), which has a higher capacity to accumulate thiocyanate than spinach (Control; week 6). In T2, spinach accumulated more thiocyanate than chard (week 4–5), although the thiocyanate concentration in chard (85 ng g⁻¹) was higher than that in spinach (57 ng g⁻¹) at week 6. In addition, a significant difference was present in thiocyanate accumulation between the roots and stems in chard ($p < 0.0001$).

3.2.2. Total aerial fraction and leaves

The thiocyanate accumulation in the leaves and total aerial fraction are presented in Fig. 2. A similar pattern to that observed in the roots and stems occurred in the total aerial fraction and leaves, with thiocyanate accumulation increasing over time. Interestingly, in the Control treatment, the total aerial fraction of chard was found to accumulate twice as much thiocyanate as that of spinach from weeks 3–5. However, these concentrations were the same at harvest. For T1 and T2, thiocyanate accumulation in the total aerial fraction of chard was always higher than that of spinach. The thiocyanate

Table 1
Thiocyanate (SCN⁻) concentrations in fertilizers.

Fertilizer	Concentration of SCN ⁻ (ng g ⁻¹)
Magnesium sulphate (MgSO ₄)	354
Basafer (Fe-EDDHA)	N.D.
Potassium nitrate (KNO ₃)	358
Monoammonium Phosphate (NH ₄ H ₂ PO ₄)	397
Calcium nitrate (Ca(NO ₃) ₂)	142

N.D.: Not detected.

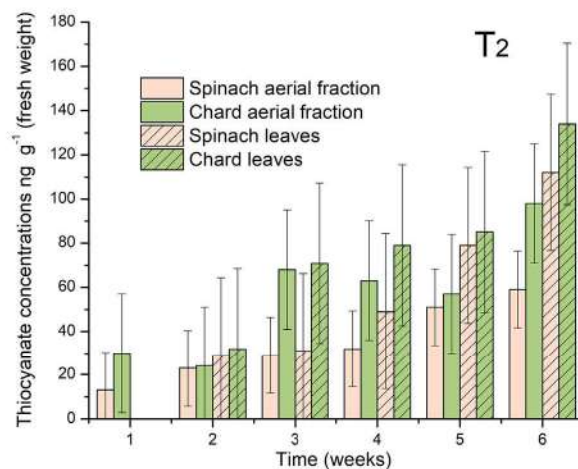
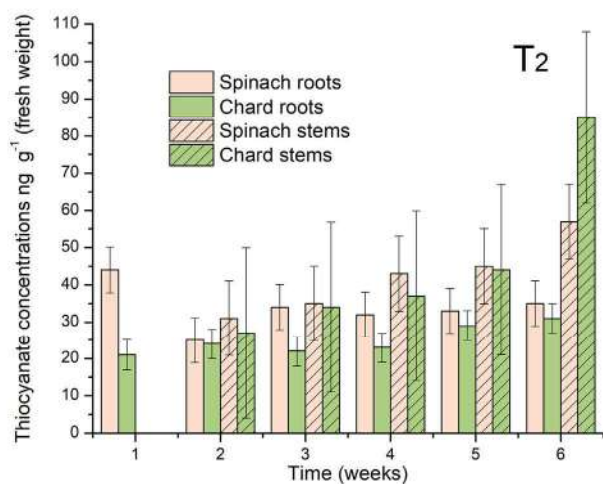
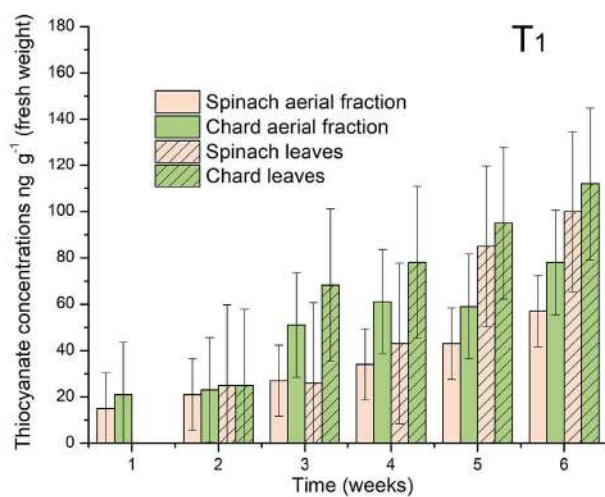
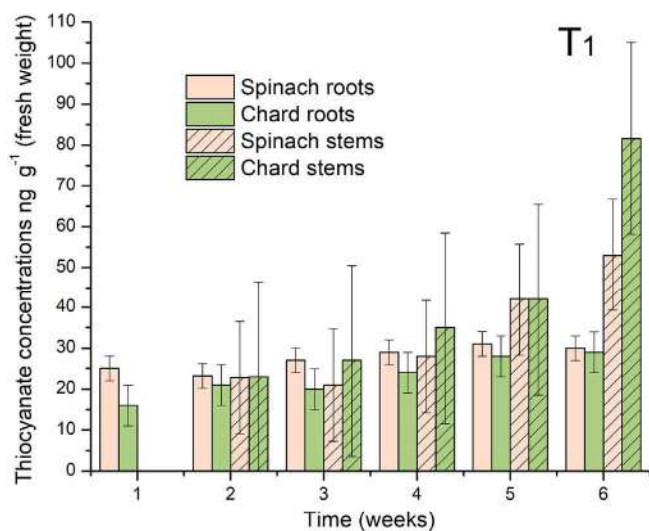
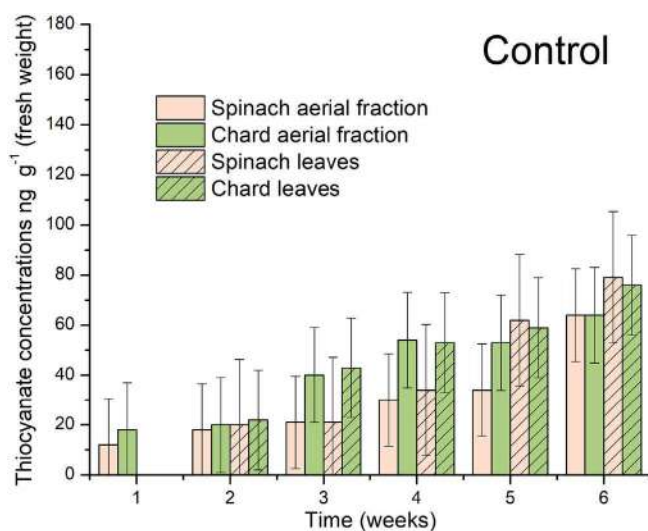
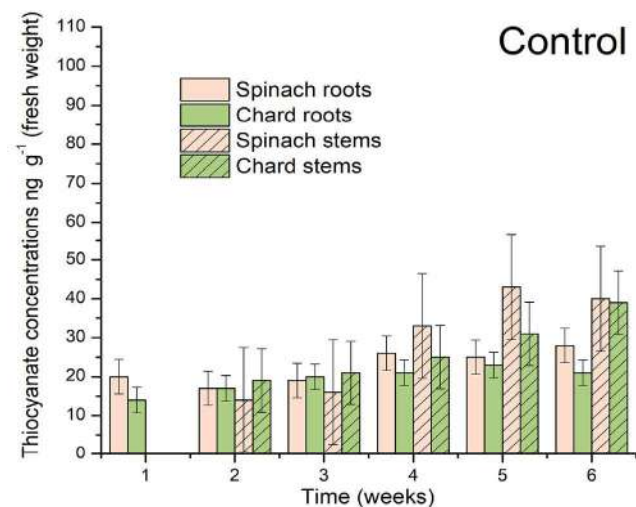


Fig. 1. Distribution of the thiocyanate concentration in the roots and stems of chard and spinach plants in the control, T1, and T2 treatments.

Fig. 2. Distribution of the thiocyanate concentration in the leaves and total aerial fractions of chard and spinach plants in the control, T1, and T2 treatments.

concentrations at harvest for chard in T1 and T2 were 78 and 98 ng g⁻¹, respectively.

When comparing thiocyanate accumulation in this study with the perchlorate accumulation in greenhouse crops of Calderón et al. (2022), notable differences are present. Calderón et al. (2022) found that perchlorate accumulation was always higher in spinach in treatments with 1 and 10 mg L⁻¹ and exceeded the permitted limits for perchlorate in baby foods (20 ng g⁻¹) (EFSA, 2017). In our study, thiocyanate accumulation in chard was significantly ($p < 0.0194$) higher than that of spinach, and thus accumulation is a function of the plant species.

In general, the volume and surface area of chard leaves are greater than those of spinach, and thus chard leaves have greater evapotranspiration potential, with the concentrations of soluble contaminants, such as thiocyanate, increasing over time. In a previous study, it was reported that the accumulation of thiocyanate in rice seedlings fertilized with NO₃⁻ was higher 4 than that of NH⁺ (Zhang et al., 2020). In the Control treatment, thiocyanate accumulation in chard leaves was higher than that of spinach leaves until week 4. However, from week 4 until harvest, the thiocyanate concentration in spinach leaves surpassed that of chard leaves. In T1 and T2, thiocyanate accumulation in chard was always greater than in spinach. The maximum thiocyanate concentrations in chard and spinach in T1 and T2 were 112 and 134 ng g⁻¹ and 100 and 112 ng g⁻¹, respectively.

The results of the statistical analyses show that there were significant differences in thiocyanate accumulation in both the leaves and stems of chard ($p < 0.0001$) and spinach ($p < 0.0005$). The BAF for both species >1, indicating that thiocyanate accumulates in both species (leaf > stem > root). In addition, the TF values indicated that thiocyanate is preferentially translocated from the roots to the leaves in both chard and spinach. Finally, significant differences were present between treatments for chard ($p < 0.0121$) but not for spinach ($p < 0.0936$).

Although thiocyanate accumulation in this study was high, without regulations it is not possible to determine if these types of vegetables represent a potential danger to human health. For example, Sanchez et al. (2008) reported elevated thiocyanate levels in Brassica sp. (1965–56,219 µg kg⁻¹). Additionally, Han and Kwon (2009) reported that the average thiocyanate intake (16.3 µmol SCN⁻ day⁻¹ person⁻¹) through Brassicaceae vegetables in Korea was lower than the dose required producing adverse effects. In this context, Bhattacharjee et al. (2012) suggest that the high thiocyanate content in both Brassica and non-Brassica vegetables (16.5–42.3 mg kg⁻¹) may be in part responsible for the persistence of the endemic goiter in people of the sub-Himalayan Tarai region. New studies are needed that generate baseline data to establish regulations for thiocyanate concentrations in fruits and vegetables to protect consumer health, especially those of vulnerable groups.

3.3. Human exposure

Table 2 shows the EDI values calculated by age group for chard and spinach. For chard, the highest EDI values were found in the age groups of 4–10 and 22–45 years, with upper limits of 281 and

348 ng kg⁻¹ day⁻¹ for T2, respectively, and 235 and 291 ng kg⁻¹ day⁻¹ for T1, respectively. These upper limits exceeded the subchronic reference dose of 200 ng kg⁻¹ day⁻¹ (EPA, 2012). In the Control treatment, the EDI values did not exceed the subchronic reference dose of 200 ng kg⁻¹ day⁻¹ (EPA, 2012).

The EDI calculations were made for spinach considering both the consumption of fresh spinach and spinach in baby foods. In fresh spinach, the EDI values for the age groups spanning 2 to 70 years exceeded the chronic reference dose of 600 ng kg⁻¹ day⁻¹. The highest EDI values of 813 (Control), 1030 (T1), and 1154 (T2) ng kg⁻¹ day⁻¹ were present in the age group of 2–3 years. The EDI values for spinach consumption in baby foods were estimated up to 3 years of age. The EDI values for the age group of newborn–1 year were greater than 1000 ng kg⁻¹ day⁻¹, whereas the EDI values for the age group of 2–3 years exceeded the subchronic reference dose but not the chronic reference dose.

In summary, the EDI values in this study are less than the lowest observed adverse effect level (LOAEL), which is 1.9×10^5 ng kg⁻¹ day⁻¹ (EPA, 2012). However, our results show that there is a potential risk to human health from the consumption of spinach and chard in different age groups, primarily in newborns and infants up to three years of age. Further studies are needed to elucidate the real impacts of thiocyanate intake on human health due to the consumption of contaminated foods.

4. Conclusions

Our study is the first to evaluate the uptake and accumulation of thiocyanate in chard and spinach grown in greenhouses. The results show that thiocyanate is a common contaminant in nitrogenous, potassic, and phosphoric fertilizers on the order of ng g⁻¹. The thiocyanate accumulation increased over time and depended on the treatment (T2 > T1 > Control), with chard accumulating more thiocyanate than spinach ($p < 0.0194$). Interestingly, statistically significant differences ($p < 0.0001$) were present with regard to thiocyanate accumulation between chard and spinach (leaf > total aerial fraction). The EDI values for chard (Control) exceeded the subchronic reference dose of 200 ng kg⁻¹ day⁻¹ (EPA, 2012). For fresh spinach, the EDI values exceeded the chronic reference dose of 600 ng kg⁻¹ day⁻¹ for the age groups spanning 2 to 70 years. For spinach in baby foods, the EDI values for the age group of newborn–1 year were higher than 1000 ng kg⁻¹ day⁻¹ and exceeded the chronic reference dose, although lower EDI values of ~500 ng kg⁻¹ day⁻¹ were found for the age group of 2–3 years. In general, the EDIs were lower than the LOAEL of 1.9×10^5 ng kg⁻¹ day⁻¹ (EPA, 2012).

Funding

This study was supported by the National Fund for Scientific and Technological Development (FONDECYT) Program [FONDECYT 11160581] of the National Commission for Scientific and Technological Research (CONICYT), Chile.

Table 2

Estimated daily intake (EDI) of thiocyanate (SCN⁻) in chard and spinach for different age groups.

Age group (years)	Chard				Spinach (fresh)				Spinach (baby food)			
	C/BM	EDI Control: 76 ng g ⁻¹	EDI T1: 112 ng g ⁻¹	EDI T2: 134 ng g ⁻¹	C/BM	EDI Control: 79 ng g ⁻¹	EDI T1: 100 ng g ⁻¹	EDI T2: 112 ng g ⁻¹	C/BM	EDI Control: 79 ng g ⁻¹	EDI T1: 100 ng g ⁻¹	EDI T2: 112 ng g ⁻¹
Newborn–1	0	0	0	0	2.3	181.7	230	257.6	12.4	979.6	1240	1388.8
2–3	0	0	0	0	10.3	813.7	1030	1153.6	5.2	410.8	520	582.4
4–10	2.1	159.6	235.2	281.4	8.4	663.6	840	940.8	0	0	0	0
11–21	0	0	0	0	5.7	450.3	570	638.4	0	0	0	0
22–45	2.6	197.6	291.2	348.4	9.6	758.4	960	1075.2	0	0	0	0
46–70	1.3	98.8	145.6	174.2	6.1	481.9	610	683.2	0	0	0	0

EDI in (ng kg⁻¹ day⁻¹).

C/BM: Consumption (g)/Body Mass (kg).

CRedit authorship contribution statement

R. Calderón: Funding acquisition, Writing – original draft, Writing – review & editing, Formal analysis, Resources. **C. Jara:** Formal analysis, Investigation, Methodology. **F. Albornoz:** Formal analysis, Supervision, Writing – review & editing. **P. Palma:** Formal analysis, Writing – original draft, Writing – review & editing. **N. Arancibia-Miranda:** Formal analysis, Investigation. **R. Karthikraj:** Formal analysis. **K. Manquian-Cerda:** Formal analysis. **P. Mejias:** Formal analysis.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Raul Calderon Araya reports financial support was provided by National Commission for Scientific and Technological Research. Raul Calderon Araya reports a relationship with National Commission for Scientific and Technological Research that includes: funding grants.

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Contents lists available at ScienceDirect

Chemosphere

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Occurrence and human exposure to bromate via drinking water, fruits and vegetables in Chile



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HIGHLIGHTS

- Bromate was detected in water, soil, fertilizers, fruits and vegetables from Chile.
- Levels of bromate in DW (median: 18.5 $\mu\text{g L}^{-1}$) exceeded the maximum contaminant level.
- Leafy vegetables accumulate higher levels of bromate than non-leafy vegetables.
- The main exposure route for bromate in humans is via drinking water.

ARTICLE INFO

Article history:

Received 2 April 2019

Received in revised form

14 April 2019

Accepted 22 April 2019

Available online 25 April 2019

Handling Editor: Xiangru Zhang

ABSTRACT

Bromate (BrO_3^-) is an anionic contaminant known possess carcinogenic potential. Although some studies have reported the occurrence of bromate in drinking water, very little is known about its presence in fruits and vegetables, especially in Chile. In this study, we quantified bromate in soils ($n = 29$), drinking water ($n = 43$), surface water ($n = 6$), groundwater ($n = 6$), fertilizers ($n = 7$), fruits ($n = 12$) and vegetables ($n = 42$) collected across Chile. The highest average concentrations of bromate in soils (11.7 ng g^{-1}) and drinking water (8.8 ng mL^{-1}) were found in northern Chile. Additionally, drinking water collected from four regions of Chile showed higher concentrations of bromate (median: 18.5 ng mL^{-1}) than the maximum contaminant level (MCL, 10 ng mL^{-1}). Concentrations of bromate in nitrogenous and non-nitrogenous fertilizers were similar (median: $2.51 \mu\text{g g}^{-1}$). Leafy vegetables (median: 9.52 ng g^{-1}) produced in the northern Chile contained higher bromate concentrations than those produced in other regions (median: 0.24 ng g^{-1}). The estimated daily intakes of bromate via drinking water in northern, central and southern were ranged between 58.6 and 447 ng/kg bw/d . Leafy vegetables were an important source of bromate for all age group. The EDI values were below the respective reference dose (RfD) of 4000 ng/kg-day .

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1. Introduction

Industrial development and new technologies continue to introduce new chemicals in the market, attracting the attention of the international scientific community and regulatory agencies to examine the impact of these emerging environmental chemicals on human health (Gravilescu et al., 2015; Geissen et al., 2015). Although great advances have been made in analytical

methodologies to identify environmental contaminants, not all contaminants are routinely monitored in many countries in Latin America.

Bromate (BrO_3^-) is an anionic compound generated as a byproduct during disinfection process via oxidation and chlorination of drinking water (Soltermann et al., 2016; Lai et al., 2018; Fischbacher et al., 2015; Fang et al., 2017). Bromate is classified as a group 2B, possible human carcinogen by the International Agency for Research on Cancer (International Agency for Research on Cancer (IARC), 2018) based on sufficient evidence that bromate induces cancer in experimental animals. The United States Environmental Protection Agency (USEPA) and the World Health

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Organization (WHO) have proposed a tolerance limit of $10 \mu\text{g L}^{-1}$ bromate in drinking water (United States Environmental Protection Agency (USEPA), 2018; World Health Organization, 2011). Japan, Canada and China have adopted the same standard whereas Australia set the limit at $20 \mu\text{g L}^{-1}$ (Kosaka, 2016).

Very little information is known about the occurrence of bromate in the environment, although some drinking water monitoring studies have been reported its occurrence in drinking water (Han and Zhang, 2018). In the drinking water collected from India and Canada, bromate was found at $5.34 \mu\text{g L}^{-1}$ and $6.11 \mu\text{g L}^{-1}$ (maximum value and average), respectively (Dong et al., 2019; Anupama et al., 2012). It was estimated that the average concentration of bromate in water after ozonation ranged from 1.9 to $3.87 \mu\text{g L}^{-1}$ (CFIA, 2010–2011). Bottled water and surface water from the United States were shown to contain bromate at $<76 \mu\text{g L}^{-1}$ and $<4.6 \mu\text{g L}^{-1}$, respectively (Snyder et al., 2005).

Some studies reported the occurrence of bromate in potato snacks, flour, and bread (Shi et al., 2006; Arias et al., 2010). Dong et al. (2019) analyzed bromate and perchlorate in vegetables from China but the concentrations of bromate were below the method detection limit in those samples (LOD: $0.5 \mu\text{g L}^{-1}$). Other than these reports, the information regarding environmental occurrence of bromate is scarce globally. Considering that bromate has characteristics similar to perchlorate, bromate can be found naturally in fertilizers of northern Chile (Calderón et al., 2014). It is probable that bromate and perchlorate coexist in arid and semi-arid environments which warrants the need for assessing bromate levels in agricultural ecosystems in Chile.

Therefore, our study was aimed to investigate the occurrence of bromate in soils, drinking water, surface water, groundwater, vegetables and fruits collected from various locations in Chile. Further, based on the measured concentrations of bromate, we estimated human exposure dose to bromate in Chile. Our study presents the first evidence of bromate in water-soil-plant system in Chile and examines its association with human exposure.

2. Materials and methods

2.1. Sampling

A total of 145 samples were collected during 2017 throughout Chile that was divided into 16 regions assigned in ascending order from north to south with exception of region (XIV and XV, Fig. 1). More information about the regional distribution in Chile is provided in the supporting information (SI). Of these 145 samples, there were 29 fertilized ($n = 3$) and unfertilized soils ($n = 26$), 43 drinking water, 6 surface water, 6 groundwater, 7 fertilizers (nitrogenous and non-nitrogenous), 12 fruits and 42 vegetables. Most of the sampling was conducted in northern Chile where agricultural production and fertilizer mining are major activities. More information about the sampling is provided in the SI.

Soil samples were collected between depths of 0 and 15 cm, sieved ($<2.0 \text{ mm}$) and stored in polyethylene bags at 4°C until further analysis. Samples from several locations within a same field were pooled to obtain a representative mixture. Drinking water samples were collected directly from the faucets after running the water for 3 min and stored in polyethylene containers. Surface water, groundwater and river water were collected in polyethylene containers and stored at 4°C . Fertilizers for national ($n = 5$) and international ($n = 2$) origin were collected from the Institute of Agricultural Research (INIA). Fruits and vegetables were collected from two systems: 1) a surveillance program of the northern Chile by the Ministry of Health (traceable) and 2) supermarkets in Santiago metropolitan region (non-traceable).

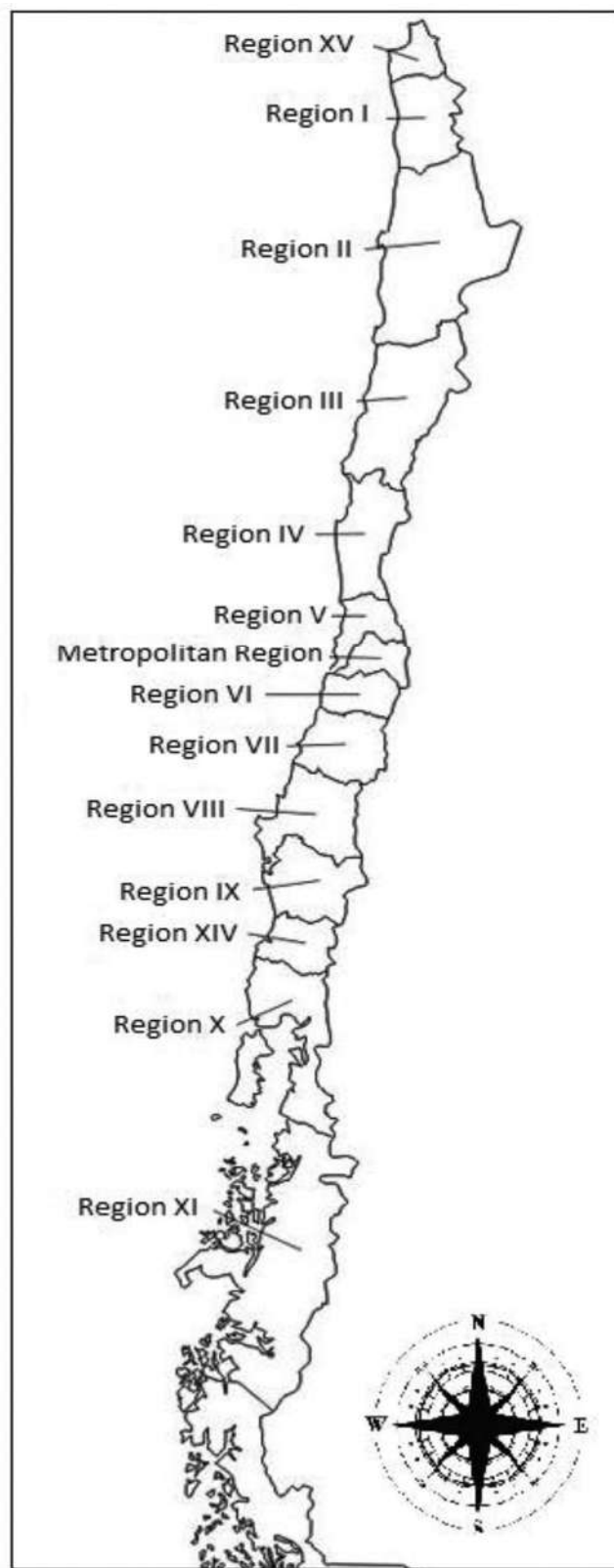


Fig. 1. Map of the sampling regions in Chile.

2.2. Sample extraction

Soil samples (1.0 g) were placed in 15-mL Falcon tubes and fortified with Br^{18}O_3 (98%) as the internal standard purchased from Cambridge Isotope Laboratories (Andover, MA). Ten milliliters of HPLC-grade water were subsequently added, and the solution was shaken in an orbital shaker for 30 min and then centrifuged at 4500 rpm for 5 min. One mL of methanol was added to the mixture, and the above procedure was repeated. The sample was subsequently passed through an Envi-carb cartridge (500 mg, 6 cc; Waters Corp, Milford, MA, USA) preconditioned with 6 mL of HPLC-grade water was purchase from J. T. Baker (Phillipsburg, NJ). Finally, 1 mL of the solution was filtered using a 0.20- μm nylon syringe filter and injected into LC-MS/MS.

Exactly 950 μL aliquot of water samples were filtered using a 0.20- μm nylon syringe filter and fortified with 50 μL of Br^{18}O_3 (98%) to make up the final volume to 1 mL and directly injected into LC-MS/MS.

For fertilizers, 0.25 g of each sample was dissolved in 10 mL of HPLC-grade water. One milliliter of the homogenized solution was then diluted to a final volume of 10 mL with HPLC-grade water. Subsequently, 950 μL of the diluted solution was fortified with 50 μL of an internal standard mixture Br^{18}O_3 (98%), and passed through an Envi-carb cartridge as described for soil samples.

Fruits and vegetables (0.25 g, freeze-drying) were homogenized, fortified with an internal standard mixture containing Br^{18}O_3 (98%) and mixed with 4 mL of acetic acid (1%), vortexed and brought to a final volume of 10 mL with acetonitrile (ACN). The solution was centrifuged, and the extract was transferred to another polypropylene tube. To the residue, 1 mL of methanol was added, and the above procedure was repeated. The extract was passed through a preconditioned (with 3 mL of ACN and 1% acetic acid) Envi-carb cartridge (500 mg, 6 cc; Water, Milford, MA, USA). One mL of the eluent was filtered using a 0.20- μm nylon syringe filter and injected into an LC-MS/MS.

2.3. Instrumental analysis

The extracts were analyzed by high-performance liquid chromatography (Agilent 1100 series HPLC; Agilent Technologies, Santa Clara, CA) coupled with electrospray triple quadrupole mass spectrometry (API 2000; ESI-MS/MS; Applied Biosystems, Foster City, CA). Data acquisition and quantification were accomplished with Analyst software. The chromatographic separation of bromate was accomplished with an anion exchange column, IonPac AS-21 (250 mm \times 2 mm, Dionex, Sunnyvale, CA, USA). Two hundred millimolar (mM) methylamine in water solution was the mobile phase and was eluted isocratically at a flow rate of 0.27 mL/min. The injection volume of the sample was 50 μL . Bromate eluted at 3.6 min and the total run time was 9 min. Electrospray negative ionization (ESI-) and multiple reaction monitoring (MRM) mode with the following ions were monitored for quantification and confirmation of bromate and $^{18}\text{O}_3$ -enriched bromate: m/z 127 ($^{79}\text{BrO}_3^-$)/111 ($^{79}\text{BrO}_2^-$), m/z 129 ($^{81}\text{BrO}_3^-$)/ m/z 113 ($^{81}\text{BrO}_2^-$), and m/z 133 ($^{79}\text{Br}^{18}\text{O}_3^-$)/ m/z 115 ($^{79}\text{Br}^{18}\text{O}_2^-$).

2.4. Quality assurance and quality control

An eight-point calibration standard encompassing concentration ranging from 1 to 200 ng mL^{-1} for bromate was injected with each batch of 100 samples. The regression coefficient of the calibration curves was >0.99 . The limit of detection (LOD) and LOQ were defined as the minimum amount of analyte that yielded a signal-to-noise ratio of 3:1 and 10:1, respectively. The LODs for bromate was 0.08 ng mL^{-1} for water, 0.2 ng g^{-1} dry weight (DW) for

soil, 2 ng g^{-1} DW for fertilizer and 0.05 ng g^{-1} fresh weight for fruits/vegetables. Procedural blank, duplicate samples, and matrix spike (5 and 15 ng mL^{-1} of bromate fortified) samples were included in each batch. Bromate was not detected in any of procedural blanks. Instrumental (water) blanks were injected after every 20–25 samples and no carry-over of bromate was found between samples. A mid-point calibration standard was injected for every 12 h to monitor for drift in instrumental response.

2.5. Exposure assessment

The daily intake (EDI) of bromate through the ingestion of fruits, vegetables and drinking water was calculated. The EDI of bromate through the ingestion of drinking water was calculated by multiplying the median bromate concentrations (ng mL^{-1}) with nominal volume of water ingestion (mL day^{-1}) divided by the body weight (kg). The drinking water ingestion rates were cited from the US EPA exposure factors handbook (United State Environmental Protection Agency (USEPA), 2011). The calculation of EDI was performed for four age groups and gender: infants (0–1 years), children (1–10 years), teens (11–19 years) and adults (20–64 years). For vegetables, the EDI of bromate was calculated using the median bromate concentrations in these products (ng g^{-1} fresh weight) multiplied by daily intake rate (g day^{-1}) and then divided by body weight (kg). The vegetable consumption data were based on the National Health Survey of Chile 2016–2017 (ENS, 2016–2017). The EDI was calculated for three groups and gender: 15–24 years, 25–44 years and 45–64 years. More information about the calculated for EDI is provided in the supporting information 2 (SI 2). The EDI values were calculated on the basis of two different concentrations of bromate: 1) bromate levels found in northern Chile and 2) for the entire country for drinking water and vegetables. Sigma Plot (version 12.0) was used for statistical analysis.

3. Results and discussion

3.1. Soils

All soil samples contained detectable levels of bromate ranging in concentrations from 0.6 to 38.6 ng g^{-1} with a median value of 4.8 ng g^{-1} . Of the 29 samples analyzed, 31% ($n=9$) contained bromate concentrations above 10 ng g^{-1} (Fig. 2). The highest occurrence of bromate was observed in soils of Regions I, III and the metropolitan region (MR) (see Fig. 1). Fertilized soils under the cultivation of olive trees contained approximately 6 times higher bromate concentrations (28.9 ng g^{-1}) than those of unfertilized soil (4.8 ng g^{-1}) (Fig. 2a). A similar pattern was found in soils under pomegranate crops, in which fertilized soils contained an order of magnitude higher bromate concentrations than those in unfertilized soil (15.1 versus 1.4 ng g^{-1}).

In soils from Region I, bromate levels were similar between different locations, with Humberstone containing the highest concentration (31.1 ng g^{-1}). Humberstone is a town with nitrate mines operated for many years (Calderón et al., 2014). Some industries currently producing fertilizers for domestic consumption and for export are located in northern Chile. Bromate was detected in all soil samples from the central region (median 6.9 ng g^{-1}), which seemed to be related with physicochemical characteristics (alfisol) different from northern region (aridisol), three times higher than those found in the southern region (median 2.3 ng g^{-1}).

3.2. Drinking water, surface water and groundwater

The measured concentrations of bromate in drinking water,

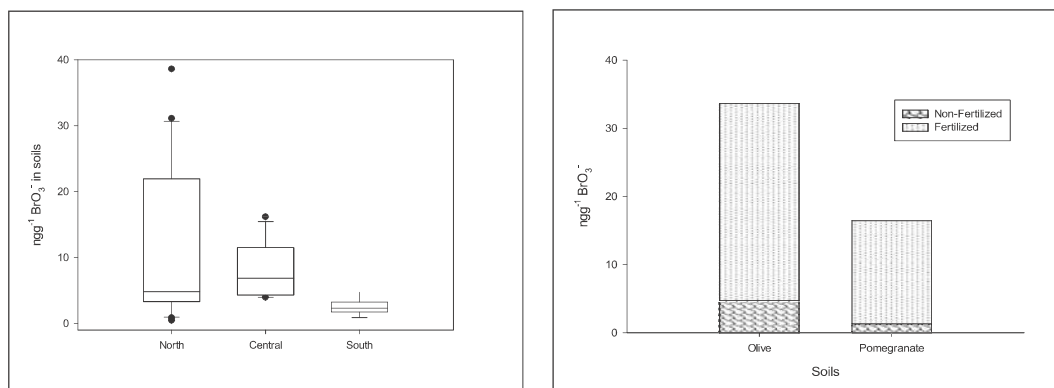


Fig. 2. Bromate levels in soils from different parts of Chile (a) and bromate in fertilized and non-fertilized soils under Olive and pomegranate cultivation (b).

Table 1

Bromate levels in drinking water, surface water and groundwater from Chile.

	N	Area	Region	Mean	Min (ng mL ⁻¹)	Max (ng mL ⁻¹)	Detection Frequency
Drinking water	35	North	XV (n:7)	ND	ND	ND	0/6
			I (n:2)	9.8	—	9.8	1/2
			II (n:7)	22.9	—	22.9	1/7
			III (n:7)	5.2	ND	7.3	2/7
			IV (n:12)	3.7	ND	21.7	7/12
			V (n:1)	ND	ND	ND	0/1
Surface water	6	Central	RM (n:5)	4.8	2.7	9.5	5/5
			V (n:1)	ND	ND	ND	0/1
Groundwater	2	South	VIII (n:2)	7.1	6.0	8.2	2/2
			II (n:1)	ND	ND	ND	0/1
Groundwater	6	North	XV (n:6)	10.5	ND	10.5	1/6

surface water and groundwater from Chile are presented in Table 1. Bromate was detected in 33% of the water samples with concentrations in the range of 1.7 and 22.9 ng mL⁻¹. The bromate levels in all surface water and groundwater samples were below the method detection limit. In the surface waters of the USA, 2 out of 13 samples contained bromate at concentrations below 4.6 µg L⁻¹ (Snyder et al., 2005). Only 1 of 6 groundwater samples from the northern region (Region XV) contained bromate (10.5 ng mL⁻¹) at concentrations higher than maximum contaminant level of 10 µg L⁻¹ (United States Environmental Protection Agency (USEPA), 2018). The groundwater is used for human consumption and for the irrigation of crops in rural areas. Forty-two percent of drinking water samples (n = 18) contained detectable concentrations of bromate. Bromate was detected in all samples from the central and southern regions of Chile. However, the largest number of positive samples (n = 11) were collected from the northern region and 3 samples contained levels equal to or greater than 10 µg L⁻¹ (Serena, 21.7 ng mL⁻¹ (IV region); Illapel, 15.6 ng mL⁻¹ (IV region) and Antofagasta 22.9 ng mL⁻¹ (II region). Additionally, our results indicate that higher bromate contamination in the northern Chile than India (5.34 µg L⁻¹) and similar to Canada (6.11 µg L⁻¹) (Anupama et al., 2012; CFIA, 2010–2011). The sources of bromate in drinking water can be associated with the formation during disinfection process in the water treatment plants (ozonation) and/or from the natural source of origin (Fischbacher et al., 2015; Fang et al., 2017). Treatment plants throughout Chile use chlorine before drinking water is distributed to households. Therefore, in Chile the bromate contamination is from natural origin.

3.3. Fertilizers

Both nitrogenous and non-nitrogenous fertilizers used

nationwide were analyzed for the presence of bromate. All analyzed fertilizers contained bromate at concentrations ranging between 0.21 and 3.44 µg g⁻¹. This is the first report of the occurrence of bromate in fertilizers. Two nitrogenous fertilizers, calcium nitrate and sodium nitrate contained 3.13 and 1.97 µg g⁻¹ bromate, respectively. Among non-nitrogenous fertilizers, bromate concentrations of 2.51 µg g⁻¹ for magnesium sulfate, 3.44 µg g⁻¹ for boric acid and 0.28 µg g⁻¹ for potassium sulfate were found (Fig. 3). Relatively lower concentrations of bromate were found in urea and triple superphosphate fertilizers (median: 0.76 µg g⁻¹). It is probable that fruits and vegetables produced in Chile could be exposed to bromate from the fertilizers.

3.4. Vegetables

A total of 24 vegetable samples were collected from supermarkets in Santiago metropolitan region of Chile (non-traceable), and 18 were from the surveillance program of the Chilean Ministry of Health (traceable). All vegetable samples contained bromate. Median bromate concentrations in vegetables from traceable and non-traceable sources were 0.15 ng g⁻¹ and 2.14 ng g⁻¹, respectively. The highest bromate levels (non-traceable) occurred in leafy vegetables, such as chard (4.04 ng g⁻¹), lettuce (*Lactuca sativa var. cos*) (0.29 ng g⁻¹), and arugula (5.87 ng g⁻¹). The bromate levels in other vegetables varied between 0.04 and 0.83 ng g⁻¹. Leafy vegetables (traceable), such as lettuce, produced in Regions I, II and III (northern zone) contained bromate levels of 23.6 ng g⁻¹, 9.66 ng g⁻¹ and 7.68 ng g⁻¹, respectively. In comparison to bromate levels reported in Santiago supermarket samples, lettuce grown in Region I contained almost two orders of magnitude higher bromate levels. For chard, a similar pattern was noted. Bromate concentrations of 11.2 ng g⁻¹ and 24.8 ng g⁻¹ were found in chard from

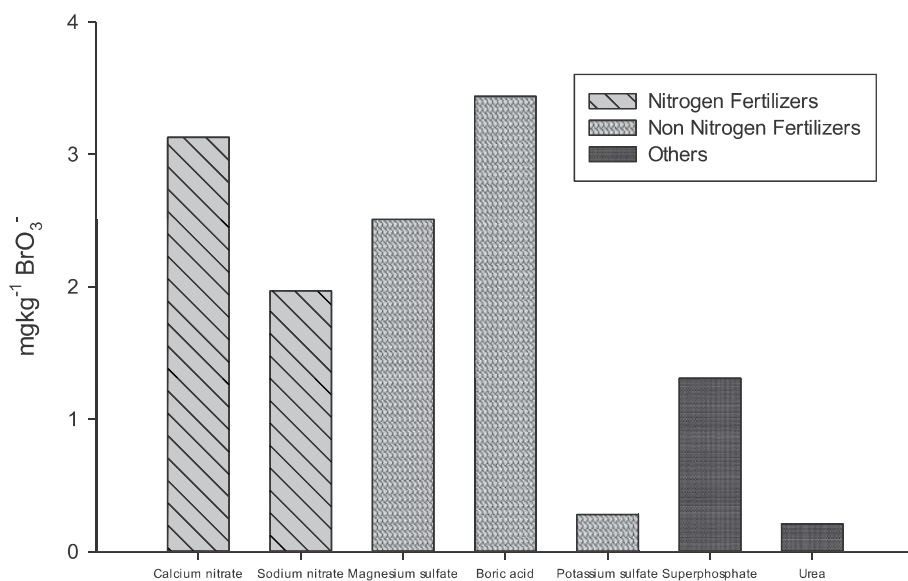


Fig. 3. Bromate levels in nitrogenous and non-nitrogenous fertilizers from Chile.

Regions I and II, respectively, which exceeded those in chard (non-traceable) by a factor between 3 and 6 (Fig. 4). For non-leafy vegetables, (e.g., tomatoes) bromate levels found in Region III (6.07 ng g⁻¹) were greater than those reported in Santiago supermarket samples (0.04 ng g⁻¹) by more than two orders of magnitude. Notable concentrations of bromate were found in cucumbers from Region II (5.96 ng g⁻¹) and carrots of Region I (3.11 ng g⁻¹). Bromate concentrations in remaining vegetables were in the ranges of between 0.05 and 0.74 ng g⁻¹. The bromate concentrations in vegetables in our study were higher than those reported for vegetables from China (Dong et al., 2019). Overall, vegetables from northern Chile contained higher bromate concentrations than those of other regions. High concentrations in vegetables from northern Chile were likely to be related with high bromate levels in soils and fertilizers.

3.5. Fruits

A total of 12 fruit samples were collected with 7 from

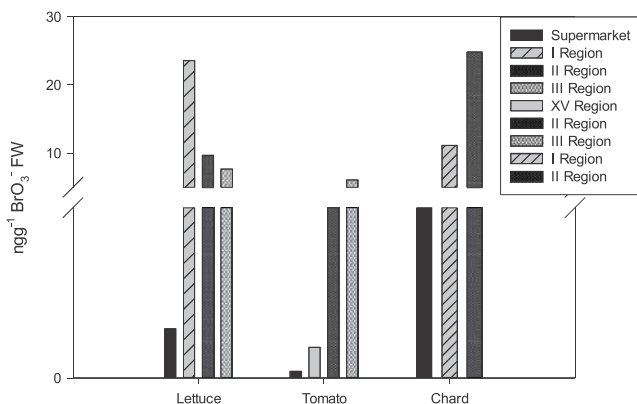


Fig. 4. Distribution of the bromate levels in lettuce, tomato and chard (traceable samples collected by the Ministry of Health and non-traceable samples from local metropolitan supermarkets).

supermarkets and 5 by the national surveillance program. Similar to vegetables, fruits were classified as traceable (ministry of health samples) and non-traceable (supermarket samples). Bromate levels in supermarket samples ranged from not detected (ND) to 0.91 ng g⁻¹. All the traceable fruit samples contained bromate at a median level of 0.08 ng g⁻¹. The levels were lower than those reported for vegetables. The highest bromate levels in fruits were observed in kiwis (0.91 ng g⁻¹) and honeydew melons (0.68 ng g⁻¹) for supermarket samples. Avocados produced in Region XV presented the highest level of bromate (2.24 ng g⁻¹).

3.6. Human exposure to bromate

The EDI (drinking water) values for bromate for the northern, central and southern regions stratified by age are listed in Table 2. The EDI of bromate ranged between 58.6 and 447 ng/kg bw/d for all age groups and regions. Inhabitants of northern region were exposed to higher doses bromate via drinking water than inhabitants from other regions of Chile (Table 2). Among various age and regional groups, infants and children (southern) had the highest EDI values (447 and 373 ng/kg bw/d) followed by infants of the northern (315 ng/kg bw/d) region. However, the EDI values are still lower than the reference dose (RfD, 4000 ng/kg-d). The EDI of bromate for all age groups in specific cities located in the northern region with level higher than MCL such as Antofagasta (22.9 ng mL⁻¹), Illapel (15.6 ng mL⁻¹) and Serena (21.7 ng mL⁻¹) was also below the RfD. The EDI values of bromate via dietary intake of vegetables from traceable and non-traceable sources were calculated separately (Table 3). The EDI values from leafy vegetables were higher than non-leafy vegetables for all age groups. In general, women had higher EDI than men. To compare the EDI of traceable and non-traceable leafy vegetables, the latter had ten times higher levels of exposure for all age groups. For men (15–24 years) the EDI through leafy vegetables was 0.608 ng/kg bw/d from non-traceable sources and 24.1 ng/kg bw/d from traceable sources, respectively. The EDI of bromate for age groups of 15–65 years through non-traceable sources was fruits > leafy vegetables > non-leafy vegetables. In the case of traceable sources, the pattern was leafy vegetables > non-leafy vegetables > fruits.

Chard from Region II, showed EDI for men (15–24 years) of 3.1 ng/kg bw/d, which was approximately one order of magnitude

Table 2

Estimated Daily intake of bromate (ng/kg bw/d) via ingestion of drinking water in Chilean population.

	NORTHERN*	CENTRAL*	SOUTHERN*	SERENA	ILLAPEL	ANTOFAGASTA
Northern						
INFANTS (<1)	315 (1403)**	245 (609)**	447	1365	982	1441
CHILDREN (1–10)	263 (1172)**	205 (509)**	373	1141	820	1204
TEENS (11–19)	75 (335)**	59 (146)**	107	326	235	344
ADULTS (20–64)	84 (373)**	65 (162)**	119	362	261	382
ADULTS (> 65)	101 (449)**	79 (195)**	143	437	314	461

Rfd for bromate: 4000 ng/kg-day.

*Median: Northern (5 ng mL⁻¹), central (3.9 ng mL⁻¹) and southern (7.1 ng mL⁻¹).

**95th Percentile.

Table 3

Estimated daily intake of bromate (ng/kg bw/d) via ingestion of vegetables and fruits in Chilean population.

	Male		Female		Male		Female	
Age group	15–24		25–44		45–64		> 65	
Supermarket								
*Leafy vegetables	0.61	0.71	0.55	0.63	0.55	0.62	0.59	0.66
*Non leafy vegetables	0.070	0.081	0.063	0.073	0.063	0.071	0.067	0.075
*Fruits	0.82	0.95	0.74	0.86	0.74	0.83	0.79	0.89
Surveillance								
*Leafy vegetables	24	28	22	25	22	25	23	26
*Non leafy vegetables	0.39	0.45	0.35	0.40	0.35	0.39	0.37	0.42
*Fruits	0.19	0.22	0.17	0.20	0.17	0.19	0.18	0.20

*Supermarket (median): Leafy vegetables (0.24 ng g⁻¹), non-leafy vegetables (0.11 ng g⁻¹) and fruits (0.35 ng g⁻¹).

RfD (Bromate): 4000 ng/kg-day.

*Monitoring (median): Leafy vegetables (9.52 ng g⁻¹), non-leafy vegetables (0.61 ng g⁻¹) and fruits (0.08 ng g⁻¹).

greater than that for non-traceable chard (0.51 ng/kg bw/d). Similarly, lettuce from Region I showed an EDI of 41.8 ng/kg bw/d, which was much higher than those of non-traceable lettuce (0.51 ng/kg bw/d). The calculated EDIs for fruits were very low for all age groups (female: 0.79–0.95 ng/kg bw/d and male: 0.17–0.22 ng/kg bw/d). The EDI for all sources and age groups were lower than the RfD of 4000 ng/kg-day for bromate.

4. Conclusion

Overall, this study establishes the first evidence of the occurrence of bromate in different environmental compartments and associated human exposure in Chile. Drinking water and leafy vegetables are an important source of exposure to bromate. Considering the current agronomic practices in Chile, using large amount of fertilizers and drip irrigation in areas with water scarcity, the contamination of bromate in soil is expected to increase overtime. Further studies are needed to understand the flux of bromate in agricultural environment.

Declarations of interest

None.

Acknowledgments

This works was funded by the Project Fondecyt 11160581, Conicyt, Chile.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.04.171>.

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Occurrence, distribution and dynamics of perchlorate in soil, water, fertilizers, vegetables and fruits and associated human exposure in Chile

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Received: 16 December 2019 / Accepted: 24 July 2020
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Abstract Perchlorate (ClO_4^-) has been identified as a persistent environmental contaminant of concern. Perchlorate exposure is a potential health concern because it interferes with hormone production by thyroid gland. Food (fruits and vegetables) and drinking water are an important source of human exposure to perchlorate. However, little is known about the occurrence of perchlorate in Chile. The purpose of this study was to determine the occurrence of perchlorate in 145 samples (soil, drinking water,

surface water, groundwater, fertilizers, fruits and vegetables) collected across Chile and estimate associated exposure to consumers. Our results show that perchlorate was detected in soil (median: 22.2 ng g^{-1}), drinking water (median: 3.0 ng mL^{-1}), fruits (median: 0.91 ng g^{-1} fresh weight [FW]), lettuce (median: 5.0 ng g^{-1} FW) and chard (median: 4.15 ng g^{-1} FW). Interestingly, perchlorate concentrations detected in drinking water from three regions (Serena, Copiapo and Illapel) exceeded the USEPA interim drinking water health advisory level of 15 ng mL^{-1} . Median concentrations of perchlorate in non-nitrogenous fertilizers (3.1 mg kg^{-1}) were higher than those in nitrogenous fertilizers

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10653-020-00680-6>) contains supplementary material, which is available to authorized users.

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(1.3 mg kg⁻¹). Estimated daily intake (EDI) of perchlorate via drinking water was lower than the USEPA's reference dose (7000 ng kg⁻¹ bw day⁻¹). The EDI of perchlorate via vegetables (chard and lettuce) produced in northern Chile was three times higher than those produced in other regions. The results of this study provide information about perchlorate sources in Chile, which will be helpful in modifying current regulations.

Keywords Perchlorate · Fruits · Vegetables · Risk assessment · Chile · Fertilizers

Introduction

Perchlorate is an emerging environmental pollutant that has caused widespread water sources (drinking water, irrigation water, groundwater, surface water), soils, fruits and vegetables in the USA and worldwide (Calderón et al. 2017; Dasgupta et al. 2005; Kumarathilaka et al. 2016). Perchlorate is an endocrine disruptor and has the potential to cause thyroid dysfunction by inhibiting the production of T₃ and T₄ hormones, thereby leading to hypothyroidism and metabolic and neurological problems in vulnerable age groups such as breastfeeding infants (Pleus and Corey 2018; Rubin et al. 2017; Steinmaus et al. 2015). Perchlorate is a contaminant released into the environment from both natural and anthropogenic sources. In the past, ammonium perchlorate salts were widely used in military and aerospace industry in the USA generating high levels of contamination into the environment (Liu et al. 2019; Lv et al. 2014). Perchlorate occurs naturally in the environment in deposits of nitrate (caliche) and can be formed in the atmosphere and precipitate into soil (Erickson 1981). Chilean sodium nitrate deposits (caliche) are known to contain naturally occurring perchlorate (Calderón et al. 2014; Urbansky et al. 2001; Rao et al. 2010). Several studies have reported perchlorate concentrations in nitrate minerals and fertilizers produced in the Atacama Desert ranged from N.D. to 5.7 g kg⁻¹ and 0.5 to 4 g kg⁻¹, respectively (Erickson 1981; Dasgupta et al. 2005). There are various possible routes through which perchlorate can enter food. The application of excessive fertilizer represents a primary source of entry for perchlorate, which can be a source

of accumulation in soil, resulting in plant uptake and food chain transfer. Several studies have shown that perchlorate can quickly bioaccumulate in leafy vegetables through contaminated soil or irrigation water or fertilizer use (Calderón et al. 2017; El Aribi et al. 2006; USFDA 2004a, b; Wang et al. 2009; Lee et al. 2012; Alomirah et al. 2016). Consumption of perchlorate-contaminated food and drinking water is the most relevant route for human exposure to perchlorate (Zhang et al. 2018). Recently, high-perchlorate contamination in a diverse range of foods has been reported (Calderón et al. 2017; EFSA 2014), indicating the potential risk from exposure to perchlorate. The highest levels were found in vegetables: Chile (apricot, 145 µg kg⁻¹), Mexico (carrot, 21.5 µg kg⁻¹; tomato, 122 µg kg⁻¹; spinach, 187 µg kg⁻¹), Canada (leafy green, 26.7 µg kg⁻¹), USA (lettuce, 46.7 µg kg⁻¹; Spinach, 175 µg kg⁻¹) and Korea (spinach, 39.9 µg kg⁻¹) (Wang et al. 2009; Alomirah et al. 2016; Guruge et al. 2011). In this context, the European Community (EC) has adopted a provisional perchlorate level for vegetables to protect consumer health (EFSA 2014). Chile is recognized as the main producer in the southern hemisphere and a world leader in the export of products such as cherries, plums and blueberries (Chilealimentos 2017). However, limited information is available about the occurrence of perchlorate in soils, water sources, fertilizers, fruits and vegetables from Chile (Wang et al. 2009; El Aribi et al. 2006; EFSA 2014).

Our primary objective in this study was to conduct a nationwide monitoring of perchlorate in soil, water sources, fertilizers, vegetables and fruits and estimate the perchlorate level to which the Chilean population is exposed. Generation of new information about perchlorate sources into the environment is important for national and international agencies to modify current regulations to ensure food safety.

Materials and methods

Sample collections

A sample set is comprised of 145 samples (29 soil samples, 55 water samples (43 drinking water, 6 surface water and 6 groundwater), 7 fertilizers, 12 fruits and 42 vegetables) which were collected during 2017 throughout Chile. Vegetables and fruits were

collected from: (a) Ministry of Health (traceable = T) and (b) supermarkets in metropolitan region (non-traceable = N.T.). Details in regard to sample collection are provided in Supporting Information (SI, Figure S1).

Sample extraction and instrumental analyses

Samples were analyzed following the method which has been previously described (Calderon et al. 2020a, b). Briefly, soil samples were extracted with 10 mL of HPLC-grade water, purified using an Envi-Carb cartridge (500 mg, 6 cc; Waters Corp., Milford, MA, USA) and stored at -20°C until analysis. Drinking water, surface water and groundwater samples were filtered (10 mL), fortified and stored at -20°C until analysis. Fertilizer samples were extracted with 10 mL of HPLC-grade water, diluted 1000 times, purified by solid-phase extraction using an Envi-Carb cartridge (500 mg, 6 cc; Waters Corp., Milford, MA, USA) and stored at -20°C until analysis. Vegetables and fruits (freeze-dried) were fortified, extracted with acetic acid (1%) and acetonitrile (ACN), vortexed, centrifuged, purified using an Envi-Carb cartridge (500 mg, 6 cc; Water Corp., Milford, MA, USA) and stored at -20°C until analysis.

Identification and quantification of perchlorate were performed on an Agilent 1100 series LC (Agilent Technologies, Santa Clara, CA) interfaced with an API 2000 triple-quadrupole (MS/MS) mass spectrometer (Applied Biosystems, Foster City, CA). Perchlorate was separated using 40 mM of methylamine in water solution as mobile phase by passing through an anion exchange column, IonPac AS-21 (250 mm \times 2 mm, Dionex, Sunnyvale, CA, USA). The limit of detection (LOD) for perchlorate was: 0.05 ng mL⁻¹ for water, 0.2 ng g⁻¹ dry weight (DW) for soil, 0.4 $\mu\text{g g}^{-1}$ DW for fertilizers and 0.05 ng g⁻¹ fresh weight (FW) for fruits and vegetables.

Daily intake estimation

The human exposure was estimated using information obtained from USEPA Exposure Factors Handbook (USEPA 2011) and the National Health Survey 2016–2017 (ENS Chile 2009–2010; 2016–2017). For

drinking water, fruits and vegetables, the estimated daily intake (EDI) was calculated based on geographical zones in Chile (northern, central and southern) for four different age groups (15–24; 25–44; 45–64; > 65). More information about the EDI calculation is provided in SI. All statistical analyses described in the following section (Kruskal–Wallis and Pearson correlation) were performed by using Statistic 10, 2019.

Results and discussion

Concentration in soils

The perchlorate concentration in the agricultural and non-agricultural soils is presented in Table 1. A total of 29 surface soil samples were classified into three zones (northern, central and southern). The highest concentration of perchlorate was observed in soils from northern Chile (ND—311 ng g⁻¹ dry weight [DW]), while those lowest values were observed in central zone (ND—8.4 ng g⁻¹ DW) and southern zone (ND—12 ng g⁻¹ DW). A similar pattern was reported by Urbansky et al. (2001) and Calderón et al. (2014). The perchlorate concentration in fertilized soils was significantly greater than in unfertilized soil (northern). The relatively higher contents of perchlorate in agricultural soils could be related to the consecutive application of fertilizers. Fertilized soils under the cultivation of tomato (region XV), olive (region III) and pomegranates (region III) contained approximately 56, 12 and 13 times higher perchlorate concentrations than unfertilized soil. Interestingly, high perchlorate concentrations were observed in soils from northern (region I) such as Canchones (138 ng g⁻¹) and Humberstone (308 ng g⁻¹). Some industries that produce fertilizers in Chile are located in regions XV, I and II (Calderón et al. 2014; Urbansky et al. 2001). Soils from central (n : 7) and southern (n : 5) regions contained perchlorate levels lower than unfertilized soils from northern Chile (Calderón et al. 2014). In general, the perchlorate levels in Chilean soils were lower than those reported in northern (0.001–216 mg kg⁻¹) and southern China (0.001–25.8 mg kg⁻¹) and Bolivian playa crust (500 mg kg⁻¹) (Gan et al. 2014; Kumarathilaka et al. 2016; Rao et al. 2007).

Table 1 Perchlorate concentration in soil (ng g⁻¹ DW)

Region	Area	Min (ng g ⁻¹)	Max (ng g ⁻¹)	Detection frequency
XV	North	2.0	113.5	3/3
I		7.2	307.8	3/3
III		0.3	311	9/9
IV		N.D.	5.9	1/2
Metropolitan	Central	N.D.	8.4	3/7
IX	South	N.D.	12	3/5

Concentration in fertilizers

The measured concentrations of perchlorate (100% detected) in fertilizers are shown in Table 2. Elevated concentrations of perchlorate were found in urea (0.99 mg kg⁻¹) and triple superphosphate (1.21 mg kg⁻¹). Similar patterns were observed in nitrogenous fertilizers such as caliche and calcium nitrate of 1.47 mg kg⁻¹ and 1.05 mg kg⁻¹, respectively. In general, Chilean nitrogenous fertilizers contain levels lower than the international standard of 50 mg kg⁻¹ (SQM 2016). In previous studies, in 45 and 21 different types of fertilizers perchlorate was detected only in sodium nitrate from Chile (Urbansky et al. 2001; Hunter 2001). Interestingly, the highest concentrations of perchlorate were found in non-nitrogenous fertilizers such as K₂SO₄ (4.63 mg kg⁻¹), MgSO₄ × 7H₂O (3.05 mg kg⁻¹) and H₃BO₃ (2.99 mg kg⁻¹). Our results are the first evidence of the presence of perchlorate in non-nitrogenous fertilizers.

Concentration in drinking water

Concentrations of perchlorate in drinking water samples collected from different regions are presented in Fig. 1. The median concentrations of perchlorate were 2.9 (northern), 4.5 (central) and 6.0 ng mL⁻¹

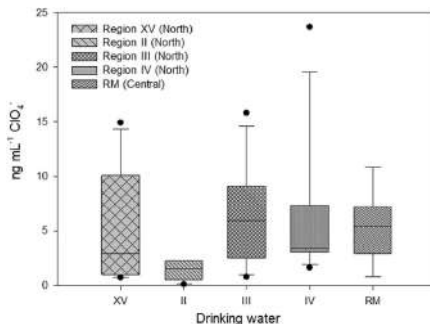


Fig. 1 Perchlorate concentrations in drinking water from different regions of Chile

(southern). Perchlorate was detected in 34 drinking water samples (97%) from the northern zone and 6 samples contained levels higher than 10 ng mL⁻¹. In contrast, perchlorate concentrations in drinking water were lower than the US drinking water contaminant limit (DWEL: 25 µg L⁻¹; EPA 2018) and guideline value suggested in France (15 µg L⁻¹; ANSES 2014). However, our results were higher than those reported in Kuwait 0.5 ng mL⁻¹ (Alomirah et al. 2016), Korea 0.11 µg L⁻¹ (Lee et al. 2012; Her et al. 2011), India 0.1 µg L⁻¹ (Kannan et al. 2009) and China 2.20 µg L⁻¹ (Gan et al. 2015; Wu et al. 2010).

Table 2 Perchlorate level fertilizers from Chile

Fertilizer class	Specific fertilizer	Perchlorate levels (mg kg ⁻¹)
Chilean nitrogenous fertilizers	Sodium nitrate	1.47
	Calcium nitrate	1.05
Non-nitrogenous fertilizers	Magnesium sulfate	3.05
	Potassium sulfate	4.63
	Boric acid	2.99
	Urea	0.99
Other fertilizers	Superphosphate	1.21

Previous studies in the USA reported peak concentration of perchlorate in Los Angeles (159 ug L^{-1}), San Bernardino (820 ug L^{-1}) and Sacramento (400 ug L^{-1}) (CDDW 2017). Additionally, Steinmaus (2016) evaluated the presence of perchlorate in the US residences ($n = 3262$) and concluded that 83% of the samples contain an average of $1.16 \text{ } \mu\text{g L}^{-1}$, which is ten times less than that in our study (maximum value).

Concentration in surface water and groundwater

A total of 11 surface and groundwater samples contained perchlorate concentrations ranging from 0.8 to 15.9 ng mL^{-1} . In region XV ($n = 6$), all the groundwater samples contained perchlorate (maximum: 15.9 ng mL^{-1}). Our results were higher than those reported in India and China (Kannan et al. 2009; Wu et al. 2010; Anupama et al. 2012). The perchlorate concentrations in all surface water (median 1.8 ng mL^{-1}) were ten times lower than groundwater samples (median 12.1 ng mL^{-1}). In general, our results (median of 1.8 ng mL^{-1}) were lower than in China (2.82 ng mL^{-1}), but higher than in India (0.05 ng mL^{-1}) (Kannan et al. 2009; Wu et al. 2010; Anupama et al. 2012). Perchlorate levels in rivers from regions XV (2.5 ng mL^{-1}) and II (4.9 ng mL^{-1}) were lower than reported for samples from Japan and Korea (Kosaka et al. 2007, Quinones et al. 2007). Interestingly, our results were higher than in the Colorado River ($5\text{--}9 \text{ ug L}^{-1}$) and Great Lakes ($0.05\text{--}0.13 \text{ ug L}^{-1}$), but lower than in San Bernardino ($11\text{--}221 \text{ ug L}^{-1}$) in the USA (CDDW 2017). The sources of perchlorate in drinking water, surface water and groundwater can be associated with natural sources (Calderon et al. 2014).

Concentrations in vegetables and fruits

The contents of perchlorate in vegetables are shown in Supplementary Material (Tables S1 and S2). In our study, the highest perchlorate levels were primarily contributed by leafy vegetables (Fig. 2). The mean perchlorate concentration in vegetables (T and N.T.) was higher than in fruits. High perchlorate levels were found in vegetables (N.T.): cabbage (15.9 ng g^{-1}), lettuce var. cos (11.3 ng g^{-1}), lettuce var. endive (6.3 ng g^{-1}) and chard (3.8 ng g^{-1}). Chard produced in region II (41.8 ng g^{-1}) was ten times higher than

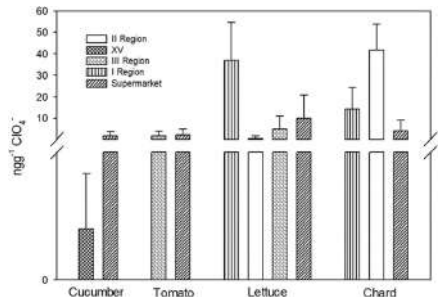


Fig. 2 Concentration of perchlorate in vegetables collected from Chile

chard from supermarket (4.2 ng g^{-1}). Our previous study found high perchlorate levels in soils from northern Chile, which may partially explain the high concentrations in leafy vegetables (N.T.). Interestingly, perchlorate levels in lettuce from region I (36.1 ng g^{-1}) were three times higher than those in lettuce from supermarket (N.T.). According to previous studies, the perchlorate concentrations in leafy vegetables (N.T.) were higher than those reported previously (USFDA 2004–2005; Wang et al. 2009; Gan et al. 2015; Canadian Food Inspection Agency 2010–2011). Exceptionally, perchlorate concentrations in carrots from region XV (47.0 ng g^{-1}) were higher than in Korea and China (Lee et al. 2012; Gan et al. 2015). Additionally, high concentrations of perchlorate were found in vegetables (N.T.): green cabbage (27.4 ng g^{-1}) and arugula (8.79 ng g^{-1}). Interestingly, celery (107 ng g^{-1}) contained ten times more perchlorate than lettuce from supermarket (Figure S2). In general, the concentrations of perchlorate in leafy vegetables (N.T.: median 8.6 ng g^{-1}) were lower than the international regulations (EFSA 2014).

A median value of 0.68 ng g^{-1} and 0.91 ng g^{-1} was found in fruits (N.T. and T). In general, perchlorate concentrations in fruits (N.T.) were 0.10 ng g^{-1} (peach) and 3.24 ng g^{-1} (banana). The perchlorate concentrations in fruits from supermarket were: avocados (0.44 ng g^{-1}), oranges (3.19 ng g^{-1}), grapes (1.71 ng g^{-1}), watermelon (0.48 ng g^{-1}) and honeydew melon (0.91 ng g^{-1}). The perchlorate levels in Chilean fruits were lower than previous studies (Canadian Food Inspection Agency 2010–2011; English et al. 2011; Gan et al. 2015; Alomirah et al.

2016), with the exception of bananas and oranges (El Aribi et al. 2006). Interestingly, perchlorate concentrations in oranges from supermarkets were five times higher than in oranges (N.T.). Finally, perchlorate levels in cantaloupe were lower than in the USA (28.6 ug kg⁻¹), Guatemala (463 ug kg⁻¹) and Costa Rica (151.6 ug kg⁻¹) (USFDA 2004–2005; El Aribi et al. 2006).

Perchlorate exposure from drinking water, vegetables and fruits

The results of EDI via drinking water and fruits and vegetables stratified by age are shown in Tables 3 and 4, respectively. The EDI from lettuce (T) of region I was almost three times higher than lettuce (N.T.) for all age groups. The EDI of perchlorate from lettuce in region I (0.057–0.074 µg kg⁻¹ bw day⁻¹) was higher than perchlorate exposure calculated for total dietary intake in the USA in 2004 (0.053 µg kg⁻¹ bw day⁻¹; United States Food and Drug Administration [USFDA 2004a, b]) and 15 times higher than the perchlorate exposure estimated only via intake of lettuce (0.003 µg kg⁻¹) (USFDA 2004). For lettuce from supermarket, the EDI (0.018–0.023 µg kg⁻¹ - bw day⁻¹) was higher than the daily intake for lettuce in the USA (0.003 µg kg⁻¹ bw day⁻¹) (USFDA 2004). Additionally, the EDI of perchlorate from chard (N.T.) was almost ten times higher than chard from supermarket for all age groups and lower than in lettuce and spinach in the USA (USFDA 2004). The

EDI for chard (T) (0.005–0.006 µg kg⁻¹ bw day⁻¹) was higher than those calculated for lettuce and spinach in the USA (USFDA 2004) for all age groups. It is worthwhile to note that our results show that inhabitants of northern Chile were exposed to higher-dose perchlorate via intake of leafy vegetables than inhabitants from other regions of Chile. The EDI in leafy vegetables from supermarket (0.019–0.023 µg kg⁻¹ bw day⁻¹) was lower than those reported from Kuwait (total: 0.062 µg kg⁻¹ - bw day⁻¹), but similar to those reported from Canada (0.024 µg kg⁻¹ bw day⁻¹) (Alomirah et al. 2016; Wang et al. 2009). Perchlorate exposure (non-leafy vegetables and fruits) was lower than those reported in other studies (USFDA 2004; Alomirah et al. 2016; Gan et al. 2015). The highest intakes occurred in leafy vegetables > fruits > non-leafy vegetables for all age groups. The EDI values of perchlorate via drinking water for all age groups were lower than the reference dose (RfD = 7000 ng kg⁻¹ bw day⁻¹), but higher than those in Kuwait (total), India (total) and China (adult age group) (Alomirah et al. 2016; Kannan et al. 2009; Wu et al. 2010).

Conclusion

The results obtained in our study indicate widespread human exposure to perchlorate by the Chilean population. High perchlorate concentrations in agricultural soil (regions XV and III) compared with unfertilized

Table 3 Estimated daily intake (EDI) of perchlorate (ng kg⁻¹ bw day⁻¹) via ingestion of vegetables and fruits in Chile

Age group	Male 15–24	Female	Male 25–44	Female	Male 45–64	Female	Male > 65	Female
Supermarket samples								
*Leafy vegetables	21.6	25.0	19.4	22.5	19.4	21.9	20.8	23.3
*Non-leafy vegetables	1.27	1.48	1.14	1.33	1.14	1.29	1.23	1.38
*Fruits	1.59	1.85	1.43	1.66	1.43	1.62	1.54	1.72
Surveillance samples								
*Leafy vegetables	7.2	8.4	6.5	7.5	6.5	7.3	7.0	7.8
*Non-leafy vegetables	1.1	1.3	1.0	1.2	1.0	1.1	1.1	1.2
*Fruits	2.1	2.5	1.9	2.2	1.9	2.2	2.1	2.3

*Supermarket (median): leafy vegetables (8.52 ng g⁻¹), non-leafy vegetables (2.01 ng g⁻¹) and fruits (0.68 ng g⁻¹)

*Monitoring (median): leafy vegetables (2.85 ng g⁻¹), non-leafy vegetables (1.76 ng g⁻¹) and fruits (0.91 ng g⁻¹)

RfD (perchlorate): 7000 ng kg⁻¹ bw day⁻¹

Table 4 Estimated daily intake (EDI) of perchlorate ($\text{ng kg}^{-1} \text{ bw day}^{-1}$) via ingestion of drinking water in Chile

	Northern	Central	Southern	Serena* Northern	Copiapo*	Arica*
Infants (< 1)	182	283	378	1491	994	761
Children (1–10)	152	2377	315	1246	831	636
Teens (11–19)	44	68	90	356	238	182
Adults (20–64)	48	75	100	396	264	202
Adults (> 65)	58	91	121	477	318	244

RfD (perchlorate): $7000 \text{ ng kg}^{-1} \text{ bw day}^{-1}$

*Serena (23.7 ng mL^{-1}), Copiapo (15.8 ng mL^{-1}) and Arica (12.1 ng mL^{-1})

soils suggest that the use of fertilizers is a significant source of perchlorate to the environment. We found that nitrogenous fertilizers (3.1 mg kg^{-1}) contained the highest levels of perchlorate compared with non-nitrogenous fertilizers (1.3 mg kg^{-1}). Drinking water from Serena (region IV) and Copiapo (region III) showed higher concentrations of perchlorate (23.7 ng mL^{-1} and 15.8 ng mL^{-1}) compared with the guideline value suggested in France ($15 \mu\text{g L}^{-1}$). The EDI values were below the respective RfD of $7000 \text{ ng kg}^{-1} \text{ bw day}^{-1}$. Our findings provide important information about perchlorate levels in soils, water sources, fertilizers, fruits and vegetables in Chile, which will be helpful in establishing appropriate regulatory guidelines.

Acknowledgements This work was funded by the Project Fondecyt 11160581, Conicyt, Chile.

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Perchlorate Levels in Soil and Waters from the Atacama Desert

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Received: 2 May 2013 / Accepted: 8 October 2013 / Published online: 29 October 2013
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Abstract Perchlorate is an anion that originates as a contaminant in ground and surface waters. The presence of perchlorate in soil and water samples from northern Chile (Atacama Desert) was investigated by ion chromatography–electrospray mass spectrometry. Results indicated that perchlorate was found in five of seven soils (cultivated and uncultivated) ranging from 290 ± 1 to $2,565 \pm 2$ $\mu\text{g}/\text{kg}$. The greatest concentration of perchlorate was detected in Humberstone soil ($2,565 \pm 2$ $\mu\text{g}/\text{kg}$) associated with nitrate deposits. Perchlorate levels in Chilean soils are greater than those reported for uncultivated soils in the United States. Perchlorate was also found in superficial running water ranging from

744 ± 0.01 to $1,480 \pm 0.02$ $\mu\text{g}/\text{L}$. Perchlorate water concentration is 30–60 times greater than levels established by the United States Environmental Protection Agency (24.5 $\mu\text{g}/\text{L}$) for drinking.

The perchlorate anion is considered a strong oxidant, but its kinetic barrier makes the reduction of Cl^{7+} to Cl^- extremely slow due to its high activation energy. Under natural conditions perchlorate is stable; it is not reduced by common agents; it does not precipitate in the presence of cations; and it is widely used in laboratory studies as counterion and in the synthesis of organometallic compounds (Urbansky 2002). Its main sources are sodium, potassium, lithium, and magnesium salts and other commercial forms such as perchloric acid. Its most largely marketed compound is ammonium perchlorate, which represents approximately 90 % of all perchlorate manufactured at the world level. Perchlorate (ClO_4^-) is used as an oxidizer and in explosive areas, such as rocket propellants (Urbansky and Schock 1999) and the manufacture of fireworks and arms.

Because of its high stability, perchlorate can remain in the soil and in running and groundwater for years. This mobility and persistence can represent a potential threat to ecological receptors and to the complete ecosystem. Recent studies have reported that perchlorate has been detected in drinking water, groundwater, and surface water in many countries, such as the United States (Parker et al. 2008), Korea (Quinones et al. 2007), Japan (Kosaka et al. 2007), China (Wu et al. 2010), and India (Kannan et al. 2009). Increased interest in perchlorate detection is derived from the adverse health effects associated with its exposure. One potential adverse effect of perchlorate on human health is that it can interfere with hormone production by competing

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with the uptake of iodide by the thyroid through the sodium (Na^+)/iodide (I^-) symporter (NIS) molecule. NIS is the protein responsible for transporting iodide into the thyroid gland for the production of two key thyroid hormones, triiodothyronine [T3] and thyroxine [T4] (Charnley 2008), which that are essential for normal development of the body (Charnley 2008). Thyroid hormones regulate several critical functions in the body, including oxygen consumption, metabolism, skeletal growth, and brain development. Perchlorate contamination poses a special danger to nursing mothers and infants because perchlorate can be passed from mother to infant through breast milk, severely affecting the development of the thyroid's function and causing physical and mental disabilities, including mental retardation, impaired hearing, and language deficits. Significant and/or sustained decreases in thyroid hormone levels could affect the development of the fetus. If the maternal thyroid is not able to maintain adequate levels of thyroid hormones, especially during the first trimester, irreversible alterations in fetal neurological development could occur. Sufficient thyroid hormone (especially T4) is required during fetal development of the central nervous system. T4 is solely supplied by the mother before the fetal thyroid gland becomes functional at the end of the first trimester. After the first trimester, the fetal thyroid is functional and can maintain its own hormone levels. However, some studies have suggested that T4 supplied by the mother throughout pregnancy has an overall protective effect from fetal neurological impairment (Morreale de Escobar et al. 2000).

Environmental perchlorate contamination was first detected in wells in California as early as 1985. In the United States, it is estimated that perchlorate is a water source contaminant in at least 26 of the states. However, in 2005 the National Resource Council recommended that the maximum daily intake of perchlorate should not exceed $0.7 \mu\text{g}/\text{kg}$ (National Research Council 2005), which is the equivalent of $24.5 \mu\text{g}/\text{L}$ for a 70-kg adult male with a daily water consumption of 2 L. The state of California, in contrast, has mandated $18 \mu\text{g}/\text{L}$ as the level at which remediation is required (Wirt et al. 1998).

Among the natural resources existing in Chile, some of the most important are caliche deposits, which are rich in sodium nitrate (NaNO_3). Caliche is extracted and leached to obtain sodium nitrate, which is refined to produce commercial fertilizers. The Atacama Desert nitrate deposits are widely known as natural perchlorate reservoirs whose origin has not been elucidated (Ericksen 1981). More recently, it has also been reported that perchlorate is naturally formed in atmospheric processes (Orris et al. 2003; Dasgupta et al. 2006; Plummer et al. 2006; Rajagopalan et al. 2006). The marked increase in frequency of perchlorate detection in recent years can be largely

ascribed to improvements in analytical methods and instrumentation. Since then, perchlorate has been found in environmental and drinking waters in many states of the United States (Massachusetts Department of Environmental Protection 2005). Perchlorate has also been detected in certain food crops (Seyfferth and Parker 2006; Sanchez et al. 2005; Yu et al. 2004; Tefera et al. 2007), milk (Kirk et al. 2003; Kirk et al. 2005), fish (Theodorakis et al. 2006), waters (Lamb et al. 2006), soils (Macmillan et al. 2006), and fertilizers (Tian et al. 2005). The accumulation of perchlorate in crops whose leaves are consumed is a present concern. The objective of this study was to conduct a survey of the occurrence of perchlorate in cultivated and uncultivated soils and in running waters used in farming in the north of Chile.

Materials and Methods

Sampling

This study a zone, located from $19^{\circ}45'$ to $20^{\circ}00'S$ and from $68^{\circ}25'W$ to the Pacific ocean, was defined as the testing area for the seven soils considered, which include a number of agriculturally significant soils. The soils came from Alto Hospicio, Canchones, Humberstone, Matilla Lama, Pica, Pozo Almonte, and Tirana (Table 1). Canchones and Pica soils are used for vegetables cultivation; the others are not agricultural soils. The soil samples were sifted in the field to pass a 2-mm sieve, stored at 4°C , and dried overnight at 110°C . The water samples were collected at Canchones and Pica (Table 2), both used for the irrigation of food crops. The ClO_4^- quantification in soil and water samples was performed in triplicate ($n = 3$).

Table 1 Geographical location of soil samples

Sample	Location
Alto Hospicio	$20^{\circ}18'39.60''S-70^{\circ}06'49.30''O$
Humberstone	$20^{\circ}12'36.76''S-69^{\circ}48'21.32''O$
La Tirana	$20^{\circ}21'00.22''S-69^{\circ}39'59.65''O$
Canchones	$20^{\circ}26'28.52''S-69^{\circ}32'06.80''O$
Matilla lama	$20^{\circ}31'19.80''S-69^{\circ}21'53.60''O$
Pica	$20^{\circ}28'30.21''S-69^{\circ}18'39.17''O$
Pozo Almonte	$20^{\circ}39'31.97''S-68^{\circ}38'45.61''O$

Table 2 Geographical location of water samples

Sample	Location
Canchones	$20^{\circ}25'10.31''S-69^{\circ}32'19.31''O$
Pica	$20^{\circ}30'34.70''S-69^{\circ}20'23.22''O$

Reagents

All solutions were prepared using 18 M Ω cm water or better. Perchlorate standards ranging from 0.03 to 10 μ g/L were prepared by dilution of a 1,000 mg/L perchlorate standard solution (SPEX; CertiPrep, Metuchen, NJ, USA).

Internal Standard

The internal standard (ISTD) used in this study was Cl¹⁸O₄[−] with ion masses of 107 and 109 (Dionex, Sunnyvale, CA, USA). SIM 107 was used for quantification. This ISTD is chemically and chromatographically similar to SIM 99 perchlorate (³⁵Cl¹⁶O₄[−]).

Analytical Details

All perchlorate analyses were performed using ion chromatography–electrospray ionization–mass spectrometry (IC–ESI–MS) (Dionex Corp. 2002a). Chromatographic analysis was performed on a DX500 ion chromatograph equipped with an AS50 autosampler and a GP50 pump ran in isocratic mode using 45 mM NaOH eluent at a flow rate of 0.3 mL/min. An injection loop of 100 μ L was used for all analyses. Background conductivity was maintained below 1 μ S/cm by means of an ASRS Ultra II (2 mm) suppressor in the external water mode and an ATC–HC trap column. Chromatographic separation was achieved using an IonPac AS16 (2 \times 250 mm) analytical column equipped with an IonPac AG16 (2 \times 50 mm) guard column. Flow from the IC was directed into a Finnigan Surveyor MSQ Plus single–quadrupole MS (Thermo Electron Corp., Waltham, MA, USA). The MS was equipped with an AXP–MS auxiliary pump, pumping 50:50 acetonitrile/water at a flow rate of 0.3 mL/min. Matrix diversion was used to divert all of the IC to waste for the first 9 min of each run, and then the IC flow joined the acetonitrile/water so that a total flow rate of 0.6 mL/min was provided to the MS for each analysis. The retention time of perchlorate was approximately 13 min under these conditions. Flow to the MS was nebulized through an ESI source using ultra high–purity nitrogen gas at a pressure of 550 kPa. The electro–spray capillary was held at 450 $^{\circ}$ C with a needle voltage of 3.5 kV. The entrance cone was held at a voltage of 70 V. Negative ion monitoring of m/z 99 (\pm 0.5), m/z 101 (\pm 0.5), and m/z 107 (\pm 0.5) (corresponding to ³⁵Cl¹⁶O₄[−], ³⁷Cl¹⁶O₄[−], and ³⁵Cl¹⁸O₄[−], respectively) was used with a dwell time of 0.30 s/ion mass. SIM 99 was used for calibration of standards exclusively, and, if preliminary results indicated the need, Cl¹⁸O₄[−] was used as the ISTD at a concentration of 1 μ g/L in all standards and samples. Identification of perchlorate in the unknowns was confirmed by the retention times of unknown peaks with those

of the standards as well as the 3:1 SIM 99 to SIM 101 ratio. Chromeleon version 6.6 (Dionex Corp. 2002a) was used to control the instrumentation and to quantify perchlorate.

Quantification of NO₃[−], SO₄^{2−}, and Cl[−]

The determination of NO₃[−], SO₄^{2−} and Cl[−] was made in an Ion DIONEX ICS 3000 (Dionex Corp. 2002b) ion chromatography system coupled with a conductivity detector and an ASRS (4 mm) conductivity suppressor. An AS–11 high–capacity column with a 30–mM NaOH mobile phase was used for the analysis (Dionex Corp. 2002b).

Electrical Conductivity and pH

The electrical conductivity (EC) of each soil was determined on the saturation paste extract. The saturation paste was allowed to stand for 24 h, filtered under vacuum, and the EC then measured on the extract. The pH of the soil was measured in a 1:2.5 water–and–soil suspension. Approximately 20 g of soil were weighed; 50 mL of double distilled water were added; the mixture was stirred for 30 min and allowed to stand for the same time; finally, the pH was measured in the supernatant (Richards 1954). In the water samples, pH and EC were determined directly in the sample after filtering it through a 0.45– μ m Millipore membrane.

Organic Carbon

Determination of easily oxidizable organic carbon (OC) in soil samples was performed according to the method of Walkley–Black (Walkley and Black 1934), which uses approximately 1.0 g of soil sample to which 10 mL of 1 M K₂Cr₂O₇ and 20 mL of concentrated H₂SO₄ are added and the mixture allowed to stand for 30 min in a fume hood. The excess K₂Cr₂O₇ was titrated with 1.0 M FeSO₄ in an automatic titrator using a combined Pt–calomel electrode and setting the end point of the titration at a potential of 630 mV (Richards 1954).

Results and Discussion

Characterization of Soils and Waters

Each of the sectors studied corresponds to interior settlements in the province of Iquique in the First Region of Chile (Table 1). Of the seven soils considered in the study, two (Canchones and Pica) are used for agricultural production of fruits and vegetables that are massively consumption in the northern part of the country. The products include citrus fruits, grapes, tangerines, and guava, among others. The other soils correspond to desert sectors located

in the Atacama Desert. According to their general characterization, the soils have alkaline pH in the range of 7.2–8.5 with EC between 1.2 and 53 dS/m, OC content <1.7 % (Table 3), and high soluble salt content (Table 4), which is characteristic of arid soils. The chemical composition of these soils is quite different from that of soils of volcanic origin from the south of Chile, which have slightly acid pH (5.0–6.0), OC contents that vary between 5.0 and 9.5 % and colloids with variable charge that give greater chemical reactivity to the soil. The water samples correspond to watercourses that cross the settlements of Canchones and Pica (Table 2) and are used mainly for irrigation of plant species and potentially for human consumption. The general characterization of the water samples shows a pH equal to 7.5 and an EC < 0.87 dS/m (Table 5), which is slightly greater than the EC established in the Chilean standard for irrigation water (0.75 dS/m).

Concentration of ClO_4^- in Soils

The results show that of a total of seven soils studied, only five present detectable and quantifiable ClO_4^- levels in concentration ranges of 290 ± 1 to $2,565 \pm 2$ $\mu\text{g}/\text{kg}$ (Table 4). The other two soils have levels <0.04 mg/kg, which is the limit of detection of the method. The sectors that were studied are located in areas with a prevalence of caliche deposits that contain significant amounts of ClO_4^- (1,500–800 mg/kg) (Michalski et al. 2004). The nitrate deposits in the north of Chile are located within the Atacama Desert, a zone known as one of the most arid in the world with a precipitation regime on the order of 2 mm/rain/year. Recent studies have shown scientific evidence that the ClO_4^- found in the Atacama Desert was formed through processes having an atmospheric origin (Dasgupta et al. 2006; Ericksen et al. 1988). At present, the development of new and better analytical methods have decreased the limits of detection of ClO_4^- , reaching the trace level and therefore increasing the number of reports of ClO_4^- in different environmental matrices, thus making it possible to quantify the existence of ClO_4^- in extensive arid and semiarid zones of the United States that are far from anthropogenic sources

(Orris et al. 2003; Rajagopalan et al. 2006; Rao et al. 2007). These detections confirm that the presence of ClO_4^- is of natural origin and that its accumulation on the surface of the soils has taken place during thousands of years. Comparing the ClO_4^- concentrations measured in the soils studied here (290 ± 1 to $2,565 \pm 2$ $\mu\text{g}/\text{kg}$) with those reported in the United States (agricultural soils), in Chile they are much greater than those reported in the United States (1.6–13 $\mu\text{g}/\text{kg}$) (Rao et al. 2007). Regarding the agricultural soil from Canchones ($465 \mu\text{g}/\text{kg} \pm 2$), its perchlorate level is approximately 36 times the highest value reported in the United State (13 $\mu\text{g}/\text{kg}$).

The existence of these kinds of ClO_4^- reservoirs in arid zones can be considered potentially nonhazardous because since there is no hydrological transport, the ClO_4^- would not be mobilized. However, a different situation occurs when these reservoirs are located in zones used for agricultural production. Considering the agricultural soils, only in Canchones was ClO_4^- detected (465 ± 2 $\mu\text{g}/\text{kg}$). The presence of ClO_4^- at significant levels in agricultural soils may result in potentially healthy risky situations considering that ClO_4^- can be absorbed by consumable vegetables. Farming activity involves the use of soil for the production of various plant species, either leaves or fruits, and the use of large volumes of water to satisfy the requirements of each species. The ClO_4^- anion is known to be highly soluble and mobile in the environment, and this can cause it to be mobilized by irrigation water to shallow zones, thus making it bioavailable to the plant species or allowing it to leach through the soil profile and reach the groundwater. The vegetables and fruits harvested in the Canchones and Pica sectors are distributed mainly in the neighboring settlements and in the city of Iquique. The potential transfer of ClO_4^- to plant species of massive consumption that are cultivated in those sectors represents a potential risk to the health of the people who consume those kinds of food. Recent studies have shown that perchlorate has accumulated in various plant species in the United States (Sanchez et al. 2005b, 2006, 2007, 2009; Seyfferth and Parker 2007) at lower concentrations than the reference dose (RfD). The interaction between perchlorate and plants is not fully understood. In northern Chile, the cultivation and consumption of different lettuce (*Lactuca sativa*) varieties is significant due to their fast growth and low cost. However, they have not been studied.

Table 3 Soil sample characterization

Sample	pH	EC (dS/m)	OC (wt%)
Alto Hospicio	7.9 \pm 0.1	1.7 \pm 0.1	0.42 \pm 0.06
Canchones	7.8 \pm 0.2	5.2 \pm 0.1	1.20 \pm 0.50
Humberstone	8.1 \pm 0.2	53.0 \pm 2.0	0.12 \pm 0.09
Matilla lama	8.5 \pm 0.1	4.2 \pm 0.1	0.15 \pm 0.07
Pica	7.6 \pm 0.2	1.2 \pm 0.2	1.10 \pm 0.50
Pozo Almonte	7.2 \pm 0.1	3.1 \pm 0.2	0.14 \pm 0.04
Tirana	8.0 \pm 0.1	15.0 \pm 1.0	1.70 \pm 0.60

Quantification of ClO_4^- in Water

Two types of surface waters from the Canchones and Pica settlements were studied. Both settlements use these types of water for irrigation of their cultures and probably for direct consumption. According to the Chilean 2012 census, the Pica and Canchones sectors have a population of

Table 4 Anion content of soil samples

Sample	NO ₃ ⁻ (mg/g)	SO ₄ ²⁻ (mg/g)	Cl ⁻ (mg/g)	ClO ₄ ⁻ (μg/kg)
Alto Hospicio	0.04 ± 0.005	0.83 ± 0.02	0.63 ± 0.03	ND
Canchones	1.24 ± 0.06	4.07 ± 0.5	1.67 ± 0.5	465 ± 2
Humberstone	69.7 ± 3	38.4 ± 3	57.7 ± 4	2,565 ± 2
Matilla lama	ND	0.83 ± 0.1	0.15 ± 0.02	291 ± 0.5
Pica	0.76 ± 0.05	3.75 ± 0.4	0.20 ± 0.02	ND
Pozo Almonte	0.74 ± 0.05	13.6 ± 1	2.37 ± 0.3	290 ± 1
Tirana	0.72 ± 0.03	7.46 ± 0.6	7.03 ± 0.4	600 ± 0.9

ND concentration in the extract is lower than the method detection limit (40 μg/kg)

Table 5 Water sample characterization

Sample	pH	EC (dS/m)	Ca* (mg/L)	Mg* (mg/L)	K* (mg/L)	Na* (mg/L)	ClO ₄ ⁻ (mg/L)
Pica	7.5 ± 0.09	0.24 ± 0.02	2.6	0.11	5.1	5.9	1.48 ± 0.02
Canchones	7.5 ± 0.1	0.87 ± 0.03	3.0	0.34	15	11	0.74 ± 0.01

* SD < 0.05

approximately 4,194 and 11,519 inhabitants (for Pozo Almonte). Thus, approximately 16,000 people are potentially consumers of this superficial water as drinking and/or irrigation water. The general characterization of the waters in terms of pH, Conductivity electric, and exchange bases is listed in Table 5. The results show that the two water samples from Pica and Canchones contain 1,480 and 740 μg/L of ClO₄⁻, respectively (Table 5). To assess the risk associated with the ClO₄⁻ levels found in these waters, they can be compared with other reports on the presence of ClO₄⁻ in the world. One of the first studies performed in the United States was that of the Colorado River, which is used for the irrigation of crops and as a source of potable water by >20 million people. The presence of ClO₄⁻ in this water source has an essentially anthropogenic origin, and the reported levels are on the order of 2–9 μg/L (Sanchez et al. 2005). These values are lower than the reference values proposed by the National Academy of Sciences (NAS) of 24.5 μg/L and accepted by the United States Environmental Protection Agency (USEPA). Meanwhile, in Chile, the levels measured in the irrigation waters whose origin is essentially natural in the Canchones and Pica sectors are 30- to 60-fold greater than the levels that would lead to exceeding the RfD if a 70-kg person consumed 2 L/day. In contrast, in Japan (Asami et al. 2009), the water of the Tone river contains ClO₄⁻ levels (10–20 μg/L) that are greater than those of the Colorado River and much lower than those reported in this study. Various studies have reported the existence of ClO₄⁻ in water for massive consumption on the order of micrograms per litre in countries such as Canada (Backus et al. 2005), India (Kannan et al. 2009), and Korea (Quinones et al. 2007). A major problem arises when the ClO₄⁻ present in

water sources is transferred to plants that are irrigated with these waters. It has been shown that ClO₄⁻ accumulates in plants, fruits, and forage crops (Jackson et al. 2005) on the order of micrograms per kilogram.

In Chile, no studies have evaluated the transfer potential of ClO₄⁻ to crops irrigated with waters that contain high concentrations of ClO₄⁻. Based on these comparisons, it is highly probable that crops existing in the areas of Canchones and Pica contain much greater ClO₄⁻ levels than those reported in the United States. However, it must be considered that depending of the volume of water used for crop irrigation, it is also probable that part of the ClO₄⁻ may seep through the soil profile and reach the groundwater (Gal et al. 2009). The waters of Canchones and Pica are also used to a lower extent for daily consumption by the people who live in those sectors. In 2005, the USEPA together with the NAS established a RfD for ClO₄⁻ of 0.7 μg/kg/day, which is equivalent to 24.5 μg/L in drinking water. Comparing the RfD established by the USEPA as a preventive level for ClO₄⁻, the values found in the water for consumption of Canchones and Pica yield a ClO₄⁻ dose that is being potentially ingested by habitants of 21.1 and 40.3 μg/kg/day, respectively. This calculation takes into account the same parameters used by the USEPA for the RfD, *i.e.*, for an adult weighing 70 kg with a minimum consumption of 2 L of water/day. Values calculated for the ingestion of ClO₄⁻ in the water of both settlements exceed that standard by approximately 30- and 60-fold, respectively. This is of vital importance because the RfD corresponds to ClO₄⁻ concentrations present in the body at which it is not possible to detect any adverse effect. (Blount et al. 2007) Toxicological studies made in Israel indicate

that there is no significant evidence that ClO_4^- causes adverse effects in persons who have been exposed to ClO_4^- concentrations $<340 \mu\text{g/L}$ (Amitai et al. 2007). Preliminary epidemiological studies performed in northern Chile on pregnant women showed no increment of TSH levels or decrease of T4 hormone when they were exposed to drinking water with ClO_4^- levels ranging from 0.5 to 114 mg/L. No adverse effect was also observed in newborn babies (Crump et al. 2000). In a similar study (Tellez et al. 2005), no clinical evidence to confirm that ClO_4^- inhibits thyroid function in newborn and school-age child was observed when they were exposed to drinking water with perchlorate levels ranging from 100 to 120 $\mu\text{g/L}$. However, the situation has changed; at present, the ClO_4^- concentrations in the water of Canchones and Pica are significant greater than those reported in the previous studies.

Conclusion

The situation in the studied locations is potentially complex because the ClO_4^- concentrations determined in the waters of Canchones and Pica are between 6- and 12-fold greater than the levels that were used in toxicological studies (100–120 $\mu\text{g/L}$) in the north of Chile. Considering the data generated in the present work, it is quite probable that there may currently be potential cases in which ClO_4^- has considerable incidence in the number of persons who present with or who are developing thyroid function-related diseases. Therefore, it is necessary to perform clinical studies to assess the real effects that ClO_4^- may be having in Canchones, Pica, and surrounding areas. Those studies should consider not only the ingestion of ClO_4^- through water consumed daily but also that ingested from plants cultivated in those areas that may contain high levels of ClO_4^- in their edible parts. The natural presence of ClO_4^- at concentrations of 744 ± 0.01 to $1,480 \pm 0.02 \mu\text{g/L}$ in irrigation waters and 290 ± 1 to $2,565 \pm 2 \mu\text{g/kg}$ in soils in the interior sectors of the north of Chile used for vegetables cultivations (Canchones y Pica) represent a potential risk to human health because the ClO_4^- can be incorporated through the ingestion of water or plants grown in those areas.

Acknowledgments The authors acknowledge with thanks the financial support of FONDECYT through Project 1070116, CED-ENNA, and the scholarship program of the Universidad de Santiago de Chile. The assistance of Stephan Hlohowskyj for the analytical measurements is gratefully acknowledged.

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Sources and fates of perchlorate in soils in Chile: A case study of perchlorate dynamics in soil-crop systems using lettuce (*Lactuca sativa*) fields. [☆]



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ARTICLE INFO

Article history:

Received 26 November 2019

Received in revised form

24 April 2020

Accepted 25 April 2020

Available online 28 April 2020

Keywords:

Perchlorate

Fertilizers

Soil contamination

Food safety

ABSTRACT

Perchlorate occurs naturally in the environment in deposits of nitrate and can be formed in the atmosphere and precipitate into soil. However, little is known about the occurrence and levels of perchlorate in soils and fertilizers in Chile and its impacts on agricultural systems and food safety. In this study, concentrations of perchlorate were determined in 101 surface soils and 17 fertilizers [nitrogenous ($n = 8$), nitrogen-phosphorous-potassium (NPK; $n = 3$), phosphate ($n = 2$) and non-nitrogenous ($n = 4$)] collected across Chile from 2017 to 2018. Our results show that perchlorate was detected mainly in agricultural soils (mean: 0.32 ng g^{-1}), grassland rotation sites (0.41 ng g^{-1}) and urban locations (0.38 ng g^{-1}). Interestingly, elevated concentrations of perchlorate (9.66 and 54.0 ng g^{-1}) were found in agricultural soils. All fertilizers contained perchlorate: nitrogenous fertilizers (mean: 32.6 mg kg^{-1}), NPK (mean: 12.6 mg kg^{-1}), non-nitrogenous fertilizers (mean: 10.2 mg kg^{-1}) and phosphates (mean: 11.5 mg kg^{-1}). Only one type of nitrogenous fertilizer (KNO_3 ; 95.3 mg kg^{-1}) exceeded the international regulation limit (50 mg kg^{-1}). For two agronomic practices, the content of perchlorate in lettuce increased as the fertilizer application rate increased, with fertigation promoting a more significant accumulation. However, the concentrations generally remained below regulatory values. Our results suggest that fertilizers constitute an important source of perchlorate in soils.

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1. Introduction

Perchlorate is both a synthetic and a naturally occurring chemical of concern, and its prevalence in the environment poses a great risk for both human and the environment (Calderon et al., 2017). Perchlorate has been widely used as a propellant in rocket

fuel, fireworks, and explosives. Due to its wide usage and natural occurrence, perchlorate is inevitably released into the environment and food products (Kumarathilaka et al., 2016). There is concern that perchlorate may represent a health risk. Perchlorate is an endocrine disruptor and has the potential to cause thyroid dysfunction by inhibiting the production of T_3 and T_4 hormones, thereby leading to hypothyroidism and metabolic and neurological problems in vulnerable age groups such as breastfeeding infants (Pleus and Corey, 2018).

According to estimates from the World Health Organization (WHO), the global population will increase to 9.5 billion by 2050 (World Health Organization (WHO), 2015). This implies the need

[☆] This paper has been recommended for acceptance by David O'Connor.

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for higher food production under scenarios of water scarcity, climate change, reduction of arable land and higher rates of fertilizer usage (Chouchane et al., 2018). Fertilizers are an important source of nitrogen, phosphorus and potassium for agricultural systems. Globally, nutrient consumption has increased approximately to 200 million tons (FAO, 2017). However, the application of fertilizers can produce an accumulation of perchlorate into the food chain (Li et al., 2018). Phosphorus is one of the most important macronutrients for plant nutrition. It is estimated that 90% of global phosphorus production is used in agriculture (Gupta et al., 2014). However, phosphate fertilizers are one of the main sources of trace elements (TE) in agricultural soils (Roberts, 2014; Azzi et al., 2017; Li et al., 2018). Nitrogen is another macronutrient with an annual global consumption of 119,418,000 tons, which is higher than for phosphorus (46,648,000 tons) or potassium (34,456,000 tons) (FAO, 2015). Furthermore, the usage rate of NPK fertilizers is estimated to increase nitrogen, phosphate and potassium by 1.5%, 2%, and 2.9%, respectively (El Sharkawi et al., 2018). Nevertheless, studies have reported that only 50% of the nitrogen applied to corn, rice and wheat crops is assimilated, and the rest accumulates in soil or leaches into groundwater (Poffenbarger et al., 2018; Raun and Johnson, 1999). Nitrogenous and potassium fertilizers contain lower levels of TE than do phosphate fertilizers (Chaney, 2012; Yang et al., 2016). However, nitrogenous fertilizers contain contaminants such as perchlorate with toxic potential similar to some TE. Excessive intake of food products containing perchlorate is a matter of public health concern (Jaishankar et al., 2014). Chile has the largest caliche reservoirs in the world, which have been used in the production of nitrogenous fertilizers for decades (Calderón et al., 2014). Compounds such as nitrates, chromates, iodates, sulphates and perchlorates are some of constituents of these reservoirs (Urbansky et al., 2001; Przybyla et al., 2018; Zoeller, 2010; Calderón et al., 2014). In recent decades, the detection of perchlorate in nitrogenous fertilizers has been reported (Susarla et al., 1999; Urbansky et al., 2001; Calderon et al., 2017). Currently, a considerable number of studies have focused on human exposure to perchlorate with an emphasis on sources such as drinking water, fruits, vegetables and other foodstuffs, indicating that the general population is continuously exposed to perchlorate in day-to-day life (Zhang et al., 2018). In this context, the European Community (EC) has adopted provisional perchlorate levels for fertilizers (50 mg kg⁻¹) and for vegetables and fruits to protect consumer health (European Food Safety Authority (EFSA), 2014). However, perchlorate's presence and levels in other commercially marketed fertilizers in the world is not known.

Chile is one of the world's leaders, among 190 countries, in the production and export of fresh and processed fruits and vegetables. Considering the extensive use of fertilizers in agriculture to increase food production, it is necessary to estimate the levels of contaminants such as perchlorate introduced into crop fields and the food chain. Although a few studies have indicated the presence of perchlorate in fertilizers, no detailed information is available concerning the sources and types of fertilizers used in Chile and perchlorate distribution in agricultural soils. The objectives of this study were to: a) measure the levels and the distribution of perchlorate in Chilean soils (MR) and selected fertilizers commonly used in agriculture and b) evaluate the impact of N fertilizer rate and agronomic practices on perchlorate content in field-grown lettuce (*Lactuca sativa*). Generation of new information about perchlorate sources and dynamics in crops of interest is important for national and international agencies to modify current regulations to ensure food safety.

2. Materials and METHODS

2.1. Sample collection

Some of the commonly used commercial fertilizers in Chile were collected (n = 17) at the Agricultural Research Institute (INIA) in Santiago, Chile. Four types of commercial fertilizers include nitrogenous (n = 8), NPK (n = 3), phosphate (n = 2) and non-nitrogenous (n = 4) fertilizers. In this study, all trademarks of fertilizers were removed, and only laboratory assigned codes were used for further discussions (Table S1 [Supporting information]). A total of 101 surface soil samples (0–20 cm) were collected in the metropolitan region (MR) in Santiago during 2017–2018 (Fig. S1). Soil samples were stored in precleaned polypropylene and transported to the laboratory, air-dried, sieved (< 2.0 mm) and stored at 4 °C until analysis. The sample sites were provided by the Servicio Agrícola y Ganadero (SAG) of the government of Chile. The soil samples were collected from agricultural (n = 34), grassland rotation (n = 37), native (n = 5), scrubland (n = 8), urban (n = 11), crop rotation (n = 4) and grassland (n = 2) sites.

2.2. Sample extraction

The method for extraction of perchlorate from the soil, water, fertilizer, and vegetable samples was similar to that previously described, with minor modifications (Calderon et al., 2020).

Briefly, 0.25–0.28 g of fertilizer was extracted with 10 mL of HPLC-Grade water, diluted 1000 times. Afterward, 900 µL of the sample and 50 µL of an internal standard Cl¹⁸O₄ (98%) were purified with an Envi-carb cartridge (500 mg, 6 cc; Waters Corp, Milford, MA, USA) previously activated with 6 mL of HPLC-grade water. Finally, the sample was filtered using a 0.20-µm nylon syringe filter and analyzed by HPLC-MS/MS.

For soils, ~1.0–1.2 g of soil was fortified with 50 µL of an internal standard Cl¹⁸O₄ (98%) and extracted in 10 mL of HPLC-grade water. The extract was subjected to the previous procedure again but with methanol. The extracts were purified using an Envi-carb cartridge (500 mg, 6 cc; Waters Corp, Milford, MA, USA). Finally, 1 mL of the solution was filtered using a 0.20-µm nylon syringe filter into a glass vial and analyzed by HPLC-MS/MS.

For vegetables, 0.25–0.03 g fresh weight (FW) samples were fortified with 50 µL of an internal standard Cl¹⁸O₄ (98%) and extracted with acetic acid (1%) and acetonitrile (ACN), vortexed and centrifuged. The extracts were purified using an Envi-carb cartridge (500 mg, 6 cc; Water, Milford, MA, USA). Finally, 1 mL was filtered using a 0.20-µm nylon syringe filter and analyzed by HPLC-MS/MS.

The irrigation water sample was filtered (10 mL) using a 0.20-µm nylon syringe filter, and then 950 µL of the sample was fortified with 50 µL internal standard Cl¹⁸O₄ (98%) to a final volume of 1 mL and analyzed by HPLC-MS/MS.

2.3. Instrumental analysis

The extracts were analyzed using high-performance liquid chromatography (Agilent 1100 series HPLC; Agilent Technologies, Santa Clara, CA) coupled with electrospray triple quadrupole mass spectrometry (API 2000; ESI-MS/MS; Applied Biosystems, Foster City, CA). Data acquisition and quantification were accomplished with Analyst software (Version 1.4.1). The chromatographic separation of perchlorate was accomplished with an anion exchange column, IonPac AS-21 (250 mm × 2 mm, Dionex, Sunnyvale, CA, USA). Two hundred millimolar (mM) methylamine in aqueous solution was used as the mobile phase with an isocratic elution at a flow rate of 0.3 mL/min (total run time: 10 min). The sample injection volume was 50 µL. The elution time for perchlorate was

3.7 min (Fig. S3). The ESI- and MRM modes with the following ion transitions were monitored for quantification and confirmation of perchlorate and $^{18}\text{O}_4$ - enriched perchlorate (labeled): m/z 99 ($^{35}\text{ClO}_4^-/83$ ($^{35}\text{ClO}_3^-$)), m/z 101 ($^{37}\text{ClO}_4^-/m/z$ 85 ($^{37}\text{ClO}_3^-$)), and m/z 107 ($^{35}\text{Cl}^{18}\text{O}_4^-/m/z$ 89 ($^{35}\text{Cl}^{18}\text{O}_3^-$)). The ratio of $^{35}\text{Cl}:^{37}\text{Cl}$ in perchlorate was estimated as the ratio of m/z 99:101 peaks and considered acceptable at $3.12 \pm 25\%$ r.s.d.

2.4. Quality assurance and quality control

An eight-point calibration standard curve encompassing concentrations ranging from 1 to 200 ng mL^{-1} was constructed for linearity and quantification. The regression coefficient of the calibration curves was >0.99 . The limits of detection (LOD) and limits of quantification (LOQ) were calculated as the signal-to-noise ratio of ≥ 3 and ≥ 10 , respectively. The LOD values for perchlorate were 0.05 ng g^{-1} (soil), 0.2 ng g^{-1} (fertilizers), 0.05 ng g^{-1} (vegetables) and 0.05 ng g^{-1} for irrigation water. We included a procedural blank, duplicate sample, and matrix spike (fortified with 5 and 15 ng mL^{-1} of perchlorate). Perchlorate was not detected in any of the procedural blanks. Recoveries of perchlorate spiked in irrigation water, soil, fertilizer, and vegetables were 102, 106, 113, and 89%, respectively. Instrumental blanks (water) were injected after every 20–25 sample injections, and no carry-over was found. A midpoint calibration standard was injected every 12 h to monitor for drift in instrumental response.

2.5. Experimental design

Field studies were carried out in 2018 during March and July. The experimental design (1200 m^2) included two rows of 20 m^2 (20×1 m) with an intermediate zone of 1 m between rows, corresponding to 200 transplanted seedlings (Fig. S2). Each row corresponded to a type of agronomic practice (manual and fertigation), and three treatments were applied: a) control (No N-fertilizer); b) optimal, which was determined according to the basic nutritional requirements and c) excess (double the fertilizer level than in the optimal treatment). The soils were fertilized under both agronomic practices with 649 g (optimal: 150 mg kg^{-1}) and 1298 g (excess: 300 mg kg^{-1}). For the manual agronomic practice, the fertilizer was applied randomly, while in fertigation, the fertilizer was dissolved in 20 L of water according to the commercial practices used by farmers in Santiago, Chile. Lettuce was collected seven times during the experiment for all treatments (Table S2). The samples were separated by zone (control, optimum and excess) placed in plastic bags for storage, and labeled. Additionally, before fertilization we performed a soil analysis to determine the natural levels of nitrogen, phosphorus and potassium (NPK).

2.6. Bio-accumulation factor (BAF)

The BAF is an index of the ability of a vegetable to accumulate a particular contaminant as a function of its concentration in the soil. The BAF from soil to lettuce was calculated according to equation (Jolly et al., 2013):

$$\text{TF} = C_{\text{plant}} / C_{\text{soil}}$$

where, C_{plant} and C_{soil} represent the perchlorate concentration in edible portions of vegetables and in soils, respectively, on a dry weight basis.

2.7. Inputs to soil via fertilizers

The input of perchlorate into agricultural soils from fertilizer use

was estimated as follows:

$$A_{ij} = \sum \cdot N_j \cdot C_{ij}$$

Where A_i is the amount of perchlorate (i) added each year (tons year^{-1}) from fertilizers (j), N_j is the amount of fertilizer (j) applied (tons) currently consumed in Chile and C_{ij} is the concentration of perchlorate in the fertilizer (mg kg^{-1}). The rate of application (g ha^{-1}) was estimated using the amount of perchlorate added annually per unit area through fertilizer the average recommended dose for the main crop and the fractions of nitrogen, phosphate, and potassium in fertilizers (Vieira Da Silva et al., 2017).

2.8. Estimation of human exposure

The estimation of human exposure was calculated based on the mean perchlorate concentration (ng g^{-1}) multiplied by the daily vegetable intake rates per age group (0–11 years) and body mass (g kg^{-1} body mass) using information obtained from the United States Food Commodity Intake Database ((FCID FCID 2005–2010)).

2.9. Data analysis

Statistical analysis was performed using SPSS 25 (SPSS Inc, Chicago, IL, USA). Before performing a one-way analysis of variance (ANOVA), the Kolmogorov-Smirnov test was used to assess the normality of original data. The Pearson correlation analysis was implemented to explore associations between perchlorate in soils and fertilizers, using a significance level of 0.05.

3. Results and discussion

3.1. Occurrence of perchlorate in soil

The distribution of perchlorate in soils was studied on the basis of land-use and by provinces: Chacabuco, Cordillera, Santiago, Talagante, Maipo, and Melipilla (Fig. S1). Over 23,000 ha (31.8% of the total) are devoted to producing leafy vegetables in the metropolitan region (MR) (Instituto Nacional de Estadísticas, 2015). Perchlorate was detected in 64% of the analyzed soils (Table 1). Agricultural, grassland rotation, and urban soils were the most contaminated soils (28%, 17%, and 11%, respectively), with maximum values of 54.0 (Melipilla), 44.3 (Melipilla) and 11.9 ng g^{-1} (Santiago), respectively. Interestingly, the maximum level found in an urban soil suggests the effect of industrial activities. Nevertheless, ubiquitous occurrence of perchlorate in soils in our study suggests the existence of other sources that contribute to contamination in Chilean soils. The perchlorate concentrations in urban soils are lower than those in agricultural and non-agricultural soils of northern Chile (290–2565 $\mu\text{g kg}^{-1}$) (Calderón et al., 2014). A similar pattern has been observed in urban soils in China (Gan et al., 2014). Although anthropogenic sources are known in China, there is no such information available in Chile (central zone).

Areas with high perchlorate contents were generally divided into two groups. The first group represents agricultural soils, and the second group grassland rotation sites (Fig. 1). The highest detection frequencies were observed in the soils from the provinces of Chacabuco (45%), Melipilla (57%) and Maipo (81%). There was no significant difference between values from agricultural and grassland rotation soils or among agricultural soils collected from different provinces ($p > 0.05$).

Soil samples collected from native soils contained lower concentrations (0.01–0.5 ng g^{-1}) than those from grassland rotation sites (0.1–44.3 ng g^{-1}). Our study suggests a potential migration of

Table 1
Summary of the perchlorate concentrations (ng g^{-1}) from sample locations.

Province	N	Median (ng g^{-1})	Min (ng g^{-1})	Max (ng g^{-1})	Detection frequency (%)
Chacabuco	20	0.41	N.D.	0.69	45
Cordillera	5	—	N.D.	0.26	20
Maipo	21	0.38	N.D.	20.3	81
Melipilla	37	0.32	N.D.	54.0	57
Santiago	4	5.01	N.D.	11.9	75
Talagante	14	0.30	N.D.	1.20	79

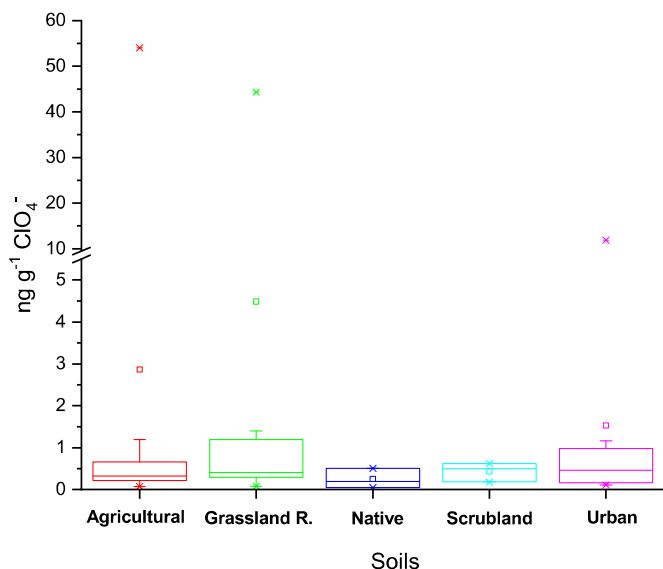


Fig. 1. Perchlorate concentrations stratified by land use pattern.

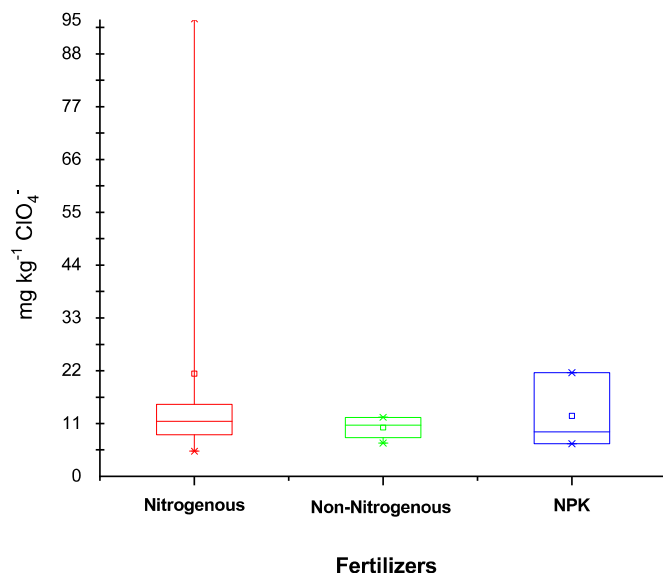


Fig. 2. Perchlorate concentrations in fertilizers.

perchlorate from agricultural areas to native soils.

Considering grassland soils that do not contain perchlorate (not detected (ND)), our study suggests that changing management practices in agriculture could increase perchlorate accumulation in soils. Levels of perchlorate in scrubland soils ranged from ND to 0.62 ng g^{-1} . A similar pattern was observed in crop rotation soil, indicating that successive alternation of different crops reduces the perchlorate levels in the soil system to a greater extent than in grassland rotation. In general, the perchlorate levels found in our study (grassland, scrubland and native) are similar to those levels reported by Rao et al. (2007) in US soils ($1.0 \mu\text{g kg}^{-1}$). In addition, in Chile perchlorate contamination in soils is both natural and resulting from the use of fertilizers, compared with the USA (where it is both natural and anthropogenic),

3.2. Fertilizers

The northern zone of Chile is known as a natural reservoir of perchlorate of exclusively natural origin (Orris et al., 2003; Rao et al., 2007). Currently, perchlorate has been reported in arid and semi-arid soils, evaporite, potassium minerals and fertilizers around the world (Rajagopalan et al., 2006; Orris et al., 2003). To elucidate the source of perchlorate in Chilean soils, we analyzed 17 types of fertilizers (nitrogenous, NPK, phosphate and non-nitrogenous).

Nitrogenous fertilizers: Nitrogenous fertilizers such as KNO_3 contained the highest levels of perchlorate, with a median concentration of 11.5 mg kg^{-1} (Fig. 2). Interestingly, perchlorate levels varied among producing companies. For example, concentrations of KNO_3 (different brands) ranged from 12.8 to 95.3 mg kg^{-1} ,

indicating different origins of contamination. In our study, only one type of KNO_3 exceeded the recommended value from European international regulations (50 mg kg^{-1}) (European Commission, 2016). Perchlorate levels in nitrogenous fertilizers and soils (Maipo and Melipilla) were positively correlated ($p < 0.01$).

Fertilizers such as calcium and ammonium nitrate contain perchlorate (17.2 and 11.5 mg kg^{-1} , respectively). The concentrations of perchlorate observed in our study were lower than previously reported values [1.5 – 1.8 mg g^{-1} (Urbansky et al., 2001), 8.4 mg g^{-1} (Susarla et al., 1999), non-detected, $< 20 \text{ mg g}^{-1}$ (Hunter, 2001)] in different types of fertilizers. In previous reports, the use of a non-selective technique such as ion chromatography with conductivity detection (IC-CD) may have overestimated levels of perchlorate (Susarla et al., 1999; Hunter, 2001). In recent years, the companies producing fertilizers in Chile modified refining techniques to produce fertilizers containing less than 0.01% perchlorate (USEPA, 2001; Calderon et al., 2017). However, many fertilizers are imported, and hence it is not possible to associate their origins to Chile (ODEPA, 2010). Considering the exponential demand for nitrogen fertilizers worldwide (119,418,000 tons) and the co-existence of perchlorate, this pollutant certainly represents a potential hazard to food safety.

NPK Fertilizers: Perchlorate was found in 2 of 3 NPK fertilizers, at lower concentrations than in nitrogenous fertilizers (except NPK2: 21.6 mg kg^{-1}) and lower than in previous studies (USEPA, 2001). Our results suggest that NPK fertilizers are also an important source of introduction of perchlorate into agricultural systems, although their levels of application are less than for nitrogenous fertilizers. However, application of both fertilizers (nitrogenous and NPK) in crop production increases the probability of contamination

in soils.

Phosphate Fertilizers: All phosphate fertilizers contained perchlorate. For diammonium phosphate (DAP) purchased from two different companies, the level of perchlorate ranged from 4.5 to 18.5 mg kg⁻¹. Chile does not produce phosphate fertilizers (Estudio de Mercado, 2018). In previous reports, perchlorate has not been detected in phosphate fertilizers (USEPA, 2001; Hunter, 2001). However, Susarla et al. (1999) measured concentrations of perchlorate in phosphate fertilizers (0.1–0.46%). Probably, the use of IC-CD overestimated the levels of perchlorate in a highly complex matrix of fertilizers (Susarla et al., 1999).

Non-nitrogenous fertilizers: Non-nitrogenous fertilizers are used in agriculture to regulate levels of elements essential for plant nutrition. In our study, perchlorate was detected in all non-nitrogenous fertilizers (mean = 10.7 mg kg⁻¹). The levels of perchlorate in non-nitrogenous fertilizers varied according to the brand/supplier. For example, two different brands of the same magnesium sulfate fertilizer exhibited a 2-fold difference in perchlorate concentration.

3.3. Field study

Excessive inputs of pollutants from fertilizers can contaminate soils and groundwater and eventually enter the food chain (Fan et al., 2018; Li et al., 2018; Jiao et al., 2012). In our study, the level of perchlorate (22.4 ng g⁻¹) in soils (field) was higher than the mean for agricultural soils in the MR (0.32 ng g⁻¹) but lower than the maximum value (54 ng g⁻¹). Perchlorate in irrigation water (0.26 ng mL⁻¹ detected in the current study) is lower than in surface waters from the Colorado River used for various lettuce types produced in the Colorado River region (Sanchez et al., 2005a). No perchlorate was detected in the seedlings before transplantation. Lettuce accumulates perchlorate throughout the cultivation period, with a maximum level of 4.4 ng g⁻¹ at harvest time. Our study shows that lettuce grown in areas with natural levels of perchlorate in soils and irrigation water accumulates perchlorate (Sanchez et al., 2005b). After the first fertilization (on May 25th), lettuce accumulated more perchlorate (optimal and excess treatments) than in the control plots. For the excess treatment (29.6 ng g⁻¹) the accumulation rate was higher than that in the optimal treatment (12.6 ng g⁻¹, Fig. 3). Currently, the global trend in agriculture is the

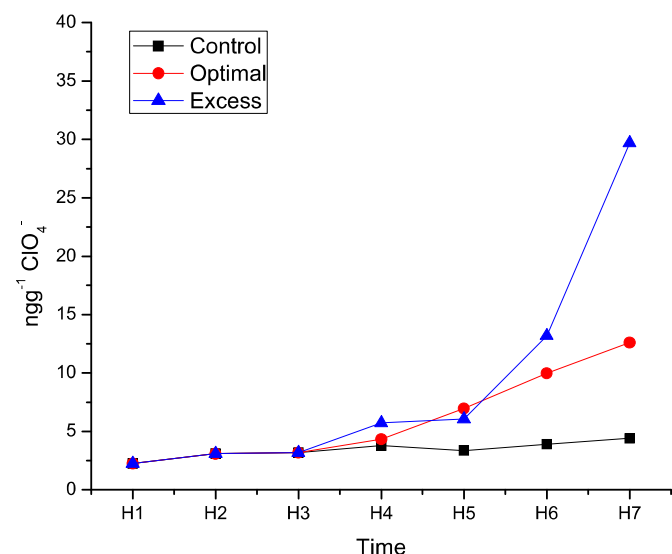


Fig. 3. Perchlorate concentrations in lettuce (*Lactuca sativa*) under manual fertilization.

use of drip irrigation, considering the current scenario of water scarcity.

For the excess treatment, perchlorate content was almost three times higher at harvest time than with the optimal treatment (Fig. 4). In our study, lettuce accumulated higher levels of perchlorate than in previous reports (USFDA, 2005; Sanchez et al., 2005b). However, the content of perchlorate (current study) is lower than in other leafy vegetables such as spinach. (USFDA, 2005; Sanchez et al., 2005b; Ha et al., 2011). Finally, levels of perchlorate remained below the international standard of 1 mg kg⁻¹ (European Food Safety Authority (EFSA), 2014).

3.4. Perchlorate contamination of soil from fertilizer application

In Chile, the annual consumption of NPK fertilizers corresponds to 63,000, 65,000 and 39,000 tons, respectively (ODEPA, 2010). For lettuce (*Lactuca sativa*), the average application of nitrogen, potassium and phosphate fertilizers corresponds to 150, 120 and 100 kg ha⁻¹. Knowing the levels of contaminants present in the fertilizers and the annual application rate of fertilizers (tons year⁻¹), we can estimate the quantities of contaminants introduced into the crop system (Luo et al., 2009; Azzi et al., 2017). A total of 7.68 tons year⁻¹ of perchlorate are incorporated into soils, considering application of nitrogen (KNO₃: 95.3 mg kg⁻¹), phosphorus (NH₄H₂PO₄: 18.5 mg kg⁻¹) and potassium (KCl: 12.2 mg kg⁻¹) fertilizers.

Considering the common use of these fertilizers as sources of N, P and K in a lettuce crop (*Lactuca sativa*), we estimated 112.0 g ha⁻¹ for each crop cycle (70 days per year). This estimated perchlorate contamination level is higher than for trace elements (TE) in phosphate fertilizers (Vieira Da Silva et al., 2017). However, perchlorate mobility in soils is completely different than for TE.

3.5. Human risk

Concentrations of perchlorate in lettuce (optimal and excess) at harvest time (June 19th) were used to calculate the estimated daily intake (EDI). In our study, the EDI of perchlorate ranged between 0.9 and 30.2 ng kg⁻¹ bwd⁻¹ for all treatments and age groups. Low risk to human health was associated with the intake of lettuce for all age groups. The highest EDI occurred in the groups aged 1–3

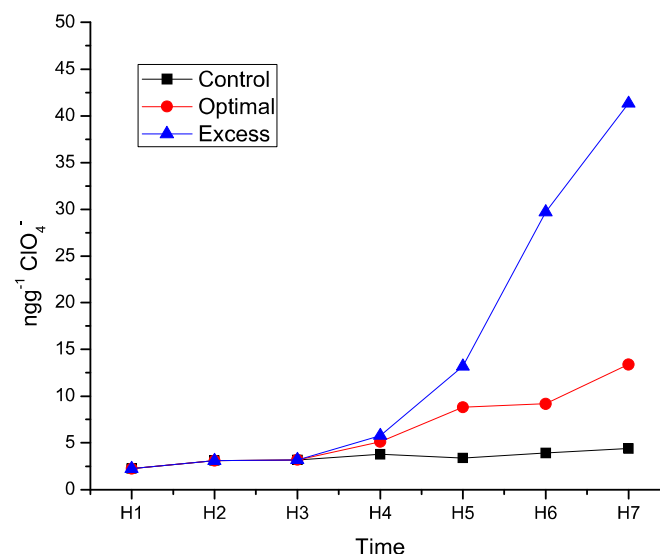


Fig. 4. Perchlorate concentrations in lettuce (*Lactuca sativa*) under fertigation.

years (fertigation). Lettuce (*Lactuca sativa*) grown under different treatments and agronomic practices increases the perchlorate content in plant tissues, generating greater exposure. However, for the entire age group range, levels did not exceed the reference dose of 7000 ng kg⁻¹ bwday⁻¹) (European Food Safety Authority (EFSA), 2014; USEPA, 2018).

4. Conclusion

This study provides data concerning perchlorate levels in soils, fertilizers and mobility of perchlorate in the soil-crop system. Our results showed lower perchlorate concentrations in soils than in previous studies. However, high concentrations in agricultural soils suggest that the use of Chilean nitrogen fertilizers is a significant source of perchlorate to the environment. All fertilizers contained perchlorate; however, the perchlorate content depended on the raw material used in production. The nitrogenous fertilizers contained the highest levels, ranging from 5.3 to 95.3 mg kg⁻¹. Treatments and agronomic practices increase the accumulation of perchlorate, which was higher with fertigation. The perchlorate levels in lettuce (*Lactuca sativa*) are lower than the those set by international regulations and do not represent a health hazard for vulnerable groups (0–11 years). Our findings provide information about perchlorate content in soils and fertilizers, which will be helpful for establishing appropriate global regulatory guidelines.

Declaration of interests

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

CRediT authorship contribution statement

P. Palma: Methodology, Formal analysis. **N. Arancibia-Miranda:** Formal analysis, Methodology. **E. Silva-Moreno:** Formal analysis. **F. Corradini:** Formal analysis. **Karthikraj Rajendiran:** Formal analysis. **Kim U.J.:** Formal analysis.

Acknowledgments

This work was funded by the Project Fondecyt 11160581, Conicyt, Chile.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.114682>.

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Trace element content in soil after a sediment-laden flood in northern Chile

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Received: 12 December 2016 / Accepted: 1 March 2017
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Abstract

Purpose Arid and hyper-arid zones worldwide are reservoirs of chemical compounds, among them are various trace elements. With climate change, abnormal precipitation is occurring in arid and hyper-arid mountainous zones, which in turn is increasing the displacement of trace elements from mountainous to populated areas. The objective of this study was to evaluate trace element displacement of a sediment-laden flood in the Copiapó River Basin on March 24–25, 2015.

Materials and methods Sixty topsoil samples were taken from 20 agricultural fields. Soil organic matter content, pH, electrical conductivity, and particle size were determined according to accepted procedures in Chile. Samples were acid-digested to determine total Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, and Zn content by flame atomic absorption spectroscopy. Hydride generation AAS was used for As and Se determination, and Hg was quantified by cold vapor AAS. Detection limits were 0.2, 0.05, 0.1, and 5.0 mg kg⁻¹ for Cd, Hg, Se, and Mo, respectively. Correlation and principal component analyses were made, and theoretical distribution functions were fitted to each element.

Results and discussion Metal concentration showed a strong correlation between SOM and particle size, explaining the first component from the principal component analysis. All trace elements correlated well between each other except for Mo and Se. Mo values were consistently below detection levels (<5.0 mg kg⁻¹). Expected values for the elements were (95% of probability): 13–37 g Al kg⁻¹, 10–50 mg As kg⁻¹, <0.2–0.6 mg Cd kg⁻¹, 13–25 mg Cr kg⁻¹, 27–281 mg Cu kg⁻¹, 27–40 g Fe kg⁻¹, <0.05–6.5 mg Hg kg⁻¹, 516–1.080 mg Mn kg⁻¹, 7–24 mg Ni kg⁻¹, 13–50 mg Pb kg⁻¹, 0.2–0.6 mg Se kg⁻¹, and 61–172 mg Zn kg⁻¹. Concentrations of As, Cu, and Hg were consistently above national standards.

Conclusions The authors conclude that the trace element contents in sediments deposited by the event are within expected values based on soil data in Chile.

Keywords Agricultural land · Atacama Desert · Debris flow · Floodplain sediment · Trace element

1 Introduction

Landslides are important geo-hazards that affect mountainous areas (Hung and McDougall 2009; Korup and Clague 2009) (e.g., Hu et al. 2016 (China); Sepúlveda et al. 2006 (Chile); Tsuchida et al. 2014 (Japan)). Flows are a type of landslide formed by spatially continuous movement of saturated masses of earth and other materials, primarily controlled by gravity. In those events, the distribution of velocities of the displacing mass resembles that of a viscous liquid (Cruden 2013). The general term debris flow will be in this work for simplicity, according to Hung et al. (2014), to indicate complex processes in which a surging debris flow passes through a steep gully, enters a depositional fan, leaves behind the coarsest fractions, and continues as a sediment-laden flood.

Responsible editor: Dong-Mei Zhou

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Because of the large amount of material that debris flows transport, these events generally cause major damage to populations, agricultural lands, and infrastructure (Kitamura and Sako 2010). Due to the topographic influence of the Andean Mountain range, landslides are important natural hazards in South America. These events are common in Argentina, Peru, Bolivia, and Chile (Keefer et al. 2003; Sepúlveda et al. 2006; Latrubesse et al. 2009; Moreiras and Coronato 2009).

A third of Chile is covered by the towering Andean range, thus the main geo-hazards are mass movements, volcanic eruptions, earthquakes, and tsunamis (Cecioni and Pineda 2009). Topography controls temperature and rainfall patterns in Chile. In fact, the Andean and Coastal ranges regulate atmospheric circulation and are involved in the dynamics of the South Pacific anticyclone along the Chilean coast. Extended droughts and major floods are strongly affected by the location and persistence of the anticyclone and the El Niño current (Muñoz et al. 2007; Vargas et al. 2006).

Rainfall in northern Chile (from 18° to 27° S) is extremely low, with an average of less than 4 mm year⁻¹. However, the El Niño phenomenon has resulted in anomalous rainfalls in northern Chile, including the Atacama Desert. To illustrate this, Vargas et al. (2000) showed that the debris flow events that occurred in the area around Antofagasta in the twentieth century were associated with heavy rainfalls during the austral winter of the development phase of El Niño. In this way, topography and climate create special conditions for sporadic debris flow events. Chilean governments have had reactive rather than proactive policies regarding geological hazards, with limited research on prevention, prediction, and hazard assessment. In fact, the lack of awareness of the hazards of debris flows results in an inclination to reoccupy affected areas soon after catastrophic events (Sepúlveda et al. 2006).

Several authors have studied the enrichment of Chilean soils with trace elements and the implications for food production (Ginocchio et al. 2004; González et al. 2014). However, there is no baseline of trace element concentrations in Chilean soils and only a few highly geographically limited studies have been made about trace elements in Chilean soils (e.g., Muñoz et al. 2005; Pizarro et al. 2016). Northern Chile in particular has the highest concentration of mining activities in the country. For example, 2397 mining operations were reported in the Atacama Region (between 25° 17' and 29° 30' S) in 2011 (SERNAGEOMIN 2011), the major products being sulfuric acid, limestone, iron, and copper.

On March 24 and 25, 2015, there were heavy rains in the Atacama Region of northern Chile, having precipitation scores of 14.6 and 35.2 mm each day (data from “Amolana” meteorological station owned by National Agricultural Research Center, located at UTM WGS84 19H 400.654 E; 6.906.839 S). That event was combined with high temperatures at lower altitudes and freezing temperatures above 3500 m.a.s.l., thus causing a series of debris flows in different

locations. Agricultural land, cities, villages, and infrastructure were damaged. After the event, the Copiapó Valley producers association surveyed producers that account for 5233 ha of horticultural crops (mainly table grapes). In an internal report, they stated that 2326 ha, representing 42% of total agricultural land, were affected directly by the event. Among those, 353 ha (7%) were lost irreversibly. In addition to the physical effect on the structures of grapevines and fruit trees, the event deposited a considerable amount of sediments on arable lands, burying the soil with deposits more than 1 m deep in some areas.

Beyond the direct effects of debris flows, a general concern emerged after the event. Given the level of mining activities, the Atacama Region has 36% of all the mining dams in Chile: 45 active and 72 inactive (Cámara de Diputados 2011). As mining dams located on steep gullies pose a risk of dragging potentially toxic material over agricultural lands and urban areas during flow events, the authorities suspect that the sediments deposited by the events in 2015 in the Copiapó Valley include high concentrations of trace elements. Moreover, the community met with a National Human Rights Institute and demanded that the authorities take action on this matter (INDH 2015). Therefore, the main objectives of this work were to (1) survey trace element concentrations along the Copiapó River Basin, (2) compare those concentrations to national and international references, and (3) evaluate the contribution of the recent floodplain sediments to trace element concentrations of the resulting soils.

2 Materials and methods

2.1 Study site

The Atacama Region presents a large number of mining operations, with copper and gold being the most economically important minerals being extracted. The region accounts for 0.4% of arable land in Chile (19,744 ha) cultivated mostly with fruit crops (ODEPA 2014). The Copiapó River flows through the communes of Tierra Amarilla, Copiapó, and Caldera, all located in Copiapó Province of the Atacama Region. Figure 1 is a map of the Copiapó River Basin, including agricultural areas (CIREN 2007). It also shows the distribution of mining operations (SERNAGEOMIN 2011). The agricultural lands located on the river floodplains were affected by a series of debris flows on March 24–25, 2015.

2.2 Soil sampling and analysis

A sampling campaign took place on April 8, 2015. Affected agricultural fields were identified, and 20 fields were chosen for sampling. Three independent samples were taken at each field, providing 60 sampling points in all. Sediments were

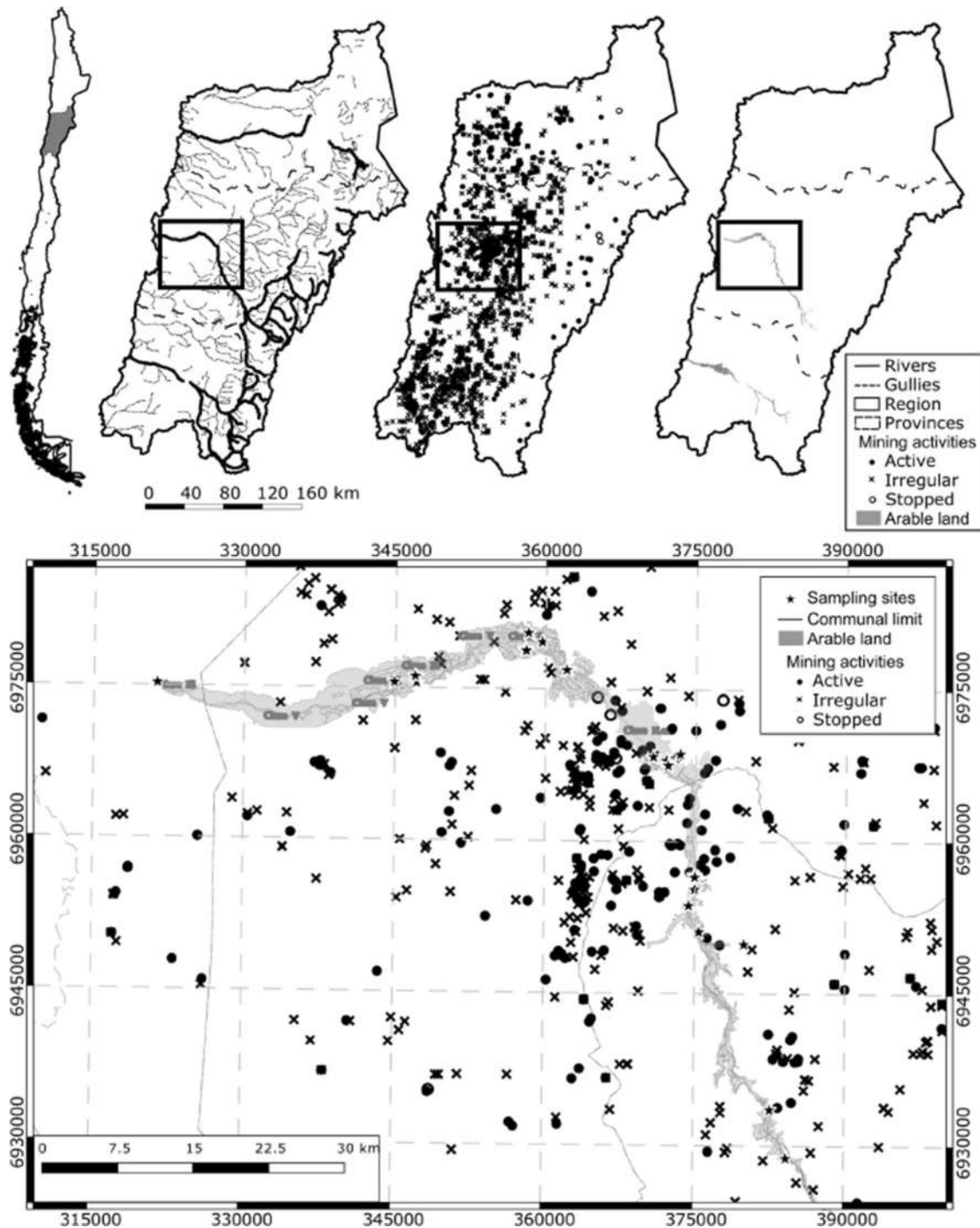


Fig. 1 Location of the Copiapó River Basin, near agricultural areas, and distribution of mining activities. Coordinates in UTM WGS84 19H

collected from the topsoil (top 50 cm) using either a shovel or a soil auger. Soil samples were taken between 0 and 50 cm deep and homogenized in a plastic pail to take a composite sample of approximately 1 kg. Additionally, four agricultural sites that were not affected by the debris flows were sampled as control sites, for a total of 12 additional soil samples. Figure 1 is a map of the Copiapó River Basin with the location of all the sampling points.

Within 2 days, soil samples were transported to the Environmental Laboratory of La Platina Regional Research Centre of the Agricultural Research Institute (INIA) in Santiago, Chile. Samples were air dried and sieved at 2 mm. Then, 2 g of each sample was acid-digested according to EPA Method 3050B (EPA 1996) to determine trace (semi)metal content (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, and Zn) by flame atomic absorption (FLAA) spectroscopy.

In addition to trace element analysis, sediment samples were air dried and sieved for chemical and physical characterization, including: pH in water (1:2.5), electrical conductivity (EC) in saturated extract (dS m^{-1}), and soil organic matter (SOM) (%), according to Sadzawka et al. (2006). Particle size was determined by the Bouyoucos hydrometer method as presented by Sandoval et al. (2012).

2.3 Quality control

Samples from the WEPAL program were used as reference to ensure the accuracy of the analytical methods. These samples were not certified but the concentration values for all elements were obtained from the analytical results provided by several laboratories around the world. Every laboratory performs the same acid digestion procedure employing similar analytical equipment. The results were within one standard deviation of reported WEPAL values. Furthermore, 20% of samples were analyzed in duplicate seeking less than 10% variation.

The detection limit for a given element was established as a function of sample dilution and the corresponding equipment detection threshold. The latter was determined by a statistical function that takes into account blank levels, equipment sensitivity, and signal to noise ratios. The equipment detection limit was defined as the concentration of the element in milligrams per liter that yields a reading equal to three times the standard deviation of a signal measured close to the blank level. Standard deviation was calculated using 10 sequential readings. Detection limits were 0.2, 0.05, 0.1, and 5.0 mg kg^{-1} for Cd, Hg, Se, and Mo, respectively.

2.4 Statistical analysis

Mean, median, and standard deviations (sd) were calculated for control sites and for sediment samples. Statistics for Cd, Hg, and Se were obtained by maximum likelihood estimation, since these variables present left-censored data. Spearman's rho was used as a correlation index to define dependency among observed values. A minimum significance level was set at 95%. Aitchison's centered log ratio transformation for compositional data was performed on trace element data prior to calculate correlations. Correlation matrix was sorted by hierarchical clustering. Within-group sum of squares was used to define the number of clusters. Euclidean method was used to obtain the distance matrix and Ward method to cluster the data. Data was processed in R (R Core Team 2016). Other packages such as Hmisc (Harrell and Dupont 2016), Hotelling (Curran 2013), gplots (Warnes et al. 2016), car (Fox and Weisberg 2011), MASS (Venables and Ripley 2002), fitdistrplus (Delignette-Muller and Dutang 2015), logspline (Kooperberg 2016), and NADA (Lee 2013) were also used.

Trace element concentration data was transformed by Aitchison's centered log ratio procedure and then scaled and centered for a principal component analysis. The calculation was done by singular value decomposition of the data matrix. The true value of the rotated data was recovered. The Kaiser-Guttman criterion (variance above 1) was used to define the number of principal components to consider. Categorical variables were obtained from SOM, pH, geographic altitude, EC, and soil texture data and tested as grouping factors. SOM, pH, EC, and geographic altitude (m.a.s.l) values were discretized, breaking the observed data down into quantiles whenever possible: (1) SOM as [0.2, 0.3] (0.3, 0.5] (0.5, 0.9] (0.9, 4.2]; (2) pH as [7.8, 7.9] (7.9, 8.0] (8.0, 8.2]; (3) altitude as [210, 302] (302, 419] (419, 504] (504, 669]; and (4) EC as [2.6, 4.0] (4.0, 4.4] (4.4, 5.1] (5.1, 33.2]. Percentages of sand, silt, and clay were classified according to the textural classes proposed by the Natural Resource Conservation Service of the USDA (Schoeneberger et al. 2012) and classified as: (1) "coarse" sediments with texture classes within sandy loam, loamy sand, and sand; (2) "loam" sediments presenting texture classes among sandy clay, sandy clay loam, and loam; and (3) as "fine" sediments within all other texture classes. To evaluate these categorical variables as grouping factors, confidence ellipses were drawn based on the true value of rotated data. A confidence interval (CI) of 68% and a lineal model for the rotated data were considered for computation.

With trace element concentration data from sediment samples, theoretical distribution functions were fitted ($n = 60$) to compare the observed data from sediment samples with Chilean and international standards for soil trace element content. For each trace element, univariate distributions were fitted by maximum likelihood. Normal, lognormal, gamma, Weibull, uniform, and logistic distributions were tested to select the model with the best fit according to Akaike's information criterion. To test whether the selected distributions were good approximations of the observed data, a p value was obtained for each as indicated by Jogesh Babu and Rao (2004). Thereafter, nonparametric bootstrap resampling was used to simulate uncertainty in the parameters of the distribution fitted to observed data. The study determined the cumulative probability of sampling values above Chilean standard thresholds from the fitted distribution of each element.

Trace element concentrations in control sites and sediments were compared to evaluate the trace element contribution of recent floodplain sediments. Element concentrations were tested to determine normality (Shapiro-Wilk) and homoscedasticity (Bartlett). Transformations were applied when data failed these criterions. Manganese, Pb, and Se were log transformed. Box-Cox transformation was used for As, Cu, Hg, and Zn. Finally, Cd and Ni were consistently abnormal. The Student's t test was used to compare control sites to sediments. The Wilcoxon test was used for Cd and Ni. Significance was evaluated at $\alpha = 0.05$.

3 Results

3.1 Critical limits and observed values

Chile does not have environmental or productive thresholds for trace elements in soil. Thus, there is no way to determine whether a soil is enriched with such elements. However, there is legislation that established threshold values for trace elements in soils where sewage could be dumped (DTO 4/2009) (Table 1). Assuming that the Chilean government is not inclined to apply potentially contaminated amendments to already polluted soil, these values are used in this paper as threshold concentrations to compare the observed values in the Chilean context. Table 2 shows the values obtained for the measured elements on control sites and sediment samples. Figure 2 presents the values for each sampling point (control sites included) and their relationship to the standards. Maximum acceptable concentrations of Cd, Pb, Cu, and Zn are also shown in Fig. 2. Ecotoxicological threshold values were calculated according de Vries et al. (2013), using a method which calculates critical site-specific limits for each element considering soil pH, SOM, and clay content. In this study, the means of all independently calculated ecotoxicological thresholds for each sampling point were used for comparison ($2.7 \text{ mg Cd kg}^{-1}$, $43.6 \text{ mg Pb kg}^{-1}$, $7.1 \text{ mg Cu kg}^{-1}$, $17.2 \text{ mg Zn kg}^{-1}$).

Observed Cd values were generally three times as low as the Chilean threshold, and four times as low as the ecotoxicological threshold calculated by de Vries et al. method. Moreover, there was no appreciable difference in Cd concentrations between sampling points and control sites or according to altitude. The latter also applies for Ni and Se, where observed levels were four times less than Chilean critical limits for both elements. Arsenic and Hg concentrations were 63.9 and 36.1% above Chilean standards, with values more than twice as high as the Chilean maximum recommended levels. Of particular concern are the samples taken from points 67, 68, and 69 (last three white bars from left to right in Fig. 2), which had As and Hg concentrations more than four times greater than recommended limits. This was also the case for Cu and Zn.

Lead, Cu, and Zn values exceeded the critical ecotoxicological limits calculated by de Vries et al. method. In terms of the percentage of samples, 12.5, 100.0, and 100.0% of observed values exceeded de Vries thresholds for Pb, Cu, and Zn, respectively. For Pb, Cu, and Zn, the Chilean threshold is much higher than that calculated by the method proposed by de Vries et al., because of which the Chilean critical values were exceeded by a lower percentage of samples: 13.9 and 11.1% for Cu and Zn. A control site far from sediment deposition presented the highest Pb concentration. Nevertheless, no observations over Chilean limits were reported for Pb. In contrast, the highest Cu and Zn concentrations, which were

above the Chilean threshold, were found in samples taken near a mining dam (points 67, 68, and 69).

In summary, soil content of Cd, Se, and Ni was consistently below established critical limits. Arsenic and Hg frequently exceeded the maximum concentration proposed by the Chilean government, while Pb, Cu, and Zn slightly exceeded these limits but were generally ten times as high as the critical ecotoxicological limits determined according to the methodology of de Vries et al.

3.2 Correlation and principal component analysis

Figure 3 shows the correlation matrix sorted by hierarchical clustering. Clay and SOM correlated positively and significantly with all trace elements determined in the study, except for Mo because observed Mo values were consistently below the detection limit ($<5.0 \text{ mg kg}^{-1}$). Conversely, sand content correlated negatively and significantly with trace element contents because, obviously, a higher sand content implies lower silt/clay content. On the other hand, pH did not correlate with any of the studied variables. However, the observed pH range was very low, between 7.6 and 8.2. Lastly, altitude correlated negatively with some trace elements (Hg, Fe, Al, and Ni) and silt. Although significant, these correlations were weak.

Sum of squares within groups was used to define clusters for the correlation matrix. Six clusters were defined, of which the first relates, Al and Ni, correlated positively with Fe, Mo, Mn, and Cr (cluster two) and negatively with Cu, Hg (cluster five), As, and Cd (part of cluster six). The second cluster aggregated Cr, Se, Fe, and Mn and obviously correlated positively with the elements in cluster one. Cluster two had similar relations to those of cluster one, but correlated strongly with Cu and Hg (with negative vector). Clusters three and four account for particle size, SOM, pH, and altitude according to their correlation vector with trace element content (cluster three was positive for silt, clay, and SOM and cluster four negative for sand, altitude, and pH). Finally, copper and Hg (cluster five) correlated negatively with all trace elements, and cluster six aggregated elements with lower rho values.

All observed values, with the exception of Mo, were centered and scaled by mean and standard deviation, constructing a matrix plot in which standardized values were plotted against sand, silt, and clay content and SOM, EC, and altitude (Fig. 4). When a linear regression was significant, the equation was added to the plot. All regression coefficients are indicated according to the same criterion. Figure 4 shows that relative trace element content decreases as the ratio of sand in the sediment increases, while the opposite is true for clay, silt, SOM, and EC. Conversely, no relationship was found between altitude and trace element content.

The principal component analysis showed that the first three components explained 78.75% of the variation. These components were the only ones that presented a variance

Table 1 Critical limits of trace elements in soils for sewage applications (Chilean DTO 4/2009), ecotoxicological thresholds calculated using the approach of de Vries et al. (2013), and standards of Finnish legislation for contaminated soil

Element	Units	Critical limit	Ecotoxicological threshold	Threshold value	Guideline
As	mg kg ⁻¹	20	–	5	50
Cd	mg kg ⁻¹	2.0	2.7	1.0	10
Cr	mg kg ⁻¹	–	–	100	200
Cu	mg kg ⁻¹	150	7.1	100	150
Hg	mg kg ⁻¹	1.5	–	0.5	2
Ni	mg kg ⁻¹	112	–	50	100
Pb	mg kg ⁻¹	75	43.6	60	200
Se	mg kg ⁻¹	4	–	–	–
Zn	mg kg ⁻¹	175	17.2	200	250

above 1 (Kaiser's criterion, Fig. 5). The correlations between the three principal components (PC) and the analyzed trace elements are presented in Table 3. Figure 6 shows the vectors obtained for each element. The PC1 presented high positive correlations with Hg and Cu, grouping these elements. The highest negative vectors were for Mn, Cr, Fe, Zn, Al, and Se. The PC2 correlated positively with Ni and Al and negatively with Pb. Finally, PC3 separated As with a negative vector.

The categorical variables obtained from particle size, EC, pH, and altitude data were used as grouping factor to draw confidence ellipses (CI = 68%) around rotated values. Ellipses for each grouping factor are presented in Fig. 6. The ellipses suggest that rotated values are higher when clay content and SOM are also high, reinforcing the idea of a strong correlation between trace elements and SOM and clay. Nevertheless, loam and coarse soil texture classes were not distinguished by the first or the second component, which means that only fine texture (higher percentage of clay) increased rotated values. Similarly, PC1 separated sampling points with different SOM content, although the range was very narrow, as it

was for pH. EC and altitude did not appear to significantly affect rotated values.

3.3 Theoretical distribution functions

Figures 7 and 8 present the theoretical and observed cumulative distribution functions for each element. The fitted distributions and their coefficients are presented in Table 4. The concentration of a given element in the samples from the study area should be in the range of the 2.5 to 97.5 percentiles, with a probability of 95%. Cd, Ni, Pb, Se, and Zn presented lower theoretical ranges than the thresholds established by the Chilean government. As, Cu, and Hg presented ranges 2.5, 1.9, and 4.3 times as high as the critical limits established by the Chilean government. The obtained theoretical distribution functions for each element were used to calculate the probability of obtaining sample values above the thresholds: close to 0 for Cd, Ni, and Se;

Table 2 Minimum, maximum, mean, median, and standard deviation for trace elements measured in soil samples (dry weight basis)

Element	Units	Control samples					Sediment samples					
		Min.	Max.	Mean	Median	SD	Min.	Max.	Mean	Median	SD	<i>p</i> value
Al	g kg ⁻¹	13.9	33.5	24.1	23.9	5.23	12.8	39.1	23.6	23.0	6.07	0.782
As	mg kg ⁻¹	15.4	50.2	31.1	30.4	10.7	12.3	93.1	28.4	23.4	17.6	0.110
Cd	mg kg ⁻¹	<0.20	0.72	0.31	0.24	0.26	<0.20	0.71	0.35	0.32	0.14	0.240
Cr	mg kg ⁻¹	15.1	27.2	21.8	21.2	3.11	13.3	25.3	19.0	19.0	3.16	0.012
Cu	mg kg ⁻¹	51.3	190	87.0	71.6	44.0	37.2	1069	146	83.1	188.7	0.430
Fe	g kg ⁻¹	26.8	36.0	31.7	31.8	2.50	25.4	43.9	34.2	33.8	3.70	0.008
Hg	mg kg ⁻¹	<0.05	5.08	2.17	0.42	10.9	<0.05	10.4	2.66	0.71	9.51	0.441
Mn	mg kg ⁻¹	528	1433	858	768	290	484	1356	787	745	183	0.530
Mo	mg kg ⁻¹	<5.00	<5.00	–	–	–	<5.00	5.01	–	–	–	–
Ni	mg kg ⁻¹	9.35	24.2	18.6	20.1	4.70	6.95	23.5	14.2	13.1	4.45	0.006
Pb	mg kg ⁻¹	10.8	67.6	28.7	23.2	17.5	13.8	60.1	28.5	27.1	10.5	0.649
Se	mg kg ⁻¹	0.31	0.73	0.51	0.50	0.11	0.15	1.00	0.32	0.30	0.11	0.000
Zn	mg kg ⁻¹	62.5	248	126	103	54.7	63.7	368	119	99.2	59.2	0.741

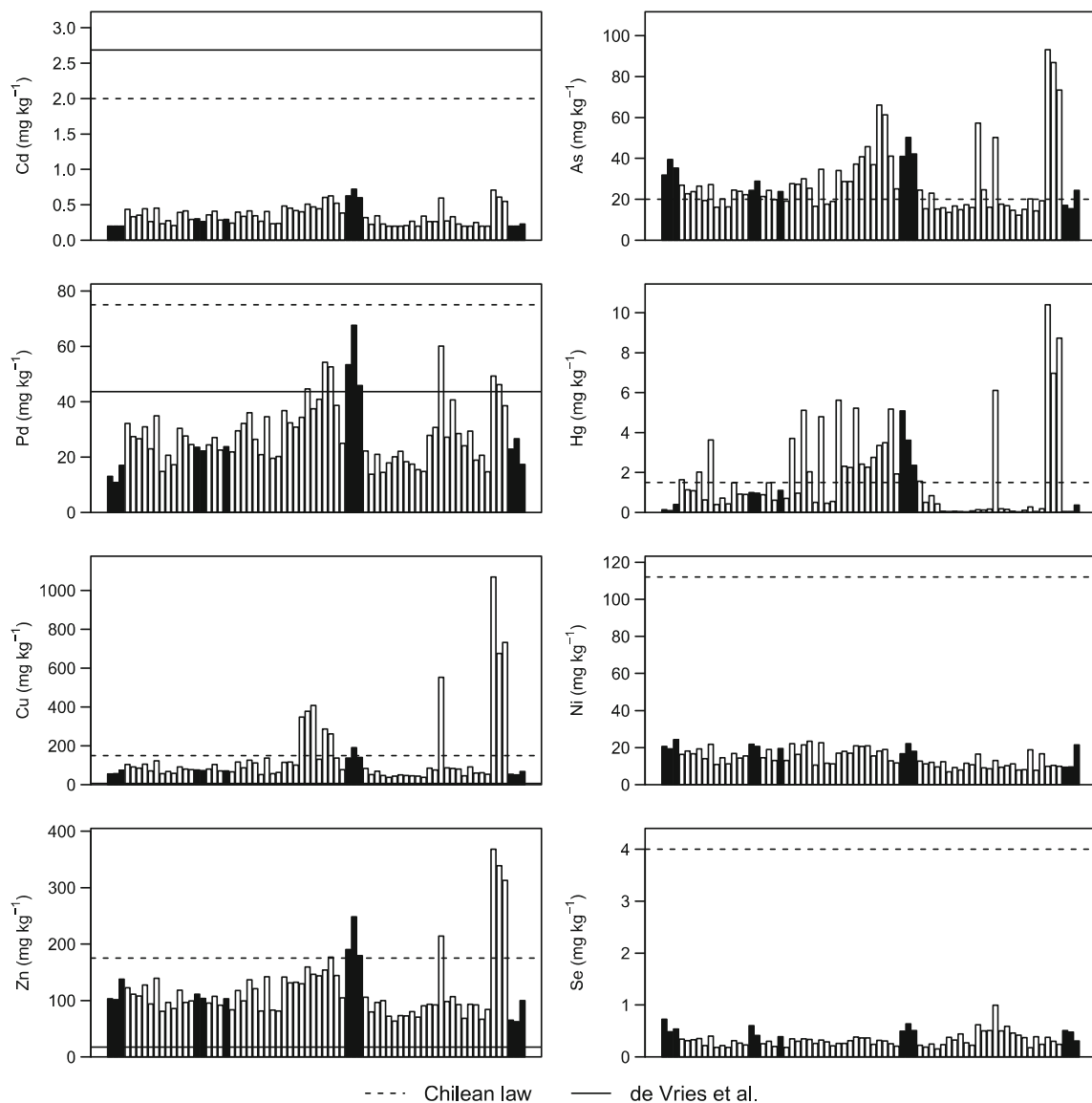


Fig. 2 Observed values of trace element concentrations at each sampling point. *Black and white bars* indicate control and sediment affected sites, respectively. Thresholds limits are indicated according to Chilean law

(*dashed line*) and de Vries et al. (2013) (*solid line*). Detection limits for Cd, Hg, and Se were 0.2, 0.05, and 0.1 mg kg⁻¹, respectively. Sites are organized by increasing altitude on the x-axis

less than 5% for Zn; and 65.2, 18.5, and 29.3% for As, Cu, and Hg, respectively.

3.4 Comparison between control sites and sediments

Table 2 provides statistical information about control and sediment samples. Comparison test results show that there were only differences in concentrations for Cr, Fe, Ni, and Se. Mean Cr concentrations in control samples (21.8 mg kg⁻¹) were higher than in sediments (19.0 mg kg⁻¹). The minimum and maximum Cr concentrations in control soils were higher than those in sediments. The same tendency was observed for Ni and Se. Nickel showed nearly 30% variation in median values

between control and sediment samples, presenting a mean concentration in control sites (18.6 mg kg⁻¹) that was 23% greater than in sediment (14.2 mg kg⁻¹). Selenium presented the greatest differences in medians, with the median in control sites being 40% higher than in sediment samples. Nevertheless, Se contents were generally low, with a maximum value of 1.00 mg kg⁻¹ in a sediment sample. The mean Fe value observed in sediment samples (34.2 g kg⁻¹) was higher than at control sites (31.7 g kg⁻¹). Standard deviations were high in general. Coefficients of variations range from 8% for Fe to 501% for Hg (data not shown). The lowest variations were for Fe, Cr, Ni, and Se. Only Fe and Cr presented variation coefficients of less than 20%.

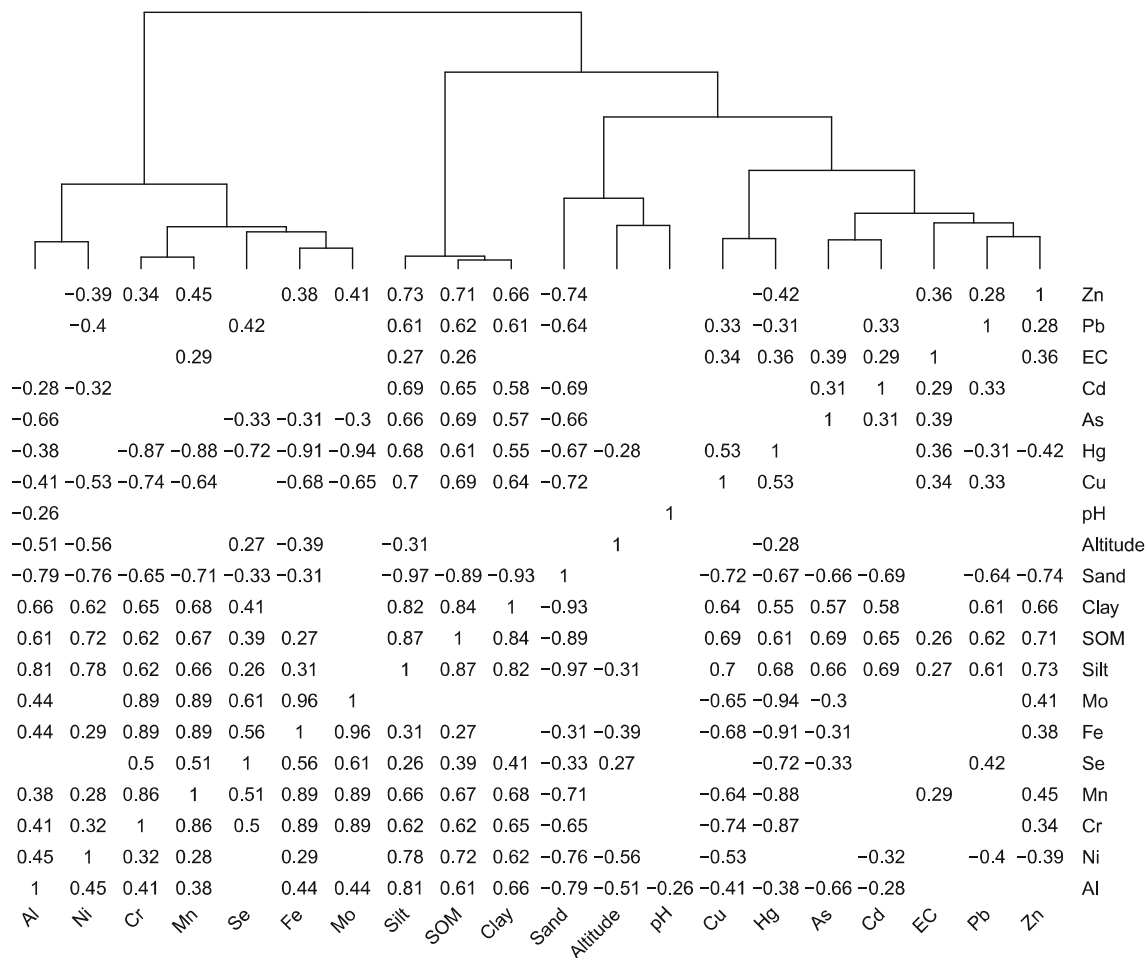


Fig. 3 Spearman correlation between studied variables. Correlations that were nonsignificant at a confidence level of 95% were removed

4 Discussion

4.1 Trace element concentration in Chilean soils

The results show that expected concentration of Cd, Ni, Se, and Mo does not pose the risk of exceeding what are considered critical limits for agricultural areas. This concurs with findings in from other studies in Chile. For example, Hirzel et al. (2016) studied Cd content in Chilean agricultural soils used for wheat production. Although all samples were taken from the southern range of Atacama Region and further south, Cd content in soils was consistently below limits considered critical for agricultural areas. Schalscha and Ahumada (1998) studied Cd, Cu, Zn, Hg, and As concentrations in soils in central Chile and also concluded that Cd concentration were consistently above accepted levels. This coincides with Bonomelli et al. (2003) who reported Cd concentrations of 0.01–0.10 mg kg⁻¹ (dry weight basis) for soils in central Chile. In 1990, INIA (Chilean Agricultural Research Center) developed a baseline for trace element concentration in Chilean topsoils between the Atacama and Bio-Bio regions. For northern Chile, the analysis

focused on the Huasco River Basin. While the basin is located approximately 100 km to the south of Copiapó, it has similar geographic and climatic conditions to those of the Copiapó Basin. Cd content in all 29 soil samples was below the detectable limit (<2.5 mg kg⁻¹ dry weight basis). On the other hand, although there have been no studies of Cd content in soils in the Copiapó Basin, Villarroel et al. (2009) assessed Cd concentrations in dust on roofs in the city of Copiapó and found that all samples were below the detectable limit.

There have been few studies of Se and Mo concentrations in Chilean soils. Pinochet et al. (1999) reported Se concentration from 0.28 to 0.49 mg kg⁻¹ (dry weight basis) for a mining impacted zone near a copper smelter in Valparaiso Region. These values are within the 95% probability range obtained in this study and below the 4 mg kg⁻¹ threshold. High concentrations of Se (up to 800 µg l⁻¹) have been found in the Atacama Desert in groundwater flowing in a copper deposit (Spence), while groundwater upflows have considerably lower Se concentrations (Leybourne and Cameron 2008). Since Se forms anionic compounds in water, there is low retention by clay or SOM in soils. The low retention of

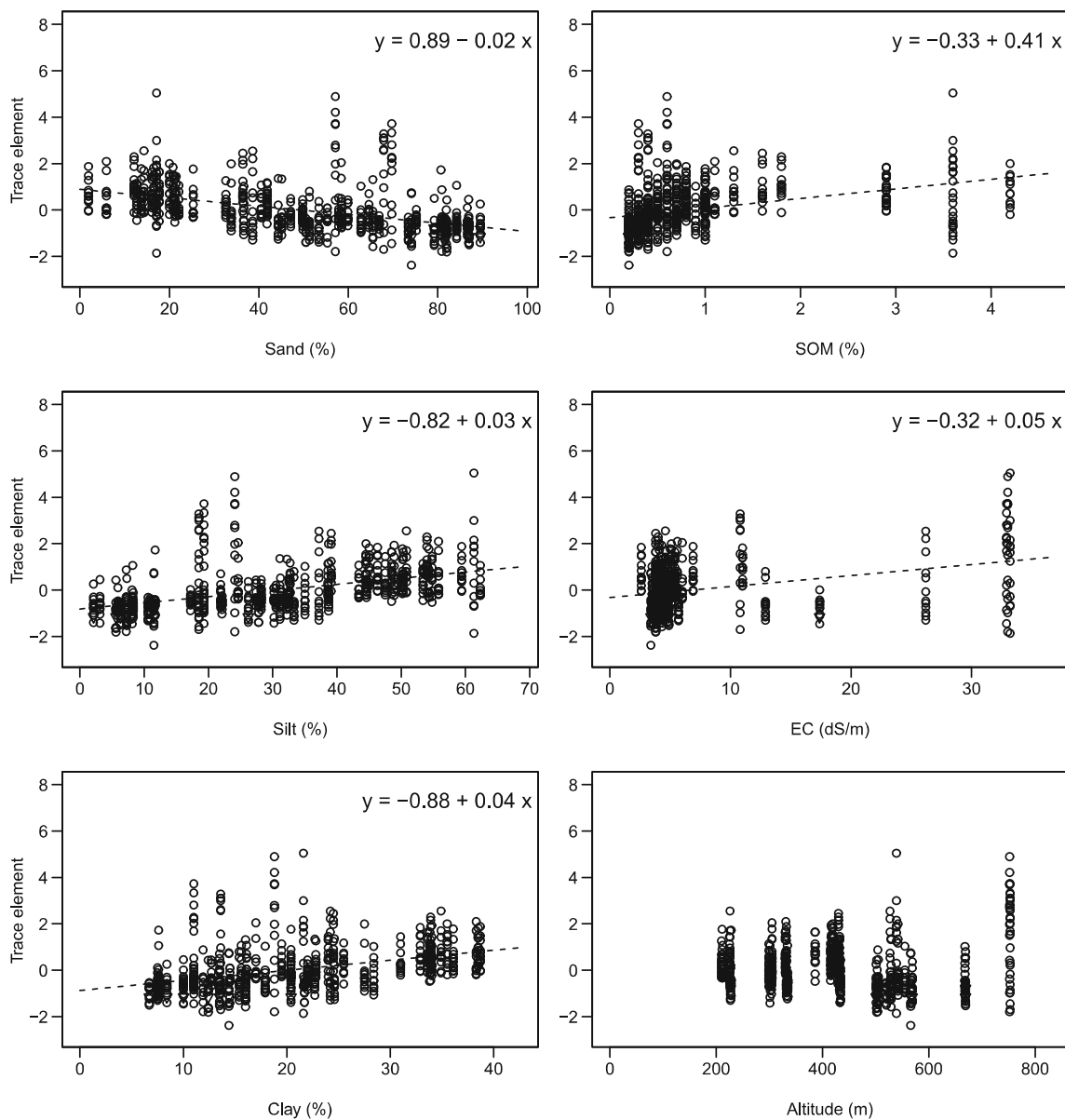


Fig. 4 Trace element content of all element scaled and centered by mean and standard deviation plotted against sand, silt, and clay content and SOM, EC, and altitude. Linear regression is presented according to its significance

Se in soils in northern Chile is due to the permanent electrostatic negative charge in these soils (Calderon et al. 2016). Molybdenum was not detected in any of

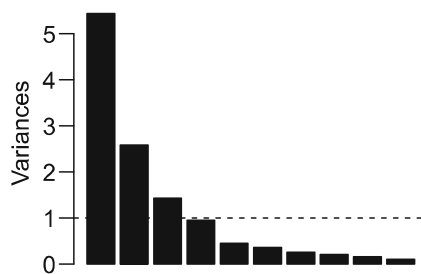


Fig. 5 Scree plot of principal component analysis. PC1 and PC2 were the only ones with variance above 1

the soil samples, which concurs with INIA (1990), which reported Mo in all samples being below detectable concentrations ($<10 \text{ mg kg}^{-1}$).

The concentrations of Pb and Zn were below Chilean maximum limits. Lead concentrations exceeded the critical levels proposed by de Vries et al. (2013) by a few points. The 95% probability range for Pb is between 13 and 50 mg kg^{-1} . These values are higher than those reported by INIA (1990) for the Huasco Basin, which ranged from 10 to 25 mg kg^{-1} with a mean of 15 mg kg^{-1} (dry weight basis). The observed values are low compared to concentrations found in soils in the Valparaiso Region, where Pb concentrations range from 29 to 103 mg kg^{-1} (Muena et al. 2010). In contrast, Zn concentrations were consistently below Chilean thresholds,

Table 3 Correlation between first, second, and third principal components and all analyzed trace elements

Element	PC1	PC2	PC3
Al	-0.70	0.50	0.33
As	-0.85	-0.20	-0.90
Cd	-0.94	-0.10	-0.49
Cr	-0.76	0.22	-0.08
Cu	-0.76	-0.49	0.18
Fe	-0.47	0.67	0.10
Hg	-0.86	-0.06	0.04
Mn	-0.80	0.26	-0.21
Ni	-0.79	0.44	-0.15
Pb	-0.83	-0.38	0.34
Se	-0.27	-0.77	0.07
Zn	-0.94	-0.20	0.14

except in samples from points 67, 68, 69, and 58, and control points 42, 43, and 44. Firstly, points 67, 68, and 69 are located approximately 200 m from a mining dam and thus constitute outliers from the general trend. According to De Gregori et al. (2003), distance from a pollution source is a key factor that determines trace element concentrations in soil. Secondly, point 58 is located near the road from Copiapó to Tierra Amarilla and thus could be affected by factors other than the flood. Thirdly, points 42, 43, and 44 were control site where no sediments were deposited. This suggests that baseline condition represents soil containing significant concentrations of trace elements. INIA (1990) reported Zn soil concentrations between 44 and 140 mg kg⁻¹ (dry weight basis), with a mean of 81 mg kg⁻¹. This range, which is reported for soil in the Huasco Basin, is slightly lower than the 95%

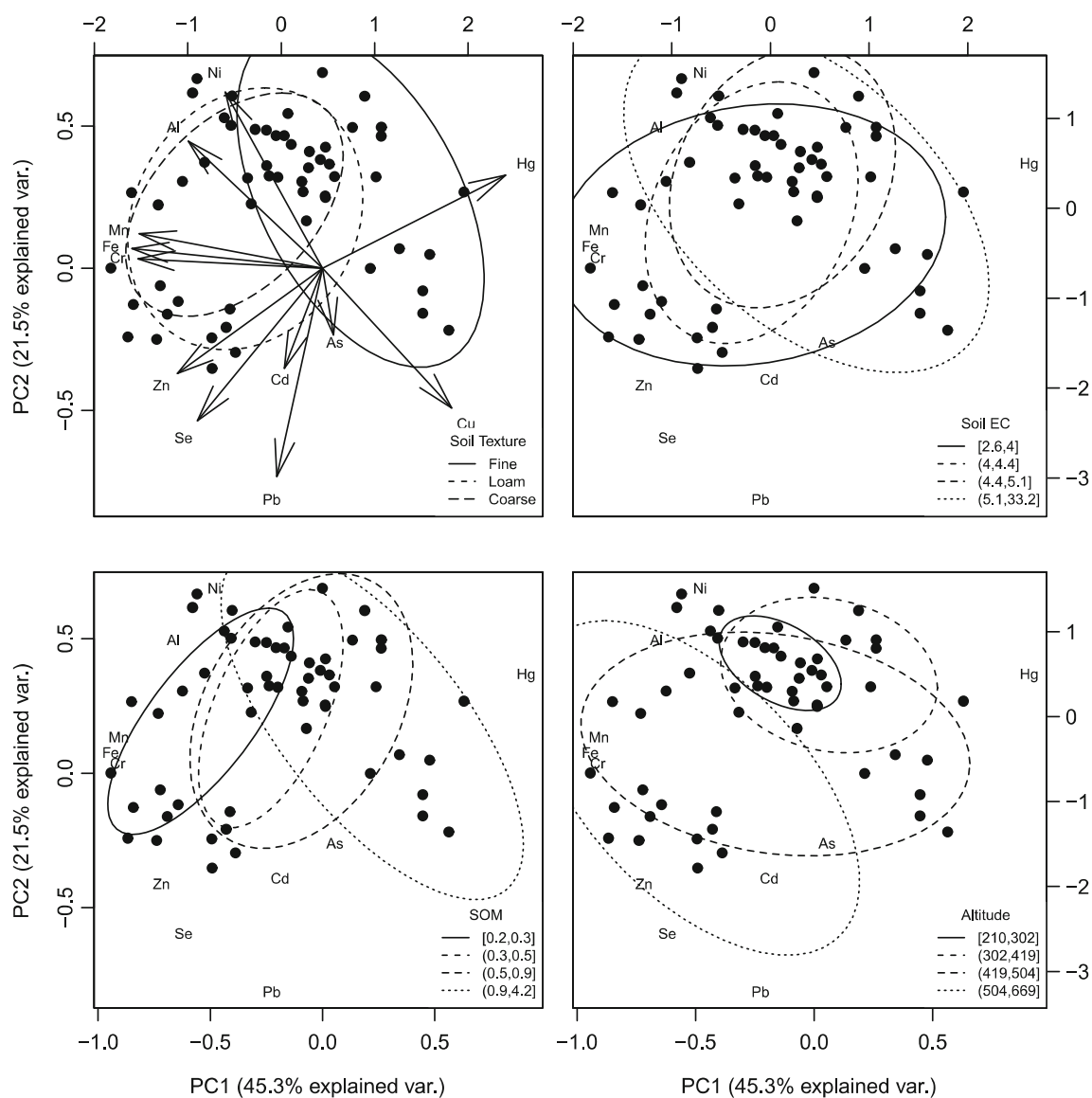


Fig. 6 Rotated PCA data and 68% confidence ellipses. *Soil texture*, *SOM*, *EC*, and *altitude* are presented as grouping factors. The first plot presents loadings for trace element contents and their vectors

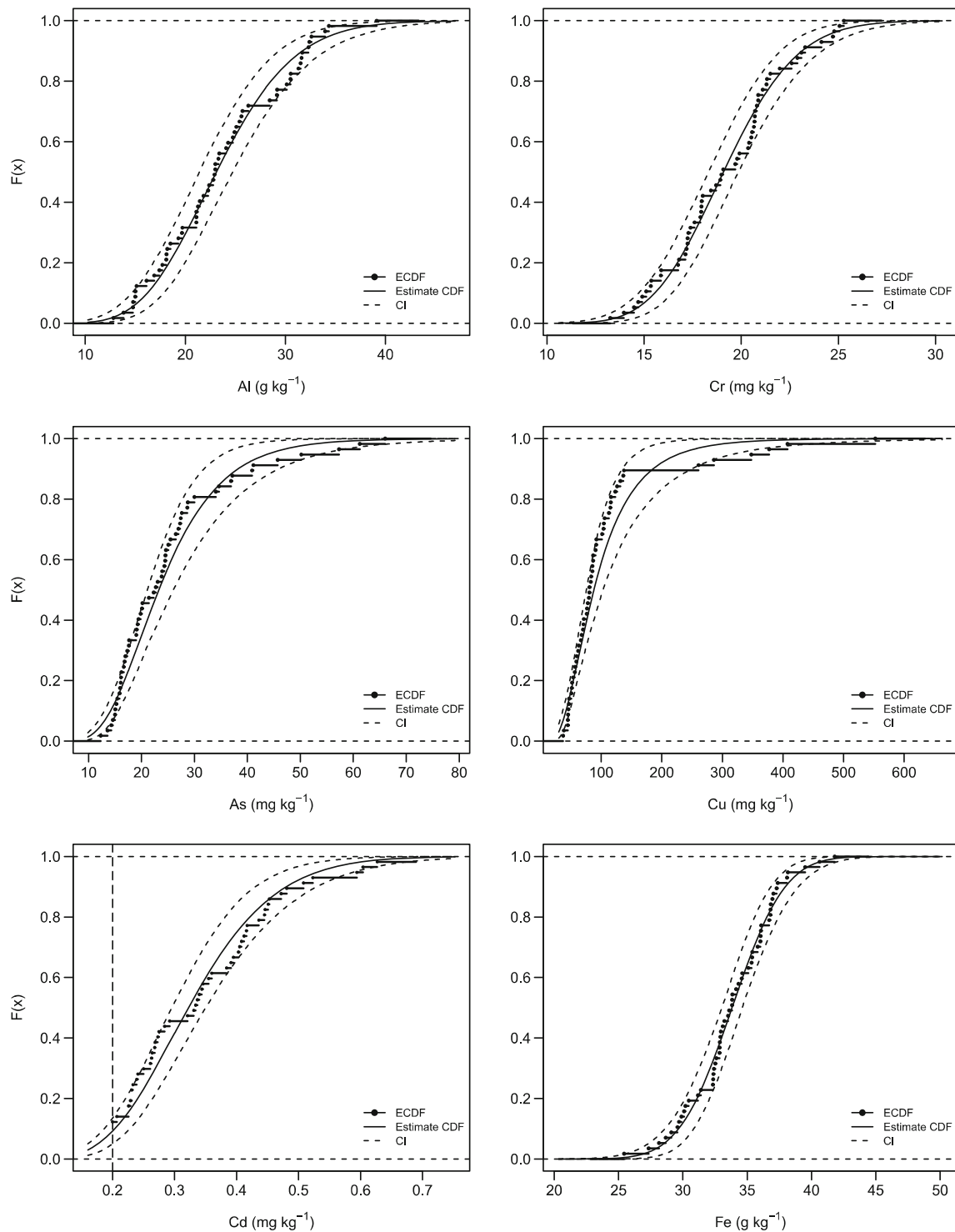


Fig. 7 Empirical (ECDF) and theoretical (estimated) cumulative distribution functions for Al, As, Cd, Cr, Cu, and Fe with 95% confidence intervals

probability range for Zn obtained for the study area (61–172 mg kg⁻¹).

Soil Cu content was consistently above the thresholds of 7.14 mg kg⁻¹ estimated by de Vries et al. (2013). The threshold established by the Chilean government of 150 mg kg⁻¹ is considerably higher than of de Vries et al. The 95%

probability range obtained is from 27 to 281 mg kg⁻¹. Several authors have reported high concentrations of Cu near mining activities: 162–751 mg kg⁻¹ (Badilla-Ohlbaum et al. 2001), 11–530 mg kg⁻¹ (De Gregori et al. 2003), 45–680 mg kg⁻¹ (Ginocchio et al. 2004), and 60–800 mg kg⁻¹ (Muena et al. 2010). The latter is probably the reason the

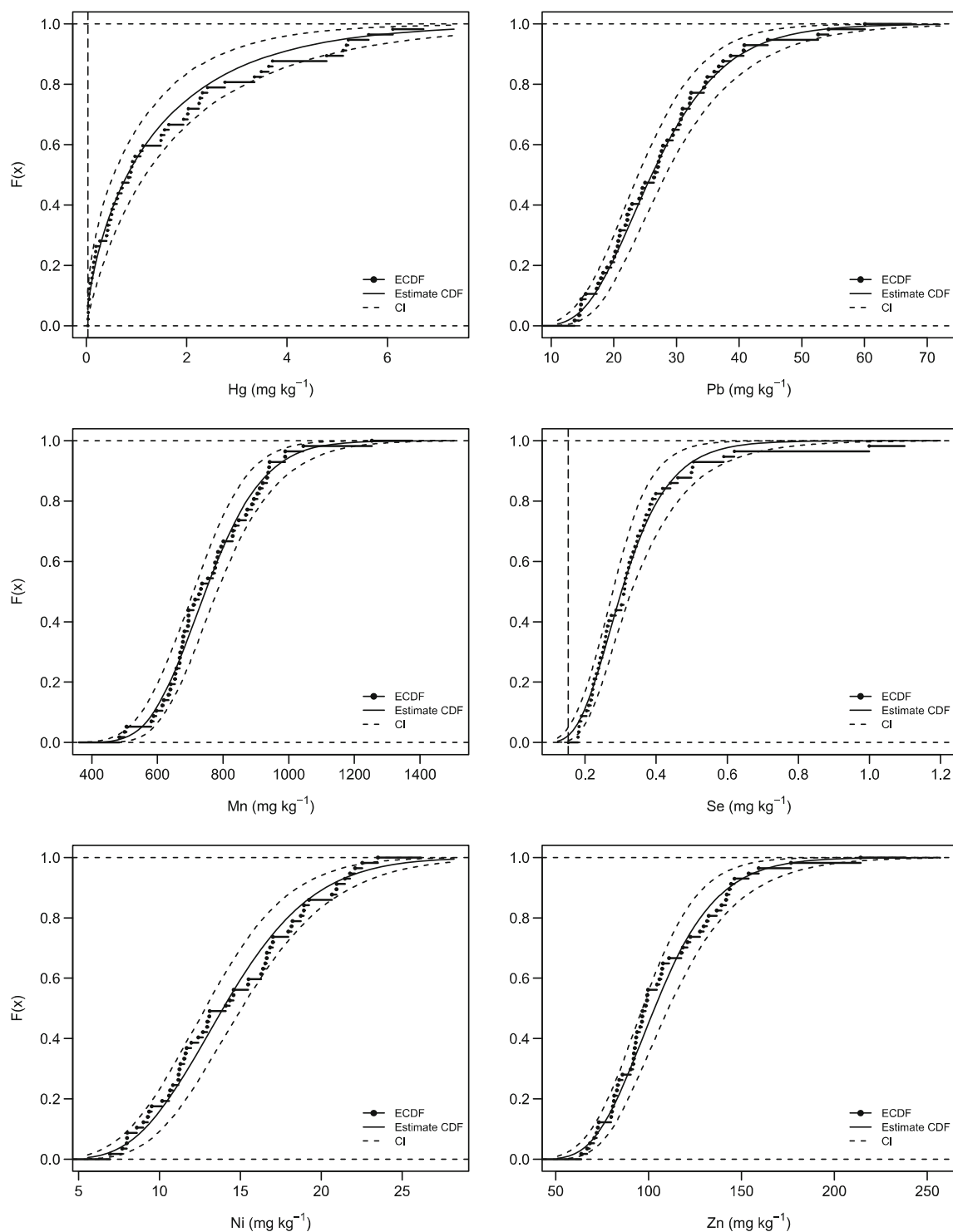


Fig. 8 Empirical (ECDF) and theoretical (estimated) cumulative distribution functions for Hg, Mn, Ni, Pb, Se, and Zn with 95% confidence intervals

government established a higher threshold. However, there is an 18.5% probability of Cu concentrations being over 150 mg kg^{-1} and 10 of 72 samples presented higher values. These samples were from 67, 68, 69, 58, and 43, sites that consistently presented high concentrations of trace elements like Zn, and from points 34, 35, 36, 38, and 39, which are

located within the boundaries of the village of San Fernando. While De Gregori et al. (2003) reported values above 100 mg kg^{-1} for soils in the Antofagasta Region (bordering the Atacama Region to the north), INIA (1990) reported Cu concentrations in samples from the Huasco Basin between 13 and 53 mg kg^{-1} with an average of 31 mg kg^{-1} , which are

Table 4 Distribution fitted, estimates, p value as goodness of fit, percentiles for a 95% probability range (in units according to laboratory analytical methods), critical values according to Chilean DTO-4, mean cumulative probability of obtaining a value beyond the critical value from a sample taken at the study area, and standard deviation of that mean

El.	Dist.	Estimate		p value	Percentiles ^c		C. limit	P-mean	P-sd
		a	b		2.5th	97.5th			
Al	Gamma ^a	14.53	0.61	0.79	13.1	37.2	–	–	–
As	Lognormal ^b	3.15	0.40	0.58	10.7	50.7	20	0.65	0.05
Cd	Gamma	7.33	22.20	0.33	<0.2	0.6	2	<0.01	<0.01
Cr	Gamma	41.46	2.15	0.58	13.8	25.5	–	–	–
Cu	Lognormal	4.48	0.59	0.21	27.7	281.0	150	0.19	0.04
Fe	Normal ^b	33.83	3.26	0.64	27.4	40.2	–	–	–
Hg	Gamma	0.69	0.46	0.44	<0.05	6.5	1.5	0.34	0.05
Mn	Lognormal	6.62	0.19	0.73	516.8	1080.4	–	–	–
Ni	Gamma	10.36	0.72	0.63	7.0	24.4	112	<0.01	<0.01
Pb	Lognormal	3.26	0.34	1.00	13.3	50.9	75	0.01	0.01
Se	Lognormal	–1.19	0.35	0.85	0.2	0.6	4	<0.01	<0.01
Zn	Lognormal	4.64	0.26	0.43	61.8	172.2	175	0.02	0.01

^a A and b estimates correspond to shape and rate, respectively

^b A and b estimates correspond to mean and sd, respectively

^c Percentiles are in grams per kilogram for Al and Fe and in milligrams per kilogram for all other elements

considerably lower than values observed in study or reported in the literature.

As and Hg present the higher probability of exceeding the Chilean standard: 65 and 34%, respectively. Those results are in agreement with the literature. Sancha and Marchetti (2008) made a prospective study of As concentrations in Chile and concluded that the highest As soil and water concentrations are found in the northern part of the country and that the concentrations are generally above levels reported internationally. De Gregori et al. (2003) reported similar results: As concentration in soils in northern Chile greatly exceeded the average concentration reported globally. Concentrations of Hg in soil are considered related to mining activities (Barrios-Guerra 2004). Higuera et al. (2004) studied Hg soil contamination caused by mining dam erosion and general mining activities. They reported soil Hg concentrations between 2.4 and 47 mg kg⁻¹ in soils affected by mining activities in the Coquimbo Region (bordering the Atacama Region to the south). As the study site is strongly influenced by mining activities, high Hg concentration in soils can be expected.

4.2 Comparison with international standards

Trace element concentrations vary widely from region to region (Essington 2015), which is why countries set different standards according to their particular context. Nevertheless, the standards set in Finnish legislation for contaminated soil (Ministry of the Environment—MEF, Finland 2007) have been used by the European Union for trace element evaluation since they present a good approximation of the mean values of different procedures (Carlson et al. 2007; UNEP 2013; Tóth

et al. 2016) and will be used from this point onward in this paper for comparison. Table 1 shows the “threshold values” that indicate when a site needs further study and “guideline values” that are meant to indicate when an area presents ecological or health risks. Although these guideline values are a valuable resource for international comparison, they are much higher than critical Chilean limits. However, these limits are meant for total trace element concentration; thus, they consider slightly more aggressive sample digestion that occurs with *aqua regia* (ISO 1995). Nonetheless, the Finnish threshold values, which were established with the goal of early detection of possibly problematic soils, are stricter than Chilean counterparts. According to these limits, all sites will require further study for As and 43, 34, and 7% of sites require further study for Hg, Cu, and Zn and none for Cd, Cr, Ni, and Pb.

4.3 Trace element behavior

The relationship between SOM and particle size and trace element concentrations is known to be related to soil electrical charge. This was described extensively in Essington (2015) and applied in de Vries et al. (2013). Although pH generally correlates with trace element content, in the present study, this correlation was not observed, probably because of the narrow range of values. Dragović et al. (2008) studied Cd, Cr, Cu, Mn, Ni, Pb, and Zn relationships with soil characteristics and found positive correlations with organic matter and clay content but not with pH for most of elements analyzed.

The correlation and the principal component analysis indicated three groups of elements with similar behaviors: (1) Cu and Hg; (2) As and Cd; (3) Al and Ni; (4) Cr, Fe, Mn, and Se;

and (5) Pb and Zn. Copper and Hg have been related to and are known to be located near mining/industrial activities (Badilla-Ohlbaum et al. 2001; Barrios-Guerra 2004; Higuera et al. 2004). In fact, samples with high Cu and Hg concentrations were taken from sampling points near mining dams. For example, the last three sediment samples (white bars) in Fig. 2, left to right, were taken within a radius of 500 m of a mining dam.

Zinc and Pb concentrations correlated with Cu and Hg, which suggests that soil concentration of these elements are partially due to by anthropogenic activities. The same applies to As and Cd, although concentrations did not correlated to any other evaluated element. Arsenic concentration in soil was high according to both Finnish and Chilean standards. Although the findings of de Gregori et al. (2003) suggest that As levels in Chilean soil are above international standards, major variations were observed in this study for Copiapó Valley (CV = 62%). Thus, a more detailed survey is suggested. Cadmium concentrations were related to As, but all observed values were below Chilean and Finnish limits, suggesting that for the moment Cd concentrations are not a matter of concern.

Another fact that connects the groups of Cu, Hg, As, Cd, Pb, and Zn is that all these elements presented high standard deviations with respect to their means. Recalling the conclusion of de Gregori et al. (2003) that the distance from a pollution source is key to determining trace element concentrations in soil, it can be assumed that in a survey that covers a wide area in which mining/industrial activities are randomly located, elements closely linked to mining will present wide variation. On the other hand, Al, Ni, Cr, Fe, Mn, and Se showed low standard deviations with respect to their means, suggesting lithogenic origin, which concurs with the findings of Dragović et al. (2008).

Comparisons of trace elements in control sites and in sediment concentrations showed no differences for anthropogenically related elements, which could be due to the high degree of variation among samples. The differences observed for Cr, Fe, Ni, and Se were statistically significant, but the differences in mean and median concentrations were low compared to threshold concentration.

Altitude was not a good predictor of trace element content. The purpose of including altitude as an independent variable was to understand if there was a significant translocation of trace elements during sediment transport. The absence of a relationship between this variable and trace element content, the observed low spatial influence of mining activities on the concentrations of trace elements of anthropogenic origin, and the lack of difference between control sites and sediments samples suggest that sediment transport of trace element has a short spatial range of influence.

5 Conclusions

Trace element contents in sediments deposited by debris flows in the studied area were within expected values. Concentrations of total Cd, Se, Zn, Ni, and Pb were below Chilean maximum limits, while As, Cu, and Hg concentrations were above the limits. Mo levels were consistently below detectable levels, so finer methodologies need to be used to make an adequate determination. There was a correlation between SOM and sediment particle size. There could be an influence of mining dams/activities on trace element concentrations in soil, but further studies are needed with finer grid sampling, particularly with elements that are associated with anthropogenic activities (Cu, Hg, As, Cd, Pb, and Zn). Our findings suggest that sediment transportation of trace element associated with the event of March 24–25, 2015 had a short range of influence. Accordingly, soils in the Copiapó Valley show no addition or dilution of trace element concentration. Finally, this study is proposed as a preliminary baseline of trace element content for an agricultural area in the hyper-arid region of northern Chile frequently exposed to sediment-laden floods.

Acknowledgements The authors thank Regina Ite, Francisco Casado, and Raúl Eguluz for their indispensable help in sampling and laboratory analysis.

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