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Arsenic and trace elements in soil, water, grapevine and onion in Jáchal, Argentina

Iván Funes Pinter^{a,*}, M. Victoria Salomon^a, Raúl Gil^b, Leandro Mastrantonio^c, Rubén Bottini^a, Patricia Piccoli^a

^a Instituto de Biología Agrícola de Mendoza (IBAM, CONICET-UNCuyo), Almirante Brown 500, M5528AHB Chacras de Coria, Argentina

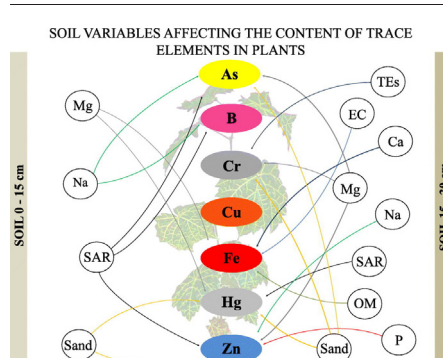
^b Instituto de Química de San Luis (INQUISAL, CONICET-UNSL), Chacabuco y Pedemera, D5700HOI San Luis, Argentina

^c Cátedra de Edafología, Facultad de Ciencias Agrarias, UNCuyo, Almirante Brown 500, M5528AHB Chacras de Coria, Argentina

HIGHLIGHTS

- In soils and water of Jáchal, high levels of trace elements were detected.
- In grapevine and onion, As, Cr, Cu, Fe and Zn exceeded limits established by law.
- Correlation analyses suggested a common source of potentially toxic metals.
- Soils characteristics enhance trace elements mobility.

GRAPHICAL ABSTRACT



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ABSTRACT

Contamination by trace elements (TE) is an increasing concern worldwide. In some areas, crop production could be limited by the presence of metals and metalloids, so it is important to determine their concentrations and mobility. The region of Jáchal, province of San Juan, Argentina, has good growing conditions for onion and grapevine production, but their quality and yield are affected by high TE concentration in soils and water. Soils, water, grapevine and onion were sampled and TE content determined. In soils elevated As, B, Cr, Hg, and Tl concentrations were detected (506 ± 46 , 149 ± 3 , 2714 ± 217 , 16 ± 7 , and $12 \pm 3 \mu\text{g g}^{-1}$, respectively, for maximum values measured), and physicochemical properties of the soil promotes these elements mobility. Water samples had high As, B, Cr, and Fe concentrations (1438 ± 400 , $10,871 \pm 471$, $11,516 \pm 2363$, and $3071 \pm 257 \mu\text{g L}^{-1}$, respectively, for maximum values measured) while in onion bulbs and grapevine berries, As, Cr, Cu, and Fe (92 ± 7 and 171 ± 20 , 1412 ± 18 and 2965 ± 32 , 17 ± 3 and 126 ± 88 , and 418 ± 204 and $377 \pm 213 \mu\text{g g}^{-1}$, respectively, for maximum values measured) exceeded the limits for food consumption established by Argentinian law. Correlation analyses indicated that: i) there is a common source of TE in this area, ii) each elements concentration in plants is associated with different soil variables and different soils depths, and iii) the lack of correlation between soil and water indicates that concentration in water is not constant over the time and/or there exists a differential accumulation of elements in soils depending on their own properties. Data obtained demonstrate very high concentration of TE in soil, grapevines, and onion plants in Jáchal region, and different remediation techniques are necessary to stabilize and minimize the bioavailability of these elements.

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* Corresponding author.

E-mail addresses: ifunespinter@fca.uncu.edu.ar (I. Funes Pinter), msalomon@fca.uncu.edu.ar (M.V. Salomon), ragil@unsl.edu.ar (R. Gil), lmastra@uncu.edu.ar (L. Mastrantonio), rbottini@fca.uncu.edu.ar (R. Bottini), ppiccoli@fca.uncu.edu.ar (P. Piccoli).

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1. Introduction

Concerns regarding contamination by trace elements (TE) has been increasing worldwide. Many studies have reported high concentration of metals and metalloids in diverse matrices, i.e. atmosphere, soil, water, and organisms, and sources are natural and anthropogenic. Although many environmental problems are products of natural mobilization of these elements, such as weathering reactions, biological activity, volcanic emissions, rocks solubilization, etc., direct and indirect anthropogenic activity are important to consider. TE are directly released due to mining, use of pesticides, fertilizers, fossil fuels, color glass, and wood preservatives (Ferguson and Gavis, 1972; Smedley et al., 2002). Indirect anthropogenic effects occur due to influences on solubility and availability through land use change.

The mobility of TE in soils is complex and responds to many different factors. In general, retention increases with soil pH, organic matter (OM), and clay content (ion exchange capacity), and diminishes with soil electrical conductivity (EC). De Matos et al. (2001) observed that Zn mobility was affected mainly by cation exchange capacity (CEC), and also, that the retention of Cu and Pb was correlated with OM content, showing that soil complexity plays an important role in TE immobilization. Metal oxides present in the soil (Fe, Al, and Mn) are the most common sorbent species, principally for As. But, while Fe-oxides adsorb As, they could increase mobility of Pb and Cd as well (Hartley et al., 2004). Also at high pH As bonds less than at low pH (Ferguson and Gavis, 1972; Frost and Griffin, 1976), contrary to the effect of others elements such as Cu and Zn. OM plays an important role in TE retention; the mobility of Hg is highly affected by humic mater and sulfides (Boszke et al., 2008), but for Cu and Pb, Harter (1979) found no significant relationship between OM and adsorption. Based on available information, TE mobility in soils depends on many factors, chemical properties and species, climate, biological activity, and their interactions. This indicates that predictions of mobility and bioavailability of TE is complicated and a single remediation technique may not be sufficient for removal or stabilization; that is while one soil factor could increase retention of one element, it may improve the mobility of another.

The limits of TE concentrations established by governmental policies vary depending on the regions, the environments, and the possible use of the soil and/or water. Argentina has several environment laws that establish limits of TE, but in some cases they overlap. The provisional guideline value of the World Health Organization (WHO, 2006) for total As in drinking water is $10 \mu\text{g L}^{-1}$, which was adopted since 2007 by the Argentinian Alimentary Code (CAA, Código Alimentario Argentino, Administración Nacional de Medicamentos, Alimentos y Tecnología Médica, <http://www.anmat.gov.ar/>). CAA also establishes limits for different TE in drinking water that overlap with those established by other Argentinian laws for dangerous residues (Ley 24.051 Residuos Peligrosos).

In Argentina, there are fewer studies of TE content in soil than in water. Some authors reported high As contents in groundwater of Chaco-pampean and Cuyo regions (Nicolli et al., 2012; Sigrist et al., 2013; Smedley et al., 2002). In the Cuyo region, water samples from Río Jáchal (San José de Jáchal, San Juan) contain total As and B concentrations up to $357 \mu\text{g L}^{-1}$ and 3.92 mg L^{-1} respectively, and As^{III} is the predominant species (O'Reilly et al., 2010). However, there are no reports of TE content in soils and plants, despite of high concentration found in water. Moreover, Jáchal is an arid zone, and as such, it has elevated soil salinity, low OM, and clay content (Adamo and Crews-Meyer, 2006; Karlin et al., 2015; Suvires, 2004), conditions that favor TE mobility.

Several studies have reported high TE content in grapevine and wines limiting yield, quality, and even more being a serious risk to human health (Komárek et al., 2010; Mirlean et al., 2005, 2007; Volpe et al., 2009). According to the Instituto Nacional de Tecnología Agropecuaria (INTA; <http://www.inta.gov.ar/>), Jáchal has exceptional conditions for high quality grapevine production, but culture expansion

is difficult due to the TE content in soils and water. Río Jáchal is the main water source in the area, used mainly for onion and grapevine irrigation, although there is a second water source called Huaco from a small dam that collects rain overflow or in some cases is filled up with Río Jáchal water.

Based on the concentrations of As and B reported for water, we hypothesized that vegetable concentrations would also be harmful, and could potentially impact human health. The processes of accumulation and desorption of TE in soils are complex, and different mobility under different conditions will influence plant intake, accumulation, and quality of the cultures. Therefore, the objective of the present study was to determine the content of As and TE in soils (TEs), water (TEw), grapevine (TEg) and onion (TEo) cultured in the Jáchal region, and the main edaphic conditions that affect the bioavailability of these elements.

2. Methods

2.1. Collection of soil and water samples

All samples were collected in triplicate from sites of Jáchal, San Juan, Argentina (Fig. 1) during grape harvest season (March 2015). Soil samples were collected at two depths: 0–15 and 15–30 cm (indicated as a sub-index ₁₅ and ₃₀ respectively in each variable measured), at 11 different sites: 8 irrigated by Río Jáchal: 1- Cuesta del Viento (J1, a dam in Jáchal river at the beginning of the agricultural area), 2- Pachinoca vineyard (J2v, 20 km downstream of Cuesta del Viento dam), 3- Pachinoca uncultured soil (J3), 4 and 5- onion fields in La Falda (J4o and J5o, located in Jáchal downtown), 6- La Falda vineyard (J6v), 7- Otra Banda vineyard (J7v), and 8- Río Jáchal Sur (J8, located 70 km downstream of Cuesta del Viento dam); and 3 irrigated by Río Huaco: 1- La Ciénaga vineyard (H1v, cultured soil located 6 km before Huaco town), 2- La Ciénaga uncultured soil (H2), and 3- Huaco vineyard (H3v, located in Huaco downtown). Samples were stored in plastic bags at 4 °C until drying and acid digestion.

Irrigation water samples were collected by triplicate in 50 mL tubes and stored at 4 °C from 6 sites irrigated by Río Huaco (H3v and H2) and Río Jáchal (J1, J6v, J2v and J8).

2.2. Soil physicochemical analysis

Each sample was granulometrically characterized by Bouyoucos (1962) method. EC in saturated paste extract and pH in saturated soil paste were measured according to Richards (1954). Soluble Ca and Mg were determined by titulation with versenate, while Na and K were assessed by flame photometer in saturation extract (Cheng and Bray, 1951); Sodium Adsorption Ratio (SAR) was calculated in base to the formula:

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{\frac{\text{Ca}^{+2} + \text{Mg}^{+2}}{2}}}$$

OM content was analyzed following Walkley and Black (1934) protocol, and available P was colorimetrically determined according to McGeorge and Breazeale (1931).

2.3. Collection of plant samples

Berries, apical and basal leaves of *Vitis vinifera* L. plants were collected from three plants of each vineyard where soil samples were taken (J2v, J6v, J7v, H1v and H3v). Also onion (*Allium cepa*) bulbs and leaves irrigated by Río Jáchal, were collected by triplicate from onion fields (J4o and J5o). The samples were stored at $-20 \text{ }^\circ\text{C}$, until drying, and acid digestion.

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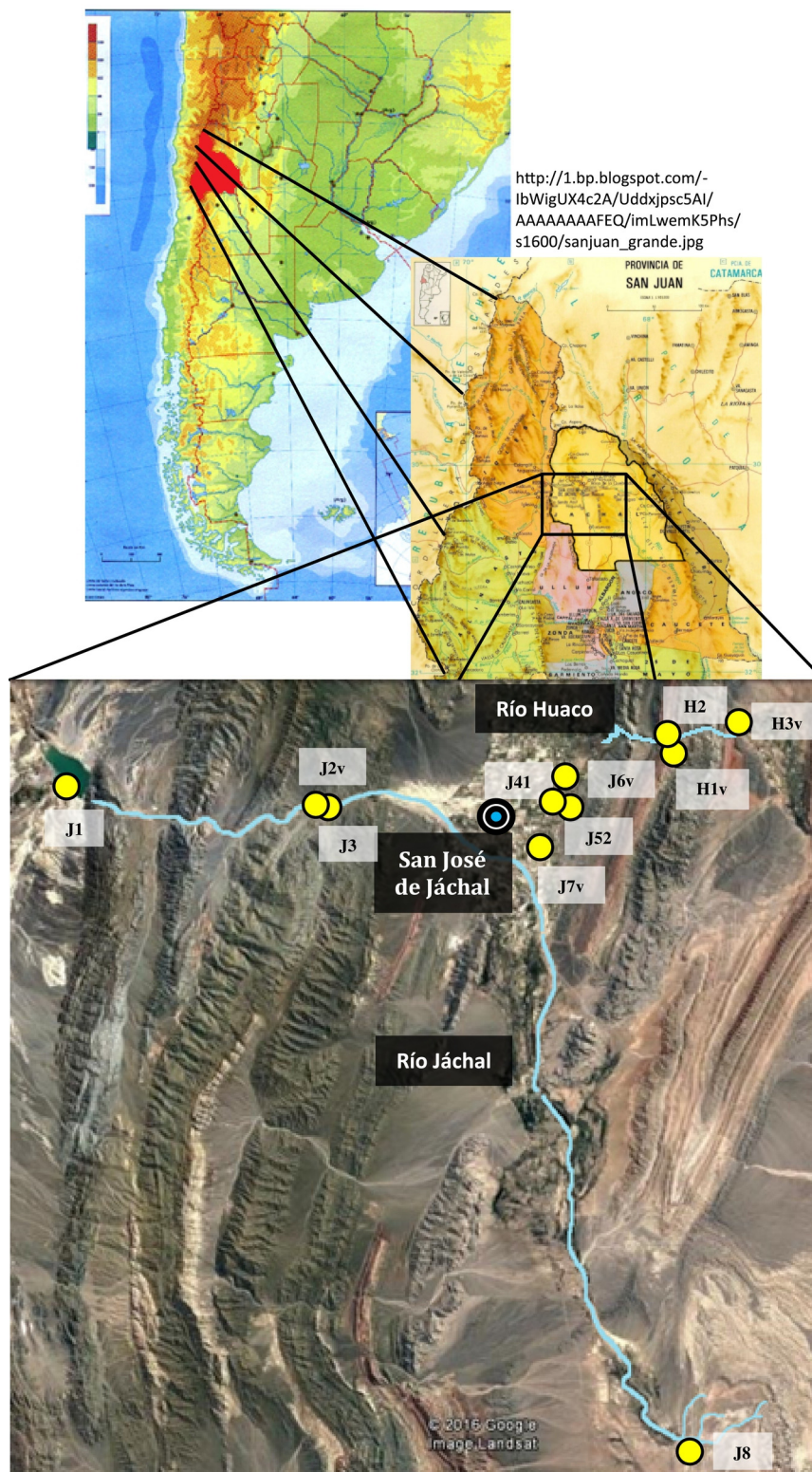


Fig. 1. Study area and sampling sites indicated by yellow circles, located in San José de Jáchal, San Juan, Argentina. Sites: J1: Cuesta del Viento; J2v: Pachinoca vineyard; J3: Pachinoca; J40 and J50: La Falda onion fields; J6v: La Falda vineyard; J7v: Otra Banda vineyard; J8: Río Jáchal Sur; H1v: La Ciénaga vineyard; H2: La Ciénaga; and H3v: Huaco vineyard. Image Landsat/Copernicus Google Earth. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.4. Acid digestion and elemental determination

Plant material was dried at 60 °C during 48 h in a ventilated oven and grounded with pestle and mortar; soil samples were dried in open air. The following protocol, developed in our laboratory, was used for both

soil and plant samples: 0.1 g of sample was placed in 15 mL Falcon tube, 1.5 mL 65% HNO₃, 0.5 mL HCl 37% and 0.5 mL 65% HClO₄ were added and vortexed 15 s. When the reaction was stopped, 100 µL H₂O₂ (30 vol%) were added and sonicated at 60 °C during 15 min, cooled at room temperature, then 200 µL H₂O₂ was added and again vortexed

15 s. A microwave digestion was carried out for 30 s at maximum potency (600 W). Finally, 200 μL H_2O_2 was added, and samples were sonicated at 60 °C for 30 min, and then centrifuged 10 min at 4000 rpm and 10 °C. The supernatant was collected and diluted in ultrapure water (18.2 M Ω ·cm) for elemental analysis. Water samples were only centrifuged and diluted in ultrapure water.

Thirteen elements were analyzed: Ag, As, Ba, B, Cr, Cu, Fe, Hg, Mn, Pb, Se, Tl and Zn. A 1:20 dilution was required to analyze by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with a PerkinElmer SCIEX, ELAN DRC-e (Thornhill, Canada) equipment. Argon with a purity of 99.99% was supplied by Air Liquid S.A. (Córdoba, Argentina). HF-resistant and high performance perfluoracetate (PFA) nebulizer model PFA-ST, coupled to a quartz cyclonic spray chamber with an internal baffle and drain line, cooled with the PC3 system from ESI (Omaha - NE, USA), Tygon black/black peristaltic pump tubing of 40 cm length and 0.76 mm i.d. was used. Instrumental calibration was carried out by double charged ($\text{B}^{++}/\text{Ba}^{+}$) and oxide ions ($\text{CeO}^{+}/\text{Ce}^{+}$) levels evaluation that should not be higher than 3%; instrumental sensitivity was monitored for Mg, In and U. On the other hand, method calibration was carried out through external calibration with acidified (1% v v⁻¹ HNO_3) aqueous standards. Both procedures were done with commercial standards purchased from Perkin Elmer (PerkinElmer® Pure Plus Atomic Spectroscopy multi-element standard solutions 1, 2, 3, 4 and 5; and Ba and Ce ELAN® 6100 DRC™ Setup/Stab/Masscal Solution. PerkinElmer, Inc., Shelton, CT USA). See Table A1 for instrument settings and data acquisition parameters for ICP-MS.

2.5. Statistical analysis

To determine association between the TE in soil, water and plant tissues, Pearson's correlation coefficient were calculated using Software InfoStat (Di Rienzo et al., 2011). Five correlation analyses were carried out: TEs versus TEw; each TEg, versus TES, TEw, and soil physicochemical parameters; each TEO versus, TEw, TES and soil physicochemical parameters; each TEg versus all TES; each TEO versus all TES. Only results of TE above Argentinian legal limits are showed in correlation analyses.

Table 1
Physicochemical analyses in soil samples at two depths (0–15 and 15–30 cm) in sites from Jáchal, San Juan, Argentina. EC: Electrical conductivity; SAR: Sodium Adsorption Ratio; OM: Organic Matter. Sites: J1: Cuesta del Viento; J2v: Pachinoca vineyard; J3: Pachinoca; J4o and J5o: La Falda onion fields; J6v: La Falda vineyard; J7v: Otra Banda vineyard; J8: Río Jáchal Sur; H1v: La Ciénaga vineyard; H2: La Ciénaga; and H3v: Huaco vineyard.

Site	Depth (cm)	pH Paste	EC ($\mu\text{S cm}^{-1}$)	Ca^{+2} (meq L ⁻¹)	Mg^{+2} (meq L ⁻¹)	Na^{+} (meq L ⁻¹)	K^{+} (meq L ⁻¹)	P ($\mu\text{g g}^{-1}$)	SAR	OM (% g g ⁻¹)	Texture	Coord (UTM)	
												X	Y
J1	0–15	7.80 ± 0.03	5487 ± 339	15.7 ± 2.2	5.3 ± 0.9	46.7 ± 5.0	2.2 ± 0.5	1.1 ± 0.7	14.4 ± 1.1	0.4 ± 0.1	Sandy loam	19S492209	6,659,510
	15–30	7.80 ± 0.08	6387 ± 400	9.0 ± 5.6	14.0 ± 5.0	44.2 ± 10.7	1.9 ± 0.2	1.8 ± 0.5	12.7 ± 2.2	0.5 ± 0.2	Clay loam		
J2v	0–15	7.60 ± 0.08	2227 ± 283	8.7 ± 2.0	5.0 ± 1.0	10.1 ± 4.8	1.6 ± 0.7	1.3 ± 0.5	3.6 ± 1.6	4.1 ± 0.4	Sandy loam	19S512411	6,658,739
	15–30	7.51 ± 0.02	2280 ± 168	7.5 ± 0.4	3.9 ± 2.1	13.0 ± 1.7	1.6 ± 0.6	2.5 ± 1.3	5.5 ± 0.7	4.2 ± 0.1	Sandy loam		
J3	0–15	7.63 ± 0.13	21,952 ± 1676	109.3 ± 30.4	67.3 ± 16.5	237.3 ± 94.3	9.2 ± 2.5	2.2 ± 0.4	28.1 ± 12.8	1.0 ± 0.3	Sandy loam	19S512899	6,658,550
	15–30	7.72 ± 0.10	17,189 ± 1252	73.3 ± 20.8	42.7 ± 4.4	186.6 ± 57.2	7.5 ± 1.3	1.1 ± 0.1	26.1 ± 9.9	0.6 ± 0.1	Sandy loam		
J4o	0–15	7.76 ± 0.05	5100 ± 1102	15.0 ± 3.5	8.0 ± 1.5	31.5 ± 6.6	2.7 ± 0.2	1.5 ± 0.1	9.3 ± 1.3	2.0 ± 0.1	Loam	19S531486	6,659,454
	15–30	7.84 ± 0.07	3443 ± 572	16.3 ± 2.3	8.0 ± 2.5	21.0 ± 2.6	2.1 ± 0.4	1.9 ± 1.0	6.2 ± 1.0	1.8 ± 0.1	Sandy loam		
J5o	0–15	7.86 ± 0.04	5640 ± 964	22.7 ± 4.4	9.0 ± 1.7	30.8 ± 4.0	2.5 ± 0.1	2.0 ± 0.4	7.8 ± 0.4	2.7 ± 0.4	Sandy loam	19S532029	6,661,518
	15–30	7.81 ± 0.07	4477 ± 956	20.0 ± 4.4	11.3 ± 2.9	22.8 ± 2.3	2.5 ± 0.3	1.2 ± 0.3	5.8 ± 0.2	2.0 ± 0.1	Loam		
J6v	0–15	7.63 ± 0.02	1537 ± 100	5.3 ± 0.7	2.5 ± 0.7	8.3 ± 0.7	1.3 ± 0.3	4.1 ± 1.4	4.2 ± 0.3	3.8 ± 1.0	Loam	19S532195	6,659,199
	15–30	7.67 ± 0.02	1410 ± 155	4.5 ± 0.3	1.7 ± 0.6	8.3 ± 2.0	1.3 ± 0.3	1.5 ± 0.8	4.7 ± 1.1	2.3 ± 0.4	Sandy loam		
J7v	0–15	7.73 ± 0.02	2230 ± 397	7.0 ± 2.6	3.0 ± 0.6	11.9 ± 1.7	1.2 ± 0.2	2.2 ± 0.6	5.5 ± 0.7	3.7 ± 0.2	Clay loam	19S530170	6,655,955
	15–30	7.69 ± 0.08	2433 ± 205	7.3 ± 1.5	1.0 ± 1.2	4.3 ± 1.9	1.0 ± 0.1	2.2 ± 0.7	2.3 ± 0.9	2.9 ± 0.3	Clay loam		
J8	0–15	7.86 ± 0.16	26,984 ± 1587	98.7 ± 23.9	39.7 ± 8.9	375.0 ± 52.2	3.3 ± 0.4	3.7 ± 2.9	45.8 ± 1.8	0.4 ± 0.1	Sandy loam	19S543496	6,607,288
	15–30	8.00 ± 0.03	24,012 ± 378	66.7 ± 9.6	26.7 ± 1.2	286.6 ± 17.0	5.1 ± 1.2	0.6 ± 0.2	42.1 ± 2.1	0.3 ± 0.1	Sandy loam		
H1v	0–15	7.78 ± 0.11	1763 ± 149	8.8 ± 0.8	6.4 ± 2.4	11.6 ± 3.2	3.1 ± 0.9	2.9 ± 1.3	4.4 ± 1.5	4.1 ± 0.4	Loamy sand	19S540668	6,664,379
	15–30	7.62 ± 0.07	2540 ± 581	11.8 ± 2.7	6.5 ± 0.7	12.0 ± 5.6	2.4 ± 0.7	2.0 ± 1.0	3.7 ± 1.6	5.2 ± 0.3	Loamy sand		
H2	0–15	7.46 ± 0.10	7493 ± 878	38.7 ± 3.3	19.3 ± 2.3	38.8 ± 4.5	2.9 ± 0.6	0.7 ± 0.4	7.2 ± 0.6	1.2 ± 0.1	Loamy sand	19S540076	6,664,842
	15–30	7.79 ± 0.14	3473 ± 777	17.7 ± 6.4	9.7 ± 2.8	15.2 ± 2.7	1.4 ± 0.3	1.9 ± 1.3	4.5 ± 0.8	0.5 ± 0.2	Loamy sand		
H3v	0–15	7.85 ± 0.07	2755 ± 1155	7.6 ± 2.4	7.2 ± 2.8	14.7 ± 7.1	0.6 ± 0.1	1.8 ± 0.8	5.2 ± 1.7	1.4 ± 0.2	Sandy loam	19S546176	6,666,081
	15–30	7.81 ± 0.01	1985 ± 95	5.7 ± 0.7	6.6 ± 0.6	12.5 ± 0.5	1.4 ± 0.6	1.0 ± 0.2	5.1 ± 0.1	1.1 ± 0.2	Sandy loam		

3. Results

3.1. Soil physicochemical analyses

Soil texture analyses indicated, in general, that sand is the main component of soils in Jáchal region (Table 1). However, J4o, J5o, and J6v samples were associated with loam and sandy loam soils, clay loam soil was present at J7v, and at J1 15–30 cm, while the rest exhibited sandy loam or loamy sand textures. The analyses indicated that in general, this region has low clay content, which facilitates TE mobility. The area has alkaline soils, the pH values ranged between 7.46 ± 0.10 and 8.00 ± 0.03 . The EC levels varied depending on the zone and soil practices; the cultured soils showed lower values than uncultured ones. In vineyards the values determined were below $4000 \mu\text{S cm}^{-1}$, but in onion fields were between 3443 ± 572 and $5640 \pm 964 \mu\text{S cm}^{-1}$, respectively. In uncultured soils the values indicated high salt content, with conductivities ranged from $3473 \pm 777 \mu\text{S cm}^{-1}$ in H2 to $26,984 \pm 1587 \mu\text{S cm}^{-1}$ in J8. In J1, J3, and J8, SAR was >15 , which implies saline-sodics soils. In the rest of the sampled sites, SAR values were below this limit, especially in cultured soils, indicating along with EC that ions could be lixiviated due to irrigation.

In general, the content of P was low, except in J6v with values of $4.1 \pm 1.4 \mu\text{g g}^{-1}$. Conversely, K content was $>0.5 \text{ meq L}^{-1}$, the limit established for and adequate provision of K in culture soils. OM was below 1% in all uncultured soils, except in H2 ($1.2 \pm 0.1\%$ at 0–15 cm), while in cultured sites and irrigated by Río Jáchal ranged from 1.8 ± 0.1 to $4.2 \pm 0.1\%$, and 0.5 ± 0.2 to $5.2 \pm 0.3\%$ in those irrigated by Río Huaco.

3.2. TE content in soils

Elemental analysis showed high concentration of TEs (Table 2). In all the sampled sites high values (according to Argentinian law) of **As**, **B** and **Cr** were detected. Total **As** showed a maximum value of $505.9 \pm 45.8 \mu\text{g g}^{-1}$ (dry weight, DW) in the onion field J4o, and a minimum of $236.3 \pm 44.0 \mu\text{g g}^{-1}$ in J8, both at 0–15 cm depth. Total **B** had a maximum value of $149.1 \pm 2.9 \mu\text{g g}^{-1}$ at 0–15 cm depth in H3v and a minimum of $7.5 \pm 0.5 \mu\text{g g}^{-1}$ at 0–15 cm in J8. **Cr** concentration was highest

Table 2

Trace elements content in soils (TEs) from Jáchal at two depths: 0–15 and 15–30 cm, determined by ICP-MS. Values are in $\mu\text{g g}^{-1}$ DW \pm standard error. Nd: no detected. Sites: J1: Cuesta del Viento; J2v: Pachinoca vineyard; J3: Pachinoca; J4o and J5o: La Falda onion fields; J6v: La Falda vineyard; J7v: Otra Banda vineyard; J8: Río Jáchal Sur; H1v: La Ciénaga vineyard; H2: La Ciénaga; and H3v: Huaco vineyard.

SOIL	J1		J3		J2v	
TEs	0–15 cm	15–30 cm	0–15 cm	15–30 cm	0–15 cm	15–30 cm
Ag	0.03 \pm 0.02	nd	0.06 \pm 0.04	nd	0.12 \pm 0.03	0.10 \pm 0.07
As	291.1 \pm 14.4	268.8 \pm 18.9	312.9 \pm 9.3	287.9 \pm 28.5	350.4 \pm 23.3	271.4 \pm 108.7
B	18.0 \pm 14.9	19.4 \pm 11.7	26.3 \pm 5.4	22.2 \pm 2.6	24.8 \pm 7.0	10.7 \pm 9.7
Ba	152.4 \pm 10.6	130.8 \pm 19.4	147.7 \pm 8.1	139.2 \pm 12.7	160.0 \pm 10.9	119.8 \pm 53.7
Cr	1177.0 \pm 223.7	1128.8 \pm 183.9	1046.9 \pm 84.2	1012.2 \pm 72.0	1153.4 \pm 90.4	1056.6 \pm 273.4
Cu	25.4 \pm 8.9	18.5 \pm 1.9	20.7 \pm 2.9	18.1 \pm 3.1	58.6 \pm 4.5	49.7 \pm 22.0
Fe	14,706.2 \pm 703.2	10,556.6 \pm 106.5	13,341.6 \pm 812.6	12,570.0 \pm 921.3	25,528.6 \pm 1285.8	22,926.2 \pm 10,635.5
Hg	nd	nd	nd	nd	3.2 \pm 0.7	2.6 \pm 0.5
Mn	584.0 \pm 19.7	437.5 \pm 31.5	488.8 \pm 43.7	475.1 \pm 42.8	1102.4 \pm 53.0	772.4 \pm 347.1
Pb	4.3 \pm 2.2	4.7 \pm 1.4	6.3 \pm 1.5	5.0 \pm 1.3	16.9 \pm 0.5	12.6 \pm 6.2
Se	nd	nd	nd	nd	nd	nd
Tl	2.4 \pm 1.2	2.6 \pm 0.8	3.6 \pm 0.8	2.8 \pm 0.7	8.3 \pm 0.3	6.2 \pm 2.9
Zn	50.5 \pm 8.3	34.2 \pm 6.4	46.0 \pm 7.4	36.8 \pm 7.5	137.9 \pm 12.4	107.8 \pm 53.9
SOIL	J4o		J5o		J6v	
TEs	0–15 cm	15–30 cm	0–15 cm	15–30 cm	0–15 cm	15–30 cm
Ag	0.5 \pm 0.1	0.4 \pm 0.04	0.09 \pm 0.05	0.14 \pm 0.04	0.7 \pm 0.1	0.7 \pm 0.1
As	505.9 \pm 45.8	470.3 \pm 2.5	281.3 \pm 14.3	324.7 \pm 7.8	400.4 \pm 46.1	436.6 \pm 74.3
B	53.6 \pm 15.0	37.4 \pm 1.2	11.3 \pm 5.1	15.5 \pm 0.5	117.6 \pm 9.7	107.9 \pm 26.6
Ba	231.5 \pm 23.8	194.0 \pm 24.3	99.7 \pm 50.1	166.0 \pm 3.0	319.7 \pm 45.1	307.3 \pm 30.5
Cr	2225.1 \pm 77.4	2189.3 \pm 23.6	1693.7 \pm 102.8	1720.1 \pm 29.1	2596.2 \pm 308.7	2713.6 \pm 216.8
Cu	76.2 \pm 8.0	64.9 \pm 6.1	35.9 \pm 16.1	58.3 \pm 0.5	95.2 \pm 16.3	92.5 \pm 9.6
Fe	33,228.8 \pm 3573.4	27,644.6 \pm 3191.6	14,103.8 \pm 7005.7	24,780.2 \pm 680.7	41,960.7 \pm 7658.4	40,550.1 \pm 6854.7
Hg	nd	nd	nd	nd	2.6 \pm 1.4	2.1 \pm 1.1
Mn	1479.5 \pm 163.7	1215.2 \pm 176.5	669.4 \pm 333.1	1158.9 \pm 10.1	2447.0 \pm 544.5	2408.0 \pm 463.9
Pb	21.6 \pm 2.0	19.4 \pm 1.9	9.8 \pm 4.9	17.3 \pm 0.5	24.8 \pm 6.6	23.1 \pm 5.6
Se	nd	nd	nd	nd	nd	nd
Tl	11.3 \pm 1.1	9.8 \pm 0.8	4.8 \pm 2.4	8.3 \pm 0.2	12.3 \pm 2.9	11.6 \pm 2.6
Zn	179.4 \pm 23.9	154.6 \pm 5.4	63.5 \pm 31.8	116.4 \pm 4.0	271.7 \pm 66.7	263.0 \pm 50.7
SOIL	J7v		J8		H1v	
TEs	0–15 cm	15–30 cm	0–15 cm	15–30 cm	0–15 cm	15–30 cm
Ag	0.2 \pm 0.1	0.4 \pm 0.2	nd	nd	1.2 \pm 0.5	0.5 \pm 0.3
As	302.9 \pm 5.7	308.7 \pm 23.3	236.3 \pm 44.0	283.4 \pm 14.0	214.7 \pm 35.8	228.7 \pm 87.5
B	23.1 \pm 3.4	18.4 \pm 0.8	7.5 \pm 0.5	16.0 \pm 10.9	134.6 \pm 3.8	137.1 \pm 22.0
Ba	147.1 \pm 10.8	149.8 \pm 5.9	76.1 \pm 39.0	88.3 \pm 44.8	364.6 \pm 56.2	278.3 \pm 99.8
Cr	1101.7 \pm 211.7	866.3 \pm 132.3	1015.0 \pm 155.5	1155.2 \pm 67.5	1637.0 \pm 480.7	1980.1 \pm 661.8
Cu	52.1 \pm 2.6	50.4 \pm 2.3	6.5 \pm 3.4	8.1 \pm 4.2	54.0 \pm 7.4	44.8 \pm 17.9
Fe	22,005.8 \pm 1241.9	22,183.4 \pm 1135.6	5193.2 \pm 2659.7	6302.3 \pm 3277.6	30,777.8 \pm 6739.7	21,153.4 \pm 6791.9
Hg	6.3 \pm 3.5	11.0 \pm 4.2	nd	nd	16.0 \pm 7.1	10.7 \pm 3.4
Mn	1027.1 \pm 70.4	998.4 \pm 61.4	212.1 \pm 109.4	259.0 \pm 132.9	2009.6 \pm 196.8	1757.7 \pm 736.8
Pb	16.5 \pm 0.8	16.0 \pm 1.3	1.6 \pm 0.9	2.0 \pm 1.0	15.0 \pm 3.0	9.7 \pm 3.9
Se	nd	nd	nd	nd	nd	nd
Tl	8.1 \pm 0.3	7.9 \pm 0.6	1.0 \pm 0.5	1.1 \pm 0.6	7.3 \pm 1.3	5.0 \pm 1.8
Zn	109.0 \pm 3.8	108.9 \pm 10.4	3.0 \pm 2.8	9.3 \pm 5.9	148.4 \pm 26.8	114.3 \pm 57.1
SOIL	H2		H3v			
TEs	0–15 cm	15–30 cm	0–15 cm	15–30 cm		
Ag	0.08 \pm 0.04	0.04 \pm 0.02	1.7 \pm 0.4	0.4 \pm 0.4		
As	379.2 \pm 56.2	325.3 \pm 35.8	369.7 \pm 203.0	139.0 \pm 86.9		
B	31.0 \pm 12.0	25.3 \pm 9.4	149.1 \pm 2.9	82.6 \pm 10.9		
Ba	165.1 \pm 4.9	193.7 \pm 28.0	376.0 \pm 108.5	56.8 \pm 22.9		
Cr	1396.1 \pm 60.9	1360.4 \pm 18.6	2781.5 \pm 1894.2	1863.7 \pm 1212.4		
Cu	50.0 \pm 15.6	46.5 \pm 25.4	62.7 \pm 5.9	8.5 \pm 0.4		
Fe	21,933.7 \pm 3704.2	18,990.6 \pm 4245.4	47,034.3 \pm 1412.0	6482.1 \pm 830.6		
Hg	0.5 \pm 0.5	0.2 \pm 0.2	15.6 \pm 15.6	8.2 \pm 8.2		
Mn	942.7 \pm 119.6	863.8 \pm 78.7	2018.0 \pm 205.6	260.2 \pm 25.0		
Pb	11.5 \pm 4.3	8.2 \pm 5.0	15.9 \pm 5.6	1.2 \pm 0.6		
Se	nd	nd	nd	nd		
Tl	5.7 \pm 2.1	4.2 \pm 2.4	7.9 \pm 2.1	1.0 \pm 0.3		
Zn	116.1 \pm 38.6	84.2 \pm 38.4	218.8 \pm 19.9	10.7 \pm 10.7		

Values in bold are above limits established for agricultural soils (law 24.051 Residuos Peligrosos. Decreto 831/93): Ag and As: $20 \mu\text{g g}^{-1}$; B: $2 \mu\text{g g}^{-1}$; Ba: $750 \mu\text{g g}^{-1}$; Cu: $150 \mu\text{g g}^{-1}$; Cr: $750 \mu\text{g g}^{-1}$; Hg: $0.8 \mu\text{g g}^{-1}$; Pb: $375 \mu\text{g g}^{-1}$; Se: $2 \mu\text{g g}^{-1}$; Tl: $1 \mu\text{g g}^{-1}$; and Zn $600 \mu\text{g g}^{-1}$. No limits are established for Fe and Mn.

at 0–15 cm in J6v ($2713.5 \pm 216.8 \mu\text{g g}^{-1}$), and the lowest at 15–30 cm in J7v ($866.3 \pm 132.3 \mu\text{g g}^{-1}$). Also high Hg content were detected in J2v, J6v, J7v, and H1v, with values > the limits established for agricultural soils ($0.8 \mu\text{g g}^{-1}$). Tl also showed high values in most areas, except in J8 with values close to the limit established for agricultural soils ($1 \mu\text{g g}^{-1}$),

and maximum value of $12.3 \pm 2.9 \mu\text{g g}^{-1}$ at 0–15 cm depth in J6v. All other elements (Ag, Ba, Cu, Pb, Se, and Zn) did not exceed the limits established by Argentinian law for agricultural soils. Finally, Fe and Mn were found at high content in soils, but there is no legislation regarding acceptable concentrations for this element.

3.3. TE content in water

Total elemental analysis in samples of irrigation water belonging to Río Jáchal and Río Huaco showed a high content of **As**, **B**, **Cr**, and **Fe** in all the cases. The maximum value for **As** was $1437.9 \pm 399.9 \mu\text{g L}^{-1}$ in J8, and the minimum $192.3 \pm 116.9 \mu\text{g L}^{-1}$ in J6v; for **B** was $10,870.6 \pm 471.3 \mu\text{g L}^{-1}$ in H3v and $3367.9 \pm 232.6 \mu\text{g L}^{-1}$ in H2; for **Cr** was $11,516.3 \pm 2362.8 \mu\text{g L}^{-1}$ in J8 and $1675.6 \pm 450.2 \mu\text{g L}^{-1}$ in J6v; and finally for **Fe** was $3071.0 \pm 257.0 \mu\text{g L}^{-1}$ in H3v and $2334.7 \pm 40.8 \mu\text{g L}^{-1}$ in J6v. Only the samples belonging to Río Huaco: H3v and H2 presented **Mn** values above limits: 168.6 ± 5.3 and $219.8 \pm 2.5 \mu\text{g L}^{-1}$ respectively. All the others elements showed lower values than those referred in Argentinian law for drinking and irrigation water (Table 3).

3.4. TE content in grapevine

In leaves, the content of **As**, **Cr**, **Cu**, and **Fe** exceeded the limit established by CAA for vegetables. **As** presented a maximum value of $189.6 \pm 2.9 \mu\text{g g}^{-1}$ in basal leaves of H3v and a minimum of $92.7 \pm 34.1 \mu\text{g g}^{-1}$ in apical leaves of J6v; **Cr** content reached to $3003.1 \pm 45.3 \mu\text{g g}^{-1}$ in basal leaves of H1v and $1454.2 \pm 674.1 \mu\text{g g}^{-1}$ in apical leaves of J6v. **Cu**, reached the maximum concentration basal leaves of H3v ($28.0 \pm 4.3 \mu\text{g g}^{-1}$), and the minimum in basal leaves of J2v ($6.3 \pm 0.4 \mu\text{g g}^{-1}$). **Fe** content ranged between 1299.3 ± 227.2 and $67.0 \pm 53.3 \mu\text{g g}^{-1}$ in basal leaves of J6v and J7v, respectively. Finally, in general, **Hg** was not detected (nd), but exceeded the limits in grapevine leaves of J2v, J6v and J7v. All the other elements analyzed were at concentrations allowed by the CAA (Table 4).

In grapevine berries, high **As**, **Cr**, **Cu**, and **Fe** concentration were detected. **As** showed a maximum value of $171.2 \pm 19.7 \mu\text{g g}^{-1}$ in grapes of J7v, and a minimum of $72.2 \pm 2.9 \mu\text{g g}^{-1}$ in grapes of J6v; **Cr** highest concentration was in grapes of H1v ($2965.0 \pm 32.2 \mu\text{g g}^{-1}$) and the lowest ($1071.8v \pm 37.4 \mu\text{g g}^{-1}$) in samples of J6v. **Cu** reached $126.2 \pm 88.4 \mu\text{g g}^{-1}$ in grapes of H1v and $7.32 \pm 1.5 \mu\text{g g}^{-1}$ in grapes of J7v; and **Fe** presented values $476.3 \pm 476.3 \mu\text{g g}^{-1}$ as maximum (high standard error was given by the no detection in several samples), and in J6v it was not found. In addition, elevated **Hg** concentrations in samples of grapevine berries (3.7 ± 1.9 , 1.0 ± 0.2 , and $0.22 \pm 0.1 \mu\text{g g}^{-1}$, respectively for J6v, J7v, and J2v samples) were detected. All the others elements were below detection limits or no current regulations were found. There is no Argentinian legislation for **B** and **Zn** concentration in food.

3.5. TE content in onion

In onion, **As**, **Cr**, **Cu**, and **Fe** contents exceeded the limits established by law, with a maximum of $91.6 \pm 7.1 \mu\text{g g}^{-1}$ in bulbs and $90.8 \pm$

$8.0 \mu\text{g g}^{-1}$ in leaves for **As**; 1412.0 ± 18.2 and $1378.4 \pm 24.7 \mu\text{g g}^{-1}$ respectively for **Cr**; 16.7 ± 2.8 and $30.2 \pm 1.6 \mu\text{g g}^{-1}$ for **Cu**; and 418.4 ± 203.9 and $9131.1 \pm 3878.2 \mu\text{g g}^{-1}$ for **Fe**. All the others elements were below legal limits or no regulation is available (Table 4).

3.6. Correlation analysis

3.6.1. Correlation analysis of TE concentration in soils and water

Table 5 shows the Pierson's correlation matrix for TEs (at both 0–15 and 15–30 cm depth) of Jáchal. In general, values indicated strong linear correlation among the TEs analyzed, which suggests a common source. **Se** had no correlation with all the other elements and was not detected in most samples. Despite the low concentration of **Hg** and **Ag** detected, they showed strong correlation ($p < 0.01$) with some others elements. While **Hg** presented correlation with **Ag** (CI: 0.64, $p < 0.01$), **B** (CI: 0.50, $p < 0.01$), **As** (CI: -0.45 , $p < 0.01$), **Ba** (CI: 0.44, $p < 0.01$), **Mn** (CI: 0.30, $p < 0.05$), **Cr** (CI: -0.25 , $p < 0.10$) and **Fe** (CI: 0.25, $p < 0.10$), **Ag** showed highly significant correlation with all elements, except with **As** and **Se**. **As** showed correlation with **Ba** (CI: 0.23, $p < 0.01$) and was highly significantly correlated with the other elements. **B**, **Ba**, **Cr**, **Cu**, **Fe**, **Mn**, and **Pb** in general, exhibited highly significant correlation with all elements, except **B-As** (CI: 0.07), **Cu-Hg** (CI: 0.11) and **Pb-Hg** (CI: 0.017). Finally, **Tl** and **Zn** were highly significant correlation with all elements except with **Hg** (CI: 0.14 in both cases). It is important to mention that the correlation index for **Pb-Tl** was 1.00. No significant correlation was detected between TE_w and TE_s (data not shown).

3.6.2. Correlation analysis of TE concentration in grapevines, soil and soil physicochemical variables

Correlation analysis between each TE_g and its corresponding TE_s indicated that different variables affect the metal content depending on the considered organ. Variables at depth at 30 cm affected metals content in grapevine organs more than at 15 cm (Fig. 2).

The **As** content in apical leaves was affected by **As**_{30 cm} (Correlation Index (CI): -0.54 , $p < 0.05$), **OM**_{15 cm} (CI: -0.49 , $p < 0.10$), and **Mg**_{30 cm} (CI: 0.48, $p < 0.10$); in basal leaves by **Sand**_{30 cm} (CI: 0.60, $p < 0.05$); and in berries by **Mg**_{30 cm} (CI: 0.73, $p < 0.01$), **SAR**_{15 cm} (CI: -0.67 , $p < 0.05$), **Sand**_{30 cm} (CI: 0.58, $p < 0.05$), **Na**_{15 cm} (CI: -0.56 , $p < 0.05$), **Sand**_{15 cm} (CI: 0.49, $p < 0.10$), and **P**_{30 cm} (CI: -0.48 , $p < 0.10$). **B** content in apical leaves was affected by **B_w** (CI: -0.66 , $p < 0.05$), **EC**_{15 cm} (CI: -0.59 , $p < 0.05$), **Ca**_{15 cm} (CI: -0.55 , $p < 0.05$), and **OM**_{15 cm} (CI: 0.46, $p < 0.10$), in basal leaves by **Mg**_{30 cm} (CI: -0.71 , $p < 0.01$), **Na**_{30 cm} (-0.68 , $p < 0.01$), **B**_{15 cm} (CI: -0.54 , $p < 0.05$), **Sand**_{30 cm} (CI: -0.55 , $p < 0.05$), **Sand**_{15 cm} (CI: -0.52 , $p < 0.10$), and **SAR**_{30 cm} (CI: -0.42 , $p < 0.10$), while in grapes by **SAR**_{15 cm} and **Na**_{15 cm} (CI: -0.59 and -0.56 , $p < 0.05$ respectively). **Cr** concentration in apical leaves was significantly correlated with **Cr_w** (CI: 0.62, $p < 0.05$),

Table 3
Trace elements content in water from Jáchal, determined by ICP-MS. Values are presented in $\mu\text{g L}^{-1} \pm$ standard error. Nd: no detected. J1: Cuesta del Viento; J2v: Pachinoca vineyard; J6v: La Falda vineyard; H2: La Ciénaga; H3v: Huaco vineyard; and J8: Río Jáchal Sur.

WATER	J1	J2v	J6v	H2	H3v	J8
Ag	3.2 ± 2.8	2.8 ± 7.3	3.5 ± 0.1	nd	2.3 ± 0.5	nd
As	592.6 ± 12.7	501.9 ± 0.0	192.3 ± 116.9	1062.6 ± 159.2	399.4 ± 65.9	1437.9 ± 399.9
B	4731.8 ± 30.0	8025.8 ± 0.4	3412.1 ± 2992.7	3367.9 ± 232.6	10,870.6 ± 471.3	3768.4 ± 561.3
Ba	46.5 ± 3.5	89.0 ± 2.0	28.0 ± 28.1	64.5 ± 2.0	123.0 ± 1.0	85.9 ± 17.8
Cr	4250.6 ± 320.0	3208.4 ± 2.7	1675.6 ± 450.2	7008.7 ± 911.9	3370.1 ± 514.2	11,516.3 ± 2362.8
Cu	8.4 ± 8.4	19.3 ± 0.7	8.3 ± 0.3	7.9 ± 4.6	24.3 ± 6.9	8.9 ± 0.3
Fe	2569.5 ± 74.5	2860.1 ± 373.4	2334.7 ± 40.8	2769.4 ± 132.0	3071.0 ± 257.0	2679.4 ± 72.5
Hg	nd	nd	nd	nd	nd	nd
Mn	46.3 ± 1.9	44.6 ± 80.2	47.5 ± 2.0	219.8 ± 2.5	168.6 ± 5.3	44.6 ± 1.2
Pb	0.7 ± 0.7	0.4 ± 5834.0	0.2 ± 0.2	nd	0.4 ± 1.1	nd
Se	nd	nd	nd	nd	nd	nd
Tl	1.7 ± 1.7	1.8 ± 904.7	1.2 ± 0.8	nd	1.3 ± 0.0	nd
Zn	290.0 ± 0.1	206.1 ± 37.0	212.5 ± 7.0	286.0 ± 62.2	259.3 ± 98.1	279.5 ± 10.1

Values in bold are above limits established for drinking water (Código Alimentario Argentino): **As**: $10 \mu\text{g L}^{-1}$; **Ag**, **Cr**, and **Pb**: $50 \mu\text{g L}^{-1}$; **B**: $500 \mu\text{g L}^{-1}$; **Cu**: $1000 \mu\text{g L}^{-1}$; **Fe**: $300 \mu\text{g L}^{-1}$; **Hg**: $1 \mu\text{g L}^{-1}$; **Mn**: $100 \mu\text{g L}^{-1}$; **Se**: $10 \mu\text{g L}^{-1}$; and **Zn**: $5000 \mu\text{g L}^{-1}$.

Table 4

Trace elements content in grapevine (TEg) and onion (TEo) from Jáchal determined by ICP-MS. Values are presented in $\mu\text{g g}^{-1}$ dry weight \pm standard error. Nd: no detected. Sites: J2v: Pachinoca vineyard; J4o and J5o: La Falda onion fields; J6v: La Falda vineyard; J7v: Otra Banda vineyard; H1v: La Ciénaga vineyard; and H3v: Huaco vineyard.

Grapevine		J2v			J6v		
TEg	Apical	Basal	Grape	Apical	Basal	Grape	
Ag	nd	nd	nd	1.1 \pm 0.9	0.4 \pm 0.4	nd	
As	148.6 \pm 4.9	155.0 \pm 3.4	141.9 \pm 6.3	92.7 \pm 34.1	107.0 \pm 19.2	72.2 \pm 2.9	
B	1520.0 \pm 585.2	2062.8 \pm 347.9	931.4 \pm 596.8	2428.5 \pm 542.8	2767.5 \pm 132.5	580.4 \pm 72.4	
Ba	13.7 \pm 6.5	18.3 \pm 5.2	10.9 \pm 4.0	17.8 \pm 2.6	20.7 \pm 4.9	1.7 \pm 0.4	
Cr	2322.7 \pm 60.9	2361.9 \pm 20.6	2275.6 \pm 59.0	1454.2 \pm 674.1	1473.1 \pm 538.2	1071.8 \pm 37.4	
Cu	8.2 \pm 0.8	6.3 \pm 0.4	30.7 \pm 9.3	22.0 \pm 3.5	24.8 \pm 5.3	31.2 \pm 3.8	
Fe	290.6 \pm 179.0	177.3 \pm 93.2	376.7 \pm 212.8	769.4 \pm 207.4	1299.3 \pm 227.2	nd	
Hg	0.6 \pm 0.1	0.5 \pm 0.1	0.2 \pm 0.1	32.8 \pm 22.6	17.2 \pm 11.3	3.7 \pm 1.9	
Mn	86.9 \pm 38.3	112.1 \pm 18.0	49.1 \pm 17.6	218.9 \pm 18.3	311.2 \pm 105.2	24.6 \pm 4.3	
Pb	nd	nd	nd	nd	nd	nd	
Se	12.6 \pm 7.1	7.6 \pm 4.2	7.6 \pm 4.2	nd	nd	3.6 \pm 2.4	
Tl	nd	nd	nd	0.3 \pm 0.3	0.0 \pm 0.0	nd	
Zn	nd	nd	2.1 \pm 2.1	20.6 \pm 16.5	52.3 \pm 32.1	0.3 \pm 0.3	
Grapevine		J7v			H1v		
TEg	Apical	Basal	Grape	Apical	Basal	Grape	
Ag	0.1 \pm 0.1	0.03 \pm 0.03	nd	nd	nd	nd	
As	126.6 \pm 23.9	144.3 \pm 39.1	171.2 \pm 19.7	169.3 \pm 14.0	186.7 \pm 17.7	158.0 \pm 9.4	
B	2242.0 \pm 1094.3	2150.4 \pm 536.5	1180.2 \pm 853.4	2789.1 \pm 260.6	2466.9 \pm 260.2	404.8 \pm 73.4	
Ba	10.4 \pm 2.5	10.8 \pm 2.8	4.4 \pm 4.1	27.6 \pm 7.5	31.1 \pm 5.9	5.3 \pm 1.3	
Cr	1716.2 \pm 388.9	2091.7 \pm 467.8	2664.3 \pm 159.4	2901.7 \pm 147.9	3003.1 \pm 45.3	2965.0 \pm 32.2	
Cu	10.3 \pm 1.9	10.2 \pm 1.0	7.3 \pm 1.5	20.6 \pm 0.7	19.8 \pm 3.1	126.2 \pm 88.4	
Fe	72.4 \pm 42.4	67.0 \pm 53.3	72.7 \pm 72.7	877.0 \pm 264.9	1110.8 \pm 224.6	232.4 \pm 185.8	
Hg	1.6 \pm 1.0	1.2 \pm 0.7	1.0 \pm 0.2	nd	nd	nd	
Mn	122.1 \pm 45.8	130.7 \pm 7.8	49.1 \pm 37.1	291.6 \pm 52.2	335.6 \pm 63.0	32.3 \pm 2.3	
Pb	nd	nd	nd	nd	nd	nd	
Se	nd	nd	3.6 \pm 2.4	nd	nd	nd	
Tl	nd	nd	nd	nd	nd	nd	
Zn	5.7 \pm 5.7	nd	12.1 \pm 12.1	21.6 \pm 1.8	27.7 \pm 11.8	5.6 \pm 5.6	
Grapevine		H3v					
TEg	Apical	Basal	Grape	Apical	Basal	Grape	
Ag	nd	nd	nd	nd	nd	0.27 \pm 0.27	
As	183.4 \pm 15.6	189.6 \pm 2.9	168.4 \pm 8.1	189.6 \pm 2.9	168.4 \pm 8.1	168.4 \pm 8.1	
B	909.9 \pm 80.9	965.8 \pm 200.9	253.8 \pm 19.9	965.8 \pm 200.9	965.8 \pm 200.9	253.8 \pm 19.9	
Ba	16.4 \pm 3.9	18.8 \pm 2.5	6.7 \pm 5.8	18.8 \pm 2.5	18.8 \pm 2.5	6.7 \pm 5.8	
Cr	2551.0 \pm 211.8	2566.9 \pm 133.2	2753.8 \pm 15.7	2566.9 \pm 133.2	2566.9 \pm 133.2	2753.8 \pm 15.7	
Cu	26.0 \pm 3.8	28.0 \pm 4.3	24.5 \pm 7.9	28.0 \pm 4.3	28.0 \pm 4.3	24.5 \pm 7.9	
Fe	380.6 \pm 72.0	644.4 \pm 98.2	476.3 \pm 476.3	644.4 \pm 98.2	644.4 \pm 98.2	476.3 \pm 476.3	
Hg	nd	nd	nd	nd	nd	nd	
Mn	296.3 \pm 61.0	278.7 \pm 32.5	36.0 \pm 14.7	278.7 \pm 32.5	278.7 \pm 32.5	36.0 \pm 14.7	
Pb	nd	nd	nd	nd	nd	nd	
Se	nd	nd	nd	nd	nd	nd	
Tl	nd	nd	nd	nd	nd	nd	
Zn	32.3 \pm 8.8	35.1 \pm 6.1	28.1 \pm 5.2	35.1 \pm 6.1	35.1 \pm 6.1	28.1 \pm 5.2	
Onion		J4o		J5o			
TEo	Bulb	Leaf	Bulb	Leaf	Leaf		
Ag	nd	nd	nd	nd	nd		
As	73.4 \pm 4.0	90.8 \pm 8.0	91.6 \pm 7.1	81.8 \pm 1.1	81.8 \pm 1.1		
B	156.6 \pm 50.9	306.8 \pm 64.1	93.6 \pm 6.7	197.9 \pm 135.0	197.9 \pm 135.0		
Ba	9.2 \pm 2.0	52.9 \pm 13.6	23.7 \pm 5.6	8.4 \pm 5.5	8.4 \pm 5.5		
Cr	1160.9 \pm 71.0	1176.8 \pm 56.6	1412.0 \pm 18.2	1378.4 \pm 24.7	1378.4 \pm 24.7		
Cu	10.3 \pm 0.8	30.2 \pm 1.6	16.7 \pm 2.8	12.2 \pm 5.8	12.2 \pm 5.8		
Fe	418.4 \pm 203.9	9131.1 \pm 3878.3	362.7 \pm 260.3	58.9 \pm 42.8	58.9 \pm 42.8		
Hg	nd	nd	nd	nd	nd		
Mn	27.4 \pm 9.9	211.6 \pm 72.6	38.8 \pm 4.3	36.3 \pm 18.2	36.3 \pm 18.2		
Pb	nd	1.0 \pm 0.7	nd	nd	nd		
Se	nd	nd	nd	nd	nd		
Tl	nd	1.1 \pm 0.6	nd	nd	nd		
Zn	6.9 \pm 3.4	106.8 \pm 21.5	206.7 \pm 58.5	28.9 \pm 21.8	28.9 \pm 21.8		

Values in bold are above limits established (Código Alimentario Argentino): As: 100 $\mu\text{g kg}^{-1}$; Cu: 10 mg kg^{-1} ; Cr: 50 $\mu\text{g kg}^{-1}$; Fe: 1.5–5 mg kg^{-1} ; Hg: 50 $\mu\text{g kg}^{-1}$; Pb: 0.1 mg kg^{-1} .

OM_{30 cm} (CI: 0.55, $p < 0.05$), K_{30 cm} (CI: 0.57, $p < 0.10$), and Mg_{30 cm} (CI: 0.50, $p < 0.10$); in basal leaves with Sand_{30 cm} (CI: 0.55, $p < 0.05$) and Cr_{30 cm} (CI: 0.49, $p < 0.10$); and in berries with Sand_{30 cm} (CI: 0.74, $p < 0.01$), Mg_{30 cm} (CI: 0.59, $p < 0.05$), P_{30 cm} (CI: -0.59, $p < 0.10$), Cr_{30 cm} (CI: 0.57, $p < 0.05$), and Sand_{15 cm} (CI: -0.51, $p < 0.10$). Cu content in

apical leaves was influenced by Sand_{30 cm} (CI: 0.69, $p < 0.01$), and pH_{15 cm} (CI: 0.52, $p < 0.10$); in basal leaves by pH_{15 cm} (CI: 0.63, $p < 0.05$), Cu_{30 cm} (CI: -0.60, $p < 0.05$) and OM_{15 cm} (CI: -0.51, $p < 0.10$), while no significant correlations were detected in grapes. Fe concentration in apical leaves was correlated with Sand_{30 cm} (CI: 0.67, $p < 0.01$)

Table 5
Pearson's correlation matrix of trace elements concentration in soils of Jáchal, San Juan.

	Ag	As	B	Ba	Cr	Cu	Fe	Hg	Mn	Pb	Se	Tl	Zn
Ag	1.00												
As	0.15	1.00											
B	0.75***	0.07	1.00										
Ba	0.77***	0.23*	0.77***	1.00									
Cr	0.43***	0.59***	0.55***	0.46***	1.00								
Cu	0.51***	0.65***	0.45***	0.64***	0.49***	1.00							
Fe	0.70***	0.58***	0.57***	0.78***	0.55***	0.92***	1.00						
Hg	0.64***	-0.45***	0.50***	0.44***	-0.25*	0.11	0.25*	1.00					
Mn	0.67***	0.36***	0.77***	0.90***	0.63***	0.77***	0.82***	0.30**	1.00				
Pb	0.50***	0.60**	0.35***	0.60***	0.39***	0.95***	0.89***	0.17	0.71***	1.00			
Se	0	0	0	0	0	0	0	0	0	0	1.00		
Tl	0.50***	0.63***	0.36***	0.59***	0.40***	0.96***	0.89***	0.14	0.70***	1.00***	0	1.00	
Zn	0.63***	0.64***	0.56***	0.71***	0.61***	0.95***	0.96***	0.14	0.82***	0.92***	0	0.92***	1.00

* p < 0.1.
** p < 0.05.
*** p < 0.01.

and EC_{15 cm} (CI: -0.47, p < 0.10), in basal leaves with Na_{30 cm} (CI: -0.46, p < 0.10), and in berries with Ca_{30 cm} (CI: 0.72, p < 0.01), EC_{30 cm} (CI: 0.62, p < 0.05), OM_{30 cm} (CI: 0.59, p < 0.05), Mg_{15 cm} (CI: 0.49, p < 0.10) and Ph_{30 cm} (CI: -0.52, p < 0.10). **Hg** concentration in apical leaves was correlated with P_{15 cm} (CI: 0.74, p < 0.01), EC_{30 cm} (CI: -0.53, p < 0.05), OM_{15 cm} (CI: 0.46, p < 0.10), in basal leaves with Sand_{30 cm} (CI: -0.48, p < 0.10), and in berries with Sand_{30 cm} (CI: -0.67, p < 0.01), Sand_{15 cm} (CI: 0.58, p < 0.05), SAR_{30 cm} (CI: -0.55, p < 0.05) and Na_{30 cm} (CI: -0.49, p < 0.10). **Zn** in apical leaves was no significantly affected by soil variables, while in basal leaves was affected only by pH_{15 cm} (CI: 0.50, p < 0.10), and in berries by Mg_{30 cm} (CI: 0.83, p < 0.01), SAR_{15 cm} (CI: 0.58, p < 0.05), Sand_{15 cm} (CI: 0.54, p < 0.05), P_{30 cm} (CI: -0.57, p < 0.05), Na_{30 cm} (CI: 0.53, p < 0.05), Mg_{15 cm} (CI: 0.50, p < 0.10), and EC_{30 cm} (CI: 0.46, p < 0.10).

3.6.3. Correlation analysis of TE concentration in onion, soil and soil physicochemical variables

Unlike what was found in grapevine, the depth variable of soil at 15 cm was more important for TEo, especially in bulbs (Fig. 3), than that at 30 cm. **As** content in bulbs was conditioned by SAR_{15 cm} (CI: 0.76, p < 0.10) and As_{30 cm} (CI: -0.74, p < 0.10), and only with P_{30 cm} (CI: 0.88, p < 0.05) in leaves. **B** concentration in bulbs had correlation with OM_{30 cm} (CI: 0.96, p < 0.01), B_{15 cm} (CI: 0.89, p < 0.05) and K_{30 cm} (CI: 0.76, p < 0.10), while in leaves, with OM_{15 cm} (CI: -0.76, p < 0.10) and K_{15 cm} (CI: 0.74, p < 0.10). **Cr** content in bulbs was affected by Cr_{30 cm} (CI: -0.89, p < 0.05), Sand_{15 cm} (CI: 0.85, p < 0.05), Cr_{15 cm} (CI: -0.82, p < 0.05), OM_{30 cm} (CI: 0.81, p < 0.05), K_{15 cm} (CI: -0.76, p < 0.10), pH_{15 cm} (CI: -0.75, p < 0.10) and EC_{30 cm} (CI: 0.59, p < 0.10); while in leaves, it was correlated with OM_{30 cm} (CI: 0.96,

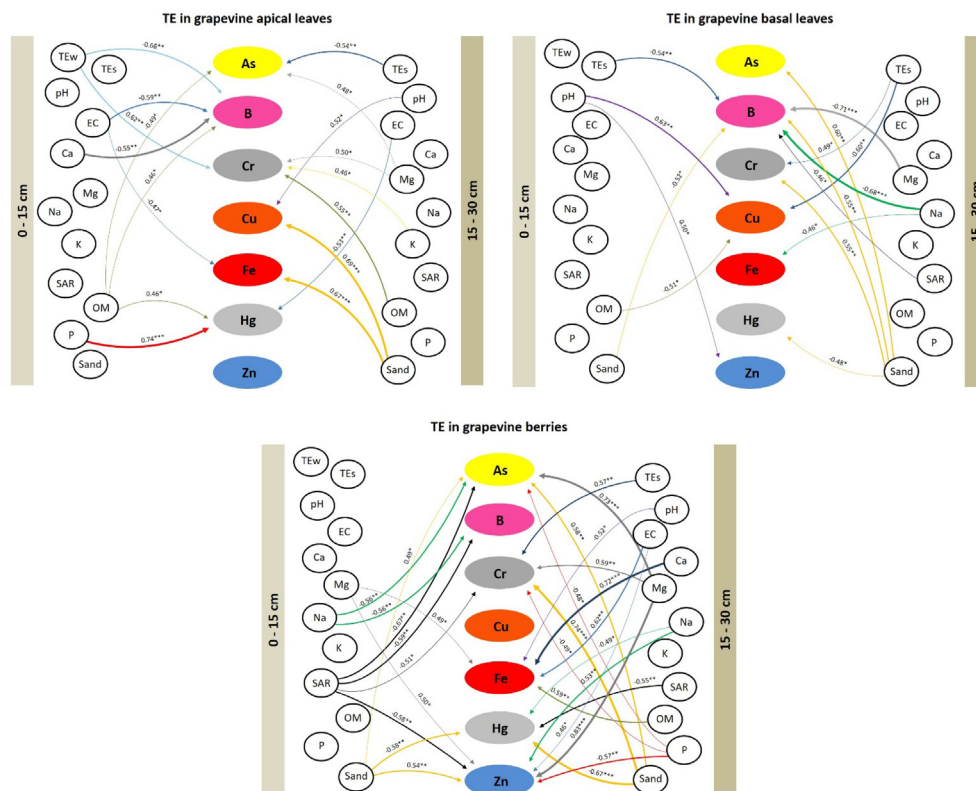


Fig. 2. Correlation between soil variables and trace elements (TE) content in different grapevine aerial organs. Only the elements that exceeded the limits established were considered. TE_s: element content in soil; EC: electrical conductivity; SAR: Sodium Adsorption Ratio; OM: organic matter content. *p < 0.10; **p < 0.05; ***p < 0.01.

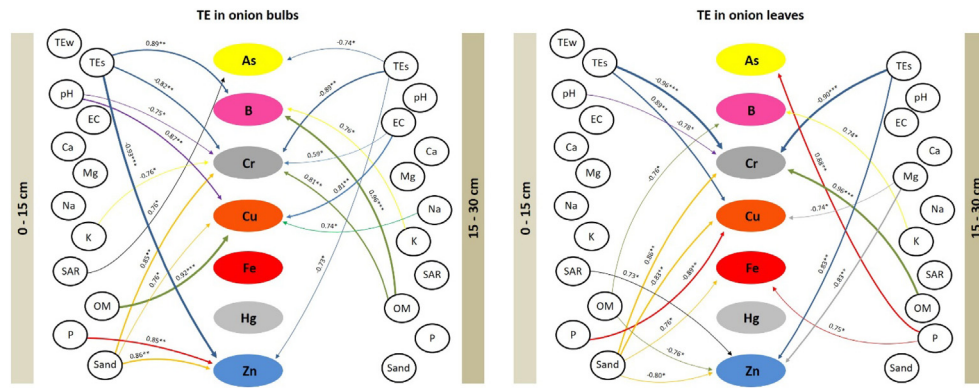


Fig. 3. Correlation between soil variables and trace elements (TE) content in different onion organs. Only the elements that exceeded the limits established were considered. TEs: element content in soil; E.C.: electrical conductivity; SAR: Sodium Adsorption Ratio; O.M.: organic matter content. * $p < 0.10$; ** $p < 0.05$; *** $p < 0.01$.

$p < 0.01$), $Cr_{15\text{ cm}}$ and $Cr_{30\text{ cm}}$ (CI: -0.96 and 0.90 , $p < 0.01$, respectively), $Sand_{15\text{ cm}}$ (CI: 0.86 , $p < 0.05$), and $pH_{15\text{ cm}}$ (CI: -0.78 , $p < 0.10$). **Cu** concentration in bulbs was affected by $OM_{15\text{ cm}}$ (CI: 0.92 , $p < 0.01$), $pH_{15\text{ cm}}$ (CI: 0.87 , $p < 0.05$), $EC_{30\text{ cm}}$ (CI: 0.81 , $p < 0.05$), $Sand_{30\text{ cm}}$ (CI: 0.76 , $p < 0.10$) and $Na_{30\text{ cm}}$ (CI: 0.74 , $p < 0.10$); and in leaves by $Cu_{30\text{ cm}}$ (CI: 0.89 , $p < 0.05$), $P_{15\text{ cm}}$ (CI: 0.89 , $p < 0.05$), $Sand_{15\text{ cm}}$ (CI: 0.83 , $p < 0.05$) and $Mg_{30\text{ cm}}$ (CI: -0.74 , $p < 0.10$). **Fe** content were significantly only in leaves with $Sand_{15\text{ cm}}$ (CI: 0.76 , $p < 0.10$) and $P_{30\text{ cm}}$ (CI: 0.75 , $p < 0.10$). Finally, **Zn** concentration in bulbs presented significant correlation with $Zn_{15\text{ cm}}$ (CI: -0.93 , $p < 0.01$), $Sand_{15\text{ cm}}$ (CI: 0.86 , $p < 0.05$), $P_{15\text{ cm}}$ (CI: 0.85 , $p < 0.05$), and $Zn_{30\text{ cm}}$ (CI: -0.73 , $p < 0.10$); in leaves with $Zn_{30\text{ cm}}$ (CI: 0.83 , $p < 0.05$), $Mg_{30\text{ cm}}$ (CI: -0.81 , $p < 0.05$), $Sand_{15\text{ cm}}$ (CI: -0.80 , $p < 0.10$), $OM_{15\text{ cm}}$ (CI: -0.76 , $p < 0.10$), and $SAR_{15\text{ cm}}$ (CI: 0.73 , $p < 0.10$). **Hg** was not significantly correlated with the analyzed variables (data not shown).

3.6.4. Correlation analysis of TE concentration in grapevines, water and soils

In grapevine apical leaves (Table A2), **As** CI was significant with $Tl_{15\text{ cm}}$ (CI: -0.69 , $p < 0.01$), $Tl_{30\text{ cm}}$ (CI: -0.66 , $p < 0.01$), $Cu_{15\text{ cm}}$ (CI: -0.65 , $p < 0.01$), $Pb_{30\text{ cm}}$ (CI: -0.65 , $p < 0.01$), $Pb_{15\text{ cm}}$ (CI: -0.64 , $p < 0.01$), $Fe_{30\text{ cm}}$ (CI: -0.59 , $p < 0.05$), Zn (CI: -0.59 , $p < 0.05$) and $Cu_{30\text{ cm}}$ (CI: -0.58 , $p < 0.05$). **B** content had significant correlation with $As_{30\text{ cm}}$ (CI: 0.57 , $p < 0.05$), $Tl_{30\text{ cm}}$ (CI: 0.57 , $p < 0.05$), $Fe_{30\text{ cm}}$ (CI: 0.56 , $p < 0.05$), $Cu_{30\text{ cm}}$ (CI: 0.55 , $p < 0.05$), $Pb_{30\text{ cm}}$ (CI: 0.55 , $p < 0.05$), $Zn_{30\text{ cm}}$ (CI: 0.54 , $p < 0.05$) and $Ba_{30\text{ cm}}$ (CI: 0.50 , $p < 0.10$). **Cr** was correlated with $Tl_{15\text{ cm}}$ (CI: -0.71 , $p < 0.01$), $Cu_{15\text{ cm}}$ (CI: -0.66 , $p < 0.01$), $Pb_{15\text{ cm}}$ (CI: -0.66 , $p < 0.01$), $Tl_{30\text{ cm}}$ (CI: -0.55 , $p < 0.05$), $Pb_{30\text{ cm}}$ (CI: -0.54 , $p < 0.05$), $As_{15\text{ cm}}$ (CI: 0.50 , $p < 0.10$) and $Zn_{15\text{ cm}}$ (CI: -0.50 , $p < 0.10$). **Cu** content in apical leaves had significant correlation with $B_{15\text{ cm}}$ (CI: 0.83 , $p < 0.01$), $Ag_{15\text{ cm}}$ (CI: 0.78 , $p < 0.01$), $Ba_{30\text{ cm}}$ (CI: 0.74 , $p < 0.01$), $Fe_{15\text{ cm}}$ (CI: 0.70 , $p < 0.01$), $B_{30\text{ cm}}$ (CI: 0.60 , $p < 0.05$), $Zn_{15\text{ cm}}$ (CI: 0.57 , $p < 0.05$) and $Mn_{15\text{ cm}}$ (CI: 0.56 , $p < 0.05$). **Fe** content was affected by $B_{30\text{ cm}}$ (CI: 0.84 , $p < 0.01$), $Mn_{30\text{ cm}}$ (CI: 0.64 , $p < 0.01$), $Ba_{30\text{ cm}}$ (CI: 0.62 , $p < 0.05$), $B_{15\text{ cm}}$ (CI: 0.61 , $p < 0.05$), $Mn_{15\text{ cm}}$ (CI: 0.61 , $p < 0.05$), $Ba_{15\text{ cm}}$ (CI: 0.52 , $p < 0.10$), and $Cr_{30\text{ cm}}$ (CI: 0.51 , $p < 0.10$). **Hg** was correlated with $Cu_{15\text{ cm}}$ (CI: 0.90 , $p < 0.01$), $Tl_{15\text{ cm}}$ (CI: 0.90 , $p < 0.01$), $Pb_{15\text{ cm}}$ (CI: 0.88 , $p < 0.01$), $Zn_{15\text{ cm}}$ (CI: 0.85 , $p < 0.01$), $Zn_{30\text{ cm}}$ (CI: 0.72 , $p < 0.01$), $Pb_{30\text{ cm}}$ (CI: 0.68 , $p < 0.01$), $Tl_{30\text{ cm}}$ (CI: 0.67 , $p < 0.01$), $Fe_{30\text{ cm}}$ (CI: 0.66 , $p < 0.01$), $Fe_{15\text{ cm}}$ (CI: 0.60 , $p < 0.05$) and $Cu_{30\text{ cm}}$ (CI: 0.58 , $p < 0.05$). Finally, **Zn** presented correlation with $Ag_{15\text{ cm}}$ (CI: 0.69 , $p < 0.01$), $B_{15\text{ cm}}$ (CI: 0.58 , $p < 0.05$), and $Ba_{15\text{ cm}}$ (CI: 0.52 , $p < 0.10$).

In basal leaves, **As** content was correlated with $B_{30\text{ cm}}$ (CI: 0.79 , $p < 0.01$), $B_{15\text{ cm}}$ (CI: 0.77 , $p < 0.01$), $Ba_{15\text{ cm}}$ (CI: 0.62 , $p < 0.05$), $Mn_{15\text{ cm}}$ (CI: 0.59 , $p < 0.05$), $Cr_{30\text{ cm}}$ (CI: 0.55 , $p < 0.05$), $Ag_{30\text{ cm}}$ (CI: 0.54 , $p < 0.05$) $Ag_{15\text{ cm}}$ (CI: 0.49 , $p < 0.10$) and $Cr_{15\text{ cm}}$ (CI: 0.47 , $p < 0.10$). **B** with $Ag_{15\text{ cm}}$ (CI: -0.81 , $p < 0.01$), $Fe_{15\text{ cm}}$ (CI: -0.65 , $p < 0.01$) and

$Ba_{15\text{ cm}}$ (CI: -0.63 , $p < 0.05$). **Cr** was significantly affected by $B_{30\text{ cm}}$ (CI: 0.72 , $p < 0.01$), $Mn_{15\text{ cm}}$ (CI: 0.68 , $p < 0.01$), $Ba_{15\text{ cm}}$ (CI: 0.65 , $p < 0.01$), $B_{15\text{ cm}}$ (CI: 0.64 , $p < 0.01$), $Ag_{30\text{ cm}}$ (CI: 0.56 , $p < 0.01$), $Ba_{30\text{ cm}}$ (CI: 0.53 , $p < 0.05$) and $Mn_{30\text{ cm}}$ (CI: 0.52 , $p < 0.10$). Finally, **Cu** content in basal leaves was correlated with $As_{30\text{ cm}}$ (CI: -0.63 , $p < 0.05$), $Tl_{30\text{ cm}}$ (CI: -0.59 , $p < 0.01$), $Fe_{30\text{ cm}}$ (CI: -0.58 , $p < 0.05$), $Pb_{30\text{ cm}}$ (CI: -0.58 , $p < 0.05$), $Zn_{30\text{ cm}}$ (CI: -0.52 , $p < 0.10$) and $Ag_{15\text{ cm}}$ (CI: 0.45 , $p < 0.10$). **Fe**, **Hg** and **Zn** content in basal leaves had no significant correlation with TEs (Table A3).

In grape (Table A4), **As** was weak correlated ($p < 0.10$) only with $B_{30\text{ cm}}$ (CI: 0.46); and **B** with $As_{30\text{ cm}}$ (CI: 0.47). **Cr** was affected by $B_{30\text{ cm}}$ (CI: 0.65 , $p < 0.01$), $B_{15\text{ cm}}$ (CI: 0.62 , $p < 0.05$), $Mn_{15\text{ cm}}$ (CI: 0.60 , $p < 0.05$), $Ba_{15\text{ cm}}$ (CI: 0.57 , $p < 0.05$), and $Fe_{15\text{ cm}}$ (CI: 0.48 , $p < 0.10$). **Cu** was correlated with $Mn_{15\text{ cm}}$ and $Mn_{30\text{ cm}}$ (CI: 0.62 and CI: 0.55 , $p < 0.05$, respectively); **Hg** with $B_{15\text{ cm}}$ (CI: -0.53 , $p < 0.05$); and **Zn** with $Ag_{15\text{ cm}}$ (CI: 0.56 , $p < 0.01$), $Pb_{30\text{ cm}}$ (CI: -0.50 , $p < 0.10$), and $Tl_{30\text{ cm}}$ (CI: -0.50 , $p < 0.10$), $As_{30\text{ cm}}$ (CI: -0.45 , $p < 0.10$), $Mn_{30\text{ cm}}$ (CI: -0.45 , $p < 0.10$), and $Ag_{30\text{ cm}}$ (CI: -0.44 , $p < 0.10$). **Fe** content in berries had no significant correlation with soils TE content.

TEg and TEw showed weak (Cr in apical leaves, Fig. 3) or no significant correlation (data not shown).

3.6.5. Correlation analysis of TE concentration in onion, water and soil

In onion bulbs, **As** content was correlated with $Tl_{30\text{ cm}}$ (CI: -0.82 , $p < 0.05$), $Zn_{30\text{ cm}}$ (CI: -0.80 , $p < 0.10$) and $Pb_{30\text{ cm}}$ (CI: -0.74 , $p < 0.10$). **B** had correlation with $As_{15\text{ cm}}$ (CI: 0.81 , $p < 0.05$), $Cr_{15\text{ cm}}$ (CI: 0.76 , $p < 0.10$), $Ag_{15\text{ cm}}$ (CI: 0.74 , $p < 0.10$) and $Zn_{15\text{ cm}}$ (CI: 0.73 , $p < 0.10$). **Cr** presented significant correlation with $Zn_{30\text{ cm}}$ (CI: -0.90 , $p < 0.05$), $Ag_{15\text{ cm}}$ (CI: -0.89 , $p < 0.05$), $B_{30\text{ cm}}$ (CI: -0.87 , $p < 0.05$), $As_{30\text{ cm}}$ (CI: -0.84 , $p < 0.05$) and $As_{15\text{ cm}}$ (CI: -0.76 , $p < 0.10$). **Cu** was correlated with $Cr_{15\text{ cm}}$ (CI: -0.82 , $p < 0.05$), $Ag_{30\text{ cm}}$ (CI: -0.79 , $p < 0.10$), $Cr_{30\text{ cm}}$ (CI: -0.77 , $p < 0.10$), $Zn_{30\text{ cm}}$ (CI: -0.75 , $p < 0.10$) and $As_{15\text{ cm}}$ (CI: -0.74 , $p < 0.10$). Finally, **Zn** had significant correlation with $Pb_{15\text{ cm}}$ (CI: -0.95 , $p < 0.01$), $Tl_{15\text{ cm}}$ (CI: -0.95 , $p < 0.01$), $Ba_{15\text{ cm}}$ (CI: -0.94 , $p < 0.01$), $Fe_{15\text{ cm}}$ (CI: -0.94 , $p < 0.01$), $Cu_{15\text{ cm}}$ (CI: -0.93 , $p < 0.01$), $Mn_{15\text{ cm}}$ (CI: -0.93 , $p < 0.01$), $Ag_{15\text{ cm}}$ (CI: -0.91 , $p < 0.01$), $B_{30\text{ cm}}$ (CI: -0.84 , $p < 0.05$), $As_{15\text{ cm}}$ (CI: -0.82 , $p < 0.05$), $As_{30\text{ cm}}$ (CI: -0.80 , $p < 0.05$), $Cr_{30\text{ cm}}$ (CI: -0.79 , $p < 0.10$), $Ag_{30\text{ cm}}$ (CI: -0.76 , $p < 0.10$) and $B_{15\text{ cm}}$ (CI: -0.76 , $p < 0.10$). **Fe** content in bulbs had no significant correlation with TEs (Table A5).

In onion leaves, **Cr** presented significant correlation with $As_{15\text{ cm}}$ (CI: -0.95 , $p < 0.01$), $B_{15\text{ cm}}$ (CI: -0.93 , $p < 0.01$), $B_{30\text{ cm}}$ (CI: -0.91 , $p < 0.01$), $Ag_{15\text{ cm}}$ (CI: -0.87 , $p < 0.05$), $As_{30\text{ cm}}$ (CI: -0.84 , $p < 0.05$), $Zn_{15\text{ cm}}$ (CI: -0.81 , $p < 0.05$), $Zn_{30\text{ cm}}$ (CI: -0.76 , $p < 0.10$) and $Fe_{15\text{ cm}}$ (CI: -0.73 , $p < 0.10$). **Cu** with $Ba_{15\text{ cm}}$ (CI: 0.91 , $p < 0.01$), $Pb_{15\text{ cm}}$ (CI: 0.91 , $p < 0.01$), $Tl_{15\text{ cm}}$ (CI: 0.91 , $p < 0.01$), $Fe_{15\text{ cm}}$ (CI: 0.90 , $p < 0.01$), $Mn_{15\text{ cm}}$ (CI: 0.89 , $p < 0.05$), $Zn_{30\text{ cm}}$ (CI: 0.88 , $p < 0.05$), $Ag_{15\text{ cm}}$ (CI: 0.84 , $p < 0.05$), $Ag_{30\text{ cm}}$ (CI: 0.80 , $p < 0.05$), $B_{30\text{ cm}}$

(CI: 0.80, $p < 0.10$), As_{15 cm} (CI: 0.78, $p < 0.10$), As_{30 cm} (CI: 0.77, $p < 0.10$) and Cr_{30 cm} (CI: 0.75, $p < 0.10$). Fe had significant correlation with Ag_{30 cm} (CI: 0.83, $p < 0.05$) and As_{30 cm} (CI: 0.77, $p < 0.10$). Finally, Zn showed correlation with Ag_{30 cm} (CI: 0.84, $p < 0.05$), Tl_{30 cm} (CI: 0.79, $p < 0.05$), Ag_{15 cm} (CI: 0.77, $p < 0.10$), B_{30 cm} (CI: 0.76, $p < 0.10$), As_{30 cm} (CI: 0.75, $p < 0.10$), Ba_{30 cm} (CI: 0.75, $p < 0.10$), Cr_{30 cm} (CI: 0.75, $p < 0.10$), Cu_{30 cm} (CI: 0.74, $p < 0.10$), Fe_{15 cm} (CI: 0.74, $p < 0.10$), Pb_{15 cm} (CI: 0.74, $p < 0.10$) and Tl_{15 cm} (CI: 0.74, $p < 0.10$). As and B content in onion leaves had no significant correlation with other elements (Table A6).

TEw and TEo showed weak or no significant correlation (data not shown).

4. Discussion

Our analyses showed that concentrations of As, B, Cr, Fe, Hg and Tl are excessive in soils being used for agricultural purposes. According to (Hu et al., 2013), the highly significant correlation among TEs tested, suggest a common and natural source for concentrations observed, and there is no evidence that support that anthropic activity is directly responsible for increase the concentration of a single metal. However, use of these soils for agricultural purposes results indirectly in anthropogenic activity influencing bioavailability. This is in concordance with O'Reilly et al. (2010) that suggest a natural source of As and B in waters from Río Jáchal.

TEw had no significant correlation with TE content in soil and plants, suggesting that TEw may not be constant and fluctuates over time. Additionally, TEw determinations indicated inputs to irrigation water from the soil system, while that of the soil reflect accumulation-lixiviation processes that occur for a period of time, so TEs determination reproduce the result of such processes (Alloway, 2013).

In grapes and bulbs, As, Cr, Cu, and Fe, exceeded the limits established for vegetables by the Argentinian laws (CAA), implying that their intake is a high risk for human health. Currently, wine production in Jáchal is not an important economic activity despite agro-ecological features that makes the activity promissory. This region however, is a national onion producer, so considering the high TEo assessed, this activity should be seriously reconsidered for human consumption. Although in plant tissues Tl concentration measured was not excessive, it was in soils, which indicates a low bioavailability of this element. In contrast, Zn and Cu levels are low in soils, but in vegetables reach concentrations above the accepted limits, suggesting high mobility of these elements and an accumulation process. Some TE do not Argentinian regulations, such as Fe, which is excessive in grape and onion according to limits established for vegetables (CAA), suggesting a relatively high concentration in soil for agricultural purpose.

It is important to note that correlation analyses determine which variables are associated with each other, but does not necessarily explain causal relationships, thus some correlations may not have biological or physicochemical meaning in the studied environment. Soil variables differentially affected each TE concentration in plant tissues depending on the species and organs tested. In grapevine, we observed that variables at depths of 15–30 cm are more influential than those at 0–15 cm, but the opposite was observed in onion, coincidentally with the root depth reached for each species. The proportion of sand had high correlation with the presence of As, B, Cr, Cu, and Fe in different parts of the grape plant indicating low soil retention capacity and high plant intake. SAR exhibited a significant negative correlation with As, B, Hg, and Zn in grapes (low effect was observed in onion), while Ca and Mg showed positive correlation. According to Harter (1992), Uwamariya et al. (2015), and Kumpiene et al. (2008), Ca and Mg could be in competition with TEs for soil binding sites, increasing their mobility and bioavailability for plants. However, Ca had no effect on the onion leaves and Mg had a negative correlation with Zn concentration, probably due to competition between the plant intake and/or the presence of Mg compounds in the soil, that can immobilize TE, such as Al, Cd, Co, and Zn (Rengel et al., 2015; Yin and Zhu, 2016; Wang et al., 2003). In our study, P and OM in soils were in low concentration, but

at other cultivated sites, where the OM content was higher, the immobilization of trace metals can be increased (Lai et al., 2010; Wightwick et al., 2010, Nessner Kavamura and Esposito, 2010). The positive correlation observed between As content in onion leaves and P in soil, indicated that these elements may compete for binding sites in soils (Goh and Lim, 2004), probably due to their chemical similarity (Ghosh et al., 2015). However, in some cases negative or no linear correlation among TEs, TEg, and TEo was observed, suggesting the importance of the soil variables and the complex interaction between elements mobility and bioavailability in the area of Jáchal (Tang et al., 2012; Wightwick et al., 2010; Jung, 2008) that may result in a higher plant intake and the subsequent decrease in the soil. In addition, the high mobility of TE also means high lixiviation in the soil, which may result in a negative correlation due to a low content of superficial TE, while at a greater depth the roots would be able to absorb them. Considering the results of the TEs correlation analysis, mostly CI were highly significant and positive, suggesting no specific lixiviation processes.

Physicochemical soil analyses indicated that conditions present at Jáchal, increase metal mobility. Low content of OM, clay, and P reduce metal retention and competition (for instances P with As) in plant intake, while high EC may influence the soil structure and thus TE mobility (Acosta et al., 2011; Kwiatkowska-Malina, 2017). High pH values could reduce metal bioavailability, except for As that shows higher solubilization in alkaline conditions (Ferguson and Gavis, 1972; Frost and Griffin, 1976). However, these effects reported for TE mobility based in soil conditions is not completely reflected in correlations analyses for TE concentration in tissues, indicating the complex interactions between soil variables with metals and biological process that produce plant metal intake.

TEg and TEo was differentially correlated with others TE in soil depending on the organ and species considered. In apical leaves As had negative correlation with other TEs suggesting competition or retention in soil. Fe oxides in soils are able to adsorb As and other TE reducing their mobility (Dixit and Hering, 2003; Elliott et al., 1986; Yin et al., 2016), but in basal leaves all correlations were positive and in grapes there was a low significant correlation only with B at 15–30 cm, which suggests that As intake and transport inside the plant is complex and independent of other TE present. In onion bulbs, As had negative correlation with Hg, Tl, and Zn. In general, TE content in grapes had few significant correlations with TEs, showing that TE in berries may be given by translocation from other organs and no by direct soil intake. Similar condition was observed in onion, but in bulbs Zn was correlated negatively with other TEs, denoting competition for plant intake.

The data obtained demonstrate very high concentration of TEs, TEw, TEg, and TEo in the region of Jáchal. Human exposure occurs through water, food consumption (fresh or passed berries, wine and onion bulbs) or direct contact with soil; although there is no information available regarding TE poisoning (especially with As) in this region.

5. Conclusions

In the region of Jáchal, Argentina, high TE content in different environmental samples were found (TEs, TEw, TEg, TEo). In soils and water, elevated As, B, Cr, Mn, Fe, Hg, and Tl concentration were detected. Moreover, grapevine and onion showed high As, Cr, Cu, Fe, and Zn content indicating high bioavailability of these elements. Also physicochemical results suggest that the soil has a low adsorption capacity and conditions that benefit the mobility of these elements. Correlation analyses indicated a common TE source and concentration in water had no significant correlation with values founded in soil and plants, implying that these elements concentration in water may not be constant over time and/or in soils complex accumulation-lixiviation processes are occurring. Human exposure will occur by the way of ingestion of water and food, or direct contact with soil. More studies and evaluation of TE concentration and mobility in arid soils are necessary to determine remediation strategies to minimize negative effects and ensure the safe production of plants.

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Appendix

Table A1

Instrument settings and data acquisition parameters for ICP-MS.

Instrument	Elan DRC-e (Perkin-Elmer SCIEX, Thornhill, Canada)
Sample uptake rate ($\mu\text{L min}^{-1}$)	1000
Sample introduction	Nebulizer model PFA-ST, coupled to a quartz cyclonic spray chamber with internal baffle and drain line, cooled with the PC3 system from ESI (Omaha - NE, USA)
RF power (W)	1100
Gas flow rates (L min^{-1})	Plasma, 13.5; auxiliary, 1.2; nebulizer, 0.85
Interface	Ni cones (sampler and skimmer)
Cell gas A	None
Standard mode	^{107}Ag (0.008), ^{75}As (0.05), ^{11}B (0.05), ^{138}Ba (0.001), ^{51}Cr (0.02), ^{63}Cu (0.01), ^{57}Fe (0.04), ^{202}Hg (0.002), ^{55}Mn (0.002), ^{208}Pb (0.001), ^{82}Se (0.02), ^{205}Tl (0.001), ^{66}Zn (0.005).
Scanning mode	Peak hopping
Dwell time (ms)	30 in standard mode
Number of replicate	10

* isotope (limit of detection as 3 s of instrumental blank in $\mu\text{g L}^{-1}$).

Table A2

Pearson's correlation between trace elements (TE) content in grapevine apical leaves and in soil. Only the elements that exceeded the limits established were considered. * $p < 0.10$; ** $p < 0.05$; *** $p < 0.01$. Significant values are shown in bold.

		TE in grapevine apical leaves						
		As	B	Cr	Cu	Fe	Hg	Zn
TE in soil	Ag _{15 cm}	0.31	-0.07	0.17	0.78***	0.24	0.03	0.69***
	Ag _{30 cm}	-0.40	0.10	-0.31	0.37	0.34	0.39	0.19
	As _{15 cm}	-0.37	-0.02	-0.50*	-0.02	-0.26	0.39	-0.12
	As _{30 cm}	-0.54**	0.57**	-0.44	-0.08	0.15	0.43	-0.03
	B _{15 cm}	0.29	0.02	0.28	0.83***	0.61**	0.11	0.58**
	B _{30 cm}	0.25	0.22	0.40	0.60**	0.84***	0.07	0.35
	Ba _{15 cm}	0.28	-0.09	0.28	0.74***	0.52*	0.13	0.52*
	Ba _{30 cm}	-0.16	0.50*	0.07	0.16	0.62**	0.31	0.00
	Cr _{15 cm}	-0.05	-0.13	-0.12	0.39	0.15	0.29	0.05
	Cr _{30 cm}	-0.06	0.29	0.02	0.39	0.51*	0.38	0.06
	Cu _{15 cm}	-0.65***	0.09	-0.66***	0.44	0.09	0.90***	0.26
	Cu _{30 cm}	-0.58**	0.55**	-0.41	-0.06	0.33	0.58**	-0.12
	Fe _{15 cm}	-0.18	-0.15	-0.32	0.70***	0.13	0.60**	0.42
	Fe _{30 cm}	-0.59**	0.56**	-0.44	-0.01	0.28	0.66***	-0.11
	Hg _{15 cm}	0.27	-0.20	0.09	0.21	-0.11	-0.14	0.04
	Hg _{30 cm}	0.19	-0.30	0.01	0.17	-0.17	-0.17	0.04
	Mn _{15 cm}	0.12	-0.07	0.18	0.56**	0.61**	0.28	0.20
	Mn _{30 cm}	-0.16	0.42	0.07	0.10	0.64***	0.31	-0.12
	Pb _{15 cm}	-0.64***	0.07	-0.66***	0.29	-0.07	0.88***	0.12
	Pb _{30 cm}	-0.65***	0.55**	-0.54**	-0.12	0.12	0.68***	-0.18
Se _{15 cm}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Se _{30 cm}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Tl _{15 cm}	-0.69***	0.10	-0.71***	0.31	-0.08	0.90***	0.17	
Tl _{30 cm}	-0.66***	0.57**	-0.55**	-0.09	0.13	0.67***	-0.13	
Zn _{15 cm}	-0.43	0.04	-0.50*	0.57**	0.13	0.85***	0.25	
Zn _{30 cm}	-0.59**	0.54**	-0.43	0.06	0.33	0.72***	-0.11	

Table A3

Pearson's correlation between trace elements (TE) content in grapevine basal leaves and in soil. Only the elements that exceeded the limits established were considered. * $p < 0.10$; ** $p < 0.05$; *** $p < 0.01$.

		TE in grapevine basal leaves						
		As	B	Cr	Cu	Fe	Hg	Zn
TE in soil	Ag _{15 cm}	0.49*	-0.81***	0.40	0.45*	-0.08	-0.21	0.17
	Ag _{30 cm}	0.54**	0.20	0.56**	-0.16	0.09	-0.34	-0.25
	As _{15 cm}	-0.11	0.03	-0.13	-0.20	-0.11	-0.04	-0.19
	As _{30 cm}	-0.03	0.25	0.11	-0.63**	-0.32	-0.12	-0.37
	B _{15 cm}	0.77***	-0.54**	0.64***	0.34	0.02	-0.36	0.06
	B _{30 cm}	0.79***	-0.19	0.72***	0.13	0.04	-0.37	-0.02

(continued on next page)

Table A3 (continued)

		TE in grapevine basal leaves						
		As	B	Cr	Cu	Fe	Hg	Zn
Ba ₁₅ cm		0.62**	-0.63**	0.65***	0.29	-0.08	-0.36	0.00
Ba ₃₀ cm		0.43	0.24	0.53**	-0.39	-0.10	-0.24	-0.27
Cr ₁₅ cm		0.47*	-0.11	0.37	0.06	0.02	-0.29	-0.16
Cr ₃₀ cm		0.55**	-0.03	0.49*	-0.14	-0.06	-0.33	-0.21
Cu ₁₅ cm		0.04	-0.29	0.34	-0.20	-0.11	-0.20	-0.24
Cu ₃₀ cm		-0.01	0.30	0.24	-0.60**	-0.21	-0.15	-0.35
Fe ₁₅ cm		0.32	-0.65***	0.43	0.23	-0.05	-0.31	-0.05
Fe ₃₀ cm		-0.06	0.19	0.21	-0.58**	-0.23	-0.16	-0.35
Hg ₁₅ cm		0.30	-0.27	0.01	0.37	0.11	-0.07	0.16
Hg ₃₀ cm		0.30	-0.18	0.04	0.37	0.15	-0.08	0.13
Mn ₁₅ cm		0.59**	-0.28	0.68***	0.15	-0.02	-0.35	-0.10
Mn ₃₀ cm		0.41	0.34	0.52*	-0.35	-0.04	-0.21	-0.25
Pb ₁₅ cm		-0.18	-0.23	0.18	-0.13	-0.02	-0.08	-0.14
Pb ₃₀ cm		-0.09	0.33	0.18	-0.58**	-0.16	-0.05	-0.31
Tl ₁₅ cm		-0.19	-0.24	0.16	-0.16	-0.05	-0.07	-0.15
Tl ₃₀ cm		-0.08	0.30	0.19	-0.59**	-0.18	-0.06	-0.32
Zn ₁₅ cm		0.22	-0.42	0.40	-0.01	-0.05	-0.26	-0.16
Zn ₃₀ cm		0.05	0.24	0.29	-0.52*	-0.13	-0.16	-0.31

Table A4

Pearson's correlation between trace elements (TE) content in grapevine berries and in soil. Only the elements that exceeded the limits established were considered. *p < 0.10; **p < 0.05; ***p < 0.01.

		TE in grapevine berries						
		As	B	Cr	Cu	Fe	Hg	Zn
TE in soil	Ag ₁₅ cm	0.38	-0.28	0.43	-0.10	0.34	-0.40	0.56**
	Ag ₃₀ cm	-0.05	-0.06	0.18	0.13	-0.22	0.15	-0.44*
	As ₁₅ cm	-0.09	0.21	0.00	-0.11	-0.33	-0.05	-0.34
	As ₃₀ cm	0.10	0.47*	0.14	0.02	-0.13	0.02	-0.45*
	B ₁₅ cm	0.42	-0.33	0.62**	0.22	0.19	-0.53**	0.27
	B ₃₀ cm	0.46*	-0.26	0.65***	0.43	0.19	-0.40	0.11
	Ba ₁₅ cm	0.42	-0.38	0.57**	0.26	0.30	-0.42	0.39
	Ba ₃₀ cm	0.20	-0.01	0.36	0.36	-0.05	-0.13	-0.39
	Cr ₁₅ cm	0.11	-0.19	0.36	0.21	-0.30	-0.21	-0.21
	Cr ₃₀ cm	0.34	-0.06	0.57**	0.30	-0.17	-0.41	-0.25
	Cu ₁₅ cm	0.04	0.07	0.23	0.03	-0.02	-0.22	-0.21
	Cu ₃₀ cm	0.15	0.37	0.23	0.18	-0.08	-0.03	-0.43
	Fe ₁₅ cm	0.32	-0.18	0.48*	-0.04	0.10	-0.38	0.27
	Fe ₃₀ cm	0.23	0.42	0.30	0.09	-0.09	-0.05	-0.31
	Hg ₁₅ cm	0.14	-0.22	0.20	-0.13	-0.03	-0.17	0.21
	Hg ₃₀ cm	0.02	-0.23	0.09	-0.13	-0.07	0.03	0.16
	Mn ₁₅ cm	0.33	-0.36	0.60**	0.62**	0.04	-0.39	0.04
	Mn ₃₀ cm	0.16	-0.05	0.37	0.55**	-0.12	-0.15	-0.45*
	Pb ₁₅ cm	0.01	0.10	0.12	-0.08	-0.03	-0.05	-0.06
	Pb ₃₀ cm	0.01	0.24	0.08	0.02	-0.12	0.05	-0.50*
Tl ₁₅ cm	-0.01	0.16	0.10	-0.11	-0.05	-0.07	-0.11	
Tl ₃₀ cm	0.02	0.28	0.09	0.01	-0.10	0.04	-0.50*	
Zn ₁₅ cm	0.21	-0.08	0.42	0.00	-0.04	-0.37	-0.05	
Zn ₃₀ cm	0.16	0.28	0.29	0.15	-0.14	-0.11	-0.44	

Table A5

Pearson's correlation between trace elements (TE) content in onion bulbs and in soil. Only the elements that exceeded the limits established were considered. *p < 0.10; **p < 0.05; ***p < 0.01.

		TE in onion bulbs						
		As	B	Cr	Cu	Fe	Zn	
TE in soil	Ag ₁₅ cm	-0.63	0.74*	-0.89**	-0.69	0.51	-0.91***	
	Ag ₃₀ cm	-0.57	0.34	-0.71	-0.79*	-0.08	-0.76*	
	As ₁₅ cm	-0.44	0.81**	-0.76*	-0.74*	0.26	-0.82**	
	As ₃₀ cm	-0.74*	0.59	-0.84**	-0.72	0.25	-0.80**	
	B ₁₅ cm	-0.29	0.89**	-0.69	-0.66	0.36	-0.76*	
	B ₃₀ cm	-0.66	0.69	-0.87**	-0.77	0.3	-0.84**	
	Ba ₁₅ cm	-0.28	0.63	-0.64	-0.61	0.38	-0.94***	
	Ba ₃₀ cm	-0.65	-0.29	-0.48	-0.37	-0.02	-0.45	
	Cr ₁₅ cm	-0.54	0.76*	-0.82**	-0.82**	0.13	-0.61	
	Cr ₃₀ cm	-0.7	0.68	-0.89**	-0.77*	0.28	-0.79*	
	Cu ₁₅ cm	-0.28	0.64	-0.63	-0.58	0.42	-0.93***	
	Cu ₃₀ cm	-0.71	-0.19	-0.58	-0.38	0.14	-0.41	
	Fe ₁₅ cm	-0.31	0.64	-0.68	-0.62	0.42	-0.94***	

Table A5 (continued)

	TE in onion bulbs					
	As	B	Cr	Cu	Fe	Zn
Fe ₃₀ cm	−0.62	−0.28	−0.5	−0.39	−0.01	−0.33
Mn ₁₅ cm	−0.26	0.63	−0.62	−0.58	0.4	−0.93***
Mn ₃₀ cm	−0.50	−0.51	−0.27	−0.11	0.03	−0.2
Pb ₁₅ cm	−0.30	0.59	−0.64	−0.58	0.42	−0.95***
Pb ₃₀ cm	−0.74*	−0.16	−0.59	−0.38	0.12	−0.33
Tl ₁₅ cm	−0.32	0.62	−0.67	−0.61	0.41	−0.95***
Tl ₃₀ cm	−0.82**	0.01	−0.71	−0.49	0.19	−0.53
Zn ₁₅ cm	−0.35	0.73*	−0.71	−0.64	0.42	−0.93***
Zn ₃₀ cm	−0.80*	0.47	−0.90**	−0.75*	0.23	−0.73*

Table A6

Pearson's correlation between trace elements (TE) content in onion leaves and in soil. Only the elements that exceeded the limits established were considered. * $p < 0.10$; ** $p < 0.05$; *** $p < 0.01$.

TE in soil		TE in onion leaves					
		As	B	Cr	Cu	Fe	Zn
	Ag ₁₅ cm	0.20	0.41	−0.87**	0.84**	0.54	0.77*
	Ag ₃₀ cm	0.64	0.4	−0.70	0.80**	0.83**	0.84**
	As ₁₅ cm	0.32	0.55	−0.95***	0.78*	0.67	0.63
	As ₃₀ cm	0.52	0.27	−0.84**	0.77*	0.77*	0.75*
	B ₁₅ cm	0.12	0.6	−0.93***	0.70	0.50	0.51
	B ₃₀ cm	0.41	0.37	−0.91***	0.80*	0.71	0.76*
	Ba ₁₅ cm	0.15	0.71	−0.72	0.91***	0.49	0.72
	Ba ₃₀ cm	0.46	−0.09	−0.08	0.51	0.42	0.75*
	Cr ₁₅ cm	0.33	0.32	−0.96***	0.57	0.63	0.59
	Cr ₃₀ cm	0.41	0.3	−0.90***	0.75*	0.69	0.75*
	Cu ₁₅ cm	0.12	0.7	−0.70	0.89**	0.46	0.7
	Cu ₃₀ cm	0.27	−0.19	−0.11	0.44	0.26	0.74*
	Fe ₁₅ cm	0.11	0.68	−0.73*	0.90***	0.46	0.74*
	Fe ₃₀ cm	0.28	−0.17	−0.05	0.37	0.23	0.72
	Mn ₁₅ cm	0.11	0.71	−0.7	0.89**	0.46	0.7
	Mn ₃₀ cm	0.20	−0.28	0.24	0.24	0.07	0.56
	Pb ₁₅ cm	0.12	0.68	−0.68	0.91***	0.45	0.74*
	Pb ₃₀ cm	0.26	−0.28	−0.14	0.35	0.24	0.69
	Tl ₁₅ cm	0.14	0.68	−0.72	0.91***	0.49	0.74*
	Tl ₃₀ cm	0.38	−0.14	−0.33	0.54	0.43	0.79*
	Zn ₁₅ cm	0.16	0.65	−0.81**	0.88**	0.52	0.70
	Zn ₃₀ cm	0.44	0.15	−0.76*	0.71	0.65	0.83**

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