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**ASSESSMENT OF POTENTIAL HEALTH RISK DUE TO CONSUMPTION OF VEGETABLES GROWN NEAR A COPPER SMELTER IN CENTRAL CHILE**

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**Summary.** *It is known that the consumption of vegetables grown in mining areas could be a source of intake of potentially toxic elements. Accordingly, this study aimed to compare concentrations of arsenic and copper in edible parts of vegetables grown in a proximity to a copper smelter and in a control area, and compare the potential children health risks of the consumption of vegetables from both areas. Alimentary habits of infants (age of 1-5 years old) were determined through one-year-period surveys. The most consumed vegetables are potato, lettuce and carrot (consumption over 10 kg of fresh weight year<sup>-1</sup>). Leafy vegetables showed a higher capacity to accumulate As in comparison to underground vegetables. Among underground vegetables, only carrot exhibited As concentration in edible tissues above the limit of detection (0.008 mg kg<sup>-1</sup>). Values of HQ showed a wide difference between mining and control areas only for As (11 versus 60% of the risk limit). This increase was mainly related to lettuce since it has both high concentration of As and high consumption in the studied scenario. In contrast of As intake, HQ-values for Cu were similar between the mining and the control area. Only a combination of high concentration of elements in a particular vegetable and high consumption of this vegetable resulted in high hazard quotient (e.g. lettuce and carrot). However, there was no health risk associated with vegetable consumption in neither the mining nor the control area, since none of the hazard quotient values surpassed 1.0.*

**Keywords:** *copper, arsenic, lettuce, cabbage, chard, potato, carrot, beetroot, risk, health.*

### **Introduction**

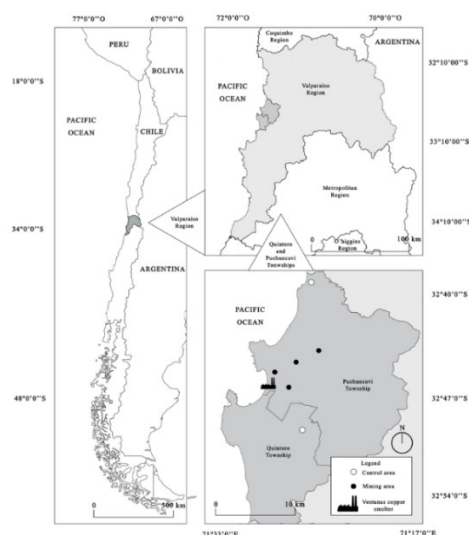
Human exposure to potentially toxic elements (PTE) has been a subject of great concern worldwide. If PTE are present in excessive concentrations, they might be hazardous to human health [1]. Specifically, several studies have reported that the influence of mining activities may increase PTE in soils [2]. Once in soils, PTE may potentially be accumulated in vegetable tissues and, consequently, enter the human food chain [3]. Thus, the consumption of vegetables grown in mining areas has been shown to be the main source of PTE intake in several locations [4, 5].

The Puchuncaví valley in the coastal area of central Chile has been exposed to massive atmospheric contamination with sulfur dioxide and PTE-rich particulate matter due to emissions from the Ventanas copper smelter [6]. In order to assess the potential impact of such emissions on the food security, the potential human health risk through vegetable consumption should be determined for a mining area and for a control area without mining activities [7]. In this way, results would allow discerning the real enrichment effect of mining activity on PTE human exposure.

**Objective of the article** – compare concentrations of arsenic and copper in edible parts of different vegetables cultivated in soils near a copper smelter and in a control area, and compare the potential human health risk of the consumption of vegetables coming from both areas.

### Materials and methods

Location of the study. We studied areas in close proximity to the Ventanas copper smelter (which will be referred to as “mining area”) and areas that were not affected by the smelter (which will be referred to as “control area”) (Figure 1). The average distance from the smelter to the mining and control areas was 3.8 and 10 km, respectively. The study was carried out from October 2016 until January 2017. Four contaminated sites (in the proximity to the Ventanas copper smelter) represented the mining area, while two uncontaminated sites (away from the Ventanas copper smelter) represented the control area. Both areas were comparable since they exhibited similar soil-climatic characteristics, such as textural class (sandy loam), moderately alkaline soil pH, rainfall rate and temperature.



**Figure 1 – Geographical location of the studied sites**

Studied vegetables. Only leafy vegetables – lettuce (*Lactuca sativa* L.), chard (*Beta vulgaris* L. var. *cicla* L.) and cabbage (*Brassica oleracea* L. var. *capitata* L.) – and underground vegetables – potato (*Solanum tuberosum* L.), beetroot (*Beta vulgaris* L. var. *crassa* (Alef.) J. Helm), and carrot (*Daucus carota* L. var. *sativus* (Hoffm.) – were considered in our investigation. According to our previous study, bulb and fruit vegetables exhibited low accumulation capacity of PTE. Thereby, they were not considered.

Once in the laboratory, edible tissues of vegetables were prepared for analyses. Special care was taken to remove external soil or dust contamination on the surface of vegetables. Leafy vegetables were thoroughly washed in the following sequence: tap water, 0.1 M HCl, distilled water, 0.05 M EDTA, distilled water, and again distilled water [8]. On the other hand, underground vegetables were washed with tap water, and then were peeled and washed with distilled water. Then, samples were cut into pieces, put into paper bags, and dried in an oven at 70 °C for 48 h. Later, samples were ground, sieved, and homogenized.

Concentrations of metals were measured using standard methods [9]. A standard reference material (NIST SRM 1570a – spinach leaves) was taken through the entire process with experimental values being within 10 % of the certified values.

Data analyses. The enrichment factor for PTE in soil and vegetables were calculated by dividing the PTE concentration in the mining area by the PTE concentration in the control area [10].

Risk estimation. Exposure to PTE was quantified using an indirect quantification method: chronic daily intake (DI) [10], which determined exposure by relating quantity of PTE ingested via vegetable consumption, body weight and consumption habits (17 children

were surveyed for this purpose). This exploratory study, conducted with a small number of children, will define the necessity of further research in other regions of Chile.

Once determined, DI is compared with the reference dose (RfD) (0.0003 and 0.04 mg kg<sup>-1</sup> for As and Cu, respectively). RfD-values represent the maximum allowed PTE intake. Then, hazard quotient (HQ) was calculated by dividing DI by RfD, taking into account that only if HQ is above 1, there may be a potential risk [10].

### Results and their discussion

Potentially toxic elements in edible tissues. Average concentrations of PTE in the edible parts of vegetables are shown in Tables 1 and 2 (in dry weight basis). In general, concentrations of PTE were higher for vegetables grown in the mining area than those grown in the control area. Analysis of EF shows that As holds the highest differences between mining and control areas, while Cu holds relatively similar values between both areas. Leafy vegetables showed a higher capacity to accumulate As in comparison to underground vegetables. Among underground vegetables, only carrot exhibited As concentration in edible tissues above the limit of detection (0.008 mg kg<sup>-1</sup>). However, As concentration in carrot grown in mining area is similar to that of lettuce and chard grown in the control area.

**Table 1 – Potentially toxic element concentration in edible tissues of leafy vegetables and the enrichment factor of PTE between the mining area and the control area (2016-2017)**

Data	Potentially toxic elements (PTE)	Species of vegetable		
		Lettuce	Chard	Cabbage
Average PTE concentration in vegetables from the control area (C), mg kg <sup>-1</sup> dry weight	As	0.23 ± 0.10	0.13 ± 0.02	< 0.008
	Cu	20.00 ± 3.60	13.00 ± 1.90	4.20 ± 0.90
Average PTE concentration in vegetables from the mining area (MA), mg kg <sup>-1</sup> dry weight	As	0.86 ± 0.49	0.35 ± 0.21	0.056 ± 0.022
	Cu	31.00 ± 15.00	37.00 ± 17.00	6.80 ± 2.00
Enrichment factor (MA/C)	As	3.7*	2.7*	>6.9**
	Cu	1.6	2.8*	1.6*

*Note.* \* Statistically significant difference between mining and control areas according to Mann-Whitney test; \*\* Statistical differences were not determined since As concentration in vegetables were below the limit of detection in the control area.

**Table 2 – Potentially toxic element concentration in edible tissues of underground vegetables and the enrichment factor of PTE between the mining area and the control area (2016-2017)**

Data	Potentially toxic elements (PTE)	Species of vegetable		
		Potato	Carrot	Beetroot
Average PTE concentration in vegetables from the control area (C), mg kg <sup>-1</sup> dry weight	As	<0.008	<0.008	<0.008
	Cu	10 ± 1.0	9.0 ± 1.0	8.0 ± 2.9
Average PTE concentration in vegetables from the mining area (MA), mg kg <sup>-1</sup> dry weight	As	<0.008	0.140 ± 0.036	<0.008
	Cu	10 ± 2.4	11 ± 2.3	5.5±2.6
Enrichment factor (MA/C)	As	-**	> 18**	-**
	Cu	1.0	1.2	0.69

*Note.* \* Statistically significant difference between mining and control areas according to Mann-Whitney test; \*\* Statistical differences were not determined since As concentration in vegetables were below the limit of detection in the control area.

Daily intake of PTE by vegetable consumption. According to US EPA [6], human exposure to PTE depends not only on PTE concentration in vegetables but also on the quantity consumed. Thereby, alimentary habits of infants (age of 1–5 years old) from Puchuncaví were determined (Table 3). Based on the results of the survey, the average

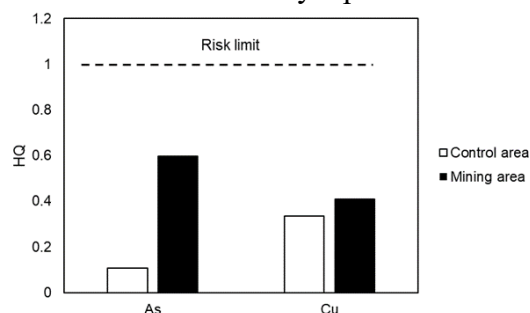
exposure time was 2.5 years (equivalent to 929 days) and the average body weight was 16 kg. The most consumed vegetables are potato, lettuce and carrot (consumption over 10 kg of fresh weight year<sup>-1</sup>).

**Table 3 – Mean vegetable consumption and alimentary habits of infants from the Puchuncaví valley (2016-2017)**

Ingestion rate (kg of fresh weight year <sup>-1</sup> ) of vegetables, based on the survey					
Leafy vegetables			Underground vegetables		
Lettuce	Chard	Cabbage	Potato	Carrot	Beetroot
14.0	1.7	3.2	18.0	12.0	2.9

Hazard quotient. Potential human health risk of PTE intake through consumption of vegetables from both areas is shown in Figure 2. Values of HQ showed a wide difference between the exposure and control areas only for As (11 % versus 60 % of the risk limit). This increase was mainly related to lettuce since it has both high concentration of As and high consumption in the studied scenario (see Tables 1 and 2).

In contrast of As intake, HQ-values for Cu were similar between the mining and the control area. Intake of Cu by children from Puchuncaví is mainly attributed to potato. Potato did not show a high concentration of Cu (see Table 1), but its high consumption implies a high daily intake. Therefore, local alimentary habits are a key factor to accurately estimate the intake of PTE. On the other hand, the similarity of the total hazard quotient for Cu in Figure 1 highlights the necessity of assessing both mining and control areas. If PTE exposure is quantified only for a mining area, as usual in literature [11], results may wrongly lead to think that all the daily intake of PTE is caused by a presumed contamination source.



**Figure 2 – Hazard quotient (HQ) of the consumption of the vegetables for each potentially toxic element in infants from the Puchuncaví valley**

In terms of risk assessment, results show that PTE exposure through vegetable consumption in the studied population is not a risk to human health in both areas. However, other PTE exposure sources as dust, soils, water and other food can increase the total hazard quotient. Thus, other environmental media must be considered in future studies. Likewise, future research should consider other age groups and other locations in Chile.

The topic of the research is relevant since several international studies have concluded that the intake of vegetables grown in contaminated areas may be a route of exposure to PTE, representing a potential human health risk [12–14].

### Conclusions

Accordingly to the objectives, the conclusions are as follow: leafy vegetables showed a higher capacity to accumulate As in comparison to underground vegetables.

Among underground vegetables, only carrot exhibited As concentration in edible tissues above the limit of detection (0.008 mg kg<sup>-1</sup>). Values of HQ showed a wide difference between mining and control areas only for As (11 % versus 60 % of the risk limit). This increase was mainly related to lettuce since it has both high concentration of As and high

consumption in the studied scenario. In contrast of As intake, HQ-values for Cu were similar between the mining and the control area.

Only a combination of high concentration of elements in a particular vegetable and high consumption of this vegetable resulted in high hazard quotient (e.g. lettuce and carrot). However, there was no health risk associated with vegetable consumption in neither the mining nor the control area, since none of the hazard quotient values surpassed 1.0.

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Алексеев И., Неаман А., Лизарди Н., Мондака П., Агилар М.  
**ОЦЕНКА ПОТЕНЦИАЛЬНОГО РИСКА ДЛЯ ЗДОРОВЬЯ ОТ  
ПОТРЕБЛЕНИЯ ОВОЩЕЙ, ВЫРАЩЕННЫХ ВБЛИЗИ  
МЕДЕПЛАВИЛЬНОГО КОМБИНАТА, В ЦЕНТРАЛЬНОМ ЧИЛИ**

**Реферат.** Цель исследования – сравнение концентраций мышьяка и меди в съедобных частях овощей (латук (*Lactuca sativa* L.), мангольд (*Beta vulgaris* L. var. *cicla* L.), капуста (*Brassica oleracea* L. var. *capitata* L.), картофель (*Solanum tuberosum* L.), свекла (*Beta vulgaris* L. var. *crassa* (Alef.) J. Helm), морковь (*Daucus carota* L. var. *sativus* (Hoffm.)), выращенных в непосредственной близости от медеплавильного

комбината, с концентрациями мышьяка и меди в овощах, выращенных контрольной зоне, и анализ потенциальных рисков для здоровья детей при потреблении овощей из обеих зон. Пищевые привычки детей (возраст 1-5 лет) определяли в ходе исследования в 2016-2017 гг. Самые потребляемые овощи – картофель, салат-латук и морковь (потребление более 10 кг свежего веса в год<sup>-1</sup>). Овощи, у которых использовали листья, показали более высокую способность к накоплению мышьяка по сравнению с овощами, у которых использовали подземные части. Среди последних только для моркови концентрация мышьяка в съедобных тканях была выше предела обнаружения (0,008 мг кг<sup>-1</sup>). Значения коэффициента риска показали значительные различия между двумя зонами исследования только для мышьяка (11 против 60 % от лимита риска). В основном, это увеличение обусловлено салатом-латуком, так как растение имеет высокую концентрацию мышьяка и значительные объемы потребления. В отличие от поглощения мышьяка, значения коэффициента опасности для меди были сходными для зоны медеплавильного комбината и контрольной зоны. Только сочетание высокой концентрации элементов в определенном овоще и высокого потребления этого овоща привело к высокому риску (например, салат-латук и морковь). Тем не менее, не обнаружено никакого риска для здоровья, связанного с потреблением овощей ни в зоне медеплавильного комбината, ни в контрольной зоне, поскольку ни одно из значений коэффициента опасности не превышало 1,0.

**Ключевые слова:** медь, мышьяк, салат-латук, капуста, мангольд, картофель, морковь, свёкла, риски для здоровья.

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