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Selenium and Copper in Vegetables and Fruits Grown on Long-Term Impacted Soils from Valparaiso Region, Chile

H. Pinochet, I. De Gregori, M. G. Lobos, E. Fuentes

Chemical Institute, Catholic University of Valparaíso, Post Office Box 4059, Valparaíso, Chile

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Studies of trace elements in ecosystems have indicated that many areas near metalliferous mines, urban complexes or major road systems contain anomalously high concentrations of these elements. The mining, manufacture and disposal of metals and metal- containing materials inevitably cause environmental pollution. This contamination concerns principally the zones where most metalurgical industries and mining activities are located (Chlopecka et al.1996). The consequences of such contamination are that toxic element concentrations in locally grown vegetables and crops may greatly exceed accepted standards, as may the element uptake by the consumers. This effect is more pronounced in areas close to the source of contamination, primarily metal smelters. More remote areas may also be contaminated because a substantial portion of toxic elements released from these sources into the environment are emitted into the atmosphere bound to small dust particles, as fumes or aerosols. Therefore a significant pathway for the pollution of terrestrial and aquatic ecosystems by toxic elements goes through the atmosphere, according to the meteorological conditions they can be transported over varying distances before deposition in different ecosystems.(Beaker and Senft 1995).

In Chile many ecosystems have been and are still susceptible to be contaminated by toxic elements produced especially by the mining and industrial processing of ores and metals, as these activities play an important role in our country. (Gonzalez et al. 1986). But these activities are well known as an important source of contamination by toxic elements, due to the enormous quantities of waste products.

This paper presents a comparative study on the uptake of selenium and copper by vegetable crops grown on two long term impacted soils and one non impacted soil from agricultural zones located in the Valparaíso region from Chile. Samples were collected at Puchuncavi and Catemu valleys, both zones impacted by smelter activities and Casablanca valley, location not subject to these activities. Cu was chosen because it is one of the most important essential elements for plants and animals and Chile is one of the most important producer of this element in the world. Se was retained due to its toxicological significance in animal nutrition. The Se present in the diet may result in either deficient or toxic responses and it is present in such significant amount in copper ores that it is obtained as a by product of the copper electrolytic refining processes.

Correspondence to: H. Pinochet

Atmospheric inputs of Cu to soils from dry and wet deposition varies considerably according to the proximity of industrial emissions containing Cu and the type and quantities of wind-blown dust (Baker et al. 1995). Se from soil is incorporated into plant tissues especially in inorganic form depending on various botanical and environmental factors (Arvy 1993,Gupta et al.1993, Landberg et al. 1994, Bell et al. 1992). The total Se concentration of soil pasture systems is important relatively to the health of grazing livestock. Concentrations less than 0.05-0.1mgkg^{-1} in animal feed produce Se deficiency; toxic effects on animals can occur when Se concentration reaches 2-5 mgkg^{-1} (Neal 1995, Hambiri 1993). The primary Se source for animals is dietary. Because of the narrow range between requirement and toxicity, treatment and prevention must be conducted with care. A quality hay, such alfalfa, can supply the Se nutritional requirements. Alfalfa has been reported as a passive selenium accumulator, the average concentrations are 0.03-0.08 µg g^{-1}, but levels as high as 57 µg g^{-1} have been repotted. (Witte et al. 1993). Although it is well established that Se is an essential nutrient for the normal functioning of animals and humans, it is less clear whether Se is essential for plants. Recent research on plant Se uptake has placed great emphasis on Se non-accumulators, including pasture plants, vegetables and serial crops and naturally established field plants. Non accumulator species generally contains less than 25 mg kg $^{-1}$. Se accumulation by these plants has been found to be profoundly influenced by the plant species, soil salinity and Se concentration, and field management strategies.

MATERIALS AND METHODS.

Soils were collected (April-May 1997) from zones located in the Valparaíso region, two affected by the emissions of mining complexes. Puchuncavi valley, an agricultural zone, at the north of Valparaíso city, receive the impact of the industrial complex “Las Ventanas”, where are located both a smelter and electrorefinery plant of Cu ore as well as a coal- fired thermoelectric power plant. Catemu valley located eastern of Valparaíso in the Aconcagua river valley, also receives the influence of a Cu ore smelter (Chagres). Both zones can be therefore regarded as strongly affected by emissions of mining complexes. The third selected zone was Casablanca valley, a rural agricultural area, located at south of Valparaíso. Two fodders (alfalfa and grass) and two fruits (grape and quince) were collected from all sampling sites. Also nine other vegetables were taken although they were not found in all studied area.

All samples were analyzed in triplicate. Cu and Se were determined in acid digested samples by atomic absorption spectrometry using a GBC model 905 AA spectrometer. Se by hydride generation AAS, using a GBC HG 3000 analytical continuous flow generator system, in samples solutions where Se (VI) was reduced previously to Se (IV) with 6 M HCl, at 90°C. Cu was determined by flame AAS. Standard addition method was used for all determinations. San Joaquin soil (SRM 2707 NIST), Irish soil (BCR) and White Clover (BCR 402) were used for the assessment of the total Cu and Se determination procedures. The % recovery for both elements ranged between 89 to 102 % in all CRM. Results are reported as mean ± confidence limits ($p < 0.05$, dry weight basis).

RESULTS AND DISCUSSION

Se and Cu concentration in soils, vegetables and fruits are presented in Tables 1 and 2, respectively. Relatively to Se concentration in soils it can be seen that the values are low and relatively constant in both impacted valleys, At Catemu valley the values are not higher than those obtained for Casablanca valley, the reference site. All values ranged in the normal levels (0.1-0.5 µg g^{-1}) and never exceeded the reported critical toxicity values (5-10 µg Se g^{-1}). On the contrary all Cu concentrations for soils are higher than those considered as critical (60-125 µg Cu g^{-1}) (Alloway, 1995), with the only exception of soils from Casablanca (28 µg g^{-1}) that have a level considered as background in agricultural soils. At Puchuncavi valley, a clear decrease is observed in Cu concentrations with distance from the smelter, this behavior is not so clear at Catemu valley where Santa Margarita soils have a Cu concentration up to 8 time the level found at Panquehue. An explanation to this fact could be that the road crossing this little village, have been filling with solids wastes from Chagres smelter. From these results it can be seen that the more impacted sites are La Greda and Santa Margarita from Puchuncavi and Catemu valley respectively.

Vegetables are important products of the human and animal diet, specially for cattle and horses. Element concentrations of soil-pasture systems are important in relation to the health of grazing livestock. Alfalfa is classified as quality hay and can supply the nutritional requirements of essential elements for livestock and horses, both kind of animals grazing in this region. For this reason in this study Alfalfa and grass were selected as vegetal matrices. They were found in all sampling sites. As can be seen in Table 1 and 2 Cu and Se concentrations in fruits are low, however the quince leaves from all samples sites have the highest values for both elements. This behavior clearly show that element concentrations in quince plant parts differ. Cu concentrations in fruits (quince and grape), from all sites, have levels lower than those reported as critical concentrations in plants, defined as the level above which toxicity effect likely (20-100 µg g^{-1}) (Alloway, 1995). However quince leaves from all sites exceed these values (whit the exception of Nogales). Alfalfa, from Nogales and Panquehue have Cu concentrations lower than the critical values, the sampling sites farther away from the respective smelter. In all vegetables and fruits from Casablanca (reference zone), the Cu levels are lower than 10 µg g^{-1}.

In Figures 1 and 2 are presented the Cu and Se concentrations respectively, in Alfalfa and quince fruit and leaves from the different zones. In Alfalfa from Puchuncavi valley Cu concentrations decrease with distances from the smelter (a similar behavior was observed for Cu in soils) (see Table 2). In Catemu valley the highest values of Cu concentration in Alfalfa were found at Santa Margarita, a contaminated site. The Se concentrations in Alfalfa have not the same pattern. On the other hand, in quince leaves, both elements have values higher than those found in the fruits. The ratio of element concentration (leaves/ fruits) ranged between 3.5 to 41.7 for Cu and 3.8 to 25.4 for Se; while the ratio values for the quinces from Casablanca were only 2.2 and 3.3 for Cu and Se respectively.

Table 1. Selenium concentration in plants and soils (μg g^{-1} d.w.) from different zones of Valparaíso region.

Zone	Site	Soil	Plants					
			Alfalfa *Medico sativa*	Grass *Poa annoa*	Quince		Grape	Others
					Fruit	Leaf		
Puchuncavi valley	La Greda (P-1)	0.49 ± 0.03	0.28 ± 0.05	0.16 ± 0.04	0.043 ± 0.001	0.34 ± 0.03	0.060 ± 0.004	Llantencillo 0.15 ± 0.03 *Plantago lanceolata*
	Maitenes (P-2)	0.31 ± 0.06	0.30 ± 0.02	0.21 ± 0.08	0.024 ± 0.003	061 ± 0.02	0.035 ± 0.002	
	Puchuncaví (P-3)	0.40 ± 0.04	0.37 ± 0.07	0.3 ± 0.1	0.020 ± 0.003	0.10 ± 0.02	0.020 ± 0.002	Yuyo*(Brassica rapa)* 0.39± 0.08 Lettuce*(Lactucasativa)*0.06±0.01 Celery *(Apium graveolens)* 0.05± 0.01
	Nogales (P-4)	0.37 ± 0.03	0.22 ± 0.06	0.04 ± 0.02	0.015 ± 0.002	0.18 ± 0.02	0.008 ± 0.001	
	Campiche (P-2b)	0.28 ± 0.05	0.23 ± 0.04					Lettuce 0.07 ± 0.01 Onion *(Allium cepa)* 0.06 ± 0.01
Catemu valley	Catemu (C-1)	0.22 ± 0.03	0.15 ± 0.02	0.021 ± 0.002	0.015 ± 0.004	0.18 ± 0.01	ND (< LD)	Celery 0.06 ± 0.01
	San José (C-2)	0.20 ± 0.02	0.10 ± 0.03	0.031 ± 0.008	0.014 ± 0.002	0.15 ± 0.01	ND (< LD)	
	Sta Margarita (C-3)	0.23 ± 0.07	0.12 ± 0.03	0.028 ± 0.001	0.040 ± 0.002	0.15 ± 0.02	0.035 ± 0.003	
	Panquehue (C-4)	0.15 ± 0.02	0.23 ± 0.03	0.042 ± 0.003	0.031 ± 0.003	0.26 ± 0.01	0.017 ± 0.003	Cabbage *Brassica oleraceae ND <LD)*
	Chagres (C-1b)	0.22 ± 0.01		0.047 ± 0.005				
Casablanca valley	Casablanca (CB)	0.10±0.01	0.08 ± 0.04		0.009 ± 0.001	0.03 ± 0.01	ND (< LD)	

Table 2. Copper concentration in plants and soils (µg g^{-1} d.w.) from different zones of Valparaíso region.

Zone	Site	Soil	Plants					
			Alfalfa *Medico sativa*	Grass *Poa annoa*	Quince		Grape	Others
					Fruit	Leaf		
Puchuncavi Valley	La Greda (P-1)	443 ± 24	60 ± 2	90 ± 1	10 ± 2	204 ± 10	16.7 ± 0.4	Llantencillo 158 ± 4
	Los Maitenes (P-2)	382 ± 10	56 ± 3	75 ± 4	13.8 ± 0.4	576 ± 30	18.4 ± 1.8	
	Puchuncaví (P-3)	143 ± 5	41 ± 1	34 ± 5	2.3 ± 0.3	49 ± 7	5.3 ± 0.2	Yuyo (*Brassica rapa*) 19 ± 2 Lettuce (*Lactuca sativa*) 43.9 ± 0.3 Celery (*Apium graveolens*) 24 ± 1
	Nogales (P-4)	59 ± 2	8.6 ± 0.2	13 ± 2	3.5 ± 0.5	10 ± 1	2.5 ± 0.2	
	Campiche (P-2b)	283 ± 8	47 ± 2					Potato (*Solanum tuberosum*) 7.5 ± 0.2 Lettuce 30 ± 1 Onion (*Allium cepa*) 5.8 ± 0.2
Catemu valley	Catemu (C-1)	113 ± 3	24.1 ± 0.7	16 ± 1	3.8 ± 0.5	52 ± 3	4.0 ± 0.3	
	San José (C-2)	127 ± 5	34 ± 3	16 ± 2	6.6 ± 0.4	202 ± 15	4.0 ± 0.2	Celery 9.8 ± 0.3
	Sta Margarita (C-3)	183 ± 3	82 ± 4	100 ± 7	10.5 ± 0.5	156 ± 8	5.4 ± 1.1	
	Panquehue (C-4)	62 ± 2	12.1 ± 0.2	28 ± 2	6.8 ± 0.3	24 ± 2	3.5 ± 1.1	
	Chagres (C-1b)	140 ± 3		42 ± 2				Cabbage (*Brassica oleraceae*) 13 ± 1 Carrot (*Daucas carota*) 5.0 ± 0.6 Garlic (*Allium sativum*) 16 ± 1
Casablanca Valley	Casablanca (CB)	27.9 ± 0.4	9.3 ± 0.4		2.5 ± 0.3	5.5 ± 5	ND(< LD)	

Table 3. Ratio plant/soil Concentration Factor (CF)

Plants	CF (plant/ soil)			
	Cu (means)	Ratio	Se (means)	Ratio
Quince leaves	0.66 (0.11-1.59)	14.5	0.85 (0.25-1.97)	7.9
Grass	0.36 (0.13-0.89)	6.8	0.30 (0.11-0.75)	6.8
Alfalfa	0.24 (0.10-0.45)	4.5	0.79 (0.50-1.53)	3.1
Quince fruits	0.05 (0.02-0.11)	5.5	0.10 (0.04-0.21)	5.2
Grape	0.04 (0.03-0.06)	2	0.09 (0.02-0.15)	7.5
Average (range)	0.27(0.04-0.66)		0.43 (0.09-0.85)	

In Figure 3 it can be seen that the quince leaves from La Greda are the samples that present the highest values for both elements, while the grape and quince fruits have the lowest values. In Puchuncavi a different pattern for Se was observed, in this site yuyo and alfalfa were the samples that have the highest values. Overall Se levels found in these vegetables permits classified all these plants as non seleniferous species.

A quantitative evaluation of the relative Se and Cu uptake by plants was made by calculating appropriate plant/soil concentration factors (CF). In Table 3 are presented the means and ranged of CF calculated for all plants found in all sampling sites; in addition the overall averages were also included. The average CF values for Se indicate that the plant uptake is almost two times greater than that for Cu. Only for grass plants, the CF values were similar for both elements. The magnitude the CF values reflected that the uptake for Cu and Se, was more pronounced in vegetables than fruits. It is important to remark that Cu CF calculated for quince leaves are 13 times higher than quince fruit. This same trend was observed for Se, in this case the Se CF for quince leaves are 8.5 time higher . Consequently, this fact seems to reflect that leaves in comparison with fruits, have a better power to bioaccumulate both elements. In addition, Cu CF for the other food crops were lettuce (0.21), potatoes (0.30) and celery (0.13), while onion only have a value of 0.02. Se CF for these same vegetables are quite similar (0.18-0.24) reflecting a similar trend relatively to the uptake of both elements by these plants. It must be emphasized that the present data where obtained for a limited number of plants under natural conditions, and more temporal trends in soils and plants for Cu and Se are needed to confirm this pattern.

The results obtained in this work have demonstrated that the Cu smelters activities developed in the Valparaíso region have contributed to increase the Cu concentration in the agricultural ecosystems studies. This metal is considerably enriched, particularly in soils, alfalfa and quince leaves from sites located near the smelters, if the levels found for samples from Casablanca are taken as reference values.

Relatively to Se a different behavior of the expected was observed, this fact taking into account that Se is obtained as by-product in the copper industry located at Las Ventanas. The low levels of Se found in soils and plants (under 0.5 µg g^{-1}) could be attributed to the percolation of soluble Se species or volatilization of Se compounds

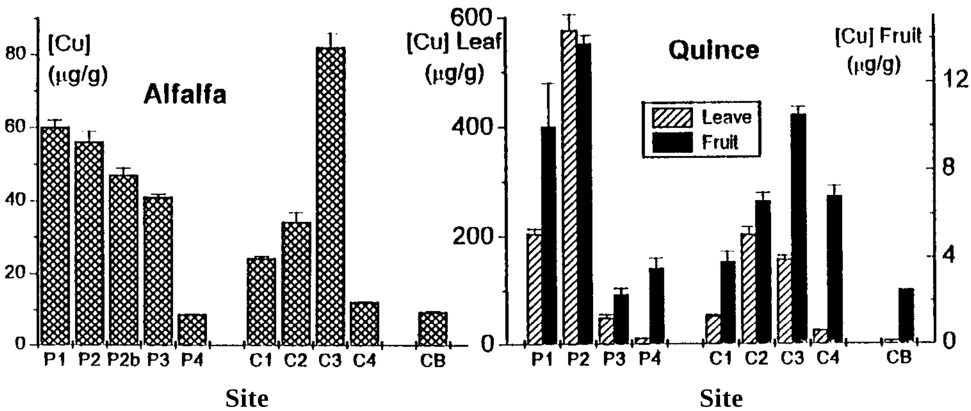
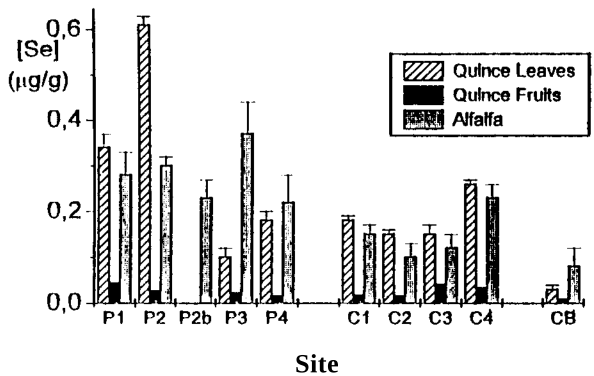


Figure 1. Cu concentrations in Alfalfa and Quince (leaves and fruits) from different zones of Valparaíso region.



	Site	Km
P1	La Greda	2
P2	Los Maitenes	2.6
P2b	Campiche	6
P3	Puchuncavi	8
P4	Nogales	26
C1	Catemu	4
C2	San José	5.5
C3	Sta. Margarita	7
C4	Panquehue	13.5
CB	Casablanca	ref

Figure 2. Se concentrations in Alfalfa and Quince (leaves and fruits) from diferent zones of Valparaíso region.

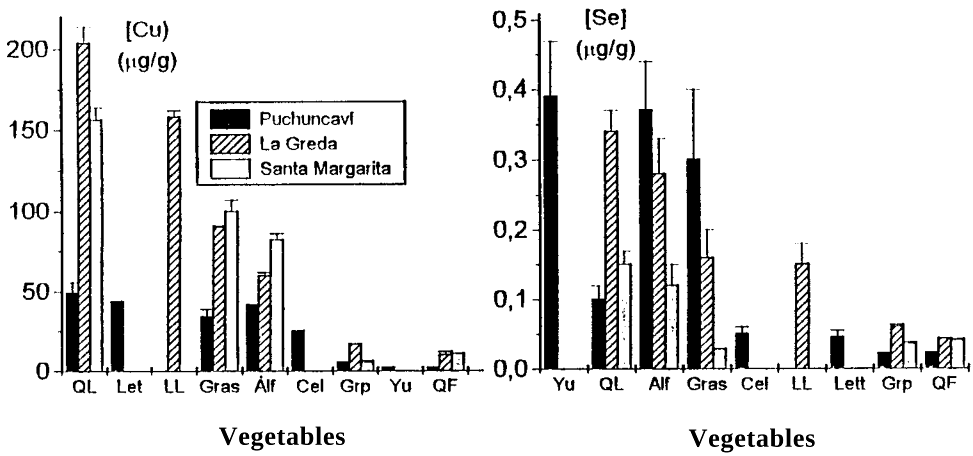


Figure 3. Cu and Se contrations in different vegetables, from 3 impacted sites.

through methylation, a mechanism used by microorganisms and plants to avoid the Se toxicity in the environment (Frankenberger et al. 1994, Terry et al. 1994). The rate and efficiency of soil Se removal by these organisms depends on soil physico-chemical properties, the plant species and the culture management strategies. For these reasons more research is needed to be understand the behavior of Se in these ecosystems.

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