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Selenium Concentration in Compartments of Aquatic Ecosystems in Central Chile

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Selenium (Se) toxicity in aquatic ecosystems has been the subject of extensive studies during the last decade. Atmospheric emissions from coal power plants and copper refineries may lead to Se deposition into aquatic systems. Congenital malformations as well as cancer in birds and fish have been detected in lakes contaminated by Se (Ohlendorf et al. 1988 and 1990; Saiki et al. 1993; Welsh and Maughan 1994; Lemly 1995; Schultz and Hermanutz 1990; Hermanutz 1992; Lemly 1993). The fact that Se can bioaccumulate and biomagnify further increases the risk of ecotoxicity (Maier and Knight 1994).

Most plants contain low amounts of Se in the order of 1 mg/ kg (dry weight) or less (Brown and Shrift 1982; Marschner 1986). These are usually termed non-accumulators. On the other hand, there are several plant species that occur only on seleniferous soils and accumulate and tolerate large concentrations of Se. This group of plants is therefore termed Se accumulators, they accumulate as much as 4000 mg Se /kg. A third group of plants are low to medium in their Se content are proposed to be called Se indicators, they can accumulate up to 1000 mg Se/kg.

In Chile, Se is produced as a by-product of the copper industry, but only a few studies have been performed to assess Se environmental concentrations in the country. Here we report a study undertaken in 1995-1996 to evaluate the concentration of Se in water, sediment and plants from aquatic ecosystems of central Chile, an area that is particularly impacted by mining activities (Figure 1).

Samples were collected from three sites (Panquehue, Chagres and Ocoa) along the Aconcagua River which presumably receives discharges from a copper refinery and a copper mine (Chagres and Sociedad Minera Andina, respectively; see Figure 1). Samples were also collected from one site on the Puchuncaví Stream which is directly contaminated by both a coal power plant and a copper refinery, located southwest of the stream (Complejo Industrial Las Ventanas in Figure 1) and was thus expected to have higher levels of Se than the other sites. Additionally, samples were also collected from one site on the Limache Stream, an urban area which has no Se-contaminating sources.

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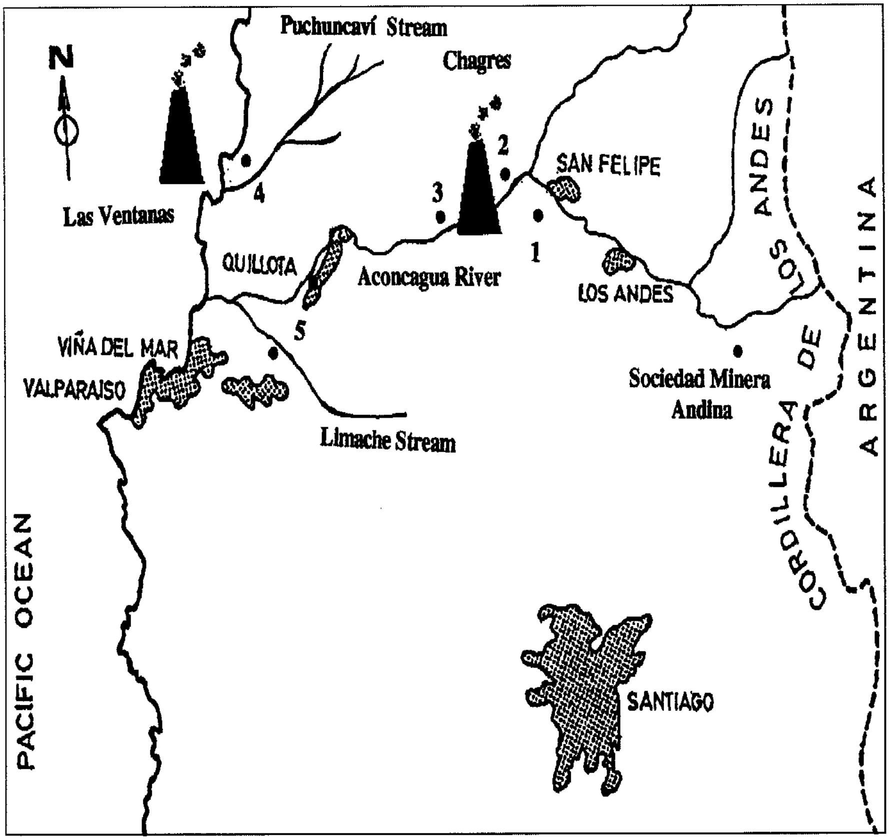

Figure 1. Sampling sites. 1: Ocoa; 2: Chagres; 3: Panquehue; 4: Puchuncaví; 5: Limache.

MATERIALS AND METHODS

Water, sediment and plants were collected in the fall of 1995 and 1996 from Puchuncaví, Chagres, Panquehue, Ocoa and Limache. In this season rainfall are scarse at this zone and therefore the effects of dilution and runoff were avoided. Water was collected in acid-cleaned polyethylene containers, filtered through a 0.45 µm membrane (MFS), acidified to pH 1-2 with concentrated HNO_3 and then frozen until analysis. Whole plants of each specie were collected from different points of a same sampling site, rinsed *in situ* to eliminate excess sediment and transported to laboratory in polyethylene bags. One composite sample for each specie from each site was made from roots, leaves and branches. This mixture was homogenized, after which samples were lyophilized and then stored in desiccators at room temperature. Sediments were collected in acid-cleaned polyethylene containers and dried in an oven at 60 °C for 48 h. The dried sediments were sieved through a series of decreasing mesh size screens until a < 65 µm fraction was obtained. The sediment samples were kept in desiccators, at room temperature, until analysis.

All samples were first digested overnight in H_2O_2, HNO_3 and $HClO_4$ and then transferred into high pressure decomposition systems (PTFE vessels, Uniseal Teflon®) for further digestion at 170 °C for 3 h. The digested samples were then filtered (Advantec, N° 2) and treated with a cationic exchange resin (Chelex 100, 100-200 mesh, sodium form, Bio-Rad Laboratories) in order to eliminate ions of metals, such as iron, copper and lead.

Prior to quantification, samples were treated with HCl 6M in order to reduce Se(VI) to Se (IV). Total selenium was quantified by cathodic stripping voltammetry (Polarographic Analyzer model 264A and Static Mercury Drop Electrode Model 303A, EG & G Instruments) as previously described (De Gregori et al. 2000).

Random samples were spiked with a standard solution containing Se (II), Se(IV) and Se (IV) for quality control. Average recovery was 105 ± 5 % for plants and 98 ± 4 % for sediments. Additionally, San Joaquin soil (SRM 2707 NIST), Irish soil (BCR) and White Clover (BCR 402) were used as reference material. Data is reported as the mean of four determinations ± 95 % confidence limits, dry weight basis for plants and sediments (confidence limit = Student coefficient × standard deviation/ $\sqrt{n}$).

RESULTS AND DISCUSSION

Total Se concentration in water, sediment and plants collected from sites along the Puchuncaví and Limache Streams and the Aconcagua River are shown in Table 1. As expected, the sediment and plant samples collected in Puchuncaví had higher Se levels which were statistically different to the concentrations in samples from other sites ($p < 0.0001$).

Sediment from Puchuncaví and Ocoa had the highest levels of Se (520 ± 46 and 440 ± 10 µg/kg, respectively) while the plant collected in Puchuncaví, *Jussiaea repens*, had a Se concentration 6.5 times higher than the sample collected in Panquehue (1161 ± 154 and 182 ± 54 µg/kg, respectively). Interestingly, water from Puchuncaví had a lower concentration of Se than water collected in other sites. In fact, the sample from Ocoa had almost twice as much Se as the one from Puchuncaví (23 ± 2 and 12 ± 2 µg/L, respectively). Soluble Se species decrease in reducing and acidic environments (Masscheleyn et al. 1990) and this behavior may explain the water concentration observed at the different sites. Water flow in the sampling site in the Puchuncaví Stream was extremely low compared to the Aconcagua River flow and so anoxic conditions may have been present. Additionally, Puchuncaví water had a more acidic pH than water from other sites (7.21 in Puchuncaví v/s 8.03 in Ocoa), thus decreasing Se solubility.

Table 1. Selenium concentration (μg/L water, μg/kg dry weight plants and sediments) in compartments of aquatic ecosystems in central Chile. (Means ± 95% confidence limit, n = 4).

SAMPLE	LIMACHE	PUCHUNCAVI	PANQUEHUE	CHAGRES	OCOA
WATER	17 ± 6	12 ± 2	20 ± 1	12 ± 2	23 ± 2
SEDIMENT	355 ± 19	520 ± 46	212 ± 11	152 ± 28	440 ±10
J. repens	na	1161 ± 154	182 ± 54	na	na
H. ranunculoides	373 ± 27	na	230 ± 42	216 ± 13	na
A. nodiflorum	na	na	na	na	333 ±31
Callitriche sp	na	na	na	309 ± 90	na
M. verticillatum		na	366 ± 67	na	na

(J. repens: Jussiaea repens; H. ranunculoides: Hydrocotyle ranunculoides; A. nodiflorum: Apium nodiflorum; M. verticillatum: Myriophyllum verticillatum; na: plant not available at that site).

Another interesting observation is that Se concentrations in sediment and water collected in Chagres - location of a copper smelter - were lower than the concentration determined in sediment and water from either Ocoa or Panquehue the sampling sites up and downstream from Chagres in the Aconcagua River, respectively. Wind direction (northwest during fall and winter and southwest during spring and summer) may help explain this situation, at least in the case of Ocoa, located west of Chagres. On the other hand, several measures were taken at Chagres in order to control the release of contaminants into the environment. Similar measures were also introduced in Las Ventanas but only after the completion of this study.

Different plant genus have different capabilities for growing on seleniferous soils. For instance, some plants, including those belonging to *Astragalus* and *Haplopappus*, can accumulate Se up to 5000 μg/g dry weight without showing signs of toxicity, while most grains and grass will not survive if the concentration of Se in the plant exceeds 50 μg/g dry weight (Mayland 1994). To the best of our knowledge, there is no information on how the plants we study here handle Se, so it is difficult to conclude anything from the data, other than suggesting that all these aquatic plants, by similarity to the terrestrial plants, can be considered as non accumulators (Mayland 1994).

Trends in Se concentrations in plants according to site cannot be discussed because not all plants were found on all sampling sites. However, plant/water and plant/sediment accumulation factors discussed below may provide insight into the capacity of these plants to accumulate Se.

Plant/water and plant/sediment accumulation factors as well as a sediment/water distribution factor for all sites are shown in Table 2. The factors are similar for all sampling sites except for Puchuncaví. The accumulation and distribution factors are higher at this site than at the other sites. Obviously, the higher concentrations at this site can account for this difference but this result also suggests that Se at this site may be present in a form that is more bioavailable to plants. Puchuncaví has been receiving emissions from Las Ventanas industrial complex (see Figure 1) for years, so it is possible that these emissions may change environmental characteristics and thus influence Se transport into plants.

It is worth noting that *Hydrocotyle ranunculoides* had practically the same plant/sediment accumulation factor at all sites while the accumulation factor for *Jussiaea repens* varied according to site. This data suggests that *Jussiaea repens* is capable of differentially accumulating Se according to the concentration of the element in the sediment and thus could be used as a biomarker for Se contamination. Additional research is necessary to further study this hypothesis.

De Gregori et al. (2000) showed that Se and Cu concentrations in rainwater sampled in and around Puchuncaví clearly decrease exponentially with distance from the industrial complex Las Ventanas, where are located a thermoelectric power plant and a smelter and copper refinery, and were significantly correlated. Additionally, Pinochet et al. (1999) quantified Se in a series of plants (including vegetables, fruits, grains and grass species) collected in the area and observed the same trend that Se levels were always higher in samples collected closer to the industrial complex Las Ventanas, an observation that is in agreement with the data we report here.

Surprisingly, samples collected in the Limache Stream, a site included in the study because of its distant location from Se-contaminating sources, had Se at equal or even higher concentrations than the other samples collected from presumably contaminated sites (except Puchuncaví). Since the Limache Stream runs through an urban area, one could propose that input of residential wastewater to the Stream could make a significant contribution to Se concentrations. Human elimination of Se occurs mainly through urine under the form of trimethyl selenonium ion with an excretion rate that varies between 7 and 160 μg/L in 24 h (Milne 1994).

Water Se concentrations from all sampling sites were above safe limits established by the US EPA (5 μg/L). In sediments the Se concentrations (0.150 to 0.520 mg/kg) are lower than 1 mg/kg, concentration that not present a potential risk (Lemly 1995). These values can also be considered as normal in nonmarine aquatic ecosystems (Skorupa 1998). The Se concentrations for all plant species are lower

Table 2. Plant/water and plant/sediment accumulation factors and water/sediment distribution factors. (Means ± 95% confidence limit, n = 4).

	LIMACHE	PUCHUNCAVI	PANQUEHUE	CHAGRES	OCOA
Plant/water					
J. repens	na	94.46	8.90	na	na
H. ranunculoides	21.90	na	11.29	17.49	na
A. nodiflorum	na	na	na	na	14.45
Calitriche sp .	na	na	na	25.07	na
M. verticillatum.	na	na	17.91	na	na
Plant/sediment					
J. repens	na	2,23	0.86	na	na
H. ranunculoides	1.05	na	1.09	1.42	na
A. nodiflorum	na	na	na	na	0,76
Calitriche sp .	na	na	na	2,04	na
M. verticillatum.	na	na	1.72	na	na
Sediment/water	20.83	42.29	10.39	12.29	19.04

(J. repens: Jussiaea repens; H. ranunculoides: Hydrocotyle ranunculoides; A. nodiflorum: Apium nodiflorum; M. verticillatum: Myriophyllum verticillatum; na: plant not available at that site).

than the value considered as critical for terrestrial plants (5-50 mg/kg) (Alloway 1995) and can be termed as non - accumulator.(Lauchli 1993). A future study should include not only the total Se determination but also its speciation in invertebrates and fish for a more comprehensive assessment of Se contamination of aquatic environments in central Chile. On the other hand sampling made at different seasons of the year could help to corroborate some of the explanations given in this study.

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