THALLIUM LEVELS AND BIOACCUMULATION IN ENVIRONMENTAL SAMPLES OF NORTHERN CHILE: HUMAN HEALTH RISKS

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ABSTRACT

Thallium (Tl) is a highly toxic heavy metal; however there is an increasing demand for thallium in the high-technology and a lack of information in the literature. On the other hand, under natural conditions, Tl occurs in large quantities rarely and plays no role in the metabolism of plants or animal. Studies on the presence of Tl in the vicinity of a copper mining-impacted region in northern Chile were carried out. A number of different types of environmental samples such as crop plants (potato, broad bean and maize), water, algae (*Myriophyllum acuaticum*, *Zannichellia palustris* L.) and one plant species (*Tessaria absinthoides*) growing wildly in the same area, were examined. All of them are exposed to a natural environmental contamination and to the impact of the copper mining activity throughout the region. Thallium concentration in plants exhibits species-dependent preferences. Thus, the enrichment of Tl in the edible parts of crop species decreases in the following order: potato > broad bean > maize grain. Thallium contents, expressed as dry weight (d.w.), varied from < 0.001 to 6.8 µg g⁻¹ in crop plants, from 0.295 to 8.3 µg g⁻¹ in algae, and between 0.010 and 0.501 µg g⁻¹ in plant samples (2-10 times the level normally found in plants, 0.05 µg g⁻¹ dry wt). Dissolved Tl concentrations in rivers were found to be 6 to 120 ng L⁻¹. In the current study, the risk for adverse health effects derived from ingestion from potatoes was assessed. It shows that there is an important risk for the infantile and adult population at present.

Keywords: Thallium; Chile; river pollution; bioaccumulation, human health risks, heavy metal.

INTRODUCTION

Thallium is widely distributed in the environment in very low concentrations. The average concentration of Tl is 0.1 – 1.0 µg/g in the lithosphere, 0.01 - 0.02 µg/l^{1,2} in seawater, and 0.01 – 14 µg/l in fresh water⁷. Thallium ores and minerals (TlAsS₂, TlAs₂SbS₅, (Cu,Tl,Ag)₂Se, Tl₂SAsS₃) are rare. The metal is recovered during processing of sulphides ores of copper, zinc and lead, containing thallium^{2,5,8}. Relatively high levels of this metal are also present in manganese nodules⁹. Inorganic Tl (I) compounds are more stable than Tl(III) compounds in aqueous solution at neutral pH. Thallium cation (I), Tl⁺, tends to form stable complexes with sulphur- containing compounds^{2,10} and is particularly toxic in its compounds, as for example: sulphate (Tl₂SO₄), and acetate (CH₃CO₂Tl), Carbonates (TL₂CO₃) and sulphide (Tl₂S), are poorly soluble and less toxic¹¹.

Thallium is one of the most toxic metals and causes chronic and acute poisoning⁶. It is more toxic to mammals than Hg, Cd, Pb, Cu or Zn. Since its discovery in 1861 it is known that Tl have caused many accidental, occupational and therapeutic poisonings in the entire world^{1,2,3,4,5,6}. Examples are “thallium poisoning” in Brazil¹², Mexico^{13,14}, Spain^{15,16}, China^{3,17}, Belgium¹⁸, Israel⁴ and USA¹⁹, “acute thallium poisoning” in Chile²⁰, chronic occupational thallium poisoning” in Japan²¹.

Thallium toxicity is related to the interference with some vital potassium-dependence biological reactions, like substitution of potassium in the (Na⁺/K⁺)-ATPase, as well as a high affinity for sulphidryl groups from proteins and other biomolecules⁵. Intoxication of thallium appears after its introduction into the body by inhalation, ingestion via contaminated food and hands, and absorption through skin and mucous membranes. It is distributed widely through the body and accumulates in bones, renal medulla and eventually, in the central nervous system. Neurological symptoms usually appear between 2-5 days after acute exposure cases. Average lethal doses for Tl in humans its also variable; lethal dose for thallium sulphate has been reported from 8 to 15 µg/g^{11,23}. Thallium levels in normal human and animals are < 1 µg/l in blood and urine²⁴, < 10 µg/kg in tissues⁵, between 5-10 ng/g in human hair²⁵, < 5 ng/g in nails, 1 – 4 ng/g (w.w.) in kidney, 0.5 – 5 ng/g (w.w.) in brain, 0.5 – 2 µg/L in whole blood and 1 µg/day in feces²⁶.

Hanzel and Verstraeten⁴² demonstrated that rat PC12 cells exposure to Tl(I) or Tl(III) cations leads to mitochondrial damage and reduced cell viability⁴².

Allus et. al²⁷ studied the effect of metals on the grown of plants. Thallium was considerably more toxic than the other elements (e.g. Cd, Pb, Zn, Fe)

in root and shoot. At water concentration of 2 – 3 µgTl/ml the activity of photosynthesis in algae is distinctly influenced and at 7µgTl/ml toxic effects have been observed. The resistance of plants to Tl in soil and water seems to be specific and not correlated with the ability of thallium accumulation²⁶.

The thallium presence in water and aquatic environments has not received much attention due, in part, to difficulties in its low levels measuring and because there is a lack of environmental reference materials having certified values. However, scientists of Canada and China demonstrate that natural sources of elevated Tl pose a potential health risk to population⁴¹.

The region of Antofagasta, in the northern part of Chile, worldwide known as the mining capital of the country and one of the most important world's copper producers, is extremely arid. Andes volcanism has always been intense in this region (eruptions, vents, geysers and thermal springs). Rainfall at the Highland takes place from December to March, ranging from 200 to 250 mm annually²⁸. Winter temperature falls to -30°C overnight with daily variations up to 35°C.

All above makes the natural waters in the Chilean pre-Andes region quite varied, their quality ranging from snow fusion to brine. Saline water predominates and thus its use is highly limited. Sodium, K, Ca, Mg, chlorides, sulphates and nitrates are major components, while Li, F and B are minor ones. Due to the extreme temperature conditions and the high salinity in water, plants habitually grow between December and March. The bulk of produced crop plants are used for self-consumption while part of it is sold at the market.

The aim of the present study was to evaluate the Tl bioaccumulation in crop plants, algae and river plants; the Tl pollution levels in salt rivers and the potential health risks for the population derived from Tl ingestion. The absence of detailed knowledge of the distribution and dispersion of Tl in this region is a matter of concern.

RESEARCH AREA

Sampling was done in the highlands of El Loa province (Fig.1), which is located between 22° 12' and 23° 45' S and 68° 20' W. The capital of the province is Calama, with approximately 140,000 inhabitants. The Atacameños and Quechua population living in the region amounts about to 4,000 people.

The location of the study has been detailed previously by Queirolo et. al.^{29,30,31} and by Stegen et al.^{32,33,34}.

Name	Altitude (m.a.s.l.)
1 Puente Posada	1100
2 Coya Sur	1170
3 La Cascada	2300
4 Yalquincha	2300
5 Yervas Buenas	2640
6 El Tatio	4250
7 Toconce	3140
8 Quinchamale	3040
9 Lequena	3300
10 Caspana	3200
11 Talabre	3600
12 Socaire	3750

Fig.1. Map showing the sampling sites at Rio Loa basin and at Salar de Atacama basin.

Collection sites

The only permanent surface water is the 440 km long Loa River which flows to the Pacific Ocean as shown in Fig.1. The Loa River and its main tributaries (Salado and San Salvador) provide water both to the cities and to the mining activity. Furthermore, they support irrigation for limited agricultural

and allow the growth of some aquatic plants (algae) and terrestrial flora around the basin. The different sampling sites are shown in Fig. 1 and they are considered representative of the environmental situation of this region.

Water samples were collected at Toconce, Lequena, Quinchamale, Ayquina, Rio Salado, Yalquincha, La Cascada, Coya Sur and Puente Posada. These places are distributed at very different elevations having different streams over them^{29,30}. The pH, conductivity, dissolved oxygen and temperature were measured *in situ*. Water samples were filtered *in situ* at 0.45 µm and acidified with HNO₃ (1% v/v suprapure grade).

Crop plants sampling was done at Yervas Buenas (potatoes), Caspana (broad beans), Talabre (broad beans and potatoes) and Socaire (broad beans, maize and potatoes).

The algae species *Myriophyllum aquaticum* (common name in the North of Chile: Hierba del sapo, Pinito de agua) and Horned pondweed *Zannichellia palustris* L. (common name in the North of Chile: cachudita de las lagunas) were collected at La Cascada, Yalquincha, Ayquina and in Rio Salado at Yervas Buenas. They were identified at the National History Museum in Santiago, Chile.

The species *Tessaria absinthioides* is proposed to evaluate the TI bioaccumulation due to its abundance and representativeness. This is a bush with new branches and ash green leaves owing to the many short hairs covering it. It has gemiferous roots and 1 – 1.5 m upright stems full of leaves. It frequently grows in the sandy and somewhat humid soils of Bolivia, Chile, Uruguay and Argentina. In Chile it is found from Arica to Lebu. A description of this species was made by Stegen et. al.³². The sampling was done at Puente Posada, Coya Sur, Yalquincha and La Cascada.

Sampling and pretreatment

Samples from several crop species (potato, broad bean, and maize grain) were collected in the field with a random sampling procedure. Each sample consisted of a number of sub-samples taken within an area of 100 x 100 m or less. Sampling procedure and sample pretreatment have been discussed previously³⁰. Potato and broad bean skin was removed with a quartz knife, since it is sometimes consumed. Water content and the mass correction factor were determined by freeze-drying because water determination by an oven is not recommended for beans and their skin³⁵. Water content values were in the 72-79 % range for potatoes, 81-86% for potato skin (pskin), 78 a 80% for broad bean, 92-90% for broad bean skin (bskin) and 75-83% for maize, depending on the sampling site.

About 5 kg of the plants (*Tessaria absinthioides* and the algae *Myriophyllum aquaticum* and *Zannichellia palustris*) were taken from each of the sampling sites by applying a random sampling procedure. They were put in polyethylene bags and transported to the laboratory in a cold box in order to avoid alterations during transport. In the laboratory, the particles adhered to the surface of the plant, mainly to the root and the upper and middle parts, were eliminated under a laminar-flow hood by using a quartz knife. The leaves were separated from the stems by hand protected with vinyl gloves. Then, the plant was quickly washed by submerging each part in an alcohol solution at 10% (CH₃OH 95% s.p.) to eliminate the particles adhered on the surface. All samples were frozen at -20°C. Due to the handling of the samples in a laboratory environment it was necessary to determine the dry mass correction factor (infrared balance at 105°C)⁵⁹.

Water samples were collected with sampling bottles (precleaned and rinsed twice with the collected water) generally no deeper than 50 cm. Temperature, pH and conductivity were recorded. Duplicate samples of 2-L (precleaned polyethylene bottles), previously filtered and acidified, were stored at 4°C. All samples were placed in polyethylene double bags to protect them from possible dust contamination.

ANALYTICAL PROCEDURES

For the determination of the total TI concentration about 0.3 g of all solid samples were treated with 2 ml of HNO₃ (65% suprapure) and 0.5 ml of HCl (37% suprapure) in a PMD Krner microwave oven (5-10 min., power setup 6-8). For samples of high silicate content 0.1 ml of HF were used. After cooling, the solutions were diluted to 25 ml with de-ionized water (18M).

Solutions were analyzed by graphite furnace atomic absorption spectrometry (GF-AAS) (Perkin Elmer Model ANALYST 700 equipped with an HGA-700 graphite furnace and an autosampler). Palladium as matrix modifier, pyrolytic graphite coated graphite tubes, and the method of standard addition were used. Detection limits (LOD) and coefficients of variation (CV) for the different matrices are reported in Table 1.

Table 1.- Limits of detection (LOD)^a and coefficients of variation (CV)^b for the analysis of Thallium performed by graphite furnace atomic absorption spectrometry (GF-AAS)

	Plants	Algae	Crop Plants
LOD($\mu\text{g g}^{-1}$ d.w.)	0.009	0.003	0.010
CV (%)	8.8	10	2.0

^aCalculated on the basis of 10 determinations of the blanks as 3 times the standard deviation of the blank

^b(CV) % relative to 10 determinations performed on the same sample.

Thallium was also determined by flame atomic absorption spectrometry (AAS) (Perkin Elmer Model ANALYST 700). LOD for the analysis performed by AAS ($\mu\text{g g}^{-1}$ d.w.) was 0.3 for the crop plants. In surface water samples, Tl was determined by induced coupled plasma - mass spectra (ICP-MS), at the Research Centre of Jülich, Germany.

The accuracy (bias) and precision (%RSD) of the methods were tested with certified reference materials: Tomato Leaves 1573, Pine Needles 1575, Citrus Leaves 1572, Bovine Liver 1577, River Sediment 1648 NBS and River Water Reference Material for Trace Metals SLRS-4 NRCC. One sample of reference material and blanks were included in each analytical batch.

Table 2.- Analysis by GF-AAS of certified reference materials: certified values and found values (means $\pm$ SD) and %RSD.

SRM	Type	Certified values Tl	Found values Tl	%RSD
1573	Tomato Leaves ($\mu\text{g/g}$)	(0.05)	0.048 ± 0.008	16
1575	Pine Needles ($\mu\text{g/g}$)	(0.05)	0.063 ± 0.009	14
1572	Citrus Leaves ($\mu\text{g/g}$)	(<0.01)	<0.01	-
1648	River Sediment ($\mu\text{g/g}$)	1.44 ± 0.07	1.70 ± 0.02	1.2
1577	Bovine Liver ($\mu\text{g/g}$)	0.05	0.056 ± 0.010	18
SLRS-4*	River Water Reference Material for Trace Metals ($\mu\text{g/L}$)	-	0.008 ± 0.001	13

*Analyzed by ICP-MS

The results obtained for Tl are in excellent agreement with the certified values as seen from Table 2 and supported by the traceability test of t Student. The test statistic t was calculated with Eq. (1):

$$t_{cal} = \frac{(X_a - X_b)\sqrt{n}}{s}$$

Where X_a = duplicated means

X_b = certified value of Certified Reference Materials (CRM)

s = standard deviation of n analysis

The t_{cal} was compared to the two-sided t-value, at a probability of 95% and n-1 degrees of freedom. If the $t_{cal} < t_{tabulated}$ the accuracy of the applied method is traceable to the CRM.

For external quality control, some of samples were analyzed by ICP-MS, at the Zentralabteilung fuer Chemische Analysen, Abteilung Massenspektrometrie of the Research Centre of Jülich, Germany (Table 3).

Results for the other matrices studied in this work are given in the next section

Table 3.- Tl concentrations (in $\mu\text{g g}^{-1}$ d.w. $\pm$ SD)* in crop plants grown at the pre-Andes northern Chile

	Crop plants parts			
Crop species	Flesh	Skin	Flesh**	Skin**
(a) <i>Potato</i>				
Socaire	2.1 (0.1)	4.5 (0.3)	1.8 (0.2)	4.3 (0.2)
Talabre	4.4 (0.6)	6.8 (0.4)	4.1 (0.1)	6.4 (0.1)
Yerbas Buenas	3.8 (0.2)	5.7 (0.6)	3.2 (0.2)	5.3 (0.3)
(b) <i>Broad bean</i>				
Socaire	0.015 (0.001)	0.031 (0.001)	0.011 (0.001)	0.029 (0.001)
Talabre	0.080 (0.001)	0.136 (0.010)	0.072 (0.001)	0.132 (0.002)
Caspana	0.006 (0.000)	0.022 (0.001)	0.005 (0.000)	0.019 (0.001)
(c) <i>Maize grain</i>				
Socaire	<0.010		0.006 (0.000)	
Talabre	0.010 (0.001)		0.008 (0.000)	
Caspana	<0.010		<0.0001	

*Mean of three independent determinations.

Coefficients of variation (CV) was always less than 10%

** Analyzed by ICP-MS in the Zentralabteilung für Chemische Analysen, Abteilung Massenspektrometrie at the Research Centre of Jülich, Germany

RESULTS AND DISCUSSION

Three parallel measurements were made in all cases. The analytical precision, determined by quality assurance and quality control procedures, using duplicates, blanks, internal standards and reference materials, was better than $\pm 10\%$.

Thallium bioaccumulation in crop species

Results on all the collected samples are summarized in Table 3, as mean values. The enrichment of Tl in crops is also characterized as species and sites dependant (Fig. 2).

Maize grains (mgrain) contained only traces of Tl ($<0.1 \text{ ng g}^{-1}$), since in most cases Tl concentration was lower than the GF-AAS detection limit. So the contribution of maize to Tl bioaccumulation via the food chain is expected to be very low in these villages.

Figure 2.- Concentration distribution of Tl in crops at the different sampling sites (p:potato, bb: broad beans; m: maize)

Smith and Carson⁶ reported Tl levels in the range of $0.02\text{--}0.125 \text{ } \mu\text{g g}^{-1}$ for edible plants, from 0.008 to $0.01 \text{ } \mu\text{g g}^{-1}$ in clover, and from 0.02 to $0.025 \text{ } \mu\text{g g}^{-1}$ in meadow hay. Broad beans Tl levels (bbskin and bbFlesh) determined at this investigation are quite comparable with concentrations at others parts of the world.

Thallium concentrations were found to be very high in potato at Talabre ($4.4 \text{ } \mu\text{g g}^{-1}$ in pFlesh and $6.8 \text{ } \mu\text{g g}^{-1}$ in pSkin) lower at Yerbas Buenas (3.8

$\mu\text{g g}^{-1}$ in pflesh and $5.7 \mu\text{g g}^{-1}$ in pskin) and also lower, but still significant, at Socaire ($2.1 \mu\text{g g}^{-1}$ in pflesh and $4.5 \mu\text{g g}^{-1}$ in pskin), showing that potatoes are efficient bioaccumulators of this metal. Queirolo et al.³⁰ reported that the tendency of Cd and Pb in these locations is also to accumulate in the skin of potatoes. Differences of Tl concentrations in vegetable organs could be due to differences in uptake and/or in differences in translocation within the whole plant. Valuable minerals contained in the potatoes are some of potassium³⁶. The explanation for this occurrence would be the behavior of Tl^+ and K^+ in soils. Both are univalent ions with similar ionic radii, so thallium is able to interfere with potassium-dependence processes²³. It seems that soils at Talabre and Yerbas Buenas are extremely polluted by Tl, highly probable related to volcanic activity (Lascar volcano) or to geochemical sources such as thallium minerals (TlAsS_2 , $\text{TlAs}_2\text{SbS}_5$, $(\text{Cu}, \text{Tl}, \text{Ag})_2\text{Se}$, Tl_2SAsS_3), since the soils in this region exhibit a very high natural arsenic content³⁸. Inputs from agricultural additives are particularly difficult to detect because the information about them is vague and the Tl content of pesticides is not well known. Additionally, the link between Tl and K may be distorted by the use of potassium fertilizers.

The minimum lethal dose (LD_{50}) of soluble thallium salts for an adult has been estimated to be 0.7-1.4 g or 10-20 mg thallium/kg for a 70 Kg adult⁴⁰. The Oral Chronic Reference Dose (RfD) for Thallium Carbonate, Thallium Chloride, and Thallium Sulfate is 8.00×10^{-5} mg/kg-day for a 70 Kg adult⁴⁰ and 3.7×10^{-4} mg/kg-day for a 15 Kg child⁴⁰. The local villagers in Socaire, Talabre and Yerbas Buenas consume potatoes during the entire year and after air-drying. Table 4 summarizes the criteria assumed in this study to calculate the daily ingestion of Tl from potatoes (flesh).

Table 4.- Estimation of daily ingestion of Tl from potatoes consumption (flesh) in different location.

Local Villagers	DW (mgTl/Kg)	Consumption amount (Kg/day)		Total ingestion mg/day	
		Adult	Children	Adult	Children
Socaire	2.1	0.200	0.100	0.420	0.210
Talabre	4.4	0.200	0.100	0.880	0.440
Yerbas Buenas	3.8	0.200	0.100	0.760	0.380

The estimated oral daily intake of Tl from potatoes as well as the risk index for adults (for a body weight of 70 Kg) and children (for a body weight of 15 Kg) are shown in Table 5. This index, known also as hazard quotient (HQ), is a numeric estimate of the systemic toxicity potential posed by a single chemical within a single route of exposure and can quantitatively be calculated by using the following equation (2):

$$HQ_i = \frac{CDI_i}{RfDi}$$

where: CDI_i = the estimate of chronic daily intake from the exposure assessment

$RfDi$ = the chronic reference dose for administered or absorbed dose, as appropriate

A quotient under 1 is assumed as safe.

Table 5. Predicted daily exposure to thallium from potatoes (flesh) and hazard quotient.

Sampling Site	Adults		Children	
	Predicted Exposure* (mg/kg-day)	Hazard Quotient**	Predicted Exposure* (mg/kg-day)	Hazard Quotient**
Socaire	6.0×10^{-3}	75	1.4×10^{-2}	175
Talabre	1.3×10^{-2}	163	2.9×10^{-2}	363
Yerbas Buenas	1.1×10^{-2}	138	2.5×10^{-2}	313

* CDI_i , based on body weights of 70 Kg for adults and of 15 Kg for children

** Calculated with $RfDi$ values of 8.00×10^{-5} mg/kg-day for adults (70 Kg) and of 3.7×10^{-4} mg/kg-day for children (15 Kg). $HQ_i < 1$ is assumed as safe

According to above results, mining and volcano activity are important

sources of thallium emission into the environment of this region. Thus, the highest hazard quotient is for the village nearest to the active Lascar volcano (Talabre). The current study also shows that the highest risk of adverse health effects comes from the ingestion of potatoes and that there is a significant risk for the infantile and adult population at present.

Thallium bioaccumulation in plants

Thallium concentration in *Tessaria absinthioides* varies considerably depending on the sampling site and on the analyzed part of the plant. Roots are the best bioaccumulators for thallium as concentration increases from leaves to roots in all sites collected (Fig. 3)

Figure 3.- Thallium levels (ng g^{-1} d.w.) in different parts of *Tessaria absinthioides* sampled at various sites.

The highest concentration of Tl was found in all parts of the plants collected at La Cascada where the water is turbid. Upstream of this sampling site, sewage water was observed. Thallium is present in this industrial area, where mean concentration levels of Tl in water are 120 ng L^{-1} (Table 7), mainly as component of sulfide ores of copper. As mentioned, Tl is present in wastewaters at this place. However, mining companies often do not want their Tl concentrations values to be published. Water concentrations of 1–80 ppb have been reported for rivers draining metal mining areas. It has been suggested that Tl in mining districts is transported in waters mainly as sulfates, arsenates and chloride complexes³⁹.

On the contrary, the lowest Tl concentration was found in Puente Posada; three times lower than in La Cascada and twice lower than in Coya Sur and Yalquincha. In these sampling places the thallium input from the ground water via roots is similar to that observed for the stems and leaves.

Concentration of Tl in *Tessaria absinthioides* and those reported for some heavy metals in the same plants (Cd, Pb, Co and Ni)³² can be compared (Fig.4). The element pattern indicates that this plant accumulates much more Cd, Co, Pb and Ni than Tl. Cadmium concentration in leaves > stems > roots in all sites collected. In opposition, Pb (exception made of La Cascada close to anthropogenic sources of heavy metals) and Ni concentrations in roots > leaves > stems. Thus, roots are the best bioaccumulator for Tl, Pb and Ni, while, in most cases, leaves are the best accumulator for Cd and Co.

Lead is generally of limited mobility in plants and is mostly found in roots, while Cd is well known to be relatively mobile in plants. The differences in the bioaccumulation of Tl and the heavy metals, however, suggest that the mode of action within the body probably also differs between these metals.

Figure 4. Tl, Cd, Pb, Co and Ni levels (ng g^{-1} dry wt.) in different parts of *Tessaria absinthioides* collected at the River Loa basin.

Thallium bioaccumulation in algae.

Table 6 shows Tl concentration in two algae. Values for As and Cu reported in previous works³³⁾ are also shown for comparison. The very high thallium concentrations found in all sampling areas corroborate the high pollution level of natural waters near to the smelter. The results show also that the species studied have wide tolerance ranges for Tl. Observed ranges are from 0.295 to 8.30 $\mu\text{g g}^{-1}$ d.w in *Myriophyllum acuaticum* and from 0.615 to 7.34 $\mu\text{g g}^{-1}$ d.w in *Zannichelia palustris*. These values indicate that the mining activity can be responsible for the distribution of high Tl concentrations in algae at La Cascada and Yalquincha. Moss and algae samples from Canada water that receives mining operation effluents contain Tl in concentrations ranging from 9.5 to 162 $\mu\text{g g}^{-1}$ dry weight¹. Our study shows that the Tl values we found were lower and reflect an elevated pollution in Canada.

Samples obtained from river Salado (it originates at the El Tatío geysers, having extremely hot water reaching 86°C) showed the highest levels of Tl. It can be concluded that Tl from water bioconcentrates in the tissues of the aquatic plants. This implies that Tl accumulation in algae increases with time throughout the growth process.

Table 6. Some trace element concentrations ($\mu\text{g g}^{-1}$ d.w. $\pm$ SD)* in *Zannichelia palustris* and *Myriophyllum acuaticum* collected at the River Loa basin.

Sampling area	Algae	Tl	As	Cu
La Cascada	<i>Zannichelia palustris</i>	7.34 (0.02)	810 (10)	12.5 (0.1)
Yalquincha	<i>Zannichelia palustris</i>	0.615 (0.055)	498 (8)	43.2 (0.6)
	<i>Myriophyllum acuaticum</i>	6.27 (0.06)	707 (4)	20.9 (0)
Ayquina	<i>Myriophyllum acuaticum</i>	0.295 (0.005)	89 (7)	117 (7)
Salado river (at Yervas Buenas)	<i>Myriophyllum acuaticum</i>	8.30 (0.05)	900 (11)	36 (1)

*Mean of three independent determinations.

Coefficients of variation (CV) for Tl and for As were less than 8%, CV for Cu determination was less than 6%.

As seen, the other two important toxic elements of interest, Cu and As, show also high contents in both algae, being higher than Tl level. According to this observation, the aquatic system under study shows clear signs of Cu and As pollution and suggests a real impact of the mining activity over the Loa basin.

Thallium levels in water

Water samples at all sampling sites were characterized in the field by determining pH, temperature, conductivity and O_2 concentration. All collected physico-chemical parameters and Tl and Pb concentrations in surface water samples are presented in Table 7. Overall, surface water shows near neutral to alkaline pH, values ranging from 6.93 to 8.56. According to the O_2 concentration (3.55 – 11.8 mg/L) and the wide range of total dissolved solids (TDS: 0.23 – 4.84 g/L), the water in the upper Loa (Toconce, Lequena and Quinchamale) has a relative low TDS while the sampling site La Cascada shows a relative high pollution.

Table 7. Physico- chemical parameters and some trace element concentrations of surface waters from the Rio Loa basin.

River	pH	T°C (water)	Conductivity [mS/cm]	O_2 [ppm]	TDS* [g/L]	Tl** [ng/ml]	Pb** [ng/ml]
Toconce	7.63	6.7	1.19	6.04	0.23	0.012	0.26
Lequena	8.56	7	1.06	11.3	0.55	0.006	0.08
Quinchamale	8.19	13	1.77	11.8	0.83	0.014	0.23
Ayquina	6.93	18	1.74	3.81	1.65	0.021	0.17
Rio Salado	7.61	9	4.96	3.65	3.12	0.005	0.06
Yalquincha	7.96	6	4.12	8.78	3.29	0.076	1.2
La Cascada	8.23	11	4.68	3.55	4.84	0.12	2.4
Coya Sur	7.87	6	4.66	6.7	2.53	0.011	0.05
Puente Posada	7.90	8	3.56	5.82	1.82	0.003	0.03

*TDS = Total dissolved solids

**Measurements done by ICP-MS

The hot spring water from El Tatío (temperatures close to 90°C, TDS 2.5 – 9.8 g/L and As 25 mg/L) is the source of the Rio Salado (Fig 1) which explains the high TDS value. However, downstream near the medium Loa basin the increase of TDS (Yalquincha 3.29 g/L and La Cascada 4.84 g/L) is related to pollution.

Results obtained in our study show that dissolved thallium concentrations in the salt rivers average 3–120 ng/L. As can be expected, at La Cascada, the nearest sampling site to Calama city, an elevated concentration of Tl and Pb was observed. In general, Tl levels declined downstream except in La Cascada where inputs from several industries presumably occasioned the observed elevated concentrations. The presence of Tl in water clearly diminishes with increasing distance from the source, particularly at the surroundings of the Chuquicamata smelter.

Cheam et al.³⁸ reported that dissolved Tl concentrations average 5–10 ng L^{-1} in unpolluted and 20–50 ng L^{-1} in polluted freshwater, but Zitko¹ indicated that the concentrations of Tl in river water receiving mining operation effluents ranged from 0.7 $\mu\text{g L}^{-1}$ to 80 $\mu\text{g L}^{-1}$ at locations in Canada.

There is a need of developing treatment technologies to reduce Tl levels in mine effluents and ground impacted water. The very dry climate in northern Chile favors strong evaporation and the lack of raining does not allow dilution.

CONCLUSIONS

In summary, found Tl concentrations in north Chile are low and quite comparable with concentrations at others parts of the world. Nevertheless, the presence of high concentrations of Tl in some environmental samples suggests an impact of the mining activity over the region. On another side, the high concentration values determined in potatoes far from the pollution source suggest as highly probable that potatoes pollution is more related to volcanic activity or to geochemical origin. The enrichment of Tl in vegetables and plants is closely related to the concentrations of Tl in soils. This study also points strongly to the conclusion that efficient bioaccumulators of Tl like potatoes should not be planted in areas of Tl-rich soils such as Talabre and Yervas Buenas. Study on the health impact of Tl over the population exposed is needed and the removal of Tl from waters and wastewaters should be investigated.

The GFAAS approach to the determination of Tl in environmental samples after wet digestion is a very reliable, sensitive and accurate method.

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