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Heavy metal and trace elements in riparian vegetation and macrophytes associated with lacustrine systems in Northern Patagonia Andean Range

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Abstract Vegetation associated with lacustrine systems in Northern Patagonia was studied for heavy metal and trace element contents, regarding their elemental contribution to these aquatic ecosystems. The research focused on native species and exotic vascular plant *Salix* spp. potential for absorbing heavy metals and trace elements. The native species studied were riparian *Amomyrtus luma*, *Austrocedrus chilensis*, *Chusquea culeou*, *Desfontainia fulgens*, *Escallonia rubra*, *Gaultheria mucronata*, *Lomatia hirsuta*, *Luma apiculata*, *Maytenus boaria*, *Myrceugenia exsucca*, *Nothofagus antarctica*, *Nothofagus dombeyi*, *Schinus patagonicus*, and *Weinmannia trichosperma*, and macrophytes *Hydrocotyle chamaemorus*, *Isöetes chubutiana*, *Galium* sp., *Myriophyllum quitense*, *Nitella* sp. (algae), *Potamogeton linguatus*, *Ranunculus* sp., and *Schoenoplectus californicus*. Fresh leaves were analyzed as well as leaves decomposing within the aquatic bodies, collected from lakes Futalaufquen and Rivadavia (Los Alerces National Park), and lakes Moreno and Nahuel Huapi (Nahuel Huapi National Park). The elements studied were heavy metals Ag, As, Cd, Hg, and U, major elements Ca, K, and Fe, and trace elements Ba, Br, Co, Cr, Cs, Hf, Na, Rb, Se, Sr, and Zn. Geochemical tracers La and Sm were also determined to evaluate contamination of

the biological tissues by geological particulate (sediment, soil, dust) and to implement concentration corrections.

Keywords Freshwater ecosystem · Patagonia native plant · *Salix* spp · Lake Futalaufquen · Lake Rivadavia · Lake Moreno · Lake Nahuel Huapi

Introduction

The Northern Patagonian Andean mountain range (39° to 45° S, 71° W; 500 to 3554 m above sea level), shared by Chile and Argentina, has numerous glacial oligotrophic lakes, which drain towards the Atlantic and Pacific oceans (Fig. 1). Precipitation in this area depends mainly on the westerly winds from the Pacific and ranges from 3000 mm in the West to a few hundreds in the East. Vegetation follows the precipitation gradient, with dense rainforest in the West, to dry shrublands in the Patagonian steppe in the East.

This region has been historically protected from anthropogenic contamination, because of its isolation and low population density. The National Park system adds additional protection to several areas and basins. Primary source of metals and trace elements is from the frequent Andes volcanic activity (Ruggieri et al. 2011; Stern 2004).

Available data on metal and trace element contents in lake waters within the study area are sparse and inconsistent. Nutrients, namely, total and reactive phosphorus (P) and total and dissolved nitrogen (N), and major ions Na⁺, K⁺, Ca⁺⁺, Mg⁺⁺, SO₄, HCO₃⁻, Cl⁻, and SiO₂, were determined in different studies and summarized for several lakes by Díaz et al. (2007). Trace element concentrations, such as arsenic (As), cobalt (Co), chromium (Cr), iron (Fe), lead (Pb), strontium (Sr), or zinc (Zn), in lakes belonging to the Northern Patagonian Andean range were reported only for L.

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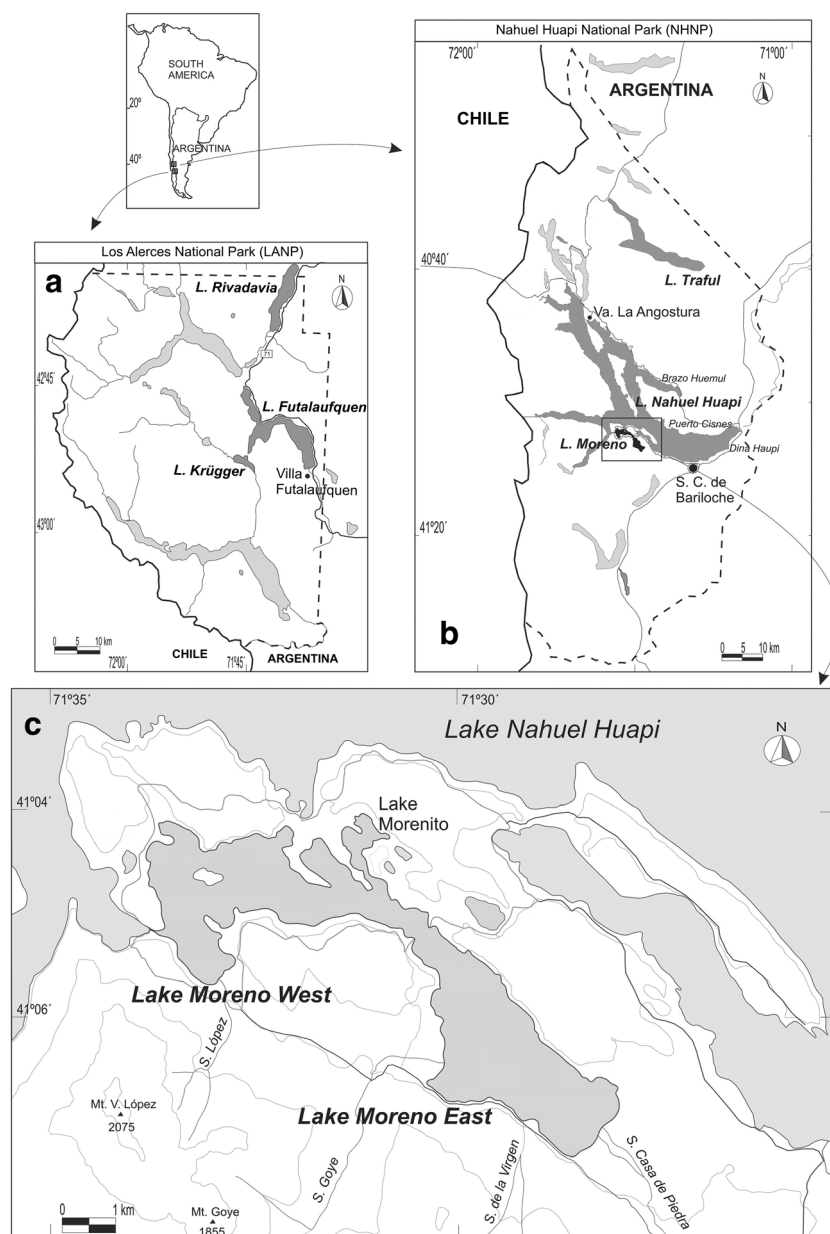
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Fig. 1 Water bodies studied for heavy metal and trace element contents in riparian and aquatic vegetation, belonging to Northern Patagonia Andean Range delimited by the Andean mountains chain to the West, and by the Patagonian steppe to the East. Water bodies Lake Futralafquen and Lake Rivadavia (a), Los Alerces National Park (42° 33' to 42° 53' S; 71° 35' to 72° 05' W). Lake Nahuel Huapi (b) and Lake Moreno (c), Nahuel Huapi National Park (40° 40' to 41° 36' S; 71° 00' to 71° 50' W)



Gutiérrez, L. Mascardi and L. Nahuel Huapi by Markert et al. (1997). Arribére et al. (2010a) reported mercury (Hg) levels for Lago Moreno. Previous survey in the area indicated that concentrations of elements such as silver (Ag), bromine (Br), cesium (Cs), Fe, Hg, selenium (Se), rubidium (Rb), sodium (Na), or Zn in muscle and liver tissues from various fish species from across Los Alerces National Park (LANP) (Fig. 1a) and Nahuel Huapi National Park (NHNP) (Fig. 1b, c) were comparable or higher than similar ones of fish species from other regions, including contaminated sites (Arribére et al. 2006; Arribére et al. 2008; Arribére et al. 2010b; Ribeiro Guevara et al. 2004; Rizzo et al. 2011). On the other hand, benthic organism values had similar or lower concentrations

than those observed in other studies (Arribére et al. 2010b). Moreover, plankton analysis showed very high Hg concentrations with high variability and also high levels of Zn and moderate As and Se (Arribére et al. 2010b; Rizzo et al. 2014).

The actual trophic structure, trophodynamics and metal transfer routes within the food webs of these particular systems are still under study. The better studied are those of Lake Moreno (Arcagni et al. 2013a; 2013b; Revenga et al. 2011; 2012; Vigliano et al. 2009), and Lake Nahuel Huapi (Arcagni et al. 2015; Juncos et al. 2016; Rizzo et al. 2014), both in NHNP. The evidence indicates that benthic and allochthonous carbon contributions are relevant in both lakes, particularly from riparian vegetation. Where the element ends up in the

plant (root, stem, leaf) is determined by cellular processes and concentration, and when the element is not needed, or is a not essential element (e.g. heavy metals), the excess element will be stored in the leaves. Therefore, primary producers, both riparian and aquatic, play a significant role as a source of elements to the aquatic ecosystem impacting heavy metal and trace elements trophodynamics. There is no comprehensive study in the literature of heavy metals and trace element contents in plants from the Patagonia, particularly for native species, and on the association with aquatic systems. This knowledge is key for the understanding of heavy metal and trace elements trophodynamics in aquatic systems, and this lack of information supports the present research.

The aim of this work is to study heavy metals and trace elements contents in riparian vegetation and macrophytes as primary producers associated with lacustrine ecosystems in Northern Patagonian Andean Range. Specifically, deep and transparent ultra to oligotrophic lakes Moreno and Nahuel Huapi, (NHNP), and lakes Futalaufquen and Rivadavia (LANP). The study includes riparian and aquatic vegetation, considering fresh leaves, and decomposing material in the aquatic media.

Material and methods

Study site

Present work was performed in water bodies situated in NHNP and LANP, in Northern Patagonia Andean Range (Fig. 1). Nahuel Huapi National Park is a protected area with an extension of 7050 km², comprising three major river systems, 13 lakes of more than 10 km², and several hundred small lakes and ponds. The climate characteristics of the park are dominated by winds moving from West to East. The west to east airflow creates a steep precipitation gradient from around 3000 mm y⁻¹ in the West to less than 400 mm y⁻¹ in the East part of the park. Associated vegetation gradient is comprised of a dense rainforest dominated by *Nothofagus* spp. and *Austrocedrus chilensis* in the West, to ecotonal forest and dry shrubland in the East (León et al. 1998; Paruelo et al. 1998). The riparian vegetation analyzed was collected in two major lakes of NHNP: lakes Nahuel Huapi (Fig. 1b) and Moreno (Fig. 1c). Los Alerces National Park is also a protected area with 2630 km² extension and has similar characteristics regarding geological, climate and biota as described for NHNP. Macrophyte samples were collected in LANP from lakes Futalaufquen and Rivadavia (Fig. 1a), and from Lake Moreno as well (Fig. 1c). These four lakes are transparent, monomictic, ultraoligotrophic to oligotrophic systems of glacial origin, fed by snowmelt and rain through numerous small tributaries (Díaz et al. 2007).

Lake Nahuel Huapi (Fig. 1b) is the largest in NHNP with 557 km² total area and 464 m maximum depth, located at 764 m above sea level. It is formed by seven branching arms, with a 357 km shoreline. The principal settlement is the city of San Carlos de Bariloche, with 140,000 inhabitants.

Lake Moreno (Fig. 1c) is a system with 10.3 km² total area divided in two basins, Lake Moreno West (88 m max. depth), and Lake Moreno East (106 m max. depth), joined by a narrow connection (Rechencq et al. 2014). Lake Moreno West flows to Lake Nahuel Huapi through a small outlet. There is an extended periurban area around the North-East margin of Lake Moreno East, as well as a small village (Colonia Suiza) in the South-East margin. On the contrary, the area around Lake Moreno West is protected and less populated than the East, with isolated houses, hotels, and a golf course located in the North-West margin.

Lake Futalaufquen (Fig. 1a) has a total area of 44.6 km² and 168 m maximum depth, receiving waters from lakes Rivadavia and Menéndez through River Arrayanes, and discharging to Lake Krüger through a short and narrow channel. Human settlements are scarce in the lake basin, with about 2000 inhabitants.

Lake Rivadavia (Fig. 1a) has a total area of 21.7 km² and a maximum depth of 147 m, receiving waters from lakes Cholila, Lezama, and Mosquito. There is one human settlement in the lake basin, a small town (Cholila) with 2000 inhabitants.

Sample collection and conditioning

Samples of riparian plants and macrophytes were collected by hand from along the lakes shoreline and from the littoral area.

Terrestrial plants Fresh leaves of the most abundant plant species from the forest located along the lakes shorelines were collected. These included trees *Amomyrtus luma* (Molina) D. Legrand. & Kausel, *Luma apiculata* (DC.) Burret, *Myrceugenia exsucca* (DC) O.Berg, *Nothofagus antarctica* (G.Forst.) Oerst., *Nothofagus dombeyi* (Mirb.) Oerst., *Lomatia hirsuta* (Lam.) Diels ex J.F. Macbr., *Maytenus boaria* Molina, *Weinmannia trichosperma* Cav. (natives species), and *Salix* spp. (exotic species); the native conifer *Austrocedrus chilensis* (D.Don) Pic.Serm. & Bizzarri; the gramineous *Chusquea culeou* Desv. (natives species), and shrubs *Desfontainia fulgens* D.Don, *Escallonia rubra* (Ruiz et Pav.) Pers., *Gaultheria mucronata* (L.f.) Hook. et Arn., and *Schinus patagonicus* (Phil.) I.M. Johnst. ex Cabrera, (natives species). Submerged decomposing leaves belonging to terrestrial plant species were collected from the littoral area near the coast. The leaf samples were rinsed repeatedly in lake water to remove any debris and stored in plastic bags until processing in the laboratory.

Aquatic plants *Hydrocotyle chamaemorus* Cham. & Schldl., *Galium* L., *Ranunculus* L., and *Schoenoplectus californicus* (Meyer) Soják (emergent), and *Isöetes chubutiana* Hickey, Macluf & Taylor, 2003, *Myriophyllum quitense* Humboldt, Bonpland & Kunth, 1823, *Nitella* C. Agardh 1824, and *Potamogeton linguatus* Hangstr. (submerged macrophytes) were collected at sampling sites described in Table 1. Submerged decomposing material from *S. californicus* was also obtained. Samples were washed in lake water to remove sediments and detritus and stored in clean plastic to be processed in the laboratory.

Biota samples were conditioned in the laboratory for analysis following clean procedures for trace element analysis. Samples were cleaned with ASTM type 1 water, freeze dried and homogenized in Teflon[®] mortars. Aliquots of about 100 mg were sealed in SUPRASIL AN[®] quartz ampoules.

Elemental analysis

Sample analysis was performed by Instrumental Neutron Activation Analysis (INAA). The ampoules were irradiated for 20 h at the RA-6 research reactor (Centro Atómico

Bariloche, Argentina). Gamma-ray spectra were collected at different decay times using an intrinsic High Purity Germanium (HPGe) n-type detector, 12.3 % relative efficiency, and 4096-channel analyzer. Gamma-ray spectra collected were analyzed by using the GAMANAL routine included in the GAANAS package, distributed by International Atomic Energy Agency (IAEA). Elemental concentrations were determined using the absolute parametric method. Corrections for spectral interferences were performed when necessary. The elements determined were Ag, As, barium (Ba), Br, calcium (Ca), cadmium (Cd), Co, Cr, Cs, Fe, hafnium (Hf), Hg, lanthanum (La), Na, potassium (K), Rb, Se, samarium (Sm), Sr, uranium (U), and Zn. Analytical errors differ for each element and sample analyzed, since they depend on the nuclear parameters of each element, on the irradiation conditions and on the composition of the sample, varying from 5 to 15 % in most cases. Concentrations were reported on dry weight basis. Certified references materials (CRM) IAEA-336 lichen and IAEA-392 algae were analyzed together with the vegetation samples for analytical quality control, as well as sample replicates in selected cases. The CRM analyses

Table 1 Riparian vegetation and macrophytes studied for trace element contents

Vegetation species	Vegetation type	Lakes sampled	Sample collection
<i>Nothofagus antarctica</i>	Riparian,	Nahuel Huapi	Fresh from shoreline
<i>Nothofagus dombeyi</i>	larger trees	Moreno, Nahuel Huapi	Fresh from shoreline, decomposing submerged
<i>Maytenus boaria</i>		Nahuel Huapi	Fresh from shoreline
<i>Salix</i> spp.		Nahuel Huapi	Fresh from shoreline, decomposing submerged
<i>Lomatia hirsuta</i>		Moreno, Nahuel Huapi	Fresh from shoreline, decomposing submerged
<i>Weinmannia trichosperma</i>		Nahuel Huapi	Fresh from shoreline
<i>Austrocedrus chilensis</i>	Riparian, conifer	Moreno, Nahuel Huapi	Fresh from shoreline
<i>Amomyrtus luma</i>	Riparian,	Nahuel Huapi	Fresh from shoreline
<i>Chusquea culeou</i> ^a	smaller trees	Moreno, Nahuel Huapi	Fresh from shoreline, decomposing submerged
<i>Luma apiculata</i>		Moreno, Nahuel Huapi	Fresh from shoreline, decomposing submerged
<i>Myrceugenia exsucca</i>		Moreno	Fresh from shoreline
<i>Desfontainia fulgens</i>	Riparian, shrubs	Nahuel Huapi	Fresh from shoreline
<i>Escallonia rubra</i>		Nahuel Huapi	Fresh from shoreline
<i>Gaultheria mucronata</i>		Nahuel Huapi	Fresh from shoreline
<i>Schinus patagonicus</i>		Moreno	Fresh from shoreline, decomposing submerged
<i>Hydrocotyle chamaemorus</i>	Aquatic	Moreno, Nahuel Huapi	Fresh living in water-
<i>Isöetes chubutiana</i>		Futalaufquen, Rivadavia	Fresh living in water
<i>Galium</i> sp.		Moreno	Fresh living in water
<i>Myriophyllum quitense</i>		Futalaufquen, Moreno	Fresh living in water
<i>Myriophyllum quitense</i>		Rivadavia	Fresh living in water
<i>Potamogeton linguatus</i>		Futalaufquen, Rivadavia	Fresh living in water
<i>Ranunculus</i> sp.		Moreno	Fresh living in water
<i>Schoenoplectus californicus</i>		Moreno	Fresh living and decomposing in water
<i>Nitella</i> sp.	Aquatic, algae	Moreno	Fresh living in water

^a Gramineous species, included here for discussion although is not a tree

showed good agreement with certified and informed concentrations, and replicate samples were consistent.

Data analysis

Although vegetation samples were carefully cleaned in the field with lake water and in the laboratory with ASTM type 1 water, geological particulate remains were detected by the determination of lithophile elements like Rare Earth Elements (REEs) La and Sm. The inclusion of geological particulate in vegetation tissues was particularly relevant after the eruption of Puyehue-Cordón Caulle volcanic system in June 2011, which dispersed fine volcanic ash all over NHNP. As well, LANP was affected by the eruption of volcano Chaiten in 2008. Therefore, it was necessary to correct the elemental concentration of biota samples by subtraction of geological particulate contributions, in order to obtain elemental concentrations representative of the biological tissues under study. This correction was implemented by the determination of REE Sm. The biological fraction of the sample, after subtraction of geological contamination, was computed as follows:

$$F_b = 1 - \frac{C_{L,V}}{C_{L,G}}$$

F_b Biological fraction of the of the vegetation sample, determined by subtraction of the geological fraction evaluated by the determination of a lithophile element (Sm)

$C_{L,V}$ Concentration of the lithophile element (Sm) measured in the biota sample

$C_{L,G}$ Concentration of the lithophile element (Sm) measured in the geological material contaminating the biota sample

The correction can be computed only when a lithophile element is measured. Detection limits in INAA determinations depend on the irradiation conditions and on the composition of the sample, which can vary significantly among samples. In this case, detection limits for Sm ranged from 0.002 to 0.05 $\mu\text{g g}^{-1}$. Method detection limit (MDL) for Sm is low enough to assure that any geological particulate interference is below analytical uncertainties.

Another condition to implement this correction is to determine elemental concentrations in the geological material contaminating vegetation samples. In the case of underwater vegetation, fine sediments collected at the same site of biota samples represent the geological contamination. Bed sediment was analyzed by INAA. The elemental concentrations were used to implement the correction by geological material contamination. For riparian vegetation, it is more difficult to obtain geological material considered to be representative of the geological contamination. Except for the contamination by fine volcanic ash, which proved to have no significant variation on the

spatial distribution on most elements in Chaiten 2008 and Puyehue-Cordón Caulle 2011 events (Daga et al. 2014). Corrections for geological material contamination in riparian plants were implemented only in NHNP samples collected after Puyehue-Cordón Caulle 2011 eruption. All other samples measured for Sm were below detection limits. The correction was computed in this case using fine volcanic ash elemental concentrations measured by Daga et al. (2014). The elemental concentrations reported in the present work include the correction for geological material contamination.

In order to evaluate variations in elemental concentrations associated to vegetation processes undergoing within the water media, elemental enrichment factors (EF) of decomposing vegetation in lake water respect to fresh samples were computed. The EF is defined as follows:

$$EF = \frac{C_d}{C_f}$$

C_d Average elemental concentration of vegetation decomposing in lake water in a sampling site

C_f Average elemental concentration of fresh vegetation in a sampling site

Non-parametric Kruskal-Wallis analysis of variance test was applied to compare between groups of plants (exotic vs native large trees; large trees vs shrubs and small trees; riparian vs aquatic plants). Analysis was performed using Statistica v8.0. The level of significance was 0.05.

The correlation between Rb and Cs concentrations was tested by linear fitting with Origin 8 including ANOVA test, considering measurement uncertainties for both elements.

The statistical analysis was performed with ANOVA by using XL-STAT (7.5.X) software. The level of considered significance was 0.05.

Results and discussion

Riparian vegetation

Exotic species: Salix spp.

In Patagonia, the riparian landscape is dominated by several species of the Salicaceae, mainly *Salix alba* L. and *Salix viminalis* L., willow species introduced by European settlers at the end of the 19th century or at the beginning of the 20th (Budde et al. 2010; Naumann 1996), with the role of wind curtains and shade casters around fruit plantations and farmyards (Naumann 1996; Peri and Bloomberg 2002). *Salix humboldtiana* Willd. is the only willow native species, distributed along the rivers from the provinces of Patagonia, but it

was not found around the study sites (Budde et al. 2010; Correa 1984).

Several works studied *Salix* spp. regarding its capacity for heavy metal accumulation, and also for phytoremediation applications (Kacálková et al. 2015; Reimann et al. 2001; Robinson et al. 2000). *Salix* spp. specimens grown in non-contaminated sites showed similar Ba, Ca, Sr, and K concentrations as those obtained in this work (Table 2), whereas Rb concentrations were twofold higher, and Cd, Cr, Sc, Fe, Na, and U concentrations were one order of magnitude higher (Reimann et al. 2001; Table 2). The concentrations reported for *Salix* spp. bioaccumulation in greenhouse and contaminated soils experiments, and phytoremediation tests (Kacálková et al. 2015; Robinson et al. 2000; 2005) were, in general, much higher than the results obtained in the present work (Table 2). Consistent with the ability observed for *Salix* spp. for bioaccumulation of metals and trace elements, the concentrations determined are, in general, higher than those determined in native species (Tables 3, 4, and 5). A nonparametric Kruskal-Wallis test showed that Br, K, Rb, Cs, Zn, and Co

concentrations were significantly higher in *Salix* spp. than in the native species, but no differences were observed in Ca, Cr, Hg, Se, and Sr. To remark, the high Cd, Cs, and Zn concentrations in *Salix* spp., that reached 4.56, 9.39 and 245 $\mu\text{g g}^{-1}$ respectively.

Autochthonous species

Until now, there have been no comprehensive studies on heavy metal concentrations and trace elements in Patagonian native plant species. However, Ferrando et al. (2001) and Gyenge et al. (2008) reported on the elemental composition of native riparian plants from Patagonia, and associated productivity in native forest settings, whereas Barrera et al. (2004) research focused on senescent leaves, and Diehl et al. (2003) in nutrients (C, Ca, K, Mg, N, and P) in mature and senescent leaves. For this study, native species from Patagonia of riparian plants were grouped into large and small trees, conifers, and shrubs (Table 1), and measured for major (Ca, K, and Fe) and trace elements (Ba, Br, Co, Cr, Cs, Hf, Na, Rb,

Table 2 Elemental concentrations determined in *Salix* spp. leaves

	<i>Salix</i> spp. ^a natural concentration	<i>Salix</i> spp. ^b natural concentration	<i>Salix matsudana</i> x <i>S. alba</i> NZ 1040 ^c	greenhouse experiment average concentration		contaminated soil average concentration	
	min.-median-max.		average concentration	<i>Salix purpurea</i> ^d	<i>Salix schwerinii</i> ^d	<i>Salix rubens</i> ^e	<i>Salix x smithiana</i> Willd. ^e
Ag ($\mu\text{g g}^{-1}$)	0.0122	0.007					
As ($\mu\text{g g}^{-1}$)	–	0.0200					
Ba ($\mu\text{g g}^{-1}$)	15.0–29.0–69.3	15.1					
Br ($\mu\text{g g}^{-1}$)	1.51–4.33–14.1						
Ca (wt%)	0.807–1.37–2.37	1.1					
Cd ($\mu\text{g g}^{-1}$)	0.690–2.31–4.56	0.678	9–167	2.2	3.5 ± 0.4	5.16–7.26	5.23–8.18
Co ($\mu\text{g g}^{-1}$)	0.112–0.339–1.52	1.757		0.8 ± 0.1	0.7 ± 0.1		
Cr ($\mu\text{g g}^{-1}$)	0.743–2.06–5.35	<0.2					
Cs ($\mu\text{g g}^{-1}$)	0.195–5.44–9.39						
Fe ($\mu\text{g g}^{-1}$)	–	79		70 ± 2	130 ± 10		
Hf ($\mu\text{g g}^{-1}$)	0.697–0.956–1.16						
Hg ($\mu\text{g g}^{-1}$)	0.00760–0.0315–0.0590	<0.04					
K (wt%)	0.793–2.45–4.42	1.65					
Na ($\mu\text{g g}^{-1}$)	–	23					
Rb ($\mu\text{g g}^{-1}$)	5.79–60.5–97.5	31.4					
Se ($\mu\text{g g}^{-1}$)	0.0150–0.0476–0.0808	<0.5					
Sr ($\mu\text{g g}^{-1}$)	13.5–42.0–89.1	37.3		165 ± 30	155 ± 40	851–1050	748–1020
U ($\mu\text{g g}^{-1}$)	0.971–1.32–1.65	<0.005					
Zn ($\mu\text{g g}^{-1}$)	16.8–123–245						

Values obtained in present work and reported in the literature. Concentrations expressed in dry weight basis

^a This work

^b Reimann et al. 2001

^c Robinson et al. 2000, Data obtained from willows grown in soils containing 0.6–60.6 $\mu\text{g g}^{-1}$ of Cd

^d Robinson et al. 2005. Greenhouse experiment with soil concentration of Cd 0.1; Zn 36.4, Co 2.1, and Fe 12644 $\mu\text{g g}^{-1}$

Table 3 Elemental concentrations in riparian vegetation studied for trace element contents

	<i>Amomyrtus luma</i> N=6 Min.-median-max.	<i>Austrocedrus chilensis</i> N=6 Min.-median-max.	<i>Chusquea culeou</i> N=8 Min.-median-max.	<i>Desfontainia fulgens</i> N=6 Min.-median-max.	<i>Escallonia rubra</i> N=6 Min.-median-max.
Ag ($\mu\text{g g}^{-1}$)	0.0091–0.0122–0.0212	0.0130	0.0159–0.0210–0.0261	0.00920	0.0200
As ($\mu\text{g g}^{-1}$)	–	0.221	0.0310–0.0890–0.147	–	–
Ba ($\mu\text{g g}^{-1}$)	6.30–11.0–22.8	7.47–33.2–38.8	13.0–25.7–30.5	13.1–15.3–34.2	18.3–33.7–70.1
Br ($\mu\text{g g}^{-1}$)	1.03–2.58–5.81	0.434–2.90–7.40	1.65–2.83–13.8	0.453–0.627–0.950	1.24–1.80–2.63
Ca (wt%)	0.654–0.735–1.07	1.41–1.74–1.84	0.239–0.407–0.690	0.718–1.04–1.48	1.25–1.78–2.34
Cd ($\mu\text{g g}^{-1}$)	–	–	–	0.136	–
Co ($\mu\text{g g}^{-1}$)	0.0703–0.0919–0.379	0.0387–0.192–0.311	0.0357–0.128–0.339	0.0197–0.0615–0.210	0.0381–0.0709–0.109
Cr ($\mu\text{g g}^{-1}$)	0.485–1.60–9.30	0.468–0.825–7.13	1.43–4.91–17.8	0.98–2.27–13.59	0.564–2.50–9.69
Cs ($\mu\text{g g}^{-1}$)	0.0444–0.0985–0.129	0.114–0.242–0.422	0.104–0.133–0.251	0.00449–0.0103–0.0162	0.0558–0.0838–0.106
Fe ($\mu\text{g g}^{-1}$)	–	–	126	–	–
Hf ($\mu\text{g g}^{-1}$)	1.19	0.665–0.772–0.880	0.896–0.949–1.00	0.541–0.695–0.850	0.775–0.970–1.17
Hg ($\mu\text{g g}^{-1}$)	0.0100–0.0373–0.114	0.0115–0.0307–0.0577	0.0159–0.0375–0.568	0.0199–0.0410–0.0779	0.0182–0.0224–0.0438
K (wt%)	0.650–1.18–1.41	0.534–0.884–1.19	0.978–1.37–1.99	1.03–1.19–1–48	0.558–1.05–1.77
Na ($\mu\text{g g}^{-1}$)	120–173–227	77.7–95.2–113	55.3–71.9–83.8	–	–
Rb ($\mu\text{g g}^{-1}$)	7.85–16.7–26.6	3.77–9.35–24.3	12.4–20.0–31.0	9.04–13.4–19.5	6.91–14.3–31.1
Se ($\mu\text{g g}^{-1}$)	0.0426–0.200–0.309	0.0383	0.0222–0.101–0.247	0.0190–0.0350–0.0780	0.0690–0.162–0.643
Sr ($\mu\text{g g}^{-1}$)	24.6–34.5–61.7	12.1–98.6–160	17.5–27.4–35.2	23.4–34.2–52.7	72.1–97.0–120
U ($\mu\text{g g}^{-1}$)	1.86	0.920–1.07–1.21	1.39–1.50–1.61	0.00832–0.974–1.30	1.85–1.88–1.92
Zn ($\mu\text{g g}^{-1}$)	18.7–21.9–31.6	10.6–16.4–25.4	14.3–24.9–36.1	20.5–33.8–40.4	25.2–60.9–82.1

Concentrations expressed in dry weight basis

Table 4 Elemental concentrations in riparian vegetation studied for trace element contents

	<i>Gaultheria mucronata</i> N=6 min.-median-max.	<i>Lomatia hirsuta</i> N=7 min.-median-max.	<i>Luma apiculata</i> N=8 min.-max.	<i>Maytenus boaria</i> N=4 min.-median-max.	<i>Myrceugenia exsucca</i> N=1
Ag ($\mu\text{g g}^{-1}$)	0.0174	0.0093–0.0122–0.0151	0.0245–0.0336–0.0530	0.0460	0.0242
As ($\mu\text{g g}^{-1}$)	–	0.0420–0.0478–0.0945	0.0310	–	–
Ba ($\mu\text{g g}^{-1}$)	11.8–28.1–48.8	13.5–31.7–74.3	7.71–13.3–30.8	–	11.5
Br ($\mu\text{g g}^{-1}$)	0.489–0.681–1.29	32.7–49.2–103	2.61–14.0–46.0	1.67–1.94–3.09	2.71
Ca (wt%)	0.660–1.28–3.60	0.386–0.780–1.13	1.06–1.54–2.45	0.831–0.881–3.06	0.757
Cd ($\mu\text{g g}^{-1}$)	0.146	–	–	–	–
Co ($\mu\text{g g}^{-1}$)	0.0482–0.0727–0.152	0.0312–0.0733–0.148	0.0671–0.207–0.298	0.0378–0.0538–0.0698	–
Cr ($\mu\text{g g}^{-1}$)	0.461–1.82–5.72	0.360–2.38–5.71	0.303–1.28–3.20	0.257–1.79–2.47	–
Cs ($\mu\text{g g}^{-1}$)	0.100–0.226–0.336	0.162–0.265–0.515	0.0743–0.839–2.52	–	0.157
Fe ($\mu\text{g g}^{-1}$)	–	–	–	–	–
Hf ($\mu\text{g g}^{-1}$)	1.03–1.14–1.25	0.563–0.686–0.810	1.27	0.737–0.739–0.742	–
Hg ($\mu\text{g g}^{-1}$)	0.00740–0.0154–0.174	0.0150–0.0370–0.119	0.0460–0.0615–0.104	0.0170–0.0369–0.0500	0.113
K (wt%)	0.679–0.773–1.41	0.404–0.547–0.759	0.689–1.13–1.87	0.497–0.648–0.848	1.02
Na ($\mu\text{g g}^{-1}$)	43.3	36.0–38.2–40.4	52.5	–	–
Rb ($\mu\text{g g}^{-1}$)	9.28–20.0–22.9	4.60–6.55–14.2	14.2–21.3–43.3	1.98–2.18–2.37	35.3
Se ($\mu\text{g g}^{-1}$)	0.0840–0.268–0.499	0.0667–0.591–0.763	0.0211–0.0417–0.0659	0.0356–0.0838–0.132	0.0859
Sr ($\mu\text{g g}^{-1}$)	41.3–45.6–82.4	24.6–56.3–76.7	26.7–41.9–71.9	15.0–21.5–65.2	26.7
U ($\mu\text{g g}^{-1}$)	0.0094–0.891–2.29	0.756–0.956–1.16	1.96	1.05–1.22–1.40	–
Zn ($\mu\text{g g}^{-1}$)	11.0–28.4–60.3	6.66–13.2–17.5	10.6–16.1–34.4	31.7–52.0–56.4	22.9

Concentrations expressed in dry weight basis

Table 5 Elemental concentrations in riparian vegetation studied for trace element contents

	<i>Nothofagus antarctica</i> N=4 Min.-median-max.	<i>Nothofagus dombeyi</i> N=14 Min.-median-max.	<i>Salix</i> spp. N=10 Min.-median-max.	<i>Schinus patagonicus</i> N=1	<i>Weinmannia trichosperma</i> N=6 Min.-median-max.
Ag ($\mu\text{g g}^{-1}$)	0.00720	0.00468–0.00680–0.0587	0.0122	–	0.0133–0.0240–0.453
As ($\mu\text{g g}^{-1}$)	–	0.0185	–	0.0140	–
Ba ($\mu\text{g g}^{-1}$)	35.9–39.4–42.8	5.18–22.5–63.2	15.0–29.0–69.3	15.8	15.7–33.0–85.2
Br ($\mu\text{g g}^{-1}$)	1.20–1.24–2.24	0.157–0.391–1.12	1.51–4.33–14.1	2.64	0.852–2.88–3.84
Ca (wt%)	1.54–2.04–2.65	0.318–0.613–1.09	0.807–1.37–2.37	0.381	1.18–1.25–1.79
Cd ($\mu\text{g g}^{-1}$)	–	–	0.690–2.31–4.56	–	0.237–0.239–0.241
Co ($\mu\text{g g}^{-1}$)	0.0883–0.121–0.155	0.0311–0.0800–0.187	0.112–0.339–1.52	0.196	0.0826–0.172–0.192
Cr ($\mu\text{g g}^{-1}$)	0.816–2.01–6.48	0.200–0.944–5.61	0.747–2.06–5.35	–	0.506–1.00–9.30
Cs ($\mu\text{g g}^{-1}$)	–	0.0133–0.0482–0.933	0.195–5.44–9.39	–	0.0219–0.0549–0.0878
Fe ($\mu\text{g g}^{-1}$)	–	106	–	–	–
Hf ($\mu\text{g g}^{-1}$)	0.627–0.684–0.740	0.819–0.826–0.834	0.697–0.956–1.16	–	0.842–0.873–0.903
Hg ($\mu\text{g g}^{-1}$)	0.0170–0.0252–0.0405	0.0191–0.0388–0.190	0.00760–0.0315–0.0590	0.0416	0.00680–0.0169–0.0597
K (wt%)	0.699–0.900–1.01	0.321–0.563–0.886	0.793–2.45–4.42	0.820	0.604–0.688–0.932
Na ($\mu\text{g g}^{-1}$)	–	36.0–43.3–50.6	–	24.6	–
Rb ($\mu\text{g g}^{-1}$)	2.38–4.31–4.91	1.41–7.93–25.2	5.79–60.5–97.5	7.58	9.58–11.6–18.7
Se ($\mu\text{g g}^{-1}$)	0.0300–0.0600–0.110	0.0121–0.0776–0.167	0.0150–0.0476–0.0808	–	0.0570–0.0809–0.200
Sr ($\mu\text{g g}^{-1}$)	31.5–38.0–46.5	11.4–27.7–85.9	13.5–42.0–89.1	75.6	47.7–63.3–105
U ($\mu\text{g g}^{-1}$)	1.31–1.31–1.32	0.0104–1.26–1.49	0.971–1.32–1.65	–	1.40–1.47–1.55
Zn ($\mu\text{g g}^{-1}$)	40.4–49.1–83.8	16.2–31.4–176	16.8–123–245	13.1	9.76–14.71–26.8

Concentrations expressed in dry weight basis

Se, Sr, and Zn), and heavy metals (Ag, As, Cd, Hg, and U). Delimitation between larger and smaller trees is not precise. *Chusquea culeou* was considered among smaller trees even though it is a gramineous species because it can reach up to 6 m tall. Median, minimum, and maximum values determined for each species are reported in Tables 3, 4, and 5.

Regarding major elements, highest Ca and K concentrations were measured in *G. mucronata* and *C. culeou*, respectively. Calcium concentrations were significantly higher in shrubs than in smaller trees, and K concentrations were higher in smaller trees and shrubs than in larger trees. Iron was similar in the few samples with significant determinations after the correction for geological material contamination. Bromine concentrations were particularly high in *L. hirsuta*, reaching $103 \mu\text{g g}^{-1}$. In other species, Br concentrations were below $15 \mu\text{g g}^{-1}$. Bromine concentrations were statistically higher in smaller trees than in larger trees and shrubs. Selenium and Zn showed a wide variation range, with Se in much lower levels (from 0.02 to $0.1 \mu\text{g g}^{-1}$ in *D. fulgens* and *N. antarctica*, to 0.07 – $0.8 \mu\text{g g}^{-1}$ in *E. rubra* and *L. hirsuta*) than Zn (from 7 to $18 \mu\text{g g}^{-1}$ in *L. hirsuta*, to 16 – $176 \mu\text{g g}^{-1}$ in *N. dombeyi*). There were no differences in Se concentrations between shrubs, larger and smaller trees. Zinc concentrations were higher in shrubs than in smaller trees, but no differences were observed between the other plant groups. Cobalt varied from 0.02 to $0.2 \mu\text{g g}^{-1}$ in *D. fulgens*, to 0.07 – $0.3 \mu\text{g g}^{-1}$ in *L. apiculata*.

Silver concentrations were below $0.06 \mu\text{g g}^{-1}$, except for *W. trichosperma* ($0.5 \mu\text{g g}^{-1}$). There were no differences in Ag and Co concentrations between the three groups of plants. Arsenic concentrations ranged between 0.03 and $0.3 \mu\text{g g}^{-1}$. Cadmium was detected only in *D. fulgens* ($0.15 \mu\text{g g}^{-1}$), *G. mucronata* ($0.14 \mu\text{g g}^{-1}$), and *W. trichosperma* ($0.24 \mu\text{g g}^{-1}$). Mercury ranged from 0.01 to $0.2 \mu\text{g g}^{-1}$, except for *C. culeou* ($0.6 \mu\text{g g}^{-1}$). There were no differences in Hg concentrations between shrubs, larger and smaller trees.

Cesium, potassium, and rubidium Potassium is an essential element for all forms of life, taken up by plants in its cationic form (K^+). It can be substituted by Rb and Cs, trace elements belonging to the same chemical group but without known biologic function, given that their chemical properties are similar, and can be incorporated from the soil as well. Intracellular Cs competition for K-binding sites in proteins was suggested to have toxic effects (Isaure et al. 2006). On the other side, despite the similar chemical behavior, Rb uptake and transportation within plants was reported to be different from K (Kabata-Pendias and Pendias 2001). Larger native trees showed significantly lower K concentrations (0.6–0.7 wt%; mean values, Table 6) than the other native plants studied (0.8–1.4 wt%; mean values, Table 6), as well as Rb, with lower concentrations (2 – $13 \mu\text{g g}^{-1}$ in larger native trees, and 8 – $27 \mu\text{g g}^{-1}$ in other native plants; Table 6). Cesium

Table 6 Mean K, Rb, and Cs concentrations in native riparian plants

Plant group	Species	K (wt%)	Rb ($\mu\text{g g}^{-1}$)	Cs ($\mu\text{g g}^{-1}$)
Exotic tree	<i>Salix</i> spp.	2.56 (0.94)	56 (28)	4.4 (3.3)
Larger trees	<i>L. hirsuta</i>	0.58 (0.13)	7.8 (3.6)	0.31 (0.14)
	<i>M. boaria</i>	0.66 (0.15)	2.18 (0.28)	–
	<i>N. dombeyi</i>	0.55 (0.15)	8.6 (5.7)	0.23 (0.31)
	<i>N. antarctica</i>	0.69 (0.18)	3.9 (1.3)	–
	<i>W. trichosperma</i>	0.72 (0.12)	12.6 (3.5)	0.55 (0.47)
Conifer	<i>A. chilensis</i>	0.87 (0.24)	11.3 (7.6)	0.26 (0.11)
Smaller trees	<i>A. luma</i>	1.10 (0.28)	16.8 (7.0)	0.93 (0.35)
	<i>C. culeou</i>	1.41 (0.29)	20.2 (5.6)	0.146 (0.045)
	<i>L. apiculata</i>	1.18 (0.37)	27 (12)	1.08 (0.90)
Shrubs	<i>M. exsucca</i>	1.02	35.3	0.157
	<i>D. fulgens</i>	1.23 (0.19)	14.1 (4.1)	0.103 (0.054)
	<i>E. rubra</i>	1.13 (0.47)	16.5 (9.4)	0.082 (0.022)
	<i>G. mucronata</i>	0.94 (0.32)	18.3 (5.0)	0.22 (0.10)
	<i>S. patagonicus</i>	0.820	7.58	0.38

Concentrations expressed in dry weight basis. Standard deviation of the average, in parenthesis

concentrations did not show a clear grouping, and no difference between the groups of plants, with highest values ($1 \mu\text{g g}^{-1}$) in *L. apiculata* and *A. luma*, and the lowest in the shrub *E. rubra* ($0.08 \mu\text{g g}^{-1}$).

Previous research found an association between the ratio of Rb and Cs concentrations in fish muscle and food source, allowing the use of Rb-Cs ratios as a diet tracer in lacustrine systems (Chiasson 1991; Kanevskii and Fleishman 1972; Ribeiro Guevara et al. 2006). Considering that Rb and Cs are nonessential for cellular process, but have similar chemical properties, the Rb-Cs ratio is not substantially modified along the transfer processes in the trophic web. Thus, keeping the value of the primary carbon source and allowing its identification. Rubidium and Cs concentrations in riparian plants are studied together with macrophytes, in order to provide background data for the potential use of Rb-Cs ratios as a diet tracer. Except for the conifer *A. chilensis*, Rb and Cs concentrations exhibited a trend of positive correlation, although the linear correlation was not significant for shrubs (Fig. 2). The slope of the Rb vs Cs concentrations linear correlation, representing the Rb-Cs ratio, was similar among small trees and *Salix* spp., ranging from 7 to 8, and higher for larger trees (shrub Rb-Cs ratios are not considered for the comparison because the correlation was no significant, but these ratios are close to that of larger trees; Fig. 2). The introduced *Salix* spp. exhibited higher Rb and Cs concentrations than the native species (Table 6), and the slope of the linear correlation was 7.39 (Fig. 2), lower than that for most native species (Fig. 2). Macrophytes Rb and Cs concentrations showed significant linear correlation for *H. chamaemorus* only ($R^2=0.32$; ANOVA $p=0.031$), with a slope of 34.3

± 3.9 , whereas Rb-Cs ratios were above 100 for *Galium* sp., *M. quitense* and *P. linguatus*, and above 25 for *S. californicus*. Macrophyte Rb-Cs ratios are far above riparian plants, allowing therefore the discrimination of both carbon sources.

Vegetation associated with the water body dynamics

Leaf and plant decomposition

Riparian plants are a significant source of allochthonous carbon to aquatic ecosystems. Once settled on the bottom of the water body, leaf litter decomposition proceeds in three distinct temporal stages: chemical leaching, microbial conditioning, and finally mechanical or biological breakdown (Gessner et al. 1999; Webster and Benfield, 1986). Primary decomposition is by microorganisms, which releases dissolved organic carbon (DOC). The decomposing leaves become covered with a complex biofilm composed of a diverse association of fungi, algae, protozoa, detritus, and bacteria (Kominkova et al. 2000; Lázaro et al. 2013). Microorganisms are known to accumulate high amounts of heavy metals and trace elements. Therefore, decomposing riparian vegetation is an important source of elements to aquatic ecosystems, entering the food web and bioaccumulating in higher trophic levels.

The incorporation of heavy metals and trace elements to the decomposing leaves from the aquatic media could be associated with leaf matrix processes. For example, adsorbing onto exposed surfaces, or by biofilm and microorganism uptake provided that leaf decomposition involves microorganism activity, which bioaccumulate high amounts of heavy metals and trace elements. Elemental concentration of decomposing leaves of riparian plants (considering also the macrophyte

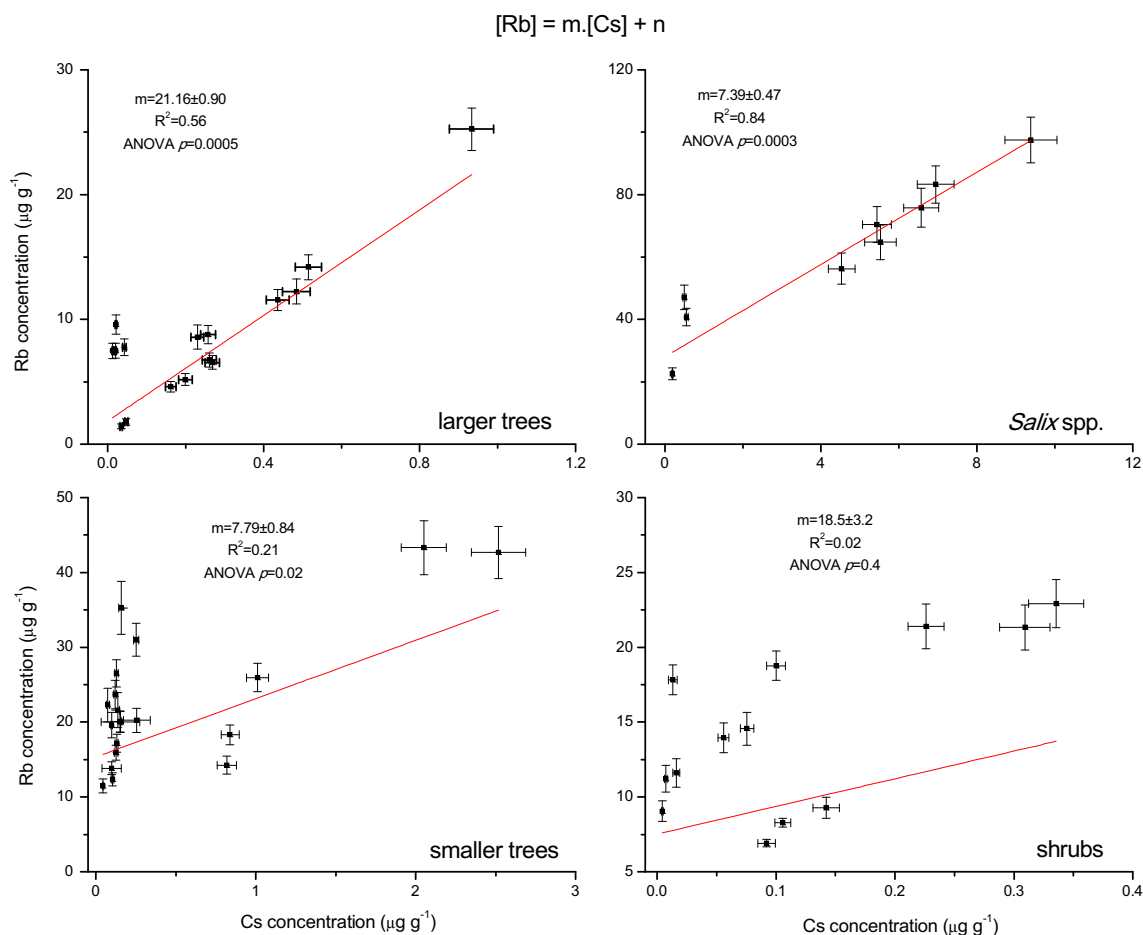


Fig. 2 Rubidium and cesium concentrations in riparian plants grouped in *Salix* spp. larger trees, smaller trees and shrubs (Table 1). Linear correlation is included for each group

S. californicus) is compared with those concentrations in fresh leaves of the same species. Elemental concentrations are reported in Table 7, whereas trace elements enrichment factors (*EF*) are shown in Table 8.

Values of *EF* around 1 indicate that there is no net effect on the release of this element at this stage of leaves decomposition, whereas values above 1 indicates net incorporation of this element and values below 1 indicates release to the aquatic body. Zinc is released by all riparian species during leaves decomposition, except for *C. culeou* (*EF* around 1), *L. hirsuta* and the aquatic species *S. californicus* with *EF* values above 1 (Table 8). On the other side, Co is incorporated by all riparian species and the aquatic *S. californicus*, except for *Salix* spp. with *EF* around 1 (Table 8). Similar for Se, with *EF* values above 1 for all species except for *C. culeou* and *N. dombeyi*, that exhibited *EF* values around 1. This is also the case of Cr for all riparian species (Table 8). Bromine exhibited a different behavior among riparian species, with *EF* values below 1 for *C. culeou*, *L. hirsuta*, *L. apiculata*, and *Salix* spp., whereas Br *EF* in other species was above 1 (Table 8). Similarly, the heavy metal Ag showed *EF* values below 1 for *L. apiculata*,

and *N. dombeyi*, but above 1 for *Salix* spp. and, the highest determined (33.4), for *L. californicus* (Table 8).

Mercury was found in high levels in the biota of lakes Moreno and Nahuel Huapi. Extremely high concentrations, up to $260 \mu\text{g g}^{-1}$, were determined in plankton, also high in fish and macroinvertebrates (Rizzo et al. 2011; 2014). Mercury in fresh riparian plants ranged from 0.01 to $0.6 \mu\text{g g}^{-1}$, with the highest values corresponding to *C. culeou* (Tables 3, 4, and 5). Mercury *EF*s were above 1 (except for *L. hirsuta* with a value slightly below), reaching a value of 24 for *S. californicus* and of 14 for *C. culeou* (Table 8), meaning a strong uptake of Hg from the water body by the decomposing leaves. Passive uptake of inorganic Hg (Hg^{2+}) from the aquatic media in exposed surface was observed in natural plankton from these lacustrine systems in laboratory experiments, and this uptake mechanism was proposed to explain the extremely high Hg concentrations in the smallest natural plankton (Soto Cárdenas et al. 2014). The same mechanism could also explain the increased Hg concentrations in decomposing leaves. Also, biofilms growing on decomposing leaves can accumulate metals through

Table 7 Elemental concentrations in decomposing leaves of riparian vegetation collected within water bodies

	<i>Chusquea culeou</i> N=1	<i>Lomatia hirsuta</i> N=2 Min.-max.	<i>Luma apiculata</i> N=2 Min.-max.	<i>Myrceugenia exsucca</i> N=1	<i>Nothofagus dombeyi</i> N=3 Min.-median-max.	<i>Salix</i> spp. N=1	<i>Schoenoplectus californicus</i> ^a N=1
Ag ($\mu\text{g g}^{-1}$)	–	–	0.0531	–	0.00983–0.0128–0.0157	0.0337	0.587
As ($\mu\text{g g}^{-1}$)	0.606	–	2.77	0.913	2.12	–	0.909
Ba ($\mu\text{g g}^{-1}$)	37.8	39.4–51.3	32.6–33.8	37.7	36.3–39.2–43.5	29.7	61.1
Br ($\mu\text{g g}^{-1}$)	2.37	4.17–4.35	4.47–4.91	3.73	1.10–6.74–41.1	3.68	10.0
Ca (wt%)	0.650	1.64–1.75	1.46–2.61	1.31	1.35–1.77–2.57	1.53	1.40
Cd ($\mu\text{g g}^{-1}$)	–	0.310	–	–	0.290–0.295–0.300	–	–
Co ($\mu\text{g g}^{-1}$)	1.15	–	4.98–7.23	1.83	0.254–0.964–4.53	0.588	2.70
Cr ($\mu\text{g g}^{-1}$)	–	1.01–3.60	–	–	2.03–3.24–4.44	2.31	5.59
Cs ($\mu\text{g g}^{-1}$)	–	–	–	–	–	–	–
Fe ($\mu\text{g g}^{-1}$)	2880	–	19200	10000	4110–12500–20900	2470	–
Hf ($\mu\text{g g}^{-1}$)	–	–	–	–	–	–	–
Hg ($\mu\text{g g}^{-1}$)	1.67	0.0356–0.0410	0.123–0.227	0.188	0.0536–0.0950–0.654	0.143	0.950
K (wt%)	–	–	–	–	0.0374	–	–
Na ($\mu\text{g g}^{-1}$)	–	–	–	–	–	–	–
Rb ($\mu\text{g g}^{-1}$)	–	–	–	–	–	–	–
Se ($\mu\text{g g}^{-1}$)	0.107	0.695–1.05	0.136	0.163	0.0389–0.0463–0.119	0.0613	0.121
Sr ($\mu\text{g g}^{-1}$)	34.1	85.7–89.9	91.2–200	85.9	78.7–10.0–120	99.3	56.6
U ($\mu\text{g g}^{-1}$)	–	0.0626–0.208	–	–	0.0640	0.0834	–
Zn ($\mu\text{g g}^{-1}$)	23.0	15.7–24.5	11.2–19.8	12.4	13.5–21.0–22.4	18.6	39.4

Concentrations expressed in dry weight basis

^a *Schoenoplectus californicus* is an aquatic plant, emerging from the water surface. The sample reported here is composed of decomposing *S. californicus* remains collected from lake bottom at littoral sites

adsorption onto organic and inorganic matter, and by bacteria and fungi uptake (King et al. 2002; Gothberg and Greger 2006), and Hg methylation may take place in the bacterial community of such matrix (Gentès et al. 2013; Hamelin et al. 2011). Some macroinvertebrate consumers inhabiting the littoral zones of lakes depend on autochthonous (e.g., epiphytes attached to macrophytes, vascular plants, phytoplankton, and decaying macrophytes) and allochthonous (e.g., tree leaves) sources of energy (Cremona et al. 2010; France 1998). Methylmercury, then, enters the food web as it is easily bioaccumulated and biomagnified (Watras et al. 1998) from

primary producers to macroinvertebrates, and finally to fish. Macroinvertebrate consumers can also be a relevant pathway of other heavy metal and trace elements from decomposing leaves to the lacustrine food web.

Submerged and emergent plants

Macrophytes are considered as important components of the aquatic ecosystems, being a food source for aquatic invertebrates and playing a relevant role in the carbon cycle. Although the elements uptake by aquatic plants from the water

Table 8 Enrichment factor of trace element concentrations of decomposing leaves of riparian vegetation collected within water bodies respect to fresh samples

	<i>C. culeou</i>	<i>L. hirsuta</i>	<i>L. apiculata</i>	<i>M. exsucca</i>	<i>N. dombeyi</i>	<i>Salix</i> spp.	<i>S. californicus</i>
Ag	–	–	0.738	–	0.490	2.76	33.4
Br	0.560	0.0750	0.211	1.38	36.3	0.624	2.02
Co	7.53	–	32.2	–	20.1	1.08	9.39
Cr	–	0.882	–	–	1.22	1.00	8.03
Hg	13.7	0.789	2.37	1.66	5.56	4.25	24.2
Se	0.885	1.59	1.54	1.89	0.950	1.33	–
Sr	1.24	1.63	3.09	3.22	3.22	1.98	–
Zn	0.950	1.60	0.841	0.544	0.445	0.145	2.62

Table 9 Elemental concentrations in aquatic plants

	<i>Galium</i> sp. N=3 Min.-median-max.	<i>Hydrocotyle chamaemorus</i> N=18 Min.-median-max.	<i>Isöetes chubutiana</i> N=2 Min.-max.	<i>Myriophyllum quitense</i> N=21 Min.-median-max.
Ag ($\mu\text{g g}^{-1}$)	0.313	0.0610–0.0847–0.108	–	0.0189–0.0696–0.203
As ($\mu\text{g g}^{-1}$)	1.77–7.78–13.8	0.0539–0.383–1.50	–	0.249–0.890–5.98
Ba ($\mu\text{g g}^{-1}$)	83.1–106–139	5.07–42.9–161	17.4–60.8	10.9–36.2–197
Br ($\mu\text{g g}^{-1}$)	19.1–21.4–23.0	2.13–9.02–57.0	6.10–42.3	3.89–23.3–77.5
Ca (wt%)	1.21	0.287–1.54–3.81	0.730–0.960	0.730–0.928–4.07
Cd ($\mu\text{g g}^{-1}$)	–	1.00	–	0.783–1.49–2.20
Co ($\mu\text{g g}^{-1}$)	4.71–6.67–8.62	0.0341–1.02–3.03	–	0.753–2.15–6.09
Cr ($\mu\text{g g}^{-1}$)	2.20	1.03–1.98–2.96	–	1.16–5.27–6.86
Cs ($\mu\text{g g}^{-1}$)	0.408–0.562–0.716	0.100–0.235–0.565	–	0.0945–0.322–0.433
Fe ($\mu\text{g g}^{-1}$)	3400	62.1–2200–4000	–	2030
Hf ($\mu\text{g g}^{-1}$)	–	2.02	–	–
Hg ($\mu\text{g g}^{-1}$)	0.321–2.52–4.72	0.0100–0.184–7.60	0.0263–0.0397	0.0152–0.111–5.60
K (wt%)	2.09–3.14–4.19	0.589–2.05–4.83	3.23–4.52	0.158–1.52–7.86
Na ($\mu\text{g g}^{-1}$)	4000	738–3000–17200	5420–6150	968–5500–36900
Rb ($\mu\text{g g}^{-1}$)	66.4–67.7–68.2	4.78–22.0–95.2	40.1–45.5	2.77–34.3–93.9
Se ($\mu\text{g g}^{-1}$)	0.160	0.0198–0.121–0.155	0.0665–0.102	0.0530–0.141–0.422
Sr ($\mu\text{g g}^{-1}$)	48.0–69.5–91.0	17.8–87.5–210	63.3–902	35.6–59.2–161
U ($\mu\text{g g}^{-1}$)	–	3.06	–	–
Zn ($\mu\text{g g}^{-1}$)	84.3–98.0–199	29.9–57.2–212	55.1–64.6	32.3–94.3–336

Concentrations expressed in dry weight basis

Table 10 Elemental concentrations in aquatic plants

	<i>Nitella</i> sp. N=4 Min.-median-max.	<i>Potamogeton linguatus</i> N=6 Min.-median-max.	<i>Ranunculus</i> sp. N=1	<i>Schoenoplectus californicus</i> N=5 Min.-median-max.
Ag ($\mu\text{g g}^{-1}$)	0.0516–0.0946–0.175	0.0503–0.0885–0.162	–	0.0176
As ($\mu\text{g g}^{-1}$)	1.13–1.49–1.89	0.232	1.90	0.095–0.104–0.142
Ba ($\mu\text{g g}^{-1}$)	191–249–255	44.9–80.7–715	172	1.48–6.72–25.4
Br ($\mu\text{g g}^{-1}$)	1.38–5.63–10.1	9.43–17.6–23.4	26.4	1.42–3.58–10.2
Ca (wt%)	1.26–1.35–1.61	0.788–0.936–1.01	1.51	0.0676–0.392–0.727
Cd ($\mu\text{g g}^{-1}$)	–	–	–	–
Co ($\mu\text{g g}^{-1}$)	1.62–1.78–1.94	0.270	8.45	0.323–0.152–0.605
Cr ($\mu\text{g g}^{-1}$)	3.11–9.99–11.6	–	5.30	0.285–0.669–1.16
Cs ($\mu\text{g g}^{-1}$)	–	0.283–0.335–0.388	0.705	0.00596–0.0143–0.0227
Fe ($\mu\text{g g}^{-1}$)	4220	–	5710	144
Hf ($\mu\text{g g}^{-1}$)	–	–	–	–
Hg ($\mu\text{g g}^{-1}$)	0.777–1.41–2.00	0.0234–0.0321–0.174	–	0.0762–0.0107–0.147
K (wt%)	–	1.42–2.23–3.25	2.59	0.0536–0.437–0.706
Na ($\mu\text{g g}^{-1}$)	–	4510–5410–6290	10600	48.7–144–1010
Rb ($\mu\text{g g}^{-1}$)	–	26.5–40.1–229.	71.8	0.614–0.618–2.04
Se ($\mu\text{g g}^{-1}$)	0.157–0.233–0.286	0.0868–0.189–0.314	0.322	0.161
Sr ($\mu\text{g g}^{-1}$)	78.11–81.0–90.4	40.0–51.6–60.5	145	24.5
U ($\mu\text{g g}^{-1}$)	–	–	–	–
Zn ($\mu\text{g g}^{-1}$)	98.3–100–106	46.4–60.0–74.2	126	4.07–16.9–25.5

Concentrations expressed in dry weight basis

phase depends on the bioavailability of the metal in the water, which in turn depends on the retention time, as well as on the interaction with other elements and substances (Fritioff and Gregor 2003), macrophytes are known to be efficient heavy metal accumulators (Chung and Jeng 1974; Devlin 1967). Some aquatic plant species can accumulate very high concentrations of toxic metals to levels which exceed by far sediment and soil levels (Baker and Brooks 1989), including Ag, Cd, Cr, Pb, and Hg (Memon et al. 2001). The aquatic plants incorporate also essential elements from the water column and from the sediments, such as Co, Cu, Fe, Mg, Mn, Mo, Ni, Se, and Zn.

Among the aquatic plants studied, *Galium* sp. had the highest As and Co concentrations (13.8 and 8.62 $\mu\text{g g}^{-1}$, respectively), *P. linguatus* the highest Ba and Rb (715 and 229 $\mu\text{g g}^{-1}$, respectively) (Tables 9 and 10). Regarding heavy metals, Hg was low in *Ranunculus* sp. and *I. chubutiana* (below 0.04 $\mu\text{g g}^{-1}$), but particularly high in *H. chamaemorus* (7.6 $\mu\text{g g}^{-1}$), *M. quitense* (5.6 $\mu\text{g g}^{-1}$), *Galium* sp. (4.7 $\mu\text{g g}^{-1}$), and *Nitella* sp. (2.0 $\mu\text{g g}^{-1}$). Silver ranged from 0.05 to 0.3 $\mu\text{g g}^{-1}$; Cd was detected in *H. chamaemorus* and *M. quitense* only in relevant concentrations (from 0.8 to 2.2 $\mu\text{g g}^{-1}$) (Tables 9 and 10).

The comparison of median values between riparian and aquatic plants shows that Ag, As, Ba, Br, Co, Fe, Hg, Na, and Zn concentrations are 1 to 3 orders of magnitude higher in aquatic plants. On the other side, similar values were observed for Ca, Cd, Cs, Cr, Hf, K, Rb, Se, Sr (except for *I. chubutiana*, with higher concentrations), and U (Tables 3, 4, 5, 9, and 10). The Kruskal-Wallis test showed significant differences in Ag, Ba, Br, Co, Hg, K, Rb, Se, Na, Sr, and Zn, between riparian and aquatic plants, having the later higher concentrations. No differences were observed in Ca, Cr, and Cs.

Conclusions

Present work studied heavy metal and trace element contents in riparian vegetation and macrophytes as primary producers associated with lacustrine ecosystems in Northern Patagonian Andean Range, including 22 native species and the exotic *Salix* spp.. The elements analyzed were heavy metals Ag, As, Cd, Hg, and U, major elements Ca, K, and Fe, and trace elements Ba, Br, Co, Cr, Cs, Hf, Na, Rb, Se, Sr, and Zn. *Salix* spp. exhibited, in general, higher concentrations than the native riparian species, particularly high for Cd, Cs, and Zn, reaching 4.56, 9.39, and 245 $\mu\text{g g}^{-1}$, respectively. Regarding critical heavy metals in riparian native species, Ag ranged from 0.005 to 0.5 $\mu\text{g g}^{-1}$, As from 0.03 to 0.3 $\mu\text{g g}^{-1}$, Cd from 0.14 to 0.24 $\mu\text{g g}^{-1}$, and Hg from 0.01 to 0.6 $\mu\text{g g}^{-1}$. Aquatic plants had Ag, As, Ba, Br, Co, Fe, Hg, Na, and Zn

concentrations 1 to 3 orders of magnitude higher than riparian vegetation, with higher Ag concentrations from 0.05 to 0.3 $\mu\text{g g}^{-1}$, As up to 14 $\mu\text{g g}^{-1}$, Cd from 0.8 to 2.2 $\mu\text{g g}^{-1}$, and Hg from 2.0 to 7.6 $\mu\text{g g}^{-1}$.

Riparian vegetation leaves collected from the water bodies showed enriched concentrations of Hg for all species (except for *L. hirsuta*), up to 24 times for *S. californicus*, and 14 times for *C. culeou*, meaning a strong uptake of Hg from the water body by the decomposing leaves. Biofilms growing on decomposing leaves can accumulate metals through adsorption onto organic and inorganic matter, and by bacteria and fungi uptake, and Hg methylation may take place in the bacterial community of such matrix. Methylmercury, then, may enter the food web as it is easily bioaccumulated and biomagnified from primary producers to macroinvertebrates feeding in the littoral zones, and finally to fish. Macroinvertebrate consumers can also be a relevant pathway of other heavy metal and trace elements from decomposing leaves to the lacustrine food web.

The results reported evidence the significance of littoral primary producers as the doorway for heavy metal and trace elements in freshwater food web.

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