

Latitudinal distribution of lanthanides contained in macroalgae in Chile: an inductively coupled plasma-mass spectrometric (ICP-MS) determination

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Abstract Lanthanide compositions of 17 Chilean macroalgal species were analyzed by inductively coupled plasma mass spectrometry. Samples were collected from four distinct areas (from 23° to 53° S) along the coast of Chile, in the spring of 2014. Lanthanides were confirmed in all samples and were found over a range of 0.0001–7.62 mg kg⁻¹ dry weight, in agreement with concentrations found in non-polluted areas around the world. The concentrations of elements varied among species, phyla, and, in some cases, by geographical distribution, highlighting the importance of local factors on lanthanide distribution. The central and northern zones of Chile contained higher concentrations of lanthanides (in total of all samples with 10.69 and 10.41 mg kg⁻¹ dry weight, respectively), although the northern samples comprised only one third of the number of samples from the central zone. The pristine area at the extreme south of Chile

also contained lanthanides in macroalgal biomass, at a total concentration of 4.77 mg kg⁻¹ dry weight. Species with the highest concentrations of these metals were the brown alga *Colpomenia sinuosa* (7.62 mg kg⁻¹ dry weight) and the red macroalga *Gracilaria chilensis* (2.92 mg kg⁻¹ dry weight), followed by *Corallina officinalis* var. *chilensis*, and *Pyropia* sp. Cerium was normally the main lanthanide (2.99 mg kg⁻¹ dry weight) followed by lanthanum (1.34 mg kg⁻¹ dry weight) and/or neodymium (1.61 mg kg⁻¹ dry weight). This is the first publication that exclusively covers the distribution of these economically important metals in Chilean marine biota. We suggest that the brown alga *C. sinuosa* could have potential as a bioindicator of lanthanides.

Keywords Cerium · Lanthanum · Rare earth elements · Seaweed · South America · Trace elements

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Introduction

Many taxonomic groups of macroalgae have been used traditionally both as ingredients in medicine and in food preparations across different regions of the world, although their biological properties are not yet fully understood (Mabeau and Fleurence 1993; Astorga-España et al. 2015). Over the past 50 years, industrial uses of algae have increased considerably, with the consequent development of applied research in various related fields (Goecke et al. 2012; Wells et al. 2016). Macroalgae are currently used extensively in the pharmaceutical, cosmetics, and food industries (Truus et al. 2001). Their use as ecological and environmental bioindicators has also increased in recent years (Amer et al. 1999). However, because macroalgae are known to concentrate metals to levels many times higher than those ones found in surrounding waters (Iwata et al. 1993; Kano et al. 2003; Serfor-Armah et al. 2006), their elemental composition is important (Truus et al. 2004).

Studies of the chemical composition of marine biota in Chile (algae, mollusks, tunicates, crustacean, or fishes) have usually focused on characterizing the main biomolecular constituents (e.g., amino acids, dietary fiber, fatty acids, phycocolloids, proteins) and a few micronutrients of economically important resource species (Gras et al. 1993; Manly et al. 1996; Román-Silva et al. 2003; Ortiz et al. 2009; Goecke et al. 2012). Other research has concentrated on the content of toxic metals originating from anthropogenic activities and their effects at different organizational levels (Ahumada 1994; Castilla 1996; Astorga-España et al. 2005; Contreras et al. 2010; Castillo and Valdés 2011). Over the last few decades, a large number of studies in marine biota have focused on the content of heavy metals and metalloids such as As, Cd, Hg, and Pb, whose toxic effects are well understood (Astorga-España et al. 2007; Gaudry et al. 2007a; Díaz et al. 2012). Conversely, much less research has focused on rare earth elements (REEs) in marine organisms (Liang et al. 2014). These elements are usually not considered in any compositional analysis, and therefore, their biodistribution in natural environments remains unresolved. Because they are considered to be non-essential, not particularly toxic, of low abundance, or simply due to methodological reasons, they have been neglected (Goecke et al. 2015b). This is particularly true for South American organisms.

Under the descriptor “rare earth elements,” 15 lanthanides, named lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), and ytterbium (Yb), are grouped together with the non-lanthanides scandium (Sc) and yttrium (Y) (Brown et al. 1990). They exhibit very similar physical and chemical properties but differ slightly in atomic number (Zhu et al. 2012). Despite the name, these elements are widely dispersed and are generally common in nature, in terrestrial and marine environments (Brown et al. 1990). On average, REEs in the Earth’s crust represent 0.015% dry weight (dw) (Kastori et al. 2010), which compares with that of copper, lead, or zinc (Hu et al. 2004). Because of their unique physical and chemical properties, they are used in a growing number of applications and have become indispensable for a number of critical technologies in modern commercial, industrial, and military products (Du and Graedel 2011). Consequently, with increasing agricultural and industrial uses of REEs, the release of these elements into the biosphere and their bioaccumulation has risen (Loell et al. 2011; Liang et al. 2014).

Among the analytical techniques used to quantify lanthanides, inductively coupled plasma mass spectrometry (ICP-MS) is nowadays widely employed due to its large dynamic range, low detection limits ($< \text{ng g}^{-1}$), and the ability to monitor a number of elements simultaneously (Bulska et al. 2012).

The presence of lanthanides (Pr, Nd, and Sm) was first reported in algae in the calcareous Rhodophyta *Lithotamnium calcareum* in Roscoff, France (Servigne and Tchakirian 1939). Further information on REEs has been rather dispersed since then. More recently, it was discovered that regardless of size (micro- or macroalgae), structural organization (unicellular, filamentous, crustose, or foliose), type of algal division (e.g., Chlorophyta, Ochrophyta, Rhodophyta, Charophyta or Cyanobacteria), or geographical origin, algae contain a diverse spectrum of lanthanides (see Hou and Yan 1998; Fu et al. 2000; Kano et al. 2001a; Mashitah et al. 2012).

Lanthanides can easily reach 1.3 mg kg^{-1} of fresh algal material (Yan et al. 1998), although this is low in comparison with macroelements such as calcium, sodium, or potassium (see Hou and Yan 1998; Amer et al. 1999). Worldwide, 37 studies on the identification and quantification of lanthanides from macroalgae have been published, most of them being carried out on Asian species (Table 1). Only two South American studies have been published so far. In those, the total level of lanthanides in macroalgae ranged from 0 to $226 \text{ mg kg}^{-1} \text{ dw}$.

Over the last decade, China has achieved a monopoly on REE production (over 95% of world production) with economic and social consequences (Hurst 2010; van Gosen et al. 2014). Due to increasing interest in REEs and serious limitations in the market, several efforts worldwide have been initiated to develop rare earth projects by prospecting for new ores or re-opening old mines. Chile, with a long tradition in mining, can produce valuable quantities of raw REEs, encouraging the emergence of companies for their exploration and production. Therefore, worldwide, there is concern about the environmental impacts of lanthanides (see Liang et al. 2014). These widely and frequently used minerals may enter the ecosystem, and consequently, determination of lanthanides in environmental samples (including algae) is becoming a very important issue (Bulska et al. 2012).

The coast of Chile, more than 4200 km, confers natural heterogeneity over a great latitudinal range. This variability generates a marked physical gradient along the coast (Valdés et al. 2011), which is reflected in significant chemical signatures in algae (Vásquez and Guerra 1996) and population demography (Guillemin et al. 2015).

The aim of this study was to measure the concentration of lanthanides in 17 macroalgal samples collected along the Chilean coast and to investigate the biodistribution of those metals in the country. We hypothesized that the northern zone of the country, with a large mining industry and with direct influence of the Atacama Desert, would have the highest concentration of lanthanides. We expect the central and southern zones of Chile to be next, both having highly populated cities on the coast, and anticipate the lowest concentration to be in the austral (extreme south) region, farthest from the continent

Table 1 Lanthanide content in marine macroalgae around the world. The detected metal, their concentration range, number of algal species, geographical origin of the samples, technique used for analysis, and references are given. Values are expressed in milligram per kilogram, and it is specified if the results are calculated from fresh weight or from dry weight

Elements	Concentration	Technique	Spp.	Origin	Reference
Dy	6.12–108.47	SRTXRF	11	Brazil	Ferreira et al. (2012)
Ce, La, Sm	0.14–20.2	INAA	12	Chile	Vásquez and Guerra (1996)
Ce, Eu, Yb	0.021–1.13 (fw)	INAA	1	China	Yan et al. (1998)
Ce, Eu, La, Lu, Nd, Sm, Tb, Yb	0.0253–2.45	INAA	35	China	Hou (1999)
Ce, Eu, La, Lu, Nd, Sm, Tb, Yb	0.0346–38.5	INAA	35	China	Hou and Yan (1998)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.78–49.1	ICP-MS	7	China	Shi et al. (2004)
Ce, La, Sm	0.118–4.86	INAA	6	China	Hou et al. (1998)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.0006–0.085	ICP-MS	1	China	Li et al. (2012)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.0036–0.9991	ICP-MS	2	China	Yao et al. (2007)
Ce, Eu, La, Nd, Sm, Yb	0.018–2.82 (fw)	INAA	8	China	Yan et al. (1999)
Ce, Eu, La, Lu, Sm, Tb, Yb	0.46–67	INAA, ENAA	2	Corsica	Roelandts and Monty (1987)
Eu, La, Lu, Sm, Tb, Yb	0.0–0.12	INAA	1	Estonia	Truus et al. (2001, 2004)
Nd, Pr, Sm	–	–	1	France	Servigne and Tchakirian (1939)
Ce, La, Sm	0.176–2.05	AAS, others	1	France	Coquery et al. (1997)
Ce, Eu, La, Sm, Tb, Yb	0.0005–7.5	INAA, ICP-MS, AES	1	Germany	Amer et al. (1999)
Ce, Eu, Sm, Tb, Yb	0.01–>10	INAA	3	Germany	Jayasekera and Rossbach (1996)
La, Sm	0.04–2.1	INAA	16	Ghana	Serfor-Armah et al. (2006)
Eu	0.01–0.06	INAA	8	Greece	Kanias et al. (1992)
Ce, La, Lu, Sm, Tb, Yb	0.61–1.1	INAA	69	Japan	Yamamoto et al. (1984)
Ce, Dy, Er, Eu, La, Lu, Nd, Pr, Sm, Tb, Yb	0.000–0.0174	INAA	1	Japan	Iwata et al. (1993)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	L kg ⁻¹ (fw)	ICEP-MS	1	Japan	Takata et al. (2010)
Ce, Eu, La, Lu, Sm, Tb, Yb	<0.01–5.3	INAA	40	Japan	Kawashima et al. (1983)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.00025–0.174	ICP-MS	5	Japan	Fu et al. (2000)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.001–1.58	ICP-MS	7	Japan	Kano et al. (2001a)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.00056–3.25	ICP-MS	21	Japan	Kano et al. (2001b)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.00145–1.96	ICP-MS	39	Japan	Kano et al. (2003)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.000–0.97	ICP-MS	29	Japan	Sakamoto et al. (2008)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.01–26.2	ICP-MS	1	Malaysia	Mashitah et al. (2012)
Ce, Dy, Er, Eu, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb	0.004–226	ICP-MS, INAA	2	Morocco	Gaudry et al. (2007a, b)
Ce, Tb, Yb	0.00–0.3	INAA	10	Norway	Kleiven (2014)
Ce, Eu, Sm, Tb, Yb	0.028–13.1	INAA	2	Sri Lanka	Jayasekera (1994)
Ce, Eu, Sm, Tb, Yb	0.01–>10	INAA	3	Sri Lanka	Jayasekera and Rossbach (1996)
Ce, Eu, La, Lu, Sm	<0.02–13	INAA	3	Yugoslavia	Martić et al. (1980)
Nd, Sm	0.001–187	INAA	2	Ukraine	Kravtsova et al. (2014, 2015)

Techniques used for analysis are AAS = flame atomic absorption spectroscopy, ENAA = epithermal neutron activation analysis, ICP-AES = inductively coupled plasma atomic emission spectroscopy, ICP-MS = inductively coupled plasma mass spectrometry, INAA = instrumental neutron activation analysis, SRTXRF = synchrotron radiation total reflection X-ray fluorescence analysis

fw fresh weight

and with fewer anthropogenic influences. In addition, we aim to identify a suitable species for future biomonitoring studies.

Material and methods

Samples

Healthy macroalgal samples from the Chilean coast were individually handpicked over the period of late spring in 2014. Samples were placed into pre-cleaned polyethylene bags into thermal boxes filled with ice. Morphologically complex species as *Durvillaea antarctica*, *Macrocystis pyrifera*, and *Lessonia spicata*, with large morphological differences and longer lifetime, were sampled in the stipe and fronds separately. The rest of the species (mostly smaller than 10 cm and with little morphological differentiation, if any) were sampled on fronds only. The samples were transferred to the laboratory, identified, cleaned from sediments and epiphytes, washed several times with (local) filtered seawater, and dried at 60 °C in an oven for at least 2 days to a constant weight (Serfor-Armah et al. 2006; Sakamoto et al. 2008). We analyzed the dry biomass by ICP-MS in the National Institute of Public Health, Czech Republic.

The study was divided into four areas of Chile (Fig. 1, Table 2):

Northern area: Antofagasta's coast, specifically Punta Coloso, Isla Santa María and Caleta Urco beach (between 23°47'08.5" S; 70°29'19.8" W and 23°27'57.5" S; 70°30'47.2" W).

Central area: coast of Quintero-Ventanas and Montemar (between 32°43'12.5" S, 71°28'42.1" W and 32°57'46.9" S, 71°32'49.4" W).

Southern area: Valdivia's coast, specifically Niebla and Mehuin beach (between 39°51'19.8" S 73°23'35.1" W and 39°25'14.53" S, 73°13'7.98" W).

Austral zone (extreme South): coast of Magallanes, specifically, Bahía Mansa (53°36'43.71" S, 70°55'43.21" W) and San Juan (53°41'28.64" S, 70°58'14.53" W).

Analytical methods

Sample digestion

Samples of dry algal biomass (0.1 g) were digested with 3 mL of 67% HNO₃ (Merck, Suprapure) and 0.5 mL of 30% H₂O₂ (Merck, Suprapure) in a PTFE vessel in a Milestone MLS-1200 MEGA closed microwave device at 250–600 W for 20 min. After evaporation of excess acid in the same system, the resulting solution was transferred to a volumetric flask

(20 mL) and filled with 0.67% HNO₃ (Merck, Suprapure) (Vítová et al. 2011).

Determination of elemental content (ICP-MS)

ICP-MS measurements were performed using an Elan DRC-e (Perkin Elmer, Canada) equipped with a concentric PTFE nebulizer, a cyclonic spray chamber, a high-efficiency quartz torch, and a dynamic reaction cell (DRC) for the elimination of spectral interference. The IS solution for determination of total metals contained Ge, In, and Re (10 µg L⁻¹) in dilute (1:100) HNO₃ (Suprapur, Merck). Distilled and demineralized water (Millipore, USA) was used to prepare all solutions. Samples were passed through a 0.45-µm nylon syringe filter and diluted 1:10 in water. Values are expressed in milligram per kilogram dw. We corrected for background noise by subtracting the blank samples from the raw data (Kleiven 2014).

Reference material underwent all the steps as measured samples; no part of the procedure was skipped. It was mainly in order to avoid possible loss of analyzed metals in the various treatment steps. The standards were always used during the measurements because of checking the accuracy of the results and for controlling of instruments. Samples were always diluted to reach the corresponding concentrations of the reference solutions.

Statistical analysis

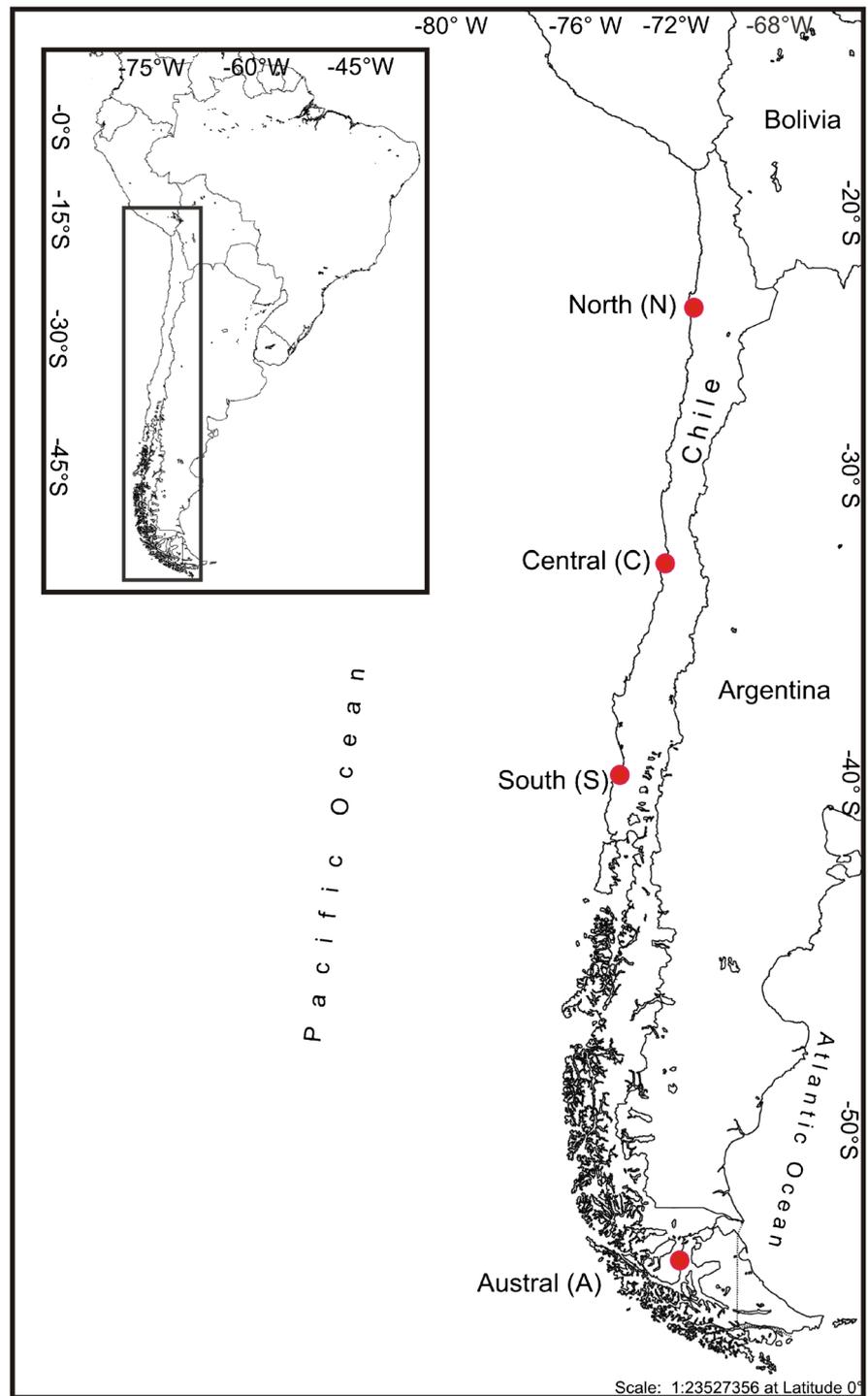
Three replicates ($n = 3$) of each species (if available) from each location were used for chemical analysis. Data were statistically analyzed using R version 3.3.1 (R Development Core Team 2016). We applied a Mann-Whitney U test in order to determine the existence of differences in REE content among algal groups, while for differences among algal species within each zone and among geographical origins, Kruskal-Wallis tests were used at a significance level of $\alpha = 0.05$. Furthermore, we used a Dunn test for multiple comparisons when differences were detected.

Results

Lanthanides were detected in all macroalgal samples collected from different areas of the Chilean coast, within a range of 0.0001–7.61 mg kg⁻¹ dw. All lanthanides detected, their concentrations, and localities are shown in Table 3 (only species of concentrations equal or above 0.01 mg kg⁻¹ dw are displayed in).

The compact brown alga *Colpomenia sinuosa* from central and northern Chile had the highest concentration (Table 3). The concentration of total lanthanides found in red algae was significantly lower than that observed in brown algae (U test, $W = 68$, $P = 0.01723$), ranging from 0.13 to 2.96 mg kg⁻¹ dw. Among Rhodophyta, the highest concentration was found in

Fig. 1 Map of Chile showing the sampling sites



Gracilaria chilensis from southern Chile (Table 3). Results show differences in the total amount (sum of all samples) of lanthanides found in macroalgae at different localities, although no significant latitudinal patterns of metal content in relation to sampling sites were observed within individual species (Kruskal-Wallis test, chi-squared = 8.027, $df = 3$, $P = 0.05$). The central and northern zones of Chile exhibited the highest concentrations of lanthanides (total of 10.69 and

10.41 mg kg^{-1} dw, respectively), although the northern samples comprised only one third of the number of samples from the central zone. The pristine area in the extreme south of Chile also exhibited lanthanides in macroalgal biomass, at a concentration of 4.77 mg kg^{-1} dw.

In all samples, cerium was the lanthanide found in highest concentrations, ranging from 0.0001 to 2.99 mg kg^{-1} dw (Table 3), except in the case of *Corallina officinalis*

Table 2 List of macroalgae investigated in the present study according to the different geographical localities from which they were isolated. They were divided into northern area (N, divided into sector s1 = Caleta Urco, sector s2 = Santa María, and sector s3 = Punta Coloso), central area (C, divided into sector s1 = Montemar and sector s2 = Quintero), southern area (S, divided into sector s1 = Mehuín and sector s2 = Niebla), and extreme southern or austral zone (A, divided into sector s1 = San Juan and sector s2 = Bahía Mansa) of Chile. Species names are according to Algaebase (see Guiry and Guiry 2015)

Algae division	Locality			
	N	C	S	A
Div. Ochrophyta				
<i>Adenocystis utricularis</i> (Bory de Saint-Vincent) Skottsberg		s1, 2		s2
<i>Colpomenia sinuosa</i> (Mertens ex Roth) Derbés and Solier	s1, 3	s1, 2		s2
<i>Desmarestia ligulata</i> (Stackhouse) Lamouroux			s2	
<i>Desmarestia</i> sp.				s2
<i>Durvillaea antarctica</i> (Chamisso) Hariot (frond)		s1, 2	s1	
<i>Durvillaea antarctica</i> (Chamisso) Hariot (stipe)		s1, 2		
<i>Lessonia spicata</i> (Suhr) Santelices (frond)		s1, 2		
<i>Lessonia spicata</i> (Suhr) Santelices (stipe)		s1, 2		
<i>Lessonia</i> spp.	s3			
<i>Lessonia flavicans</i> Bory de Saint-Vincent				s2
<i>Macrocystis pyrifera</i> (Linnaeus) C Agardh (frond)	s1, 2	s2	s1, 2	s2
<i>Macrocystis pyrifera</i> (Linnaeus) C Agardh (stipe)		s2		
Div. Rhodophyta				
<i>Chondrus</i> sp.	s2			
<i>Corallina officinalis</i> var. <i>chilensis</i> (Decaisne) Kützing		s1		s2
<i>Gracilaria chilensis</i> CJ Bird, McLachlan and EC Oliveira			s2	
<i>Iridaea cordata</i> (Turner) Bory de Saint-Vincent			s1	
<i>Mazzaella laminarioides</i> (Bory de Saint-Vincent) Fredericq		s1	s1, 2	s1
<i>Nothogenia fastigiata</i> (Bory de Saint-Vincent) PG Parkinson		s1, 2	s2	
<i>Pyropia</i> sp.			s2	
<i>Sarcothalia crispata</i> (Bory de Saint-Vincent) Leister				s1

var. *chilensis* from the austral zone, which had slightly higher levels of Nd, followed by La and Ce. Samples from the northern area of Chile contained lanthanides in the order Ce > Nd > La > Gd (with Sm > Dy > Pr also in considerable concentrations). Samples from the central and southern areas contained Ce > La/Nd > Nd/La > Pr, while samples from the austral zone contained Ce > La > Nd as the main lanthanides. The main lanthanides and their concentrations in the different macroalgal species by zone are displayed in Table 3. Samples such as *Lessonia* spp. (s3) in the north, *D. antarctica* and *L. spicata* in the central zone, and *L. flavicans* in the austral zone that contained less than 10^{-5} mg kg⁻¹ dw are not displayed in table, but did contain lanthanides.

Certain species collected from distant localities contained similar concentrations of total lanthanides: *Nothogenia fastigiata* (0.24–0.62 mg kg⁻¹ dw), *C. officinalis* var. *chilensis* (1.03–1.13 mg kg⁻¹ dw), and *Mazzaella laminarioides* (0.14–0.53 mg kg⁻¹ dw), the latter in samples extracted from central, southern, and austral zones of the country (Table 3). Other species showed great variation in the concentrations of total lanthanides. For example, samples of *C. sinuosa* from the central part of Chile and from two localities in the north contained the highest concentration of total lanthanides, but samples of

the same species extracted in the extreme south (austral zone of Chile) contained only low levels of those elements (Table 3). Another brown macroalga, *M. pyrifera*, also showed variations in the concentrations of metals, although they were less evident (0.0001 in central Chile to 0.65 mg kg⁻¹ dw in the south).

Despite this variation among algal species, only Ce was present in *C. sinuosa* at a concentration significantly higher than other lanthanides (Dunn test, $H = 44.8$, $df = 13$, $P < 0.01$).

Discussion

Lanthanides were present as trace elements in all macroalgae sampled from different geographical sites. This result confirms the presence of these non-essential elements in macroalgae, living either with or without anthropogenic influences. REEs are usually not measured when performing elemental analyses of living organisms, making comparisons difficult. In Chile, a large number of studies on the composition of sediments have considered many elements but, as is also the case for marine biota, almost none included lanthanides (e.g., Salamanca et al. 1986; Ramírez et al. 2005; Valdés et al. 2011; Chandía and Salamanca 2012; Astorga-España et al. 2015). On the contrary, many Chilean land studies associated with environmental research,

Table 3 Concentrations of single lanthanides in the selected marine macroalgae collected at four distant coastal areas of Chile: northern zone (N), central zone (C), southern zone (S), and extreme south or austral zone (A) from different sites (s1, s2, s3 behind species names). For more details of sampling places, see Table 2. Arithmetic mean from three analyses and their standard deviations are shown. The total concentration of lanthanides (TCLn) and origin of the samples expressed as algal division (Rhodophyta—“Rho” or Ochrophyta—“Och”) or algae section (frond—“f” or stipe—“s”) are given. All results are expressed in milligram per kilogram dry weight. Lanthanides were detected within a range of 0.0001–7.61 mg kg⁻¹ dw (only species of concentrations equal or above 0.01 mg kg⁻¹ dw are illustrated in this table)

Location	Species name	Division	Ce	Dy	Er	Eu	Gd	Ho	La	Lu	Nd	Pr	Sm	Tb	Tm	Yb	TCLn	
N	<i>C. sinuosa</i> s1	Och	2.41 ± 0.08	0.38 ± 0.04	0.18 ± 0.02	0.11 ± 0.015	0.40 ± 0.02	0.07 ± 0.006	1.11 ± 0.07	1.43 ± 0.06	0.33 ± 0.03	0.38 ± 0.04	0.07 ± 0.003				6.87	
	<i>C. sinuosa</i> s3	Och	1.41 ± 0.09	0.09 ± 0.04	0.04 ± 0.001	0.03 ± 0.001	0.12 ± 0.02	0.02 ± 0.001	0.68 ± 0.03	0.64 ± 0.04	0.17 ± 0.02	0.12 ± 0.003	0.02 ± 0.001				3.34	
	<i>M. pyrifera</i> (f) s2	Och	0.06 ± 0.03	0.02 ± 0.005	0.001 ± 0.001	0.001 ± 0.001	0.02 ± 0.005	0.03 ± 0.005	0.001 ± 0.002	0.03 ± 0.005	0.01 ± 0.002	0.02 ± 0.002	0.003 ± 0.002				0.07	
	<i>Chondrus</i> sp. s2	Rho	0.05 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.003 ± 0.003	0.13
	Total 10.41																	
	<i>A. utricularis</i> s1	Och	0.16 ± 0.03	0.02 ± 0.003	0.01 ± 0.003	0.01 ± 0.003	0.02 ± 0.003	0.01 ± 0.003	0.09 ± 0.002	0.09 ± 0.002	0.08 ± 0.002	0.02 ± 0.002	0.02 ± 0.002	0.02 ± 0.002				0.42
	<i>A. utricularis</i> s2	Och	0.12 ± 0.06	0.01 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.06 ± 0.02	0.06 ± 0.02	0.06 ± 0.02	0.02 ± 0.02	0.01 ± 0.02	0.01 ± 0.02				0.29
	<i>C. sinuosa</i> s1	Och	2.99 ± 0.2	0.23 ± 0.02	0.12 ± 0.01	0.07 ± 0.06	0.32 ± 0.04	0.04 ± 0.002	1.34 ± 0.06	1.61 ± 0.06	1.61 ± 0.06	0.40 ± 0.02	0.32 ± 0.02	0.04 ± 0.06	0.04 ± 0.06	0.02 ± 0.006	0.10 ± 0.06	7.62
	<i>C. sinuosa</i> s2	Och	0.36 ± 0.04	0.03 ± 0.002	0.01 ± 0.001	0.01 ± 0.001	0.04 ± 0.002	0.04 ± 0.002	0.17 ± 0.02	0.16 ± 0.02	0.16 ± 0.02	0.05 ± 0.002	0.04 ± 0.002	0.04 ± 0.002				0.87
	<i>L. spicata</i> (f) s1	Och	0.02 ± 0.004	0.002 ± 0.002	0.001 ± 0.001	0.001 ± 0.001	0.002 ± 0.002	0.002 ± 0.002	0.02 ± 0.003	0.02 ± 0.003	0.02 ± 0.004	0.02 ± 0.004	0.02 ± 0.004	0.02 ± 0.004	0.02 ± 0.004	0.02 ± 0.004	0.02 ± 0.004	0.06
<i>L. spicata</i> (s) s1	Och	0.01 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.002 ± 0.002	0.01	
<i>M. pyrifera</i> (f) s2	Och	0.03 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001	0.03	
S	<i>C. officinalis</i> v. <i>chilensis</i> s1	Rho	0.32 ± 0.06	0.04 ± 0.004	0.02 ± 0.003	0.01 ± 0.003	0.05 ± 0.003	0.05 ± 0.003	0.28 ± 0.04	0.20 ± 0.03	0.05 ± 0.004	0.04 ± 0.003	0.04 ± 0.003				1.01	
	<i>M. laminarioides</i> s1	Rho	0.06 ± 0.004	0.004 ± 0.004	0.004 ± 0.004	0.004 ± 0.004	0.004 ± 0.004	0.004 ± 0.004	0.05 ± 0.006	0.03 ± 0.002	0.03 ± 0.002	0.03 ± 0.002	0.03 ± 0.002				0.14	
	<i>N. fastigiata</i> s1	Rho	0.09 ± 0.004	0.004 ± 0.004	0.004 ± 0.004	0.004 ± 0.004	0.01 ± 0.001	0.01 ± 0.001	0.07 ± 0.002	0.05 ± 0.002	0.05 ± 0.002	0.01 ± 0.001	0.01 ± 0.001				0.24	
	Total 10.69																	
	<i>D. antarctica</i> (f) s1	Och	0.03 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.02 ± 0.003	0.02 ± 0.003	0.02 ± 0.002	0.02 ± 0.002	0.02 ± 0.002	0.02 ± 0.002			0.01 ± 0.002	0.09
	<i>M. pyrifera</i> (f) s1	Och	0.24 ± 0.02	0.02 ± 0.002	0.02 ± 0.002	0.02 ± 0.002	0.02 ± 0.002	0.02 ± 0.002	0.12 ± 0.02	0.13 ± 0.02	0.13 ± 0.02	0.03 ± 0.002	0.03 ± 0.002	0.03 ± 0.002				0.55
	<i>M. pyrifera</i> (f) s2	Och	0.09 ± 0.005	0.01 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.05 ± 0.005	0.06 ± 0.005	0.06 ± 0.005	0.01 ± 0.005	0.01 ± 0.005	0.01 ± 0.005				0.25
	<i>G. chilensis</i> s2	Rho	1.32 ± 0.04	0.09 ± 0.002	0.05 ± 0.002	0.03 ± 0.001	0.12 ± 0.02	0.02 ± 0.002	0.56 ± 0.03	0.49 ± 0.04	0.49 ± 0.04	0.12 ± 0.02	0.10 ± 0.02	0.02 ± 0.002				2.92
	<i>I. cordata</i> s1	Rho	0.09 ± 0.005	0.02 ± 0.005	0.02 ± 0.005	0.02 ± 0.005	0.02 ± 0.005	0.02 ± 0.005	0.10 ± 0.05	0.08 ± 0.05	0.08 ± 0.05	0.02 ± 0.005	0.02 ± 0.005	0.02 ± 0.005				0.35
	<i>M. laminarioides</i> s1	Rho	0.09 ± 0.006	0.02 ± 0.003	0.02 ± 0.003	0.02 ± 0.003	0.02 ± 0.003	0.02 ± 0.003	0.08 ± 0.002	0.09 ± 0.002	0.09 ± 0.002	0.02 ± 0.002	0.02 ± 0.002	0.02 ± 0.002				0.34
<i>M. laminarioides</i> s2	Rho	0.16 ± 0.04	0.02 ± 0.002	0.01 ± 0.002	0.01 ± 0.002	0.03 ± 0.002	0.03 ± 0.002	0.14 ± 0.04	0.12 ± 0.04	0.12 ± 0.04	0.03 ± 0.004	0.02 ± 0.002	0.02 ± 0.002				0.53	
<i>P. columbina</i> s2	Rho	0.45 ± 0.02	0.05 ± 0.003	0.03 ± 0.002	0.01 ± 0.002	0.06 ± 0.002	0.06 ± 0.002	0.22 ± 0.03	0.24 ± 0.02	0.24 ± 0.02	0.03 ± 0.002	0.03 ± 0.002	0.03 ± 0.002				1.12	
Total 6.15																		
<i>A. utricularis</i> s2	Och	0.03 ± 0.005	0.005 ± 0.005	0.005 ± 0.005	0.005 ± 0.005	0.005 ± 0.005	0.005 ± 0.005	0.02 ± 0.004	0.02 ± 0.004	0.02 ± 0.005	0.02 ± 0.005	0.02 ± 0.005	0.02 ± 0.005				0.07	
<i>C. sinuosa</i> s2	Och	0.27 ± 0.04	0.03 ± 0.002	0.02 ± 0.004	0.01 ± 0.001	0.03 ± 0.002	0.03 ± 0.002	0.13 ± 0.04	0.14 ± 0.04	0.14 ± 0.04	0.04 ± 0.004	0.03 ± 0.004	0.03 ± 0.004				0.70	

Table 3 (continued)

Location	Species name	Division	Ce	Dy	Er	Eu	Gd	Ho	La	Lu	Nd	Pr	Sm	Tb	Tm	Yb	TCLn
	<i>D. ligulata</i> s2	Och	0.07 ± 0.001	0.02 ± 0.001	^a	^a	0.02 ± 0.001		0.06 ± 0.001		0.06 ± 0.001	0.01 ± 0.001	0.02 ± 0.001			^a	0.26
	<i>Desmarexia</i> sp. s2	Och	0.18 ± 0.04	0.04 ± 0.004	0.02 ± 0.004	0.01 ± 0.001	0.04 ± 0.004	^a	0.12 ± 0.03		0.14 ± 0.02	0.03 ± 0.004	0.03 ± 0.004	^a			0.61
	<i>L. flavicans</i> s2	Och	0.15 ± 0.04	^a	^a	^a	0.01 ± 0.002		0.12 ± 0.03		0.07 ± 0.004	0.02 ± 0.004	0.01 ± 0.002				0.38
	<i>M. pyrifer</i> (f) s2	Och	0.10 ± 0.005	^a	^a	^a	^a		0.05 ± 0.005		0.03 ± 0.005	^a	^a				0.18
	<i>C. officinalis</i> v. <i>chilensis</i> s2	Rho	0.24 ± 0.05	0.06 ± 0.003	0.04 ± 0.003	0.01 ± 0.003	0.06 ± 0.004	0.01 ± 0.002	0.27 ± 0.03	^a	0.28 ± 0.03	0.06 ± 0.003	0.06 ± 0.002	0.01 ± 0.003	^a		1.10
	<i>M. laminaroides</i> s1	Rho	0.09 ± 0.004	0.02 ± 0.003	^a	^a	0.02 ± 0.003		0.09 ± 0.004		0.08 ± 0.003	0.02 ± 0.003	0.02 ± 0.003	^a		^a	0.34
	<i>N. fastigiata</i> s2	Rho	0.19 ± 0.05	^a	^a	^a	0.01 ± 0.005		0.15 ± 0.05		0.10 ± 0.05	0.03 ± 0.005	0.01 ± 0.005				0.49
	<i>S. crispata</i> s1	Rho	0.24 ± 0.04	0.02 ± 0.004	^a	^a	0.03 ± 0.004	^a	0.14 ± 0.04		0.15 ± 0.04	0.03 ± 0.004	0.03 ± 0.004	^a		^a	0.64
	Total																

^aThe species with concentrations below 0.01 mg kg⁻¹ dw

mining, and geology measured lanthanides in the elementary composition of soil and rock (e.g., Cortés et al. 1980; Montecinos et al. 2008; Ruggieri et al. 2012).

The tendency worldwide is not different; we found only 37 studies on the trace element composition of macroalgae that measured environmental concentrations of lanthanides (Table 1). The total amount of REEs measured in those studies ranged from 0.0001 to 226 mg kg⁻¹ dw. Only two cases involved South American species, from which, one case corresponded to Brazilian macroalgae and the other to Chilean macroalgae. In the latter research, Vásquez and Guerra (1996) studied 12 macroalgal species from the north of Chile and found four REEs (La, Ce, Sm, Sc). In the present study, we confirmed the presence of those elements and incorporated others in the latitudinal sampling, counting 14 lanthanides in 17 macroalgal species. Nevertheless, the concentrations that we observed were lower than observed by those authors.

Although it was not possible to establish a clear latitudinal gradient in the concentration of lanthanides, north-central samples contained the highest concentrations of lanthanides by biomass unit (the total of all samples) in comparison with the southern samples (south and austral zones of Chile). This result was expected since the distribution of REEs on the Earth's crust is not homogeneous. Topographical and climatic conditions, orogenetic processes, submarine groundwater discharge, hydrothermal inputs, and recent volcanic activities increase metal concentrations (Vásquez and Guerra 1996; Schacht et al. 2010; Takata et al. 2010). Geographical variations are likely due to the presence of intensive mining activity and a desert climate in the northern zone, whereas the central zone of Chile is associated with the most urban areas of the country, although activities related to mining processing are also carried out in this region.

The lowest content of lanthanides by biomass unit corresponded to the pristine austral zone. Nevertheless, lanthanides were detected in all macroalgal samples (Table 3). This suggests that anthropogenic pollution is not the only source of these metals and indicates the importance of local natural factors such as rainfall, wind, rivers, erosion, and presence of natural mineral ores on the presence of lanthanides in macroalgae. Among them, annual rainfall and consequent weathering effect on land are extremely important sources of REEs; this changes drastically in the country according to latitude. In Chile, annual precipitation increases southward from a few millimeters per year in the north of Chile (Antofagasta = 1.7 mm) to more than 2000 mm in the southern part of the country, e.g., central area/Valparaíso = 386 mm, south area/Valdivia = 2138 mm, and austral zone/Punta Arenas = 376 mm of rainfall a year (Quintana and Aceituno 2012; Herrera and Custodio 2014). Factors such as wind are also important because they serve as a vector of dust from inland. For example, evidence suggests that high concentrations of lanthanides in fresh snow of the austral zone of Chile (Grigholm et al. 2009) may represent a natural input of dust

from a crustal source. Kim et al. (2015) also detected a concentration of trace elements including REEs in ice or snow one or two orders of magnitude higher than that in seawater from Antarctica. Even the influence of volcanic ashes carried by wind may contribute to REEs in the area, as shown by Ruggieri et al. (2012).

Furthermore, natural continental runoff and atmospheric deposition of trace elements to the oceans can be dramatically increased in coastal waters due to anthropogenic activities (Kravtsova et al. 2015). Important anthropogenic sources of REEs are phosphoric mineral fertilizers, phosphorus plaster, industrial wastewater, sewer mud, mining processes, and atmospheric depositions (Volokh et al. 1990; Olmez et al. 1991; Elbaz-Poulichet and Dupuy 1999; Kulkarni et al. 2006; Sahoo et al. 2012; Zhu et al. 2012; Liang et al. 2014). Gaudry et al. (2007a) observed a drastic increase in the concentration of lanthanides such as Ce (an increase of 31,667%), La (an increase of 45,200%), Nd (an increase of 30,222%), and Dy (an increase of 45,100%), among other metals, in macroalgae under the influence of wastewaters coming from the phosphoric acid production/industry in Morocco. In agreement with this, the central zone of Chile exhibited the highest concentration of lanthanides, although concentrations were still in line with others found in non-polluted areas around the world (Table 1).

In the north of Chile, Vásquez and Guerra (1996) studied the concentrations of elements in macroalgae from polluted and non-polluted intertidal areas and found a higher concentration of REEs in samples associated with polluted coasts. Chile is an important mining country, with a great number of metallic and non-metallic deposits. The northern region is the zone where the principal and larger mines of copper ores are located, representing one of the most important global reserves of this element. The mining of copper ores has produced adverse effects on the environment due to discharge of tailing wastes into rivers or sea and release of particulate material and gases into the atmosphere by the smelters, etc. (Castilla 1996; De Gregori et al. 2003). Lanthanides associated with copper extraction and processing have already been determined (Cortés et al. 1980). Dust elements coming from the Atacama Desert also represent an important natural source of metals found in the water of the adjacent bay (Salamanca et al. 2000). In agreement, our samples from northern Chile also contained high concentrations of lanthanides.

The present findings are comparable with the relative abundance of lanthanides found generally in macroalgae. Irrespective of geographical origin, Ce is usually the most abundant lanthanide found in macroalgae (Martić et al. 1980; Kawashima et al. 1983; Iwata et al. 1993; Hou et al. 1998; Yan et al. 1999; Kano et al. 2001a, b; Yao et al. 2007). Our results on macroalgae from four geographically distinct areas of Chile support this pattern. Probably this is related to the natural abundance of this lanthanide, the highest when comparing the upper crust abundances of REEs (Liang et al. 2014). In algae,

Ce normally has values of 26.2 mg kg⁻¹ dw (Mashitah et al. 2012), a value ten times higher than our highest results, but it has been reported to reach 114.0 mg kg⁻¹ dw in polluted environments (Gaudry et al. 2007a). Other frequently found lanthanides are La, Nd, Sm, Gd, and Dy (see Roelandts and Monty 1987; Fu et al. 2000; Gaudry et al. 2007a; Sakamoto et al. 2008), which were within the ranges observed here. The less abundant lanthanides found in macroalgae, as recorded in our results, corresponded to Lu, Tm, and Tb (Shi et al. 2004; Takata et al. 2010; Mashitah et al. 2012; Table 3).

Concentrations of lanthanides varied greatly within the same algal division and even the same species, depending on geographical locations (Table 3). Nevertheless, our results do not allow for comparisons among all species because there was not a significant number of shared species in the sampled sectors. Nevertheless, our data confirms that the environment as well as characteristic features of each taxonomic group (e.g., morphological characteristics, growth strategy) are important factors in determining the pattern of lanthanide bioaccumulation (Yamamoto et al. 1984; Kawashima et al. 1983; Yan et al. 1999; Fu et al. 2000; Kano et al. 2001a, b; Sakamoto et al. 2008; Kleiven 2014; Kravtsova et al. 2015). As an example, in the austral zone of the country, the alga with the highest concentration of lanthanides was *C. officinalis* var. *chilensis*. We speculate that this high content of lanthanides may be a consequence of the ability of this calcareous Rhodophyta to replace calcium with these metals (see Goecke et al. 2015a).

It is known that metal accumulation can vary in algal thalli structures, for instance, in holdfasts, stipes, and fronds; this has been well described, especially for morphologically complex species within the kelps (e.g., Sáez et al. 2012; Stengel et al. 2005). In the present study, there was no clear difference on the REE content between fronds and stipe in morphologically complex species such as *D. antarctica*, *M. pyrifera*, and *L. spicata* (Table 3). Nevertheless, the latter two species do presented differences at Quintero area (sector s2), according to which part of the algae were sampled. Such potential variation in patterns of metal accumulation in the algal thallus may have implications for biomonitoring and need to be well considered.

The measurement of trace elements in marine organisms is critical for ecological studies, as well as for a better understanding of their functions in biological processes and the cycling of materials throughout the biosphere (Martić et al. 1980; Kano et al. 2001a; Sakamoto et al. 2008). The reason algae accumulate lanthanides remains unknown. These elements might be non-essential, but it has been repeatedly reported that high concentrations of lanthanides can be toxic to algae, plants, and animals. Low concentrations of lanthanides, on the other hand, may produce beneficial effects (e.g., Hu et al. 2004; Goecke et al. 2015a). Nevertheless, the waste footprints and environmental impacts from mining operations that extract rare earth mineral ores are expected to be significant (EPA 2012; Liang et al. 2014). In areas where REE contamination is likely, the slow accumulation of

these elements in the environment could become problematic (Thomas et al. 2014), emphasizing the urgency to support additional environmental and ecological studies on REEs, and to use this information to conduct risk assessments related to REE mining, processing, transport, and recycling (Goecke et al. 2015b).

Almost nothing is known about the concentration of lanthanides in Chilean wildlife, so there is no comparison on a national scale. This is the first study of lanthanides in Chilean marine organisms, focusing on those metals at different and distant geographical areas. The Chilean environmental legislation is quite recent, and over the last few years, work has been dedicated to the generation of environmental regulations and especially, the configuration of environmental quality guidelines (Valdés et al. 2011). Lanthanides are not yet considered in the aquatic environmental regulations from Chile (e.g., CONAMA 2003), but because of the uncertainty of the effect of lanthanides on plants, animals, and human health, knowledge of their content in algae is necessary (Yan et al. 1998; Kleiven 2014).

If the implementation of industries related to the exploitation of rare earth elements in Chile succeeds, the present study will serve as a precedent for future environmental impact studies. Furthermore, according to our results, we are able to identify the brown algae *C. sinuosa* as an interesting organism with potential as an environmental bioindicator of lanthanides. This species is cosmopolitan, is commonly presented in many coastal areas of Chile, and is relatively easy to identify, and because of its compact (round) body, there is no need to classify different sections of the algae for analysis. This alga clearly showed different concentrations of lanthanides at different geographical localities but has not yet been considered as an economic resource in Chile.

Conclusion

We have used ICP-MS to detect all 14 lanthanides in Chilean macroalgae growing in four distinct geographical areas. The concentrations of the REEs are comparable to those obtained by other authors in not severely polluted zones in different areas of the world. Local as well as species-specific factors influence the concentration of lanthanides in algae. We suggest that the influence of deserts, mining industry, and closeness to populated urban areas enhances the local concentration of lanthanides, although those elements are common in biological samples. Macroalgae such as *C. sinuosa* may be useful bioindicators of pollution related to this mineral industry.

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References

- Ahumada R (1994) Nivel de concentración e índice de bioacumulación para metales pesados (Cd, Cr, Hg, Ni, Cu, Pb y Zn) en tejidos de invertebrados bénticos de Bahía San Vicente, Chile. *Rev Biol Mar* 29:77–87
- Amer HA, Ostapczuka P, Emons H (1999) Quality assurance in measuring the elemental composition of the alga *Fucus vesiculosus*. *J Environ Monit* 1:97–102
- Astorga-España MS, Rodríguez-Rodríguez EM, Díaz-Romero C (2005) Sodium, K, Ca, Mg, Fe, Cu and Zn concentrations in molluscs from the Strait of Magellan (Chile): their contribution to dietary intake. *Int J Food Sci Nutr* 56:337–347
- Astorga-España MS, Rodríguez Galdón B, Rodríguez-Rodríguez EM, Díaz-Romero C (2015) Mineral and trace element concentrations in seaweeds from the sub-Antarctic ecoregion of Magallanes (Chile). *J Food Comp Anal* 39:69–76
- Astorga-España MS, Rodríguez-Rodríguez EM, Díaz-Romero C (2007) Application of chemometric studies to metal concentrations in molluscs from the Strait of Magellan (Chile). *Arch Environ Contam Toxicol* 52:519–524
- Brown PH, Rathjen AH, Graham RD, Tribe DE (1990) Rare earth elements in biological systems. In: Gschneidner Jr KA, Eyring L (eds) *Handbook on the physics and chemistry of rare earths*, vol 13. Elsevier Science Publishers, Amsterdam, pp 423–452
- Bulska E, Danko B, Dybczyński RS, Krata A, Kulisa K, Samczyński Z, Wojciechowski M (2012) Inductively coupled plasma mass spectrometry in comparison with neutron activation and ion chromatography with UV/VIS detection for the determination of lanthanides in plant materials. *Talanta* 97:303–311
- Castilla JC (1996) Copper mine tailing disposal in northern Chile rocky shores: *Enteromorpha compressa* (Chlorophyta) as a sentinel species. *Environ Monit Assess* 40:171–184
- Castillo A, Valdés J (2011) Contenido de metales en *Cancer polyodon* (Crustacea: Decapoda) en un sistema de bahías del norte de Chile (27°S). *Lat Am J Aquat Res* 39:461–470
- Chandía C, Salamanca M (2012) Long-term monitoring of heavy metals in Chilean coastal sediments in the eastern South Pacific Ocean. *Mar Pollut Bull* 64:2254–2260
- CONAMA (2003) Proyecto definitivo de normas de calidad primaria para la protección de las aguas marinas. Comisión Nacional de Medioambiente de Chile, Santiago
- Contreras L, Moenne A, Gaillard F, Potin P, Correa JA (2010) Proteomic analysis and identification of copper stress-regulated proteins in the marine alga *Scytosiphon gracilis* (Phaeophyceae). *Aquat Toxicol* 96:85–89
- Coquery M, Carvalho FP, Horvat M, Azemard S (1997) Report on the world-wide intercomparison run IAEA-140/TM: Trace elements in *Fucus* sample IAEA/AL/139; IAEA/MEL/64, Monaco
- Cortés E, Muñoz L, Cassorla V (1980) Determination of trace elements in copper concentrates. *J Radioanal Chem* 59:429–434
- De Gregori I, Fuentes E, Rojas M, Pinochet H, Potin-Gautier M (2003) Monitoring of copper, arsenic and antimony levels in agricultural soils impacted and non-impacted by mining activities, from three regions in Chile. *J Environ Monit* 5:287–295
- Díaz O, Tapia Y, Muñoz O, Montoro R, Velez D, Almela C (2012) Total and inorganic arsenic concentrations in different species of economically important algae harvested from the coastal zones of Chile. *Food Chem Toxicol* 50:744–749

- Du X, Graedel TE (2011) Global in-use stocks of the rare earth elements: a first estimate. *Environ Sci Technol* 45:4096–4101
- Elbaz-Poulichet F, Dupuy C (1999) Behaviour of rare earth elements at the freshwater-seawater interface of two acid mine rivers: the Tinto and Odiel (Andalucia, Spain). *Appl Geochem* 14:1063–1072
- EPA (2012) Rare earth elements: a review of production, processing, recycling, and associated environmental issues. United States Environmental Protection Agency, Washington, D.C. EPA 600/R-12/572/December 2012
- Ferreira LS, Lopes RP, Costas Ulbrich N, Guaratini T, Colepicolo P, Lopes NP, Garla RC, Oliveira Filho EC, Pohlit AM, Zucchi OLAD (2012) Concentration of inorganic elements content in benthic seaweeds of Fernando de Noronha archipelago by synchrotron radiation total reflection X-ray fluorescence analysis (SRTXRF). *Int J Anal Chem* 2012:407274
- Fu FF, Akagi T, Yabuki S, Iwaki M, Ogura N (2000) Distribution of rare earth elements in seaweed: implication of two different sources of rare earth elements and silicon in seaweed. *J Phycol* 36:62–70
- Gaudry A, Zeroual S, Gaie-Levrel F, Moskura M, Boujrhah F-Z, Cherkaoui El Moursli R, Guessous A, Mouradi A, Givernaud T, Delmas R (2007a) Heavy metals pollution of the Atlantic marine environment by the Moroccan phosphate industry, as observed through their bioaccumulation in *Ulva lactuca*. *Water Air Soil Pollut* 178:267–285
- Gaudry A, Zeroual S, Cherkaoui el Moursli R, Guessous A, Chouak A, Mouradi A, Givernaud T, Moskura M, Delmas R (2007b) Neutron activation analysis applied to the study of heavy metal marine pollution observed through bioaccumulation in macroscopic algae near El Jadida, Morocco. *J Radioanal Nucl Chem* 271:165–171
- Goecke F, Escobar M, Collantes G (2012) Chemical composition of *Padina fernandeziana* (Phaeophyceae, Dictyotales) from Juan Fernández Archipelago, Chile. *Rev Latinoam Biotecnol Amb Algal* 3:95–104
- Goecke F, Jerez CG, Zachleder V, Figueroa FL, Řezanka T, Bišová K, Vitová M (2015a) Use of lanthanides to alleviate the effects of metal ion-deficiency in *Desmodesmus quadricauda* (Sphaeropleales, Chlorophyta). *Front Microbiol* 6:2. doi:10.3389/fmicb.2015.00002
- Goecke F, Zachleder V, Vitová M (2015b) Rare earth elements and algae: physiological effects, biorefinery and recycling. In: Prokop A, Bajpai RK, Zappi ME (eds) *Algal Biorefinery products and refinery design*, vol 2. Springer, Cham, pp 339–363
- Gras N, Muñoz L, Thieck M, Hurtado S (1993) A study on some trace elements in Chilean seafood. *J Radioanal Nucl Chem* 169:247–253
- Grigholm B, Mayewski PA, Kurbatov AV, Casassa G, Contreras Staeding A, Handley M, Sneed SB, Introne DS (2009) Chemical composition of fresh snow from glacier Marinelli, Tierra del Fuego, Chile. *J Glaciol* 55:769–776
- Guillemin M-L, Contreras-Porcia L, Ramírez ME, Macaya EC, Bulboa Contador C, Woods H, Wyatt C, Brodie J (2015) The bladed Bangiales (Rhodophyta) of the south eastern Pacific: molecular species delimitation reveals extensive diversity. *Mol Phylogenet Evol* 94(Pt B):814–826
- Guiry MD, Guiry GM (2015) AlgaeBase. World-wide electronic publication, National University of Ireland, Galway. <http://www.algaebase.org> Accessed 11 March 2015
- Herrera C, Custodio E (2014) Origin of waters from small springs located at the northers coast of Chile, in the vicinity of Antofagasta. *Andean Geol* 41:314–341
- Hou X (1999) Study on chemical species of inorganic elements in some marine algae by neutron activation analysis combined with chemical and biochemical separation techniques. *J Radioanal Nucl Chem* 242:49–61
- Hou XL, Yan XJ (1998) Study on the concentration and seasonal variation of inorganic elements in 35 species of marine algae. *Sci Total Environ* 222:141–156
- Hou XL, Li CS, Ding WJ, Qian QF, Chai CF (1998) Determination of 24 elements in four algae reference materials by neutron activation analysis and inductively coupled plasma mass spectrometry. *Fresenius J Anal Chem* 360:423–426
- Hu ZH, Richter H, Sparovek G, Schnug E (2004) Physiological and biochemical effects of rare earth elements on plants and their agricultural significance: a review. *J Plant Nutr* 27:183–220
- Hurst C (2010) China's rare earth elements industry: what can we West learn? Institute for the Analysis of Global Security (IAGS). www.iags.org. Accessed 9 November 2015
- Iwata Y, Imura H, Suzuki N (1993) Determination of nanogram levels of lanthanoids in a marine macro-alga by neutron activation analysis combined with separation by selective precipitation. *J Radioanal Nucl Chem* 172:305–312
- Jayasekera R (1994) Pattern of distribution of selected trace elements in the marine brown alga, *Sargassum filipendula* Ag. from Sri Lanka. *Environ Geochem Health* 16:70–75
- Jayasekera R, Rossbach M (1996) Use of seaweeds for monitoring trace elements in coastal waters. *Environ Geochem Health* 18:63–68
- Kanias GD, Skaltsa H, Tsitsa E, Loukis A, Bitis J (1992) Study of the correlation between trace elements, sterols and fatty acids in brown algae from the Saronikos Gulf of Greece. *Fresenius J Anal Chem* 344:334–339
- Kano N, Aoyagi Y, Imaizumi H (2001a) Determination of rare earth elements in seaweed and seawater samples on the coast in Niigata Prefecture by ICP-MS after solvent extraction. *Anal Sci* 17(suppl): 1011–1014
- Kano N, Aoyagi Y, Imaizumi H (2001b) Determination of rare earth elements in some seaweed samples on the coast in Niigata Prefecture by inductively coupled plasma mass spectrometry. *J Environ Chem* 11:221–231
- Kano N, Aoyagi Y, Matsui K, Imaizumi H (2003) Chemical characteristics of seaweed and seawater samples on the coast in Niigata Prefecture in recent years from rare earth elements pattern. *J Environ Chem* 13:789–798 (in Japanese)
- Kastori RR, Maksimović IV, Putnik-Delić MI, Zeremski-Škorić TM (2010) Rare earth elements: yttrium and higher plants. *Matica Srpska Proc Nat Sci* 118:87–98
- Kawashima T, Yamamoto T, Kohda Y (1983) Neutron activation analysis of Japanese seaweeds. *Nippon Kagaku Kaishi (J Chem Soc Japan)* 1983:368–379
- Kim I, Kim G, Choy E (2015) The significant inputs of trace elements and rare earth elements from melting glaciers in Antarctic coastal waters. *Polar Res* 34:24289. doi:10.3402/polar.v34.24289
- Kleiven W (2014) Elemental composition in various marine brown, green and red macroalgae with respect to season and tissue-age. Master thesis, Department of Biology, Norwegian University of Science and Technology, Trondheim, Norway.
- Kravtsova AV, Milchakova NA, Frontasyeva MV (2014) Elemental accumulation in the Black Sea brown algae *Cystoseira* studied by neutron activation analysis. *Ecol Chem Eng S* 21:9–23
- Kravtsova AV, Milchakova NA, Frontasyeva MV (2015) Levels, spatial variation and compartmentalization of trace elements in brown algae *Cystoseira* from marine protected areas of Crimea (Black Sea). *Mar Pollut Bull* 97:548–554
- Kulkarni P, Chellam S, Fraser MP (2006) Lanthanum and lanthanides in atmospheric fine particles and their apportionment to refinery and petrochemical operations in Houston, TX. *Atmos Environ* 40:508–520
- Li Y, Yang JL, Jiang Y (2012) Trace rare earth element detection in food and agricultural products based on flow injection walnut shell packed microcolumn preconcentration coupled with inductively coupled plasma mass spectrometry. *J Agric Food Chem* 60:3033–3041
- Liang T, Li K, Wang L (2014) State of rare earth elements in different environmental components in mining areas of China. *Environ Monit Assess* 186:1499–1513

- Loell M, Reiher W, Felix-Henningsen P (2011) Contents and bioavailability of rare earth elements in agricultural soils in Hesse (Germany). *J Plant Nutr Soil Sci* 174:644–654
- Mabeau S, Fleurence J (1993) Seaweed in food products: biochemical and nutritional aspects. *Trends Food Sci Tech* 4:103–107
- Manly R, Blundell SP, Fifield FW, McCabe PJ (1996) Trace metal concentrations in *Mytilus edulis* L. from the Laguna San Rafael, southern Chile. *Mar Pollut Bull* 32:444–448
- Martić M, Ajdacic N, Stjepčević J, Gašić MJ (1980) Determination of trace elements in marine organisms by neutron activation analysis. *J Radioanal Nucl Chem* 59:445–451
- Mashitah SM, Shazili NAM, Rashid MKA (2012) Elemental concentrations in brown seaweed, *Padina* sp. along the east coast of peninsular Malaysia. *Aquat Ecosys Health Manage* 15:267–278
- Montecinos P, Schärer U, Vergara M, Aguirre L (2008) Lithospheric origin of Oligocene-Miocene magmatism in central Chile: U-Pb ages and Sr-Pb-Hf isotope composition of minerals. *J Petrology* 49:555–580
- Olmez I, Sholkovitz ER, Hermann D, Eganhouse RP (1991) Rare earth elements in sediments off southern California: a new anthropogenic indicator. *Environ Sci Technol* 25:310–316
- Ortiz J, Uquiche E, Robert P, Romero N, Quiral V, Llantén C (2009) Functional and nutritional value of the Chilean seaweeds *Codium fragile*, *Gracilaria chilensis* and *Macrocystis pyrifera*. *Eur J Lipid Sci Tech* 111:320–327
- Quintana JM, Aceituno P (2012) Changes in the rainfall regime along the extratropical west coast of South America (Chile): 30–43° S. *Atmósfera* 25:1–22
- Core Team R (2016) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna URL <https://www.R-project.org/>
- Ramírez M, Massolo S, Frache R, Correa JA (2005) Metal speciation and environmental impact on sandy beaches due to El Salvador copper mine. *Chile Mar Pollut Bull* 50:62–72
- Roelands I, Monty CLV (1987) Rare-earth elements in recent calcareous benthic organisms. *J Radioanal Nucl Chem* 112:531–543
- Román-Silva DA, Rivera L, Morales T, Ávila J, Cortés P (2003) Determination of trace elements in environmental and biological samples using improved sample introduction in flame atomic absorption spectrometry (HHPN-AAS; HHPN-FF-AAS). *Intern J Environ Anal Chem* 83:327–341
- Ruggieri F, Fernandez-Turiel JL, Saavedra J, Gimeno D, Polanco E, Amigo A, Galindo G, Caselli A (2012) Contribution of volcanic ashes to the regional geochemical balance: the 2008 eruption of Chaitén volcano, southern Chile. *Sci Total Environ* 425:75–88
- Sahoo PK, Tripathy S, Equeenuddin SM, Panigrahi MK (2012) Geochemical characteristics of coal mine discharge vis-à-vis behavior of rare earth elements at Jaintia Hills coalfield, northeastern India. *J Geochem Explor* 112:235–243
- Sáez CA, Lobos MG, Macaya EC, Oliva D, Quiroz W, Brown MT (2012) Variation in patterns of metal accumulation in thallus parts of *Lessonia trabeculata* (Laminariales; Phaeophyceae): implications for biomonitoring. *PLoS One* 7:e50170
- Sakamoto N, Kano N, Imaizumi H (2008) Determination of rare earth elements, thorium and uranium in seaweed samples on the coast in Niigata Prefecture by inductively coupled plasma mass spectrometry. *Appl Geochem* 23:2955–2960
- Salamanca M, Chuecas L, Carrasco F (1986) Heavy metal in surface sediments from three embayments of central-south Chile. *Mar Pollut Bull* 17:567–568
- Salamanca M, Camaño A, Jara B, Rodríguez T (2000) Cu, Pb and Zn distribution in nearshore waters in San Jorge Bay, northern Chile. *Gayana* 64:195–204
- Schacht U, Wallmann K, Kutterolf S (2010) The influence of volcanic ash alteration on the REE composition of marine pore waters. *J Geochem Explor* 106:176–187
- Serfor-Armah Y, Carboo D, Akuamoah RK, Chatt A (2006) Determination of selected elements in red, brown and green seaweed species for monitoring pollution in the coastal environment of Ghana. *J Radioanal Nucl Chem* 269:711–718
- Servigne M, Tchakirian A (1939) Sur la présence d'éléments des terres rares dans les algues calcaires (*Lithothamnium calcareum*). *CR Acad Sci Paris* 209:570–572
- Shi Q, Guo WD, Hu MH, Yang YP, Wu YM, Gong ZB (2004) The content of rare earth elements in benthic organisms from the Xiamen Bay and their distribution and environmental implications. *Acta Oceanol Sinica* 26:87–94
- Stengel DB, McGrath H, Morrison LJ (2005) Tissue Cu, Fe and Mn concentrations in different-aged and different functional thallus regions of three brown algae from western Ireland. *Estuar Coast Shelf S* 65:687–696
- Takata H, Aono T, Tagami K, Uchida S (2010) Concentration ratios of stable elements for selected biota in Japanese estuarine areas. *Radiat Environ Biophys* 49:591–601
- Thomas PJ, Carpenter D, Boutin C, Allison JE (2014) Rare earth elements (REEs): effects on germination and growth of selected crop and native plant species. *Chemosphere* 96:57–66
- Truus K, Vaher M, Taure I (2001) Algal biomass from *Fucus vesiculosus* (Phaeophyta): investigation of the mineral and alginate components. *Proc Estonian Acad Sci Chem* 50:95–103
- Truus K, Vaher M, Koel M, Mähar A, Taure I (2004) Analysis of bioactive ingredients in the brown alga *Fucus vesiculosus* by capillary electrophoresis and neutron activation analysis. *Anal Bioanal Chem* 379:849–852
- Valdés J, Román D, Rivera L, Ávila J, Cortés P (2011) Metal contents in coastal waters of San Jorge Bay, Antofagasta, northern Chile: a base line for establishing seawater quality guidelines. *Environ Monit Assess* 183:231–242
- van Gosen BS, Verplanck PL, Long KR, Gambogi J, Seal RR (2014) The rare earth elements—vital to modern technologies and lifestyles. U.S. Geological Survey fact sheet 2104–3078
- Vásquez JA, Guerra N (1996) The use of seaweeds as bioindicators of natural and anthropogenic contaminants in northern Chile. *Hydrobiologia* 326:327–333
- Vítová M, Bišová K, Hlavová M, Zachleder V, Rucki M, Čížková M (2011) Glutathione peroxidase activity in the selenium-treated alga *Scenedesmus quadricauda*. *Aquat Toxicol* 102:87–94
- Volokh AA, Gorbunov AV, Gundorina SF, Revich BA, Frontasyeva MV, Pal CS (1990) Phosphorus fertilizer production as a source of rare earth elements pollution of the environment. *Sci Total Environ* 95:141–148
- Wells ML, Potin P, Craigie JS, Raven JA, Merchant SS, Helliwell KE, Smith AG, Camire ME, Brawley SH (2016) Algae as nutritional and functional food sources: revisiting our understanding. *J Appl Phycol*. doi:10.1007/s10811-016-0974-5:1-34
- Yamamoto T, Otsuka Y, Aoyama K, Okamoto KI (1984) Character of each element on its distribution in seaweeds. *Hydrobiologia* 116/117:510–512
- Yan XJ, Hou XL, Sun B, Fan X, Han LJ (1998) Element composition of *Sargassum thunbergii*. *Chin J Oceanol Limnol* 16:189–192
- Yan XJ, Fan X, Hou XL (1999) Determination of rare earth elements in seaweeds. *Oceanol Acta Sinica* 30:558–563
- Yao JM, Gong ZB, Li YC, Wen YY, Li J, Wang T (2007) Determination of rare earth elements in marine organisms inductively coupled plasma-mass spectrometry with microwave digestion. *J Instrument Anal* 26:473–477
- Zhu ZZ, Wang ZG, Li J, Li Y, Zhang ZG, Zhang P (2012) Distribution of rare earth elements in sewage-irrigated soil profiles in Tianjin, China. *J Rare Earth* 30:609–613