

Original Research

First Report of Rare Earth Elements and Other Chemical Elements in Sediments of Rivers throughout Chile

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Received: 29 January 2022

Accepted: 30 March 2022

Abstract

The increase in demand for emerging technologies has also increased the presence of rare earth elements and other lesser-known elements in the environment that were previously stable in the Earth's crust. The aim of this study was to determine the current status of five rare earth elements such as cerium (Ce), lanthanum (La), neodymium (Nd), praseodymium (Pr) and yttrium (Y), and barium (Ba), niobium (Nb), rubidium (Rb), thorium (Th) and zirconium (Zr), in superficial sediments from rivers of northern, central and southern Chile. Data showed that the order of abundance of elements in the river sediments was Ba > Nd > Pr > La > Ce > Zr > Rb > Y > Th > Nb. We found higher Ba, Ce, La, Nd and Pr contents in northern and central Chile. Our findings showed that probably these chemical elements are adsorbed into sediments, which could facilitate remobilization to the water column, thus being more bioavailable to biota. Considering that rivers of northern and central Chile are usually used for human consumption and irrigation purposes, further studies to understand the processes involved in the recycling of elements in the watersheds are necessary. Our results may serve as a basis for environmental impact studies that are required by the Chilean legislation before any productive investment.

Keywords: rare earth elements, trace elements, sediments, river, emerging technologies, freshwater ecosystem

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Introduction

Rivers have chemical, physical and biological features that provide habitat for different components of aquatic biota, such as algae, benthic invertebrates, and fish [1]. Moreover, due to the unidirectional nature of rivers, these aquatic systems play a fundamental role in the transport of a multiplicity of elements derived from natural processes and anthropogenic activities, where sediments are crucial as they participate in the adsorption and resuspension-deposition of a wide variety of elements [2]. In this regard, chemical elements can interact strongly with river sediments through various processes, and their concentrations can reveal the degree of anthropogenic presence and pressure in the watershed [3]. For that reason, chemical elements are usually parameters selected for monitoring programs due to their toxicity, bioaccumulation and persistence in the natural environment [4].

The rivers in Chile flow from the Andes Mountains to the Pacific Ocean, and their hydrological patterns vary spatially due to climate, the presence of glaciers, lakes or volcanoes, the slope of the terrain, altitude, geology, land use and water consumption, with these three last factors having the greatest influence on water quality, along with the amount and quality of the transported sediments [5, 6]. As a consequence, river sediments are excellent indicators of chemical element pollution [7] as such chemicals will be adsorbed to the sediment, depending on the physical-chemical properties of the element, natural and anthropogenic factors, and the nature of the sediments [8]. Among the main anthropic activities affecting Chilean Rivers and sediment transportation is the modification of the hydrological regime due to channeling, damming of rivers, extraction of water for irrigation, extraction of aggregates, replacement of native forest by artificial forest, and alteration of the physicochemical quality of the water, thus affecting the habitat of the biota [6]. The most common anthropogenic actions resulting in river contamination are wastewater from households and industries, mining tailings, pulp/paper mill wastewater, and agricultural practices [5, 9].

The presence of metals in Chilean river sediments has been associated with the presence of metallogenic strips in the upper part of the Andes Mountains as a natural factor, and to the extractive mining activities that take place mainly in the northern part of the country, whereas impacts of the agricultural practices and urban development can be found in the central valley, while southern Chile presents low human presence and impacts [10].

To develop guidelines for environmental protection of rivers, it is necessary to establish chemical element concentrations in sediments at baseline to distinguish natural source levels from those from anthropogenic sources [11]. Recently, new potentially toxic elements, which had been usually stable in the Earth's crust, have emerged as consequence of the increase in mining

related to the development of modern technologies, such as cell phones, portable computers, biomedicine, and photovoltaic cells [12, 13]. Among them are some rare earth elements such as Ce, La, Nd, Pr or Y, and other lesser-known elements such as Ba, Nb, Rb, Th or Zr, which are increasingly being released into the environment, with a potential change of natural biogeochemical cycles and possible severe effects on wildlife and the natural environment [14-16]. In Chile, river rare earth elements contamination is an issue not considered yet in public management. To our knowledge, no data are available on the distribution of these less-studied chemical elements in the sediment of the Chilean Rivers. Consequently, the aim of this study was to determine a current status for ten little studied chemical elements (Ba, Ce, La, Nb, Nd, Pr, Rb, Th, Y, Zr) to establish a tool for future monitoring programs.

Materials and Methods

Selected Rivers and Sampling

During 2019-2020, we collected sediment samples (~50 grams) from several rivers throughout Chile (Fig. 1). The rivers in northern Chile (A) show a typical nival regime and the basins are characterized by major mining activities and the presence of volcanoes. In central Chile (B), river discharges show mixed regimes, which depend on snow and rain precipitation, with strong influence of volcanoes, urban development and agricultural activities. In the southern area (C), rivers show a strong pluvial regime, and they are located in one of the most austral regions of South America, considered as a pristine area with no mining or volcanic activity.

The Loa River is the longest river in Chile (440 km) and flows through the Atacama Desert from its source in the Andes Mountains to the Pacific Ocean; it is of great importance in the development of human life, such as Calama, the main city with a population of more than 140,000 inhabitants, mainly dedicated to the mining industry; the Loa River supplies water to the towns in the area and to the mines located in the area, including Chuquicamata, the largest open-pit copper mine in the world, and the cultivation of various vegetables for local consumption. The Elqui River is located 470 km north of Santiago, Chile; it rises in the Elqui valley at 815 m a.s.l. and flows into the Pacific Ocean near the city of La Serena; one of its tributaries is the Turbio River. The Choapa River is a natural watercourse, whose basin extends from the watershed in the Andes Mountains to its mouth at the Pacific Ocean, receiving the waters of several tributaries. The Maipo River is a watercourse that flows through the Metropolitan Region (highest population density of Chile, where the capital city of Santiago is located) and then through the Valparaíso Region, reaching the Pacific Ocean; because of the large amount of population and productive

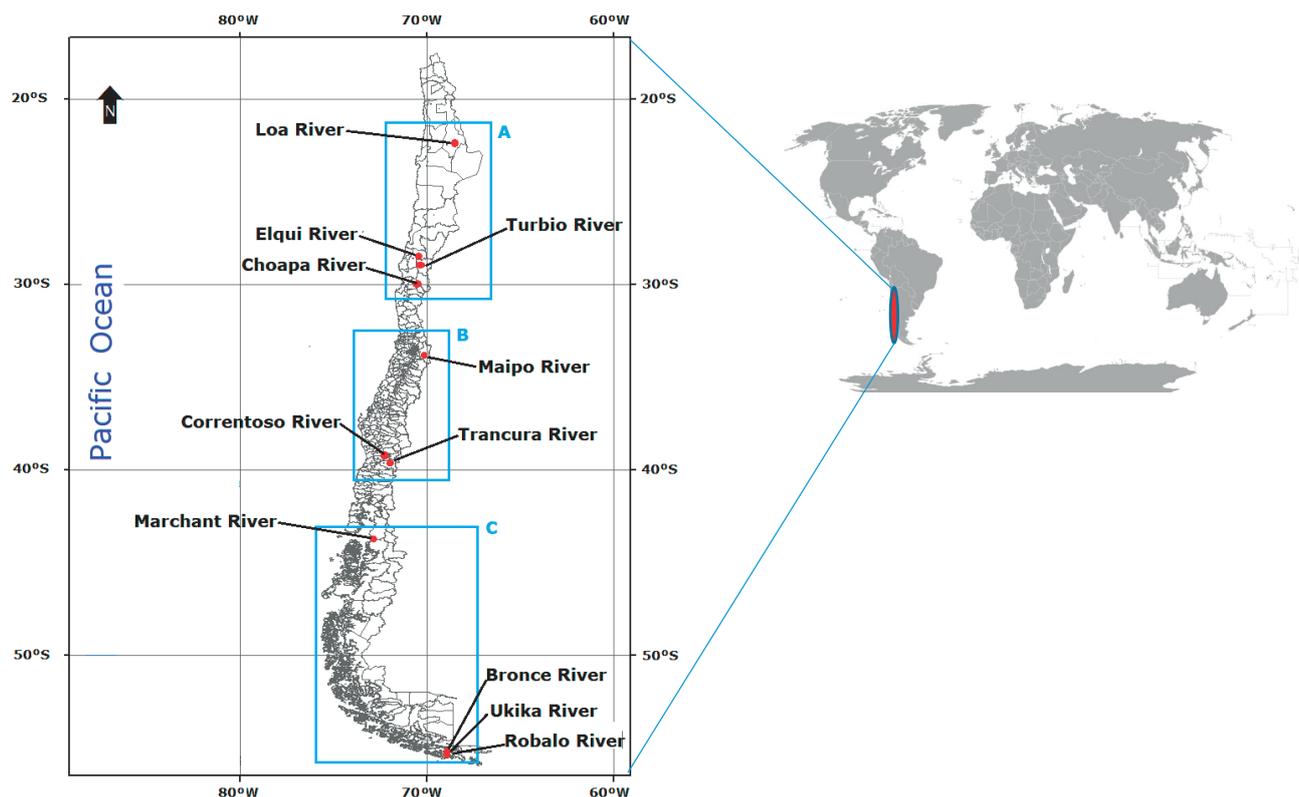


Fig. 1. Geographical locations of the rivers studied along Chile (A: northern area; B: central area; C: southern area).

activities in its basin, it is one of the most important rivers of Chile. The Maipo River is located in an area where there are different deposits in the geology of the Cajón del Maipo, with fluvial, fluvio-glacial and alluvial deposits strongly linked to the formation of terraces throughout the Cajón. The Trancura River is a watercourse that flows in the Araucanía Region, which originates in the Quillehue Lagoon and flows into the Villarrica Lake. The Correntoso River is a watercourse that originates from other tributaries in the Araucanía Region, which flows into the Pucón River. The Correntoso and Trancura rivers are located in an area that represents the evolution of the South American southwest margin, from the Mesozoic to the Holocene. The Marchant River is located in the Aysén Region (300 km south of Puerto Montt) is influenced by the Melimoyu volcano, and it originates from snow and rainfall, flowing into the Pacific Ocean. The Bronce, Robalo and Akika rivers, which flows into the Beagle Channel, are located on Navarino Island, Tierra del Fuego, Southern Chile, with the absolute absence of volcanoes. The relief of Navarino Island is of subglacial origin, where the summits rarely exceed 1,000 m a.s.l., with the Dientes de Navarino peak being the highest elevation summit on the island, reaching 1,118 m a.s.l.

At all sites, superficial sediment samples (~20 cm depth) were collected in the middle part of the rivers by means of a pre-cleaned plastic shovel ($n = 3$ per site), and then stored at -20°C in clean polypropylene bags (Whirl-Pak®) until their arrival at the laboratory.

Sample Preparation and Analysis

In the laboratory, all samples were freeze-dried until dry masses were constant, and then homogenized to a fine powder using a glass mortar previously cleaned with a 2% Conrad solution (Merck) for 24 h, washed with deionized water + 1M HCl, and then rinsed with distilled water [17]. Afterwards, the samples were heated (oven at 100°C for 12 h) to remove adsorbed water prior to analysis [18]. Then, the samples were analyzed for chemical elements at the Analytical Laboratory of the Faculty of Veterinary Sciences, Universidad de Concepción (Chile), using a portable battery-operated energy dispersive X-ray fluorescence spectrometer (Thermo Scientific Niton XL3t 950 He GOLDD+). The instrument was set up with the instrument tip up on a shielded laboratory test stand, which was remotely operated. The precision and accuracy were verified by means of international reference standards such as GSS-5, GSS-7, GXR-6 and GSR-3 [18], being the precision $<2\%$ and accuracy within 1-5%.

Data were statistically analyzed by means of nonparametric statistical methodologies because of the assumptions of normality and homoscedasticity were not met. Differences between chemical element concentrations were assessed by means of the Kruskal-Wallis analysis of variance and Mann-Whitney U tests. Post hoc tests were carried out by means of Kruskal-Wallis analyses, using the critical differences of mean rank. Spearman rank correlation

coefficients were calculated between chemical element levels. A significance level of $p \leq 0.05$ was considered to indicate statistical significance. Data were analyzed by using the R program.

Results and Discussion

Chemical Element Concentrations by Geographical Locations

For the detected elements found in northern Chilean rivers (Table 1), the highest concentration corresponded to Ba detected in the sediments of the Turbio River (654.73 $\mu\text{g/g}$), whereas the lowest levels were for Nb in the Loa River (3.47 $\mu\text{g/g}$). For central Chilean rivers (Table 2), the highest levels of the chemical elements corresponded to Nd found in the sediments of the Correntoso River with 426.98 $\mu\text{g/g}$, whereas the lowest contents corresponded to Nb in the sediments of the Trancura River (2.69 $\mu\text{g/g}$). In southern Chile (Table 3), the highest levels of the chemical elements corresponded to Ba in the sediments of Marchant River (457.59 $\mu\text{g/g}$), and the lowest to Nb (2.91 $\mu\text{g/g}$) in the sediments of Bronce River. For the detected elements found from northern Chilean rivers (Table 1), the highest concentration corresponded to Ba detected in the sediments of Turbio River (654.73 $\mu\text{g/g}$), whereas the lowest levels for Nb in the Loa River (3.47 $\mu\text{g/g}$).

Across Chilean rivers studied here (Table 1, 2 and 3), the highest means contents of Ba, Ce, La and Nd were found in the sediments of Loa River in northern Chile,

as well as the highest mean levels of Rb were found in Turbio River. The highest mean values of Nb, Pr, Y and Zr are in the sediments of Marchant River (southern Chile), while the highest mean Th contents were found in the sediments of Robalo River. The highest concentrations of the lanthanide group (Ce, La, Nd, and Pr) and Ba in the river sediments along Chile may be associated with the presence of volcanoes in the regions where the Loa River, Turbio River, and Marchant River are located. The presence of Ba and rare earth elements (such as Ce, La and Nd) could be linked to volcanic activity [19]. Additionally, there is evidence that mining activities related to copper and molybdenum tend to impact watercourses with rare earth elements [20, 21], a situation observed in northern Chile which has a generally strong copper-mining activity. On the other hand, the Robalo, Ukika and Bronce rivers presented lower concentrations of Ce, La, Nd and Pr, which could be explained by the fact that these rivers are located in an area with no volcanic activity and with little anthropic intervention.

Comparison to Worldwide Studies

To date, there are few studies on the same chemical elements studied here at global level, thus making it difficult to discuss our results. The comparison to other previous studies elsewhere revealed that the highest mean concentrations of Ba (591.7 $\mu\text{g/g}$, Turbio River), Ce (249.5 $\mu\text{g/g}$, Loa River), La (251.63 $\mu\text{g/g}$, Loa River), Nd (453.2 $\mu\text{g/g}$, Loa River), Pr (432.95 $\mu\text{g/g}$, Marchant River) and Th (16.68 $\mu\text{g/g}$, Robalo River) are higher

Table 1. Mean concentrations \pm SD of chemical elements in sediments of rivers from northern Chile. Maximum and minimum values in parentheses ($\mu\text{g/g}$, d.w.).

Elements	Loa River	Turbio River	Elqui River	Choapa River
Ba	543.8 \pm 22.41 (556.99-517.95)	591.7 \pm 55.54 (654.73-549.92)	498.12 \pm 37.48 (533.08-458.53)	433.58 \pm 55.34 (469.9-369.88)
Ce	249.53 \pm 33.32 (274.37-211.66)	195.71 \pm 53.13 (255.31-153.32)	188.18 \pm 33.60 (222.65-155.52)	203.21 \pm 28.20 (231.4-175.01)
La	251.63 \pm 10.09 (261.41-241.25)	210.1 \pm 20.52 (233.02-193.46)	169.26 \pm 15.39 (183.72-170.98)	178.8 \pm 10.8 (185.23-167.19)
Nb	3.75 \pm 0.28 (4.02-3.47)	6.25 \pm 2.05 (8.59-4.8)	5.75 \pm 1.14 (6.89-4.61)	4.53 \pm 0.95 (5.55-3.67)
Nd	453.2 \pm 78.8 (544.2-406.83)	293.4 \pm 43.75 (333.38-246.68)	265.36 \pm 36.17 (304.45-233.07)	252.69 \pm 36.48 (289.49-216.54)
Pr	422.40 \pm 83.5 (488.89-328.72)	360.96 \pm 83.42 (440.83-274.39)	314.99 \pm 27.88 (346.28-292.78)	343.9 \pm 34.3 (368.84-304.78)
Rb	30.03 \pm 9.19 (38.87-20.53)	48.39 \pm 1.81 (50.25-46.64)	45.57 \pm 2.90 (48.71 - 43.0)	30.31 \pm 2.79 (32.37-27.14)
Th	10.61 \pm 0.11 (10.71-10.5)	10.15 \pm 2.52 (11.92-7.27)	10.49 \pm 0.23 (10.71-10.25)	9.26 \pm 0.21 (9.47-9.06)
Y	9.29 \pm 2.29 (11.62-7.04)	15.32 \pm 0.69 (15.72-14.52)	18.07 \pm 2.87 (20.51-14.91)	17.60 \pm 7.98 (19.63-16.34)
Zr	77.06 \pm 9.33 (87.17-68.78)	134.83 \pm 5.01 (139.0-129.27)	77.72 \pm 16.11 (96.17-66.45)	124.54 \pm 7.98 (130.25-115.42)

Table 2. Mean concentrations \pm SD of chemical elements in sediments of rivers from central Chile. Maximum and minimum values in parentheses ($\mu\text{g/g}$, d.w.).

Elements	Maipo River	Trancura River	Correntoso River
Ba	275.62 \pm 24.98 (293.66-247.11)	225.0 \pm 26.08 (254.39-204.62)	265.35 \pm 12.77 (279.4-254.44)
Ce	Bdl	194.57 \pm 32.90 (231.49-168.34)	242.60 \pm 55.59 (302.28-192.29)
La	Bdl	213.02 \pm 18.61 (227.74-192.11)	230.93 \pm 33.30 (269.37-210.86)
Nb	4.81 \pm 0.86 (5.74-4.04)	3.07 \pm 0.56 (3.71-2.69)	Bdl
Nd	Bdl	352.02 \pm 65.40 (414.84-284.31)	414.26 \pm 13.56 (426.98 – 400.0)
Pr	Bdl	397.50 \pm 31.52 (421.8-361.88)	360.80 \pm 44.35 (410.22-324.46)
Rb	28.02 \pm 1.43 (29.08-26.4)	8.53 \pm 0.60 (9.0-7.85)	8.00 \pm 0.61 (8.62-7.4)
Th	12.70 \pm 1.69 (14.37-10.99)	8.26 \pm 0.65 (8.99-7.75)	8.44 \pm 0.65 (9.16-7.88)
Y	18.47 \pm 2.19 (20.99-17.1)	20.94 \pm 0.94 (21.57-19.86)	18.65 \pm 0.82 (19.17-17.71)
Zr	128.96 \pm 3.15 (131.79-125.57)	86.53 \pm 4.19 (91.11-82.88)	73.43 \pm 3.77 (77.35-69.82)

Bdl: below detection limit.

Table 3. Mean concentrations \pm SD of chemical elements in sediments of rivers from southern Chile. Maximum and minimum values in parentheses ($\mu\text{g/g}$, d.w.).

Elements	Marchant River	Bronce River	Ukika River	Robalo River
Ba	434.84 \pm 20.15 (457.59 -419.22)	331.83 \pm 22.83 (356.79-311.99)	231.95 \pm 68.37 (278.33-153.43)	Bdl
Ce	233.03 \pm 37.84 (276.29-206.06)	152.71 \pm 42.30 (197.79-113.89)	Bdl	Bdl
La	220.25 \pm 6.64 (226.73-213.47)	159.40 \pm 45.34 (207.49-117.41)	Bdl	Bdl
Nb	8.52 \pm 0.35 (8.87-8.17)	3.36 \pm 0.47 (3.84-2.91)	3.85 \pm 0.63 (4.47-3.22)	7.74 \pm 0.80 (8.3-6.83)
Nd	440.85 \pm 14.55 (451.15-263.67)	259.25 \pm 8.05 (267.74-250.75)	Bdl	Bdl
Pr	432.95 \pm 10.45 (444.08-423.33)	270.61 \pm 41.85 (317.95-238.51)	Bdl	Bdl
Rb	18.98 \pm 1.41 (20.58-17.87)	22.17 \pm 0.86 (23.16-21.61)	21.12 \pm 0.22 (21.35-20.91)	18.76 \pm 2.96 (22.1-16.44)
Th	12.32 \pm 0.20 (12.52-12.12)	7.19 \pm 0.79 (8.1-6.69)	7.88 \pm 2.38 (10.25-5.5)	16.68 \pm 3.05 (20.07-14.16)
Y	24.81 \pm 1.68 (26.66-23.37)	17.28 \pm 1.29 (18.32-15.83)	16.35 \pm 1.23 (17.5-15.05)	18.76 \pm 2.96 (22.32-17.15)
Zr	163.0 \pm 18.5 (182.71-145.99)	80.57 \pm 1.55 (82.31-79.33)	80.06 \pm 3.12 (83.03-76.8)	75.17 \pm 8.30 (82.82-66.34)

Bdl: below detection limit.

Table 4. Maximum and minimum levels of chemical elements in sediments of different rivers worldwide.

Location	Chemical elements	Levels ($\mu\text{g/g}$)	Reference
Chile (several locations)	Ba	654.73-153.43	Own study
	Ce	302.28-113.89	
	La	269.37-117.41	
	Nb	8.87-2.69	
	Nd	544.2-216.54	
	Pr	488.89-238.51	
	Rb	50.25-7.4	
	Th	20.07-5.5	
	Y	26.66-7.04	
Punta Arenas (southern Chile)	Ba	408-323	[24]
	Rb	42.6-32.4	
Northern Chile (Loa River)	Ba	290-60	[25]
England (Europe)	Ce	924.4-59.0	[26]
	La	382.4-28.8	
	Nd	408.2-26.1	
	Pr	111.54-6.84	
	Y	540.4-24.7	
Korea (Asia)	Ce	113.34-80.0	[27]
	La	57.35-40.66	
	Nd	49.23-36.22	
	Pr	12.22-8.71	
	Y	33.02-24.92	
China (Asia)	Ce	92.63-45.98	[27]
	La	45.79-23.1	
	Nd	42.49-22.12	
	Pr	10.07-5.12	
	Y	39.05-18.66	
Mongolia (Asia)	Ce	12.7-3.94	[20]
	La	5.12-1.4	
	Nd	5.63-1.58	
	Pr	1.44-0.43	
	Y	2.47-0.92	
Tajikistan (Central Asia)	Ba	770-370	[23]
	Ce	152-20	
	La	80-10	
	Nd	45-9	
	Rb	183-51	
	Zr	415-95	
Brazil (South America)	Ba	450-275	[11]
	Nb	18.9-7.8	
	Rb	142.7-53.2	
	Th	17.7-7.1	
	Y	34.9-16.0	

than those levels reported in the sediments of rivers of the northern hemisphere such as Mississippi, Nile, Rhine or Volga [22].

According to Table 4, our maximum Ba levels are lower than those levels reported in stream sediments of the Varzob River, Tajikistan, while higher than those levels found previously in sediments of rivers from Brazil and Chile. Our maximum Ce levels are lower than those levels reported in south-west England, but higher than those levels reported in river sediments from Korea, China, Mongolia and Tajikistan. For

La, the maximum levels are lower than those levels reported from England, but higher compared to the rest of rivers listed. For Nb, our maximum levels are around half of those levels found in river sediments of Brazil. For Nd and Pr, our maximum values are higher than those levels reported in sediments of rivers from the northern hemisphere (Table 4). For Rb, our maximum levels are lower than those levels reported from Tajikistan and Brazil, whereas are higher than those levels reported previously from Chile. For Th, our maximum levels are higher than those levels reported

Table 5. Spearman correlation coefficients among the elements studied ($* \leq 0.05$).

	La	Ce	Pr	Nd	Nb	Rb	Y	Zr	Ba
Ce	0.72	1							
Pr	0.84	0.80	1						
Nd	0.84	0.86	0.80	1					
Nb	-0.26	-0.21	-0.14	-0.28	1				
Rb	-0.15	-0.07	-0.03	-0.26	0.39*	1			
Y	-0.02	-0.07	0.06	0.08	0.13	-0.49*	1		
Zr	0.07	-0.01	0.24	-0.01	0.39	0.26	0.27*	1	
Ba	0.47	0.49	0.48	0.39*	0.20	0.68*	-0.45*	0.28*	1
Th	-0.13*	-0.22*	-0.10	-0.20*	0.69	0.16	0.18	0.22	0.03

from Brazil. For Y, our maximum levels are lower than those levels reported from England, Korea, China and Brazil, whereas are higher than those Y levels found in Mongolia. Finally, our maximum Zr levels are 2.3 times lower than those levels found in stream sediments of the Varzob River, Tajikistan. When comparing with background earth's crust levels reported worldwide [28], the maximum Ce, La, Nd and Pr levels found in the present study are 5, 7, 13 and 53 times higher, respectively, whereas the Y contents are 0.8 times lower. On the other hand, the minimum Ce, La, Nd and Pr levels are 2, 3, 5, 26 times higher whereas our Y levels are 0.2 times lower than those Earth's crust levels.

Correlations Among Chemical Elements

Considering all the sampling sites together, the order of abundance of chemical elements in surface sediments of Chilean rivers are as follows: Ba > Nd > Pr > La > Ce > Zr > Rb > Y > Th > Nb. This pattern differed a little from the enrichment factor reported in rivers from

the northern hemisphere, which was observed to be Ba > Zr > Ce > La > Nd > Y > Pr > Th [22].

The Spearman correlation analysis (Table 5) showed some significant positive correlations between Nb-Rb, Y-Zr and Ba-Zr, suggesting these metals have a common source or are redistributed in the surface sediments following the same processes, as noted by some researchers [23, 29]. On the other hand, negative correlations were observed between La-Th, Ce-Th, Nd-Th, Rb-Y and Ba-Y.

With the exception of Marchant River, the contents of the rare earth elements studied here in the river sediments are very dissimilar, with coefficient of variation values (CVs) > 10% (Fig. 2), reflecting large heterogeneity in element contents. Our results differ from those reported by researchers in sediments of Chinese and Korean rivers [27], who found high uniformity in Ce, La, Nd, Pr and Y contents. The differences of geographical, mineralogical, chemical, hydrological and climatic conditions over more than 4,000 km of the Chilean territory, as well as particular nearby anthropogenic sources throughout

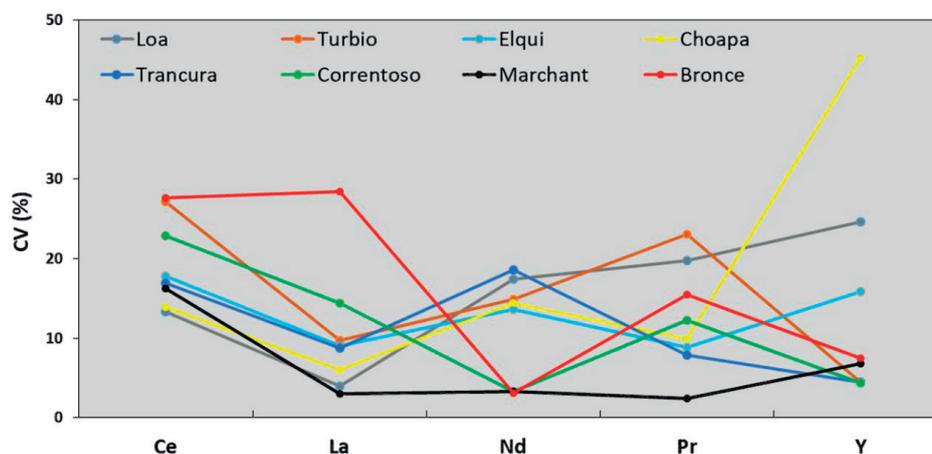


Fig. 2. Values of the coefficient of variation (CV) of rare earth element contents in Chilean river sediments (CV = standard deviation/mean value \times 100).

the basins, could explain why the chemical element contents studied here in the river sediments are very dissimilar.

Conclusions

The study of chemical elements in river sediments is important for understanding the process of pollution and transport of particles occurring in a watershed. This is the first report of Ba, Ce, La, Nb, Nd, Pr, Rb, Th, Y and Zr in the river sediments along Chile. The chemical element concentrations in river sediments indicate different fates and destinations of these elements among Chilean rivers. The river sediments showed that chemical elements remain either bound or adsorbed to carrier phases even at superficial depths (under 20 cm), which means they are available for eventual remobilization to the water column. From a health point of view, this is an issue particularly important in northern and central Chile, where water of rivers is usually extracted for human consumption and irrigation purposes. Considering the rapid development of emerging technologies, systematic studies of chemical elements some of which are the focus of this paper could be helpful in assessing the ecological status of catchments and related river sediments. Future studies should consider the analysis of deeper sediment cores along with radioisotope dating techniques, which are required to add data about the processes and sources involved in the cycling of chemical elements in the basins studied here.

Acknowledgments

This study was financially supported by the Agencia Nacional de Investigación y Desarrollo (ANID) through postdoc project FONDECYT 3200302 (W. Espejo), FONDECYT Initiation 11180914 ANID/BASAL FB210018 (P. Bahamonde) and Millennium Science Initiative NCN16_034 and NCN2021_056. Thanks to Diane Haughney for reviewing the English of the manuscript.

Conflict of Interest

The authors declare that they have no either financial or personal conflicts of interest that could have influenced this paper.

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