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ORIGINAL ARTICLE

Trace element distribution in pristine Patagonia River sediments using multivariable analysis

Daniela Nassini[1] · Georgina De Micco[1,2] · Ana Ester Bohé[1,2,3]

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Abstract
Surface sediments may serve as a metal sink that can release metals to the water body causing negative effects to the ecosystems. The analysis of trace-level metals in sediments allows detect pollution that might not be detected in water samples. In this study, the distribution and concentration of selected elements in surface sediment samples were determined in Pichileufu River in Patagonia, Argentina, to corroborate their pristine characteristic. The surface sediment samples from 6 points along the river were collected using the method across and throughout the waterway. All of them were analyzing first by X-ray fluorescence (XRF) determining the major element concentrations. Then, they were acid digested and the selected trace element (V, Cr, Ni, Cu, Mo, Cd and Pb) concentrations were determined by inductively coupled plasma mass spectrometer (ICP-MS). The correlation analysis and principal component analysis indicated that the major and minor elemental compositions allowed quickly identified specific sample that differ from the rest and understood the reason. The obtained results show that all the selected element concentrations were below the PEL of the sediment quality guidelines. There were no significant differences between the selected element contents in the surface sediments of the Patagonia River among the years. The observed differences in the 3-site samples may be related to that it is a stream of the main river. Therefore, this study result could work as reference pristine site. The study highlights the need to make tremendous efforts to monitor and control trace elemental pollution in the Pichileufu Patagonia River to avoid their future contamination from both anthropogenic and natural sources. Among the natural factors, it is very important to consider the desertification process suffered by these steppe areas. In this context, the presented results could be used as background concentrations or as starting point for these studies.

Keywords Pristine river · Major elements · Trace elements · River sediments · Acid digestion

Background and summary

Waterways like rivers are essential to the humanity prosperity, but sometimes they are not given the importance they deserve. Because water sources in rivers are constantly flowing, it is necessary continuously monitoring their quality and quantity. These control studies are pioneers to find some problems that could affect the watersheds in the future. Sometimes, the low contaminant concentrations in water samples impede the early detection. Furthermore, surface sediments have higher precipitated or decanted contaminant concentrations and could indicate changes in water column (Tomczyk-Wydrych and Swiercz 2021; Nawrot et al. 2021; Baldantoni et al. 2005; Protano et al. 2014).

Sediments are considered as free particles of soil found at the bottom of a water body. They can be made of clay, sand, organic material, or silt (Valentine 2019). Probably, erosion and decomposition of natural elements, animals, and plants were the origin of them. Their quantities and characteristics can affect the physical, chemical and biological integrity of aquatic ecosystems because they are a natural part of them (Ribeiro Carvalho et al. 2022; U.S. EPA 2006a).

✉ Daniela Nassini
dnassini@cab.cnea.gov.ar

[1] Department of Physical-Chemistry and Quality Control, Pilcaniyeu Technological Complex, National Commission of Atomic Energy (CNEA), San Carlos de Bariloche, Argentina

[2] National Council of Scientific and Technical Researches (CONICET), San Carlos de Bariloche, Argentina

[3] National University of Comahue, San Carlos de Bariloche, Argentina

Surface sediments may serve as a metal sink that can release metals to the water body causing negative effects to the ecosystems because their toxicity, persistence and non-degradability in the environment (Pavoni et al. 2021; Rakib et al 2022). The analysis of trace level metals allows detect pollution that might not be detected in water samples (Chuan and Yunus 2019).

Heavy metals in sediments can be present both for their geogenic and for anthropogenic origin. The last ones enter into rivers as hydrated ions or inorganic complexes and they are adsorbed on surface particles constituting the labile fraction of sediments (Vukovic et al. 2014). Remobilization of contaminated surface is caused by storms, seasonal flooding, turbulences, and changes in pH and in redox-potential of water, as some others ecosystem and environmental variables (Osakwe et al. 2014). Therefore the sediments are considered a potential source of heavy metals, as it was demonstrated in previous studies (Wang et al. 2011; Sorokina 2021), that 30–98% of heavy metals are transported in sediment-associated forms in rivers.

The metal contamination in aquatic environments was widely studied due to its toxicity, persistence and bioaccumulation characteristics (Ribeiro Carvalho et al. 2022). The main danger of heavy metals in sediments is because of how they travel up the food chain and become harmful to animals and humans (Arshad et al 2023) understood the reason (Couto 2022; Sugumaran et al 2023). Hence, the distribution and pollution levels of heavy metals in sediments have been extensively studied (Pandey and Singh 2017; Raju et al. 2012; Salah et al. 2012; Guo and He 2013; Li et al. 2020; Ferati et al. 2015; Sakan et al. 2020; Sakan et al. 2007; Salati and Moore 2010; Varol and Sen 2012; Shanbehzadeh et al. 2014; Martin and Meybeck 1979; Abdusamadzoda et al. 2020; Edokpayi et al. 2016).

Mainly human waste disposal sites, such as sewage treatment plants, sanitary sewers, storm-water drains, and waste industry discharge sites, are the sources of anthropogenic origin (Meybeck 2013; Couto 2022; Ribeiro Carvalho et al 2022; Decena et al. 2018). But other important contaminations sources are storm-water runoff, mining and manufacturing runoff, and atmospheric pollutant spread, and they cannot easily trace back their origin (Niu et al. 2021; Baubekova et al. 2021; Ribeiro Carvalho et al 2022).

Numerous sediment quality guidelines (SQGs) have been established since the 1980s, each incorporating different criteria, factors and approaches to try and account for the varied conditions in which sediment contamination occurs (Smith et al. 1996; Batley and Simpson 2013; Frančišković-Bilinski 2007; Gashi et al. 2011). Generally, these approaches predict adverse ecological effects from sediment contamination by the response of benthic organisms, which live on or in the sediments and are used as an indicator of a toxic environment because of their function as an important food chain link and food source for fish, birds, and mammals residing in the same ecosystem (Hübner et al. 2009).

The Pichileufu Patagonia River is one of the most important rivers in the steppe area that is introduced as a source of biodiversity. The surrounded soil of the river is characterized of water and wind erosion and has an extensive ovine breeding making necessary the desertification control (Panigatti 2010). These natural processes (such as weathering, erosion and dissolution of water-soluble salts) constitute the background level of the elemental composition in sediments, but if the desertification proceeds this level could increase and become dangerous (IPCC 2019).

In addition, there is a lack of information on the concentrations and distributions of heavy metals in water and sediments of all Patagonian area watersheds. Therefore, it is necessary to investigate the spatial distributions of these elements and their ecological risks to provide data for maintenance water quality and to prevent ecosystem contamination.

Materials and methods

Study area description

The Pichileufu Patagonia River is located in the steppe area of Rio Negro province (Argentina) with approximately 70 km of length and discharges into a freshwater dam. It is generated from thaw and mallines and it is characterized by a large daily temperature range. The location and difficult access in determined places of the River protect and preserve naturally this waterway. The main activities are the small-scale ranching and sport fishing. Surface sediments were collected from six sites along the river (Fig. 1).

Fig. 1 Location of the study area in Patagonia River showing sampling points

Collection of sediment samples

The sediment collection procedure was made taken a portion of the sediments along the river stretch (longitudinal samples—L) and a portion across the river (transversal samples—T) with a depth of 10 cm. The sediment samples were air dried at 60 °C, well-mixed and passed through a 500 µm sieves (USS #10). Sampling was carried out annually between 2016 and 2019 in six sampling sites along an important river in north Patagonia, Argentina. 3 samples were collected from each location at the same time of the year.

The identification of the sediment samples is listened in Table 1, which is composed of the year of sampling, the number site and the type of sampling procedure.

The river flows from sampling site 0 to 5 distanced 14 km. The sampling site 3 is located in a tributary.

Organic matter content in sediments

The sediment samples were dried at 65 °C for 24 h in an oven and were weighted to determine the humidity. This procedure was done up to a constant weight loss (differences below 1%). Then the samples were calcined at 450 °C for 1 h in a muffle and the weight losses were determined. An additional calcination period was done to corroborate the constant weight (differences below 1%). The mass difference between before and after calcination represents the organic matter content (calculation in dry basis).

Major elemental composition analysis

Elemental analysis of the sediment samples was done with a wavelength dispersive X-ray fluorescence (WDXRF) spectrometry (S8 Tiger—Bruker) for triplicate. This study was essential to the geochemical characterization of the region and to construct the elemental composition background of the river sediments. The crystalline structures of the sediments were identified by X-ray Diffraction (D8 Advance-Bruker) with Cu Kα ($\lambda = 1.54184$ Å) radiation in a single Silisium crystall sampler.

Table 1 Identification of surface sediment samples taken from the 6 sites from 0 to 5 in spring of the years 2016, 2017, 2018 and 2019

Sampling sites	2016	2017	2018	2019
0L	ns	17-0L	18-0L	19-0L
0T	ns	ns	ns	19-0T
1L	16-1L	17-1L	18-1L	19-1L
1T	16-1T	17-1T	ns	19-1T
2L	16-2L	17-2L	ns	19-2L
2T	16-2T	17-2T	18-2T	19-2T
3	16–3	17–3	18–3	19–3
4L	16-4L	17-4L	18-4L	19-4L
4T	16-4T	17-4T	18-4T	19-4T
5L	16-5L	ns	18-5L	19-5L
5T	16-5T	ns	18-5T	19-5T

L: longitudinal-sampling; T: transversal-sampling; ns: not sampling

Preparation of sediment samples

The sediment samples were digested using microwave digestion system (Milestone, Ethos One microwave oven) in accordance with US Environmental Protection Agency 5051A (USEPA 1996, 1998, 2006b, 2007). This method is not a total digestion technique, but it is a very strong acid digestion that will dissolve almost all elements that could become environmental available (CCME 2001).

A well-mixed sediment sample of 0.5 g was placed in a fluoropolymer digestion vessel and 10 ml of concentrated nitric acid was added in a fume hood. The concentrated nitric acid was sub-boiling distilled before use. The vessel was sealed, and the temperature reached 175 ± 5 °C in approximately 15 ± 0.25 min and remained at 175 ± 5 °C for 15 min. Then, the sample was filtered through a 0.45-µm filter into a volumetric ware and the digest was diluted to a volume of 100 ml with deionized water. The final nitric acid concentration was approximately 5% (v/v) that allows maintaining appropriate sample solution acidity and stability of the elements. The solution was transferred in a polyester container ready for analysis for elements of interest.

Selected minor element composition analysis

Sediment digests were analyzed by iCAP Q ICP-MS Thermo Scientific in accordance with standard method US Environmental Protection Agency 6020A. The selected minor elements were V, Cr, Ni, Cu, Mo, Cd and Pb because of their toxicity and persistent in the sediments. Calibration curves were performed with pattern solutions of each element. Internal patterns (IP) were used to evaluate the matrix effect. Bi was used as IP for Pb, In as IP for Mo and Cd. For lighter elements, the ^{45}Sc was not used as IP, because samples contained significant native amounts of it. A multi element ICP standard solution in 5% HNO_3 was used as reference standard (provided by Chem-Lab).

Quality control for preparation and analysis

Concentrated nitric acid (HNO_3) was employed, but previously it was sub-boiling distilled. A blank of HNO_3 was prepared and analyzed in each batch to track potential contamination of samples during the extraction and analysis processes (method blank). Three types of blanks were required: the calibration blank was used in establishing the calibration curve; the method blank was used to monitor for possible contamination resulting from reagents or equipment used during sample preparation; and the rinse blank was used to flush the system.

The effect of the matrix included the analysis of one matrix spike and one duplicate unspiked sample per analytical digestion batch. The analyte to be spiked was selected randomly in each batch assuring different sampling site. A laboratory control sample (LCS) was included with each analytical batch. It consisted of a clean (control) matrix similar to the sample matrix and of the same volume. The LCS was spiked with the same analyte at similar concentrations as the matrix spike.

The concentrations determined in the digest were reported on the basis of the dry weight of the sample. Total solid levels were below 0.2% (2000 mg/L) and were determined separately. The appropriate interference corrections, internal-standard normalization and the summation of signals at 206, 207 and 208 m/z for lead were included.

To generate acceptable accuracy and precision data, the LCS, the spiked sample and the duplicate recoveries were within ± 25% of the actual value. When the analyte had less recovery, the batch samples were discarded, and a new digestion process was applied for these sediment samples. No additional reference materials were used in theses determinations.

If the percent recovery of the internal standard in a sample was less than 80% or greater than 120% the intensity of that IS in the initial calibration standard, then a significant matrix effect must be suspected, and it can be removed by dilution of the affected sample.

Pearson correlation analysis was employed to assess linearity in relationship between variables. The analysis and interpretation of the obtained data were made using Principal Component Analysis (PCA), which is the most used lineal technique to reduce variables (Malinowski 1991; Kadhum et al. 2020; Li et al. 2020). PCA was employed to identify the cause of element concentration differences. Because the concentrations of the sediment elements varied greatly, the raw data were standardized before PCA (Wold 1987).

Results and discussion

Review of initial results

The chemical analysis results for sediment samples taken since 2016 to 2019 from 6 sampling sites of the study area are summarized in Tables 2 and 3. The values of maximum, minimum, median, mean and standard deviation for all of the selected elements are delineated there.

The main elemental composition of the sediment samples was Si, Fe and Al and the presence of Na, K and Ca indicating the salinity characteristic of the soil. Calcium and sodium aluminum silicate and silicon oxide were identified by XRD. No significant differences were presented in the different station samples showing the same sediment origin.

Generally, concentrations of selected elements in the sediment samples followed the order V > Cu > Cr > Ni > Mo > Cd in all the station except 3-station. In that site the concentration of Cu is higher than the concentration of Cr but Ni varies between these concentrations depended on the year. The Pb concentration has not a regular behavior in any sampling stations, but in the 3-station it had the lower value. The highest contents for Cr, Ni and Mo were found at the 3-station

Table 2 Summary statistics of major elements from 6 sampling stations in the years 2016 to 2019 (% wt. dry weight)

	Na	Mg	Al	Si	P	S	K
Max	3.880	3.192	16.490	60.110	0.860	0.550	5.820
Min	2.355	1.230	13.580	44.176	0.511	0.045	1.926
Median	3.154	1.870	15.051	51.374	0.651	0.130	4.014
Mean	3.180	1.924	14.994	51.286	0.654	0.148	4.067
SD	0.398	0.326	0.777	3.052	0.095	0.102	0.970

	Ca	Ti	Mn	Fe	Cu	Zn
Max	10.302	2.139	0.742	19.070	0.030	0.080
Min	4.450	0.900	0.250	8.380	BDL	BDL
Median	6.099	1.547	0.355	14.764	0.012	0.030
Mean	6.269	1.568	0.416	14.768	0.013	0.035
SD	1.275	0.300	0.129	2.514	0.008	0.015

Maximum, minimum, median, mean and SD are % wt. dry weight for sediments

BDL, below detection limit

Table 3 Summary statistics of selected minor elements from 6 sampling stations in the years 2016 to 2019 (mg/kg dry weight)

	V	Cr	Ni	Cu	Mo	Cd	Pb
Max	76.235	17.464	21.987	35.821	1.129	2.249	28.692
Min	23.068	6.791	4.379	6.419	0.038	0.047	1.891
Median	39.044	10.051	8.531	13.964	0.398	0.106	5.905
Mean	42.537	10.853	9.160	15.866	0.427	0.178	8.051
SD	13.826	2.916	3.169	7.317	0.278	0.310	7.056

Maximum, minimum, median, mean and SD are mg/kg dry weight for sediments

showing a different element distribution than in the other stations (Fig. 2).

Table 4 shows the comparison of the Pichileufu Patagonia sediment element concentrations with threshold effect level (TEL) and probable effect level (PEL) above which negative effects should be expected in aquatic ecosystem.

As can be seen in Table 4, all the selected element concentrations were below the PEL of the sediment quality guidelines, but Ni, Cu and Cd were slightly above the TEL, but only the 3% of samples exceeded the TEL value.

In the following Table 5, there is a comparison of average concentration of the three metals that presented values above the TEL in sediment of Pichileufu Patagonia River with other world rivers and with pristine-river estimations (Chen and Wang 1995; Savenko 2006). These values show that the sediment samples in the present study had concentration significantly below the others indicating that the Pichileufu Patagonia River can be consider as a background level of the studied elements (pristine place). Also, it can be used as a level to compare sediment samples from other part of the world.

Mean concentration of Ni, Cu and Cd are mg/kg dry weight for sediments. All concentrations were obtained before the same digestion process.

Organic matter content in sediments

In general, the annually organic matter average was increased from 2.15%wt. to 6.11%wt. Analyzing site-specific data, it can be mentioned that station 0 and 2 had the highest values

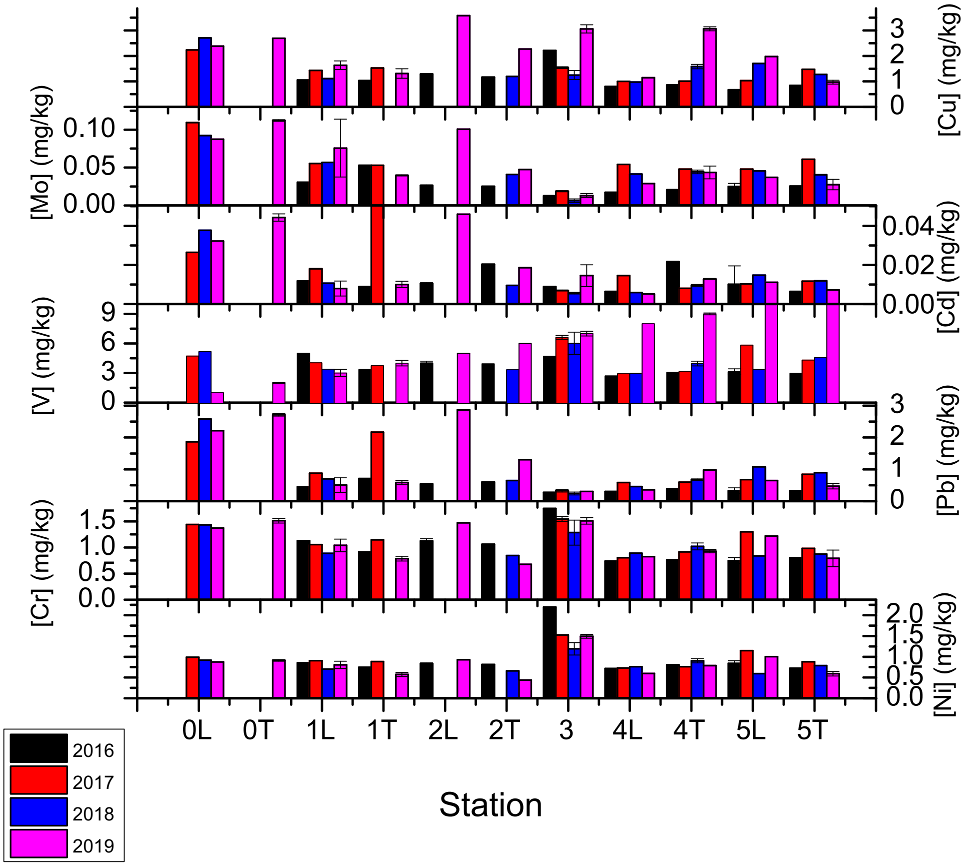

Fig. 2 Spatial and temporal distribution of selected elements in sediments of the Pichileufu Patagonia River

Table 4 Comparison between sediment quality guidelines (SQGs) and selected elements in the present study (mg/kg dry weight) with percentage of sample in each guideline

	Zn	Cr	Ni	Cu	Cd	Pb
In this study						
Range	0–80	6.8–17.5	4.4–22.0	6.4–35.8	0.005–2.25	1.9–28.7
Mean	35	10.9	9.2	7.3	0.18	8.1
SQGs						
TEL	123	37.3	18	35.7	0.596	35
PEL	315	90	36	90	3.53	91.3
Compared with TEL and PEL						
%samples < TEL	100	100	97	97	97	100
%samples between TEL-PEL	0	0	3	3	3	0
%samples > PEL	0	0	0	0	0	0

TEL: threshold effect level (Smith et al. 1996)

PEL: probable effect level (Smith et al. 1996)

Range, mean, TEL and PEL are mg per kg dry weight for sediments

Table 5 Comparison of average concentration of selected metals in sediment of Patagonia River with other world rivers

Sediment of	Country	Mean concentration			Reference
		Ni	Cu	Cd	
Patagonia river	Argentina	9.2	7.3	0.18	Present study
Trepça and Sitnica rivers	Kosovo	113.7	124.7	432	Ferati et al. (2015)
Khoshk river	Iran	107.6	42.25	1.23	Salati and Moore (2010)
Tigris river	Turkey	284.0	1257.76	3.02	Varol and Sen (2012)
Tembi river	Iran	150	100	40	Shanbehzadeh et al. (2014)
World average	World rivers	102.1	122.9	1.4	Martin and Meybeck (1979)
Suspended sediments average	World rivers	74.5	75.9	1.55	Viers et al. (2009)
Pristine-river estimation	World rivers		50	0.2	Chen and Wang (1995)
Pristine-river estimation	World rivers	50	45	0.5	Savenko (2006)

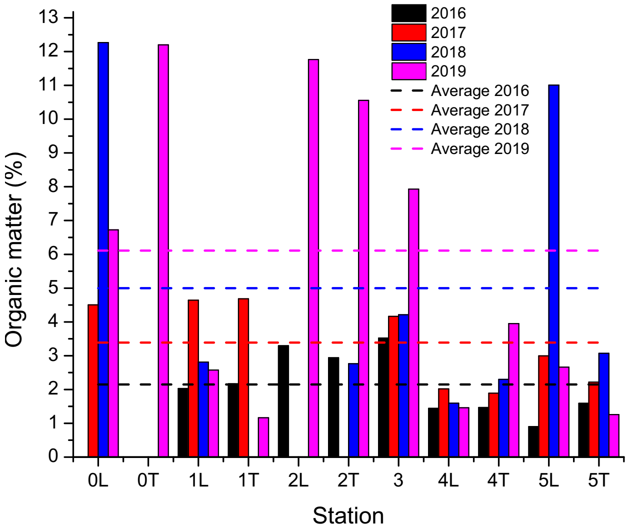

Fig. 3 Organic matter contents in sediments samples

of organic content, 12.2 and 11.76%wt., respectively, due to the small population living around these points (Fig. 3).

Major elemental composition of sediments

In this section, the principal component analysis is presented to characterize differences between the sediment samples in the major elemental compositions.

The Pearson correlation coefficient matrix of 20 element concentrations in 36 sediment samples was obtained using Mathlab software, but no important correlations between the variables were observed.

The PCA were done with the 13 elements which had a concentration upper that the limit of quantification. The eigenvalues to determine the principal components are shown in Table 6A and the eigenvectors or loadings are plotted in Fig. 4A.

PCA results suggested three principal components controlling major elements variability in sediments (Table 6A), which accounted for 37.73% (factor 1), 26.29% (factor 2) and 12.21% (factor 3) of the total variance.

Table 6 Eigenvalues of the PCA considering: (A) 13 elements and 36 sediment samples; and (B) 13 elements and 35 sediment samples

(A) Eigenvalues			(B) Eigenvalues		
Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
4.905	37.73	37.73	5.116	39.35	39.35
3.417	26.29	64.02	3.063	23.56	62.91
1.588	12.21	76.23	1.639	12.61	75.52
1.023	7.87	84.11	1.046	8.05	83.57
0.805	6.19	90.30	0.826	6.35	89.93
0.446	3.43	93.73	0.520	4.00	93.93
0.337	2.59	96.32	0.336	2.58	96.51
0.169	1.30	97.62	0.146	1.12	97.64
0.108	0.83	98.46	0.112	0.86	98.50
0.076	0.58	99.04	0.091	0.70	99.19
0.058	0.45	99.49	0.054	0.42	99.61
0.050	0.38	99.87	0.034	0.26	99.87
0.017	0.13	100.00	0.017	0.13	100.00

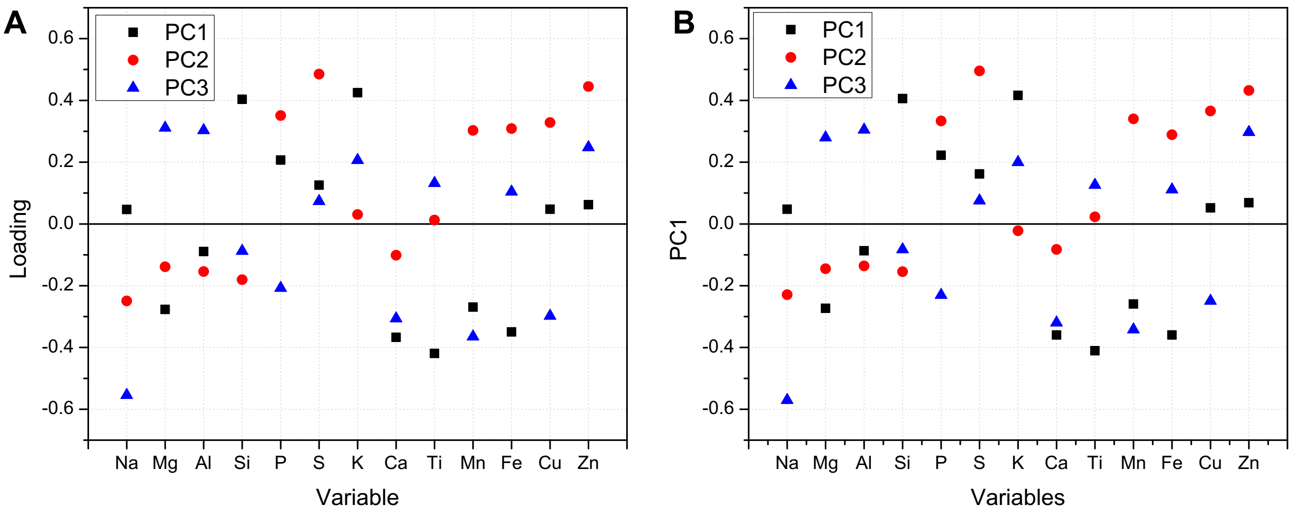

Fig. 4 Loadings of the PCs considering: **A** 13 elements and 36 sediment samples; and **B** 13 elements and 35 sediment samples

The sediment sample corresponding to the sampling site ¨0¨ with transversal-sampling method (19-0T) was segregated from the rest, because of their higher PC2 value (Fig. 5A). The major variable that contributed to PC2 was the S concentration. Unfortunately, it was not possible to take sediment sample of that site in other year, so we discarded it from the next PCA. The new eigenvalues and eigenvectors are shown in Table 6B and Fig. 4B, respectively.

PCA results suggested also three principal components controlling major elements variability in sediments (Table 6B), which accounted for 39.35% (factor 1), 23.56% (factor 2) and 12.61% (factor 3) of the total variance. These results do not differ significantly with those of the previous analysis with considering of the 19-0T sample.

Figure 5B shows clearly the separation of the sampling station ¨3¨ from the rest. This result is consistent with the fact that the 3-site is a sampling station in a stream that flow into the main river. So, it is not expected that the major composition of these sediments is similar to those of the main river.

The main phases determined by DRX of the sediment samples from Pichileufu Patagonia River corresponded to the presence of silicon oxide and calcium and sodium aluminum silicate phases. The diagrams of all the sediment samples were similar despite the differences observed in the major elemental compositions.

Selected minor elemental composition of sediments

In this section, the principal component analysis is presented to identify differences between the sediment samples despite the low trace element concentrations.

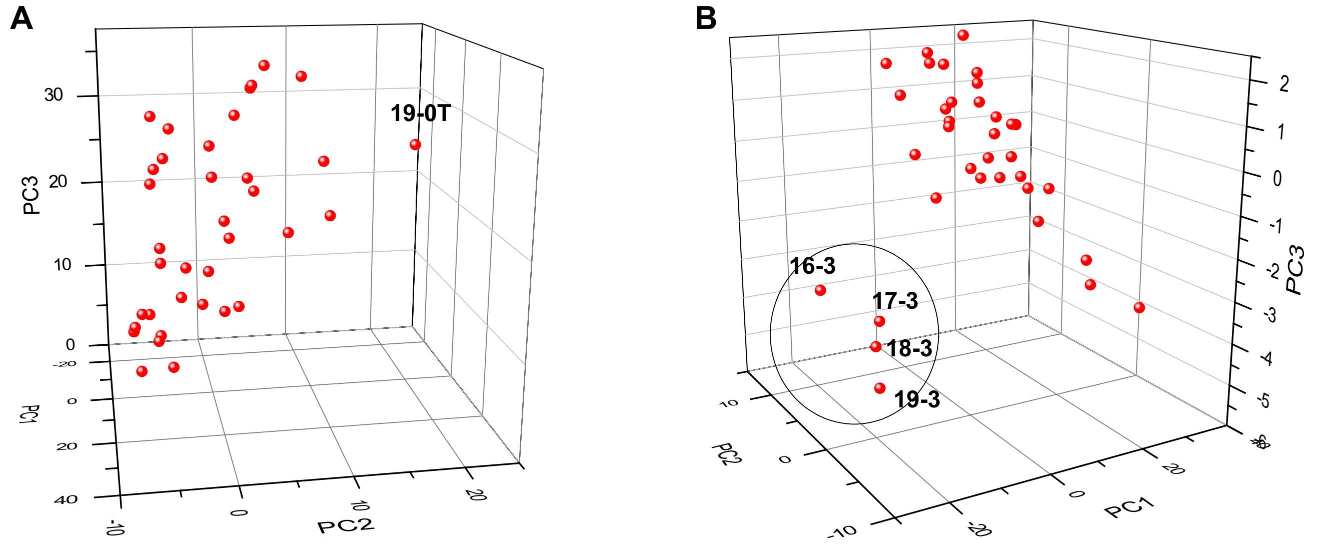

Fig. 5 PCA of major elemental composition of sediments from Patagonia River. **A** Segregation of the 19-0T sample; and **B** segregation of the 3-station samples after removing the 19-0T sample

Table 7 Eigenvalues of the PCA considering: (A) 7 minor elements and 36 sediment samples; and (B) 7 minor element concentrations and 35 sediment samples

(A) Eigenvalues			(B) Eigenvalues		
Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
3.404	48.62	48.62	3.956	56.52	56.52
2.046	29.22	77.85	2.166	30.94	87.46
0.850	12.14	89.98	0.349	4.99	92.45
0.347	4.95	94.93	0.258	3.68	96.13
0.254	3.63	98.56	0.196	2.80	98.93
0.065	0.93	99.50	0.044	0.64	99.56
0.035	0.50	100.00	0.031	0.44	100.00

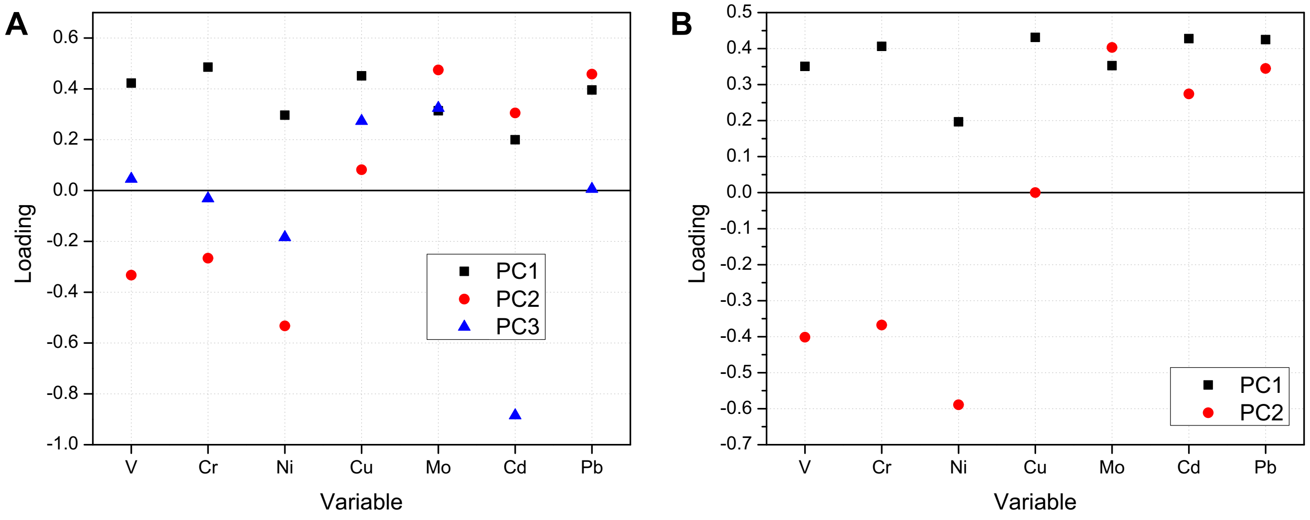

Fig. 6 Loadings of the PCs considering: **A** 7 minor elements and 36 sediment samples; and **B** 7 minor element concentrations and 35 sediment samples

The PCA for the ICP-MS results were analyzed considering the 7 selected minor elements (V, Cr, Ni, Cu, Mo, Cd, Pb). Table 7A contains the eigenvalues and Fig. 6A shows the loadings of the PCs.

PCA results suggested three principal components controlling trace elements variability in sediments (Table 7A), which accounted for 48.62% (factor 1), 29.22% (factor 2) and 12.14% (factor3) of the total variance.

In Fig. 7A the separation of the sample 17-1T is shown, because it had atypically the highest Cd concentration. Compared with the 17-1L and the samples of the same site in others sampling years, it can be considered as an outlier.

Not considering the 17-1T sample, PCA results suggested two principal components controlling trace elements variability in sediments, which accounted for 56.5% (factor 1: V, Cr, Ni, Cu, Mo, Cd and Pb) and 30.9% (factor 2: -V, -Cr, -Ni, Mo, Cd and Pb) of the total variance. The eigenvalues are shown in Table 7B and the eigenvectors o loading of the PCs are plotted in Fig. 6B.

Figure 7B shows differences in all the samples of the site ¨0¨ and in the sample 19-2L, because they presented the highest concentrations of the selected elements. Also, the samples of the site ¨3¨ had little differences from the rest, because they had the highest Ni concentrations. The site ¨0¨ showed higher differences from the rest of the sites in minor element concentrations, because their samples contained higher concentration of all the elements in comparison from the pool of samples.

Conclusions

Despite the likeness in the diffractograms, the elemental analysis by XRF and ICP-MS allowed to clearly identify the tributary of the 3-station samples that does not correspond to the main stream of Pichileufu Patagonia River sediments.

No correlation between the analyzed minor and major element concentrations was found indicating that these elements could have different origins or controlling factor in the analyzed samples.

The PCA of the major element concentration allows identifying the origin of the samples differentiating the sediment samples coming from the main river from those of the tributary.

The overall results of this study show that selected minor element concentrations in river sediments are below the sediment quality guidelines and below the reported world rivers values of pristine rivers. Furthermore, no significant temporally variations were observed. This fact converts the Patagonia River in a pristine area that can be considered as background levels of trace elements for steppe areas. The minor elemental concentrations in this study can be used as pre-industrial level references or concentrations in a free contaminant area to calculate the ecological risk assessments in other rivers.

Future analysis will consider seasonal variations of the content of selected elements, specially analyzing the water periods of the river and more monitoring will be required in the site ¨0¨because of its observed minor elemental differences.

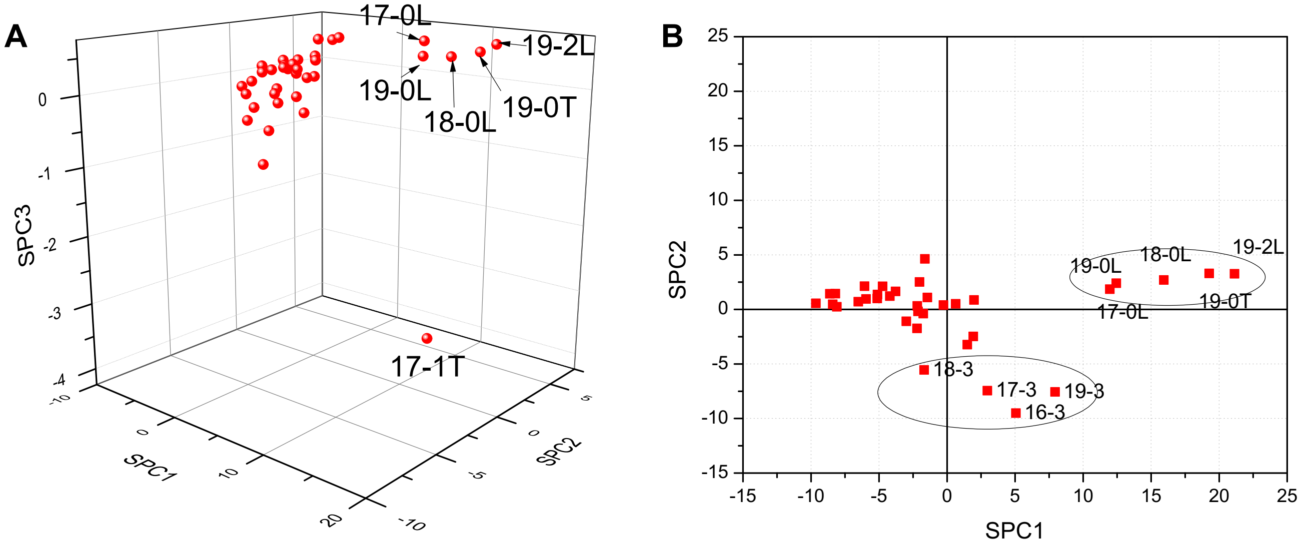

Fig. 7 PCA of selected minor elemental composition of sediments from Patagonia River. **A** Segregation of the outlier 17-1T sample; and **B** separation of the 3-station and 0-station from the rest after the outlier was removed

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Data availability The datasets generated during and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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