

Determining sedimentary material sources in a Brazilian urban lake using Zn stable isotope compositions of bottom sediments: a preliminary study

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RESUMO

As razões dos isótopos de zinco fornecem informações qualitativas e quantitativas sobre as contribuições de diferentes fontes de zinco no ambiente. Apresentam-se os resultados de um estudo preliminar para identificar as principais fontes que controlam as assinaturas de isótopos de Zn em sedimentos do Lago Paranoá (Brasil), um reservatório urbano de água. As razões isotópicas de Zn foram medidas por MC-ICP-MS e expressas como notação $\delta^{66/64}\text{Zn}$ em relação à solução JMC 3-0749-L. Os sedimentos estudados mostraram valores em um intervalo restrito (+0,00 a +0,13‰; n = 10), semelhante àquele reportado para solos intensamente intemperizados de várias partes do mundo (-0,4 a + 0,2 ‰). O Índice de Geoacumulação (I_{geo}) também sugere influência baixa ou desprezível de fontes antropogênicas para o Zn. Esta pesquisa fornece uma avaliação das assinaturas de isótopos de Zn em ambientes sedimentares lacustres sob a influência de solos intemperizados.

Palavras-chave: isótopos estáveis; MC-ICP-MS; espectrometria de massa; poluição ambiental; contaminação por metais; intemperismo; isótopos de zinco

ABSTRACT

Zinc isotope ratios provide qualitative and quantitative information about contributions from different Zn sources in the environment. Here, results of a preliminary study to identify the main sources controlling Zn isotope signatures are presented for sediments from Lake Paranoá (Brazil), an urban water reservoir. The Zn isotope ratios were measured by MC-ICP-MS and expressed as $\delta^{66/64}\text{Zn}$ notation relative to the JMC 3-0749-L solution. The studied sediments showed a narrow isotopic range (+0.00 to +0.13 ‰; n = 10) similar to that reported for intensely weathered soils worldwide (-0.4 to +0.2‰). The Geoaccumulation Index (I_{geo}) also suggests low or negligible influence of Zn from anthropogenic sources. This research provides a baseline assessment of the Zn isotopic signatures in lacustrine sediments under the influence of weathered soils.

Keywords: stable isotopes; MC-ICP-MS; mass spectrometry; environmental pollution; metal contamination; weathering; zinc isotopes

1. INTRODUCTION

In the past two decades, technological and methodological advances in inorganic mass spectrometry, notably the advent of the multicollector-inductively coupled plasma mass spectrometry (MC-ICP-MS), have enabled researches to determine the variation of Zn isotope compositions in the environment (MOYNIER *et al.*, 2017). The understanding of the main processes leading to isotopic fractionation (i.e., sorption, redox reactions, biological uptake, evaporation, etc.), their magnitudes and the effect of chemical equilibrium and kinetics fractionation mechanism opened the possibility to use the isotope systematics to obtain important qualitative and quantitative information about sources, transport and behavior of these elements in the environment (WIEDERHOLD, 2015).

Expressed in $\delta^{66/64}\text{Zn}$ notation relative to the JMC 3-0749-L standard, Zn isotopic variations in silicate rocks (including igneous, metamorphic and sedimentary) are small and tend to cluster within a narrow range from +0.20 to +0.40‰ (MOYNIER *et al.*, 2017). Soils present larger ranges of isotope compositions in relation to the parental rock variation from -0.18 to +0.55‰, which can be attributed to the combination of natural abiotic and biological processes in the redistribution of Zn into different soil horizons during pedogenesis (FEKIACOVA; COMU; PICHAT, 2015). The Zn isotope compositions of soils are affected by uptake, translocation and distribution of Zn between the internal compartments of plants (CALDELAS; WEISS, 2016). In turn, man-

made materials and byproducts produced in metallurgical and coal plants tend to be isotopically distinct from the Earth crust due to the significant Zn isotopic fractionation involved in processes such as electrolysis and high-temperature combustion (ARAÚJO *et al.*, 2017a; OCHOA GONZALEZ; WEISS, 2015). In aquatic systems, Zn isotopes may be fractionated the adsorption on solid surface (such as mineral particles and membranes) or uptake by phytoplankton (GUINOISEAU *et al.*, 2016; JOHN *et al.*, 2007; MOYNIER *et al.*, 2017; SZYNKIEWICZ; BORROK, 2016). Variations of $\delta^{66/64}\text{Zn}$ values in particulate matter from a temperate Swiss lake (Lake Greifen) over the seasons were associated to biological isotope fractionation during primary productivity (PEEL; WEISS; SIGG, 2009). In coastal systems, the Zn isotope signatures of sediments, including surface, core and SPM samples, have been successfully applied to infer source mixing processes involving anthropogenic, marine and terrigenous sources (ARAÚJO *et al.*, 2017a,c; 2018; 2019a,b).

The aim of this work is to measure the Zn isotope compositions in sediments from the Lake Paranoá, an urban reservoir near the city of Brasília (Brazil) to identify the possible sources, i.e. detrital input from weathered soils or anthropogenic sources. To support the Zn isotope data interpretation, the Geo-Accumulation Index (Igeo) (OCH *et al.*, 2012), mineralogical characterization and source signature data available in the literature were used.

2. EXPERIMENTAL

2.1 STUDY AREA AND SAMPLING

Paranoá Lake (38 km² surface area, 498 x 106 m³ volume, 13m and 40m mean and maximum depths, respectively) is located in Central Brazil (Fig. 1), east of Brasília city and metropolitan region with a population of about 2.3 million (2.6 million; Distrito Federal), in the Cerrado-biome region (Brazilian savanna) at an altitude

between 850 m and 1300 m above sea level (STARLING *et al.*, 2002). This lake was created in 1959 to provide electricity to the Brasília capital and as a place for sports, leisure, tourism, landscape composition and dilution of wastewater treatment plants, sewage and storm water drainage (MAR DA COSTA *et al.*, 2016).

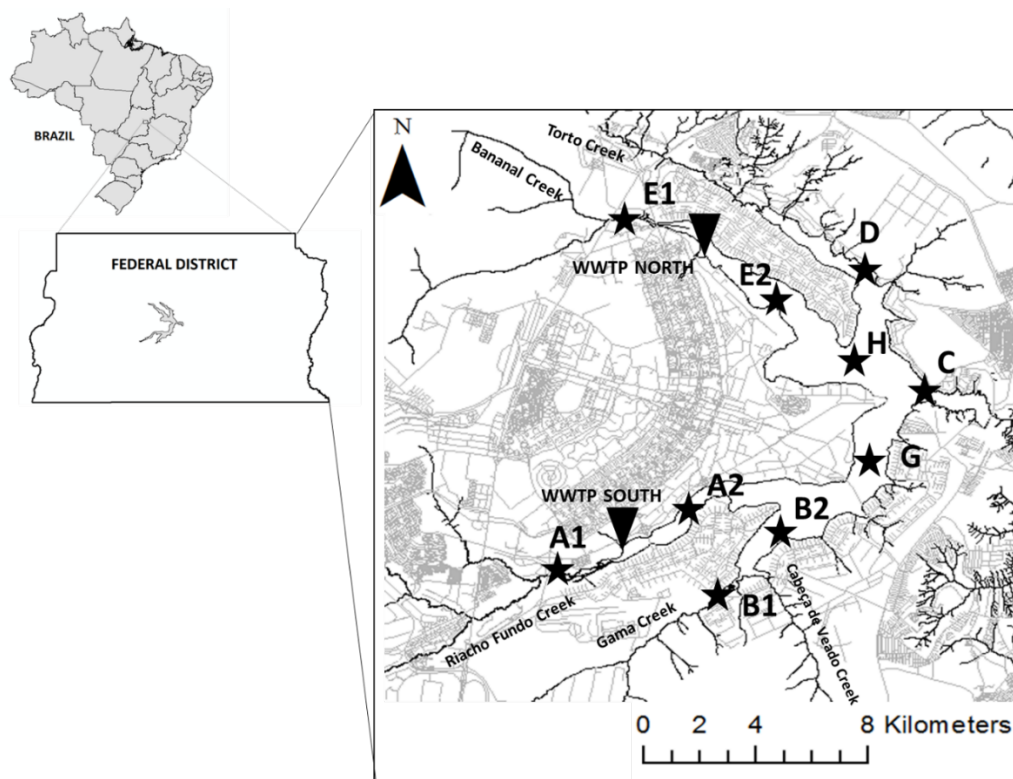


Figure 1
Sampling sites for sediment samples (stars) in the Lake Paranoá and its tributaries. The South and North Waste Water Treatment Plants (WWTP) positions are also indicated.

The regional geology consists of low-grade metamorphic rocks, comprising pelitic, psammitic and carbonate metasediments. Most part of the Paranoá Lake watershed is geologically dominated by the Paranoá Group, which comprise units formed by metasilites, metarhythmites, quartzites, dolomites and limestones (CAMPOS *et al.*, 2013). More than 85% of total area of Distrito Federal is covered by extensive lateritic soil and cambissols. They are rich in Fe and Al and poor in macro- and micronutrients (GIOIA *et al.*, 2006). The lake has five main tributaries: Riacho Fundo Creek, Gama Creek in its south portion, and Bananal and Torto Creeks in the north. The south region of the lake and the region around its tributaries

are densely populated and suffer from rapid processes of pollution (domestic sewage), deforestation and erosion (FRANZ *et al.*, 2014; MAI *et al.*, 2006; MAR DA COSTA *et al.*, 2016; PADOVESI-FONSECA, 2009). In this work, ten sediment samples were taken encompassing the different branches and main creeks that feed the lake (Fig. 1). The samples were collected from the lake using an Ekman grab, while the samples from the creeks were collected using plastic shovels. These sediments were stored in plastic bags and carried to the laboratory, where sediment drying at 40 °C, crushing and sieving at 63 μm were carried out. This grain size fraction (< 63 μm) was used for elemental, mineralogical and isotopic analyses.

2.2 DETERMINATION OF ZN CONCENTRATIONS AND ISOTOPE COMPOSITIONS BY MC-ICP-MS

Sediments and reference materials (BCR-2 or BHVO-2) were weighed in Savillex® Teflon beakers with sample masses ranging from 20 to 150 mg and digested using a multiple-step acid attack (21 mol L⁻¹ HF 14 mol L⁻¹ HNO₃ and 6 mol L⁻¹ HCl) on a hot plate, as described in Araújo *et al.* (2017b). Subsequently, the samples were dried again and re-dissolved in 1 ml of 2

mol L⁻¹ HCl prior to Zn chromatographic purification. Blanks and the reference materials (BCR-2 or BHVO-2) were included in every sample batch as analytical control in the elemental analysis. Only ultrapure acids (Merck®) distilled by sub-boiling in Teflon stills and de-ionized water (Milli-Q, 18.2 M Ω) were used in the sample preparation. Multi-element

standard solutions (Merck®) were used to produce calibration curves to measure total Zn concentrations by inductively coupled plasma-optical emission spectrometer ICP-OES (*Spectro Analytical Instrumental GmbH*, model *Spectroflame FVM03*). Accuracy was determined by comparing the measured concentration with the certified value and expressed using percentage relative error (BCR-2 and BHVO-2, USGS). The relative errors were within ±10% in relation to the certified values.

Zinc isotope ratios were measured using the ThermoFinnigan Neptune and Neptune *Plus* MC-ICP-MS at the Laboratório de Estudos Geodinâmicos e Ambientais at University of Brasília and at the Centro de Pesquisas Geocronológicas (CPGeo) at the São Paulo University, respectively. A detailed description of the methodology is found elsewhere (ARAÚJO *et al.*, 2017b). Briefly, sample aliquots were pre-concentrated to provide about 1-4 µg of Zn dissolved in 1mL of 2 M HCl. The acidified sample was then loaded onto Bio-Rad® plastic columns with about 2 mL of pre-cleaned 100–200 mesh AG MP-1 resin (Bio-Rad®). Matrix elements were eluted by addition of 2 M ultra-pure sub-boiling HCl. After, Zn was eluted using 0.05 M HNO₃. This fraction was evaporated to dryness, doped with Cu NIST SRM 976 standard and re-dissolved in 3% HNO₃

to reach a concentration between 100-300 µg/L. The raw ratios were corrected for instrumental mass fractionation using the exponential law and the certified ratio (0.4456) for Cu of the NIST SRM 976 standard. The Zn isotope ratios were reported in δ-notation relative to the Johnson Matthey 3-0749-L (JMC) reference material, as below:

$$\delta^{66}\text{Zn}(\text{‰}) = \left(\frac{{}^{66}\text{Zn} / {}^{64}\text{Zn}_{\text{sample}}}{{}^{66}\text{Zn} / {}^{64}\text{Zn}_{\text{standard}}} - 1 \right) \text{ eq.1}$$

The isotopic certified reference material Zn IRMM 3702 (-0.27 ± 0.06 ‰, *n*=30, 2σ) and six reference materials (BHVO-2 basalt; BCR-2 basalt; AGV-2 andesite; 2709 San Joaquin soil, 1646a estuarine sediment and 1573a tomato leaves) prepared in different replicates (full protocol including digestion, ion-exchange chromatography and twice isotopic measurements for each replicate) showed good reproducibility (<0.1 ‰, 2σ, 5 ≤ *n* ≤ 1). All certified materials results are available in Araújo *et al.* (2017b). Sediment samples of Paranoá Lake were prepared in duplicate with distinct digestion and chromatography, and double measurements were carried out for each one. The average external reproducibility of sediment samples was ± 0.08‰ (2σ, *n*=40) and represents external reproducibility for the entire procedure.

2.3 THE GEO-ACCUMULATION INDEX

The geo-accumulation index (*I_{geo}*) method was used to evaluate the contamination levels of Zn in sediments using Muller's expression (eq.2) and regional average background available for the Distrito Federal region (Zn = 48.7 µg g⁻¹, Arraes Moreira; Boaventura, 2003)

$$I_{geo}(\text{Zn}) = \log \left(\frac{\text{Zn sample}}{1.5 * \text{Zn nat. background}} \right) \text{ eq.2}$$

2.4 MINERALOGY

Mineralogical composition was determined by X-ray diffraction (XRD), using a RIGAKU Ultima IV diffractometer (at the University of Brasília, Brazil). The XRD patterns were obtained for powders (0-2 mm fraction) and air-

dried, using a Ni-filtered Cu-Kα radiation and graphite monochromator with an operating voltage of 45 kV; beam current of 15 mA; and a scanning speed of 2°/min between 2 and 80° 2θ.

3. RESULTS

The sediments of Lake Paranoá and tributary creeks presented Zn isotope compositions within a narrow range (+0.00 to +0.13 ‰) and Zn concentration between 21 to 130 $\mu\text{g g}^{-1}$ (Table 1, Fig. 2A). The highest concentrations were found in samples A2 (102 $\mu\text{g g}^{-1}$) and E2 (131 $\mu\text{g g}^{-1}$), both collected at downstream points from the south and north Waste Water Treatment Plants (WWTPs), respectively (Fig. 1). The sediments collected in the creeks (A1, B1, E1) showed Zn concentrations lower than those in sediments from the lake. This is explained by their coarser grain size in these environments, in contrast with the finer particles of lake sediments.

Sediment samples A2, B2 and E2 are classified as low contaminated (Igeo values

between 0 and 1), while all other samples are classified as uncontaminated (Igeo values ≤ 0). The $\delta^{66}\text{Zn}$ values and Zn concentrations were not correlated ($R^2 = 0.07$, $p < 0.05$) and the scatter plot of these variables did not appoint any tendency of mixing source processes or sample grouping. Despite the gradient of Zn concentrations, analysis of variance (ANOVA) indicated no significant statistical difference on $\delta^{66}\text{Zn}$ values of sediments ($p > 0.05$).

The X-ray diffraction (XRD) of samples showed that quartz, gibbsite, kaolinite and illite are dominant minerals in the samples, while vermiculite, rutile, muscovite, goethite, hematite and anatase occur as accessory minerals.

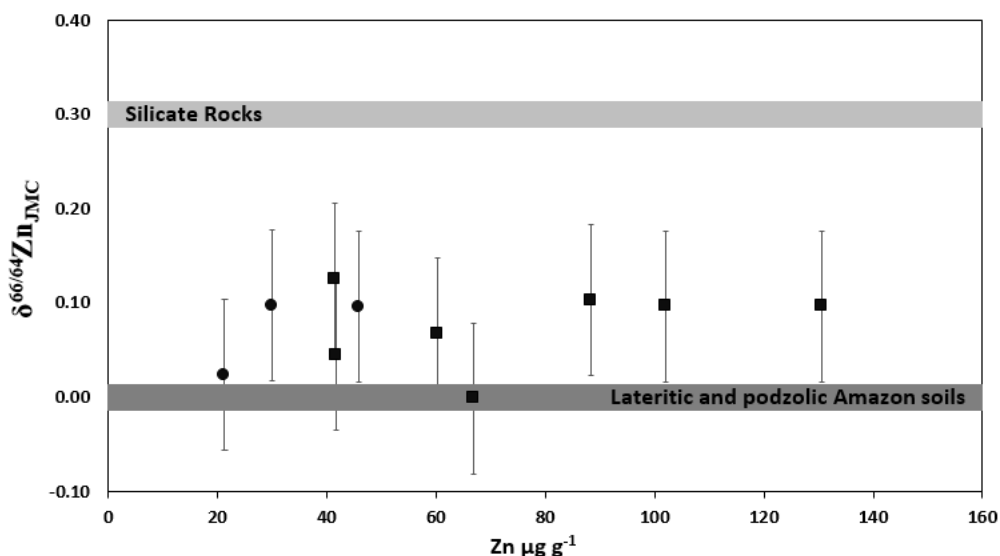


Figure 2

Scatter plot of $\delta^{66}\text{Zn}$ values versus Zn concentrations for sediments from the Paranoá Lake. Circle dots represent sediment collected in the creeks; square dots represent sediments collected in the branches and in the central area of the Paranoá Lake.

4. DISCUSSION

4.1 MAIN CONTROLLING FACTOR OF ZINC ISOTOPE COMPOSITIONS IN SEDIMENTS OF PARANOÁ LAKE

The Central Plateau of Brazil contains soils formed over long periods of pedogenic weathering under acid pH. In general, these soils tend to be leached and depleted in divalent trace element such as Zn (MARQUES *et al.*, 2004) The main minerals in these soils are 1) primary resistant minerals (i.e., quartz), and 2) iron and aluminum-rich weathering products (i.e., goethite, hematite, and kaolinite)

(MARQUES *et al.*, 2004). The mineralogical assemblies of Lake Paranoá sediments, composed mostly by clay minerals and Al and Fe oxyhydroxides, are consistent with highly weathered materials derived from these soils.

Zinc isotope ratios of Paranoá Lake sediments are isotopically lighter than the continental crust, which an isotope average estimated about $+0.28 \pm 0.08\text{‰}$ (Fig. 2). In turn,

the studied samples are similar to Zinc isotope compositions of lateritic ($-0.07 \pm 0.1\%$, 1σ , $n=3$) and podzolic soils ($+0.04 \pm 0.1\%$, 1σ , $n=3$) from the Rio Negro (Amazon) (GUINOISEAU *et al.*, 2017). The Zn isotopic variability in soils have been associated to the pedogenesis processes transformation of the saprolite horizon into a ferruginous and clay-rich horizons (VIERS *et al.*, 2007a). The mechanisms of this process have been attributed to the equilibrium fractionation between aqueous organic species that are removed from the soil versus sorption on clay minerals and (Fe-Mn)-oxyhydroxides. In this processes the Zn present in solution is slightly enriched in heavy isotopes while the Zn reminiscent in the residual solid phase is slightly enriched in light isotopes (GUINOISEAU *et al.*, 2017; MOYNIER *et al.*, 2017; VIERS *et al.*, 2007b). Amazon soils, under an extreme weathering regime, showed lighter Zn isotope composition which were associated to the enrichment of light Zn isotope in residual crystalline phases (such as kaolinite in laterite) (GUINOISEAU *et al.*, 2017, 2018). These soils contrast with soils developed on granitoid (Scotland) and basaltic (Hawaiian Islands) rock substrates, or in Siberian regions, where small isotope fractionation of Zn was observed in relation to silicatic rocks (MOYNIER *et al.*,

2017; VANCE *et al.*, 2016; VIERS *et al.*, 2015). The Zn isotopic variability in soils remains poorly understood but weathering regime and drainage patterns (that may affect Fe-Mn oxyhydroxides formation and dissolution) seem to be the major controlling factors (VANCE *et al.*, 2016). Thus, it is plausible that the wide occurrence of kaolinite and Mn/Fe-oxyhydroxides in the sediments of Paranoá Lake, originated mostly from weathered soils, reflecting the light isotopic composition of Zn in these samples.

In addition to the natural soil source influence on the Zn isotope compositions of sediment samples, potential anthropogenic Zn sources could affect their isotopic signatures. Recent studies have demonstrated the influence of diffuse (urban traffic load and domestic untreated) and punctual anthropogenic sources (Wastewater Treatment Plants (WWTPs) on trace elements and nutrients budgets (FRANZ *et al.*, 2014; GIOIA *et al.*, 2006; MAR DA COSTA *et al.*, 2016). However, the low I_{geo} values suggest low or negligible anthropogenic Zn source influence on Zn isotope compositions of lake sediments. Moreover, the plot of $\delta^{66/64}Zn$ values *versus* Zn concentrations does not show evidence of any mixing source processes.

Table 1. Zinc isotope compositions, Zinc concentrations and I_{geo} values of sediment samples in the Lake Paranoá.

Samples	* $\delta^{66/64}Zn_{JMC}$	2σ	Zn $\mu g g^{-1}$	I_{geo}
A1	0.02	0.06	21	-1.8
A2	0.10	0.07	102	0.5
B1	0.10	0.11	46	-0.7
B2	0.10	0.07	88	0.3
C	0.00	0.06	67	-0.1
D	0.04	0.13	42	-0.8
E1	0.10	0.11	30	1.3
E2	0.10	0.06	131	0.8
G	0.07	0.07	60	-0.3
H	0.13	0.11	42	-0.8
Average		0.08		

* $\delta^{66/64}Zn$ values of sediment samples of Paranoá lake were calculated based on the average of four measurements

5. CONCLUSIONS

Zinc isotopic signatures in sediments of the Paranoá Lake occurred within a narrow range ($+0.00$ to $+0.13\%$). The homogenous Zn isotope compositions likely reflects dominant input of intensely weathered soils typically found in the region (composed mostly of lateritic soils), which probably underwent light Zn isotope

enrichment during pedogenesis. The low I_{geo} values suggest low influence of anthropogenic Zn sources. Therefore, this research provides a natural baseline assessment of the Zn isotopes signatures in sediments of lacustrine environments under the influence of weathered soils.

6. ACKNOWLEDGEMENTS

This work was financially supported by CNPQ (D.F. Araújo Ph.D. grant, number: 161944/2012-4 and postdoctoral grant number: 150310/2017-0). The authors thank all the technical staff of the Institute of Geosciences of Brasília especially, Erico N. P. Zacchi, Myller

Tonh  Fernando Cavalcante and B. Alcant ra for their collaboration with this work. A special thanks to Professor Dominik Weiss for his cooperation and support in the last years. The authors also thank Timothy Mulholland for his help in reviewing the manuscript.

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