Sources, Mobility, and Accumulation of Major and Trace Elements in Sediments: Implications for Environmental Quality and Management of an Urbanized Tropical Lake (Brasília, Brazil)

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Research Article

Additional Declarations: No competing interests reported.

Abstract

The quality of aquatic ecosystems can be significantly impacted by the input of nutrients and trace elements. Identifying the sources and bioavailability of these components is crucial for understanding their cycling and assessing the environmental effects in lakes subjected to increased anthropogenic pressure, such as Lake Paranoá, a man-made reservoir in Brasília, Brazil. This study explores the spatial distribution and geochemical partitioning of sedimentary nutrients and metals in Lago Paranoá, aiming to pinpoint their origins and behaviors. The sediment distribution patterns in Lago Paranoá reflect the lake's hydrodynamics, including water currents and proximity to material sources. Human-induced erosion due to urban expansion contributes to the influx of terrigenous and anthropogenic compounds into the lake. Our findings indicate that Ca, Mg, P, and Zn are associated with anthropogenic sources, likely from domestic sewage discharge and/or leaching from construction activities. Notably, sediments near the Wastewater Treatment Plant (WWTP) show elevated concentrations of P, Ca, Mg, and Zn, identifying the WWTP as a key source. Additionally, the high levels of P, Mn, and Zn in weakly acidic phases suggest these elements may readily desorb from sediments, potentially migrating into the water column during early diagenetic processes. This study provides essential insights for evaluating the potential impacts of the upcoming sediment dredging project in Lago Paranoá.

Introduction

Urban lakes and rivers are among the most vulnerable aquatic systems to pollution. The expansion of urbanization and the suppression of vegetation have led to significant changes in land use, which directly impact the quality of nearby freshwater bodies. These changes are primarily associated with increased surface runoff, soil erosion in urbanized catchments (Tang et al. 2019), and the release and transport of chemical contaminants into freshwater ecosystems (Cyril and Weng 2010; Guan et al. 2016). Elevated concentrations of metals and nutrients pose a serious threat to these ecosystems, often leading to eutrophication and contamination, which can have adverse effects on aquatic biota and human health (Søndergaard et al. 2013; Julian et al. 2023). The behavior of chemical components in lacustrine systems is complex, as these elements can either be trapped in sediments or released into the water column due to sediment cycling, changes in water chemistry, and post-deposition processes (Furrer and Wehrli 1996; Brown and Calas 2011; Rigaud et al. 2013; Vieira et al. 2019).

The geochemical composition of lake and river sediments, as well as Suspended Particulate Matter (SPM), integrates data related to both natural and anthropogenic processes. Analyzing sediment profiles can provide crucial proxies for pollution levels, biogeochemical changes, and human-induced erosion processes (De Miguel et al. 2005; Horowitz 2008; Horowitz and Stephens 2008; United Nations 2014; Vieira et al. 2019). To fully evaluate the environmental impact of sediments, it is essential to consider not only the overall concentration of elements but also their availability, mobility, and ecotoxicity (Brown and Calas 2011; Díaz-de Alba et al. 2011).

Lake Paranoá, located in Brazil's capital, Brasília, is an artificial reservoir built in the 1950s with the primary purposes of energy production, recreation, navigation, and, more recently, public water supply (Starling 1998). Over the course of Brasília's development, the lake has received inputs from domestic sewage, urban greywater, and soil runoff. Previous studies have documented changes in land use and cover (Brandão and Paviani 2018; Menezes et al. 2010), increased sediment input leading to the siltation of tributaries (Castro et al. 2019), and alterations in sediment and water quality, including periodic eutrophication (Gioia et al. 2006; Wong et al. 2006; Franz et al. 2013; Franz et al. 2014a; Aquino et al. 2018; Batista and Fonseca 2018; Araújo et al. 2020), largely attributed to excess dissolved phosphorus input (Angelini et al. 2008; Mar da Costa et al. 2016; Da Silva et al. 2021).

Despite the extensive research on the water quality of Lake Paranoá, there has been little investigation into the geochemical partitioning of elements in both historical and recent sediments. Consequently, there is limited information on the sources and geochemical processes affecting the behavior of metals and nutrients within these sediments. Given the increasing demand for water resources in Brasília and the local water shortages during the dry season, understanding these processes is becoming increasingly critical (Starling 1998). Additionally, recent proposals for dredging the reservoir, due to the advanced siltation of Lake Paranoá, underscore the importance of assessing sediment quality and the environmental risks associated with the re-suspension of particles and the release of weakly bound contaminants and nutrients.

This study aims to provide insights into the sources, transport, and retention processes of nutrients and potentially toxic metals in Lake Paranoá. We first investigate the mineralogical and geochemical composition of soils, gutter materials (road sediments), suspended particulate matter, and surficial sediments. Next, we examine the geochemical partitioning of phosphorus and metals using a sequential extraction method to assess their mobility and availability in sediments. Finally, this study offers valuable information for assessing the potential impacts of the proposed sediment dredging project and for improving the management of this urban aquatic ecosystem.

Study site

The hydrographic basin of Lake Paranoá is situated at an elevation of 1,000 meters in the city of Brasilia (Federal District's central region, Fig. 1). The lake has a surface area of 38 km², a drainage basin of around 1,000 km², a maximum depth of 39 meters in its central region, a water volume up to 500 million m³, and a retention time of less than a year. The four main tributaries are the do Riacho Fundo and Ribeirão do Gama creeks in the south; and Ribeirões Bananal and Torto creeks in the north. The Branch of Riacho Fundo has a history of disordered human occupation that led to high urban and population density. This population density was created by industrial sectors, planned and unplanned urban districts, and dumps that resulted in significant sediment, nutrient, and potentially toxic metal inputs (Menezes et al. 2010; Castro et al. 2019).

The geology of the Paranoá basin is composed of rocks from the Paranoá Group (Mesoproterozoic era), partially covered by tertiary-quaternary cover by recent quaternary alluviums composed by the detritus-lateritic material. Within the basin boundaries, there are silt, slate, sandy metarrhythmites, and quartzites from the Paranoá Group (Campos et al. 2013). The Lake Paranoá catchment is dominated by Ferralsols, with the occurrence of Cambisols, and Gleysols (Freitas-Silva and Campos 1998, Reatto et al. 2004). With a tropical climate the annual rainfall is approximately 1.500 mm distributed from December to March. The average temperature is between 18 and 22°C.

Materials and methods

Sampling

Sediment profiles (n = 16) from Lake Paranoá were collected using a Uwitec core-piston sampler equipped with 50 cm polyethylene tubes. Sampling sites across the four lake branches were strategically selected based on sediment dynamics and local input sources, including the three Wastewater Treatment Plants (WWTPs) (Fig. 1).

Water samples were collected during both wet and dry seasons from an average depth of 10 cm below the surface to isolate Suspended Particulate Matter (SPM, n = 30). The water was collected in polyethylene bottles and filtered using a frontal vacuum filtration unit with 0.20 μm cutoff membranes, which were pre-washed with a 10% HCl acid solution and rinsed with Milli-Q water.

To determine the chemical composition of sediments, surficial soils and materials accumulated in road gutters were sampled. The surficial horizons (n = 5) of Ferralsols and Cambisols, ranging from 0 to 10 cm in depth, were collected from natural forested and agricultural areas. Road sediment samples (n = 12), referred to as gutter samples, were collected from urban and industrial areas. The supplementary material provides detailed information on the type, location, and identification of the samples (Table S1).

Sample preparation

Sediment, soil, and gutter samples were dried in an oven at 50°C, ground using agate grade mortar and pestle, and sieved. Aliquots of about 100 mg of each sample were digested in Teflon reactors (Savillex®) using a sequential four-step acid digestion method (Tonhá et al. 2020). The steps are as follows: step I – 5 mL of HF (40%, v/v) and 2 ml of HNO_3 (65%, v/v) at 130°C; II – 3 mL of HCl (6M, v/v) and 1 ml of HNO_3 (65%, v/v) mixture at 130°C; III – 2 mL of HNO_3 and 1 ml of H_2O_2 (35%, v/v) at 90°C and IV -Finally, samples were dissolved in 10 mL of HCl (2M, v/v) and centrifuged to remove solid residues. SPM membranes were digested using the same acidic digestion procedure. Additionally, for soils, gutter and sediment samples, $LiBO_2$ fusion were performed in order to quantify the SiO_2 concentration.

Sediment samples also went through a sequential extraction procedure to assess speciation, solid partition of elements, and the labile and reactive fractions (Tessier and Campbell 1987; Ure et al. 1993;

Rauret et al. 1999; Lu et al. 2014). The procedure was firstly standardized by the European institution Bureau Communautaire de Référence (BCR) developed by Ure et al. (1993) and further modified by Rauret et al. (1999). The BCR protocol uses four stages, ranging from F1 to F4, to analyze elements associated with fractions weak acid soluble fraction, which includes carbonate mineral (F1); reducible fraction (F2); oxidizable fraction (F3); and residual fraction retained in mineral crystalline structure (F4).

Sample Analyzes

The mineralogy characterization of sediment total (fraction < 2mm) and clay fractions (clay fraction separated by centrifugation) was performed by the X-Ray Diffraction (XRD) method at the X-Ray Laboratory (Institute of Geoscience, University of Brasilia) using a RIGAKU - ULTMA IV diffractometer. The XRD determination operates with a copper tube and nickel filter with an under-current of 35 kV and 15 mA, scanning speed of 2°/minute, 0.05° steps, in the range 2φ to 40°. The percentage of organic matter and volatile solids was obtained by their loss in a muffle at 1000°C using the gravimetric method and reported as the percentage of Loss to Ignition (LOI) (Heiri et al. 2001). Major (Si, Al, Fe, Mn, Ca, Mg, Ti, Na and K) and trace concentration determinations were performed using an ICP-OES (5100 dual view, AGILENT, at University of Brasilia) and ICP-MS (Q-Thermo Scientific, USA, at HSM Montpelier).

Quality Assurance and Quality Control

Analytical blanks, i.e., vessel blanks, reagent blanks, and procedural blanks, were determined. Blank measurements showed values lower than the Limit of Detection (LD) of the methods. Certified reference materials were used for analytical control: NIST (San Joaquin Soil SRM 2709a and Estuarine sediment 1646a) and BCR-701® (Freshwater Lake Sediment). The precision of the standard samples was mean within ± 5% of the certified values. The detection limit for screening metals was less than 0.030 and 0.0010 µg L-1 for the ICP-OES and ICP-MS analyses. All reagents used during labware cleaning, sample preparation, and chemical extractions were of high-grade purity and the acids were distilled by sub-boiling in Teflon™ vessels.

Multivariate statistics and sediment guidelines

The XLSTAT tool available for the Excel software was used to perform Principal Component Analysis (PCA) and descriptive statistics (mean, median, and standard deviation) to analyze the sample data set. Principal Component Analysis (PCA) with varimax rotation was employed to minimize the number of variables while maintaining their statistical significance. PCA was performed using data normalized to thorium (Th) concentrations to minimize the bias associated with sediment particle size and provide more robust insights into geochemical sources. Thorium was selected due to its conservative behavior, low mobility, and prevalence in fine-grained sediments, which dominate the collected samples.

The sediment metal potential toxicity was evaluated using reference levels proposed by the United States Environmental Protection Agency - USEPA, the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, and the Ministry of Environment (Thomas, 1987; CCME, 2003).

Results and Discussion

Mineralogy signatures of sediments, soils, and gutter sample

The mineralogy analysis of both total and clay fractions confirms the predominant presence of quartz and kaolinite, followed by gibbsite and illite in soils, gutter and sediments (Fig. S1 and Table S3). In the clay fraction of soils and sediments, kaolinite is the main mineral, followed by gibbsite, illite, and also quartz. Hematite, rutile, and anatase were consistently present as trace minerals in soils and sediments. The mineral composition of soils and sediment reflects the cachtment's pedogeological character, mainly composed of lateritic soils developed on Mesoproterozoic silicate sediments (Freitas-Silva and Campos 1998; Reato et al. 2004). Calcite is only found as a trace mineral in soils from agricultural areas and gutters samples (Fig. S1 and Table S3), consistent with previous studies (Carvalho Júnior et al. 1998; Franz et al. 2013; Franz et al. 2014b). Due to the intense weathering conditions and the absence of carbonate outcrops in the Lake Paranoá catchment, the presence of calcite mineral in these samples evidence anthropogenic sources related to agriculture intrants and sediments from civil construction and industry.

Geochemical signatures of sediments, SPM, soil, and gutter samples

The composition and spatial distribution of the analyzed sediments and SPM elements (Table S2) are reported in Figs. 2 and 3. The sediments, soils, and gutter samples were mainly composed of SiO2. Although the HF acid digestion protocol used for SPM samples does not allow for the determination of SiO_2 concentrations, it is expected that SiO2 concentration in SPM are similar to those in fine sediments collected from Lake Paranoá. Gutter samples exhibited higher CaO and MgO content, while soils and sediments were richer in terrestrial elements such as Fe_2O_3, MnO, and TiO_2 (Table S2). Large concentrations of Ca and Mg were observed in SPM and sediments (Fig. 2a and b, and Fig. 3a), with values reaching 29.60 and 2.38 wt% in P5SAR, respectively. These concentrations are more significant than expected for natural sources, since no carbonate occurs in the basin. Notably, higher Ca, Mg, and Zn concentrations were found in gutter samples from areas with higher urban density (G1 and G4B), low infrastructure standards, and commercial/industrial activities (Menezes et al. 2010). Conversely, soils and gutter samples (G2A, G2B, and G5) from less urbanized areas exhibited lower mean concentrations of Ca, Mg, Zn, and P.

The P_2O_5 concentrations in the solid samples (soil, gutter, sediment) varied significantly, ranging from 0.08 wt% (gutter sample G5) to 22.45 wt% (P1SC). Sediment and SPM collected in the Riacho Fundo

Branch close to the WWTPs showed notably high P content (Fig. 2c). Additionally, high concentrations of Cu and Zn were observed in both SPM and sediment collected in front of WWTP-S (Table S2 and Fig. 2d and 3b). Zn concentrations in SPM and sediment ranged from 19.23 mg.kg⁻¹ (P2SAR) to 2120.2 mg.kg⁻¹ (P1SC, downstream of the WWTP of the Riacho Fundo Creek). Cu concentrations in SPM and sediment reached 307.4 mg.kg⁻¹ (P1SC). SPM collected in the Ribeirão da Gama branch (P2L) exhibited high levels of As, Cd, Cr, and Ni, with concentrations of 31.38, 10.75, 489.86, and 252.30 mg kg⁻¹, respectively. Finally, Pb concentrations in the data samples ranged from 3.20 to 143.45 mg kg⁻¹, with lower concentrations observed in natural soil and higher concentrations in gutter samples.

Suspended Particulate Material sources

The PCA analysis of the elemental data set, normalized with Th concentrations, helps distinguish different geochemical signatures of SPM (Fig. 4). The PCA accounts for 82.5% of the total variance and yielded two principal components: the first (PC1), with 71%, and the second (PC2), corresponding to 11.5% of the total variance. PC1 identifies correlations between terrigenous elements (Ti, Al, K, ∑REE, and Rb) with P, Zn, and Cu (cluster 1), while PC2 regroups redox-sensitive elements such as Fe and Mn with also Co (cluster 3). An intermediate group of elements composed by Mg and Sr (cluster 2) is likely related to carbonate contribution. Since carbonate minerals and rocks are not outcropping in the geology catchment, these elements seem to have an urban origin. Higher Ca and Mg concentrations may be related to anthropogenic activities such as cement processing plants, leaching from civil construction materials, and highly urbanized catchments (Wright 2011, Tippler et al. 2014).

Notably, SPM collected downstream the WWTP exhibits a higher concentration of carbonate, and terrigenous elements grouped between clusters 1 and 2 (Fig. 4). Elevated concentrations of P, Zn, Ca, and Mg in both sediments and SPM are typically associated to untreated sewage inputs (greywater) discharged in the Riacho Fundo Creek (RFC) or more recently in the Bananal Creek (Chen et al. 2008 and 2009; Franz et al. 2013; Garnier et al. 2024). This chemical signature is consistent with the observations in SPM samples collected downstream effluents output from the WWTP-RF and WWTP-S directly spilled into RFC and Lake Paranoá (Table S2).

Sediment sources

PCA analysis of surface sediments (0−1 cm), not normalized, yielded two main components, corresponding to 69.66% of the total variance (Fig. 5). It allowed identifying five different geochemical clusters for this compartment. The clusters A, rich in SiO_2 and Zr, and B, rich in Ti, Th, Al, Fe, and Mn, may represent terrigenous sediments. Cluster A may represent the sandy contribution (S4LB), and conversely, the second one may represent fine sediments rich in clay and hydroxides (samples S3L, S2L, and S1L).

Naturally occurring terrigenous compounds, including SiO_2, have higher fluxes into Lake Paranoá due to accelerated soil erosion in urban areas. The high average contents of SiO_2 in the Riacho Fundo Branch (sites S4LB (62.8%), S4LC (43.5%), and S4LE (43.4%)) align with a previous study conducted by Aquino et

al. (2018), as the Riacho Fundo transports large volumes of sandy sediment during high rainfall events in the basin. Conversely, C, D1, and D2 cluster are rich in CaO, MgO, P, and metals such as As, Cd, Cu, Cr, Pb, Zn and likely indicate anthropogenic sources. As observed in SPM composition, sediment sampled downstream the WWTP-S (S4LC) was significantly richer in those elements, with 1.09 wt% of CaO, 1.92 wt% of P, 314.5 mg.kg^{-1} of Zn, and 0.51 mg.kg^{-1} of Cd.

The average concentration of P and Zn in S4LC, were eight and four times higher, respectively, than the average found in other Lake Paranoá sediments and ten times higher than in the sediments of the Riacho Fundo stream. The Zn concentrations in S4LC exceeded previously recorded levels in uncontaminated alluvial sediments from Lake Paranoá (Franz et al. 2014a). Additionally, the LOI measured in this sediment reached 28.7%, the highest value in our dataset. Despite the tertiary level treatment of the WWTP-S (Omoike and Vanloon 1999), these results suggest a significant input of materials with a high organic load from the WWTP-S into the lake. The average concentrations of Ca and Mg in S4LC sediments, which were higher than in other Lake Paranoá sediments (8.308 and 3.246 mg.kg^{-1}, respectively), are likely related to the use of carbonates in the WWTP-S process as a flocculation agent and to adjust wastewater pH level. This finding highlights the impact of effluents released by the sewage treatment plant on the lake´s sediment composition.

Sediment chemical partitioning

The results obtained from surface sediments sequential extractions reveal the metal partition (Al, Fe, Mn, Ca, Mg, P, Zn, Cu, Pb and Cr) across different phases at various sediment core depths, i.e., 0−1 and 4−5 cm (Figs. 6 and 7). Fe and Al are predominantly associated with the residual fraction (F4), accounting for 82 and 95% of their total concentrations, respectively (Fig. 6). The similar distribution and partitioning of both elements suggest that they primarily occur as refractory minerals. The average Fe concentration of 17.1%, in the reducible fraction (F2) indicates that Fe is partially present as iron oxyhydroxides. Notably, Al concentrations in the F2 fraction are significantly higher in sediment surrounding the WWTP-S, reaching 16.4%. This suggests that, in addition to its geogenic source, Al may be linked to sewage treatment processes, as aluminum sulfate is used in the flocculation process (CAESB 2013).

Mn is predominantly associated with the weak acid-soluble fraction (F1), which includes carbonate minerals. Mn concentrations were significantly higher in the 0−1 cm layer compared to the 4−5 cm layer (139 and 88 mg.kg^{-1}, respectively) (Fig. 6), likely reflecting post-depositional processes, such as the reduction of Mn oxides in deeper sediment layers. The reducing conditions observed in the sediments (Eh = -130 ± 35 mv) support this statement. The more oxidizing conditions at the sediment-water interface may lead to the precipitation of Mn as poorly crystallized Mn oxides or carbonates (Brown and Calas 2011; Rigaud et al. 2013). The correlation between Mn, Fe, Cr, and Al in F1 leachates suggests similar behavior (fig S2). Fe and Mn, being redox-sensitive elements, are prone to remobilization under anoxic conditions, which are typically found in deep lakes with sediments enriched in organic matter (Davison 1993; Brown and Calas 2011; Raiswell and Canfield 2012; Rigaud et al. 2013; Makri et al. 2021).

In the F1-PCA (Fig. S2), the cluster formed by redox-sensitive elements such as Mn, Fe, Cr, and Al corroborates this observation. Given the affinity of trace metals for Mn oxyhydroxides, the Mn-F1 fraction may play a crucial role in the availability of trace metals in S4LC sediments. The redox conditions and early diagenetic reactions occurring in surface sediments may significantly influence the cycles of manganese, iron, and sulfur, thereby affecting the bioavailability of associated trace elements in Lake Paranoá (Berner 1984; Audry et al. 2006).

The elevated concentrations of Ca and Mg in the F1 and F2 fractions observed in sediment samples near the WWTP-S and downstream (S4LC, S4LD, and S4LE) are particularly noteworthy (Figs. 6 and 7). In S4LC, Mg concentrations in the F1 and F2 fractions reached 34%, compared to less than 9% in other sediments, indicating a localized source of Ca-Mg-rich material. This is likely related to the use of Mg-rich carbonate during the tertiary treatment process at the WWTP-S for phosphorus fixation (as confirmed by personal communication with WWTP staff). The PCA of the F2 fraction (Fig. S2) shows a cluster of Ca, Mg, Zn, P, and Al, suggesting a common source for these elements.

In sediments near the WWTP-S, phosphorus (P) concentrations in the F1 and F2 fractions together reach up to 70%, indicating the presence of reactive P-rich phases that could lead to P release into the water column (Julian et al. 2023). This finding underscores the need for targeted P monitoring in this area of the lake (Wildman and Hering 2011; James et al. 2017) particularly to quantify the role of Lake Paranoá's sediments in the P cycle. Previous studies have shown significant P releases from sediments into overlying water, associated with sediment resuspension and early diagenetic processes (Wildman and Hering 2011; Julian et al. 2023). Given the recurring eutrophication in Lake Paranoá and the fact that improvements in water quality can take more than five years even after P reserves are depleted (Sharpley et al. 2013), P and its role in eutrophication remains a global environmental issue in the Lake Paranoá for decade.

The high concentrations of Ca, Mg, and P in the F1 and F2 fractions near the WWTP-S (Fig. 8) highlight the significant influence of WWTP-S effluents. The PCA (Fig. S2) supports this, showing clusters formed by Ca, Mg, P, and Zn. However, there is a rapid decrease in P concentration in sediments downstream of the WWTP-S, with levels dropping below 200 and 60 mg/kg in S4LE and S3L sediments, respectively. This suggests that the influence of WWTP-S as a P source is primarily confined to the upper course of the Riacho Fundo branch.

Additionally, Zn is predominantly associated with the F1 and F2 fractions (Fig. 8), particularly in the 0−1 cm and 4−5 cm sediment layers near the WWTP-S. In S4LC, Zn concentrations in those fractions range from 45 to 51% of the total Zn sediment concentration, exceeding 125 mg.kg^{-1}. In other Lake Paranoá sediments, total Zn concentration is lower, but the Zn under F1 and F2 fractions remains high, ranging from 50 to 63%. Although the total Zn concentration in S4LC exceeds the established Probable Effect Level (PEL) and Threshold Effect Level (TEL) (314.5 and 340.1 mg/kg in the 0−1 cm and 4−5 cm layers, respectively), the most bioavailable fractions (F1 and F2) did not exceed 157.3 mg/kg (Fig. 8).

The concentration of Cu in Lake Paranoá sediments remained consistently low and uniform, with slightly higher levels observed at points S3L and S4LC. Notably, Cu concentration at these locations exceed the established Threshold Effect Level (TEL). Cu was relatively evenly distributed among the F2, F3, and F4 fractions (Fig. 8). Its strong affinity of Cu for organic matter likely accounts for the higher concentrations observed in the F3 and F1 fractions in sediments near the WWTP-S (Turner and Millward, 2002). In the F3 PCA, Cu and Pb are clustered with P, Zn, and Mg, particularly in sediments collected in front of the WWTP-S (Figure S2).

Lead (Pb) concentrations in the sediments were relatively uniform, remaining below 35 mg/kg, which is below the TEL, with the majority of Pb associated with the F2 fraction (Fig. 8). Previous studies have linked Pb levels to changes in land use and land cover in the Lake Paranoá region (Moreira and Boaventura 2003; Franz et al. 2013; Franz et al. 2014a). Gioia et al. (2006) also identified sewage and transport activities as anthropogenic sources using Pb isotopic tools, a finding supported by the F3-PCA. Finally, Cr concentration in Lake Paranoá sediment exceed the TEL. Cr concentrations in the F1 fraction were low and uniformly distributed around the lake, with at least 77% of Cr associated with the F4 fraction in all Lake Paranoá sediments.

Conclusion

The geochemical spatial distribution of sediments in Lake Paranoá reflects three main factors: (i) the influx of terrigenous and anthropogenic compounds into the lake, (ii) the proximity of sediment sources, and (iii) the lake's hydrodynamics. Our findings confirm that sediment degradation is accelerating due to human-induced erosion resulting from intensive land use. The total concentrations of Ca, Mg, P, and Zn observed in sediments and SPM indicate significant inputs from anthropogenic sources.

The sources of phosphorus and metals in Lake Paranoá sediments are linked to historical human activities in the surrounding catchments. This study identifies two primary types of anthropogenic sources: the first is associated with the irregular release of domestic sewage into tributaries and effluent discharge from sewage treatment plants in Lake Paranoá and Riacho Fundo Creek. The second source is related to diffuse inputs from road traffic, urban activities, and construction materials. These anthropogenic activities contribute to the elevated concentrations of Ca, Mg, Zn, and P in the lake sediments.

Sequential extraction reveals that significant fractions of phosphorus and trace metals, such as Mn and Zn, are present in reactive geochemical phases (F1 and F2 fractions), making them susceptible to desorption and/or release following the reduction of oxyhydroxide phases. Anoxic conditions in surface sediments, induced by microbial activity during early diagenesis, may lead to the diffuse release of phosphorus and manganese from the sediments into the water column. These diffuse fluxes of phosphorus, manganese, and zinc are critical contributors to eutrophication processes and the deterioration of water quality.

This study confirms the value of sediment solid partition studies in improving freshwater ecosystem management. It underscores the need to monitor dissolved phosphorus and its behavior in association with sediments. Based on the solid partition results, dredging operations in reservoirs may increase the fluxes of phosphorus, manganese, and zinc into the water column due to sediment resuspension, potentially compromising the viability of public water supply from Lake Paranoá. Ultimately, our study demonstrates that an integrated approach, combining total concentrations and partial chemical extractions, provides new insights into the dynamics of potentially toxic trace metals and nutrients in urbanized lakes.

Declarations

The authors report there are no competing interests to declare.

Funding

Author Contribution

All authors contributed to the conception and design of the analysis, as well as the provision of data and analysis tools.E.S.O., J.G., D.F.A., M.T., and D.F. D-R. were responsible for sample collection and performing the analysis.E.S.O., J.G., D.F.A., and D.S.M. drafted the main manuscript text and prepared the figures.All authors reviewed and approved the final manuscript.

Acknowledgement

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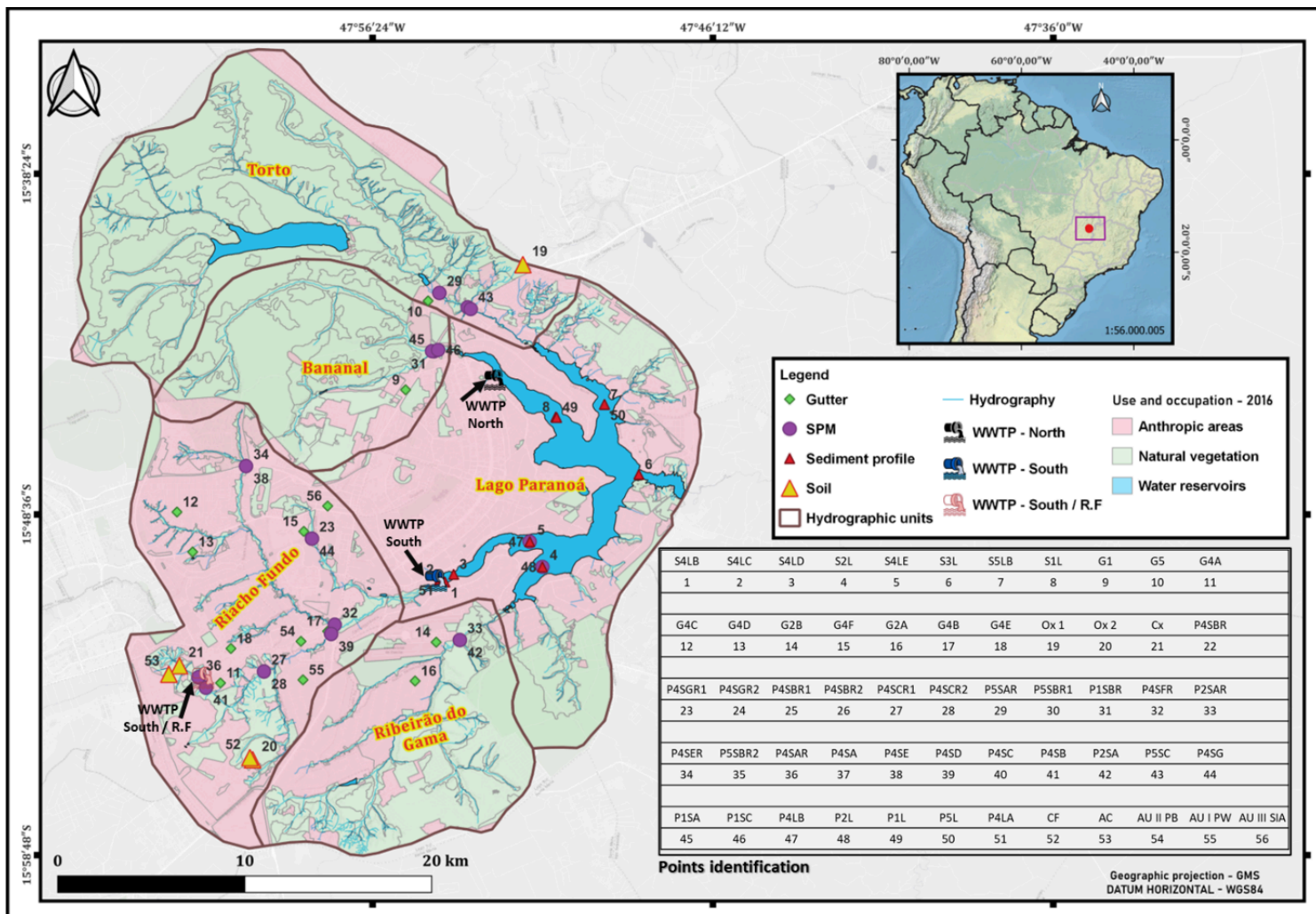
Figures

Figure 1

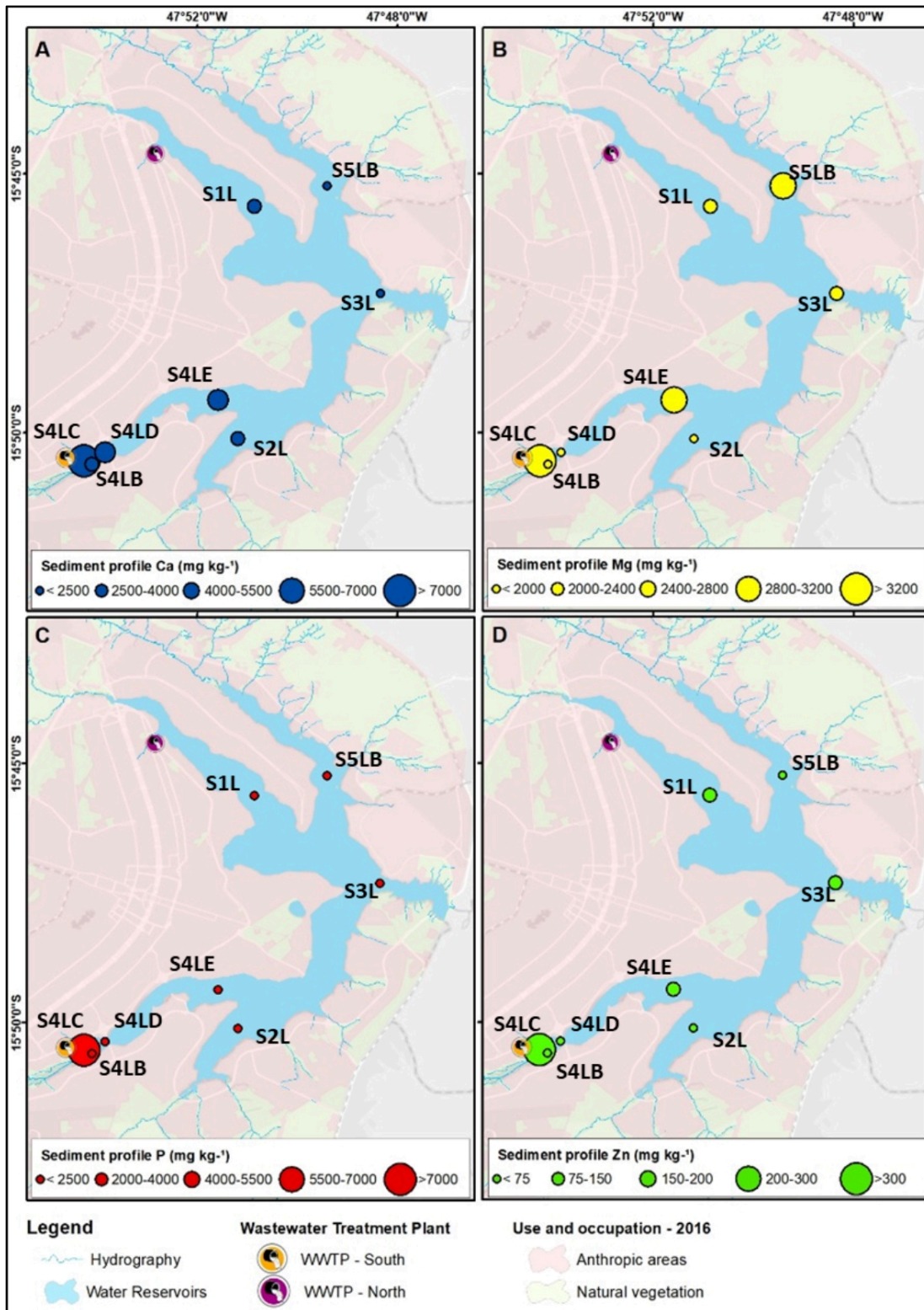Map of Lake Paranoá, including its tributaries, land use distribution, WWTP, and sampling location.

Figure 2

Spatial distribution of Ca (a), Mg (b), P (c) and Zn (d) concentrations in surficial sediment (layer 0-1cm) of the Lake Paranoá
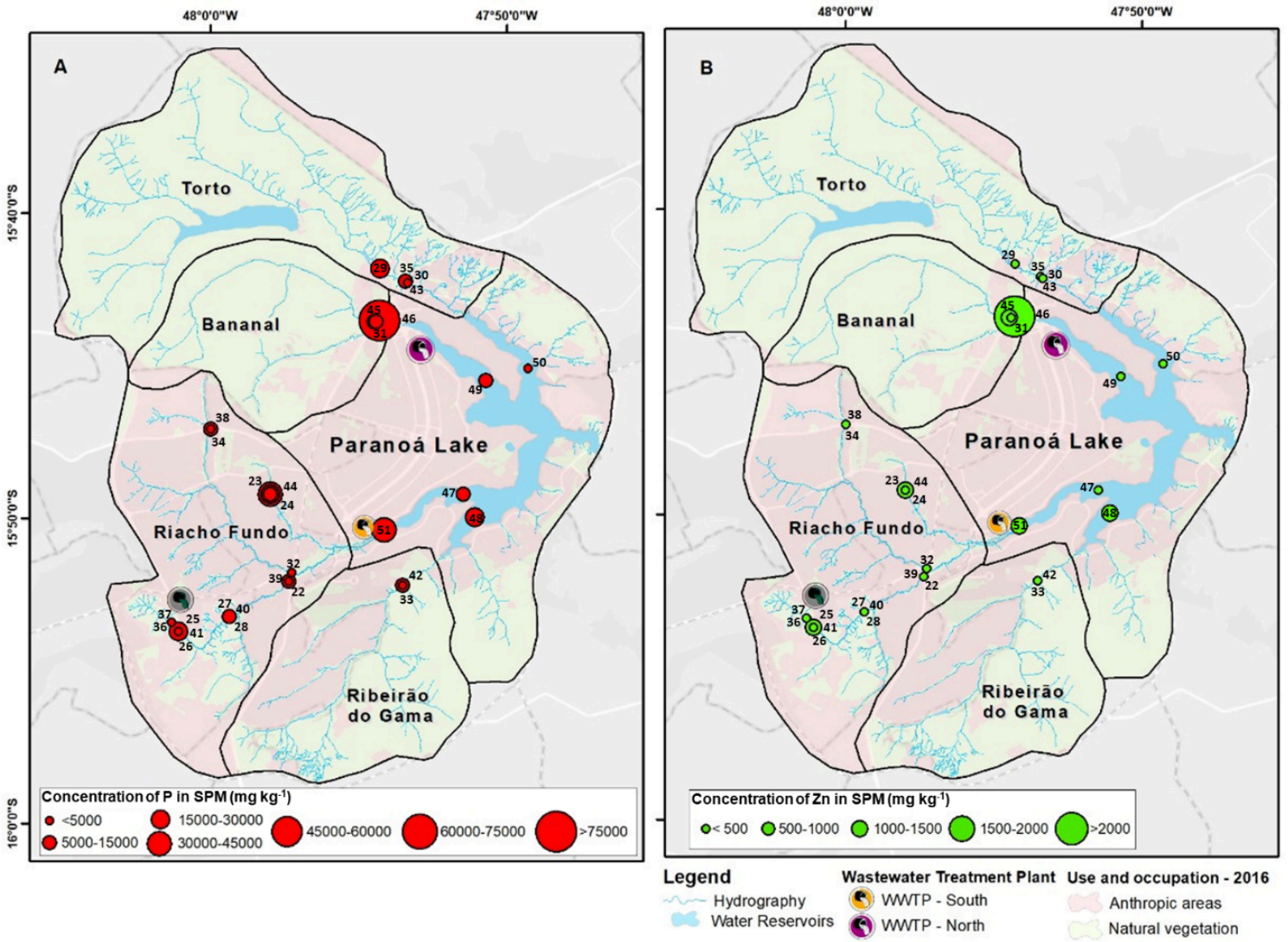
Figure 3

Spatial distribution of P (a) and Zn (b) concentrations in Suspended Particulate Matters of the Lake Paranoá.
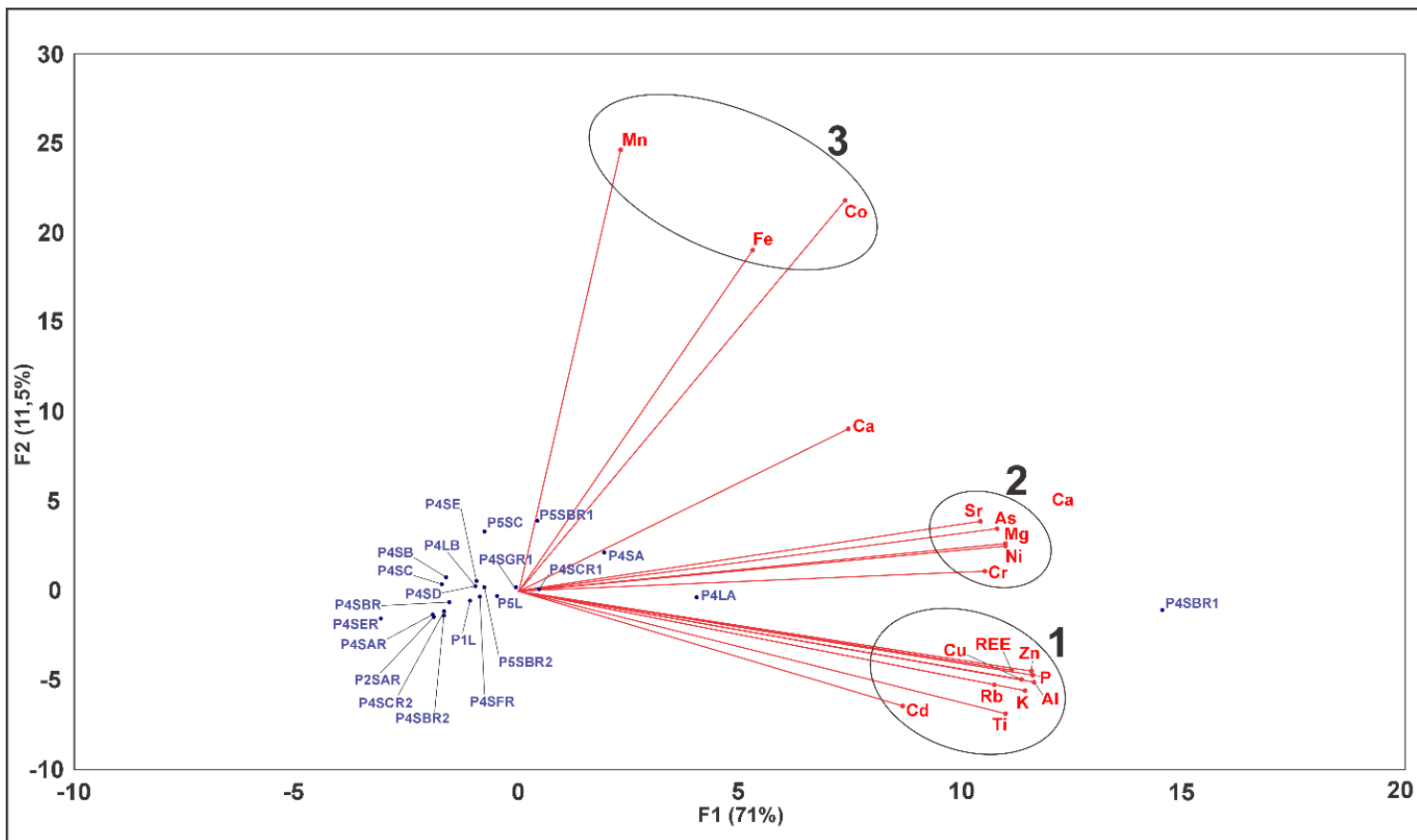
Figure 4

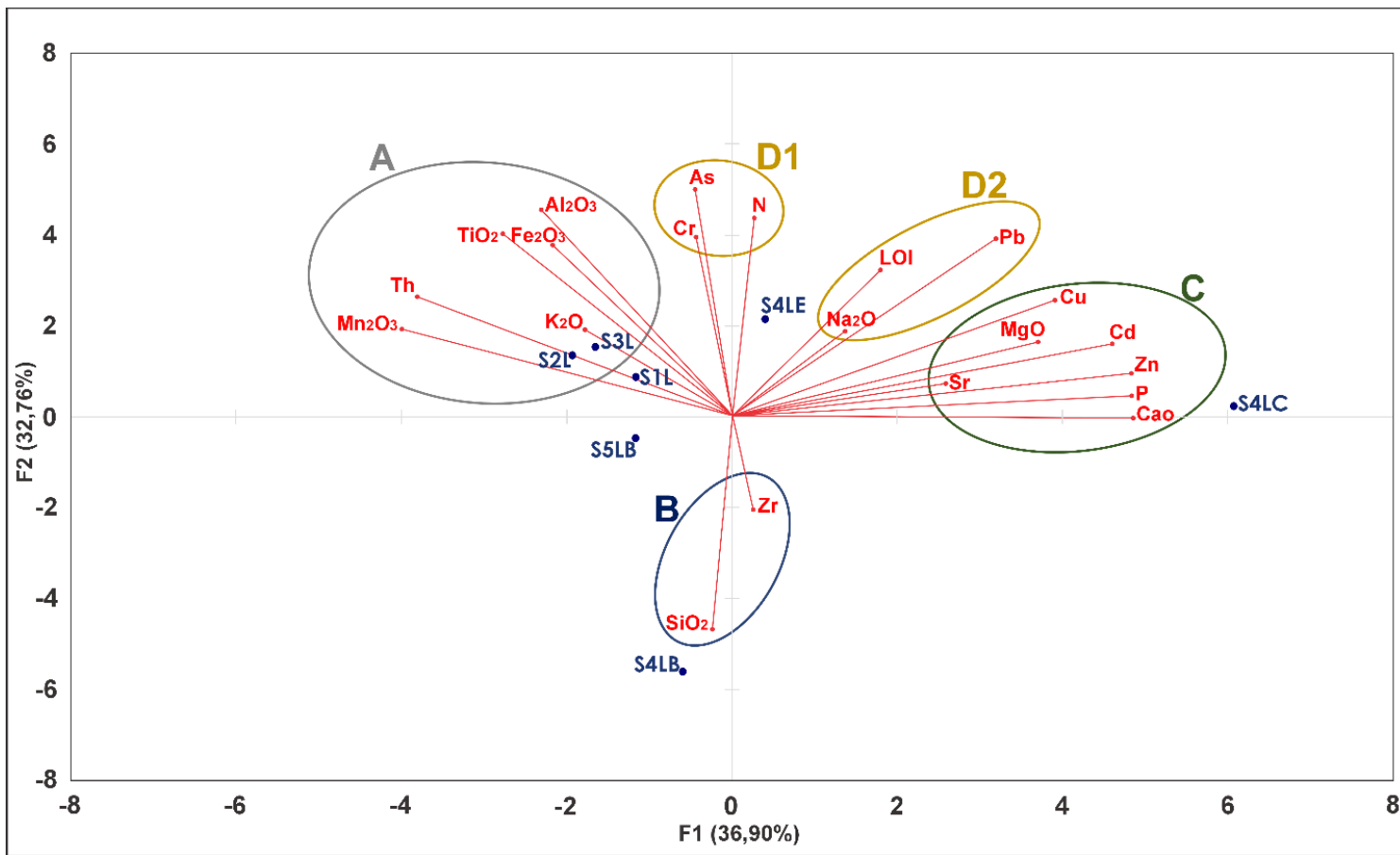Principal Component Analysis (PCA), of SPM total chemical composition normalized with Th.

Figure 5

Principal Component Analysis (PCA) of surficial sediments (depth 0-1cm) total Chemical composition.
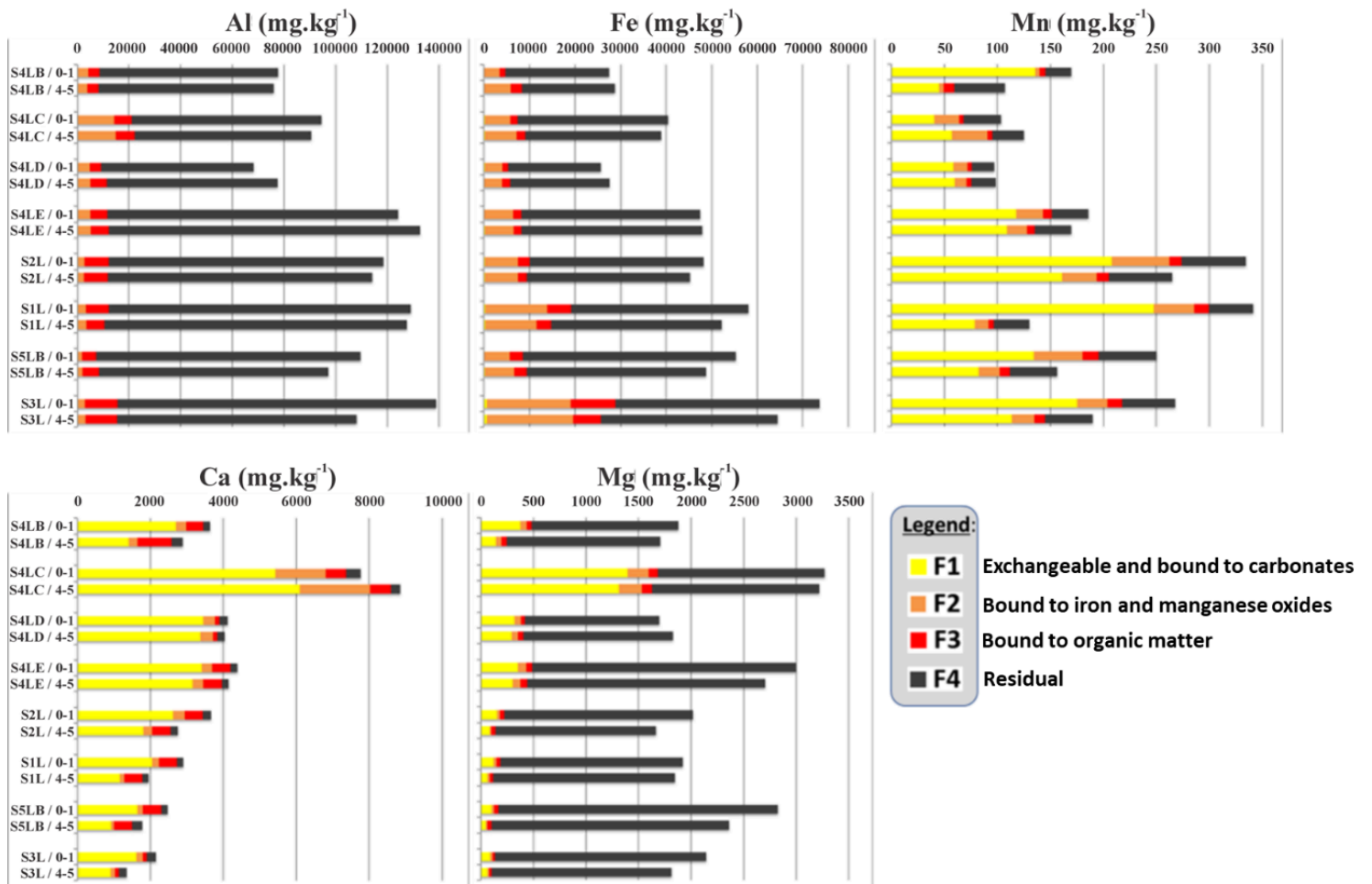
Figure 6

Geochemical partitioning of metals following sequential extraction (BCR protocol) in Lake Paranoá surface sediments.
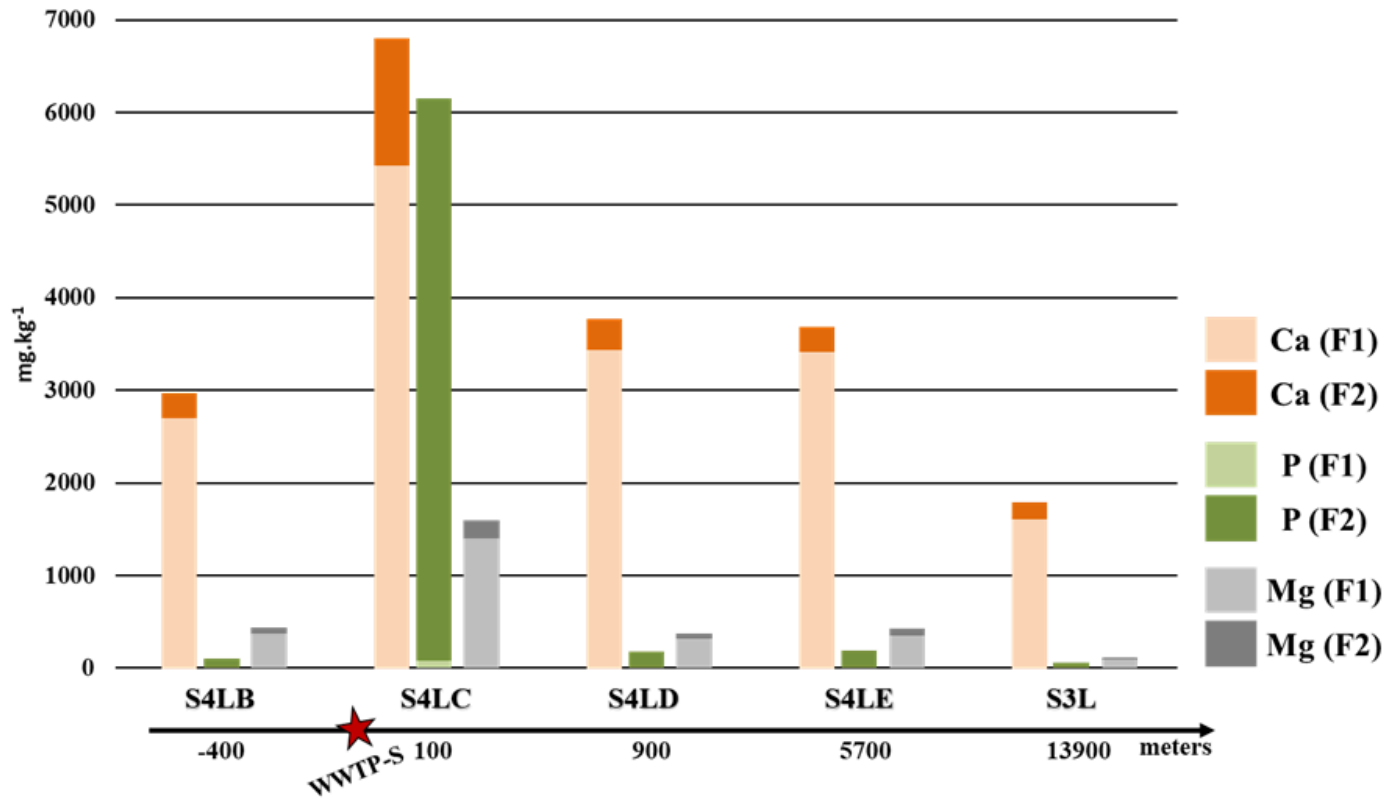
Figure 7

The Ca, P, and Mg distribution associated with F1 and F2 fraction (BCR results) in the Riacho Fundo Branch. * F1 and F2 fractions concentration in mg.kg^{-1} of the surficial sediments (0-1cm) collected at different points of the lake Paranoá. The red star relates to WWTP-S.
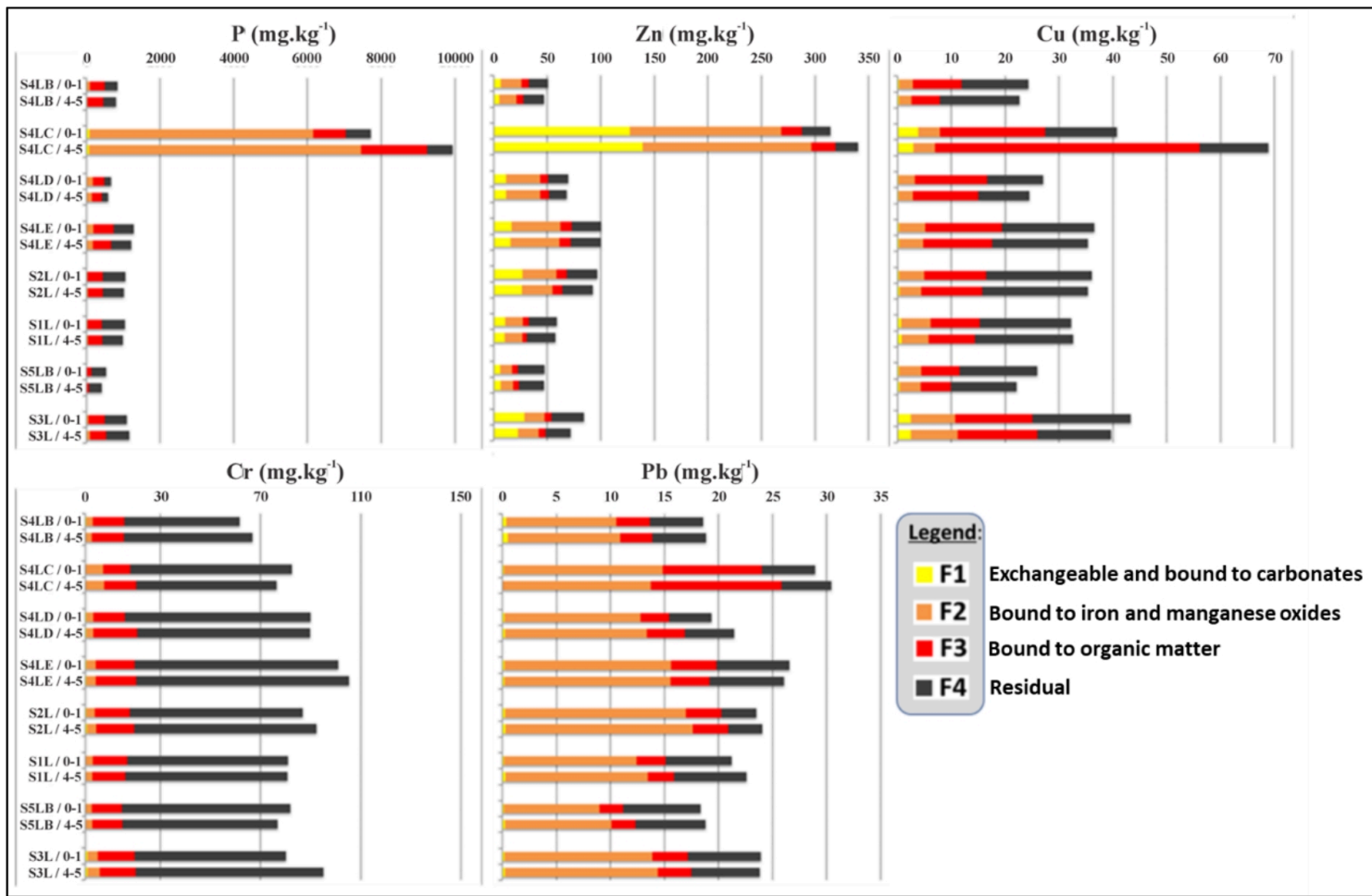
Figure 8

Geochemical partitioning of trace metals and phosphorus following sequential extraction (BCR protocol) in Lake Paranoá surface sediments.

Supplementary Files

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