

Geochemistry of the Upper Paraná River floodplain: study of the Garças Pond and Patos Pond

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Abstract The aim of this study was to investigate the temporal evolution of the supply of chemical elements to the Upper Paraná River floodplain and identify trends in the geochemistry of its drainage basin. The primary factor that regulates the supply of chemical elements of the Upper Paraná River floodplain is the flood pulse, which can be magnified by the El Niño—Southern Oscillation. Garças Pond is affected by agriculture, urbanization, discharge of industrial effluents and hydroelectric power production

activities. Patos Pond is affected by sugarcane burning, gold mining, agriculture and urbanization.

Keywords Heavy metals · ^{210}Pb · Lacustrine sediment · Paleolimnology

Introduction

The drainage basin of the Paraná River is the third largest in Brazil. It occupies approximately 10 % of Brazil and extends into the states of São Paulo, Paraná, Mato Grosso do Sul, Minas Gerais, Goiás, Santa Catarina and the Federal District. The basin contains 32 % of the country's population and 30 % of the water demand but provides only 7 % of the nation's available water supply. The primary sources of water quality degradation in the Paraná River basin are domestic sewage, of which only 44 % undergoes treatment before disposal in the watersheds [1]; improper disposal of solid waste; industrial pollution, particularly in headwaters such as the Upper Tietê River, which is home to 40 % of the industrial facilities in the country, and in the Piracicaba River basin, which is the location of the second largest industrial center in the country and the largest steel complex in Latin America; deforestation and improper soil management caused by agricultural activities; and hydroelectric power production. 60 % of the electrical power capacity of the nation is located in this drainage basin, much of which is supplied by the Itaipu Hydroelectric Plant, although there are 27 other hydroelectric plants in operation in the Upper Paraná River basin [2].

The area is located between the reservoirs of the Porto Primavera Hydroelectric Plant and the Itaipu Hydroelectric Plant in Guaíra (22°32'S–22°59'S and 53°08'W–53°40'W)

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at an elevation of 250 m [3] (Fig. 1). The study reach has been described as the last stretch of the Paraná River in Brazilian territory and has an ecosystem dominated by river-floodplain interactions [4, 5].

Because of its unique features, this reach of the Upper Paraná River floodplain has been the subject of many studies since 1980. These studies have focused on ecologic and taxonomic aspects including the various communities of phytoplankton [6, 7], zooplankton [8], periphyton [9, 10], benthic macroinvertebrates [11, 12], ichthyofauna [13, 14], aquatic macrophytes [15, 16] and birds [17, 18] and on the geomorphologic [19, 20] and hydrologic aspects of the area [21].

According to Thomaz et al. [22], the Upper Paraná River floodplain contains a wide variety of habitats and a great diversity of terrestrial and aquatic species and has a flood pulse that is believed to exert primary control on the community structure and functioning of the ecosystem. Although strongly altered by the operation of the hydroelectric plant reservoirs upstream [20], the hydrosedimentologic cycles are still affected by the climate phenomenon

of the El Niño—Southern Oscillation (ENSO), which increases precipitation in the drainage basin of the Upper Paraná River floodplain [23, 24]. The Upper Paraná River floodplain is characterized by annual flood pulses that are concentrated in the summer. The magnitude of the flood pulses is correlated with the amount of suspended matter. Stronger flood pulses result in more particles being carried into the river channel and adjacent systems, which leads to an increased sedimentation rate and increased input of nutrients and contaminants [20].

Studies have been performed in this area with the goal of assessing the concentration of chemical elements in the surface sediments [25, 26]. These studies document conditions spanning 3 years and may be considered short-term studies. Reference (background) values and an understanding of the supply of chemical elements resulting from the evolution of anthropic activities in the drainage basin have been obtained using geochronologic techniques. Among these techniques, measurements of the natural radionuclide ^{210}Pb were important for dating recent deposits, i.e., those as much as 100 years old [27, 28].

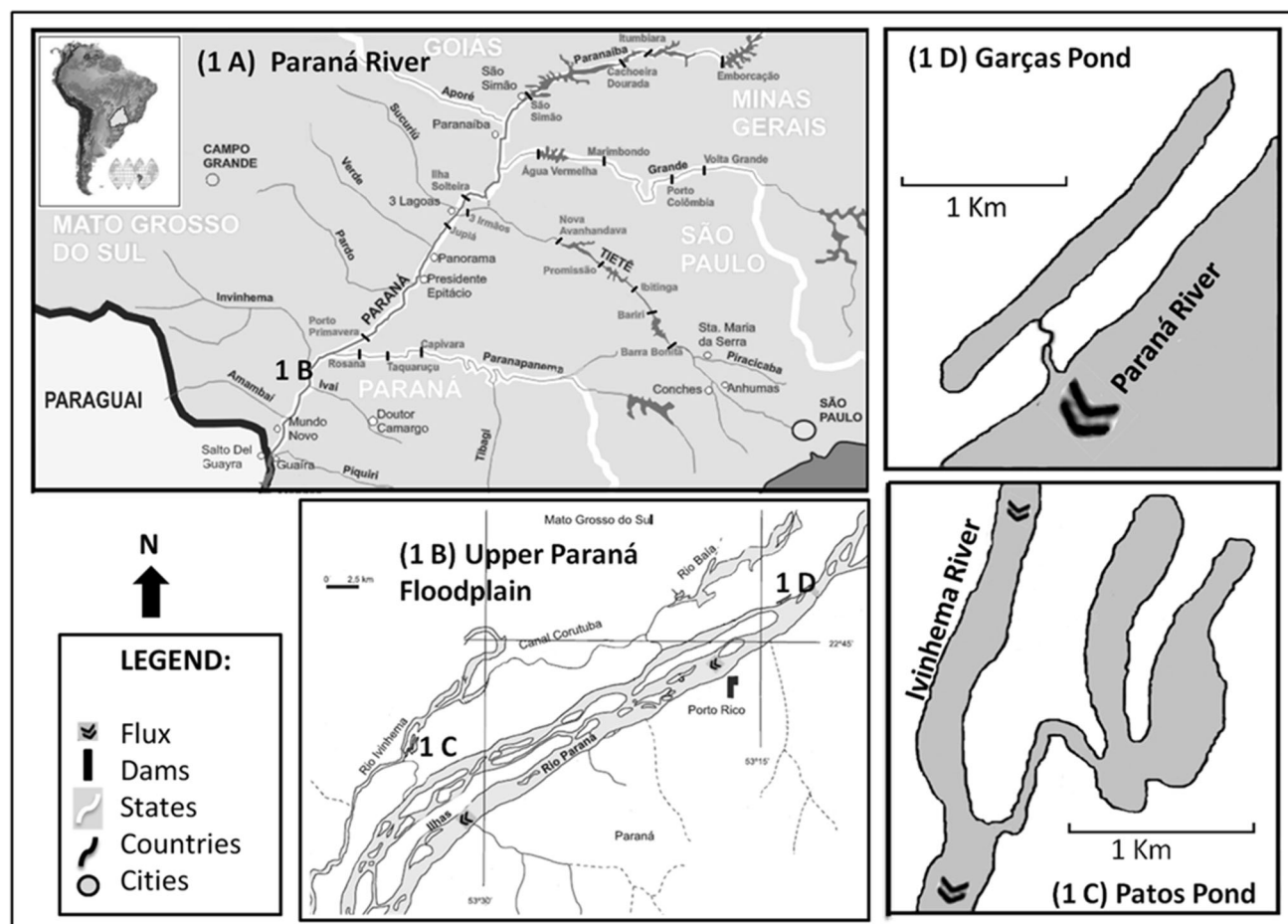


Fig. 1 Location of the study area. 1 A: Drainage basin of the Upper Paraná River; 1 B: The study reach floodplain is defined by the Paraná, Baía and Lower Invinhema rivers.; 1 D: Garças Pond; 1 C: Patos Pond

The radionuclide ^{210}Pb has been used in studies of the sedimentation dynamics, nutrient supply and environments contaminants in lakes [29, 30], seas [31, 32], estuaries [33] and floodplains [34, 35]. The method of calculating the age of a sediment as a function of its depth depends of the sedimentation model of the study area. The constant initial concentration (CIC) method is recommended in environments where the atmospheric and sediment ^{210}Pb fluxes are constant; the constant rate of supply (CRS) method is recommended in environments where the atmospheric ^{210}Pb flux is constant but the sediment supply is not; the constant initial reach clay activity, unknown sedimentation (CIRCAUS) model is used in heterogeneous environments where the other methods do not apply [36].

In floodplains, the sedimentation rate regulates the accumulation of nutrients, and contaminants are associated with the sediments in environments that are seasonally flooded by flood pulses. The enrichment in surface sediments and potential remobilization of chemicals to the system are known consequences of this phenomenon [37–39]. Floodplains are unique systems that differ from one another in terms of their climates and geomorphologic and anthropogenic features.

This study fills a gap in knowledge regarding the geochemistry of recent sedimentary records in the Upper Paraná River floodplain and temporal variability in the supply of chemical elements. The aim of the study was to investigate the temporal evolution of the concentrations of chemical elements in the sediment and to identify historical trends in the drainage basin of the Upper Paraná River floodplain.

Experimental

Study area

According to Stevaux et al. [20] 811 km of the Paraná River is located in Brazil, the stretch corresponding to the Upper Paraná River floodplain flows in its natural channel for a distance of only 200 km. The climate of the Upper Paraná River floodplain is classified as Cfa in the Köppen system, i.e., tropical-subtropical; the average annual temperature is 22 °C, and the average annual rainfall is 1,500 mm. The native vegetation of the region is seasonal semideciduous forest, which has been reduced to small fragments near the Paraná River and its islands. The floodplain landscape is a complex mosaic that includes forest remnants, stretches of riparian forest, swamp forests, buriti orchards, shrub vegetation, grasslands and wetlands. In addition to the segments of large rivers such as the Paraná, Ivinhema and Baía, there are floodplain lakes,

secondary channels, more than 100 islands and sandy and marshy beaches in the region [40].

Sediment cores were extracted from Garças Pond (GP) and Patos Pond (PP) (Fig. 1).

GP (22°43'30.7"S and 53°18'15.5"W) is located on the right side of the Paraná River, to which it is permanently connected by a channel. The pond is approximately 150 m wide and 2.0 km long and has an area of 0.3 km² and an average depth of 2.5 m [41]. PP (22°49'30.64"S and 53°33'12"W) is located on the left bank of the Ivinhema River, to which it is permanently connected by a channel. This pond has an area of 1.14 km² (0.65 km wide and 1.75 km long) and a depth between 2.8 and 4.8 m [42].

Sampling

The sediment cores were collected in October 2011. The cores were extracted from the deepest areas of the ponds because the fine particles (silt/clay) that adsorb the chemical elements are deposited in such areas. In the deepest area of each pond (depths of 3.5 and 4.5 m in GP and PP, respectively), a square meter was delineated from which six cores were collected. The samples were collected using polyvinyl chloride (PVC) hand corers that were 80 mm in diameter and 1.2 m long. Divers inserted the hand corers vertically into the sediment and then carefully extracted them. To minimize deformation of the cores, the bottom end was sealed with a stopper immediately after the hand corers were extracted.

The six sediment cores taken at the GP and PP were sliced at uniform intervals of 2.0 and 2.2 cm, respectively, to obtain sub-samples. The sub-samples were placed in expanded polystyrene trays and dried at room temperature while protected from sunlight to avoid the loss of volatile chemical elements. After drying, the sub-samples were weighed.

Chronological analysis

The chronological analysis of the sediment cores using the ^{210}Pb method was performed at the Laboratory of Environmental Radiometry of the Institute of Nuclear Energy Research.

The measurements of the radionuclides ^{226}Ra and ^{210}Pb were used to determine the dates of deposition of each slice of the sediment cores collected from the ponds. The radionuclide activity concentration was measured every 4 cm from the first slice of each profile.

All the samples previously dried at 60 °C were passed through a 63- μm sieve and digested in concentrated HNO_3 , 40 % HF and 30 % H_2O_2 for the radiochemical determination. The procedure included the initial precipitation of ^{226}Ra and ^{210}Pb with 3 M H_2SO_4 , dissolution of the

precipitate with nitrilotriacetic acid at an alkaline pH, precipitation of $\text{Ba}^{(226}\text{Ra})\text{SO}_4$ in a solution of ammonium sulfate and precipitation of $^{210}\text{PbCrO}_4$ in a solution of sodium chromate. The ^{226}Ra concentration was determined by gross alpha counting of the $\text{Ba}^{(226}\text{Ra})\text{SO}_4$ precipitate, and ^{210}Pb was analyzed based on its decay product ^{210}Bi by measuring the gross beta activity of the $^{210}\text{PbCrO}_4$ precipitate. The chemical yields of both radionuclides were determined by a gravimetric analysis of the precipitate, and the ages were calculated using the constant rate supply (CRS) model [43]. We assumed constant accumulation of ^{210}Pb because the results that we obtained for its concentration decreased exponentially, except for the results associated with flood events. The same occurred in previous work performed for us in the Brazilian wetland of Pantanal [29].

The method detection limits were 2.2 ± 0.2 mBq kg^{-1} for ^{226}Ra and 4.9 ± 0.4 mBq kg^{-1} for ^{210}Pb . For validation of the procedures, the reference materials Pacific Ocean Sediment 367 and Irish Sea Sediment 385, both from IAEA, were analyzed, and the results were in agreement with the certified values; the relative standard deviation and relative error for ^{226}Ra were 16.1 and 10.3 %, respectively, and the relative standard deviation and relative error for ^{210}Pb were 13.5 and 1.1 %, respectively.

Analysis for chemical elements

The sediment samples were sieved through a PVC and nylon sieve with 63- μm mesh, and the analyses for the chemical elements were performed on the silt/clay (<63- μm) fraction as recommended by the World Health Organization [44].

The concentrations of calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb) and zinc (Zn) were determined by flame atomic absorption spectrophotometry (FLAA). The opening of the samples and extraction of metals were conducted by wet digestion in accordance with USEPA method 3050B [45], which is indicated for the digestion of sediment and organic mud. The method detection limit for the analyses for chemical element concentrations was 1 ppm.

The analysis for mercury (Hg) was conducted by AAS based on the Zeeman differential coupled with a pyrolysis reactor. The principle of this analysis is based on the thermal destruction of the sample followed by the measurement of Hg vapor. The method detection limit for the analyses of the solid samples was 5 ppb [46].

The certified reference materials IAEA 356 and IAEA 433 (marine sediment) were used to calculate the accuracy of the elemental analyses. Only analyses that displayed an accuracy between 93 and 107 % for the element recovery relative to the reference samples were accepted.

Data analysis

The data were first analyzed using descriptive statistics for measures of central tendency. Subsequently, the concentration of each trace element over time was represented and evaluated using the statistical method of the Shewhart control chart for individual variables. In samplings of more than 25 points ($n \geq 25$), the data can be considered as having a normal distribution for the application of the Shewhart control chart in accordance with the central limit theorem [47]. The upper control limit (UCL) and lower control limit (LCL) for each element were calculated using Eqs. (1) and (2), respectively [47].

$$\text{UCL} = \bar{X} + 3 \times \left(\frac{\overline{\text{MR}}}{d_2} \right) \quad (1)$$

$$\text{LCL} = \bar{X} - 3 \times \left(\frac{\overline{\text{MR}}}{d_2} \right) \quad (2)$$

Where, \bar{X} represents the data mean; $\overline{\text{MR}}$ represents the mean moving range of the data; and d_2 represents the constant used for the moving range of $n = 2$ ($d_2 = 1.128$).

Results

Figure 2 shows the age dates of the slices from both cores (GP and PP), which were estimated using the ^{210}Pb radioisotope geochronology method. The lowermost slice from the GP core, which was at a depth of 76 cm, was deposited in 1912 (age of 99 years) and yielded a sedimentation rate of 7.7 mm year^{-1} (2.66 $\text{kg m}^{-2} \text{year}^{-1}$) in the deepest area of the lake. The lowermost slice of the PP core, which was at a depth of 84 cm, was deposited in 1876 (age of 135 years) and yielded a sedimentation rate of 6 mm year^{-1} (1.94 $\text{kg m}^{-2} \text{year}^{-1}$) in the deepest area of the pond.

The minimum, mean and maximum concentrations (ppm) of the chemical elements in GP and PP are shown in Table 1 along with reference values for the Tietê River (RVTR) as proposed by Nascimento [48], global geological reference levels (GGRLs) compiled by Turekian and Wedepohl [49], and background levels that were estimated from the concentrations of metals in the fractions deposited before 1931. The background levels were estimated based on the mean and standard deviation of the concentrations of the elements deposited before 1931. The GP core contained four samples that had been deposited during this period, and the PP core contained 14. The Cd concentration in the GP cores was below the method detection limit (1 ppm).

The concentrations of the chemical elements in the GP and PP cores as a function of time are shown in Figs. 3 and 4, respectively. At GP, the concentrations of Ca and

Fig. 2 Formation date of the slices of sediment cores estimated by the ²¹⁰Pb method. A: Garças Pond, B: Patos Pond

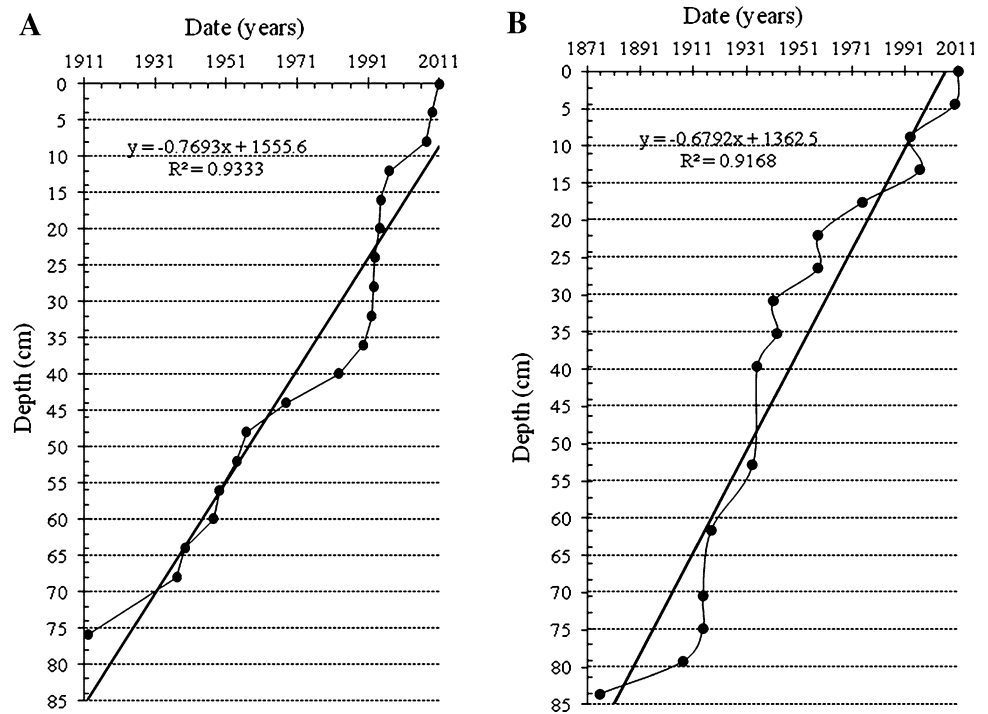


Table 1 Minimum, mean and maximum concentrations of the chemical elements (ppm) at the Patos Pond and Garças Pond

Elements	Garças Pond				Patos Pond				RVTR	GGRL
	Min	Mean	Max	Back	Min	Mean	Max	Back		
Cd	nd	nd	nd	nd	0.64	1.18	1.72	1.40 ± 0.20	0.22 ± 0.04	0.3
Co	19.70	22.72	33.45	27.60 ± 5	36.00	58.46	83.00	71.60 ± 8.80	22.00 ± 4	19
Cr	24.13	31.27	51.51	36.30 ± 3.2	23.00	31.36	37.00	30.30 ± 3.90	76.00 ± 64	90
Cu	37.82	51.81	79.12	49.60 ± 2.8	67.00	87.49	109.00	88.40 ± 10.00	52.00 ± 44	45
Hg	0.036	0.055	0.067	0.05 ± 0.01	0.025	0.078	0.125	0.05 ± 0.01	0.11 ± 0.04	0.4
Mn	254.00	325.60	528.00	475.00 ± 77	163.00	307.00	509.00	333.50 ± 82.00	*	850
Ni	12.00	20.44	31.00	15.00 ± 2.5	20.50	32.14	49.00	34.90 ± 4.80	39.00 ± 17	68
Pb	17.00	22.58	39.00	23.40 ± 2.5	7.50	15.37	22.40	17.70 ± 3.00	42.00 ± 15	20
Zn	57.00	63.56	89.00	62.70 ± 3.4	66.00	88.49	117.00	96.40 ± 8.80	90.00 ± 22	95
Ca	3.71	19.18	48.75	19.20 ± 9.5	11.00	31.37	60.00	25.80 ± 3.50	*	22,100
K	2069.00	2517.00	3998.00	2647.00 ± 199	610.00	1063.00	1280.00	1083.00 ± 177	*	26,600
Mg	2818.00	3361.00	4268.00	3403.00 ± 187	1898.00	2475.00	3103.00	2332.00 ± 272	*	15,000
Na	195.00	353.00	747.00	249.00 ± 9	409.00	584.80	791.00	600.00 ± 65	*	9600

RVTR reference values for the Tietê River (ppm) proposed by Nascimento [48] along with the standard deviation, *GGRL* global geological reference level (ppm) values compiled by Turekaian and Wedepohl [49]

* Nonexistent value, *nd* not detected, *Min* minimum; *Max* maximum; *Back* reference values were estimated from the mean and standard deviation of the concentrations of the elements sedimented before 1931

Ni increased over time, whereas the concentrations of Co, Cr and Mn decreased. At PP, the concentration of Ca and Hg increased over time, whereas the concentrations of Cd, Co, Ni and Zn decreased. The concentrations of other elements in both ponds showed no clear trend and remained close to the overall mean except for a few outliers.

Discussion

The sediment cores from both ponds (Fig. 2) were younger than the recommended age limit for analysis using the ²¹⁰Pb radioisotope, which is a maximum of 150 years [27, 28]. The cores from both ponds contained sediments dating from the Brazilian pre-industrial period before 1939.

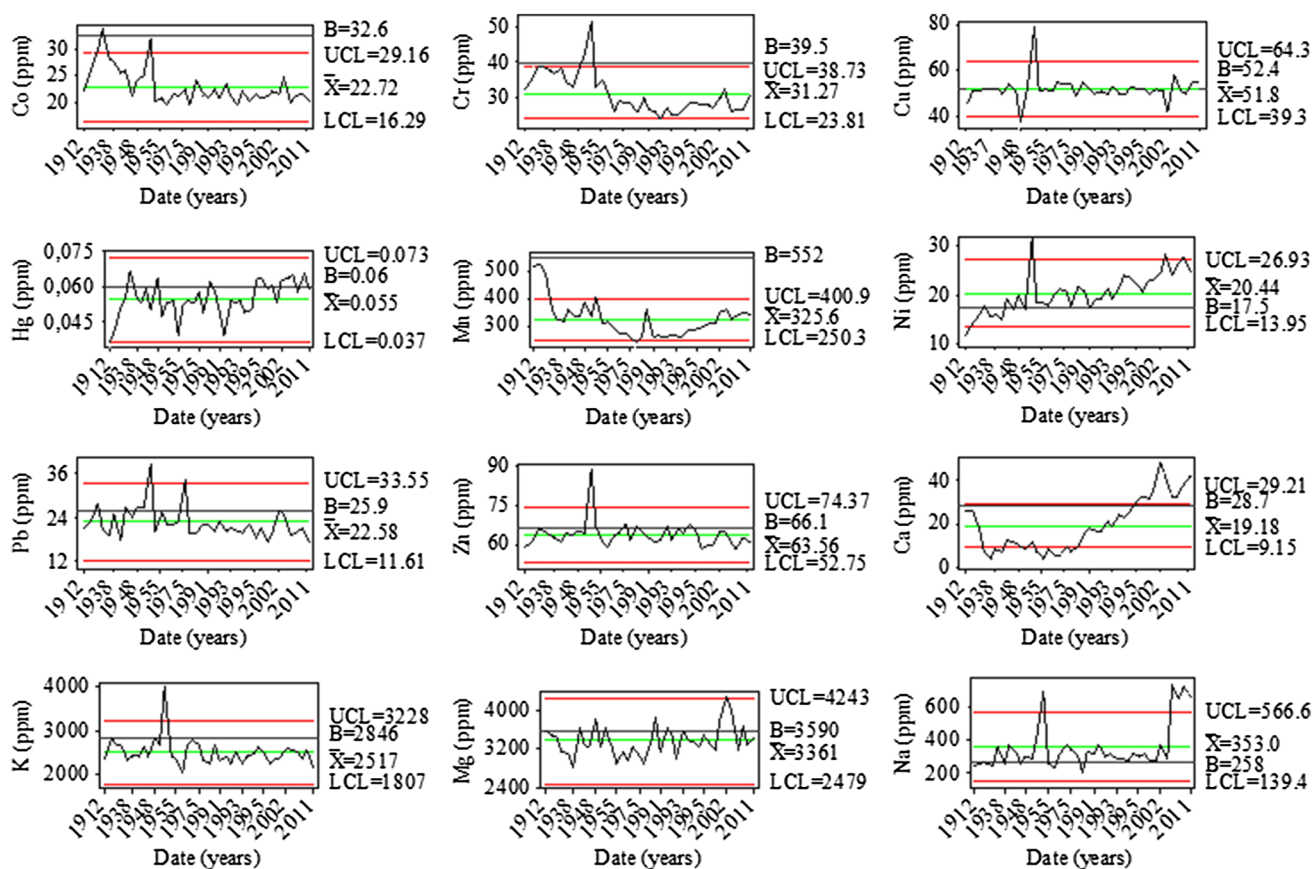


Fig. 3 Shewhart control chart for individual variables in the time series of the concentration of chemical elements at Garças Pond

The Brazilian industrial period started after the beginning of World War II because the industries in European countries had been destroyed and these countries were in need of imported manufactured goods from other countries such as Brazil. Thus, the concentrations in these samples can be considered to be background levels that predate anthropic activities [50]

The sedimentation rates obtained from the two ponds, i.e., 7.7 mm year^{-1} at GP and 6 mm year^{-1} at PP (Fig. 2), are consistent with the study of Fávoro et al. [29], who reported a sedimentation rate of 6.1 mm year^{-1} at Salina do Meio Pond (0.126 km^2 area) in the Brazilian Pantanal, whose environment is similar to that of the Upper Paraná River floodplain. However, other studies in the Brazilian Pantanal yielded lower sedimentation rates. Godoy et al. [51] reported sedimentation rates of 4.1 and 3.7 mm year^{-1} in two lakes of the Taquari River, and McGlue et al. [52] calculated a sedimentation rate of 2.4 mm year^{-1} in Gaíva Lake (area of 80 km^2). In general, sedimentation rates are lower in larger lakes because such lakes are less affected by particle entrainment from the margins, although this is only one of the factors that control the sedimentation rate.

High sedimentation rates can be detrimental to aquatic environments: higher sedimentation rates cause a higher contaminant load to enter the system along with the sediment. Consequently, chemical elements can become bioavailable through biogeochemical processes and can affect the aquatic biota [53].

The minimum and maximum concentrations of the chemical elements in the sediment from the GP and PP are presented in Table 1 along with the RVTR [48], GGRL [49] and the reference values estimated based on the fractions deposited before 1931.

The concentrations of Ca, Cd, Cr, Hg, K, Mg, Mn, Na, Ni, Pb and Zn in the GP sediment did not exceed the GGRL and RVTR reference values (Table 1). In the PP sediment, the concentrations of Ca, Cr, Hg, K, Mg, Mn, Na, Ni and Pb did not exceed the reference values.

In the GP sediment, the Co concentrations exceeded the RVTR ($22 \pm 4 \text{ ppm}$) and GGRL (19 ppm) reference values (Table 1). The highest concentrations were recorded during the period of 1912–1954, and the lowest concentrations were recorded during the period of 1997–2011.

The concentrations of the remaining chemical elements (Ca, Cd, Co, Cr, Cu, Hg, K, Mg, Mn, Na, Ni, Pb and Zn) at

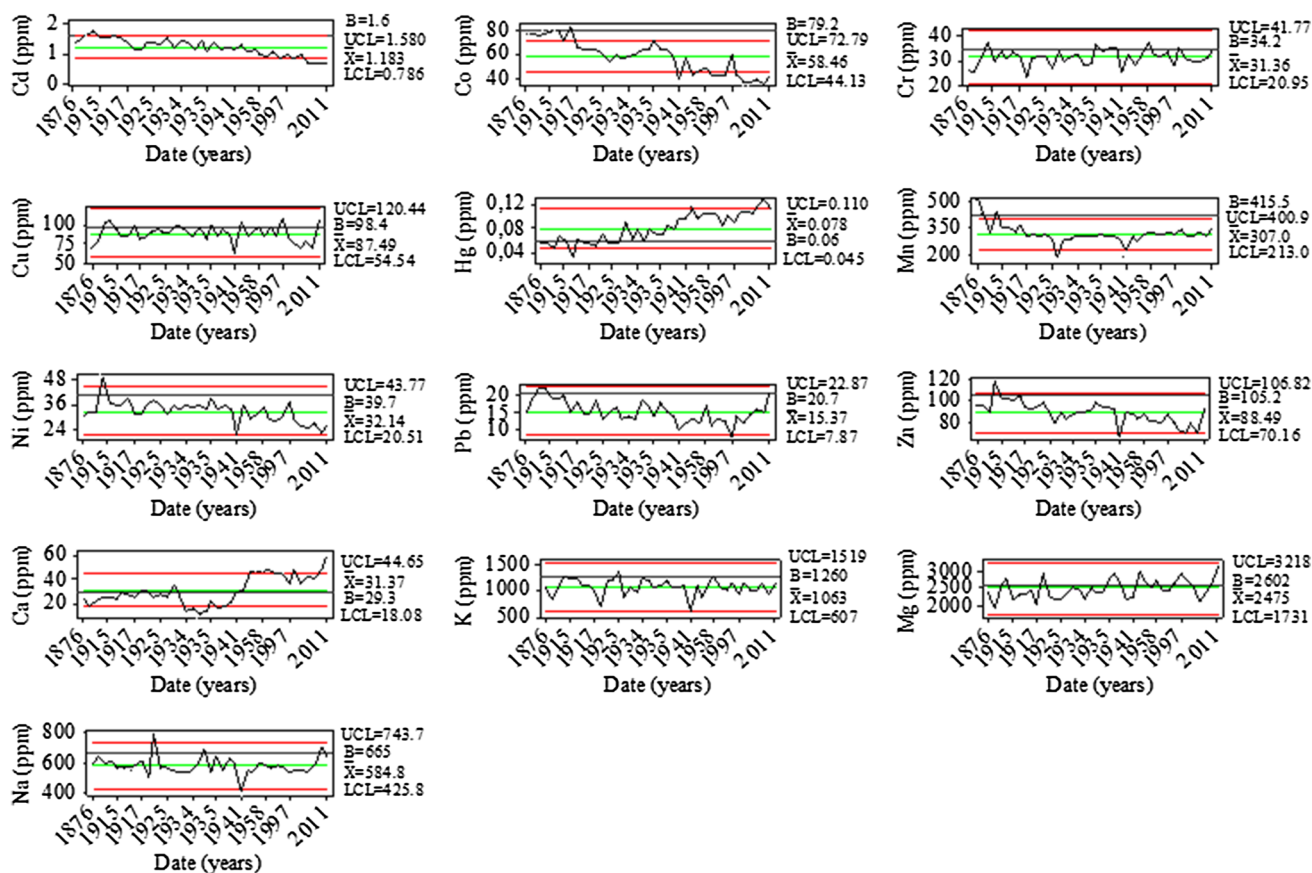


Fig. 4 Shewhart control chart for individual variables in the time series of the concentration of chemical elements at Patos Pond

GP did not exceed the RVTR reference value; however, the Cu and Pb concentrations exceeded the GGRL reference value (Table 1). The Pb concentrations were highly variable during the period of 1912–1980, and the variability decreased during the period of 1980–2011 and displayed a decreasing trend over time. The Cu concentrations fluctuated little around the overall mean except for a few outliers.

At PP, the Cd concentrations in the sediment exceeded the RVTR (0.22 ppm) and GGRL (0.30 ppm) reference values (Table 1). The highest Cd concentrations were recorded during the period of 1915–1917, and the lowest concentrations were recorded during the period of 1997–2011. The Co concentrations exceeded the RVTR (22 ± 4 ppm) and GGRL (19 ppm) reference values. The highest Co concentrations were recorded during the period of 1876–1917, and the lowest concentrations were recorded during the period of 1997–2011. The maximum concentration of Zn was recorded in 1915 (117 ppm), and this was the only sample in which the concentration exceeded the RVTR (90 ± 22 ppm) and GGRL (95 ppm) reference values. The Cu concentrations exceeded the GGRL reference value (45 ppm). The lowest Cu concentrations did not exceed the RVTR reference value (52 ± 44 ppm). The

maximum concentrations of Cd, Co and Zn were recorded during the period of 1876–1917. Anthropogenic activity did not cause these high concentrations because the drainage basin of the Ivinhema River was minimally populated at that time. The variation in Cu concentrations over time displayed a fluctuation around the mean without any clear trend, which indicates that anthropic factors did not affect the Cu concentrations of the PP sediment.

The fluctuations in the concentrations of the chemical elements in the sediments below both ponds were caused by flood pulses. When a flood pulse occurs, the amount of particulate matter entering the system increases. This sediment pulse is primarily a result of particle entrainment by runoff, which enriches the system with nutrients and contaminants [4]. Another factor that must be considered is the El Niño climate phenomenon, which causes increased rainfall in the drainage basin of the Paraná River (GP) [23, 24] and can increase the volume of the flood pulses.

More recently, the Ca concentrations at GP and PP were above the reference value, i.e., the mean concentration of Ca in the slices deposited before 1931 below both ponds (Figs. 3 and 4, respectively). The increase in Ca concentration over time at GP and PP is related to agriculture and

urbanization. Ca is used in agriculture to reduce soil acidity, and approximately 80 % of the drainage area of both ponds is used for agricultural activities [2]. Urbanization also contributed to the increase in the concentration of Ca because Ca is used in construction for the preparation of mortar. The population of Brazil has quadrupled during the previous 65 years, and in 1950 more than 60 % of the population lived in rural areas. Brazil's rural population percentage decreased to 16 % in 2010, and the rural percentage in the drainage basin is even lower: 7 % [54]. This trend was accompanied by an expansion of the construction industry and, consequently, the inappropriate disposal of construction waste.

More recently, the Ni concentrations at GP exceeded the reference value, i.e., the mean concentration of Ni in the slices deposited before 1931 at the pond (Fig. 3). The increase in the Ni concentration at GP is primarily associated with industrialization. Ni is primarily used in the manufacturing of stainless steel and other metal alloys and in casting. The largest city and largest industrial park (São Paulo) and the largest steel complex (Piracicaba) in Latin America are located in the drainage basin of the Paraná River [2]. Improper disposal of industrial waste, particularly waste from electroplating and porcelain enameling and from the production of paints, batteries and copper sulfate, explains the increase in the concentration of Ni [55].

Recently, the concentrations of Hg at PP were above the reference value, i.e., the mean pre-1931 concentration of Hg (Fig. 4). The concentration of Hg at PP displayed a gradual increase over time that is associated with the burning of sugarcane. According to Friedli et al. [56], 13 % of global Hg emissions to the atmosphere are from the burning of biomass. In the Ivinhema River basin, 175,000 hectares are planted with sugarcane, which is equivalent to approximately 4 % of the total basin area [57]. Sugarcane burning is the predominant technique to facilitate manual harvesting. Gold mining also contributes to the increased Hg concentrations. Although there are no reports of mining activity or illegal mines in the Ivinhema River basin, the Hg levels in the youngest samples (0.12 ppm) were similar to those in sediment where there is gold mining activity, such as in the northern Brazilian Pantanal region (0.18 ppm) [58].

The concentrations of Co, Cr and Mn in the GP sediment (Fig. 3) decreased over time due to oligotrophication of the Paraná Upper River floodplain in the study area. Oligotrophication is caused by the extensive installation of hydroelectric dams across the hydrographic area. Such dams sequester sediment along with nutrients and chemical elements [56]. Typically, the dams sequester only the coarse fraction of the sediment and allow the finer fraction, which is rich in contaminants, to flow downstream of the

dam. However, because of the large number of dams in the Paraná River basin, a portion of the fine fraction is stored. In the study reach, the suspended sediment concentration decreased from 35 mg L⁻¹ in the 1980s to 0.5 mg L⁻¹ after the raising of the last large dam in the basin (approximately 40 km upstream of the ponds under investigation) [20]. In addition, to supply the cities of São Paulo and Piracicaba, the two most industrialized areas of the basin, there are ten hydroelectric dams, which collectively hold approximately 600 km of backwater along the river. This backwater is sufficiently extensive to settle a portion of the fine fraction from the suspended sediment. Another factor that contributes to the decrease in the concentrations of the elements is an increase in the density of aquatic macrophytes, which adsorb nutrients and chemical elements from the medium. Mishra et al. [59] reported concentrations of trace elements that were 10–15 times greater in aquatic macrophytes than in the sediment. According to Thomaz et al. [60], submerged macrophytes were rarely observed in early studies of the floodplain but were more frequently observed after 1995 in lakes linked to the Upper Paraná River, such as GP.

The decline in the concentrations of Cd, Co, Ni and Zn in the PP sediment (Fig. 4) is associated with the increase in density of aquatic macrophytes in the environment. PP supports a diverse population of aquatic macrophytes, primarily floating macrophytes [61], which absorb nutrients and chemical elements from the medium. Furthermore, PP is connected to the Ivinhema River by a channel. The Ivinhema River's main channel may be shifting farther from the PP due to migration of the river meanders. Thus, it is possible that these elements are being deposited in the connection channel before reaching PP because they can be linked to the easily deposited particles. To confirm this hypothesis, it is necessary to perform a speciation analysis of these elements.

Conclusions

The primary factor regulating the supply of chemical elements in the Upper Paraná River floodplain is flood pulses, which may increase in size due to the El Niño—Southern Oscillation (ENSO).

The increase in agricultural area, urbanization and discharge of industrial effluents resulted in increases in the concentrations of calcium and nickel in the sediment of Garças Pond. Oligotrophication due to dams upstream of the floodplain and adsorption by aquatic macrophytes resulted in a decrease in the concentrations of cobalt, chromium and manganese in the Garças Pond sediment.

The burning of sugarcane, gold mining and increases in agricultural areas and urbanization resulted in increases in

the concentrations of mercury and calcium in the Patos Pond sediment. The adsorption by aquatic macrophytes and the migration of river meanders resulted in the decrease in the concentrations of cadmium, cobalt, nickel and zinc in the PP sediments.

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