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Temporal variation and risk assessment of heavy metals and nutrients from water and sediment in a stormwater pond, Brazil

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ABSTRACT

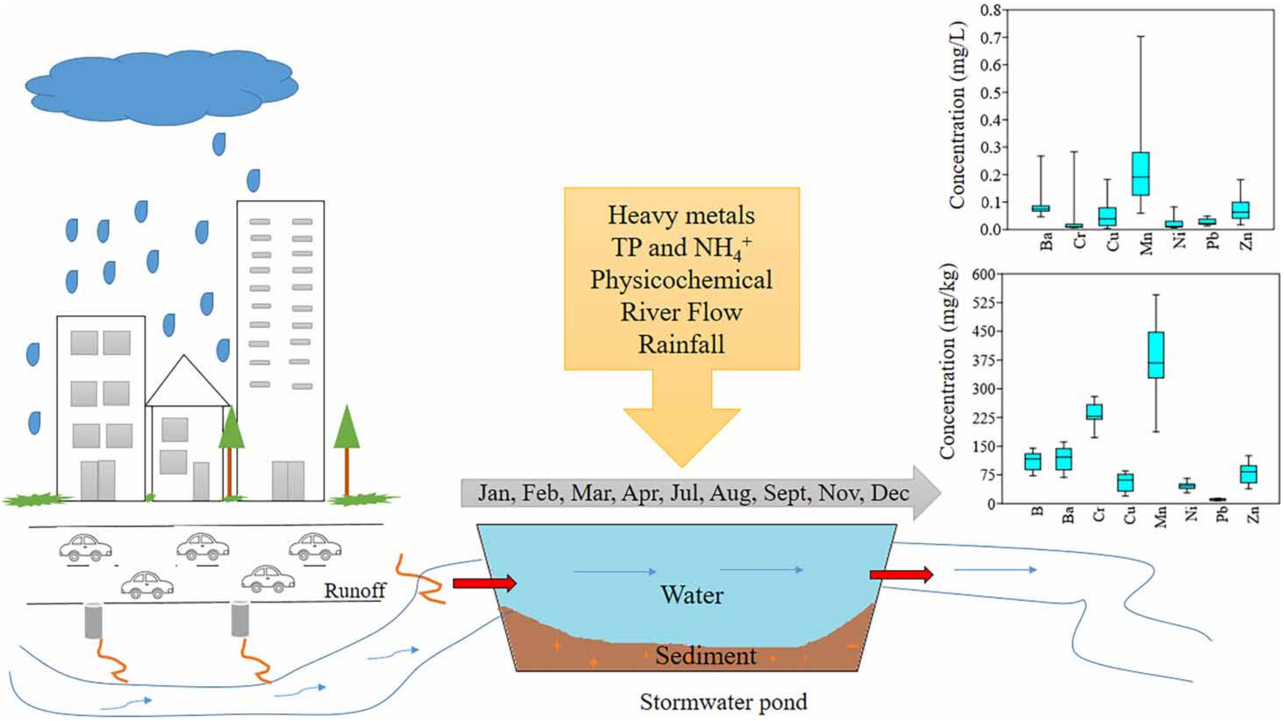
Urban watercourses are under pressure owing to the inflow of environmental pollutants from stormwater and effluent. The concentrations of heavy metals, ammoniacal nitrogen, total phosphorus (TP), and physicochemical parameters were monitored in a sediment pond in the Brazilian Midwest. The correlation between the variables and the degree of sediment contamination was verified using the Geoaccumulation Index (Igeo), Contamination Factor (CF), and Pollutant Load Index (PLI). The general concentrations of the metals were in the order Mn > B > Ba > Zn > Cu > Cr > Pb > Ni in the water and Mn > Cr > Ba ≥ B > Zn > Cu > Ni > Pb in the sediment. The concentrations of Ba, Cr, Cu, Mn, Ni, Pb, and TP in the water exceeded the regulatory limits at least one time. The mean concentrations of Cr, Cu, and Ni in the sediment samples were 6.32, 1.63, and 2.61 higher than standard values. The applied geochemical indices indicated a moderate to a very high degree of sediment contamination, suggesting the anthropogenic origin of Cr, Cu, and Ni. Significant Pearson correlations were observed between turbidity and total suspended solids (TSS), Ba, Cr, Mn, Zn, and TP. Ponds and urban lakes require maintenance or may become a source of environmental pollutants.

Key words: heavy metals, risk assessment, sediment ponds, sediment quality, stormwater, urban river basins

HIGHLIGHTS

- We assessed annual water and sediment quality of stormwater ponds.
- Water, TF showed a strong correlation with turbidity, TSS, Ba, Cr, Mn, and Zn.
- Sediment, Cr, Cu, and Ni were 6.32, 1.63, and 2.61 higher than the background values.
- Sediment, TF concentrations during the dry season exceeded legislative limits by an average of 1.73 times.
- Cu and Zn were not correlated with precipitation.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Urban growth is a global trend that causes changes to hydro-sedimentology processes that challenge water resource management (Taylor & Owens 2009; Wijesiri *et al.* 2019). Typical effects of urbanization are the decrease in vegetation space and water infiltration. The urban land use given by paved surfaces also induce the increase of surface runoff, erosive processes, effluent discharge, and river channeling. These factors cause flood control and pollution problems in urban basins (House *et al.* 1993; Islam *et al.* 2015; Wang *et al.* 2021).

The quality of watercourses is affected by natural and anthropogenic sources, such as atmospheric deposition, stormwater runoff, geological processes, land use, distribution of precipitation, and discharge of industrial effluents and domestic sewage (Sakson *et al.* 2018; Hamid *et al.* 2020; Charters *et al.* 2021). In urban areas, stormwater runoff is appointed as the main source of suspended solids and heavy metal (HM) pollution (Merchan *et al.* 2014; Behbahani *et al.* 2022) because most of the pollutants are washed off from the catchment and transported to the rivers during floods (Rügner *et al.* 2019; Costa *et al.* 2021). These pollutants came mostly from traffic vehicles (e.g. exhaust emissions, tire wear and motor oil), industrial activities and surface degradations (Egodawatta 2007; Jeong *et al.* 2020).

The suspended sediments are an important index in stormwater. They accumulate in water channels and lakes, reduce the water storage capacity contributing to flooding (Morales-Marín *et al.* 2017), and adsorb various pollutants (Ho & Burgess 2013; Yi *et al.* 2015). The land use (commercial, residential or industrial) and the proximity of those sources to rivers interfere with the nature and concentration of the pollutants (Aryal *et al.* 2010; Pulley *et al.* 2016; Yazdi *et al.* 2021). HMs like Co, Cu, Cd, Cr, Pb, Ni, and Zn are the elements most documented in the urban environment (Nawrot *et al.* 2020). This group has attracted attention due to persistence, toxicity, and bioaccumulation (Kumar & Singh 2018; Pulley *et al.* 2016). Nutrients such as phosphorus and nitrogen are mainly associated with sewage (Aryal *et al.* 2010). They provoke the eutrophication of rivers, and the reduction of dissolved oxygen (DO), which causes the death of some aquatic organisms and the loss of biodiversity (Yang *et al.* 2021).

To manage the quality and flooding issues of urban rivers, sustainable drainage systems (SuDS) have been developed to reduce the effects of urbanization and improve the quality of stormwater runoff (Flanagan *et al.* 2021). In this context, sediment ponds decrease sediment loads by decanting suspended particles and minimizing flooding (Merchan *et al.* 2014).

However, these structures require specific maintenance and management, such as dredging and proper waste management. Hence, it is essential to know the qualitative properties, especially the concentrations of heavy metals (German & Svensson 2005) because accumulated sediments can be resuspended during flooding, making the pollutants viable again for entering the receiving body of water (Lusk & Chapman 2021).

Some studies analyzed the quality of sediment by geochemistry index in rivers, lakes, and stormwater ponds (Patel *et al.* 2018; Liu *et al.* 2022; Waara & Johansson 2022). Geochemical information on sediment is essential to evaluate environmental pollution and different pollutant sources in natural (weathering processes of rocks) or anthropogenic sources (Yap & Pang 2011; Kayembe *et al.* 2018). However, more than indicating the pollution level, it is necessary to understand the spatiotemporal factors that imply the entry of pollutants into rivers (Yang *et al.* 2021). In this context, seasonality and rainfall are the main variables in environmental analysis (Taka *et al.* 2022). They may help assess the sources and the mobility of the pollutants from water to sediment (Ouyang *et al.* 2006). Therefore, continuous time monitoring is important to understand the exchanges and shades of the pollutants in a sediment pond. In addition, few studies analyzed the integral quality of these settings, including dissolve fractions and bound in sediment. The concentrations of the pollutants, such as MHs, are dynamic and are influenced by physicochemical and hydrologic conditions.

Therefore, this study aims to: (1) determine the concentration of heavy metals, TP, ammoniacal nitrogen, and physicochemical parameters in water and sediment from a sediment pond; (2) verify the correlation between pollutants with hydrologic conditions (flow and precipitation); and (3) assess the environmental risk associated with (Cr, Cu, Ni, Pb, and Zn) using geochemical indexes such as Igeo, CF, and PLI. The correlation between the variables with precipitation can provide an indication of the main source of pollution (runoff or sewage), given by seasonality (dry and wet). Even simultaneous analysis of water and sediment may indicate the release of the HMs stored in the bed sediment into overlying waters under favorable conditions. In addition, it is one of the first studies on a stormwater pond in Brazil, heavy different climatic conditions of other studies are published in Europe and USA.

2. MATERIAL AND METHODS

2.1. Description of the study area

The study area was a sediment pond on the Antas River, city of Anápolis (Central-West Brazil). The monitoring point was the output of the pond at the geographical coordinates 16°20′43″S and 48°58′06.8″N, an altitude of 1000 m (Figure 1). The municipality functions as relevant agro-industrial production and a logistics hub for Brazil and houses several pharmaceutical industries. The Antas River originates in the urban area and runs through the entire city in a north-south direction. It is affected by the waterproofing of its basin area, which results in advanced erosive processes and siltation. The sediment pond studied is on the stream and has the function of retaining suspended sediments and minimizing channel silting and downstream flooding. The catchment area of the basin is 13.3 km², with a perimeter of 18.2 km and a length of 5.5 km. The regional climate is humid and tropical, with two distinct seasons: dry (May–September) and wet (October–April). The average annual rainfall is 1586 mm. Soil use and cover data show that 35.5% of the basin area is impermeable, 27.7% pasture, 20.2% exposed soil, and 16.1% vegetation. Data were obtained through the Geocentric Reference System of the Americas/SIRGAS 2000, which are images from Google Earth Pro, with a spatial resolution of 2 m, obtained free of charge. The images were processed using the ArcMap SIG.

2.2. Collection of rain-flow, water, and sediment data

For rainfall data, three rain gauges (Onset) were installed in the basin area (pluviographs, Figure 1). The precipitation was measured every 1 minute. The average rainfall was done by interpolating the data rainfall by the basin area. Flow measurements were determined monthly by the Acoustic Speed Doppler method using a portable Flow Tracker (SonTek) in the inlet of the basin. Water and sediment samples were collected on the output of the pond (at monitoring, Figure 1). In this section, duplicate samples were collected and mixed through, so subsequent analyses were done for one composite sample for each month. Twelve samples were sampled between February 2019 and January 2020 in the sediment pond. The water samples were collected directly from the river surface in polyethylene bottles (10–20 cm depth) and sent to the laboratory under refrigeration conditions. Sediment samples were obtained using a Peterson dredger and stored in plastic packaging.

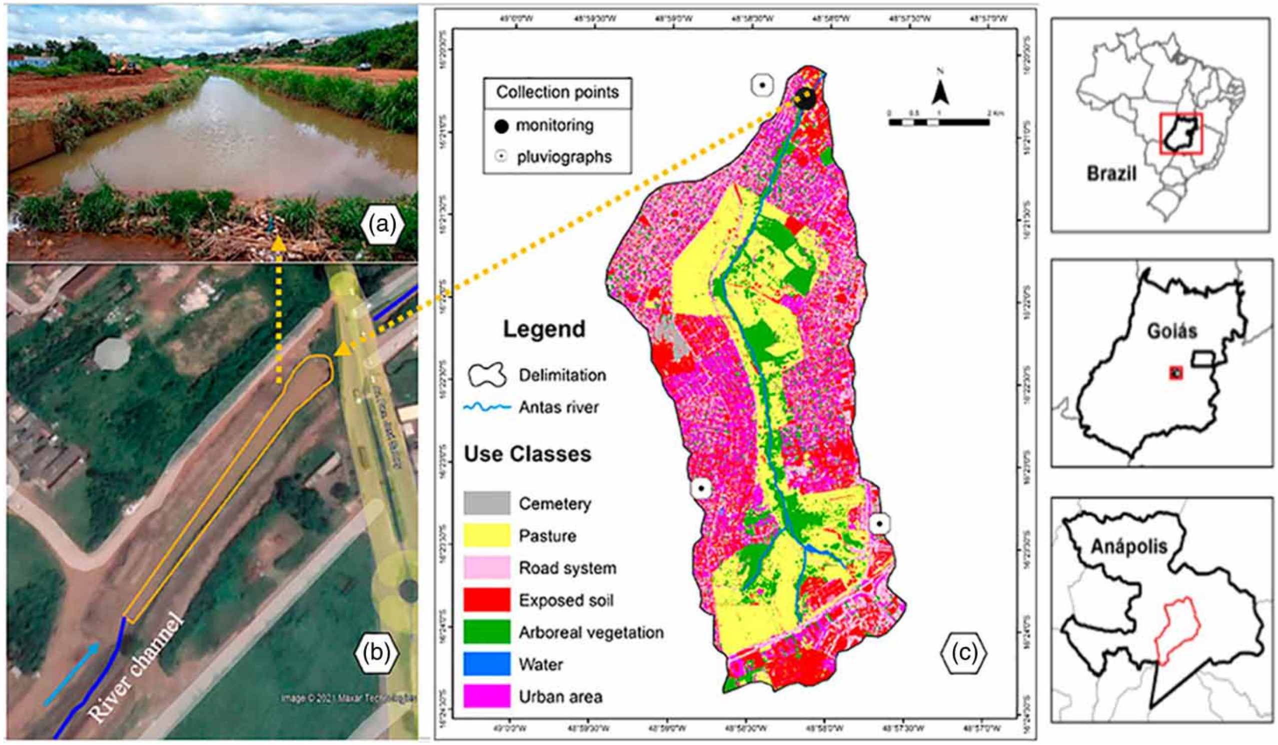


Figure 1 | Study area: (a) photograph of the sediment pond; (b) aerial view of sediment pond (Google Earth); (c) land use and occupation of the Antas River Basin, Anápolis-GO, Brazil.

2.3. Physicochemical analyses

Water samples were analyzed *in situ* for physicochemical parameters such as temperature (°C), pH, total dissolved solids (TDS), DO, electrical conductivity (EC), turbidity, and oxidation-reduction potential (ORP) using the HANNA multiparametric probe (HI 9829). Three readings were made. Total suspended solids (TSS), ammoniacal nitrogen (NH_4^+), and total phosphorus (TP) were measured in the laboratory. For TSS, 250 mL of samples were filtered through pre-weighed cellulose membranes (Whatman, 0.45 μm), dried at 105 °C, and reweighed (Method 2540-D). Nitrogen ammoniacal was done by a titrimetric method where the samples were distilled in boric acid and titled with H_2SO_4 0.02N. The concentration of NH_4^+ is directly proportional to the volume of acid spent in the titration (Method 4500 C). TP was done by the colorimetric method: digestion with $K_2S_2O_8$ followed by a reaction of mist reagent of ascorbic acid (Method 4050-P E).

Sediment samples were dried in an oven at 50 °C for 3 days. They were then disaggregated into grade and pistil, passed through a 2 mm sieve, and subjected to nutrients, pH, and organic matter (OM) analyses. For NH_4^+, the titrimetric method was also applied by dissolution of 1 g of sediment in 250 mL of water. For TP the ignition method was used (550 °C for 1 hour) followed by acid dissolution (in 0.5 g add 25 mL of HCL 1N) boiling in a thermal plate for 10 min (Aspila *et al.* 1976). The filtered extract follows the ascorbic acid method. To measure pH a suspension was prepared. A proportion of 10 g of sediment to 25 mL of water was mixed, left resting for 1 h, and then the reading was performed. Further, 2 g of sediment was calcined in a muffle at 550 °C for 4 h, and the weight difference between the dry material and the final residue corresponded to the organic matter contented in the sample. All the methods of analysis followed the protocols of the Standard Methods of Water and Wastewater (APHA 2005).

2.4. Metal analysis

Elements such as Boron (B), Barium (Ba), Cadmium (Cd), Chrome (Cr), Cooper (Cu), Manganese (Mn), Nickel (Ni), Lead (Pb), and Zinc (Zn) were analyzed in the water and sediment samples, following the digestion protocols 3015A and 3051A (USEPA 2007a, 2007b). They use a combination of nitric acid (HNO_3) and hydrochloric acid (HCl) to extract environmentally available metals. For water, 45 mL of the sample was added to 4 mL of HNO_3 and 1 mL of HCl. Digestion vessels were placed in a microwave system (Milestone ETHOS UP) at a temperature of 170 ± 5 °C for approximately 20 min. Sediment fractions < 63 μm were used because they contain the highest concentrations of metals. For 0.5 g of dry sediment, 9:1 mL (HNO_3: HCl) was added at a temperature of 175 ± 5 °C for 10 min in a microwave. Finally, the samples were filtered through white band filter paper until a volume of 50 mL was reached. Quantification was performed using inductively coupled plasma optical emission spectroscopy – ICP-OES (iCAP 6300 Duo, Thermo Fisher Scientific). The limits of detection of the method are as follows (mg/L): 0.002 for B, 0.001 for Ba, 0.001 for Cd, 0.002 for Cr, 0.001 for Cu, 0.001 for Mn, 0.001 for Ni, 0.003 for Pb, and 0.004 for Zn. Standards and samples were analyzed in triplicate.

2.5. Assessment of sediment contamination

Indexes are important analysis tools when evaluating sediment quality to measure metal contamination and anthropogenic and geogenic effects (Kayembe *et al.* 2018; Kulbat & Sokołowska 2019). In these studies, the background values depend on regional geochemical factors and therefore should be considered. The background values adopted in this study were recommended by CONAMA 454 (2012) which establishes guidelines for the evaluation of the quality of materials dredged from Brazilian river systems. There are two levels of contamination: the threshold effect level (TEL), a concentration below which adverse effects are expected to occur rarely, and the probable effect level (PEL), a concentration that is expected to occur frequently (MacDonald *et al.* 2000).

The Geoaccumulation Index (Igeo) was used to evaluate the degree of contamination by metals in sediments and to compare anthropogenic and geogenic effects (Xia *et al.* 2018; Siddiqui & Pandey 2019). They were calculated by Equation (1) and classified into six levels according to the intensity of metal enrichment. The Contamination Factor (CF) is estimated as the ratio between the concentration of the metal in the sample and its reference value (Equation (2)) (Islam *et al.* 2015; Dash *et al.* 2021). The Pollution Load Index (PLI) is estimated by Equation (3) and provides an overview of the overall pollution at a given site (Kulbat & Sokołowska 2019; Dash *et al.* 2021). All equations mentioned and the classifications of the indices analyzed are shown in Table 1.

2.6. Statistical analyses

The distribution data of metals in water and sediment throughout the year were plotted using Excel Microsoft Office 2013. Statistical analysis was performed using Pearson's correlation analysis and hierarchical cluster analysis (HCA) using Euclidean distance. These methods were applied to verify the similarity between the parameters and their potential common sources. For a cluster analysis, data were normalized. All analyses were performed using Library GGally functions using the R package version 1.66.0.

Table 1 | Equations and contamination classes of Igeo, CF, and PLI

Equation	Index	Class	Pollution intensity
$Igeo = \mathrm{Log}_2 \frac{(C_n)}{1.5\,[(B_n)]}$ (Eq. 1)	Igeo	<0	Unpolluted
C_n is the concentration of metal in sediment; B_n the concentration of metal in the geochemical background and 1.5 the lithological variability constant.		0–1	Lightly polluted
		1–2	Moderately polluted
		2–3	Moderately polluted
		3–4	Moderately to heavily polluted
		>5	Heavily polluted
$\mathrm{CF} = C_i/C_o$ (Eq.2)	CF	<1	Low
C_i concentration of metal in sediment; C_0 metal concentration in background		1–3	Moderate
		3–6	Considerable
		≥6	Very high
PLI(site) = CF1 x CF2 x CF_n (Eq. 3)	PLI	0–1	Unpolluted
CF is the contamination factor; n is the number of metals at the site		1–2	Moderately to unpolluted
		2–3	Moderately polluted
		3–4	Moderately to highly polluted
		4 –5	Highly polluted
		>5	Very highly polluted

3. RESULTS

3.1. Temporal description of physicochemical parameters

The physicochemical parameters of water samples are summarized in Table 2. The temperature ranged from 20.9 to 27.8 °C. The pH range of 5.2–7.4 characterizes an acidic to neutral environment. The OD ranged from 3.9 to 8.0 mg/L, being below the limit recommended by the legislation in May, October, and November. The TDS (23–71 mg/L) were higher in January and May at 71 mg/L, as well as the EC (46–142 μS/cm). TSS concentration ranged from 6.4 to 1071 mg/L, and turbidity ranged from 2 to 949. The values were higher in January than those in other months because the collection was carried out during the rain event. Regarding ORP, July was the month in which the water presented the highest oxidizing potential (100 mV) and November had the lowest (4.2 mV).

Ammoniacal nitrogen concentrations were higher at the end of the dry season and the beginning of the rainy season (September). For total phosphorus, concentrations ranged from 0.2 to 4.2 mg/L, and over the whole year, values were higher than that recommended for freshwater (CONAMA 2005). Regarding the flow rate, the variation was minimal because of the small size of the basin. However, during flood, the average flow was more than ten times higher than the regular flow. The months with the most rainfall were January, March, November, and December.

The physicochemical parameters of the sediment are presented in Table 3. The pH ranged from 5.5 to 7.4, with acid to neutral ambient. Nitrogen ranged from 28 to 420 mg/kg, with March and April having the highest concentrations. The TP ranged from 198 to 4693 mg/kg. The highest concentrations were in the months of lower rainfall (Jun, Jul, Aug, and Set), where the values exceeded an average 1.73 of legislative limit for sediment quality of river systems (CONAMA 2012). Organic matter ranged from 5.91 to 33.4%, and the highest percentages were observed in December and March, respectively. Values higher than 6% are considered as contaminate sediments to freshwater systems (Kayembe *et al.* 2018).

3.2. Distribution of heavy metals in water and sediment samples

Tables 4 and 5 shows a variation over the year of heavy metals concentration in water and sediment samples. Cd was the only element not detected in the water or sediment samples. B was detected only in the water sample collected in January (0.124 mg/L) during rainfall. For all metals, the highest concentrations were observed in January 2020. In this month the collection was carried out during the rainfall event. In some months, all metals presented above the recommended limit for Brazilian freshwater (CONAMA 2005). Cu and Mn concentrations were at odds virtually every month. In August and

Table 2 | Temporal variation of physicochemical and hydrologic parameters in the water of sediment pond of Antas River, Anápolis-GO

	Parameters											
Months Units	**T °C**	**pH -**	**DO mg/L**	**TDS mg/L**	**EC μS/cm**	**ORP mV**	**TSS mg/L**	**Turb UNT**	**NH_4^+ mg/L**	**TP mg/L**	**Q m³/s**	**Pec mm**
Jan	23.3	6.9	7.1	71	142	45	1,071	949	0.3	**4.2**	0.25	384
Feb	23.4	6.5	6.7	38	77	67	4.4	8.3	0.6	**0.3**	0.22	168
Mar	26.2	6.5	5.6	37	74	52	6.8	13	1.1	**0.5**	0.29	333
Apr	23.6	6.5	5.3	40	80	–	21	58	0.8	**0.2**	0.32	125
May	25.2	7.1	**3.9**	71	135	25	40	15	0.7	**0.3**	0.25	45
Jun	22.1	7.4	5.4	31	64	45	8.0	6.7	0.3	**0.4**	0.25	0
Jul	20.9	**5.2**	6.5	23	46	100	4.8	2.0	0.3	**0.5**	0.13	0
Aug	21.6	6.8	8.0	30	59	62	11	2.1	ND***	**0.2**	0.13	0
Sep	25.1	7.1	5.6	40	81	53	21	28	3.6	**0.8**	0.11	9.4
Oct	27.8	6.1	**4.8**	45	90	65	6.8	38	1.4	**0.2**	0.08	146
Nov	24.7	7.3	**4.4**	63	126	4.2	6.4	23	2.0	**0.5**	0.11	197
Dec	26.2	7.3	5.2	54	108	88	58	65	2.0	**0.5**	0.20	190
Average	24.2	6.7	5.7	45	90	55	105	101	1.2	0.7	0.19	–
SD	2.0	0.6	11.	15	25	30	292	257	1.0	1.1	0.08	–
CONAMA*	NR**	6–9	> 5	< 500	NR	NR	NR	≤ 100	3.7	< 0.1	NR	NR

*Resolution of the do Conselho Nacional do Meio Ambiente (CONAMA) Number 357/2005 Class 2; ** Unregulated; *** Not detected; bold values above the legislative limit.

Table 3 | Temporal variation of the physicochemical parameters of the sediment of sediment pond of Antas River, Anápolis-GO

	Parameters			
Months	**pH**	**NH_4^+ mg/Kg**	**TP mg/Kg**	**OM (%)**
Jan	6.9	112	1980	19.2
Feb	6.9	84	450	11.1
Mar	6.5	140	505	33.4
Apr	6.5	420	198	20.3
May	7.4	28	280	6.95
Jun	5.5	84	**3716**	19.8
Jul	5.6	56	**2240**	5.91
Aug	6.1	56	**4693**	25.6
Sep	6.2	112	**3212**	22.2
Oct	6.2	28	624	26.6
Nov	6.9	28	1481	24.5
Dec	5.9	364	518	35.6
Average	6.4	126	1658	20.9
SD	0.6	130	15%	9.3
CONAMA*	NR**	NR	2000	NR

*Resolution of the National Council of the Environment (CONAMA) Number 454/2012; ** Unregulated.

September, there was a jump in the concentration of metals, particularly Cu, Ni, Zn, and Mn. These months precede the rain season and dredging of the pond is performed. The changes on heavy metals concentrations can be attributed to release of HMs presents in mobile fractions of the sediment under to water (Friese *et al.* 2010; Al-Rubaei *et al.* 2017). The concentration order for metals in the water samples were as follows: Mn > B > Ba > Zn > Cu > Cr > Pb > Ni. Moreover, the mean concentrations (mg/L) were as follows: Ba, 0.088 $\pm$ 0.06; Cr, 0.036 $\pm$ 0.08; Cu, 0.056 $\pm$ 0.06; Mn, 0.231 $\pm$ 0.17; Ni, 0.023 $\pm$ 0.03; Pb, 0.026 $\pm$ 0.02; and Zn, 0.073 $\pm$ 0.05 (supplementary data, Figures S2 and S3).

Table 4 | Concentration of heavy metals in (mg/L) at water phase from sediment pond

Months	**B**	**Ba**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
Jan	0.124	0.268	**0.283**	**0.146**	**0.703**	0.030	**0.049**	0.182
Feb	<LQ*	0.078	0.011	0.005	**0.276**	0.012	0.009	0.041
Mar	<LQ	0.077	0.01	**0.015**	**0.15**	0.009	0.019	0.041
Apr	<LQ	0.088	0.019	**0.039**	**0.234**	0.014	**0.038**	0.066
May	<LQ	0.086	0.009	**0.036**	**0.231**	0.011	0.013	0.063
June	<LQ	0.072	0.007	0.004	**0.159**	0.010	<LQ	0.057
Jul	<LQ	0.054	<LQ	<LQ	0.059	0.006	<LQ	0.026
Aug	<LQ	0.067	0.007	**0.183**	**0.125**	**0.082**	<LQ	0.017
Sept	<LQ	0.079	0.014	**0.079**	**0.286**	<LQ	<LQ	0.146
Oct	<LQ	0.067	0.008	**0.058**	0.073	<LQ	<LQ	0.074
Nov	<LQ	0.047	0.008	**0.04**	**0.191**	<LQ	<LQ	0.099
Dec	<LQ	0.075	0.02	**0.014**	**0.281**	<LQ	<LQ	0.065
Avarege	0.124	0.088	0.036	0.056	0.231	0.023	0.023	0.073
SD	–	0.058	0.082	0.059	0.168	0.026		0.048
CONAMA*	0.5	0.7	0.05	0.009	0.1	0.025	0.01	0.18

*Resolution of the do Conselho Nacional do Meio Ambiente (CONAMA) Number 357/2005 Class 2; LQ: *below limit quantification.

Table 5 | Concentration of heavy metals in (mg/kg) at upper sediment from sediment pond

Months	B	Ba	Cr	Cu	Mn	Ni	Pb	Zn
Jan	124.5	105.6	**249.5**	**69.3**	350.4	**45.3**	12.4	86.7
Feb	116.6	141.7	**279.4**	**56.9**	545.3	**51.1**	13.1	79.4
Mar	109.0	160.9	**244.4**	**61.5**	477.1	**50.0**	13.7	83.1
Apr	72.5	68.5	**172.0**	32.5	187.0	**28.0**	7.9	50.5
May	88.6	88.1	**227.9**	**35.9**	418.3	**39.7**	10.8	54.2
June	90.0	90.9	**207.9**	28.7	237.7	**42.0**	11.4	66.4
Jul	83.0	76.2	**221.9**	19.9	372.7	**34.5**	12.7	38.7
Aug	123.6	133.7	**227.1**	**76.5**	327.8	**61.7**	7.2	88.5
Sept	145.0	143.6	**277.5**	**84.8**	364.4	**66.0**	7.6	99.1
Oct	124.2	126.9	**241.6**	**73.1**	367.3	**51.4**	7.4	95.9
Nov	130.3	150.4	**220.1**	**81.8**	447.3	**47.0**	9.4	125.0
Dec	131.7	121.3	**258.3**	**76.6**	416.4	**46.3**	11.0	99.0
TEL	–	–	37.3	35.7	–	18.0	35.0	123.0
PEL	–	–	**90.0**	197.0	–	35.9	91.3	315.0
Average	111.6	117.3	235.6	58.1	376.0	46.9	10.4	80.5
SD	22.8	30.8	30.0	22.9	97.9	10.5	2.4	24.4

TEL, threshold effect level; PEL, probable effect level.

For the sediment samples, the general order of concentration was Mn > Cr > Ba ≥ B > Zn > Cu > Ni > Pb. The mean concentrations (mg/kg) were as follows: B, 116.6 ± 22.8; Ba, 117.3 ± 30.8; Cr, 235.6 ± 30.0; Cu, 58.1 ± 22.9; Mn, 376.0 ± 97.9; Ni, 46.9 ± 10.5; Pb, 10.4 ± 2.4; and Zn, 80.5 ± 24.4 (supplementary data, Figures S2 and S3). Of the metals analyzed, Pb was the only element within the limit from quality of dredged sediments (CONAMA 2012) followed by Zn, which only exceeded the limit in November. For Cr, the concentrations were above level 2 of contamination (PEL). Adverse effects are expected to occur frequently at this level. For Cu, only levels in April, June, and July met the limit, and for Ni, this was only in the months of April and July. These months corresponded to the dry season. The inlet of these pollutants may be associated with runoff of the catchment.

Data on heavy metal contamination in sediments from stormwater systems in Brazil are too narrow. The elements analyzed on sediment samples were compared with data from other studies at urban lakes and stormwater (Table 6). The heavy metals mainly searched in urban areas are Cd, Cr, Cu, Ni, Pb, Zn, and Mn. In this study, Cd was not detected; Cr was the metal with the highest concentration among all studies; and Zn was one of the lowest levels.

3.3. Assessment of sediment contamination

Figure 2 presents an evaluation of the geological and anthropogenic influences and the degree of contamination of the sediment pond of the Antas River. Through the application of CF (Figure 2(a)), Cr contamination was at a very high degree (≥ 6), which was associated with months of higher rainfall. For Pb and Zn, the CF was low (<1), whereas for Cu, it was between 1 and 2, indicating moderate contamination. The PLI of the pond ranged from highly polluted to heavily polluted. Igeo values (Figure 2(c)) showed that Cr presented high values, ranging from moderately polluted to heavily polluted. It indicates sediment enrichment and evidence of contamination by anthropogenic activities. Regarding Cu and Ni, sediment samples were classified from unpolluted to moderately polluted. Pb and Ni were not enriched. In general, the rainiest months exhibited an increase of metals levels. Other studies have reported significant correlation by rainfall and export of heavy metals; and the seasonality with heavy metals (Cu, Cr, Pb, Mn, and Zn) (Yang *et al.* 2021; Taka *et al.* 2022).

3.4. Pearson correlation and cluster analysis between the parameters

The Pearson correlation values for water and sediment samples are shown in Figures 3 and 4, respectively. For water, heavy metal concentrations were positively correlated with TSS and turbidity, with correlation coefficients higher than 0.715 ($p <$ 0.01), except for Cu. Ammonia was not associated with any other variable. TP showed a strong correlation with turbidity

Table 6 | Comparation of heavy metals concentration in sediment samples in mg/kg (dry weight) of stormwater ponds or urban lakes to previous studies

Reference	B	Ba	Cr	Cu	Mn	Ni	Pb	Zn
This study[a]	72.5–145	68.5–160.9	172–279.4	19.9–84.8	187–545.3	28.0–66.0	7.2–13.7	38.7–125.0
German and Svensson (2005)[b]	n.a	285 ± 29	40–118	114–424	513 ± 29	26–102	127–231	478–2153
Friese *et al.*, (2010)[c]	n.a	271–720	81.9–210	30.2–71	364–1878	34.7–66.0	40.7–46.8	242–522
Merchan *et al.* (2014)[d]	n.a	n.a	113–158	213–280	n.a	60–97	135–325	1508–1766
Abreu *et al.* (2016)[e]	n.a	n.a	24.6–157	n.a	141–1363	1.1–15.9	14.6–107	89.9–456
Araújo *et al.* (2017)[f]	n.a	n.a	55–76	20–76	369–1904	18–26	33–118	181–21,960
De Andrade *et al.* (2018)[g]	n.a	139–1,448	5.7–72.7	13.8–132.1	n.a	7.8–43.4	7.9–53	32–261
Kulbat and Sokołowska (2019)[h]	n.a	n.a	14.4–260.9	2.3–25.6	n.a	0.3–26.1	1.3–49.2	14.7–92.5
Xia *et al.* (2020)[i]	n.a	n.a	94.4–111.3	46.6–93.7	590–710	40.5–45.4	35.4–62.8	115.4–166.7
Waara and Johansson (2022)[j]	n.a	39–194	9.0–45.6	20.9 –126.0	n.a	6.4–34.9	6.5–87.6	78.6–1190

n.a, not available.
[a]Stormwater pond, Brazil.
[b]Stormwater pond, Sweden.
[c]Pampulha Lake, Brazil.
[d]Detention basin, France.
[e]Guanabara Bay, Brazil.
[f]Sepetiba Bay, Brazil.
[g]Guaíba Lake, Brazil.
[h]Straszyn Lake, Poland.
[i]Urban Lakes, Chine.
[j]Stormwater ponds, Sweden.

(0.986, $p < 0.001$), TSS (0.988, $p < 0.001$), Ba (0.982, $p < 0.001$), Cr (0.999, $p < 0.001$), Mn (0.899, $p < 0.001$), and Zn (0.771 $p < 0.01$) (Figure 4). The precipitation acted moderately on the mobility of Cr (0.610, $p < 0.05$), Ba (0.599, < 0.05) and Mn (0.587, $p < 0.05$) into water, and Cu and Zn were not correlated. A strong association of Cu-Zn had already been observed,

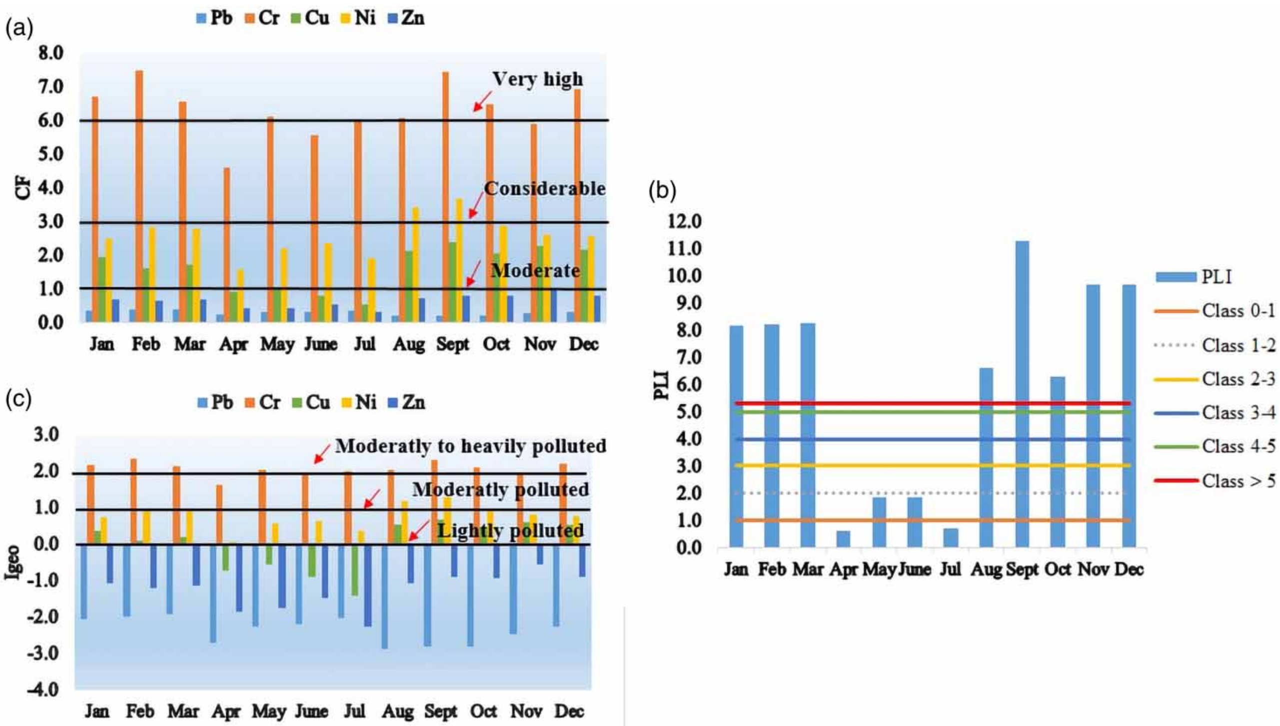


Figure 2 | CF, PLI, and Igeo of the surface sediment of the sediment pond, Antas River, Brazil.

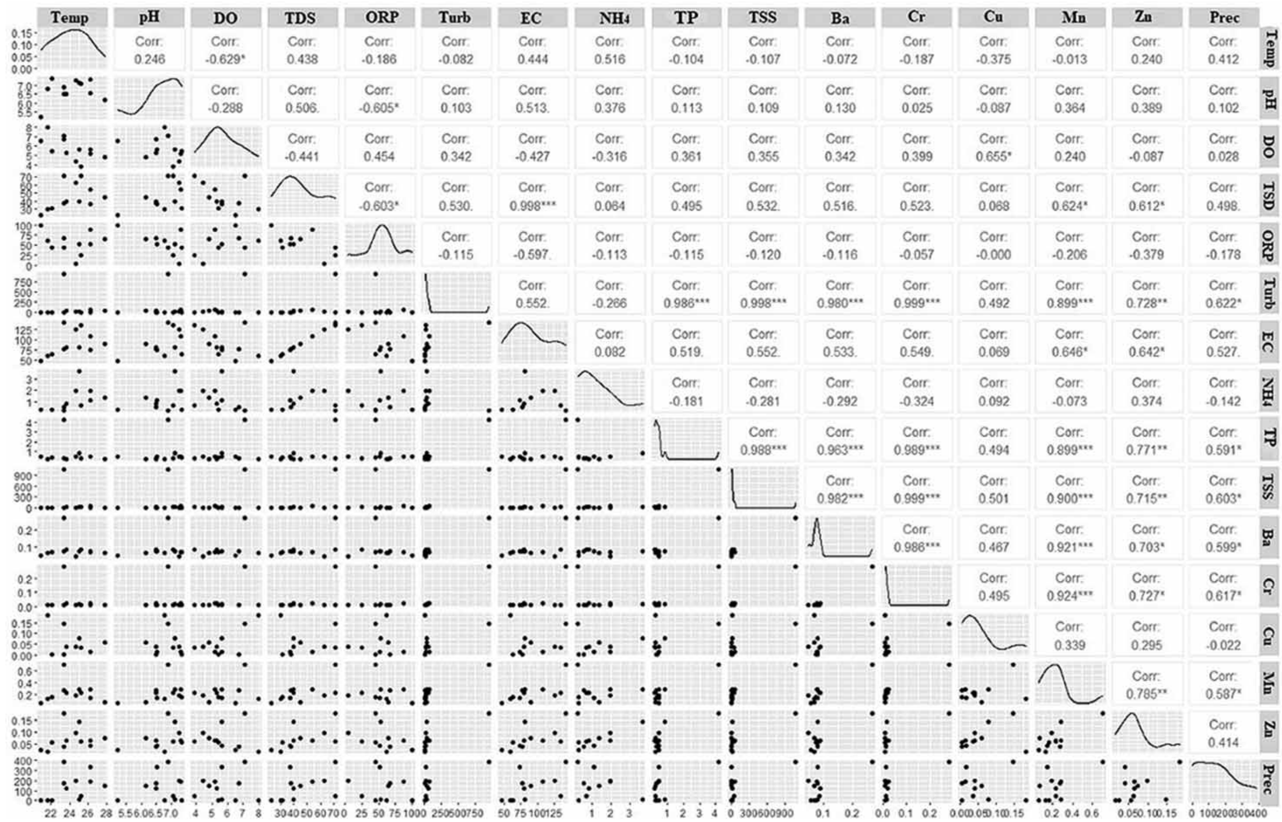


Figure 3 | Pearson correlation analysis between physicochemical parameters and heavy metals in the water of the sediment pond, Antas River, Brazil. Temp, temperature; DO, dissolved oxygen; TDS, dissolved total solids; ORP, oxidation redox potential; Turb, turbidity; EC, electrical conductivity; NH_4^+, ammoniacal nitrogen; TP, total phosphorus; Prec, precipitation; $^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$.

as well as similar seasonal distribution indicating shared sources and pathways (Taka *et al.* 2022). Copper was the only element that had a positive correlation with DO (0.655, $p < 0.01$). For the sediment, the OM (%) was moderately associated with Cu (0.648, $p < 0.05$) and Zn (0.645, $p < 0.05$). Precipitation, pH, ammoniacal nitrogen, TP, and Pb showed no correlation with any other variable. The other metals showed a strong correlation with each other, especially B with Cu, Zn, Ni, Ba, and Cr, with correlation coefficients higher than 0.642 ($p < 0.05$) (Figure 5).

Cluster analysis of water and sediment parameters is shown in Figure 5. For water, the January parameters were outside the curve due to turbidity and TSS concentrations that were higher than observed in other months (Figure 5(a)). It is because sampling during a flood event causes an increase in the concentration of particulate matter in the water. This effect is evident in the color gradient, where warmer colors indicate higher values. The grouping of months into two seasons was clear. May–September is the dry season, and October–April is the rainy season. As for the parameters, three clusters were observed that showed the similarity of the variables: (1) TSS and turbidity; (2) precipitation, EC, NH_4^+, Mn, Cr, Cu, and Zn; and (3) metals. In sediment samples, the TP showed no similarity with any variable. The metals Cr and Mn showed strong grouping, as well as Zn, Ni, Cu, B, Ba, OM (%), and Pb (Figure 5(b)). For sediment, the two seasons were not very clear, and other factors may affect the concentration of the sediments. August and September samples (8 and 9) showed high similarity, followed by June. During these months, upper values of TP, Cu, and Ni were observed. Another cluster was composed of January, April, May, July, and November samples (1, 4, 5, 7, and 11). In addition, the last cluster grouped the rainiest months.

4. DISCUSSION

The advance of this article is the range of parameters analyzed on a monthly scale in water and sediment samples, such as heavy metals in urban stormwater. Water and sediment contamination in urban areas were influenced by the modification in land use/land cover (Hamid *et al.* 2020). As reported, stormwater is one of the largest sources of pollutants, including suspended solids and metals, which pollute water bodies (Aryal *et al.* 2010). Knowledge and control of urban runoff and

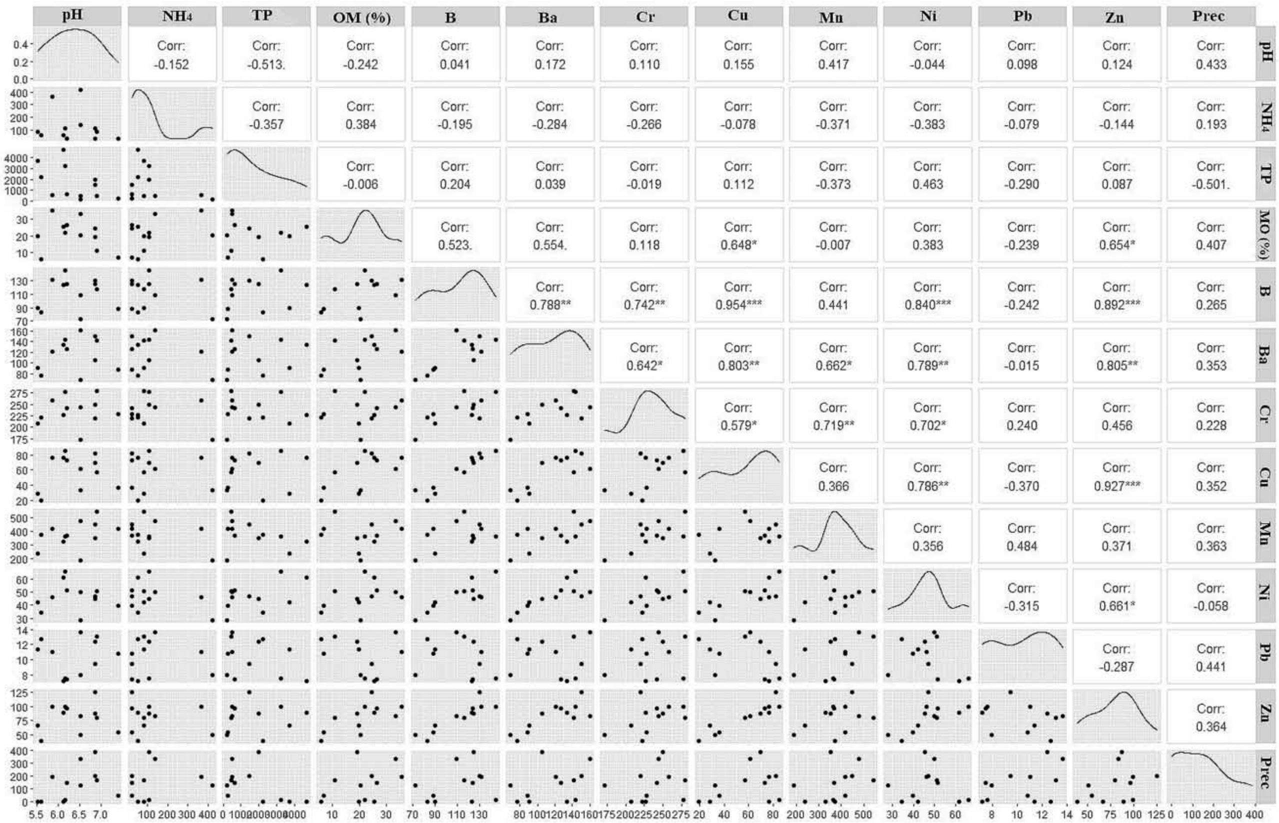


Figure 4 | Pearson correlation analysis between the physicochemical parameters and heavy metals in sediment of the sediment pond, Antas River, Brazil. NH_4^+, ammoniacal nitrogen; TP, total phosphorus; OM, organic matter; Prec, precipitation; $^*p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$.

interfering factors are essential for management measures (Valeo *et al.* 2021). There are few studies about stormwater ponds, especially in tropical countries. The inlet of higher levels of heavy metals and other pollutants can be dangerous to the ecosystem and the communities that live in the surroundings (Xia *et al.* 2020).

In this study, the water samples in the sediment pond in the Antas River had concentrations above the Brazilian low for Cu, Mn, Pb, and TP (CONAMA 2005). The levels of these elements are much higher than described by Friese *et al.* (2010) in Pampulha Lake in Brazil and by Xia *et al.* (2020) in urban lakes of China. The sediment had high concentrations of Cr, Cu, and Ni, with mean values exceeding 6.32, 1.63, and 2.61, respectively, over the TEL value. TP concentrations during the dry season exceeded the permissible limit by an average of 1.73 times. These results had similar findings in previous studies performed in Brazil in Pampulha Lake, Belo Horizonte (Friese *et al.* 2010), Guanabara Bay, Rio de Janeiro (Abreu *et al.* 2016), and Lake Gauíba, Porto Alegre (De Andrade *et al.* 2019).

These studies address that the proximity to large residential, commercial, and industrial areas raises the levels of heavy metals. De Andrade *et al.* (2018), evaluating the quality of sediments, found that Cr, Cu, Ni, and Zn had higher concentrations near Porto Alegre, a large urban center compared to other sites. German & Svensson (2005) characterized stormwater pond sediments in Sweden and found concentrations twice higher from Cr, Ni, and Zn in a pond which receives the discharge from an industrial area. However, Cu was the most critical metal in the ponds in general. Al-Rubaei *et al.* (2017) studied 12 sediment ponds in Sweden and reported that these basins have the potential to reduce metal concentrations. However, dredged sediment can be dangerous, and its disposal can increase the mobility and transport of pollutants downstream. They found that 40% of the ponds were contaminated with Cr, Cu, Ni, and Zn. Kayembe *et al.* (2018) reported these elements at higher levels in an urban river in the Democratic Republic of the Congo. They concluded that metal pollution in the urban basin is a global problem that is associated with urban runoff.

In this study, Zn was an exception compared to the reported studies. Sediment samples were not polluted by Zn (Table 6). The levels of Zn (38.7–125 mg/kg) were similar to those detected by Kulbat & Sokołowska (2019) in Straszyn Lake, Poland.

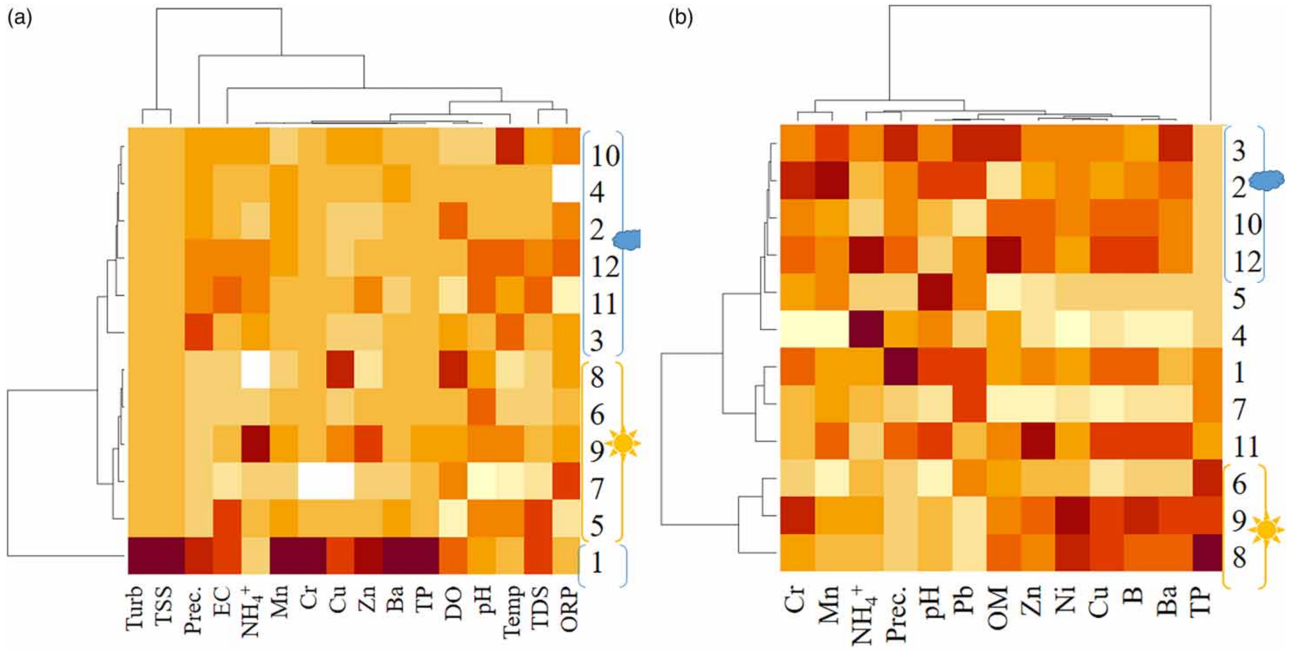


Figure 5 | Hierarchical cluster analysis by Euclidean distance for physicochemical parameters, metals, and nutrients over a year (a) in water and (b) in the sediment from a sediment pond of the Antas River. The numbers on the right correspond to the months. Turb, turbidity; TSS, total suspended solids, Prec, precipitation; EC, electrical conductivity; NH_4^+, ammoniacal nitrogen; TP, total phosphorus; DO, dissolved oxygen; Temp, temperature; TDS, total dissolved solids; OM, organic matter. More intense colors (red to orange) indicate higher values, while less intense colors (yellow to white) indicate lower values.

On the other hand, in the present study, the concentration of Cr was higher (maximum of 279.4 mg/kg) as compared to that reported by Merchan *et al.* (2014) from the stormwater pond in France (158 mg/kg); Abreu *et al.* (2016) from Guaíba Lake (157 mg/kg), and by Waara & Johansson (2022) from stormwater ponds, Sweden (45 mg/kg). An earlier study has also shown high concentrations of Cr (210 mg/kg) in Brazil (Friese *et al.* 2010).

Elements such as Mn and Cu are essential but, in excess, could be toxic (Dević *et al.* 2016). However, Cr, Ni, and Pb represent high ecological hazards (Kumar & Singh 2018). Silva *et al.* (2020), in this study area, found that the elements Ba, Mn, Zn, Cr, and Ni were strongly associated with genotoxic damage in native fish species. In addition, the association of these metals can raise toxicity in the aquatic environment. TP in urban areas originates from domestic and industrial wastewater and surface runoff (Hamid *et al.* 2020). Higher concentrations can lead to eutrophication, oxygen depletion, and a change in metal mobility.

Aryal *et al.* (2010) reported that the concentrations of Cr, Cu, Pb, and Zn are related to the intensity of traffic vehicles, and levels are affected by seasonality. Charters *et al.* (2021) studied the effect of the type of urban surface on stormwater quality and found that the contribution of metals is related to the surroundings of the urban area, atmospheric deposition, and rainfall/seasonality. Elements such as Cu, Ni, Zn, and Pb were strongly influenced by anthropogenic sources (Luo *et al.* 2022). Cr was mostly connected to industry sources, solid waste, and sewage, which can explain the high concentrations of Cr found in this study. The city of Anápolis is the second largest pharmaceutical pole in Brazil and shelters about 17 industries in the chemical sector (DAIA –Agroindustrial District of Anápolis).

The concentration of metals in water or sediment is influenced by physicochemical variables related to the availability and mobility of metals. Precipitation was correlated with turbidity and SST, which was strongly associated with TP, Ba, Cr, Mn, and Zn, as discussed in the correlation and cluster analyses. Such was earlier reported by Friese *et al.* (2010), mainly to Zn and Cr. Kayembe *et al.* (2018) and Khan *et al.* (2020) corroborate that the correlation between the variables indicates that they probably come from a common source and are controlled by the same factors. In this respect, suspended particles are extremely important for the mobility of heavy metals and nutrients in rainwater, as observed in other studies (Liu *et al.* 2019; Yazdi *et al.* 2021).

Based on the mobility of metals, Cr concentrations were low in water and high in sediments. This phenomenon is explained by the fact that Cr is associated with reducible and oxidizable fractions in the sediment and therefore has a lower ability to dissolve in water, so resuspension occurs only in anoxic, dredging, or flooding conditions (Patel *et al.* 2018; Dash *et al.* 2021). The same phenomenon was observed for Cu, and according to de Castro-Català *et al.* (2016), this metal is strongly attracted to the organic matter of the sediment, forming strong metal complexes. This corroborates our results (Figure 4(b)), in which Cu was positively correlated with OM (%). Xia *et al.* (2018) also reported a significant correlation between Cu, Zn, and organic materials.

The applied quality indices (CF, PLI, and Igeo) showed that the sediment accumulated in the sediment pond of the Antas River was enriched in the order Cr > Ni > Cu, suggesting the anthropic origin of these contaminants because the mean values were higher than the geochemical standards. Kulbat & Sokołowska (2019) observed similar results, where Cr was also the metal that had the higher effect on the pollution of sediments in a lake in Poland. Dash *et al.* (2021), applying CF and PLI, found a moderate level (1–3) of contamination in the sediment of a lake in India, where Cr, Mn, Cu, and Pb were the dominant metals associated with anthropogenic sources. Furthermore, the months with higher rainfall, except for September, showed higher pollution rates (Figure 2(a) and 2(b)). A possible explanation for the increase in metal concentrations in September was dredging carried out in the sediment pond at the beginning of the rainy season to reestablish the retention capacity for the first rains, which brings a large load of sediment and pollution.

5. CONCLUSION

The analysis of heavy metals and nutrients in the water and upper sediment of the sediment pond from the Antas River showed that precipitation acts in the mobility of suspended particles (turbidity and TSS). Such particles are positively correlated with TP, Ba, Cr, Mn, and Zn. This study appointed that in a static land use condition, the main sources of HMs came from runoff of the catchment area. The wet months showed a high concentration of HMs, less for Cu. The values of sediment quality indices Igeo, CF, and PLI indicated that sediment pollution varied from moderate to strong for Cr, Ni, and Cu, suggesting that these elements have an anthropic origin. Correlation and cluster analyses showed the similarity of the elements, which may indicate a common source. Therefore, seasonality and physicochemical parameters affect the mobility and availability of heavy metals in water and sediment. This study draws attention to the importance of understanding and monitoring the levels of pollutants in urban basins for the construction of stormwater management measures to ensure the safety of water resources as well as the neighborhood. Our data highlight that finding heavy metals in high concentrations may be very dangerous for the environment. The stormwater ponds must have a risk assessment and management plan so that the basin does not become a waste pond in the future. As suggestion remedies, it is necessary to decrease the areas of exposed soil near the pond by increasing green space. It may reduce the velocity of the water, erosion process, and transport of sediments to the pond. Also, disposal of the dredged sediment in an appropriate area, observing the risk assessment. The shortcomings explain how rainfall increases the concentration of HMs in sediment ponds. In future research, we plan to focus on the viability of the variation of these metals during rainfall events. Analyze variables such as duration and intensity of precipitation to understand how rainfall acts on wash-off the HMs in the hygrogram moments (rise, peak and recession).

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COMPETING INTERESTS

The authors have no relevant financial interest to disclose.

ETHICAL APPROVAL

Not applicable

CONSENT TO PARTICIPATE AND PUBLISH

All the authors participated and consent publish the article.

AUTHORS CONTRIBUTIONS

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by [Emanoelle Pereira da Silva and Julião Pereira, formal analysis and resources by Nelson Roberto Antoniosi Filho and Klebber Teodomiro Martins Formiga and supervision by Klebber Teodomiro Martins Formiga. The first draft of the manuscript was written by Emanoelle Pereira da Silva and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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