

A system (water-sediment) under prolonged anaerobiosis: harmful levels of chemical species

Um sistema (água-sedimento) sob anaerobiose prolongada: níveis prejudiciais de espécies químicas

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ABSTRACT

Models for assessing sediment quality describe the occurrence of a continuous matter and energy exchange process at the *sediment-water interface*, and the displacement of nutrients and metals from the sediments to the water column affecting its quality. Although these models are highly used for studying reservoirs and lakes, there is a gap between them regarding the assessment of rivers in heavily urbanized areas without access to basic sanitation, where high loads of untreated effluents from domestic and industrial sources arrive. This work evaluated this condition on the Barigüi River, an urban water system in southern Brazil. During hypoxic incubations (45 days), the concentrations of dissolved oxygen (DO), pH, redox potential (Eh), orthophosphate (P_{Oro}), total phosphorus (P_T), ammonia (NH_3), total alkalinity (TA), and metals Cr, Fe, Cd, Zn, and Cu were monitored in incubated systems (water/sediment). In this study, we present the evidence of the possible resuspension of ammonia from the sediments to the water column by mass balance. We have determined the accumulation rate in relation to time for concentrations of total phosphorus, total Fe, ammonia, and total alkalinity of $d(\phi)/dt = 4.2 \text{ mg.L}^{-1}$ per day, deteriorating its quality.

Keywords: hypoxia response; sediment quality; urban pollution; urban sediments.

RESUMO

Modelos para avaliação da qualidade dos sedimentos descrevem a ocorrência de um processo contínuo de troca de matéria e energia na interface sedimento-água, além do deslocamento de nutrientes e metais dos sedimentos para a coluna d'água, afetando sua qualidade. Embora esses modelos sejam amplamente utilizados para o estudo de reservatórios e lagos, há uma lacuna em relação à avaliação de rios em áreas altamente urbanizadas sem acesso a saneamento básico, no qual chegam altas cargas de efluentes não tratados provenientes de fontes domésticas e industriais. Este trabalho avaliou essa condição no rio Barigüi, um sistema hídrico urbano no Sul do Brasil. Durante incubações hipóxicas (45 dias), foram monitoradas as concentrações de oxigênio dissolvido (OD), pH, potencial redox (Eh), ortofosfato (P_{Oro}), fósforo total (PT), amônia (NH_3), alcalinidade total (TA) e os metais Cr, Fe, Cd, Zn e Cu em sistemas incubados (água/sedimento). Neste estudo, apresentamos evidências da possível ressuspensão de amônia dos sedimentos para a coluna d'água por meio do balanço de massa. Determinamos a taxa de acumulação em relação ao tempo para as concentrações de fósforo total, ferro total, amônia e alcalinidade total de $d(\phi)/dt = 4,2 \text{ mg.L}^{-1}$ por dia, deteriorando sua qualidade.

Palavras-chave: resposta à hipóxia; qualidade dos sedimentos; poluição urbana; sedimentos urbanos.

INTRODUCTION

In the last decades, public policies such as large urbanization projects in the metropolitan region of Curitiba promoted structural transformations that caused environmental impacts beyond their immediate limits (Gadens, 2018; Benvenuti, 2019; IBGE, 2021). One such case is the implementation of the so-called "Green Line." The project consisted of the functional reconversion of the

old BR 166 highway (30-km long, east-west section) into an important connection axis on an urban and metropolitan scale that allowed for the integration of 22 neighborhoods, about 30% of the city area (Gadens, 2018; Benvenuti, 2019; Souza; Samora, 2022).

In Curitiba's metropolitan region, the water urban systems ensure that tributaries drain densely occupied areas, where industrial activities are practiced

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simultaneously, in addition to irregularly populated areas that lack treated water and basic sanitation (Silva *et al.*, 2017; Silva *et al.*, 2019; Cervi *et al.*, 2021). Several studies have shown that urban rivers are polluted by various inorganic chemicals (such as metals, semi-metals like arsenic and non-metals like the bromine or selenium), organic chemicals (such as labile and recalcitrant organic matter, fertilizers, agrochemicals, and domestic and industrial effluents), nutrients (nitrogen, phosphorus, and potassium), and emerging contaminants (drugs, personal care products, surfactants), among others (Nascimento *et al.*, 2018; Mizael *et al.*, 2020; Heinrich *et al.*, 2021; Jia *et al.*, 2023).

In particular, water contamination by metals and nutrients is a persistent and significant problem in urban areas due to continuous inputs and high concentrations compared to the local baseline (Nascimento *et al.*, 2018; Silva *et al.*, 2019; Vergilio *et al.*, 2020; Cervi *et al.*, 2021; Jia *et al.*, 2023). Therefore, sediments from water systems are very important for assessing the pollution of aquatic ecosystems (Vieira *et al.*, 2019; Vergilio *et al.*, 2020; Mizael *et al.*, 2020; Jia *et al.*, 2023).

Sediment contamination by several chemicals threatens aquatic ecosystems due to possible toxicity, persistence, bioavailability, bioaccumulation, and biomagnification in the food chain (Pompêo *et al.*, 2013; Silva *et al.*, 2019; Mizael *et al.*, 2020; Jia *et al.*, 2023). Sediments represent an active environmental compartment, capable of accumulating and suspending chemical compounds under favorable conditions, negatively affecting the quality of the water column (Nascimento *et al.*, 2018; Vieira *et al.*, 2019; Vergilio *et al.*, 2020; Silva *et al.*, 2023).

The control of nutrients and inorganic chemical species available in the sediments is associated with the presence of organic matter, clays, carbonates, and mineral oxides of iron and manganese (Banks *et al.*, 2012; Silva *et al.*, 2019; Cervi *et al.*, 2021; Jia *et al.*, 2023). In urban sediments, usually rich in organic (and hypoxic) matter and hypoxia (low levels of dissolved oxygen), sulfides act on the complexation of metals (Schnitzler; Grassi; Quinaia, 2009; Torres *et al.*, 2014; Vieira *et al.*, 2019; Cervi *et al.*, 2021). Sulfides are formed when a significant part of the organic matter reaching the sediment is oxidized by bacteria that use sulfate as an electron acceptor (Banks *et al.*, 2012; Wagner, 2019; Zhang *et al.*, 2021; Jia *et al.*, 2023). This process produces hydrogen sulfide and other reduced sulfur compounds. In uncontaminated sediments, sulfides are mostly precipitated by Fe, Cu, Zn, Pb, Hg, Ca, and As, among others such as thiosulfate and sulfur. In environments strongly influenced by human activities, such as rivers in metropolitan regions, which receive high levels of organic matter, the presence of NO_3^- , Mn (IV), and Fe (III) ions is observed, which function as electron receptors, with the consequent minimization of sulfide production (Fagnani *et al.*, 2011; Pompêo *et al.*, 2013; Zhang *et al.*, 2021; Cervi *et al.*, 2021).

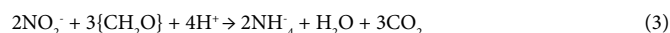
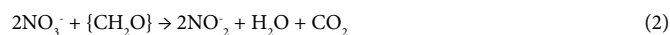
A divalent metal entering the aquatic environment promotes an exchange reaction with iron sulfide and associates with the sulfide, forming a poorly soluble metal complex, according to Equation 1. Therefore, metal levels remain reduced and retained in the solid phase (Fagnani *et al.*, 2011; Silva *et al.*, 2012; Heinrich *et al.*, 2021):



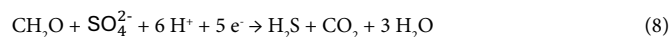
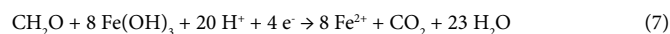
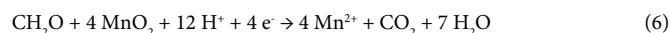
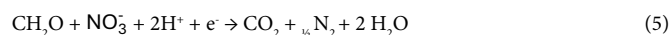
The reduction process, the gain of electrons by a chemical element, induces the release of elements from the sediments to the water column and is influenced by the dissolved oxygen concentration in the water column (Banks *et al.*,

2012; Pompêo *et al.*, 2013; Torres *et al.*, 2014). In this sense, hypoxia and anoxia episodes lead to a reduction in the redox state of sediments, accelerating the desorption of contaminant metals (linked to Fe and Mn oxides) and the sequential reduction of nitrate (Rocha; Rosa; Cardoso, 2009; Fagnani *et al.*, 2011; Banks *et al.*, 2012; Torres *et al.*, 2014; Wang *et al.*, 2022).

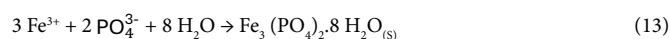
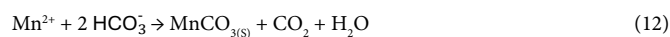
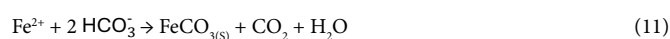
Prolonged decreased dissolved oxygen events cause the sediments in the water column to become anaerobic, thus reducing sulfate to sulfide, precipitating soluble Mn and Fe as insoluble MnS and FeS while forming subsequently insoluble sulfide complexes (Silva *et al.*, 2012; Wagner, 2019; Wang *et al.*, 2022). Decreasing dissolved oxygen levels in the sediments favors the growth of facultative aerobic and anaerobic microorganisms that obtain energy to maintain their functions by the oxidation of organic matter (Rocha; Rosa; Cardoso, 2009; Campos, 2010; Silva *et al.*, 2012). Lack of free oxygen and microbiological action reduces the nitrogen to lower oxidation states, according to Equations 2 and 3:



These microorganisms, mainly algae, fungi, and bacteria of acidophilic species, use oxygen as the final electron acceptor in the respiratory chain and transfer electrons from organic compounds to other reduced compounds, changing Mn^{4+} into Mn^{2+} , Fe^{3+} into Fe^{2+} , SO_4^{2-} into H_2S (Garcia Junior, 2001; Rocha; Rosa; Cardoso, 2009; Silva *et al.*, 2012; Jia *et al.*, 2023). Equations 4, 5, 6, 7, 8 and 9 involved in the process are summarized below:



In the presence of sulfide, bicarbonate, and phosphate, precipitation of iron and manganese salts and other associated metals may occur (e.g., Equations 10 to 13). Simultaneously, acidic conditions increase phosphate solubilization, which in turn accelerates the eutrophication process (Campos, 2010; Fagnani *et al.*, 2011; Torres *et al.*, 2014; Cervi *et al.*, 2021):



Thus, under anaerobic conditions, the elements are continuously exchanged between the water column/sediment interface, favoring the dissemination of nutrients and metals. In the last decade, mesocosm experiment models have been used to evaluate how the water column/sediment interface systems evolve over time under anaerobic conditions (Janke *et al.*, 2011; Yamada *et al.*, 2012; Torres *et al.*, 2014; Cervi *et al.*, 2021; Wang *et al.*, 2022; Jia *et al.*, 2023).

These systems seek to reproduce some environmental conditions on a small scale and show promise for the understanding of the exchange processes between sediments and the water column. The main criticism of this approach concerns the fact that the mathematical models do not account for the system dynamics since the waters and sediments are neither replenished nor subjected to hydrodynamic effects or load dilution as they normally are (Banks *et al.*, 2012; Torres *et al.*, 2014; Zhang *et al.*, 2021).

However, these models can provide a useful basis for predicting changing behavior of metals and their toxicity during hypoxia episodes, guiding follow-up, and environmental management actions (Banks *et al.*, 2012; Wang *et al.*, 2022). Therefore, this paper evaluates the over time flux/flow of dissolved oxygen (DO), pH, redox potential (*Eh*), orthophosphate (P_{Oro}), total phosphorus (P_T), ammonia (NH_3), total alkalinity (AT), and metals Cr, Fe, Cd, Zn, and Cu in incubated systems (water/sediment) kept in jars in the dark under hypoxia at controlled temperature. It is believed that prolonged sediment hypoxia in water systems favors the resuspension of harmful elements accumulated in the water column, influencing its quality.

EXPERIMENT

Study site and sampling sites

The Barigüi River, located in Curitiba metropolitan region, southern Brazil, drains an area of 279 km² and extends over 66 km, crossing the limits of the municipalities of Almirante Tamandaré (AT), between the source located in Santa Felicidade (SF) neighborhood in Curitiba, and its mouth in Araucária (A) (Machado *et al.*, 2014; Silva *et al.*, 2017). Figure 1 shows the Barigüi River on the map and the sampling stations for collecting water and sediment samples.

The region upstream of the Barigüi River, in AT (25° 22' 49.5" S and 49° 18' 03.7" W), has small and dispersed urban centers. The object of this study, the river middle region in the SF neighborhood (25° 24' 37.4" S and 49° 18' 24.7" W), Curitiba, is a highly populated urban occupation, with several commercial establishments and services.

The downstream region in Araucária City (25° 33' 20.56" S and 49° 20' 32.70" W) shelters the industrial area of Curitiba City, industrial hub of the City of Curitiba (CIC), part of the Industrial City of Araucária (CIAR), and the Petrobras Refinery (REPAR). Additionally, the industrial zones attracted several regular and irregular occupations, small metallurgical companies, and service providers (Froehner; Martins 2008; Machado *et al.*, 2014; Silva *et al.*, 2017).

Sampling

Sediment (2 kg) and natural water (1 L) samples were collected following clean technique protocols (ANA; CETESB, 2011) and stored in double Ziploc bags and wide-mouth bottles, both made of polypropylene. The samples were labeled, placed in coolers containing cryogel, and transported to the laboratory (Silva *et al.*, 2019; Silva *et al.*, 2023). Water quality and physical and chemical parameters were obtained in situ using multiparametric equipment (HANNA, HI 9829).

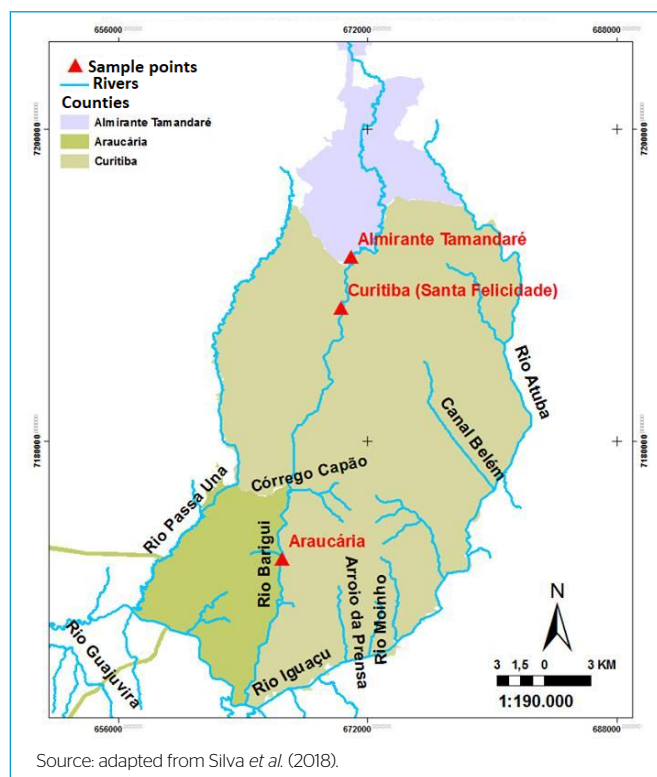


Figure 1 – Map showing the sampling sites of Araucária (A), Santa Felicidade (SF), and Almirante Tamandaré (AT) on the Barigüi River, southern Brazil.

Within the incubation systems setup, multiple subsamples of the water column and bottom sediments were randomly collected along the cross section of the Barigüi River, at the Araucária sampling site (Figure 1A). For water sampling, high-density polypropylene buckets of 10 L capacity were used, and, for sediment sampling, stainless steel scoops were used below the water column, close to the water column–sediment interface superficially with unconsolidated layers approximately 5 cm deep (Janke *et al.*, 2011; Yamada *et al.*, 2012).

To set up the incubation systems, 20 kg of sediment and 45 L of water were also collected from the Araucária sampling site, using scoop shovels, hoes, buckets, and polypropylene gallons.

Sample preparation and incubation systems

In total, 16 incubation systems were built using cylindrical jars (12 cm diameter × 25 cm height) with a 5-L capacity, made of high-density polypropylene and closed with screw caps (Janke *et al.*, 2011; Yamada *et al.*, 2012). Approximately 1 kg of sediment from the Araucária sampling site (A) was added to 12 of the jars.

Then, 2.5 L of water collected from the water column at the same sampling site was also added using a low-flow pump (Amicus, flow 170 L.h⁻¹, power 2.5W) to avoid possible suspension of sediments. The four remaining jars were filled with 2.5 L of water only (without sediment), as blank/control systems (Janke *et al.*, 2011; Yamada *et al.*, 2012). All containers were identified, sealed, and covered with aluminum foil to prevent light from entering. The jars were stored in a DBO incubator (Novatecnica, 340 L), without photoperiod, and kept at 18°C throughout the experiment (water column temperature on the day of sample collection). After resting for 48 h for stabilization, four opening times were defined, namely *t* = 0 days (stabilization), *t* = 7 days, *t* = 21 days, and *t* = 45 days.

At each set date, four jars were carefully removed from the BOD and opened (one jar, the control, containing only water and three jars containing water and sediments), avoiding disturbances that could lead to sediment resuspension (Banks *et al.*, 2012). Physical and chemical parameters (pH, Eh, NH_3) of the water column were immediately analyzed, and water samples and later sediments were collected for analysis (TA, orthophosphate, total phosphorus, and the element Fe in the total and available fraction).

Analytical methods

Physical and chemical parameters of the water column

Temperature, resistivity, conductivity, dissolved oxygen, dissolved solids, pH, and redox potential were measured (in triplicates) using a multiparameter equipment (HANNA, HI 9829). The electrodes HI 7609829-2 (DO), HI 7609829-1 (PH/ORP), and HI 7609829-4 (EC/Turbidity) used were calibrated with standard solutions as recommended by the manufacturer.

Particle size and moisture content of sediment samples

The sediment samples for determining particle size (triplicate) were prepared as follows: 0.2 kg of sediment sample was oven-dried at 50°C for 48 h (SpLabor, SL-100). After that, the samples were manually ground using a mortar and pestle, followed by fractionation in an electromagnetic stirring system (MBL, 60 Hz, 15 min) with sieves of different mesh sizes: 250, 150, 106, 53, 45, and 38 μm (Ferreira Pinto 2018).

The moisture content of sediments was determined by gravimetric technique, where 50-g samples were placed in crucibles of porcelain and weighed using an analytical balance scale (Shimadzu, AY 220), followed by oven drying at 105°C for 24 h. Subsequently, the samples were placed in a desiccator containing silica gel until reaching room temperature. After that, they were weighed again on the analytical scale until constant mass in triplicate (CETESB, 1995; Filizola; Gomes; Souza, 2006). Thus, the moisture content can be determined by Equation 14:

$$u(\%) = \left(\frac{m_1 - m_2}{m_1} \right) \times 100 \quad (14)$$

Where $u(\%)$ is the moisture percentage, m_1 and m_2 are the wet and dry mass/weight of sediment samples, respectively.

Thermal analysis of sediment samples

Sediment samples were submitted to thermal analysis of the type TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) in a simultaneous equipment by Netzsch (model STA 449 F3 Jupiter), with a temperature range of 30–1200°C, heating rate of 20 K/min, and under a nitrogen atmosphere.

Determining major elements in the sediment samples of the Araucária point

The sediment samples were deposited in a sample holder coated with thin film Mylar® (thin fractions < 63 μm), to receive direct excitation on the energy dispersive X-ray fluorescence spectrometry (EDXRF), brand Shimadzu equipment (model EDX-720, irradiation time of 200 s, air atmosphere, rhodium source (Rh) with applied voltage of up to 50 keV, semiconductor detector Si (Li), collimator 10 mm).

Determining phosphorus, ammonia, and TA of water

The inorganic orthophosphate fractions (P_{orto}) were identified following the 4500 PC protocol, the ascorbic acid method (APHA, 2017). The total phosphorus (P_T) followed the 4500 P protocol (APHA, 2017), based on acid digestion followed by heating in order to change all phosphorus forms into orthophosphate. The analytical curve was established from the dilution of a standard phosphate solution (50 mgP.L^{-1}), quantified in a spectrophotometer (Varian, Cary 50) at 890 nm wavelength. The analytical curve was described by the following equation $y = 625.42x - 0.013$ ($R^2 = 0.99$), prepared at concentrations of 0.1, 0.2, 0.3, 0.5, and 0.9 mg.L^{-1} for quantifying inorganic phosphorus. For quantifying total phosphorus, the analytical curve was described by $y = 605.9x - 0.016$ ($R^2 = 0.99$), for concentrations of 0.1, 0.2, 0.3, 0.5, and 0.9 mg.L^{-1} .

Ammonia concentrations were determined following the 4500 N protocol (APHA, 2017). Analytical curves were prepared from a standard solution of HANNA 4001-03 ammonia diluted in the following concentrations: 0.10, 0.20, 0.50, 2.00, and 4.00 mg.L^{-1} ($y = -26.59\ln x - 64.41$; $R^2 = 0.99$). Water aliquots of 25 mL were taken using a volumetric pipette and transferred to a 50 mL beaker on a magnetic stirrer under gentle stirring, followed by the addition of 3 mL of sodium hydroxide solution (10 mol.L^{-1}) using a micropipette.

TA was determined by the titrimetric method (100 mL of the sample titrated with a hydrochloric acid solution until color change as shown by the specific phenolphthalein indicator), according to protocol 2310B (APHA, 2017).

Determining metals in water by inductively coupled plasma optical emission spectrometry

The dissolved fraction of the metals Cd, Cu, Fe, Zn, and Cr present in the water was quantified following protocol 3030 (APHA, 2017), whereas the metals in the total fraction were determined following method 200.2 (USEPA, 1994). The concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP OES) in a PerkinElmer Optima 8300 device operating in the following conditions: power 1300 W; axial/radial view plane; plasma 8 L min^{-1} ; 0.55 L min^{-1} nebulizer; auxiliary gas 0.2 L min^{-1} ; 60 s read delay; integration time 1–5 s; peristaltic pump flow rate of 1 mL min^{-1} ; three readings; autosampler pump flow rate of 1.5 mL min^{-1} and cleaning time of 15 s between samples. The analytical curves of the metals were prepared with a standard multi-element solution for AAS and ICP (TraceCERT®, brand Fluka) and ultrapure water for dilution.

Statistical and graph-building methods

The outliers were excluded from the sample dataset using the QuickCalcs outlier calculator software (GraphPad Software, 2022). The means, confidence intervals, and coefficients of variation were calculated using Microsoft Excel spreadsheets. The graphs were plotted using the SciDAVis software (Sourceforge, 2022).

The mass balance

The mass balance determined the accumulation rate in relation to time $\left(\frac{d(\phi)}{dt} \right)$, considering the average concentration of chemical species entering and leaving the water–sediment system, allowing to infer the ability to retain or export elements (Aprile; Bianchini Júnior; Lorandi, 2007; Vidal; Capelo Neto, 2014). Equation 15 was used in order to obtain the mass balance (Aprile; Bianchini Júnior; Lorandi, 2007; Vidal; Capelo Neto, 2014):

$$\frac{d(\phi)}{dt} = \phi_{input} - \phi_{output} \quad (15)$$

Where ϕ_{input} represents the sum of masses that are transferred from the sediment to the water column and ϕ_{output} represents the sum of masses that are transferred from the water column to the sediment column.

RESULTS AND DISCUSSION

Physicochemical parameters of the water column *in situ*

Table 1 presents the physicochemical parameters of the water column measured *in situ* during sampling.

The results show that the physicochemical parameters are significantly different within the sampling site(s). At the Araucária sampling site (A), the concentration of dissolved oxygen (DO) was lower than the detection limit of the instrument ($0.05 \text{ mg L}^{-1} \leq \text{LD}$, HANNA HI 9829), thus confirming hypoxia (Banks *et al.*, 2012; Zhang *et al.*, 2021). This result may be associated with the high discharge of industrial effluents rich in organic matter since the sampling site (A) is located at the exit of the third largest industrial district in Brazil (Machado *et al.*, 2014; Silva *et al.*, 2017).

Furthermore, the DO concentration must not be less than 5 mg L^{-1} in rivers classified as Class II by Resolution 357 (CONAMA, 2005; CETESB, 2020). It is noteworthy that some aquatic organisms, such as fungi and bacteria, consume dissolved oxygen to perform the mineralization of organic matter in their metabolic process, and their proliferation is favored in environments with a high concentration of labile organic matter (Campos, 2010; Cervi *et al.*, 2021; Jia *et al.*, 2023).

Also, sampling site (A) exhibited high turbidity (NTU), electrical conductivity (EC), and total dissolved solids (TDS) compared to the other sampling site. The EC values above $100 \text{ }\mu\text{S/cm}$, associated with turbidity values above 100 NTU and TDS values above 500 mg L^{-1} , can indicate impacted environments (CONAMA, 2005; Silva *et al.*, 2017; CETESB, 2020; Zhang *et al.*, 2021).

The pH can influence the precipitation of chemical species and favor the solubility of nutrients in natural aquatic ecosystems. Resolution 357 (CONAMA,

2005) establishes that for Class II rivers, pH values range from 6 to 9, thus classifying as basic the Barigüi River waters. Note that for (A) the pH was 7.2 ± 0.4 , indicating slight basicity favoring an increase in the alkalinity and the formation of calcium oxides (Rocha; Rosa; Cardoso, 2009; CETESB, 2020). Another study in the Barigüi River reported pH values ranging between 5.8 and 7.5 (Gonçalves, 2008; Machado *et al.*, 2014; Silva *et al.*, 2017).

On the other hand, the redox potential (*Eh*) can determine electron deficiency, reducing medium, or electron transfer, oxidizing medium (Rocha; Rosa; Cardoso, 2009; Cervi *et al.*, 2021). The *Eh* results demonstrate that sampling site (A) has a reductive environment, thus favoring the flow of chemical species from the water column to the sediments, unlike the upstream (AT) and (SF) sampling sites in the Barigüi River. The dissolved oxygen (DO) values ranged from 0.4 to 5.6 mg.L^{-1} , EC from 285 to $590 \text{ }\mu\text{S.cm}^{-1}$, and turbidity from 7 to 32 NTU .

Physical characteristics of sediments

The moisture content of sediment samples indicates the presence of hygroscopic substances, resulting in a greater possibility of retention of organic matter, nutrients, and contaminants (Cervi *et al.*, 2021; Jia *et al.*, 2023). Figure 2A shows the moisture percentages determined in the sediment samples from the Araucária (A), SF, and AT sampling sites in the Barigüi River. Figure 2A shows that the sampling site (AT) has the highest moisture content (%) compared to the other collection points.

This result is in accordance with the clay fraction obtained for this sediment sample shown in Figure 2B. Figure 2B shows the particle size distribution of sediment fractions of the Barigüi River collected at Araucária (A), SF, and AT sampling sites.

Resolution 344 (CONAMA, 2004) classifies sediments into sand, silt, and clay according to particle size. The reactivity of chemical species in the sediments increases with decreasing particle size; therefore, the finer the particles in the sediment, the greater the deleterious potential (Silva *et al.*, 2019; Mizael *et al.*, 2020; Wang *et al.*, 2022).

Figure 2B shows the predominance of fractions $\geq 250 \text{ }\mu\text{m}$, corresponding to sand. Among the sampling sites, (SF) had the highest percentage of sand, whereas (AT) had a predominant clay fraction, smaller than $53 \text{ }\mu\text{m}$ (fine fraction), which is more absorbent and reactive, facilitating the accumulation and resuspending of chemical elements (Silva *et al.*, 2019; Cervi *et al.*, 2021).

TGA has been used in sediments to distinguish labile organic matter (between 300 and 350°C) such as aliphatic structures and carbohydrates, from recalcitrant organic matter (400 and 530°C) aromatic-type structures such as lignins, recalcitrant carbons, and polycondensate structures (700 and 900°C) such as lipids and aromatics (Capel *et al.*, 2006; Oikonomopoulos *et al.*, 2013; Cimbaluk *et al.*, 2018). The TGA graphs, Figure 3A and Table 2, show eight events of mass loss for the SF and AT environments and six events for Araucária (A).

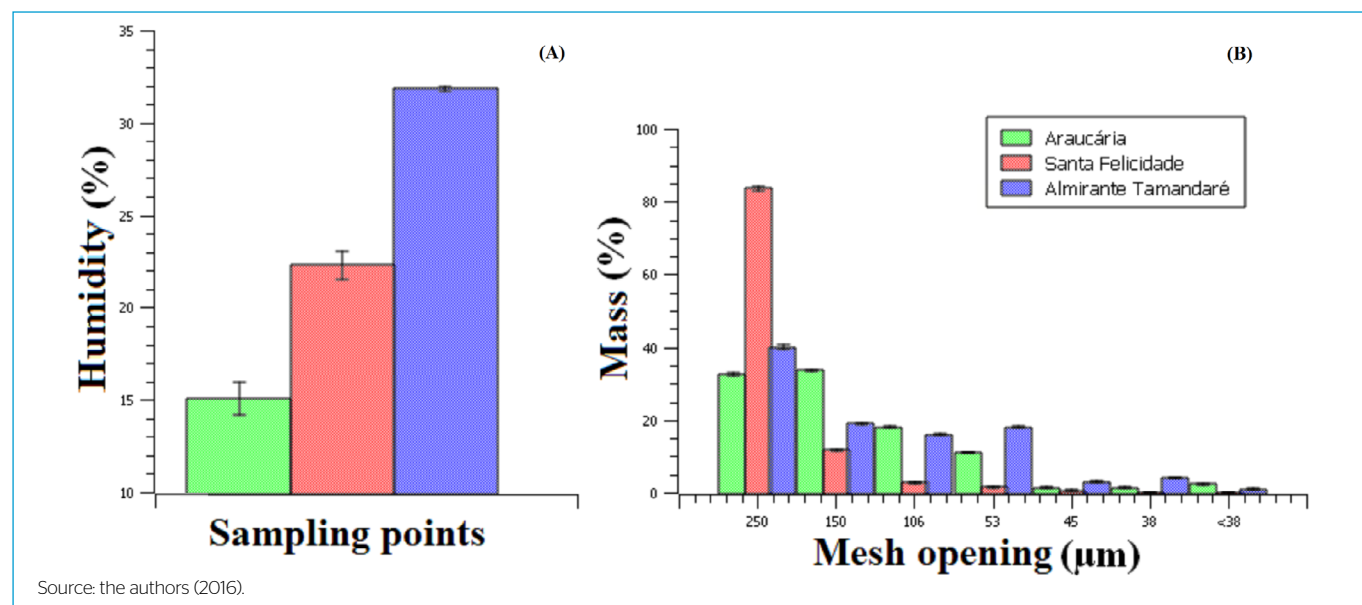
Although (A) presents a smaller number of events, it was the environment that presented the greatest mass loss, 44.0% , mainly in regions characteristic of the presence of labile organic matter that may be associated with the input of effluents (Li *et al.*, 2022; Beluco; Ionashiro; Brito, 2023). Note in (A) a distinction in behavior in relation to (SF) and (AT), evidenced between temperatures from 222.2 to 440.5°C referring to the burning of young organic matter, possibly associated with the disposal of industrial effluents (Capel *et al.*, 2006; Liu *et al.*, 2018).

Table 1 – Physical and chemical parameters measured *in situ* during water and sediment sampling in the Barigüi River, southern Brazil.

Parameters	(A)	(SF)	(AT)
Dissolved oxygen (mg L^{-1})	< LD*	7.7 ± 0.3	9.9 ± 0.5
Conductivity ($\mu\text{S.cm}^{-1}$)	582.0 ± 2.5	337.0 ± 12.4	363.0 ± 6.7
Resistivity ($\mu\Omega\text{cm}^{-1}$)	0.0017	0.0030	0.0027
Dissolved solids (mg L^{-1})	$294.0 \pm 12.$	169.0 ± 15	183.0 ± 14
Salinity (PSU)	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
Turbidity (NTU)	52.8 ± 8.4	11.7 ± 6.2	14.4 ± 2.8
Temperature ($^\circ\text{C}$)	17.8 ± 1.2	16.9 ± 0.8	16.6 ± 1.1
Pressure (psi)	13.4 ± 0.2	13.4 ± 0.1	13.3 ± 0.1
Redox potential (mV)	-26.5 ± 4.6	53 ± 3.8	48 ± 2.8
pH	7.2 ± 0.4	6.4 ± 0.2	6.2 ± 1.2

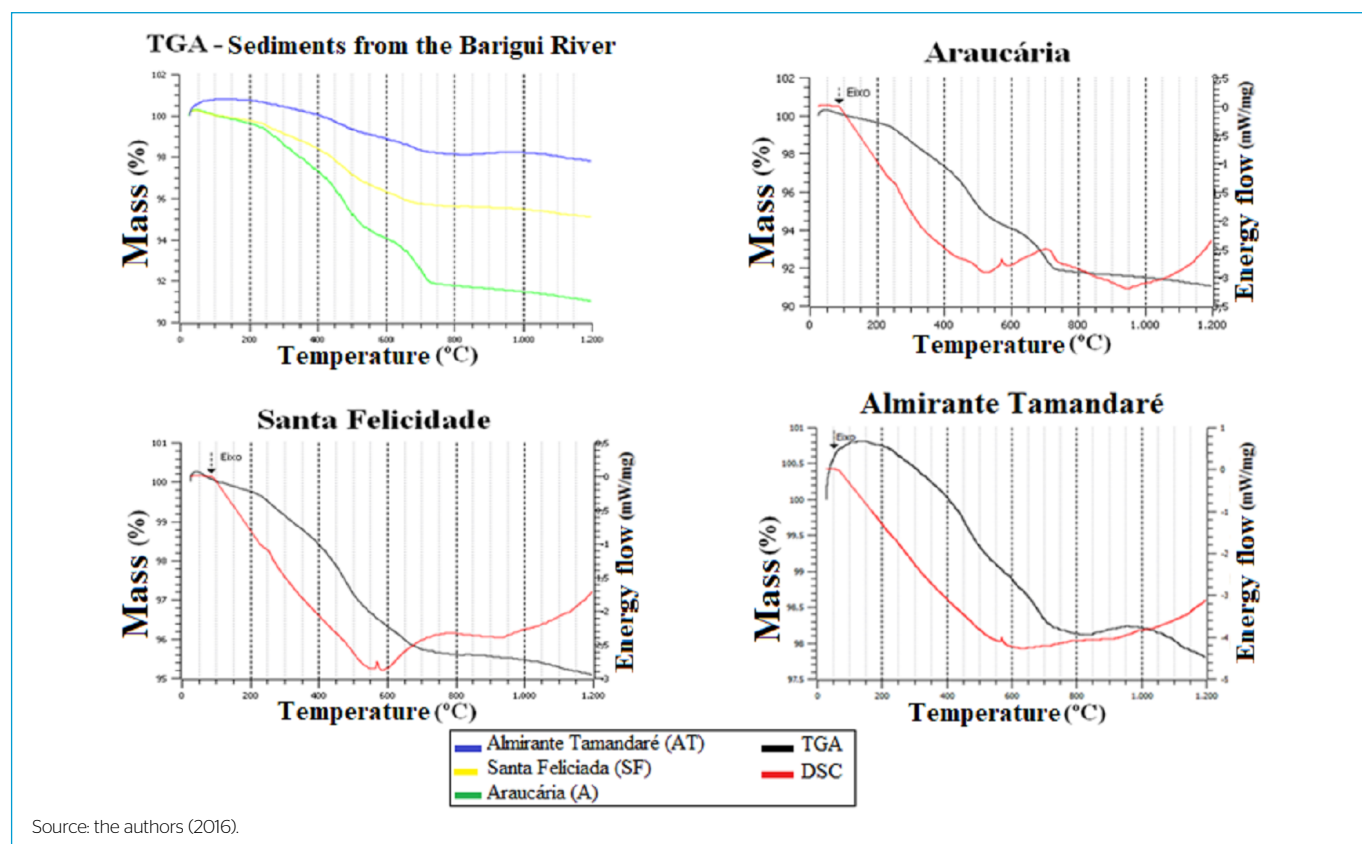
Source: the authors (2016).

*LD: method detection limit; (A): Araucária sampling site; (SF): Santa Felicidade sampling site; (AT): Almirante Tamandaré sampling site.



Source: the authors (2016).

Figure 2 – (A) Moisture (%) of sediment samples collected from the Barigüi River and quantified by gravimetry. (B) Mesh opening distribution of the sediment samples from the Barigüi River, determined by fractionation.



Source: the authors (2016).

Figure 3 – Thermal analysis of sediment samples from the Barigüi River, southern Brazil. (A) Variation in the mass of sediment samples from the sampling points as a function of temperature rise. (B) Thermal analysis of sediment sample from the Araucária point. (C) Thermal analysis of sediment sample from the Santa Felicidade point. (D) Thermal analysis of sediment sample from the Almirante Tamandaré point.

Despite presenting a smaller number of events, environment (A) had the highest mass loss, 44.0% mainly in regions characterized by the presence of labile organic matter that may be associated with the inflow of effluents. The characteristics of environment (A) differed

from environments (SF) and (AT), as evidenced by the burning of young organic matter, possibly associated with the disposal of industrial effluents in temperatures ranging from 222.2 to 440.5°C (Capel *et al.*, 2006; Zhang *et al.*, 2021).

The thermal analysis (DCS) shows the results of the energy flow processes over the matrix, in Figures 3B, 3C, and 3D. Figure 3 shows the endothermic processes related to the decreasing sediment mass that starts at about 50°C and continues up to 675°C (Liu *et al.*, 2018; Zhang *et al.*, 2021).

The absorption of energy in this system is related to the decomposition of organic matter and the breaking of carbon bonds, linked to both labile and recalcitrant fractions. The exothermic processes (beginning between 675 and 700°C) are somehow related to the combustion of aromatic compounds and the breaking of bonds between carbons present in sediment samples (Capel *et al.*, 2006; Oikonomopoulos *et al.*, 2013).

The analyses of EDXRF were conducted with the goal of establishing a multi-elemental profile of the majority of the chemical element constituents in the sediment samples (Supplementary Table 1: <https://docs.google.com/document/d/1vz-MgbLP5M15nIT1xc3k0OXYN-q01LkT/edit?usp=sharing&oid=106882126832372820439&rtfpof=true&sd=true>). The EDXRF performance was evaluated by retrieving the Green River Shale (SGR-1b) certified sample from the United States Geological Survey (Supplementary Figure 1: <https://docs.google.com/document/d/1vz-MgbLP5M15nIT1xc3k0OXYN-q01LkT/edit?usp=sharing&oid=106882126832372820439&rtfpof=true&sd=true>). In Table 3, we can observe the results of the chemical element concentrations of five sediment samples obtained from the Araucária (A) sampling site.

Sediment incubation over time

For stabilization and sedimentation of the particulate material, the flow over time was measured 48 h after incubation had started, kept at a constant temperature of 18°C in a DBO oven (Janke *et al.*, 2011; Yamada *et al.*, 2012). The sediment–water and control (water) systems were opened on the following days $t = 0$; $t = 7$; $t = 21$; and $t = 45$ days. To determine the physical and chemical parameters in the water column, four jars were opened, three with sediment–water and one system control with water

Table 2 – Analysis of thermogravimetric curves of sediment samples.

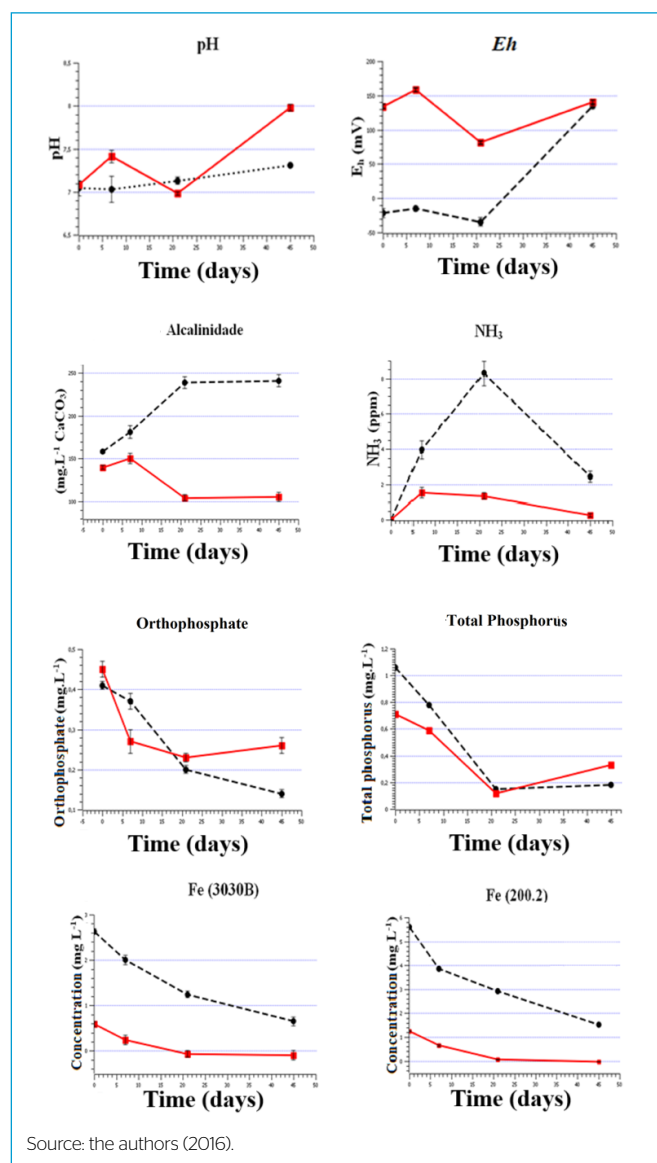
Site	Temperature (°C)	Weight/mass loss (mg)	Weight loss (%)
(A)	379-222.2	0.8	4.2
	222.2-440.5	2.8	14.2
	440.5-517.6	1.8	9.2
	517.6-645.8	1.2	6.0
	645.8-738.6	1.7	8.8
	738.6-993.3	0.3	1.7
Total	6 events	8.8	44.0
(SF)	39.4-103.8	0.3	1.3
	103.8-230.9	0.3	1.4
	230.9-364.1	0.9	4.1
	364.1-457.4	0.9	2.4
	457.4-512.6	0.8	3.6
	512.6-612.5	0.7	3.3
	612.5-662.4	0.4	1.6
	662.4-998.9	0.4	1.7
Total	8 events	4.8	19.4
(AT)	61.15-212.7	0.3	1.7
	212.7-379.5	0.6	3.4
	379.5-526.1	0.9	5.1
	526.1-642.2	0.5	2.8
	642.2-718.5	0.5	2.6
	718.5-807.6	0.1	0.8
	807.6-987.3	-0.1	-0.7
	987.3-1089.0	0.2	0.9
Total	8 events	2.9	16.6

Source: the authors (2016).

only (Supplementary Table 2: <https://docs.google.com/document/d/1vz-MgbLP5M15nIT1xc3k0OXYN-q01LkT/edit?usp=sharing&oid=106882126832372820439&rtfpof=true&sd=true>). The analytical results of the evolution of pH and Eh over time are shown in Figure 4. The graphs show the evolution of the parameters in the systems: sediment–water and the control (water) systems during the 45 days of incubation.

Figure 4 shows that the pH values remained practically neutral, with a small change to basicity that may be due to the presence of carbonates that neutralize acid formation, acting on the system buffering.

A similar result was found by Janke *et al.* (2011), Banks *et al.* (2012) and Heinrich *et al.* (2021). Figure 4 also shows the stabilization of Eh up to $t = 21$ days, after which the system evolves, becoming an oxidant at $t = 45$ days. The control, on the other hand, exhibited small oscillations reaching the oxidizing condition throughout the period. Janke *et al.* (2011), Yamada *et al.* (2012), and Zhang *et al.* (2021) reported similar results for the evolution of the redox potential of such systems, indicating the equilibrium condition of the chemical reactions.

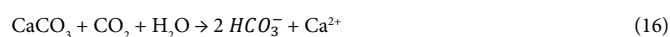


Source: the authors (2016).

Figure 4 – Temporal changes of variables (pH, Eh, total alkalinity, NH_3 , orthophosphate, total phosphorus, and Fe concentrations) during the 45-day incubation period.

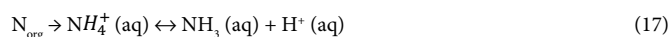
Figure 4 shows that TA increased in the S+W systems up to $t = 21$ days, followed by stabilization up to $t = 45$ days. In the control, it increased up to $t = 7$ days, and decreased at $t = 21$ days, followed by subsequent stabilization up to $t = 45$ days. This increase in TA is explained by the mineralization of organic matter, which produces bicarbonate ions. These carbonate ions are then transformed into carbon dioxide. The presence of calcium carbonate, which is found in the sediment samples (Table 3) and whose solubility is altered depending on the mineralization of organic matter demonstrated using TGA in Table 2 (Zhang *et al.*, 2021; Wagner 2019; Wang *et al.*, 2022).

Major minerals, such as calcium oxide (CaO), quantified in sediment samples (Table 3) from the Araucária (A) sampling site, are abundant in rocks such as granites and gneisses, which are common in the states of the southern region of Brazil and contribute to the alkalinity of the waters (Mineropar, 2001; Froehner; Martins, 2008; Gonçalves, 2008). The reaction of calcium carbonate with carbon dioxide in an aqueous medium is represented below (Equation 16):



Still, in Figure 4, ammonia (NH_3) concentrations increase up to $t = 21$ days. Under anoxic conditions, the reduced forms of nitrogen resulting from the decomposition of organic matter and ammonia prevail (Wagner, 2019; Heinrich *et al.*, 2021). The ammonia generated in the anaerobic layers of the sediment can diffuse to the aerobic layer of the water column (Cervi *et al.*, 2021; Zhang *et al.*, 2021; Jia *et al.*, 2023).

Furthermore, the presence of calcium in the matrix can reduce the phosphorus release to the water column and lead to an increase in the concentrations of (NH_3) produced from the nitrate and nitrite forms, according to Equation 17:



This result can be seen in Figure 4 and was similar to that found by Janke *et al.* (2011), Banks *et al.* (2012), and Zhang *et al.* (2021). Ammonia is a toxic compound that restricts the presence of aquatic species such as fish. Usually values above 0.01 mg.L^{-1} of ammonia in the water column can induce toxicity effects on these organisms and concentrations above 5 mg.L^{-1} of ammonia are not tolerated by most species (CETESB, 2020).

Table 3 - Average concentration of majority chemical elements obtained in thin fractions ($< 63 \mu\text{m}$) of sediments of the Barigüi River analyzed by energy dispersive X-ray fluorescence spectrometry.

Araucária (A)*		
Majority chemical	$\bar{x} \pm \text{IC}$	C.V. (%)
SiO_2	29.52 ± 0.03	0.2
Al_2O_3	6.91 ± 0.30	7.1
Fe_2O_3	2.32 ± 0.03	1.5
K_2O	0.96 ± 0.01	0.5
CaO	0.70 ± 0.01	0.4
TiO_2	0.50 ± 0.02	7.2
P_2O_5	0.46 ± 0.01	3.9
MnO	0.03 ± 0.01	1.1
ZnO	0.05 ± 0.01	1.0

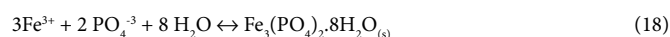
Source: the authors (2016).

*(A): Araucária sampling point; $\bar{x}$: average concentration; IC: confidence interval; C.V. (%): coefficient of variation.

At 21 days of the induced hypoxia experiment, we found values of average ammonia concentrations greater than 8 mg.L^{-1} . Where it is observed in Figure 4 that the orthophosphate (P_{orto}) and total phosphorus (P_T) concentrations decrease up to $t = 21$ days. In this sense, the average concentrations of Ca, Fe, and Mn present in the sample of sediments (Table 3), which can interact with water-soluble phosphates in the ionic form, can lead to the precipitation of phosphorus forms in the sediments, as shown in Equations 10, 11, 12, and 13.

Additionally, in the presence of sulfide, bicarbonate, phosphate, iron, and manganese salts, and other associated metals may precipitate from the water column to the sediments (Wagner, 2019; Heinrich *et al.*, 2021; Zhang *et al.*, 2021). Figure 4 shows the evolution of Fe concentrations (total and dissolved form) over the incubation period of 45 days. Figure 4 shows the decay of the average concentrations of Fe in the total (protocol 3030B) and dissolved fractions (protocol 200.2) compared to the beginning of the incubated experiment and the control.

The resuspension of the elements Ca, Fe, and Mn present in the sediment samples into the water column, which in ionic form can interact with soluble inorganic phosphates, precipitated them in the sediments, according to Equation 18:



During the experiment, no detectable changes were observed in the Cd, Cu, Zn, and Cr concentrations present in the water column (Supplementary Table 3: <https://docs.google.com/document/d/1vz-MgbLP5M15nIT1xc3k0OXYN-q01LKt/edit?usp=sharing&ouid=106882126832372820439&rtfpof=true&sd=true>).

Figure 5A shows the experimental setup and identification of incubation (sediment + water) and control (water only) systems. Figure 5B allows visualizing the formation of iron oxides on the surface of the incubation systems after 45 days.

Dissolved oxygen concentrations in all systems at the opening events were below the detection limit of the multiparameter probe.

The concentrations of total phosphorus, total Fe, ammonia, and TA were used in the mass balance, which in turn determined the accumulation rate in relation to time, considering the average concentration of chemical species entering and leaving the water-sediment system, allowing to infer the ability to retain or export elements. The concentrations of total phosphorus, total Fe, ammonia, and TA were used in the balance, and only inputs and outputs in the liquid medium were taken

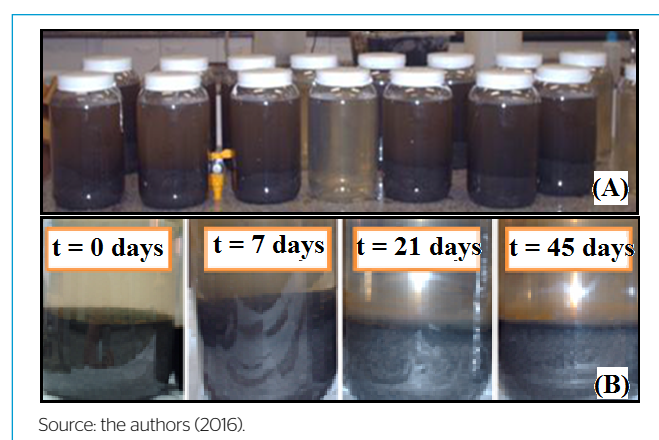


Figure 5 - (A) Study of hypoxic behavior: set of incubation systems with samples of water and sediments from the Barigüi River. (B) Formation of an oxidation layer on the surface of the incubation systems during the opening events.

into account. The accumulation rate in relation to time is $\frac{d(\phi)}{dt} = 4,2mg.L^{-1}$ per day. Figure 6 shows the flow of species used in the mass balance.

CONCLUSIONS

Degraded aquatic ecosystems, such as the Barigüi River, are normally known as reducing/reduction agents, with high concentrations of organic matter and under hypoxia. Under these conditions, the proliferation of bacteria that degrade organic matter and use of alternative electron receptors trigger processes that can influence the release of phosphorus, ammonia, and metals into the water column.

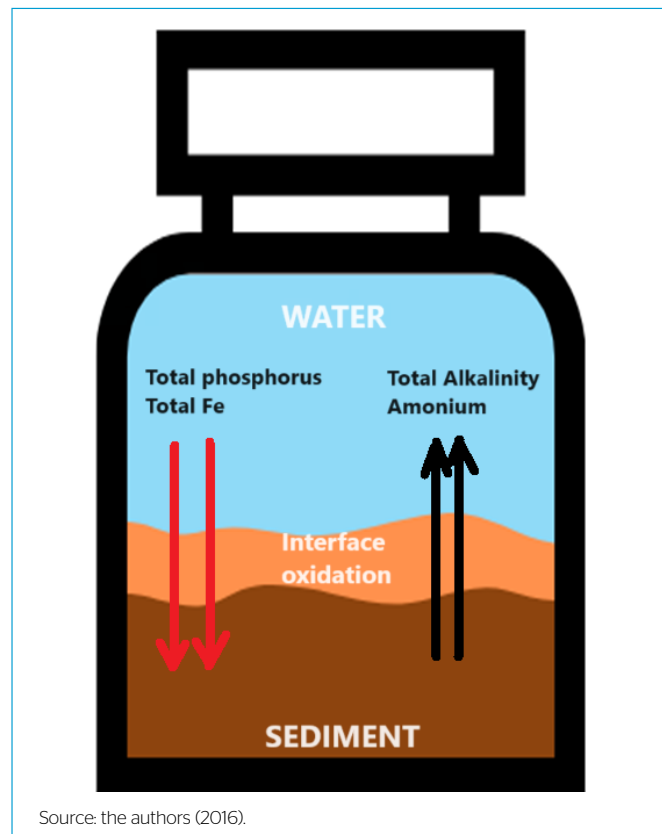


Figure 6 – Flux of chemical species between water and sediment compartments in the incubated system (t = 21 days).

In this study, the concentrations of phosphorus and metals in the water column decreased, leading to the deposition of the sediments. Thus, under prolonged hypoxia, changes at the water column/sediment interface, originating from the Barigüi River, at the Araucária sampling site, are influenced by the presence of calcium (as carbonates and nitrates) acting on the buffering of the water system to stabilize the pH, inhibit the release of phosphorus from the sediment to the water column, and thus increase the ammonia concentrations and TA of the water.

The river conditions influence the exchange between the water column and the sediments. Under conditions of high pollutant load, such as those presented in the Barigüi River at the Araucária sampling point (A), the sediment (the sediments become) became a reservoir of pollutants that can return to the water column. We present evidence of possible resuspension of ammonia, a highly toxic element, at 21 days of the hypoxia experiment from the sediments to the water column, deteriorating its quality.

In addition, there was a suspension of phosphorus, a nutrient that favors the proliferation of algae in water systems, leading to eutrophication events. Although there are inherent limitations in transferring a real-scale sample of what occurs in a river section to a controlled system without hydrodynamic influence, it was possible to evaluate the changes resulting from prolonged hypoxia events at the water-sediment interface. In future work, we recommend exploring ecotoxicity assessments and evaluating and characterizing the behavior of microorganisms in the sediment and water column.

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AUTHORS' CONTRIBUTIONS

Silva, P.R.B.: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Software, Validation, Writing – original draft. Makara, C.N.: Formal analysis, Writing – original draft, Writing – review and editing. Munaro, A.P.: Formal analysis, Writing – review and editing. Cruz, L.A.D.: Data curation, Formal analysis, Writing – review and editing. Wastowski, A.D.: Data curation, Formal analysis, Resources. Schnitzler, D.C.: Conceptualization, Project administration, Resources, Supervision.

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