UNIVERSIDADE FEDERAL DO PARANÁ

ANGELA ETHELIS JIMENEZ MARTINEZ

DISENTANGLING THE ENVIRONMENTAL IMPACT ON THE BIOGEOCHEMISTRY OF WATER RESERVOIR SUBTROPICAL IN SOUTHERN, BRAZIL



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Tese apresentada ao curso de Pós-Graduação em Engenharia Ambiental, Setor de Tecnologia, Universidade Federal do Paraná, como requisito parcial à obtenção do título de Doutora em Engenharia Ambiental.

Orientador: Prof. Dr.Sandro Froehner

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"Dedicated to the Virgin Mary Help of Christians as light and guide of my life"

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RESUMO

Sabe-se que a biogeoquímica dos lagos pode ser influenciada por mudanças climáticas, assim como atividades antrópicas. Tais mudanças podem ser refletidas nas variações da composição da matéria orgânica (MO). Para estudar as mudanças ambientais ocorridas na bacia do reservatório Passauna, sul do Brasil, foram coletados dois testemunhos sedimentares, os quais contém matéria orgânica depositada no período compreendido de aproximadamente 136 anos para o testemunho I e 97 anos para o testemunho II. Com base em diversos marcadores geoquímicos (metais, δ^{13} C, δ^{15} N, n-alcanos e hopanos), foi possível identificar que durante o período de 1930-1970 as atividades antropogênicas controlaram os impactos e a qualidade da água. Também foram utilizadas razões entre metais Mn/Fe, Cu/Ni e V(V+Ni) como indicadores paleoredox e paleoproductividade (Capitulo 2). Já o Capítulo 3, mostra a evolução da produção da matéria orgânica alóctone e autóctone no reservatório, assim como reconstrução histórica da deposição atmosférica da cidade Curitiba, portanto, a implicância de atividades antropogênicas nesse período (Capitulo 4).

Os valores de EF (Fator de Enriquecimento) dos seguintes metais diminuíram: no testemunho I, EF(Fe) > EF(Mn) > EF(Cd) > EF(Sb) > EF(Zn) > EF(Cu) > EF(Cr) > EF(Pb); e no testemunho II, EF(Sb) > EF(Pb) > EF(Cd) > EF(Cr) > EF(Fe) > EF(V) > EF(Zn) > EF(Cu) > EF(Ni) > EF(Mn), assim mostrando o enriquecimento dos metais durante o período de 1930-1970. No testemunho II, durante o período 1973-2013 há um aumento na concentração de alcanos de cadeia curta, indicando contribuição do fitoplâncton. Em contrapartida, no testemunho I prevalece a fonte terrestre para composição da matéria orgânica. Atividade microbiana e presença de bactérias metanotróficas foram confirmadas com a presença dos seguintes hopanos: 17α , 21β (H)-30-norhopane; 18α (H)-30-nor-neo-hopane; 17α , 21β (H)-hopane; and 17β , 21α (H)-hopane (moretane), depois de 1940. As concentrações totais de HPAs variaram de 5,13 ng.g-1 a 444,60 ng.g-1 (testemunho I) e de 124,55 ng.g-1 a 3.018,14 ng.g-1 (testemunho II). As concentrações atingiram o pico em 1944 e 1958, refletindo o crescimento da economia local.

Em geral, este estudo fornece informações mais precisas que podem auxiliar na construção de cenários pretéritos vinculados a mudanças climáticas e antrópicas. Tais resultados podem ser utilizados posteriormente no planejamento futuro para restauração e gerenciamento de corpos hídricos em situação semelhante.

Palavras chaves: Eutrofização, matéria orgânica, biomarcadores lipídicos, lago e reservatório.

ABSTRACT

It is known that the biogeochemistry of lakes can be influenced by climate change and human activities. Such changes can be reflected in variations in the composition of organic matter (OM). To study the environmental changes that occurred in the Passauna reservoir basin, south of Brazil sedimentary cores were collected, which contain organic matter deposited in the period comprised approximately 136 years for core I and 97 years for core II. Based on several geochemical markers (metals, δ^{13} C, δ^{15} N, n-alkanes, and hopanes), it was possible to identify that during the period 1930-1970, anthropogenic activities-controlled impacted water quality. In addition, we applied the Mn/Fe, Cu/Ni, and V(V+Ni) ratios as paleoredox and paleoproductivity indicators (Chapter 2). To better understand the evolution of the production of allochthonous and autochthonous organic matter in the reservoir (Chapter 3), as well as the historical reconstruction of the atmospheric deposition of the Curitiba city, therefore, the implications of anthropogenic activities in this period (Chapter 4).

The Enrichment Factor (EF) values of the following metals decreased: in core I, EF(Fe) > EF(Mn) > EF(Cd) > EF(Sb) > EF(Zn) > EF(Cu) > EF(Cr) > EF(Pb); and in core II, EF(Sb) > EF(Pb) > EF(Cd) > EF(Cr) > EF(Fe) > EF(V) > EF(Zn) > EF(Cu) > EF(Mn), showing the largest enrichment of the metals during the period 1930-1970. In the core II, during the period 1973-2013 shows an increase in short-chain n-alkanes concentration, indicating contribution by phytoplankton. In contrast, in core I, terrestrial source prevails for organic matter composition. Microbial activity and presence of methanotrophic bacteria was confirmed with the presence of the following hopanes: 17α , 21β (H)-hopane; 18α (H)-30-nor-neohopane; 17α , 21β (H)-hopane; and 17β , 21α (H)-hopane (moretane), after 1940. Total concentrations of PAHs varied from 5.13 ng g⁻¹ to 444.60 ng g⁻¹ (core I) and from 124.55 ng.g⁻¹ to 3,018.14 ng.g⁻¹ (core II). The concentrations peaked at 1944 and 1958, reflecting the boom in local economics.

Overall, this study provides more accurate information that can help in the construction of past scenarios linked to anthropic changes. These results can be used later to develop plans for the restoration and management of water bodies in similar conditions.

Keywords: Eutrophication, organic matter, lipid biomarkers, lake and reservoir

RESUMEN

Se sabe que la biogeoquímica de los lagos puede verse influenciada por el cambio climático, así como por las actividades humanas. Dichos cambios pueden reflejarse en variaciones en la composición de la materia orgánica (MO). Para estudiar los cambios ambientales ocurridos en la cuenca del embalse de Passauna, sur de Brasil, fueron recolectados dos núcleos sedimentarios que contienen materia orgánica depositada aproximadamente en un periodo 136 años para el núcleo I y 97 años para el núcleo II. Con base en varios marcadores geoquímicos (metales, δ^{13} C, δ^{15} N, n-alcanos y hopanos), fue posible identificar que durante el período 1930-1970, las actividades antrópicas controlaron los impactos y la calidad del agua. Las relaciones entre los metales Mn/Fe, Cu/Ni y V(V+Ni) se utilizaron como indicadores de paleoredox y paleoproductividad (Capítulo 2). El Capítulo 3, por otro lado, muestra la evolución de la producción de materia orgánica alóctona y autóctona en el embalse, así como la reconstrucción histórica de la deposición atmosférica de la ciudad de Curitiba, por lo tanto, las implicaciones de las actividades antrópicas en este período. (Capítulo 4).

Los valores de EF (Factor de Enriquecimiento) de los siguientes metales disminuyeron: en el núcleo I, EF(Fe) > EF(Mn) > EF(Cd) > EF(Sb) > EF(Zn) > EF(Cu) > EF (Cr) > EF(Cu) > EF(Mn), mostrando así el enriquecimiento de metales durante el período 1930-1970. En el núcleo II, durante el período 1973-2013 se presenta un incremento en la concentración de alcanos de cadena corta, indicando el aporte de fitoplancton. En cambio, en el núcleo I predomina la fuente terrestre para la composición de la materia orgánica. Despues de 1940, la actividad microbiana y la presencia de bacterias metanotróficas se confirmaron con la presencia de los siguientes hopanos: 17α , 21β (H)-hopano; y 17β , 21α (H)-hopano (moretano). Las concentraciones totales de PAH oscilaron entre 5,13 ng.g⁻¹ y 444,60 ng.g⁻¹ (nucleo I) y entre 124,55 ng.g⁻¹ y 3018,14 ng.g⁻¹ (nucleo II). Las concentraciones alcanzaron su punto máximo en 1944 y 1958, lo que refleja el auge de la economía local.

En general, este estudio proporciona información más precisa que puede ayudar en la construcción de escenarios pasados vinculados a los cambios climáticos y antrópicos. Dichos resultados pueden utilizarse posteriormente en la planificación futura para la restauración y gestión de cuerpos de agua en una situación similar.

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LIST OF SYMBOLS, ACRONYMS, AND ABBREVIATIONS

δ ¹³ C	-isotopic carbon ratio
$\delta^{15}N$	-isotopic nitrogen ratio
β	-Beta position
α	-alpha position
‰o	-Per mil
Σ	-Sum
ACL	-Average chain length
AHs	-Aliphatic hydrocarbons
ANT	-Anthracene
Acenaf	-Acenaftilene
Baa	-Benzo(a)anthracene
Bap	-Benzo(a)pyrene
BkF	-Benzo(k)fluoranthene
BbF	-Benzo(b)fluoranthene
Bghip	-Benzo (g,h,i)perylene
CFCS	-Constant flux constant sedimentation
CPI	-Carbon preference index
Cmax	-Carbon maximum
Cfb	-oceanic temperate climatic
Chry	-Chrysene
CONAMA	-Conselho Nacional de Meio Ambiente
DCM	-Dichloromethane
F1	-Fluoranthene
Flu	-Fluorene
US EPA	-U.S. Environmental Protection Agency
GC/MS	-Gas Chromatography coupled to Mass Spectrometry
g	-grams
HC1	-Hidrochloric acid
HMW	-High Molecular Weight
IAP	-Instituto Ambiental do Paraná
Ind	-Indeno (1,2,3-cd)pyrene
IQAR	-Dam Water Quality Index

km ²	-square kilometers
LMW	-Low Molecular Weight
MeOH	-Methanol
PAHs	-Policyclic Aromatic Hydrocarbons
Paq	- Proxy of aquatic macrophytes input
PCA	-Principal Component Analysis
Ph	-Phytane
PMF	-Positive Matrix factorization
Pr	-Pristane
Pyr	-Pyrene
²¹⁰ Pb	-Lead
¹³⁷ Cs	-Cesium
ОМ	-Organic matter
OEP	-Odd carbon predominance
RMC	- Região Metropolitana de Curitiba
SUDERSA	-Superintendência de desenvolvimento de recursos hídricos e ambiental
TAR	-Terrestrial/Aquatic Ratio
TEQs	-Toxic Equivalent
TOC	-Total Organic Carbon
TLE	-Total Lipid Extract
ТМ	-Trace Metal
TN	-Total Nitrogen
μg	-micro grams
VPDB	-Vienna Pee Dee Belemnite

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1 INTRODUCTION

Recently, there is an increasing concern to preserve freshwater bodies, especially because most are used as water suppliers. Pollution and climate can interfere with the water quality of the urban reservoirs. In this study, we examine two sedimentary cores from Passauna reservoir, attempting to assess how to land occupation and climate interfere with the biogeochemistry of this reservoir. The Passauna reservoir is considered vital for the water supply to the city of Curitiba (VEIGA and DZIEDZIC, 2010). The Passauna reservoir is located between S 25°25'48" and W 49° 15' 16". Passauna sub-basin has a drainage area of 217 km², the reservoir is a shallow mean depth of 6.5 m, an artificial reservoir with a dam. The Passauna reservoir-initiated operation in 1989. ERHSA, 2007; CARNEIRO et al., 2016; IAP, 2017).

The study region has, in the Köppen classification, a temperate oceanic climate (Cfb), which is not very constant, with sudden variations during the same day. In general, winters have an average temperature of the coldest month below 18°C, while in the hottest month the average temperature remains above 10°C and below 22°C. Mean annual precipitation ranges from 1400 mm to 1600 mm (ARAUCARIA, 2003; NOGAROLLI, 2007). According to Xavier et al. (2005), the quality of the Passauna reservoir can be classified as moderately degraded. To better understand the biogeochemical processes in the lake reservoir, were collected sedimentary cores and examine the occurrence and distribution of metals, aliphatic hydrocarbons, hopanes and polycyclic aromatic hydrocarbons (PAHs) used as geochemical markers. The geochemical markers tend to remain accumulated in the sediments over time, which allows the analysis of recent and previous contamination (surface sediment), such as the reconstruction of past scenarios related to natural and anthropic events that occurred in the watershed (PETERS et al., 2005).

The use of biomarkers as paleoenvironmental proxies has been considered an effective tool to understand the anthropogenic and natural influences on the water quality of a water body over time (BIANCHI and CANUEL, 2011). Heavy metals such as Pb, Cr, As and Cu are widely used to source fingerprint and trace contaminant transport pathways and assess pollution stress over time in aquatic environments (WANG et al., 2011). The deposition of metals can be altered by climatic changes, by modifying their input from surface sources in the basin, by changing the atmospheric wet and dry chemical disposition through changes in precipitation and affecting mixing and stratification processes, or by changing water chemistry, in some cases resulting in the release of metals from bottom sediments (XU et al., 2017). Cd, Co, Zn, and Ni are biologically essential elements (enzyme metabolites) scavenged to the sediments during

sedimentation, recent studies used them as indicators of changes in primary productivity in aquatic environments (CHAILLOU et al., 2002; PAYTAN and GRIFFITH, 2007).

The n-alkane profiles, from different organisms, can be preserved in the sediments as geochemical records, that could be used as a fingerprint to infer the sources of depositional organic matter in the reservoir (MEYERS, 2003; WANG et al., 2006). It is known that short-chain odd-carbon n-alkanes (nC₁₅, nC₁₇, and nC₁₉) are abundant in phytoplankton, while medium-chain and long-chain n-alkanes are prominent in submerged/floating macrophytes and terrestrial plants, respectively (PETERS et al., 2005; JENG, 2007). On the other hand, PAHs are used as indicators of environmental pollution caused by emissions from burning fossil fuels, oils, and diesel, as well as from burning vegetation for agricultural purposes (YUNKER et al., 2002). Thus, determining the relative contribution of organic matter sources will be critical to understanding how climate and land occupation can control/interfere with the biogeochemical processes in water bodies. A better understanding of those processes could be essential to applying good practices in designing and further establishing good management.

1.1 JUSTIFICATION

The Passauna reservoir, currently, is one of the largest water suppliers for the metropolitan region of Curitiba. More than 650.000 inhabitants receive water from Passauna. It is among the springs threatened by urban influence, representing 22% of the public water supply (IAP, 2009).

Studies have been carried out that are related to post-anthropic impact periods. Passauna reservoir has been studied in various areas since the analysis of water quality and sediment (BUSCH, 2008; CARNEIRO; KELDERMAN, IRVINE, 2016) modeling (SMAHA; VEIGA; DZIEDZIC, 2010), land use and occupation (SAUNITI; FERNANDES; BITTENCOURT, 2003; BUSCH, 2008), ecological evaluation (COQUEMALA, 2005), ebullition (MARCON, 2018), temperature and stratification (POLI, 2018) and suspended solids (WOSIAKI, 2017). Meanwhile, there is no long-term information that covers a time scale (pre and post anthropic impact) in the ecosystems, the initial conditions being unknown.

Thus, the following study seeks to infer the biogeochemical processes and the historical process of eutrophication associated with anthropogenic activities in the water body (DUMISTRESCU and BRASSEL, 2005). For this, we used a multi-biomarker approach that includes saturated hydrocarbons, polycyclic aromatic hydrocarbons, and compound-specific analysis in two sedimentary cores, to examine recent changes in autochthonous and allochthones organic carbon inputs in the reservoir Passauna. It would be the first contribution

detailing temporal variation of multi-proxy analysis to understand and reconstruct eutrophication episodes in this aquatic environment.

Therefore, this study is accounted for by the unprecedented paleolimnological data about study in aquatic environments, also it will contribute to knowing the baseline state, access to environmental variability, and alterations over time. This information is useful to understand the operation of lakes and identify possible sources that cause deterioration of water quality. Understanding those multiple stressors that influence the past helps to anticipate future responses that are vital for water resources management.

1.2 HYPOTHESIS

The sediments retain all compounds which reflect the external influence provoked by natural factors or by anthropogenic activities. Thus, the distribution of the geochemical markers can be associated with those facts.

1.3 OBJECTIVES

1.3.1 General Objective.

Assess the possible effects of land occupation in Passauna reservoir concerning through analysis of aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, and isotopic compositions (δ^{13} C and δ^{15} N). All these data will be considered within a robust chronological framework attained by measuring ²¹⁰Pb and ¹³⁷Cs decay in two sediments cores.

1.3.2 Specific objectives

- Determine the source of organic matter input; natural or anthropogenic source.
- Compare sedimentation rates based on a chronological determination by ²¹⁰Pb and ¹³⁷Cs decay;
- Associate the temporal chemical markers with anthropogenic to reconstruct scenarios of paleoenvironmental changes.

Structure of thesis

This thesis is structured into chapters:

Chapter 1: presents an introduction to the research topic, the objectives, justification, and a bibliographic review of the concepts of biomarkers, lentic environments, and organic matter.

Chapter 2: 136-years of variations of metals in sediment from a subtropical reservoir in southern Brazil: Implications for the environmental change.

Chapter 3: Insights into the origin of organic matter from saturated hydrocarbons and isotopic analysis of sediments from a subtropical reservoir in southern Brazil.

Chapter 4: Forensic assessment of polycyclic aromatic hydrocarbons to reconstruct anthropogenic activities in a nearby urban reservoir.

Chapter 5: presents a general conclusion; recommendations for future work and publications.

1.4 LITERATURE REVIEW

1.4.1 Eutrophication

Globally, one of the biggest environmental problems in water bodies is eutrophication (CARPENTER, 2005). The eutrophication process occurs when there is an additional supply of limiting nutrients, especially nitrogen and phosphorus in a water body. The sources of these nutrients can be punctual or non-punctual (RICKLEFS, 2010). The abundance of these nutrients causes an increase in primary production and also causes an imbalance in the ecosystem favoring certain groups of organisms (RICKLEFS, 2010).

Eutrophication in natural and artificial lakes is a product of multiple uses of the watersheds. These ecosystems accumulate information because they are a point of convergence of all the activities carried out in the river basin. Water quality is a reflection of socioenvironmental and economic aspects, anthropic activities, and their derived impacts. The environmental problems caused by these are depletion of dissolved oxygen in the water, loss of biodiversity, the boom of algae, cyanobacteria, and aquatic macrophytes, the release of CO_2 into the atmosphere; water use with restrictions; effects on human health, and increased costs for water treatment (TUNDISI AND MATSUMURA, 2002).

The eutrophication process can be of natural or anthropogenic origin. In the natural condition when the contribution of nutrients by surface runoff causes erosion on the earth's surface, consists of a gradual and continuous process. And in an unnatural condition when induced by anthropic activities, the eutrophication process is accelerated and can have different origins: domestic effluents, industrial effluents, and agricultural activities (ESTEVES, 1998).

The trophic state of a water body can be classified according to the trophy levels (TUNDISI, 1988):

• Oligotrophic: they have low organic enrichment and nutrients: the low presence of plankton, clear waters, and high concentration of dissolved oxygen, the value of total phosphorus dissolved is $<0.01 \text{ mgP L}^{-1}$;

• Mesotrophic: moderate nutrient enrichment and planktonic growth; an intermediate state. The total phosphorus dissolved between 0.01 to 0.035 mg L⁻¹;

• Eutrophic: high nutrient enrichment, high plant growth, low levels of dissolved oxygen at the bottom of deep-water bodies, minerals in suspension and on the benthic surface. The total phosphorus dissolved 0.035 to 0.1 mg L^{-1} ;

• Hypereutrophic: the value phosphorus dissolved is $> 0.1 \text{ mg L}^{-1}$.

1.4.2 Lentic environments

Reservoirs are bodies of water that according to their hydrological behavior, physicochemical and biological characteristics are classified into lotic, flowing water, such as rivers, and lentic whose speed is small or none, being represented by natural lakes (KENEDDY, 1999).

The need for the accumulation of water for various purposes determined the river dam, creating artificial lakes or reservoirs. These reservoirs are formed from the construction of a dam, which changes the natural conditions of the watercourse, reducing the flow velocity and increasing the deposition rate of sediments in the reservoir, which is gradually silted up over time (ANDRADE, 2013).

An important factor in the structure of reservoirs is their compartmentalization. In a reservoir, three compartments can be observed: one with characteristics close to the river (Fluvial), located in the upper part of the reservoir, another similar to the lake environment (lacustrine), near the dam; and one of transition between those of the environments (RIBEIRO FILHO, 2006).

The fluvial compartment presents a higher flow velocity; therefore, it has a characteristic shorter retention time, less light penetration, a higher concentration of suspended sediment and nutrients, and a greater source of allochthones material. The lake area has characteristics opposite to the river. In the transition zone, there is a higher phytoplankton primary productivity, and a great relation between nutrients and luminosity, providing good conditions for algae growth (CUNHA, 2012).

Compartmentalization in a reservoir produces a large number of subsystems, which can impact water quality, for example, anoxia processes due to reduced circulation caused by the accumulation of decaying biological material (TUNDISI and MATSUMURA, 2002).

One of the main differences between reservoirs and rivers is mass transportation. The rivers are completely mixed, in exchange in the reservoirs, and transport of the mass is affected by the occurrence of thermal stratification in the water column, and the compartmentalized

system (MIHELCIC and ZIMMERMAN, 2012). A feature in common between reservoirs and lakes, environments with a buffering capacity, can resist certain levels of contamination and alterations (XAVIER, 2005). Table 1.1 presents the differences between lakes, reservoirs, and rivers.

Characteristics	Lake	Reservoir	River
Water level	Small, stable	According to the operating rules and management	The function of climatic conditions
Thermic stratification	Depending on the natural regimen	Variable, irregular	Depending on the natural regime
Water inlet	Depending on small tributaries and sources superficial diffuse or underground	Depends on superficial tributaries	Depending on the weather and the basin geomorphology
Water outlet	Stable, superficial	Irregular depends on the operating rules and management	Usually flow continuously
Resident time	Long, from one to several years	Variable, from days to years	A few hours a week
Oxygen dissolved	Slight variation horizontal, gradient vertical with oxygen	Big variation, vertical gradient	Horizontal variation is more expressive
Light Extinction	Vertical gradients predominant, low light extinction	Horizontal gradients, predominant, extinction irregular light	Depending on the color of the water and the amount of suspended material
An external load of nutrients	Loads moderated the bay biogeochemical influence of ecotones	Higher than in lakes, river function tributaries, and soil type	Side entrances, and depending on geology and land use
Dynamic of nutrients	Predominate gradients vertical, low load inland lakes not eutrophicated by action human	Predominate gradients horizontal, depending on sedimentation rate, residence time, and hydraulic regime	Related to flow and flow rate
Phytoplankton	Limited by availability of light and inorganic nutrients, can form blooms seasonal	Limited by light availability, inorganic nutrients, and residence time can form blooms	Limited growth by the flow rate of the water
Nutrient source	Internal Recycling	Advection and recycling intern	Advection
Source organic matter	Autochthone predominance	Autochthone and Allochthone	Allochthone predominance

TABLE 1.1 DIFFERENCES BETWEEN LAKES, RESERVOIRS, AND RIVERS.

Source: CUNHA (2012).

The quality of water in reservoirs or lakes is conditioned by the level of water and the circulation and sedimentation mechanisms, these three factors promote nutrient removal in the water column. Therefore, lentic aquatic systems with eutrophication characteristics and the

removal mechanism are reduced by the recycling of ions and metals conditioned by sediment, keeping or neutralizing eutrophication (ESTEVES,1998).

Productivity in aquatic systems depends on the interactions of the watershed properties (climatic and geological factors, physicochemical properties of water flow rate, turbidity, presence of humic substances, macro ions, nutrients, and toxic substances, and limnologic properties morphometry, residence time, thermal stratification, biochemical cycles, temperature, optical and light conditions), also anthropogenic activities have an important role in the productivity of the system (ESTEVES,1998).

1.4.3 Early diagenesis

Recent sediment suffers from decomposition and degradation of organic matter that is an important process in the carbon cycle. The decomposition occurs a few meters from the water-sediment interface (MEYERS and ISHIWATARI,1993).

Diagenesis is defined as the chemical (oxygen, pH, etc.), physical (pressure and temperature) and biological (benthos) processes that affect the products of the primary production before disposal and during sedimentation under low temperature and pressure conditions (MOLDOWAN et al. 1986). Degradation of organic matter commensurate in the water column and continuing after sedimentation, the principal agents responsible for biological agents, and chemical transformations may also exist (KILLOPS and KILLOPS, 2013). Different classes of organic components present different degradation tables, where they are the ones that maintain their original structure. Lipids are more resistant to diagenetic processes and suffer from changes in their original structure. This feature enables them to be used as biomarkers, order for the resistance of lipid groups in anoxic sediments and the following: alkanes> sterols > saturated carboxylic acids> alcohols> monounsaturated carboxylic acids (RODRIGUEZ NETO, 1998).

During the initial phase of diagenesis, lipid compounds during and after sedimentation participate in several biogeochemical processes: defunctionalization, isomerization and polycondensation (KILLOPS and KILLOPS,2013). Lipids that contain oxygen in their structure predominate at the onset of diagenesis. Due to the dehydration and decarboxylation reactions during the diagenetic process, these compounds can lose the functional group. The process of defunctionalization occurs at the end of the diagenesis, there may be saturated hydrocarbon formations as well (MEYERS, 1993). Double bond migration in unsaturated markers is the main process of isomerization during diagenesis. It also happens configurational isomerization of chiral centers that are mainly associated with the increase in temperature. 1.4.4 Geochemical Markers of Organic Matter.

Characterizing the sources of organic matter is one of the important steps in the evaluation of environmental processes. The processes and sources that carbon undergoes during transport can be deciphered by the composition of organic matter. Bottom sediment is a potential report for historical removals that occurred in the drainage basin. Knowing the organic characteristics of the sediments, it is possible to evaluate the history of the processes to determine their composition from the moment of formation and deposition to the present (PETERS et al., 2005).

Different studies determined that materials originating in soils and vegetation are respectively the primary and final sources of carbon for river organic matter (BERNANDES et al., 2004).

Geochemical markers are defined as the specific compounds produced and/or altered by organisms whose identification in natural envi vronments allows inference about the origin, transport mechanism, alterations, and sedimentation of organic matter (ZIMMERMAN and CANUEL, 2001; JAFFE et al., 2001), widely applied in studies on Earth sciences (environmental geochemistry, petrochemicals, paleoclimatology, etc.) (VOLKMAN et al., 1998), and are divided into three categories biogenic markers, contemporary fossil biomarkers, and anthropogenic markers.

A group widely used as contemporary and anthropogenic markers are lipid markers. Lipids form fat in animals and are used as energy sources, structural, thermal insulators, and mechanical protection; in vegetables, they form oils and waxes with protective functions for the leaves (KILLOPS AND KILLOPS, 2013). They are water-insoluble compounds but can be extracted from the solid or liquid matrix by low polarity organic solvents. Lipid markers can be used to identify the origin, transformation, and evolution of sedimentary organic matter because they are compounds with a high preservation potential in aquatic environments (REITEFFAR et al., 2016).

The lipid extraction may contain more than 16 subclasses of biogenic and anthropogenic origin, but the most important for the characterization of organic matter are n-alkanes, fatty acids, and sterols, which are specific to the source and have a greater resistance to bacterial degradation processes (VOLKMAN et al., 1998) (Figure 1.1).



FIGURE 1-1 CLASSIFICATION OF LIPID BIOMARKERS

1.4.1 Elemental composition of carbon and nitrogen (C/N)

The concentration of total organic carbon (TOC) is a bulk value that represents the fraction of organic matter that was not remineralized during sedimentation. TOC concentrations are influenced by both the initial production of biomass and the subsequent degree of degradation, so it integrates the different origins of organic matter, delivery routes, deposit processes and the amount of conservation (MEYERS, 2003).

Nitrogen, together with phosphorus, are two of the major constraints in the primary production of aquatic environments. Nitrogen fixation is one of the most important processes in the dynamics of natural ecosystems since it is the only form of nitrogen transfer from the atmosphere to aquatic or terrestrial systems (MARTINELLI et al., 2009).

The TOC/TN ratio can be used (REDFIELD et al., 1963) to determine sources (algae) and terrestrial sources. The organic matter of phytoplankton origin, are rich in protein and poor in cellulose, presenting molar values of C/N that vary between 4 and 10; while terrestrial vascular plants, which are poor in proteins and rich in cellulose, create organic matter with C/N relations of 20 (MEYERS, 1993). Ratios between 11 and 20 may be associated with a mixture of sources. However, the elementary composition can suffer alterations during the transport and sedimentation processes, such that only the use of this parameter by itself can erroneously

estimate the sources of organic matter. Therefore, different studies use geochemical markers together with their isotopic ratios of stable carbons to better determine the sources of organic matter in the sediments.

1.4.2 Saturated Hydrocarbons as biomarkers

The hydrocarbons are formed by atoms of hydrogen and carbon, are classified according to their structure in aliphatic and aromatic hydrocarbons. These compounds can be found in aquatic environments, which are derived from multiple sources, natural or anthropic (KILLOPS and KILLOPS, 2013).

The hydrocarbons from biogenic sources can be of autochthone origin, products of the primary phytoplankton production, and/or allochthones, which are from land plants (READMAN et al., 2002).

Those from anthropic sources, their origin could be domestic and industrial effluents, products resulting from the combustion of fossil fuels, oil spills or derivatives, or deposits of oil and derivatives (DASKALOU et al., 2009).

Among the hydrocarbons, the most analyzed in environmental studies are n-alkane, branched alkanes, and polycycloalkanes (WANG et al., 2006; ZHANG et al., 2007; BAKTIARY et al., 2010). The higher plants developed a form of protection against environmental variations and water loss, called the cuticle. This membrane has flexible and hydrophobic characteristics, with a thickness of 0.1-10 mm. Lipids are the main components of the cuticles, lining the external periclinal walls of epidermal cells (EGLINTON et al., 1962).

The coating of the primary cellulosic walls is composed of the secondary cuticle, primary cuticle, and epicuticular wax on the outermost part. The function of epicuticular wax is to form an insulating coating against the action of pathogens, insect attack, solar radiation, pollutant entry, and also in the control of excessive perspiration, limiting the loss of water and solutes through the cuticle (HEREDIA et al., 1998).

The n-alkanes are one of the compounds of epithelial waxes in vascular plants, which are used as chemotaxonomic frameworks for good comparison between different families and plants. The n-alkanes of biogenic origin are compounds with an odd number of carbon (Figure 1.2). According to the concentration of n-alkanes in the sediments, for each carbonic length, it is possible to infer the origin of the n alkanes (terrestrial or aquatic) (WANG, 2015b). The long-chain compounds between 23 and 33 carbons are of terrestrial origin derived from the cuticle waxes of the upper plants. Land plants predominate compounds C_{27} , C_{29} , and C_{31} (MEYERS, 2003). On the other hand, those with short chains between 15 and 21 carbon atoms are produced by phytoplankton with a predominance of n-C₁₅ and n-C₁₇. Furthermore, submerged and

emergent aquatic plants are the main producers of mid-chain (n-C₂₁, n-C₂₃, and n-C₂₅) n-alkanes (FICKEN et al., 2000).

FIGURE 1-2 EXAMPLES OF ALIPHATIC HYDROCARBONS

Saturated Aliphatic Hydrocarbonate-C₁₅H₃₂



Unsaturated Aliphatic Hydrocarbonate-C₁₅H₃₀



Branched Aliphatic Hydrocarbonate - C₁₆H₃₄



In environmental studies ratios are used for a better evaluation of the contribution of aquatic and terrestrial organic matter:

• TAR (Terrestrial/aquatic), the proportion of long-chain (represent terrigenous sources of OM) to short chain biomarkers (reflect aquatic sources) (BOUBOMNIERE and MEYERS, 1996).

$$TAR = \frac{C_{27} + C_{29} + C_{31}}{C_{15} + C_{17} + C_{19}}$$

• Paq, (odd mid chain alkanes/odd mid and long chain alkanes), discriminate the relative contribution of non-emergent/emergent macrophytes and terrestrial vegetation using the relative proportion of mid chain to long chain homologues (FICKEN et al., 2000).

$$P_{aq} = \frac{(C_{23} + C_{25})}{(C_{23} + C_{25} + C_{31} + C_{33})}$$

• CPI (carbon preference index), odd/even predominance to determine the quality of soil OM and the contribution from source such as terrestrial, microbial and/or petroleum hydrocarbons (WANG et al., 2007)

$$CPI = \left[\frac{\sum (C_{25} - C_{33})odd}{\sum (C_{24} - C_{32})even} + \frac{\sum (C_{25} - C_{33})odd}{\sum (C_{26} - C_{34})even}\right]/2$$

 ACL (Average chain length) could be interpreted in terms of changes in vegetation types (ROMMERSKIRCHEN et al., 2003), climate (SIMONEIT et al. 1991; SARKAR et al., 2014) and contribution from petrogenic sources (AHAD et al.,2011).

$$ACL = \frac{(23 X C_{23} + 25 X C_{25} + 27 X C_{27} + 29 X C_{29} + 31 X C_{31})}{(C_{23} + C_{25} + C_{27} + C_{29} + C_{31})}$$

Table 1.3 shows the ranges of values of the ratios for a better identification of the sources of organic matter in the sediments.

Ratio	Value	Source	Reference
	<0,1	Terrestrial Plant	FICKEN et al., 2000
D	0,1-0,4	Emergent macrophytes	
r _{aq}	0,4-1	Submerget/floating	
		macrophytes	
CDI	> 5	Terrestrial vascular plants	AHAD (2011)
CFI	≤ 1	Petroleum hydrocarbons	
ТАР	>1	Terrestrial MO	BOURBONNIERE
IAK	<1	Aquatic MO	AND MEYERS (1996)

TABLE 1.2 RATIOS OF N-ALKANES

Source: Author (2022).

Isoprenoid alkanes belong to branched-chain hydrocarbons with a molecular structure derived from isoprene (BICEGO et al., 2006). Phytane (2,6,10,14-tetramethyl hexadecane) and pristane (2,6,10,14 -tetramethylpentadecane) are the most common isoprenoids in lacustrine and marine sediments, they are the product of the geological alterations of phytol and other natural isoprenoids (BIANCHI and CANUEL, 2011).

Under anoxic conditions and/or reducing environments, the separation of the phytol group from the chain is promoted, producing phytol ($C_{20}H_{40}O$), which undergoes a reduction to dihydrofitol and is then transformed into phytane (C_{20}). In this case, in the sediment with the presence of oxygen, the conversion of phytol to pristane occurs due to the oxidation of phytol to fetenic acid, then a decarboxylation occurs to pristane, and finally a reduction to pristane (C_{19}) (PETERS, et al., 2005). Thus, the concentrations of phytane and pristane can be used to indicate the oxic or anoxic conditions in the sedimentation of aquatic environments (Figure 1.3) (DIDYK et al., 1978).



FIGURE 1-3 CHLOROPHYLL, PHYTOL, PRISTANE, AND PHYTANE STRUCTURES

Source: Modified from DE SOUZA (2011)

In the Pr /Ph ratio, values > 1 indicate the presence of compounds of biogenic origin, while values close to 1 indicate probable petroleum contamination. This reason can be used to infer whether the presence of these compounds is biogenic or anthropic (JENG et al., 2007; WAGENER et al., 2010).

1.4.2.1 Polycyclic hydrocarbons.

Hopanoids are natural pentacyclic (5-ring) compounds based on the chemical structure of the hopane triterpene. Hopanoids are found in bacterial membranes, their main function is to stiffen the bacterial plasma membrane (prokaryotes). The function in the membranes of eukaryotes is made by cholesterol (OURISSON AND ALBRECHT, 1992; BIANCHI & CANUEL et al., 2011).

Hopanoids are lipids that can be found in modern biota, in recent sediments, and sedimentary rocks with low maturity (PEARSON et al., 2007). Its presence in both modern and ancient sediments reflects the resistance of polycyclic hydrocarbons to biotic and abiotic degradation.

According to their molecular structure, these hydrocarbons can be divided into hopenes and hopanes. And the hopanes can be divided into biological configuration $17\beta(H),21\beta(H)$ -hopane ($\beta\beta$ -hopane) and geological configuration $17\alpha(H),21\beta(H)$ -hopane ($\alpha\beta$ -hopane) (XIONG et al., 2010).

 $\beta\beta$ -hopanes and hopenes are found in recent and ancient sediments, as well as rocks on thermal stress. During the burial process, the thermodynamically unstable $\beta\beta$ -hopanes are gradually replaced by the geologically stable $\alpha\beta$ -hopanes (BOULOUBASSI et al., 2001). The latter exhibit carbon numbers from C₂₇ to C₃₅, they do not occur in living systems but are generally abundant in petroleum products and mature rocks of hydrocarbon origin (PETERS et al., 2005

Bacteriohopanepolyol are precursors of a variety of hopanoids found in the environment (BIANCHI & CANUEL, 2011). For example, diplotene its presence can be attributed to the bacteria that contain it (ELVERT et al., 2001), cyanobacteria, purple non-sulfur bacteria, acetic acid bacteria, nitrifying bacteria, heterotrophic bacteria, ammonium oxidation bacteria, methylotrophic and methanotrophic bacteria (SARKAR et al., 2014). $\beta\beta$ -homohopane was identified in marine sediment, lignite deposit, and lake sediments, and is also derived from methanogenic bacteria, chemoautotrophic and heterotrophic bacteria (DUMITRESCU and BRASSELL, 2005; BECHTEL et al., 2003; BECHTEL; 2007; WOSZCZYK et al., 2011).

In aquatic environments, hopenes and $\beta\beta$ -hopanes may reflect the history of bacterial productivity in overlying water and the contribution of soil-based allochthone bacteria (ZANG et al., 2019). In contrast, thermodynamically stable $\alpha\beta$ -hopanes found in recent sediments cannot be produced biologically in situ, therefore they are indicators of allochthone fossil fuel inputs (OLIVEIRA and dos SANTOS MADUREIRA, 2001). The distribution and composition of $\alpha\beta$ -hopanes have been used to determine anthropogenic contamination by oil in soils, oceans, and lakes (RUSHDI et al., 2016; BOULOBASSI et al., 2001).

1.4.3 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that have two or more condensed benzene rings, and may also have rings with fewer than six carbons (KILLOPS and KILLOPS, 1993). PAHs are poorly soluble in water and have a high octanol/water partition coefficient (Log Kow), ranging from 3.37 to 6.84, and are fat-soluble and can be used as exposure markers. In sediments, PAHs with high polar mass can be strongly absorbed (SHEIKH FAKHRADINI et al., 2019).

Sixteen types of PAHs are considered priority pollutants for environmental monitoring according to the EPA's Clean Water Act (CWA), they are: naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, indene[1, 2,3-c,d]pyrene (ASTDR, 1995). Of these, seven are considered by the USEPA to be carcinogenic to humans: benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g, h,i]perylene and indene[1,2,3-c,d]pyrene (BOJES and POPE, 2007). The chemical structure of these compounds is shown Annex in A1.

The origin of PAHs in aquatic environments is determined by the molecular structure of these compounds. Naphthalene and phenanthrene (low molecular weight), are made up of three aromatic rings, are associated with petroleum and derivatives, petrogenic origin. PAHs with more than three aromatic rings in their molecular structure, are mainly caused by combustion and are the pyrogenic sources (high molecular weight) (PETERS, 2005).

PAHs are present in the environment from domestic, mobile, industrial, agricultural, and natural sources (RAVINDRA et al., 2008). Domestic emissions are fueled by wood, oil, or coal and are observed in urban areas. Mobile sources include emissions from all types of vehicles, in urban areas vehicle emissions have a large contribution. The processing of aluminum, cement, waste incineration, and the petrochemical industries contribute to a large part of the industrial sources of PAHs. As natural sources are natural fires and volcanic eruptions (HAUGLAND et al., 2008; JENSEN et al., 2012; ANDERSSON et al., 2014).

Mobile sources of PAHs, diesel trucks are the main sources of low molecular weight PAHs and gasoline vehicles are the main sources of heavier PAHs molecular, such as benzo(a)pyrene and dibenzo(a,h)anthracene (PETERS et al., 2005). Oil combustion is associated with high concentrations of fluorene, fluoranthene, and pyrene, together with moderate levels of higher molecular weight composts, such as benzo(b)fluoranthene and indeno (1,2,3-cd) pyrene (AZEVEDO, ARAÚJO, and SILVA, 2013). Phenanthrene, fluoranthene, and pyrene were identified by Azimi et al. (2005) as the most abundant composts, confirming the pyrogenic origin of aromatic composts in atmospheric deposition.

1.4.4 Isotopic composition of carbon

The great complexity of microorganisms in ecosystems can be evidenced by the organic matter present. The organic matter in the sediments is incorporated by a diversity of organisms that live both in the water column and in the sediments and also by the contribution of terrestrial material. This complexity makes it difficult to infer biological precursors and paleo-environmental conditions, analysis techniques such as isotopic ratios are being used as a complementary tool (NGUYEN TU et al., 2004).

Carbon has two stable isotopes. Carbon-12 (¹²C, 98.295%) is more abundant than Carbon-13 (¹³C) (SCHMIDT et al., 2004). In biological systems, there is a preference for more

easily incorporating the light isotope (¹²C) at a higher rate in biologically synthesized organic molecules above ¹³C (heavy). This preference is because the ¹²C has weaker links, which translates into lower energy requirements when the links on the ¹³C links are broken. This isotopic discrimination is known as isotopic fractionation or Kinetic Isotopes Effect (KIE) (MEIER-AUGENSTEIN, 1999).

The proportion of stable isotopes of an element is represented by delta notation (δ) concerning a standard, according to the Equation 5:

$$\delta = \left(\left(\frac{R_{sample}}{R_{standard}} \right) - 1 \right) \times 1000\%$$
 (5)

Where R_{sample} and $R_{standard}$ are the molar ratios of the stable heavy isotopes over the light ones present in the sample and the standard, respectively. For carbon, the standard used is called Vienna PeeDee Belemnite (VPDB) which corresponds to the isotopic carbon ratio of a Cretaceous (marine fossil) sample found in the Pee Dee formation in South Carolina, USA, whose δ^{13} C by definition it is equal to zero. Therefore, the isotopic composition of a sample is relative to that of the standard, when a sample has positive values, it indicates that the sample has isotopic ratios greater than the standard (more heavy isotopes than the mild one) (ROSMAN and TAYLOR, 1998).

The aquatic and terrestrial plants present an isotopic fraction with a difference of an approximate factor of 10 ‰. This difference exists due to the way plants fix CO₂ during photosynthesis. Plants use three paths, 85% of all plant species use the photosynthetic path of Calvin (or C₃) (REIFFART et al., 2016). The isotopic ratio for this type of plant varies between -24 to -30 ‰. C₄ is the other known photosynthetic path that is more efficient than C₃, which is only used by 5% of species, for example, phytoplankton. Their values of δ^{13} C -10 to -16 ‰, are more enriched (BIANCHI and CANUEL, 2011). The other photosynthetic path is the plants that use the C₃ path during the day and the C₄ during the night, this is called Crassulacean Acid Metabolism (CAM). They have intermediate δ^{13} C values between -15 to -25 ‰, the plants that use this system are common in desert environments (BIANCHI and CANUEL, 2011). Table 1.4 presents the values of δ^{13} C for different types of samples.

Vegetal Group Photosintetic $\delta^{13}C$ (%) Group Tree Vegetation and shrubbery -38 to-24 ‰ C_3 C4 Grasses C_4 -15 to -10‰ Succulents CAM -15 to -11 phytoplankton C_3 -30 to -24‰

TABLE 1.3 THE VALUES δ^{13} C ACCORDING WITH PHOTOSINTETIC GROUP.

Source: Author (2022).

The isotopic composition of plants can be affected by environmental factors: temperature, humidity, and atmospheric CO₂ concentration. These factors affect the biological processes in aquatic and terrestrial plants (photosynthesis, growth, development, and absorption of nutrients), causing differences in isotopic discrimination and difference in δ^{13} C values (STREET-PERROT et al., 2004).

In C₃ plants, the magnitude of isotopic fractionation varies according to environmental factors, especially with humidity and temperature (STREET-PERROT et al., 2004). In terrestrial plants, dry conditions in the environment cause a reduction of stomatal conductance as a mechanism to prevent the loss of water through perspiration while also reducing the diffusion of CO₂ in the leaf. Which leads to an enrichment of ¹³C and consequently high δ^{13} C values (CERLING, et al., 1997). Something similar happens with the temperature. A decrease in temperature increases the viscosity of the water, therefore the transport of water from the soil to the areas of slower evapotranspiration, as a consequence the stomatal conductance and the diffusion of CO₂ in the leaves is reduced, resulting also high values of δ^{13} C (RODERICK and BERRY, 2001).

The CO₂ plays an important and complex role in photosynthesis, different steps occur to incorporate it into plant matter (TIPLLE et al., 2010). The discrimination of ¹³CO₂ occurs in all the steps that transfer CO₂ from the atmosphere to the chloroplast and in the carboxylation reactions (FUNG et al., 1997). Causing changes in the isotopic composition of atmospheric CO₂ that strongly influence the isotopic discrimination of plants and is reflected in their δ^{13} C values.

In terrestrial plants, they are the ones used by the C₃ pathway for carbon fixation using only CO₂ as a substrate, consequence they are extremely sensitive to changes in CO₂ in the atmosphere. The increase in atmospheric CO₂ implies a direct decrease in the δ^{13} C values of the terrestrial plants (WEISENBERG et al., 2008a).

High amounts of CO₂ in the atmosphere lead to a disturbance in the carbonate system in the aquatic environment (CO₂ (aq), HCO³⁻, CO₃⁻²). The dissolved carbonate species are isotopically lighter than atmospheric CO₂ and are indicated by an increase in the δ^{13} C values of aquatic plants (STREE-PERROT et al., 2004). Because aquatic plants mitigate this effect by assimilating bicarbonates and dissolved CO₂.

1.4.5 Metals as markers in aquatic environments

Metals have ecological importance because they are not removed from the water as a result of self-purification and accumulate in reservoirs, entering the food chain. When they
exceed certain concentrations, most of them have toxic effects on living organisms (GHREFAT et al., 2006). The presence of metals in aquatic environments is attributed to natural processes, such as weathering of rocks and soil erosion. They are also related to residues from anthropogenic activities, discharge of domestic and industrial effluents, agricultural activities, and mining activities (MAR and OKAZAKI, 2012). The difference between the two is the frequency (occasional, continuous, or intermittent) and the duration (days, months, or years), causing alterations in the water body. The contribution of metals by natural processes, depending on their magnitude and frequency, is more assimilable by ecosystems. On the contrary, the anthropogenic process contributes to higher concentrations and longer durations, being more difficult to assimilate in the ecosystems and accumulating (YUAN et al., 2016).

Metals in aquatic environments, their distribution in the water column can be affected by pH conditions and redox potential. Due to this characteristic, metals are used as tracers of metal contamination sources (DUAN et al.,2014). Sediments can act as a sink (deposition) for metals from surface waters or depending on the environment if it is anoxic or oxic, they can represent a source (release through physical, chemical, or biological processes)(FIELDING et al., 2020).

Meteorological factors and anthropogenic activities can influence the sedimentation process of metals. For example, heavy rainfall can increase the leaching effect of metals from mineral zones and aggravate the spread of agricultural pollution. The increase in temperature can accelerate the adsorption process of heavy metals by suspended sediments in the aquatic environment, and improve the weathering process (WEBER et al., 2007). According to Duan et al., 2014, metals are associated with the eutrophication process in aquatic environments due to contamination by the diffusion of phosphorous fertilizers that are composed of heavy metals.

By combining radiochronology, heavy metal distribution, and tracing in sedimentary profiles, it is possible to reconstruct the sedimentary history, including the input of metals and toxic elements and the relationship with biological activity and redox changes in the lake sediment (FIELDING et al., 2020).

1.5 STUDY AREA AND METODOLOGY

1.5.1 Study Area

The watershed of Passauna river is located between S 25 °25'48" and W 49 ° 15' 16". Passauna sub- basin has a drainage area of 217 km², covering the municipalities of Almirate Tamandaré, Campo Magro, Campo Largo, Araucaria and Curitiba (Figure 1.4) (SUDERHSA, 2007). The Passauna reservoir was formed in 1989 for public water supply. It is located in Araucaria, PR, near to Curitiba, Brazil. The Passauna reservoir is responsible for supplying 22% of the population in Curitiba and RMC, with an operating capacity ranging from 1300 L/s to 2000 L/s of treated water available for supply (AISSE et al., 1990) The normal operation level is 890 m, the reservoir has a water sheet area of 11 km² and average depth of 9,4m. The resident time of reservoir is 292 days (CARNEIRO; KELDERMAN; IRVINE, 2016), the main water inflow comes from Passauna river with a mean flow rate of 1 m³ s⁻¹. Along its course of approximately 22 km, it receives the contribution of small watercourses from six sub-basins (Custodio, Cachoeirairinha, Cachoerinha, Ferraria, Margem direita A and Norte).

FIGURE 1-4 LOCALIZATION OF POINTS FROM SAMPLING PASSAUNA RESERVOIR.



1.5.1.1 Precipitation

The local climate according to the Koppen climate map is classified as Cfb which is a temperate climate with a mean temperature of 22 °C.

Monthly precipitation data for the period 1986-2017 are presented in Table 1. Obtained from the meteorological station Colonia Dom Pedro (2549080) operating for Instituto das Aguas Paraná.

According to the precipitation data, greater rainfall rate season is observed in the months of January and February (Table 1.5). On the other hand, the dry months are April and August. Precipitation data show that this sub-basin presents favorable conditions so that throughout the year the rains events contribute loads of nutrients and pollutants to the body of water. Since the greatest economic activity in this area is agriculture.

Vear	Ian	Feb	Mar	Anr	May	Iun	Iul	Δ11σ	Sen	Oct	Nov	Dec
108/	5411	100	Ivitui	7101	ivitay	5411	541	Thus	Bep	42.5	204.5	122.2
1985	73.4	243 5	72.4	93.6	117	34.4	30.4	4.6	119.0	68.1	50.7	100.3
1986	125.4	00 2 00 2	176.6	100.8	94.6	89	42 2	141 2	59.3	112.2	149.3	262.8
1987	137.9	148.8	20.3	189.9	289.7	127.8	49.0	55 5	92.1	140.2	67.6	130.4
1988	1793	138.5	179.2	106.9	285.0	64 7	17.2	2 0	120.5	91.0	53 1	106.4
1989	200 5	209 5	1131	152.6	117.1	60.2	139.4	34.4	114.0	93.8	72 2	131 3
1990	281.1	38 3	98.0	81.9	34.4	66.1	211.4	93.4	197.1	134.8	75 3	14.6
1991	71.3	140.0	191.6	72.8	40.0	78.9	0.1	81.3	38.1	176.5	47.5	267.6
1992	51.6	128.7	147.7	22.5	301.7	22.2	118.8	101.1	53.4	84.8	73.7	50.0
1993	210.0	179.2	120.0	76.6	174.8	773	105.6	30.6	370.7	124.0	64.8	100.1
1994	180.6	87.5	67.4	108.3	64.1	107.5	109.1	5.0	27	185.0	125.7	185.3
1995	385.7	175.2	152.5	67.9	15.6	100.3	93.9	14.2	124.8	100.0	37.1	193.5
1996	239.9	209.8	179.2	10.1	0.0	134.9	66.1	70.6	249.4	176.3	62.1	310.5
1997	267.7	155.3	90.3	0.7	48.4	151.3	48.6	110.5	189.8	275.7	219.0	254.9
1998	212.0	175.3	197.7	260.8	21.8	112.0	148.2	224.0	426.3	323.9	24.0	136.8
1999	190.8	411.2	99.7	118.3	31.0	103.5	126.7	4.0	68.8	142.6	38.7	81.4
2000	77,1	166,5	174,4	10,0	35,0	129,0	87.2	139.6	310,7	108,3	125,2	143,2
2001	265,1	283,3	224,6	47,9	226,9	118,2	185,6	69,5	86,6	278,0	98,3	80,2
2002	270,2	172,4	134,0	40,7	190,8	116,4	39,7	59,7	245,9	151,4	254,9	262,6
2003	160,2	198,3	184,9	50,1	17,4	170,0	148,8	7,8	138,7	90,9	115,4	146,8
2004	148,8	132,2	132,6	92,4	162,9	91,0	123,1	4,2	82,5	239,8	108,2	134,8
2005	201,3	82,3	124,0	70,0	152,7	49,0	186,5	167,0	335,0	208,0	51,0	32,0
2006	51,0	125,5	140,5	20,0	10,0	29,5	40,0	49,8	275,0	133,0	255,1	126,3
2007	196,2	275,5	139,0	120,0	225,1	0,0	136,8	0,0	61,2	187,6	246,9	180,8
2008	101,2	34,5	190,5	241,2	94,0	180,3	28,6	233,3	29,4	255,0	56,0	30,0
2009	198,7	79,0	112,0	36,0	45,3	65,9	186,2	54,6	250,4	139,2	181,7	95,3
2010	412,5	151,0	192,4	141,4	70,8	51,4	107,2	28,1	45,0	119,2	103,6	268,1
2011	135,5	292,7	71,5	35,2	48,9	87,5	103,4	224,7	27,5	172,0	85,5	186,4
2012	127,5	198,1	60,7	183,6	77,4	224,9	104,0	15,4	55,9	125,3	40,3	248,2
2013	70,7	250,6	111,9	78,1	80,8	288,6	140,7	40,6	215,1	68,3	139,0	75,2
2014	213,2	113,8	134,1	72,8	70,1	210,3	47,3	68,0	206,0	179,9	121,7	224,9
2015	162,5	253,3	220,8	71,3	142,7	86,6	224,0	37,7	143,2	290,6	267,3	331,4
2016	207,7	223,6	139,0	71,7	187,0	107,9	119,3	214,1	97,6	251,4	156,1	197,8
2017	319,8	223,9	89,3	88,0	104,3	160,2	5,1	101,9	49,0	284,4	150,5	221,9
2018	305,9	172,2	372,9	0,0	37,5	108,2	5,4	49,1	64,8	275,2	35,0	145,5
Month	Jan	Fev	Mar	Abr	Mai	Jun	Jul	Ago	Set	Out	Nov	Dez
Med.	189,2	175,6	142,8	86,3	103,2	103,7	97,8	74,6	145,5	1665	113,1	159,4
Min.	51,0	34,5	20,3	0	0,0	0,0	0,1	0,0	2,7	42,5	24,0	14,6
Max	412,5	411,2	372,9	260,8	301,7	288,6	224,0	233,3	426,3	323,9	267,3	331,4
D.	88,7	76,8	62,6	62,3	86,0	61,7	60,9	72,1	107,4	74,2	70,5	81,4
pad.												

TABLE 1.4 PRECIPITATION DATA FROM PASSUAN WATERSHED.

Source: IAP, 2019

1.5.1.2 Land used and occupation

The Passauna River catchment is protected by an APA (Environmental Protection Area). APA is an instrument of Brazilian environmental legislation, which aims at sustainable use, allowing human occupation in a disciplined manner, which can become a problem when it is established in urbanized regions, as is the case of RMC.

The vegetation in the Passauna watershed area is formed by natural fields, divided into two types of grassy-woody steppes: dry fields and wetlands (floodplains); Mixed Ombrophilous Forest, also divided into two classes; Montana Mixed Ombrophilous Forest, or the Araucaria forest, which occupies a small part of the reservoir amount; and the Alluvial Mixed Ombrophilous Forest, also called riparian, gallery or riparian forest. According to Ansolin (2018) the land use of the watershed is grouped considering the following classes: "agricultural area", "urban area", "vegetation" (forests), "exposed soil" and "water" as presented in Table 1.6.

Land use	Area (ha)	Percentage (%)
Water	1.057,13	4,88
Exposed soil	145,63	0,68
Vegetation	8.847,45	40,81
Agricultural area	9.990,26	46,11
Urban Area	1.627,83	7,52
Total	21.668,33	100

TABLE 1.5 LAND USE AND OCCUPATION OF PASSAUNA WATERSHEDS

Source: IAP, 2019

The agricultural area is defined as the grouping of the following subclasses: all productive areas, any area built in the rural perimeter, pastures, and fields. Already urban area comprises all built areas in the urban perimeter. The vegetation component corresponds strictly to the area, tree and shrub vegetation, and the exposed soil area, which characterizes mining and degraded areas. The "water" class, composed of the hydrography of the basin, nascent rivers, lakes, and drainage ducts.

The agricultural area represents 46.11% of the total area of the basin, this fact is very important concerning the water quality of the reservoir, and that in these areas fertilizers are applied to crops. There may be an increase in nutrient concentrations in the body of water due to surface runoff. The class of vegetation use, which corresponds to the forest, occupies 40, 81% and has the second largest coverage. The urban area has only 7.52% of coverage in the basin.

In the Passauna watersheds we can also find two industrial centers: Cidade Industrial de Curitiba (CIC) and Cidade Industrial de Araucaria (CIAR). According to IAP and SUDERHSA, the main industrial in this area are: Höerlle Cardboard Industry, Lunardon Farinheira, Volvo of Brazil, Bel Paladar Refrigerator, Campo Novo Slaughterhouse and Ouroplast.

1.5.1.3 Water quality

The Passauna reservoir is classified as bake Class III as moderately degraded according to the Reservoir Water Quality Index (IAQR) values calculated for each sampling campaign conducted from 1999 to 2013 by IAP (Instituto de Aguas Paraná). The reservoir is within the limits considered acceptable to be used for public water supply.

During this study period a small concentration of cyanobacterial cells with a value typically below 100000 cells / ml were detected. According with final report (2005/2013) of IAP, the vertical profiles of temperature and oxygen concentrations in the water column. It is

observed that the upper layers have high values and deep anoxic behavior. This behavior contributes to the higher growth of phytoplankton in the euphotic zone and poor circulation in the deepest layers.

According to the EIT classification in the period (2005/2013), the Passauna reservoir presented a final mesotrophic classification.

- 1.5.2 Methodology
- 1.5.2.1 Sampling sediment cores

Two sediments cores (core I and core II) were collected on February 2018. The cores were retrieved using a piston percussion corer fitted with 86-mm internal diameter acrylic tubes (Figure 1.5). In the laboratory, cores were subsampled by slicing at 2.0 cm intervals. All samples were transferred to polyethylene bags and frozen at 0°C. Samples were later freeze-dried a ground by an agate mortar and pestle 39 and 18 sub samples were taken in sedimentary cores , core I and core II, respectively (Table 1.7).

FIGURE 1-5 SAMPLING CORES



TABLE 1.6 SAMPLING POINTS

Sampling point	Geographical coordinates				
	Latitude	Longitude			
Passauna Reservoir					
P1- Buffer	25,450152	49,383142			
P2- Dam	25,52723	49,38797			

1.5.1 Dating core

The core dating will be by 210 Pb decay and 137 Cs precipitation in the previously prepared sediment and with particle size <63 µm using a gamma spectrometer, following the method described by FIGUEIRA (2007). The accuracy of the methodology will be assessed using certified references IAEA-326-(soil), IAEA-327 (soil) and IAEA-385(marine sediment) to determine the radionuclides of interest.

To calculate the sedimentation velocity two models will be used: the initial concentration of 210 Pb (CIC) and the constant supply velocity of 210 Pb models according to Neves et al. 2014. Mass accumulation rates (MAR) will be calculating from measurements of bulk density measurements, 210 Pb data and 137 Cs precipitation. The age of the samples will be determines considering the core depth (z), core collection time (A₀) and sedimentation speed (v) according to equation 1.1.

$$I = A_0 - \frac{v}{z}$$
 (1.1)

1.5.2 Elemental Analysis

1.5.2.1 Total Organic Carbon (TOC) and Total Nitrogen (TN)

The 2 g dry sediment was weighed for each sample and 10 mL of 1 M HCl, was added and placed on a heating plate at a temperature of approximately 170 ° C to remove inorganic carbon (carbonates). Subsequently, 25 mg of the total mass of each sample were used for the determination of TOC and TN by the combustion method (Figure 1.7). The analysis of organic carbon content and total nitrogen were performed by the combustion method using a CNHOS Elementar Vario EL III.

FIGURE 1-6 SAMPLE WEIGHING FOR ELEMENTAL ANALYSIS.



1.5.2.2 Extraction of Total Lipid Extract (TLE)

Saturated hydrocarbons (n-alkanes, branched aliphatic alkanes, hopanes and PAHs) were separated from the total lipid extract (TLE). The TLE was obtained starting by weighing 1 g dried sediment and adding 10 mL dichloromethane: methanol mixture (2:1) in an extraction tube, homogenizing it in a vortex, and subsequently taken to an ultrasonic bath for 30 min (SANEZ et al., 2013). The solvent (containing the TLE) was separated, repeating the process three times. The volumes were then combined. Activated copper chips were added to remove possible sulfur. TLE was concentrated and the volume was reduced to approximately 1 mL through evaporation in a rotary evaporator and then dried under a gentle flow of N₂. The dried extracts, containing n-alkanes and other compounds, were stored at - 20 °C for further analysis. n-Alkanes were extracted and separated from TLE following the procedure described in Galoski et al. (2019). Briefly, TLE was fractionated using a flash chromatography column filled with silica gel, alumina, and sodium sulfate. Silica gel and alumina were previously activated. TLE was separated into four fractions: saturated hydrocarbons (fraction 1) and aromatic compounds (fraction 2). Fraction 1 was obtained after elution with 7 mL n-hexane and polycyclic aromatic hydrocarbons (Fraction 2) with 7 mL of a mixture of hexane: dichloromethane (2:1).

Fraction 1, containing the n-alkanes, steranes, and hopanes, were analyzed in a gas chromatograph (GCMS-QP2010 Plus, Shimadzu) coupled with a mass detector. The gas chromatograph operated with ultra-pure helium as the carrier gas at a flow of 0.70 mL min⁻¹ and the separation was performed using a capillary column (RTx-5MS), 30 m x 0.25 mm I.D. with 0.25 µm film thickness), in a column oven at 60 °C, followed by heating at 20 °C min⁻¹ up to 60 °C, then 12.50 °C min⁻¹ up to 120, subsequently heated at a rate of 3.50 °C min⁻¹ up to 60 °C to 240 °C and finally at a rate of 5.50 °C min⁻¹ to 315 °C and held for 11.20 minutes. Aliphatic hydrocarbons were identified by their retention time and mass spectra in full scan. Previously, a mixture of C8–C40 n-alkanes (C8–C40 Alkanes Calibration Standard, Supelco, Germany), within the range of 0.1–100 ng mL⁻¹, was used to obtain a calibration curve to quantify the n-alkane

In this study we sought the 16 target PAHs: Naphthalene (Nap), Acenaphthene (Ace), Acenaphthylene (Acy), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a,h) anthracene (BahA), Dibenzo(a,h)anthracene (DahA), Indene (1,2,3-cd)pyrene (IcdP) and benzo(g,h,i)perylene (BghiP). Analyses of standards and samples prepared in dichloromethane were performed in triplicate, using a Perkin Elmer branded Clarus SQ 8 T gas chromatograph coupled with a mass spectrometer (Turbomass, Perkin Elmer). The capillary column used was Sigma Aldrich brand fused silica with the reference 5-MS (0.25 mm x 30 m x 0.25 μ m) phase 5% diphenyl and 95% dimethylpolysiloxane. The carrier gas used was helium at a constant flow of 1.0 ml min⁻¹ and a pressure pulse of 25 psi with a duration of 0.50 min. The injected volume was 1.5 μ L in splitless mode. The oven temperature was programmed as follows: 1 min at 40 °C, heated at a rate of 10 °C min⁻¹ to 200 °C and held for 5 min, subsequently heated at a rate of 6 °C min⁻¹ to 240 °C and held for 10 min and finally heated to 300 °C in sequence at a rate of 10 °C min⁻¹ and held for 5 minutes. Previously, a mixture of 16 PAHs (TCL PAH mix, Supelco, Germany), within the range of 5-250 ppb (μ g L⁻¹), was used to obtain the calibration curve to quantify the PAHs.

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2 136-YEARS OF VARIATIONS OF METALS IN SEDIMENT FROM A SUBTROPICAL RESERVOIR IN SOUTHERN BRAZIL: IMPLICATIONS FOR THE ENVIRONMENTAL CHANGE

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ABSTRACT

Two sediment cores from the Passauna reservoir in Curitiba, Brazil were examined to follow the accumulation of heavy metals, including lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), zinc (Zn), and nickel (Ni) and major elements aluminum (Al), iron (Fe), manganese (Mn), potassium (K) and barium (Ba), and association to pollution. Enrichment factor (EF) and geoaccumulation index (I_{geo}) were applied to the identified accumulation of metals as well as to the level of pollution. The decay of radionuclides, including ²¹⁰ Pb and ¹³⁷ Cs, were used to find the rate of sedimentation over the years. The results showed a spatial variation, with the highest concentration of metals found in the upstream part of the reservoir. The EF values of the following metals decreased: in core I, EF(Fe) > EF(Mn) > EF(Cd) > EF(Sb) > EF(Zn) > EF(Cu) > EF(Cr) > EF(Pb); and in core II, EF(Sb) > EF(Pb) > EF(Cd) > EF(Cr) > EF(Cr) > EF(Cr) > EF(Cu) > EF(Cu) > EF(Cu) > EF(Cu) = EF(Ni) > EF(Mn). We observed that during the period 1930-1970, anthropogenic activities controlled the impacts on reservoir and water quality. In addition, paleoredox and paleoproductivity showed periods with different rates of productivity as well as alternate periods of trophic level. We used the Mn/Fe, Cu/Ni, and V(V+Ni) ratio.

Keywords: Heavy metals, sediment core, Environmental changes, Passauna reservoir, and paleoredox

2.1 INTRODUCTION

In many places around the world, including Brazil, the growth of urban areas occurs around water bodies, mainly rivers. It is estimated that by 2050, two-thirds of the global population will be residing in metropolitan regions, in contrast to the one-third in 1950 living in urban areas (Horowits, 2009). The anthropogenic influence in the hydric bodies causes a series of natural and anthropogenic disturbances such as overfishing, contamination by toxic metals, organic contamination, nutrient enrichment, and regional climate change (Yuan et al., 2014).

Natural as well as man-made lakes and reservoirs are hotspots of biodiversity and are often sensitive to environmental changes. Lakes, in general, are interconnected with the surrounding environment. The concern with the water quality of reservoirs has grown a lot recently, notably due to the growth of urbanization, where difficulty in preventing pollution and problems with an excessive inflow of sediments exists (Davis and Fox, 2009; Fran et al., 2014). Sediments in water bodies have great potential to retain metals and nutrients, therefore making it important to manage any effects caused by pollution or even resulting from environmental changes (Varol and Sen, 2012). Assessing sources of pollution is necessary to subsequently design measures to mitigate the potential impacts of current changes on ecosystem functioning. In addition, it is essential to know how lakes have responded to past environmental changes. This is accomplished by studying chemical markers deposited along the years which are associated with environmental changes, therefore are proxies for evaluating long-term ecosystem changes that have occurred in a watershed (Ha et al., 2015a; Bing et al., 2016; Chen et al., 2016).

Trace elements in natural aquatic systems play an important role in sustaining life, mainly acting as essential micronutrients and controlling multiple biogeochemical processes across the trophic levels (Nuruzzama et al., 2021). Trace metals like Mn, Cu, Mo, Ba, and Cd

are important for metabolic functions, enzyme formations, and primary productivity (Brand et al., 1986; Horner et al., 2013; Lane et al., 2005; Maldonado et al., 2006; Peers and Price, 2006; Takano et al., 2014; van den Berg et al., 1987; Wu et al., 2014). Heavy metals like Pb, Cr, Zn, and U are widely used as fingerprints to trace the reactive-transport pathways of contaminants and to assess the pollution stress in the aquatic environments (Maceda-Veiga et al., 2013; Wang et al., 2011)

Analysis of the metals, as well as their contents and accumulation rates, in sediment cores, is necessary for studies related to the mechanisms of biogeochemical cycles and the contribution of anthropogenic vs natural processes. Detection of heavy metals and trace elements in sediment can help to determine the peculiarities of the metal accumulation process in limnic systems. Heavy metals in lake/reservoir sediments are mainly from two sources i.e., natural sources such as rock-weathering and anthropogenic activities such as mining, agriculture, and industrialization. For example, Cd is associated with phosphoric fertilizers (Mar and Okazaki, 2012). The presence of Zn and Cd in waters indicates inputs of industrial effluents as well as combustion of fossil fuels (Gao et al., 2018). The importance of sediments was already proved, for example, it is known that fine sediments can carry metals and organic compounds to water bodies by surface runoff (Garcia-Ordiales et al., 2016). To better understand the source and infer about paleoproductivity and paleoredox, ratios among metals can replicate past scenarios (Yuan et al., 2014). For example, Fe and Mn have a redox-sensitive behavior in aquatic environments (Calvert and Pederson, 2007; Och et al., 2012), Thus, Fe (II) / Fe (III) and Mn (II) / Mn (IV) are coupled pairs that result in precipitation or redissolution. In Fe and Mn cycles in lakes/dams, these are products of the seasonal redox changes in the hypolimnion (Balistrieri et al., 1992, Davison, 1993). The release of Fe and Mn from sediments reduction conditions is the result of the consumption of O2 during the remineralization of organic matter (Nealson and Saffarini, 1994; O'Sullivan and Reynolds, 2005). After

oxygenation at the chemocline due to partial or total mixing of the water column, Fe and Mn precipitates are deposited and potentially preserved in the sediment (Schaller and Wehrli, 1996). Mn/Fe ratios have been used repeatedly to reconstruct changes in redox conditions in lakes (Dean and Doner, 2012; Melles et al., 2012). Lower values of Mn/Fe ratios indicate lower O₂ amounts in the lower column, whereas higher ratios suggested higher O₂ levels (Mackereth, 1966). This is because Mn is reduced faster than Fe under anoxic conditions, causing a preferential release of Mn, which results in low Mn/Fe ratios (Balistrieri et al., 1992; Loizeau et al., 2001). Under oxic conditions, Fe oxidizes faster than Mn, resulting in an accumulation of Mn and high Mn/Fe ratio values (Naeher et al., 2013).

The Passauna reservoir, located in the Metropolitan Region of Curitiba, contains 48 million cubic meters, installed in 1988 to supply the growing demand for treated water. It supplies 30% of the population of the Metropolitan Region of Curitiba (MRC) (Xavier, 2005). Since the reservoir was constructed, suspicions about contamination have risen due to the presence of a landfill and several agricultural areas with intensive use of pesticides and agricultural fertilizers. In the 1990s, disorderly residential growth around the Passauna River basin, followed by deforestation for agricultural purposes and lack of basic sanitation (Xavier, 2005), led to research being carried out to assess the impacts of land use on the water quality of the river and the reservoir. As of 2005, the reservoir has shown a continuous decline in water quality in the basin. Previously, monitoring programs demonstrated eutrophication of the reservoir due to the excess of macronutrients (Xavier, 2005), the annual fluctuations of phytoplankton with the physical and chemical parameters of the water (Coquemala, 2005), the microbiological quality of river waters (Da Silva, 2007), trace metal contamination in river sediments (Bocalon, 2007) and sedimentation rate in the reservoir (Sotiri, 2021). In this study, we applied geochemical proxies, including total organic carbon (TOC), total nitrogen (TN), TOC/TN ratio, and the metals Fe, Mn, Cu, Zn, Ni, Pb, Cr, V, Cd, Mo, Al, Ba, Mg, K, and Sb,

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in two sediments cores from the Passauna reservoir to assess inputs of pollutants in the reservoir that induced low water quality. The aims of this study included a) to assess the sources and the ecological risk of heavy metals in sediments; b) identify toxic or anoxic events in the water column during sediment deposition; c) identify the source and influencing factor of metals throughout the past years.

2.2 MATERIAL AND METHODS

2.2.1 Study area

The watershed of Passauna River is located between S $25^{\circ}25'48"$ and W $49^{\circ}15'16"$. Passauna sub-watersheds have a drainage area of 217 km², covering the municipalities of Almirate Tamandaré, Campo Magro, Campo Largo, Araucária and Curitiba (Figure 2.1) (SUDERHSA, 2007). The Passauna reservoir was formed in 1988 for public water supply. It is located in Araucária, PR, near Curitiba, Brazil. The Passauna reservoir is responsible for supplying 30% of water to Curitiba and MRC, with an operating capacity ranging from 1 300 L/s to 2 000 L/s of treated water available for supply (Sotiri, et al., 2021) The normal operation level is 890 m, and the reservoir has a water sheet area of 11 km² and medium depth of 9.4 m. The residence time of the reservoir is 292 days (Carneiro et al., 2016) and most of the water inflow is from Passauna River with a mean flow rate of 1 m³s⁻¹. Along its course of approximately 22 km, it receives the contribution of small watercourses from six sub-basins: Juruqui, Cachoeirinha, Cachoeira, Ferraria, Taquarova, and Jaguaruva (Coquemala, 2005).



Figure 2-1 Localization of points from sampling Passauna reservoir

According to the Environmental Institute of Paraná (IAP, 2009), Passauna reservoir has been ranked as Class III (moderately degraded) and with an oligotrophic trophic status. Thermal/chemical stratification takes place in deeper parts of the reservoir, with warm periods (September-March) showing substantial oxygen deficits in the upper water column (epilimnion) and anoxic conditions in the deepest zones of the hypolimnion (Carneiro et al., 2016).

The local climate according to the Koppen climate map is classified as Cfb which is a temperate climate with a mean temperature of 22 °C. According to the precipitation data, the mean annual ranges from 1400 mm to 1600 mm, and the season of high rainfall rates is observed in January and February; the dry months are April and August. Precipitation data show that this sub-basin presents favorable conditions so that throughout the year, rain events contribute loads

of nutrients and pollutants to the body of water since the greatest economic activity in this area is agriculture.

2.2.2 Land use and occupation in the Passauna watershed.

The Passauna River catchment is inserted in a Protected Area (APA – Area de Proteção Ambiental). APA is an instrument of Brazilian environmental legislation which aims at sustainable use allowing human occupation in a controlled manner, which can become a problem when it is established in urbanized regions, as is the case of MRC.

The vegetation in the Passauna watershed area is formed by natural fields divided into two types of grassy-woody steppes (dry fields and wetlands (floodplains)) and Mixed Ombrophilous Forest also divided into two classes (Montana Mixed Ombrophilous Forest or the Araucária Forest, which occupies a small part of the reservoir amount, and the Alluvial.

Mixed Ombrophilous Forest, also called riparian, gallery or riparian forest). Following Mapbiomas (2020), land use of the watershed is grouped considering the following classes: "agricultural and pasture area", "urban infrastructure", "vegetation" (forest, grassland and forest plantation), and "river, lake and ocean" as presented in Figure 2.2. The agricultural area is defined by grouping the following subclasses: all productive areas, an area built in the rural perimeter, pastures, and fields. An urban area comprises all constructed zones in the urban perimeter. The vegetation component corresponds strictly to the local tree and shrub vegetation, and the exposed soil which characterizes mining and degraded plots. The "water" class is composed of the hydrography of the basin, headwaters, lakes, and drainage ducts (Ansolin, 2018).



Figure 2-2 Land Use and Occupation of Passuana watersheds between 2014-2019.

Source: Adapted from Mapbiomas 2020

The agricultural area represents 46.11% of the total area of the basin; this fact is very important concerning the water quality of the reservoir, as in these areas fertilizers are applied to crops, thus there may be an increase in nutrient concentrations in the body of water due to surface runoff. The class of vegetation use, which corresponds to the forest, occupies 40.81% and has the second-largest coverage. The urban area has only 7.52% of coverage in the basin.

2.2.3 Sample collection

Two sediment cores (core I and core II) (Table 2.1) were collected in February 2018 and May 2019 respectively. The cores were retrieved using a piston percussion core fitted with 86mm internal diameter acrylic tubes. In the laboratory, cores were subsampled by slicing at 2.0 cm intervals. All samples were transferred to polyethylene bags and frozen at 0 °C. Samples were later freeze-dried and ground by an agate mortar and pestle. Of these, 39 and 18 subsamples were taken from sedimentary cores C1 and C2, respectively. The point I, is located in the pre-reservoir region, , a shallow with a depth varying from 0.5 to 2 meters, flooded region, bounded by a grounded cord with a bridge that strangles the flow. And Point II, presents a greater depth of 10-14 meters, near the outlet of the reservoir.

 Geographical coordinates

 Sampling point
 Geographical coordinates

 Latitude
 Longitude

 C1
 25,450152
 49,383142

 C2
 25,52723
 49,38797

Table 2.1 Samplings points and coordinates in the Passauna reservoir

2.2.4 Geochronology

Approximately 5 g of dry sediment from 57 samples collected from the P1 core and P2 core were disaggregated into a mortar and analyzed for ²¹⁰Pb and ¹³⁷Cs contents in an EG&G ORTEC low-background gamma spectrometer (hyperpure Ge, model GMX25190P) at LaQIMar (Laboratorio de Quimica Inorganica Marinha, University of São Paulo-Brazil) The sediment core chronologies were determined using the CFCS (constant flux constant sedimentation) model. This model assumes a constant flux to the sediment surface and constant mass accumulation rate (Appleby and Oldfield, 1983), an exponential decrease of C_i with depth should be observe, C₀ is the Pb_{excess} in the water- sediment layer, λ is the decay constant (0.03118 yr⁻¹), *r* is the mass accumulation rate (kg m⁻² yr⁻¹) and m_i is the accumulative mass depth to the *i*th layer (kg m⁻²). To obtain mass accumulation rates, the following Equation 1 is solved by linear regression between the Ci and the mass depth (Crozaz et al., 1964):

$$lnC_i = lnC_o - \frac{\lambda}{r}m_i \tag{1}$$

from the linear regression equation (y = a +bx), the slope is b= $-\lambda/r$, then $r = -\lambda/b$. So, the layer age t_i can be given by Equation 2

$$t_i = \frac{m_i}{r} \tag{2}$$

2.2.5 Elemental analyses Total Organic Carbon (TOC) and Total Nitrogen (TN)

Two grams of dry sediment were treated with 10 mL of 1 M HCl to be placed on a heating plate at a temperature of approximately 170 °C to remove inorganic carbon (carbonates). Subsequently, 25 mg of the total mass of each sample was used for the determination of TOC and TN by the combustion method. The analysis of organic carbon content and total nitrogen was performed by the combustion method using a CNHOS Elementar Vario EL III.

2.2.6 Determination of metals

For the determination of bioavailable metals, sediment samples previously dry and with a granulometry, less than 63 µm were prepared according to the EPA 3050-B method (USEPA, 1996) and with the adaptation made by Schimitz (2018) that allows the use of the digestion block. The extraction and reading of the bioavailable metals were carried out in the Plant Nutrition Laboratory of the UFPR. The following metals were analyzed with ICO-ES Varian 720: Al, Pb, Cu, Ni, Zn, Fe, Mn, Mg, Ba, Ca, K, Sc, and V.

2.2.7 Enrichment factors and Igeo

Enrichment factors (EF) and the geochemical index (I_{geo}) were used to determine the level of pollution indicated by metal content in these sediment cores, similar to other studies (Guo et al. 2015; Barik et al., 2017; Zhang et al., 2013). The EF is calculated by the following Equation 3:

$$EF = \frac{\left[\frac{Me}{Al}\right]_{sample}}{\left[\frac{Me}{Al}\right]_{background}}$$
(3)

where [Me/Al]_{sample} is the ratio of the concentration of metal to the reference element (Al) in the sediment, and (Me/Al)_{background} is the ratio of the background concentration of metal to the background value of Al.

The I_{geo} is method used to evaluate soil metal pollution and is calculated as follows Equation 4:

$$I_{geo} = \log_2 \frac{C_n}{K \times C_b} \tag{4}$$

Where Cn is the measured concentration of the element n in the sedimentary core, C_b is the background concentration of the element n; and the constant K is a coefficient used to eliminate the change of background values caused by regional differences (K= 1.5) (Guo et al., 2015a). Table 2.2 shows the values of background concentration of the elements in core I and core II. In both sedimentary cores, the average concentrations of the elements were used as background, core I (1883-1894) and core II (1916).

Elements	Core I	Core II		
	$(mg kg^{-1})$	$(mg kg^{-1})$		
Al	16003.320	532.711		
Sb	1.568	0.543		
V	113.376	33.950		
Cd	0.179	0.103		
Cr	61.602	24.369		
Cu	18.655	19.279		
Fe	15366.078	424.179		
Mn	283.854	240.431		
Ni	12.670	11.697		
Pb	34.025	6.367		
Zn	31.760	25.628		
Ba	234.811	176.023		
Κ	419.156	335.329		
Mg	816.900	1206.97		
Mo	0.172	0.642		

Table 2.2 The values of background concentrations of the elements in core I and core II

2.2.8 Statistical Analysis

Univariate and multivariate statistical methods of analysis were applied. The normality of the data was tested for all variables using the Shapiro-Wilk test. To determine the degree of relationship between the variables, non-parametric correlation analyses were performed using the Spearman correlation coefficient, considering them significant at $p \le 0.05$.

Principal component analysis (PCA) was applied to identify the significant ordering pattern of the samples based on their characteristics using the metal concentrations as variables. This ordering method consists of defining the position of the samples about a set of axes. Each of these axes and a linear combination of the used variables were centered about the mean (μ) and reduced to the standard deviation (σ) so that the variables have comparable scales and can be effectively compared (Valentin, 2000).

2.3 RESULTS

2.3.1 Age Model

 210 Pb_{total} and 137 Cs (Bq kg⁻¹) activity profiles (Figure 2.3) showed a decreasing trend with depth, except it does not show this behavior in core I in the first 20 cm. These few deviations from the expected exponential decay may be related to variations in sediment flows. Core II shows a decreasing trend with depth throughout the core. According to the CFCS model, core I have a sedimentation rate of 0.56 ± 0.06 cm year⁻¹ and core II a rate of 0.35 ± 0.04 cm year⁻¹. The maximum fallout for 137 Cs, corresponding to 1963, was recorded at the sediment layer of 30 cm (core I) and 20 cm (core II). According to the age model, core I is composed of sediment deposited since 1883 and core II since 1916. Sotiri et al 2020, determined by the echobathymetry method a sedimentation rate of 3.11. Also Ono (2020), determined a rate between 0.94 -1.34, by installing traps at different points in the reservoir.

Figure 2-3 The chronological results showing ¹³⁷Cs and ²¹⁰Pb and age-depth model of sediment cores: core I (a) and core II (b) from the Passauna reservoir



2.3.2 Total Organic Carbon and Total Nitrogen

The TOC in point I presented a minimum value of 0.989% and the maximum value was 3.997%. The TOC presented high values in the years ~1911, ~1972, and ~2019. The TN content had an average of 0.207% and varied from 0.122% to 0.388%. The TN also presented the same behavior as the TOC, with notable peaks of increases in the years ~1911, ~1972, and ~2019. The TOC and TN had a strong positive correlation (r > 0.927, p < 0.05). The ratio of TOC/TN ranged from 7.64 to 12.84 and an average of 7.64. The ratio of TOC/TN has the same pattern as the TOC. The values of TOC/TN were positive and strongly correlated to TOC (r = 0.769, p < 0.05) than the TN (r = 0.514, p < 0.05).

The TOC and TN of point II ranged from 3.824% to 32.843% and from 0.357% to 2.189% with averages of 15.947% and 1.272% respectively. The TOC/TN ratio averaged 12.145 and

varied from 7.418-15.273. The long-term ratios of TOC/TN increased starting from the year ~1916. In this core, the TOC/TN ratio record is positively correlated to TOC ($r^2 = 0.89$, p < 0.05) Figure 2.4.

TOC/TN ratios in general distinguish terrestrial from aquatic OM sources in the sediments (Hu et al., 2014; Liu et al., 2015). The TOC/TN in the aquatic-derived OM is less than 8, while it is more than 20 from the terrestrial-derived OM. This discrepancy is attributed to vascular plants containing more cellulose and less protein than phytoplankton (Wu et al., 2015b). Both sediment cores have values between 7-12, suggesting mixed OM sources of aquatic and terrestrial input, probably related that most of the cores correspond to before the formation of the reservoir.

2.3.3 Chronological variation in heavy metal and trace metal concentrations in sediments of
Figure 2-4 The temporal variation in TOC, TN, and TOC/TN in sediments cores;
core I;
core II of the Passauna reservoir



The vertical distribution of metals in the sediment cores from the Passauna reservoir is shown in Figure 2.5. For core I, the average concentration of Fe, Al, Mn, V, Cr, Zn, Cu, Pb, Ni, Sb and Cd were 40,455.81 \pm 10,367.87 mg kg⁻¹, 23,9454 \pm 4,090.69 mg kg⁻¹, 668.8 \pm 284.59 mg kg⁻¹, 81.18 \pm 14.93 mg kg⁻¹, 57.23 \pm 5.31 mg kg⁻¹, 55.82 \pm 13.01 mg kg⁻¹, 32.97 \pm 6.13 mg kg⁻¹, 25.32 \pm 4.73 mg kg⁻¹, 19.39 \pm 2.86 mg kg⁻¹, 3.06 \pm 0.86 mg kg⁻¹, 0.41 \pm 0.096 mg kg⁻¹, respectively. For sediment core II, the average concentrations of Fe, Al, Mn, V, Cr, Zn, Cu, Pb, Ni, Sb and Cd were 712.31 ± 298.46 , $991 \pm 258.77 \text{ mg kg}^{-1}$, $279.71\pm85.63 \text{ mg kg}^{-1}$, $56.29 \pm 15.68 \text{ mg kg}^{-1}$, $40.51 \pm 5.90 \text{ mg kg}^{-1}$, $35.07 \pm 21.13 \text{ mg kg}^{-1}$, $25.74 \pm 3.87 \text{ mg kg}^{-1}$, $13.52 \pm 3.86 \text{ mg kg}^{-1}$, $15.43 \pm 3.24 \text{ mg kg}^{-1}$, $1.13 \pm 0.73 \text{ mg kg}^{-1}$, $0.21 \pm 0.045 \text{ mg kg}^{-1}$, respectively (Table 2.3).

Metal	Core I	Core II		
	C± SD	C± SD		
	(mg kg ⁻¹)	(mg kg ⁻¹)		
Sb	307±0.87	1.33±0.63		
V	81.13±14.93	56.29±15.68		
Al	23952.97±4090.67	991.21±258.77		
Cd	0.40±0.10	0.21±0.05		
Cr	56.09±5.32	40.51±5.91		
Cu	32.98±6.14	25.74±3.88		
Fe	40455.81±10367.87	712.32±298.46		
Mn	668.18±284.59	279.71±85.63		
Ni	19.40±2.86	15.43±3.24		
Pb	25.32±4.73	13.52±3.87		
Zn	55.82±13.01	35.07±21.13		
Ba	182.59±32.71	172.54±14.89		
Κ	1057.19±328.35	733.00±307.23		
Mg	1737.14±568.34	1432.45±134.49		
Mo	0.23±0.14	0.81±0.42		

Table 2.3 Concentration average \pm standard deviation (C \pm SD) of metals in the sediments from Passauna reservoir

The chronological variations in concentrations of metals in core I and core II are shown in Figure 2.5, respectively. In core II, Al shows an increase in concentration from ~1908, having two peaks in ~1917 and ~1926. Then, it gradually decreased and had a behavior without significant fluctuations. The Cd decreased according to the depth; its concentration peak was in the year ~1951 in core I and core II three peaks were observed in ~1920, ~1950, and ~2010. The Cu peak concentration was observed in ~1917 in core I, then gradually decreased and did not present relevant changes. The highest concentration of Cr in core I was observed in ~1890 then decreased until ~1926. It presented another peak of concentration in the year ~1944 and the last segment, the control gradually decreased. In core II, the highest concentration of Cu was observed in ~1970. The concentrations of Fe vary between 392.56 - 50,494.00 mg kg⁻¹ showing its concentration peak in ~1917 in core I. Fe in core II decreased with depth, showing its highest concentration in ~1960. Mn also decreased its concentration according to depth; its highest concentration was in the year ~1904 (1565.89 mg kg⁻¹). It then decreased rapidly until ~1911 (415 mg kg⁻¹), after which it began to gradually increase until 1972 (1085.61 mg kg⁻¹). Mn in core II decreases considerably with depth, showing growth from ~1939 on. Whereas the concentration peak of Ni was observed in ~1947 (22.66 mg kg⁻¹) in core I, it also showed peaks in ~1915 (22.21 mg kg⁻¹) and ~1980 (22.01 mg kg⁻¹). In core II, Ni presents its peak concentration in ~1920 (27.27 mg kg⁻¹), and again in 1970 and ~1983. In core II, Pb began with a concentration of 36.42 mg kg⁻¹ then gradually decreased until ~1929 (21.76 mg kg⁻¹). After 1929 the concentration of Pb began to increase until the year ~1980 (30.30 mg kg⁻¹), then decreased considerably. The highest concentration of Pb in core II is ~1922 (23.00 mg kg⁻¹) and decreased until ~1940; it then shows the same behavior as core I, with a concentration peak in ~1979 (17.38 mg kg⁻¹). Zn in core I showed a concentration peak in the year ~1980 (80.94 mg kg⁻¹). On the contrary, in core II Zn concentration peaks were observed in ~1922 (117.13 mg kg⁻¹) and ~1990 (37.39 mg kg⁻¹).





2.3.4 Enrichment factor (EF) and Igeo for heavy metals.

Al was used as a normalized element to remove the influences of geological and hydrodynamic processes and to estimate the anthropogenic impacts on heavy metals and trace metals. The mean EF in core I decreased in the following order: Fe > Mn > Cd > Sb > Zn > Cu > Cr > Pb. And in core II decreased in the order Sb > Pb > Cd > Cr > Fe > V > Zn > Cu > Ni > Mn. The presence of Cu and Zn in sediment samples could be associated with two sources of pollution and one anthropic source, indicated by the positive correlation between Cu and Zn which was previously evidenced by Xavier (2005). The fixed pollution source is represented by the Lamenha Pequena landfill, operated without control between the years 1964-1974 (Pitrat, 2010). This became a contracted sanitary landfill until 1989 when it was closed. As shown in Figure 2.6 this episode is revealed by the enrichment of Cu, Ni, and Zn between the years ~1965-1980, and after ~1980 their concentrations decreased.

In sediment core I, concentrations of Cd, Zn, Fe, and Mn increased after ~1937, ~1965, ~1918, and ~1962, respectively, with EF > 1.5 and I_{geo} < 1 (Figure 2.6). The concentrations of Cu, Ni, Pb, and Cr are enriched, but not strongly, with EF < 1.5 and I_{geo} < 1. In this core, it showed increases in metal concentrations in ~1930, ~1960, and ~1980. TOC concentrations were significantly and positively correlated with the concentration of Sb, Cd, Mn, Zn, Mg (p < 0.01) and negatively correlated with the concentrations of V and Cr. The concentration of Zn in the Passauna reservoir is significantly correlated with a majority of the metals, i.e., Sb. Al, Cu, Fe, Ni, K, Mg. In contrast, in sediment core II the metal concentration profiles exhibited no significant increases and showed similar concentration fluctuations (EF < 1.5 and I_{geo} < 1). The concentrations of Cd, V, Pb, and Fe increased after ~1973. This core showed a sedimentary transition in ~1980 the metal concentrations showed a slight increase in the enrichment factor, stabilizing in the last layers. TOC and TN concentrations are positively correlated with the concentrations of Ba and negatively correlated with the concentrations of Sb, V, Al, Cd, Cr, Fe, Mn, Ni, Pb, Zn, K, and Mg. The concentration of Fe is correlated with the concentrations of Sb, V, Al, Cd, Cr, Mn,

Ni, Pb, Zn, K, and Mg. The Pb is positively correlated with the concentrations of V, Cd, Fe, Ni, Zn, K, Mg, and Mo.




2.3.5 Multivariate Statistical

To identify the sources of metals and factors that regulate biogeochemical characteristics in the lake/reservoir, statistical tools were employed on the geochemical data. Principal components analysis (PCA) indicates possible sources/factors that control the supply and distribution of the metal concentrations (Figure 2.7). In this study, for core I three principal components can be extracted; these explain about 81.88% of the total variance and are the major contributors of the former two PCs (PC1 PC2 and PC3). In core, I, Cd, Cu, Fe, Ni, Zn, TOC, and TN showed stronger positive loadings on PC1 with values of 0.950, 0.923, 0.936, 0.883, 0.858, 0.509, and 0.583, respectively. The metals V, Cr, Pb, and Ba were negatively loaded on PC1 (-0.928, -0.757, -0.780, and 0.765, respectively). For PC2 in core I, Al and Cr exhibited positive loading with values of 0.459 and 0.375, respectively. In PC3, Mo was significantly loaded with the value of 0.738.

For core II, three PCs were derived loading for approximately 85.2% (PC1 and PC2) of the total variation. In PC1, V, Al, Fe, Mn, K, and Mg were positively loaded with the values 0.979, 0.941, 0.974, 0.863, 0.983, and 0.773, respectively. TOC and TN showed strongly negative loading with values -0.976 and 0.970. Metals Cu, Ni, Pb, Zn and Mo exhibited strong

positive loading on PC2 (0.894, 0.952, 0.778, 0.961 and 0.956, respectively). In PC3, Cr was

significantly loaded with a value of 0.723.



PC1-58%

Figure 2-7 Principal Components Analysis loading concentrations of metals from the Passauna Reservoir: a) core I b) core II.

2.3.6 Redox- sensitive trace elements

PC1-58.56%

Redox-sensitive trace elements (for example: V, Ni, Cr, Re, Mo, U, Cu, Cd, Se, Tl, and Sb), ratios of trace elements (e.g., Th/U, Ni/Co, V/(V + Ni), V(V + Cr), C/Zn, and V/Mo), and Mn concentrations were used to assess changes in the redox conditions in the lake. In this study, we used V/(V+Ni), V/(V+Cr), Cu/Zn, Cu/Ni, Pb/Cu, Cd/Pb, and Mn/Fe High values of the V/ (V + Ni) and Cu/Zn ratios could indicate anoxic conditions (Goodarzi et al., 2019). In core I, high V/ (V + Ni) ratios (range: 0.76-0.91; average: 0.80) and Cu/Zn ratios (range: 0.43-1.79; average: 0.60) were detected. In core II, V/ (V + Ni) ratios (range: 0.63-0.83; average: 0.77) and Cu/Zn (range: 0.32-1.20; average: 0.82) (Figure 2.8) were also observed. The V/(V+Cr) ratios were measured for core I (range: 0.65-0.50; average: 0.58) and for core 2 (range: 0.50-0.64, average: 0.57). The variations in the V/ (V + Ni) and V/ (V + Cr) ratios could indicate more strongly reducing conditions.

The Mn/Fe ratio values for the samples collected in core I were (range: 0.004-0.04, average: 0.017) and core II (range: 0.31-0.58, average: 0.42).

Figure 2-8 The vertical distribution of ratios Cu/Ni, Pb/Cu, Cd/Pb, V(V+Ni), Mn/Fe in sediment cores a) core I and b) core II from the Passauna reservoir



2.4 DISCUSSION

2.4.1 Organic elements and their sources

The TOC/TN ratio is widely used to identify the source of organic matter in the lake and river sediments. A value of TOC/TN between 4 and 10 indicates a predominance of algae and cyanobacteria, while the value indicating terrestrial organic matter is above 20 (Meyers, 1997; Meyers, 2003). Marine and freshwater phytoplankton are rich in nitrogen and have a TOC/TN ratio of 5-6, while terrestrial vascular plants are poor in nitrogen and have a TOC/TN ratio of 12-14 (Meyers and Teranes, 2002). In core I the TOC/TN ratio varied from 7.14-12, indicating that algae and cyanobacteria (allochthonous) are the predominant sources of organic matter. The TOC/TN ratio of core II was found to be relatively higher in the bottom section of the core due to the presence of terrestrial vascular plants. In the upper section of core I, from ~1956, TOC/TN ratio was found to be low (< 10); the decrease in TOC/TN values indicates an increase in the contribution of algal-derived organic matter in the sediments (Meyers, 1994, 2003). Thus, these values evidenced an increase in primary productivity at this layer. However, such low TOC/TN values have also been attributed to the presence of inorganic nitrogen in sediments with low organic matter contents (Lehmann et al, 2002). To estimate the inorganic nitrogen contents, the correlation between TOC and TN contents was tested. The strong correlation coefficients in the two sediment cores ($R^2 = 0.87$ for core I and $R^2 = 0.97$ for core II) indicate that the majority of nitrogen is organically bound. The regression line intercepts the y-axis for core I at 0.06% and core 2 at 0.07%. This suggests that the percentage of inorganically bound is small, with 0.06% (core I) and 0.07% (core II) corresponding to the maximum amount of inorganic nitrogen to be expected in these sediments (Veres et al, 2008).

2.4.2 Source and disentangling the distribution of metals

According to Sotiri et al. (2021), 19 of 30 sediment core samples from the Passauna reservoir consisted of more than 95% of silt-clay material and the average Wet Bulk Density (WBD) was 1.12 g cm⁻³. In a previous study, it was shown that granulometry composition of samples near the point I predominate the fraction 63 μ m (silt and clay), contributing to 95.77%. The fraction > 0.125 mm (fine sand) and 0.25 mm (medium sand) varies between about 0.68% and 1.29%, respectively. For the two of the coarsest fractions, > 0.5 mm (coarse sand) and > 2.0 mm (gravel), with average of 1.51% and 0.68%. Furthermore, for sampling point II the fraction < 63 μ m was the most predominant with an average of 99.59%: fine sand (< 0.125 mm) 0.13%, medium sand (0.25 mm) 0.04%. and 0% for coarse sand and gravel.

The metal concentration profiles in the sediment core from the Passauna reservoir exhibit a higher concentration of the elements in core I than core II. For example, the concentration of Fe was 55 times higher than that of core II, and the concentration of Cd was two times higher. This can be explained by different pollution sources around the sampling sites. In addition, the point I is located at the entrance to the reservoir; it receives and accumulates all-metal load received by the upstream river in dissolved form and the form absorbed in finer particles such as clay and silt. Such particles are easily dragged from the bottom of the river by the current and taken to the reservoir, where they are deposited. This point has a greater content of clay fraction than point II (Sotiri et al., 2019). Also, point I receive more natural and anthropic organic matter than point 2, located in a more urbanized area (Pitrat, 2010).

The EF has frequently been used to infer the increase of metal concentration over a long time. The EF value of > 1.5 (core I), suggests that a significant portion of metals is delivered from non-crustal materials or non-natural weathering processes (Gao et al., 2018). Alternatively, the metals can have other sources, e.g., point and non-point pollution sources, and biota (Klerks and Levinton, 1989; Liu, 2014). As shown in figure 6, the vertical EF vertical profile at the core I that the EF<1 values of the relatively low for Ni, Pb, Ba, V, Cr, Mo, at a minor enrichment (1-3) for Sb, Cd, Cu, Fe, Mn, Ni, Zn, K, and Mg. In the core II, EF values of the sediments are relatively low for Mn, Ni, Fe, Cr, V, Zn, Ba, Mg, Mo, and at minor enrichment Sb, Cd, Pb, and K.

The concentrations of metals are higher in core I due to the difference in the hydrodynamics of the sample sites. Sampling point I have lotic characteristics and acts as a buffer at the entrance of the reservoir with a higher sedimentation rate. In contrast, point II is a totally slow system where a lower sedimentation rate was determined.

In addition to EF, the sources of the metals found in the core sediments in the Passauna reservoir were investigated using multiple statistical analyses including correlation analysis and PCA. The TOC and TN content was included in the PCA to determine whether the metals, organic matter, and total nitrogen had a common source.

According to Sartor and Boyd (1972), urbanization and industrial activity generate high concentrations of Zn, Cu, and Cr among the metals found in drainage water. In core I, Zn was also positively correlated with Cd, Cu, Ni, Fe, K, and Mg, indicating a similar source. The TOC concentrations were significantly and positively correlated with the concentrations Cd, Mn, Zn, and Mg, indicating these metals are significantly controlled by algae-derived organic matter. Phytoplankton can absorb and assimilate heavy metals from aqueous environments (Duan et al., 2014). Concurrently, they can form extracellular organic bonds that are capable of complexing with metals. After the phytoplankton dies, their OM together with the metals are settled down into the sediments (Xu et al., 2013; Wu and Xia, 2014). Also, the concentration of Fe and Mn in the Passuna reservoir is significantly correlated with most of the metals including Al, Ni, and K (all with p < 0.01). These results indicate that the deposition of most metals has been influenced by organic matter and Fe-Mn oxides (Guo et al., 2015). Al is extremely immobile and is a typical lithogenic element (Price et al., 1999). Al is positively correlated with Fe, suggesting that Fe and Al are mainly originating from the erosion of soils in the reservoir watershed. Agricultural fertilizers, herbicides, and pesticides typically alter the soil chemistry (Huang et al., 2013). According to Dias (1970) and Xavier (2005), the application rate of NPK fertilizer (Nitrogen, Phosphorus and Potassium) or urea fertilizers varies between 200 and 300 kg/ha. The main agricultural inputs of metals are fertilizers and pesticides containing metal, other than soil acidity correctors. Concentrations of Cd and Zn in chemical fertilizers used in Brazil can range from 0.6-6.7 mg kg⁻¹ and 2-810 mg kg⁻¹, respectively. In pesticides the concentration of these metals varies 3-6 mg kg⁻¹ and 6.8-37.5 mg kg⁻¹,

respectively (Malavolta,1994). Thus, Cd can be used as an indicator of agricultural growth. Between the 1930-1960 period, the state of Paraná presented the greatest deforestation coupled with the implementation of extensive agriculture (Carvalho, 2007). The metals Cd, Cu, and Zn in this period showed an increase in their concentrations and EF values > 1.5. The application of agricultural inputs can lead to the leaching of metals from the soil and, therefore, into water bodies, through drainage and erosion. The expressive use of agricultural inputs in the study area, particularly pesticides, was highlighted by several studies in the Passauna watershed (Bagatin, 1988; Dias; 1997; Xavier, 2005). In 2000, more than 20% of the area was covered by agricultural use and 21.8% by livestock use (Meger, 2007). Therefore, the heavy metals including Cd, Zn, Ni, and Cu in the sediments of the Passauna reservoir mainly originated from soil erosion and agricultural non-point source pollution. Similar results by Xia et al. (2011a, 2011b) and Tang et al. (2014) found that the increasing heavy metals including Cr, Zn, As and Cd in the sediment were primarily from extensive use of phosphate fertilizer.

In 1991 the Passauna Environmental Preservation Area was created (Curitiba City Hall Decree n° 80/91 of 03/06/1991), and in effect, several measures to reduce pollutant loads from fixed sources present in the basin were implemented, including, among others, the removal of polluting industries (Xavier, 2005). As can be seen in Figure 2.6, the enrichment of heavy metals decreased after 1991.

In core II, TOC presented a negative correlation with most metals indicating that the deposition of these metals is not related to organic matter. On the other hand, Fe and Mn did show a positive correlation with Sb, V, Al, Cd, Cr, Ni, Pb, Zn; their disposition is influenced by Fe-Mn oxides. The significant correlation of Al with Fe and Mn (two redox-sensitive elements), indicated the accumulation of these elements is primarily regulated by the input of terrigenous materials, which could indicate the diagenetic migration of trace metals (e.g. Ni, V, and Sb) along the sediment cores is unlikely (Ontiveros-Cuadras et al., 2021). The mean of the

EF values varies between 0.62-1.20, while it is generally recognized that an EF value below 1.5 indicates natural sources such as rock weathering (Gao et al., 2018).

Copper is a natural mineral that is abundant in nature, but it has wide use in industry and other places. Its anthropogenic sources are pesticides, fertilizers, corrosion-resistant materials, and domestic waste (Wu et al., 2017). In core II, the increase in copper concentration begins after 1930. These concentrations reflect the changes in the environment or the waters of the Rio Passauna from the 1930s to the 1960s, attributed to the expansion of industrialization in Curitiba during this period or population growth, as well as urbanization of the region (Loeffler, 2009). In 1953, it was observed that the population growth rate was 7.8% per year (Loeffler, 2009). The increase in Cu concentrations in the sediment may be influenced by the disposal of domestic sewage, due to its high affinity of copper with organic matter (Yang et al.,2010). In core II its source is more related to natural origin, with EF value < 1.5. It has a decreased concentration in the layers close to the surface which also has a lower percentage of TOC.

The Pb profile in both cores showed a gradual increase from 1962 to 1980 when it presented its maximum concentration of 30.82 mg kg⁻¹ (core I) and 17.38 mg kg⁻¹ (core II). The use of Pb as an additive in gasoline may have resulted in an increase of this metal through atmospheric emissions from the 1940s to 1992, after which Brazilian gasoline no longer had a leaded additive (Fontenele, 2006). Brazilian legislation, through CONAMA resolution 452/2012, establishes the maximum limit of heavy metals in sediments for dredging purposes. Within the sediments from core I, the metals that exceed level 1 of their concentrations were copper, chromium, and nickel. In core II, only Cr and Ni go beyond level 1. Sediments from the Passuna reservoir to be used for dredging purposes would be subject to ecotoxicological tests to comply with the criteria provided by the resolution.

2.4.3 Cu/Ni as a proxy of productivity and Mn/Fe as a proxy of paleoredox

Some trace metals (TM) are closely related to primary productivity because there are biologically essential elements scattered to the sediments during organic matter sedimentation (Yuan et al., 2014; Calvert and Pederson, 2007). To evaluate the degree of ecosystem changes in the reservoir lake, we applied ratios of Cu/Ni, Pb/Cu, and Cd/Pb.

In core I, in the 100-year record of metals, large and lasting trends in the proportions of trace metals indicated that a change in the regime in the ecosystem occurred between the period 1939-1980.

Variations in Cu/Ni of sediment reflect changes in trace metal inputs, biological productivity, and other factors (Yuan et al., 2014). Cu/Ni changes in the water column can be induced by variations in anthropogenic emissions of metals and differentiation processes of these metals in the lake (Yuan et al., 2014). The variation of Cu/Ni in relation to anthropogenic inputs could be insignificant because the ratio of Cu/ Ni consumption has changed little over time, suggesting that these records are responding to biological changes in the lake. The Cu/Ni changes can be attributed to the cumulative effect of phytoplankton preferential uptake of Ni over Cu, both metals being organically complexed to varying degrees (Odzak et al., 2002). The organic complexation of Cu with organic matter is stronger, which limits its bioavailability and absorption by phytoplankton (Sunda et al., 1998). In core I, the Cu/Ni ratio showed an increase of 35.29%, 16.28%, and 44.67% during the periods 1897-1925, 1929-1980, and 1983-2019, respectively. The increase in Cu/Ni between 1983 and 2019 corresponds to a change in the biological productivity of the lake due to the commencement of reservoir operations in 1990 (Carneiro et al., 2016). High Cu/Ni values in Lake Erie (1.0) are related to contemporary episodes of algal blooms (Yuan et al., 2014). The use of Cu/Ni as a proxy for productivity is supported by the ratios V/ (V + Ni), Cu/Zn, and V/ (V + Cr) that present high values related to anoxic periods, which occurs when the system presents a reduced circulation due to circulation and accumulation of decomposing organic material (Yun et al., 2014). Also observed in these

three periods are low values of TOC/TN. Additionally, in core II, between the period 1940-1980 the Cu/Ni values decreased 21.36%, and after 1980 it presents almost constant values. This result can be confirmed with the V (V + Ni), Cu/Zn, and V/ (V + Cr) indices that show an increase after 1980 indicating a change in the redox conditions of the environment. According to Xavier (2005), the Passauna reservoir was classified as mesotrophic during the period 1993-2004.

Mn and Fe are elements sensitive to redox conditions (Davison, 1993). Fe (II) oxidizes more rapidly than Mn (II) and Mn oxyhydroxides are relatively easily reduced than the oxides of Fe. According to these differences between these two elements, the Mn/Fe ratio of the oxide forms a change in the ratio to low values indicating a depletion of Mn, which is interpreted as a Mn dissolution event due to suboxic or anoxic conditions at the time of deposition (Wersin, et.al, 1991). In both cores, Fe and Mn profiles are relatively similar (Figure 2.8). In core I, the ratio Mn/Fe showed the highest values from ~1904 and ~1964. The lowest values are recorded between ~1925 to ~1933. Core II showed the highest value in the bottom part of the core, and after ~1939 the values began to decline until 1973. After ~1980 there is a slight increase in the value of the index, along with relevant changes with a decreasing trend. The low Mn/Fe ratio can be reflecting a tendency of low oxygen concentration in the reservoir, however without the development of complete anoxia, which favors the dissolution of Mn oxyhydroxides. In both cores, fluctuating Mn/Fe ratios are observed between ~1904 to ~2000. These observations could be evidence of degradation of climatic conditions, which reduced the primary production and improvement in water circulation (Wersinet al., 1991; Loizeau et al., 2001).

The results of the indices showed fluctuations overtime during some periods, the Passauna reservoir had increased its primary productivity (For example, the construction of the dam in 1989) caused by the input of nutrients due to it being a watershed with increasing anthropogenic pressure, and this situation may affect the quality of the water.

2.5 CONCLUSIONS

The Passauna reservoir receives metallic loads from diffuse sources, that is, drainage from agricultural and urban areas. The fixed sources identified would be sewage, landfill, and drainage from a nearby highway (BR 277), and these sources are evidenced by the enrichment of heavy metals (Pb, Zn, Cd, Cu, and Cr) along with the cores. The factor of enrichment via metals was observed during the period 1930-1960, attributed to this period of greatest deforestation occurring in the basin for the opening of agriculture, in the 1960s alone, Paraná lost about 240 thousand ha/year of forests, at the expense of agricultural expansion in the western region (Maack, 1968). In core II a natural source predominates for metals, related to strong rock erosion in the study area together with local geochemical characteristics. Fluctuations in metal concentrations were also observed after 1980, the year the reservoir was built, when the site was no longer a river.

The Passauna reservoir is currently an oligotrophic lake, and according to the Mn/Fe index, it shows signs of reduced oxygenation in the bottom waters. This could mean that in the future a combination of high nutrient concentrations in the lake water and a warmer climate than the current one can lead to higher primary production, causing an anoxic environment due to the decomposition of organic matter.

Sediments are of fundamental importance for environmental assessment as they can transport and accumulate toxic substances, releasing them into the environment under certain conditions. Therefore, monitoring the quality of water bodies through the analysis of sediments is of great importance.

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3 INSIGHT INTO THE ORIGIN OF ORGANIC MATTER FROM SATURATED HYDROCARBONS AND ISOTOPIC ANALYSIS OF SEDIMENTS FROM A SUBTROPICAL RESERVOIR IN SOUTHERN BRAZIL.

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ABSTRACT

The composition and distribution of saturated hydrocarbons, besides indices among nalkanes in two dated sediment cores from Passauna reservoir, were analyzed to identify changes in environmental and trophic state conditions in the overlying water time. In this study, two cores were examined according to organic matter source and compared using saturated hydrocarbons occurrence and indices among n-alkanes. According to the n-alkanes indices (CPI, TAR, Pr/Ph, ACL), the distribution of n-alkanes between cores is remarkable. For example, during the period 1973-2013 core II, shows an increase in short-chain alkanes concentration, suggesting significant contribution by phytoplankton for organic matter, probably as a consequence of higher nutrient input. That period presented a constant increase in urbanization and industries in that area. In contrast, in the core I prevail terrestrial sources for organic matter composition. Those results are reinforced by analysis of stable isotope values of δ^{13} C and δ^{15} N. Values of δ^{13} C ranged from -23.0 ‰ to -25.7‰ (core I), -28.4‰ to -29.2‰ (core II); values of δ^{15} N ranged from 6.6‰ to 10.8‰ (core I) and 3.8‰ to 7.6‰ (core II), respectively. Microbial activity and presence of methanotrophic bacteria were confirmed by the presence of hopanes: $17\alpha,21\beta(H)$ -30-norhopane; 18α (H)-30-nor-neo-hopane; $17\alpha,21\beta(H)$ -hopane; and $17\beta,21\alpha(H)$ -hopane (moretane), after 1940. The presence of methanotrophic bacteria implies an anoxic environment, caused by high bacterial productivity.

Keywords: hopane, methanotrophic bacteria, sediment core, eutrophication, Passauna reservoir and hydrocarbons aliphatic

3.1 INTRODUCTION

Urban reservoirs are exposed to the effects of anthropogenic activities (land clearing, agriculture, deforestation, and urbanization). Those activities, sometimes, increase the input of nutrients, therefore causing an imbalance in nutrient concentration (Das et al., 2008). The industrial revolution contributed to that in many cases. The sediment deposition reflects climate change as well as the anthropogenic influence on the lakes and their catchments (Huang et al., 2001). In general, organic matter derives from two main sources, being autochthonous - primary production (algae, zooplankton, bacteria) and allochthonous - terrestrial material (Bianchi and Canuel, 2011).

Disentangling the organic matter composition of lake sediments has great importance in understanding external factors. The composition of organic matter can be revealed by number of methods, which include elemental composition, isotopic analysis, lipids distribution (biomarkers) that can be used to reconstruct paleoenvironments of lakes and surrounding areas. Geochemical markers are organic molecules that have not undergone significant changes in their chemical structure despite the biological or geochemical processes to which they were subjected (Peters et al., 2005). The analysis of geochemical markers in sedimentary profiles provide insights and understanding the changes that occurred reconstructing geological scenarios and events that occurred over time (Froehner et al., 2010; Machado et al., 2014). Organic geochemical markers can be divided into acyclic, cyclic, and aromatic, their distribution in sediments is used to show environmental changes that have occurred, such as carbonic, phytoplanktonic, and zooplanktonic composition (Zimmerman and Canuel, 2002). Aliphatic hydrocarbons (AHs) as one the most abundant lipid molecules, due to their functional groups. AHs are relatively resistant to degradation and are well preserved in sediments (Mejanelle et al., 2017). The source-specific of aliphatic hydrocarbons are allochthonous and autochthonous in sediments. The allochthonous AHs originate from terrestrial plants and petroleum residues, while the autochthonous sources come from aquatic organisms such as algae, microbes, and aquatic macrophytes (Ficken et al., 2000; Meyers, 2003; Duan et al., 2017). The source of organic matter can be identified according to the number of carbons in the chain, n-alkanes with long chains ($n-C_{26}-n-C_{33}$) with a predominance of odd carbons are indicators of terrestrial plants (Meyers, 2003). Short chains of n-alkanes ($n-C_{15}-n-C_{20}$) with an even or odd predominance are indicators of phytoplankton and bacteria (Killops and Killops, 2013). Middle-chain n-alkanes ($n-C_{21}-nC_{25}$) with a predominance of odd carbons originate from submerged and floating aquatic macrophytes (Hostettletr et al., 1999). For a better distinction of the sources of organic matter between terrestrial and aquatic sources, indices are used, such as carbon preference index (CPI), odd-carbon predominance (OEP), low molecular weight to high molecular weight ratio (LMW/HMW), terrigenous/aquatic ratio (TAR), average chain length (ACL) and aquatic macrophyte (Paq).

Hopanes are produced as membranes lipids by bacteria of diverse taxonomic groups (Innes et al., 1997). The presence of hopanes, including 17β , 21β -22R-hopanes ($\beta\beta$ -hopanes), in recent sediments has been reported frequently (Cranwell and Koul, 1989). The abundance of hopanes in recent sediments reflects the intensity of bacterial activity, combined with favorable conditions for organic matter (Ishiwatari et al., 2014). The molecular composition and distribution of hopanes differ between lakes and sediment depth (Uemura and Ishiwataru, 1995). The $\alpha\beta$ type of hopane, frequently detected in surface sediments, is generally derived from oil pollution, as hopanes with this configuration are the transformation products of hopanes with $\beta\beta$ configuration under thermal stress (Peters et al., 2005). However, hopanes with $\alpha\beta$ configuration have been found in acid peat and forest soils and it has been shown that $\alpha\beta$ can be formed by microbial activity (Crossman et al., 2001; Pancost et al., 2003).

Passauna reservoir is used for supplying 30% of public water of the Metropolitan Region of Curitiba (MRC) population, for approximately half a million inhabitants, with a regularized intake flow of 2 m.s⁻¹ by local sanitation company (SANEPAR, 2013). According to Veiga and

Dziedzic (2010), there are loads of 93.904 kg year⁻¹ of total nitrogen and 5.789 kg year⁻¹ of total phosphorus. The region suffers from anthropogenic actions since the 1980s, with the occurrence of irregular riverbank occupations, the presence of industries and agricultural areas without adequate management methods (Xavier, 2005). The increase in nutrient input, the influence of anthropogenic activities, and climatic changes contribute to a deterioration of the water quality of the reservoir. Environmental changes exert a strong influence on the growth of algae, aquatic macrophytes, and bacteria in lakes, which imply the occurrence and distribution of hydrocarbons in sediments (Lu and Meyers, 2009; Zhang et al., 2014).

There is a lack of information about the main sources of organic matter of Passauna reservoir as well as the consequence in the trophic state of the reservoir. Combining saturated hydrocarbons (n-alkanes and hopanes) with isotopic analysis shed light on understanding changes in the trophic state of the reservoir induced by climate change and anthropic activities. The aims of this study included: a) identifying the main sources of OM through occurrence and distribution of n-alkanes in two sedimentary cores; b) discussing the controlling factors (natural and anthropogenic activities) of AHs in the Passauna reservoir; and C) distinguishing microbial activity between two sedimentary cores examining the occurrence of hopanes, typically derived from bacteria (Summons and Jahnke, 1990).

3.2 MATERIAL AND METHODS

3.2.1 Study area

The watershed of Passauna river is located between S 25 °25'48" and W 49 ° 15' 16". Passauna sub-watersheds has a drainage area of 217 km², covering the municipalities of Almirate Tamandaré, Campo Magro, Campo Largo, Araucária and Curitiba (Figure 3.1) (Sauniti et al., 2004). The Passauna reservoir was formed in 1989 for public water supply. It locates in Araucária, PR, near to Curitiba, Brazil. The Passauna reservoir is responsible for supplying 30% of the population in Curitiba and MRC, with an operating capacity ranging from 1300 L/s to 2000 L/s of treated water available for supply (Sotiri, et al., 2021). Table 2.1 shows the physical and chemical parameters of the reservoir. The normal operating level is 890 m, the reservoir has a water sheet area of 11 km² and an average depth of 9.4 m. The residence time of the reservoir is 292 days (Carneiro et al., 2016), being the main water inflow is the Passauna River representing 65.6% of the reservoir tributaries. Along its course of approximately 22 km, it receives the contribution of small watercourses from six sub-basins (Juruqui, Cachoeirinha, Cachoeira, Ferraria, Taquarova, Jaguaruva).

According to the Environmental Institute (IAP-Environmental Institute of Paraná State 2017), Passauna reservoir has been ranked as Class III (moderately degraded) and oligotrophicmesotrophic state trophic. Thermal/chemical stratification takes place in the deeper part of the reservoir, during warm periods (September-March) showing substantial oxygen deficits in the upper water column (epilimnion) and anoxic conditions in the deepest zones of the hypolimnion (Carneiro et al., 2016). The reservoir is classified as warm monomythic. Presenting mixed water column during the winter (April-August) (IAP, 2017).

Parameter	Values
Elevation (m)	889.5
Average annual temperature(°C)	17.3
Catchment area (km ²)	152.6-188
Lake surface area (km ²)	9-11
Mean depth (m)	6.5-9.4
Secchi depth (m)	2.55
Total nitrogen (kg year ¹)	93.904
Total phosphorus (kg year ¹)	5.789

Table 3.1 Physical and chemical characteristics of the Passauna reservoir

According to the monitoring of IAP (2017), during the period 1999-2013, the results show that the reservoir has oligotrophic characteristics, but is sometimes mesotrophic. The pH values ranged between 6 to 9, values within the limits of legislation. About the primary production, a small concentration of cyanobacteria cells (blue algae), with values below 10,000 cells.mL⁻¹. Furthermore, it showed good water transparency conditions, low to moderate nutrient concentrations, and low levels of organic matter.

The local climate according to the Koppen climate map is classified as Cfb which is a temperate climate with a mean temperature of 22 °C. According to the precipitation data mean annual ranges from 1400 mm to 1600 mm, greater rainfall rates season is observed in January and February. On the other hand, the dry months are April and August. Precipitation data show that this sub-basin presents favorable conditions so that throughout the year, during the rain events contribute loads of nutrients and pollutants to the body of water. Since the greatest economic activity in this area is agriculture.



Figure 3-1 Localization of sampling points from Passauna Reservoir.

3.2.2 Sample collection

Two sediments cores (core I and core II) were collected in February 2018 and May 2019, respectively. The cores were retrieved using a piston percussion core fitted with 86-mm internal diameter acrylic tubes. In the laboratory, cores were subsampled by slicing at 2.0 cm intervals. All samples were transferred to polyethylene bags and frozen at 0°C. Samples were later freeze-dried on the ground by an agate mortar and pestle. 39 and 18 subsamples were taken

in sedimentary core I and core II, respectively. Point 1, is located in the pre-reservoir region, a shallow with a depth varying from 0.5 to 2 meters, flooded region, bounded by a grounded cord with a bridge that strangles the flow. And point 2, presents a greater depth of 10-14 meters, near the outlet of the reservoir.

3.2.3 Geochronology

Subsamples for isotope analysis (δ^{13} C; δ^{15} N), total organic carbon (TOC), and total nitrogen (TN) analyses were treated with 10 mL of 1M HCl to remove inorganic carbon (carbonates). The carbonate-free subsamples were then measured for TOC and TN contents on a CNHOS Elementar Vario EL III at Lamir (Laboratorio de Minerais e Rochas/UFPR).

The analyses of δ^{13} C and δ^{15} N were on the sediment subsamples, using a Delta V Advantage mass spectrometer (Thermo Fisher Scientific). The isotope ratios are reported in part per mil (‰) as followed Equation 3.1:

$$\delta(\%_0) = \left(\frac{R_{sample}}{R_{std}} - 1\right) \times 1000, \tag{3.1}$$

where $\delta(\%_0) = \delta^{13}C(\%_0)$ or $\delta^{15}N(\%_0)$, $R_{sample} =$ the isotopic ratios of the sample, $R_{std} =$ the isotopic ratios of the standard. For carbon, the standard is VPDB (Vienna Pee Dee Belemnite) and for nitrogen, it is N₂ present in air composition.

3.2.4 Determination of hydrocarbons aliphatic

Saturated hydrocarbons (n-alkanes, branched aliphatic alkanes, and hopanes) were separated from the total lipid extract (TLE). The TLE was obtained starting by weighing 1 g dried sediment and adding 10 mL dichloromethane: methanol mixture (2:1) in an extraction tube, homogenizing it in a vortex, and subsequently taken to an ultrasonic bath for 30 min (Sanez et al., 2016). The solvent (containing the TLE) was separated, repeating the process three times. The volumes were then combined. Activated copper chips were added to remove possible sulfur. TLE was concentrated and the volume was reduced to approximately 1 mL through evaporation in a rotary evaporator and then dried under a gentle flow of N₂. The dried

extracts, containing n-alkanes and other compounds, were stored at -20 °C for further analysis. n-Alkanes were extracted and separated from TLE following the procedure described in Galoski et al. (2019). Briefly, TLE was fractionated using a flash chromatography column filled with silica gel, alumina, and sodium sulfate. Silica gel and alumina were previously activated. TLE was separated into four fractions: saturated hydrocarbons (fraction 1) and aromatic compounds (fraction 2). Fraction 1 was obtained after elution with 7 mL n-hexane. Fraction 1, containing the n-alkanes, steranes, and hopanes, were analyzed in a gas chromatograph (GCMS-OP2010 Plus, Shimadzu) coupled with a mass detector. The gas chromatograph operated with ultra-pure helium as the carrier gas at a flow of 0.70 mL min⁻¹ and the separation was performed using a capillary column (RTx-5MS), 30 m x 0.25 mm I.D. with 0.25 µm film thickness), in a column oven at 60 °C, followed by heating at 20 °C min⁻¹ up to 60 °C, then 12.50 °C min⁻¹ up to 120, subsequently heated at a rate of 3.50°C min⁻¹ up to 60 °C to 240 °C and finally at a rate of 5.50 °C min⁻¹ to 315 °C and held for 11.20 minutes. Aliphatic hydrocarbons were identified by their retention time and mass spectra in full scan. Previously, a mixture of C8-C40 n-alkanes (C8-C40 Alkanes Calibration Standard, Supelco, Germany), within the range of 0.1–100 ng mL⁻¹, was used to obtain a calibration curve to quantify the n-alkanes. To better understand the source of organic matter, we applied the following proxies:

$$\frac{LMW}{HMW} = \frac{\sum nC_{11} - nC_{20}}{\sum nC_{21} - nC_{35}}$$
(3.2)

Carbon Preference Index (CP1; Allan and Douglas, 1977) (Equation 3.3 and Equation 3.4).

$$High \ CPI_{24-35} = 0.5 \times \frac{\sum nC_{25} - nC_{23}}{\sum nC24 - nC32} + \frac{\sum nC_{25} - nC_{33}}{\sum nC_{26} - nC_{34}}$$
(3.3)

$$Low \ CPI_{14-24} = 0.5 \times \frac{\sum nC_{15} - nC_{23}}{\sum nC_{14} - nC_{22}} + \frac{\sum nC_{25} - nC_{33}}{\sum nC_{16} - nC_{24}}$$
(3.4)

Average Chain Length (ACL; Meyers et al., 2003) (Equation 3.5)

ACL =
$$\frac{27 \times nC_{27} + 29 \times nC_{29} + 31 \times nC_{31} + 33 \times nC_{33}}{nC_{27} + nC_{29} + nC_{31} + nC_{33}}$$
(3.5)

Terrigenous Aquatic Ratio (TAR; Bourbonniere ad Meyers, 1996), (Equation 3.6 and Equation 3.7).

$$TAR = \frac{nC_{27} + nC_{29} + nC_{31}}{nC_{15} + nC_{17} + nC_{19}}$$
(3.6)

$$OEP = \frac{nC_{21} + (6 \times nC_{23}) + nC_{25}}{4 \times (nC_{22} + nC_{24})}$$
(3.7)

Proxy of Aquatic macrophyte input (Paq; Ficken et al., 2000) (Equation 3.8).

$$Paq = \frac{nC_{23} + nC_{25}}{nC_{23} + nC_{25} + nC_{27} + nC_{29}}$$
(3.8)

Hopanoid hydrocarbons were identified by comparison of mass spectra and relative GC retention times with those of standards and those reported in the literature.

3.3 RESULTS

3.3.1 δ^{13} C, δ^{13} N and TOC values of reservoir sediments

The δ^{13} C values in organic matter (OM) ranged from -23.0 to -25.7 ‰ (core I). Values recorded in core II were moderate and relatively constant, between -28.4 and -29.2 ‰ (core II); in both cores, the lower values occurred in surface sediments (Figure 3.2). The δ^{13} N values fluctuated between 5.6 to 10.8 ‰ (core I) and from 3.8 to 7.6 ‰ (core II). The more negative δ^{13} C values of the sedimentary cores were obtained in point II, near the dam of the reservoir. Abundances of TOC were exceptionally high in core II, averaging 15.90%, and varying from 3.82 % to 32.84%. In core II values ranged from 0.98% to 3.99% (average 2.02%).



Figure 3-2 Variation vertical of δ^{13} C and δ^{15} N verses year in Passauna reservoir sediment cores: • core I; • core 2

3.3.2 Distribution of n-alkanes in sediments cores

In the two cores, the n-alkane distributions range from C_{14} to C_{37} . The total concentration of n-alkanes (Σ n-alkanes) ranges from 0.27 to 37.02 µg.g⁻¹ (core I) and from 9.58 to 60.62 µg.g⁻¹ (core II). According to individual n-alkanes, the concentrations varied with carbon number. For the odd-carbon fraction, short-chain n-alkane abundances (sum of C_{15} , C_{17} , C_{19}) amounted 0.032 to 1.23 µg.g⁻¹ (average 0.32 µg.g⁻¹) and 0.23 to 1.16 µg.g⁻¹ (average 0.67 µg.g⁻¹) in the core I and core II, respectively. The middle-chain n-alkanes (sums of C_{21} , C_{23} , and C_{25}) ranging from 0.080-10.02 µg.g⁻¹ (average 5.04 µg.g⁻¹) in the core I and from 0.50 to 9.50 µg.g⁻¹ (average 3.70 µg.g⁻¹) in the core II. The long-chain n-alkanes (sums of C_{29} , C_{31} , and C_{33}) were higher abundant in core II, ranging from 1.32 to 26.21 µg.g⁻¹ with an average of 10.14 µg.g⁻¹. In core, I values range from 0.72 to 10.44 µg.g⁻¹ with an average of 3.87 µg.g⁻¹.

The carbon number maximum of n-alkanes (C_{max}) varied between cores (Figure 3.3). In core, I, C_{max} for the long-chain (> C_{21}) occurred at C_{25} or C_{29} , at C_{29} or C_{31} in core II. For the middle and short-chain n-alkanes (< C_{20}) C_{max} occurred at C_{17} , C_{18} , C_{19} , or C_{20} in core I, at C_{16} , C_{17} , C_{19} , or C_{20} in core II. The Pr/Ph ratio varies with the depth from 3.98 (1987) to 0.45 (1901) and 0.38 (2013) to 1.52 (1928), in core I and core II, respectively. High CPI₂₄₋₃₃ values range from 0.30 (2013) to 5.22 (1922) in core I and from 0.72 (1886) to 149 (1965) in core II. Low CPI₁₄₋₂₄ values range from 1.30 (2013) to 10.66 (1966) in core I and from 1.22 (1886) to 21.34 (1980) in core II. The ACL proxy values range from 29.21 (1894) to 30.41 (1983) in core I and 29.00 (1990) to 30.44(1939) in core II. The TAR reflects the terrigenous/aquatic ratio of the hydrocarbons in the samples, with the values ranging from 1.33 (1901) to 32.64 (1965) in core I and from 1.14 (2013) to 30.44 (1939) in core II. The OEP values range from 0.42(2019) to 9.23(1958) in core I and from 0.32(2013) to 4.41(1922) in core II. The Paq values of core I range from 0.058(2019) to 1 (1890), while in the core II values range from 0.14 (1968) to 0.41 (1922).

Figure 3-3 Values of Low CPI₁₄₋₂₄, High CPI₂₄₋₃₃, ACL, TAR, OEP and Paq in sediment cores from the Passauna reservoir; \blacksquare core I; \bullet core II.



3.3.3 Hopane

Hopanoid hydrocarbons were present in saturated hydrocarbons fractions. Figure 3.4 shows a vertical distribution of hopanoid hydrocarbons $(17\alpha,21\beta(H)-30-norhopane; 18\alpha(H)-30-nor-neo-hopane; 17\alpha,21\beta(H)-hopane; 17\beta,21\alpha(H)-hopane)$ for the two cores. The abundance between $17\alpha,21\beta(H)-30-norhopane$, $17\alpha,21\beta(H)-hopane$ and $17\beta,21\alpha(H)-hopane$

was similar for both cores. The highest values are observed in the years 1944, 1965, and 1983 (core I) and 1933 and 1980 (core II) (Figure 3.4). The presence of moretane $(17\beta,21\alpha(H)-hopane)$, starts in both sediment cores from 1911, which might be reasonable (Moldowan et al., 1991; Innes et al., 1993). We identified the C₃₁ and C₃₂ hopanes throughout the cores. The most abundant were the $17\alpha,21\beta$ (H)-29-homohopane (22S-22R) and $17\alpha,21\beta$ (H)-29-bis-homohopane (22S-22R).

Figure 3-4 Distribution vertical of H29 (17α , 21β (H)-30-norhopane), C₂₉TS, H30(17α , 21β (H)-hopane) and M₃₀ (17β , 21α (H)-hopane) in sediments cores from Passauna reservoir.



3.4 DISCUSSION

3.4.1 Lake productivity

Molecular biomarkers (saturated hydrocarbons, δ^{13} C and δ^{15} N) were identified and quantified to reconstruct changes in biological sources or environmental conditions during the deposition of sediments in the Passauna reservoir. δ^{13} C, δ^{15} N, and TOC are used as a proxy to estimate the productivity of lakes. The TOC found in Passauna reservoir sediments indicates some important changes in organic matter supply. In core I, it presents a gradual upward increase in TOC concentrations from the bottom of the core until ~1912 and in 1973. In contrast, in core II, TOC concentrations gradually decrease upward, indicating a disturbance in the lake watershed and an increase in nutrient delivery into the Passauna reservoir.

The δ^{13} C values are extensively used to trace organic matter sources and changes in lake productivity (Meyers, 2006; Bernasconi et al., 1997; Whitmore et al., 2006). The isotopic composition of organic matter is rarely affected by post-photosynthesis or diagenetic processes (Shelske and Hodell, 1994). Freshwater phytoplankton has δ^{13} C values between -30 ‰ to -24‰ (Ortiz et al. 2004). The organic matter produced by C₃ plants (terrestrial and vascular plants) has δ^{13} C values -38 ‰ to -24 ‰ (Boutton et al., 1991). In contrast, the organic matter originated from algae and C₄ plants have values between -10% to -15% (Meyers, 2006), and the macrophytes have δ^{13} C values between -30% to -12 %. The organic matter produced under conditions of high primary productivity presents less negative δ^{13} C values (Meyers and Lallier-Verges, 1999). Because algae remove ¹²C from the water column causing a decrease in dissolved carbon (Bianchi and Canuel, 2011). Therefore, when the productivity of a lake increases, the availability of ¹²CO₂ decreases and a greater fraction of ¹³CO₂ is incorporated into the organic matter (Das, et al., 2008). The δ^{13} C values in the reservoir show a variation between the two sampling points, -23.0 % to -25.7 % (core I) and -28.4 % to -29.2 % (core II). These values indicate a predominance of organic matter produced by C3 plants (terrestrial and vascular plants). A study on the isotopic variation of aquatic plants showed that most macrophytes (including floating, emergent and rooted ones) show variation in the δ^{13} C signal from -25% to -30%. In core I, there is a gradual decrease in the values δ^{13} C -23.0 (1922) to -25.2‰ (2019), showing a decrease in primary productivity that could be caused by the change in the regime in the Passauna River after the construction of the reservoir in 1987 (Coquemala,

2005). In core II, it presents relatively constant values between -28.4‰, to -29.2‰, indicating a predominance of organic material of terrestrial origin or vascular plants. An indirect indicator to determine the sources of organic matter and state of transformation of organic matter in an aquatic environment is the isotope δ^{15} N (Teranes and Bernasconi, 2000). The most common form of dissolved inorganic nitrogen in aquatic environments is a nitrate, used by non-N₂ fixing algae, whereas land plants receive N₂ from atmospheric N₂ fixers in soil (Meyers,2003). A comparison of atmospheric N₂ with typical high δ^{15} N (7 to 10‰) values of NO₃, helps to investigate the source of N, and as a consequence the source of organic matter (Das et al., 2008).

The nitrogen isotopic signal (δ^{15} N) reached the highest value in 1922 in core I (upstream) and after 1972 in core II (dam), accordingly indicating the the contribution of sewage or nutrient runoff from agricultural areas. Due external nitrate loading from agricultural and sewage will progressively increase the nitrogen isotopic composition of dissolved inorganic nitrogen in lakes, as nitrate derived from human and animal waste is enriched in ¹⁵N (δ^{15} N: 10 to 25 ‰) (Kendall, 1998).

3.4.2 Source of aliphatic hydrocarbons

Aliphatic hydrocarbons (AHs) were originated from both natural biogenic and anthropogenic petroleum sources (Peters et al., 2005). The characteristic parameters, such as Pr/Ph, LMW/HMW, CPI-15-20, CPI25-34, OEP, ACL, TAR, and Paq, were employed to identify the AHs sources.

The Pristane and Phytane could originate from zooplankton and/or aquatic animals and oxidation or reduction of chlorophyll (Zaghden et al., 2017). The Pr/Ph ratio < 1 represents anoxic conditions, while the value > 1 indicates oxic conditions (Didyk et al., 1978). In the present study, Pr and Ph were not detected in all samples. In the core, I, after ~1969 presented values 1 suggestion oxic conditions. On the other hand, in core II, the years ~1939, ~1933 and ~1928 have values >1 and at the top of the profile, after ~1973, values are <1 (anoxic conditions), suggesting predominant biogenic source rather than petrogenic and under aerobic

depositional condition. The variations of the Pr/Ph ratio could be indicated a change in trophic status resulting from soil erosion and intense human activities (population growth changes of cropping varieties and intensity and application of fertilizer) after 1973. In fact, C_{max} of short-chain n-alkanes, C_{17} dominates during the period 1973-2013 in the core II, suggests a significant contribution from phytoplankton, because this alkane is predominant in diatoms (e.g., Rhizolenia setigera), green algae (e.g., Chlorella pyrenoidosa), dinoflagellates (e.g., Peridinium trochoideum), euglenophyceae (e.g., Eutrepiella sp.), cyanobacteria (e.g., Nostos muscorum) and in photosynthetic bacteria (Han and Calvin, 1969; Blumer et al., 1971). In core I, prevalent C_{16} , C_{18} , C_{20} , and C_{17} , these results indicates that major source of short-chain n-alkane in the cores are biogenic.

The terrestrial higher plant-derived long-chain n-alkane was evidenced by the carbon preference index (CPI) for the C_{25} - C_{31} . In the core I, observed values > 8 in 1894, 1944, and after 1965, indicating a greater contribution for sedimentary OM from vascular plants. Interesting that for core II, values do not exceed the value 8. In the period between 1916-1985 values are higher than 3 (terrestrial plants origins) and after 1985 the values decrease to less than one. Low CPI (~1) indicates the mid-long chain n-alkanes derived from microorganisms and recycled OM (Fang e al., 2014). This indicates that core II shows evidence of high bacterial productivity in the interface between sediment and water during the depositing sediments (Neunlist et al., 2002).

The OEP, TAR, and ACL were used to indicate the types of terrestrial higher plants. OEP values between 0.42 to 9.22 (core I) and 0.97 to 4.14 (core II), suggest odd carbon predominance of long-chain n alkanes (terrestrial source) in the Passauna reservoir. ACL in both sedimentary cores show values > 29, which corresponded to the C_{max} at C_{29} and C_{31} , suggesting the terrestrial source of n-alkanes, likely derived from higher plants. The ACL tends to be higher in drier and/or warmer environments. Also, when change the proportion of C_3 and

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C₄ plants (Rommerskirchen et al., 2006). ACL value was the lowest in 1958 and 1901 (core I) and 1990 and 1945 (core II). TAR ratio supports the evidence of terrestrial input in the period 1940-2019 (core I) and before 1973 (core II). It is known that terrestrial sources of organic matter are mainly represented by vascular plants, and this observation could indicate erosion and runoff (Jimenez Martinez et al., 2022; Galoski et al., 2019).

Middle chain n-alkanes are associated with aquatic plants (including emergent aquatic plants and submerged macrophytes) (Duan et al., 2019). In core, I, Paq the period between 1883-1937 shows values of 0.6 suggesting a predominance of submerged aquatic plants and after 1937 the values < 0.6 indicated emergent aquatic macrophytes plants.

The comparison of different indices for two sedimentary profiles highlights that in reservoirs the processes of OM dispositions can vary in space as a function of the peculiar hydrodynamics of these ecosystems. Due to the hydrodynamic influences in the basin, the quality of the sediments and their mobility is governed by the density of the currents. The results showed that the dam region (deeper) is considered as the region with the greatest accumulation of information in the reservoir.

3.4.3 Evidence of Microbial Activity

Hopane can be used as bacterial community indicators (Rohmer et al., 1984). In sediments, with increasing diagenesis, geohopanoids undergo stereochemical transformations, and the biologically-derived 17β , 21β (H) hopanoid is transformed into the more thermally stable 17β , 21α (H) and 17α , 21β -stereoisomers (Peter and Moldowan, 1991). The presence of hopane C_{31} 17α (H), 21β (H)-22R, which might be a contribution from the natural and thermogenic sources. In this case, the isomerization of the hydrogen atom at the C-17 position is not caused by thermal stress. The predominance of the $C_{31} \alpha\beta$ hopane in recent peat deposits which have not undergone thermal maturation could result from the direct input of $\alpha\beta$ hopanoids by indigenous bacteria (Rosa-Putra et al., 2001).
Different studies have determined in the Passauna reservoir, a stable thermal stratification in the summer months causing a decrease in the concentration of oxygen throughout the water column (Marcon et al, 2019; Godoy, 2017), resulting in the promotion of the activity of methane-producing bacteria (Ishiwatari et al., 2014). According to Marcon et al., (2019), the average methane emission in the Passauna reservoir was 3.9 mgCH₄.m⁻² day⁻¹, 61.8 mgCH₄.m⁻²day⁻¹, and 22.6 mgCH₄.m⁻²day⁻¹ at different sampling points. As a result, moretene derived from methanotrophic bacteria would become abundant in the upper section of the cores. Moretene has been suspected to be derived from methanotrophic bacteria by several authors based on its carbon isotopic composition (Aichner et al., 2009; Kristen et al., 2010).

3.4.4 Recent nutrient collaboration

Between 1999 and 2013, the Passauna reservoir was estimated as predominantly classified as moderately degraded" and mesotrophic trophic status according to the values of the Dam Water Quality Index (IQAR). During the summer, it presents a thermal stratification, distribution of dissolved oxygen in the upper layers with high values, and reaching anoxia in the bottom layers. Therefore, it is linked to a higher production of phytoplankton, mainly in the euphotic zone, and a lack of oxygen circulation in the bottom litters. During this period, 60 phytoplanktonic taxa were identified, with greater representativeness of the Chlorophyceae, predominating the species Pediastrum simplex (IAP, 2017). Caused by an increase in nutrients in the reservoir, it has a notable impact on phytoplankton productivity and community structure, with consequences for n-alkanes production and sediment distribution (Lu and Meyers, 2009). Under these conditions, the deposited sediment would present high concentrations of alkanes with short odd chains and low values of long odd chains (terrestrial plants) (Meyers, 1997; Bianchi and Canuel, 2011; Zhang et al.; 2018c). In core II more than core I of the Passauna reservoir, the increase in nutrients in the reservoir is reflected in the n-alkane sediment profiles. For better visualization, Figure 3.5 shows the temporal variations in the distribution of nalkanes in the two cores (core I and core II). The core I presents a considerable variation, in

layers before 1945, the points are distributed around the final member of long-chain n-alkanes with an odd number of carbons. Later, between 1985 and 2013, the dots show a shift towards the short and medium-chain odd carbon end member (phytoplankton indicator). The difference in the distribution of n-alkanes between the two sedimentary profiles may be associated with the height of the water column at these two points, point 2 being deeper than point 1. Alternatively, point 1 being a point Before the entrance of the reservoir, it is more influenced by terrigenous sources.

Figure 3-5 Ternary plots showing the relative abundances of short-chain $(C_{15}+C_{17}+C_{19})$, middlechain $(C_{21}+C_{23}+C_{25})$ and long-chain $(C_{29}+C_{31}+C_{33})$ n-alkanes in core I and core II over time.



3.5 CONCLUSIONS

The contribution and distribution of aliphatic hydrocarbons, hopane, and stable isotopes (δ^{13} C; δ^{15} N) were determined in two sedimentary profiles of the Passauna reservoir, Brazil. Due to changes in anthropogenic influences, currents, and sedimentary environment, distribution patterns of aliphatic hydrocarbons were observed in the sediments. The distribution patterns combined with the characteristic indices identified that after 1973 (core II) the C₁₇ alkane predominates, suggesting an increase in the biogenic contribution (phytoplankton, algae). Therefore, identifying changes in the trophic state of the lake. Until 1965, in both sedimentary profiles, alkanes with odd long chains between C₂₅-C₃₁ predominated, indicating the contribution of OM from vascular plants. The comparison between the two sedimentary profiles shows that the distribution of alkanes is influenced by hydrodynamic differences and anthropogenic activities. These patterns help in understanding the factors that control the distribution of the OM, which will help in the management of the reservoir and use the AHs as tools to indicate environmental and ecological changes in and around the lake.

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4 FORENSIC ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS TO RECONSTRUCT ANTHROPOGENIC ACTIVITIES IN A NEARBY URBAN RESERVOIR.

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ABSTRACT

This work examined the presence of polycyclic aromatic hydrocarbons (PAHs) in two sediment cores from the Passauna reservoir, in southern Brazil. The sediment cores contain organic matter deposited in the period comprising approximately 136 years for core I and 97 years for the core II. The distribution of PAHs reconstructs the historical atmospheric deposition for the city of Curitiba and therefore implies the anthropic activities in that period. Total concentrations of PAHs varied from 5.13 ng g^{-1} to 444.60 ng g^{-1} (core I) and 124.55 ng g^{-1} to 3,018.14 ng g⁻¹ (core II). The concentrations peaked in 1944 and 1958, reflecting the boom in the local economy. We identified the sources of PAHs by applying positive matrix factorization (PMF) and diagnostics ratios among PAHs compounds. According to PMF in core I 45.58% of PAHs are from diesel combustion, 32.19% from coal combustion and biomass burning, and 14.54% from vehicle emissions. In core II, vehicle emission contributed 40.91%, while 28.70% corresponds to traffic and biomass or coal combustion, 20.86% from petroleum sources, and 9.53% originated from biomass burning. The toxic level of sediments was determined considering the toxicity of PAHs equivalent to benzo(a)pyrene (TEQ) showed low carcinogenic risk, and considering the total concentration for core I (1.70 to 47.70 ng g⁻¹) was lower than that of core II (11.64 ng g^{-1} to 899 ng g^{-1}).

Keywords: Polycyclic aromatic hydrocarbons (PAHs), source apportionment, sediment core, Passauna reservoir, ecological risk.

4.1 INTRODUCTION

Sediments, soil, and suspended sediments carry countless organic and inorganic compounds, most of them named chemical markers (Jimenez et al., 2022). Therefore, the determination of the concentration of such compounds in core sediment from reservoirs provides a useful tool for evaluating and reconstructing historical records of anthropic activities nearby that might be impacting the ecosystem (Gsechwend and Hites, 1981; Meyers et al., 2001; Machado et al., 2014).

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds formed by aromatic hydrocarbons with two or more fused benzene rings (Yunker et al., 2002; Bianchi and Canuel, 2011). PAHs are one of the most important classes of environmental pollutants, due to their persistence, toxicity, mutagenic and carcinogenic characteristics (Liu et al., 2014; Xu et al., 2016; Zhang et al., 2013b). The sorption of compounds (organic and inorganic) is a usual characteristic of sediments, mainly due to the silt and clay contained in its granulometric composition. The sorption of compounds like PAHs is fully registered by literature in order to study contamination of environments (Machado et al., 2014; Vieira et al., 2019).

PAHs are ubiquitous compounds in the environment. In aquatic environments, it arises mainly from pyrogenic (incomplete combustion) and petrogenic sources (Liu et al., 2005). PAHs are introduced in the water body through polluted water, runoff, industrial processes, vehicle traffic, and fossil fuel spills (Moghaddam et al., 2021). Pyrogenic and petrogenic sources are two major origins of anthropogenic PAHs in the aquatic environment (Liu et al. 2009). In addition, PAHs compounds with lower molecular weight are major components in crude and refined petroleum products (Liu et al 2009; Yunker et al; 2002); in contrast, incomplete combustion implies PAHs with high molecular weight (wood, fossil fuels, industrial waste, etc.).

In an aquatic environment, PAHs, due to their hydrophobic characteristics, tend to adhere to particulate matter and are ultimately deposited in lake sediments. These compounds accumulate over time in the sediments because they are lipophilic and present low chemical and biological degradation rates in aquatic environments (Tolosa et al., 2004; Bianchi and Canuel, 2011). The continuous deposition of PAHs over time makes it possible to use sediments as a tool for mapping and reconstructing general environmental changes (Lima et al., 2003).

The Passauna reservoir is located in the watersheds of Rio Iguaçu, the hydrographic unit of Alto Iguassu, sub-basin of Rio Passauna. The Passauna reservoir is located between the cities of Curitiba and Araucária, in Parana state, Brazil. It is one of the most important reservoirs in the city, supplying water to more than 650,000 inhabitants of the metropolitan region of Curitiba. Approximately 67,000 inhabitants live around the reservoir (Carneiro; Kelderman; Irvine, 2016), however, near to the reservoir there is an important industrial area. According to IBGE (2010), Curitiba and its metropolitan area had approximately 3.4 million inhabitants in the recent decade, and the numbers of established industries has increased (IPPUC, 2009). Therefore, the presence of PAHs in sediments of the Passauna reservoir could be used to determine the main sources that have contributed negatively to water quality. As mentioned previously, in general, PAHs compounds have two main sources: pyrogenic and petrogenic. Notwithstanding, individual PAHs can degrade, even slowly, and the source indication could be uncertain. In order to avoid misinterpretation, the literature provides identification of sources through ratios among PAHs (Feng et al. 2007; Malik et l., 2001), for example, Fluoranthene / (Fluoranthene + Pyrene); Anthracene / (Anthracene + Phenanthrene); Benzo(a)Anthracene / (Benzo(a)Anthracene + Chrysene; and Indene(1,2,3-cd) pyrene / (Indeno(1,2,3-cd) pyrene + Benzo(ghi)perylene (Yunker et al., 2002) (Table 4.1).

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Diagnostic ratio	Petrogenic source	Liquid fossil fuel	Biomass or coal	Reference
		combustion	combustion	
BaA/(BaA+Chr)	<0.20	0.20-0.35	>0.35	Zhao et al.,
				2017
$Fl_{a}/(Fl_{a}+D_{vr})$	<0.40	0.40-0.50	>0.50	Yunker et
11a/(11a+1 y1)				al.,2002
IndD/(IndD + DahiD)	<0.20	0.20-0.50	>0.50	Yunker et
icur/(icuP +BgniP)				al.2002

Table 4.1 Diagnostic ratios used for source estimate of PAHs

Receptor models are mathematical procedures; these models use the chemical and physical characteristics of the components detected at the sources and at the receptor to identify and quantify the predominance of the sources at the receptor (Guide, E.P.A, 2008). The receptor model can be employed to make quantitative assessments in media such as the atmosphere (Manuosakas et al., 2017), soil (Wang et al., 2015), and sediments (Zhang et al., 2013a). Three important receptor models, namely principal component analysis-multiple linear regression (PCA-MLR) (Bzdusek et al., 2004; Shi et al., 2009, 2011), unmix model (Hopke, 2003), and positive matrix factorization model (PMF) (Paatero, 1997), are the most frequently used and prove to be useful tools in source apportionments studies (Platiknov et al., 2007; Li et al., 2012, Mohammed et al., 2021). In this study, based on the identification of 16 PAHs from two sediment core samples from the Passauna reservoir, the sources of these PAHs were quantitatively assessed by the PMF EPA model.

This work aimed: 1) to reconstruct the PAHs depositing history in the Passauna reservoir; 2) to assess the sources and possible variation in sources; and 3) to evaluate the toxicity risk. Results of this study could supply information on levels, sources, and potential risks of PAHs in the Passauna reservoir.

4.2 MATERIAL AND METHODS

4.2.1 Study area

The watershed of the Passauna river is located between S 25 ° 25' 48" and W 49° 15' 16". Passauna sub-watersheds have a drainage area of 217 km², covering the municipalities of Almirante Tamandaré, Campo Magro, Campo Largo, Araucaria, and Curitiba (Figure 4.1) (SUDERHSA, 2007). The Passauna reservoir was formed in 1989 for public water supply and is located in Araucaria, PR, near Curitiba, Brazil. The Passauna reservoir is responsible for supplying water to 30% of the population in Curitiba and its metropolitan area, with an operating capacity ranging from 1300 L/s to 2000 L/s of treated water available for supply (Sotiri, et al., 2021). The normal operation level is 890 m, and the reservoir has an area of 11 km² and an average depth of 9.4 m. The residence time of the reservoir is 292 days (Carneiro et al., 2016), and the main water inflow is from Passauna River with a mean flow rate of 1 m³ s⁻¹. Along its course of approximately 22 km, the river receives the contribution of small watercourses from six sub-basins: Juruqui, Cachoeirinha, Cachoeira, Ferraria, Taquarova, and Jaguaruva (Coquemala, 2005).

The local climate, according to the Koppen climate map, is classified as Cfb, with a mean temperature of 22 °C. According to the precipitation data mean annual ranges from 1400 mm to 1600 mm, greater rainfall rates season is observed in January and February. On the other hand, the period from April to August is colder and the precipitation is low. Precipitation data show that this sub-basin presents favorable conditions so that throughout the year, during the

rain events contribute loads of nutrients and pollutants to the body of water. Since the greatest economic activity in this area is agriculture.



Figure 4-1 Localization of sampling points from Passauna Reservoir

4.2.2 Sample collection

Two sediment cores (core I and core II) were collected in February 2018 and May 2019, respectively. The cores were retrieved using a piston percussion corer with an internal acrylic tube with an 86-mm internal diameter. In the laboratory, cores were subsampled by slicing at 2.0 cm intervals. All samples were transferred to polyethylene bags and frozen at 0 °C. Samples were later freeze-dried on the ground by an agate mortar and pestle. Slicing of core I resulted in 39 sub-samples, whereas in core II there were 18 sub-samples. Core I is in the pre-reservoir area, with a depth varying from 0.5 to 2 meters. Core II presents a greater depth of 10-14 meters, near the outlet of the reservoir.

4.2.3 Extraction of PAHs

The total lipid extract (TLE) was obtained from 1 g of freeze-dried treated with 10 mL of a mixture of dichloromethane and methanol (2:1) by ultrasonic bath for 30 min (Sanez et al., 2013); this step was repeated three times. Activated copper was added for 24 hours to remove possible sulfur. The extracts were concentrated in a rotatory evaporator to approximately 1 mL. The TLE concentrate was fractionated and cleaned up on a column of silica gel and sodium sulfate; the silica gel was previously activated. The TLE was separated into two fractions: saturated hydrocarbons containing the aliphatic compounds (Fraction 1) with 7 mL of hexane, and polycyclic aromatic hydrocarbons (Fraction 2) with 7 mL of a mixture of hexane: dichloromethane (2:1).

4.2.4 Determination of PAHs compounds

In this study we sought the 16 target PAHs: Naphthalene (Nap), Acenaphthene (Ace), Acenaphthylene (Acy), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a,h) anthracene (BahA), Dibenzo(a,h)anthracene (DahA), Indene (1,2,3-cd)pyrene (IcdP) and benzo(g,h,i)perylene (BghiP). Analyses of standards and samples prepared in dichloromethane were performed in triplicate, using a Perkin Elmer branded Clarus SQ 8 T gas chromatograph coupled with a mass spectrometer (Turbomass, Perkin Elmer). The capillary column used was Sigma Aldrich brand fused silica with the reference 5-MS (0.25 mm x 30 m x 0.25 μ m) phase 5% diphenyl and 95% dimethylpolysiloxane. The carrier gas used was helium at a constant flow of 1.0 ml min⁻¹ and a pressure pulse of 25 psi with a duration of 0.50 min. The injected volume was 1.5 μ L in splitless mode. The oven temperature was programmed as follows: 1 min at 40 °C, heated at a rate of 10 °C min⁻¹ to 200 °C and held for 5 min, subsequently heated at a rate of 6 °C min⁻¹ to 240 °C and held for 10 min and finally heated to 300 °C in sequence at a rate of 10 °C min⁻¹ and held for 5 minutes. Previously, a mixture of 16 PAHs (TCL PAH mix, Supelco, Germany), within the range of 5-250 ppb (μ g L⁻¹), was used to obtain the calibration curve to quantify the PAHs.

4.2.5 Geochronology

Approximately 5 g of dry sediment from 57 samples collected along with core I and core II were disaggregated into a mortar and analyzed for ²¹⁰Pb and ¹³⁷Cs contents in an EG&g ORTEC low-background gamma spectrometer (hyperpure Ge, model GMX25190P) at LaQIMar (Laboratorio de Quimica Inorganica Marinha, University of São Paulo-Brazil). The sediment core chronologies were determined using the CFCS (constant flux constant sedimentation) model (Sanchez-Cabeza and Ruiz-Fernandez, 2012).

4.2.6 Positive matrix factorization model and statistical analysis.

For identification of predominant sources of PAHs in the two sediment cores, it was used the US EPA PMF v. model. PMF (Positive Matrix Factorization), is a mathematical receptor model that is used to analyze data from different environmental media such as sediments, surface water, and atmospheric particles (Balgobin and Ramroop Singh, 2019). This mathematical model decomposes the data into two matrices: factor contribution and factor profiles (Liu et al., 2018). The factor analysis model is represented by the following matrix relationship (Equation 4.1):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{X_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{U_{ij}} \right)^2 \qquad \text{Equation 4.1}$$

Where U_{ji} is the uncertainty estimate of source *j* measures in sample *I*, *p* is the number of factors of each sample, and f_{kj} *r* is a species profile of each source. In this study, the uncertainty (U_{nc}) matrix was determined based on detection limits of the PAHs using the following equations in the PMF user guide (Equation 4.2 and Equation 4.3):

$$U_{nc} = \frac{5}{6} \times MDL$$
 Equation 4.2

$$U_{nc=\sqrt{(Error F \times Conc.E \times Conc.)^2} + (0.5 \times MDL)^2}$$

Equation 4.3

where Error F: Error fractions, CE : Concentration Error and Conc.: concentrations of PAHs

4.2.7 Potential cancer risk assessment

The potential cancer risk for PAHs was calculated using equation (4). Multiplying the concentration of each PAHs by its corresponding TEF (Toxic equivalency factor) value (Bentrend et al., 2015; Sun et al., 2018) (Equation 4.4).

$$\sum TEQs = \sum PAH_i \times TEF_i$$
 Equation 4.4

where PAH_i is the concentration of individual PAH and TEF_i is the corresponding TEF. 4.3 RESULTS

4.3.1 Total concentrations of PAHs in sediment core

The total concentration of the 16 PAHs (Σ PAHs), excluding acenaphthene, in the two core sediments from the Passauna reservoir are presented in Table 1. Σ PAHs concentration in core I ranged from 5.13 ng g⁻¹ to 444.60 ng g⁻¹, with a mean concentration of 129.65 ng g⁻¹. In core II, values ranged from 124.55 ng g⁻¹ to 3018.15 ng g⁻¹, with an average concentration of 731.06 ng g⁻¹ (Figure 4.2). Individually, core I presents higher values of total PAHs in 1944, 1958, 1998, and 2015. In core II, the maximum values are observed in 1945 and 1955. Variations in concentrations of individual PAHs are highlighted in Figure 4.3. BghiP, DahA, BbF, Phe, Flu and Pyr predominate in core I, and Phe, BbF, BghiP, IcdP and Chry have been the most abundant PAHs in core II.



Figure 4-2 Vertical profile of total PAHs, percentages of HMW and LMW of PAHs in those cores of Passauna a) and b) \blacksquare core I; c) and d) \bullet core II from Passauna reservoir.

0 Figure 4-3 Vertical profile of total PAHs (ZPAHs), percentages of HMW and LMW of PAHs in those cores of Passauna. a) and b) \blacksquare core I; c) and d) \bullet core II from Passauna reservoir.



According to the CFCS model, core I has a sedimentation rate of 0.56 ± 0.06 cm year⁻¹ and core II has a rate of 0.35 ± 0.04 cm year⁻¹(Jimenez-Martinez et al., 2021). The maximum fallout for ¹³⁷Cs, corresponding to 1963, was recorded at the sediment layer of 80 cm (core I) and 20 cm (core II). According to the age model, core I is composed of sediment deposited since 1883 and core II since 1916. In core I it starts to show moderate levels of contamination from ~1915. In 1998, it presented the highest value of Σ PAHs, followed by 1958 and 1944. In core II, it presents high levels of contamination in the years 1955 and 1945; in the other years, it can be classified as moderately contaminated. At both sediment cores, the compounds with lesser predominance were Acenaphthylene and Anthracene. Figure 4.2 shows the variation of PAHs separated into categories of molecular weight. Since 1947, in core, I, the percentage of low molecular weight (LMW) PAHs (2 + 3 rings) gradually decreased until 1983, when their concentration began to increase. Conversely, the percentage of high molecular weight (HMW) PAHs (6+5 rings) to the total PAHs increased from 18.40% in 1908 to 65.58% in 1915. In core II, HMW represents 83.65% of the total PAHs.

4.3.2 Diagnostic isomeric ratios

Traditional ratios among PAHs compounds are useful to indicate precisely the source of contamination by hydrocarbons. The profile of ratios is shown in Figure 4.4. The Fla / (Fla + Pyr) ratio is in the range of 0.34 to 0.55 (core I) and 0.31 to 0.50 for core II. The ratio BaA / (BaA + Chr) values varied between 0.11 to 1 (core I) and 0.01 to 0.9 (core II). The ratios for IcdP / (IcdP + BghiP) are in the range 0.24 to 0.55 (core I) and 0.046 to 0.30 (core II). The ratio Ant / (Ant + Phe) was only possible to determine in core II, and the values range between 0.08 to 0.22.





4.3.3 PMF model

The positive matrix factorization (PMF) model had been used to describe PAHs source contribution for both sediment cores I and II. To further ascertain the validity of PAHs sources, 39 sub-samples from core I and 18 sub-samples from core II were analyzed. Fifteen compounds (PAHs) with their uncertainties were used as the input data. Factor numbers ranging from three to six were considered to select the best solution. A high correlation between measured and modeled PAHs concentrations verified the option of the selected factor ($r^2 = 0.90$). Four sources were determined in Figure 4.5. For core I, the first factor is responsible for a 14.54% contribution rate and is heavily weighted in Flu, BaA, BbF, and DahA. BaA was a typical pollutant of biomass or coal combustion. IndP and DahA were an indication of traffic emission (Zhao et al.,2020). Factor 2 is predominantly composed of PAHs with 2-4 rings, including Phen, Nap, Ant, BaA, BkP, BaP, and IcdP. The higher level of Nap and Acy relative to other PAHs suggests a petroleum source (Khalili et al., 1995). Factor 3 could represent the contribution from coal and biomass burning which were found to be heavily loaded by Ant, Phe, Flu, and Fl (Miankhan, et al., 2020). Factor 4 was identified for diesel combustion (Liu et al.,2020), which displayed higher loads of Flu, Pry, Chry, BbF, BkF, and Bap.

For core II, the first factor was loaded with InP, BaA, and DahA, prevailing IcdP, and DahA, which were used as a marker for vehicle emission. The Factor 2 recognized source was categorized by a high level of Flu, Phe, Fla, and Acy and the contribution signified biomass burning. Factor 3 was identified for traffic and biomass or coal combustion, and was predominantly composed of BbF, BkF, IcdP, BaA, DahA Chry, and Pry (Khalili et al., 1995; Jenkis et al., 1996; Larsen et al., 2003). Finally, Factor 4 was composed of Nap, BkF, BaP, and Ant, which suggests petroleum sources (Khalili et al., 1995).

4.4 DISCUSSION

4.4.1 Source identification with a diagnostic ratio

ΣPAHs concentrations in sediments can be classified into four contamination categories: low (up to 100 ng g⁻¹), moderate (100 to 1,000 ng g⁻¹), high (1.00 to 5,000 ng g⁻¹), and very high (more than 5,000 ng g⁻¹) (Baumard et al., 1998). We applied these numbers to classify the level of contamination of samples in the core. According to the results found for ΣPAHs in the Passauna reservoir, core I and core II are classified as moderately contaminated areas when we consider the average concentration of ΣPAHs values. The Passauna reservoir presents the following average values of PAHs contamination in rivers located in the MRC (Metropolitan Region of Curitiba): Barigui River in Araucária (1,206 ng g⁻¹), Iguaçu River in São José do Pinhais (1,713 ng g⁻¹), and in the Irai reservoir the values are found between 131 and 358 ng⁻¹. The Irai reservoir has a lower anthropogenic influence (Leite, 2010).

The diagnostic ratios can be used to infer possible sources of the PAHs found in the sediment cores of the Passauna reservoir. In this study, we applied the following ratios: Fla / (Fla + Pry), BaA / (BaA + Chry), Ant / (Ant + Phen), and Icdp / (Icdp + BghiP. According to Yunker et al. (2002; 1999), the presence of PAHs in sediments with ratio values of Fla / (Fla + Pry) lower than 0.4 suggests petroleum contamination; values higher than 0.5 indicate combustion of grass, wood, and coal; and 0.4 < Fla / (Fla + Pry) > 0.5 indicate combustion of petroleum. In core I, the ratio of Fla / (Fla + Pry) was 0.50 to 0.55 comprised the period between 1883 and 1929, prevailing pyrogenic source (biomass combustion). In the period from 1933 to 2019, the ratio Fla / (Fla + Pry) varied from 0.42 to 0.48, therefore indicating combustion of a petroleum source. During the period 1965 – 1985, a slight change in values was observed, probably associated with the increase in vehicular traffic attributed to the rapid economic development of Brazil between the period 1960-1980 (Azevedo and Barcellos, 2011). For core II, values ranged between 0.4 to 0.5, indicating liquid fossil fuel combustion (Deng et al., 2013; Yang et al., 2005).

The Ant / (Ant + Phe) ratio can be used to distinguish sources of PAHs, between pyrolysis and petrogenic sources. In general, Ant / (Ant + Phe) values close to 0.10 indicate combustion pyrogenic sources (wood and biomass burning), while < 0.1 ratios indicate petrogenic origin of PAHs (Yunker et al. 2002). After 1928, the ratio values ranged between 0.11 to 0.22, suggesting combustion of oil and gasoline (0.22), kerosene (0.16), gasoline, diesel, and crude oil combustion (0.11 to 0.27) (Yunker et al., 2002), supporting the interpretation of the (Fla / (Fla + Pry) ratio. Additionally, the BaA / (BaA + Chry) ratio indicates petroleum sources when values are < 0.20, whereas values higher than 0.35 indicate combustion of coal, grass, and wood. Petroleum combustion (liquid fossil fuel and vehicle and crude oil spillage) is indicated if the ratio is between 0.20 - 035 (Zhao et al., 2017).

The diagnostic characteristic ratio demonstrated that the PAHs in sediments of the Passauna reservoir showed to be predominantly from pyrogenic sources (wood and biomass burning) between 1883-1929. And for the period between 1933-2019, petroleum combustion prevails (Figure 4.4).

4.4.2 Source identification with PMF

The identification of the source was based on the occurrence and distribution of molecular markers, i.e., the PAH compounds. The goal in source apportionment is to determine the percentage contribution of different sources of sedimentary PAHs in the Passauna reservoir. We used the model PMF EPA to determine the percentage of major sources of PAHs. Figure 4.5 shows the composition of each factor. In core I, the mean contribution percent is 45.58% for diesel combustion (Factor 4), 32.19% for coal combustion and biomass burning (Factor 3), 14.54% for vehicle emissions (Factor 1), and 7.68 for the petroleum source (Factor 2). On the other hand, in core II, the major source determined were 40.91% for vehicle emission (Factor 1), 28.70% for traffic and biomass or coal combustion (Factor 3), 20.86% for the petroleum source is the first contributor to the PAHs in both sedimentary cores. In recent decades, a rapid increase

in motor vehicles near the Passauna reservoir aggravated the pollution, as is registered in the sediments.

Figure 4-5 Source contributions profiles using PMF model and contributions of each factor (source) to the PAHs in two sediment cores (A) core I and (B) core II from a Passauna reservoir.

a)



4.4.3 Relation PAHs with regional socioeconomic data

PAHs are produced mainly from the incomplete combustion of fossil fuels, which makes them good indicators of anthropogenic activities (Ishitake et al., 2007; Machado et al., 2014). The Passauna reservoir watershed is located between the Araucária and Curitiba municipalities. The municipality of Araucária has had remarkable economic development in the last five decades and has become one the most important industrial centers in the Paraná state (Loeffler, 2009). In this study, we used regional socioeconomic data to determine the relationship between PAHs pollution and socioeconomic development. According to the vertical distribution of the PAHs in the sediment cores, it can be divided into three periods for better analysis: a) 1883-1929 b) 1933-1965 and c) 1969-2019.

A) 1883-1929:

European migration began in 1829 on the banks of the Passauna River. The Thomas Coelho colony was founded in 1870 by Polish immigrants, with activities such as mining, keeping of livestock, and agriculture utilized for subsistence. The construction of the first railroad in the state of Paraná was in 1871; in this period the concentration of Σ PAHs varied between 4.71 - 117.12 ng g⁻¹, falling within the low pollution category. The diagnostic ratios suggest a predominance of biomass combustion (Figure 4.4).

B) 1933-1965

In this period, the state of Paraná was marked by predatory logging, which was caused by the scarcity of mineral coal and the growing import of oil. The country was supported by deforestation policies and the consumption of charcoal (Loeffler, 2009). In 1930, the economy of the state of Paraná was based on agriculture, mainly on the cultivation of coffee, which grew rapidly from 1950. Also in 1940, Curitiba presented a population growth of 78.1% (IBGE, 2010). As a result, the number of cars and mechanic shops in Curitiba (IPPUC, 2021) increased. In Figure 4.2, it is possible to observe an increase in the concentrations of PAHs, and this period presents a mixture of pyrogenic and petrogenic sources of PAHs.

C) 1969-2019

In the second half of the 20th century, Brazil experienced its greatest urban population explosion. Between the 1960s and 1980s, the country's cities gained about 50 million inhabitants, a number practically equal to the total population of the country in 1950 (Santos, 1993). In the city of Curitiba in 1960, there was a population growth of 97.6%, in 1970 an increase of 80%, and in 1980 an increase of 59.6% (IBGE, 2010). This increase in urbanization in the country is a consequence of the rural mechanization process that took place in the countryside, which was promoted by the Federal Government. In 1970, the Industrial City of Curitiba and Industrial City of Araucária were founded to promote the economic growth of the state of Paraná. Between 1960-1980, Brazil experienced the "Economic Miracle" period with greater economic development (Kroetz, 1985) The increase in urbanization is evidenced by the increase in PAH concentrations after 1960. It was also demonstrated in the diagnostic ratios that after 1960 there was a switch from pyrogenic sources to petroleum combustion.

4.4.4 Carcinogenic potency of the sediments core

The toxic equivalency factor was used to quantify the carcinogenicity of other PAHs relative to benzo(a)pyrene. The TEF of seven carcinogenic PAHs (BaA, Chr, BbF, Bkf, BaP, DahA, and Icdp) show the vertical distribution in Figure 4.6. The values of TEFs for BaA, Chr, BbF, Bkf, BaP, DahA and Icdp are 0.1, 0.001, 0.1, 0.001, 1, 1, and 0.1, respectively (USEPA 1993). The TEQ segments of seven carcinogenic PAHs in sediment core I presents values ranging from 1.70 ng g⁻¹ (1928) to 47.40 ng g⁻¹ (1972), and in core II from 11.64 ng g⁻¹ (1928) to 899 ng g⁻¹ (1951). Both sedimentary cores present an increase after 1940 and 1970, coinciding within those years with the increase in urbanization and industry in the region.

Figure 4-6 Vertical profile of toxic equivalency factor (TEF) of PAHs in sediment cores (**•** core I; **•** core II) from Passauna reservoir.

4.5 CONCLUSIONS



In this study, 15 priority PAHs in two sediment cores from the Passauna reservoir, Brazil were investigated, and possible sources were estimated by diagnostic ratio, PCA, and a receptor model (PMF EPA). During two periods, 1933-1965 and 1969-2019, an increasing trend of total PAH concentrations might be associated with the local economic development. Four sources identified with PMF were vehicle emission, coal and biomass burning, petroleum source, and diesel combustion. The results of diagnostic ratios show the predominant source of PAHs was from pyrogenic source, coinciding with the result obtained with PMF. The risk assessments showed that the TEQs in core I are very low (1.70 ng g^{-1} - 47.40 ng g^{-1}) and higher in core II (11.64 ng g^{-1} -899.91 ng g^{-1}).

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5 GENERAL CONCLUSION

Based on the sedimentary cores collected in the Passauna Reservoir, it was possible to study the upstream and downstream regions. From several geochemical markers, it was possible to estimate the variation of metal sources, estimate the sources of autochthonous and allochthonous organic matter and reconstruct scenarios of anthropogenic activities over time.

Regarding the heavy metal, the fixed sources identified would be sewage, landfill, and drainage from a nearby highway (BR 277), and these sources are evidenced by the enrichment of heavy metals (Pb, Zn, Cd, Cu, and Cr) along with the cores. The factor of enrichment via metals was observed during the period 1930-1960, attributed to this period of greatest deforestation occurring in the basin for the opening of agriculture.

According to the distribution of aliphatic hydrocarbons, a change in the trophic state of the lake was identified by increasing the contribution of short-chain alkanes, suggesting a source of biogenic organic matter (phytoplankton). The Passauna reservoir is currently an oligotrophic lake, and according to the Mn/Fe and short-chain n-alkanes, it shows signs of reduced oxygenation in the bottom waters.

During two periods 1933-1965 and 1969-2019, an increasing trend of total PAHs concentrations might be associated with the local economic development in the region.

Thus, the results found here support the use of a set of geochemical markers with different characteristics complementary to each other, to obtain an assessment of the system closer to the accuracy and precision indispensable for the detection of the state of a water body.

5.1 RECOMMENDATIONS FOR FUTURE WORK

- According with the presence 17α, 21β (H)-30-norhopane; 18α (H)-30-nor-neo-hopane; 17α, 21β (H)-hopane; and 17β,21α(H)-hopane (moretane) activity microbial was identified. Deepen the study of saturated hydrocarbons, identifying branched hydrocarbons that are indicators of the presence of cyanobacteria and methanotrophic bacteria in water bodies.
- Expand the characterization of organic matter, including fatty acids for a better determination of microbial activity. Use Glycerol Dialkyl Glycerol Tetraether (GDGT) to reconstruct temperature change scenarios in this region.
- According to the variation of the n-alkanes, in the upper part of the sedimentary profile it shows a predominance of short-chain alkanes, which shows an increase in primary

production. It is recommended to analyze the sedimentary pigments in order to discuss the spatial distributions of phytoplankton primary production.

5.1 PUBLICATIONS

- Jimenez Martinez, A.E., Froehner, S., Macedo Neto, D., Galoski, C. Detailing the organic matter in suspended sediments as a tool to assess the impact of land occupation in water bodies: a case of Barigui Watershed (Southern Brazil). Environ Geochem Health (2022). https://doi.org/10.1007/s10653-021-01167-8
- Jimenez Martinez, A.E., Galoski, C. Froehner, S. Marcadores moleculares organicos para determinação do estado trófico e mudanças climáticas no reservatório Passauna, Curitiba, Paraná. Poster in XVI Congresso Brasileiro de Geoquímica, September, Fortaleza, 2019.
- Trancing sources of organic matter in suspended sediments from tropical river thought distribution of fatty acids, Extended Summary, XV Latin America Congress of Organic Geochemistry, Alago, 2018.
ANNEX-A1 STRUCTURE OF PAHS



Benzo(g,h,i)perylene

Indeno(1,2,3 c-d)perylene

ANNEX-A2 SAMPLINGS SEDIMENTARY CORES





ANNEX-A3 VARIATION OF LAND AND USED OCCUPATION BETWEEN 1985-2014





ANNEX-A4 PASSAUNA SUB-BASIN HYDROGRAPHY