UNIVERSIDADE ESTADUAL DO MARANHÃO - UEMA
CENTRO DE CIÊNCIAS AGRÁRIAS - CCA
PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA ANIMAL - PPGCA
TESE

THIAGO MACHADO DA SILVA ACIOLY

MONITORAMENTO AMBIENTAL DO MÉDIO RIO TOCANTINS: ELEMENTOS POTENCIALMENTE TÓXICOS E ESSENCIAIS EM ÁGUA, SEDIMENTOS E PEIXES, BIOMARCADORES E IMPLICAÇÕES PARA A SAÚDE RIBEIRINHA

SÃO LUÍS – MA
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Tese apresentada ao Programa de Pós-graduação em Ciência Animal (PPGCA/UEMA) como parte das exigências para obtenção do título de Doutor em Ciência Animal.

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Linha de pesquisa: Conservação, Morfologia, Citogenética e Reprodução Animal.

Orientador: Prof. Dr. Diego Carvalho Viana, Núcleo de Estudos Morfofisiológicos Avançados (NEMO)/UEMA e UEMASUL

Coorientador: Prof. Dr. José Iannacone Oliver (Federico Villarreal National University - UNFV, Lima-Peru)

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MONITORAMENTO AMBIENTAL DO MÉDIO RIO TOCANTINS: ELEMENTOS POTENCIALMENTE TÓXICOS E ESSENCIAIS EM ÁGUA, SEDIMENTOS E PEIXES, BIOMARCADORES E IMPLICAÇÕES PARA A SAÚDE RIBEIRINHA

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*"Apenas quando a última árvore for derrubada, o último peixe
for pescado e o último rio for envenenado, entenderemos
que não se pode comer dinheiro."*

*"Only when the last tree has been cut down, the last fish caught,
and the last river poisoned, will we
realize that we cannot eat money."*

AGRADECIMENTOS

A Deus, por conduzir meus passos até aqui.

À minha família, base de tudo, por compreender as ausências e celebrar cada conquista.

Ao meu orientador e coorientador, pela confiança, pelas críticas construtivas e pelo rigor científico que fortaleceram esta pesquisa.

A UEMA e UEMASUL, por proporcionar as condições acadêmicas para o desenvolvimento deste estudo.

Às comunidades ribeirinhas e aos pescadores do médio rio Tocantins, cuja realidade inspira a busca por conhecimento comprometido com a transformação social.

Aos colegas e amigos que compartilharam desafios, coletas sob sol e chuva, análises laboratoriais e reflexões científicas.

Que este trabalho contribua, ainda que modestamente, para a preservação do rio Tocantins e para a saúde das populações que dele dependem.

MONITORAMENTO AMBIENTAL DO MÉDIO RIO TOCANTINS: ELEMENTOS POTENCIALMENTE TÓXICOS E ESSENCIAIS EM ÁGUA, SEDIMENTOS E PEIXES, BIOMARCADORES E IMPLICAÇÕES PARA A SAÚDE RIBEIRINHA

RESUMO. A bacia Tocantins–Araguaia é uma das maiores bacias hidrográficas da América do Sul, abrangendo os estados do Maranhão, Tocantins e Pará, e está inserida na Amazônia Legal brasileira. Apesar de drenar extensos ecossistemas de Cerrado e de floresta tropical, essa bacia tem sofrido degradação ambiental nas últimas décadas, em decorrência da expansão da agricultura, do desmatamento e da introdução de espécies não nativas. Esse cenário é particularmente relevante para as comunidades ribeirinhas do médio rio Tocantins, que dependem do rio para abastecimento de água, recreação e consumo de peixes. Nesse contexto, os peixes podem atuar como biomonitores da exposição a contaminantes em ambientes aquáticos, por integrarem processos ecológicos e representarem importante recurso alimentar e econômico. Dessa forma, o objetivo desta pesquisa foi realizar o monitoramento ambiental do médio rio Tocantins por meio de uma abordagem integrada, envolvendo a análise de parâmetros físico-químicos da água, a determinação de elementos potencialmente tóxicos e essenciais em água, sedimentos e peixes, e a avaliação de biomarcadores enzimáticos em peixes nativos. As coletas foram realizadas em quatro pontos de amostragem: P1 (Beira Rio – zona urbana), P2 (povoado Bananal), P3 (povoado Embiral) e P4 (povoado Cidelândia). A tese está estruturada em cinco capítulos. O Capítulo 1 consiste em uma revisão de literatura sobre a bacia Tocantins–Araguaia e aspectos ecotoxicológicos associados à presença de contaminantes em ambientes aquáticos. O Capítulo 2 apresenta o estudo socioambiental, no qual se investigou a percepção dos ribeirinhos sobre a qualidade da água por meio de questionários estruturados. Os resultados indicaram que 34% dos entrevistados consomem e comercializam peixes nativos, 62% os utilizam para consumo próprio e 4% não consomem peixes, além de 84% relatarem ausência de sistema de esgotamento sanitário, evidenciando elevada dependência dos recursos naturais e vulnerabilidade socioambiental. O Capítulo 3 avaliou os níveis de elementos potencialmente tóxicos e essenciais na água e parâmetros físico-químicos. Os resultados mostraram que alumínio, cobre, ferro, magnésio e selênio excederam padrões legais em determinados pontos e períodos, com variações sazonais influenciadas por fatores climáticos. O ponto P1 apresentou maiores valores de condutividade elétrica, sólidos totais dissolvidos, clorofila e compostos nitrogenados, indicando influência antrópica e potenciais riscos associados ao consumo de água sem tratamento. No Capítulo 4, a análise dos sedimentos revelou concentrações elevadas de alumínio, ferro, manganês e selênio, além de cromo, níquel, cobre, zinco e chumbo acima de diretrizes de qualidade, especialmente em áreas com influência urbana. A maior ocorrência desses elementos no período chuvoso evidenciou a importância da sazonalidade nos processos de mobilização e deposição. O Capítulo 5 investigou a bioacumulação de elementos potencialmente tóxicos e essenciais e as respostas enzimáticas em peixes nativos (*Psectrogaster amazonica* e *Caenotropus labyrhinthicus*). Foram observadas concentrações elevadas de arsênio, chumbo e selênio nos tecidos, com valores acima dos limites recomendados. As atividades enzimáticas (AChE, AST, ALT e ALP) indicaram respostas fisiológicas associadas à exposição ambiental, sendo interpretadas como alterações subletais, sem permitir inferências diretas de causalidade ou mecanismos específicos. De forma integrada, os resultados indicam que a dinâmica dos elementos no médio rio Tocantins é controlada pela interação entre processos naturais e influências antrópicas. As concentrações de elementos como ferro, alumínio e manganês refletem, em parte, o contexto geoquímico regional, caracterizado por solos altamente intemperizados, enquanto parâmetros físico-químicos e padrões espaciais evidenciam a influência de atividades humanas, especialmente em áreas urbanas. A bioacumulação em peixes e as respostas enzimáticas observadas indicam exposição dos organismos a contaminantes e alterações fisiológicas associadas. Esses achados, aliados à dependência das populações ribeirinhas dos recursos hídricos e pesqueiros, destacam a importância de abordagens integradas para o monitoramento ambiental, considerando as especificidades regionais e suas implicações para a saúde ambiental e a segurança alimentar, em consonância com a abordagem One Health.

Palavras-chave: Avaliação de risco; Metais pesados; One Health; Poluição ambiental; Segurança alimentar

ENVIRONMENTAL MONITORING OF THE MIDDLE TOCANTINS RIVER: POTENTIALLY TOXIC AND ESSENTIAL ELEMENTS IN WATER, SEDIMENTS, AND FISH; BIOMARKERS AND IMPLICATIONS FOR RIVERSIDE HEALTH

ABSTRACT. The Tocantins–Araguaia basin is one of the largest hydrographic systems in South America, spanning the states of Maranhão, Tocantins, and Pará, and is part of the Brazilian Legal Amazon. Despite draining extensive Cerrado and tropical forest ecosystems, this basin has undergone significant environmental degradation in recent decades due to agricultural expansion, deforestation, and the introduction of non-native species. This scenario is particularly relevant for riverine communities along the middle Tocantins River, which depend on the river for water supply, recreation, and fish consumption. In this context, fish can act as biomonitors of contaminant exposure in aquatic environments, as they integrate ecological processes and represent an important food and economic resource. Thus, the aim of this study was to perform environmental monitoring of the middle Tocantins River through an integrated approach, including the analysis of physicochemical water parameters, the determination of potentially toxic and essential elements in water, sediments, and fish, and the assessment of enzymatic biomarkers in native fish species. Sampling was conducted at four sites: P1 (Beira Rio – urban area), P2 (Bananal village), P3 (Embiral village), and P4 (Cidelândia village). The thesis is structured into five chapters. Chapter 1 presents a literature review on the Tocantins–Araguaia basin and ecotoxicological aspects related to contaminants in aquatic environments. Chapter 2 describes a socio-environmental study assessing riverine perceptions of water quality through structured questionnaires. The results showed that 34% of respondents consume and commercialize native fish, 62% use them for subsistence consumption, and 4% do not consume fish. Additionally, 84% reported the absence of sewage systems, highlighting high dependence on water and fish resources and significant socio-environmental vulnerability. Chapter 3 evaluated potentially toxic and essential elements in water, along with physicochemical parameters. Aluminum, copper, iron, magnesium, and selenium exceeded regulatory limits at certain sites and periods, with seasonal variations influenced by climatic factors. Site P1 exhibited higher electrical conductivity, total dissolved solids, chlorophyll, and nitrogen compounds, indicating anthropogenic influence and potential risks associated with untreated water consumption. In Chapter 4, sediment analysis revealed elevated concentrations of aluminum, iron, manganese, and selenium, as well as chromium, nickel, copper, zinc, and lead exceeding quality guidelines, particularly in areas influenced by urban activities. Higher concentrations during the rainy season highlighted the role of seasonality in contaminant mobilization and deposition processes. Chapter 5 investigated the bioaccumulation of potentially toxic and essential elements and enzymatic responses in native fish species (*Psectrogaster amazonica* and *Caenotropus labyrhinthicus*). Elevated concentrations of arsenic, lead, and selenium were detected in fish tissues, exceeding recommended limits. Enzymatic activities (AChE, AST, ALT, and ALP) indicated physiological responses associated with environmental exposure and were interpreted as sublethal alterations, without allowing direct inference of causality or specific mechanisms. Overall, the results indicate that the dynamics of elements in the middle Tocantins River are controlled by the interaction between natural processes and anthropogenic influences. The concentrations of elements such as iron, aluminum, and manganese partly reflect the regional geochemical background, characterized by highly weathered tropical soils, while physicochemical parameters and spatial patterns indicate the influence of human activities, particularly in urban areas. The observed bioaccumulation in fish and enzymatic responses indicate organism exposure to environmental contaminants and associated physiological alterations. These findings, combined with the strong dependence of riverine populations on water and fish resources, highlight the importance of integrated environmental monitoring approaches that consider regional specificities and their implications for environmental health and food safety, in line with the One Health framework.

Keywords: Risk assessment; Heavy metals; One health; Environmental pollution; Food safety

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Certificado da Comissão de Ética no Uso de Animais

Este estudo foi aprovado pelos Comitês de Ética no Uso de Animais da Universidade Estadual da Região do Tocantins (CEUA nº 1025220722) e da Universidade Estadual do Maranhão (CEUA nº 040/2023), com autorização de coleta pelo SISBIO (Autorização nº 87310-1). Todos os procedimentos experimentais envolvendo animais foram realizados de acordo com as diretrizes e regulamentações institucionais, nacionais e internacionais pertinentes ao cuidado e ao uso de animais em pesquisa.

Sumário

Considerações gerais

O rio Tocantins, juntamente com o rio Araguaia, forma a segunda maior bacia hidrográfica inteiramente brasileira, com mais de 960.000 km², o que corresponde a 11% do território nacional (ANTAQ, 2013; PRYSTHON et al., 2022; SERRÃO, 2022). Esta bacia é de grande importância ecossistêmica para os biomas Amazônico e Cerrado, por se localizar numa zona de transição entre ambos. O rio Tocantins é o segundo maior curso d'água 100% brasileiro, com 2.400 km de extensão, que atravessa Maranhão, Tocantins e Pará e deságua (ANA, 2024). Ele é subdividido em Alto (sub-bacias 20 e 21), Médio (sub-bacias 22 e 23) e Baixo (sub-bacia 29), sendo que a região Tocantina maranhense está na sub-bacia 23 (PEREIRA; QUEIROZ, 2021).

A ictiofauna deste rio é bastante diversificada, com cerca de 520 espécies, das quais 30% são endêmicas, incluindo principalmente Characiformes (ordem) e Siluriformes (ordem), além de Ciclídeos (família) (SANTOS et al., 1984; LIMA; CAIRES, 2011). Isso ocorre, pois, embora a bacia Araguaia-Tocantins não esteja diretamente ligada ao rio Amazonas, ela compartilha com este um estuário (BARTHEM; GOULDING, 1997; CHAMON et al., 2022). Salienta-se que o rio é essencial para a população local, sustentando turismo, artesanato tradicional e pesca artesanal, que gera trabalho, renda, segurança alimentar e identidade cultural para milhares de famílias ribeirinhas.

O crescimento populacional, o avanço tecnológico e o aumento no uso de químicos industriais (fertilizantes, inseticidas e herbicidas) têm agravado a contaminação por xenobióticos em ecossistemas aquáticos (QAYOOM et al., 2024; SHARMA; KUMAR, 2024; SIVAKUMAR et al., 2024). Esse cenário pode comprometer a qualidade ambiental, afetando organismos aquáticos e potencialmente impactando a saúde humana, sobretudo em populações que dependem diretamente desses recursos. Mais especificamente, essa situação pode impactar negativamente a qualidade de vida da população, bem como contaminar a fauna e a flora local com diversos xenobióticos de origem antrópica (ABRANTES; BARRELLA, 2019; WAQAS et al., 2024; SABLE et al., 2024). A exposição a misturas de contaminantes pode desencadear respostas fisiológicas e bioquímicas, resultando em alterações estruturais e funcionais nos organismos.

A rica e endêmica ictiofauna da bacia do rio Tocantins–Araguaia enfrenta graves ameaças decorrentes do aumento das atividades antrópicas nas últimas décadas, incluindo a construção de barragens, mineração, introdução de espécies exóticas e projetos de hidrovias (PERÔNICO et al., 2020; AZEVEDO-SANTOS et al., 2021; PELICICE et al., 2021). Além disso, a expansão da agricultura na região do MATOPIBA, estabelecida pelo Decreto Presidencial nº 8.447/2015, intensifica essas pressões ambientais (CHAMON et al., 2022). Essas atividades contribuem para a introdução e mobilização de elementos químicos no ambiente aquático, os quais podem ser classificados em essenciais e potencialmente tóxicos, dependendo de sua função biológica e dos níveis de exposição.

Elementos essenciais, como ferro (Fe), zinco (Zn), cobre (Cu) e selênio (Se), desempenham funções metabólicas fundamentais, atuando como cofatores enzimáticos e reguladores fisiológicos. No entanto, quando presentes em concentrações elevadas, podem causar efeitos adversos, evidenciando um estreito intervalo entre essencialidade e toxicidade. Por outro lado, elementos potencialmente tóxicos, como chumbo (Pb), cádmio (Cd), arsênio (As) e mercúrio (Hg), não possuem função biológica conhecida e podem provocar efeitos deletérios mesmo em baixas concentrações. Exemplos como o chumbo (Pb) e o mercúrio (Hg) têm impactos que variam conforme sua concentração e forma química. Associados à poluição por resíduos domésticos, agrícolas e industriais (IANNACONE et al., 2022; HABIB et al., 2024; SHARMA et al., 2024), esses elementos representam um risco à saúde humana, à biota aquática e ao meio ambiente, podendo ser incorporados pelos organismos principalmente por meio da ingestão de água e alimento. Nesse contexto, a exposição humana a esses elementos ocorre principalmente por meio da ingestão de água e do consumo de organismos aquáticos, como peixes, podendo resultar em efeitos adversos à saúde, que variam desde alterações metabólicas e neurológicas até efeitos crônicos, dependendo da dose, forma química e tempo de exposição. Dessa forma, populações ribeirinhas apresentam maior vulnerabilidade, em função da forte dependência dos recursos hídricos e pesqueiros para sua subsistência.

Neste cenário, os peixes podem atuar como biomonitores de possíveis contaminantes no meio aquático, visto que é um importante componente do ecossistema, possui ciclo de vida totalmente aquático e é um recurso econômico ou de consumo da população local (IYIOLA et al., 2024; KUMAR; GUPTA; DHIMAN, 2024). Elementos potencialmente tóxicos podem ser incorporados pelos organismos aquáticos por meio da ingestão de água, sedimentos e alimento, podendo se acumular em diferentes tecidos. Estudos indicam que, após o contato do tóxico com o organismo exposto, pode ocorrer sua absorção por meio de processos fisiológicos, condicionada à biodisponibilidade do contaminante, seguida de sua distribuição nos diferentes tecidos (SAIDON et al., 2024; SINGH; KOSTOVA, 2024; VIDYALAKSHMI et al., 2024). Em seguida, o xenobiótico pode atingir e interagir com órgãos, tecidos ou células-alvo. Contudo, a ocorrência de efeitos tóxicos depende da eficiência dos mecanismos de biotransformação, excreção e compartimentalização do organismo. Quando esses mecanismos são sobrecarregados ou ineficientes, desencadeiam-se alterações fisiológicas capazes de comprometer a integridade estrutural e funcional das células, em função do nível e do tempo de exposição. A toxicidade se estabelece quando essas alterações ultrapassam a capacidade de adaptação e regeneração do sistema biológico.

A interpretação das concentrações de elementos em ambientes aquáticos deve considerar o contexto geoquímico regional, especialmente em regiões tropicais altamente intemperizadas, como o médio rio Tocantins. Nessa região, predominam Latossolos, Plintossolos e formações lateríticas, naturalmente enriquecidos em ferro (Fe), alumínio (Al) e manganês (Mn). Sob condições de elevada pluviosidade, processos de intemperismo químico e lixiviação promovem a mobilização natural desses elementos para a água e os sedimentos. Assim, concentrações elevadas desses elementos, especialmente durante o período chuvoso, podem refletir processos geogênicos naturais, não sendo necessariamente indicativas de contaminação antrópica. Dessa forma, a distinção entre fontes naturais e antrópicas é fundamental para a interpretação adequada da qualidade ambiental.

Muitos tecidos e órgãos de organismos aquáticos, como brânquias, fígado, hepatopâncreas, rins, sangue e músculos, são utilizados como matrizes para a quantificação de biomarcadores em análises de monitoramento ambiental (EMARA et al., 2024; LIU et al., 2024; WAQAS et al., 2024). A identificação de alterações bioquímicas, histológicas e fisiológicas nesses tecidos indica exposição/efeitos a tóxicos, servindo para avaliar a qualidade ambiental e os níveis de poluição em sistemas aquáticos, do ponto de vista biológico. Por exemplo, quando o metabolismo hepático de peixes é exposto a poluentes, pode haver alterações bioquímicas, com a liberação de enzimas hepáticas na circulação sanguínea. Como biomarcadores enzimáticos, destacam-se a aspartato aminotransferase (AST), alanina aminotransferase (ALT) e fosfatase alcalina (FA), associadas ao metabolismo hepático, e a acetilcolinesterase (AChE), relacionada à atividade colinesterásica, podendo indicar interferências na atividade enzimática decorrentes da exposição a contaminantes (HU et al., 2024; LIU et al., 2024; NAYAK et al., 2024; TAWFIK et al., 2024; WANG et al., 2024; ZAHRAN et al., 2024). Essas enzimas não são específicas para metais, mas refletem danos celulares e podem ser utilizadas para detectar exposição a diversos poluentes ambientais, incluindo metais traço, pesticidas, produtos químicos industriais, entre outros.

A ecotoxicologia tem ganhado importância, refletindo um aumento na conscientização ambiental e alinhando-se aos Objetivos de Desenvolvimento Sustentável da ONU. Há também uma crescente percepção de que atividades humanas podem causar danos aos ecossistemas e à saúde pública (BJERREGAARD et al., 2022). Em ecossistemas aquáticos, os sedimentos acumulam metais, que os organismos podem bioacumular, podendo, em alguns casos, contaminar a cadeia alimentar, especialmente em níveis tróficos superiores (LIU et al., 2024; SAIDON et al., 2024). A biomagnificação, embora possível, ocorre apenas em situações específicas e não constitui uma regra geral, dependendo de fatores como a natureza do metal e as interações ecológicas. A aplicação de conceitos ecotoxicológicos proporciona benefícios, permitindo a caracterização dos cenários de contaminação antropogênica e a compreensão das interações entre compostos tóxicos e biota, o que facilita a determinação de ações adequadas para remediar os impactos ambientais causados por atividades humanas.

Este estudo visa preencher lacunas de pesquisa no médio rio Tocantins (interface Cerrado-Amazônia), fornecendo informações sobre o perfil e percepção dos ribeirinhos quanto à qualidade da água, níveis de poluição, presença de elementos tóxicos e essenciais em amostras de água, sedimento e peixes, e distribuição espacial. Apesar da rica biodiversidade, há poucos estudos sobre os impactos ambientais nos compartimentos hídricos e na saúde da ictiofauna local na região de Imperatriz, Maranhão. A pesquisa é crucial para o monitoramento ambiental e manejo preventivo dos impactos da intervenção humana, visando à preservação dos ecossistemas e à qualidade da água. Identificar e criar estratégias para mitigar os impactos da ação antrópica na região é crucial, assim como fornecer subsídios para políticas públicas de responsabilidade social que atendam às necessidades dos cidadãos vulneráveis.

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OBJETIVOS

Objetivo geral

Realizar o monitoramento ambiental do médio rio Tocantins por meio da avaliação multicompartimental de parâmetros físico-químicos da água, elementos potencialmente tóxicos em água, sedimentos e peixes, biomarcadores enzimáticos em peixes nativos e da percepção socioambiental de populações ribeirinhas, visando à interpretação integrada dos riscos ambientais e à saúde.

Objetivos específicos

- ✓ Analisar a percepção socioambiental de populações ribeirinhas quanto à qualidade da água, ao uso dos recursos hídricos e pesqueiros e às condições de saneamento básico no médio rio Tocantins, como subsídio à interpretação dos riscos ambientais e à saúde ambiental.
- ✓ Avaliar os parâmetros de qualidade da água, incluindo aspectos físicos e químicos, bem como a presença de compostos nitrogenados (NH_4, NO_2 e NH_3) no médio rio Tocantins.
- ✓ Determinar a concentração de elementos potencialmente tóxicos (metais pesados) na água e nos sedimentos do médio rio Tocantins.
- ✓ Avaliar a bioacumulação de elementos potencialmente tóxicos nos tecidos muscular e hepático de peixes capturados em diferentes pontos do médio rio Tocantins.
- ✓ Quantificar a atividade enzimática de aspartato aminotransferase (AST) e alanina aminotransferase (ALT) no fígado, bem como de acetilcolinesterase (AChE) e fosfatase alcalina (FA) no fígado e no músculo de peixes capturados no médio rio Tocantins.

Perguntas de pesquisa e hipóteses

Com base nos objetivos propostos, esta tese foi orientada pelas seguintes perguntas de pesquisa:

- ✓ A pergunta central que norteia este estudo é: como a presença de elementos potencialmente tóxicos no médio rio Tocantins se distribui entre água, sedimentos e peixes, e quais são suas implicações ecotoxicológicas e para a saúde das populações ribeirinhas?

A partir dessa questão central, foram estabelecidas as seguintes perguntas específicas:

- ✓ Como as populações ribeirinhas percebem a qualidade da água, a poluição e os riscos associados ao uso dos recursos hídricos e pesqueiros no médio rio Tocantins?

- ✓ Os níveis de elementos potencialmente tóxicos na água do rio Tocantins excedem os padrões legais e representam risco à saúde humana?
- ✓ Os sedimentos do rio atuam como reservatórios e potenciais fontes de contaminação por elementos potencialmente tóxicos no ambiente aquático?
- ✓ Há bioacumulação de elementos potencialmente tóxicos em peixes nativos do médio rio Tocantins e respostas enzimáticas associadas à exposição?
- ✓ O consumo de água e de peixes provenientes do médio rio Tocantins representa risco potencial à saúde das populações ribeirinhas?

Para responder a essas questões, foram formuladas as seguintes hipóteses:

- ✓ A hipótese geral deste estudo é que a presença de elementos potencialmente tóxicos no médio rio Tocantins apresenta distribuição heterogênea entre água, sedimentos e biota, promovendo bioacumulação em peixes, alterações em biomarcadores enzimáticos e potenciais riscos à saúde das populações ribeirinhas.

As hipóteses específicas são:

- ✓ Os níveis de elementos potencialmente tóxicos na água são influenciados por fontes antrópicas e podem exceder os limites estabelecidos por normas ambientais, especialmente em áreas urbanizadas.
- ✓ Os sedimentos apresentam maiores concentrações de elementos potencialmente tóxicos em comparação à água, atuando como reservatórios e fontes secundárias de contaminação.
- ✓ Peixes expostos a ambientes contaminados apresentam bioacumulação de elementos potencialmente tóxicos e alterações em biomarcadores enzimáticos.
- ✓ O consumo de água e peixes contaminados pode representar risco potencial à saúde humana, especialmente para populações ribeirinhas com alta dependência desses recursos.
- ✓ A percepção socioambiental das populações ribeirinhas reflete, ao menos parcialmente, as condições reais de qualidade ambiental do médio rio Tocantins.

Esta tese está estruturada em cinco capítulos. O Capítulo 1 apresenta uma revisão de literatura sobre a bacia Tocantins–Araguaia, abordando aspectos ambientais, socioeconômicos e ecotoxicológicos relacionados à presença de contaminantes em ambientes aquáticos, e foi publicado como capítulo de livro. O Capítulo 2 é um estudo socioambiental que discute a percepção ambiental das comunidades ribeirinhas do médio rio Tocantins acerca da poluição e da qualidade da água. O Capítulo 3 avalia os níveis de elementos potencialmente tóxicos e essenciais na água do rio, bem como os riscos à saúde humana associados ao consumo dessa água. O Capítulo 4 analisa a concentração, a distribuição espacial e os riscos associados a elementos tóxicos e essenciais presentes nos sedimentos do rio Tocantins. O Capítulo 5 apresenta uma avaliação ecotoxicológica integrada da bioacumulação de elementos tóxicos e essenciais, bem como das respostas enzimáticas em peixes nativos do médio rio Tocantins. Além disso, foram avaliados os índices de risco à saúde humana associados ao consumo de peixe, destacando-se os potenciais impactos na população local. Todos os capítulos de 2 a 5 foram desenvolvidos como artigos científicos e publicados em revistas internacionais de alto impacto, incluindo a Scientific Reports (A1, Nature), com fator de impacto próximo de 4. Por fim, apresentam-se as considerações finais, que sintetizam os principais resultados e destacam suas implicações ambientais e de saúde pública.

This thesis is structured into five chapters. Chapter 1 presents a literature review on the Tocantins–Araguaia Basin, addressing environmental, socioeconomic, and ecotoxicological aspects related to the presence of contaminants in aquatic environments, and was published as a book chapter. Chapter 2 consists of a socio-environmental study that examines the environmental perception of riverine communities in the middle Tocantins River regarding pollution and water quality. Chapter 3 evaluates the levels of potentially toxic and essential elements in river water, as well as the associated human health risks related to its consumption. Chapter 4 analyzes the concentration, spatial distribution, and associated risks of toxic and essential elements in the sediments of the Tocantins River. Chapter 5 presents an integrated ecotoxicological assessment of the bioaccumulation of toxic and essential elements, along with enzymatic responses in native fish species from the middle Tocantins River. Additionally, human health risk indices associated with fish consumption were evaluated, highlighting potential impacts on the local population. Chapters 2 to 5 were developed as scientific articles and published in high-impact international journals, including Scientific Reports (A1, Nature), with an impact factor close to 4. Finally, the concluding remarks synthesize the main findings and highlight their environmental and public health implications.

CAPÍTULO 1 – QUALIDADE DA ÁGUA E CONSERVAÇÃO NO RIO TOCANTINS (MARANHÃO, BRASIL): UMA ANÁLISE DOS IMPACTOS ANTRÓPICOS E DAS ESTRATÉGIAS DE MITIGAÇÃO

QUALIDADE E CONSERVAÇÃO DA ÁGUA NO RIO TOCANTINS (MARANHÃO, BRASIL): UMA ANÁLISE DOS IMPACTOS ANTROPOGÊNICOS E ESTRATÉGIAS DE MITIGAÇÃO

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Resumo - O Rio Tocantins desempenha um papel fundamental na biodiversidade aquática, servindo como habitat para uma rica ictiofauna cuja preservação é crucial para a saúde ecológica do sistema, especialmente diante das pressões antropogênicas. Este artigo de revisão resume informações relevantes sobre os impactos humanos na região, destacando a importância ambiental e socioeconômica do rio para a população do Maranhão, Brasil. Examina os efeitos da contaminação ambiental, incluindo metais potencialmente tóxicos, a geração excessiva de radicais livres e o estresse oxidativo, bem como os mecanismos de biotransformação de xenobióticos. Além disso, discute-se o uso de biomarcadores, com ênfase em peixes e parâmetros bioquímicos, como transaminases, acetilcolinesterase e fosfatase alcalina, como ferramenta eficaz para monitorar e avaliar danos ambientais. Os dados compilados ressaltam a necessidade de estratégias integradas de monitoramento, conservação e mitigação de impactos, contribuindo assim para o desenvolvimento sustentável e para a preservação dos ecossistemas aquáticos da região.

Palavras-chave: Bacia Tocantins-Araguaia. Ecossistemas de Água Doce. Poluição Aquática. Qualidade Ambiental.

Water quality and conservation in the Tocantins river (Maranhão, Brazil): an analysis of anthropogenic impacts and mitigation strategies

Abstract - The Tocantins River plays a fundamental role in aquatic biodiversity, serving as a habitat for a rich ichthyofauna whose preservation is crucial for the ecological health of the system, especially in the face of anthropogenic pressures. This review article summarizes relevant information about human impacts in the region, highlighting the environmental and socioeconomic importance of the river for the population of Maranhão, Brazil. It examines the effects of environmental contamination, including potentially toxic metals, the excessive generation of free radicals, and oxidative stress, as well as the mechanisms of xenobiotic biotransformation. Furthermore, the use of bioindicators, with an emphasis on fish and biochemical parameters such as transaminases, acetylcholinesterase, and alkaline phosphatase, is discussed as an effective tool for monitoring and assessing environmental damage. The compiled data underscore the need for integrated strategies for monitoring, conservation, and impact mitigation, thereby contributing to sustainable development and the preservation of the region’s aquatic ecosystems.

Keywords: Aquatic Pollution. Environmental Quality. Freshwater Ecosystems. Tocantins-Araguaia Basin.

INTRODUCTION

The Tocantins River plays a fundamental role in aquatic biodiversity, serving as a habitat for a rich diversity of fish species. Preserving this diversity is essential for maintaining the river’s ecological health, especially in the face of anthropogenic pressures. Human activities, such as pollution and habitat alterations, have negatively impacted on the aquatic environment, directly affecting water quality and, consequently, fish populations’ health. In this context, the use of biomarkers has proven to be an effective tool for monitoring environmental quality and detecting ecosystem changes caused by human actions (Sumudumali; Jayawardana, 2021).

This study investigates the ecological and environmental aspects of the Tocantins River, emphasizing fish diversity and anthropogenic impacts. It assesses biomarkers in environmental monitoring, considering oxidative stress, xenobiotic biotransformation, and the influence of potentially toxic metals in water, sediments, and fish tissues. Additionally, it examines biochemical biomarkers such as transaminases, acetylcholinesterase, and alkaline phosphatase. Environmental monitoring is crucial for mitigating impacts and supporting public policies focused on conservation and socio-environmental responsibility (Acioly et al., 2024; Machado da Silva Acioly et al., 2024). Moreover, raising awareness among the local population strengthens river conservation efforts and promotes governmental and institutional actions for more effective environmental management (Machado da Silva Acioly et al., 2025).

This review adopts a broad approach, aiming to compile and synthesize relevant findings from existing scientific research. An in-depth literature search was conducted using databases such as Science Direct, Scielo, CAPES Periódicos, and Wiley Online Library. The research employed keywords in both English and Portuguese: “Tocantins River,” “environmental monitoring,” “fish,” “oxidative stress,” “antioxidant enzymes,” and “potentially toxic metals,” combined using the Boolean operators “AND” and “OR” to ensure greater precision. Inclusion criteria were limited to original research articles and literature reviews published in scientific journals. Excluded materials included articles unrelated to the proposed topic, those outside the central research scope, paywalled content, monographs, dissertations, theses, opinion articles, and duplicates.

LITERATURE REVIEW

Tocantins River: Importance, Fish Diversity, and the Presence of Pollutants

The Araguaia-Tocantins watershed, as described by the Tocantins and Araguaia Waterways Administration (Ahitar, 1999), is located between 4° and 18° South latitude and 46° and 55° West longitude. The Tocantins River, which flows through this basin, is recognized for its ecological and economic significance, playing a central role for the region's inhabitants. It originates in the Goiás Plateau and flows through the states of Goiás, Tocantins, and Maranhão, eventually emptying into the Pará River estuary/Baía de Marajó system, which is hydrodynamically connected to the greater Amazon coastal-estuarine complex (Oliveira Lopes, 2020).

The Tocantins River, divided into upper, middle, and lower sections, features numerous rapids and waterfalls (Bezerra et al., 2020; Americo, 2022). Most of the river is navigable, facilitating the transport of goods such as soy and minerals for export. Additionally, the river has significant hydroelectric potential, with several projects developed in recent decades (Americo, 2022), including the Tucuruí Dam in Pará, which generates 8.370 MW. Hydropower plants are the world's leading source of renewable energy, accounting for approximately 16% of the global energy matrix (Balkhair; Rahman, 2017; IEA, 2019). However, both river navigation and hydroelectric energy generation can have significant environmental impacts.

The middle Tocantins River, approximately 980 km long with a 150-meter elevation drop, extends from Lajeado Falls (Tocantins) to Itaboca Falls (Pará) (Americo, 2022). Along its course lies the city of Imperatriz, which has 273.110 inhabitants and covers an area of 1.369.039 km², of which 65.07 km² is urbanized (IBGE, 2022). Imperatriz is the second most populous municipality in Maranhão and one of the most economically significant, serving as a major transit route between large commercial centers.

River navigation is deeply rooted in the cultural history of the Araguaia-Tocantins basin, as Portuguese colonizers used these waterways to access northern Brazil in search of valuable goods and indigenous slaves. Over time, local populations incorporated this riverine lifestyle into their social, economic, cultural, and environmental contexts. Viana et al. (2022) report that fishing remains a traditional and income-generating activity, practiced for generations in the region. It serves as a primary protein source for the Maranhão population and supplies fish to neighboring states such as Pará, Tocantins, and Piauí.

Aquatic ecosystems function as sinks, absorbing various substances from land runoff and leaching (Bashir et al., 2020; Bjerregaard et al., 2022). Human activities, including sewage discharge, nutrient input, terrigenous materials, crude oil, potentially toxic metals, and plastics, have severely impacted these environments. Additionally, global climate change, urban and tourism development, and the unsustainable exploitation of aquatic resources have intensified these challenges (Häder et al., 2020). Specifically, metals can enter aquatic ecosystems through natural processes such as weathering, atmospheric deposition, and rainfall, as well as through anthropogenic sources.

Recent studies indicate that fish species in northern Brazil are heavily influenced by local climatic conditions, human activities, deforestation, and river damming, often for energy production (Carvalho et al., 2017; Berlatto, 2018; Santana et al., 2021). It is important to note that fish exhibit diverse responses to xenobiotic exposure, with variations depending on factors such as sex, diet, size, genetic polymorphism, and developmental stage (Adeogun et al., 2020; Campbell et al., 2021; Topić Popović et al., 2023).

Imperatriz, located in northeastern Brazil along the right bank of the Tocantins River (Maranhão), has a population strongly connected to the river in socio- economic, cultural, and environmental aspects. A recent study found that 34% of riverine residents both consume and sell native fish, while 62% use them solely for personal consumption. Additionally, 84% reported lacking a sewage system, while many rely on untreated river water (Acioly et al., 2025). The same study revealed that 84% of interviewed riverside dwellers perceive the middle Tocantins River as polluted. Among the most noticeable changes over time, they mentioned a decrease in river levels during the dry season, a decline in fish availability, especially in the dry season and increasing water pollution.

Studies by Acioly et al. (2024) and Machado da Silva Acioly et al. (2024) provide key insights into the concentration, distribution, pollution levels, and sources of toxic and essential elements in water and sediment. Water monitoring revealed that aluminum, copper, iron, magnesium, and selenium exceeded legal limits, with seasonal variations suggesting climatic influences, particularly in February when concentrations peaked. Additionally, the urban area showed higher conductivity, total dissolved solids (TDS), and chlorophyll levels, highlighting the need for ongoing monitoring. Sediment analysis in 2023 indicated excessive levels of aluminum, iron, manganese, and selenium, while chromium, nickel, copper, zinc, and lead surpassed guideline thresholds.

Anthropic Activity and Bioindicators for Environmental Quality Monitoring

The main anthropogenic impacts that can compromise the functioning of aquatic ecosystems include industrial, urban, agricultural, and mining pollution; construction of dams, reservoirs, and roads; salinization; sedimentation resulting from deforestation; removal of riparian forests; intensive exploitation of fishery resources; introduction of exotic plant and animal species; and habitat destruction (Trivinho et al., 2008; Azevedo-Santos et al., 2021; Ogidi; Akpan, 2022; Swain, 2024). Contaminants from these activities, when entering aquatic environments, can disrupt the ecosystem by generating oxidants and free radicals in organisms. These compounds intensify oxidative stress, causing harmful biological effects on the morphology, physiology, and biochemistry of living organisms.

Potentially toxic elements, such as metals, metalloids, and non-metals, are of environmental concern due to their effects on different components of aquatic ecosystems (Guabloche et al., 2024).

Hernández-Fernández et al. (2020) highlight the presence of metals and metalloids in organic and inorganic forms, such as methylated mercury (Hg), the most toxic form of this element in the food chain. Depending on its concentration in animal tissue, Hg can denature and inactivate enzymes, interfere with cellular metabolism, and alter cell membranes. Elements with no essential metabolic functions, such as mercury (Hg), cadmium (Cd), lead (Pb), and aluminum (Al), can produce highly reactive compounds, such as H_2O_2 (hydrogen peroxide), being among the most prevalent contaminants causing damage to the human body (Shiry et al., 2021; Merola et al., 2021; Rajkumar et al., 2023).

Bioindicators are organisms whose presence, abundance, and distribution reflect environmental quality and can be used to detect anthropogenic impacts. Nevertheless, in ecotoxicological approaches, fish are more appropriately considered biomonitors, as they integrate contaminant exposure over time through bioaccumulation. In such cases, the use of biomarkers, including enzymatic responses, enables the detection of sublethal and early biological effects of exposure. Thus, while biomonitors indicate exposure, biomarkers provide evidence of biological effect at molecular and physiological levels. The responses observed in analyzed specimens depend on their physiological characteristics and capacity to accumulate contaminants, being influenced by nutritional, immunological, and environmental conditions (Prestes and Vincenci, 2019).

Environmental monitoring biomarkers are subdivided into exposure, effect, and susceptibility biomarkers (Chandana, 2019; Manno, 2024). Exposure biomarkers are used to detect and quantify the presence of contaminants or their metabolites in the organism, reflecting the intensity and duration of exposure to these agents. Their use indicates that the organism has been exposed to toxic substances and can also provide information on bioaccumulation levels. Effect biomarkers measure the biological damage caused by exposure to contaminants, assessing physiological, biochemical, or morphological changes at the cellular or molecular level. These biomarkers help identify adverse impacts (preclinical, sublethal, or lethal) resulting from exposure.

Free Radicals, Oxidative Stress, and Xenobiotic Biotransformation

Oxidation is the process by which an atom, group, or ion loses electrons during a chemical reaction. This process is natural and essential for the survival of aerobic organisms that breathe oxygen. During metabolism, these organisms generate oxidants and free radicals, which interact with the environment. Oxidants are small, inorganic molecules that attack and oxidize other molecules and cells. Over evolution, aerobic organisms have developed antioxidant defenses to manage these compounds, including enzymes such as superoxide dismutase, catalase, and glutathione peroxidase. In addition to these enzymes, non-enzymatic compounds such as bilirubin, uric acid, melatonin, and glutathione also help maintain cellular balance (Gordon, 2012; Alam et al., 2024).

Free radicals are unstable molecules that contain atoms with unpaired electrons due to an odd number of electrons in their valence shell. According to the octet rule, a molecule requires eight electrons in its valence shell to achieve stability. Free radicals are frequently produced by mitochondria during the electron transport chain in metabolic processes such as redox reactions. However, when produced in excess, they can induce oxidative stress. Reactive oxygen species (ROS), such as hydrogen peroxide (H_2O_2), are reactive molecules that, despite not having unpaired electrons, can still cause damage, acting similarly to free radicals in terms of chemical reactivity (Silva, 2016). Oxidative stress occurs when there is an imbalance between the production of reactive oxygen species (ROS) and the organism's antioxidant defense system, leading to damage to essential biomolecules such as lipids, DNA, and proteins. In response, cellular metabolism may increase the activity of antioxidant enzymes or reduce the activity of enzymes that generate oxidative stress to restore physicochemical balance. The antioxidant defense system acts to mitigate the damage caused by ROS, which, besides being associated with oxidative stress, also play essential roles as secondary messengers in cellular signaling pathways, regulating processes such as immune response and cellular adaptation. Moreover, responses to xenobiotic exposure involve distinct but interconnected processes. Detoxification can be evaluated through the quantification of enzymes involved in biotransformation pathways (phase I and phase II), which mediate the metabolism of contaminants. In addition, xenobiotic exposure may lead to the generation of reactive oxygen species (ROS), triggering oxidative stress. This condition can be assessed by analyzing enzymatic and non-enzymatic antioxidant systems responsible for maintaining cellular redox balance.

The increased release of ROS in aquatic environments is strongly associated with environmental stressors such as ultraviolet (UV) radiation and the presence of contaminants, including trace metals (Silva et al., 2016; Anetor et al., 2022; Sharma et al., 2024). Microparticles of potentially toxic metals catalyze metabolic reactions, generating oxidative stress and releasing free radicals, particularly hydroxyl radicals (-OH). The accumulation of environmental contaminants compromises the organism's antioxidant defenses, reducing its ability to neutralize these radicals and causing oxidative damage to biomolecules such as proteins, lipids, and nucleic acids. Recent studies show that ROS can damage these macromolecules, resulting in metabolic dysfunction and apoptosis, both in vivo and in vitro (Stark et al., 2022; Rauf et al., 2024; Yu; Luo, 2024).

The Fenton and Haber-Weiss reactions explain how metals contribute to ROS generation. In the Fenton reaction, iron (Fe^{2+}) or copper (Cu^{2+}) ions react with hydrogen peroxide (H_2O_2), generating highly reactive hydroxyl radicals (-OH), which can cause severe cellular damage. In the Haber- Weiss reaction, the interaction between superoxide (O_2^-) and metal ions, such as Fe^{3+}, can regenerate Fe^{2+}, which then reacts with H_2O_2, forming hydroxyl radicals (-OH) again. These metal-catalyzed processes are crucial in ROS generation, intensifying oxidative stress and exacerbating cellular and molecular damage, particularly in aquatic organisms exposed to contaminants. ROS are generated not only through these reactions but also when certain metals, such as Cu, As, Fe, Pb, Cd, Cr, Hg, Ni, and Zn, interact with each other, amplifying cellular and molecular damage in exposed aquatic organisms

(Wasif et al., 2024).

It is crucial to note that many potentially toxic metals are not metabolized by organisms and accumulate in soft tissues, as living beings struggle to excrete them efficiently. These pollutants are highly persistent in the environment and can impact various metabolic systems, including blood and cardiovascular pathways, colon, liver, kidneys, endocrine system, enzymatic energy production pathways, gastrointestinal system, immune system, nervous system, and reproductive and urinary systems (Budi et al., 2024; Singh; Kostova, 2024; Parui et al., 2024; Tyagi et al., 2024). This can lead to cytotoxic, mutagenic, and carcinogenic effects in animals and humans, particularly through the consumption of contaminated food (Rivera et al., 2018).

Potentially Toxic Metals: General Aspects, Adsorption, Mobility, and Accumulation in Water, Sediments, and Tissues

Potentially toxic elements are chemical substances that can cause harmful effects on living organisms and ecosystems, depending on their concentrations and chemical forms in the environment. These elements include both heavy metals and non-metals and metalloids, which can be toxic at high levels or even in small quantities, depending on environmental and biological conditions. Among the heavy metals of greatest toxicological and ecotoxicological relevance in aquatic environments are mercury (Hg), arsenic (As), chromium (Cr), lead (Pb), cadmium (Cd), nickel (Ni), and zinc (Zn). For most organisms, exposure to concentrations above a specific threshold can be extremely toxic (Alvariño et al., 2024). However, some, such as cobalt (Co) and zinc (Zn), are essential for living organisms (Obasi; Akudinobi, 2020). Essential trace elements may pose risks if their levels exceed the tolerance limits of organisms, while non-essential metals are toxic even at relatively low concentrations.

These contaminants, from both natural and anthropogenic sources, are present in nature. Natural sources include forest fires, rock weathering, volcanic activities, and the chemical evolution of hydrochemical facies. However, it is evident that the excessive release of heavy metals occurs mainly due to anthropogenic activities, such as urbanization, industrialization, mining, municipal and domestic activities, agriculture, wastewater, and metallurgical processes (Masindi et al., 2018; Adnan et al., 2024; Swain et al., 2024). Therefore, recognizing the risk of heavy metal contamination and its consequences for biodiversity is essential (Savassi et al., 2020); only by doing so can we control and prevent harm to the aquatic ecosystem's balance.

Unlike organic compounds, potentially toxic metals are not easily degraded and can accumulate in various compartments of aquatic ecosystems (Jalilian et al., 2024), including sediments, water columns, and the tissues of organisms. This characteristic makes them a significant environmental concern, as they can cause negative impacts at different trophic levels, depending on their concentration, chemical form, and environmental conditions. The term "Potentially Toxic Metals" includes not only heavy metals but also other elements such as Cr, Cu, Zn, and Ni, which, although essential in small quantities, can cause damage at relatively low concentrations (Alvariño et al., 2024). Essential elements like Na, Ca, Mn, Zn, and Fe are crucial for organisms in small amounts, while non-essential or toxic elements like Cd, Hg, and Pb pose risks even at low concentrations (Alvariño et al., 2024; Kacini tarhane et al., 2024).

Excessive accumulation of potentially toxic elements in the food chain can lead to severe systemic health issues, highlighting the need to control this contamination and its health risks. Thus, their presence in the environment must be monitored through samples of soil, water, air, or bioindicator organisms (Shawai, 2017). For instance, Cd can be introduced into the soil through tire residues, oil, urban waste, sewage sludge, and phosphate fertilizers (Roberts, 2014; Jayakumar et al., 2021). Meanwhile, the discharge of urban wastewater may contain elevated levels of Zn, Pb, and Cu (Ancieta, 2012; Rosado et al., 2024).

Typically, potentially toxic metals are associated with suspended organic particles, settling at the bottom of water bodies. Thus, sediments play a crucial role in the dynamics, conversion, and transport of metal-organic complexes (Sun et al., 2023; Tripathi et al., 2024). Due to their organic matter content, sediments can retain trace elements. Therefore, the bioavailability of metals depends on physicochemical factors like pH, salinity, organic matter, temperature, dissolved oxygen, and alkalinity (Pontoni et al., 2022; Harmesa; Taufiqurrahman, 2022; Linnik et al., 2023). For example, salinity can influence the bioavailability and toxicity of As, Cd, Cu, Cr, Hg, Ni, Pb, and Zn (Rebolledo et al., 2021; Cui et al., 2024).

Mountouris et al. (2002) emphasize that the bioavailability of trace metals is influenced by the concentration of iron, manganese, and aluminum oxides, and the amount of organic matter present in the sediment. Among the soil properties that affect the retention and mobility of heavy metals are is, which is the main force governing the adsorption of metal cations; the oxidation- reduction potential (ORP); cation exchange capacity (CEC); percentage of organic matter; clay fraction, which includes silicate clays and oxides; and ionic competition (Matos, 1995; Zhang et al., 2020). These properties interact to determine how potentially toxic metals behave in the environment, influencing their mobility and bioavailability.

The presence of trace metals in aquatic ecosystems can affect water quality parameters, such as hydrogen ion concentration (pH), dissolved oxygen, and turbidity, as well as impact aquatic biota, including plankton, algae, crustaceans, fish, and benthic organisms (Dhanaraj et al., 2024; Dey et al., 2024; Khan et al., 2024; Kashyap et al., 2024; Sharma et al., 2024). However, these effects depend on the chemical speciation, concentration, and bioavailability of the metals, as well as environmental conditions. These metals can directly induce toxicity in aquatic organisms or indirectly disrupt the food chain, resulting in ecological imbalances (Samuel et al., 2023). It is known that several potentially toxic metals, including Cd, Pb, Hg, Cu, and Zn, cause harmful effects on fish growth and development, as well as on specific organs such as the liver and in the reproductive and respiratory systems of these animals (Wasif et al., 2024; Sharma et al., 2024).

Studies indicate that the presence of these elements in natural aquatic ecosystems can lead to algae proliferation, oxygen deficiency, and even the death of aquatic organisms (Bashir, 2020; Lafta et al., 2024; Wasif et al., 2024). Pb, for example, is a metal that, in fish, can reduce survival, growth, development, and metabolism rates, as well as increase mucus formation in the organism (Eisler, 1988). Sukardi et al. (2024) observed that Pb caused liver damage, such as the accumulation of inflammatory cells, necrosis, and hydropic degeneration. Pb exposure rapidly damages and disrupts biological functions in the organism, affecting its survival and growth. Potentially toxic metals like Cr, Cd, and As cause genomic instability, promoting defects in DNA repair following oxidative stress and DNA damage (Balali-mood et al., 2021).

Special attention is drawn to the ability of these chemical elements to bioaccumulate in the tissues of living organisms, triggering the biomagnification process along the aquatic food chain (Li et al., 2024; Saidon et al., 2024). Biomagnification refers to the transfer of heavy metals between at least two trophic levels in a food web. However, it is important to note that bioaccumulation is much more common than biomagnification, as substances can be continuously absorbed by organisms but not eliminated, resulting in a progressive accumulation along trophic networks.

Simmons et al. (2005) indicate that, regardless of the concentration of Cd in organisms, it predominantly accumulates in the renal and hepatic tissues, potentially interfering with phosphorus and calcium metabolism due to the inhibition of vitamin D synthesis. This metal is also highly carcinogenic to both humans and animals, and exposure to or consumption of contaminated food can impair quality of life. Additionally, a recent study by Rocha (2022) suggests that the intake of large quantities of this pollutant, or prolonged contact, as in the case of fish, can interfere with the functioning of endocrine glands.

Farombi, Adelowo and Ajimoko (2007) observed that concentrations of potentially toxic metals in fish organs exceeded the acceptable limits established by regulatory institutions. In their research, they identified the following bioaccumulation priority order: arsenic (As) accumulated most in the kidneys, followed by the liver, gills, and heart, while zinc (Zn) accumulated primarily in the gills, followed by the liver, kidneys, and heart. Meanwhile, Cagni et al. (2022) found higher levels of mercury (Hg) in fish muscles and gills, in addition to identifying fifteen perfluoroalkyl substances (PFASs) when analyzing the fish.

Recent studies highlight a variety of aquatic organisms, such as mollusks, fish, turtles, and cetaceans, as models for environmental monitoring (Herceg Romanić et al., 2024; Otero et al., 2024; Polizzi et al., 2024). Historically, fish have been the main models for assessing the effects of potential environmental contaminants. They play crucial ecological roles in maintaining the food chain and represent a significant economic resource for humans (Alvariño et al., 2024). To investigate the association between potentially toxic and essential elements, statistical tools such as correlation matrices and principal component analysis (PCA) are used.

Fish, fully aquatic vertebrates, allow for direct observation of the effects of exposure to xenobiotics, providing valuable insights into biological mechanisms and improving the extrapolation of these effects to other organisms and humans. In addition to their ecological role, fish are an important food source, rich in proteins and low in saturated fats, with omega fatty acids that support good health (Tur et al., 2012; Kumar et al., 2024). Therefore, muscle tissue is often analyzed due to its ability to store metals and its role as the main edible part of the fish. The liver is also analyzed, as it is crucial for processing toxins in vertebrates and plays a vital role in removing toxic substances from the organism.

Biochemical Indicators of Environmental Contamination: Transaminases, Acetylcholinesterase, and Alkaline Phosphatase in Fish

Biochemical parameters are widely used in environmental monitoring due to their sensitivity to toxic substances (xenobiotics). When living organisms are exposed to contaminated environments, a common response is oxidative stress. In the case of organic compounds, the xenobiotic is mainly metabolized by phase I enzymes (such as CYP450), which promote oxidation reactions, potentially generating free radicals and reactive oxygen species (ROS) in excess. The accumulation of ROS can lead to oxidative stress, causing cellular damage. Subsequently, phase II enzymes act on the conjugation of metabolites generated in phase I, facilitating the excretion of compounds. In the case of metals, metabolism occurs differently. Although they are not metabolized by phase I or phase II enzymes, metals can bind to proteins and enzymes, directly affecting cellular processes and often being bioaccumulated. Biotransformation enzymes, including those involved in phase I and phase II reactions, play a key role in the detoxification of xenobiotics. In parallel, antioxidant enzymes are essential for protecting cells against oxidative stress generated during contaminant exposure. Hepatic enzymes, including both biotransformation and antioxidant enzymes, have been widely studied as indicators of exposure to environmental contaminants (Lionetto et al., 2019; Aprocallao, 2006; García; Arceo, 2018; Carmen et al., 2022).

Transaminases are intracellular enzymes involved in amino acid metabolism and are highly active in hepatic tissue (Yadav et al., 2022; Youssef; Wu et al., 2024). Elevated levels in plasma or serum are commonly interpreted as indicators of hepatocellular damage, reflecting leakage of these enzymes into the circulation. In contrast, tissue activity is naturally high in the liver and may vary with metabolic status; therefore, its interpretation requires comparison with appropriate reference or control conditions. The two main aminotransferases are aspartate aminotransferase (AST) (EC 2.6.1.1), also known as glutamic-oxaloacetic transaminase (GOT), and alanine aminotransferase (ALT) (EC 2.6.1.2), also known as glutamic- pyruvic transaminase (GPT). Both transaminases are important organ-specific biomarkers for hepatotoxicity and physiological stress in fish (Malarvizhi et al., 2012; Temiz; Kargin, 2024).

These enzymes play an important role in the metabolism of biomolecules such as carbohydrates and amino acids in fish tissues and other living organisms. AST and ALT are leakage enzymes; under normal conditions, their presence is low or absent. However, if there is destruction of hepatocyte tissue or mitochondrial membrane, serum levels will increase. In other words, an increase in serum activity of transaminases can be caused by necrosis or sublethal damage to hepatocytes and muscle cells (Galeb, 2010). It is worth noting that the levels of AST and ALT can vary between organisms. Alves (2003), for example, found AST levels three times higher than ALT in tilapia (*Oreochromis niloticus*), due to the lower specificity of AST, which can bind to more sites. The use of biomarkers in fish populations to measure chemical toxicity is ecologically relevant due to their sensitivity, specificity, and precision (Alvariño et al., 2023). This assessment has become a powerful predictive tool, allowing the development of protection and remediation strategies before chemical damage becomes irreversible in aquatic ecosystems. Alvariño et al. (2023) indicate that fish in the assessed ecosystem are affected by anthropogenic activities and show changes in enzymatic biomarkers. The species *Sciaena deliciosa* and *Odontesthes regia* served as sensitive models for monitoring potentially toxic metals, showing altered liver function with elevations of AST and ALT. High ALT concentrations can be used with some specificity in diagnosing toxic liver damage (Haque et al., 2021; Llewellyn et al., 2021).

Cholinesterases are enzymes from the serine-esterase family, present in the nervous system, muscle tissues, liver, and circulatory system of vertebrates and invertebrates. Acetylcholinesterase (AChE, EC 3.1.1.7) regulates the transmission of nerve impulses between neurons by inactivating the neurotransmitter acetylcholine, hydrolyzing it into acetate and choline, ensuring the intermittency of nerve impulses responsible for neuronal communication. The most widely used biomarker for responding to neurotoxic compounds is acetylcholinesterase inhibition, a key enzyme in the nervous system that catalyzes the hydrolysis of the neurotransmitter acetylcholine (Lionetto et al., 2019).

In vertebrate animals, such as fish, AChE is found in higher concentrations in brain and muscle tissues, liver, heart, plasma, and eyes. Its activity can be inhibited when the organism is exposed to certain xenobiotics, such as potentially toxic metals, metalloids, and non-metals. AChE plays a crucial role in the physiological metabolism of the organism, influencing processes such as neuritogenesis, cell adhesion, synaptogenesis, activation of dopaminergic neurons, amyloid fiber assembly, hematopoiesis, and thrombopoiesis (Fulton; Key, 2001; Olivares-Rubio; Espinosa-Aguirre, 2024). When its activity is inhibited, non-hydrolyzed acetylcholine accumulates in synaptic clefts, disrupting normal nervous system function. This can lead to continuous stimulation of muscles, resulting in paralysis and eventually death of the organism (Payne et al., 1996; Olivares-Rubio; Espinosa-Aguirre, 2024).

Many potentially toxic metals are considered non- specific anticholinesterase agents (Lionetto et al., 2013). This anticholinesterase activity is primarily associated with metals like Hg, Cd, and Pb, which can interfere with the function of cholinesterase enzymes essential for nerve transmission. Additionally, the combination of different classes of chemicals can have a synergistic effect on AChE activity inhibition. In most cases, cholinesterase recovery depends on the synthesis of new enzymes. According to Lionetto et al. (2013), this inhibition likely occurs through binding to protein-SH residues, and the authors suggest that the presence of metal cations may alter the enzyme's conformation.

FINAL CONSIDERATIONS

The Tocantins River, which is ecologically and economically significant to the region, was shown in this study to be affected by anthropogenic pressures. This is supported by the elevated concentrations of potentially toxic elements detected in water and sediments, their bioaccumulation in fish tissues, and the enzymatic responses observed in native species. Additionally, the high dependence of riverine populations on untreated water and fish consumption reinforces the environmental and public health relevance of these findings. The results indicate that sediments may act as reservoirs of contaminants, influencing their bioavailability and potential transfer to aquatic organisms. The patterns observed across environmental compartments suggest the need for continuous and integrated monitoring strategies that consider water, sediments, and biota.

The assessment of biochemical parameters, such as transaminases, acetylcholinesterase, and alkaline phosphatase, provided insights into physiological and metabolic responses associated with exposure to contaminants. However, these biomarkers should be interpreted with caution, as they indicate biological responses rather than directly confirming specific tissue damage or causality. Overall, the integration of physicochemical data, bioaccumulation patterns, enzymatic biomarkers, and socio-environmental information contributes to a more comprehensive understanding of environmental quality and supports the development of management and mitigation strategies aimed at protecting aquatic ecosystems and riverine populations.

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CAPÍTULO 2 – PERCEPÇÃO AMBIENTAL DOS RIBEIRINHOS SOBRE A POLUIÇÃO E QUALIDADE DA ÁGUA DO MÉDIO RIO TOCANTINS, MARANHÃO

ACIOLY, T. M. da S.; BILIO ALVES, M.; ALMEIDA BARBOSA, L.; FRANCISCO DA SILVA, M.; IANNACONE, J.; CARVALHO VIANA, D. Percepção ambiental dos ribeirinhos sobre a poluição e qualidade da água do médio rio Tocantins, Maranhão. **Revista GeoUECE**, [S. l.], v. 13, n. 25, 2025. https://doi.org/10.52521/geouece.v13i25.12334

PERCEPÇÃO AMBIENTAL DOS RIBEIRINHOS SOBRE A POLUIÇÃO E QUALIDADE DA ÁGUA DO MÉDIO RIO TOCANTINS, MARANHÃO

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RESUMO - O rio Tocantins é essencial para o sustento da população maranhense, porém, apesar de sua importância, a região enfrenta problemas de degradação ambiental pelo crescimento urbano acelerado, como desmatamento de encostas, exploração intensa de recursos pesqueiros, poluição do ar e água, assoreamento, dragagem e falta de saneamento. Objetivou-se investigar a percepção ambiental dos ribeirinhos quanto à qualidade da água do médio rio Tocantins através da aplicação de questionários estruturados. A pesquisa foi realizada entre os meses de agosto e dezembro de 2023, contando com um universo amostral de 50 entrevistados. Ainda, foi utilizada uma abordagem multimétodo para a integração de dados quantitativos e qualitativos. A população atingida foi composta por famílias ribeirinhas distribuídas entre quatro pontos de aplicação de questionário ao longo do médio rio Tocantins (P1: Beira Rio – zona urbana, P2: povoado Bananal, P3: povoado Embiral e P4: povoado Cidelândia). Percebe-se que a maioria dos ribeirinhos envolvidos no estudo reside na região há um período significativo, predominantemente acima de 10 anos (88%). Além disso, 34% dos entrevistados consomem e comercializam peixes nativos, enquanto 62% os utilizam apenas para consumo próprio, e 4% não os consomem. É importante destacar também que 84% dos participantes afirmam não possuir rede de esgoto em suas residências. Esses dados evidenciam a importância dos recursos pesqueiros e da água do rio para essa população, destacando a necessidade de medidas que promovam a conservação ambiental e o acesso a serviços básicos de saneamento.

Palavras-chave: Meio ambiente; Poluentes; Recursos pesqueiros.

ENVIRONMENTAL PERCEPTION OF RIVERINE PEOPLE ON POLLUTION AND WATER QUALITY OF THE MIDDLE TOCANTINS RIVER, MARANHÃO

ABSTRACT - The Tocantins River is essential for the sustenance of the population in Maranhão; however, despite its importance, the region faces environmental degradation problems due to rapid urban growth, such as deforestation of hillsides, intense exploitation of fishery resources, air and water pollution, siltation, dredging, and lack of sanitation. The objective was to investigate the environmental perception of riverside dwellers regarding the water quality of the middle Tocantins River through the application of structured questionnaires. The research was conducted between August and December 2023, with a sample universe of 50 respondents. Additionally, a multimethod approach was used to integrate quantitative and qualitative data. The affected population consisted of riverside families distributed among four questionnaire application points along the middle Tocantins River (P1: Beira Rio - urban area, P2: Bananal village, P3:

Embiral village, and P4: Cidelândia village). The majority of riverside dwellers involved in the study have been residing in the region for a significant period, predominantly over 10 years (88%). Furthermore, 34% of respondents consume and market native fish, while 62% use them only for their consumption, and 4% do not consume them. It is also important to highlight that 84% of participants claim not to have a sewage system in their homes. These data highlight the importance of fishery resources and river water for this population, emphasizing the need for measures to promote environmental conservation and access to basic sanitation services.
Keywords: Environment; Pollutants; Fishing resources.

PERCEPCIÓN AMBIENTAL DE LOS RIBERANOS SOBRE LA CONTAMINACIÓN Y LA CALIDAD DEL ÁGUA DEL MEDIO RÍO TOCANTINS, MARANHÃO

RESUMEN - El río Tocantins es esencial para el sustento de la población en Maranhão; sin embargo, a pesar de su importancia, la región enfrenta problemas de degradación ambiental debido al rápido crecimiento urbano, como deforestación de laderas, intensa explotación de recursos pesqueros, contaminación del aire y el agua, sedimentación, dragado y falta de saneamiento. El objetivo fue investigar la percepción ambiental de los habitantes ribereños con respecto a la calidad del agua del río Tocantins medio mediante la aplicación de cuestionarios estructurados. La investigación se llevó a cabo entre agosto y diciembre de 2023, con un universo muestral de 50 encuestados. Además, se utilizó un enfoque multimétodo para integrar datos cuantitativos y cualitativos. La población afectada consistió en familias ribereñas distribuidas entre cuatro puntos de aplicación de cuestionarios a lo largo del río Tocantins medio (P1: Beira Rio - área urbana, P2: aldea Bananal, P3: aldea Embiral y P4: aldea Cidelândia). Es evidente que la mayoría de los habitantes ribereños involucrados en el estudio han estado residiendo en la región durante un período significativo, predominantemente más de 10 años (88%). Además, el 34% de los encuestados consumen y comercializan pescado nativo, mientras que el 62% los utilizan solo para su consumo propio y el 4% no los consume. También es importante destacar que el 84% de los participantes afirman no tener un sistema de alcantarillado en sus hogares. Estos datos resaltan la importancia de los recursos pesqueros y del agua del río para esta población, enfatizando la necesidad de medidas para promover la conservación ambiental y el acceso a servicios básicos de saneamiento.

Palabras clave: Meio ambiente; Contaminantes; Recursos pesqueros.

INTRODUÇÃO

O rio Tocantins é um curso de água que atravessa os estados brasileiros do Maranhão, Tocantins e tem sua foz no Pará; por isto, também é nomeado de Araguaia-Tocantins. Esse corpo hídrico é o segundo maior totalmente brasileiro, possuindo 2.400 km de extensão, com potencial de geração de energia elétrica de aproximadamente 11.500 MW, a terceira maior do Brasil (Agência Nacional De Águas, 2020). Entretanto, esse rio vem enfrentando degradação ambiental, afetando diretamente as comunidades tradicionais que vivem no seu entorno, dentre elas, as comunidades ribeirinhas (SANTOS, 2019).

A água é o principal recurso natural renovável e com relevante interesse para manutenção da vida no planeta Terra, embora abundante, parte desse recurso apresenta parâmetros físico-químicos diferentes dos exigidos pelo Ministério da Saúde para o consumo da população e serviços agropecuários (RIBEIRO, 2017). Nesse sentido, a manutenção da qualidade da água torna-se fator preocupante devido ao rápido crescimento urbano nas proximidades dos cursos hídricos, resultando no acúmulo de poluentes (CHIDIAC, 2023).

A inexistência e precariedade do saneamento ambiental são motivos de preocupação mundial, sendo essencial para a manutenção da integridade ecológica, bem-estar e saúde humana, tendo sido incluída como meta da Agenda 2030 da Organização das Nações Unidas (ONU) (BRITO *et al.*, 2021). Diversos estudos têm observado situações em que efeitos adversos à saúde humana surgem em decorrência do consumo de peixes e frutos do mar contaminados por poluentes emergentes e algumas doenças conhecidas têm sido associadas a metais traços, como, por exemplo, os episódios recorrentes de intoxicação por mercúrio em áreas que houve exploração de minérios no Brasil (ALVARIÑO *et al.*, 2023; JOB *et al.*, 2023; RAKIB *et al.*, 2021; MILHOMEM *et al.*, 2016).

A contaminação humana por peixes ganha importância quando se considera a preferência dos ribeirinhos amazônicos por esta fonte proteica, em detrimento de outros tipos de alimentos (JUNIOR *et al.*, 2020). Para as comunidades ribeirinhas, os recursos pesqueiros representam uma importante fonte de proteína na dieta diária, devido à elevada disponibilidade de espécies aquáticas na região. De acordo com Corrêa *et al.* (2023), a principal fonte de contaminação por metais pesados, como mercúrio (Hg), chumbo (Pb) e cádmio (Cd) para humanos é através da ingestão de peixes e outros organismos aquáticos. Além disso, as comunidades ribeirinhas vivem em estreita conexão com o rio, utilizando de suas águas para rotina diária e até para consumo humano e animal.

O município de Imperatriz é o segundo município mais populoso do estado do Maranhão, possui 273.110 habitantes e área de 1.369.039 km², localizada na Região Nordeste, estendendo-se pela margem direita do rio Tocantins (IBGE, 2022). Diante desta proximidade, a população foi influenciada pelas atividades do rio em seu contexto social, econômico, cultural e ambiental. Sua percepção ambiental é de extrema importância, pois são os primeiros a notar qualquer mudança ou impacto que ocorra no ambiente em que vivem. A partir de seu conhecimento íntimo da região, suas percepções podem fornecer informações valiosas sobre problemas ambientais, como contaminação da água, poluição e mudanças nos ecossistemas locais (PARENTE, 2019).

Ao sensibilizar e educar as populações ribeirinhas, visa-se incentivar práticas sustentáveis e a proteção de rios brasileiros. É esperado que essas ações também estimulem o poder público e outras instituições a se envolverem no desenvolvimento de programas de conscientização e remediação, promovendo uma gestão ambiental mais eficaz e colaborativa. Em última análise, podem inspirar iniciativas similares em todo o Brasil, beneficiando a preservação dos recursos hídricos, a qualidade de vida das populações ribeirinhas e a saúde do ecossistema local (MATSUOKA, 2019). Nesse sentido, pode-se observar que os objetivos da agenda 21 buscam a promoção da sustentabilidade, incluindo a gestão sustentável (SCHIEBELBEIN, 2018).

> A elaboração da Agenda 21 foi um dos principais resultados deste encontro e definiu objetivos para a promoção do desenvolvimento sustentável dos assentamentos humanos, incluindo: proporcionar habitação adequada para todos; melhorar a gestão dos assentamentos humanos; promover o planejamento e a gestão sustentável do uso do solo; e promover a prestação integrada de infraestrutura ambiental, considerando os temas água, esgoto, drenagem e manejo de resíduos sólidos (SCHIEBELBEIN, 2018, p. 67).

As ações antrópicas têm modificado a dinâmica natural do meio ambiente e acelerado os impactos ambientais que causam o aceleramento dos processos que alteram as bacias hidrográficas e curso dos rios (COLOMBO *et al.*, 2019). Impactos negativos tem sido motivo de degradação físico-química como a diminuição do volume de água, contaminação das águas superficiais e subterrâneas, além disso, a água é fonte de consumo animal, humano, assim como turístico, além de ser importante para futuras gerações, exigindo assim dos governos e da população a preservação e conservação do recurso (RIBEIRO *et al.*, 2017).

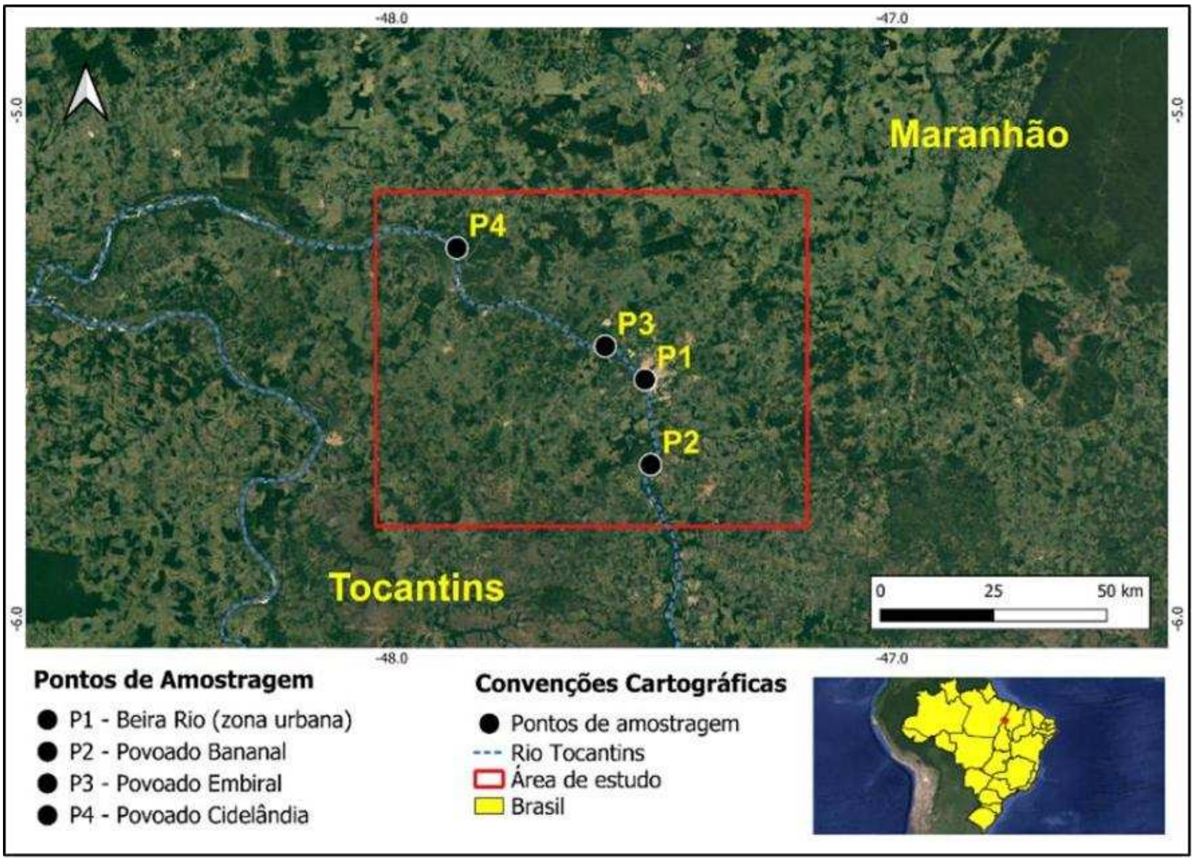
Este estudo socioambiental busca dar o primeiro passo para diagnóstico, entendimento e sensibilização da população ribeirinha sobre a poluição e qualidade das águas do médio rio Tocantins, no Maranhão. Mais especificamente, investigar a percepção ambiental dos ribeirinhos quanto à qualidade da água do médio rio Tocantins através da aplicação de questionários estruturados, sensibilizando-os e orientando-os quanto à conservação e recuperação do meio ambiente. Ao sensibilizar e educar as populações ribeirinhas, compreendemos a importância de incentivar práticas sustentáveis e a proteção de rios brasileiros.

METODOLOGIA

Caracterização da área de estudo

A pesquisa foi desenvolvida em trechos ao longo do médio rio Tocantins, localizados no município de Imperatriz e regiões circunvizinhas, com ribeirinhos residente dos trechos Beira Rio (zona urbana), povoado Bananal, povoado Embiral e povoado Cidelândia (Figura 1) pelo Núcleo de Estudos Morfofisiológicos Avançados (NEMO) da Universidade Estadual da Região Tocantina do Maranhão. A cidade de Imperatriz faz divisa com o estado do Tocantins e é margeada pelo rio Tocantins (IBGE, 2022). Salienta-se que, diante da proximidade dessa população com o rio, as pessoas foram influenciadas pelas atividades fluviais e incorporaram a vida ribeirinha em seu contexto social, econômico, cultural e ambiental.

Figura 1 - Pontos de aplicação do questionário de percepção ambiental aos ribeirinhos do médio Rio Tocantins, Maranhão.



Fonte: Autor (2024, p. 04).

A ocupação urbana nas proximidades e, consequentemente, as externalidades ambientais negativas desestruturam o ambiente e a ictiofauna aquática da região, resultando no desmatamento de encostas, exploração intensa de recursos pesqueiros, destruição de habitats, assoreamento e contaminação das águas do rio. Logo, atividades antrópicas acabam por elevar os níveis de degradação ambiental, alterando o equilíbrio do ecossistema e causando efeitos nocivos à população residente.

O primeiro ponto amostral (P1) no entorno do médio rio Tocantins fica cerca de 600 m de distância da Beira Rio, região potencialmente contaminada e urbanizada (Figura 2). É um local intensamente populado por comerciantes, turistas, pescadores ribeirinhos e cidadãos em busca de lazer às margens do rio. Além disso, a área conta com a presença de animais domésticos, embarcações, despejo de lixo e esgoto diretamente no corpo hídrico.

Figura 2 – Beira Rio (P1), primeiro ponto de aplicação dos questionários, com evidências de despejo de lixo e esgoto diretamente no corpo hídrico do rio, presença de animais, embarcações e ribeirinhos.

Fonte: Autor (2024, p. 05).

O segundo ponto de estudo (P2) está localizado no povoado Bananal, na Praia Talismã, a cerca de 30 km de distância de do município de Imperatriz (MA). É considerada uma área mais afastada do perímetro urbano, com algum fluxo de embarcações advindas de atividades pesqueiras (ribeirinhos) e de lazer (praia de rio) (Figura 3).

Figura 3 – Povoado Bananal (P2), segundo ponto de aplicação dos questionários, com a presença de ribeirinhos e embarcações nas imediações do médio rio Tocantins.

Fonte: Autor (2024, p. 06).

O terceiro local de aplicação de questionários (P3) é localizado no povoado Embiral, zona rural de Imperatriz e a cerca de 40 km de distância do município de Cidelândia (MA). Esta área é muito empregada para atividades de lazer no rio Tocantins (praias de rio e chácaras), além de atividades pesqueiras de ribeirinhos (Figura 4).

Figura 4 – Povoado Embiral (P3), terceiro ponto de aplicação dos questionários, com a presença de ribeirinhos e embarcações nas imediações do médio rio Tocantins.

Fonte: Autor (2024, p. 06).

O último ponto de aplicação dos questionários (P4) é localizado na região da Praia da Viração, que fica a 20 km de distância do centro do município de Cidelândia (MA). Este, pertence à zona rural de Imperatriz (MA) e concentra uma grande quantidade de ribeirinhos que dependem da água do rio para grande parte de suas atividades domésticas. É uma região considerada de destaque por apresentar intensa dragagem, atividade pesqueira e de lazer, o que pode contribuir para a contaminação dos recursos hídricos do rio Tocantins (Figura 5).

Figura 5 – Praia da Viração no povoado de Cidelândia (P4), quarto ponto de aplicação de questionários, com a presença de dragas em atividade e embarcações de ribeirinhos.

Fonte: Autor (2024, p. 07).

Procedimentos metodológicos

Aplicação de questionários sobre percepção ambiental dos ribeirinhos

A pesquisa foi realizada entre os meses de agosto e dezembro de 2023, contando com um universo amostral de 50 entrevistados. Foi utilizada uma abordagem multimétodo para a integração de dados quantitativos e qualitativos, a fim de obter informações complementares sobre o objeto de estudo (PINHEIRO *et al.*, 2008). O questionário foi constituído de 23 questões sobre a percepção dos entrevistados a respeito de qualidade/contaminação ambiental, recursos hídricos e pesqueiros, distribuídas entre questões fechadas (14) e abertas (9) (Quadro 1).

Quadro 1 - Questionário de percepção sobre poluição ambiental e qualidade da água do médio rio Tocantins, Maranhão.

Nome do entrevistado (a): Sexo: ( ) Feminino ( ) Masculino Idade: Nome da Região:
Nível de escolaridade: ( ) Ensino Fundamental incompleto ( ) Ensino Fundamental completo ( ) Ensin

médio incompleto ( ) Ensino médio completo ( ) Nível superior incompleto ( ) nível superior completo	
Tempo que reside no local: Número de pessoas que moram na casa:	
Qual sua ocupação/ profissão?	
Renda média mensal: ( ) Até um salário mínimo ( ) Até dois salários mínimos ( ) Acima de dois salários mínimos	
Possui rede de esgoto? ( ) Sim ( ) Não. Para onde vai o esgoto produzido na sua residência?	
1. Você usa a água do rio no seu cotidiano? Se sim, quais são os usos?	
2. Você sabe qual é o órgão responsável por fiscalizar e proteger o rio Tocantins e a área ao entorno?	
3. Em sua vivência na região, você considera que o rio Tocantins mudou ao longo do tempo? Quais foram as principais mudanças?	
4. Acredita que a água do rio Tocantins possa estar de alguma forma poluída?	
5. Na sua concepção, quais os principais impactos causados pela ação do homem ao rio Tocantins? () dragagem; ( ) poluição por sabão e combustível; ( ) urbanização; ( ) queimadas e ocupação indevida; ( ) lançamento de lixo e esgoto no rio; ( ) assoreamento e desmatamento; outros __________	
6. Quais ações de recuperação e preservação poderiam ser desenvolvidas no rio?	
7. Você consome ou comercializa os peixes do rio Tocantins? Consumo próprio? Se comercializa, onde? Quais as principais espécies (tipos de peixes)?	
8. O que você acha da qualidade da água do rio Tocantins da sua região? (aparência, cheiro, higiene, gosto etc) ( ) Muito boa; ( ) Boa; ( ) Razoável; ( ) Ruim; ( ) Muito ruim.	
Legenda para as questões 9 a 15: 1 – Discordo totalmente; 2 – Discordo; 3 – Nem discordo, nem concordo; 4 – Concordo; 5 - Concordo totalmente.	
9. Para você, a urbanização da região exerce influência na qualidade da água do rio?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
10. Considera que atividades próximas do rio (ou no rio) podem contribuir para a poluição e contaminação do rio Tocantins?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5

11. Você considera que o rio Tocantins está poluído?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
12. Você acredita que o uso da água do rio Tocantins pode veicular doenças?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
13. Está satisfeito com a qualidade da água do rio nesta região?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
14. Você considera a água desta região do rio imprópria para consumo?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
15. Você se considera satisfeito em morar na região onde vive?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
Legenda para as questões 16 a 20: 1 – Nunca; 2 – Pouco; 3 – Raramente; 4 – Muito, 5 – Sempre.	
16. Frequência que usa água do rio para beber. Se usa, faz algum tratamento antes de beber ou para cozinhar? Qual?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
17. Frequência que usa a água desta região do rio para atividades de recreação (banho, por exemplo).	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
18. Participa, ou já participou de algum programa/atividade desenvolvida com objetivo de conservar ou preservar a área na extensão do rio Tocantins?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
19. Frequência que consome peixes do rio Tocantins?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
20. Você utiliza a água do rio Tocantins para agricultura ou pecuária?	( ) 1 ( ) 2 ( ) 3 ( ) 4 ( ) 5
21. Se o rio deixar de existir (secar), o que iria interferir em sua vida? O que você faria para continuar suas atividades que dependiam da água do Rio?	
22. Você acredita que o rio se manterá para as gerações futuras de sua família (netos, bisnetos)?	
23. Que atividades sua você julga que pode fazer mal à qualidade do rio? Quais?	

Fonte: Autor (2024, p. 8).

Dentre as questões fechadas, analisadas por meio da estatística descritiva, doze (12) foram construídas segundo o modelo da escala de Likert, com cinco níveis de respostas, enquanto duas (2) foram em modelo simplificado. O objetivo é calcular a frequência percentual para cada alternativa de respostas. A escala de Likert consiste em uma série de afirmações ou itens aos quais os participantes respondem indicando seu nível de concordância, ou discordância (GÜNTHER, 2003). Essa escala, que varia de 'discordo totalmente' a 'concordo totalmente', com pontos intermediários, foi escolhida devido à sua capacidade de fornecer uma medida quantitativa das opiniões ou atitudes dos participantes. Isso permite uma análise mais detalhada e uma compreensão mais precisa das percepções da amostra em estudo.

Critérios de seleção dos participantes

Como critérios de inclusão na seleção dos participantes, foram aplicados questionários às pessoas que residiam nas proximidades das margens do rio Tocantins, com idade igual ou superior a 18 anos. A aplicação foi feita de maneira aleatória com os moradores presentes durante as entrevistas, buscando atingir principalmente a população que trabalhava com atividade pesqueira. Foi garantido o sigilo e confidencialidade dos entrevistados, que concordaram em participar voluntariamente da pesquisa, concordando com os objetivos do trabalho descritos no Termo de Consentimento Livre e Esclarecido (TCLE).

Constituição da amostra

A população atingida foi composta por famílias ribeirinhas, distribuídas pelos quatro pontos de aplicação do questionário. Os eixos das perguntas visavam obter informações sobre escolaridade, qualidade da água, fiscalização ambiental, espécies de peixes consumidas, percepção da poluição, alterações cronológicas e percepções futuras sobre o corpo hídrico.

RESULTADOS E DISCUSSÃO

Caraterização da população objeto de estudo

Foi realizado o levantamento do perfil dos ribeirinhos do médio rio Tocantins para caracterização da população, que posteriormente é analisada quanto à sua percepção ambiental. Os entrevistados apresentaram uma idade média de 44 anos, variando entre 18 e 82 anos, sendo 60% do sexo masculino e 40% do sexo feminino (Tabela 1). A grande maioria apresenta uma renda mensal familiar de até um salário mínimo (86%) e uma escolaridade até o ensino fundamental incompleto (42%), seguido pelo ensino médio completo (32%).

Tabela 1 - Perfil dos ribeirinhos entrevistados em pontos do médio Rio Tocantins, Maranhão.

Variável	Categoria	n (%)
Sexo	Feminino	20 (40%)
	Masculino	30 (60%)
	Fundamental incompleto	21 (8%)
	Fundamental completo	4 (42%)

Nível de escolaridade	Ensino médio incompleto	3 (6%)
	Ensino médio completo	16 (32%)
	Superior incompleto	6 (12%)
Tempo que reside no local	Menos de 01 ano	1 (2%)
	Entre 1 - 5 anos	3 (6%)
	Entre 6 - 10 anos	2 (4%)
	Acima de 10 anos	44 (88%)
Número de pessoas que moram na residência	Apenas 1 pessoa	4 (8%)
	Entre 2 – 5 pessoas	42 (84%)
	Acima de 6 pessoas	4 (8%)
Profissão	Autônomo (a)	9 (18%)
	Dona de casa	6 (12%)
	Pescador (a)	18 (36%)
	Outras	17 (34%)
Renda média mensal	Até um salário mínimo	43 (86%)
	Até dois salários mínimos	7 (14%)
Possui rede de esgoto	Sim	8 (16%)
	Não	42 (84%)

Fonte: Autor (2024, p. 10).

Percebe-se que a maioria dos ribeirinhos envolvidos no estudo reside na região há um período significativo, predominantemente acima de 10 anos (88%) (Tabela 1). Esse dado é relevante, pois indica uma ligação duradoura dessas comunidades com o meio ambiente local. A longa permanência na região pode ter impactos significativos na percepção ambiental dos habitantes, no conhecimento adquirido sobre os recursos naturais e na relação das comunidades com o rio Tocantins ao longo do tempo. Essa conexão prolongada pode influenciar as atitudes, práticas e perspectivas das comunidades ribeirinhas em relação ao ambiente ao seu redor.

A ocupação profissional "Pescador" foi a mais citada no estudo, representando a significativa parcela de 36% (Tabela 1). Estes ribeirinhos são os cidadãos que residem nas proximidades do rio e dependem diretamente dele para sustento e segurança alimentar da família. Outras profissões citadas foram "Autônomo (a)", "Dona de casa", "Garçom", "Lavrador", "Estudante", "Zelador" e "Aposentado (a)". Isso, revela uma grande diversidade de atividades para geração de renda, sendo, eles, os principais atores envolvidos no estudo, e suas percepções e ações são fundamentais para o sucesso das atividades socioambientais propostas. Afinal, a percepção pode ser julgada como algo seletivo que está vulnerável a uma série de quesitos como os significados, as memórias e as experiências vividas pelo sujeito sobre aquele objeto (PINTO *et al.*, 2016).

A ausência e precariedade das condições de saneamento ambiental representam uma preocupação mundial, tendo sido alvo de discussões e incluída como meta da Agenda 2030 da ONU (BRITO *et al.*, 2021). Neste contexto, 8 entrevistados (16%) informaram possuir em sua residência rede de esgoto, enquanto 42 entrevistados (84%) afirmaram não possuir (Tabela 1). Quando questionados a respeito do tipo de estrutura de saneamento, foram citadas as seguintes situações: fossa séptica (6%), céu aberto (6%), CAEMA (Companhia de Saneamento Ambiental do Maranhão) (2%), despejo de esgoto direto no rio (70%) ou não souberam informar (16%). Nesse sentido, observa-se que existe ineficiência no sistema de coleta de esgoto da região, corroborando com Silva (2022) que relatou que 440 bilhões de litros de esgoto são derramados nos cursos de água do estado do Maranhão, e que a cidade de Imperatriz possui índice de 70,8% em relação à falta de sistema de coleta de esgoto.

Percepção ambiental sobre a qualidade da água do médio rio Tocantins da população objeto de estudo

Dentre os ribeirinhos entrevistados, a grande maioria utiliza a água do rio em seu cotidiano (94%), seja para uso doméstico (56%), recreativo (15%) ou geração de renda (26%). Salienta-se que o uso doméstico envolve desde cozinhar, beber, tomar banho até lavar roupa; o que é uma preocupação, afinal, a população despeja diretamente no rio grande quantidade de lixo e esgoto doméstico. A ONU reconhece que o direito à água é interdependente com outros direitos, uma vez que a escassez ou precariedade desse recurso impacta diretamente a saúde e a qualidade de vida do cidadão (BRITO *et al.*, 2021).

Na questão 02, os entrevistados foram questionados: “Você sabe qual é o órgão responsável por fiscalizar e proteger o rio Tocantins e a área ao entorno?”. A maioria respondeu que não sabe informar (56%), enquanto alguns órgãos governamentais foram citados: IBAMA (14%), Marinha (28%) e Defesa Civil (2%). O Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis (IBAMA) desempenha diversas funções essenciais para a proteção e preservação do meio ambiente no Brasil, incluindo fiscalização e controle ambiental, gestão de unidades de conservação, licenciamento ambiental e educação ambiental/conscientização pública.

Para Fernandes *et al.* (2019) e Nascimento *et al.* (2021), a ausência de informações ambientais e políticas de conscientização popular são prejudiciais ao bem comum. Logo, para que a educação ambiental colabore na conscientização e formação de um novo cidadão, os princípios de uma ação ambiental educativa devem ser respeitados. Estes princípios são participação, pensamento crítico-reflexivo, ecologia de saberes, conscientização, coletividade, responsabilidade, continuidade, igualdade, emancipação e transformação social (GONZALEZ *et al.*, 2007).

Na percepção da maioria dos ribeirinhos entrevistados, o médio rio Tocantins está de alguma forma poluído (84%). Além disso, em resposta à questão 03 “Em sua vivência na região, você considera que o rio Tocantins mudou ao longo do tempo?” a maioria dos entrevistados observa mudanças no rio ao longo dos anos, sobretudo aqueles que residem nas regiões estudadas há mais de 10 anos (88%). Dentre as mudanças mais citadas, estão diminuição no nível do rio (seca), menor quantidade de peixes (principalmente, no período sem chuvas) e água poluída (Tabela 2).

Tabela 2 − Problemas de qualidade ambiental percebidos pelos ribeirinhos de trechos do médio rio Tocantins, Maranhão.

Ponto de estudo	Quais foram as principais mudanças observadas no rio Tocantins ao longo do tempo?	Quais os principais impactos causados pela ação do homem ao rio Tocantins?
Beira rio (zona urbana)	Diminuição do nível do rio; assoreamento do rio; maior temperatura da água; menor quantidade peixes; água poluída	Lançamento de lixo e esgoto no rio; urbanização e assoreamento
Povoado Bananal	Diminuição do nível do rio; água poluída	Lançamento de lixo e esgoto no rio; assoreamento e desmatamento
Povoado Embiral	Diminuição do nível do rio; Menor quantidade peixes	Lançamento de lixo e esgoto no rio; barragem do rio pela represa de Estreito, Maranhão
Povoado Cidelândia	Diminuição do nível do rio; água poluída	Lançamento de lixo e esgoto no rio

Fonte: Autor (2024, p. 12).

O entrevistado 37 diz "o rio mudou muito, nos últimos tempos a água tá poluída, o rio mais seco e a cidade mais quente". Em complemento, os impactos causados pelo homem ao rio Tocantins citados foram "Lançamento de lixo e esgoto no rio" (50%), "Urbanização" (30%), "Assoreamento e desmatamento" (14%), "Barragem" (2%), "Dragagem" (2%) e não sabe informar (2%). Esses dados são valiosos para o desenvolvimento de políticas públicas, programas de conservação ambiental e a implementação de práticas sustentáveis. Além disso, entender a percepção ambiental das comunidades locais é crucial para promover a participação ativa dessas comunidades na gestão e preservação do meio ambiente.

Na questão 06, quando questionados "Quais ações de recuperação e preservação poderiam ser desenvolvidas no rio?" as mais citadas foram "Não jogar lixo e esgoto no rio" (34%), "Tratamento de esgoto" (18%), "Fiscalização e conscientização" (12%) e "Evitar desmatamento" (8%); enquanto, 8% citaram outras opções (coleta de lixo, proibir uso de dragas para retirada de areia e implementação de políticas públicas de apoio) e 20% não souberam informar (Tabela 2). Braga *et al.* (2023) também observou uma grande diversidade de respostas no que tange às propostas sugeridas pela população para melhorar a qualidade do rio, com destaque para os atos de fiscalizar e conscientizar por meio de ações de Educação Ambiental. Os autores reforçam a importância da própria comunidade se mobilizar para que as melhorias ocorram e reflitam em seu cotidiano.

Frisa-se que a descarga de esgoto não tratado diretamente no rio pode comprometer a biota e a qualidade da água (SOUZA, 2014), tanto para fins domésticos como geração de renda. Pádua (2021) afirma que o lançamento de esgotos não tratados impacta seriamente o corpo receptor, podendo causar diminuição no nível do oxigênio dissolvido, intensificação de eutrofização e mudanças na biota aquática. Assim, a relação entre a qualidade da água do rio e a subsistência socioeconômica dos ribeirinhos é interdependente; e, a degradação ambiental pode ter impactos diretos na renda familiar destas pessoas (ADGER, 2006).

> O Art. 3º da Resolução n.º 430/2011, do Conselho Nacional do Meio Ambiente (CONAMA), institui que os efluentes de qualquer fonte poluidora somente poderão ser lançados, direta ou indiretamente, em corpos de água, após o devido tratamento e apenas após obedecer às condições, padrões e exigências dispostos na referida Resolução (BRASIL, 2011, p. 01).

Na questão 07, os entrevistados foram questionados sobre o consumo e comercialização de peixes nativos do rio Tocantins, e foi observado que 34% consomem e comercializam, 62% usam apenas para consumo próprio e 4% não consomem. As famílias de pescadores ribeirinhos da região de Imperatriz (Maranhão) têm o pescado como principal fonte proteica na alimentação, se alimentando de espécies predadoras e não predadoras (FILHO *et al.*, 2016). Neste estudo de percepção, as principais espécies consumidas e comercializadas são Avoador (*Brycon pesu*) (citado por 62% dos entrevistados), Branquinha (50%) (*Psectrogaster amazonica*), Tambaqui (26%) (*Abramitis hypselonotus*), Curimatá (18%) (*Prochilodus nigricans*), Tucunaré (16%) (*Cichla kelberi*), Mapará (14%) (*Hypophthtalmus marginatus*) e Sardinha (12%) (*Lycengraulis batesii*).

Quando questionados quanto a qualidade da água do rio na sua região, a maioria considera "Boa" (44%), seguido por "Razoável" (26%), "Ruim" (14%) e "Muito boa" (16%). Porém, caso essa qualidade deteriore ao longo dos anos, 87,5% informam que não teriam condições de continuar na região, pois a renda familiar seria totalmente prejudicada. O entrevistado 39 diz "Não teria opção, ficaria sem trabalho e até sem água para beber". Esta abordagem de percepção ambiental se faz necessária para identificar e compreender questões socioambientais, sendo o primeiro passo para o diagnóstico, conscientização e ação sustentável.

Frequência de respostas como ferramenta de percepção ambiental da população objeto de estudo

Os ribeirinhos afirmam que a urbanização da região exerce influência na qualidade da água do médio rio Tocantins, uma vez que 46% concordam e 42% concordam totalmente com o questionamento (Tabela 3). Além disso, a grande maioria também concorda que atividades próximas ao rio (ou no rio) podem contribuir para a poluição e contaminação do rio (34% concordam e 46% concordam totalmente). Quando questionados sobre a possível poluição do rio, 48% dos entrevistados concordam totalmente, indicando uma preocupação significativa com a qualidade da água. Essa percepção pode ser reflexo das condições ambientais observadas na região.

Tabela 3 - Frequência de respostas dos entrevistados sobre aspectos relacionados a urbanização, poluição da água do rio, veiculação de doenças por meio hídrico e satisfação de moradia.

Perguntas	**Frequência de resposta dos entrevistados**				
	1	**2**	**3**	**4**	**5**
Para você, a urbanização da região exerce influência na qualidade da água do rio?	2%	-	10%	46%	42%
Considera que atividades próximas do rio (ou no rio) podem contribuir para a poluição e contaminação do rio Tocantins?	2%	6%	12%	34%	46%
Você considera que o rio Tocantins está poluído?	14%	8%	16%	14%	48%
Você acredita que o uso da água do rio Tocantins pode veicular doenças?	14%	6%	18%	28%	34%
Está satisfeito com a qualidade da água do rio nesta região?	10%	14%	36%	28%	12%
Você considera a água desta região do rio imprópria para consumo?	56%	12%	-	8%	24%
Você se considera satisfeito em morar na região onde vive?	-	2%	10%	62%	26%

1 – Discordo totalmente; 2 – Discordo; 3 – Nem discordo, nem concordo; 4 – Concordo; 5 - Concordo totalmente. **Fonte:** Autor (2023, p. 14).

Quando o foco se volta para a segurança sanitária, 36% dos entrevistados expressam uma posição neutra em relação à possibilidade de a água do rio Tocantins veicular doenças. Essa resposta indica uma considerável parcela da população que não concorda nem discorda, sugerindo uma incerteza ou falta de informação sobre os riscos associados ao uso de água contaminada. Surpreendentemente, apesar das preocupações com a possível poluição, 56% dos entrevistados discordam totalmente que a água da região seja imprópria para consumo. Essa aparente contradição pode sugerir uma desconexão entre a percepção e a realidade, destacando a importância da conscientização e educação ambiental. Um impressionante percentual de 88% dos entrevistados concorda ou concorda totalmente que estão satisfeitos em viver na região. A alta satisfação das respostas pode ser atribuída a diversos fatores, como a beleza natural da região, a comunidade local ou outros elementos positivos que superam as preocupações ambientais.

O uso da água do médio rio Tocantins para atender às necessidades dos ribeirinhos é uma preocupação constante, pois pode expor essas famílias a contaminantes e microrganismos presentes em águas poluídas (OLIVEIRA, 2019). Em estudo realizado nos mesmos locais de coleta, verificou-se que os níveis de alumínio, cobre, ferro, magnésio e selênio na água excederam os padrões legais (ACIOLY et al., 2024). Notadamente, a região urbanizada (P1) apresentou concentrações elevadas de nitrogênio, levantando sérias preocupações sobre a qualidade da água para consumo direto. A análise dos sedimentos desses mesmos pontos de coleta revelou que os níveis de cromo, níquel, cobre, zinco e chumbo ultrapassaram os limites estabelecidos por diretrizes ambientais, sendo que os maiores valores foram encontrados na região urbanizada (P1) para alumínio e no povoado Embiral (P3) para níquel e chumbo (MACHADO DA SILVA ACIOLY et al., 2024). Além disso, há a possibilidade de ocorrência de *Salmonella spp.*, agente causador da salmonelose, um dos principais patógenos transmitidos pelo consumo de água contaminada (MENDONÇA, 2023). Esses fatores configuram um risco significativo, sobretudo porque 18% dos participantes e suas famílias relataram utilizar a água do rio como única fonte para consumo, incluindo a ingestão direta (Tabela 4).

Tabela 4 - Frequência de respostas dos entrevistados sobre aspectos relacionados a participação em atividades de conservação, percepção futuras sobre o corpo hídrico e atividades poluidoras.

Perguntas	**Frequência de resposta dos entrevistados**				
	1	**2**	**3**	**4**	**5**
Frequência que usa água do rio para beber. Se usa, faz algum tratamento antes de beber ou cozinhar?	80%	2%	-	-	18%
Frequência que usa água desta região do rio para atividade de recreação (banho, por exemplo)?	2%	8%	10%	44%	36%
Participa ou já participou de algum programa/ atividade desenvolvida com o objetivo de conservar ou preservar o rio Tocantins?	92%	4%	2%	-	2%
Frequência que consome peixes do rio Tocantins?	10%	6%	8%	20%	28%
Você utiliza a água do rio Tocantins para agricultura ou pecuária?	86%	-	4%	-	10%

1 – Nunca; 2 – Pouco; 3 – Raramente; 4 – Muito, 5 – Sempre. **Fonte:** Autor (2023, p. 15).

Quando se trata do uso da água para atividades recreativas, como o banho, a frequência é notável. Um expressivo percentual de 44% dos entrevistados afirma utilizar a água desta região do rio Tocantins com muita frequência, enquanto 36% a utilizam sempre para tais atividades; destacando a importância do rio não apenas como fonte de recursos, mas também como espaço de lazer. Apesar desta relação complexa e multifacetada, a pesquisa indica que a grande maioria (92%), nunca participou ou atualmente não participa de programas ou atividades voltadas para a conservação e preservação do rio Tocantins (Tabela 4).

Quanto ao consumo de peixes provenientes do rio Tocantins, observa-se que existe uma relação ativa entre população local e recursos naturais. A maioria dos entrevistados consome peixes nativos do rio, sendo que 20% afirmam fazê-lo com muita frequência e 28% sempre. Esses dados correspondem com Milhomem et al. (2016), que dos 59 ribeirinhos entrevistados, 90% consumiam mais que 2 refeições, e mais de 60% ingeriam acima de 4 refeições de pescado por semana. Ainda nesse estudo, as concentrações de mercúrio (Hg) nos peixes mais consumidos estavam normais, mas, considerando que esse metal está envolvido com doenças neurológicas nos humanos, e, em outras regiões, como no Pará e em Rondônia, foram encontrados níveis anormais, isso evidencia a importância do monitoramento constante da ictiofauna. Ademais, 10% responderam que usam água do rio com frequência para atividades agrícolas ou pecuárias, revelando a importância do monitoramento da qualidade desse recurso hídrico.

Durante as entrevistas, o cenário hipotético de futuramente o médio rio Tocantins deixar de existir, seja devido à seca ou a qualquer outra razão, levantou reflexões profundas sobre a interdependência entre as comunidades locais e os recursos hídricos. Para um significativo percentual de 32% dos entrevistados, a perspectiva de ficar sem renda é uma preocupação iminente, enquanto 28% temem ficar sem água tanto para uso doméstico quanto para consumo e outros 10% indicaram disposição para mudar de cidade em busca de melhores condições de vida. Apesar disso, 84% dos ribeirinhos acreditam que o rio se manterá para as gerações futuras de sua família (netos, bisnetos) (questão 22).

A última questão da pesquisa (questão 23) buscou promover um pensamento crítico- reflexivo ao entrevistado, ao abordar possíveis atividades humanas que podem ter impactos negativos na qualidade do rio Tocantins. A maioria expressiva, representada por 52%, identifica a combinação de jogar lixo e esgoto como uma atividade que pode ser prejudicial à qualidade do rio, enquanto 10% citaram o desmatamento. É notável a discrepância entre o conhecimento e o comportamento, visto que alguns entrevistados estão cientes das atividades prejudiciais à qualidade do rio Tocantins, como o descarte inadequado de lixo e esgoto, enquanto simultaneamente admitem que realizam tal prática.

Além disso, fatores como a percepção da qualidade da água do rio e o tempo em que os moradores residem na região podem ser correlacionados. Nesse sentido, 18% dos entrevistados com tempo de residência entre 21 a 40 anos na região concordam totalmente que a água do rio está poluída e 16% com 41 a 60 anos de residência também concorda com está afirmação. Quanto os moradores com mais de 60 anos na região somente concordam que o rio está poluído 2% e as pessoas com moradia entre 1 e 20 anos discordam totalmente que a água não está poluída (Tabela 5).

Tabela 5. Relação entre o tempo de residência e qualidade da água do médio rio Tocantins, Maranhão.

Tempo de residência na região (em anos)	**Frequência de resposta sobre a pergunta: "Você considera que o rio Tocantins está poluído?"**				
	1	**2**	**3**	**4**	**5**
Entre 1 – 20 (13)	3 (23,08%)	1 (7,69%)	2 (15,38%)	-	7 (53,85%)
Entre 21 – 40 (22)	2 (9,09%)	2 (9,09%)	4 (18,18%)	5 (22,73%)	9 (40,91%)
Entre 41 – 60 (14)	2 (14,29%)	1 (7,14%)	2 (14,29%)	1 (7,14%)	8 (57,14%)
Acima de 60 anos (1)	-	-	-	1 (100%)	-

1 – Discordo totalmente; 2 – Discordo; 3 – Nem discordo, nem concordo; 4 – Concordo; 5 - Concordo totalmente. **Fonte:** Autor (2023, p. 17).

CONCLUSÕES

A ausência e precariedade das condições de saneamento ambiental é preocupante, visto que a maioria dos entrevistados diz não possuir rede de esgoto, além de despejar os resíduos domésticos do esgoto diretamente no rio. Apesar de quase todos os entrevistados indicarem utilizar a mesma água para uso doméstico, que inclui tomar banho, lavar roupas ou até beber.

Embora os residentes indiquem perturbações na qualidade da água do rio, a expressiva maioria dos entrevistados, nunca participou ou atualmente não participa de programas, ou atividades voltadas para a conservação e preservação do rio Tocantins. Desta forma, revela-se uma lacuna na conscientização ambiental e na participação da comunidade em iniciativas de proteção ambiental, ressaltando a necessidade de promover programas educativos e de engajamento.

A maioria dos entrevistados consome peixes nativos do rio, com muita frequência ou sempre. Enquanto, alguns participantes e suas famílias utilizam da água do rio para beber sempre, sendo esta a única fonte disponível. Isso evidencia a importância do rio e seus recursos pesqueiros para a subsistência das famílias ribeirinhas da região.

Os principais impactos causados pelo homem ao rio Tocantins percebidos foram urbanização, lançamento de lixo e esgoto no rio; enquanto, as ações de recuperação e preservação mais recomendadas pelos ribeirinhos foram não jogar lixo e esgoto no rio, realizar tratamento de esgoto e maior fiscalização e conscientização. Espera-se que essas ações também estimulem o poder público e outras instituições a se envolverem no desenvolvimento de programas de conscientização e remediação, promovendo uma gestão ambiental mais eficaz e colaborativa.

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Thiago Machado da Silva Acioly – conceitualização, metodologia, curadoria de dados, análise formal, investigação, validação, redação do rascunho original, revisão e edição; Matheus Bilio Alves – revisão do texto; Letícia Almeida Barbosa – investigação; Marcelo Francisco da Silva – visualização e metodologia; José Iannacone – validação e revisão do texto; Diego Carvalho Viana – recursos, supervisão, administração do projeto e validação.

DECLARAÇÃO DE CONFLITO DE INTERESSES

Os autores declaram que não possuem interesses financeiros concorrentes ou relações pessoais que possam ter influenciado o trabalho relatado neste artigo.

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CAPÍTULO 3 – NÍVEIS DE ELEMENTOS POTENCIALMENTE TÓXICOS E ESSENCIAIS NA ÁGUA E ESTIMATIVA DOS RISCOS À SAÚDE HUMANA EM UM RIO LOCALIZADO NA INTERFACE ENTRE OS BIOMAS CERRADO E AMAZÔNICO (RIO TOCANTINS)

DESTAQUES

- Fontes industriais podem adicionar elementos tóxicos, ressaltando a importância do tratamento de águas residuais.
- O alumínio excede os padrões; elementos essenciais levantam preocupações ambientais e de saúde.
- Elementos químicos, principalmente Al, Fe, Cu e Mg, apresentaram variação sazonal.
- Avaliações de risco à saúde para Al, Cu, Fe, Mg e Se não indicam risco.

Acioly, T.M.d.S.; da Silva, M.F.; Barbosa, L.A.; Iannacone, J.; Viana, D.C. Levels of potentially toxic and essential elements in water and estimation of human health risks in a river located at the interface of brazilian savanna and amazon biomes (Tocantins River). **Toxics**, v. 12, n. 7, p. 444, 2024. https://doi.org/10.3390/toxics12070444

LEVELS OF POTENTIALLY TOXIC AND ESSENTIAL ELEMENTS IN WATER AND ESTIMATION OF HUMAN HEALTH RISKS IN A RIVER LOCATED AT THE INTERFACE OF BRAZILIAN SAVANNA AND AMAZON BIOMES (TOCANTINS RIVER)

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Abstract - The Tocantins–Araguaia basin is one of South America's largest river systems, across three Brazilian states (Maranhão, Tocantins, and Pará), within the Legal Amazon region. Despite draining extensive Cerrado savanna and rainforest ecosystems, it has suffered significant degradation, notably in the past 40 years. Human activities, including agricultural expansion, deforestation, and the introduction of non-native species, have worsened the environmental damage, which is alarming since many residents and villages along the middle Tocantins River rely on it for water supply, recreation, and fishing. This study assessed the concentration of potentially toxic and essential elements in water samples from four sampling sites distributed along the middle Tocantins River. The monitoring occurred throughout 2023, involving the measurement of parameters both on-site and in the laboratory. Water quality and its health implications were evaluated using the Weighted Arithmetic Water Quality Index (WAWQI), the Water Quality Index (WQI), and the health risk assessment index. The levels of aluminum, copper, iron, magnesium, and selenium exceeded legal standards. Seasonal fluctuations indicate a complex dynamic influenced by climatic or seasonal factors, with February showing the highest values. Site P1, located in urban areas, exhibited elevated mean concentrations for conductivity, total dissolved solids (TDS), and chlorophyll, indicating the need for continuous monitoring. The nitrogen concentrations at P1 raise concerns regarding drinking water quality, which is a concern for the region's residents who use untreated river water. Despite seasonal variations in element concentrations, the overall WAWQI categorized all sections as "Excellent," and the WQI rated as "Good." Human health risk assessments detected no risks, but continuous monitoring and interventions are crucial for sustained water quality improvement.

Keywords: biomonitoring; drinking water quality; environmental quality; pollutant; heavy metals

1. INTRODUCTION

Contaminated water poses significant risks to human health, leading to waterborne diseases and impacting communities and healthcare systems. Access to clean and safe water directly correlates with improved global health indicators [1,2]. Despite efforts to expand access to clean drinking water, millions of people around the world still suffer from preventable illnesses due to contamination, emphasizing water's critical role in sustaining human health [3]. Consequently, the declining water quality not only affects the environment but also imposes substantial economic and public health burdens [4,5].

Anthropogenic impacts on aquatic ecosystems stem from diverse sources, including industrial, urban, agricultural, and mining pollution [6,7]. Human interventions, such as dam construction, salinization, deforestation-driven sedimentation, riparian vegetation clearance, and intensive fishery exploitation, further exacerbate this imbalance [8]. Consequently, contaminants from these activities disrupt the ecosystem equilibrium when introduced into aquatic environments. Notably, approximately 80% of infections in low- income and developing countries are directly attributable to contaminated drinking water and unhygienic settings [9]. Potentially toxic and essential elements, sourced from domestic, agricultural, and industrial waste, pose hazards to humans, marine life, and the environment [10]. Heavy metal pollution, particularly prevalent in developing countries, is a global concern affecting rivers worldwide [11–13].

Nitrogenous compounds such as total ammoniacal nitrogen ($NH_3^{-}NH_4^{+}$) from agri- cultural and industrial effluents significantly contribute to groundwater pollution [14,15]. Understanding these processes is crucial for effective water resource management and the implementation of preventive measures to mitigate pollution impacts. Nitrogen exists in water in various forms, and careful monitoring of its levels is crucial due to the potential for excess. Elevated ammonium levels, often resulting from excessive wastewater-based chemical usage, have been associated with eutrophication [16]. This condition increases water purification costs, stimulates algal growth, poses health risks to humans and live- stock, diminishes the recreational value of water bodies, causes objectionable changes in aquatic environments, and leads to oxygen depletion [17–19].

After persistent pollutants are released into the environment, they can accumulate in various environmental compartments, such as water, sediment, and biota, in different chemical forms, posing a threat to human health through multiple absorption pathways [20,21]. These pathways for human exposure to contaminants include the soil–food chain, skin contact, inhalation, and oral intake. Excessive dietary accumulation of potentially toxic elements in the human body can lead to severe systemic health problems [22,23], emphasizing the importance of addressing this type of contamination and its associated health risks.

Water quality monitoring typically generates a large and intricate database that includes biological, physical, and chemical variables, making it challenging to manage [24]. To address this complexity, the suitability of water sources for human consumption has been assessed using the Water Quality Index (WQI), which is considered an effective form of characterizing water quality. Water quality assessment employs various methods, with the Weighted Arithmetic Water Quality Index (WAWQI) and the Water Quality Index (WQI) standing out as prominent examples of multiple objective decision-making methods [25,26]. The WQI offers a simplified approach but may not fully capture all nuances of water quality. In contrast, the WAWQI enables a more detailed and customized assessment by assigning weights to parameters based on their relative importance to water quality and human health [27,28]. This approach can provide a more accurate and specific assessment of water quality by considering the relative importance of each parameter.

Among the largest river systems in South America, the Tocantins–Araguaia basin stands out due to its extensive drainage area of 767.000 km^2, traversing three Brazilian states (Maranhão, Tocantins, and Pará) and falling within the Legal Amazon region [29,30]. Additionally, this river's ichthyofauna is highly diverse, comprising approximately 300 species, 126 genera, and 34 families, primarily Characiformes (order), Siluriformes (order), and Cichlids (family) [31]. Although the Araguaia–Tocantins basin is not directly connected to the Amazon River, it shares an estuarine region with it [32]. This basin drains a vast area of the Cerrado savanna and rainforest ecosystems, known for their large and biodiverse floodplains [33]. However, this basin has experienced significant degradation, particularly over the last 40 years, primarily due to the expansion of dams, croplands, irrigation, mining, and aquaculture [33].

The middle Tocantins River region has seen a surge in various human activities, from agricultural expansion to deforestation, along with the introduction of non-native species, exacerbating environmental degradation. Around 32.244 individuals (12% of the population) lack access to clean water at home, while a staggering 181.533 lack a sewage system (69.83%) [34]. Due to this shortfall, many residents dispose of domestic waste directly into the river. Despite using the same untreated water for essential tasks such as bathing, laundry, and even consumption, the absence of proper sanitation facilities poses significant health risks. In many rural or low-income areas, people place pumps on the riverbanks to draw untreated water, exposing individuals to chemical and biological contaminants. This degrades water quality and increases disease risks for those dependent on the river, highlighting the necessity of appropriate mitigation measures to protect public health.

Starting in the 1970s and 1980s, population growth and waste accumulation began to degrade the quality of streams that traverse the city and feed into the Tocantins River [35]. For example, the Bacuri stream lacks proper banks, causing houses to be built in the water and leading to unsanitary conditions as household waste, especially from bathrooms and kitchens, is dumped directly into the stream, turning it into an open sewer [36]. This stream has shown concentrations of metals such as Cu, Pb, Fe, and Cr exceeding national standards, indicating that these elements are being carried to the Tocantins River as suspended particulate matter [37]. It is worth noting that fish sourced from the Tocantins River, near Imperatriz city, serve as a primary protein source for riverside dwellers, albeit with observed mercury concentrations averaging 0.2775 µg/g for dogfish and 0.1360 µg/g for mapará [38]. Many riverside residents in the region and neighboring villages depend on the waters of the

Tocantins River for direct household water supply, recreational purposes (bathing), and artisanal fishing for family consumption and/or commercialization.

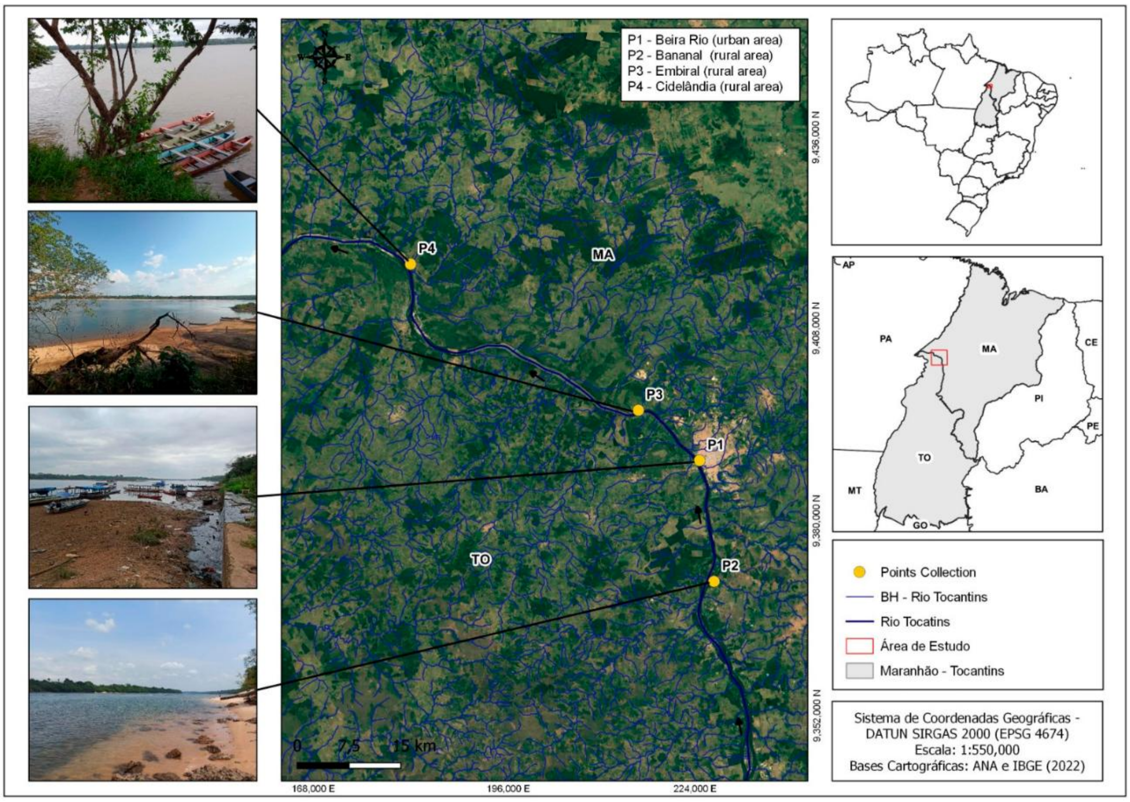
The information gaps this study seeks to fill revolve around the lack of comprehensive studies and environmental monitoring in the middle Tocantins River. Essentially, this study assessed the concentration of potentially toxic and essential elements in water samples from this region. Additionally, it investigated various physicochemical parameters related to water quality (air and river water temperature, chlorophyll, total dissolved solids, pH, turbidity, conductivity, oxidation–reduction potential, luminescent dissolved oxygen, and salinity) and the presence of nitrogenous compounds (NH_4^+, NO_2, and NO_3^-). The quality of water and its impacts on human health were also evaluated using the Weighted Arithmetic Water Quality Index (WAWQI), the Water Quality Index (WQI), and the health risk assessment index. The environmental fragility of the middle Tocantins River under- scores the urgency for increased attention to environmental monitoring in this vital aquatic ecosystem.

2. MATERIALS AND METHODS

2.1.Study Area and Sampling

This research was conducted in the middle Tocantins River, within the Imperatriz area of influence (Maranhão, Brazil) (Figure 1). This region holds strategic importance both regionally and nationally as a key transportation hub and gateway to the Amazon. Its thriving agribusiness and industrial sectors drive economic growth, providing employment and fostering development. The municipality serves as the headquarters of the southwestern metropolitan region of the state (5°31′32″ S; 47°26′35″ W) and stretches along the right bank (South-North) of the Tocantins River. The precipitation and temperature data in the region throughout the year are depicted in Figure S1. This allows for the identification of the rainiest/coldest period (Janury to June) and the hot/dry season (July to December) [39].

Figure 1. Location, main characteristics, and geographic coordinates of the sampling sites in the middle Tocantins River, Maranhão, Brazil. P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area).



The level of inorganic contamination was monitored from January to December 2023 by measuring parameters both in situ and in the laboratory and collecting water samples from different sections of the middle Tocantins River. Four sampling sites were established, each with GPS georeferencing (Figure 1). Water samples were collected monthly, with three repetitions in each section, totaling 121,000 mL polyethylene containers that had been previously prepared and washed with milli-Q water. The samples were collected at a depth of 1.5–2 m, with a distance from the riverbanks of 5–10 m and 100 m between repetitions. The river had an average depth of 30 m, an average width of 500 m, and a flow volume of 13,600 m^3/s. After being collected with the assistance of the Center for Advanced Morphophysiological Studies (NEMO), the containers were labeled and refrigerated at 4 °C until they reached the laboratory.

The first sampling site (P1) was in front of "Beira Rio", an urbanized and recreational area, and was susceptible to contamination due to factors such as heavy vessel traffic, river beaches, solid waste disposal, and urban sewage input. Conversely, the second sampling site (P2), known as "Ribeirãozinho", is situated farther from the city (30 km) and was expected to exhibit a lower contaminant potential. The third site (P3) is situated upstream of the paper mill manufacturing plant, 20 km from the city in another direction, which could be a possible contamination source.

Lastly, the fourth sampling site (P4), “Praia da Viração”, located approximately 100 km downstream from the city, is situated in the Cidelândia village and is affected by industrial activities, particularly from the paper and cellulose industry.

The region grapples with challenges such as deforestation driven by agricultural expansion, monoculture cultivation (e.g., Eucalyptus), and sanitation issues due to urbanization. These activities collectively degrade water quality, impacting ecological health and community well-being. Deforestation leads to increased soil erosion and sedimentation, resulting in water turbidity and pollutant introduction. Urbanization causes runoff from impermeable surfaces, carrying pollutants such as oils, heavy metals, and nutrients into water bodies. The Tocantins–Araguaia basin is currently the most targeted area for expanding agricultural activities, as stated in Presidential Decree 8447 of 2015, which created the MATOPIBA Federal Plan for the Development of the Brazilian Cerrado. Data from 2019 indicate that pastures and monocultures covered more than 42% of the basin [33]. Agricultural expansion has dramatically increased the use of pesticides [40,41], which invariably end up in aquatic ecosystems. Broad changes in land use have resulted in the elimination of riparian forests and modifications to hydrological dynamics [42–44].

These activities result in numerous discharges being emitted into the atmosphere and the aquatic system, causing harm to the health of the Tocantins River (both fauna and flora) and impacting the quality of life of the population dependent on the river. Threats are escalating as public policies continue to prioritize maximizing economic growth at the cost of environmental sustainability [33]. Fishing is a cultural activity that has been generating income for generations in the region [45]. It serves as a vital protein source for the population of Maranhão, which is the 5th state with the highest fish consumption in Brazil and supplies the demands of the states of Pará, Tocantins, and Piauí [46,47].

2.2. Water Physicochemical Parameters and Presence of Nitrogenous Compounds

Physicochemical determinations were conducted monthly throughout 2023, in triplicate, covering the following parameters: air and river water temperature (°C), chlorophyll (µg/L), total dissolved solids (TDS) (g/L), pH, turbidity (NTU), conductivity (µS/cm), oxidation–reduction potential (ORP) (MV), luminescent dissolved oxygen (LDO) (mg/L), and salinity (ppt). These measurements were obtained in situ using the Hydrolab mul- tiparameter probe (model SX751—SANXIN), totaling 12 readings for each parameter (4 sampling sites, with 3 repetitions each).

Sampling occurred monthly, on over 12 occasions throughout the year, to collect this comprehensive dataset. The water samples were filtered to detect the presence of NH_4^+, NO_2, and NO_3^-. NH_4^+ was quantified using Nessler colorimetric analysis, with spectrophotometer readings at 450 nm. For NO_2, the Alphanaphthylamine colorimetric method was employed, with spectrophotometer readings at 520 nm. NO_3^- was determined by the brucine colorimetric method, with readings at 415 nm.

2.3.Determination of Potentially Toxic and Essential Elements in Water

The concentrations of potentially toxic elements (aluminum—Al, antimony—Sb, arsenic—As, barium—Ba, cadmium—Cd, chromium—Cr, lead—Pb, lithium—Li, nickel—Ni, strontium—Sr, titanium—Ti, and silver—Ag) and essential elements (boron—B, selenium—Se, silicon—Si, phosphorus—P, copper—Cu, iron—Fe, calcium—Ca, cerium—Ce, potassium—K, magnesium—Mg, manganese—Mn, molybdenum—Mo, sodium—Na, vanadium—V, cobalt—Co, tin—Sn, and zinc—Zn) were determined using inductively coupled plasma emission spectrometry (ICP-EAS) (SHIMADZU, ICPE-9000, Kyoto, Japan). The analyses were conducted using 50 mL samples in Falcons, pre-filtered on qualitative film paper, following the analytical methodology of the U.S. Environmental Protection Agency (US EPA Method 3015A). Calibration standards and blanks were treated in the same manner. Mercury (Hg) analysis for the samples was conducted following EPA Method 6020A.

2.4.Comparison of Data with National and International Standards

The results from physicochemical parameters, nitrogen compounds, and potentially toxic and essential elements in water were compared with the National Environmental Quality Standards [48], which serve as a benchmark (Table 1). These standards establish specific limits for each substance within every classification, providing a comprehensive framework for water quality assessment and regulation. Additionally, comparisons were made with international standards, such as the World Health Organization [49,50] and the Environmental Protection Agency [51].

Table 1. Values for comparison of physicochemical parameters, nitrogenous compounds, and elements in the waters of the middle Tocantins River, Maranhão, Brazil.

Standards for Drinking Water			
Parameters	**CONAMA**	**WHO**	**USEPA**
T Air (°C)	<30 °C	-	-
pH	6.0–9.0	6.5–8.5	-
Conductivity (µS/cm)	100	-	-
Salinity (PPT)	0.01	-	-
TDS (g/L)	0.5	0.3–0.9	-
LDO (mg/L)	≥6.0	-	-

Turbidity (NTU)	≤40	5	-
Chlorophyll (μG/L)	10	-	-
NH_4^+ (mg/L)	3.7 (pH < 7.5); 2.0 (7.5–8); 1.0 (8–8.5); 0.5 (pH > 8.5)	1.24	-
NO_2 (mg/L)	1	0.1	-
NO_3^- (mg/L)	10	10	-
Al	0.1	0.1–0.2	-
Hg	0.002	0.006	0.002
Cu	0.009	2	0.013
Fe	0.3	0.3	-
Mg	0.1	0.1	-
Na	-	200	-
Se	0.01	0.01	0.290

T: temperature, TDS: total dissolved solids, LDO: luminescent dissolved oxygen, NTU: nephelometric turbidity units. NH_4^+: ammonium, NO_2: nitrite, and NO_3^- : nitrate. CONAMA: National Environmental Council Resolution n° 357/2005 [48]. WHO: World Health Organization [49]. USEPA: Environmental Protection Agency [50].

2.5. Weighted Arithmetic Water Quality Index (WAWQI) and Water Quality Index (WQI)

The WAWQI is an index that comprehensively assesses water quality by combining various characteristics. This approach uses a weighted average, assigning weights to each parameter based on its relative importance. Studies [51,52] recommend processing the data using Equation (1):

$$\mathrm{WAWQI} = \sum_{i=0}^{n} \mathrm{QiWi} \qquad (1)$$

The sub-quality index for each variable is denoted as Qi, with the specified variable's weight unit represented by Wi. There were 13 physicochemical characteristics (n = 13): water temperature, pH, TDS, Al, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Ni, and Zn. They are expressed in mg/L, except for water temperature and pH. To calculate the quality of each parameter (qi), Equation (2) is used:

$$(\mathrm{qi}) = (\mathrm{Ci}/\mathrm{Si}) \times 100 \qquad (2)$$

where Ci represents the concentration of the parameter in the water sample, and Si is the established quality standard for that parameter. Additionally, the unit weight (Wi) for each parameter needs to be calculated using Equation (3):

$$Wi = wi/\sum wi \qquad (3)$$

Wi represents the unit weight of the pollutant variable; n is the total number of pollutant variables; and wi is the weight of each parameter (temp. = 0.00007; pH = 0.00002; TDS = 0.00001; Al = 0.00623; Ba = 0.01245; Cd = 0.62253; Cr = 0.06225; Cu = 0.15563; Fe = 0.00208; Pb = 0.08893; Mn = 0.01245; Ni = 0.02490; Zn = 0.01245) [52]. Finally, one should multiply the unit weight (Wi) of each parameter by the parameter's quality (qi) an sum the results to obtain the WAWQI. Based on these data, water quality is classified on a scale from excellent to unsuitable for consumption, with numerical values calculated using Equation (1). Values falling within the range of 0 to 25 are classified as excellent, while those between 26 and 50 are considered good. Bad quality is indicated by values ranging from 51 to 75, and very bad quality by values between 76 and 100. Any value exceeding 100 is deemed unsuitable for consumption.

The Water Quality Index (WQI) is an effective method for assessing water quality, determined by the calculated IQA value. This value can range from very poor ($WQI < 25$) to excellent ($91 < WQI \leq 100$) [53]. Each parameter contributing to the WQI is assigned a specific weight based on its relative impact on water quality [54]. The parameters considered include pH, water temperature difference, LDO, turbidity, and NO3-. Equation (4) is used to determine the WQI [54].

$$WQI = \sum_{i=1}^{n} qi^{wi} \qquad (4)$$

2.6. Quantitative Health Risk Assessment: Average Daily Intake (ADI), Target Hazard Quotient (THQ), and Hazardous Index (HI)

For metals and metalloid contamination in water, food, and soils, ingestion and dermal contact play the most important roles among the potential exposure pathways [55,56]. Furthermore, risk assessment entails evaluating adverse health effects on humans exposed to substances over a specified period [57]. In this investigation, health risk was assessed by measuring contamination levels in the water of the middle Tocantins River, Brazil. Both adults and children were considered in this analysis (Table 2).

Table 2. Health risk assessment of different exposures through parameters.

Parameter	Children	Adults
Exposure Frequency (EF) (Day/year)	365	365
Body Weight (BW) (kg)	15	70
Ingestion Rate (IR) or Daily intake (DI) (L/day)	1.8	2.2
Exposure Duration (ED) (Years)	6	70
Skin Surface Area (SA) (cm^3)	6600	18,000
Exposure Time (ET) (Hours/day)	1	0.58
Conversion Factor (CF) (L/cm^3)	0.001	0.001
Averaging Time (AT) (Days)	365 × 6	365 × 70
Particular Emission Factor (PEM) (m^3/kg)	1.3×10^9	1.3×10^3

Source: USEPA [58,59].

To calculate the exposure dose through ingestion of water (EXPing) (mg/kg/day), Equation (5) is utilized, while for exposure dose through dermal absorption (EXP-der) (mg/kg/day), Equation (6) is applied [60]. In this case, Cw represents the concentration of the chemical in water (mg/L), Kp is the permeability constant (1 cm/h), and the other terms are provided in Table 1.

To calculate the exposure dose through ingestion of water (EXPing) (mg/kg/day), Equation (5) is utilized, while for exposure dose through dermal absorption (EXP-der) (mg/kg/day), Equation (6) is applied [60]. In this case, Cw represents the concentration of the chemical in water (mg/L), Kp is the permeability constant (1 cm/h), and the other terms are provided in Table 1.

$$\text{EXPing} = \frac{\text{Cw} \times \text{IR} \times \text{EF} \times \text{ED}}{\text{Bw} \times \text{AT}} \quad (5)$$

$$\text{EXPder} = \frac{\text{Cw} \times \text{SA} \times \text{Kp} \times \text{EF} \times \text{ED} \times \text{ET}}{\text{Bw} \times \text{AT}} \quad (6)$$

Equation (6) is utilized to determine the THQ index. EFr represents total exposure frequency, ED is exposure duration, WiR stands for rate of water ingestion, C denotes the average concentration of trace elements in water, RfD indicates oral reference dose according to the USEPA, BW represents mean body weight, and AT signifies mean exposure time. The oral reference doses (RfD) for the trace elements are as follows: 1 mg/kg/day for aluminum (Al), 0.40 mg/kg/day for copper (Cu), 0.8 mg/kg/day for iron (Fe), 0.14 mg/kg/day for magnesium (Mg), and 0.005 mg/kg/day for selenium (Se) [10,61,62].

$$\text{THQ} = \left(\frac{\text{EFr} \times \text{ED} \times \text{WiR} \times \text{C}}{\text{RfD} \times \text{BW} \times \text{AT}} \right) \times 10^{-3} \quad (7)$$

The target hazard quotient (THQ) assesses the non-carcinogenic risk level from pollutant exposure. THQ values below 1 indicate insignificant health threats, while THQ values ≥1 indicate potential health risks requiring corrective action [63]. The Hazardous Index (HI) is the cumulative sum of the Target Hazard Quotient (THQ) values for all trace elements present in an individual's exposure. It is calculated using Equation (8). An HI value of ≥1 indicates a potential non-carcinogenic risk to human health [64].

$$HI = \Sigma\, THQ = THQ\,(iAl) + THQ\,(iCu) + THQ\,(iFe) + THQ\,(iMg) + THQ\,(iSe) \quad (8)$$

2.7. Statistical Analysis

To evaluate significant differences in the average total concentration of toxic and essential elements across sampling stations or within the same station during various samplings, an Analysis of Variance (ANOVA) was employed. Before the analysis, normality was assessed using the Kolmogorov–Smirnov test, and variance homogeneity was assessed using Levene's test. Means were compared using the Tukey test (<0.05). Data analysis was conducted using SPSS version 22. Additionally, principal component analysis (PCA) was utilized to investigate and interpret water quality data results, facilitating the grouping of information and visualization of hidden structures and relationships. PCA was performed using software PAST 4.03 (latest version 2020).

PCA was used to identify patterns or relationships among the concentrations of toxic and essential elements, physicochemical parameters, and the presence of nitrogenous compounds relevant to water quality. The data remained untransformed, and the results are expressed as correlations. Selection and interpretation criteria involved analyzing principal components and their respective weights or loadings, emphasizing those explaining most of the data variability. The technique was employed to reduce data dimensionality and facilitate the interpretation of inter-variable relationships, enabling a comprehensive analysis of factors influencing water quality in the Tocantins River.

3. RESULTS AND DISCUSSION

3.1. Water Physicochemical Parameters and Presence of Nitrogen Compounds

During the 2023 monitoring period, the observed average pH values were 7.23 (P1), 7.18 (P2), 7.41 (P3), and 7.00 (P4) (Table 3). The average pH values for each section conform to the National and International Environmental Quality Standards guidelines [48–50]. It is worth mentioning that water availability influenced this factor, with higher values being found during the dry season, explaining the wide range for some variables studied. Thus, during this period, there were months when maximum values exceeded legal standards. Furthermore, the spatial data collected throughout 2023 are available in the Supplementary Material (Tables S1–S12).

Table 3. Physicochemical parameter values and presence of nitrogen compounds in the middle Tocantins River waters during 2023, Maranhão, Brazil.

Parameters		Middle Tocantins River			
		P1	**P2**	**P3**	**P4**
T air (°C)	Range	26.5–32.2	25.5–30.3	24.5–33.1	25.7–32.0
	Mean ± SD	28.8 ± 1.7 [a]	27.8 ± 1.4 [a]	28.7 ± 2.1 [a]	29.2 ± 1.8 [a]
T water (°C)	Range	27.8–31.3	27.8–30.8	27.8–31.3	28.1–32.6
	Mean ± SD	29.3 ± 0.9 [a]	29.2 ± 0.9 [a]	29.4 ± 1.1 [a]	29.9 ± 1.5 [a]
pH	Range	4.25–9.19	5.38–9.5	5.48–9.52	4.81–9.01
	Mean ± SD	7.23 ± 1.03 [a]	7.18 ± 0.67 [a]	7.41 ± 1.04 [a]	7.00 ± 1.03 [a]
Conductivity (µS/cm)	Range	13.3–193.6	22.9–51.3	24–49	24.9–78.5
	Mean ± SD	51.67 ± 34 [a]	37.70 ± 8.24 [b]	36.93 ± 9.19 [b]	39.68 ± 10.87 [b]
Salinity (PPT)	Range	0.01–0.02	0–0.01	0–0.01	0–0.01
	Mean ± SD	* 0.02 ± 0.02 [a]	0.01 ± 0.01 [a]	0.01 ± 0.01 [a]	0.01 ± 0.01 [a]
TDS (g/L)	Range	0.1002–0.0471	0.0144–0.0328	0.0100–0.0318	0.0060–0.0502
	Mean ± SD	0.0326 ± 0.02 [a]	0.0242 ± 0.01 [b]	0.0239 ± 0.01 [b]	0.0251 ± 0.01 [b]
LDO (mg/L)	Range	7.56–13	8.53–13.68	7.64–13.42	6.71–13.28
	Mean ± SD	8.91 ± 3.25 [a]	9.36 ± 3.33 [a]	8.74 ± 3.14 [a]	8.77 ± 3.10 [a]
Turbidity (NTU)	Range	18.5–117.7	21.6–113.8	23.7–123.7	24.6–114.5
	Mean ± SD	49.56 ± 24.34 [a]	45.04 ± 23.55 [a]	40.92 ± 28.25 [a]	42.84 ± 28.63 [a]
Chlorophyll (µG/L)	Range	0.52–3.7	0.41–2.8	0.52–2.84	0.47–2.7
	Mean ± SD	1.47 ± 0.95 [a]	1.24 ± 0.80 [b]	1.35 ± 0.75 [a]	1.28 ± 0.80 [ab]
ORP (mV)	Range	5–297	18–273	21–195	20–380
	Mean ± SD	123 ± 63.22 [a]	152 ± 132.85 [a]	131 ± 38.40 [a]	150 ± 75.41 [a]
NH_4^+ (mg/L)	Range	1.55–12.82	<0.01–4.97	<0.01–3.66	<0.01–6.2
	Mean ± SD	* 3.96 ± 2.46 [a]	* 1.59 ± 1.13 [b]	* 1.65 ± 0.97 [b]	* 1.91 ± 1.64 [b]
NO_2 (mg/L)	Range	<0.01–0.43	<0.01–0.08	<0.01–0.06	<0.01–0.07
	Mean ± SD	* 0.07 ± 0.10 [a]	0.03 ± 0.03 [b]	0.02 ± 0.02 [b]	0.02 ± 0.02 [b]
NO_3^- (mg/L)	Range	<0.01–6.23	<0.01–3.86	<0.01–3.44	<0.01–3.48
	Mean ± SD	0.98 ± 1.59 [a]	0.86 ± 1.28 [a]	0.60 ± 1.14 [a]	0.60 ± 1.04 [a]

P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area). T: temperature, TDS: total dissolved solids, LDO: luminescent dissolved oxygen, NTU: nephelometric turbidity units, ORP: oxidation reduction potential. NH_4^+: ammonium, NO_2: nitrite, and NO_3^-: nitrate. * Parameter concentrations above the quality standards of some regulations in comparison. The Tukey test was performed ($p < 0.05$) for mean comparison, where "[a]" and "[b]" alone denote significant differences among other groups.

The urban area (P1) showed elevated and statistically significant levels of conductivity (51.67 µS/cm), total dissolved solids (TDS) (0.0326 g/L), and chlorophyll (1.47 µg/L) (Table 3). However, these readings remained within CONAMA's recommended limits. High conductivity values might lead to unpleasant taste and digestive issues [65]. Although turbidity did not exhibit statistically significant differences among the data, the values slightly surpassed the recommended levels. To provide a meaningful comparison, it is useful to look at turbidity levels in other, cleaner rivers. Typically, cleaner rivers have turbidity levels well below those observed, often less than 5 NTU, indicating clearer water with lower concentrations of suspended particles [49]. Elevated turbidity levels can indicate higher concentrations of bacteria, microalgae, nutrients, pesticides, or metals [66,67].

The pH, conductivity, salinity, and nitrite concentration are among the parameters that can serve as effective water quality indicators based on statistical analyses [68]. This type of analysis is essential for environmental biomonitoring studies [69,70], given the sensitivity of ichthyofauna to environmental variations and physical–chemical contamination involving dissolved organic and inorganic compounds.

Site P1 exhibited elevated mean concentrations of NH_4^+ (3.96 mg/L) and NO_2 (0.07 mg/L) (Table 3). The region has an open sewage system that directly disposes of untreated wastewater from the neighborhood into the middle Tocantins River (Figure 1), with an average daily flow of approximately 411.6 L per second (calculated based on city indices and the average flow rate of the collection area). Additionally, domestic wastewater serves as a significant source of inorganic nutrients, including nitrogen (NH_3^-N) and phosphorus (PO_4^-P) [71,72]. The NH_4^+ and NO_2 levels exceed the established limits for drinking water, while NO_3^- content falls below thresholds [49]. Therefore, wastewater must be treated to reduce contaminants, pollutants, and undesirable components before being discharged into freshwater or water sources [73]. Additionally, physicochemical parameters and nitrogenous compound data collected throughout the region are provided in Table S1.

3.2. Temporal Distribution and Annual Average Concentration of Potentially Toxic and Essential Elements in Water from the Middle Tocantins River

February exhibited elevated levels of Al (Figure 2a), Fe (Figure 2b), Cu (Figure 2c), and Mg (Figure 2d) in the water of the middle Tocantins River. This month falls within the rainy and cooler period (January to June). Interestingly, aluminum and iron were undetectable (<0.01 mg/L) in March, August, and September. This seasonal fluctuation indicates a complex dynamic influenced by climatic or seasonal factors. Additionally, copper and magnesium remained below the detection limit only in March.

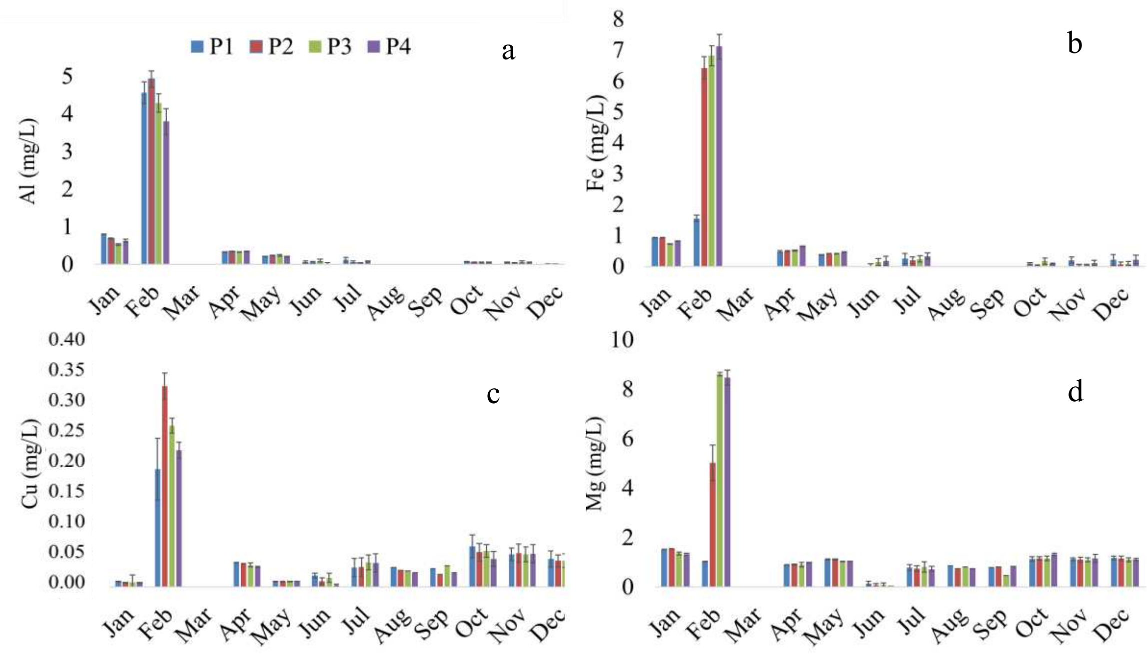


Figure 2. Temporal distribution of potentially toxic and essential elements in the waters of the middle Tocantins River throughout 2023, Maranhão, Brazil. (**a**) Aluminium (Al); (**b**) iron (Fe); (**c**) cooper (Cu); (**d**) magnesium (Mg). P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area). Rainiest/coldest (January to June) and hot/dry (July to December) seasons [39].

The rains began weakly in January; February experienced heavy rain and thunderstorms interspersed with sunny days, while in March, the rain was heavy and constant [74]. These variations highlight the need for further investigation to elucidate temporal patterns and potential influencing factors related to these elements in the middle Tocantins River waters. The results of potentially toxic and essential elements for the year 2023 are available in the Supplementary Material (Tables S12–S24).

Studies have investigated the influence of natural factors, including seasonal variations, on the pollution of potentially toxic elements in surface water, yielding diverse findings [25,75,76]. Factors such as changes in water velocity, storage capacity, and spatial location can contribute to significant variations in the pollution levels of potentially toxic elements in water bodies [77].

Among the potentially toxic elements, only aluminum (Al) presented annual averages that exceeded national and international standards for water quality (P1: 0.69 mg/L; P2: 0.71 mg/L; P3: 0.63 mg/L; P4: 0.58 mg/L). Regarding essential elements, copper (Cu), iron (Fe), manganese (Mn), and selenium (Se) concentrations raise significant concerns for environmental and health quality (Table 4). No statistical differences were observed in the average concentrations among the studied sections of the middle Tocantins River.

Table 4. Comparison of the concentration of potentially toxic and essential elements (annual average, mg/L) in water from the middle Tocantins River with national and international regulations.

Elements (Detection Limit)	Tocantins River			
	P1	P2	P3	P4
Potentially toxic elements				
Al (0.01)	* 0.69 ± 1.42	* 0.71 ± 1.54	* 0.63 ± 1.34	* 0.58 ± 1.19
Au (0.01)	0.08 ± 0.16	0.11 ± 0.24	0.10 ± 0.20	0.09 ± 0.19
Hg (0.01)	0.0002 ± 0	0.0002 ± 0	0.0002 ± 0	0.0002 ± 0
In (0.03)	0.58 ± 1.05	0.64 ± 1.20	0.51 ± 0.89	0.44 ± 0.80
Essential elements				
Ca (0.01)	8.24 ± 3.38	10.78 ± 8.98	12.59 ± 17.47	13.89 ± 17.88
Cu (0.02)	* 0.05 ± 0.05	* 0.06 ± 0.09	* 0.05 ± 0.07	* 0.05 ± 0.06
Fe (0.02)	* 0.46 ± 0.49	* 0.95 ± 2.00	* 1.02 ± 2.11	* 1.11 ± 2.19
K (0.02)	0.48 ± 0.40	0.59 ± 0.85	0.65 ± 0.89	0.87 ± 1.77
Mg (0.02)	* 0.96 ± 0.35	* 1.31 ± 1.29	* 1.59 ± 2.28	* 1.61 ± 2.23
Na (0.02)	0.92 ± 0.75	0.83 ± 0.83	1.14 ± 1.37	1.45 ± 1.72
S (0.01)	0.17 ± 0.16	0.09 ± 0.11	0.14 ± 0.15	0.21 ± 0.28
Se (0.02)	* 0.20 ± 0.01	* 0.19	* 0.17 ± 0.02	* 0.13 ± 0.01
Si (0.01)	4.46 ± 2.16	6.11 ± 7.16	6.96 ± 9.66	7.61 ± 9.71
Sn (0.02)	0.27 ± 0.50	0.39 ± 0.80	0.34 ± 0.66	0.29 ± 0.60

P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area). * Parameter concentrations above the quality standards of some regulations for comparison.

The chemicals released from industrial sources may contaminate drinking water, either through direct discharges or indirectly, through widespread sources resulting from the use and disposal of materials and products containing these chemicals. Various chemicals may find their way into water bodies due to improper disposal of household or industrial products. Specifically, potentially toxic elements can be identified in domestic wastewater [78–80].

Aluminum (Al) is commonly found in food, drinking water, and antacid preparations, posing acute toxicity risks to humans upon oral ingestion. Exposure to aluminum has been linked to the development or acceleration of Alzheimer's disease and various other health issues affecting nervous, reproductive, respiratory, mammary, skeletal, and immune tissues [49,81–83]. Health risk assessments for aluminum should consider individual factors such as age, renal function, diet, and gastric pH [84]. Elevated aluminum levels in brain tissues have been associated with encephalopathy, particularly notable in dialysis patients [85].

Copper (Cu) is an essential element for maintaining body metabolism but becomes toxic when present in higher concentrations [73]. Each metal, metalloid, and non-metal exhibit specific characteristics and toxicity. Its toxicity manifests gastrointestinal irritation, particularly from drinking water contamination [49]. Furthermore, exposure to excessive levels of copper can lead to liver and kidney damage, anemia, immunotoxicity, and developmental toxicity [86].

The Tocantins–Araguaia region hosts the two largest iron ore deposits globally: the Carajás mine in Pará State (with 17 billion tons) and the Serra do Carmo iron deposit in Tocantins State (with 159 billion tons) [33]. Continuous monitoring of this water resource is essential for addressing and mitigating water pollution, as contaminated water poses serious health risks to human and animal health. Elements in drinking water such as fluoride, copper, zinc, or iron may exacerbate cognitive impairment or modify the neurotoxic effects of aluminum [87]. Selenium (Se) is also concerning due to its presence in the aquatic food chain, where it bioaccumulates in higher life forms [88].

3.3. Weighted Arithmetic Water Quality Index (WAWQI), Water Quality Index (WQI), and Quantitative Health Risk Assessment

In this study, the WAWQI values were calculated using Equation (1) for four different locations in the middle Tocantins River: 7.42 (P1), 7.52 (P2), 8.27 (P3), and 8.65 (P4) (Table 5). According to the established classification criteria, where values between 0 and 25 are considered "Excellent," the water quality in the middle Tocantins River can be categorized as such. The accessibility of safe drinking water is highlighted in this context, contributing significantly to various aspects of public health and well-being. This includes promoting healthy bodies, ensuring food security, reducing poverty, and fostering the overall development of a population, both socially and economically [89,90].

Table 5. The WAWQI and WQI estimates for surface water parameters with arithmetic weights in the middle Tocantins River, Maranhão, Brazil.

Index	Tocantins River			
	P1	**P2**	**P3**	**P4**
WAWQI	7.42	7.52	8.27	8.65
WQI	83.37	83.75	84.82	84.81

P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area). Weighted Arithmetic Water Quality Index (WAWQI) [45,46]. WQI: Water Quality Index. All physicochemical parameters are expressed in mg/L except temperature (water temperature °C) and pH.

It is important to note that different studies or water quality assessment methodologies may have slightly different categorizations. Therefore, for comparison, the Water Quality Index (WQI) was applied using the national parameters [48]. The WQI values express freshwater quality as a percentage of an optimum situation, with 100% representing the best possible quality. The values were calculated using Equation (4) for four different locations in the Middle Tocantins River: 83.37 (P1), 83.75 (P2), 84.82 (P3), and 84.81 (P4) (Table 5). This indicates that all the analyzed sections are classified as "Good".

The concentrations of Al, Cu, Fe, Mg, and Se through ingestion and dermal pathways (primarily through activities such as swimming and bathing in untreated water) for both adults and children are detailed in Table S25. Direct ingestion and dermal absorption (excluding inhalation through the mouth and nose) are recognized as the primary exposure routes for trace elements in river water for humans [91]. Importantly, the human health risk assessment values for both adults and children were found to be less than 1, indicating no risk.

Environmental exposure to metals through water may raise concerns regarding human exposure to potentially toxic elements [60]. Despite the studied elements showing average levels above national and international standards, human health risk assessment indices were found to be less than 1, indicating no risk (Table S25). This index assesses the probability of an individual developing cancer over their lifespan due to exposure to carcinogenic metal(loid)s. However, in this study, carcinogenic elements were not detected.

3.4. Correlation Coefficients and Principal Component Analysis (PCA)

The highlighted correlations reveal strong linear relationships: conductivity/TDS ($r = 0.999$), Al/Ca ($r = 0.989$), Ca/Si ($r = 0.997$), conductivity/NH_4^+ ($r = 0.996$), salinity/TDS ($r = 0.993$), Al/In ($r = 0.989$), and Fe/Ca ($r = 0.947$) (Table S26). Conversely, significant negative correlations were observed, such as Al/Na ($r = -0.992$), Fe/NO_2 ($r = -0.992$), K/Se ($r = -0.989$), and chlorophyll/ORP ($r = -0.966$). High positive correlations (close to 1) imply a strong linear relationship, indicating that when one’s concentration increases, the other is expected to increase as well. Conversely, negative correlations suggest an inverse relationship between the variables. For instance, a negative correlation between Al/Na indicates that an increase in Al concentration is associated with a decrease in Na concentration.

Correlation coefficients offer valuable insights into the strength and direction of relationships among the analyzed parameters, enhancing our understanding of water quality dynamics and potential contaminant sources [92]. Therefore, numerous studies employ both univariate and multivariate statistical analyses to identify highly correlated water pollutants and relevant industries [93,94]. This enables researchers to effectively trace these pollutants and industries, resulting in the development of more efficient pollution management strategies.

The PCA results show that the first two components explain 89% of the data variability (Figure 3). The first component accounted for 52.79% (variance) and was positively loaded by conductivity, salinity, TDS, NH_4^+, NO_2, NO_3^-, Al, and Se; this component presented negative loadings for Ca, Fe, K, Mg, Na, and Si. Conversely, the second component accounted for 35.88% (variance) and was positively loaded by LDO, Au, In, Cu, and Sn, while presenting negative loadings for T surface (air temperature), chlorophyll, and S. The second graph showing PC1 vs. PC3, along with the loadings, scores, and eigenvalues of the principal component analysis are available in the Supplementary Material (Tables S27–S30).

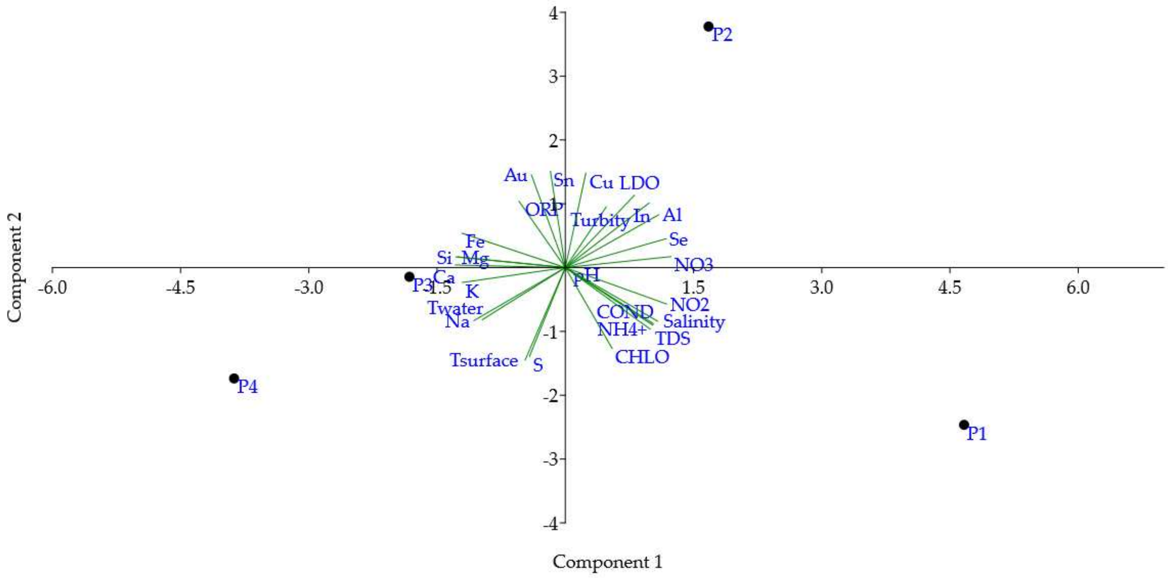


Figure 3. Principal component analysis (PCA) of water quality monitoring data of the middle Tocantins River, Maranhão, Brazil. P1: Beira Rio, P2: Bananal, P3: Embiral, P4: Cidelândia. T: temperature, TDS: total dissolved solids, LDO: luminescent dissolved oxygen. ORP: oxidation reduction potential. CHLO: chlorophyll. NH_4^+: ammonium, NO_2: nitrite, and NO_3^-: nitrate.

PCA serves as a valuable tool for identifying pollution sources and extracting meaningful insights to facilitate eco-conservation and management efforts [94–96]. In this study, PCA analysis revealed three distinct groups based on water quality. The first group consisted solely of the P1 station, located within an urban area known as “Beira Rio,” which showed a positive association with the first component and a negative association with the second.

The second group comprised only the P2 station, situated near the village of “Bananal” in a rural area, and exhibited a negative association with the second component of PCA. The third group consisted of the P3 and P4 stations, also situated in rural areas, being close to industrial waste discharge sites (pulp and paper production), and both stations showed a negative association with both the first and the second components. This underscores the utility of PCA in identifying pollution sources and guiding conservation and management efforts.

4. CONCLUSIONS

The levels of aluminum, copper, iron, magnesium, and selenium exceeded legal standards during 2023. The seasonal fluctuation indicates a complex dynamic influenced by climatic or seasonal factors, with February showing the highest values. Particularly, in urban areas such as P1, there are increased levels of conductivity, TDS, and chlorophyll, indicating the need for continuous monitoring. The presence of nitrogen compounds at P1 raises specific concerns regarding drinking water quality, which is a concern for the residents of the region, who use untreated river water for recreational and domestic purposes.

Despite seasonal fluctuations in element concentrations, the overall Water Quality Index (WAWQI) categorizes all sections as "Excellent," while the Water Quality Index (WQI) is labeled as "Good." This emphasizes the importance of ensuring safe drinking water for both public health and socioeconomic development. Human health risk assessments for aluminum, copper, iron, magnesium, and selenium indicate no risk, but ongoing monitoring and interventions are essential to maintain sustained water quality in the region.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1. Climatology and weather forecast history of 2023 in Imperatriz, Brazil; Table S1. Temperature (air and water) of the middle Tocantins River throughout 2023; Table S2. pH (unit) in the waters of the middle Tocantins River throughout 2023; Table S3. Conductivity (mS/cm) in the waters of the middle Tocantins River throughout 2023; Table S4. Salinity (PPT) in the waters of the middle Tocantins River throughout 2023; Table S5. Total dissolved solids (g/L) in the waters of the middle Tocantins River throughout 2023; Table S6. Luminescent dissolved oxygen (mg/L) in the waters of the middle Tocantins River throughout 2023; Table S7. Turbidity (NTU) in the waters of the middle Tocantins River throughout 2023; Table S8. Chlorophyll (µG/L) in the waters of the middle Tocantins River throughout 2023; Table S9. ORP (mV) in the waters of the middle Tocantins River throughout 2023; Table S10. Ammonium (NH_4^+) (mg/L) in the waters of the middle Tocantins River throughout 2023; Table S11. Nitrite (NO_2) (mg/L) in the waters of the middle Tocantins River throughout 2023; Table S12. Nitrate (NO_3^-) (mg/L) in the waters of the middle Tocantins River throughout 2023; Table S13. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S14. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S15. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S16. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S17. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S18. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S19. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S20. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S21. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S22. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S23. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S24. Results of essential and potentially toxic elements in the waters of the middle Tocantins River throughout 2023; Table S25. The human health risk assessment indices for cancer risks from ingestion and absorption of studied metals for children and adults; Table S26. Pearson correlation coefficients for water quality monitoring data of the middle Tocantins River, Maranhão, Brazil; Table S27. Principal component analysis (PC1 vs. PC3) of water quality monitoring data of the middle Tocantins River, Maranhão, Brazil; Table S28. Loadings from principal component analysis (PCA); Table S29. Scores from principal component analysis (PCA); Table S30. Summary from principal component analysis (PCA).

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CAPÍTULO 4 – NÍVEIS DE ELEMENTOS POTENCIALMENTE TÓXICOS E ESSENCIAIS NOS SEDIMENTOS DO RIO TOCANTINS: RISCOS À SAÚDE NA INTERFACE SAVANA-AMAZÔNIA, NO BRASIL

DESTAQUES

- ✓ Os níveis de Al, Fe, Mg e Se nos sedimentos excederam os padrões legais até 2023.
- ✓ Elementos químicos, principalmente Al, Cr, Ni e Pb, apresentaram variação sazonal.
- ✓ Os índices de poluição consistentemente apontaram chumbo e níquel como contaminantes preocupantes.
- ✓ Risco ecológico geral: "Baixo", apesar de alguns elementos excederem as diretrizes.

Machado da Silva Acioly, T., Francisco da Silva, M., Iannacone, J., & Viana, D. C. Levels of potentially toxic and essential elements in Tocantins River sediment: Health risks at Brazil's Savanna-Amazon interface. **Scientific Reports**, v. 14, n. 1, p. 18037, 2024. https://www.nature.com/articles/s41598-024-66570-4

LEVELS OF POTENTIALLY TOXIC AND ESSENTIAL ELEMENTS IN TOCANTINS RIVER SEDIMENT: HEALTH RISKS AT BRAZIL'S SAVANNA-AMAZON INTERFACE

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ABSTRACT - The field study aims to address identified research gaps by providing valuable information on the concentration, spatial distribution, pollution levels, and source apportionment of toxic and essential elements in sediment samples from four sampling sites (P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area) distributed along the middle Tocantins River, Brazil. Samples were collected in 2023 from river sections and analyzed using various contamination indices (geoaccumulation index, contamination factor, enrichment factor, pollution load index, sediment pollution index, potential ecological risk coefficients, and integrated risk index). Results indicated that the levels of aluminum, iron, manganese, and selenium exceeded legal standards in that year. Chromium, nickel, copper, zinc, and lead exceeded guidelines, mainly in section P1 for aluminum and section P3 for nickel and lead. Rainy months showed increased presence, indicating seasonal variability. The geoaccumulation index indicated low pollution levels, with lead and nickel notably present near urban and industrial areas. The enrichment factor highlighted elevated concentrations of lead and zinc in industrial areas. Both PLI and SPI indices raise concerns regarding Pb (P4) and Zn (P3) concentrations at specific times of the year. Overall, potential ecological risks were deemed low for most sites. Continuous monitoring and interventions are crucial to preserving water and environmental quality in the region.

Keywords: Aquatic Toxicology, Biomonitoring, Ecotoxicology, Environmental Impact, Heavy metals.

1. INTRODUCTION

The aquatic environment faces constant threats from contamination due to various anthropogenic pollutants, which stem from different industrial, agricultural, and urban activities. These pollutants can have diverse origins and compositions, depending on the specific activities occurring in a given region[1]. For instance, mining, agrochemicals, and industrial wastewater contribute to sediment heavy metal contamination[2,3]. Urban wastewater discharge may contain high levels of Zn, Pb, and Cu[4].

Sediments serve a crucial role in preserving the ecological status of water bodies, functioning as essential ecological components in aquatic reservoirs[5]. However, despite their significance, sediments also act as repositories for various pollutants, especially heavy metals, significantly contributing to the mobilization of contaminants within aquatic systems under favorable conditions[6,7]. Acknowledging their importance as hosts for trace metals, it is imperative to integrate sediments into environmental monitoring programs[8].

Studies highlight the contamination of potentially toxic elements as a severe ecological crisis in aquatic environments due to their destructive, non-degradable, and bioaccumulative impact on organisms throughout the food web[9,10,11]. While essential elements like Na, Ca, Mn, Zn, and Fe are vital for organisms in trace amounts, non-essential or toxic elements like Cd, Hg, and Pb pose significant risks, even at minimal concentrations[12,13]. Additionally, these elements strongly adhere to suspended sediments, leading to their rapid deposition in bed sediments and detrimental effects on aquatic diversity[14]. In cases of strong sorption, suspended particle settling and sediment formation scavenge contaminants from the water phase, contributing to their accumulation in river and lake beds[15].

The quality of sediments serves as a crucial indicator of water pollution, providing valuable insights into pollutant levels. Sediment contamination, as emphasized by Alsamadany et al.[16], is a significant factor in degrading aquatic environments, leading to the development of various monitoring and management methods. Monitor- ing sediment quality is essential for assessing water pollution, and it's imperative to share this information with the community and government to develop plans for safeguarding valuable freshwater resources. Only through such measures can we effectively control and prevent damage to the balance of the aquatic ecosystem and the health of the population.

Various indices can be used to assess potential metal pollution levels in sediment. It's important to note that all risk assessment methods provide theoretical, probabilistic results[17]. These indices are widely employed for detecting metal contamination and are firmly established in the literature, often mandated by legislation[18]. For instance, the Pollution Load Index (PLI) offers a comprehensive assessment of sediment quality regarding metal pollution, aiding in categorizing pollution levels based on established criteria. Spatial analyses of metal levels in sediments, along with differentiation from natural backgrounds, are essential and can help recognize the methods of accumulation and geochemical behavior of metals in aquatic ecosystems.

The Tocantins River, also known as the Araguaia-Tocantins due to its mouth in Pará, flows through the states of Maranhão and Tocantins. This watercourse stands out due to its extensive drainage area of 767,000 km^2 and hosts the two largest iron ore deposits globally: the Carajás mine in

Pará State and the Serra do Carmo iron deposit in Tocantins State[19]. Situated in the transitional area between the Amazon and the Cerrado biomes, it plays a crucial ecological role[20]. The river harbors a highly diverse ichthyofauna, boasting approximately 300 species, 126 genera, and 34 families, predominantly Characiformes, Siluriformes, and Cichlids[21]. Notably, the river is vital for the local population's sustenance, supporting fishing for commerce and subsistence, tourism activities such as river beaches, and traditional crafts. However, over the last 40 years, it has experienced significant degradation, primarily due to the expansion of dams, croplands, irrigation, mining, and aquaculture[19].

The region faces challenges such as deforestation for agriculture, monoculture (e.g., *Eucalyptus*), and sanitation issues driven by urban growth, leading to soil erosion, sedimentation, and the introduction of pollutants[22]. This degradation affects water and sediment quality, impacting ecological health and community well-being. Several polluted streams flow into the study area, causing unsanitary conditions due to the direct dumping of household waste from bathrooms and kitchens, effectively turning them into open sewers[23]. Elevated levels of metals such as Al, Cu, Fe, Mg, and Se exceeding national standards have been observed, indicating these elements are carried into the Tocantins River as suspended particulate matter[24]. A recent study also found that levels of Al, Cu, Fe, Mg, and Se exceed legal standards. Particularly in urban areas, increased levels of conductivity, total dissolved solids, chlorophyll, NH_4^+, and NO_2 raise concerns about drinking water quality[22]. This is critical for residents who rely on untreated river water for recreational and domestic purposes.

The field study aims to address identified research gaps by providing valuable information on the concentration, spatial distribution, pollution levels, and source apportionment of toxic and essential elements in sediment samples from sampling sites distributed along the middle Tocantins River. Additionally, contamination levels have been assessed using various indices such as the Geoaccumulation Index (Igeo), Contamination Factor (CF), Enrichment Factor (EF), Pollution Load Index (PLI), Sediment Pollution Index (SPI), Potential Ecological Risk Coefficients (Er), and their Integrated Risk Index (RI). The lack of studies and the environmental fragility of the middle Tocantins River highlight the urgent need for greater attention to environmental monitoring of this important water resource. Given those anthropogenic activities, particularly urbanization and deforestation, degrading environmental quality, they lead to compromised water and sediment conditions, posing risks to eco- systems and human health.

2. Material and methods

2.1. Study área, sampling, and ethical aspects

The study was carried out in the middle Tocantins River within the Imperatriz area of influence (Maranhão, Brazil). There are four sampling station areas, each equipped with GPS georeferencing using the GARMIN 4215 (Fig. 1). This region is strategically vital as a major transportation hub and gateway to the Amazon, often referred to as the portal to the Amazon. Its strong agribusiness and industrial sectors drive economic growth, generating employment and promoting development. The rainiest/coldest period (January–June) and the hot/dry season (July–December) are highlighted[25].

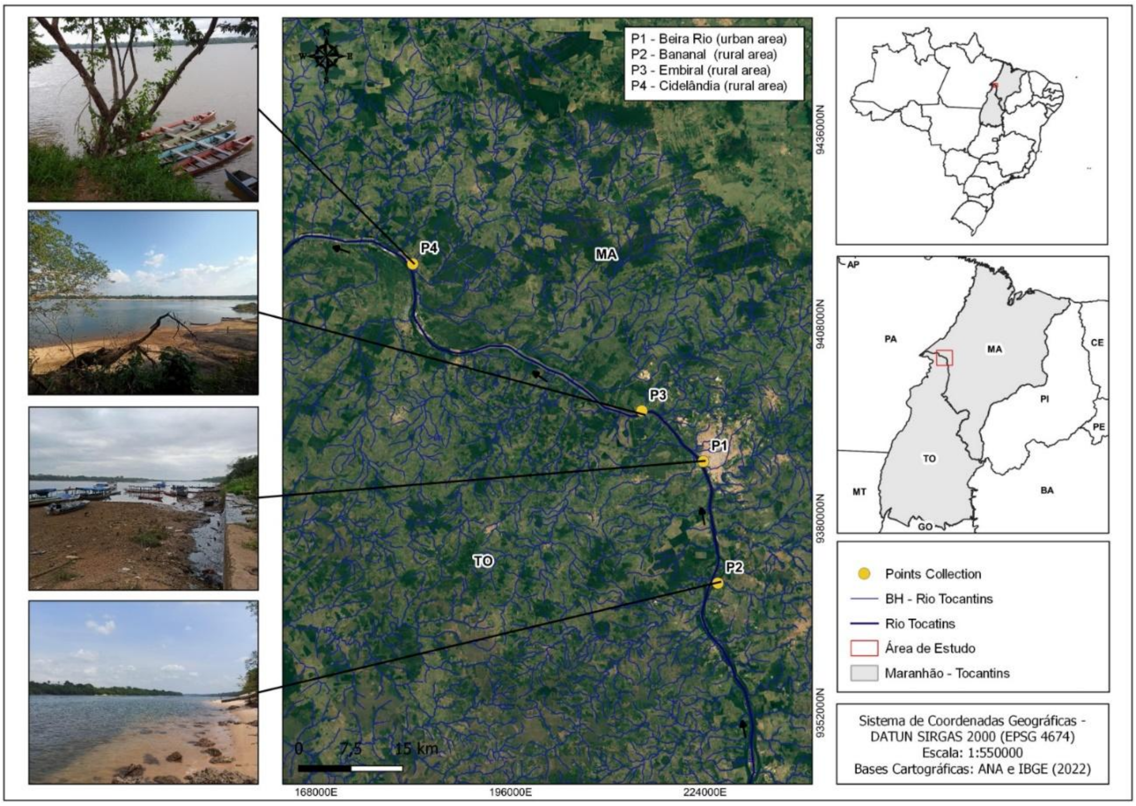

Figure 1. Geographic coordinates of sampling points in the middle Tocantins River, Maranhão, Brazil.

It's worth noting that the region faces several challenges, including deforestation on hillsides, intensive exploitation of fishery resources, sedimentation, sanitation issues, and direct disposal of waste and sewage into the water body, all contributing to contamination of the river waters. Consequently, these activities lead to damage to the health of the Tocantins River ecosystem, affecting both fauna and flora and negatively impacting the quality of life for the population relying on the river.

A recent study provides insights into characterizing the region, where P1 is situated in an urbanized area with significant human activity[22]. This site is potentially contaminated due to high vessel traffic, recreational beach use, waste disposal, residues from commercial iceboxes, and urban sewage. On the contrary, P2 has a lower potential for contamination, being situated farther away from the city. P3 is located upstream of a paper and cellulose manufacturing and processing industry, while P4 is approximately 100 km downstream from the city, downstream from the paper and cellulose industry.

The degree of inorganic contamination was monitored from January to December 2023, by collecting sediment samples from sections of the middle Tocantins River. Sediment samples were systematically collected monthly, with three replicates at each designated point, resulting in a total of

12 containers. These samples were carefully preserved in pre-cleaned plastic vials, thoroughly rinsed with metal-free water, and maintained within a cold chain (refrigerated at 4°C) until they reached the laboratory at the State University of the Tocantina Region of Maranhão (UEMASUL).

Both the field collection and subsequent laboratory procedures followed ethical guidelines and were formally reviewed and approved by the Institutional Ethics Committee of the State University of the Tocantins Region of Maranhão (CEUA No: 1025220722) and the State University of Maranhão (CEUA Nº 040/2023). Furthermore, scientific activities were conducted with explicit authorization (SISBIO Number: 87310-1) by Normative Instruction No. 748/2022 as outlined in the ICMBio Ordinance.

2.2. Determination of potentially toxic and essential elements in sediments

Samples of 500 g of surface sediments were collected, with subsamples taken from the central part to avoid contamination. Subsequently, the samples were dried in a drying oven at 70˚C (CienlaB) for three days or until a constant mass was obtained. For the determination of total concentrations of elements in sediments, a 0.5-gram sample (dry weight) was taken and 1 mL of HCl (50%), 1 mL of nitric acid (50%), and 8 mL of water were added; following the analytical methodology of the U.S. Environmental Protection Agency (US EPA Method 3050B). The digestion was then accelerated in a digestion block (ECO 16, VELP Scientifica) for 2 hours at 120ºC.

The concentrations of both potentially toxic elements (aluminium—Al, antimony—Sb, arsenic—As, barium— Ba, cadmium—Cd, chromium—Cr, mercury—Hg, lead—Pb, lithium—Li, nickel—Ni, strontium—Sr, titanium— Ti, and silver—Ag) and essential elements (beryllium—Be, boron—B, selenium—Se, silica—Si, phosphorus—P, copper—Cu, iron—Fe, calcium—Ca, cerium—Ce, potassium—K, magnesium—Mg, manganese—Mn, molybdenum—Mo, sodium—Na, vanadium—V, cobalt—Co, tin—Sn, and zinc—Zn) were determined using inductively coupled plasma emission spectrometry (ICP-EAS) (SHIMADZU, ICPE-9000, Kyoto, Japan). Mercury (Hg) was determined following the specific methodology EPA 245.7:2005[26].

The results were compared with the National Environmental Council resolution no 454/2012[27]. Additionally, the results were compared with international sediment guidelines, including those from the Canadian Council of Ministers of the Environment (CCME)[28], the National Oceanic and Atmospheric Administration (NOAA)[29], and the United States Environmental Protection Agency guidelines for sediments (USEPA)[30].

2.3. Assessment of anthropogenic pollution in sediments

2.3.1. Geoaccumulation index

The Geo-accumulation Index (Igeo) has been calculated for the six studied metals: Al, Cr, Cu, Ni, Pb, and Zn. Igeo serves as a measure to assess metal contamination in sediments, soils, or other environmental samples, providing insights into the degree of accumulation or contamination relative to natural background levels[31]. The data should be processed using Eq. (1):

$$\text{Igeo} = \log_2 \left(\frac{\text{Cn}}{1.5\times\text{Bn}}\right) \quad (1)$$

In this context, Cn represents the measured concentration of the metal in the sediment samples, while Bn denotes the geochemical background value in the Earth's crust[32]. To address potential variations in background values resulting from lithogenic variations, a factor of 1.5 is introduced[33].

Muller[31] categorized the geoaccumulation index into six classes. The classification of contamination levels in sediment, as indicated by the Geo-accumulation Index (Igeo), is determined based on specific ranges[34,35]. When Igeo is less than or equal to 0, it suggests no contamination. For values between 0 and 1, the sediment is categorized as experiencing no contamination to being moderately contaminated. A range of 1–2 indicates a state of moderate contamination, while 2–3 signifies a condition of moderate to heavy contamination. The levels intensify as Igeo progresses: 3–4 suggests heavy contamination, 4–5 indicates contamination from heavy to extremely contaminated, and an Igeo equal to or greater than 5 denotes an extremely contaminated state.

The logarithm to base 2 is utilized to express the concentration relationship more clearly. It is important to note that understanding the nature of concentration values, especially about background concentration levels, is crucial for interpreting the index correctly. This classification system offers a comprehensive understanding of the contamination degree in sediment samples, thereby assisting in environmental assessments and the development of management strategies.

2.3.2. Enrichment factor (EF)

In the present study, the concentrations of elements in the Earth's crust were utilized as reference values, sourced from Turekian and Wedepohl[36]. The Enrichment Factor (EF) assesses the ratio of elemental concentrations in each sample to those in the Earth's upper continental crust (background). This ratio is calculated using Eq. (2) as proposed by Loring[37]. The EF serves as a valuable metric for understanding the extent to which elemental concentrations in a sample deviate from the natural background levels, providing insights into potential anthro- pogenic influences and environmental impacts.

$$\text{EF}=\frac{\left(\frac{\text{CM}}{\text{CX}}\right)\text{sample}}{\left(\frac{\text{CM}}{\text{CX}}\right)\text{earth crust}} \quad (2)$$

CM represents the concentration of the target element in the sample, while CX denotes the concentration of the same element in the Earth's crust. A value of EF greater than 1 indicates enrichment, signifying an elevated concentration relative to the Earth's crust. Conversely, an EF less than 1 indicates depletion, suggesting a lower concentration compared to the typical Earth's crust. EF is extensively employed in geochemistry and environmental studies to evaluate contamination or the anomalous presence of elements in a sample. Its application provides valuable insights into potential anthropogenic influences and environmental implications.

2.3.3. Pollution load index (PLI)

The Pollution Load Index (PLI), developed by Tomlinson et al.[38], serves as a tool to assess the extent of sediment contamination by metals in diverse locations. This index can be calculated using Eq. (3):

$$PLI=\sqrt[n]{(CF1 \text{ x } CF2 \text{ x} \ldots CFi)} \quad (3)$$

The PLI indicates how many times the metal content in the sediment exceeds background levels (Soliman et al., 2021), where n represents the number of metals studied. Therefore, interpreting the PLI involves comparing the calculated value with established limits or standards. A PLI equal to 1 suggests that the area is within acceptable limits and is not significantly polluted. Values above 1 indicate an increase in the pollution load, suggesting rising levels of contamination. According to Soliman et al. (2021), a PLI < 1 indicates "Unpolluted," PLI > 1 "Polluted," and PLI > 5 "Very highly polluted".

2.3.4. Sediment pollution index (SPI)

The Sediment Pollution Index (SPI) serves as a comprehensive multi-metals index for assessing sediment quality in terms of both metal content and toxicity. The methodology for calculating SPI, as proposed by Rubio et al.[39], is outlined, and it is expressed through Eq. (4):

$$SPI=\frac{\sum(EFm \text{ x } Wm)}{\sum Wm} \quad (4)$$

Toxicity weights (Wm) are assigned to each metal, with values of 2, 5, 5, 5, 1, and 1 for Cr, Cu, Ni, Pb, Al, and Zn, respectively[40,41]. Additionally, EFm represents the Enrichment Factor for each metal. The SPI index is classified into five categories based on the classification by Soliman et al. (2021): 0–2 (Natural sediment), 2–5 (Low-polluted sediment), 5–10 (Moderately polluted sediment), 10–20 (Highly polluted sediment), and > 20 (Dangerously polluted sediment).

2.3.5. The potential ecological risk coefficients (Epr) and integrated risk index (RI)

To assess potential toxic hazards posed by metals, the potential ecological risk index (RI) derived by Hakanson[40] was estimated. According to this index, the potential ecological risk coefficient (E_r^i) for a specific metal and the overall potential ecological risk index (RI) induced by the combined impacts of the studied metals were evaluated using the following formulas:

$$C_f^i = \frac{C_s^i}{C_n^i} \quad (5)$$

$$E_r^i = T_r^i \; x \; C_f^i \quad (6)$$

$$\mathrm{RI} = \sum_{i=1}^{n} E_r^i \quad (7)$$

The ecological risk indices (RI) and potential ecological risks (E_r^p) were computed using pollution coefficients (C_f^i), metal content in sediment (C_s^i), baseline values (C_n^i), and toxicity coefficients (T_r^i) (Okbah et al. 2018; Soliman, Younis, and Elkady 2019). The pollution coefficients for Cr, Cu, Ni, Pb, Al, and Zn were 2, 5, 5, 5, 1, and 1, respectively. Based on the calculated indices, the ecological risk levels were categorized.

RI values below 150 indicate low risk, while values between 150 and 300 suggest moderate risk[42]. RI values ranging from 300 to 600 indicate considerable risk, and values equal to or exceeding 600 represent significant risk. Similarly, Epr values below 40 signify low risk, while values between 40 and 80 indicate moderate risk. Consider- able risk is denoted by Epr values between 80 and 160, while high risk corresponds to values between 160 and 320. Epr values equal to or exceeding 320 indicate very high risk. These categorizations enable a comprehensive assessment of ecological risk levels based on metal concentrations in sediment samples.

2.4. Statistical analysis

To evaluate significant differences in the average total concentration of essential and toxic elements across sampling stations or within the same station during different periods of 2023, Analysis of Variance (ANOVA) was employed. Before conducting the analysis, it was essential to perform the Kolmogorov-Smirnov normality test and Levene's test to assess variance homogeneity. The Tukey test ($p < 0.05$) was also employed to compare means. The data were analyzed using statistical software SPSS version 22.

To identify the association between potentially toxic and essential elements analyses, statistical tools such as correlation matrix and principal component analysis (PCA) were explored on raw data using the free software PAST 4.03 (latest version 2020). The technique reduces data dimensionality, emphasizing principal components explaining most variability, and aiding interpretation of inter-variable relationships for a comprehensive sediment quality analysis.

3. RESULTS AND DISCUSSION

3.1. Spatial distribution and annual average concentration of potentially toxic and essential elements in sediments from the middle Tocantins River

The sediment monitoring of the middle Tocantins River has revealed significant trends in the concentration of chemical elements throughout the year 2023. Notably, the months of February, April, and May show heightened levels of Al (Fig. 2A), Cr (Fig. 2B), Ni (Fig. 2C), and Pb (Fig. 2D). This period coincides with the rainiest and coldest months (January to June). However, these elements are undetectable (<0.01 mg/kg) in January and March due to excessive rainfall, which dilutes the metals.

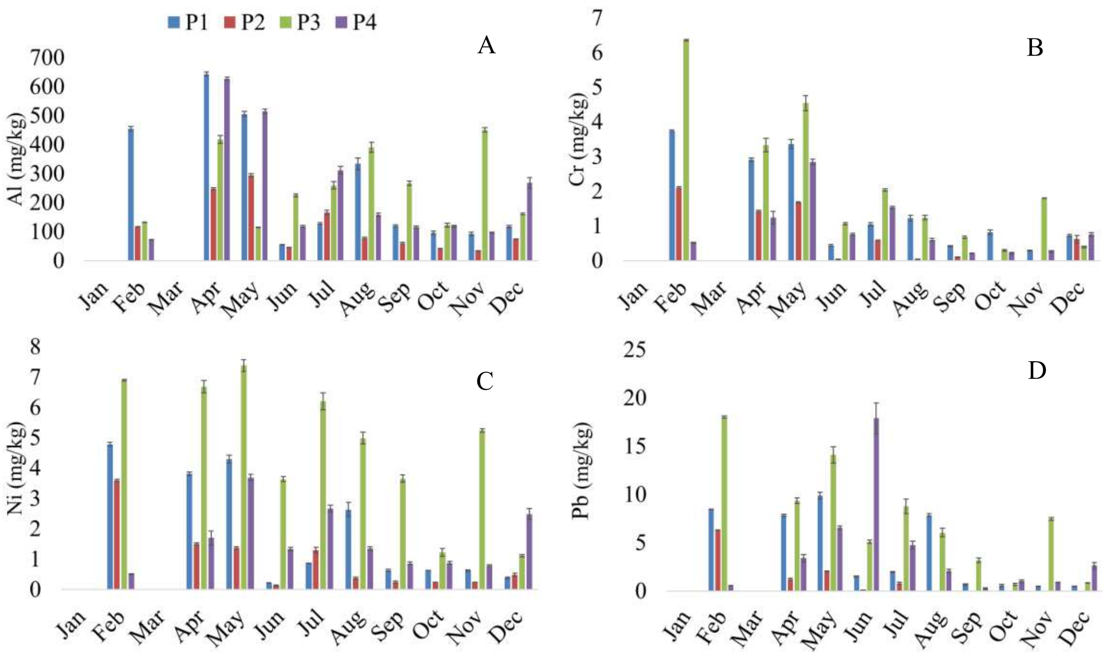

Figure 2. Spatial distribution of potentially toxic elements in the sediments of the middle Tocantins River throughout 2023, Maranhão, Brazil.

P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area). Rainiest/coldest period (January to June) and the hot/dry season (July to December) (Koppen and Geiger, 1928). A: Aluminium (Al); B: Chromium (Cr); C: Nickel (Ni); D: Lead (Pb). Values represent mean concentrations (mg/kg) of each metal. Error bars indicate the standard deviation (SD) of the mean concentrations.

The rain began in January weakly; February saw heavy rain and thunderstorms punctuated by sunny days, while March brought continuous and heavy rainfall[43]. This seasonal fluctuation suggests a multifaceted interaction influenced by climatic and seasonal factors. At Site P1, there is a higher presence of Al, while Ni exhibits a greater concentration in P3 (Fig. 2). Silva et al.[44] state that urban activities disrupt natural metal levels in sediments and aquatic ecosystems by altering geochemical processes that mobilize, transport, and disperse hazardous metals. Pb seems to be more prevalent in P3, except in June, where a greater concentration is observed at point P4. These concentration fluctuations underscore the necessity for a more thorough investigation to comprehend the temporal patterns and potential influencing factors linked to the presence of these elements in the waters of the middle Tocantins River. Additionally, spatial analysis of sediments can provide insights into the transport and deposition of contaminants[15].

Senze et al.[45] also observed that the seasonal variations were reflected in the levels of Al detected in the sediments. The authors noted that across all rivers and their tributaries, autumn values significantly exceeded spring levels, indicating aluminum retention in sediments during the summer months. Conversely, in water, the opposite trend was observed, likely attributed to abundant precipitation and the leaching of aluminum from the catchment. Acioly et al.[22] reported that February, part of the rainiest and coldest period (January–July), recorded the highest values of elements in the water of the middle Tocantins River. In this recent study, annual concentrations of Al exceeded both national and international water quality standards (P1: 0.69 mg/L, P2: 0.71 mg/L, P3: 0.63 mg/L; P4: 0.58 mg/L). Elevated levels of essential elements such as Cu, Fe, Mn, and Se also raise significant concerns for environmental and health quality.

Aluminum demonstrated higher values among the potentially toxic elements; however, it is noteworthy that national and international standards do not provide specific limits for this element (Table 1). Meanwhile, values for Cr, Ni, and Pb exceeded only the sediment guideline set by the National Oceanic and Atmospheric Administration[29]. The same holds for essential elements, Cu and Zn surpassed the guidelines established by NOAA. No statistical differences were observed in the average concentrations among the studied sections of the middle Tocantins River.

Table 1. Comparison of the concentration of potentially toxic and essential elements (annual average, mg/kg) in sediment from the middle Tocantins River with national and international regulations.

Elements	CONAMA	CCME	USEPA (Not Polluted)	NOAA		Tocantins River			
				TEL	PEL	P1	P2	P3	P4
Potentially toxic elements									
Al						254.97±43.13	116.04±16.94	254.51±29.74	240.32±39.91
As	5.9	5.9	3			0.57±0.13	0.15±0.06	2.38±0.34	0.63±0.13
Au						3.08±0.34	1.52±0.20	5.29±0.60	2.75±0.27
Ba						5.10±0.83	2.66±0.31	9.64±1.30	4.35±0.48
Cr	37.3	37.3	25	0.0523	0.16	*1.50±0.25	*0.66±0.15	*2.18±0.39	*0.90±0.18
Hg	0.17	0.17		0.13	0.7	<0.06	<0.06	<0.06	<0.06
In						1.86±0.31	1.08±0.26	3.51±0.54	1.81±0.25

Ni	18		20	0.0159	0.0428	*1.78±0.36	*0.90±0.21	*4.70±0.54	*1.63±0.25
Pb	35	35	40	0.03024	0.112	*3.98±0.73	*1.05±0.35	*7.37±1.19	*4.02±1.60
Sb						1.41±0.28	0.62±0.17	4.04±0.51	1.55±0.22
Essential elements									
B						2.05±0.43	1.14±0.24	2.25±0.34	1.07±0.18
Ca						291.65±26.34	133.19±17.19	399.93±48.36	145.47±18.29
Cu	35.8	35.7	25	0.0187	0.39	*1.32±0.13	*0.60±0.05	*2.11±0.23	*0.94±0.10
Co						2.98±0.43	1.18±0.24	5.35±0.66	2.58±0.34
Fe						774.50±139.39	378.81±57.50	1105.75±163.97	549.99±83.79
K						16.72±3.82	11.75±2.76	31.92±6.47	14.87±2.33
P						2.72±0.43	0.79±0.20	5.29±0.72	1.85±0.32
Mg						47.19±8.02	30.00±4.50	136.02±17.60	50.35±6.77
Mn						13.63±1.42	7.95±0.96	29.14±2.69	14.04±1.49
Na						15.88±3.09	11.69±1.48	15.02±2.38	11.38±1.65
S						9.24±2.77	12.09±7.34	24.74±4.70	4.32±0.66
Se						7.50±0.93	3.55±0.67	13.37±1.55	6.16±0.70
Si						255.84±31.71	186.83±20.04	341.25±46.73	218.79±22.74
Sn						3.85±0.54	2.27±0.44	8.55±0.99	3.52±0.41
V						1.57±0.24	1.01±0.26	2.12±0.32	1.11±0.18
Zn	123	123		0.124	0.271	*4.15±1.11	*2.11±1.04	*9.03±4.35	*3.08±1.58

P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area). CONAMA: National Environmental Council resolution no 454/2012[27]. USEPA: United States Environmental Protection Agency guidelines for sediments[30]. CCME: Canadian Council of Ministers of the Environment[28]. NOAA: National Oceanic and Atmospheric Administration[29], Sediment Guidelines. TEL: Threshold Effects Level. PEL: Probable Effects Level. These are metrics similar to the effects range metrics (i.e., Effects Range Low and Effects Range Median) used to assess the potential effects of contaminants on sediments. The Threshold Effects Level is the average of the 50th percentile and the 15th percentile of a dataset and the Probable Effects Level is the average of the 50th percentile and the 85th percentile of a dataset. *Parameter concentrations above the quality standards of some regulations in comparison. The Tukey test was performed ($p < 0.05$) for mean comparison, where "a" and "b" alone denote significant differences about other groups. The detection limit was 0.01 mg/kg for Al, Au, Hg, Ca, Pb, S, and Si,0.02 mg/kg for Ar, B, Ba, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, Se, Sn, and Zn, and 0.03 mg/kg for In, Cd, Co, P, Sb, and V.

The elements with the highest mean values followed this order: Fe > Al > Si > Mg > K > Na > S. The sediment's mercury content was below the detection limit (Table 1). Manganese and Iron are not explicitly addressed in national and international standards. However, according to Aiman et al.[46], its safety level is established at 30 mg/kg for sediment quality guidelines (SGV). The same source mentions a safety level of 15 mg/kg for Fe. It is crucial to underscore the lack of specific regulations for aluminum, highlighting a potential gap in standards. Continued monitoring is essential to assess the environmental and health implications of exceeding guidelines for other elements.

Aluminum ranks as the third most abundant element and the predominant metal in the Earth's crust[47]. While commonly present in rocks where they are considered inert and non-bioavailable, weathering of these minerals gradually releases potentially toxic forms of aluminum into the environment, such as Al + and Al hydroxides[47,48]. Both natural and human activities contribute to the presence of aluminum in aquatic systems. In sediment, aluminum is typically inert when bound with dissolved organic carbon (DOC) or in the form of silt or clay, serving as a storage reservoir. However, changing conditions, such as a decrease in pH, can mobilize aluminum back into the water column[49,50]. In such cases, riverbed sediment acts as a pollution store. Health effects of aluminum exposure include impacts on the respiratory, nervous, skeletal, hematological, cardiovascular, hepatic, renal, and endocrine systems, as well as skin, eyes, and body weight[51–53].

According to Ohiagu et al.[54], elements such as Cr, As, Pb, Cu, Fe, Cd, Zn, and Ni are among the metals raising high public health concerns. Several studies indicate that the presence of Cr, Cd, Pb, Mn, and Ni above threshold limits suggests potential carcinogenic and genotoxic effects on humans[55,56]. This situation is alarming and demands continuous monitoring, public awareness, and stringent governmental policy. Notably, Point P3 exhibited slightly elevated values for Cr (2.18 mg/kg), Ni (4.70 mg/kg), and Pb (7.37 mg/kg).

3.2. Assessment of anthropogenic pollution in sediments: Geoaccumulation Index, Enrichment Factor, Contamination Factor, Pollution Load Index, Sediment Pollution Index, and Potential Ecological Risk Index

For the Igeo, the samples of Al, Cr, and Cu consistently show only negative values, indicating a low level of pollution (Tab. 2). Among the metals analyzed, Ni and Pb stand out as the highest contaminants. When examining the average data for 2023, only Pb recorded a positive value for P3 (0.54); nevertheless, it still falls within the range of no contamination to moderately contaminated. However, considering the maximum values obtained for metal concentration in the Igeo equation, both Ni and Pb recorded values higher than 1 for points P1 (1.50), P3 (1.92), and P4 (3.00).

Table 2. Geoaccumulation index and enrichment factor for investigated metals in the sediment from the Middle Tocantins River, Maranhão, Brazil.

Elements	Index value	Igeo				Enrichment factor			
		P1	P2	P3	P4	P1	P2	P3	P4
Al	Min	-3.96	−4.83	−3.52	−3.47	0.00062	0.00028	0.00083	0.00088
	Average	−2.39	−3.26	−2.40	−2.45	0.00319	0.00145	0.00318	0.00300
	Máx	−2.82	−2.82	−1.61	−1.39	0.01097	0.00433	0.00858	0.01053
Cr	Min	−4.29	−4.80	−3.91	−4.48	0.00078	0.00056	0.00189	0.00067
	Average	−2.00	−2.88	−1.72	−2.42	0.01667	0.00733	0.02422	0.01000
	Máx	−1.20	−2.11	−0.95	−1.47	0.05278	0.02667	0.07844	0.04078
Cu	Min	−2.18	−3.04	−2.08	−2.63	0.01133	0.00489	0.01333	0.00667
	Average	−1.49	−2.35	−1.08	−1.93	0.02933	0.01333	0.04711	0.02089
	Máx	−0.84	−1.72	−0.37	−1.14	0.08356	0.02800	0.13644	0.06467

Ni	Min	−5.15	−7.14	−2.20	−4.05	0.00138	0.00016	0.01926	0.00441
	Average	−1.16	−2.10	−0.43	−1.32	0.02618	0.01324	0.06912	0.02397
	Máx	0.61	−0.10	**1.08**	0.02	0.08588	0.05882	0.17471	0.06941
Pb	Min	−2.39	−2.85	−1.79	−1.73	0.035	0.022	0.0545	0.0595
	Average	−0.22	−2.12	**0.54**	−0.03	0.199	0.0525	0.369	0.201
	Máx	**1.50**	0.85	**1.92**	**3.00**	**0.695**	0.33	**0.93**	**2.41**
Zn	Min	−6.01	−7.62	−3.34	−6.01	0.00105	0.0002526	0.01036	0.0003368
	Average	−1.38	−2.53	−0.65	−2.06	0.04368	0.02221	0.09474	0.03242
	Máx	−0.54	−0.41	**0.92**	−0.14	0.2653	0.3021	**1.347**	0.4811

Min: minimum value observed for the element; Average: average value observed for the element; Máx: maximum value observed for the element. P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area). Igeo values: ≤ 0 (no contamination), 0-1 (none to moderate contamination), 1-2 (moderate contamination), 2-3 (moderate to heavy contamination), 3-4 (heavy contamination), 4-5 (heavy to extreme contamination), ≥ 5 (extreme contamination). An EF > 1 indicates enrichment (elevated concentration relative to Earth's crust), while an EF < 1 indicates depletion (lower concentration than typical Earth's crust).

The calculations indicate a minimal presence of zinc pollution in the samples. The Igeo serves as a valuable tool for evaluating the prevailing contamination levels in specific sedimentary areas[57,58]. For the majority of points and situations, the Igeo values were predominantly negative, indicating a lack of contamination. These values offer a descriptive investigation of sediment contamination status and the accumulation profile of heavy metals[59,60]. The average EF for the studied metals exhibited a decrease in the following order: Pb > Ni > Zn > Cu > Cr > Al. Moreover, when evaluating the maximum metal concentration values in the EF equation, Pb was the sole ele- ment surpassing a value of 1 (P4 = 2.41), whereas Zn recorded a value above 1 for P3 (P3 = 1.347) (Table 2). The EF stands out as a crucial index for identifying the sources of metals in both soil and sediment61. A value of EF greater than 1 indicates enrichment, signifying an elevated concentration relative to the Earth's crust[62,63]. Conversely, an EF less than 1 indicates depletion, suggesting a lower concentration compared to the typical Earth's crust.

The mean values for the metals studied revealed a higher PLI for Ni (0.235) and Pb (0.184), both observed at P3 (Table 3). On the other hand, considering the observed maximum values obtained through ICPE analysis, the PLI hierarchy is as follows: Pb (1.205 at P4) > Zn (1.041 at P3) > Ni (0.595 at P3) > Cr (0.282 at P3) > Cu (0.246 at P3). These results suggest that, based on the mean values, there is no imminent concern. However, at certain moments or periods of the year, there is an escalation in pollution levels (PLI > 1 "Polluted" according to Soliman et al. 2021), particularly for lead and zinc. This emphasizes the importance of monitoring and implementing environmental management strategies to mitigate further contamination risks.

Table 3. Pollution load index and sediment pollution index for investigated metals in the sediment from the middle Tocantins River, Maranhão, Brazil.

Elements	Index value	Pollution load index (PLI)					Sediment pollution index (SPI)				
		P1	P2	P3	P4	Global	P1	P2	P3	P4	Global
Al	Min	0.089	0.074	0.112	0.097		0.00062	0.00028	0.00083	0.00088	
	Average	0.153	0.114	0.147	0.145	0.135	0.00319	0.00145	0.00318	0.00300	0.011
	Máx	0.200	0.151	0.182	0.196		0.01097	0.00433	0.00858	0.01053	
Cr	Min	0.003	0.002	0.007	0.002		0.00156	0.00112	0.00378	0.00134	
	Average	0.060	0.026	0.087	0.036	0	0.03334	0.01466	0.04844	0.020	0.044
	Máx	0.190	0.096	0.282	0.147		0.10556	0.05334	0.15688	0.08156	
Cu	Min	0.020	0.009	0.024	0.012		0.01133	0.00489	0.01333	0.00667	
	Average	0.053	0.024	0.084	0.038	0.066	0.02933	0.01333	0.04689	0.02089	0.043
	Máx	0.150	0.050	0.246	0.116		0.08356	0.028	0.13644	0.06467	
Ni	Min	0.005	0.0005	0.065	0.015		0.00138	0.00016	0.01926	0.00441	
	Average	0.089	0.045	0.235	0.081	0.128	0.01309	0.00647	0.03397	0.01176	0.024
	Máx	0.292	0.200	0.595	0.236		0.04294	0.02941	0.06985	0.02765	
Pb	Min	0.017	0.011	0.027	0.030		0.035	0.022	0.0545	0.0595	
	Average	0.099	0.026	0.184	0.100	**0.305**	0.199	0.052	0.368	0.201	**0.444**
	Máx	0.347	0.165	**0.465**	**1.205**		0.695	0.330	**0.930**	**2.410**	
Zn	Min	0.0008	0.00019	0.008	0.00026		0.00105	0.00025	0.01037	0.000337	
	Average	0.034	0.017	0.073	0.025	0.112	0.01379	0.00705	0.03063	0.01047	0.090
	Máx	0.205	0.234	**1.041**	0.372		0.08526	0.09726	0.43158	0.15410	

Min: minimum value observed for the element; Average: average value observed for the element; Máx: maximum value observed for the element. P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area). A PLI < 1 indicates "Unpolluted," PLI > 1 "Polluted," and PLI > 5 "Very highly polluted." SPI index: 0–2 (Natural), 2–5 (Low), 5–10 (Moderate), 10–20 (High), >20 (Dangerous).

A variety of pollution indices are at our disposal for evaluating the quality of soil and sediment. The selection of these indices is intricately tied to specific objectives, considering factors such as contamination levels, metal origins, and potential ecological risks[64–66]. Furthermore, the mathematical and statistical methodology behind these indices makes them practical and highly efficient tools for environmental studies61. Each index specializes in investigating contamination, emphasizing the need to tailor the choice based on the distinct goals of the assessment.

Similar to the PLI index, the SPI provides a composite measure of sediment contamination by various pollutants, allowing for a comprehensive assessment of sediment quality concerning pollution[67,68]. In this study, all investigated metals showed low pollution levels (Natural sediment), with Pb being the most concerning, having a global SPI value of 0.444 (Table 3). The overall PLI value was also higher for Pb. However, when considering the maximum concentration of metals found, Pb stands out with a SPI of 2.410 (P4), classified as “Low-polluted” sediment. Despite Al showing among the highest mean values, its accumulation index values were low, likely due to its high reference value (a relatively abundant element in the Earth's crust).

The estimation results of potential ecological risk coefficients (Epr) and their integrated risk index (RI) for sediment samples are presented in Table 4. The order of Epr for the studied metals is Pb > Ni > Zn > Cu > Cr > Al. Consequently, the estimated Er values for these elements are all lower than 40, indicating a low level of eco- logical risk[42]. As for the RI values, the combined potential ecological risks are assessed to be at a low degree of contamination for most of the studied sites. The highest RI value was observed for Pb (15.749) (Table 4). However, even with this value, the overall risk level for the middle Tocantins River remains classified as "Low-grade" in terms of potential ecological risk.

Table 4. The potential ecological risk index for investigated metals in the sediment from the middle Tocantins River, Maranhão, Brazil.

Sampling site	Index value	Potential ecological risk coefficients (Epr)					
		Al	Cr	Cu	Ni	Pb	Zn
P1	Min	0.001	0.016	0.056	0.070	0.175	0.001
	Average	0.003	0.033	0.147	0.131	**0.995**	0.044
	Máx	0.008	0.106	0.419	0.416	**1.724**	0.265
P2	Min	0.001	0.011	0.024	0.009	0.110	0.000
	Average	0.002	0.015	0.067	0.059	0.262	0.022
	Máx	0.004	0.053	0.140	0.294	0.825	0.303
P3	Min	0.001	0.038	0.067	0.101	0.272	0.010
	Average	0.003	0.052	0.233	0.410	**1.842**	0.096
	Máx	0.006	0.157	0.687	0.882	**2.790**	**1.347**
P4	Min	0.001	0.013	0.033	0.022	0.297	0.000
	Average	0.003	0.020	0.104	0.114	0.402	0.033
	Máx	0.008	0.082	0.305	0.319	**6.055**	0.482
Integrated risk index (RI)		0.041	0.596	2.282	2.827	**15.749**	2.603

P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area). Min: minimum value observed for the element; Average: average value observed for the element; Máx: maximum value observed for the element. Epr values: <40 (Low risk), 40-80 (Moderate risk), 80-160 (Considerable risk), 160-320 (High risk), ≥ 320 (Very high risk). RI values: <150 (Low risk), 150-300 (Moderate risk), 300-600 (Considerable risk), ≥ 600 (Significant risk).

All estimations were conducted across the minimum, average, and maximum values observed in sediment samples collected in 2023. This approach allows for a comprehensive understanding of the temporal variability of the risks involved. By considering the full range of values within the sediment samples, we can better grasp how ecological risk levels fluctuate over time. This comprehensive analysis enhances our ability to assess and manage potential environmental risks associated with metal contamination in sediment ecosystems. Comprehensive ecological risk assessment is of great significance for the restoration of watershed ecosystem health, and the appropriate and effective assessment method is the premise of ecological risk assessment[66].

3.3. Correlation Coefficients and Principal Component Analysis (PCA)

The strongest positive correlations are observed within specific pairs of data: Cu/Si (r= 0.999), Ni/Sn (r= 0.999), Au/Co (r= 0.999), As/Mg (r= 0.999), and Cr/Fe (r= 0.996) (Tab. S1). A negative correlation was not observed. Correlation coefficients offer valuable insights into the strength and direction of relationships among different parameters related to water quality. They are commonly used to analyze associations between persistent contaminants in aquatic ecosystems[69–71]. A coefficient closer to 1 or -1 indicates a stronger correlation, while values near 0 suggest a weaker or nonexistent linear relationship.

Correlation coefficients provide valuable insights into the strength and direction of relationships among analyzed parameters, enhancing our understanding of sediment quality dynamics and potential aquatic contaminant sources[72,73]. Consequently, numerous studies utilize both univariate and multivariate statistical analyses to identify highly correlated sediment pollutants and relevant industries[74,75]. This enables researchers to effectively trace these pollutants and industries, leading to the development of more efficient pollution management strategies and mitigation efforts.

The PCA results indicate that the first two components explain 99.38% of the data variability (Fig. 3). The first component accounts for 97.5% of the variance and is positively loaded with As, B, Ba, Ca, Co, Cr, Cu, and Fe. Conversely, the second component accounts for 1.92% of the variance and is positively loaded with Al and Pb, while exhibiting negative loadings for Ca, Mg, S, and Zn. In this study, the correlation matrix was used to better capture the relationships between metals, minimizing the impact of different variance scales among them. The loadings, scores, and eigenvalues of the principal component analysis are available in the supplementary material (Tables S2, S3, and S4).

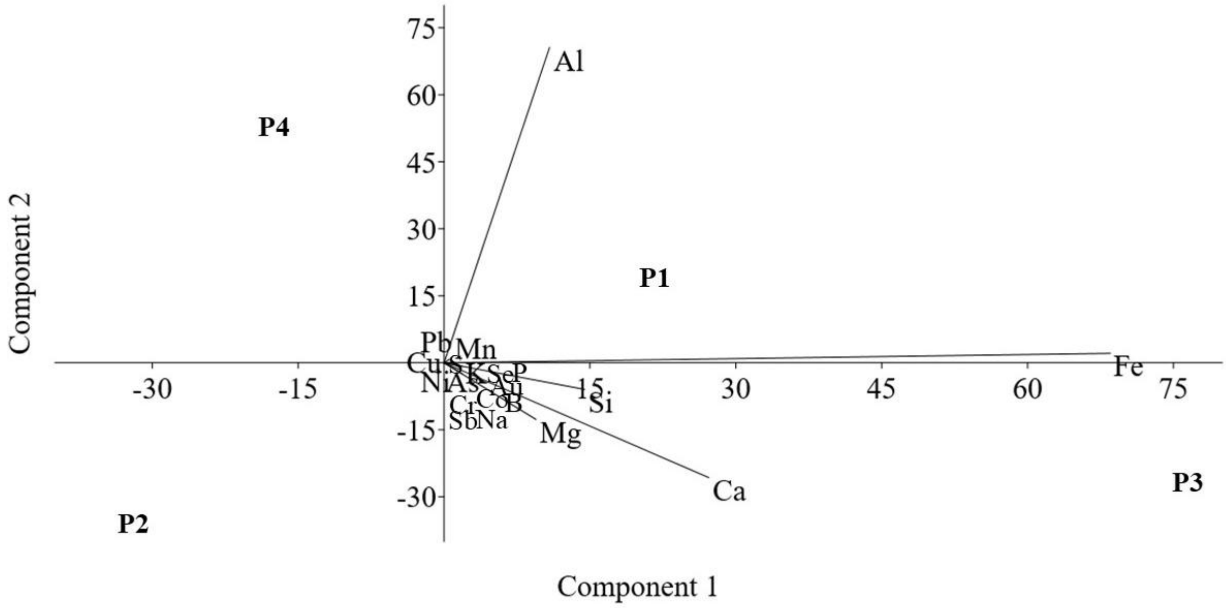

Figure 3. Principal component analysis (PCA) of sediment quality monitoring data of the middle Tocantins River, Maranhão, Brazil.

P1: Beira Rio (urban area), P2: Bananal (rural area), P3: Embiral (rural area), P4: Cidelândia (rural area).

Highlighting the considerable role of aluminum in sediment contamination, PCA offered valuable insights into the underlying dynamics. These sediments can serve as significant sources of metal contamination in aquatic environments, as deposited or stored contaminants may re-suspend or dissolve back into the water. Hence, employing this technique was crucial for pinpointing pollution sources and extracting reliable information to elucidate clearer relationships[76,77].

The PCA analysis unveiled three distinct groups based on sediment quality. The first group comprised stations P1 (located in an urban area) and P3 (close to industrial waste discharge). P1 showed a positive association with the first and second components but a negative association with the third, whereas P3 exhibited a positive association with the first and third components. The second group solely included station P2, situated near the village of "Bananal" in a rural area, which displayed a negative association with all PCA components. The third group consisted solely of station P4, also located in rural areas but in proximity to industrial waste discharge (from pulp and paper production). P4 showed a positive association with both the second and third components but a negative association with the first. This underscores the effectiveness of PCA in identifying pollution sources and providing valuable insights for conservation and management efforts.

This research is one of the few studies on the quality of sediments in the middle Tocantins River, highlighting high concentrations of metals such as Al, Cr, Ni, Pb, Cu, and Zn in an urbanized region of the river. Unregulated urbanization has led to environmental changes, adding high loads of untreated domestic and industrial waste- water, and altering biological, physical, and chemical processes in natural systems, directly or indirectly affecting the population's quality of life[78–80]. The river's maximum flow is approximately 11.000 m3/s, contributing 8.388 t/ day of suspended solid discharge to the ocean[81], supporting marine biodiversity at its mouth. Additionally, the Tocantins River basin is among the most degraded in the Amazon[19,82]. According to Schmitz[83], tropical deforestation and unsustainable policies pose current challenges in this basin, which serves as the ecotone between the Amazon and Cerrado biomes. This region is a primary target for agricultural expansion in Brazil, as indicated in Presidential Decree 8447 of 2015[19,84]. Furthermore, Brazil stands as the world's second-largest agricultural producer and is forecasted to undergo substantial growth in agricultural output over the next four decades[85,86]. Despite these challenges, freshwater ecosystems in this region play vital roles in biodiversity preservation, water purification, and flood control.

In this scenario, this region emerges as a pivotal case study, and measures might be implemented to decrease the levels of these potentially toxic elements. Effective measures to address these issues include the treatment of industrial and urban effluents and the reforestation and conservation of riparian forests[87,88]. Industries and urban areas should be required to properly treat their effluents before discharging them into the river. Water treatment technologies such as chemical precipitation, adsorption, and filtration can effectively remove heavy metals[89–91]. Additionally, vegetation along riverbanks (riparian forests) acts as a natural filter, reducing the amount of sediment and contaminants reaching the river[92,93]. Reforestation projects can help restore these areas, enhancing their capacity to mitigate pollution and protect aquatic ecosystems.

Often, environmental degradation stems from a lack of environmental responsibility and ineffective public policies. Thus, the ongoing deforestation, even in conservation-oriented scenarios, raises questions about the effectiveness of current protection measures, highlighting the need for reassessment and strengthening of conservation strategies. Therefore, ongoing monitoring and enforcement, along with education and awareness efforts, are essential[94–96]. Establishing a continuous monitoring system for pollution levels and rigorous enforcement to ensure adherence to environmental laws is crucial. Furthermore, educational campaigns for local communities and industries on the impacts of pollution and the importance of sustainable practices can foster changes in behavior.

4. CONCLUSION

The levels of aluminum, iron, manganese, and selenium exceeded legal standards through 2023. Although aluminum showed the highest value among the potentially toxic elements, there are no specific limits in national and international standards for this element. Chromium, nickel, copper, zinc, and lead only surpassed the guidelines established by NOAA (National Oceanic and Atmospheric Administration). The seasonal fluctuation indicates a complex dynamic influenced by climatic or seasonal factors. The rainy months of February, April, and May showed heightened levels of aluminum, chromium, nickel, and lead. Particularly, in urban area P1 had a higher presence of Al, while Ni and Pb were more concentrated in P3.

Igeo indicates low pollution levels, with lead and nickel standing out in urban areas (P1) and near the pulp and paper industry (P3 and P4). The EF highlights high concentrations of Pb (P4) and Zn (P3). Both PLI and SPI indices raise concerns regarding Pb (P4) and Zn (P3) concentrations at specific times of the year. The overall risk level for the middle Tocantins River remains classified as "Low-grade" concerning potential ecological risk. These findings stress the importance of continuous monitoring and interventions to uphold water and environ- mental quality in the region.

Credit author statement

Thiago Machado da Silva Acioly – conceptualization, methodology, data curation, formal analysis, investigation, validation, writing-original draft, writing-review, and editing; Marcelo Francisco da Silva – visualization and methodology; José Iannacone – methodology, validation, and writing-review; Diego Carvalho Viana – resources, supervision, project administration, and validation.

Declaration of competing interest

The authors declare that they have no known competing financial and non-financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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CAPÍTULO 5 – BIOACUMULAÇÃO DE ELEMENTOS TÓXICOS E ESSENCIAIS E RESPOSTAS ENZIMÁTICAS EM PEIXES NATIVOS DO MÉDIO RIO TOCANTINS

DESTAQUES

- ✓ *Psectrogaster amazonica* (zona urbana) apresentou concentrações de As, Pb e Se até 266%, 1.850% e 4.537% acima dos limites recomendados, com evidências enzimáticas de estresse hepático.
- ✓ *Caenotropus labyrhinthicus* (zona rural) apresentou Se e As até 5.180% e 470% acima dos limites, respectivamente, além de redução na atividade da AChE, indicando possível distúrbio neurofisiológico.
- ✓ Os valores do Fator de Bioconcentração (BCF) revelaram acúmulo moderado de Fe, S e Ca, indicando retenção específica nos tecidos.
- ✓ O Quociente de Risco (RQ) para Se atingiu 53.13, e a Ingestão Diária Estimada (EDI) de As excedeu os limites seguros para crianças em sete vezes, evidenciando riscos ecológicos e à saúde.

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BIOACCUMULATION OF TOXIC AND ESSENTIAL ELEMENTS AND ENZYMATIC RESPONSES IN NATIVE FISHES FROM THE MIDDLE TOCANTINS RIVER

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Abstract. This study provides the first ecotoxicological evaluation of potentially toxic elements (PTEs), essential elements (EEs), and enzymatic biomarkers in two native fish species, Branquinha (*Psectrogaster amazonica*) and Branquinha-cascuda (*Caenotropus labyrhinthicus*), from the middle Tocantins River, Brazil. Specimens were collected from the urban riverside zone of Beira Rio (P1) and a fluvial beach near the rural community of Embiral (P2). PTEs and EEs concentrations were measured in liver and muscle tissues, and biochemical biomarkers included acetylcholinesterase (AChE), aspartate aminotransferase (AST), alanine aminotransferase (ALT), and alkaline phosphatase (ALP). Human health risks associated with fish consumption were assessed using the bioconcentration factor (BCF), risk quotient (RQ), and estimated daily intake (EDI). In *P. amazonica* (urban zone), arsenic (As) exceeded limits by 83–266% in muscle and 60–220% in liver, lead (Pb) in liver by 95–1850%, and selenium (Se) by up to 4537%. In *C. labyrhinthicus* (rural zone), As and Se in muscle exceeded limits by 185–470% and 5–200%, respectively, while Pb and zinc (Zn) were not detected. BCF values indicated moderate bioaccumulation of sulfur (S) (2867.29) and iron (Fe) (2641.30). Risk assessment revealed a high level of concern, with an RQ for Se reaching 53.13 and As intake exceeding child safety thresholds sevenfold, highlighting significant food safety risks.

Keywords: food safety; dietary intake; heavy metals; freshwater fish; risk assessment; one health

1. INTRODUCTION

Environmental contamination from domestic effluents, agricultural practices, industrial waste, and urban expansion has emerged as a critical global issue, compromising the integrity of aquatic ecosystems and posing risks to organisms and human populations that depend on these environments (Alvariño et al., 2023; Thakur et al., 2025). Among the most hazardous elements in freshwater environments are arsenic (As), chromium (Cr), lead (Pb), cadmium (Cd), mercury (Hg), nickel (Ni), and zinc (Zn), which may become highly toxic when exceeding biological thresholds (Alvariño et al., 2024; Sharma et al., 2025). These contaminants can impair food webs and fish safety, triggering cytotoxic, mutagenic, reproductive, developmental, and carcinogenic effects in exposed organisms (US EPA, 2000; Mitra et al., 2022; Babaniyi et al., 2025).

Fish occupy key ecological and nutritional roles and are recognized as effective bioindicators of aquatic pollution due to their physiological sensitivity, trophic position, and ability to accumulate contaminants throughout their life cycle (Dietrich et al., 2022; Iyiola et al., 2024). Exposure occurs through multiple routes, including ingestion of contaminated food sources, branchial respiration, and dermal absorption resulting from contact with suspended particles and sediments (Chandel et al., 2024; Singh et al., 2024). Many contaminants, particularly trace metals such as As, Cd, Hg, and Pb, tend to accumulate in metabolically active organs like the liver and in muscle tissues consumed by humans, posing health risks even at low environmental concentrations (US EPA, 2000; Islam et al., 2025; Mititelu et al., 2025). In recognition of their toxicity, the International Agency for Research on Cancer (IARC) classifies As, Cd, and hexavalent Cr as Group 1 carcinogens (carcinogenic to humans), while Pb is categorized as Group 2B (possibly carcinogenic) (IARC, 2024).

The bioaccumulation of potentially toxic metals in fish has been increasingly documented worldwide, reflecting a widespread environmental and public health concern. Rapid agricultural expansion, industrial effluent discharge, and urban and peri-urban runoff have contributed to the transport of these elements (including As, Pb, Cd, Hg, and Se) into freshwater systems, promoting their entry into the food chain (Xu et al., 2014; Masindi & Muedi, 2018; Shifaw, 2018). Once accumulated in fish tissues, these elements can biomagnify, ultimately reaching human consumers. Chronic consumption of contaminated fish can lead to neurological impairments, hematological disturbances, developmental delays, carcinogenesis, gastrointestinal damage, cardiovascular disease, and elevated cancer risk, even when ingestion occurs in low but continuous doses (Munir et al., 2021; Al-Sulaiti et al., 2023; Mititelu et al., 2025). Studies in Bangladesh (Sarker et al., 2022; Chakma et al., 2025; Shetty et al., 2025), Serbia (Milošković & Simić, 2023), the Pearl River Basin in China (Fan et al., 2025), and the Orashi River in Nigeria (Ossai et al., 2025) consistently demonstrate that rivers affected by agroindustrial, mining, and urban pressures exhibit elevated metal concentrations in fish tissues, underscoring the universality of this issue across distinct geographic and socioeconomic contexts.

Despite these risks, fish remain an essential source of macro- and micronutrients, including proteins, iron (Fe), zinc (Zn), copper (Cu), Selenium (Se), and particularly long-chain omega-3 polyunsaturated fatty acids such as docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA). These compounds play key roles in maintaining cardiovascular and neurological functions and have been associated with reduced risks of coronary disease and with modulation of inflammation (Ghasemi Fard et al., 2019; Zhuzzhassarova et al., 2024). To minimize exposure-related risks, organizations such as the European Commission (EC), the World Health Organization (WHO), the Food and Agriculture Organization (FAO), and the United States Environmental Protection Agency (USEPA) have established maximum permissible limits and intake guidelines to evaluate dietary exposure risks for both general and vulnerable populations, including children (Ossai et al., 2025). These regulatory frameworks are essential for guiding risk assessments that support public health protection.

The Tocantins River is an important watercourse that flows through the states of Maranhão and Tocantins, Brazil, emptying into Pará, and forms part of the Araguaia-Tocantins system (Acioly et al., 2025). Located in the transitional zone between the Cerrado and Amazon biomes, it plays a vital strategic role both regionally and nationally, serving as a major transportation corridor and gateway to the Amazon region. Its surrounding areas host dynamic agribusiness and industrial activities that significantly contribute to economic development and job creation. The river averages 30 meters in depth, 500 meters in width, and has a discharge of approximately 13.600 m³/s (Acioly et al., 2024). Communities along its banks, as well as nearby villages, depend heavily on the river for domestic water use, recreation (such as bathing), and artisanal fishing, which supports both subsistence and local commerce (Acioly et al., 2025). However, environmental pressures such as agricultural expansion, monoculture practices (e.g., eucalyptus plantations), aquaculture, and inadequate urban sanitation infrastructure have contributed to water quality degradation (Jesus, 2023; Acioly et al., 2024; Araújo et al., 2024). Moreover, urban runoff can transport potentially toxic metals, oils, excess nutrients, pesticides, polycyclic aromatic hydrocarbons (PAHs), and emerging contaminants such as pharmaceutical metabolites into the river (Singh et al., 2022; Gunasekara et al., 2025; Labad et al., 2025; Mishra & Botlaguduru, 2025; Ullah et al., 2025). This situation is particularly concerning for local communities that rely on fishing as a traditional source of food and income (Acioly et al., 2025). Riverside families depending on water and fish from the middle Tocantins River face risks from contaminants, highlighting the urgent need for effective monitoring and management.

This study provides the first comprehensive assessment of potentially toxic elements (PTEs) and essential elements (EEs) in the muscle and liver tissues of two native fish species, *Psectrogaster amazonica* Eigenmann & Eigenmann, 1889 and *Caenotropus labyrhinthicus* (Kner, 1858), from the middle Tocantins River, addressing a notable gap in regional knowledge. These species are ecologically important and widely consumed by riverside communities, making them suitable sentinel organisms for monitoring contaminant exposure, as documented in previous ecological and socio-environmental studies (Freitas et al., 2021; Acioly et al., 2025; Barbosa et al., 2025). To evaluate potential human health risks, the Bioconcentration Factor (BCF), Risk Quotient (RQ), Risk Index (RI), and Estimated Daily Intake (EDI) were calculated. This integrated approach directly links environmental contamination to real dietary exposure in traditional Brazilian Amazonian riverine communities.

2. MATERIALS AND METHODS

2.1. Sampling Sites

The study was conducted in the middle stretch of the Tocantins River, within the area influenced by the municipality of Imperatriz (sub-basin 23), Maranhão, Brazil. Sampling campaigns took place during the hot and dry season of 2023 (July to December), according to the Köppen-Geiger climate classification (Köppen & Geiger, 1928). Located at the interface between the Brazilian savanna (Cerrado) and Amazon biomes, this river holds considerable regional and national relevance as a transportation corridor and gateway to the Amazon. Fish specimens were collected from two key sites: the urban riverside area known as "Beira Rio" (coordinates: 2°34'57.82"S; 44°21'34.92"W) (P1) and a fluvial beach near the rural community of Embiral (coordinates: 5°41'17.6658"S; 47°28'30.40752"W) (P2), approximately 40 km from the municipality of Cidelândia (Figure 1). Sampling points were georeferenced in the field using a GARMIN 4215 GPS receiver. The map was created using QGIS software (version 3.40.9; https://qgis.org/) under the SIRGAS 2000 geographic coordinate system (EPSG:4674). Cartographic base layers were obtained from publicly available datasets provided by the Brazilian National Water Agency (ANA, 2017) and the Brazilian Institute of Geography and Statistics (IBGE, 2024).

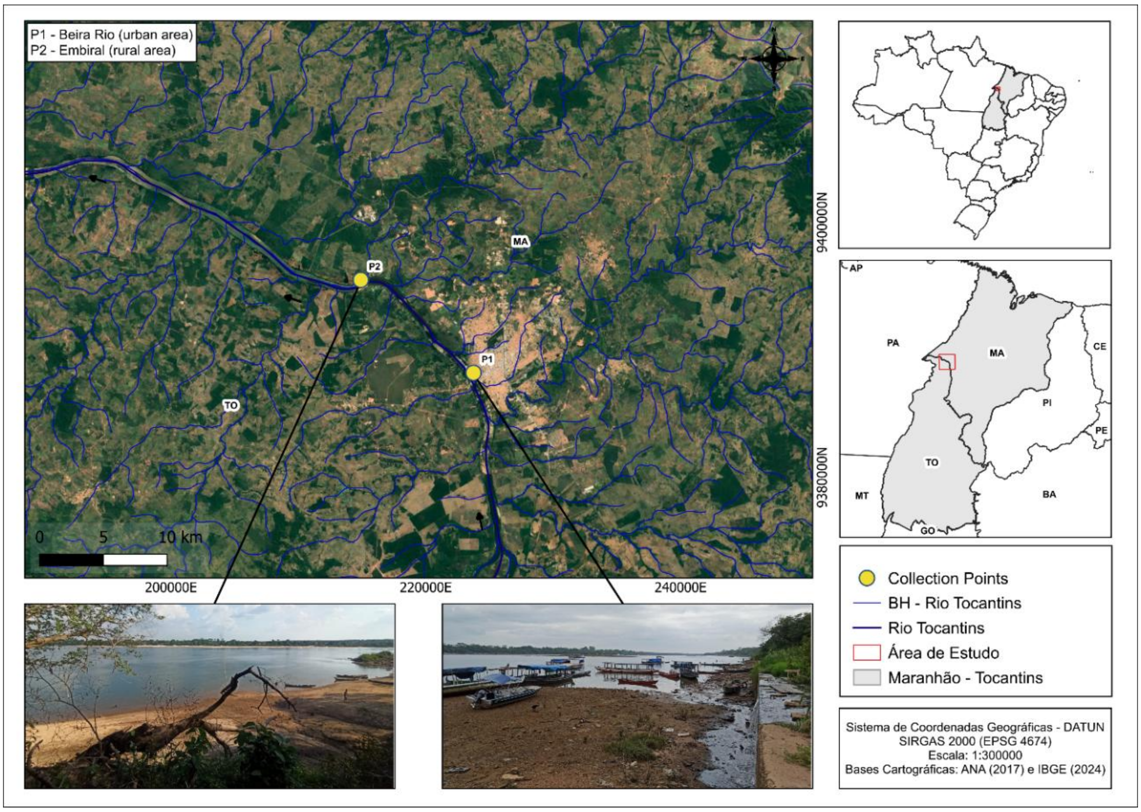

Figure 1. Location, main characteristics, and geographic coordinates of the sampling sites in the middle Tocantins River, Maranhão, Brazil.

A recent study conducted in the middle Tocantins River, Maranhão, Brazil, offers a detailed environmental characterization of two distinct sampling sites. The first site (Beira Rio), located within an urban zone, is heavily influenced by anthropogenic activities, including boat traffic, recreational use, improper waste disposal, and discharge from iceboxes and untreated urban sewage. This area is notably affected by high viral loads in sewage, with concentrations reaching 260 billion copies per liter (REMONAR, 2023). The second site, located upstream from the urban area, lies near a pulp and paper industry and is subject to its effluent discharge, representing a potential source of pollution. Despite this, the area is frequently used for recreational activities on river beaches and private estates and is also a site for small-scale artisanal fishing by residents. Previous studies conducted at four sites along the middle Tocantins River, Maranhão (Acioly et al., 2024; Machado da Silva Acioly et al., 2024), served as the basis for selecting the current sampling locations, representing an urban site under greater anthropogenic influence and a rural site under lower impact. This selection strategy aimed to minimize environmental disturbance and reduce the number of animals required for the study, in accordance with ethical research principles.

2.2. Fish Sampling

Fish specimens were captured using gill nets with mesh sizes ranging from 1.5 to 8.0 cm (measured between opposite knots), in addition to cast nets. A total of 30 individuals were collected, comprising 15 specimens of *P. amazonica* from the urban site (P1) and 15 specimens of *C. labyrhinthicus* from the rural site (P2). The use of different species at each site was based on local species availability, ecological representativeness, and relevance to human consumption (Freitas et al., 2021; Acioly et al., 2025; Barbosa et al., 2025), as *P. amazonica* predominated at P1 and *C. labyrhinthicus* at P2. This approach is consistent with ecotoxicological and biomonitoring studies that employ locally abundant, site-specific fish species as sentinel organisms when paired sampling of the same species is not feasible (Barrett & Munkittrick, 2010). Biometric data (total weight, g; standard length, mm) were recorded using a portable scale and an ichthyometer, and sex was determined. Species identification was based on morphological characteristics, supported by taxonomic literature and the traditional ecological knowledge of local fishers.

Muscle and liver tissues were collected for the analysis of PTEs and EEs. Evisceration was performed in the field using sterile surgical scalpels, and samples were stored in polyethylene containers at −4 °C for transport and at −20 °C upon arrival at the laboratory at the State University of the Tocantina Region of Maranhão (UEMASUL) until analysis. Anesthesia and euthanasia followed internationally and nationally recognized ethical guidelines. Eugenol was used as the primary anesthetic, with auxiliary ice slurry to reduce metabolic activity, followed by anesthetic overdose and spinal cord sectioning, in accordance with the AVMA Guidelines for the Euthanasia of Animals (2020) and the Brazilian Guidelines for Best Practices in Animal Euthanasia (CFMV, 2012).

2.3. Preparation and Chemical Processing of Fish Samples

To determine the total concentration of elements in fish tissues, approximately 0.5 g of dried muscle tissue was accurately weighed and digested using an acid mixture composed of 1 mL of hydrochloric acid (HCl) (50%), 1 mL of nitric acid (HNO_3) (50%), and 8 mL of deionized water. The procedure followed the guidelines outlined in Method 3050B by the U.S. Environmental Protection Agency (US EPA, 1996). The digestion was conducted using a heating block (ECO 16, VELP Scientific) at 120 °C for 2 hours. Subsequently, the quantification of PTEs, Al (aluminum), As (arsenic), Au (gold), Sb (antimony), Cd (cadmium), Cr (chromium), Pb (lead), Ni (nickel), Sr (strontium), Ti (titanium), and In (indium); and EEs, B (boron), Ba (barium), Be (beryllium), Ca (calcium), Co (cobalt), Cu (copper), Fe (iron), K (potassium), Mg (magnesium), Mn (manganese), Na (sodium), P (phosphorus), S (sulfur), Se (selenium), Si (silicon), Sn (tin), and Zn (zinc) was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES) with a SHIMADZU ICPE-9000 (Kyoto, Japan). All measurements were performed in triplicate, and results were expressed in mg/kg of fish tissue, as calculated using Equation 1 (NYANTAKYI et al., 2021). Elements that were below detection limits or occurred at very low concentrations were retained in the analytical protocol but are not discussed in detail in the Results section due to their limited ecological or toxicological relevance. The measured concentrations were then evaluated against established national and international regulatory standards to assess compliance and potential environmental risk (Table 1).

$$\text{Concentration of the metal (mg / kg)} = \frac{\text{(Instrument reading × volume of the extract)}}{\text{mass of fish digested}} \quad (Eq. 1)$$

Table 1. Guidelines for element concentrations (mg/kg) in edible fish tissues.

Elements	**Brazil**	**Mercosul** (GMC/RES. Nº 12/11)	**Chile**	**FAO** (n◦ 66/2003)	**WHO/FAO** (CODEX)
As	1.0	1.0	1.0		0.5
Cd	1.0	0.05		0.05	0.5
Cu			10		
Se			0.3		
Pb	2.0	0.3	2	0.2	0.3
Zn			100		

Brazil (ANVISA, 1998). MERCOSUL (2011). Chile (Ministerio de Salud, 2016). FAO (2003). WHO/FAO Codex Alimentarius Commission (2023).

To ensure the reliability of elemental analyses in fish tissues, rigorous quality assurance (QA) and quality control (QC) procedures were implemented following the U.S. EPA Quality Management System (US EPA, 2002) and the internal standards of the analytical laboratory. These procedures included: (a) strict adherence to equipment manufacturers' specifications, (b) regular instrument calibration, (c) proper sample handling with documented custody and storage, (d) standardized procedures before and after sample collection, and (e) comprehensive documentation of all analytical steps. Only analytical-grade reagents and chemicals (Merck, PA grade) were used throughout the study (US EPA, 1991; US EPA, 2007; Osorio et al., 2022). Multi-element ICP standards (Merck), calibrated according to DKD-accredited procedures (DKD-K-14302), were used for external calibration curves. Instrument calibration was performed prior to analysis and routinely verified throughout analytical runs, with recalibration conducted whenever necessary, in accordance with manufacturer specifications. All calibration curves exhibited high linearity, with correlation coefficients (r) exceeding 0.998. Method performance was evaluated through linearity, precision, and recovery. Precision was assessed by replicate analyses, while recovery was determined using matrix spike experiments, in which known concentrations of multi-element standards were added to fish tissue samples prior to analysis. Recovery rates ranged from 90% to 109%, confirming satisfactory analytical accuracy and reliability. No certified reference material (CRM) specific to fish tissues from the Tocantins River or to the studied species was available at the time of analysis, which represents a limitation of the study. However, this work constitutes the first ecotoxicological assessment of elemental contamination in these species and this river section, and data quality was supported by consistent calibration linearity, acceptable recovery rates, and reproducible analytical performance.

2.4. Fulton Condition Factor (Q)

The Fulton condition factor (Q), also known as the condition index, was used to assess the length-weight relationship of the fish samples and their condition in the river according to Equation 2 (Fulton, 1904). This index provides an estimate of the nutritional status, health, and well-being of the fish, and is useful for understanding how the physical condition of the fish can vary with environmental and nutritional factors.

$$Q=\frac{W}{L^3}\times 100 \text{ (Eq. 2)}$$

Where W is the total body weight of the fish in grams (g), and L is the total length of the fish in centimeters (cm). According to Sekitar et al. (2015) and Datta et al. (2013), a $Q \leq 1$ indicates poor condition (possibly due to factors such as lack of food, environmental stress, or disease), a $Q = 1.2$ indicates moderate condition (expected for the length and weight), and a $Q \geq 1.4$ indicates proportionally good condition (good health status). This index is widely used in ecological and fisheries biology studies to monitor the conditions of different fish populations and to better understand the impacts of environmental factors on these populations (Nyantakyi et al., 2021; Nodehi et al., 2024).

2.5. Bioconcentration Factor (BCF)

The BCF quantifies how readily a compound accumulates in aquatic organisms relative to its concentration in the surrounding water, as expressed in Equation 3 (Guabloche et al., 2024). This parameter is calculated by dividing the compound's concentration in the organism by its concentration in the aquatic environment, with water concentration data, in this case, sourced from Acioly et al. (2025). The BCF is a critical metric for evaluating the ecological and health risks associated with contaminants of emerging concern (Ruan et al., 2020; Irshad et al., 2024) and can be determined in various organs or tissues such as liver, muscle, kidney, or brain (Del Carmen Gómez-Regalado et al., 2023).

$$BCF=\frac{\text{concentration of the substance in the body}}{\text{concentration of the substance in water}} \text{ (Eq. 3)}$$

Fish are commonly used in BCF assessments due to their ecological and nutritional significance, as well as the availability of standardized test methods. According to the classification proposed by the US EPA (2010), compounds with a BCF below 1000 are considered not bioaccumulative, those between 1000 and 5000 are classified as bioaccumulative, and values exceeding 5000 are indicative of high bioaccumulation potential. Thereby, a BCF of 1000 means that the organism concentrates the product up to a value a thousand times higher than that of the environment (INECC, 2023).

2.6. Risk Assessment for Human Health from Fish Consumption

Human health risk from fish consumption was evaluated using the Risk Quotient (RQ) and the cumulative Risk Index (RI). The RQ for each metal was calculated as the ratio between its concentration in fish muscle tissue and the corresponding maximum permissible limit (ML) established by Brazilian and international regulations (ANVISA, 1998; ANVISA, 2013), as shown in Eq. (4). Values of $RQ < 1$ indicate no expected risk, whereas $RQ \geq 1$ suggest potential adverse effects (US EPA, 2010).

$$RQ = \frac{C}{ML} \quad \text{(Eq. 4)}$$

Where C is the concentration of the metal in fish muscle (mg/kg, wet weight) and ML is the regulatory maximum limit (mg/kg). To assess the combined risk from multiple metals, the RI was calculated as the sum of individual RQ values (Eq. 5). Higher RI values indicate greater potential health concern from dietary exposure (Viana et al., 2023).

$$RI = \sum RQi \quad \text{(Eq. 5)}$$

Where RQ_i represents the risk quotient of each metal i.

2.7. Estimated Daily Intake (EDI)

To improve human health risk assessment, the EDI of each bioaccumulated metal in fish muscle tissue was determined by dividing its concentration by the average daily fish consumption rate, normalized by average adult body weight (Souza et al., 2025). This evaluation followed the methodology proposed by the US EPA (2000), with adaptations described by Naji et al. (2016). Two fish consumption scenarios were considered: the national average for the Northern region of Brazil of 23 kg/person/year (Arruda, 2017) and the higher regional estimate of 151.98 kg/person/year for the Brazilian Amazon population (Isaac et al., 2015; Souza-Araujo et al., 2022). Risk characterization and safe consumption thresholds were established according to the approach developed by Naji et al. (2016).

EDI was calculated using Equation 6, where C is the concentration of metals in fish muscle (mg/kg), IR is the ingestion rate—63 g/day for the general Brazilian population (Arruda, 2017) and 416.39 g/day for individuals in the Amazon region (Isaac et al., 2015; Souza-Araujo et al., 2022)—and BW is body weight (70 kg for adults, 15 kg for children), based on standard reference values widely used in human health risk assessment (Smith, 1995; US EPA, 2000; US EPA, 2008; Abdel-Kader et al., 2023). The resulting EDI values were compared against reference doses (RfDs) defined by ANVISA (2019) for most elements, and by FAO/WHO (2010) for lead (Pb), which represent the maximum daily intake considered safe. Including both ingestion scenarios allows for a broader assessment of potential health risks and supports the development of consumption guidelines, especially for Amazonian populations with high fish consumption habits.

$$EDI = \frac{C}{IR/_{BW}} \text{ (Eq. 6)}$$

2.8. Enzyme biomarkers assay

The liver and muscle samples were processed as follows: 100 mg of each tissue was weighed on an analytical balance and placed in a 1.5 ml glass test tube. Next, 0.4 ml of cold 1X phosphate-buffered saline (PBS) was added, and the tissue was homogenized using a micro-homogenizer. The tubes were centrifuged at 4.000 rpm for 15 minutes. The supernatant was transferred to microtubes and kept refrigerated (4°C) until all analyses were completed. The activities of acetylcholinesterase (AChE), aspartate aminotransferase (AST), alanine aminotransferase (ALT), and alkaline phosphatase (ALP) were then measured using a spectrophotometer (Model 800 XI) with thermostatted cuvettes (37ºC).

2.8.1. Quantification of AChE in muscle and liver

AChE activity was determined using the Enzymatic Kinetic Test (Bioclin K094). The enzyme activity catalyzes the hydrolysis of butyrylthiocholine to thiocholine and butyrate; thiocholine reduces potassium hexacyanoferrate (III), a yellow compound, to colorless hexacyanoferrate (II). The decrease in absorbance is measured at 405 nm. The minimum detection limit is 50 U/L, and the test is linear up to 20.000 U/L.

For the assay, 10 µL of supernatant was added to a cuvette, followed by 400 µL of reaction buffer (pyrophosphate, potassium hexacyanoferrate (III), stabilizer, and preservative). The contents in the cuvette were mixed, homogenized, and incubated for approximately 3 minutes at 37°C. Then, 100 µL of substrate (butyrylthiocholine, buffer, stabilizer, and preservative) was added. After homogenization, the mixture was incubated for exactly 2 minutes in a thermostatted cuvette at 37°C, and absorbance was measured at 405 nm. The readings were taken again after 1, 2, and 3 minutes.

AChE activity was expressed as nmol/mg/min. The absorbance value was multiplied by 62.000 to obtain the value in U/I (international units). The linear equation obtained was Y = 1.0028X - 170.85, with a correlation coefficient of 0.9964.

2.8.2. Quantification of AST in the liver

AST activity was determined using the Enzymatic Kinetic Test (Bioclin K048). AST catalyzes the transfer of amino groups from aspartate to α-ketoglutarate, forming glutamate and oxaloacetate. In the presence of malate dehydrogenase (MDH), oxaloacetate reacts with NADH, converting to malate and oxidizing NADH to NAD+. The rate of oxidation is proportional to the AST activity in the sample, in the absorbance readings taken at 340 nm. The minimum detection limit is 1.756 U/L, and the test is linear up to 400 U/L.

For the assay, 100 µL of supernatant was added to a cuvette, followed by 1 mL of working reagent (substrate + coenzyme). The contents in the cuvette were mixed, homogenized, and incubated for approximately 1 minute at 37°C. An initial absorbance reading was taken, with the timer started simultaneously. Subsequent readings were taken at 1, 2, and 3 minutes. The average differences in absorbance per minute (A/min) were calculated and used for the result calculation. AST activity was expressed as nmol/mg/min. The absorbance value was multiplied by 1.746 to obtain the value in U/I (international units). The linear equation obtained was Y = 0.9765X + 1.0283, with a linear correlation coefficient of 0.9999.

2.8.3. Quantification of ALT in the liver

ALT activity was determined using the Enzymatic Kinetic Test (Bioclin K049). In this assay, the kinetic determination of ALT follows this sequence: ALT catalyzes the transfer of the amino group from alanine to α-ketoglutarate, forming pyruvate and glutamate. Pyruvate, in the presence of lactate dehydrogenase (LDH), reacts with NADH, converting to lactate and oxidizing NADH to NAD+. The rate of oxidation is proportional to the ALT activity in the sample, in the absorbance readings taken at 340 nm. The minimum detection limit is 0.998 U/L, and the test is linear up to 400 U/L.

For the assay, 100 µL of supernatant was added to a cuvette, followed by 1 mL of working reagent (substrate + coenzyme). The contents in the cuvette were mixed, homogenized, and incubated for approximately 1 minute at 37°C. An initial absorbance reading was taken, with the timer started simultaneously. Subsequent readings were taken at 1, 2, and 3 minutes. The average differences in absorbance per minute (A/min) were calculated and used for the result calculation. ALT activity was expressed as nmol/mg/min. The absorbance value was multiplied by 1.746 to obtain the value in U/I (international units). The linear equation obtained was Y = 0.9693X + 1.33, with a correlation coefficient of 0.9995.

2.8.4. Quantification of ALP in liver and muscle

ALP activity was determined using the Enzymatic Kinetic Test (Bioclin K021). The methodology employed was the IFCC Kinetic method, where ALP catalyzes the transfer of the phosphate group from the substrate p-Nitrophenylphosphate (pNPP) to 2-Amino-2-Methyl-1-Propanol (AMP), forming p-Nitrophenol. The rate of p-Nitrophenol release, which has high absorbance at 405 nm, is proportional to the ALP activity in the sample. The minimum detection limit is 3.08 U/L, and the test is linear up to 1500 U/L.

For the assay, 20 µL of supernatant was added to a cuvette, followed by 1 mL of working reagent (buffer, p-Nitrophenylphosphate substrate, stabilizer, and preservative). The contents in the cuvette were mixed, homogenized, and incubated for approximately 1 minute at 37°C. An initial absorbance reading was taken, with the timer started simultaneously. Subsequent readings were taken at 1, 2, and 3 minutes. The average differences in absorbance per minute (A/min) were calculated and used for the result calculation. ALP activity was expressed as nmol/mg/min. The absorbance value was multiplied by 2,757 to obtain the value in U/L (international units). The linear equation obtained was $Y = 0.9979X - 0.486$, with a correlation coefficient of 0.9996.

2.9. Statistical Analysis

Statistical analyses were conducted using PAST software, version 4.03 (2020), with the significance level set at $p < 0.05$. Data normality was assessed using the Kolmogorov–Smirnov and Shapiro–Wilk tests, and the homogeneity of variances was verified with Levene's test. Since the data did not meet the assumptions of normality (Shapiro–Wilk, $p < 0.05$), differences in metal concentrations and enzymatic activities between sites (P1 and P2) were evaluated using the non-parametric Mann–Whitney U test. Correlation analyses (e.g., Pearson or Spearman) were not performed because only two sampling sites were available, which precludes meaningful estimation of inter-variable relationships. The association between two variables is expressed by the correlation coefficient r, ranging from −1 to +1, where values close to zero indicate no linear relationship and values approaching ±1 indicate a perfect correlation (Akoglu, 2018). Positive values of r ($r > 0$) indicate direct relationships between variables, whereas negative values ($r < 0$) indicate inverse relationships. The strength of the associations was interpreted following Akoglu (2018), considering $|r| \leq 0.30$ as weak, 0.40–0.60 as moderate, and $|r| \geq 0.70$ as strong.

2.10. Ethical statement

This study was approved by the Ethics Committees on Animal Use of the State University of the Tocantins Region (CEUA No: 1025220722) and the State University of Maranhão (CEUA Nº: 040/2023), with collection authorized by SISBIO (Authorization N°: 87310–1). All experimental procedures involving animals were performed in accordance with relevant institutional, national, and international guidelines and regulations for the care and use of animals in research. This study is reported in accordance with the ARRIVE guidelines 2.0 for the reporting of animal research (Du Sert et al., 2020).

3. RESULTS AND DISCUSSION

Previous environmental assessments conducted in the middle Tocantins River basin provide essential context for interpreting the present findings. Acioly et al. (2024) performed an integrated evaluation of physicochemical and biological parameters in surface waters, including temperature, pH, turbidity, electrical conductivity, redox potential, dissolved oxygen, salinity, chlorophyll, total dissolved solids, nitrogenous compounds, and trace elements, thereby characterizing baseline ecosystem conditions. In a complementary study, Machado da Silva Acioly et al. (2024) investigated the same elements in bottom sediments using contamination and ecological risk indices, revealing marked spatial variability and clear signals of anthropogenic influence along different sectors of the basin. Together, these studies establish a robust baseline for environmental quality in the middle Tocantins River. Building upon this environmental framework, the results of the present study provide biological evidence that such contamination is not restricted to abiotic compartments but is effectively transferred to aquatic biota. The detection of toxic elements such as As, Pb, and Se in fish tissues indicates that metals present in the environment are biologically available. Moreover, differences in metal accumulation patterns between fish collected from urbanized and rural areas highlight the influence of localized anthropogenic pressures on contaminant exposure. Collectively, these findings establish a direct link between environmental contamination and biological uptake, providing the foundation for the subsequent discussion of bioaccumulation dynamics, physiological responses, and potential ecological and human health implications.

3.1. Biometric Data and the Fulton Condition (Q)

For *P. amazonica*, individual weights ranged from 83 to 110 g and standard lengths from 17 to 21 cm. *C. labyrhinthicus* individuals weighed 28–57 g with lengths of 10.8–13 cm (Table 2). The Q factor, a widely used indicator of fish health, indicated good body condition for both species (*P. amazonica*: Q = 1.40; *C. labyrhinthicus*: Q = 2.20). According to Datta et al. (2013), Q values above 1.4 typically reflect good physiological status, suggesting that the captured individuals were not under significant stress at the time of sampling. This apparent maintenance of good body condition, despite the presence of elevated metal concentrations, suggests sublethal exposure scenarios in which fish are able to sustain somatic growth while undergoing biochemical and physiological adjustments. Such a pattern indicates that condition indices alone may not fully capture underlying toxic stress.

Table 2. Taxonomy of biological material and biometric measurements.

Common Name (Scientific name)	Environment/ Trophic level	Sampling point	Number of fish collected	Standard length (CP)		Weight (W)		Fulton Condition Factors (Q)
				Mean ± SD	Min-Max	Mean ± SD	Min-Max	
P. amazonica	d/ 2.2 and 2.79	P1	15	19±1.72	17-21	96±10.15	83-110	1.40
C. labyrhinthicus	d/ 2.2 and 2.79	P2	15	12±0.68	10.8-13	38±6.88	28-57	2.20

P1: Beira Rio (urban area). P2: Embiral (rural area). bp: benthopelagic, d: demersal, pn: pelagic-neritic, Trophic level: herbivores may have values of trophic level between 2.0 and 2.19; tc: consumers who consume 'mainly animals' (carnivores) may have trophic levels equal to or greater than 2.8; and fish which are partly herbivore and partly carnivore, i.e. omnivores which consume 'plants/detritus + animals' may have trophic levels between 2.2 and 2.79.

3.2. PTEs and EEs in Branquinha (P. amazonica) (urban zone)

The highest concentrations of elements in muscle tissue of *P. amazonica* were Ca > K > Mg > Na > Fe > Zn > P, whereas in liver the order was Fe > Ca > K > Na > Mg > Zn > P (Table 3). Al, although not among the most abundant elements, is noteworthy due to its toxicological relevance, with concentrations of 7.19 mg/kg in muscle and 3.34 mg/kg in liver. These values are below the No Observed Adverse Effect Level (NOAEL) of 30 mg/kg body weight/day established by FAO/WHO (ANVISA, 2019), suggesting no immediate health risk. Nevertheless, the detection of aluminum in both muscle and liver tissues indicates continuous environmental exposure and bioavailability, which may contribute to cumulative effects when combined with other elements present in the system. Therefore, the absence of acute risk does not exclude potential long-term ecological or health implications. In contrast, Se was markedly elevated, reaching 9.30 mg/kg in muscle and 13.91 mg/kg in liver, exceeding the international safety limit of 0.3 mg/kg by approximately 3100% in muscle and 4537% in liver. Se intake in humans primarily occurs through dietary sources such as meat, cereals, and seafood. Excessive dietary intake can lead to selenosis, with symptoms including dermatologic and neurologic disorders, gastrointestinal disturbances, hepatotoxicity, fatigue, irritability, and mild neurological effects (Zwolak, 2020; Aktaş & Bilgiç, 2025). These findings highlight a significant health concern for both fish and consumers.

Table 3. Average, maximum, and minimum values of PTEs and EEs concentrations (mg/kg) in tissues of *P. amazonica* from the middle Tocantins River (P1: urban zone).

	Minimum (mg/kg)		**Maximum (mg/kg)**		**Average (mg/kg) ± Standard deviation**	
Elements (Detection limit)	**Muscle**	**Liver**	**Muscle**	**Liver**	**Muscle**	**Liver**
			PTEs			

Al (0.014)	2.27	1.2	13.27	6.93	7.19±4.49	3.34±2.36
As (0.002)	1.06	0.96	2.75	1.99	**1.83±0.65***	**1.6±0.41***
Au (0.001)	0.35	0.62	1.31	7.44	0.71±0.37	3.95±2.71
Cr (0.003)	0.78	-	3.70	-	1.83±1.15	-
In (0.033)	0.19	-	2.31	-	0.31±0.17	-
Pb (0.012)	-	1.44	-	6.74	-	**3.90±2.53***
Ni (0.002)	1.85	1.76	3.18	3.20	2.53±1.04	2.66±0.59
EEs						
Ba (0.002)	0.13	0.13	0.48	0.36	0.31±0.25	0.14±0.18
Ca (0.007)	77.38	139.04	759.31	489.09	590.14±132.36	394.70±128.16
Co (0.003)	-	3.60	-	7.80	-	5.54±2.01
Cu (0.003)	0.14	6.52	0.66	13.71	0.31±0.2	9.56±3.10
S (0.001)	274.54	168.36	368.13	274.54	298.79±34.68	210.57±46.19
Se (0.024)	5.24	8.51	15.62	17.93	**9.30±4.13***	**13.91±3.92***
Sb (0.003)	1.23	1.64	2.78	4.09	1.94±0.59	3.12±1
Sn (0.021)	5.16	4.31	10.60	7.40	6.97±2.2	6.15±1.29
Si (0.015)	6.34	11.40	14.98	19.64	9.44±3	15.04±3.39
Fe (0.002)	7.64	432.88	20.92	2189.8	11.07±5.1	1215.93±703.1
Mg (0.001)	169.09	142.02	249.19	163	212.47±32.12	150.45±9.22
Mn (0.001)	0.18	1.11	3.55	1.62	1.04±1.28	1.47±0.21
Na (0.020)	163.76	149.90	229.39	305.07	186.90±24.31	202.42±73.23
P (0.004))	0.89	12.95	6.40	22.54	2.67±2.01	17.33±3.70
K (0.018)	207.45	280.22	284.86	572.73	257.33±26.53	384.88±110.41
Zn (0.002)	0.085	17.04	9.30	26.73	3.99±4.25	21.72±3.52

*Elements that are above national or/and international standards.

As concentrations in *P. amazonica* exceeded recommended limits, with 1.83 mg/kg in muscle (83–266% above Brazil/MERCOSUL and WHO/FAO limits, respectively) and 1.60 mg/kg in liver (60–220% above limits). Pb in liver (3.90 mg/kg) surpassed thresholds by 95% (Brazil/Chile), 1200% (MERCOSUL/WHO), and 1850% (FAO). These results indicate site-specific contamination and underscore the liver’s key role in bioaccumulation and detoxification of toxic elements. Zn was detected only in specimens from this area, with elevated hepatic levels, suggesting significant environmental exposure. The presence of As in muscle tissue raises concerns for food safety and human health. As, a well-known toxicant, is associated with gastrointestinal, neurological, cardiovascular, and hematological disorders (Edition, 2000; Munir et al., 2021; Rahaman et al., 2022), reinforcing the need for ongoing environmental monitoring in urbanized and ecologically sensitive regions (MERCOSUL, 2011).

Exposure to Pb represents a significant public health concern, particularly for populations consuming contaminated fish (Nkansah et al., 2024; Zhuzzhassarova et al., 2024). Pb is persistent, non-biodegradable, and one of the most prevalent aquatic contaminants. It acts as an immunotoxicant and is associated with various physiological, biochemical, and neurological disorders in humans (Dietert & Piepenbrink, 2006; Das et al., 2022). In fish, Pb exposure affects reproduction, growth, and behavior (Burden et al., 1998; Mobarak & Sharaf, 2010; Reddy et al., 2023). Its hepatotoxic effects are primarily linked to oxidative stress, including excessive reactive oxygen species (ROS) generation, which can disrupt antioxidant enzyme activity and lead to cell death.

3.3. PTEs and EEs in tissues of Branquinha-cascuda (C. labyrhinthicus) (rural zone)

In muscle tissue, the most abundant elements were Ca > K > Mg > Na > Fe > P, whereas in liver the order was Fe > Ca > K > Na > Mg > P (Table 4). As and Se were detected in muscle tissue, with As at 2.85 mg/kg (185–470% above Brazil/MERCOSUL and WHO/FAO limits, respectively) and Se at 15.94 mg/kg (5180% above the international safety limit). Pb and Zn were not detected in rural specimens, suggesting lower local contamination. Nevertheless, the elevated As and Se concentrations indicate the need for ongoing environmental monitoring to safeguard both aquatic ecosystems and human health. The occurrence of elevated As and Se in fish from a rural setting indicates that contamination is not restricted to urban effluents. However, may also reflect upstream transport, natural geochemical background, or diffuse anthropogenic inputs. This reinforces that rural areas are not necessarily free from contamination risks.

Table 4. Average, maximum, and minimum values of PTEs and EEs concentration (mg/kg) in tissues of *C. labyrhinthicus* from the middle Tocantins River (P2: rural zone).

	Minimum (mg/kg)		**Maximum (mg/kg)**		**Average (mg/kg) ± Standard deviation**	
Elements (Detection limit)	**Muscle**	**Liver**	**Muscle**	**Liver**	**Muscle**	**Liver**
			PTEs			
Al (0.014)	5.27	0.58	19.60	3.52	13.06±3.99	1.82±1.24
As (0.002)	0.30	-	6.70	-	**2.85±0.70***	-
Au (0.001)	0.66	0.004	4.25	1.23	1.26±0.27	0.39±0.48
Cr (0.003)	0.31	-	12.85	-	3.61±3.22	-
In (0.033)	0.10	-	4.30	-	2.33±1.19	-
Pb (0.012)	-	-	-	-	-	-
Ni (0.002)	0.37	-	6.56	-	3.32±1.04	-
			EEs			
Ba (0.002)	0.22	-	11.82	-	1.92±0.61	-
Ca (0.007)	951.68	113.92	87608.17	265.08	20757.3±11173.31	183.52±55.35
Co (0.003)	-	-	-	-	-	-
Cu (0.003)	0.16	0.37	1.9	2.60	0.79±0.5	0.83±0.81
S (0.001)	281.74	23.94	536.63	95.24	401.42±73.46	44.15±24.72

Se (0.024)	9.98	-	46.59	-	**15.94±10.55***	-
Sb (0.003)	1.62	-	6.94	-	3.12±1.39	-
Sn (0.021)	8.24	-	37.93	-	12.19±8.74	-
Si (0.015)	6.98	8.71	14.40	13.72	9.47±2.74	10.65±1.99
Fe (0.002)	1.65	30.22	18.5	683.70	12.11±4.06	229.66±230.99
Mg (0.001)	32.78	11.01	496.50	36.26	258.76±104.69	18.54±9.15
Mn (0.001)	0.04	0.14	4.22	0.58	1.29±1.12	0.35±0.16
Na (0.020)	25.99	42.82	631.91	91.74	173.21±58.57	67.90±18.14
P (0.004))	3.66	-	9.21	-	4.85±1.89	-
K (0.018)	138.49	30.22	694.83	685.56	470.27±176.74	230.35±231.09
Zn (0.002)	1.65	0.16	3.94	28.20	11.86±8.55	1.37±1.22

*Elements that are above national or/and international standards.

In fish from water bodies in Macapá, concentrations of Pb, Cr, Ni, Hg, Cu, and Zn remained below Brazilian maximum limits (ML), indicating low risk to consumers (Souza et al., 2025). However, Cd levels exceeded the legal threshold of 0.05 mg/kg, with average concentrations of ~0.06 (20% above the limit) and peak values reaching 0.09 in *Acaronia nassa* (Heckel, 1840) (80% above the limit). Other species, including *Acestrorhynchus altus* (Menezes, 1969), *Leporinus friderici* (Bloch, 1794), *Serrasalmus spilopleura* (Kner, 1858) and *Pygocentrus nattereri* (Kner, 1858), showed Cd concentrations of 0.07 (40% above the limit). These findings indicate that all sampled species are potentially unsafe for human consumption due to Cd contamination, regardless of size, weight, foraging behavior, or urban aquatic environment. Similarly, in fish from the lower Araguari River (Amapá), both Cd and Pb in muscle tissues exceeded national MLs, posing cumulative health risks from exposure to metal mixtures (Viana et al., 2023). These findings are consistent with the pattern observed in the middle Tocantins River and indicate that metal contamination in Amazonian River systems arises from spatially distributed anthropogenic pressures rather than from isolated point sources.

The contamination observed in these urban areas reflects a broader environmental concern across the Amazon. It is estimated that nearly 90% of wastewater from urban zones in this region is discharged without treatment, introducing various pollutants, including potentially toxic metals, into rivers and tributaries (Rico et al., 2021). A similar context is observed in the middle Tocantins River region, where this study was conducted. The local riverside population (96%) relies on native fish for food, 20% consume untreated river water, and 84% lack access to basic sanitation infrastructure, highlighting significant public health vulnerabilities (Acioly et al., 2025). Under such socio-environmental conditions, dietary exposure through fish consumption becomes a primary pathway for chronic metal intake, amplifying health risks in communities with limited access to sanitation and alternative protein sources. The spatial differences observed between sampling sites should not be interpreted as a strict control–impact contrast, but rather as a gradient of anthropogenic pressure along the middle Tocantins River. Both sampling areas are influenced, to varying degrees, by human activities, and the differences in metal accumulation in fish patterns reflect variations in land use, urbanization intensity, and proximity to potential contamination sources. The urban area is characterized by higher population density and greater exposure to industrial and domestic effluents, which may contribute to increased metal inputs into the aquatic system. In contrast, although the rural area is less urbanized, it is not free from anthropogenic influence, as agricultural activities, diffuse runoff, and changes in land use can also act as sources of metal contamination. This gradient-based interpretation provides a more ecologically realistic framework for understanding spatial variability in metal bioavailability and supports the subsequent analysis of bioaccumulation dynamics and physiological responses in fish.

3.4. Bioconcentration Factor (BCF)

In the muscle of *P. amazonica*, S showed the highest BCF (1757.59), followed by K (536.10) and Na (203.15), indicating significant accumulation (Table 5). In the liver, the element with the highest BCF was Fe (2641.30), suggesting its higher concentration in this organ. No element exceeded the 5000 thresholds, but some, such as sulfur, fall within the moderate bioaccumulation range (BCF between 1000 and 5000). In and Si had low BCFs (<10), suggesting limited *accumulation. For C. labyrhinthicus*, in the muscle, S also had the highest BCF (2867.29), followed by Ca (1648.62) and K (723.49). In the liver, K (354.38) dominated, with a significant BCF, reflecting its higher concentration in this organ. The bioaccumulation of macronutrients remained predominant, but In and Cu showed low value, indicating limited accumulation (Table 5). The predominance of higher BCF values for EEs reflects their metabolic demand and physiological regulation, whereas the accumulation of certain PTEs in specific tissues highlights the role of organ function in modulating exposure and detoxification processes.

Table 5. Bioconcentration Factor (BCF) of PTEs and EEs in the middle Tocantins fish.

Elements	Branquinha *(P. amazonica)* (urban zone)		Branquinha-cascuda *(C. labyrhinthicus)* (rural zone)	
	BCF Muscle	BCF Liver	*BCF Muscle*	BCF Liver
		PTEs		
Al	10.42	*4.84*	20.71	2.89
Au	8.88	49.38	12.60	3.90
In	0.53	-	4.57	-
		EEs		
Ca	71.63	47.91	**1648.62**	14.58

Cu	6.20	191.20	15.80	16.60
Fe	24.07	**2641.30**	11.87	225.16
Na	203.15	219.15	151.06	59.56
K	536.10	801.83	723.49	354.38
S	**1757.59**	**1239.82**	**2867.29**	315.36
Se	46.50	69.55	93.76	-
Sn	*25.81*	22.78	35.85	-
Si	*2.12*	3.37	1.36	1.53

BCF < 1000 is non-bioaccumulative, 1000–5000 is bioaccumulative, and > 5000 indicates high bioaccumulation potential (US EPA, 2010).

3.5. Human Health Risk Assessment from Fish Consumption

There is a potential risk to human health associated with the consumption of the analyzed fish species, particularly due to elevated levels of Se and As. Se exhibited the highest RQ values across all tissues, with notable levels in the liver of *P. amazonica* (RQ = 49.16) and the muscle of *C. labyrhinthicus* (RQ = 53.13), exceeding the Brazilian regulatory limit of 0.3 mg/kg by more than 150 times (Table 6). It is important to note that selenium is an essential micronutrient and may reflect both environmental availability and physiological regulation related to homeostasis and detoxification, including protective interactions with other metals (Kessi et al., 1999; Hossain et al., 2021). Consistent with this interpretation, the normal Q factor suggests that elevated Se levels may partly represent an adaptive response in fish; however, concentrations exceeding food safety limits remain a concern for human consumption. These results indicate potential for adverse effects (US EPA, 2010) in frequent consumers. As also exceeded the legal threshold of 1.0 mg/kg in the muscle tissue of *P. amazonica* (1.83), yielding an RQ of 1.83 and representing an additional health concern.

Table 6. Risk quotients (RQ) and cumulative risk index (RI) of studied elements in muscle and liver tissues of fish species from the middle Tocantins River.

Elements	Branquinha *(P. amazonica)* (urban zone)		Branquinha-cascuda *(C. labyrhinthicus)* (rural zone)	
	RQ Muscle	RQ Liver	*RQ Muscle*	RQ Liver
Potentially toxic elements				
As	**1.83***	-	-	-
Pb	-	**1.95***	-	-
Essential elements				
Cu	0.03	0.96	0.08	0.08
Se	**31.00***	**46.37***	**53.13***	-
RI	32.86	49.16	53.21	47.20

RQ < 1 indicates no risk to human health; *RQ > 1 suggests potential adverse effects (US EPA, 2010). RI values below 150 indicate low risk, while values between 150 and 300 suggest moderate risk (Dash et al., 2021).

Although it was only detected in the urban zone with *P. amazonica*, its RI was low, suggesting minimal immediate risk. Selenium, however, was the primary contributor to the elevated RQ values in both muscle and liver tissues, indicating that its concentration, despite being an essential element, can reach concerning levels. Pb, found in the liver of *P. amazonica*, may not pose a direct risk to human health, as liver is not typically consumed. However, even at low concentrations in aquatic environments, Pb poses a significant threat to aquatic organisms due to its toxicity and bioaccumulation potential, which can harm biodiversity and affect local fisheries (Viana et al., 2020; Souza et al., 2025). Cu showed RQs well below the threshold, indicating no significant risk. The results highlight the importance of monitoring Se and Pb concentrations and implementing fish consumption guidelines to protect public health. Taken together, these results indicate that health risks are driven not by a single contaminant, but by the combined presence of multiple elements (Pose-Juan et al., 2016; Niede & Benbi, 2022), particularly those exceeding regulatory limits in edible tissues.

The EDI assessment demonstrated that while Al, Cr, Ni, Fe, Mn, Cu, and Zn concentrations remained below reference doses (EDI < RfD) for both adults (Table 7) and children (Table 8) (FAO/WHO, 2010; ANVISA, 2019), arsenic presented concerning exposure levels. In Scenario 2 (Amazonian consumption: 416.39 g/day), arsenic EDI values exceeded the FAO/WHO RfD by 7-fold for children (15 kg BW) versus 1.6-fold for adults (70 kg BW), revealing children experience 4.6× greater exposure per kg body weight. This disproportionate risk for pediatric populations stems from their lower body mass and higher metabolic susceptibility to toxic elements. These health effects are dose-dependent and cumulative, meaning that even moderate daily intake can become hazardous over time (Gorini et al., 2014; Balali-Mood et al., 2021; Teschke, 2024). The findings underscore an urgent need for: (1) species-specific consumption guidelines prioritizing low-As fish, particularly for vulnerable groups; (2) targeted monitoring programs in high-intake regions; and (3) community education about differential risks between adult and child consumption patterns.

Table 7. Estimated daily intake (EDI, mg/kg/bw day) of metals for adults (70 kg body weight) through consumption of fish muscle tissue from species collected in the middle Tocantins River, Maranhão, Brazil.

Fish species	EDI (Adult)								
	Scenario	Al	As	Cr	Ni	Fe	Mn	Cu	Zn
Branquinha *(P. amazonica)* (urban zone)	1	0.0065	0.0016	0.0016	*0.0023*	0.0100	0.0009	0.0003	0.0036
	2	0.0428	0.0109	0.0109	*0.0150*	0.0658	0.0062	0.0018	0.0237
Branquinha-cascuda *(C. labyrhinthicus)* (rural zone)	1	0.0118	0.0026	0.0033	0.0030	0.0109	0.0012	0.0007	-
	2	0.0777	0.0170	0.0215	0.0197	0.0720	0.0077	0.0047	-

RfD (mg/kg/day)	0.286	0.003 (revoked)	0.045	1	3.47	2.3	6.935	23.5

Scenario 1: 63 g/day for the general Brazilian population (Arruda, 2017). Scenario 2: 416.39 g/day for individuals in the Amazon region (Isaac et al., 2015; Souza-Araujo et al., 2022). RfD (Reference dose): ANVISA (2019), FAO/WHO (2010). Body weight (70 kg for adults, 15 kg for children) is based on standard reference values widely used in human health risk assessment (Smith, 1995; US EPA, 2000; US EPA, 2008; Abdel-Kader et al., 2023).

Table 8. Estimated daily intake (EDI, mg/kg/bw day) of metals for children (15 kg body weight) through consumption of fish muscle tissue from species collected in the middle Tocantins River, Maranhão, Brazil.

Fish species	EDI (Children)								
	Scenario	Al	As	Cr	Ni	Fe	Mn	Cu	Zn
Branquinha *(P. amazonica)* (urban zone)	1	0.008	0.001	0.0005	*0.002*	0.015	0.0007	0.0003	0.004
	2	0.053	0.007	0.003	*0.013*	0.099	0.005	0.002	0.026
Branquinha-cascuda *(C. labyrhinthicus)* (rural zone)	1	0.055	0.012	0.015	0.014	0.051	0.005	0.003	-
	2	0.363	0.079	0.100	0.092	0.336	0.036	0.021	-
RfD (mg/kg/day)		0.286	0.003 (revoked)	0.045	1	3.47	2.3	6.935	23.5

Scenario 1: 63 g/day for the general Brazilian population (Arruda, 2017). Scenario 2: 416.39 g/day for individuals in the Amazon region (Isaac et al., 2015; Souza-Araujo et al., 2022). RfD (Reference dose): ANVISA (2019), FAO/WHO (2010). Body weight (70 kg for adults, 15 kg for children) is based on standard reference values widely used in human health risk assessment (Smith, 1995; US EPA, 2000; US EPA, 2008; Abdel-Kader et al., 2023).

Evidence from human health risk assessments based on the consumption of contaminated fish strongly supports these concerns. Numerous studies worldwide have shown that arsenic concentrations in edible fish tissues frequently exceed regulatory limits and pose both non-carcinogenic and carcinogenic risks, particularly for populations with high fish intake (Fakhri et al., 2021; Cobbinah et al., 2025). For example, investigations in riverine and marine systems across South America have reported HQ and EDI values for arsenic above national and international safety thresholds, indicating increased lifetime cancer risk as well as potential hepatic, neurological, and cardiovascular effects in frequent consumers (Custodio et al., 2020; Bundschuh et al., 2021; Marrugo-Madrid et al., 2022; Ignacio et al., 2025). Consistent with these reports, our results show that arsenic intake from fish consumption in the middle Tocantins River exceeds safe limits, particularly under high-consumption scenarios, with children exhibiting exposure levels several-fold higher than adults. Collectively, these findings demonstrate that chronic dietary exposure to arsenic via contaminated fish represents a tangible public health risk and underscores the need for site-specific consumption advisories, long-term biomonitoring, and mitigation strategies for vulnerable riverine populations.

3.6. Enzymatic biomarkers

The enzymatic responses evaluated in this study—AChE, AST, ALT, and ALP—represent sublethal physiological responses associated with contaminant exposure. Alteration in the activity of these enzymes reflect adaptive adjustments in detoxification, antioxidant defense, and neurophysiological regulation pathways, allowing the early detection of environmental stress before the onset of clinical or population-level effects. Similar biomarker-based responses have been widely reported in aquatic and semi-aquatic organisms exposed to environmental contaminants, including neotropical fish species subjected to pesticides and metal mixtures (Alvariño et al., 2023; Saboia-Morais et al., 2024; Carnib et al., 2025). In the present study, the modulation of enzymatic biomarkers is consistent with the bioaccumulation of toxic elements observed in fish tissues and with the simultaneous exposure to multiple metals, which may act additively or synergistically on redox balance and metabolic homeostasis (Abdallah et al., 2024; Sarkar et al., 2025; Wu et al., 2025). Thus, the observed biomarker patterns provide functional evidence of physiological stress linked to metal exposure and complement the chemical data by demonstrating biologically relevant effects in fish from the middle Tocantins River.

The biochemical responses presented in Table 9 reveal significant site- and tissue-specific variations in enzymatic activities and should not be interpreted as direct quantitative comparisons among distinct species. In *P. amazonica* from the urban site (P1), AChE activity was elevated in both muscle and liver when compared with basal values reported for Characiformes under non-impacted conditions. In contrast, *C. labyrhinthicus* from the rural site (P2) exhibited a marked reduction in muscle AChE activity. It is important to emphasize that phylogenetic, physiological, and ontogenetic differences among species, including variation in body size, metabolic rate, and the relative expression of cholinesterase isoforms, preclude direct interspecific comparisons of absolute AChE activity. Accordingly, interpretations were based on qualitative patterns of enzymatic responses within each site, rather than on cross-species numerical differences. The observed enzymatic alterations, even in individuals with normal condition factors, demonstrate that metal exposure is biologically active and capable of inducing functional responses before the onset of overt physiological impairment.

Table 9. Average, maximum, and minimum values of some enzymes in the muscle and liver tissue (U/I) of *P. amazonica* (urban zone) and *C. labyrhinthicus* (rural zone) from the middle Tocantins River.

Species	Enzyme	Minimum (U/I)		Maximum (U/I)		Average (U/I) ± Standard deviation	
		Muscle	Liver	Muscle	Liver	Muscle	Liver
P. amazonica (urban zone)	AChE	12263.87	12263.87	38376.78	18481.23	19207±9794	15372.55±3405
	AST	-	191.29	-	410.22	-	294.39±88

	ALT	-	94.41	-	822.14	-	528.89±260
	ALP	18.77	384.68	274.64	604.78	121.72±96	471.13±74
C. labyrhinthicus (rural zone)	AChE	1818.71	1818.71	3994.78	3994.78	2544±1071	2352.36±991
	AST	-	115.26	-	430.38	-	290.02±152
	ALT	-	35.18	-	41.95	-	38.28±3
	ALP	82.05	82.05	170.09	170.09	89.39±25	104.06±40

AchE: Acetylcholinesterase; AST: Aspartate Aminotransferase; ALT: Alanine Aminotransferase; ALP: Alkaline Phosphatase.

The increased AChE activity observed in *P. amazonica* at the urban site (P1) is consistent with a compensatory or adaptive biochemical response to chronic exposure to metals such as As and Pb, which are characteristic of urban effluents and surface runoff. Experimental and field studies indicate that prolonged sublethal exposure to neurotoxicants may elicit an initial upregulation of AChE activity as a mechanism to sustain cholinergic neurotransmission, frequently preceding enzymatic inhibition under more advanced or prolonged toxic stress (Richetti et al., 2011; Jonsson et al., 2014; Olagoke et al., 2024). Conversely, the reduction of AChE activity in *C. labyrhinthicus* from the rural site (P2) suggests subclinical neurotoxic inhibition, compatible with arsenic exposure even at comparatively lower environmental concentrations. A reduction in AChE activity is widely recognized as early biomarkers of neurotoxicity in Neotropical fish species, reflecting functional impairment of cholinergic signaling prior to overt behavioral or histopathological alterations (De la Torre et al., 2002; Lionetto et al., 2013; Sandoval-Herrera et al., 2019). Additionally, the analytical method employed (Bioclin K094) may present partial cross-reactivity with butyrylcholinesterase, potentially amplifying interspecific variability. This methodological constraint further supports the avoidance of absolute interspecies comparisons and reinforces the focus on site-specific enzymatic trends.

Elevated hepatic ALT and AST activities in *P. amazonica* indicate hepatocellular stress likely associated with higher bioaccumulation of Pb and As at the urban site, consistent with the liver's central role in metal detoxification and biotransformation (Jomova & Valko, 2011; Fu & Xi, 2020; Kumar, 2025). Moreover, experimental studies demonstrate that combined exposure to metals, particularly lead and arsenic, markedly enhances oxidative stress and hepatotoxicity compared to single-metal exposure (Agrawal et al., 2015). The concomitant increase in ALP activity reflects non-specific physiological stress associated with chronic sublethal contamination. In *C. labyrhinthicus* from the rural site, lower and more stable enzymatic activities suggest reduced systemic biochemical stress, although the inhibition of AChE indicates that neurophysiological effects may occur even under diffuse or low-intensity contamination scenarios. When integrated with concentrations of PTEs and human health risk metrics (EDI and RQ), these enzymatic biomarkers provide early, sensitive, and biologically meaningful indicators of environmental degradation in the middle Tocantins River.

In addition to chemical contamination, the observed alterations in biochemical biomarkers indicate that metal exposure is biologically active, inducing increases in AST, ALT, and ALP and reductions in AChE activity. The integration of chemical and biochemical biomarkers with human health risk assessment strengthens the ecological relevance of the findings and enhances their translational value for public health. These results are directly relevant to environmental management and food safety policies and align with the United Nations Sustainable Development Goals (SDGs), particularly SDG 3 (Good Health and Well-being), SDG 6 (Clean Water and Sanitation), SDG 14 (Life Below Water), and SDG 15 (Life on Land) (United Nations, 2015). Framed within a One Health perspective, this study highlights the interconnectedness of environmental quality, fish health, and human well-being.

3.7. Correlation coefficients

Correlation analysis revealed several relevant associations among metal concentrations and biomarker responses (Figure S1). Strong positive correlations were observed between Fe and Al ($r = 0.6985$, $p < 0.05$; the same significance level applies to all correlations reported below) and between Mn and Zn ($r = 0.7112$), suggesting common geochemical or environmental sources, possibly linked to lithogenic inputs or sediment resuspension. A moderate positive correlation between Cu and Ni ($r = 0.5749$) indicates potential overlap in contamination sources, such as industrial effluents or agricultural runoff. Regarding enzymatic biomarkers, AChE activity showed a moderate negative correlation with hepatic Fe concentrations ($r = -0.6234$), suggesting possible neurophysiological inhibition associated with metal-induced oxidative stress. Conversely, ALP activity correlated positively with Ca ($r = 0.6481$) and P ($r = 0.5927$), consistent with its role in phosphorus metabolism, membrane transport, and tissue turnover processes.

Weak or non-significant correlations ($|r| \leq 0.50$) were observed for most other metal–enzyme pairs, indicating independent biochemical regulation, low-level exposure effects, or complex multivariate interactions. Overall, these patterns suggest that the bioaccumulation of specific elements, notably Fe, Mn, and Zn, may modulate enzymatic responses, although enzyme activities likely reflect the combined influence of metal exposure and intrinsic physiological regulation. Taken together, the correlation coefficients indicate weak to moderate associations between metal concentrations and enzymatic biomarkers (e.g., $r = -0.62$ for the Fe–AChE relationship), supporting the interpretation that biochemical responses are driven by multiple concurrent stressors rather than by single-element exposure alone (Figure S1). The integrated chemical and biochemical evidence indicate that fish from the middle Tocantins River are undergoing multi-element exposure capable of eliciting relevant physiological disturbances, with direct implications for ecosystem integrity and human health.

The marked accumulation of As, Pb, and Se, together with alterations in AChE, ALT, AST, and ALP activities, demonstrates that PTEs are not only present but bioavailable and capable of compromising essential metabolic and neurophysiological functions. The two native species evaluated proved to be effective bioindicators due to their ecological relevance, trophic position, abundance, and significant contribution to traditional riverside diets. Their contrasting feeding strategies and habitat use enhance the detection of contaminants originating from both urban effluents and diffuse agricultural sources, allowing a more comprehensive assessment of the basin.

Overall, the integration of chemical and biological evidence indicates that metal contamination in the middle Tocantins River operates across multiple environmental compartments and levels of biological organization. The presence of toxic elements in surface waters and sediments, as documented in previous assessments, is reflected in their accumulation in fish tissues, demonstrating effective transfer from abiotic matrices to aquatic biota. This bioaccumulation is accompanied by sublethal biochemical responses, as evidenced by changes in enzymatic biomarkers such as AChE, AST, ALT, and ALP, which reflect physiological alterations associated with contaminant exposure. From a One Health perspective, these findings highlight interconnected risks linking environmental degradation, fish health impairment, and human dietary exposure, particularly among vulnerable riverside populations that rely on fish as a primary protein source. Therefore, continuous biomonitoring, improved sanitation infrastructure, and stricter environmental regulation are essential to prevent further ecological degradation and reduce long-term public health risks in the Tocantins River basin.

4. CONCLUSION

This study demonstrates that metal contamination in the middle Tocantins River is not only detectable but also associated with biological responses, as evidenced by the bioaccumulation of elements in fish tissues and the observed changes in enzymatic biomarkers, with potential implications for food safety and public health. The co-occurrence of elevated As and Se concentrations in edible fish tissues and variations in enzymatic activity suggests that these elements are bioavailable and that fish are exposed to environmental contamination, resulting in measurable physiological responses. Importantly, the identification of disproportionate dietary exposure among children under high-consumption scenarios highlights a specific vulnerability that links environmental contamination directly to human health concerns. Rather than representing isolated contamination events, the contrasting patterns observed between urban and rural sites reflect the combined influence of point and diffuse anthropogenic sources within the Cerrado–Amazon ecotone. These results underscore that areas perceived as less impacted may still sustain contaminant levels sufficient to pose chronic risks through food-web transfer. From a management perspective, the findings support the implementation of routine biomonitoring using locally consumed sentinel species, the development of age-specific fish consumption advisories, and the targeted identification and control of As and Se sources within the Tocantins River basin. Framed within a One Health perspective, this work reinforces that the protection of riverine ecosystems is intrinsically linked to food security and community health, providing a scientific basis for informed environmental regulation and public health strategies in one of Brazil's most socioecologically sensitive regions.

Credit author statement

T.M.S.A. (conceptualization, methodology, data curation, formal analysis, investigation, validation, visualization, software, writing-original draft, writing-review, and editing); J.I. (conceptualization, methodology, and writing-review); K.S.S.A. (writing-review); J.M.O. (writing-review, editing); M.I. (writing-review); J.F.F.O. (conceptualization, methodology); D.C.V. (resources, supervision, project administration, and validation).

Availability of data

The data that support the findings of this study are available from the corresponding author upon reasonable request. Supplementary material available at: https://static-content.springer.com/esm/art%3A10.1038%2Fs41598-026-39611-3/MediaObjects/41598_2026_39611_MOESM1_ESM.docx

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CONSIDERAÇÕES FINAIS

- ✓ Os resultados desta tese contribuíram para a ampliação do conhecimento sobre a qualidade ambiental do médio rio Tocantins, especialmente na região de influência do município de Imperatriz (MA), ao integrar, de forma inédita na região, análises físico-químicas da água, sedimentos, bioacumulação em peixes, biomarcadores enzimáticos e percepção socioambiental. Essa abordagem multidisciplinar permitiu uma compreensão mais abrangente dos processos que controlam a dinâmica de elementos potencialmente tóxicos e essenciais no sistema aquático, fornecendo subsídios relevantes para o monitoramento ambiental e a gestão sustentável dos recursos hídricos.
- ✓ De forma integrada, os resultados indicam que a dinâmica dos elementos no médio rio Tocantins é condicionada pela interação entre processos naturais e influências antrópicas. A interpretação das concentrações observadas em água e sedimentos deve considerar o contexto geoquímico regional, caracterizado pela predominância de Latossolos, Plintossolos e formações lateríticas, naturalmente enriquecidos em elementos como ferro, alumínio e manganês. Nesse sentido, o aumento desses elementos, especialmente durante o período chuvoso, está associado a processos naturais de intemperismo e lixiviação típicos de ambientes tropicais, não podendo ser atribuído exclusivamente a fontes antrópicas.
- ✓ Por outro lado, parâmetros como condutividade elétrica, sólidos totais dissolvidos, compostos nitrogenados e clorofila, especialmente mais elevados na área urbana (P1), indicam a influência de pressões antrópicas relacionadas ao uso e ocupação do solo, lançamento de efluentes e ausência de saneamento básico. Esses resultados evidenciam que a qualidade ambiental do rio Tocantins é resultado da sobreposição de processos naturais e impactos antrópicos, exigindo abordagens integradas para sua interpretação. A análise dos sedimentos reforça seu papel como compartimento-chave no sistema, atuando como reservatório de elementos e potencial fonte secundária para a coluna d'água e organismos aquáticos. A maior ocorrência de elementos no período chuvoso evidencia a influência da sazonalidade na mobilização e redistribuição desses materiais no ambiente.
- ✓ A bioacumulação observada nos tecidos de peixes confirma a transferência de elementos presentes no ambiente para a biota aquática, evidenciando a exposição dos organismos. As respostas enzimáticas (AChE, AST, ALT e ALP) indicam alterações fisiológicas associadas à exposição ambiental, devendo ser interpretadas como respostas biológicas gerais, não permitindo, de forma isolada, estabelecer relações causais específicas ou inferir mecanismos como estresse oxidativo ou efeitos neurotóxicos

diretos, especialmente na ausência de condições de referência. Do ponto de vista socioambiental, a forte dependência das populações ribeirinhas dos recursos hídricos e pesqueiros, aliada à elevada proporção de residências sem acesso a saneamento básico, configura um cenário de vulnerabilidade, no qual a exposição a contaminantes pode ocorrer por múltiplas vias, incluindo o consumo de água e pescado.

- ✓ Esses resultados evidenciam a necessidade de considerar o background geoquímico regional na avaliação da qualidade ambiental, uma vez que padrões legais generalistas nem sempre contemplam as especificidades de ambientes tropicais altamente intemperizados. Nesse contexto, interpretações baseadas exclusivamente em limites normativos podem superestimar ou subestimar riscos ambientais, reforçando a importância de abordagens contextualizadas. Dessa forma, os achados desta tese sustentam um modelo conceitual no qual a dinâmica de elementos no médio rio Tocantins é controlada por três componentes principais: (i) processos naturais de origem geoquímica, associados ao intemperismo e à sazonalidade; (ii) pressões antrópicas relacionadas ao uso do solo, urbanização e deficiência de saneamento; e (iii) processos de transferência e resposta biológica nos organismos aquáticos.
- ✓ Por fim, a abordagem integrada adotada, caracterizada como uma das primeiras investigações na região a articular, de forma conjunta, dados físico-químicos, biológicos e socioambientais, evidencia a importância do monitoramento ambiental contínuo como ferramenta para subsidiar políticas públicas mais eficazes. Sob a perspectiva da abordagem One Health, este estudo reforça que a compreensão integrada dos sistemas naturais e sociais é fundamental para a proteção dos ecossistemas aquáticos, a segurança alimentar e a saúde das populações ribeirinhas.