UNIVERSIDADE ESTADUAL PAULISTA
"JÚLIO DE MESQUITA FILHO"
Câmpus de Sorocaba

PROGRAMA DE PÓS-GRADUAÇÃO em
Ciências Ambientais

IVAN EDWARD BIAMONT ROJAS

HETEROGENEIDADE ESPACIAL ECOTOXICOLÓGICA DE METAIS E SUAS IMPLICAÇÕES EM RESERVATÓRIOS PAULISTAS (BRASIL) E PARA O LAGO TITICACA (PERU)

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Tese apresentada como requisito para a obtenção do título de Doutor em Ciências Ambientais da Universidade Estadual Paulista "Júlio de Mesquita Filho" na Área de Concentração Diagnóstico, Tratamento e Recuperação Ambiental

Orientador: Prof. Dr. Marcelo Luiz Martins Pompêo
Coorientador: Prof. Dra. Marisa Dantas Bitencourt Pereira

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TÍTULO DA TESE: HETEROGENEIDADE ESPACIAL ECOTOXICOLOGICA DE METAIS E SUAS IMPLICAÇÕES EM RESERVATORIOS PAULISTAS (BRASIL) E PARA O LAGO TITICACA (PERU)

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“... detrás del ventisquero llameante
fogata en plenitud
las aguas crespas de germen se bifurcan al solsticio en anchas marejadas
BERMELLON DE LAGOS VESPERTINOS
RISAS AGRIAS
DE AMANECERES JOYANTES...”

Gamaliel Churata

RESUMO

Os ambientes aquáticos, principalmente os lacustres e de transição, sofreram com as mudanças e impactos como consequência dos fenômenos (naturais e artificiais) que acontecem dentro da sua bacia hidrográfica. Eventos como o crescimento urbano somado à falta de sistemas de tratamento de esgoto ameaçam também o equilíbrio existente nestes corpos hídricos. O aporte de altos teores de nutrientes origina ocorrências de florações de algas que, em alguns casos, são inibidos por métodos paliativos e não resolvem o problema principal. O presente trabalho objetivou avaliar a heterogeneidade ecotoxicológica do sedimento superficial, mediante a quantificação e classificação dos metais segundo a sua qualidade, aplicando técnicas cartográficas, de sensoriamento remoto empregando guias de qualidade e índice de enriquecimento nos reservatórios Rio Grande (RG), Itupararanga (ITU) e Paiva Castro (PC) no Brasil, e no Lago Titicaca no Peru. Foi analisado o sedimento em perfil na Baía de Puno (BP), para quantificar a concentração de metais, bem como a geocronologia do sedimento para assim propor pela primeira vez valores regionais de referência na Baía de Puno. Para o sedimento superficial foram amostrados 47 pontos no RG, 52 no ITU, 50 no PC e 11 na BP. No caso do sedimento em perfil, foram dos pontos na Baía de Puno de 48 e 45 cm de profundidade ambos em triplicata, os que foram fatiados a cada 3 cm. A análise de metais foi realizada num espectrômetro de emissão óptica com plasma indutivamente acoplado (ICP-OES) e sua classificação segundo o nível de efeito limiar TEL e o nível de efeito provável PEL. A geocronologia utilizou ^{210}Pb, ^{226}Ra e ^{137}Cs num espectrômetro gama de germânio hiper puro (ORTEC), além disso, foram calculadas as taxas de sedimentação segundo o modelo de Fluxo Constante Sedimentação Constante (CFCS). O Cu foi o metal mais significativo nas amostras brasileiras, chegando a superar valores de 10 vezes o PEL no RG, enquanto o As foi relevante nas amostras peruanas com teores por cima de 3 vezes o PEL. A análise de sedimentação na Baía de Puno (0.48 ± 0.08 cm a^{-1} and 0.64 ± 0.07 cm a^{-}1, para a baía externa e interna, respectivamente) indicam que as taxas estão relacionadas a eventos climáticos, isto na baía externa, e para a baía interna além dos climáticos, eventos de origem humano também foram observados. Estes resultados são fundamentais para os tomadores de decisões, bem como a população em geral para um melhor gerenciamento e conservação destes ambientes aquáticos.

Palavras-chave: Ecotoxicologia, reservatórios, sedimento, Lago Titicaca, cobre, arsênio, paleolimnologia.

ABSTRACT

Aquatic environments, mainly lacustrine and transition ones, have experienced trends and impacts as a consequence of natural and artificial phenomena which take place in its basin. Events, such as urban growth linked to the lack of a proper sewage treatment system threaten the equilibrium in these water bodies as well. The high nutrient concentration inlet leads to algal bloom occurrences which, in some cases, are inhibited throughout palliative methods without solving the main problem. This study aimed to assess the ecotoxicological heterogeneity of superficial sediment, by means of metal quantification and classification according to their quality, applying cartographic, remote sensing techniques employing quality guidelines and enrichment index in Rio Grande (RG), Itupararanga (ITU) e Paiva Castro (PC) reservoirs in Brazil, and Lake Titicaca in Peru. Profile sediment samples were analyzed in Puno Bay (BP), to quantify metal concentration, as well as sediment geochronology and in this way propose for the first-time background values in Puno Bay. To evaluate superficial sediment 47 sites in RG, 52 sites in ITU, 50 in PC and 11 in BP were collected. Talking about the profile sediment, two sample sites were considered, outer and inner bays, the first core of 48 cm and the second of 45 cm depth, both in triplicate, the sediment was sliced at each 3 cm. Metal analysis was performed using an inductively coupled plasma optical emission spectrometry (ICP-OES) and its classification according to the threshold effect level (TEL) and probable effect level (PEL). The geochronological analysis used ^{210}Pb, ^{226}Ra and ^{137}Cs in a low-background hyperpure Ge gamma spectrometer (ORTEC, model GMX50P), moreover, sedimentation rates were calculated following the Constant Flux Constant Sedimentation (CFCS). Copper was the most significative metal in the Brazilian samples, sometimes overpassing ten times the PEL value in RG, meanwhile, As was relevant among the Peruvian samples with concentrations higher than three times the PEL. The sedimentation analysis in Puno Bay (0.48 ± 0.08 cm a^{-1} and 0.64 ± 0.07 cm a^{-1}, for the outer and inner bays, respectively) indicate that the rates are related to climatic events, this in the outer bay, and added to climatic events, human derived are also observed in the inner bay. These results are fundamental for decision makers, as well as for the entire population for a better management and conservation of these aquatic environments.

Keywords: Ecotoxicology, reservoirs, sediment, Lake Titicaca, copper, arsenic, paleolimnology.

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LISTA DE ABREVIATURAS E SIGLAS

HNO_3	= Ácido nítrico
Bq kg^{-1}	= Becquerel por quilograma
CCME	= *Canadian Council of Ministers for the Environment*
cm	= Centímetro
cm^2	= Centímetro quadrado
cm a^{-1}	= Centímetro por ano
FE	= Fator de Enriquecimento
°C	= Grau Celsius
df	= Grau de liberdade
hm^3	= Hectômetro cúbico
H	= Hora
ISQGs	= *Interim Sediment Quality Guidelines*
IDW	= *Inverse Distance Weighting*
m	= Metro
m^3	= Metro cúbico
m^3/s	= Metro Cúbico por segundo
µm	= Micrometro
µg/kg	= Micrograma por quilograma
mg As/kg	= Miligrama de arsênio por quilograma de sedimento
mg Pb/kg	= Miligrama de chumbo por quilograma de sedimento
mg Cu/kg	= Miligrama de cobre por quilograma de sedimento
mg Cr/kg	= Miligrama de cromo por quilograma de sedimento
mg Ni/kg	= Miligrama de níquel por quilograma de sedimento
mg Zn/kg	= Miligrama de zinco por quilograma de sedimento
mg/L	= Miligrama por litro
mg/kg	= Miligrama por quilograma
mg/kg dw	= Miligrama por quilograma de peso seco
ml	= Mililitro
PEL	= *Probable Effect Level*
kg	= Quilograma
km	= Quilometro
km/h	= Quilometro por hora

km^2	= Quilometro quadrado
RMSP	= Região Metropolitana de São Paulo
ITU	= Reservatório Itupararanga
PC	= Reservatório Paiva Castro
RG	= Reservatório Rio Grande
SQGs	= *Sediment Quality Guidelines*
TEL	= *Threshold Effect Level*
Ton	= Tonelada
VRR	= Valor de Referência Regional

SUMÁRIO

APRESENTAÇÃO

Os corpos hídricos apresentam características particulares as quais as diferenciam umas de outras, isto devido às atividades que acontecem em suas bacias. No caso brasileiro, as complicações ecológicas dos reservatórios avaliados estão relacionadas à acumulação de metais em grande medida como consequência das atividades humanas, a falta de ações coerentes no gerenciamento dos reservatórios e a necessidade de uma melhor comunicação entre o município, o gestor da barragem e a agencia de abastecimento. No caso peruano, trata-se de duas zonas de um corpo hídrico, um apresenta maiores impactos a causa das atividades antrópicas, relacionadas também à deficiência no gerenciamento do corpo hídrico e o segundo uma maior relação com eventos climáticos, que aos poucos também vem sendo afetado por atividades produtivas (piscicultura). A presente tese foi desenvolvida de modo para examinar a qualidade do sedimento nos reservatórios Rio Grande (RG), Itupararanga (ITU) e Paiva Castro (PC), no Brasil e a Baía de Puno (baía externa e interna) no Peru.

A análise foi realizada de uma maneira integral abrangendo a química ambiental, geologia e o uso de geotecnologias para a construção e mapeamento do relevo subaquático desde uma perspectiva espacial. Nesse cenário, o documento foi estruturado em capítulos sendo:

Capítulo 1. Introdução geral.

Capitulo 2. Intitulado *Heterogeneidade espacial e ecotoxicidade de metais no sedimento em três reservatórios paulistas aplicando um enfoque geoestatístico*. Neste capítulo foram analisados metais (Cr, Ni, Pb e Zn), em três reservatórios (RG, ITU e PC), levando em consideração suas concentrações e classificando-as segundo categorias de qualidade ambiental para sedimentos. Este documento foi escrito como capitulo no livro “Aspectos da Ecotoxicidade em ambientes aquáticos”, o qual já foi publicado.

Capítulo 3. Intitulado *Técnicas de ecotoxicologia e geostatistica empregadas no sedimento de reservatórios subtropicais depois de décadas de aplicação do sulfato de cobre*. Neste trabalho o cobre foi avaliado espacialmente nos reservatórios RG e ITU, também foi considerado a categorização do metal segundo guías de qualidade utilizando métodos geostatisticos (krigagem). Este capitulo foi escrito como artigo, o qual foi aceito na revista Environmental Geochemistry and Health.

Capitulo 4. Intitulado *A distribuição espacial do arsênio e outros metais sugerem um elevado potencial ecotoxicológico no Lago Titicaca.* Este estudo analisou a distribuição de metais com potencial tóxico (As, Cu, Ni, Pb, Cr, Zn) no sedimento superficial bem como a sua classificação seguindo os guias de qualidade, utilizando técnicas de sensoriamento remoto e geoprocessamento. O documento foi submetido na revista Science of the Total Environment, encontra-se sob revisão.

Capitulo 5. Intitulado *Novas perspectivas sobre a contribuição e acumulação do sedimento e metais no Lago Titicaca.* O trabalho visou analisar o sedimento em perfil de dois pontos na Baía de Puno, esse analise considerou a geocronologia das amostras. Além disso foram propostos pela primeira vez teores de metais para ambas baías.

Capitulo 6. Contempla uma avaliação comparativa entre os ambientes brasileiros e peruanos. Este capitulo teve o objetivo de uma análise crítica dos ambientes avaliados e as considerações finais da tese.

Capítulo 1

Introdução Geral

Os corpos hídricos apresentam características particulares as quais as diferenciam umas de outras. Os chamados fatores extrínsecos que envolve a toda atividade que acontece em suas bacias hidrográficas e também os fatores intrínsecos que as faz particulares e independentes. Devemos considerar que as áreas urbanas, presentes nas bacias, de rápido crescimento apresentam maiores necessidades de abastecimento de água. Segundo o Sistema Nacional de Informações sobre Saneamento (SNIS), o abastecimento de água abrange 83,6% dos brasileiros, porém, apenas 53,2% possuem o esgotamento sanitário e somente 46,3% tem tratamento de esgoto (SNIS, 2019). Essa situação se vê ainda pior ao ver o Atlas Esgotos: Despoluição de Bacias Hidrográficas, um reporte da Agência Nacional de Águas e Saneamento Básico (ANA), onde apontam que 38,6% dos esgotos produzidos não são coletados, nem tratados, e que 18,8% são coletados, mas lançados sem tratamento aos corpos hídricos (ANA, 2017). No caso peruano, para o 2020, segundo a Superintendência Nacional de Serviços de Saneamento (SUNASS), 56,9% tem abastecimento de água e 53% possuem esgotamento sanitário (SUNASS, 2022). O esgoto coletado é somente o 79,2% dos quais nem todo é tratado prévio a sua liberação ao ambiente.

Na Região Metropolitana de São Paulo (RMSP), o saneamento básico foi e ainda é um desafio (KAWAI; BRANCO, 1969; POMPÊO et al., 2020), devido à rápida expansão urbana e o crescimento populacional experimentado desde a segunda metade do século XX. A RMSP possui um sistema integrado de abastecimento público, compondo os seguintes sistemas: Cantareira, Baixo Cotia, Alto Cotia, Guarapiranga, Rio Grande, Ribeirão da Estiva, Rio Claro e Alto Tietê. Esses oito sistemas produtores possuem uma capacidade nominal de produzir 68,2 m3/s (ANA, 2010). Já fora da RMSP, muitos municípios também tem demonstrado um crescimento populacional significativo. Assim, o abastecimento da cidade de Sorocaba, que opera mediante o Serviço Autônomo de Água e Esgoto (SAAE), capta 85% da água bruta de três represas, os reservatórios Clemente, Itupararanga e Ipaneminha, sendo que outros 10% do córrego Pirajibu-Mirim e o 5% restante proveniente de 23 poços tubulares (SAAE, 2020). Finalmente, no caso da cidade de Puno o abastecimento provem de três fontes, sendo 93,2% do próprio Lago Titicaca, outros 5,9% do rio Totorani e 0,9% de água subterrânea (EMSA, 2022).

O saneamento deficitário é um dos principais fatores de degradação da qualidade da água no Brasil como um todo (POMPÊO; MOSCHINI-CARLOS, 2012; POMPÊO et al., 2020). Além do déficit no saneamento, que intensifica o processo de eutrofização, outros problemas associados à perda da qualidade da água são o adensamento urbano e os usos e ocupação da bacia hidrográfica sem o planejamento adequado. Tais atividades levam à alteração da ciclagem de elementos e o aporte de contaminantes como metais, poluentes orgânicos, poluentes emergentes, entre outros. Dentre os eventuais contaminantes merece destaque as alterações no ciclo e aporte de metais, já que estes elementos são reconhecidos pelo seu potencial tóxico, persistência e capacidade de se bioacumular (LUOMA; RAINBOW, 2008). Esse mesmo panorama também é observado na região do Lago Titicaca no Peru, carecendo de um sistema de tratamento nas zonas urbanas (MORENO TERRAZAS *et al.*, 2018) e em áreas, principalmente, de mineração na parte alta da bacia. Todas as mudanças físicas que ocorrem dentro da área de drenagem conduzem a mudanças no ciclo e sistemas hidrológicos (padrões de precipitação, evapotranspiração entre outros) devem ser considerados.

O efeito visível do desequilíbrio, devido à ausência de planos sanitários, é a eutrofização artificial como consequência do ingresso de grandes quantidades de nutrientes, fosforo e nitrogênio, levando a cenários de florações de algas e consequentemente a problemas com a saúde pública devido à presença de toxinas em cianobactérias(DOS SANTOS MACHADO *et al.*, 2022; YANG *et al.*, 2020). Essas florações podem afetar o processo de produção da água potável e desse modo incrementa o custo dos produtos químicos utilizados. Nesse contexto o controle das algas prévio ao tratamento é importante. No Brasil e vários outros países são aplicados o sulfato de cobre e o peroxido de hidrogênio para realizar esse controle (ANDERSON *et al.*, 2019; HULLEBUSCH *et al.*, 2003; KANSOLE; LIN, 2017; POMPÊO, 2017; REIS; CAPELO, 2022; SKLENAR; HORNE, 1999; ZHANG *et al.*, 2022). Nos Estados Unidos com aplicações desde 1905 (HANSON; STEFAN, 1984; MCKNIGHT *et al.*, 1983), no Canada (PREPAS; MURPHY, 1988) na Região Metropolitana de São Paulo no reservatório Guarapiranga desde 1979 (MANCUSO, 1987). Tudo isso devido a sua ampla aceitabilidade e baixo custo são os paliativos mais simples para evitar as florações de algas (LEAL *et al.*, 2018; ZHANG *et al.*, 2022). A pesar da presença natural do cobre na crosta terrestre, teores altos do metal apresentam um potencial toxico provável (CERVI *et al.*, 2021; LUOMA;

RAINBOW, 2008). Somado a reportes de conteúdos de cobre de até 120 vezes o valor de referência regional, o valor do ambiente originário antes da intervenção do homem.

A bacia do Lago Titicaca localiza-se no sudeste peruano e que continua no território boliviano. Aqui aparece um planalto de alta montanha conhecido como “O Planalto do Collao” ou mais comumente chamado “Altiplano” localizado em formado entre as Cordilleras ocidentais e orientais dos Andes Centrais. Seu baseamento é de rocha Paleozoica sobre rocha Mesozoica (Jurássico e Cretáceo) convertas por uma potente sequencia vulcânica do Cenozoico (INGEMMET, 1995). O arsênio (As) presente na água superficial e subterrânea é naturalmente alta na área dos Andes (SARRET *et al.*, 2019). A poluição e contaminação do ambiente deve-se à liberação de As de minerais ricos em sulfeto formados devido a atividades magmáticas e hidrotermais, além do vulcanismo ao longo das montanhas dos Andes (BUNDSCHUH *et al.*, 2017; COOMAR *et al.*, 2019; MAITY *et al.*, 2017; MORALES-SIMFORS *et al.*, 2020). A presença do As na água subterrânea no noroeste do Lago apresenta valores quase quatro vezes o limiar (VALENZUELA ANTEZANA; YUCRA LIMAHUAYA, 2022) estabelecido pela lei (PERU, 2010), o cenário é parecido no Sul onde o sedimento coletado de poços chega a teores com risco à saúde pública (CALCINA BENIQUE; APAZA CAMPOS, 2019).

Nesse intuito de caracterizar o sedimento segundo seu potencial toxico, temos disponíveis os Guias de Qualidade do Sedimento (SQGs). Os SQGs desenvolvidos pela Agencia Ambiental Canadense, apresentam o nível de efeito limiar TEL (Threshold Effect Level) e o nível de efeito provável PEL (Probable Effect Level) (CCME, 1999) que é amplamente utilizado e reconhecido pela comunidade cientifica (BROCE *et al.*, 2022). Os valores indicam que teores abaixo do TEL sugerem um efeito toxico não muito provável de ocorrência, e concentrações por cima do PEL indicam que há uma probabilidade que os efeitos tóxicos aconteçam, porém, os valores entre o TEL e PEL são incertos. Contudo, a caracterização do sedimento fica incompleta se não demostramos a fonte do metal. Assim, temos índices como o fator de enriquecimento que mensura a concentração do metal considerando um outro elemento de referência na litosfera (MOHAN; KRISHNAKUMAR, 2022; PAN *et al.*, 2022). O elemento de referencia deve ser um metal, utilizado para quantificar o grau de poluição (LEE *et al.*, 1997; PASSOS *et al.*, 2022; WU *et al.*, 2022) e assim diferenciar a sua origem, natural ou antropogênica (BERN *et al.*, 2019; CARDOSO-SILVA *et al.*, 2021; MARTINS *et al.*, 2021).

Outro aspecto importante é a dinâmica de sedimentação porque podem estar relacionados a mudanças de fontes naturais ou artificiais. Inclusive as variações do processo de sedimentação podem se relacionar com eventos históricos. Técnicas de datação radiométricas são ferramentas amplamente utilizadas, que num primeiro momento foram aplicadas na datação de gelo glaciar (GOLDBERG, 1963) logo em ambientes lacustres (KRISHNASWAMY *et al.*, 1971). A utilização do ^{210}Pb em estudos geocronológicos pode ser atribuído a: i) tempo de vida-média de 22.2 anos, ii) é presente tanto na atmosfera quanto nos sedimentos (APPLEBY; OLDFIELD, 1992). A datação do sedimento usando ^{210}Pb é alcançado aplicando o excesso deste metal ($^{210}Pb_{xs}$) resultando num decaimento atmosférico, este é um método globalmente usado (BLASS *et al.*, 2005; DAS; VASUDEVAN, 2021; FONTANA *et al.*, 2022; SHARMA *et al.*, 2012). Por outro lado, ^{137}Cs é relacionado a eventos de explosões nucleares de grande escala que começaram em 1961 – 1962, que após sua difusão atmosférica chegou a um decaimento máximo (maximum fallout), que implica a acumulação de radionuclídeos nos sedimentos lacustres entre 1963 e 1964 (BONOTTO *et al.*, 2022; ROUT; VASUDEVAN, 2022).

Alguns dos modelos baseados em ^{210}Pb tem sido desenvolvidos para avaliar a taxa de sedimentação. Este se fundamenta na acumulação uniforme do sedimento (APPLEBY, 2001). Primeiro, o modelo de fluxo constante sedimentação constante (CFCS) é recomendado quando a taxa de sedimentação e $^{210}Pb_{xs}$ ambos são constantes (um decaimento exponencial) (BONOTTO *et al.*, 2022; CARDOSO NERY; BONOTTO, 2022; KRISHNASWAMY *et al.*, 1971). Segundo, o modelo de concentração inicial constante (CIC) que considera um $^{210}Pb_{xs}$ inicial constante sem levar em conta nenhuma mudança na sedimentação (ABBASI, 2019; ROBBINS; EDGINGTON, 1975). Terceiro, o modelo suprimento de taxa constante (CRS) que assume um fluxo constante de $^{210}Pb_{xs}$ à superfície e consequentemente a concentração inicial de $^{210}Pb_{xs}$ é inversamente proporcional à taxa de sedimentação (APPLEBY; OLDFIELD, 1978; FONTANA *et al.*, 2022).

No sedimento em perfil cada camada avaliada tem suas próprias características, salvando certos aspectos históricos, inclusive quando não houve interferências ambientais. É possível observar mudanças relacionadas à biologia, clima e variações dos teores de metais (CARDOSO-SILVA *et al.*, 2021, 2022;

MATAMET; BONOTTO, 2019a; 2019b). Os metais, devido a seu potencial toxico precisam de um monitoramento constante, recomenda-se acompanhar seu incremento (FERREIRA *et al.*, 2021; MARTINS *et al.*, 2021; MIZAEL *et al.*, 2020).

Assim este trabalho visou:

1. Quantificar as concentrações de metais e analisar a sua distribuição espacial no sedimento superficial ao longo dos reservatórios de Rio Grande, Paiva Castro e Itupararanga, no Brasil (Capítulos 2 e 3), e na Baía de Puno, no Peru (Capítulo 4).
2. Categorizar a toxicidade potencial do sedimento superficial, em função dos valores background (valores de referência regional) e os valores dos guias de qualidade para o sedimento "*Threshold Effect Level*" – TEL e "*Probable Effect Level*" – PEL. (Capítulos 2 – 5)
3. Avaliar, cartograficamente, a ecotoxicidade e índices de enriquecimento dos metais no sedimento superficial em Rio Grande, Paiva Castro e Itupararanga (Capítulos 2 e 3) e na Baía de Puno (Capítulo 4).
4. Mensurar as concentrações de metais em perfis de sedimento em duas áreas dentro da Baía de Puno para propor valores background (Capítulo 5).
5. Calcular a taxa de sedimentação segundo o modelo de *Constant Flux Constant Sedimentation* (CFCS) e analisar baseado numa abordagem geocronologica o sedimento em perfil de duas áreas dentro da Baía de Puno (Capítulo 5).
6. Comparar a qualidade do sedimento entre os ambientes brasileiros e os peruanos que nos permitam atingir recomendações que estimulem a adoção de ações de controle para amenizar impactos futuros tanto nos ambientes avaliados como em outros corpos hídricos de características similares (Capítulo 6).

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Capítulo 2

Heterogeneidade espacial e ecotoxicidade de metais no sedimento em três reservatórios paulistas aplicando um enfoque geoestatístico[1]

2.1. RESUMO

Os metais de origem geogênica ou antrópica, podem ser incorporados pela biota, porém, grande parte tende a sedimentar permanecendo retidos no sedimento. De modo geral, as pesquisas que avaliam os metais no sedimento, quase sempre o fazem de forma pontual e são relativamente poucos os trabalhos que mostram a distribuição espacial das concentrações de metais no sedimento superficial, particularmente em reservatórios. Este trabalho visou avaliar a heterogeneidade espacial da qualidade do sedimento, com base nas concentrações de metais e em guias de qualidade, em três reservatórios paulistas. Foi feita uma classificação das concentrações do Cr, Ni, Pb e Zn nos reservatórios de Rio Grande (RG), Paiva Castro (PC) e Itupararanga (ITU) segundo os Valores de Referência Regional (VRR), *Threshold Effect Level* (TEL) e *Probable Effect Level* (PEL). O modelamento da distribuição espacial foi realizado pelo *Inverse Distance Weighting* (IDW). Os mapas temáticos obtidos, demonstram que o RG apresentou uma classificação Regular para Cr e em certas porções do sedimento, Ruim para Zn. No PC somente o Cr foi classificado como Regular e para ITU, Cr e Pb mostram áreas categorizadas como Regular. O Cr foi o metal com maior potencial de risco nos três reservatórios avaliados, com valores por cima do TEL. De modo geral o RG foi o reservatório que apresentou condições mais preocupantes de toxicidade potencial, com base nos critérios de qualidadeas aplicados, seguido de ITU e depois por PC, o menos impactado entre eles, levando em consideração as concentrações dos metais estudados.

2.2. INTRODUÇÃO

A necessidade de abastecimento de água para áreas urbanas de rápido crescimento, é um desafio para as companhias envolvidas no saneamento da água. Segundo o Sistema Nacional de Informações sobre Saneamento (SNIS), o abastecimento de água abrange 83,6% dos brasileiros, porém, apenas 53,2%

[1] Capítulo publicado no livro “Aspectos da Ecotoxicidade em Ambientes Aquáticos”

possuem o esgotamento sanitário e somente 46,3% possuem tratamento de esgoto (SISTEMA NACIONAL DE INFORMAÇÕES SOBRE SANEAMENTO, 2019). Para piorar o panorama, a Agência Nacional de Águas e Saneamento Básico (ANA) mediante o Atlas Esgotos: Despoluição de Bacias Hidrográficas, aponta que 38,6% dos esgotos produzidos não são coletados, nem tratados, e que 18,8% são coletados, mas lançados sem tratamento aos corpos de água (ANA, 2017).

Na Região Metropolitana de São Paulo (RMSP), o saneamento básico foi e ainda é um desafio (KAWAI; BRANCO, 1969; POMPÊO *et al*., 2020), devido à rápida expansão urbana e o crescimento populacional experimentado desde a segunda metade do século XX. A RMSP possui um sistema integrado de abastecimento público, compondo os seguintes sistemas: Cantareira, Baixo Cotia, Alto Cotia, Guarapiranga, Rio Grande, Ribeirão da Estiva, Rio Claro e Alto Tietê. Esses oito sistemas produtores possuem uma capacidade nominal de produzir 68,2 m^3/s (ANA, 2010). Já fora da RMSP, muitos municípios também tem demonstrado um crescimento populacional significativo. Assim, o abastecimento da cidade de Sorocaba, que opera mediante o Serviço Autônomo de Água e Esgoto (SAAE), capta 85% da água bruta de três represas, os reservatórios Clemente, Itupararanga e Ipaneminha, sendo que outros 10% do córrego Pirajibu-Mirim e o 5% restante proveniente de 23 poços tubulares (SAAE, 2020).

O saneamento deficitário é um dos principais fatores de degradação da qualidade da água no Brasil como um todo (POMPÊO; MOSCHINI-CARLOS, 2012; POMPÊO *et al*., 2020). Além do déficit no saneamento, que intensifica o processo de eutrofização, outros problemas associados à perda da qualidade da água são o adensamento urbano e os usos e ocupação da bacia hidrográfica sem o planejamento adequado, que não tenha impactos negativos ao meio ambiente em geral. Tais atividades levam à alteração da ciclagem de elementos e o aporte de contaminantes como metais, poluentes orgânicos, poluentes emergentes, entre outros. Dentre os eventuais contaminantes merece destaque as alterações no ciclo e aporte de metais, já que estes elementos são reconhecidos pelo seu potencial tóxico, persistência e capacidade de bioacumular (LUOMA; RAINBOW, 2008).

Os metais podem ter origem natural (geogênica) ou artificial (antrópica) (GARCÍA-ORDIALES *et al*., 2016), e são introduzidos nos corpos de água através de eventos climáticos, como pela chuva, a erosão ou a deposição atmosférica seca, além de fontes pontuais e difusas. Alguns exemplos de fontes antrópicas são os efluentes industriais, o uso de agrotóxicos (DEFARGE *et al*., 2018), os fertilizantes aplicados em áreas agrícolas (MORTEVEDT, 1995), a aplicação de algicidas a base de metais, como o sulfato de cobre (MARIANI; POMPÊO, 2008; CARDOSO-SILVA *et al*., 2016; BEYRUTH; PEREIRA, 2018; LEAL *et al*., 2018), o desmatamento e as queimadas de florestas (uma das fontes de Hg na região amazônica) (CRESPO-LOPEZ *et al*., 2021).

No meio aquático os metais podem ser diretamente adsorvidos e absorvidos pela biota (MAGALHÃES *et al*., 2015), e, em grande parte, tendem a sedimentar, permanecendo retidos neste compartimento. Entretanto, dependendo das condições físicas e químicas, os metais sedimentados podem ser re-suspendidos para a coluna de água, e se presentes em elevadas concentrações, podem impactar significativamente a qualidade do ambiente aquático (LUOMA; RAINBOW, 2008). Desta forma, mesmo após uma fonte de poluição ser cessada, os metais adsorvidos ao sedimento podem por um longo período ser liberados à coluna de água e exercer seus efeitos potenciais tóxicos adversos à biota. Na ocorrência de eventos climáticos extremos, como chuvas, sequias ou o mesmo vento, construção de infraestrutura ao redor do ambiente aquático, entre outras causas. Desta forma, é imprescindível que medidas de controle da emissão de metais, restauração e recuperação e uma ampla rede de monitoramento sejam implementadas nos ecossistemas aquáticos, visando acompanhar suas concentrações e distribuição no sedimento nos reservatórios.

A distribuição espacial de compostos químicos presentes em uma dada massa de água ou no sedimento. Isto permite conhecer se há heterogeneidade dentro desse corpo de água, auxiliando na categorização dessas regiões, segundo seus níveis de toxicidade potencial. Essa espacialização também permite visualizar a dinâmica da poluição e identificar fontes importantes que influenciam o equilíbrio pré-existente. Os dados fornecem informações primordiais aos tomadores de decisões, contribuindo no desenvolvimento de políticas públicas entre o meio ambiente e a planificação estratégica a médio e longo prazos, bem como para o planejamento de programas de monitoramento da qualidade da água e do sedimento.

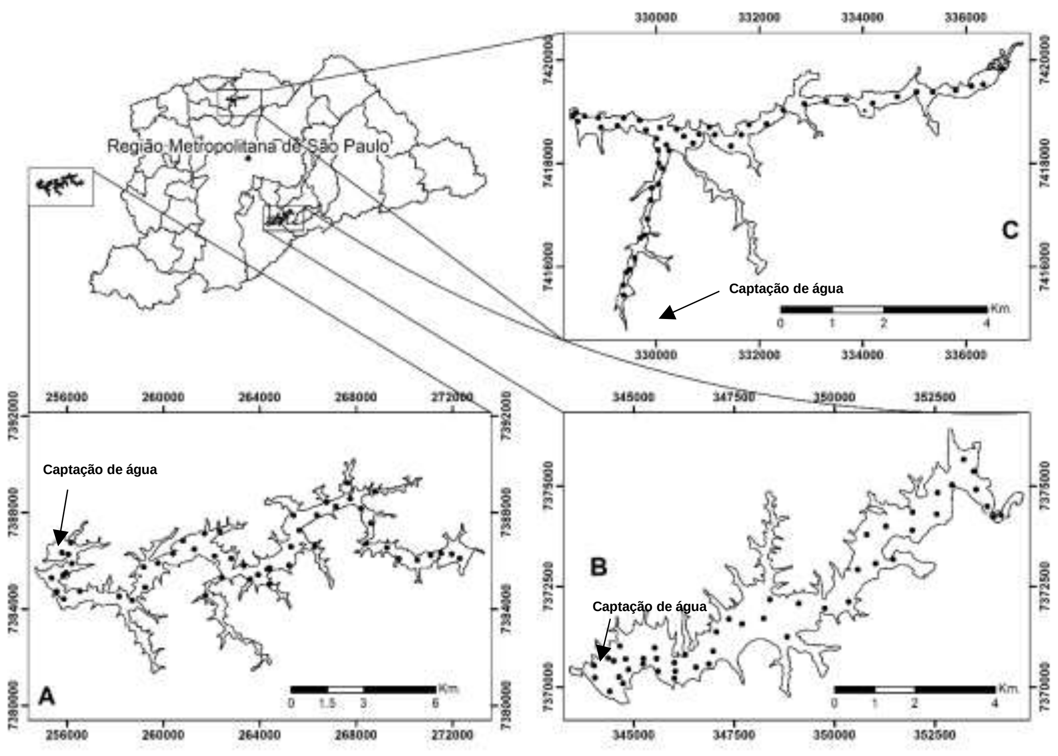
O presente trabalho teve como objetivo avaliar a heterogeneidade espacial da qualidade do sedimento, com base nas concentrações de metais e em guias de qualidade, em três reservatórios paulistas, com uma categorização das regiões segundo os valores de referência regional (VRR), *Threshold effect level* (TEL) e *Probable effect level* (PEL).

2.3. MATERIAL E MÉTODOS

2.3.1. Local de estudo

Nesta pesquisa, foram estudados três reservatórios empregados no abastecimento público, os reservatórios Rio Grande, do Complexo Billings, o Paiva Castro, do Sistema Cantareira, e o de Itupararanga (Fig. 1).

Figura 1 – Mapa de localização dos reservatórios e dos pontos de coleta (●) em Itupararanga (A), Rio Grande (B) e Paiva Castro (C)



Fonte: Autoria própria

O reservatório Rio Grande (RG) (46°29’49”W 23°45’46”S) foi isolado do Complexo Billings pela barragem Anchieta em 1982, e é destinado ao abastecimento de água de 1,2 milhões de pessoas nos municípios de São Bernardo do Campo, Santo André e Diadema. A pressão urbana é muito grande ao redor desse reservatório e os efluentes de atividades antrópicas (domesticas e industriais), são lançados *in natura* e até diretamente no reservatório. Visando o controle do crescimento fitoplanctônico, existem registros de aplicações de algicidas nesse reservatório, em especial do sulfato de cobre pentahidratado, desde a década de 1980 (MARIANI; POMPÊO, 2008; BEYRUTH; PEREIRA, 2018).

Já o reservatório de Paiva Castro (PC) (46°39’27”W 23°20’5”S), pertence ao Sistema Cantareira, que faz a transposição entre duas bacias hidrográficas, importando água desde a bacia do Piracicaba para a bacia do Alto Tietê. Deste modo, o reservatório Paiva Castro recebe água dos reservatórios Jaguari, Jacareí, Atibainha, Cachoerinha, e mais recentemente do Igaratá, produzindo até 33 m^3/s, abastecendo 9 milhões de pessoas (POMPÊO *et al*., 2017; POMPÊO *et al*., 2021). Este reservatório tem registros de aplicações de sulfato de cobre desde meados de 1990 (CARDOSO-SILVA *et al*., 2016).

O reservatório de Ituparamanga (ITU) (47°20’18”W 23°36’49”S) foi construído em 1912, pelo barramento dos rios Sorocabuçu, Sorocamirim e Una. Tem sua área de drenagem compreendendo os municípios de Ibiúna, Piedade, São Roque, Cotia, Vargem Grande Paulista, Mairinque e Votorantim (TANIWAKI *et al*., 2013). O reservatório faz parte da Área de Proteção Ambiental (APA) de Itupararanga desde 1998, e apresenta um tempo de residência de 250 dias. Neste reservatório não existe registro de aplicação de algicidas baseados em metais.

2.3.2. Coleta e processamento das amostras

A coleta de sedimento no reservatório RG foi realizada em 16 de novembro de 2017, em PC em 23 de novembro de 2017 e no reservatório ITU no dia 28 de setembro de 2017. Em todos eles as estações de coletas foram distribuídas ao longo dos reservatórios, com 47 amostras georeferenciadas em RG, 50 em PC e 52 pontos de amostragem em ITU (Fig. 1).

Para a coleta do sedimento superficial (4 cm), foi empregado um coletor de sedimento Lenz de 225 cm^2. A porção superficial do sedimento foi armazenada em frascos coletores e estéreis de 100 ml, e guardados em bolsas térmicas e no escuro. No laboratório as amostras foram secas em estufa a 50 °C e trituradas em almofariz de vidro. Para a análise dos metais Cromo (Cr), Níquel (Ni), Chumbo (Pb) e Zinco (Zn), o sedimento foi preparado seguindo o método 3050B (USEPA, 1996). As amostras após a digestão foram armazenadas a 4 °C antes da análise no Espectrômetro de Emissão Atômica de Plasma Acoplado Indutivamente (ICP-AES), utilizando um equipamento Agilent Série 720. O material de vidro utilizado no processamento das amostras para análise de metais foi deixado numa solução de 10% de ácido nítrico por 24 horas e depois lavadas com água ultrapura.

2.3.3. Ecotoxicologia do sedimento

A avaliação da concentração de metais e seu potencial de toxicidade foi baseada nos guias de qualidade de sedimento canadenses (ISQGs), como o *Threshold Effect Level* (TEL) e *Probable Effect Level* (PEL) (CCME, 1999); em conjunto com os valores de referência regional (VRR) (Tab. 1) de Cardoso-Silva *et al*. (2016), para PC, de Nascimento ; Mozeto (2008) para RG e de Cardoso-Silva *et al*. (2021) para ITU. O VRR é determinado mediante a coleta de sedimento em perfil e identificando camadas desse sedimento pertencentes a épocas antes da intervenção humana. Logo a média aritmética é calculada a partir dos teores das camadas mais profundas, resultando no VRR. As classificações associadas ao risco ecotoxicológico foram definidas em quatro categorias, segundo à qualidade do sedimento como Excelente, Bom, Regular e Ruim, adaptado de Leal *et al*. (2018) (Tab. 2).

2.3.4. Geoestatística

Neste trabalho o interpolador determinístico utilizado foi o Ponderador Pelo Inverso da Distância ou *Inverse Distance Weighting* (IDW). Para estimar os valores em locais não amostrados. O interpolador IDW utiliza valores próximos ao local de predição. Este algoritmo assume que zonas próximas aos pontos de avaliação são mais parecidas do que de regiões maiss distantes. Deste modo, os valores estimados próximos aos locais de avaliação terão maior influência na interpolação que outros localizados mais distantes. A equação utilizada para calcular os valores desconhecidos foi:

$$\hat{Z}_j = \frac{\sum_{i=1}^{n} \frac{Z_i}{d_{ij}^2}}{\sum_{i=1}^{n} \frac{1}{d_{ij}^2}} \qquad (1)$$

onde Ẑj é o valor estimado para o ponto não amostrado; d é a distância de dado ponto conhecido; z é o valor de z do ponto conhecido i; n é o número de pontos a serem incluídos na procura; e i é o número do ponto conhecido a ser tomado em conta.

A ponderação mais usada é o inverso do quadrado da distância euclidiana do ponto da grade à amostra considerada, sendo:

$$d_{ij}\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2} \qquad (2)$$

Tabela 1 – Valores de referência regional (VRR), ISQG/TEL= Threshold effect level; PEL= Probable effect level

METAL	Reservatorio	VRR	TEL	PEL
Cromo			37.3	90
	Paiva Castro	24*		
	Rio Grande	36**		
	Itupararanga	31***		
Níquel			18	36
	Paiva Castro	33*		
	Rio Grande	23**		
	Itupararanga	7***		
Chumbo			35	91.3
	Paiva Castro	27*		
	Rio Grande	61**		
	Itupararanga	25***		
Zinco			123	315
	Paiva Castro	70*		
	Rio Grande	82**		
	Itupararanga	40***		

*Fonte: Cardoso-Silva *et al*. (2016)
**Fonte: Nascimento e Mozeto (2008)
***Fonte: Cardoso-Silva *et al*. (2021)
TEL e PEL: CCME (1999)

Tabela 2 – Classificação qualitativa do sedimento, adaptado segundo Leal *et al*. (2018), onde [M]= concentração do metal; VRR= Valor de referência regional, ISQG/TEL= Threshold effect level; PEL= Probable effect level.

Classes	Limites/Intervalos	Potencial ecotoxicologico
Excelente	0 µg/Kg ≤ [M] < VRR	Região com mínimo risco ecotoxicológico. Concentração basal.
Bom	VRR ≤ [M] < ISQG/TEL	Região com possível contaminação antrópica, mas com risco ecotoxicológico mínimo ou improvável.
Regular	ISQG/TEL ≤ [M] < PEL	Região com contaminação antrópica e com risco ecotoxicológico incerto.
Ruim	> PEL	Região com contaminação antrópica e com risco ecotoxicológico provável

Fonte: Leal et al. (2018)

2.4. RESULTADOS E DISCUSSÕES

2.4.1. Heterogeneidade espacial de metais no sedimento

Rio Grande

Para o reservatório Rio Grande a espacialização das concentrações de metais resultou em uma heterogeneidade ao longo do corpo de água (Fig. 2).

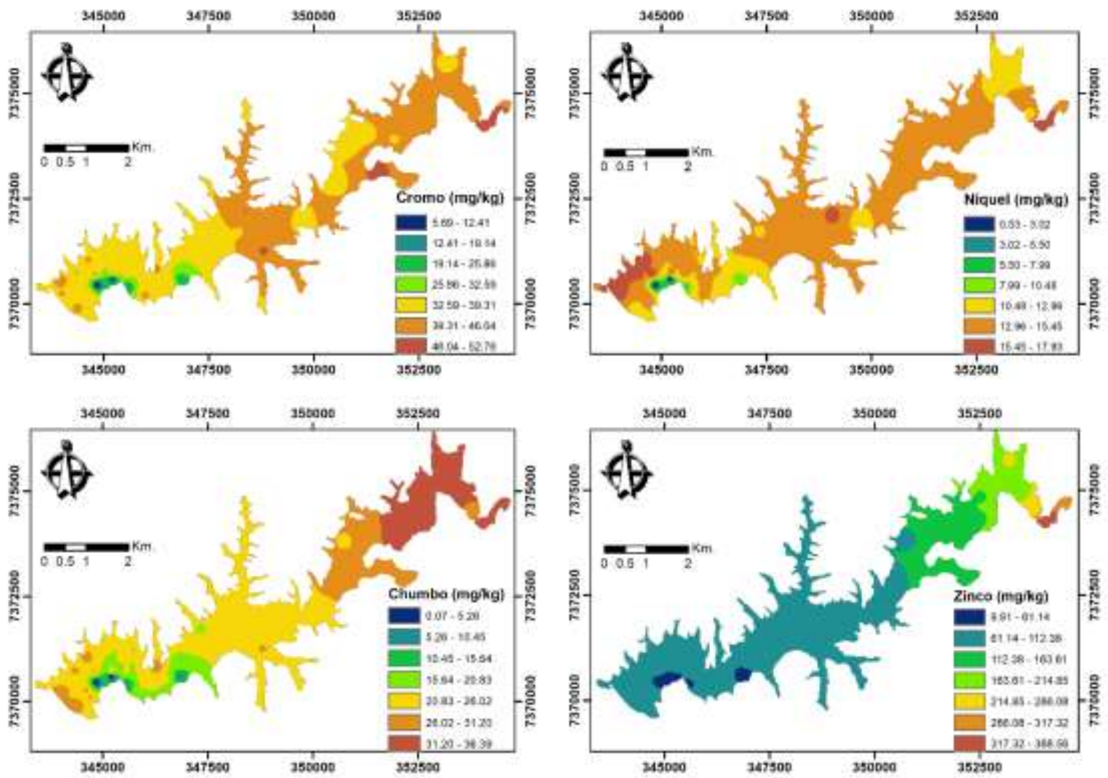
Para o Cr, as maiores concentrações, de 39,31 mg Cr/kg até 52,76 mg Cr/kg, estão localizadas na parte alta do reservatório, e os teores vão diminuindo em direção à barragem. A concentração elevada é intensificada na margem inferior (Sul), onde as atividades antrópicas estão distribuídas (áreas urbanas, agrícolas e industriais). Os teores mais elevados do Cr (acima de 39,31 mg Cr/kg) estão presentes até aproximadamente a porção central do reservatório, perto de áreas urbanas e industriais. É provável que fontes de poluição urbanas exerçam uma alta influência na presença dos metais no sedimento (LEI *et al*., 2019; SAIDI *et al*., 2019). A parte baixa do reservatório apresenta valores abaixo de 39,31 mg Cr/kg, chegando até 32,59 mg Cr/kg perto da barragem. Porém, existe uma área na região da barragem, na frente do ponto de captação da SABESP que apresenta os menores teores de Cr (5,69 mg Cr/kg até 25,86 mg Cr/kg), o que também foi reportado por Mariani; Pompêo (2008).

Para o Ni, foram observadas concentrações acima dos 12 mg Ni/kg em grande parte do reservatório, estendendo-se desde regiões próximas à entrada até a região central, principalmente em áreas próximas às zonas urbanas. Como foi visto no caso do Cr, a porção que se encontra na margem contrária ao ponto de captação d´água da SABESP continua sendo o setor com a menor concentração, de 0,53 mg Ni/kg até 10,48 mg Ni/kg. Já no caso do Pb está presente desde a entrada do rio principal, com teores acima dos 26 mg Pb/kg, mas evidenciando uma diminuição da concentração em direção à barragem. A partir da metade do reservatório a maior parte do sedimento apresenta concentrações entre 20,83 mg Pb/kg e 26 mg Pb/kg. Na região da barragem, na margem contrária ao ponto de captação da SABESP apresenta, em todos os casos avaliados, baixos teores de metais. Este fenômeno é contrário ao comum de outros reservatórios como Guarapiranga (LEAL *et al*., 2018) onde as maiores concentrações são observadas na região da barragem.

O Zn foi o metal que apresentou a maior variação de concentrações, desde 9,91 mg Zn/kg até 368,56 mg Zn/kg. Na porção referente à entrada de água do rio principal, o sedimento apresentou valores acima dos 112 mg Zn/kg. A partir do meio do reservatório, a concentração diminui até 61,14 mg Zn/kg. Também para Zn é possível observar que a área na margem oposta do ponto de captação d´água exibe os menores teores desse elemento, de 9,91 mg Zn/kg até 61,14 mg Zn/kg.

De maneira geral, observou-se um gradiente de diminuição nos teores de metais no sentido montante-jusante, exceto para o Ni. Este padrão de maiores teores na entrada de RG pode estar associado à fatores como a entrada do rio principal que passa pelo município de Ribeirão Pires. Além disso, processos erosivos poderiam influenciar tal distribuição. Apesar dos maiores teores de Cr, Pb e Ni na entrada do reservatório, tais valores estão em conformidade com os valores de referência regional (VRR).

Figura 2 – Distribuição espacial da concentração de Cromo, Níquel, Chumbo e Zinco no sedimento do reservatório Rio Grande

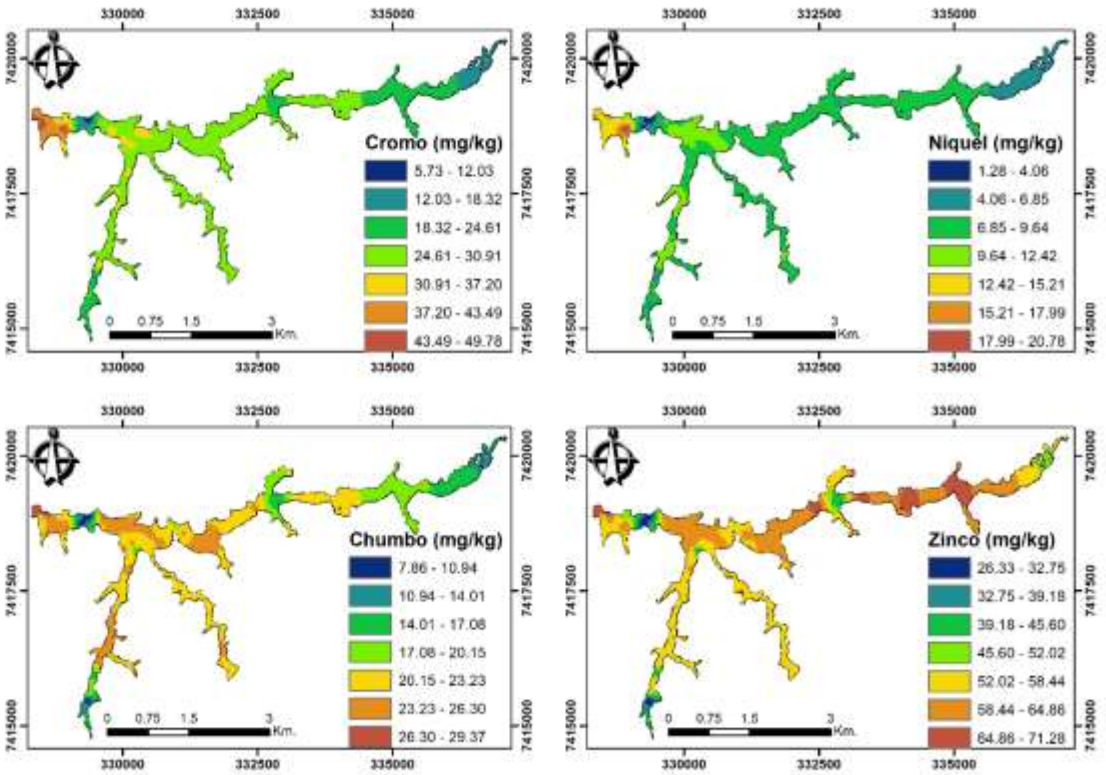


Fonte: Autoria própria

Paiva Castro

Para o Cr (Fig. 3), suas concentrações apresentaram variação de 5,7 mg Cr /kg até 24 mg Cr /kg. Na porção central o Cr apresentou valores acima de 24,5 mg Cr /kg, chegando a 37 mg Cr /kg, que se manteve até o ponto de captação da SABESP. Levando em conta o curso natural, deste ponto até à barragem, existe um aumento nos teores de Cr, chegando até 49,7 mg Cr/kg. Ao redor do reservatório especialmente na margem sul, há grandes áreas urbanas, mas não foi observada uma relação direta entre a presença de atividades humanas e as elevadas concentrações de Cr, como sugerido em RG. O acúmulo de Cr na região da barragem e em pontos isolados, provavelmente é devido à vazão e o tempo de retenção (aproximadamente 5 dias).

Figura 3 – Distribuição espacial da concentração de Cromo, Níquel, Chumbo e Zinco no sedimento do reservatório Paiva Castro



Fonte: Autoria própria

O Ni também segue o padrão de distribuição exibido pelo Cr, com teores baixos na região de entrada do rio principal, com uma amplitude entre 1 e 6 mg Ni /kg. Já na parte central, pode chegar a 9,84 mg Ni /kg ou acima desse valor. Em referência à porção da barragem, os valores estão na casa de 20,78 mg Ni /kg, que pode ser resultado do fluxo d´água.

Já o Pb apresentou as menores concentrações na parte alta, na região de ingresso da água do rio principal, com concentrações de 7,8 mg Pb/kg até 17 mg Pb/kg. Na porção central e de uma forma similar ao observado para o Cr e Ni, a concentração vai aumentando em direção à barragem, chegando a 29,37 mg Pb/kg.

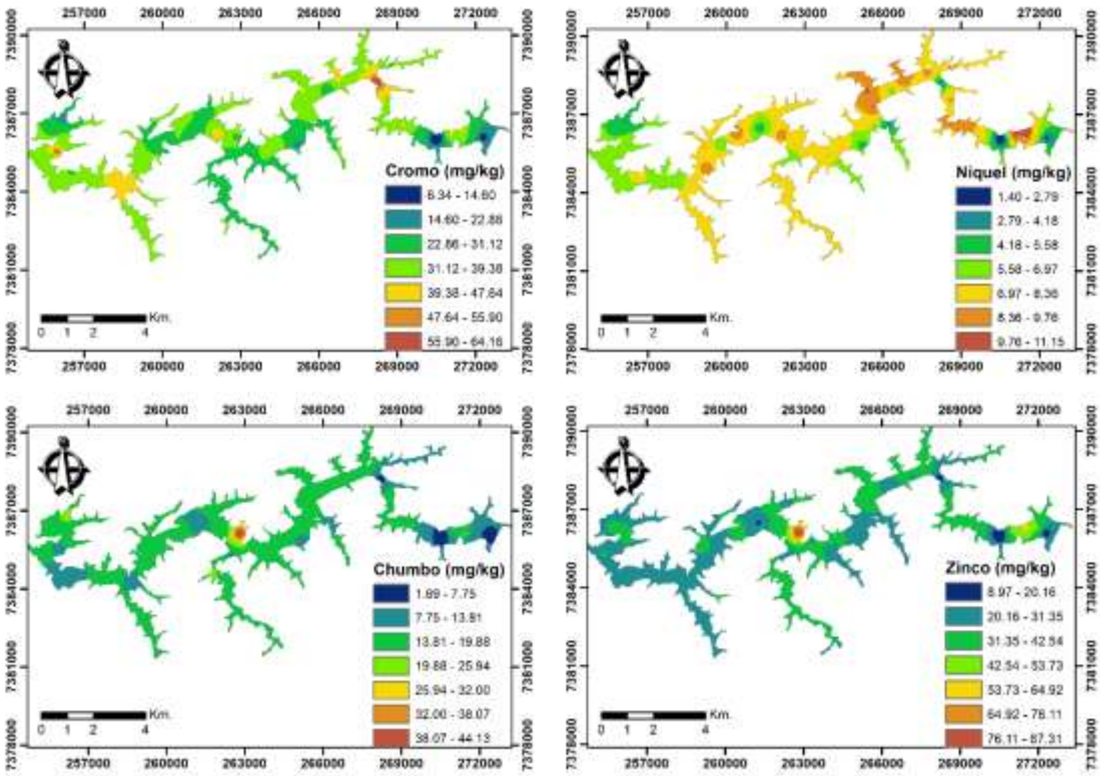
Esse valor máximo é também evidenciado na região perto do ponto de captação da SABESP.

Para o Zn, na parte alta do reservatório e no braço do ponto de captação da SABESP, as concentrações variaram de 45,6 mg Zn/kg até 58 mg Zn/kg. Também é observado o mesmo fenômeno com aumento nos teores em direção à barragem. Na porção central essas concentrações chegam a 71,28 mg Zn/kg indicando, provavelmente, uma maior taxa de sedimentação desse metal.

Itupararanga

A distribuição das concentrações do Cr no sedimento de ITU encontra-se de forma heterogênea ao longo do reservatório (Fig. 4). Há baixas concentrações na parte alta do reservatório, com valores de até 22 mg Cr/kg. Entretanto, uma grande parte do reservatório apresenta valores entre 22,8 mg Cr/kg e 39,3 mg Cr/kg. Na confluência de afluentes na porção ao leste (parte alta do reservatório) e também na porção oeste, os valores chegaram a 64,1 mg Cr/kg. Na área da barragem foram registradas concentrações menores que 39,38 mg Cr/kg. Comparando as concentrações de Cr no ITU, PC e RG, os teores presentes em ITU são superiores aos valores observados nos reservatórios RG e PC.

Figura 4 – Distribuição espacial da concentração Cromo, Níquel, Chumbo e Zinco no sedimento do reservatório Itupararanga



Fonte: Autoria própria

Na parte alta do reservatório, foram observadas baixas concentrações de Ni (Fig. 4), de 1,4 mg Ni/kg até 5,5 mg Ni/kg, mas aparecem como pontos isolados. É possível identificar numa zona adjacente e na zona central do reservatório, concentrações altas entre 8,3 mg Ni/kg até 11,15 mg Ni/kg. Deste modo, a maior parte do reservatório mostra valores entre 5,58 mg Ni/kg e 8,36 mg Ni/kg, chegando até a barragem. Já na área da barragem, são observadas as menores concentrações de Ni.

Para o Pb (Fig. 4), para grande parte do sedimento superficial, as concentrações variaram entre 1,6 mg Pb/kg a 19,8 mg Pb/kg. Já na região central é possível observar uma pequena região com a maior concentração de Pb observada, chegando ao valor de 44,1 mg Pb/kg. Na região da barragem, há um setor que exibe valores entre 19,8 mg Pb/kg e 25,9 mg Pb/kg.

Grande parte do reservatório apresenta concentrações de Zn entre 20,1 mg Zn/kg e 42,5 mg Zn/kg (Fig. 4). A forma do reservatório provavelmente faz com que a sedimentação ocorra nas porções que se localizam perto dos braços. Também podemos observar valores acima dos 42,5 mg Zn/kg na parta alta do reservatório, de até 64,9 mg Zn/kg. No corpo central do reservatório, e como observado para o Pb, há um ponto isolado que apresenta concentrações mais elevadas, chegando a 87,3 mg Zn/kg.

2.4.2. Análise comparativa

Considerando as concentrações de metais, numa comparativa na literatura, é possível observar que no caso do Cr, Ni, Pb e Zn, o reservatório RG apresentou valores similares, embora as médias calculadas nestes trabalhos sejam menores (Tab. 3). Para PC se observa um incremento nas concentrações do Ni, Pb e Zn, sugerindo uma acumulação destes metais. Finalmente no RG, as concentrações dos metais no sedimento foram ligeiramente menores comparado a outros estudos.

Tabela 3 – Concentração de metais no sedimento dos reservatórios de Rio Grande, Paiva Castro, Itupararanga e outros reservatórios (mg/kg)

Reservatório / Lago	Cr	Ni	Pb	Zn	Tipo de uso	Referência
Rio Grande	37,98 ± 8,93	13,53 ± 3,48	25,21 ± 7,78	115,96 ± 68,14	Abastecimento	Este trabalho
Rio Grande	46,37 ± 2,96	18,91 ± 3,33	32,85 ± 4,25	128,22 ± 26,49	Abastecimento	Frascareli *et al*., 2018
Paiva Castro	27,12 ± 6,84	8,86 ± 2,92	20,85 ± 4,71	56,39 ± 10,36	Abastecimento	Este trabalho
Paiva Castro	-	1,4 ± 1,6	13,5 ± 6,6	12,9 ± 7,7	Abastecimento	Cardoso-Silva *et al*., 2016
Itupararanga	33,14 ± 9,32	7,12 ± 1,94	15,44 ± 5,61	32,27 ± 10,84	Uso Múltiplo	Este trabalho
Itupararanga	36,17 ± 1,67	7,82 ± 0,95	16,87 ± 1,01	33,24 ± 1,28	Uso Múltiplo	Frascareli *et al*., 2018
Keban (Turquia)	143,63 ± 82,85	106,64 ± 46,04	10,64 ± 2,91	76,73 ± 19,89	Uso Múltiplo	Varol, 2020
Ross Barnett (EUA)	40,2 ± 26,6	-	13,5 ± 6,8	53,7 ± 36,0	Uso Múltiplo	Paul *et al*., 2021
Changshou (China)	99,1	50,8	35,7	149,0	Uso Múltiplo	Xie *et al*., 2020
Luhan (China)	59,17	26,65	201,1	187,07	Uso Múltiplo	Wang *et al*., 2020
Barra Bonita (Brasil)	82,0	54,5	11,6	162,0	Energia elétrica	da Conceição *et al*., 2020
Rożnów (Polonia)	24,58	26,5	8,68	66,28	Energia elétrica	Szara *et al*., 2020

Fonte: Autoria própria

No contexto internacional, ao comparar reservatórios com características similares (Tab. 3), com todos os reservatórios recebendo despejos de esgotos tanto domésticos quanto industriais, é possível observar que a represa Keban apresenta as maiores concentrações de Cr (143,63 mg Cr/kg) e Ni (106,64 mg Ni/kg), no caso do Pb é o reservatório Changshou (35,7 mg Pb/kg) é o que apresenta o maior teor e finalmente para o caso do Zn o reservatório Barra Bonita (162,0 mg Zn/kg) e Changshou (149,0 mg Zn/kg).

Em um outro grupo, podemos comparar os reservatórios PC, Ross Barnett e Luhun, que são utilizados quase que exclusivamente para o abastecimento público. Entre estes três reservatórios, Luhun apresentou os maiores teores para todos os metais avaliados (Cr - 59,17 mg Cr/kg, Ni - 26,65 mg Ni/kg, Pb - 201,1 mg Pb/kg, Zn - 187,07 mg Zn/kg). Neste caso, para Luhun, essas maiores concentrações são explicadas, pois sua bacia hidrográfica é rica em minérios, incluindo a maior exploração de Molibdênio da China, assim como de Pb e Zn. No caso do reservatório Ross Barnett, as concentrações de Cr (40,2 mg Cr/kg), Pb (13,5 mg Pb/kg) e de Zn (53,7 mg Zn/kg), apresenta valores similares aos do PC.

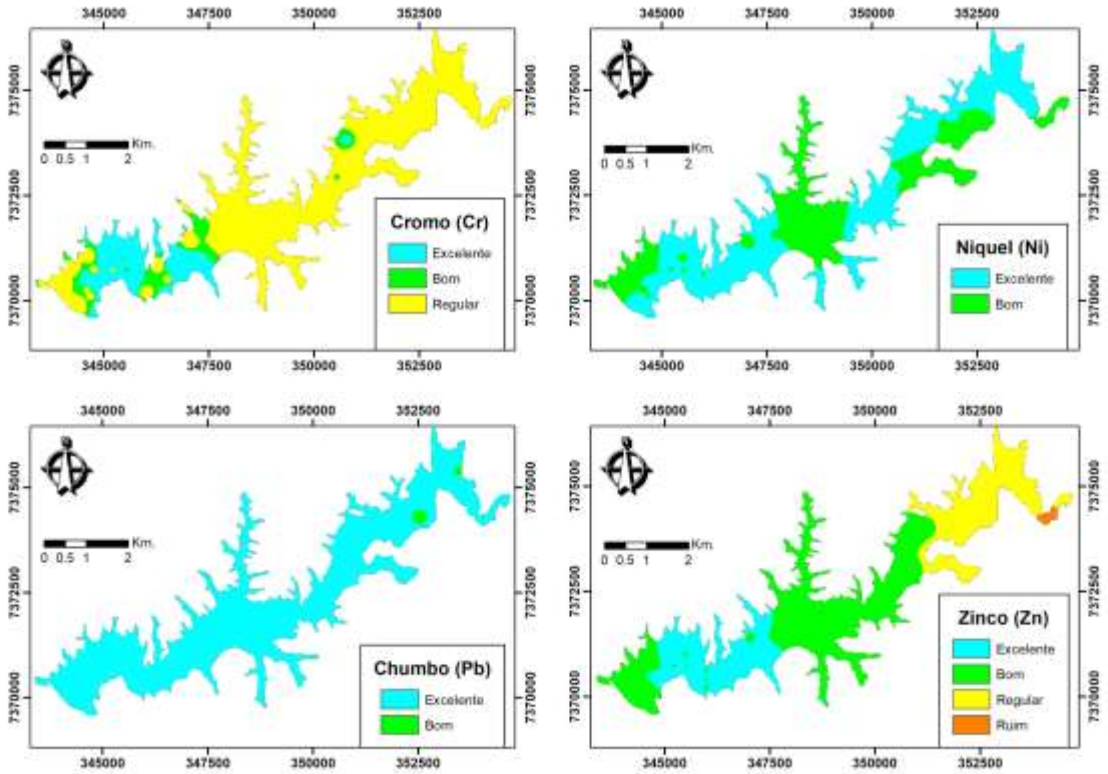
Já os reservatórios de ITU e Rożnów, apresentam características de uso similares, pois recebem despejos de esgoto doméstico e ficam numa bacia com atividade agrícola. O reservatório Rożnów apresenta valores de Cr da ordem de 24,58 mg Cr/kg, de Ni, de 26,5 mg Ni/kg e para Zn de 66,28 mg Zn/kg, mais elevados aos observados no PC. Somente para Pb (8,68 mg Pb/kg) o reservatório Rożnów apresentou concentração menor do que o observado no PC para esse elemento.

2.4.3. Classificação ecotoxicológica de metais no sedimento

Rio Grande

A categorização da toxicidade potencial dos metais no sedimento superficial dos reservatórios estudados, segundo guia de qualidade de sedimento canadense, como aplicado por Leal *et al*. (2018), demostra que no caso do Cr existem três classes de sedimentos para RG (Fig. 5): Excelente (17,6%), Bom (8,2%) e Regular (74,2%). As porcentagens apresentadas em parênteses, se referem à respectiva área do sedimento em termos de porcentagem. Desta maneira, para RG, a maior porção do sedimento se encontrou na classe Regular. Observa-se que há um incremento na concentração do Cr no sedimento, acima do VRR e também acima do TEL. No caso do Ni, foram observadas as seguintes classes: Excelente (58,9%) e Bom (41,1%); para Pb de Excelente (99,1%) e Bom (0,9%). Embora estes valores indiquem que a toxicidade é improvável, para o caso do Ni o incremento da concentração em quase a metade do reservatório poderia indicar fontes antrópicas deste metal. Finalmente para o Zn, as classes foram: Excelente (23,2%), Bom (50,6%); Regular (25,3%) e Ruim (0,8%), com a parte alta do reservatório com as classes acima do TEL e PEL.

Figura 5 – Categorização da qualidade do sedimento para Cromo, Níquel, Chumbo e Zinco no reservatório de Rio Grande



Fonte: Autoria própria

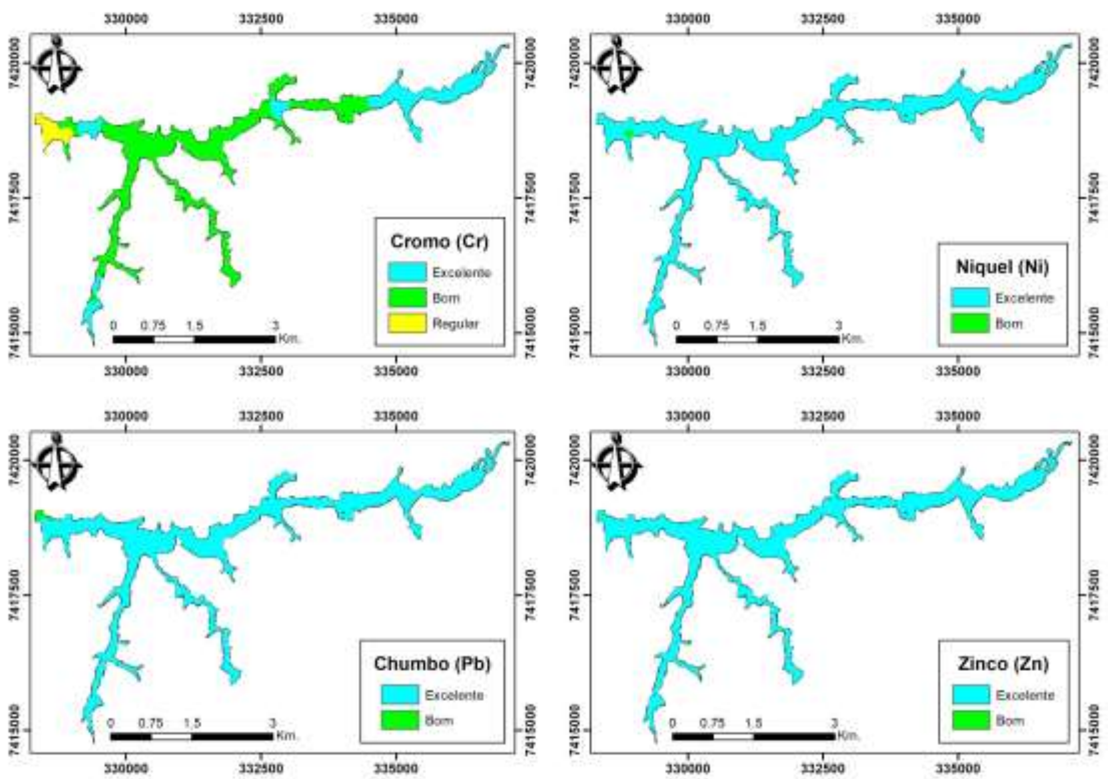
Paiva Castro

A maior variação na classificação dos sedimentos no reservatório PC (Fig. 6), foi observada para os teores de Cr: Excelente (26,9%), Bom (67,7%) e Regular (5,4%). Neste caso em específico, a região do reservatório que está acima do nível do TEL localiza-se na proximidade da região da barragem e a maior parte do sedimento se apresentou com teores acima do VRR, indicando o ingresso deste metal de fontes artificiais. Para o caso de Ni, as classificações foram Excelente (99,5%) e Bom (0,5%), para Pb de Excelente (99,2%) e Bom (0,8%) e para Zn de Excelente (99,9%) e Bom (0,1%). De maneira geral, para os metais Ni, Pb e Zn, as concentrações determinadas no sedimento superficial de PC mostram que não há um incremento do valor, acima do VRR para esse reservatório.

Itupararanga

A categorização dos sedimentos no reservatório de Itupararanga (Fig. 7) indica que o Cr se apresentou com as seguintes classificações: Excelente (37,5%), Bom (42,4%) e Regular (20,1%), representando valores acima do TEL localizados no corpo central e em porções da parte alta do reservatório, indícios de aportes por atividades humanas. No caso do Ni, as classes foram: Excelente (37,4%) e Bom (62,6%), com o corpo central do reservatório com valores ligeiramente acima do VRR. Para o caso do Pb, as classes foram, Excelente (98,6%), Bom (0,9%) e Regular (0,5%), com apenas uma pequena porção localizada no corpo central do reservatório, com valores acima de TEL. Finalmente para o Zn, as classes foram Excelente (94,2%) e Bom (5,8%), com a grande maioria do sedimento superficial do reservatório com valores similares ao VRR, particularmente para Pb e Zn.

Figura 6 – Categorização da qualidade do sedimento para Cromo, Níquel, Chumbo e Zinco no reservatório Paiva Castro



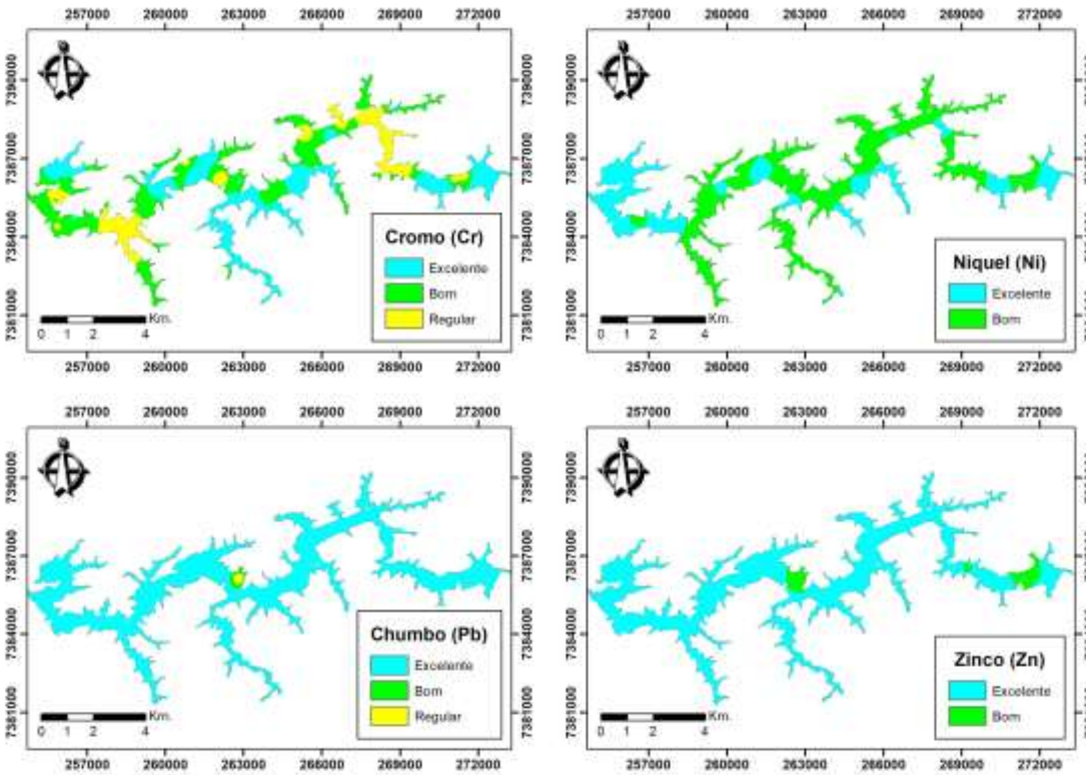
Fonte: Autoria própria

2.5. CONSIDERAÇÕES FINAIS

Como foi possível observar, nos reservatórios estudados há algumas semelhanças, mas também algumas diferenças.

No reservatório Rio Grande, ao comparar os teores dos metais, o Cr apresentou teores acima do VRR, desde a parte alta até a região central do reservatório. Embora, o Ni não exceda os valores do VRR em nenhuma região, há um acumulo importante na área da barragem. O Pb exibiu os maiores teores em relação ao VRR na entrada do reservatório. Os teores de Zn, por sua vez, são maiores do que o VRR em praticamente todo o reservatório. No que se refere à qualidade do sedimento, os quatro metais avaliados seguem um padrão onde as classificações mais péssimas foram observadas na parte alta do reservatório e diminui em direção à barragem. Este fenômeno pode estar relacionado tanto a vazão, à sedimentação e o tempo de residência da água do reservatório. Tanto Ni e Pb apresentaram qualidade categorizada como Excelente e Bom. No caso do Cr a maior parte do reservatório foi classificado como Regular e o Zn mostra um sedimento Ruim na região da entrada do reservatório.

Figura 7 – Categorização da qualidade do sedimento para Cromo, Níquel, Chumbo e Zinco no reservatório de Itupararanga



Fonte: Autoria própria

Para o reservatório Paiva Castro, somente o Cr seguiu um padrão, que é contrário ao descrito no RG, com teores abaixo do VRR e que foi aumentando em direção à barragem do reservatório. Tanto o Ni quanto o Pb apresentaram concentrações abaixo do VRR ao longo de todo o reservatório. O Zn mostra um caso diferenciado, com pontos de maiores teores, quando comparado ao VRR, na região central do reservatório. Já no caso da qualidade do sedimento, para o Ni, Zn e Pb a classificação é Excelente em quase toda a extensão do reservatório. Já o Cr mostra o sedimento categorizado como Regular somente na região da barragem.

Já no reservatório de Itupararanga, tanto o Cr quanto o Ni apresentaram concentrações maiores em relação ao VRR em áreas isoladas, mas com uma característica importante, esses locais ficam em regiões de confluência dos braços e o corpo central do reservatório. Já no caso do Pb e Zn outra característica importante foi observada, os teores acima do VRR ficam num ponto especifico na região central do reservatório, em frente a uma área urbana. Na qualificação do sedimento, para Ni e Zn, apresentaram áreas classificadas como Excelente e Bom, sendo que o Ni apresentou maiores porções do sedimento categorizadas como Bom. Na qualificação do Pb, este mostrou uma única região, no corpo central, classificada como Regular. O Cr apresentou maiores áreas categorizadas como Regular nas áreas de confluência dos braços e o corpo principal do reservatório.

Ao compararmos os reservatórios PC e RG, observamos que ambos estão localizados em zonas urbanas. Já ITU e PC, ambos fazem parte de uma Área de Proteção Ambiental (APA). Embora o PC esteja também inserido na RMSP e tenha a cidade de Mairiporã localizada logo na entrada do reservatório, os níveis de pressão das atividades agrícolas, industriais e urbanas, com base nas concentrações de metais e nas classes de toxicidade potencial empregadas neste trabalho, não chegam àqueles observados em RG. ITU e PC mostram valores aceitáveis para Ni, Pb e Zn, o que não acontece com o Cr, que apresenta o sedimento com possíveis efeitos negativos ao ambiente.

A distribuição espacial e os valores guia de qualidade do sedimento empregados neste trabalho, mostraram que no caso do reservatório Rio Grande o Cr e Zn apresentaram concentrações acima do TEL e o Ni mostra zonas acima do VRR. Em PC unicamente o Cr exibiu áreas classificadas acima do TEL na porção da barragem. Em ITU, Cr mostrou o maior acúmulo do metal, com valor acima do TEL e VRR, principalmente na convergência dos braços com o corpo principal. Portanto, o Cr foi o metal com maior potencial de risco nos três reservatórios avaliados. No entanto, para todos os reservatórios e metais estudados, apenas para o elemento Zn e em uma pequena porção do Rio Grande, há níveis de toxicidade potencial para a biota, com concentrações acima de PEL. Também com base nesses metais, o reservatório Paiva Castro se apresentou com os menores níveis de toxicidade potencial, com apenas uma pequena porção na zona da barragem com valores entre TEL e PEL, o que confere toxicidade potencial incerta. Comparativamente o reservatório de Itupararanga se mostrou com características intermediárias, com maiores porções do sedimento superficial com qualidade Regular, enquanto que o Rio Grande para Cr e Zn apresentou grandes porções do sedimento superficial com valores entre TEL e PEL. Desta maneira, do ponto de vista da toxicidade potencial, os dados levantados sugerem toxicidade potencial para grande porção do sedimento do Rio Grande, seguido de Itupararanga e o Paiva Castro, como o reservatório com o sedimento superficial mais preservado.

Finalmente, a alternativa mais eficiente para enfrentar a problemática atual e possivelmente futura de outros reservatórios fica relacionada ao tratamento de esgoto. Deste modo evitaria a adição de nutrientes e outros compostos provenientes dos efluentes municipais e industriais. Consequentemente, os paliativos utilizados atualmente não seriam necessários para o controle das florações de algas como o sulfato de cobre e o peroxido de hidrogênio.

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CAPÍTULO 3

Ecotoxicology and geostatistical techniques employed in subtropical reservoirs sediments after decades of copper sulfate application[2]

3.1. Abstract

Spatial distribution linked to geostatistical techniques contribute to sum up information in to an easier to comprehend knowledge. This study compares copper spatial distribution in surface sediments and subsequent categorization according to its toxicological potential in two reservoirs, Rio Grande (RG) and Itupararanga (ITU) (São Paulo - Brazil), where copper sulfate is applied and not applied, respectively. Sediments from 47 sites in RG and 52 sites in ITU were collected then copper concentrations were interpolated using geostatistical techniques (kriging). The resulting sediment distributions were classified in categories based on sediment quality guides: Threshold effect level (TEL) and Probable effect level (PEL); Regional reference values (RRV) and enrichment factor (EF). Copper presented a heterogenic distribution and higher concentrations in RG (2283.00±1308.75 mg/kg) especially on the upstream downstream, associated to algicide application as well as the sediment grain size, contrary to ITU (21.81±8.28 mg/kg) where a no clear pattern of distribution was observed. Sediments in RG are predominantly categorized as "Very Bad" whereas in ITU sediments are mainly categorized as "Good", showing values higher than RRV. The classification is supported by the EF categorization, which in RG is primarily categorized as "Very High" contrasting to ITU classified as "Absent/Very Low". Copper total stock in superficial sediment was estimated for RG is 4515.35 Ton of Cu and for ITU is 27.45 Ton of Cu.

Keywords: ecotoxicology, spatialization, copper sulfate, variogram, geostatistics

3.2. Introduction

Physical changes in the environment mainly in warmer areas lead to changes in the hydrological cycle and systems (precipitation patterns and evapotranspiration, among others) must be counted (CHANG *et al.*, 2015; IPCC, 2021). Reservoirs, being hybrid ecosystems, are not only influenced by human activities but natural factors as well, such as climate change (CHANG *et al.*, 2015). Changes in the global temperature are expected, this will concern not just the physical environment, aquatic

[2] Artigo aceito para publicação na revista "Environmental Geochemistry and Health"

organisms will experience changes in their metabolism and phenology (DAUFRESNE *et al.*, 2009). Aquatic species have different responses to natural and artificial trends or adaptations to a non-equilibrated environment (ROLAND *et al.*, 2012).

One visible effect of this unbalance, due to the lack of sanitary plans, is the artificial eutrophication as a consequence of the excessive inputs of nutrients such as, phosphorus and nitrogen, leading to algal bloom events and cause public health problems due to toxins in some cyanobacteria species (DOS SANTOS MACHADO *et al.*, 2022; WU *et al.*, 2017; YANG *et al.*, 2020). With global warming, these algal blooms tend to become more frequent (HOU *et al.*, 2022; PAERL; HUISMAN, 2008). The blooms can affect the drinking water supply processes increasing costs of chemical products employed to remediate water organoleptic properties (KO; SAKAI, 2021; LEAL *et al.*, 2018). In this context, algal bloom control before treatment process is highly important.

Copper sulfate and hydrogen peroxide application are widely used for algal bloom control around the world (ANDERSON *et al.*, 2019; HULLEBUSCH *et al.*, 2003; KANSOLE; LIN, 2017; POMPÊO, 2017; REIS; CAPELO, 2022; SKLENAR; HORNE, 1999; ZHANG *et al.*, 2022). In the United States, there are application records since 1905 (MCKNIGHT *et al.*, 1983) as well as in Fairmont lakes, Minnesota (HANSON; STEFAN, 1984), and in Canada there are also records in small springs of farms (Alberta Agriculture, 1980, *apud* Prepas and Murphy, 1988). In São Paulo, Brazil, there are records of copper sulfate applications since 1979 in Guarapiranga reservoir (MANCUSO, 1987). $CuSO_4$ is responsible for increasing the Regional Reference Value (RRV) up to 120 times (CARDOSO-SILVA *et al.*, 2021; LEAL *et al.*, 2018).

Due to its wide acceptability and low cost, copper sulfate and hydrogen peroxide are some of the cheapest and quickest solution to avoid algal blooms (LEAL *et al.*, 2018; ZHANG *et al.*, 2022). Despite its natural presence in the terrestrial crust, copper is considered a toxic metal in aquatic communities (CERVI *et al.*, 2021; LUOMA; RAINBOW, 2008). High copper concentrations reduce algal cell division up to 50% causing cellular lyses (HADJOUDJA *et al.*, 2009; WU *et al.*, 2017) and hydrogen peroxide effectively inhibits the metabolic activity and photosynthesis in a very short time(ZHANG *et al.*, 2022).

In the aquatic environment metals, e.g., copper, tend to accumulate in sediment at the bottom of the reservoir. In certain environmental conditions those metals can be released to the water column again. The main concern is the accumulation of metals in the aquatic environment from anthropogenic activities including fertilizers leaching, domestic and industrial sewage (FRASCARELI *et al.*, 2018; MELO *et al.*, 2019; PEDRAZZI *et al.*, 2013; WENGRAT *et al.*, 2019). Thus, sediment needs to be constantly monitored to understand transport and suspension processes in aquatic environments, from a spatial standpoint (ALEXANDER *et al.*, 1993; HAO *et al.*, 2021; MELO *et al.*, 2019) which is useful to assess the bioavailability of those potential pollutants (CARDOSO-SILVA *et al.*, 2016a).

Sediment quality guidelines (SQGs) have been applied to characterize sediments according to its toxicity potential. The SQGs developed by the Canadian Environmental Agency, present the TEL (Threshold Effect Level) and PEL (Probable Effect Level) (CCME, 1999) which is widely applied and recognized by the scientific community (BROCE *et al.*, 2022; CARDOSO-SILVA *et al.*, 2016a; LEAL *et al.*, 2018; YÜKSEL *et al.*, 2022). Concentrations below TEL suggest toxic effects are unlikely to occur, values above PEL indicate that the toxic effects are likely to occur, meanwhile, the toxic effect when concentrations are between TEL and PEL are uncertain. However, sediment characterization is incomplete since it does not demonstrate the metal origin.

Therefore, enrichment factor is a mean to measure the metal concentration increase considering another reference element in the lithosphere (LEE *et al.*, 1994; MOHAN; KRISHNAKUMAR, 2022; PAN *et al.*, 2022). The reference element must be a metal, used to quantify the degree of pollution (LEE *et al.*, 1997; PASSOS *et al.*, 2022; WU *et al.*, 2022) to differentiate the natural or anthropogenic origin (BERN *et al.*, 2019; CARDOSO-SILVA *et al.*, 2021; MARTINS *et al.*, 2021). Aluminum is a widely used reference element around the world and specifically in Brazil, because it has a natural origin.

In order to assess the metal’s toxic potential, it is necessary to evaluate the sediment quality with representative number of sampling sites that cover the area of interest. Combining traditional sampling techniques and the geostatistical approach, to plot the spatial distribution of certain element. For this purpose, it is possible to employ the kriging interpolation method (GOLIA *et al.*, 2021), widely used for mining activities (BELKHIRI *et al.*, 2017; GUO *et al.*, 2018; JIA *et al.*, 2018) as well as in reservoir assessments (OLADOSU *et al.*, 2019; RAKHMATULLAEV *et al.*, 2011) or lakes (KOSTKA; LEŚNIAK, 2020) assessments and even few studies that provide the toxic potential of metals in the sediment of reservoirs (CHEN *et al.*, 2018; LEAL *et al.*, 2018). This method uses geostatistical models such as autocorrelation among a cloud of points to create predictions with specific weights for the collected points. These weights are based in the distance and its spatial autocorrelation (BAUX *et al.*, 2022; SZATMÁRI *et al.*, 2022).

Kriging considers the anisotropy, which is related to the spatialization of natural events, assuming that the area of interest does not present a uniformity from one point to another. This method takes into account how a given property varies in space through the variogram function (SAITO *et al.*, 2021). The difference between kriging and other interpolation methods relies how weights (properties under analysis) are distributed among all sampling sites. In addition, kriging provides unbiased estimates with minimal variance (FERREIRA *et al.*, 2013). Those weights, are calculated from the spatial analysis, which is based on the experimental variogram. There are distinct types of kriging divided in linear and nonlinear models (SAITO *et al.*, 2021). Finally, due to the natural events happening in the environment and the lack of uniformity, particular events or properties cannot be mapped by simple mathematical functions (FERREIRA *et al.*, 2013).

Despite the copper pollution evidence in Rio Grande reservoir (Mariani and Pompêo, 2008; Cardoso-Silva et al. 2021), no study explored in a wide manner the sediment in these reservoirs. As far as it is known, this is one of a few studies (e.g., Leal et al., 2018) developed in subtropical reservoirs associating metal analysis, toxicological quality categorization and the kriging technique. This research presents a relevant contribution to geochemistry performed in reservoirs and results can be applied in other geographical contexts with the same or other metal contamination. It has been expected that: a) Rio Grande reservoir (RG) with a major urban pressure, added to the lack of a proper sewage treatment system, shows higher copper concentrations in sediment than Itupararanga reservoir (ITU). b) The sediment in ITU, located inside an Environmental Protection Area, presents copper values lower than the threshold level. c). The management in these reservoirs led to copper accumulation since their installation originated from human applications.

The objectives of the present research are (1) to evaluate copper concentration, its stock and its spatial distribution in surface sediments of two reservoirs; (2) assess toxicity and categorize sediments using Sediment Quality

Guidelines, and Enrichment Factors (3) analyze the water quality management applied in two reservoirs, with and without copper sulfate applications.

3.3. Study area

3.3.1. General description

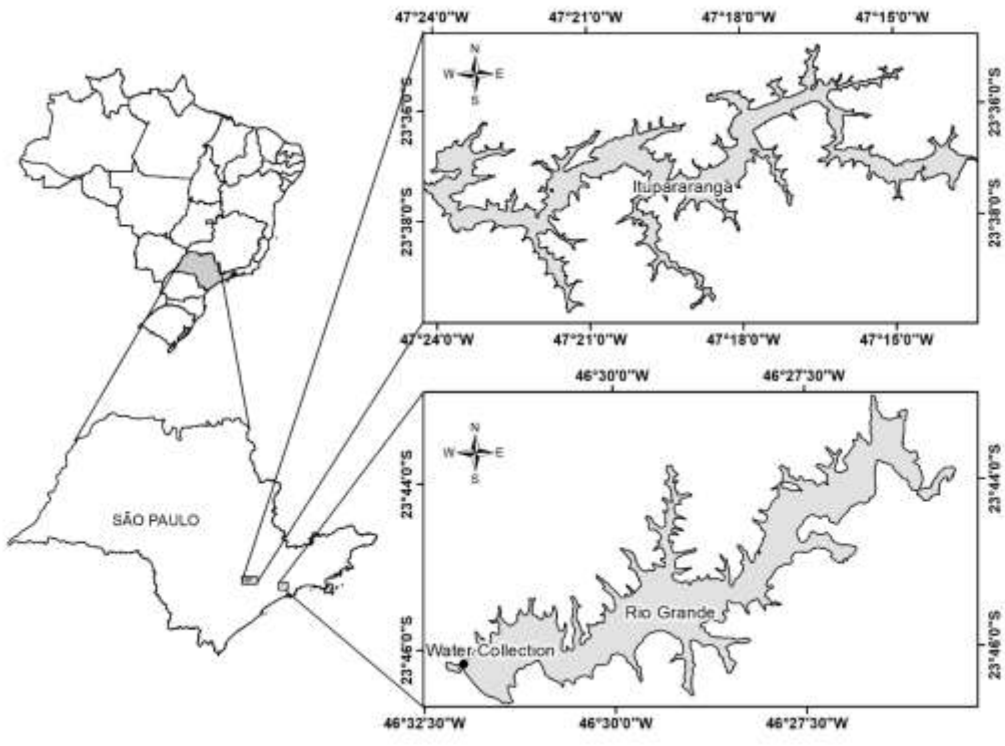
Rio Grande (23°45’46”S 46°29’49”W) and Itupararanga (23°36’49”S 47°20’18”W) reservoirs, are located in the Billings-Tamanduateí subbasin and in the high course of Sorocaba river respectively. RG belongs to Alto Tietê hydrographic basin, meanwhile ITU, to the Middle Tietê watershed, São Paulo State, Brazil (Fig. 1). Rio Grande reservoir (RG) has been isolated from the Billings Complex, through the Anchieta dam in 1982, intended for drinking water supply to 1.2 million people from São Bernardo do Campo, Santo André and Diadema municipalities, but it also receives domestic sewage from the surrounding area (WENGRAT *et al.*, 2019). RG is at an altitude of 750 m, it has an area of 7.4 km^2, an inlet volume of 194 m^3/s, an average depth of 26.2 m and a residence time of 306 days (CARDOSO-SILVA *et al.*, 2021). According to the Köppen classification (1900), the region has a humid subtropical climate (Cwa), characterized by summer rains with an average annual precipitation of 1500 mm.

The area is dominated by the Atlantic Forest and is originally formed by dense ombrophilous forest (COPOBIANCO; WHATELY, 2002). However, due to intense urbanization, the vegetation has been restricted to small patches. Anthropogenic activities occupy an average of 27% of the basin, 20% of which are considered urban areas (BONZI *et al.*, 2017). It is estimated that around 900,000 people live in its drainage area, most of them in irregular settlements (BONZI *et al.*, 2017). For 2017, about 75% of the sewage generated in the municipalities that make up the Rio Grande reservoir microbasin was collected, and only 40% of this total was treated, which contributes to the eutrophication process in the region (CBH-AT, 2022). In Rio Grande reservoir (RG) (São Bernardo do Campo, SP – Brazil) copper sulfate pentahydrate has been applied since 1985 (BEYRUTH; PEREIRA, 2018) in order tocontrol algal bloom.

Itupararanga reservoir (ITU) was built in 1912 by damming the Sorocabaçu, Sorocamirim and Una rivers; its drainage basin has a total area of 936.51 km^2 and covers Ibuúna, Piedade, São Roque, Cotia, Vargem Grande Paulista, Mairinque and Votorantim municipalities (TANIWAKI *et al.*, 2013). ITU belongs to an Environmental

Protection Area (Área de Proteção Ambiental - APA) of Itupararanga since 1998, created by State Law n° 10.100, aiming to preserve the hydrological quality and important extensions of the Atlantic Forest Biome remnants as a wildlife refuge (BEU *et al.*, 2011). ITU is at an altitude of 849 m, has an area of 26 km^2, a volume of 286 m^3, an average depth of 11 m and a residence time of 250 days (Cardoso-Silva et al, 2021). The region has also a humid subtropical climate (Cwa), characterized by summer rains with an average annual precipitation of 1370 mm.

Figure 1 – Study area, Itupararanga reservoir (scale, 1:120,000) and Rio Grande (scale, 1:80,000) – São Paulo, Brazil. Itupararanga near the Metropolitan Region of Sorocaba and RG near the Metropolitan Region of São Paulo. The black point indicates the SABESP water collection site in RG



Fonte: Autoria própria

In the Middle Tietê basin, where the Itupararanga reservoir is located, for the year 2016, 86.4% of the generated domestic sewage was collected and 64.6% was treated (CBH-MT, 2022). In Itupararanga reservoir (ITU) (Ibiúna, SP) there are no algicide application record for algae blooms control. Frascareli et al. (2018) evaluated three different areas in ITU and observed a spatial heterogeneity in copper distribution in sediments.

3.3.2. Geology and geomorphology

RG watershed is located in the Planalto Paulistano, covering part of the crystalline relief of the Planalto Paulista, according to Ross and Moroz (2011) classification, characterized by an area of granites, and some outcrops of mica schists and micaceous gneisses from the regional Precambrian formations (AB’SABER, 2007). The most abundant minerals in the sediment, in decreasing order of importance, are: kaolinite, vermiculite, illite, gibbsite and goethite (IPT, 2005). This particular geological characteristic explains the occurrences of aluminium natural sources in this area of the State of Sao Paulo.

In ITU, six major geological groups integrate the watershed: Massif Caucaia (9.24%), Cenozoic covers (10.64%), Embu complex (20.87%), Ibiúna Complex (48.54%), São Francisco Complex (4.24%), São Roque Group (6.41 %) (Secchin,2012). Six shear zones are also present, covering periods from the Upper Middle Proterozoic to the Quaternary (FF, 2009). The predominant composition is monzogranites and syenogranites (SECCHIN, 2012). The morphological unit to which the hydrographic basin belongs is the Planalto Ibiúna/São Roque, where sharp hills and convex tops predominate (ROSS; MOROZ, 2011).

3.4. Material and methods

3.4.1. Bathymetry and morphometry

The bathymetric survey in RG was performed on April 13th, 2016 and in ITU was carried out on September 21st, 2017. This survey followed the method applied in (LEAL *et al.*, 2018), who navigated in a zig zag pattern through the reservoir to better describe the bottom of the reservoir. The followed track began near the dam and went upstream, maintaining a mean vessel speed of 17 km/h to reduce water disturbance. Data were collected using a Garmin Fishfinder GPSmap 421S paired to a data-log and georeferenced with Datum WGS84 and projection UTM 23S. This survey corrected its sampling error due to two previously known points located in bridges. The circuit, which covered all the extension of the reservoir, was performed in a zigzag pathway, the Fishfinder was placed at the stern (BILHALVA, 2013; LEAL *et al.*, 2018). This bathymetric sonar has been chosen since it is inexpensive, easy to install, manipulate and capable to storage large amount of data. It has to be considered that in ITU, additionally to data gathered in this study, another database collected by the Department of Biology from the Federal University of Sao Carlos, Sorocaba Campus (2011) was employed. In that survey an ecobathymeter model Bathy 500-MF® (Ocean Data), coupled to a GPS model GS20 Professional Data Mapper (Leica Geosystems) were employed. The bathymetric survey database for RG were 9,429 points, added to 4,186 additional points from the shoreline vectorization process and 47 points from the sediment sampling sites, with a total of 13,662 points. In ITU from the fish finder survey we gathered 8,589 points, joined to the complementary bathymetric record list of 79,091 points and 28,439 points from the shoreline vectorization with a total of 116,119 bathymetric points. The benchmark used to correct water depth was 746.77 m in RG, from April 13th, 2016 (SABESP, 2022), and 822,45 m in ITU from September 21st, 2017 (ANA, 2022).

In order to calculate the accumulation of Cu, the morphometrical parameters were updated, throughout georeferencing and remote sensing techniques. To define the shoreline in RG and ITU were used Sentinel-2 imagery from the European Spatial Agency (ESA), of April 7th, 2016 and September 19th, 2017, respectively. The water portions were highlighted via the Normalized Difference Water Index (NDWI), which uses Band 3 (GREEN) and the Near infrared (NIR) following: NDWI= (GREEN - NIR) / (GREEN + NIR) (MCFEETERS, 1996), both with a spatial resolution of 10 m. The vectorization was performed through a semi-automatic manner. The shoreline vector, together with the bathymetric data were used for modelling the bottom of the reservoir, as well to calculate the copper concentration to transform the bathymetric data into altimetric. the methodology described in Leal et al. (2018) and (BILHALVA, 2013) was followed, considering the altitude values.

The previous process resulted in a Digital Elevation Model (DEM) applying the Triangular Irregular Net (TIN) based in the Delauney criteria (circumscribed circumference) widely used due to its rapid interpretation and availability in Geographic Information System (GIS) software (SHELKE *et al.*, 2016). The sextant extension was to the DEM Sá (2018), these algorithms allowed to determine the partial slope aspect of sediment, in north – south (dY) and east – west (dX) for each pixel in the matrix, based in Horn (1981) criteria. With the UTM Datum and projection the 2D and 3D surface area were calculated. The morphometric analysis was performed with QGIS v. 3.4.9 software and ArcGIS 10.4 software.

3.4.2. Sediment sampling and copper concentration assessment

Sediment sampling in RG (47 sites) was performed on November 16th, 2017 and in ITU (52 sites) was on September 28th, 2017. These collections sites we georeferenced (WGS84; UTM 23S) and distributed along the reservoirs to better understand the spatial variation in both study sites. Sediment sampling strategy followed the conditions employed in Leal et al. (2018). A collector type Lenz (225 cm2) was employed, collecting 4 cm from the superficial sediment. The gathered samples were stored in collecting flasks (100 ml) completely loaded, kept in thermal bags and in the dark.

The laboratory process, samples were dried in an oven at 50 °C and ground in a glass mortar. For near-total metal assessment (Cu and Al), the sediment was processed following the 3050B method from US EPA series SW 846 (U.S.EPA, 1996). The samples were stored at 4°C prior to analysis of copper and aluminum by inductively coupled plasma atomic emission spectrometry (ICP-OES), using an Agilent Series 720 instrument. Analytical grade reagents (obtained from Merck and Sigma-Aldrich) were used in all the analyses. All glassware items and equipment used to storage and processing the samples for metal assessment were left in 10% nitric acid for at least 24 h, followed by rinsing with ultrapure water. The accuracy of the data obtained was evaluated in recovery assays performed using sample solutions fortified with metals. These assays employed SpecSol® G16 V standard solutions containing 100 mg/L of the metals in 2% HNO_3. A value between 75 to 125% was considered as the acceptance criterion. The recovery efficiencies ranged from 89.67 up to 112.63% and limits of quantification and detection were calculated according to Vogel (2000) (Table 1). The metal data were expressed as milligrams per kilogram of dry weight (mg/kg dw).

Table 1 – Analytical recovery (AR) (%) from solutions with 0.10; 0.25; 0.50 and 1.00 mg/L and R^2 value of the calibration curves and limits of detection (LD) and quantification (LQ)

Metal	AR 0.10 mg/L	AR 0.25 mg/L	AR 0.50 mg/L	AR 1.00 mg/L	R^2	LD	LQ
Al	112.63	110.63	110.62	109.33	0.9997	0.007	0.024
Cu	105.56	101.27	89.67	90.29	0.9991	0.002	0.006

Fonte: Autoria própria

3.4.3. Spatial analysis and copper stock calculation

We applied the kriging interpolation method, using non converted data (original values), to recognize and understand copper concentration distribution, using the GS + v. 7.0 software. Copper stock calculation was performed according the equation used in Leal et al. (2018) Equation: $S = \left[\left(\frac{FS}{Kv} * SRS * h\right) - (Wm)\right] * [Cu] * 10^{-3}$. Where FS/Kv is the ratio between fresh sediment and the container volume, SRS is the sediment surface, h is the sampler penetration, Wm is the mean water mass and Cu is the mean copper concentration in the reservoir.

The Grub test was applied to evaluate outliers. Following data normality and homogeneity was tested. A t test ($p < 0.05$) was performed to check if mean Copper concentrations were different between the two reservoirs and to evaluate whether metal concentrations were homogeneous along each reservoir. The calculations were performed using PAST 2.7 software (HAMMER *et al.*, 2001).

3.4.4. Enrichment factor and copper toxic potential assessment

The EFs were calculated as follows, *EF=(Me/El)/(Mer/Elr)*. Where *Me/El* is the ratio between the concentrations of the analyzed metal and the conservative element in the sample, and *Mer/Elr* is the ratio of the background values for the metal to be analyzed and the conservative element. Aluminum was used as a conservative element (FÖRSTNER; WITTMANN, 1981; LUOMA; RAINBOW, 2008), since aluminosilicates are part of the composition of the fine-grained fractions (<63µm, silt and clay) and are important metal-binding phases (DEVESA-REY *et al.*, 2011). The EF categorization were labelled in five categories: Absent / Very Low, Moderate, Considerable, High and Very High (Table 2) according to the classification for enrichment factor described by Sutherland (2000).

Table 2 – Classification for enrichment factor (EF) according to Sutherland (2000)

Classes				
Absent/Very Low	Moderate	Considerable	High	Very High
<2	2 ≤ EF < 5	5 ≤ EF <20	20 ≤ EF < 40	>40

Fonte: Autoria própria

This assessment was based in the Canadian Interim Sediment Quality Guidelines (ISQGs) such as TEL and PEL (CCME, 1999); simultaneously to the Regional Reference Values (RRV) for ITU (Cardoso-Silva et al., 2021) and RG (NASCIMENTO, 2003). To categorize the ecotoxicological risk associated to sediment quality five classes were labelled as follows: Excellent, Good, Regular, Bad and Very bad, as described in (LEAL *et al.*, 2018) (Table 3).

Table 3 – Qualitative classification of sediment according to Leal et al. (2018), where: [M]= Metal concentration; RRV= Regional reference value, TEL= Threshold effect level; PEL= Probable effect level; 10*PEL= Ten times PEL. Cu data: RRV= 15 mg/kg; TEL= 35.7 mg/kg; PEL= 197.0 mg/kg

Classes	Limits/Intervals	Ecotoxicological Potential
Excellent	0 mg/Kg ≤ [M] < RRV	Region with minimal ecotoxicological potential. Basal concentrations.
Good	RRV ≤ [M] < TEL	Region with possible anthropic contamination, but with little to improbable ecotoxicological activity.
Regular	TEL ≤ [M] < PEL	Region with anthropogenic contamination of unknown ecotoxicological activity and, medium occurrence probability
Bad	PEL ≤ [M] < 10*PEL	Region with high ecotoxicological activity and, occurrence probability
Very bad	10*PEL ≤ [M] < +∞	Region with maximum ecotoxicological effect and, maximum occurrence probability.

Fonte: Autoria própria

3.5. Results and discussions

3.5.1. Bathymetry and morphometry

Water depth (considering the shoreline as 0 m), in RG varied from 0.4 to 13.2 m; in ITU from 0.35 to 22.21 m. The regions presenting the maximum values of water depth are located close to the dam in both reservoirs (Fig. 2), which agrees with the hydrographic patterns described by (SPERLING, 1999).

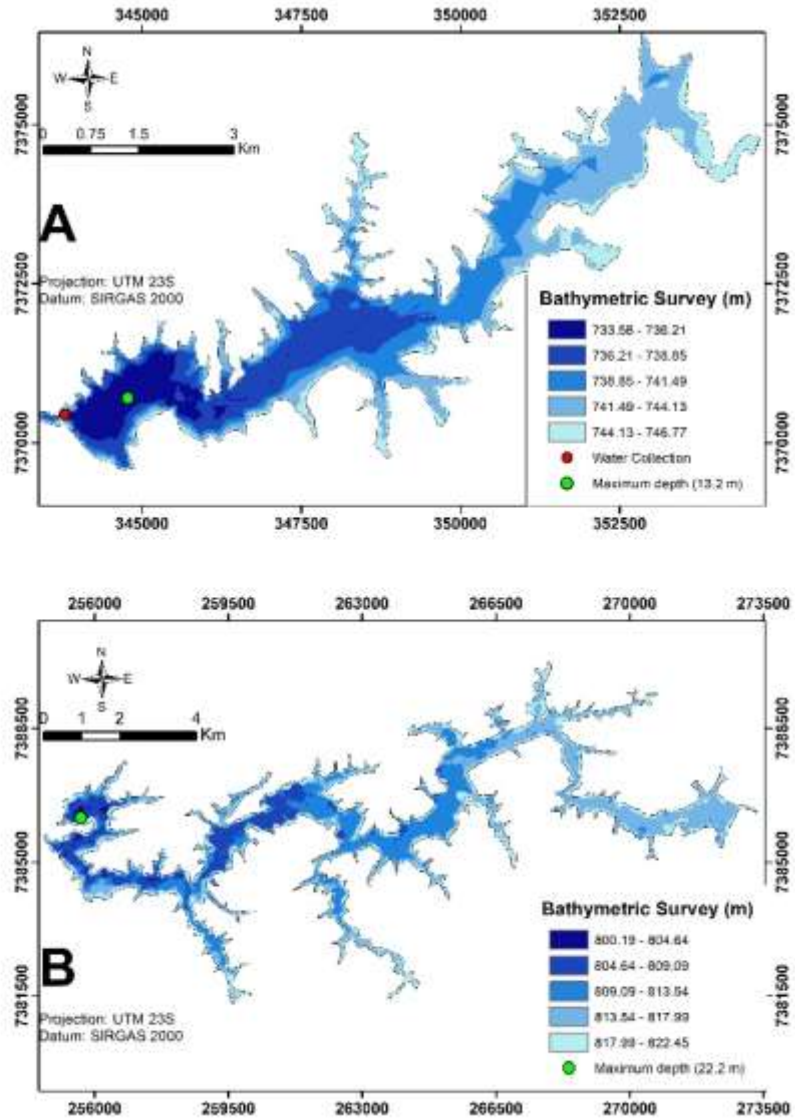
The calculated morphometric values are presented in Table 4, as well as previous studies developed in the areas. As observed, there are differences in the evaluated studies. We must consider that the bathymetry is variable, since it is influenced by weathering and sedimentation rates presented in the basin. This phenomena of area, water depth and volume variation in RG and ITU can be assigned to seasonal characteristics, sedimentation and in specific the date when the satellite image has been taken.

Table 4 – Morphometric parameters from Rio Grande and Itupararanga reservoirs in a comparison with previously reported values for the reservoirs

Reservoir	Total planar area (km^2)	Sediment surface area (Km^2)	Perimeter (km)	Max. depth (m)	Mean depth (m)	Volume (hm^3)	References
Rio Grande	14.12	15.561	80.57	13.2	5.91	89.61	This study
	7.4	-	-	-	26.2	110	Frascareli et al. (2018)
	16.17	-	-	-	6	-	Wengrat et al. (2018)
	15	-	-	-	-	155	Maier et al. (1985)
	-	-	-	13	-	85	Souza et al. (2018)
	15	-	-	-	-	-	Barbieri & Godinho Orlandi (1989)
Itupararanga	23.28	30.949	199.61	22.21	9.19	174.83	This study
	29.9	-	-	-	7.8	260	Frascareli et al. (2018)
	24.48	-	-	-	7.8	-	Wengrat et al. (2018)
	-	-	-	-	-	249.58	ANEEL (2004)
	-	-	-	-	-	286	Smith and Petrere (2008)
	27.23	-	-	-	-	-	Beu et al. (2011)

Fonte: Autoria própria

Figure 2 – Maps from the bathymetric surveys in A) Rio Grande (Scale, 1:60,000) and B) Itupararanga (Scale, 1:100,000). Darker colored zones represent deeper areas in the reservoirs, "Green" point shows the maximum depth in both reservoirs and "Red" point indicates the SABESP water collection. Water depth correction performed with 746.73 m in RG, and 822. 45 m in RG as benchmarks



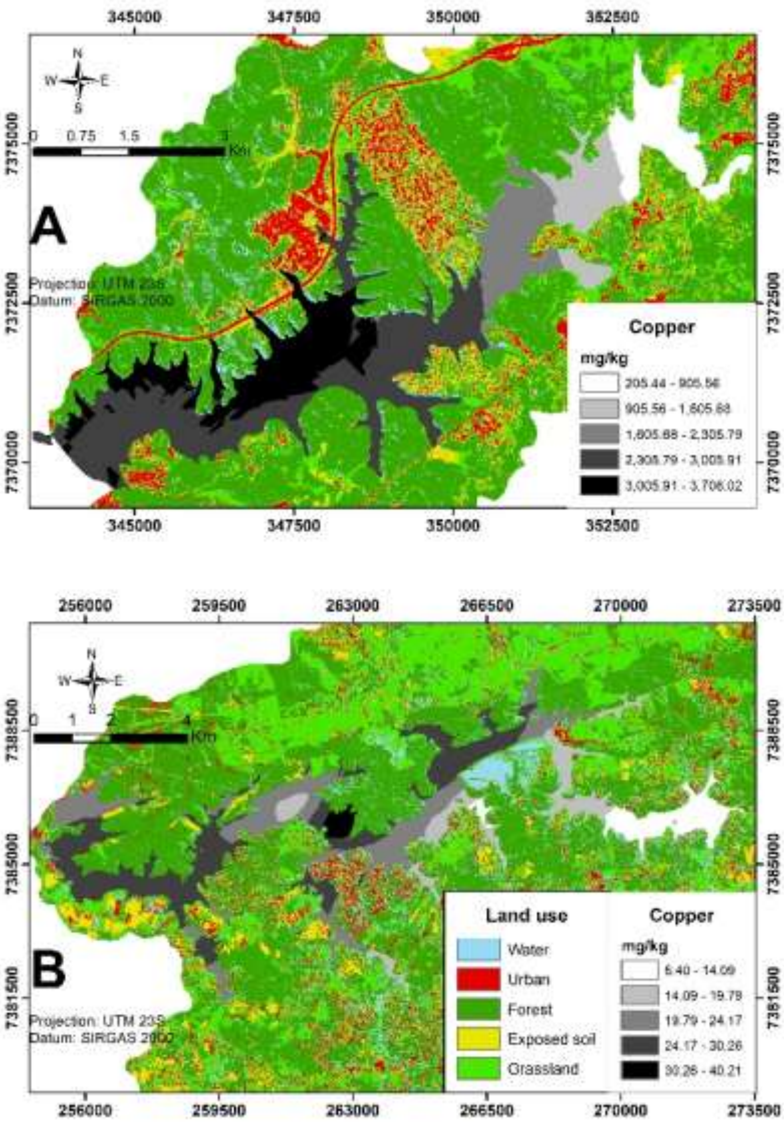
Fonte: Autoria própria

3.5.2. Copper in sediment assessment

Copper mean values were significantly different between the two reservoirs and in each reservoir suggesting a heterogenous distribution ($p < 0.05$). The spatial distribution concentrations in RG and ITU showed compartments (Fig. 3). In RG there is a significant increasing, but disperse copper concentration in direction to the dam, this spatial heterogeneity is related to algicide application process. The company in charge of the drinking water treatment (SABESP) starts the algicide application near the dam, where the water collection for drinking water treatment occurs (Fig. 3), and continues in direction to the reservoir entrance (Mariani and Pompêo, 2008; CETESB, 2018;). The Cu spatial heterogeneity can also be consequence of sediment re-suspension due to physical factors and granulometric influence, since fine grained sediment (< 63 µm) presence increases from upstream to downstream (Mariani and Pompêo 2008; Frascarelli et al., 2018).

In ITU there is not a uniform distribution as well, the observed pattern can be associated due to the dendritic format, as well as the water flow by the reservoir tributaries in different points along the reservoir. However, areas where high copper concentrations are located close to zones intended to agriculture and urban expansion. Therefore, in geostatistical studies to evaluate contamination by metals, it is important to consider the main contamination sources, as well as the morphometry of the reservoir, whether dendritic or not, and if it predominantly follows the compartmentalization proposed by Kimmel et al. (1990).

Figure 3 – Visual representation of copper concentration spatial variability in reservoirs. Land use classification performed by Maximum Likelihood method A) Rio Grande: Sentinel-2 imagery (2016/04/07) and B) Itupararanga: Sentinel-2 imagery (2017/06/24)



Fonte: Autoria própria

It is possible to observe in Table 5, that the copper mean concentration in RG (2282.996 mg/kg) exceeds 12x the PEL (197.0 mg/kg); also, the minimum concentration assessed (100.07 mg/kg) is 7x the RRV value (NASCIMENTO, 2003). Despite the high copper concentrations, a previous study suggested Cu is not being bioavailable in RG because of the high levels of sulfide, organic matter, and the predominance of the grain size < 63 µm (MARIANI; POMPÊO, 2008). However, this does not mean that the metals are not exerting adverse effects. A study developed by Beghelli et al. (2016), show the bioaccumulation of Cu in a reservoir in which there are records of Cu only three-fold the background.

Despite, the maximum concentration (56.62 mg/kg) is almost 3x the RRV (CARDOSO-SILVA *et al.*, 2021) this referring an isolated area in the middle of the reservoir. In ITU, the copper mean concentration (21.82 mg/kg) is lower than TEL (35.7 mg/kg) value, indicating that it preserves its original characteristics, considering copper concentration in sediment, but there is evidence that are sites with copper accumulation that eventually could compromise the aquatic ecosystem.

Likewise, in Table 5, we can see that copper mean concentration, which Frascareli et al. (2018) previously reported in RG is 21.65% higher than our data. Nevertheless, it is important to note that the authors evaluated only three sampling points, which does not necessarily indicate a decrease in copper values in the reservoir. Our research presents a much wider range of points showing more assertively the copper distribution along the reservoir. When comparing RG and Guarapiranga reservoir (GUA), which is another SABESP managed reservoir, where copper-based algicides are applied as well. Copper mean values in RG are 6.8% higher than the values in GUA (LEAL *et al.*, 2018; POMPÊO *et al.*, 2013) which is preoccupant due to their morphometric differences (GUA is 10 km^2 bigger) indicating a higher pressure in RG. In the case of ITU copper mean concentration in sediment is similar to the values reported previously by Frascareli et al. (2018), this indicates a geogenic accumulation within the basin. When comparing RG and Paiva Castro (PC), a reservoir which presented CuSO4 applications in its main tributary (Cardoso-Silva, et al. 2016), the minimum copper concentration in RG is 5x the maximum concentration in PC.

The application of copper sulphate, despite its low cost, is a palliative and controversial measure since it can promote a series of adverse effects on a variety of non-target aquatic species (JANČULA; MARŠÁLEK, 2011) as many fish and aquatic invertebrate species (CLOSSON; PAUL, 2014; SILVA *et al.*, 2014). Besides that, repetitive copper sulphate dosing can lead to resistance of phytoplankton communities (GARCÍA-VILLADA *et al.*, 2004) and its application leads to cell damage releasing cyanotoxins into the water (JANČULA; MARŠÁLEK, 2011).

When comparing RG with other in-land water bodies considering attributes such as inflows of domestic and industrial sewage, and agricultural pollutants, it has been observed that copper concentrations in RG are the highest, in a regional (Souza and

Wasserman 2015; de Andrade et al. 2018) or international context (Wang et al. 2016; Li et al. 2020) (Table 5), in water bodies with or without CuSO4 applications. In Daheiting reservoir – China (LI *et al.*, 2020), for example, the maximum copper concentration (163.50 mg/kg) is very alike with the minimum values registered in RG; or Taihu lake – China (WANG *et al.*, 2016) that presents areas dominated by algae as well, the maximum copper concentration (113.0 mg/kg) being above TEL values, is slightly higher than the minimum copper value in RG. When comparing RG with Qinggeda lake – China (FENG-LAN *et al.*, 2019), which shows a similar area (17 km^2) and it is located near an urban area as well, it has been observed that the maximum copper concentration (59.78 mg/kg) is half the minimum copper value registered in RG. In our research we did not find any reservoir with Cu concentration as high as those recorded in RG, except for GUA. Therefore, further studies addressing ecotoxicological effects, including synergistic and additive effects, as well as effects on the trophic cascade, be carried out in RG. Some other reservoirs where Cu-based algicide were used reported by (JACINTHE *et al.*, 2010) in Eagle Creek - USA and (MILOŠKOVIĆ *et al.*, 2013) in Gruža Reservoir – Serbia. Eagle Creek presents concentrations higher than PEL but below the reported values in RG. Gruža Reservoir presents values below the TEL which are similar to ITU.

Table 5 – Comparison of copper concentration in sediments in different water bodies. Descriptive statistics mean, standard deviation, range (minimum - maximum), values in mg/kg and coefficient of variation (CV) expressed in (%)

References	**Reservoir**	**Mean ± SD**	**Range**	**CV**	**Cu-based algicide application***
This study	Rio Grande	2,282.996 ± 1,294.76	100.07 - 4827.57	56.71	Yes
Leal et al. (2018)	Guarapiranga	1,241.64 ± 1,135.62	0 – 3011.99	91.46	Yes
Mariani and Pompêo (2008)	Rio Grande	1,644.1 ± 1,067.9	8.2 – 3582.6	64.95	Yes
Cardoso-Silva et al. (2016a)	Paiva Castro	3.9 ± 6.6	3.5 – 21.00	169.23	Yes
Frascareli et al. (2018)	Rio Grande	2,914.08 ± 1,704.52	-	58.85	Yes
Pompêo et al. (2013)	Guarapiranga	1,157.2 ± 1,125.6	29.2 – 2902.4	97.27	Yes
Mozeto et al. (2014)	Ibirité - Brazil	142.05	115.8 – 170.8	-	Yes
de Andrade et al. (2018)	Lago Guaíba – Brazil	78	13.8 – 132.1	-	Yes
(JACINTHE *et al.*, 2010)	Eagle Creek - USA	59.9	-	-	Yes
(MILOŠKOVIĆ *et al.*, 2013)	Gruža Reservoir - Serbia	10.53 ± 0.006	-	0.00005	Yes
This study	Itupararanga	21.82 ± 8.28	3.09 – 56.62	37.95	No
Frascareli et al. (2018)	Itupararanga	20.9 ± 1.51	-	7.22	No
Mizael et al. 2020)	Broa – Brazil	32.65 ± 1.82	-	5.57	No
Souza and Wasserman (2015)	Juturnaíba – Brazil	14.2	2.8 – 21	-	No
(WANG *et al.*, 2016)	Lake Taihu - China	35.18	12.5 – 113	-	No
(LI *et al.*, 2020)	Daheiting - China	82.97 ± 14.61	33.93 – 163.50	17.61	No
(FENG-LAN *et al.*, 2019)	Qinggeda Lake - China	46.73 ± 6.87	30.06 – 59.78	14.70	No
(MANOJ *et al.*, 2018)	Vembanad Wetland System - India	21.66 ± 12.45	2.88 – 40.92	57.48	No

*Cu-based algicide application in the reservoir or in their main tributaries at least in some period.

3.5.3. Enrichment factor

The EF categorization (Fig. 4) in ITU, copper shows enrichment classified as “Absent/Very Low”, which suggests a geogenic source. Contrasting with RG, where the EF is represented by three categories: “Considerable” 5.46%, “High” 5.62%, and “Very High” 88.92%, where we can infer that copper presence has an anthropogenic source mainly due to metal-based algicide, such as CuSO4.5H2O (Copper Sulfate Pentahydrate).

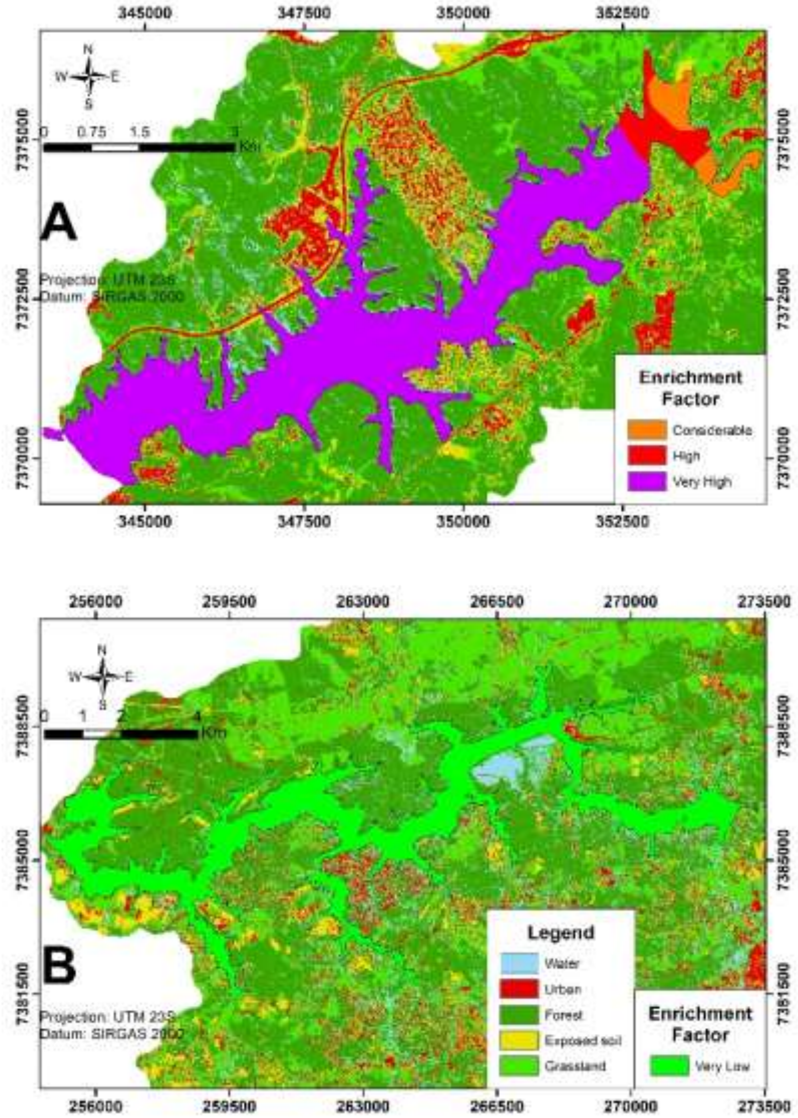
It is worth mentioning that, similarly, as observed in the Guarapiranga reservoir (LEAL *et al.*, 2018), Rio Grande reservoir has been receiving periodically copper sulfate and hydrogen peroxide applications for almost 50 years (Pompêo, 2020). The use of hydrogen peroxide is a recommended alternative to reduce impacts caused by copper present in algicides. In Table 6, are presented total values applied each year in Rio Grande reservoir. These data are worthy of comparison with CETESB registers mentioned in Leal et al. (2018) that in 2007, total copper sulfate application reached 360 Ton. It is important to consider that 25% of copper sulfate molecular mass is related to copper.

Table 6 – Annual total amounts of copper sulfate and hydrogen peroxide applications as algicide in Rio Grande reservoir

YEAR	2012	2013	2014	2015*
Hydrogen peroxide (ton)	700	226	1109	181
Copper sulfate pentahydrate (ton)	109	60	97	106

Fonte: SABESP, * Applications until October 9th, 2015.

Figure 4 – Copper enrichment factor categorization in reservoirs. Land use classification performed by Maximum Likelihood method A) Rio Grande: Sentinel-2 imagery (2016/04/07) and B) Itupararanga: Sentinel-2 imagery (2017/06/24)



Fonte: Autoria própria

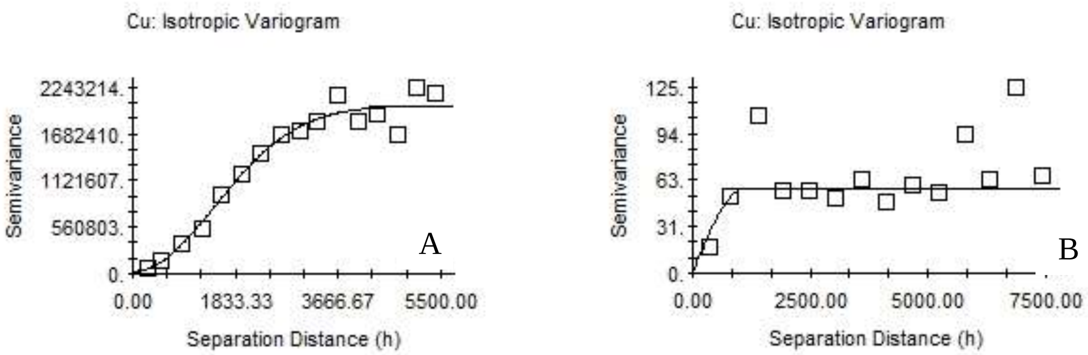
3.5.4. Superficial sediment potential toxicity

Fig. 6 shows the sediment categorization in RG and ITU according the methods described in the Canadian Interim Sediment Quality Guidelines (ISQG) (CCME, 1999), as applied by Leal et al. (2018). In the case of RG the quality conditions after applying the kriging interpolation to sediment data it shows that all the superficial sediment are above PEL values. Worse, 71.05% of the total area in the reservoir surpasses the PEL(x10) categorized as “Very Bad”. In ITU occurs the opposite, the superficial sediment presents mean quality values that area classified as “Good”.

Considering the reservoir's total planar area, a minimum area shows concentrations above the TEL, classified as "Regular". On the other hand, 75.57% of superficial sediment was categorized as "Good", but there are concentrations above the Regional Reference Values (RRV) (CARDOSO-SILVA *et al.*, 2021; NASCIMENTO, 2003). This growth can be related to soil deterioration due to rapid urban expansion, deforestation and increasing agricultural areas, where artificial fertilizers and pesticides are applied, in the basin (MARTINS *et al.*, 2021; TANIWAKI *et al.*, 2013)

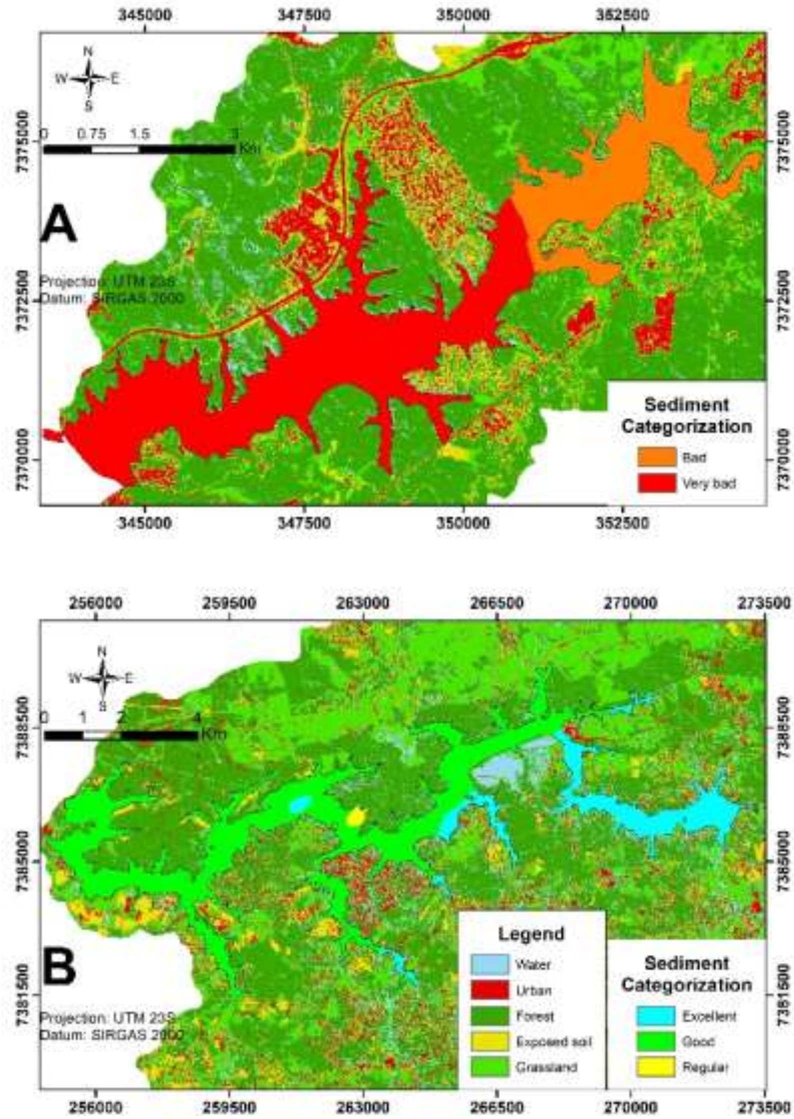
The kriging geostatistical method was performed due to the sediment sample sites spatialization, the separation among these points was considerable, and the heterogeneity both spatial and the range of copper concentration that showed being irregular. Looking at the experimental variograms, these, RG follows a Gaussian structure while ITU a spherical one, demonstrating the existence of a spatial correlation between the copper variability and the assessment distance, with a relevant SILL and a Nugget Effect, which is result of the sample points distribution in both reservoirs. In RG the variogram evaluation (Fig. 5A) demonstrates that there is a strong correlation due to the positive variation of copper concentrations along the reservoir, from upstream to downstream direction until the dam. In ITU (Fig. 5B) this correlation is present as well, but it is not as strong as in RG, probably due to minor variations of copper in the sediment along the reservoir.

Figure 5 – Copper experimental variograms. A) Rio Grande: Isotropic variogram type; Lag= 5500 m.; Angular tolerance= 22,5; Sill= 2022000; Nugget= 37000. B) Itupararanga: Isotropic variogram type; Lag= 7500 m.; Angular tolerance = 22,5; Sill= 57,0; Nugget= 0,1



Fonte: Autoria própria

Figure 6 – Sediment quality categorization in reservoirs. Land use classification performed by Maximum Likelihood method A) Rio Grande: Sentinel-2 imagery (2016/04/07) and B) Itupararanga: Sentinel-2 imagery (2017/06/24)



Fonte: Autoria própria

It is possible to infer that the copper sulfate application, since the decade of 1980’s, has directly influenced the very high values that surpass the international sediment patters. This copper concentration categorization in sediments is directly related to enrichment factor, because the classes “High” and “Very High” cover 94.54% of the reservoir’s area, indicating artificial sources of copper. It is possible to state that, due to the geological composition of the basin (kaolinite, vermiculite, illite, gibbsite and goethite), natural accumulation at the observed scales might be unlikely.

On the other hand, in ITU the copper concentration is not directly related with anthropogenic sources and the whole reservoir was classified as “Absent/Very Low”.

To calculate the copper concentration total stock in superficial sediment, we used the equation proposed in Leal et al. (2018). In RG, we used the copper concentration mean values from kriging, [Cu]= $2{,}267*10^{-3}$ kg (Cu)/kg(sediment), in addition to bathymetry and sediment data. From the sediment sampling: the fresh sediment, FS=0.1 kg., sample height, h=0.04 m., sample volume, v= 0.0001 m^3. From the bathymetric survey and interpolation: area 3D= 15,560,731.94 m^3. This calculation resulted in a value of 1,411.047 Tons Cu. Considering the sedimentation rates, in RG, reported by Franklin et al. (2016), there is an accumulation of 0.4 cm a^{-1}, and considering that copper sulfate pentahydrate started being applied in 1985 according to Beyruth and Pereira (2018), in total 32 years, it results in 4,515.35 Ton Cu. This value is close to the estimation reported by Leal et al. (2018) in Guarapiranga reservoir, SP, approximately 4,540 Ton Cu.

In ITU, the mean copper concentration value from kriging was [Cu]= $2{,}217*10^{-5}$ kg(Cu)/kg(sediment). From the sediment collection: Fresh sediment weigh, FS=0,1 kg., sample heigh, h= 0.04 m., sample volume, v= 0.0001 m^3. From the bathymetric survey and interpolation: Area 3D= 30 949264.69 m^3. This calculation resulted in 27.45 Tons Cu.

3.6. Conclusions and final considerations

The geostatistical method applied clearly demonstrated the spatial heterogeneity and potential toxicity of copper in both reservoirs, being more perceivable in RG, which was caused by inorganic metal-based algicide to control algal blooms.

RG, presented 71% of its sediment higher than PEL(x10) and the enrichment factor corroborates the anthropic source. Meanwhile Itupararanga showed 75% of the sediment is higher than regional reference values however the enrichment factor indicates a geogenic source.

Although previous works suggest that Cu is not being bioavailable in RG, this does not mean that the metal is not exerting toxic effects on the biota. Our data suggests adverse effects and it is possible that Cu bioaccumulation is occurring. Therefore, Cu high concentrations can promote a trophic cascade effect.

The application of copper sulfate as an algaecide is a palliative and controversial practice since Cu is recognized for its toxic character to aquatic communities. The copper sulfate application has already been banned in several European Union countries but is still being continuously applied in several other regions. Although the cost of applying this algaecide represents a lower monetary cost to the government compared to investments in sewage collection and treatment (Leal et al., 2018), the ecosystem services of the water bodies are threatened by this practice. As pointed out by Pompêo (2020), in almost 32 years of continuous copper sulfate application, under no circumstances this treatment can be considered a success. On the contrary, this palliative effort mismatches and appropriate quality management system, potentially polluting the sediments.

Our study shows the potential of using the kriging technique to reveal areas most potentially affected by a given contaminant, as well as, allowing to calculate its stock. Thus, it can contribute to risk analysis studies and the proper management of the water body. Moreover, Geostatistical techniques and enrichment factor, demonstrated being replicable to analyze the toxicological potential of metals in sediments and advantageous to assist decision makers.

New strategies to keep algal blooms under control must be considered, we believe that implementing proper sewage treatment systems to prevent the entrance of raw sewage is of the utmost importance. Consequently, copper based algicide will no longer be necessary, therefore, the reservoir’s original equilibrium might be restored. The same scenario is recommended for ITU, even though, it is inserted in a natural protected area, human derived impacts are increasing inside the drainage area.

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CAPÍTULO 4

Spatial distribution of Arsenic and other metals suggests a high ecotoxicological potential in Lake Titicaca[3]

4.1. **Abstract**

Spatial distribution and interpolation methods provide a summarized overview about the pollution dispersion, concerning the environment's quality. A high-altitude lake was taken as a model to assess As and other metals (Cr, Cu, Ni, Pb, Zn) distribution in superficial sediment and classify them according to their ecotoxicological potential in the aquatic environment. Surface sediments were collected from 11 sites along Puno Bay and analyzed for pseudo total-metals. Sediment concentration data and quality were plotted using the Inverse Distance Weighting (IDW) as an interpolation method. High concentrations of As were found especially in the outer bay (81.73 mg/kg). Spatial heterogeneity was evidenced for metal by the coefficient of variation, although no significative differences were observed between the two bays applying a Kruskall Wallis test ($p<0.05$, df=1). Sediment quality classification showed that most metal values were below TEL and toxicity was unlikely to occur, only As exceeded threefold PEL values, which categorized sediment as "Very Bad", indicating a rather high ecotoxicological potential to the aquatic environment. In conclusion, spatial analysis connected to interpolation methods demonstrated the superficial sediment heterogeneity in Puno Bay.

Keywords: Arsenic, spatial heterogeneity, superficial sediments, Puno Bay, Lake Titicaca

4.2. Introduction

Spatial distribution analysis is a key factor in the pollutant's transportation assessment, through the air, soil and water. Among the factors that influence the dispersion of pollutants are prominent the erosion process, weathering and even atmospheric deposition occurrences (ANAMAN *et al.*, 2022; IFTIKHAR *et al.*, 2022). In addition, anthropogenic activities contribute to these events increasing the production, deposition and subsequently the concentration of certain elements in a short period (IFTIKHAR *et al.*, 2022; LI *et al.*, 2021).

The spatial distribution offers tools to assess the dispersion of different phenomena, not only restricted to environmental, but social and even economic

[3] Manuscrito em etapa de revisão na revista "Science of the Total Environment"

affairs. Some examples of this approach from the social stand point are related to human mobility, to enhance tourism attractions (MA *et al.*, 2022), or to improve maternal continuum of care (MELAKU *et al.*, 2022). In the environment, relating spatial analysis to suspended particles in the air to assess health risks (GUO *et al.*, 2022; MOHD SHAFIE *et al.*, 2022; XU *et al.*, 2022). There are also some spatialization studies associating groundwater quality distribution as a source for drinking water supply (BUX *et al.*, 2022; LIMA *et al.*, 2019). Another approach is related to atmospheric deposition tracking of certain metals in the air and soils (DI *et al.*, 2022), and even to calculate chlorophyll and calculate cell number of phytoplankton (POMPÊO *et al.*, 2021). It is possible to address some anthropic-related scenarios or outcomes such as ore exploration and their related impacts (LIU *et al.*, 2022; TENDE *et al.*, 2021), or human consumption habits linked to solid waste i.e., microplastics (WU *et al.*, 2022). In the economics, to understand how spatial factors influence real estate prices and values (KOBYLIŃSKA, 2021), also, the valuation of certain environmental services (BALDERAS TORRES *et al.*, 2015). Furthermore, the understanding of this spatial distribution is limited, due to its specificity to the assessed area, being each site unique and different compared to other ones.

Mapping associated to spatial distribution analysis identifies, throughout models, regions of interest. Plotting the characteristic differences in a certain area, turns data more comprehensible (MARTINS *et al.*, 2021; POMPÊO *et al.*, 2021; URBINA-SALAZAR *et al.*, 2021). This simplified outcome summarizes the information which identifies certain occurrences of pollutants in the environment.

Environmental pollution is caused by both human activities and natural occurrences which is related to the catchment itself (MARTINS *et al.*, 2021; RANI *et al.*, 2021). Inlets can contain high concentration of contaminants and this occurrence could have taken place for a prolonged time (CUSTODIO *et al.*, 2022). Different eroding events (physical, chemical or biological) transport contaminants from the sources (natural or human made) to water bodies (ponds, rivers, lakes, etc.) (MARTINS *et al.*, 2021; SALEH *et al.*, 2021). Once in the aquatic system, elements as metals remain stored in the sediment (ZERROUQI *et al.*, 2021), due to their molecular weight, charge and density (ALI; KHAN, 2018).

Sediment deposits in limnetic water bodies are used worldwide to describe the environmental pollution within a basin (KHALIKOV *et al.*, 2021). Activities taking place in the catchment (industrial, mining, agricultural, etc.) are connected to increasing pollution rates (DAI *et al.*, 2018; ZHANG *et al.*, 2022). This contamination can be direct or indirect, because the compounds used in the processes of each activity may contain metals (YANG *et al.*, 2021). Therefore, monitoring these elements alone or in complexes in the sediment must be evaluated periodically. A clue factor is to distinguish regions with differences in concentrations, sediment quality and sedimentations rates in the aquatic environment. Subsequently identify the possible sources or climatic conditions that influence the presence of those elements (REN *et al.*, 2021). Finally, the data provides facts for a better comprehension of the aquatic system and give real solutions to certain phenomena.

Metals adsorbed to sediment represent a constant source of pollution to the aquatic environment. In some cases, sediment can transform the aquatic system, due to its interaction with the biota, increasing metal availability and consequently interfering with natural processes (FERREIRA *et al.*, 2021; DE FERNICOLA *et al.*, 2004). The ecotoxicological potential in a water body can affect the entire food web and modify the processes occurring in it (SILVA *et al.*, 2020). To assess the presence of certain compounds in the aquatic system, i.e., benthic environment, periphyton, algae or phytoplankton can be used (DE SOUSA *et al.*, 2021). It is possible to evaluate the potential toxicity in the aquatic environment through zooplankton and macroinvertebrates bioassays (DE ALBUQUERQUE *et al.*, 2021). The amounts absorbed by the living organisms, because of metals persistence in the system, can be bioaccumulated (ASARE *et al.*, 2022; LI *et al.*, 2022). In addition, some studies demonstrate how submerged, floating and emerging macrophytes, because of the physiological characteristics, are used to restore the environmental equilibrium (CARPIO, 2016; DAI *et al.*, 2012; WANG *et al.*, 2021). It is in this scenario where potential pollutants in the aquatic system are present that research and monitoring are crucial to maintain or preserve the ecological quality and promote public health (EISSA *et al.*, 2022).

Arsenic (As) concentration which is present in the superficial freshwater and underground water is naturally high in the Andes area (SARRET *et al*., 2019). The elevated content in this particular environment is related to As releasing by sulfide-rich minerals formed se to magmatic and hydrothermal activity, beyond the volcanism along the Andes mountains (BUNDSCHUH et al., 2017; COOMAR et al., 2019; MAITY et al., 2017; MORALES-SIMFORS et al., 2020). The As presence in the underground water at the northwest side of the lake is up to four times the threshold level (VALENZUELA ANTEZANA; YUCRA LIMAHUAYA, 2022) established by the law (PERU, 2010), this scenario is similar at the southern area where reports about the sediment indicate As concentrations with a risk to public health (CALCINA BENIQUE; APAZA CAMPOS, 2019). In this particular concern, Herrera-Añazco et al. (2016), associated a high mortality rate in Puno region attributed to renal failure, even higher to the national mean, as a consequence of a prolonged exposure of elevated contents of arsenic. Another risk diseases reported in the Titicaca basin, due to high arsenic concentrations, are the carcinogenic ones (CCANCAPA-CARTAGENA *et al.,* 2021). However, since the indigenous people have been in contact with natural high arsenic concentrations a genetic variation is the product to the adaptation of native communities in the Andes (DE LOMA *et al*., 2022). Despite of this genetic modification, high or extremely high environments will continue threating the environment and the public health.

Lake Titicaca has fascinated people around the world due to its unique characteristics, not just geographical but limnological. Even though the lake is located in a high-altitude plateau, Richerson et al. (1977) highlights similarities with low-altitude tropical lakes in almost all limnological aspects. Dejoux and Iltis (1992), briefly comment that the scientific interest in the lake began with Alcide D'Orbigny taking biological collections from his expeditions to South America (1826-1833). On the other hand, Joseph Pentland as a geographer made the first precise maps of the lake and regions in two expeditions (1827-28 and 1837-38). In the last century limnologists as Gilson (1939, 1964) and Richerson et al. (1975, 1977)centered their efforts in the larger water portions (Lago Mayor and Menor). It was until the 1980's when (DEJOUX; ILTIS, 1992) studied several characteristics in Lake Titicaca Basin and Northcote et al. (1991) focused on pollution in the inner bay (Puno Bay). There is still a lack of knowledge about the trends the lake has been experiencing particularly in ecological and limnological characteristics. Data necessary to analyze and unveil certain aspects are still needed in this special but unusual ecosystem.

This study takes a high-altitude subtropical lake, the Lake Titicaca (Peru), as a model to assess As and other metals' spatial distribution in superficial sediment and classify them according to their ecotoxicological potential in the aquatic environment. We hypothesize that: 1) metals concentrations may be higher in the proximity to urban areas due to domestic and industrial effluents and lower in distant areas; 2) spatial distribution might suggest a sediment heterogeneity which also be related to the basin’s geomorphology. This approach of spatial distribution and sediment quality fulfills a gap of knowledge related to this unique highland lake. There are still gaps on how high-altitude aquatic environments respond to high concentrations of metals and subsequently public health. Finally, the data will show a novel point of view about Puno Bay as part of the Lake Titicaca.

4.3. Study area

4.3.1. General description

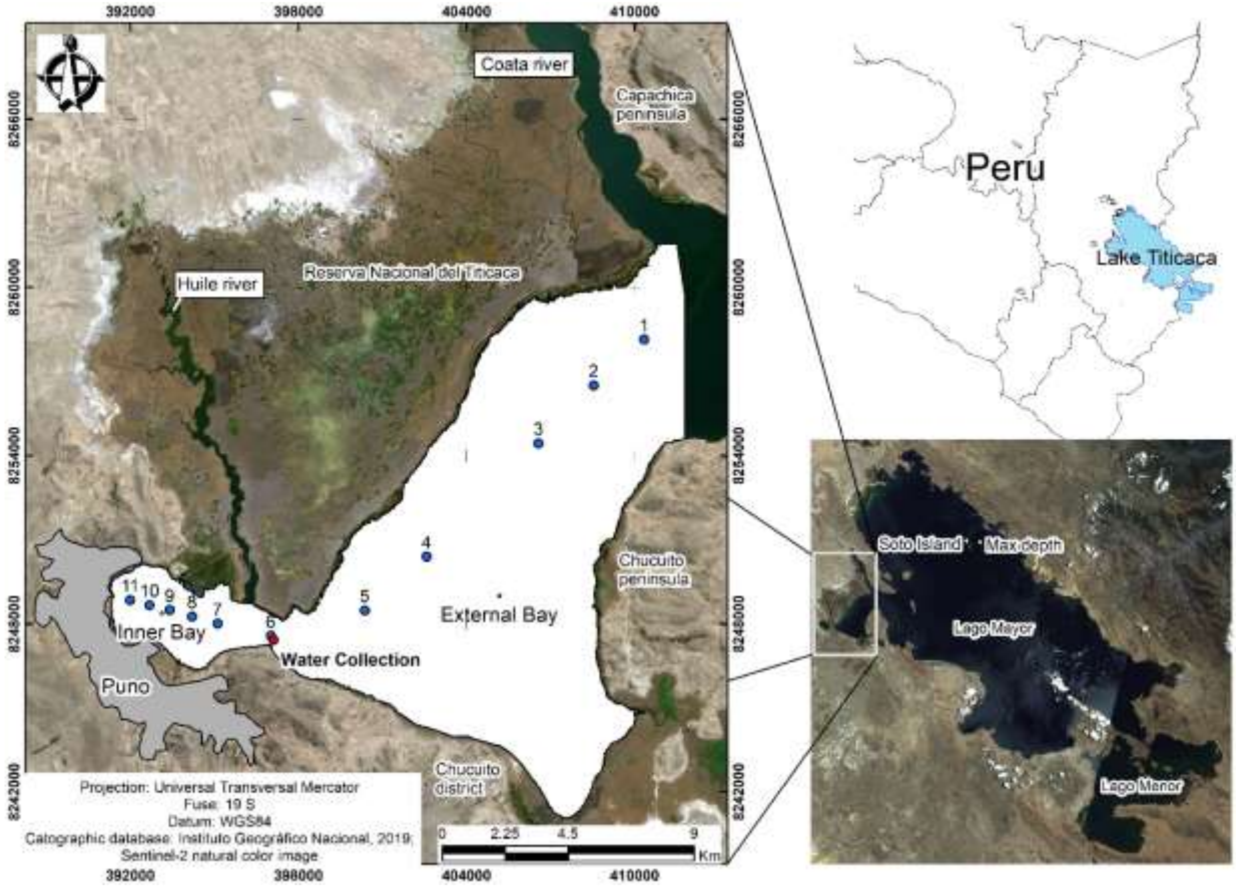
Lake Titicaca is one of the largest lakes in South America and it is the highest navigable lake in the world. This antique lake (ARGOLLO; MOURGUIART, 1995; LAVENU, 1995) has experienced variations specially morphometrical (i.e., altitude, extension, volume, etc.) (LAVENU, 1992). The oldest deposit registered is called “Mataro”, which water surface reached 3,950 m (LAVENU, 1995). Throughout the years, environmental and climatic events turned that antique lake into the current Lake Titicaca at 3,810 m (LAVENU, 1992; LOZA DEL CARPIO *et al.*, 2016). Lake Titicaca has an area of 8,562 km^2, with maximum depth of 284 m, located near Soto island, and a mean depth of 105 m (GOYZUETA *et al.*, 2009; WIRRMANN, 1992). Lake Titicaca basin is divided in two sub-basins, Lake Chucuito or “Lago Grande” (where Puno Bay is located) in the north and Lake Huiñaimarca or “Lago Menor” in the south.

Puno Bay (15º37’15’’ S e 70º02’00’’ W) is located in the west margin of Lake Titicaca. It is delimited in the east side by the Capachica and Chucuito peninsulas, in the south by Chucuito district, to the west by the city of Puno and in the north by the Reserva Nacional del Titicaca (Fig. 1). Puno Bay is divided in two by submerged and emergent macrophytes, 1) the region closer to the city (inner bay) and 2) the bigger and father portion from the city (outer bay).

The inner bay receives the non-treated sewage (domestic and industrial) from the city. Being Lake Titicaca a touristic place itself, there are some attractions located near the city of Puno. These touristic sites are islands linked to Puno through aquatic transportation which start point is located in the inner bay. This area has evidenced contamination and eutrophication signal (Northcote and Morales, 1991).

The outer bay has two tributaries (Huile and Coata rivers), keeping a better water quality than the inner bay. However, Coata river has experienced a significant urban development along its course and a subsequently non-treated sewage inlet. In addition, a natural area called “Reserva Nacional del Titicaca” protected by the Peruvian government is located, which is also considered as a wetland of international importance (Ramsar site). Unique biodiversity can be found, i.e., birds, *Rollandia microptera* “Titicaca grebe”, fish, Orestidae family “carachi”, amphibians, *Telmatobius culeus* “Titicaca water frog”. This protected area is dominated by marshes conformed by *Schoenoplectus tatora* locally known as “Totora”, an emergent macrophyte (SERNANP, 2021).

Figure 1 – Puno Bay (scale 1:150,000) demonstrating the inner and outer bays, as well as the eleven sample sites. Red point indicates the water collection site for Puno’s drinking water supply



Fonte: Autoria própria

4.3.2. Geomorphology

The Titicaca basin is located at the southeast of Peru, continuing into the Bolivian territory. Appears the highland plateau known as the “Collao Plateau” or most commonly the “Altiplano” located and formed between the western and eastern Cordilleras in the central Andes. The Vilcanota Cordillera bounds the Andean depression in the north constituting an endorheic watershed with a radial drainage. Its basement is made up by Paleozoic rock over them Mesozoic rocks (Jurassic and Cretaceous) appear, covered by a potent Cenozoic volcanic sequence (INGEMMET, 1995).

The western Cordillera presents mountains with elevations overpassing 4600 m which conform the *divortium aquarium*. According to INGEMMET (2020), in this Cordillera, we can differentiate some geological formations. i) high slope mountains with juvenile valleys, these are formed by sandstone, limestone and lute from the

Socosani formation and Yura group and a minor proportion of limestone form the Ayabacas formation. ii) hills and mountains with canyon valleys, these areas present volcanic structures from the Sillapaca and Barroso groups, additionally, volcanic-sedimentary sequences from the Pichu formation. iii) hills and mountains with slight slopes, even though the geological formation is similar to canyon valleys, the drainage erodes volcanic-sedimentary sequences from the Pichu formation and from the Maure and Tacaza groups.

The Altiplano, is formed by plains, hills and aligned mountains between 3800 to 4200 m with other geological formations inside. 1) sedimentary plains, the principal characteristic of the Altiplano, they can reach 3900 m and are composed by sediments from the Azangaro formation. 2) volcanic plains, located at the west of the lake up to 4000 m, composed by lava from the Umayo formation. 3) carbonated rock hills, located in the middle of, previously mentioned, sedimentary plains, these hills can overpass 4200 m, composed by a chaotic mass of limestone and silt from the Ayabacas formation. 4) isolated dendritic and volcanic rock mountains, composed by sandstones from the Puno group and volcanic sequence from the Mitu group. 5) mountains, composed by sandstone and conglomerates from the Puno group and in a lower proportion of limestone from the Ayabacas formation, as well as, by a volcanic sequence from Tacaza group and Umayo formation. these can reach 4300 m. 6) structural dome of Cabanillas, the highest peaks are around 4600 m. they have a semicircular shape conformed by lute and sanstone from the Cabanillas group (INGEMMET, 2020; NEWELL, 1949; SAMPERE *et al.*, 2000).

4.4. Material and Methods

4.4.1. Sampling and analytical procedures

Sediment sampling was performed on January 3rd, 2019. Eleven (11) sampling sites were georeferenced (WGS84; UTM 19S) distributed in a straight transect from nearby the city of Puno to closer zones of Capachica and Chucuito peninsulas (Fig. 1). This transect is used mainly in people (tourists) and goods transportation to outer areas in “Lago Mayor”, i.e., Taquile and Amantani islands.

A collector type Ekman (225 cm^2) was employed. Collecting the first 4 cm of the superficial sediment. These samples were stored in sterile flasks (100 ml) kept and transported in thermic bags.

The laboratory process, samples were dried in an oven at 60 °C, then ground in a glass mortar. To analyze arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), the sediment was processed following the 3050B method (U.S.EPA, 1996). The extract from acid digestion were stored at 4 °C before its analysis by inductively coupled plasma atomic emission spectrometry (ICP-OES), using a Varian 710-ES model instrument. The quantification limits for all metal assessed were as follows: As (2.22 mg/kg), Cr (0.5 mg/kg), Cu (0.71 mg/kg), Ni (0.89 mg/kg), Pb (1.48 mg/kg) and Zn (1.44 mg/kg). Analytical grade reagents (obtained from Merck and Sigma-Aldrich) were used in all the analyses. All glassware items and equipment used to storage and processing the samples for metal assessment were left in 10% nitric acid for at least 24 h, followed by rinsing with ultrapure water. The metal data were expressed as milligrams per kilogram of dry weight (mg/kg dw).

4.4.2. Spatial distribution analysis

The Inverse Distance Weighting (IDW) was used to estimate values in non-sampled areas employing values from known sites. This interpolation method IDW, considers highly similar values when the prediction site is closer to the sampling point and lower values when the prediction site gets farther. IDW uses the following equation to calculate unknown values (KOUTROULIS *et al.*, 2013; WEI; MCGUINNESS, 1973; YANG *et al.*, 2020):

$$\hat{z}_j = \frac{\sum_{i=1}^{n} \frac{z_i}{d_{ij}^2}}{\sum_{i=1}^{n} \frac{1}{d_{ij}^2}} \qquad (1)$$

Where: “Ẑj” it is the estimated value for a non-sampled site; “d” it is the distance of both points sampled in the equation; “z” it is the z value of the known ‘i’ point; “n” it is the number of points being included in the survey; and “i” it is the number of known points considered in the interpolation.

4.4.3. Sediment ecotoxicology

Metal concentration and its toxicity potential assessment was based in the Interim Sediment Quality Guidelines (ISQGs), such as the Threshold Effect Level (TEL) and Probable Effect Level (PEL) (CCME, 1999). The classifications associated to the ecotoxicological risk were defined in four categories, according to the sediment quality, as Good, Regular, Bad, Very Bad, adapted from (LEAL *et al.*, 2018) (Tab. 1)

Table 1 – Sediment qualitative classification, were [M]= metal concentration; ISQG/TEL= Threshold effect level; PEL= Probable effect level

Classes	Limits/Intervals	Ecotoxicological Potential
Good	0 mg/kg ≤ [M] < ISQG/TEL	Region with possible contamination, but with little to improbable ecotoxicological activity.
Regular	ISQG/TEL ≤ [M] < PEL	Region with contamination of unknown ecotoxicological activity and, medium occurrence
Bad	PEL ≤ [M] < 3*PEL	Region with high ecotoxicological activity and, occurrence probability.
Very	3*PEL ≤ [M] < +∞	Region with maximum ecotoxicological effect and, maximum occurrence probability.

Fonte: Autoria própria

4.4.4. Organic matter and granulometric analyses

To determine organic matter (OM), part of the previously dried sediment employed for metal concentration assessment was used. These samples were put in washed, dried and identified crucibles, calcinated at 550 °C for 4 h (HEIRI *et al.*, 2001). All crucibles were cooled in a pressured desiccator for at least two hours. Then 0.5 g of dried sediment were weighted and returned to the muffle for 4 h at 550 °C, then cooled once more and finally weighted. OM was calculated and expressed as percentage, being the difference between the first (crucible and sediment) and second weight, considering the burned material as OM.

The granulometry assessment followed the steps in Martins et al. (2021). To determine the granulometric composition, the resulting sediment passed through sieves, then classified according to its size, medium size (> 0.212 mm), fine and very fine sand (< 0.212 - >0.032 mm) and silt/clay (< 0.032 mm)

4.4.5. Statistics

The Principal Component Analysis (PCA) was used to describe the characteristics among sampling sites regarding their correlation. PCA reduces all data set to a lower number of variables (usually the first two components), for plotting purposes. The graphical biplot correlation in the PCA was based on (LEGENDRE; LEGENDRE, 1998). A Kruskal Wallis analysis was performed to evaluate significant differences between the inner and outer bays (p < 0.05, df = 1) The analysis was performed using a free statistical software Paleontological Statistics (PAST) Version 4.03. To observe the relationship between metals, a Spearman's rank correlation will be calculated (SPEARMAN, 1904).

4.5. Results

4.5.1. As and other metal concentrations

Metal concentration results represent the pseudo-total value of the metals analyzed in sediment (Tab. 2). It has been observed that higher concentrations are present in the central portion in both areas of Puno Bay (inner and outer bays). In the outer bay, As (81.73 mg/kg), Cr (14.06 mg/kg), Cu (35.49 mg/kg), Ni (13.23 mg/kg), Pb (36.96 mg/kg) and Zn (130.99 mg/kg) show their maximum values, then the concentration decreased until reaching the macrophyte areas that divide the bays. It is in this region where the minimum values are observed (As - 11.32 mg/kg, Cr - 2.81 mg/kg, Cu - 3.83 mg/kg, Ni - 2.48 mg/kg, Pb - 2.75 mg/kg, and Zn - 16.48 mg/kg). Once in the inner bay, these concentrations increase again in the central part reaching maximum values, (As - 43.18 mg/kg, Cr - 8.93 mg/kg, Cu - 29.33 mg/kg, Ni - 8.80 mg/kg), Pb - 28.50 mg/kg, and Zn - 120.44 mg/kg).

The basic statistical analysis showed that the coefficient of variation for As, Cu, Pb and Zn is higher to 52%, in the case of Cr and Ni even though the variation is still high it does not overpass 48.5%. This suggested the existence of a spatial heterogeneity in the metal concentration distribution.

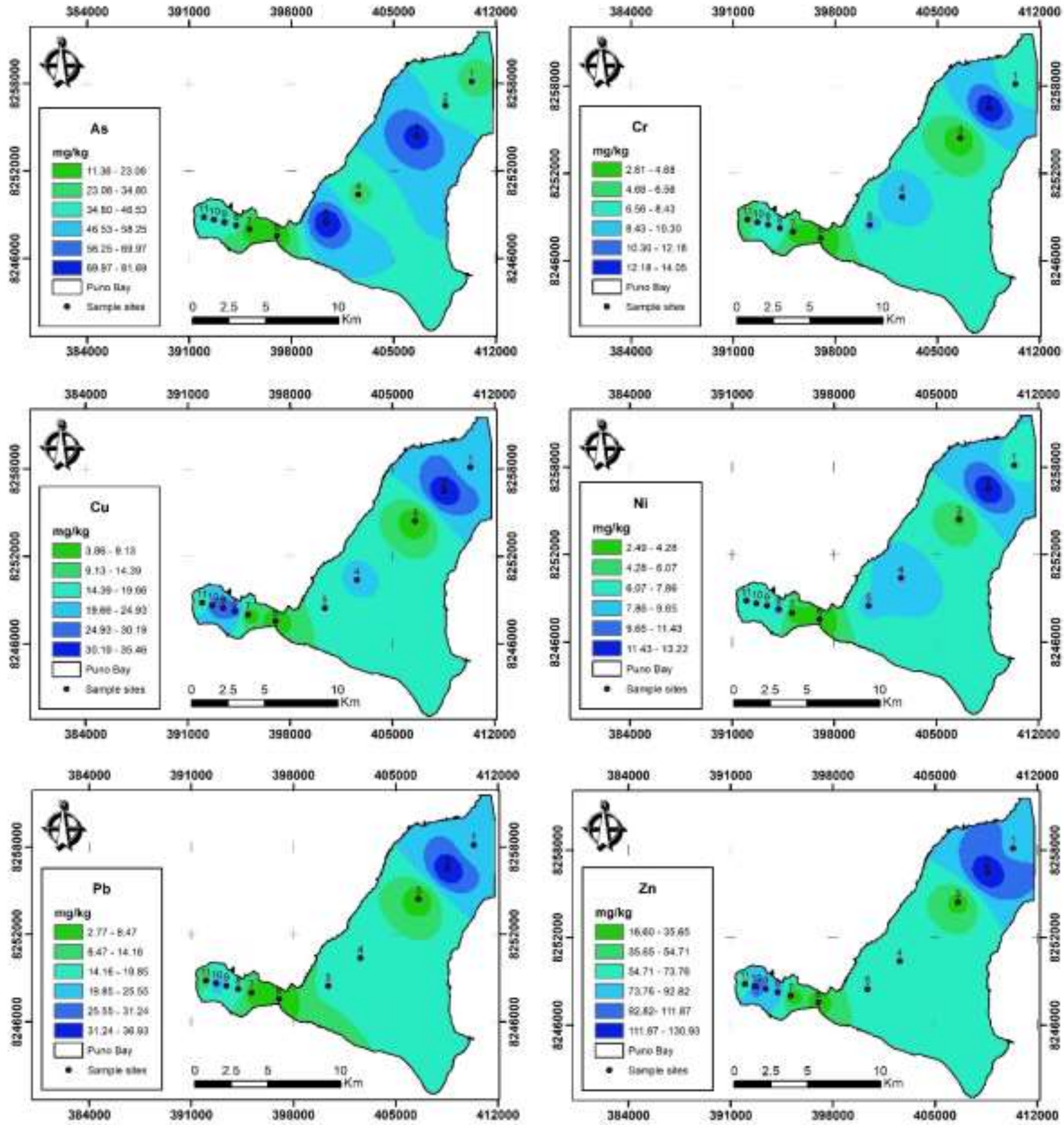
Table 2 – Descriptive statistics outcome, mean, standard deviation and variation coefficient in Puno Bay (mg/kg), as well as Threshold Effect Level (TEL) and Probable Effect Level (PEL)

	Metals					
	As	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Max	81.73	14.06	35.49	13.23	36.96	130.99
Min	11.32	2.81	3.83	2.49	2.75	16.48
Mean	40.59	7.00	18.71	6.98	15.86	70.61
St. Dev.	21.35	3.39	11.14	3.11	10.98	38.47
Var. Coef.	52.60	48.45	59.52	44.53	69.24	54.48
TEL	5.9	37.3	35.7	18	35	123
PEL	17	90	197	36	91.3	315

Fonte: Autoria própria

Since the cartographic and spatial standpoint, As and Cr show higher concentration distributions in the outer bay with values higher than 75.0 mg/kg and 14.0 mg/kg, respectively. However, despite the higher values in the outer bay, no significative differences, for each meta in the two analyzed bays were observed (Kruskal Wallis, $p<0.05$, df=1). For Cu, Ni, Pb and Zn the distribution areas with high concentrations are visible in both bays (Fig. 2). Another evidence that this spatial analysis offers is referred to the channel which joins both bays (inner and outer) in these surroundings the lowest values of all metals are present. There is a high probability that macrophytes retain the pollution in the inner bay preventing the propagation throughout the outer bay.

Figure 2 – Metal concentration spatial variability for the metals analyzed in the superficial sediment in Puno Bay



Fonte: Autoria própria

4.5.2. Principal Component Analysis outcome

The PCA states that 94.3% of the variance is explained by the first two components (Tab. 3). In the first component the loadings of Cr, Cu, Ni, Pb and Zn are similar above 0.44 (see Table 3) except As in which the loading drops to 0.09. In the second component only As shows a high loading of 0.97 dominating the scenario.

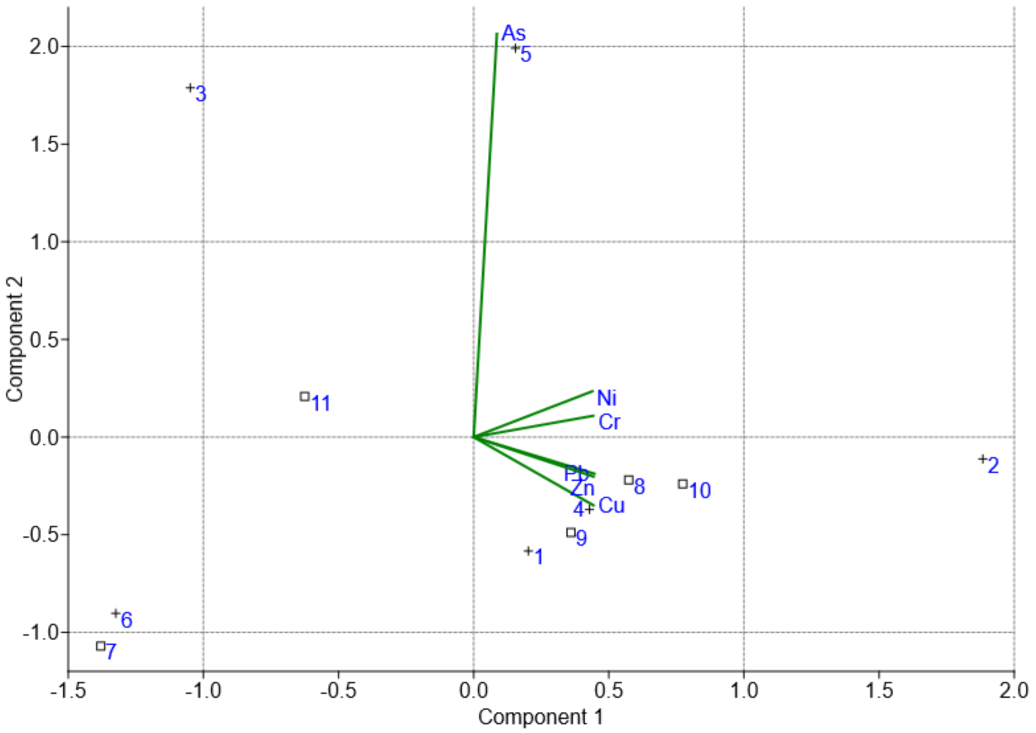
Table 3 – Loadings for the first two components from the metal concentration analysis in superficial sediments for Puno Bay

Metal	PC 1	PC 2
As	0.09	**0.97**
Cr	**0.44**	0.05
Cu	**0.45**	-0.16
Ni	**0.44**	0.11
Pb	**0.45**	-0.08
Zn	**0.45**	-0.09

Fonte: Autoria própria

From the resulting scatter plot (Fig. 3), it is possible to observe that sampling sites 1, 9, 4, 8 and 10 are inversely related to sites 3, and 11 when considering Pb, Zn and Cu. Sampling sites 6 and 7 are negatively related, in the case of Ni and Cr, while site 2 is slightly positively related to the same metals. Finally sampling site 5 presents a high correlation to As.

Figure 3 – Resulting scatter plot from the Principal Component Analysis for metals assessed in the sediment, outer bay (1 - 6), and inner bay (7 - 12)

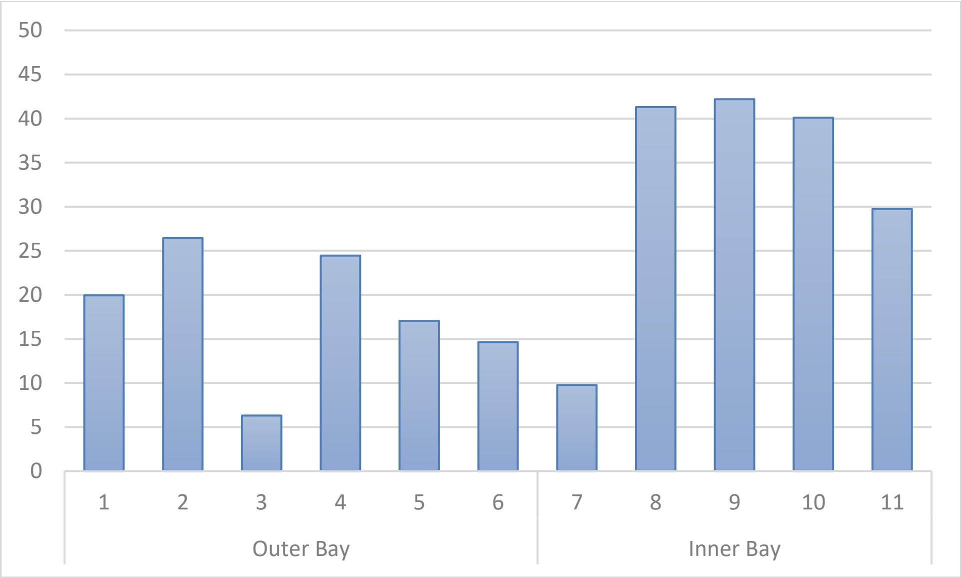


Fonte: Autoria própria

4.5.3. Organic matter and granulometric assess

While the organic matter in outer bay ranges from 6.3% to 26.43%, the inner bay presents in almost all sites values higher than the maximum percentage in the outer bay. Only sample site 7, presents a lower percentage similar to the values in the outer bay. Organic matter mean value in the inner bay (32.61%) is almost the double than the mean in the outer bay (18.13%) (Fig 4).

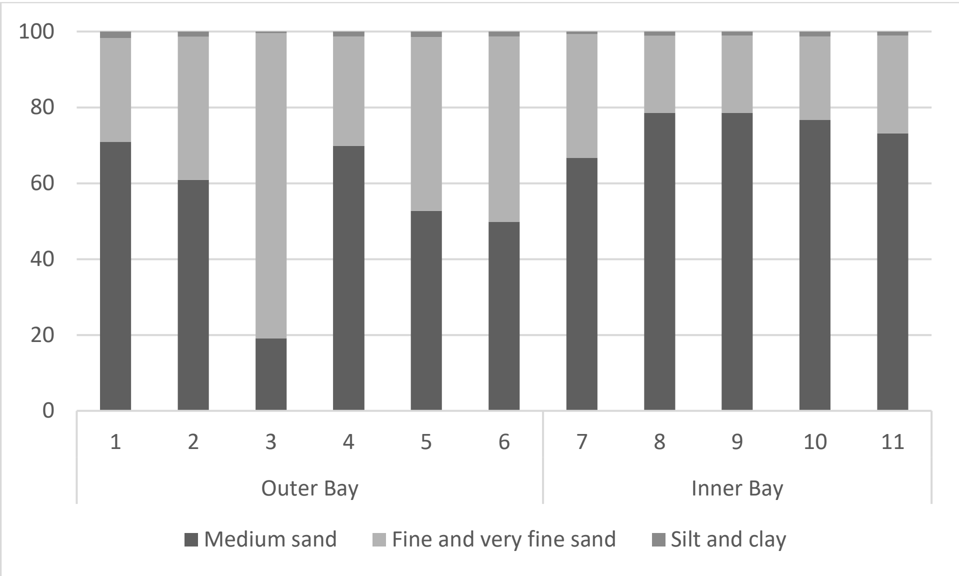
Figure 4 – Organic matter percentages (OM, %) of the superficial sediment in Puno Bay, distributed in the outer and inner bays



Fonte: Autoria própria

The granulometric analysis (Fig. 5), indicates the presence of medium sand size grains in high percentages (from 49% to 78%) in ten sites. Despite the distinct values for both variables, granulometry and organic matter, the Kruskal Wallis test did not indicate significant differences between these two portions of the bay (Kruskal Wallis, p = 0.05, df = 1).

Figure 5 – Particle size (%) composition of the superficial sediment at each sampling site. Medium sand, fine and very fine sand, and silt and clay percentages in Puno Bay are shown, divided in outer and inner bays



Fonte: Autoria própria

4.5.4. Correlation

Significative Spearman correlations (r > 0.5) were observed between metals, suggesting a similar origin, between metal and organic matter, as well as metals and silt and clay fractions (Tab 4), two important biding phases which retain metals in sediments. Only As did not present significative correlations with any evaluated variable.

Table 4 – Spearman correlation among metals, organic matter (OM) and grain size: silt and clay (S-C), medium sand (MS) and fine and very fine sand (FS), in bold, correlations r > 0.5

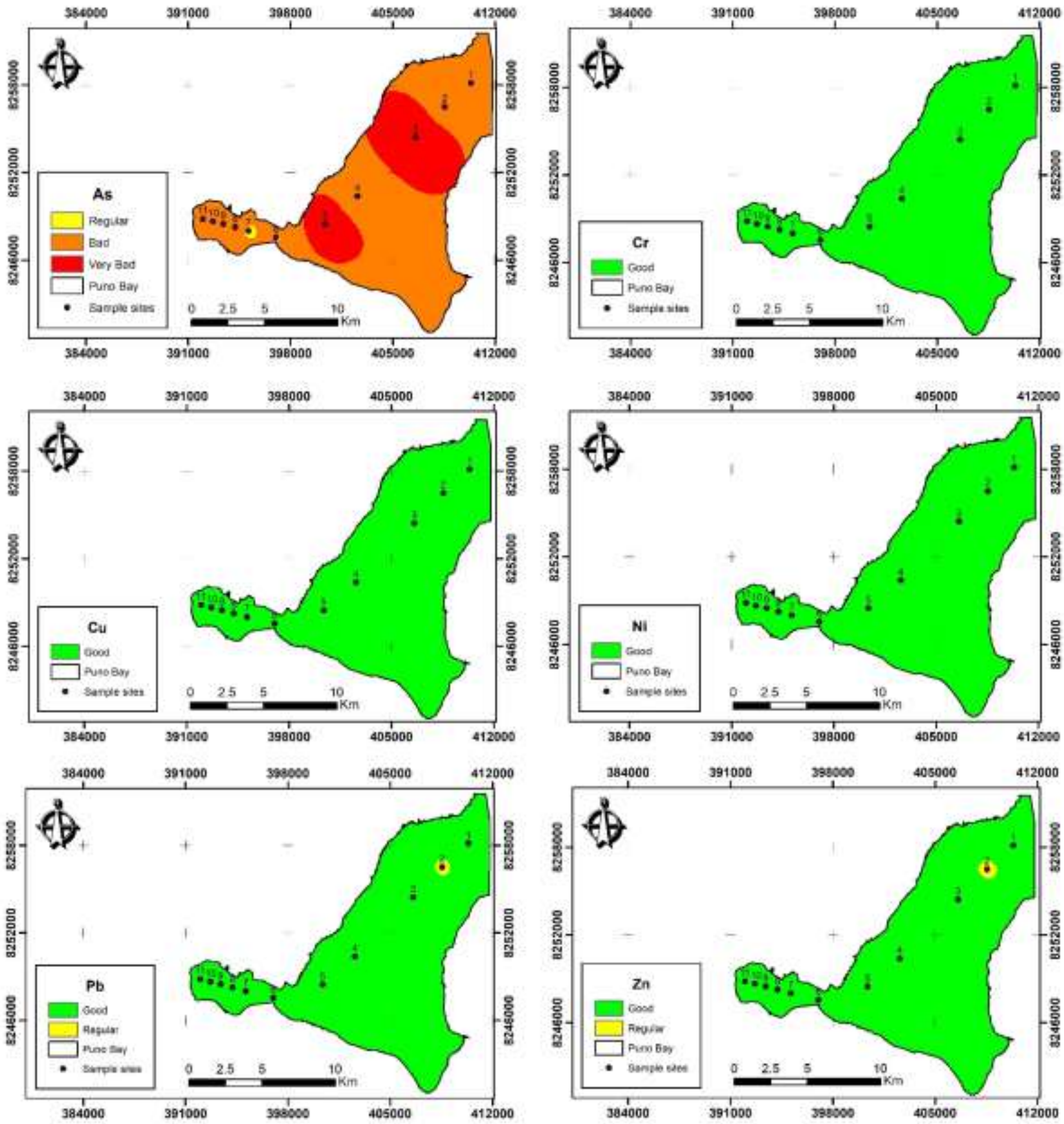
	OM	As	Cr	Cu	Ni	Pb	Zn	S-C	MS	FS
OM	0.000									
As	0.100	0.000								
Cr	**0.536**	0.436	0.000							
Cu	**0.773**	0.291	**0.782**	0.000						
Ni	**0.555**	0.409	**0.991**	**0.764**	0.000					
Pb	**0.582**	0.282	**0.773**	**0.909**	**0.745**	0.000				
Zn	**0.700**	0.345	**0.791**	**0.982**	**0.764**	**0.936**	0.000			
S-C	0.036	0.109	**0.500**	**0.527**	0.464	**0.645**	**0.555**	0.000		
MS	**0.882**	-0.173	0.327	**0.564**	0.336	0.400	**0.527**	-0.064	0.000	
FS	-0.882	0.173	-0.327	**-0.564**	-0.336	-0.400	**-0.527**	0.064	-1.000	0.000

Fonte: Autoria própria

4.5.5. Ecotoxicological potential classification

When comparing the data to TEL and PEL (Fig. 6), As is the only metal, that surpasses 3xPEL (51 mg/kg). Despite native flora and fauna are adapted to this particular high concentration, extremely high contents indicate the occurrence of potential ecotoxicological effects to the aquatic environment.

Figure 6 – Ecotoxicological potential classification according to sediment quality guidelines in Puno Bay. The areas where no sampling collection occurred were filled according to the interpolation of data applied through geostatistics



Fonte: Autoria própria

Sediment classification according to its ecotoxicological level, shows the presence of a potential risk in the case of As. In the visual categorization according to TEL, PEL and 3xPEL, only two sites are below PEL but above TEL classified as “Regular”, seven sites are higher than the PEL classified as “Bad” and two sites present values higher than 3xPEL classified as “Very Bad”. Cr, Cu and Ni do not show values higher than the TEL, in the whole Puno Bay, being classified as “Good”. Finally, Pb and Zn show as well a general classification as “Good”, just in one site, both cases show a concentration over the TEL classifying it as “Regular”.

4.6. Discussion

For a better understanding and general perspective when analyzing the presence of these metals (As, Cr, Cu, Ni, Pb and Zn), human activities inside the catchment must be considered. On the premise that Lake Titicaca basin is endorheic, and according to UNESCO (2022), there are 25 tributary rivers. The most important are Ramis, Ilave, Coata Huancane in the Peruvian side, Katari in the Bolivian territory and Suches which along its course flows in both territories (ALT, 2022). It is in the upper basin where mining activities are developed in different scales, including the artisanal mining (LOZA DEL CARPIO; CCANCAPA SALCEDO, 2020) which in many cases is informal (BROUSETT-MINAYA *et al.*, 2021; MAMANI VILLALBA *et al.*, 2021). In these cases where there is no control by the government or any environmental agency, compounds from the processing stages, are disposed carelessly. The result is mine tailings lack of containment reaching small stream, important rivers and subsequently lakes.

There are evidences that in the upper basin, where mining activities take place, as well as rivers that have their origin in this area, higher concentrations of metals with a potential toxicity to human health are found. The sediment in water bodies (springs, ponds, lagoons and streams) close to ore extraction and processing zones present concentrations with potential toxicity. (BROUSETT-MINAYA *et al.*, 2021) identified As in two lagoons where tailing residues flow into, this near processing areas in La Rinconada – Peru, located in the Ramis river watershed. Those values reached 56.92 mg/kg and 66.71 mg/kg during dry and rainy seasons, respectively. In this research, according to sediment quality guidelines As is above PEL, Cu and Pb are below TEL, Ni and Zn are above TEL but below PEL.

The same condition is observed in certain rivers inside the Titicaca basin. Vasquez Choque (2018) reported in Chacapalca river, located in the Coata river watershed, As presence (9.41 ± 0.01 mg/kg) which is above TEL. Other metals such as Cu, Ni, Pb and Zn showed values higher than TEL, in contrast, Cr was the only metal below TEL. Salas Mercado (2017) in Azangaro river which belongs to Ramis river watershed, reported that metals such as Cr, Cu, Pb where below TEL. In the same watershed but in Crucero river catchment Salas-Mercado et al. (2020) found As and Zn (36.72 mg/kg and 1227 mg/kg, respectively) above the PEL value. At the east side of Lake Titicaca, in the Suches river, Mamani Villalba et al. (2021) observed that As, Cr, Cu, Pb and Zn values were below TEL, only Ni showed concentrations above this guide value.

Once in the lacustrine zone, this panorama with high concentrations of metals is still evident. In the inner bay (Puno Bay) Moreno Terrazas et al. (2018) sampled six sites in this area, reporting really low As values (0,00013 ± 0,00005 mg/kg) which differs greatly from the results presented previously.. When we compare other metals concentrations, Cu (6.95 ± 0.88 mg/kg), Zn (8.20 ± 0.96 mg/kg) and Pb (0.039 ± 0.019 mg/kg), the discrepancy continues. Another analysis in the inner bay, Mamani Arce (2020) presents concentrations similar to the ones obtained in this research, As (45.37 ± 6.02 mg/kg) which shows to be higher than PEL as well. In the case of Cu and Zn there is a huge difference between the values reported by Mamani Arce (2020) and the ones presented in this study, exceeding up to 10 times. This can be explained due to the sampling location (shoreline). We have to consider that organic matter (OM) plays an important role in metal retention (FÖRSTNER, 1981) which explains the significative Spearman correlation between metals and OM.

The outer bay, receives two important tributaries (Huile and Coata river) which can influence the presence of the higher metal concentrations. Quispe Yana (2017) analyzed the sediment quality at the mouth of Coata river, finding differences in concentrations between rainy and dry seasons, i.e. As presented 0.80 mg/kg and 7.08 mg/kg, respectively. In general almost all metals assessed (Cr, Cu, Ni and Zn) increased from dry to rainy season, due to precipitation inside the basin resulting in a higher erosion in the catchment. Escobar Mamani (2019) collected the sediment in an area close to the city of Chucuito, in the south part of the outer bay. As showed similar concentration (41.10 mg/kg) as obtained in this research, other metals such as Cr (2.8 mg/kg), Cu (4.3 mg/kg), Ni (3.5 mg/kg), Pb (<1.0 mg/kg) and Zn (15.1

mg/kg) showed to be lower, this can be explained due to the heterogeneity in the spatial distribution of the analyzed metals. Particle size in this area can be related to low metal concentrations because this is dominated with medium size sand.

To discuss the source of As in Lake Titicaca, we have to analyze the basin itself and the possible forms in which As is presented. According to Bia et al., (2021) As(V) arsenate, is the dominant As species determined in carbonated rocks. The basin presents carbonate reservoirs within the Paleozoic and Mesozoic sections (PERUPETRO, 2008). Not only physical processes (weathering, precipitation, wind erosion, etc.) are responsible for carbonate precipitation, chemical and biological processes are as well, because they are part of metabolic process of organisms (BIA *et al.*, 2021). The As presence, according to (TAPIA *et al.*, 2019) in the Altiplano, is associated to arsenopyrite and tennantite in the west side of the lake. Another sources are hot springs and according to INGEMMET (2022) there are more than ten active thermal water sites in the Peruvian side of Lake Titicaca Basin. In a complementary study where sediment profiles were analyzed (unpublished data), the outcome suggests a Regional Reference Value of 32.91 mg/kg for As.

Table 5 – Comparative of high-altitude water bodies and their metal concentrations around the world to Puno Bay resulting values

Lake name	Country	Altitude (m)	Metals (mg/kg)						Reference
			As	Cr	Cu	Ni	Pb	Zn	
Puno Bay Lake Titicaca	Peru	3810	40.59 ± 21.35	7.00 ± 3.39	18.71 ± 11.14	6.98 ± 3.11	15.86 ± 10.98	70.61 ± 38.47	This research
Erhai Lake	China	1974	28	101.6	65.1	57.5	50.2	135	Yu et al. 2021
Dimon Lake	Italy	1857	39.5 ± 0.7	-	-	-	109.6 ± 1.2	138.8 ± 0.6	Pastorino et al. 2020
Cohana Bay Lake Titicaca	Bolivia	3610	50	-	-	-	-	-	Sarret et al. 2019
Lake Repomuso	Spain	2130	49.69 ± 42.17	31.53 ± 9.62	13.13 ± 11.23	23.12 ± 10.98	36.46 ± 28.92	81.99 ± 34.53	Zaharescu et al. 2009
Lake Blanc Huez	France	2543	40	-	-	-	-	-	Chapron et al. 2007

Fonte: Autoria própria

When comparing Puno Bay metals concentrations with other water bodies of high altitude around the world show some differences (Tab 5). Although Lake Titicaca is shared by Peru and Bolivia there are some contrast aspects regarding metals concentrations in sediment. As has pointed relevance due to the geomorphology in the Titicaca Basin (Peruvian and Bolivian side). Contrasting As in Puno and Cohana Bay (SARRET *et al.*, 2019) in the south area of the Lake, the concentrations are similar. The only difference are the sampling areas, while in this study were non-vegetated areas the Bolivian side were located in emergent macrophyte zones. Puno Bay is also used for drinking water supply, mainly to the city of Puno. When compared to another highland lake with the same purpose Erhai Lake (YU *et al.*, 2021), this shows As mean values lower than in Puno Bay. One possible explanation is that Erhai watershed is dominated by forest (53%) in contrast to the Titicaca basin. Comparing Puno Bay to another protected natural area, Dimon Lake (PASTORINO *et al.*, 2020) this last lake presents lower concentrations. If the geomorphology is considered Lake Respomuso (ZAHARESCU *et al.*, 2009) presents limestone in its formation similar to the west side of Lake Titicaca. The values observed in both studies are similar considering As. This can lead us think about that local geology influences the natural presence of this metal. In addition, the altitude, water origins (glaciers) give certain characteristics to the sediment as well. Lake Blanc Huez (CHAPRON *et al.*, 2007) gives a hint when comparing As concentrations to Puno Bay's these are quite similar.

4.7. Conclusions

Spatial distribution analysis associated to mapping techniques and interpolation methods demonstrated the superficial sediment heterogeneity in Puno Bay. We could not associate higher metal concentrations nearby urban areas as well. Regarding the sediment quality just As presented concentrations, in the outer bay as well, higher than threefold PEL values, sediment was considered as "Very Bad". This category relates very bad sediment quality to rather high ecotoxicological potential and maximum occurrence probability in the aquatic environment. However, it is possible to say that the As presence in Puno Bay, based on the geological and chemical composition of the basin, is natural. Since water collection for drinking water supply happens in the outer bay, As could represent a problem to public health and continuous monitoring is required. Finally, this report fulfills the lack of information concerning the sediment quality in the west area of Lake Titicaca and highlights the sediment quality from a spatial approach.

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CAPÍTULO 5

New insights about the contribution and accumulation of sediment and metals in Lake Titicaca[4]

5.1. Abstract

All changes taking place in a watershed have repercussions to lacustrine environments, being these ones, the sink of all pollutants generated by activities occurring in the basin. Lake Titicaca, the world's highest and navigable lake is not unfamiliar to these phenomena that can alter the sedimentation dynamics and metal accumulation. This study aimed to identify temporal trends of sedimentation rates by means of a geochronological analysis (^{210}Pb, ^{137}Cs). As well as to identify metal concentrations (As, Ba, Ca, Cr, Cu, K, Mg, Mo, Ni, Pb, Zn) in the projected timeline in order to propose, for the first-time, background values in Puno Bay. Two sediment cores were collected from the outer and inner bays. Sediment Rate (SR) was calculated through the excess of ^{210}Pb ($^{210}Pb_{xs}$) applying the Constant Flux Constant Sedimentation Model (CFCS). Results show that SR in the outer bay was 0.48±0.08 cm a^{-1}, and for the inner bay was 0.64±0.07 cm a^{-1}. Sediment Quality Guidelines (SQGs) did not indicate toxicity was likely to occur, except for As. However, Enrichment Factors (EFs) indicated that all metal accumulation is geogenic. Climatic factors had marked influence in sedimentation rates for the outer bay and in the case of the inner bay it was a sum of climatic and human based factors.

Keywords: Lake Titicaca, Puno Bay, sedimentation rate, high-altitude lake, CFCS model.

5.2. Introduction

Lakes are sinks for all the phenomenon taking place (natural and artificial) within the basin (KANG *et al.*, 2022; ZHANG *et al.*, 2021). These fragile environments have experienced trends in their physical (CARDOSO-SILVA *et al.*, 2021; NDIAYE *et al.*, 2022), chemical (LIM *et al.*, 2022) and biological (CARDOSO-SILVA *et al.*, 2022; DE SOUSA *et al.*, 2021; MONCHAMP *et al.*, 2021) components, due to increased human activities in the catchment. There are multiple causes, e.g., inadequate land use, release of untreated domestic and industrial sewage, deforestation, mining, agriculture among others (BROUSETT-MINAYA *et al.*, 2021; FERREIRA *et al.*, 2021; MAMANI VILLALBA *et al.*, 2021; MARTINS *et al.*, 2021;

[4] Manuscrito na etapa final de elaboração prévia à submissão

MATAMET; BONOTTO, 2019a; 2019b). These trends, influenced by the watershed, potentially affect the aquatic equilibrium. The consequences can be related to loss of habitat, algal blooms, aquatic transportation interferences, metal accumulation and several others.

A key aspect is to have the knowledge about sedimentation dynamics because they can be related to changes from natural and artificial sources. It is even possible to relate the trends observed in sediment profiles to historical events. Radiometric dating techniques are tools widely used that were first applied in glacier ice dating (GOLDBERG, 1963) then in lacustrine environments (KRISHNASWAMY *et al.*, 1971). The use of ^{210}Pb in geochronologic studies can be ascribed to, i) useful half-life of 22.2 years, ii) it is presented both in the atmosphere and in sediments (APPLEBY; OLDFIELD, 1992). Sediment dating using ^{210}Pb is achieved applying the excess of it ($^{210}Pb_{xs}$) resulting in an atmospheric decay, this is a globally used method(BLASS *et al.*, 2005; DAS; VASUDEVAN, 2021; FONTANA *et al.*, 2022; SHARMA *et al.*, 2012). On the other hand, ^{137}Cs is linked to large scale nuclear explosion events which began in 1961 – 1962, that after its atmospheric diffusion reached a maximum fallout (radionuclides accumulation) in lacustrine sediments between 1963 and 1964 (BONOTTO *et al.*, 2022; ROUT; VASUDEVAN, 2022).

Some models based on ^{210}Pb have been developed to assess sedimentation rates. This is based in the sediment accumulation uniformity (APPLEBY, 2001). First, the constant flux constant sedimentation model (CFCS) is recommended when sedimentation rate and $^{210}Pb_{xs}$ are both constant (an exponential decay) (CARDOSO NERY; BONOTTO, 2022; KRISHNASWAMY *et al.*, 1971). Second, the constant initial concentration model (CIC) that considers a constant initial $^{210}Pb_{xs}$ without taking into account any changes in the sedimentation (ABBASI, 2019; ROBBINS; EDGINGTON, 1975). Third, the constant rate supply (CRS) that assumes a constant $^{210}Pb_{xs}$ flux to the surface and consequently the initial $^{210}Pb_{xs}$ concentration is inversely proportional to sedimentation rate (APPLEBY; OLDFIELD, 1978; FONTANA *et al.*, 2022). In nature not all the aquatic environments completely meet the requisites, such as constant initial concentration of 210Pbxs and constant sedimentation rate, therefore can produce some inconsistent dating results or they can be related to particular environmental conditions (CHEN *et al.*, 2019).

In a sediment profile each layer assessed has its own characteristics, recording certain historical aspects, even when no environmental interferences occurred. It is possible to observe changes related to biological, climatic and metal trends(CARDOSO-SILVA *et al.*, 2021, 2022; MATAMET; BONOTTO, 2019a; 2019b). Metals due to their toxic potential need to be monitored constantly, track their increment is recommended (FERREIRA *et al.*, 2021; MARTINS *et al.*, 2021; MIZAEL *et al.*, 2020). Approaches as superficial sediment assessment need values to compare with, e.g., background value, which is the value when no human disturbances were observed (CARDOSO-SILVA *et al.*, 2021; KIM *et al.*, 2017; NASCIMENTO; MOZETO, 2008). These are useful for calculating enrichment sources and future environmental restorations projects.

In this sense, human activities performed within the Titicaca Basin affect directly the lake's equilibrium. Puno Bay, part of Lake Titicaca, has important affluent inlets that present serious pollution signs, in the upper, middle and lower basins(MATAMET; BONOTTO, 2019a; 2019b), affecting specially the outer bay. Urban development, the lack of a sewage treatment plan, industrial activity and its proximity to the inner bay represents an issue to the aquatic ecosystem. We have to highlight that this is the first study that evaluates sediment geochronology and metal concentrations in sediment profiles to propose background values for the outer and inner bays. These values can be applied to the rest if the lake and to other Andean lakes with similar basin characteristics.

Thus, this study aimed to identify temporal trends of sedimentation rates by means of a geochronological analysis (^{210}Pb, ^{137}Cs). In addition to identify metal concentrations in the projected timeline in order to propose, for the first-time, background values in Puno Bay.

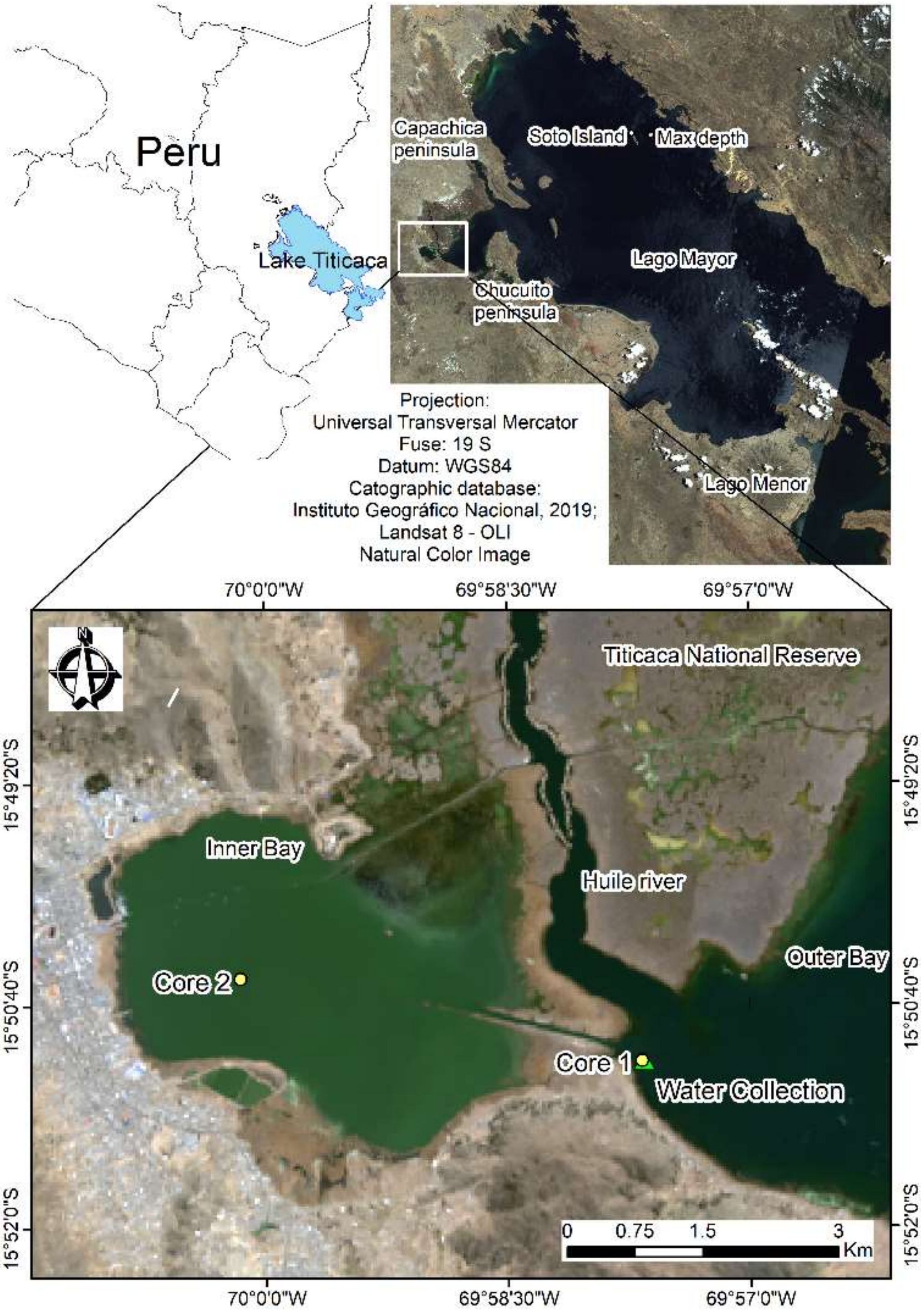
5.3. Study area

Lake Titicaca is one of the largest lakes in South America and it is the highest navigable lake in the world. This lake has experienced morphometric (LAVENU, 1992)and water level (LAVENU, 1995) transformations until it stabilized at 3810 m (LOZA DEL CARPIO *et al.*, 2016). Lake Titicaca has an area of 8,562 km^2, a maximum depth of 284 m, located near Soto Island and a mean depth of 105 m (GOYZUETA *et al.*, 2009; WIRRMANN, 1992). The Titicaca basin is divided in two sub-basins, Lake Chucuito or “Lago Grande” (where Puno Bay is located) in the north and Lake Huiñaimarca or “Lago Menor” in the south (Fig. 1).

The Titicaca basin is located in the Collao plateau, commonly known as "Altiplano" covering Peru and Bolivia. The basin is settled between the western and eastern Cordilleras in the central Andes. Its basement is made up by Paleozoic rock over them Mesozoic rocks (Jurassic and Cretaceous) appear, covered by a potent Cenozoic volcanic sequence (INGEMMET, 1995).

Puno Bay is located in the western margin of Lake Titicaca, connected to "Lago Mayor". It is delimited by the Capachica and Chucuito peninsulas in the east, the district of Chucuito in the south, the district of Puno in the west and The Titicaca National Reserve in the north (Fig. 1). Puno Bay is divided in two water bodies throughout an emergent macrophyte (*Schoenoplectus tatora*) wall, locally known as "Totora". The outer bay, located farther from the city of Puno and the inner bay, closer to the city.

Figure 1 – Lake Titicaca is located at the south east of Peru, in the department of Puno. The lake presents two major water bodies “Lago Mayor” and “Lago Menor”, this one located in the south of the lake. Maximum depth (284 m) is located near Soto Island at the northern part of the lake in “Lago Mayor”. Puno Bay appears at the west side of the lake delimited by the Capachica and Chucuito peninsulas. Inferior map: Sediment core stations located in the outer and inner bays. In the outer bay, appear the Titicaca National Reserve and Huile river, a tributary. Sediment cores = yellow dots; water collection point = green point. Scale (1:50,000).



Fonte: Autoria própria

The outer bay presents two main tributaries, Huile and Coata rivers. Huile river passes through the Uros floating islands and Coata river inlet is located in the north area. The last-mentioned river has been experimenting an increasing ecological pressure due to the activities in the watershed (mining, agriculture, cattle raising, etc.) (MATAMET; BONOTTO, 2019a). The raw water collection point is located in this area, collecting 300 liters per second, representing 93% of the total collected water. This water is subsequently transported, treated and distributed to the City of Puno. The collection point is located at 438 m, in straight line, from the shore.

The inner bay, due to its proximity with the city of Puno, receives the untreated sewage (domestic and industrial). The primary treatment (stabilization ponds), installed in 1972 (EMSAPUNO, 2021) when the population was 40,000 people (INEI, 1995), is still used nowadays not meeting the sanitary basic standards. These ponds are located almost inside the inner bay. The high nutrient loading turns the inner bay with a higher content of organic matter and triggers more frequent floating macrophytes blooms (*Lemna sp.*) (NORTHCOTE *et al.*, 1991). In addition, presents a high traffic of boats (diverse sizes) from and into the inner bay. Both bays (outer and inner) are interconnected through a channel that crosses the macrophyte wall, summed to the shallowness, the sediment has to be dredged periodically.

5.4. Material and methods

5.4.1. Sediment sampling

Sediment cores (triplicate) were collected with a gravity core sampler and an acrylic tube from two sites in Puno Bay, both georeferenced (WGS84, UTM 19S), on November 22nd, 2019. Core 1, located in the outer bay (15º51’0.06’’S 69º57’39.84’’W) approximately 30 m apart from the water collection point (Fig. 1), the sediment core was 48 cm length. Transparency, measured with a Secchi disk, was about 3 m and the water column depth reached 11.5 m (Tab 1.). Core 2, located in the inner bay (15º50’30.42’’S 70º0’9.12’’W) at 1.2 km from the city’s shoreline (Fig. 1), the sediment core was 45 cm length. Transparency was 0.45 m and water column depth reached 5 m (Tab. 1). The extracted sediment was sectioned into 3 cm intervals (subsamples), 16 and 15 subsamples per core were obtained for the outer and inner bays, respectively. These final samples were stored in sterile flasks kept into dark and transported in thermic bags.

Table 1 – Characteristics of the two bays, where water transparency and water column depth were taken before sediment core extraction.

Characteristics	Outer Bay	Inner Bay
Lat/Long	15º 51' 0.06"S 69º 57' 39.84"W	15º 50" 30.42"S 70º 0' 9.12"W
Secchi disk (m)	3	0.45
Water column depth (m)	11.5	5
Water surface area (km^2)	572.09**	15.91*
Maximum depth (m)	51***	7.19*
Trophic state	Mesotrophic****	Eutrophic*****

Fonte: Autoria própria
*(LOZA DEL CARPIO *et al.*, 2016); ** It is the difference between the area in (WIRRMANN, 1992) and (LOZA DEL CARPIO *et al.*, 2016); ***(WIRRMANN, 1992); ****(RICHERSON *et al.*, 1977); *****(NORTHCOTE *et al.*, 1991)

5.4.2. Geochronological analysis

Radiometric analysis

High resolution gamma spectrometry was the technique used to measure the levels of radionuclides in the sediment samples. Each sample was prepared following the same procedure. Between 4-10 g of dry sediment were ground into a fine powder, transferred to an air-sealed cylindrical polyethylene container, and counted for 70,000 s in a low-background hyperpure Ge gamma spectrometer (ORTEC, model GMX50P). This equipment has a mean resolution of 2,0 keV and a peak-to-Compton ratio of 62:1 for the 1332.51 keV 60Co photopeak. The method used in this study followed the guidelines of (Ferreira et al. 2015) and involved daily detector calibration, determination of counting efficiency, background radiation assessment, self-absorption correction, and the analysis of the 46.52 (^{210}Pb), 351.92 (^{226}Ra) and 661.67 (^{137}Cs) keV photopeaks. The quality of the results was ensured with measurement (n = 8) of certified reference materials IAEA326 (soil) and IAEA385 (marine sediment). The statistics of this quality control showed high precision and accuracy, with relative standards deviations and errors below 10% for all radionuclides of interest.

Unsupported ^{210}Pb model

The chronology of the sediment cores was established using an excess ^{210}Pb ($^{210}Pb_{xs}$) model. ^{210}Pb dating is based on the environmental difference between two different sources of this radionuclide: one atmospheric-originated, unsupported by the sedimentary matrix, and the other supported by the decay of ^{238}U decay products unable to escape the sedimentary matrix (ROBBINS; EDGINGTON, 1975). We used the CFCS (Constant Flux and Constant Sedimentation) model (KRISHNASWAMY *et al.*, 1971), an unsupported ^{210}Pb model that assumes two main premises: there is a constant flux of $^{210}Pb_{xs}$ to the sediments and there is a continuous sediment input to the system. Unsupported ^{210}Pb was estimated as the difference between total ^{210}Pb and ^{226}Ra. If the model assumptions are considered met, an exponential decay along with the depth should be observed in the vertical profile of unsupported $^{210}Pb_{xs}$. Equations 1 and 2 were used to calculate the mean sedimentation rate and the age-depth model, respectively.

$$\nu = -\frac{\lambda}{b} \qquad [1]$$

$$t = \frac{\nu}{z} \qquad [2]$$

In which: v = sedimentation rate, λ = ^{210}Pb decay constant, b = slope of the linear regression between ln $^{210}Pb_{xs}$ and z, t = age of the sediment layer at depth z.

5.4.3. Metal concentration in sediment

The sectioned samples were dried in an aeration oven at 60 ºC until a constant weight was reached then ground in a glass mortar and pestle. A partial digestion was applied following the SW 846 US EPA 3050B method (U.S.EPA, 1996). This process consists in an acid digestion, using HNO3 and HCl, which dissolves the environmentally available elements. Eleven metals were studied (As, Ba, Ca, Cr, Cu, K, Mg, Mo, Ni, Pb, Zn). The extracts form the digestion were stored at 4 ºC before its analysis by inductively coupled plasma optical spectrometry (ICP-OES). The accuracy and precision of the method were validated using a certified reference material (SS-2) from EnvironMAT™ CRM SPC Science. The results were between 75% and 125% which is a recommended range (U.S.EPA, 1996). All glassware items and equipment used for sample storage and processing were left in 10% nitric acid solution for at least 24 h, followed but rinsing with ultrapure water. Resulting data were expressed in milligrams per kilogram of dry weight (mg/kg).

5.4.4. Background values and enrichment factor

Background values were calculated considering the three deepest subsamples (layers), for the outer bay (42 – 48 cm) and in the inner bay (39 – 45 cm), the resulting mean concentrations were considered the background value. Background data was subsequently used to determine the enrichment factor (EF). The EF, first defined by Zoller et al. (1974), is based on the standardization of a studied element against its reference (background) value (LIU *et al.*, 2022; MARTINS *et al.*, 2021; SHAH *et al.*, 2021). This reference element is characterized due to its low variability, some common elements used for this purpose are Sc, V (KIM *et al.*, 2017), Fe, Al (CARDOSO-SILVA *et al.*, 2021), as well as Ca (LOSKA *et al.*, 2004). Since Ca is one of the principal components of the earth's crust and its potential use was confirmed by Loska et al. (2003). This study will use Ca as a normalizer element to calculate the metal enrichment in the sediment. A log-transformation was applied on Ca concentrations because it gives more realistic evaluation on the sediment contamination (LOSKA *et al.*, 2003). The EF was calculated according to the following equation:

$$EF = \frac{(M/X)_{sample}}{(M/X)_{background}} \quad (3)$$

Where M is the element of interest and X is the normalizer element (Ca). In this basis, five contamination classes are recognized to classify the enrichment factor (SUTHERLAND, 2000)

- EF < 2 depletion to minimal enrichment
- EF 2 – 5 moderate enrichment
- EF 5 – 20 significant enrichment
- EF 20 – 40 very high enrichment
- EF > 40 extremely enriched

5.4.5. Organic matter and granulometric analyses

To determine organic matter (OM), previously dried sediment was put in washed, dried and identified crucibles, calcinated at 550 ºC for 4 hours (HEIRI *et al.*, 2001). All crucibles were cooled in a pressured desiccator for at least two hours. Then ~0.5 g of dried sediment was weighted put in the crucibles and returned to the muffle for another 4 hours at 550 ºC, then cooled once more to finally be weighted. OM was calculated and expressed in percentage, being the difference between the pre calcinated weight (crucible and sediment) and the post-calcinated weight, considering the burned material as OM.

The granulometric assessment followed the steps mentioned in (MARTINS *et al.*, 2021), where a OM digestion with hydrogen peroxide solution (H_2O_2 10%, v/v) at 80 ºC for 16 to 40 h was performed. Samples were weighted to determine the granulometric composition the sediment passed through sieves, then classified according to its size, with the following categories, medium sand (> 0.212 mm), fine and very fine sand (< 0.212 - > 0.032 mm) and silt and clay (< 0.032 mm).

5.4.6. Statistics

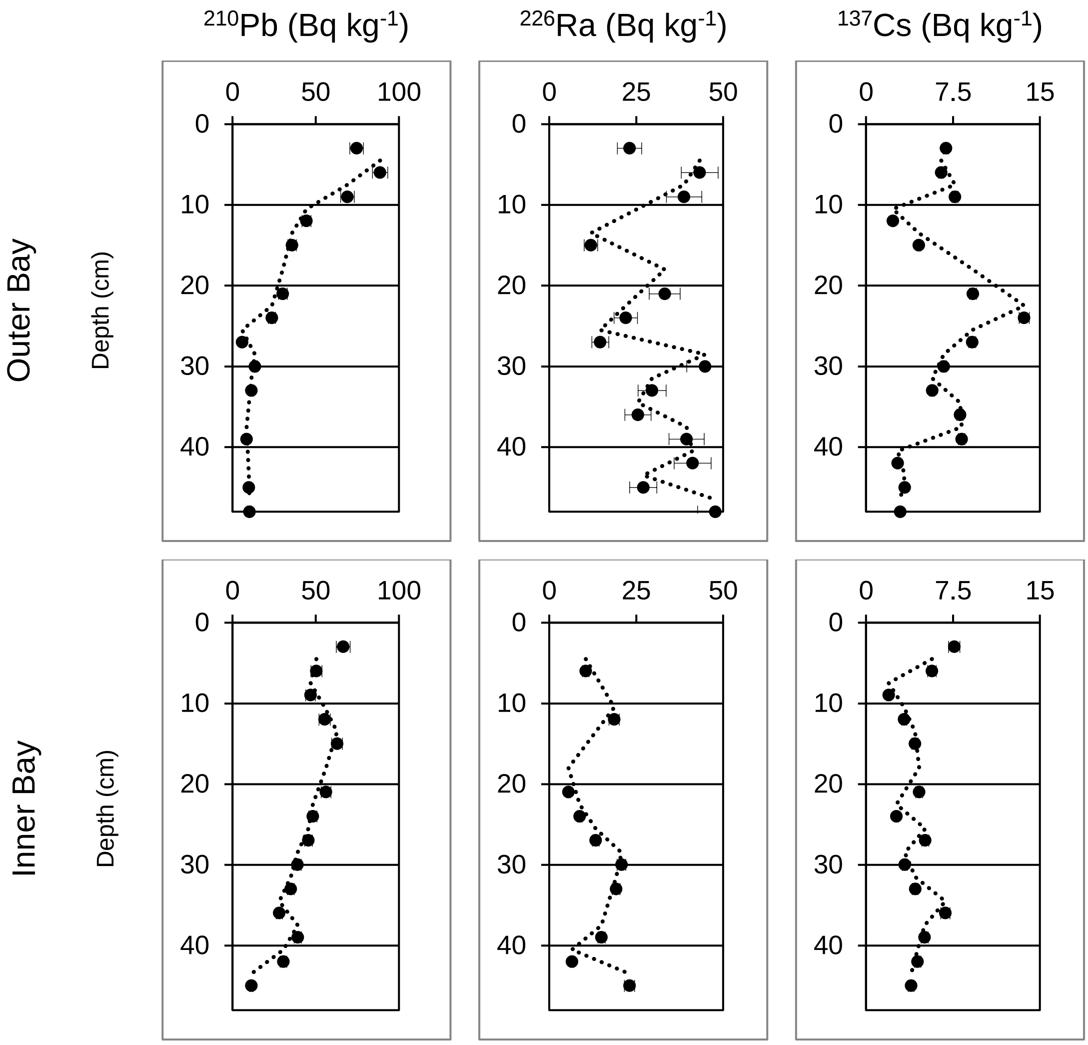
The Principal Component Analysis (PCA) was used to describe the characteristics among sampling sites regarding their correlation. PCA reduces all data set to a lower number of variables (usually the first two components), for plotting purposes. The graphical biplot correlation in the PCA was based on (LEGENDRE; LEGENDRE, 1998). A Spearman correlation was performed among all variables in the outer and inner ays ($p < 0.05$). The analysis was performed using a free statistical software Paleontological Statistics (PAST) Version 4.03.

5.5. Results

5.5.1. Geochronology

The results of the ^{210}Pb, ^{226}Ra and ^{137}Cs of the two sediment cores (outer and inner bays) are shown in Fig 2. The vertical profiles of ^{210}Pbexhibited a decay in the levels of this nuclide along with the depth, consistent with the CFCS premises.

Figure 2 – Levels of ^{210}Pb, ^{226}Ra and ^{137}Cs (Bq kg^{-1}) in sediment cores. Dashed lines = moving average; Dots = obtained value showing the error bars.



Fonte: Autoria própria

Both cores showed a layer with a maximum ^{137}Cs activity, at 24 cm in the outer bay and 36 cm in the inner bay. The higher levels of ^{137}Cs in the topmost samples of the cores can be attributed to unconsolidated sediments with high water content, since ^{137}Cs is a very soluble element. The dissimilarity between the ^{137}Cs and ^{226}Ra range levels may indicate different sediment sources (Tab 2).

Table 2 – Descriptive statistics, mean, median and range (minimum - maximum) for ^{210}Pb, ^{226}Ra, ^{137}Cs obtained values (in Bq kg^{-1}) in the sediment cores

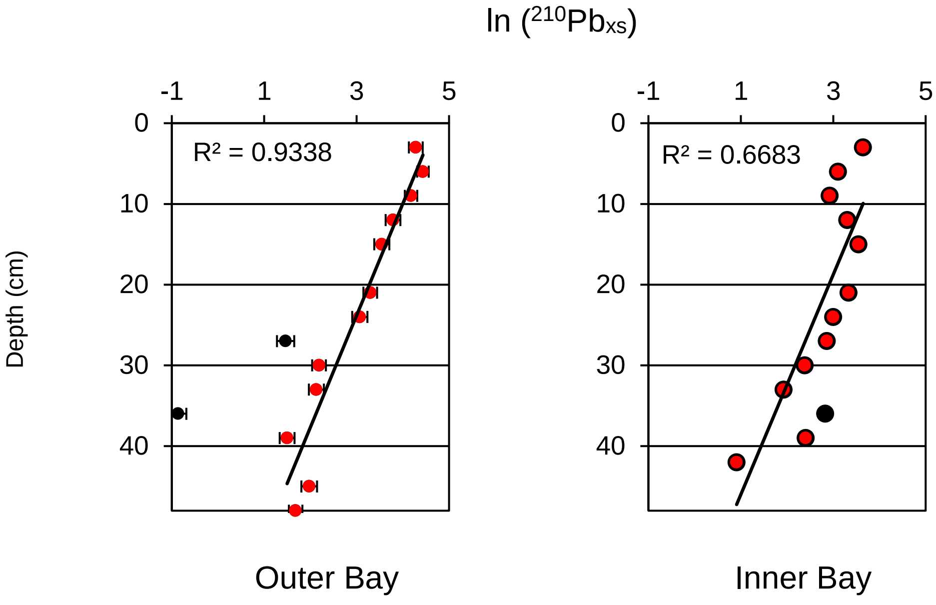
		Sediment cores	
Nuclide	**Value**	**Outer Bay**	**Inner Bay**
^{210}Pb	Mean (Median)	32.75 (23.73)	43.97 (46.26)
	Range	5.79 - 88.69	11.29 - 66.52
^{226}Ra	Mean (Median)	31.61 (31.39)	19.32 (15.06)
	Range	12.00 - 47.79	5.52 - 70.95
^{137}Cs	Mean (Median)	6.52 (6.71)	4.50 (4.35)
	Range	2.32 - 13.65	1.96 - 7.61

Fonte: Autoria própria

The age model created based on CFCS model for the outer bay core showed that the sediments at 27 cm layer were deposited in 1963, and it is consistent with the global fallout peak observed in this core. This same scenario is observed in the inner bay core where ^{137}Cs maximum activity is presented at 36 cm, while the CFCS model shows the same depth.

According to the Constant Flux Constant Sedimentation (CFCS) model applied and the resulting $^{210}Pb_{xs}$ outcome (Fig 3). The calculated SR for the outer bay is 0.48 cm a^{-1}, while in the inner bay is 0.64 cm a^{-1}. There is a notorious sedimentation increase in both bays, since 1967 (outer bay) and 1948 (inner bay).

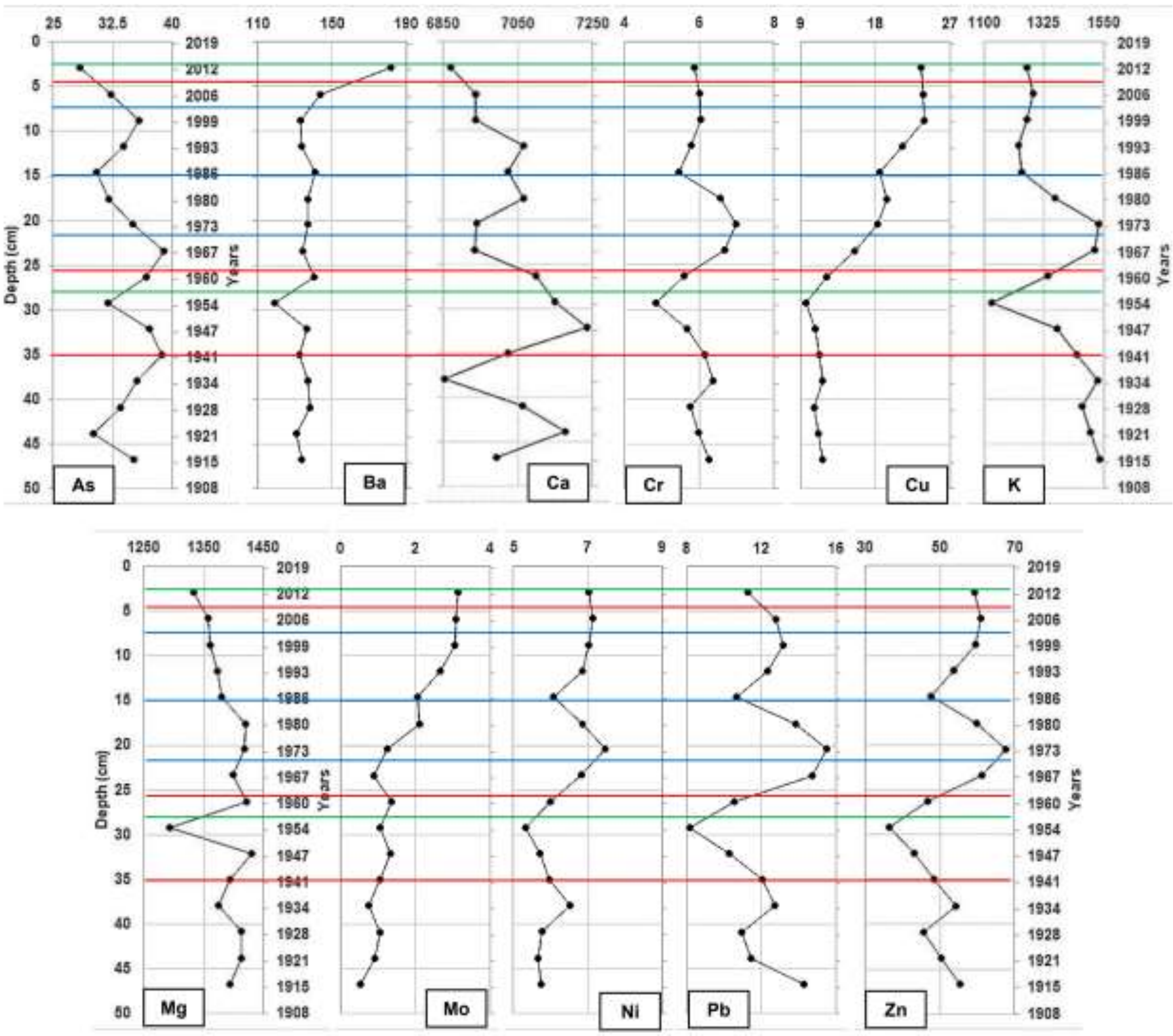
Figure 3 – ^{210}Pb excess ($^{210}Pb_{xs}$) in the sediment cores. Red dots = selected points for regression analysis; black dots = calculated point but not used in the regression; black lines = show the linear regression slope with respective R-square index, for the both bays (outer and inner).



5.5.2. Metal concentration, background values and enrichment factor

Metal content calculated at every 3 cm interval in the outer bay is shown in Fig 4. In the outer bay, there are some particular variations along the assessed period, but none of them present major changes. This suggests that the aquatic ecosystem has not experienced meaningful impacts. As, Ca, K, Mg, Pb and Zn present, in their timeline, high concentrations followed by abrupt falls, some of them before the 1950's (As, Ca, K and Mg). There is a group of elements that particularly show high concentrations in the 1970's (Cr, K, Ni, Pb and Zn). Finally, there are three metals that have experienced a constant increase in their concentrations up to superficial layers (Ba, Cu and Mo).

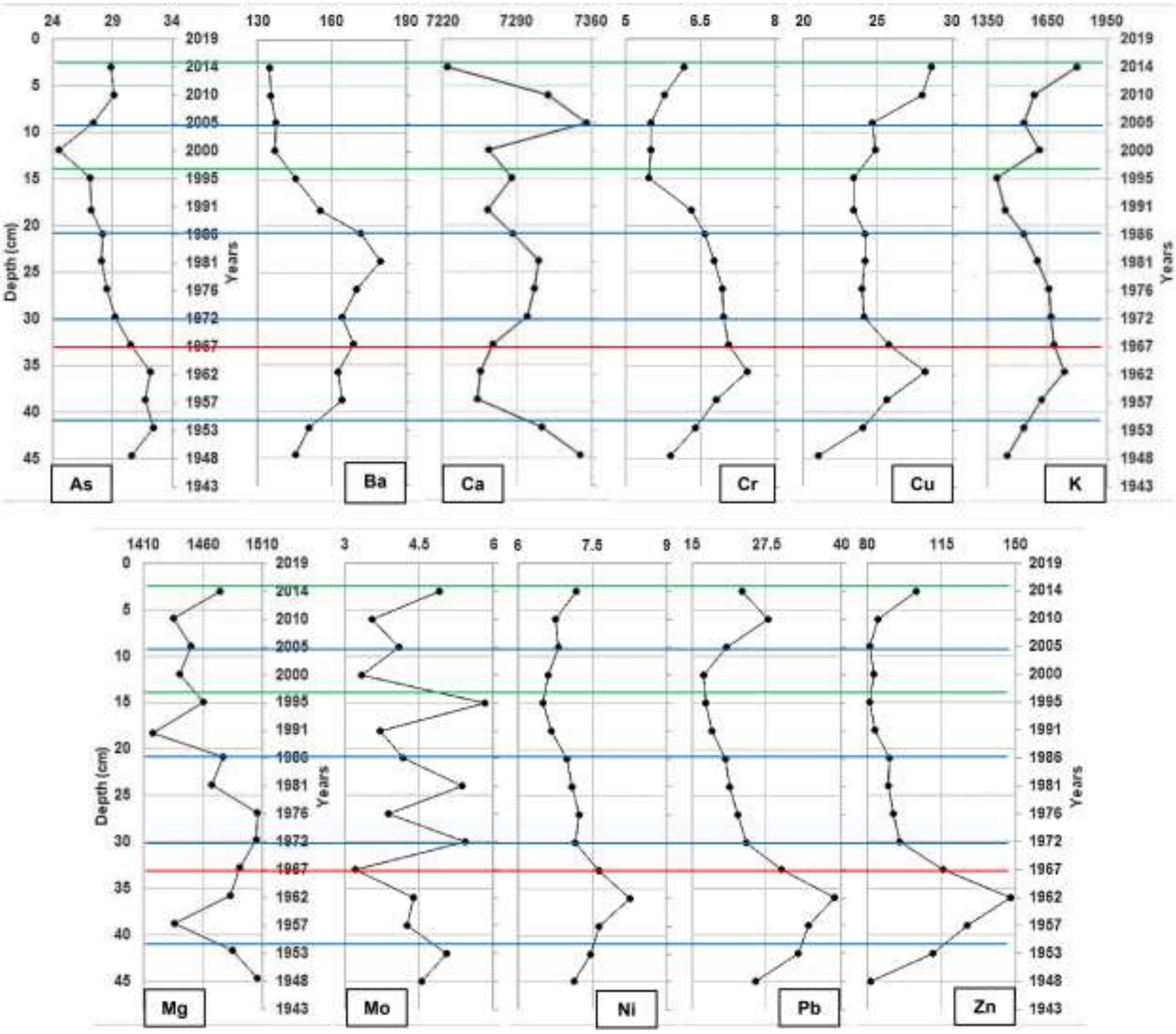
Figure 4 – Metal concentrations (mg/kg) distributed along the sediment cores collected in the outer bay. Left bar = sediment depth (cm), upper bar = concentration values; right bar = year projection according $^{210}Pb_{xs}$. Red line = refers to low rainfall or drought event for the reported year; Blue line = refers to high rainfall or flood event for the reported year; Green line = El Niño Southern Oscillation (ENSO) event for the reported year.



Fonte: Autoria própria

In the inner bay (Fig. 5), as seen in the outer bay there are no important fluctuations on the metal concentrations. However, some metal concentrations became lower along the years (As, Ba, Ca and Pb). Some metals showed their highest content in the timeline in the 1920's and experiencing a sustained concentration fall (Cr, Cu, K, Ni, Pb and Zn). From this last-mentioned group Cr, K, Ni, Pb and Zn demonstrated a similar pattern in the outer bay as well but in a different interval of time. Finally, two metals showed a constant increment since the late 1970’s (Cu and K).

Figure 5 – Metal concentrations (mg/kg) distributed along the sediment cores collected in the outer bay. Left bar = sediment depth (cm), upper bar = concentration values; right bar = year projection according $^{210}Pb_{xs}$. Red line = refers to low rainfall or drought event for the reported year; Blue line = refers to high rainfall or flood event for the reported year; Green line = El Niño Southern Oscillation (ENSO) event for the reported year.



Background values proposed for each metal are presented in Tab 3. Which is the mean content calculated from the three deepest sub samples (layers) in each sediment core (outer and inner bays).

Table 3 – Background values proposed for metals (mg/kg) in the outer and inner bays. Mean and standard deviation

Metal	Outer Bay	Inner Bay
As	32.91 ± 2.44	31.62 ± 3.87
Ba	134.09 ± 5.94	153.49 ± 14.29
Ca	7077.51 ± 299.61	7305.20 ± 65.93
Cr	6.00 ± 0.45	6.37 ± 0.8
Cu	11.11 ± 0.96	23.56 ± 4.16
K	1502.95 ± 115.21	1533.95 ± 119.95
Mg	1407.31 ± 20.75	1475.63 ± 48.22
Mo	0.83 ± 0.22	4.62 ± 2.03
Ni	5.74 ± 0.45	7.41 ± 0.77
Pb	12.24 ± 1.49	31.04 ± 6.85
Zn	50.52 ± 6.29	106.57 ± 31.27

Fonte: Autoria própria

The EFs (Tab. 4) for the outer bay, each metal mean values (all of them < 2) indicate a minimal enrichment. Nevertheless, looking carefully each layer value, two metals (Cu and Mo) show higher values mainly in the superficial layers. Cu, in the nine first centimeters present EF values higher than 2 (moderate enrichment). Mo, up to 18 cm, shows EF values varying from 3.7 – 2.5 indicating a moderate pollution. On the other hand, the EF calculated for the inner bay indicates a minimal enrichment for all the metals assessed.

Table 4 – Mean enrichment factor (EFs) for sediment in the outer and inner bays. All values show minimal enrichment (< 2) for Puno Bay

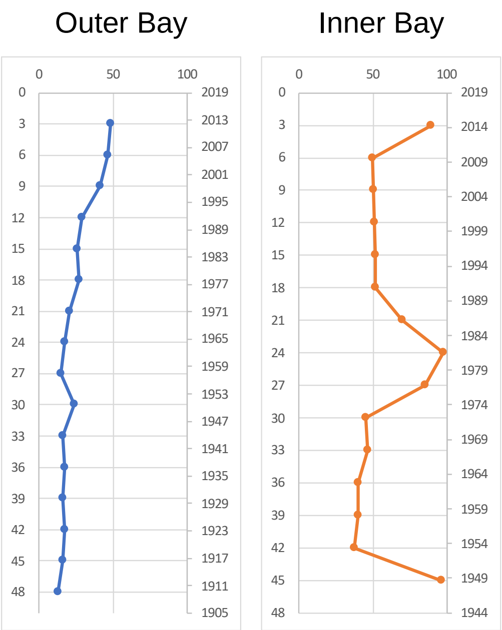
Metal	Outer Bay	Inner Bay
As	1.04 ± 0.09	0.92 ± 0.07
Ba	1.03 ± 0.10	1.01 ± 0.10
K	0.92 ± 0.09	1.04 ± 0.08
Cr	1.00 ± 0.09	1.00 ± 0.10
Cu	1.42 ± 0.48	1.06 ± 0.09
Mg	0.99 ± 0.03	1.00 ± 0.02
Mo	1.98 ± 1.09	0.95 ± 0.17
Ni	1.11 ± 0.12	0.96 ± 0.06
Pb	1.00 ± 0.16	0.81 ± 0.21
Zn	1.05 ± 0.16	0.92 ± 0.18

Fonte: Autoria própria

5.5.3. Organic matter and granulometry

The organic matter analysis (Fig. 6) exposes a decreasing pattern, with a slight increase at 30 cm for the outer bay. On the contrary, the inner bay does not exist an apparent pattern, with high percentages in the superficial layer and even higher values in intermediate (24 cm) and the deepest level (45 cm).

Figure 6 – Organic matter percentage presented at each layer of the sediment profile according to years observed. Blue presents data from the outer bay and orange displays percentages in the inner bay.



Fonte: Autoria própria

The granulometry (Fig. 7) evidences that both environments are dominated by medium sand. The outer bay presents an increase of fine and very fine sand while approaching deeper layers, while silt and clay portions remain similar along the sediment column.

Figure 7 – Granulometric analysis presented in percentages according to the sediment profile observed. Where: Medium sand (green), Fine and very fine sand (blue) and Silt/clay (orange)

Fonte: Autoria própria

5.5.4. Correlation

Significative Spearman correlations (r > 0.5) were observed in the outer bay among metals, suggesting a similar source, between metals and silt and clay fractions (Tab. 5), an important binding phase that retains metals in sediment. Nevertheless, It has been observed a lower correlation between metals and OM.

Table 5 – Spearman correlation among metals, organic matter (OM) and grain size: medium sand (MS), fine and very fine sand (FS) and silt and clay (SC) for the outer bay, in bold, correlations r > 0.5

	As	Ba	Ca	K	Cr	Cu	Mg	Mo	Ni	Pb	Zn	OM	MS	FS	SC
As	0.000														
Ba	0.327	0.000													
Ca	**0.699**	0.172	0.000												
K	0.148	**0.715**	0.362	0.000											
Cr	0.206	**0.724**	0.030	0.009	0.000										
Cu	**0.608**	0.088	0.034	0.202	0.269	0.000									
Mg	0.154	**0.882**	0.077	0.049	**0.516**	0.190	0.000								
Mo	0.245	0.051	**0.785**	0.008	0.362	0.004	0.344	0.000							
Ni	**0.964**	0.060	0.012	**0.758**	0.050	0.001	0.432	0.017	0.000						
Pb	0.344	**0.811**	0.025	0.040	0.000	0.068	**0.900**	**0.682**	0.017	0.000					
Zn	**0.829**	**0.459**	0.009	0.206	0.001	0.007	**0.724**	0.459	0.002	0.000	0.000				
OM	0.121	0.236	0.142	0.013	**0.973**	0.004	0.017	0.003	0.007	**0.577**	0.113	0.000			
MS	0.106	0.327	**0.964**	0.020	**0.616**	0.012	0.350	0.001	0.056	**0.846**	0.459	0.003	0.000		
FS	0.106	0.327	**0.964**	0.020	**0.616**	0.012	0.350	0.001	0.056	**0.846**	0.459	0.003	0.000	0.000	
SC	0.269	**0.820**	**0.592**	**0.733**	0.356	0.339	0.020	**0.657**	0.406	0.316	0.374	**0.699**	**0.509**	**0.509**	0.000

Fonte: Autoria própria

Important correlations were observed in the inner bay (Tab. 6) among metals indicating a similar origin. Organic matter and silt and clay phases turned out to be more relevant, this can be related to their characteristic for retaining metals.

Table 6 – Spearman correlation among metals, organic matter (OM) and grain size: medium sand (MS), fine and very fine sand (FS) and silt and clay (SC) for the inner bay, in bold, correlations r > 0.5

	As	Ba	Ca	K	Cr	Cu	Mg	Mo	Ni	Pb	Zn	OM	MS	FS	SC
As	0.000														
Ba	**0.557**	0.000													
Ca	**0.989**	**0.979**	0.000												
K	0.190	**0.557**	0.071	0.000											
Cr	0.027	0.006	0.310	0.018	0.000										
Cu	0.392	0.378	0.118	0.007	0.438	0.000									
Mg	0.073	0.145	0.343	0.297	0.073	0.371	0.000								
Mo	**0.539**	**0.759**	**0.800**	**0.621**	**0.989**	0.273	0.285	0.000							
Ni	0.002	0.145	0.371	0.014	0.002	0.181	0.041	**0.852**	0.000						
Pb	0.000	**0.659**	**0.862**	0.098	0.023	0.145	0.219	**0.820**	0.002	0.000					
Zn	0.006	0.157	0.054	0.008	0.002	0.061	0.285	**0.904**	0.001	0.005	0.000				
OM	0.048	**0.831**	**0.575**	**0.513**	0.240	0.240	**0.659**	**0.659**	0.128	0.033	0.054	0.000			
MS	0.044	0.053	**0.841**	**0.936**	0.430	0.240	**0.852**	0.364	0.310	0.080	**0.504**	0.267	0.000		
FS	0.044	0.053	**0.841**	**0.936**	0.430	0.240	**0.852**	0.364	0.310	0.080	**0.504**	0.267	0.000	0.000	
SC	**0.748**	0.001	0.454	0.407	0.021	**0.602**	**0.612**	0.407	0.350	**0.894**	0.316	**0.630**	0.007	0.007	0.000

Fonte: Autoria própria

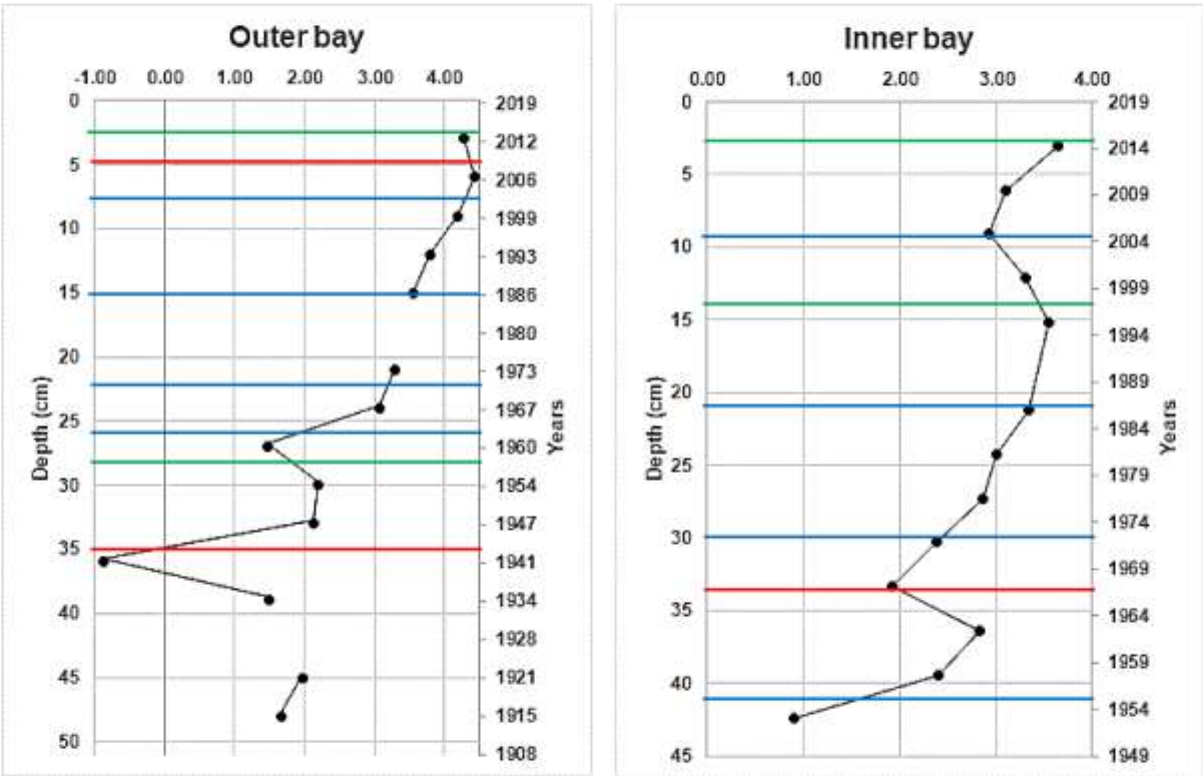
5.6. Discussion

Based on the radionuclides analyzed, there is an evident difference between the bays. It has been noticed that ^{210}Pb profile, for the inner bay, presents more variations along the calculated values than the exponential decay presented in the outer bay. Those higher fluctuations can be related to sedimentation processes intensity along the period studied (BONOTTO *et al.*, 2022; CARDOSO NERY; BONOTTO, 2022) and it is possible to infer that, different events (natural or artificial) affected each water body. The horizon with maximum ^{137}Cs activity supports the previously mentioned differences about the sedimentation processes. In the inner bay, the ^{137}Cs maximum fallout occurs at a similar depth than the calculated with ^{210}Pb (36 cm). The collected sediment core length in both bays were similar, but the projection obtained shows a clear difference in the years calculated. These differences can be related to organic matter distribution or the grain size along the profile (BOULANGÉ *et al.*, 1981; FONTANA *et al.*, 2022; RODRIGO; WIRRMANN, 1992). It is possible to state that, man-made residuals from different activities since rural to urban areas migration (INEI, 1995) had a higher impact in the inner bay. The basin's geochemical composition is another relevant factor to differentiate these water bodies and future paleolimnological will better clarify and unveil this relation.

Focusing on the outer bay, the sedimentation rate (SR), indicates that the sedimentation process was constant along the profile. Even though, some outliers were removed to calculate the unsupported $^{210}Pb_{xs}$, to calculate the regression slope. We have to consider that the outliers represent years where severe drought events took place, and the natural sedimentation process was altered. Finally, it is possible to state that, the high $^{210}Pb_{sx}$ correlation, reinforced with the ^{137}Cs maximum fallout (~1963), indicate that the projected years are solid.

On the other hand, the inner bay does not show a constant SR throughout the profile. The linear correlation is lower than in the outer bay, implying that the model detected differences in sedimentation dynamics, therefore, the range of years calculated was lower than in the outer bay. The maximum ^{137}Cs activity and ^{210}Pb projection are located in deeper horizon (36 cm), indicating a higher sedimentation rate in comparison to the outer bay profile. These variations can be related to anthropic activities due to its proximity to an urban area (city of Puno). Due to this phenomenon and even that similar sediment cores had been collected, the calculated years range in the inner bay was shorter.

Figure 8. ^{210}Pb excess ($^{210}Pb_{xs}$) in the sediment cores collected in the outer and inner bays. Left bar = sediment depth (cm), upper bar = $^{210}Pb_{xs}$ values; right bar = year projection according $^{210}Pb_{xs}$. Red line = refers to low rainfall or drought event for the reported year; Blue line = refers to high rainfall or flood event for the reported year; Green line = El Niño Southern Oscillation (ENSO) event for the reported year.



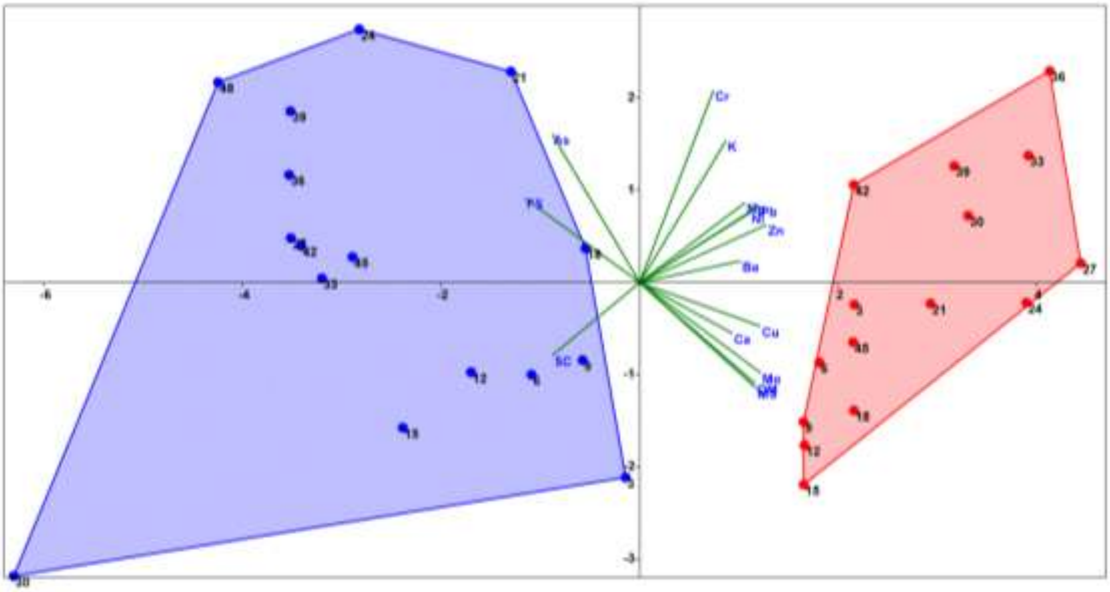
Some climatic events are the main factor that influenced sedimentation rate in the outer bay (Fig. 8). An important climatic event, which happens periodically, is El Niño Southern Oscillation (ENSO). This provokes severe and prolonged rainless seasons in the Altiplano affecting water availability for drinking water supply and agriculture (LAVADO CASIMIRO *et al.*, 2012; SENAMHI, 2022a). Droughts, as the one happened in 1943-44, which according to historical data the lake's water level fell up to 3806.21 m. (ESPINO *et al.*, 2018; ROCHE *et al.*, 1992; RONCHAIL *et al.*, 2014). This event is recognizable in the sediment profile, at 36 cm projected as the period between 1941-48 the SR appears to be not constant. Following the timeline in the late 1950's and beginning of the 1960's the SR falls once more, this can be related to another historical low level of the lake (3808.53 m) and also correlated to El Niño event in 1957 (NOAA, 2022). In contrast a flood occurrence took place during 1986 when the water level reached 3812.58 m (ESPINO *et al.*, 2018), nevertheless, it did not affect the sedimentation process. Finally, it is distinguishable that the upper layers 2006 up to 2019 there is fall in the sedimentation, this can be related to another El Niño event in 2015-16 provoking droughts in the south of Peru (NOAA, 2022).

In the inner bay the SR can be related to both climatic and anthropogenic source events along the projected period. The first observable event happens in the interval 1948 to 1958 where a SR increase occurred, this can be influenced by high precipitation reflected in a higher lake level registered in 1955 (RONCHAIL *et al.*, 2014; SENAMHI, 2014). It is possible to correlate this to the severe drought of 1943 which triggered a massive migration from rural to urban areas, using more water than before which entered to the lake as well. This is corroborated when comparing the 1940 and 1961 censuses, where urban areas population almost doubled in that period (INEI 1995). The city of Puno at that moment did not have a sewage treatment system until 1972 (EMSAPUNO, 2012), therefore all domestic and industrial waste entered directly to the inner bay. The drinking water and sanitation agency (EMSAPUNO) installed a basic treatment system (stabilization ponds), when population was of 40,000 people (INEI, 1995), and covered just the 40-45% of the population. Continuing in the timeline there is a decrease in SR from 1962 to 1967, this rate can be related to lower precipitation and a drought registered in 1966 to 1967 (SENAMHI, 2022b). Later it is seen an increment in the period from 1967 to 1972 due to precipitation and the end of the drought. The big flood event (1986) can also be seen in the period of 1986 to 1995 showing an increment in the SR. During this phenomenon the stabilization ponds where completely covered and the raw sewage run to the inner bay without any treatment. In the 1990’s a very intense El Niño event took place (1997-98) resulted in a drought in the Altiplano (NOAA, 2022; SENAMHI, 2022a), this is perceivable in the timeline from 1995 to 2005 where the SR falls. Then the SR increases again in the period of 2005 to 2010. The inefficient system (stabilization ponds) is still being employed to treat the sewage generated from 129,922 people (INEI, 2022). In addition, since the inner bay presents a low depth and boat traffic, due to tourism, the main channel that links the inner to the outer bay is dredged, permitting sediment re-suspension occurrences consequently altering the natural sedimentation dynamics.

The calculated background values (Cr, Cu, Ni, Pb, Zn), for both, the outer and inner bays are below threshold values for the applied sediment quality guidelines (SQGs) (CCME, 1999; MACDONALD *et al.*, 2000). In a comparison between the bays, the proposed values for the inner bay are higher than the ones proposed for the outer bay. This occurrence may be related to its proximity to the urban area, as well as the lack of a suitable sewage treatment.

It is clearly observable that As is the metal with high presence in Puno Bay. These high concentrations, even at lower depths, resulted in proposed background values over the threshold concentrations and even probable effect levels (CCME, 1999). The applied Principal Component Analysis (Fig. 7) shows the difference between the bay. The inner bay presents a higher correlation to OM and metals such as, Cr, Ni, Cu, Pb and Zn. However, the outer bay is related to As and granulometric characters as fine and very fine sand, and silt/clay.

Figure 9 – The Principal Component Analysis (PCA) for the mean values of all variables considered. Blue dots = outer bay variables, red dots = inner bay variables, organic matter (OM), medium sand (MS), fine and very fine sand (FS), silt and clay (SC).



Fonte: Autoria própria

To address the concern about the potential sources of these metals, enrichment factor has demonstrated its natural origin, when observing mean values. Even though As presents elevated concentrations, higher than some SQGs, the calculated enrichment indicates that the source is geogenic. The Titicaca basin geochemistry is the main source of arsenic accumulated in the lake, on the other hand it is important to characterize it, to recognize the predominant oxidation state in the sediment. It did not escape to our observation that in the outer bay Cu and Mo have experienced an unusual enrichment (moderate) since late 1980’s. This may be related to the water collection point that started the catchment of raw water sin 1989 (EMSAPUNO, 2012). This is not related to the water point itself but it might be related to the materials that the pipes are made. Cu and Mo are used in steel manufacture, e.g., water pipes. There is a high probability that the higher enrichment of these metals is connected to the devices used in the water collection.

Table 7 – Sedimentation rate outcomes comparison among different areas in Lake Titicaca and other high-altitude lakes around the world

Lake	Country	Altitude (m)	SR (cm.a^{-1})	Characteristics	Reference
Outer Bay - Puno Bay	Peru	3808.56*	0.48	Mesotrophic**	This study
Inner Bay - Puno Bay	Peru	3808.56*	0.64	Eutrophic***	This study
Inner Bay - Puno Bay	Peru	3810	0.41	Eutrophic***	Loza del Carpio et al. 2016
Lago Menor	Bolivia	3808	0.5	Eutrophic	Boulangé et al. 1981
Lago Mayor	Bolivia	3808	0.05	Oligotrophic	Boulangé et al. 1981
Lago Menor	Bolivia	3808	0.02	Eutrophic	Rodrigo and Wirrmann 1992
Lago Menor	Bolivia	3810	0.10 – 0.22	Eutrophic	Binford et al. 1992
Chandratal	India	4300	1.49 ± 0.04 2.71 ± 0.1	Ramsar site	Rout and Vasudevan 2022
Satopanth	India	4600	0.79 ± 0.04	Glacial origin	Das and Vasudevan 2021
Lake Naini	India	1937	0.48 ± 0.4	Drinking water	Saravana Kumar et al. 1999
Lake Sils	Switzerland	1800	0.06	Oligotrophic	Blass et al. 2005
San Pablo	Ecuador	2660	0.35	Eutrophic	Gunkel 2003
Gokyo lake (4th lake)	Nepal	4700 - 5000	0.083	Ramsar site	Sharma et al. 2012
Lake Garba Guracha	Ethiopy	3950	0.095	Glacial origin	Tiercelin et al. 2008

*(IMARPE, 2019); **(RICHERSON *et al.*, 1992); ***(NORTHCOTE *et al.*, 1991)
Fonte: Autoria própria

So far, Puno Bay itself has been the focus of the discussion, however, the lake is bigger than just this portion. The sedimentation process approach must consider the watershed. Human activities (land use, untreated sewage release, agriculture, cattle raising, deforestation, mining) developed within some sub-basins have impacted in water bodies (rivers, lakes, lagoons, springs) (Matamet and Bonotto, 2019a). Coata River is an important affluent, which is impacted by human activities along its course (upper, medium and lower basin). Coata river flows into the northern area of Puno Bay (near the Capachica peninsula), Matamet and Bonotto (2019a) reported sedimentation rates of 0.28 cm a^{-1} and 0.66 cm a^{-1} in the upper and lower basin of the river, respectively. Another important river is Ramis, that, as happens in Coata river, presents mining activities in the upper basin releasing high quantities of mercury to the river (BROUSETT-MINAYA *et al.*, 2021; LOZA DEL CARPIO; CCANCAPA SALCEDO, 2020; SALAS MERCADO, 2017). Matamet and Bonotto (2019b) have reported sedimentation rates of 0.15 cm a^{-1} and 0.31 cm a^{-1} for the upper and lower basin, respectively. Lower basin SR in Coata river is similar to the inner bay values, this can be related to raw sewage release into the river when it crosses Juliaca, another important city with approximately 250,000 habitants.

The Bolivian side of the lake has presented some differences with the data presented in this study (Peruvian side). Boulangé et al. (1981) describe a sedimentation rate of 0.05 cm a^{-1} in “Lago Mayor”, whereas, a ten times higher value for “Lago Menor”. Binford et al. (1992) have reported in “Lago Menor”, from a core located in the south, values that are similar to the ones presented in this study. The difference is about the sampling location, that was settled near emergent macrophytes. In addition, Rodrigo and Wirrmann (1992) mention 0.02 cm a^{-1} for organo-detrital facies. The inner bay, as mentioned by Loza del Carpio et al. (2016) has a detrital behavior, therefore, the study reported a sedimentation rate of 0.41 cm a^{-1} lower than this study but similar with the values in “Lago Menor”.

In an international context (Tab. 7), Puno Bay compared to glacial origin lakes, such as Chandratal lake (ROUT; VASUDEVAN, 2022) or Satopanth (DAS; VASUDEVAN, 2021), the Himalayan lakes are characterized by higher sedimentation rates. The reason is that both glacial lakes experience ice melt event that carry on higher amounts of sediment. Another factor is the morphometry because when comparing Puno Bay to other glacial lakes Gokyo lake (SHARMA *et al.*, 2012) and Lake Garba Guracha (TIERCELIN *et al.*, 2008), Puno Bay presents higher sedimentation rates. Taking into account the altitude, Puno Bay presents similar values as seen in Lake Naini (SARAVANA KUMAR *et al.*, 1999) but differs from the values in Lake Sils (BLASS *et al.*, 2005). The geochemistry in the basin plays a main role, in the case of Lake Naini the watershed has principally carbonated rocks (more susceptible to weathering), whereas, Lake Sils basin is dominated by clastic rocks influencing the sedimentation process. Finally, compared to another Andean lake (San Pablo) (GUNKEL, 2003), it is clearly seen that the sedimentation rates are similar, not just because of the geology but similar climatic events.

5.5. **Conclusions**

The sediment geochronology in Puno Bay obtained applying ^{210}Pb allowed the quantification of sedimentation rates in the outer and inner bays using the CFCS model. The result permitted to correlate some climatic aspects (outer bay) and human activities (inner bay) to these sedimentation rates since the beginning of the 20^{th} century. In the outer bay sedimentation trends are linked to drought events (1943-1944) and El Niño phenomenon (1957). The inner bay, aside climatic events such as flooding, urban population growth and other human activities gained importance.

With regard to metal analysis in the sediment profile, these permitted to establish, for the first time, background values for Puno Bay. Enrichment factors and sediment quality guidelines values showed that there are no significative impacts in both bays. Just Arsenic demonstrated values above probable effect values. However, analyzing the sediment profile results the values are constant along the projected years, inferring a geogenic accumulation. The drinking water agency must take actions about the Cu and Mo increment in the surroundings of the collection point. In sum, the results presented in this study provide valuable data to decision makers for future management plans to maintain or recover these aquatic ecosystems. As well as contributing chronological information for future paleolimnological studies in these ecosystems.

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CAPÍTULO 6

Analise comparativa entre os ambientes aquáticos brasileiros e peruanos

6.1. Introdução

Os corpos lacustres e de transição funcionam como sumidouros, recebendo os despejos de todas as atividades dentro de uma bacia hidrográfica. As fontes podem ser de origem natural, causadas pela erosão, intemperismo, chuva, etc. ou provenientes de fontes artificias (antropogênicas). As partículas resultantes são transportadas até os ambientes previamente mencionados onde se acumulam no sedimento. Devido a essa característica, o sedimento torna-se uma fonte potencial de metais, já que estes não permanecem completamente retidos neste compartimento. Dependendo das condições químicas do ambiente e de fenômenos como a ressuspensão do sedimento por bioturbação ou dragagem, os metais podem ser liberados à coluna de água e causar efeitos adversos às comunidades biológicas e à saúde pública.

A poluição por este tipo de agentes é difícil de observar, somado a que basta um curto período para impactar o ecossistema. Deste modo, as concentrações dos metais devem ser monitoradas periodicamente, em todos os ambientes, particularmente naqueles destinados ao abastecimento público. Esse monitoramento deve abranger uma visão completa do corpo de água para detectar mudanças espaço-temporais. Estas informações primordiais aos tomadores de decisões, para propor melhores planos de conservação ou de recuperação.

Os ambientes analisados em capítulos anteriores demostram que as há uma intervenção das atividades humanas que interferem com o equilíbrio do ecossistema aquático. Principalmente, são os efluentes domésticos e industriais que causam o desequilíbrio e que provoca florações que afetam o processo de abastecimento de água. Observou-se que a carência de uma abordagem de solução das fontes primarias de poluição provoca uma aplicação de paliativos temporais. Os ambientes que ficam em áreas de conservação, embora apresentem teores de metais abaixo dos limiares de poluição, demostraram que houve um incremento em relação a seus valores de referência.

O intuito deste capitulo é comparar criticamente os ambientes brasileiros (reservatório Rio Grande, Itupararanga e Paiva Castro) com o peruano (Baía de Puno, baía interna e externa do Lago Titicaca).

6.2. Análise

Num primeiro instante, é plausível pensar que os ambientes aquáticos envolvidos nesta pesquisa não têm relação alguma. Podemos partir do ponto de vista espacial, os quatro ambientes encontram-se na região tropical do planeta. A clara diferença fica no aspecto das altitudes, enquanto que os ambientes brasileiros localizam-se em altitudes que variam entre os 750 a 800 m, o Lago Titicaca, em especial a Baía de Puno fica nos 3810 m. Desde a perspectiva da produtividade primaria, trabalhos prévios mostraram que o Lago mostra uma produtividade similar a outros lagos tropicais, mas a temperatura média é muito mais parecida com a dos lagos temperados. Também devemos salientar que os corpos hídricos brasileiros são todos de transição, construídos com fins diversos, como para a geração de energia e o abastecimento para consumo humano, por exemplo, em contraste com o Lago Titicaca, um lago natural de altitude.

Contudo, o comum denominador em ambos os países é o incremento dos impactos gerados, principalmente, por fontes derivadas das atividades humanas. No caso brasileiro, o desmatamento, a indústria, a agricultura, o crescimento urbano e populacional, a falta de um sistema de tratamento de despejos municipais, foram aspectos observados nas bacias dos reservatórios. Toda essa pressão ambiental fez que os processos ecológicos, principalmente aqueles relacionados à acumulação de metais sejam alterados. Para o caso peruano, a bacia do Titicaca, também apresenta impactos gerados pelas atividades humanas, principalmente a exploração mineral. A região de mineração, localizada a montante, ao não aplicar técnicas adequadas contamina o rio, que somado à falta de um tratamento adequado do esgoto municipal, potencializam os impactos ao lago. Além disso, existem pequenos povoados instalados dentro do próprio lago, em ilhas naturais e outros em ilhas artificias (Ilhas flutuantes dos Uros) que também contribuem para degradar o ecossistema.

A análise de metais no sedimento indicou que o metal de importância nos ambientes brasileiros é o cobre (Cu). O Cu é empregado em grande quantidade para o controle de florações de algas e vem sendo aplicado desde a década de 1980, principalmente no braço Rio Grande da Billings. Deste modo, este metal se apresenta com concentrações muito cima dos valores do potencial tóxico, segundo os guias de qualidade do sedimento (SQGs) como o PEL (*Probable Effect Level*). No reservatório Paiva Castro também já se observa concentrações acima do TEL (*Threshold Effect Level*), que segundo os guias, o potencial toxico é incerto. Já para o reservatório Itupararanga, localizado em numa Área de Proteção Ambiental, a presença deste metal, mesmo ficando por baixo do TEL mostrou incrementos comparados aos anos anteriores. Estas observações foram corroboradas pelo fator de enriquecimento, indicando fontes artificias nos reservatórios Rio Grande e Paiva Castro e fontes naturais na maior parte do sedimento do reservatório Itupararanga.

Numa forma análoga, na Baía de Puno o metal de relevância foi o arsênio (As), tanto na baía externa quanto na interna. Em média os valores de ambas as baías ficaram acima do TEL, indicando um efeito tóxico potencial no ambiente. Num primeiro momento indicamos que a acumulação deste metal era da mesma formação geológica que contém a bacia do Titicaca. Ao analisarmos o sedimento em perfil, ficou mais evidente que essa acumulação de As é originaria da mesma bacia. Ao calcularmos o fator de enriquecimento conseguimos confirmar a observação inicial. Mas também foi possível constatar que há metais com um incremento não natural, como para o Cu e Mo. Estes metais foram relacionados à infraestrutura instalada para captar água. Na baía interna, existem processos similares aos mencionados nos ambientes brasileiros, como o despejo direto do esgoto municipal. O sistema de tratamento instalado na cidade de Puno é de inícios dos anos 1970 quando existiam 40 mil habitantes e foi planejado para o tratamento de 45% da população. Esse sistema ainda continua sendo utilizado, mas a população de Puno hoje é de 120 mil habitantes. Além disso, devido a uma inundação em 1986, onde o lago subiu mais de dois metros, a estação de tratamento ficou temporariamente inoperante. Consequentemente essa enorme quantidade de nutrientes resultou, e continua até nos dias de hoje, em florações de uma macrófita flutuante, a Lemna sp. (lentilha de água).

Cabe ressaltar que a taxa de sedimentação tanto no Brasil quanto no Peru, são parecidas. No âmbito da Baía de Puno, há uma diferença entre os fatores que influenciam a mesma. Tendo que a variação climática (chuvas, inundações, sequias e presença do fenômeno El Niño) é relevante na baía exterior e na baía interior além do aspecto climático as atividades antrópicas possuem relevância. Atividades registradas desde inícios do século XX como as migrações devido a secas, o trânsito de embarcações de pequeno e médio porte, chegando à falta de tratamento de esgoto. No âmbito brasileiro também é influenciado pela periodicidade das chuvas, bem como a influência do fenômeno de “EL Niño”.

Em relação ao gerenciamento, para o tratamento e abastecimento de água, os ambientes brasileiros, bem como o peruano, são administrados por empresas majoritariamente públicas. A Companhia de Saneamento Básico do Estado de São Paulo – SABESP, nos reservatórios Rio Grande e Paiva Castro; O Serviço Autônomo de Água e Esgoto – SAAE para o reservatório Itupararanga; e a Empresa Municipal de Saneamento Básico de Puno – EMSAPUNO, para a Baía de Puno. A SABESP e EMSAPUNO têm estratégias de gerenciamento parecidas, ao aplicar paliativos nos efeitos resultantes sem atender a fonte principal da poluição dos ambientes que administram. Um aspecto importante é o financeiro, a procura de baixar os custos na produção da água pode significar custos elevados nos intentos de recuperação das áreas afetadas. Uma melhor forma de gerenciamento sempre será a prevenção da causa, e resulta ser muito mais econômica.

Finalmente, é preciso salientar um detalhe referente à pesquisa desenvolvida nos dois países, referidas aos ambientes avaliados respectivamente. Os reservatórios paulistas apresentam um maior número de publicações em revistas e demais documentos científicos. No entanto, para o Titicaca há uma menor quantidade de trabalhos revisados por pares e a quase totalidade das informações podem ser encontradas nos trabalhos de conclusão de curso (TCC), dissertações ou teses. Tomamos isso como um limitante ao avaliar processos em longos períodos. Porém, é uma oportunidade para que a comunidade cientifica, os tomadores de decisão tenham em mãos nova informação que forneça a planos de conservação ou recuperação do ambiente aquático.

6.3. Considerações finais

Os ambientes avaliados no Brasil e Peru, embora localizados a altitudes marcantemente diferentes apresentam processos limnológicos similares. As atividades humanas dentro da bacia hidrográfica influenciam a dinâmica e a acumulação de metais em ambientes lacustres ou de transição. Essa influência se extrapola no caso brasileiro devido a demografia existente. Tanto o Cu quanto o As em ambos países deve ser monitorado de forma espacial e temporal.

Nesse intuito recomenda-se um monitoramento constante dos ambientes avaliados para ver as mudanças tanto espaciais quanto temporais que o cobre ou arsênio, bem como outros metais de importância existirem. No caso peruano, é necessário conhecer o estado do arsênio, e assim verificar de vez a toxicidade potencial presente neste ambiente. Como foi observado nos ambientes brasileiros, uma grande quantidade de artigos publicados, o Lago Titicaca, no lado peruano, ainda carece de conhecimento sobre os distintos estratos e interações. Finalmente precisamos de politicas mais adequadas e atualizadas, porque como foi indicado anteriormente, cada corpo hídrico é particular e independente de outros. Assim a legislação para a conservação do sedimento, a água, a flora e fauna deve considerar estas novas informações.

Devemos considerar que para muitos países na América do Sul as maiores ameaças incluem aos estressores da bacia e as alterações hidrológicas (a causa do uso do solo, abstração da água, reservatórios). Estas mudanças se tornam mais relevantes devido à falta ou o inadequado quadro legal de gerenciamento, que consequentemente se vê na falta de regulamentação e rigor no cumprimento.

Com tudo, são os governos quem devem fortalecer aquelas instituições governamentais focadas na proteção e controle. Para que com regulamentos baseados no conhecimento cientifico disponível, além de financiamento para sua implementação e controle. Deste modo, possam reduzir as ameaças atuais e futuras aos ecossistemas aquáticos no Brasil e Peru. Dentro disto, precisamos salientar que as agências envolvidas no gerenciamento da água, precisam identificar estratégias de monitoramento baseadas no conhecimento cientifico atualizado, abrangendo métodos de monitoramento espaço temporais para compreender a relação causa – efeito entre os impactos e o estado ambiental.