UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL

FACULDADE DE AGRONOMIA

PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA DO SOLO

IMPACTOS DO AMBIENTE URBANO NA POLUIÇÃO DOS SEDIMENTOS DO LAGO GUAÍBA

Leonardo Capeleto de Andrade

(Tese)

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LEONARDO CAPELETO DE ANDRADE

Engenheiro Ambiental (UPF)
Mestre em Ciência do Solo (UFRGS)

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BANCA EXAMINADORA:

Prof. Tales Tiecher
UFRGS

Dra. Maria Lúcia Kolowski Rodrigues
FEPAM

Dra. Elba Calesso Teixeira
FEPAM

Prof. Orientador: Flávio Anastácio de Oliveira Camargo
UFRGS

“Se vi mais longe foi por estar sobre os ombros de gigantes”

(Isaac Newton, 1676)

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IMPACTOS DO AMBIENTE URBANO NA POLUIÇÃO DOS SEDIMENTOS DO LAGO GUAÍBA [1]

Autor: Leonardo Capeleto de Andrade

Orientador: Prof. Flávio Anastácio de Oliveira Camargo

RESUMO

O Lago Guaíba possui importância ambiental, econômica e histórico-cultural, para Porto Alegre e região metropolitana, no sul do Brasil. O lago é a principal fonte de abastecimento de água para a capital do estado desde sua colonização. O objetivo geral desta pesquisa foi analisar a poluição dos sedimentos do Lago Guaíba. Os estudos envolveram a discussão do contexto histórico-cultural da poluição do lago, a avaliação da poluição dos sedimentos superficiais nas margens, nas águas transicionais (riverina para lacustrina) e ao longo de todo o Lago Guaíba, assim como de dados históricos de monitoramento no entorno do Delta do Jacuí (encontro dos rios formadores do lago). Os sedimentos foram coletados de forma composta, avaliando a concentração dos metais e compostos orgânicos. A poluição do Lago Guaíba já era observada desde o século dezenove, seguindo pelas décadas. A qualidade da água e do sedimento no Delta do Jacuí é dependente dos rios tributários (conhecidos por sua poluição) e fluxos prioritários dos canais. A granulometria do sedimento e a concentração de carbono influenciam o potencial de sorção dos elementos e compostos. As margens possuem maior concentração de sedimentos arenosos, ocorrendo o inverso nas áreas centrais do lago. O Lago Guaíba apresenta características de um lago fluvial, sendo a deposição dos sedimentos dependente dos fluxos hídricos. A poluição do Lago Guaíba foi mais evidente próximo da margem de Porto Alegre e da foz de arroios (Dilúvio, Cavalhada e Salso), com alterações nas concentrações de carbono, fósforo e nitrogênio, assim como de Zn, Pb, Cu, Cr, Ni, Cd e Hg. O controle da poluição do Lago Guaíba é complexo em função de suas fontes diversas que perpassam diversas cidades.

[1] Tese de doutorado em Ciência do Solo. Programa de Pós-Graduação em Ciência do Solo, Faculdade de

IMPACTS OF THE URBAN ENVIRONMENT IN THE SEDIMENT POLLUTION OF THE LAKE GUAÍBA [2]

Author: Leonardo Capeleto de Andrade

Adviser: Prof. Flávio Anastácio de Oliveira Camargo

ABSTRACT

Lake Guaíba has environmental, economic and historical-cultural importance for Porto Alegre, and metropolitan region, in southern Brazil. The lake is the main source of water supply for the state's capital since its colonization. The main objective of this research was to evaluate the sediment pollution in Lake Guaíba. The studies involved the discussion of the historical-cultural context of lake pollution, the evaluation of surface sediments pollution in the margins, in transitional waters (riverine to lacustrine), and throughout Lake Guaíba, as well as historical monitoring data on the surrounding of Jacuí's Delta (meeting of the forming rivers). The sediments were collected as composite, evaluating the concentration of metals and organic compounds. The pollution of Lake Guaíba had been observed since the nineteenth century, following the decades. The quality of the water and sediment in the Jacuí's Delta is dependent on the tributary rivers (known for their pollution) and priority channel flows. Sediments granulometry and carbon concentration influences the sorption potential of the elements and compounds. The margins have higher concentration of sandy sediments, being the inverse in the central areas of the lake. The Lake Guaíba shows characteristics of a fluvial lake, being the deposition of the sediments dependent on the water flows. The pollution of Lake Guaíba was more evident near the Porto Alegre margin and the outflow of streams (Dilúvio, Cavalhada, and Salso), with changes in carbon, phosphorus and nitrogen concentrations, as well as Zn, Pb, Cu, Cr, Ni, Cd, and Hg. The control of Lake Guaíba pollution is complex due to its diverse sources that surpass through several cities.

[2] Doctoral thesis in Soil Science. Programa de Pós-Graduação em Ciência do Solo, Faculdade de Agronomia, Universidade Federal do Rio Grande do Sul. Porto Alegre. (116 p.) February, 2018.

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1. INTRODUÇÃO GERAL

As civilizações historicamente se formaram em áreas com boa disponibilidade hídrica em função de sua total dependência de água para diversos fins. Em função do transporte hídrico e outros usos das águas, a maior parte das capitais brasileiras se localizou próximo ao litoral e/ou corpos hídricos conectados ao oceano. Com a proximidade de grandes centros, os rios e lagos sofreram os efeitos decorrentes da falta de adequado saneamento.

A poluição de corpos hídricos superficiais em regiões urbanas é um problema recorrente em diversos países. Estes poluentes são provenientes de fontes diversas, como indústrias, esgotos e veículos motorizados. Este problema ambiental se agrava ainda mais com a grande impermeabilização urbana, carregando estes poluentes para os corpos hídricos próximos. Estas alterações ambientais acarretam em potenciais riscos à saúde, seja por danos agudos ou crônicos.

Poluentes potencialmente tóxicos que adentram nos corpos hídricos acabam se ligando às partículas de sedimento. Desta forma, os sedimentos são um indicador do histórico ambiental do ecossistema hídrico. Ao mesmo tempo, os sedimentos agem como destinos e fontes potenciais dos poluentes para o sistema hídrico, principalmente em caso de movimentação dos sedimentos estáveis.

Porto Alegre, capital do estado do Rio Grande do Sul (RS), se desenvolveu nas margens do Lago Guaíba, conectando o interior do estado ao oceano. O lago é a principal fonte de abastecimento hídrico da capital, desde sua fundação no século XVIII, tendo importância ambiental, econômica e histórico-cultural para região. Entretanto, ao longo dos séculos o lago sofreu os efeitos da poluição que persiste até os dias atuais.

Os sedimentos do Lago Guaíba apresentam uma histórica poluição por metais potencialmente tóxicos, derivados de fontes diversas em seu entorno. A grande urbanização no entorno do Lago Guaíba gerou diversos passivos ambientais o longo dos anos, em função do adensamento populacional, industrialização e impermeabilização superficial.

O objetivo desta pesquisa foi analisar a poluição dos sedimentos do Lago Guaíba. Especificamente foram estudados: 1) o contexto histórico-cultural da poluição do lago; 2) dados históricos de monitoramento de água e sedimento no entorno do Delta do Jacuí (rios formadores); 3) a poluição nas margens do lago; 4) a geo-acumulação de metais na região de transição riverina-lacustrina; 5) as características físico-químicas e potenciais fontes de contaminação ao longo do Lago Guaíba.

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2. CAPÍTULO I (REVISÃO BIBLIOGRÁFICA) - LAGO GUAÍBA: UMA ANÁLISE HISTÓRICO-CULTURAL DA POLUIÇÃO HÍDRICA EM PORTO ALEGRE, RS, BRASIL [3]

2.1 Introdução

O desenvolvimento e a qualidade de vida das civilizações possuem intrínseca ligação com a disponibilidade de água, entretanto, a poluição e a degradação dos recursos hídricos são realidades recorrentes do acelerado crescimento demográfico, especialmente nas regiões metropolitanas, afetando direta e indiretamente as populações (BLUME et al., 2010; LONDE et al., 2014; PRESTES, 2014). A falta de planejamento no desenvolvimento urbano somado ao grande adensamento populacional pode acarretar na contaminação e poluição dos recursos hídricos, que, muitas vezes, servem de abastecimento para esta mesma população.

A poluição pode ser definida como a “degradação da qualidade ambiental” que, direta ou indiretamente, afete as populações (BRASIL, 1981). Embora danos letais sejam relacionados com grandes concentrações de poluentes e fontes pontuais de emissão, distúrbios podem ser observados mesmo em pequenas concentrações, afetando o equilíbrio ambiental. Poluentes persistentes podem ser são acumulados nos níveis tróficos inferiores (bioacumulação) e transferidos para os superiores (biomagnificação), de acordo com os hábitos alimentares das espécies – com peixes no topo da cadeia alimentar aquática e sendo parte importante da dieta humana, a presença destes contaminantes se torna ainda mais agravante (COSTA; HARTZ, 2009; GONÇALVES et al., 2012).

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[3] Artigo aceito para publicação na revista “Engenharia Sanitária e Ambiental”, 2018.

O Lago Guaíba possui ligação direta com o desenvolvimento de Porto Alegre (RS) e região metropolitana: os primeiros colonos que adentraram no estado navegaram por suas águas, fixando residência nas margens dos rios que fazem parte da Bacia do Guaíba (ASSIS, 1960; RÜCKERT, 2013). O lago é um canal de ligação navegável entre o interior do estado e o mar, em função de sua conexão com os rios (ao norte) e a Laguna dos Patos (ao sul).

Porto Alegre foi oficialmente fundada em 1772 (ainda no período colonial brasileiro), porém seu povoamento iniciou em 1752 com a chegada de 60 casais portugueses, trazidos por meio do Tratado de Madri - esta colonização gerou um dos antigos nomes da capital, “Porto dos Casais”. Atualmente, Porto Alegre possui uma população de 1,4 milhões de habitantes (censo 2010), distribuídos em uma área territorial de 496,7 km² (pouco maior que o Guaíba), com uma densidade demográfica de 2,8 mil hab/km² (IBGE, 2017).

O Lago Guaíba possui importância ambiental, econômica e histórico-cultural, para Porto Alegre - capital do estado do Rio Grande do Sul (RS), Brasil - e região metropolitana. Entretanto, a negligência com a qualidade de suas águas acompanhou o desenvolvimento urbano desde a colonização da região. Assim, esta revisão discute o contexto histórico-cultural da poluição do Lago Guaíba.

2.2 Guaíba: bacia de todas as águas

O Lago Guaíba localiza-se na região metropolitana de Porto Alegre (29°55'-30°24' S; 51°01'-51°20' W), Rio Grande do Sul (RS), Brasil, sendo o principal manancial de abastecimento hídrico da capital gaúcha, desde sua fundação, no início no século XVIII (DMAE, 2017). Em sua história, o Guaíba já foi classificado como “rio”, “ria”, “estuário” e “lago” e ainda, por certo tempo, “na dúvida entre o correto termo recomendou-se a utilização do nome apenas como ‘Guaíba’, sem designação” (CHEBATAROFF, 1959; OLIVEIRA, 1976, 1981). Sendo um ambiente transicional, este “acidente geográfico” possui particularidades que dificultam sua simples denominação topológica, persistindo continuamente a discussão. Atualmente, conceituado por especialistas como lago - embora ainda popularmente chamado de rio - o

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Guaíba é comparável, em suas dimensões e importância para a paisagem, às grandes baías do litoral brasileiro (MENEGAT; CARRARO, 2009; PRESTES, 2014).

Na cartografia dos séculos XVII e XVIII (e até princípios do XIX) o Lago Guaíba e a Laguna dos Patos eram denominados conjuntamente de "Rio Grande", o que gerou o nome do estado: Rio Grande do Sul (OLIVEIRA, 1976, 1981; SPALDING, 1961). Em relação ao Lago, o nome "*Guahyba*" origina-se do Tupi-Guarani (primeiros moradores da região), podendo ser traduzido como "encontro das águas" (MENEGAT et al., 2006), "baía de todas as águas" (NICOLODI; TOLDO JR; FARINA, 2013) ou "ponto de encontro" (PRESTES, 2014), denotando, em todos os casos, a grande convergência de seus afluentes. Entretanto, até o início do século XIX, este manancial foi conhecido por outros nomes, como "Lagoa de Viamão" ou "de Porto Alegre" (OLIVEIRA, 1981; SAINT-HILAIRE, 2002; SPALDING, 1961).

No Rio Grande do Sul (RS) são delimitadas três Regiões Hidrográficas: Uruguai, Litorânea e Guaíba. A Região Hidrográfica do Guaíba possui 84.751,48 km², abrangendo 251 municípios gaúchos - 1/3 da área territorial do estado, 50 % da municipalidade e mais de 60 % dos habitantes, gerando uma concentração de mais de 2/3 do PIB estadual (MENEGAT et al., 2006; NICOLODI; TOLDO JR; FARINA, 2013). A Região é formada por nove Bacias Hidrográficas: Taquarí-Antas - 26.491,82 km²; Baixo Jacuí - 17.345,15 km²; Alto Jacuí - 12.985,44 km²; Vacacaí-Vacacaí Mirim - 11.077,34 km²; Caí - 4.945,70 km²; Sinos - 3.746,68 km²; Pardo - 3.658,34 km²; Lago Guaíba - 2.523,62 km²; e Gravataí - 1.977,39 km² (DMAE, 2017; FEPAM, 2018; SEMA/RS, 2010).

A Bacia Hidrográfica do Lago Guaíba (Unidade G80 do Sistema Estadual de Recursos Hídricos) situa-se entre as coordenadas 29º55'-30º37'S e 50°56'-51°46'O, com área de 2.523,62 km² (0,9 % do total do estado), abrangendo 14 municípios: Barão do Triunfo, Barra do Ribeiro, Canoas, Cerro Grande, Eldorado do Sul, Guaíba, Mariana Pimentel, Nova Santa Rita, Porto Alegre, Sentinela do Sul, Sertão Santana, Tapes, Triunfo e Viamão. Neste território residem até 2,2 milhões de habitantes (20 % da população do estado, sendo 98 % residente na área urbana), gerando uma densidade flutuante de quase 900 hab/km² (IBGE, 2017; SEMA/RS, 2010). As principais atividades econômicas desenvolvidas na bacia são agricultura, pecuária, indústria, comércio e serviços - gerando cerca de 30 % do PIB estadual (ANDRADE et al., 2012; BASSO, 2012; IBGE, 2017). A região enquadra-se como clima subtropical úmido (“Cfa” na classificação de Köppen-Geiger), com médias anuais de: temperatura do ar - 19 °C (15,2 - 24,9); umidade do ar – 76 %; precipitação acumulada - 1.324 mm (LIVI, 2006).

Geologicamente, a história do Lago Guaíba se inicia no período Quaternário (há mais de 400 mil anos), com a primeira transgressão marinha que inunda a planície regional e deixa ilhados os morros de Porto Alegre. As sequentes variações do nível no mar (há 325, 120 e 5 mil anos) dão forma ao Guaíba e à Laguna dos Patos, mantendo um elo indireto com o Oceano Atlântico - o que permitiu a posterior rota de entrada dos colonizadores (MENEGAT et al., 2006). Em sua configuração final o Lago Guaíba se estabelece como parte de um sistema lagunar (juntamente com outros grandes corpos hídricos - como a Laguna dos Patos, a Lagoa do Casamento e a Lagoa Mirim), que atuam como "vasos comunicantes", influenciando mutuamente em seus níveis (MENEGAT; CARRARO, 2009).

O Lago Guaíba possui uma área média de 496 km², com variações sazonais influenciadas pelas precipitações e dinâmica dos ventos (ANDRADE et al., 2012; MENEGAT et al., 2006; NICOLODI; TOLDO JR; FARINA, 2013). O Lago localiza-se 4 metros acima do nível do mar, com profundidade média de pouco mais de 2 m (classificando-se como um grande lago raso e aberto) - chegando a 12 m no canal de navegação e uma máxima pontual de 31 m na Ponta de Itapuã (DMAE, 2017; MENEGAT et al., 2006; MENEGAT; CARRARO, 2009). O Lago Guaíba possui uma vazão (média histórica) de entrada de 780 m³/s (com eventos pontuais ultrapassando os 3000 m³/s), sendo alimentado principalmente pelos rios: Jacuí - 84,6 %; dos Sinos - 7,5 %; Caí - 5,2 %; e Gravataí - 2,7 % (ANDRADE NETO et al., 2012; DMAE, 2017; MENEGAT et al., 2006). Segundo Menegat; Carraro (2009, p. 62), o Guaíba possui "influxo fluvial e canal sub-lacustrino, e margens definidas por enseadas vegetadas por matas de restinga, alternadas por pontas graníticas com matas altas e baixas, banhados e juncais".

O Lago Guaíba possui 85 km de margem esquerda e 100 km de margem direita - banhando os municípios de Porto Alegre, Viamão, Eldorado

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do Sul, Guaíba e Barra do Ribeiro (MENEGAT et al., 2006; MENEGAT; CARRARO, 2009). O lago possui aproximadamente 50 km de comprimento (entre o Delta do Jacuí e o emissário na Laguna dos Patos), 19 km de largura máxima (entre as praias de Itapuã e da Faxina) e 900 m de mínima (entre a Ponta do Gasômetro e a Ilha da Pintada). Segundo a Lei Orgânica de Porto Alegre (PORTO ALEGRE, 1990), as margens do Guaíba são “áreas de preservação permanente” - com incentivo para sua recuperação e impedimento de atividades poluidoras no lago e seus afluentes.

O sedimento do Lago Guaíba caracteriza-se por uma predominância de frações arenosas, com a deposição das frações silte, argila e matéria orgânica principalmente nas partes mais profundas, a partir da isóbata de 3 m (BACHI; BARBOZA; TOLDO JR., 2000; LAYBAUER; BIDONE, 2001). A turbulência das ondas induz a ressuspensão dos sedimentos finos, permanecendo apenas os sedimentos arenosos nas áreas mais rasas (BACHI; BARBOZA; TOLDO JR., 2000; NICOLODI; TOLDO JR; FARINA, 2013). Segundo Laybauer; Bidone (2001), grande parte dos sólidos suspensos argilosos que adentram no Lago acaba sendo exportado diretamente para a Laguna dos Patos, ficando retidos no Guaíba apenas os materiais dominantemente sílticos (além dos arenosos).

Com uma grande bacia de drenagem, o Lago Guaíba se transforma em um receptor potencial de toda a poluição gerada nas sub-bacias que o formam. Apesar disso, a maior fonte de contaminação direta de suas águas deriva da carga orgânica oriunda dos esgotos domésticos de Porto Alegre (BASSO, 2012). Apenas no território de Porto Alegre podem ser delimitadas 27 sub-bacias hidrográficas, compostas principalmente por arroios e riachos, como o Arroio Dilúvio (MENEGAT et al., 2006).

O Lago Guaíba possui uma dinâmica de escoamento bidimensional, controlada pelas flutuações do nível da Laguna dos Patos e a direção e intensidade dos ventos (MENEGAT et al., 2006). Na região da Ponta do Gasômetro, o fluxo de água pode variar, num mesmo dia, tanto no sentido Sul como Norte, o que pode ocasionar o represamento das águas. Com este regime hídrico, grande parte da água do Guaíba fica retida no reservatório por um grande período de tempo (MENEGAT et al., 2006; MENEGAT; CARRARO, 2009), o que gera uma menor circulação da massa d’água e,

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consequentemente, menor diluição dos poluentes. Segundo Laybauer; Bidone (2001), apenas a estreita região do canal (utilizado na navegação) apresenta uma hidrodinâmica diferente do restante do Lago, com um tempo de residência reduzido.

Com a região metropolitana às suas margens, o Lago Guaíba possui usos múltiplos, como: manancial de abastecimento hídrico, diluição de efluentes, transporte e navegação, pesca, turismo, lazer, entre outros. Estes usos modificaram-se com o tempo, tendo a poluição do lago como um limitante para algumas atividades.

2.3 A relação histórica, econômica e cultural com a região

2.3.1 O abastecimento público e as origens da poluição

Durante a primeira metade do século XIX a principal forma de acesso dos porto-alegrenses à água potável ocorria por meio de chafarizes e fontes públicas (e poucas privadas), na zona central da cidade. Entretanto, estas fontes não atendiam a demanda da população, ocorrendo o comércio de água (pelos chamados “pipeiros” ou “aguadeiros”), além da captação direta do Guaíba, sobretudo pela população mais desfavorecida (RÜCKERT, 2013).

O aumento populacional - e consequente demanda de água potável - levou (ainda no período imperial brasileiro) à criação da “Companhia Hydraulica Porto-Alegrense” (1861) - captando águas na nascente do “Riacho do Sabão” (atual Arroio Dilúvio) - e posteriormente (já no período republicano) da “Companhia Hydraulica Guahybense” (1891) - com sua captação no Guaíba (DMAE, 2017; RÜCKERT, 2013). O então “Presidente da Província de São Pedro” (RS) descreve as complexidades do abastecimento hídrico em seu relatório anual (FERNANDES LEÃO, 1861) e conclui que: o Guaíba não podia satisfazer as condições necessárias, “oferecendo águas potáveis apenas no canal central”, confirmando (através de análises) que as águas do Riacho do Sabão possuíam qualidade superior em comparação ao Guaíba, citando ser “essa água a melhor de todas quantas podem ser obtidas para Porto Alegre” (FERNANDES LEÃO, 1861, p. 39). Ressalta-se que atualmente o Arroio Dilúvio percorre mais de 15 km em áreas de grande concentração populacional –

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tornado-se um dos córregos mais poluídos de Porto Alegre, sendo comparável ao Rio Tietê (em São Paulo) –, tendo em sua foz um dos principais pontos de entrada da poluição orgânica e de metais no Lago Guaíba.

O acesso à água tratada era considerado um símbolo de modernização e civilidade, sendo recomendado pelas autoridades sanitárias (RÜCKERT, 2013). Entretanto, no início do século XX, com o aumento das reclamações sobre qualidade da água e com a forte concorrência no "negócio das águas" pelas empresas, houve o encampamento da Hydraulica Guahybense (DMAE, 2017; RÜCKERT, 2013).

Durante o século XIX, grande parte dos porto-alegrenses consumia diretamente a água do mesmo lago que recebia seus dejetos sem qualquer tratamento, pois os "cubos" (ou "cabungos") – recipientes colocados sob os assentos das privadas e patentes – eram lançados (por trapiches) no Guaíba, como uma forma de compensação da Intendência Municipal para a falta de coleta de esgotos. Visando atender a crescente demanda de "materiais" e eliminar a inicial poluição, no final do século XIX os cubos passaram a ser transportados por trens a vapor que percorriam uma estrada de ferro em direção à Zona Sul da cidade, levando o passivo para longe das áreas centrais (GUIMARAENS, 2015, p. 86). Em 1878, por incentivo da Câmara de Vereadores, ocorreram ações de remoção dos "cubos" do Lago Guaíba, entretanto os lançamentos não cessaram após estas operações, persistindo os "odores e cenas desagradáveis", além da contaminação orgânica no lago. Os cubos foram inicialmente lançados na "Ponta da Cadeia" (Gasômetro), posteriormente (até 1890') na "Ponta do Dionísio" - atual local do Clube Veleiros do Sul, no bairro Assunção - e após este período na "Ponta do Melo" (ou "do Asseio") - onde funcionou o "Estaleiro Só", no bairro Cristal (RÜCKERT, 2013).

Segundo Rückert (2013), a poluição do Lago Guaíba no século XIX (e início do século XX) ocorreu principalmente com o despejo de dejetos humanos ("cubos"), lavagem de roupas nas praias e arredores (incluindo da Santa Casa de Misericórdia), ausência de fiscalização sanitária nos matadouros e navios nos portos e da localização da Cadeia Pública (ao lado do Gasômetro - gerando a denominação de "Ponta da Cadeia"). Ao mesmo tempo, segundo Prestes (2008), a poluição do Guaíba segue um padrão de cidades

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litorâneas, onde os corpos hídricos eram comumente vistos, até meados do século XIX, como um natural destino para seus dejetos.

As epidemias mundiais de cólera de 1855 e 1885 alertaram as autoridades sobre as águas consumidas pela população, mas a prática dos despejos no Guaíba era antiga e estava incorporada no cotidiano da sociedade porto-alegrense (RÜCKERT, 2013). A construção da rede de esgotos levou anos de discussão, passando pela Proclamação da República, com início somente em 1907 e finalização em 1912. Todavia, estas obras não finalizaram os despejos de “cubos” no Guaíba e o lago acabou como o destino final da rede de esgotos (DMAE, 2017; RÜCKERT, 2013).

2.3.2 A histórica degradação do Lago Guaíba

A poluição do Lago Guaíba já era observada durante o século XIX, pela população e poder público, em função de fatores ambientais como coloração e odor das águas, gradualmente ganhando importância na agenda do governo e na imprensa local (RÜCKERT, 2013). Apesar dos notórios danos ambientais, a degradação do Lago seguiu pelas décadas. Segundo (PRESTES, 2008, 2014) o processo de degradação do Guaíba foi uma consequência do intenso crescimento populacional de Porto Alegre e região metropolitana, especialmente acelerado entre as décadas de 1940 e 1970, quando passou de 272 mil para 903 mil habitantes.

A degradação histórica dos recursos hídricos locais não foi exclusividade de Porto Alegre. Dentre os afluentes do Lago Guaíba, destaca-se o Rio dos Sinos, em função de sua grande poluição - com origens ligadas à colonização da região. Segundo Figueiredo et al. (2010), a colonização sistemática na região do Rio dos Sinos teve início no século XIX, com a imigração de colonos alemães, estimulada pelo Império Português. Na metade do século XX, a instalação de fábricas do ramo coureiro-calçadista (na região de São Leopoldo e Novo Hamburgo) gerou um rápido e não planejado crescimento das áreas urbanas, afetando negativamente a bacia hidrográfica. Os impactos ambientais causados pelo desenvolvimento industrial possuem ligação econômica e cultural com a população, sendo que, segundo Figueiredo et al. (2010), “o mais importante problema é que a população que vive na Bacia

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do Rio dos Sinos reconhece no desenvolvimento industrial o único meio de visualizar o progresso".

No início do século XX ocorreram transformações urbanas sistemáticas e articuladas, com o objetivo de modernizar as estruturas herdadas do período colonial nas metrópoles brasileiras. Em Porto Alegre esta remodelação dos espaços públicos ocorre através dos aterramentos no Lago Guaíba (Rua da Praia, Praia de Belas, Beira Rio e outros), similar ao ocorrido nas cidades litorâneas, com a expansão de territórios, entre o final do século XIX e o início do século XX (BOHRER, 2002). O maior aterramento de Porto Alegre, na antiga Praia de Belas (área de banho da população no passado), foi idealizado na década de 1930 e concretizado entre as décadas de 1950 e 1970. O aterro possui mais de 200 ha, ocupados pelos Parques "Marinha do Brasil", "Maurício Sirotsky Sobrinho" (Harmonia) e centros administrativos (BOHRER, 2002; PRESTES, 2008).

Situada nas margens do Lago Guaíba, Porto Alegre sempre ocupou uma posição geograficamente estratégica, mas também perigosa, uma vez que nas sub-bacias dos rios que compõem o Lago ocorrem algumas das maiores precipitações pluviométricas do estado (RAUBER; ILGENFRITZ, 2006). Deste modo, os aumentos do nível do Lago foram frequentes ao longo da história, com a maior enchente ocorrida em 1941, cuja cota atingiu 4,75 m (sendo a média de 1 m). Segundo Bohrer (2002, p. 154), "com a necessidade do dique de contenção, a partir da década de 1950, a potencialidade da orla desvincula-se da cidade existente, que passa a ser equacionada pelo paradigma da cidade moderna".

2.3.3 A visão dos viajantes sobre o Lago Guaíba

O Lago Guaíba foi, até o século XIX, a principal via de acesso para Porto Alegre e região, tendo sua entrada pelo oceano, passando pela Laguna dos Patos e chegando a capital - podendo ainda seguir viagem para o interior do estado pelo Rio Jacuí ou outros afluentes. Alguns viajantes registraram suas impressões em seus diários de viagem.

O botânico francês Auguste de Saint-Hilaire (1779-1853), em seu diário "Viagem ao Rio Grande do Sul" (SAINT-HILAIRE, 2002) - escrito em

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1820-21 e publicado originalmente em 1887 - já descrevia o Guaíba como uma "lagoa originada de rios navegáveis e numerosos afluentes", formando uma grande bacia. Saint-Hilaire também descreveu os portos, embarcações e a relação destes com a comunicação com o mar e o interior do estado. Entretanto, a falta de saneamento e o princípio da poluição no Lago Guaíba também foram descritos pelo viajante: "as margens da lagoa são entulhadas de sujeira"; "os habitantes só bebem água da lagoa e, continuamente, vêem-se negros encher seus cântaros no mesmo lugar em que os outros acabam de lavar as mais emporcalhadas vasilhas" (SAINT-HILAIRE, 2002).

Outro naturalista francês, Arsène Isabelle (1807-1888), também registrou suas observações durante sua passagem por Porto Alegre, em 1834 - na época "uma cidade muito nova", com "cerca de 12 a 15 mil habitantes". Entre seus relatos, Isabelle descreve o Lago Guaíba: "Cinco rios, que trazem o tributo de suas águas fecundas e se reúnem ali para formar o Rio Grande do Sul". Segundo Arsène Isabelle, o Lago Guaíba era descrito como uma "mão de cinco dedos", formada pelos rios Jacuí (o polegar), Caí, Sinos, Gravataí e "Riacho" (antigo nome do Arroio Dilúvio) – esta visão teria originado o nome do vizinho município, "Viamão". O naturalista também descreve o Delta do Jacuí e a "enseada coberta de navios" (nacionais e estrangeiros), em uma economia fortemente dependente do Guaíba (ISABELLE, 2006).

No diário de viagem de Dom Gastão de Orléans (Conde d'Eu) – acompanhando o imperador Dom Pedro II, em 1865, durante Guerra do Paraguai (1864-1870) – o príncipe também descreve o Lago Guaíba, enaltecendo sua beleza e importância: "o palácio da presidência ocupa o alto da cidade; é esplêndida a vista que dali se goza. As águas da lagoa estendem-se de três lados, pois que a cidade fica num promontório. Para Sudeste, na direção de onde vínhamos, dilata-se a lagoa até o horizonte" (CONDE D'EU, 1936, p. 35).

2.3.4 A percepção da degradação ambiental no Lago Guaíba

Disfarçada pela beleza de sua orla, a poluição no Lago Guaíba progrediu juntamente à população. Os diversos usos de suas águas foram cada vez mais reduzidos aos indiretos e gradativamente se popularizou o

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ditado de que “Porto Alegre virou as costas para o Guaíba”. Segundo Bohrer (2002), “o porto-alegrense nunca alicerçou um convívio permanente com o Guaíba na escala de cidade”. As praias do Guaíba já foram intensamente frequentadas por banhistas, especialmente entre as décadas de 1940 e 1970, sendo sistematicamente abandonadas com o aumento da poluição do lago desde a década de 1950. Apesar da forte ligação histórica, cultural e emocional com o lago, a aceitação da poluição e da “perda das praias” foi vista pela população, em geral, como algo natural, “consequência inevitável do crescimento de economias subdesenvolvidas” (PRESTES, 2008) – fato semelhante ao ocorrido na Bacia do Rio dos Sinos (FIGUEIREDO et al., 2010).

O histórico da degradação do Lago Guaíba é relatado na cobertura jornalística local, onde durante os anos 1950 e início de 1960 se retratavam positivamente a “imagem dos clubes náuticos, veleiros e lanchas no Guaíba”, sendo, já no final da década de 1960, mais comum a abordagem da poluição, doméstica e industrial (PRESTES, 2008). No final da década de 1950, Henrique Luiz Roessler já criticava, em artigos jornalísticos, a poluição hídrica e os lançamentos de efluentes não-tratados na Bacia do Lago Guaíba (ROESSLER, 2005). Roessler foi um dos primeiros representantes gaúchos do crescente movimento ambientalista mundial. Nesta época, em função das críticas ambientais, fábricas instaladas próximas ao Lago Guaíba alegavam que a instalação de sistemas de tratamentos de efluentes teria custos “proibitivos” (PRESTES, 2008).

Em 1958 o jornalista Kleber Borges de Assis também relata a realidade do Lago Guaíba em uma série no jornal Correio do Povo – compilada no livro “O rio que não é rio” (ASSIS, 1960). Assis cita que “O Guaíba dispõem de ‘lugares pitorescos’ às suas margens, bem como de belas praias onde, no verão, se refugia parte da população porto-alegrense”, tendo importância social e econômica, com funções de transporte, abastecimento e recreação. Segundo Assis (1960), nos séculos XIX e XX, havia competições de remo, vela, natação, saltos ornamentais e pólo aquático no Lago Guaíba. Todavia, ainda no fim da década de 1950, já eram notórias as alterações ambientais no Guaíba, principalmente relacionadas às lavouras de arroz da região (por seus efeitos negativos na atividade pesqueira), aos coliformes (provenientes dos esgotos

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domésticos) e aos “despejos industriais” - não apenas de forma direta, mas também nos rios que fazem parte da bacia e deságuam no lago.

No início da década de 1960, Rocha Freitas - engenheiro sanitarista e professor do Instituto de Pesquisas Hidráulicas (IPH/UFRGS) - também alertava sobre a qualidade do Guaíba, em sua tese “O destino dos esgotos de Porto Alegre em face da poluição do Guaíba” (FREITAS, 1962). Neste trabalho, Freitas (1962) disserta sobre a qualidade da água e conclui que: “Porto Alegre depende do Guaíba para seu abastecimento de água potável”; “Não existe outro manancial capaz de suportá-lo no futuro”, “por isso, é imprescindível preservá-lo”. Nesta mesma época (1961) é criado o Departamento Municipal de Água e Esgotos (DMAE) de Porto Alegre (DMAE, 2013).

Durante a crescente pressão ambiental mundial, entre as décadas de 1960 e 1970 - somada ao renascimento do movimento sindical e ao contexto histórico da reabertura política do regime militar -, surgem diversos ativistas ambientais. Dentre eles, o agrônomo José Lutzenberger, um dos nomes mais lembrados no ambientalismo brasileiro e ícone na luta contra a poluição do Guaíba, especialmente no caso da “Borregaard” - indústria de celulose que iniciou suas operações em 1972, no município de Guaíba (RS). Por muitos anos esta indústria foi um popular símbolo da poluição na região (pelos efluentes e, principalmente, pelo odor das emissões atmosféricas) e, também, um catalisador do movimento ambientalista no Rio Grande do Sul (PRESTES, 2008).

Com a poluição do Lago Guaíba cada vez mais evidente, em 1973 ocorrem interdições de grande parte das praias lacustres e a colocação de placas de advertência de qualidade. Em 1975 o DMAE conclui a instalação de um emissário sub-fluvial para despejo da maior parte do esgoto não tratado de Porto Alegre no canal de navegação do Guaíba, a partir da Ponta da Cadeia (Gasômetro), apesar da oposição de diversos ambientalistas e especialistas ao projeto (PRESTES, 2014). Entre 1979-1985, com a implantação do Polo Petroquímico, em Triunfo (RS), região metropolitana de Porto Alegre, houve uma constante preocupação dos ecologistas com a poluição química do Guaíba. Com isso surgem programas governamentais visando à despoluição do lago, como os projetos “Rio Guaíba” (1981), “Guaíba Vive” (1989) e “Pró-Guaíba” (1989), que se somam ao monitoramento da qualidade pelo DMAE,

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que já ocorria desde a década de 1970 (GUIMARAENS, 2015). Desde a década de 2000 a Prefeitura de Porto Alegre executa o Programa Integrado Socioambiental (PISA), que visa “melhorar a qualidade de vida da população, melhorando a qualidade da água do Lago Guaíba” e a “retomada da balneabilidade” de suas águas (DMAE, 2013). Todavia, apesar das diversas tentativas, a poluição do Lago Guaíba está ligada ao consciente coletivo da população local, que persistirá mesmo com a reversão do quadro ambiental.

Apesar de um maior controle com a poluição das águas da Bacia, em função dos programas de despoluição, em outubro de 2006 ocorreu uma das maiores tragédias ambientais da região, gerando a morte de toneladas de peixes no Rio dos Sinos, decorrente de um conjunto de fatores que levou à redução do oxigênio dissolvido em função de uma grande concentração de carga orgânica no corpo hídrico (RODRIGUES et al., 2010). O fato se repetiu em novembro de 2010 (com menor magnitude), pela “presença de compostos químicos” (MENDES, 2010). Segundo Rodrigues et al. (2010), as altas temperaturas e a baixa vazão do rio nestas épocas contribuíram para estes eventos, entretanto, “embora as diferentes fontes industriais pudessem, isoladamente, atender à legislação vigente para disposição de efluentes no corpo receptor, o trecho final do Rio dos Sinos estava recebendo uma carga de micro-poluentes (em uma complexa mistura) muito superior à sua capacidade de suporte”. Estes casos reacenderam a preocupação com a poluição nas bacias hidrográficas da região e alertou para a necessidade de estudos ambientais na área.

2.4 Alterações na qualidade ambiental da bacia do Lago Guaíba

Os rios que compõem a Bacia Hidrográfica do Guaíba contribuem para os impactos negativos no lago. A economia e usos do solo da região envolvem: represamento (barragens); agricultura (arroz irrigado, tabaco, erva-mate, fruticultura) e pecuária; indústria (coureiro-calçadista, petroquímica, metal-mecânica, automobilística, celulose, bebidas); além do descarte de grande volume de esgotos domésticos (PRO-GUAÍBA, [s.d.]). Estas atividades contribuem para a potencial contaminação por metais, agrotóxicos e carga orgânica do Lago Guaíba (BASSO, 2012).

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As águas do Lago Guaíba apresentam variações de qualidade, com maior prejuízo nas áreas marginais, onde ocorre menor dispersão dos poluentes (DMAE, 2017). Diversos estudos na Bacia do Lago Guaíba citam alterações nas concentrações de macronutrientes (principalmente P) e metais (Tab. 2-1), refletindo na redução de oxigênio dissolvido (OD) e aumento da toxicidade ambiental (ANDRADE; GIROLDO, 2014; BENDATI, 2000; BLUME et al., 2010; CERVEIRA et al., 2011; COSTA; HARTZ, 2009; GONÇALVES et al., 2012; RODRIGUES et al., 2011; TERRA; GONÇALVES, 2013).

Tab. 2-1. Concentrações de metais em água e sedimento reportados em estudos na Bacia Hidrográfica do Lago Guaíba e padrões de qualidade.

Metais	**Água (mg/L)**		**Sedimento (mg/kg)**	
	Valores	**Padrão [a]**	**Valores**	**Padrão [b]**
Arsênio (As)	-	0,01	4,0 [c]	5,9
Cádmio (Cd)	0,01 [d]	0,001	0,10 [d]	0,6
Chumbo (Pb)	0,08 [d]	0,01	8,85 [d]	35
Cobre (Cu)	0,32 [d]	0,009	6,77 [d]	35,7
Cromo (Cr)	0,06 [d]	0,05	4,96 [d]	37,3
Mercúrio (Hg)	0,0007 [e]	0,0002	0,54 [e]	0,17
Níquel (Ni)	0,15 [f]	0,025	-	18
Zinco (Zn)	0,55 [d]	0,18	36 [d]	123

[a] Res. CONAMA Nº 357 – Classe 2 (BRASIL, 2005); [b] Res. CONAMA Nº 454 – Nível 1 (BRASIL, 2012); [c] Rio Caí (RODRIGUES; ROCHA; FORMOSO, 2010) - fração <63 µm; [d] Lago Guaíba (BENDATI, 2000); [e] Rio dos Sinos (CERVEIRA et al., 2011) - fração <63 µm; [f] Rio dos Sinos (TERRA; GONÇALVES, 2013).

Bendati (2000) avaliou a concentração de metais (Cd, Cr, Cu, Pb e Zn) em água, sedimento e moluscos bivalves, em sete pontos do Lago Guaíba, em 1994. Os resultados obtidos encontravam-se acima dos padrões de referência para a água, mas abaixo para o sedimento (Tab. 2-1). Nos moluscos os valores encontrados foram até seis vezes superiores aos obtidos no sedimento e os resultados não apontaram variações sazonais significativas.

Costa; Hartz (2009) avaliaram a concentração de metais (Cd, Cr, Cu e Zn) em *Leporinus obtusidens* (piava) no Lago Guaíba. Os resultados apontaram concentrações menores no músculo do que no fígado dos peixes. Os maiores teores destes metais foram encontrados em peixes da região

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central do lago, onde haveria maiores concentrações de matéria orgânica e poluentes no sedimento. Segundo os autores, as concentrações médias encontradas nos peixes não apresentavam risco considerável à saúde humana.

Blume et al. (2010) avaliaram a qualidade da água no Rio dos Sinos e observaram baixas concentrações de oxigênio dissolvido (com alterações sazonais) e de metais nas camadas superficiais da água (Tab. 2-1), recomendando-se, porém, estudos em amostras de águas nas camadas mais profundas e nos sedimentos. Períodos de nível e fluxo reduzidos relacionam-se à menor capacidade de diluição de poluentes e suprimento de oxigênio (BLUME et al., 2010), entretanto em épocas de grande precipitação há maior perturbação do leito e aumento da entrada de poluentes por erosão e enxurradas (GONÇALVES et al., 2012; TERRA; GONÇALVES, 2013).

Rodrigues; Rocha; Formoso (2010) e Cerveira et al. (2011) avaliaram teores de Arsênio (As) e Mercúrio (Hg) em sedimentos, respectivamente nas bacias hidrográficas do Rio Caí e do Rio dos Sinos, afluentes do Lago Guaíba (Tab. 2-1). O Arsênio foi utilizado no curtimento de peles durante o século XX. O Hg foi utilizado por muitos anos em diversas indústrias como reagente, catalisador e biocida. Estes metais provavelmente foram liberados no ambiente com os efluentes de indústrias presentes na região metropolitana de Porto Alegre. A grande preocupação com estes metais encontra-se na sua extrema toxicidade e potencial de persistência no ambiente.

Rodrigues et al. (2011) avaliaram teores de cianeto em amostras de águas superficiais na Bacia do Rio dos Sinos, encontrando teores de até 0,750 mg/L e valores médios ultrapassando o limite estabelecido pela Resolução CONAMA nº 357 (BRASIL, 2005). Os cianetos são compostos de tríplice ligação entre o átomo de carbono e o de nitrogênio (C≡N), com toxicidade ligada ao bloqueio do transporte de oxigênio nas rotas metabólicas dos organismos aquáticos, podendo ter correlação com eventos de mortandade de peixes ocorridos na região (RODRIGUES et al., 2011).

Andrade et al. (2012) avaliaram os resultados dos monitoramentos realizados em 26 pontos do Lago Guaíba utilizando o Índice de Qualidade da Água (IQA), no período de 2000 a 2009. Os menores valores de IQA (maior comprometimento ambiental) localizaram-se principalmente na parte norte da margem esquerda do lago (próximos a zona central de Porto Alegre). Segundo

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Andrade et al. (2012), “os resultados permitiram verificar que a foz dos rios Gravataí, Sinos e Dilúvio, bem como alguns pontos da margem esquerda do lago, estão mais comprometidos em função de maior adensamento populacional associado à menor vazão de tributários relacionados”.

Gonçalves et al. (2012) avaliaram a influência de xenobióticos na reprodução e sobrevivência de microcrustáceos, no Rio Taquari (parte da Bacia do Rio Jacuí, afluente do Lago Guaíba). Foram encontrados valores acima dos limites da Resolução CONAMA Nº 357 (BRASIL, 2005), para fósforo e fenóis, além da ocorrência de toxicidade aguda (*Daphnia magna*) em alguns pontos. O fósforo (P) é um elemento essencial para os organismos autotróficos fotossintetizantes, porém, seu excesso (causado por descargas de esgotos sanitários e usos do solo) altera a qualidade da água e do sedimento, estimulando a eutrofização e interferindo nos processos tróficos do sistema. Segundo Andrade; Giroldo (2014), os níveis mais baixos de P no Guaíba ocorrem no verão e, em períodos de alta retenção hidráulica (baixa pluviosidade), o sedimento é possivelmente a principal fonte de P para o sistema.

Terra; Gonçalves (2013) observaram a ocorrência de toxicidade crônica (*Daphnia magna*), na maior parte das amostras de sedimento do Rio dos Sinos, havendo pontos com toxicidade aguda. As principais alterações encontradas em água foram as concentrações de coliformes fecais, fósforo e metais (Tab. 2-1) acima dos limites e de oxigênio dissolvido abaixo dos padrões de qualidade (BRASIL, 2005).

Andrade; Giroldo (2014) avaliaram dados de caracterização limnológica do Lago Guaíba e observaram variações espaciais e sazonais, sendo que as maiores temperaturas no verão relacionam-se com: maiores valores de clorofila *a*, pH, densidade de fitoplâncton; e menores concentrações de sólidos suspensos totais e oxigênio dissolvido. Segundo os autores, alguns dos resultados obtidos contrastaram com os encontrados em reservatórios subtropicais, assemelhando-se ao observado em rios brasileiros subtropicais.

A água e o sedimento da Bacia do Lago Guaíba apresentam (mesmo que pontualmente) alterações nas concentrações de metais (Tab. 2-1) e fósforo (P), que, mesmo que não ultrapassem os limites legalmente estabelecidos, podem afetar (direta ou indiretamente) as populações -

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acordando com a definição de “poluição” proposta na Política Nacional de Meio Ambiente (BRASIL, 1981). Considerando a realidade ambiental e a importância do Guaíba para a população metropolitana de Porto Alegre, ainda são escassos os estudos científicos especificamente no Lago.

2.5 Considerações finais

Apesar da grande importância do Lago Guaíba para a região metropolitana de Porto Alegre, há um histórico descaso com sua qualidade. O lago apresenta-se poluído, com percepção pública dessa realidade e limitação de usos diretos de suas águas. Diversos programas de despoluição foram e estão sendo aplicados, com perspectivas futuras favoráveis, contudo, os resultados ainda não estão visíveis com respeito à qualidade ambiental e mais estudos devem ser direcionados para essa área. A qualidade do Lago Guaíba possui direta ligação com a qualidade de vida das populações que usufruem direta ou indiretamente de suas águas e sua revitalização deve ser uma prioridade pública para a região. Além disso, pelo uso e ocupação das áreas da bacia hidrográfica do Guaíba, é imprescindível o uso sustentável dos recursos naturais, bem como a redução das descargas orgânicas e resíduos industriais e urbanos nos corpos hídricos adjacentes à bacia.

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3. CAPÍTULO II – THE HISTORICAL INFLUENCE OF TRIBUTARIES ON THE WATER AND SEDIMENT OF JACUÍ'S DELTA, SOUTHERN BRAZIL [4]

3.1 Introduction

The high development of big cities results in environmental impacts on local water resources, which often serve as a source of water for the same populations (CAVALCANTI et al., 2014). Trace metals entering aquatic ecosystems through runoff or atmospheric deposition, accumulating eventually in the sediments (BING et al., 2016).

Lake Guaíba is the major source of water in the capital of the Rio Grande do Sul State. The lake has historical, economic and cultural importance for the region since the 18th century. With almost 500 km² of shallow waters, Lake Guaíba is the final destination to rivers Jacuí, Caí, dos Sinos, and Gravataí - accumulating potential liabilities generated in the drainage basin. Water pollution in the Lake Guaíba's watershed has been alerted since the end of 1950' (FREITAS, 1962; ROESSLER, 2005), persisting for decades as a public perception. Nowadays, the waters have multiples uses, as water supply, sewage dilution, navigation, as well as fishing (DE ANDRADE et al., 2018).

The Jacuí's Delta (Fig. 3-1) is an area of protection and great socio-environmental interest, being the archipelago a State's Conservation Unit. The aim of this work was to evaluate the historical data (between 2000 and 2014) of the water and sediments monitoring, developed by the Municipal Department of Water and Sewage (Dmae) of Porto Alegre, in the Jacuí's Delta region and to analyze a relationship between the sites.

[4] Artigo publicado na revista "Ambiente & Água", 2018. doi: 10.4136/ambi-agua.2150

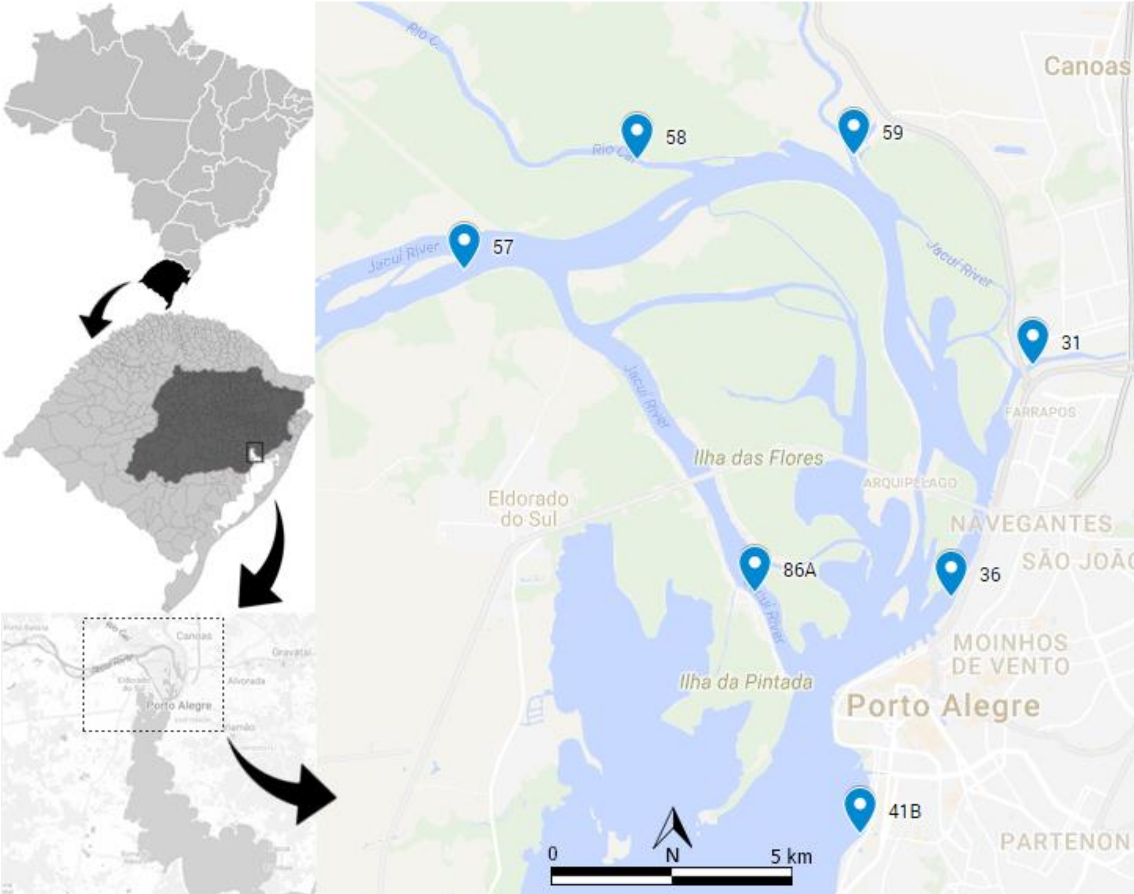

Fig. 3-1. Sampling sites (31 - River Gravataí; 36 – channel Navegantes ; 41B - Lake Guaíba; 57 - River Jacuí; 58 - River Caí; 59 - River dos Sinos; 86A – channel Ilha da Pintada) of water and sediment in Jacuí's Delta. Darkest area in state map represents the lake drainage basin. Source: Google Maps.

3.2 Materials and methods

Analyses of water and sediment monitoring were carried out by the Municipal Department of Water and Sewage (Dmae) of Porto Alegre, RS, between 2000 and 2014. The seven sites evaluated around the Jacuí's Delta (Fig. 3-1) were: 31 - Gravataí River outflow (29°58'12,6"S; 51°11'53,6"W); 36 – channel Navegantes (30°00'52,1"S; 51°12'54,2"W); 41B - Lake Guaíba (30°03'32,7"S; 51°14'10,3"W); 57 - Jacuí River outflow (29°57'07,3"S; 51°19'21,2"W); 58 - Caí River outflow (29°55'51,7"S; 51°17'05,3"W); 59 - Sinos River outflow (29°55'49,0"S; 51°14'14,9"W); and 86A – channel Ilha da Pintada (30°00'49,0"S; 51°15'34,2"W). Some of these sites are points of water catchment to Water Treatment Plants (WTP): 36 - São João and Moinhos de Ventos; 41B - Menino Deus; and 86A - Ilha da Pintada. Sites numbers are standards codes defined by Dmae.

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Water data (with monthly repetitions between the years 2000 and 2014) were evaluated to: air and water temperature; depth; pH; electrical conductivity (EC); transparency (secchi disk); turbidity (NTU); dissolved oxygen (DO - modified Winkler); biochemical oxygen demand (BOD_5 - manometric); total phosphorus (P - titulometric); total nitrogen (N - titulometric); total residues at 105°C (TR_{105} - gravimetric); and *Escherichia coli* (enzymatic substrate). Sediment (bulk) was oven dried (50°C) and evaluated, with two annual repetitions (in distinct seasons) between the years of 2000 and 2011, to pseudo-total (USEPA, 1996) concentrations (dry basis) of metals (Al, Fe, Ca, Mn, Ba, V, Zn, Cu, Pb, Cr, Ni, Co, Li, Be, Cd, Hg, As, and Ag) analyzed by atomic absorption spectrophotometry.

Data were submitted to analysis of variance (ANOVA) and, when significant, means were compared by Tukey test with 95 % confidence interval (p<0.05). All graphs and statistical analyzes were developed in Statistica® v13 software.

3.3 Results and discussion

The quality of water and sediment in the Jacuí's Delta are linked with the tributaries and priority flows of the channels (Fig. 3-1). Lake Guaíba has a historical mean water inflow of 780 m^3/s (with occasional events exceeding 3000 m^3/s). This inflow is composed mostly (85 %) for waters from Jacuí River (site 57) and the remaining by the rivers Sinos, Caí, and Gravataí (flowing into the Jacuí's Delta), as well small streams along the margins (ANDRADE NETO et al., 2012; DMAE, 2017; MENEGAT et al., 2006).

The relationship of the forming rivers with the Jacuí's Delta is observed in the cluster analysis (Fig. 3-2a), such as sites 57 (Jacuí River outflow) and 86A (channel of the Jacuí Delta - Ilha da Pintada). Nevertheless, the major influence of the tributaries is verified by the accumulation of liabilities of the rivers Caí (58), Sinos (59), and Gravataí (31) over the channel Navegantes (36) and Lake Guaíba (41B). Rivers Caí and Sinos flow through regions with many industries, especially Leather and Footwear's; and river Gravataí flow through the metropolitan region of Porto Alegre.

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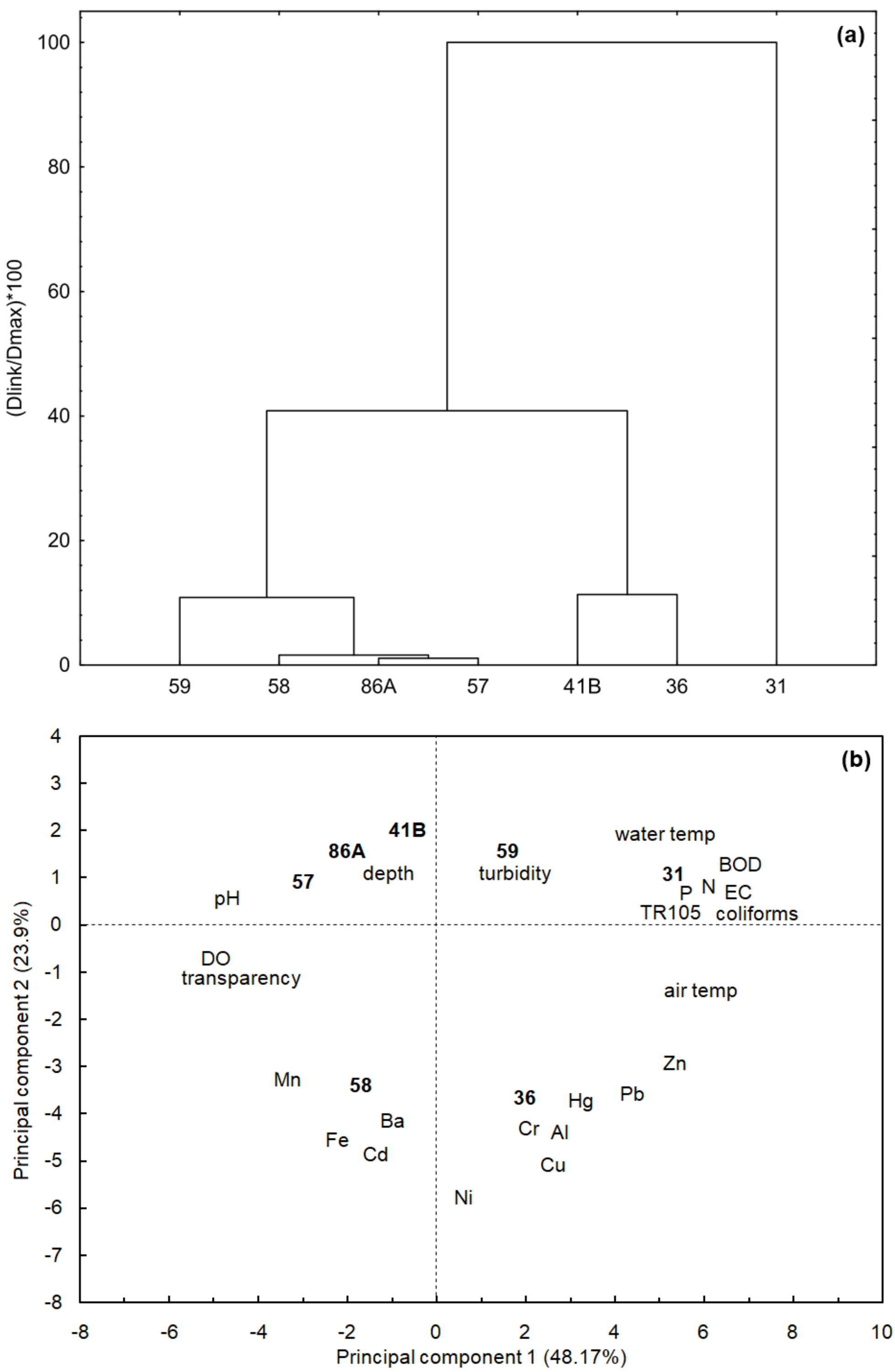

Fig. 3-2. Analysis of (a) clusters for the sites and (b) principal components for water and sediment in Jacuí's Delta.

The pollution from tributaries can be verified by the increasing in electrical conductivity (EC), biochemical oxygen demand (BOD_5), P, N, TR_{105}, and coliforms in water (Tab. 3-1), and metals (such as Zn, Cu, Pb, Cr, Ni, and Hg) in the surface sediment (Tab. 3-2) in the downstream sites (as 36 and 41B).

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Consequences of these changes are reductions in pH, dissolved oxygen (DO), and water transparency - which can result in damage to local biota.

These parameters have direct and indirect connection with the urban pollution commonly present in metropolitan regions (Fig. 3-2b). Metals and other pollutants enter the aquatic environment from various ways and sources (natural and anthropogenic), such as runoff, sewage, atmospheric deposition, and vehicular traffic (BING et al., 2016; SMOL, 2008). High vehicular traffic has been reported as a potential source of pollution by metals around the world (SHARLEY et al., 2016; ZHANG et al., 2016). Motor vehicles have a variety of emissions and releases involving many toxic metals (such as Zn, Cr, Cu, Hg, Ni, and Pb), which can cause damages to humans health and the environment (ADAMIEC; JAROSZ-KRZEMIŃSKA; WIESZAŁA, 2016).

According to the Brazilian reference values for surface waters (Tab. 3-3), Conama No. 357 – Class 2 (BRASIL, 2005), sites 31 (Gravataí River) and 59 (dos Sinos River) surpasses the mean values for DO and Coliforms (Tab. 3-1). However, the self-purification re-establishes the DO levels in the channel Navegantes (36), but cannot reduce the coliform levels below the resolution limits.

According to the Brazilian reference values for dredged sediments (level 1) of Conama No. 454 (BRASIL, 2012), the mean values were above the limits proposed in sediment for Zn (at sites 31, 36, 41B, 58, and 59), Pb (31 and 36), Cr (36, 58, and 59) and Hg (36). The site that presented more values above the limits (besides the highest concentrations) was the 36 (channel Navegantes), where are accumulated the water flow from all those rivers. The sites 57 (Jacuí River) and 86A (channel Ilha da Pintada) did not present any values above the proposed limits. Site 41B (Lake Guaíba) only present the concentrations of Zn above the limit.

The association of the analyzed parameters is corroborated by the correlation (r) of their attributes. The increase in P and N concentrations leads to an increase in BOD_5 (0.72 and 0.70, respectively; $p<0.05$), which in turn reduces DO concentrations (-0.62; $p<0.05$). This chain reaction occurs by the eutrophication of the water, consuming the oxygen available for the decomposition of the organic compounds from urban pollution (ANDRADE; GIROLDO, 2014).

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Previous studies in the Jacuí's Delta and Lake Guaíba show the seasonal variations and the negative influence of the polluted forming rivers over the water quality and phytoplankton composition (ANDRADE et al., 2012; ANDRADE; GIROLDO, 2014; RODRIGUES; TORGAN; SCHWARZBOLD, 2007). These studies point to the Gravataí River outflow (site 31) as a highly degraded local relative to others, as can be seen in the clusters analysis (Fig. 3-2a).

Considering the historical values, the time (years) and the seasonality (months) had influences on the water parameters (Tab. 3-3) in Lake Guaíba (site 41B). Time (years) present correlations (r) with the depth (-0.80), pH (-0.73), and electrical conductivity (0.73); and the air temperature (seasonal variation in the months) present correlations (r) with the depth (-0.86), pH (0.83), dissolved oxygen (-0.85) and phosphorus (-0.80). The monthly variations (depth, pH, DO, and P) can be explained by the rainy seasons, with more rainfall in the winter (Aug - 140 mm) and less between the summer-autumn (Apr - 86 mm), influencing the water flow in the lake (CEIC, 2017). The reduction in the depth through the years (2000-2014) is natural, due to the deposition of sediments. However, the reduction of pH and increase of electrical conductivity (EC) probably occurred due to pollution.

The time (years) also had influence in the sediment (Tab. 3-4), reducing the concentration of some elements (Ca, Mn, Ba, V, Pb, Co, Li, Be, and Hg). The reduction in the values of Pb ($r = -0.90$; $R^2 = 0.80$) and Hg ($r = -0.82$; $R^2 = 0.67$) is especially significant by the high toxicity of both metals. This decrease occurred in the entire world by the environmental pressure to control these priority metals (BING et al., 2016).

The rivers Caí, Gravataí, and Sinos are publicly known for their pollution, flowing through industrial areas, in a metropolitan region, suffering many environmental impacts. Thus, the remediation and protection of Jacuí's Delta and Lake Guaíba become even more complex by the liabilities upstream.

3.4 Conclusions

The historical data of water and sediment around the Jacuí's Delta shows the influence of the tributaries with low quality in the downstream sites.

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The pollution of the rivers Caí, Sinos, and Gravataí negatively affect the environmental quality of channel Navegantes and Lake Guaíba (catchment points to water supply); the water in those sites present reductions in dissolved oxygen and higher values of coliforms, and the sediment shows higher concentrations of metals Zn, Pb, Cr, and Hg. Despite the reduction along the years in the concentration of metals as Pb and Hg, in the sediment, the pollution from the tributary rivers still persists.

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Tab. 3-1. Historical means (2000 to 2014) of water parameters around the Jacuí's Delta.

Parameters	**31** Gravataí River	**36** Navegantes	**41B** Lake Guaíba	**57** Jacuí River	**58** Caí River	**59** Sinos River	**86A** Ilha da Pintada
air temperature (ºC)	22.0±0.4 [a]	21.8±0.4 [a]	21.0±0.4 [a]	21.0±0.4 [a]	21.2±0.4 [a]	21.5±0.4 [a]	21.5±0.4 [a]
water temperature (ºC)	21.6±0.4 [a]	21.2±0.4 [a]	21.2±0.4 [a]	21.1±0.4 [a]	20.8±0.4 [a]	20.9±0.4 [a]	21.1±0.4 [a]
depth (m)	4.5±0.1 [ed]	6.6±0.0 [c]	9.6±0.1 [a]	8.7±0.0 [b]	4.4±0.1 [e]	4.6±0.0 [d]	4.0±0.0 [f]
pH	6.9±0.0 [d]	7.0±0.0 [bc]	7.0±0.0 [b]	7.2±0.0 [a]	7.0±0.0 [b]	6.9±0.0 [cd]	7.2±0.0 [a]
EC (µS/cm)	185.6±7.7 [a]	88.1±1.4 [cd]	80.8±1.1 [d]	54.0±0.6 [e]	97.6±2.7 [c]	132.8±3.9 [b]	54.4±0.7 [e]
Transparency (cm)	26.1±0.7 [d]	43.1±1.2 [bc]	44.6±1.3 [abc]	54.2±2.3 [a]	48.4±1.9 [abc]	39.2±1.1 [c]	51.3±2.7 [ab]
Turbidity (NTU)	38.9±1.6 [a]	31.1±1.1 [a]	32.5±1.4 [a]	36.4±2.6 [a]	36.6±2.5 [a]	33.2±1.5 [a]	36.7±2.3 [a]
DO (mgO_2/L)	2.65±0.16 [e]	5.92±0.09 [c]	6.06±0.07 [bc]	7.93±0.08 [a]	6.54±0.09 [b]	3.86±0.12 [d]	7.76±0.08 [a]
BOD_5 (mgO_2/L)	8.22±0.48 [a]	1.95±0.06 [bc]	1.77±0.06 [bcd]	0.77±0.04 [e]	1.22±0.06 [cde]	2.64±0.11 [b]	0.87±0.05 [de]
Phosphorus (mg/L)	0.54±0.03 [a]	0.19±0.01 [bc]	0.16±0.00 [cd]	0.08±0.00 [e]	0.12±0.01 [de]	0.21±0.00 [b]	0.08±0.00 [e]
Nitrogen (mg/L)	5.96±0.27 [a]	2.17±0.07 [c]	2.00±0.06 [c]	1.29±0.03 [d]	1.97±0.05 [c]	3.17±0.12 [b]	1.26±0.04 [d]
TR_{105} (mg/L)	161.1±4.4 [a]	104.5±2.2 [d]	99.8±1.8 [d]	93.8±3.2 [d]	118.3±2.9 [c]	131.9±2.9 [b]	92.8±2.7 [d]
Coliforms (NMP/100 mL)	$3.8 \times 10^4 \pm 2 \times 10^3$ [a]	$1.5 \times 10^4 \pm 1 \times 10^3$ [b]	$1.2 \times 10^4 \pm 690$ [b]	210±46 [c]	446±117 [c]	$2.9 \times 10^3 \pm 249$ [c]	423±79 [c]
N	170	161	161	173	174	173	162

The means (±SE) followed by the same letter (in the comparative between sites) did not differ statistically from each other by the Tukey test at 95 % confidence. EC - Electrical Conductivity; DO - Dissolved Oxygen; BOD_5 - Biochemical Oxygen Demand; TR_{105} = Total solid residue at 105°C. N = average number of data per sampling site.

Tab. 3-2. Historical means (2000 to 2011) of metals in surface sediments around the Jacuí's Delta.

Parameters	**31** Gravataí River	**36** Navegantes	**41B** Lake Guaíba	**57** Jacuí River	**58** Caí River	**59** Sinos River	**86A** Ilha da Pintada
Al (mg/g)	45.9±3.2 [abc] [(1)]	54.3±4.3 [a]	44.5±5.5 [abc]	33.9±2.5 [bc]	47.7±3.5 [ab]	30.4±2.9 [c]	31.5±2.9 [bc]
Fe (mg/g)	28.6±2.9 [b]	38.4±1.9 [b]	34.4±4.6 [b]	36.3±3.5 [b]	52.5±2.9 [a]	30.6±2.9 [b]	32.2±1.8 [b]
Ca (mg/g)	-	3.6±0.2 [a]	1.9±0.3 [b]	-	-	-	2.3±0.2 [b]
Mn (mg/kg)	276.4±12.4 [d]	484.7±36.0 [bc]	423.6±40.8 [cd]	661.7±48.6 [b]	929.2±42.4 [a]	438.6±31.8 [cd]	539.3±62.7 [bc]
Ba (mg/kg)	179.1±11.5 [ab]	196.0±11.4 [a]	138.7±16.9 [bc]	196.9±11.2 [a]	229.0±9.4 [a]	121.9±9.1 [c]	187.5±14.7 [ab]
V (mg/kg)	-	120.0±10.6 [a]	72.5±13.7 [a]	60.0 [(2)]	-	-	110.4±11.4 [a]
Zn (mg/kg)	295.8±19.8 [a]	347.7±16.7 [a]	131.3±16.4 [b]	79.3±5.1 [c]	141.1±8.4 [b]	172.5±15.0 [b]	74.5±4.6 [c]
Cu (mg/kg)	64.3±4.7 [b]	103.5±6.2 [a]	41.0±6.7 [c]	52.4±5.0 [bc]	65.5±4.5 [b]	43.2±3.7 [c]	39.2±3.1 [c]
Pb (mg/kg)	50.0±4.2 [a]	62.7±4.6 [a]	26.1±3.7 [b]	20.7±3.4 [b]	29.9±3.5 [b]	19.7±3.5 [b]	24.8±2.9 [b]
Cr (mg/kg)	33.1±3.6 [b]	51.8±3.6 [a]	22.1±2.8 [bc]	21.6±1.7 [bc]	51.1±4.8 [a]	54.4±4.4 [a]	18.0±1.2 [c]
Ni (mg/kg)	22.8±2.1 [b]	37.3±2.5 [a]	18.9±2.5 [b]	22.9±2.3 [b]	42.2±2.9 [a]	26.2±2.6 [b]	20.8±2.0 [b]
Co (mg/kg)	-	28.5±1.8 [a]	15.3±2.0 [b]	15.0 [(2)]	-	-	21.6±1.6 [b]
Li (mg/kg)	-	14.8±1.1 [a]	8.2±1.5 [b]	-	-	-	8.3±0.7 [b]
Be (mg/kg)	-	2.53±0.30 [a]	2.11±0.34 [a]	1.00 [(2)]	-	-	2.26±0.33 [a]
Cd (mg/kg)	0.22±0.02 [a]	0.25±0.04 [a]	0.21±0.03 [a]	0.25±0.03 [a]	0.29±0.04 [a]	0.20±0.03 [a]	0.23±0.03 [a]
Hg (mg/kg)	0.16±0.01 [b]	0.43±0.04 [a]	0.12±0.02 [bc]	0.05±0.00 [c]	0.08±0.01 [bc]	0.16±0.02 [b]	0.06±0.00 [c]
As (mg/kg)	ND	ND	ND	ND	ND	ND	ND
Ag (mg/kg)	ND	ND	ND	ND	ND	ND	ND
N	16	16	17	17	16	17	16

[(1)] The means (±SE) followed by the same letter (in the comparative between sites) did not differ statistically from each other by the Tukey test at 95 % confidence. [(2)] No repetitions. ND = not detected. N = average number of data per sampling site.

Tab. 3-3. Historic data (means) of water parameters in the site 41B - Lake Guaíba.

Parameters	air	water	depht	pH	EC	Secchi	Turbidity	DO	BOD_5	P	N	TR_{105}	Coliforms
dates	ºC	ºC	m	-	µS/cm	cm	NTU	mg/L	mg/L	mg/L	mg/L	mg/L	MPN
2000	20.7	21.2	10.5	7.4	79.9	27.9	47.0	6.19	1.72	-	2.15	112.2	12,575
2001	23.1	22.2	10.4	7.2	73.3	31.7	38.4	5.68	1.66	-	2.40	103.6	13,575
2002	21.7	21.0	10.8	7.2	72.1	35.8	32.6	6.32	1.63	0.14	1.58	97.4	10,191
2003	22.8	22.1	10.3	7.0	77.9	36.8	36.9	5.65	1.44	0.19	1.77	91.0	7,339
2004	20.4	21.1	9.8	6.9	80.5	48.8	27.7	6.37	2.01	0.15	1.66	92.0	9,591
2005	21.4	21.3	9.2	7.1	84.3	52.5	25.1	6.46	2.15	0.14	1.78	99.4	12,091
2006	21.3	21.5	9.5	7.1	82.3	53.3	27.2	6.24	2.01	0.15	2.40	90.7	11,308
2007	21.6	21.3	9.3	6.8	77.7	44.6	31.9	5.88	1.65	0.15	2.15	112.3	11,083
2008	19.5	21.2	9.4	7.0	79.8	46.7	29.4	5.95	1.87	0.19	1.95	104.3	14,854
2009	20.6	21.2	9.4	7.0	80.8	46.3	31.0	6.06	1.55	0.15	1.97	99.7	13,308
2010	19.6	20.3	9.5	7.1	80.4	40.0	32.0	6.38	1.48	0.17	1.84	93.7	13,366
2011	21.0	20.6	8.7	6.8	79.7	41.3	36.4	6.26	1.95	0.18	2.47	93.3	19,250
2012	22.0	22.0	8.7	7.0	92.9	53.8	28.6	5.72	2.28	0.15	2.56	104.7	9,336
2013	19.5	20.7	8.5	6.9	88.1	44.5	29.3	5.72	1.51	0.15	2.04	99.4	14,872
2014	17.3	17.8	9.7	6.9	88.6	36.7	40.4	5.60	1.05	0.14	2.08	113.5	6,750
r_{year}	-0.62	-0.57	-0.80	-0.73	0.73	0.41	-0.26	-0.29	-0.16	-0.01	0.29	0.10	0.14
Jan	27.2	27.1	9.3	7.2	75.5	48.2	25.9	5.79	1.59	0.14	1.82	92.3	9,743
Feb	26.5	27.2	9.3	7.2	81.4	49.3	22.3	5.84	1.82	0.12	1.76	82.7	10,057
Mar	26.2	25.7	9.3	7.1	76.2	50.0	24.4	5.64	1.63	0.13	1.54	96.1	10,621
Apr	22.0	22.6	9.2	7.1	84.3	54.6	25.2	6.02	1.72	0.14	1.58	86.7	10,909
May	18.0	18.3	9.7	6.9	84.1	51.3	25.1	6.33	1.48	0.15	1.85	100.1	12,260
Jun	17.0	16.0	9.9	7.0	85.3	43.5	30.8	6.69	1.70	0.18	2.10	101.6	16,115
Jul	13.3	14.8	9.8	6.9	86.9	37.5	47.3	6.86	2.35	0.20	2.48	110.4	13,564
Aug	16.7	15.8	9.7	6.9	81.1	37.9	35.0	6.56	1.70	0.17	2.30	108.4	11,179
Sep	17.1	17.7	9.9	7.0	78.3	32.5	41.0	6.23	1.91	0.17	1.96	105.4	13,254
Oct	20.6	20.7	9.8	6.9	76.6	34.7	45.0	5.57	1.69	0.18	2.19	111.2	13,847
Nov	23.9	23.7	9.4	7.1	80.6	33.9	41.2	5.53	1.82	0.17	2.30	101.9	11,577
Dez	23.5	24.9	9.5	7.1	79.6	43.2	26.4	5.71	1.90	0.16	1.82	99.9	14,700
$r_{air\,ºC}$	-	0.99	-0.86	0.83	-0.62	0.45	-0.60	-0.85	-0.43	-0.80	-0.65	-0.71	-0.59
Conama No. 357	-	-	-	6 - 9	-	-	100	5	5	0.05	3.7	-	1,000

Secchi – transparency (Secchi disc); NTU - nephelometric turbidity units; EC – electrical conductivity; DO – dissolved oxygen; BOD_5 - biochemical oxygen demand; TR_{105} - total residues at 105°C; MPN - Most Probable Number (in 100 mL^{-1}). r - Pearson correlation (relative to years/air temperature). Conama No. 357 – Class 2 (Brazil, 2005) - Brazilian reference values for surface waters.

Tab. 3-4. Historic data (means) of metals in surface sediments in the site 41B - Lake Guaíba.

Year	Al	Fe	Ca	Mn	Ba	V	Zn	Cu	Pb	Cr	Ni	Co	Li	Be	Cd	Hg
	.... mg/g			.... mg/kg												
2000	45.8	57.0	2.7	680	275	130	218	81.0	49.0	38.5	23.0	23.0	18.0	4.0	0.30	0.25
2001	72.4	47.7	2.8	696	220	185	219	-	50.0	40.5	36.5	27.0	17.5	3.5	0.25	0.24
2002	69.5	47.1	2.8	695	-	130	209	-	30.0	39.0	42.0	33.0	13.0	4.0	0.10	0.21
2003	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2004	27.3	25.5	1.7	425	140	75	93.0	-	25.0	11.0	16.5	13.5	6.00	1.5	0.30	0.08
2005	13.6	15.3	1.3	281	85	35	83.0	28.0	30.0	9.5	11.0	11.5	2.00	1.0	0.10	0.08
2006	13.6	18.5	1.2	317	80	30	70.5	28.5	25.0	13.0	12.0	10.0	2.50	1.0	0.20	0.07
2007	33.6	28.3	1.0	505	175	70	125	49.0	10.0	22.0	19.5	14.0	9.50	2.0	0.10	0.06
2008	40.7	34.4	-	335	140	40	212	68.0	13.0	33.5	27.5	18.5	8.00	1.0	0.30	0.14
2009	84.9	-	-	313	93	24	65.5	27.1	11.4	14.5	9.19	5.50	4.50	-	0.16	0.08
2010	48.5	-	-	214	75	20	58.2	28.0	10.3	12.0	8.21	5.14	3.78	0.6	0.17	0.04
2011	60.1	-	-	249	70	20	78.0	23.0	16.0	14.0	9.00	6.00	4.00	1.0	0.10	0.07
R^2	0.00	0.54	0.92	0.76	0.66	0.76	0.47	0.44	0.80	0.42	0.47	0.67	0.59	0.72	0.15	0.67
r	0.02	-0.74	-0.96	-0.87	-0.81	-0.87	-0.69	-0.66	-0.90	-0.65	-0.69	-0.82	-0.77	-0.85	-0.39	-0.82
mean	46.4	34.2	1.93	428	135	69.0	130	41.6	24.5	22.5	19.5	15.2	8.07	1.96	0.19	0.12
±se	7.1	5.3	0.31	56	22	16.9	21	7.8	4.4	3.8	3.5	2.8	1.74	0.43	0.03	0.02

No detection for As and Ag. No differences between months. R^2 - coefficient of determination; r - correlation coefficient; ±se – standard error.

4. CAPÍTULO III - SEDIMENT POLLUTION IN MARGINS OF THE LAKE GUAÍBA, SOUTHERN BRAZIL [5]

4.1 Introduction

Metropolitan areas have high population densities that increase the environmental impacts over the water resources. This damage is even greater in lakes due to the reduced water flow and consequently increasing the degradation of the environmental quality (AMORIM et al., 2009; CAVALCANTI et al., 2014). Urban lakes are important to the maintenance of anthropic ecosystems and the quality of life of the population. However, they are distinguished from the lakes in rural or natural areas, suffering major impacts from development in surrounding areas, making them vulnerable to environmental impacts (HENNY; MEUTIA, 2014). Metals are a common pollutant in urban lakes originating from agriculture, industry and urban development, as well as from natural sources, entering in the sediment by punctual or diffuse ways (LANDRE et al., 2011).

Bed sediments are formed by deposition of organic and inorganic particles that accumulate on the bed of the water bodies, especially in lentic waterways such as lakes. This environment plays an important role in aquatic ecosystems, influencing biogeochemical cycles, nutrients redistribution, and maintenance of environmental quality (BEVILACQUA et al., 2009; CAVALCANTI et al., 2014; COTTA; REZENDE; PIOVANI, 2006). The risk associated with the sediment pollution involves the input of toxic metals in food chains by biomagnifications; being fish on the top of the aquatic food chain, and an important part of human diet, becomes even more aggravated with the presence of contaminants, even in low concentrations.

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Sediments are able to act as a sink or a source of essential nutrients, metals and pollutants, even after long periods following their inputs on the water body (BEVILACQUA et al., 2009; PRADIT; PATTARATHOMRONG; PANUTRAKUL, 2013). Thus, sediments play an important role recording the processes and changes that occurred directly in the water body or in its watershed (AMORIM et al., 2009), allowing its use as an indicator of environmental quality and potential pollution to aquatic organisms (BELO; QUINÁIA; PLETSCH, 2010; CAVALCANTI et al., 2014; COTTA; REZENDE; PIOVANI, 2006).

Lake Guaíba has historical, economic and cultural importance to Porto Alegre, the capital of Rio Grande do Sul, the southernmost State of Brazil, and its metropolitan region. Water and sediments of Lake Guaíba have environmental quality issues (ANDRADE; GIROLDO, 2014; BENDATI, 2000; COSTA; HARTZ, 2009). However, there is still a lack of studies on sediment pollution in Lake Guaíba. The environmental analysis of the sediments might promote important information on environmental pollution and help with future prevention of the waste disposal and water use. Therefore, the aim of this study was to evaluate the pollution of surface sediments in margins of Lake Guaíba, Rio Grande do Sul (RS), Brazil.

4.2 Materials and methods

Sediment sampling was performed on November 2015, in 12 sites located in the denominated "left margin" of Lake Guaíba (Fig. 4-1), comprising the cities of Porto Alegre (state capital) and Viamão (Tab. 4-1). All materials used in the procedures were decontaminated with hydrochloric acid solution. Analyzes were made at the Laboratory of Soil and Waste Bioremediation and Laboratory of Soil Analysis (LAS), from the Federal University of Rio Grande do Sul (UFRGS), Brazil.

Tab. 4-1. References and characterization on sampling sites of surface sediment in margins of the Lake Guaíba.

sites	Reference [a]	Distance [j]	Geographic coordinates	Time [k]	Air [k]	Water [k]	pH	EC_w
		km			°C	°C		µS/cm
1	Ponta do Gasômetro	0.0	30°02'25.46" S; 51°14'26.73" W	09:15	21	23	6.8	79
2	Parque da Harmonia	0.7	30°02'34.82" S; 51°14'06.19" W	09:30	22	23	6.8	78
3	Anfiteatro Pôr-do-sol [b]	1.5	30°02'45.84" S; 51°14'02.85" W	10:00	22	23	7.0	450
4	Parque Marinha do Brasil	2.1	30°03'11.52" S; 51°13'58.72" W	10:15	20	23	6.9	95
5	Museu Iberê Camargo	4.8	30°04'27.61" S; 51°14'34.83" W	10:30	21	23	7.0	92
6	Cristal [c]	7.1	30°05'29.43" S; 51°14'58.49" W	11:00	31	24	6.9	92
7	Tristeza [d]	11.1	30°06'58.05" S; 51°15'33.24" W	14:00	27	24	7.1	171
8	Pedra Redonda [e]	13.1	30°07'24.13" S; 51°14'58.47" W	14:30	26	25	7.1	89
9	Praia de Ipanema [f]	15.9	30°08'14.64" S; 51°13'45.32" W	15:00	26	25	7.1	84
10	Av. Guaíba [g]	16.5	30°08'35.18" S; 51°13'32.19" W	15:30	28	25	7.1	82
11	Ponta dos Coatis [h]	36.0	30°15'45.17" S; 51°09'03.37" W	16:30	22	23	7.3	75
12	Praia de Itapuã [i]	48.5	30°17'00.46" S; 51°01'19.23" W	18:00	20	23	7.3	76

[a] Public reference location close to sampling sites; [b] Near to Dilúvio Stream outflow; [c] Near to Cavalhada Stream outflow; [d] Dr. Mario Totta Street; [e] Evaristo do Amaral Street; [f] Near to Capivara Stream outflow; [g] Near to Clube do Professor Gaúcho; [h] Rural zone of Porto Alegre; [i] Itapuã District - Viamão, RS. [j] Accumulated interval between sites (water route). [k] Data from the moment of sample collection; EC_w - Electrical Conductivity (water).

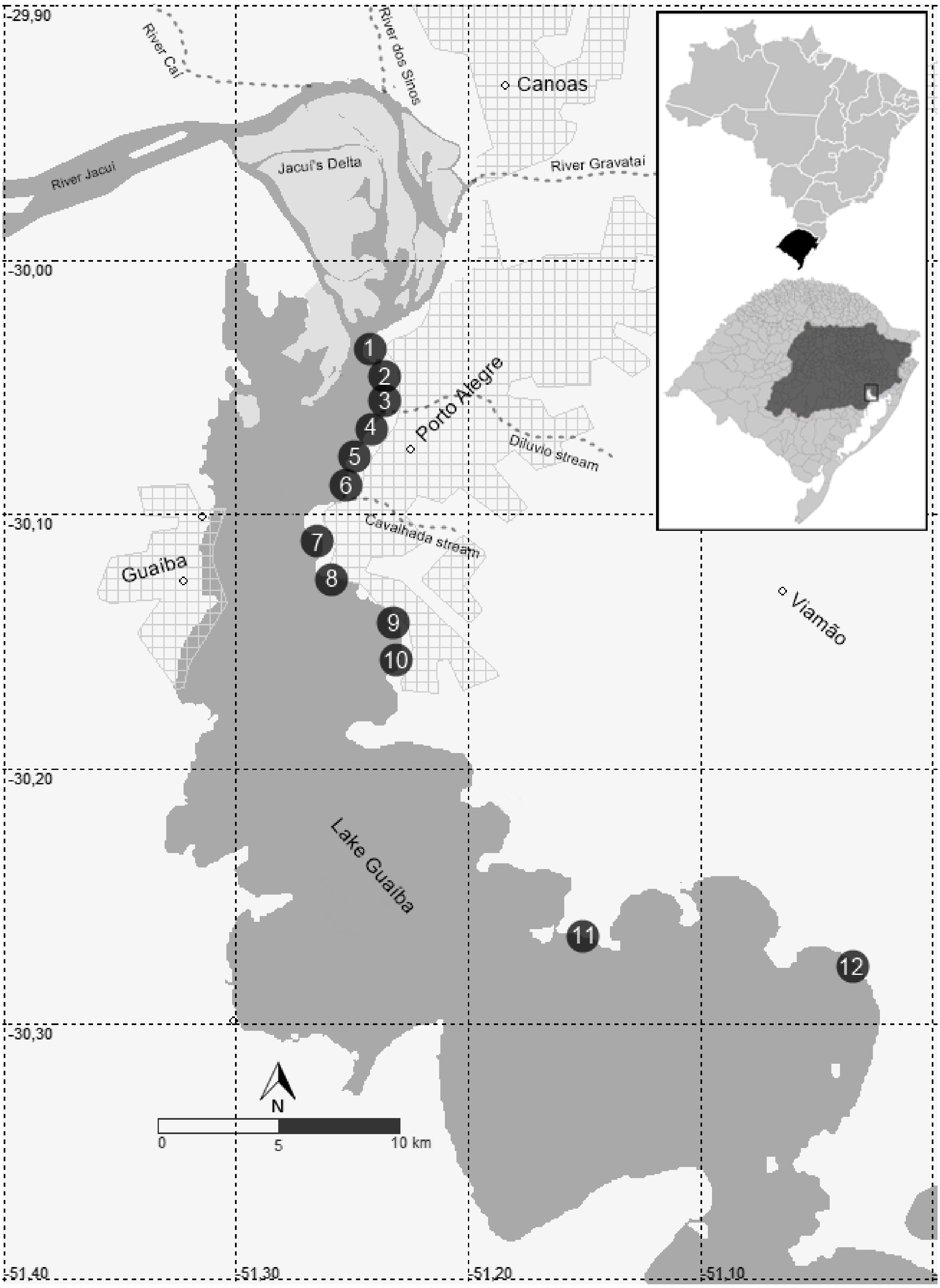

Fig. 4-1. Sampling sites of surface sediment in margins of the Lake Guaíba, Porto Alegre, RS, Brazil. Darkest area in state map represents the lake drainage basin.

4.2.1 Study Area

Lake Guaíba is located in the metropolitan region of Porto Alegre (29°55'-30°24'S; 51°01'-51°20'W), the capital of Rio Grande do Sul State (Fig. 4-1), Southern Brazil. The lake is the main water source for the capital since its founding in the early XVIII century. Presently, it supplies water for approximately 2 million people. The lake forms a navigable link channel between the state's countryside and the ocean (Fig. 4-1), due to its connection with Jacuí's Delta (north) and Patos Lagoon (south). Guaíba covers an area of 496 km^2 with 2 m of average depth, with variations influenced by rainfall and dynamic of winds (ANDRADE; GIROLDO, 2014; MENEGAT et al., 2006; NICOLODI; TOLDO JR; FARINA, 2013), classifying as a "large urban open shallow lake" (JANSSEN et al., 2014).

The drainage basin of the Lake Guaíba covers 84,700 km^2, which represents half of the municipalities and one third of the state's area (Fig. 4-1). Lake Guaíba watershed (29º55'-30º37'S; 50°56'-51°46'W), specifically, has 2,523.62 km^2 (0.9 % of state's area), covering 14 municipalities and up to 2.2 million inhabitants (IBGE, 2017; SEMA/RS, 2010). The climate is characterized as humid subtropical ("Cfa" in Köppen-Geiger classification), with annual climate averages: 19°C of air temperature; 76 % of air humidity; and 1,324 mm of annual precipitation (MENEGAT et al., 2006).

With a large drainage area, Lake Guaíba accumulates impacts of different water bodies, which persist for a long period due to lower water movement and, therefore, lower pollutant dilution. Currently, the lake has multiple uses such as water supply source, effluent dilution, navigation, recreation, and fishing. Until the mid-XX century, the lake uses were even more varied, being a popular destination for beachgoers, athletes, and tourists; these activities were restricted overtime due to increase on water pollution, already reported in the XIX century (PRESTES, 2014; RÜCKERT, 2013). The margins of the Guaíba were highly frequented by bathers, especially between the 1940s and 1970s; however, by the 1950s they began to systematically abandon due to the increase in Lake Guaíba pollution (PRESTES, 2008). According to Prestes (2008), despite the strong historical, cultural and emotional connection, the acceptance of pollution and "beaches loss" was seen by the population in general as something natural and an "inevitable consequence of growth of underdeveloped economies".

4.2.2 Sediment sampling

Sediment was sampled in the surface layer (0-5 cm), below 50 cm of water column, with a scoop-shaped sampler (crafted with PVC pipes). Each sample was composed by five sub-samples per site. In the sampling sites were measured the air and water temperature (with thermometer); electrical conductivity and pH of water samples (Tab. 4-3) were measured immediately after its arrival to the laboratory (with bench meters). Samples were transported to the laboratories (immediately after the collection) in coolers at 4°C and maintained refrigerated until preparation for analysis.

4.2.3 Sample preparation and analysis

Sediment samples were dried (45 °C), sieved (2 mm), and then stored in plastic flasks. Natural samples were maintained refrigerated as counterproofs. Grain size analyzed (2 mm) followed guidelines of CONAMA Resolution 454 (BRASIL, 2012). The samples were evaluated for: electrical conductivity (sediment/deionized water ratio 1:5), pH 1:2.5 (H_2O, KCl, and $CaCl_2$), bulk (Ds) and particle (Dss) densities, particle-size (pipette), total organic carbon (TOC; Walkley-Black), available phosphorus (P; Melich-1), Total Kjeldahl Nitrogen (TKN); and pseudo-total elements (Fe, Al, Ca, Mg, Na, K, Mn, Ba, Zn, V, Pb, Cu, Cr, Ni, Cd, Mo, and Se) according to the method 3050B (USEPA, 1996). The quantification of elements was analyzed in ICP-OES, using external (NIST) and internal control standards (PSJ-1 and PSJ-M) to quality assurance control (Tab. 4-2). All analyzes were performed in triplicate.

X-ray diffraction (XRD) analyses were made on powder blades of total sediments (sand, silt, and clay fractions) at a *Bruker-D2-Phaser* equipment, over CuKα radiation [λ = 1.54 Å], steps 0,020º and range 4 to 70 º2θ. Identification of minerals was performed with EVA/3.0 program and results are interpreted according to Brindley and Brown(1980).

4.2.4 Statistical analysis

Results were submitted to analysis of variance (ANOVA) and, when significant, means were compared by Scott-Knott test, with a 95 % confidence interval (*p*<0.05), using statistical software Assistat v7 (SILVA; AZEVEDO, 2016). Graphical models and regressions were performed with the software SigmaPlot v11 and multivariate analysis with the software Statistica v13.

Tab. 4-2. Quality assurance control with external (NIST) and internal (PSJ) Standard Reference Materials (SRM).

	Zn	Pb	Cu	Cr	Ni	Cd	Co
	.... µg/g						....
LD	2.0	2.0	0.6	0.4	0.4	0.2	0.4
NIST 1646a [1]	49	12	10	41	23	0.1	5.0
Measured values	38±1.6	13±1.8	7.1±0.0	24±0.8	20±0.8	<LD	4.9±0.3
Recovery (%)	**77**	**113**	**71**	**60**	**88**	**-**	**98**
NIST 2704 [2]	408	150	-	122	43	2.9	14
Measured values	386±7.2	155±4.1	98±1.1	90±1.7	38±0.5	3.0±0.1	11±0.2
Recovery (%)	**96**	**103**	**-**	**74**	**89**	**103**	**83**
PSJ-1 [3]	13	13	4.7	30	9.0	0.1	1.9
Measured values	13±0.8	12±0.5	4.2±0.1	32±7.7	7.3±0.5	<LD	1.6±0.2
Recovery (%)	**96**	**91**	**89**	**105**	**81**	**-**	**83**
PSJ-M (fortified) [4]	13	50	4.7	90	40	10	40
Measured values [5]	13±0.5	48±0.0	4.3±0.1	91±2.0	43±0.6	11±0.1	40±0.3
Recovery (%)	**100**	**96**	**91**	**101**	**107**	**114**	**101**

Limit of Detection (LD); [1] Estuarine Sediment; [2] Buffalo River Sediment; [3] São Jerônimo Soil - internal control standard of LAS/UFRGS; [4] Metals fortified over PSJ-1 (µg/g): Pb – 40; Cr – 60; Ni – 40; Cr – 10; Co – 40. [5] Measured value ± standard error.

4.3 Results

Surface sediment in margins of the Lake Guaíba presented as sandy (>95 %) in all analyzed samples, with fine fraction (clay+silt) ranging from 1 to 4 % (Tab. 4-3).The coarse sand fraction (0.2-2 mm) prevails in all sites. The highest values of fine sand fraction (0.05-0.2 mm) occurred at the sites 11 (Ponta dos Coatis) and 12 (Praia de Itapuã) and fine fractions (<65 µm) at the sites 3 (Anfiteatro Pôr-do-sol) and 4 (Parque Marinha do Brasil), in central area of the Porto Alegre, as well as at the site 12 (Praia de Itapuã). Apparent (bulk) density (Ds) of sediments evaluated range were from 1.46 to 1.63 g/cm³ and particle density (Dss) range were from 2.55 to 2.63 g/cm³. Total porosity (Pt) ranged from 0.38 to 0.43 cm³/cm³, with highest values (p<0.05) at the sites 3 and 11 (Tab. 4-3).

Based on the intensity of the reflections in the diffractograms, in all samples, the quartz was the predominant mineral associated with feldspars, especially in the samples of the sites 1, 3, and 6 (Fig. 4-2). It was also observed the presence of pyroxenes of high intensity at the site 2 and 9 and, also, a reflection at 1.58 nm for 2:1 clay minerals (vermiculite or smectite) at site 11. In general, the sediments of Guaíba can be classified as quartzites.

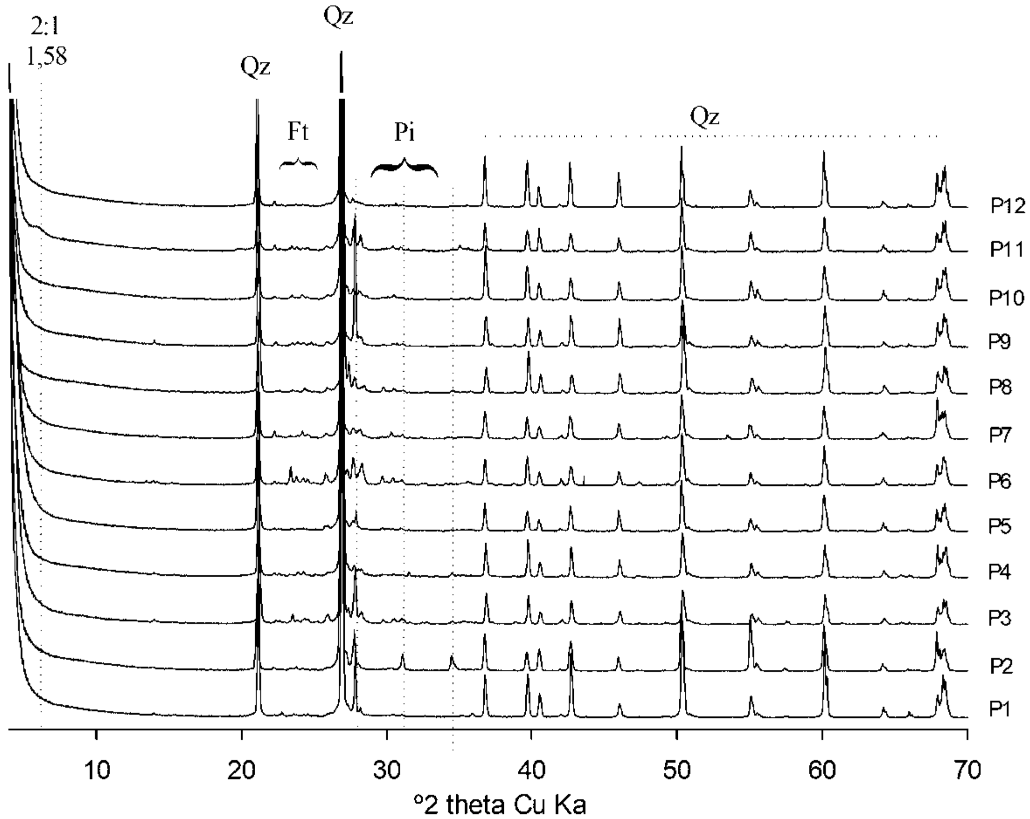

Fig. 4-2. X-ray diffraction (XRD) of total surface sediments in margins of the Lake Guaíba. 2:1 minerals Vermiculite or Smectite – (1,58 nm); Qz – Quartz (3,34 nm); Ft – Feldspar (4,04-4,02 nm;); Pi – Pyroxene (3,25; 2,91-2,87; 2,60 nm).

Electrical conductivity (EC) of sediment showed a great variation in the evaluated sites, mainly between the sites 1 (Ponta do Gasômetro, near to the Jacuí's Delta) and 3 (Dilúvio Stream outflow), ranging from 24 to 187 μS/cm, respectively (Tab. 4-3). Lower pH (KCl) values occurred at the sites 4, 6, and 9 (near to the outflows of streams Dilúvio, Cavalhada e Capivara, respectively).

Total organic carbon (TOC) ranged from 0.35±0.02 to 5.54±0.22 g/kg in margins of sites 1 to 4, respectively (Fig. 4-3a). Total nitrogen (TKN) ranged from 42±2 to 350±18 mg/kg (Fig. 4-3b), and presented a strong correlation (Tab. 4-6) with TOC (R^2 =0.94; p<0.01) and clay fraction (r = 0.83; p<0.01). Available phosphorus (P) ranged from 10±0.2 to 109±4.6 mg/kg (Fig. 4-3c), with the highest values at the sites 3 (Dilúvio Stream outflow) and 6 (Cavalhada Stream outflow). Available P was correlated with clay fraction (r = 0.58; p<0.01).

The average magnitude of pseudo-total concentration of elements followed the order (Tab. 4-4 and Tab. 4-5): Fe > Al > Ca > Mg > Na > K > Mn > Ba > Zn > V > Pb > Cu > Cr > Ni > Cd (Mo and Se were not detected). The lowest values (Fe, Al, Ca, Mg, K, Na, Mn, Ba, Zn, and V) were found at the sites 1 (Ponta do Gasômetro), 2 (Parque da Harmonia) and 12 (Praia de Itapuã), as well as at the sites 8 (Pedra Redonda), 9 (Praia de Ipanema), and 10 (Av. Guaíba), in south of the Porto Alegre (Fig. 4-1). The sites with more heavy metals concentration (Tab. 4-5) above the third quartile (Q3) were the 3 and 4 (near to Dilúvio Stream outflow), followed by the site 6 (near to Cavalhada Stream outflow); the same occurring to TOC, TKN, and P (Fig. 4-3).

4.4 Discussion

Surface sediment in margins of the Lake Guaíba showed significant differences among the evaluated sites, with indications of punctual water pollution. Guaíba is a large urban lake, fed by rivers (Jacuí, Sinos, Caí, and Gravataí) wide spread through a large part of the Rio Grande do Sul (RS) state, Brazil. Along the way, the watershed suffers many punctual and diffuse (non-punctual) impacts (as runoff, sewage and industrial wastewater releases, dredging), influencing on the lake sedimentary deposits. Studies on Lake Guaíba Watershed refers alterations in macronutrients and metals concentrations, reflecting in reductions of dissolved oxygen and increasing the environmental toxicity (ANDRADE; GIROLDO, 2014; ÁVILA; BIANCHIN; ILLI, 2015; BENDATI, 2000; COSTA; HARTZ, 2009).

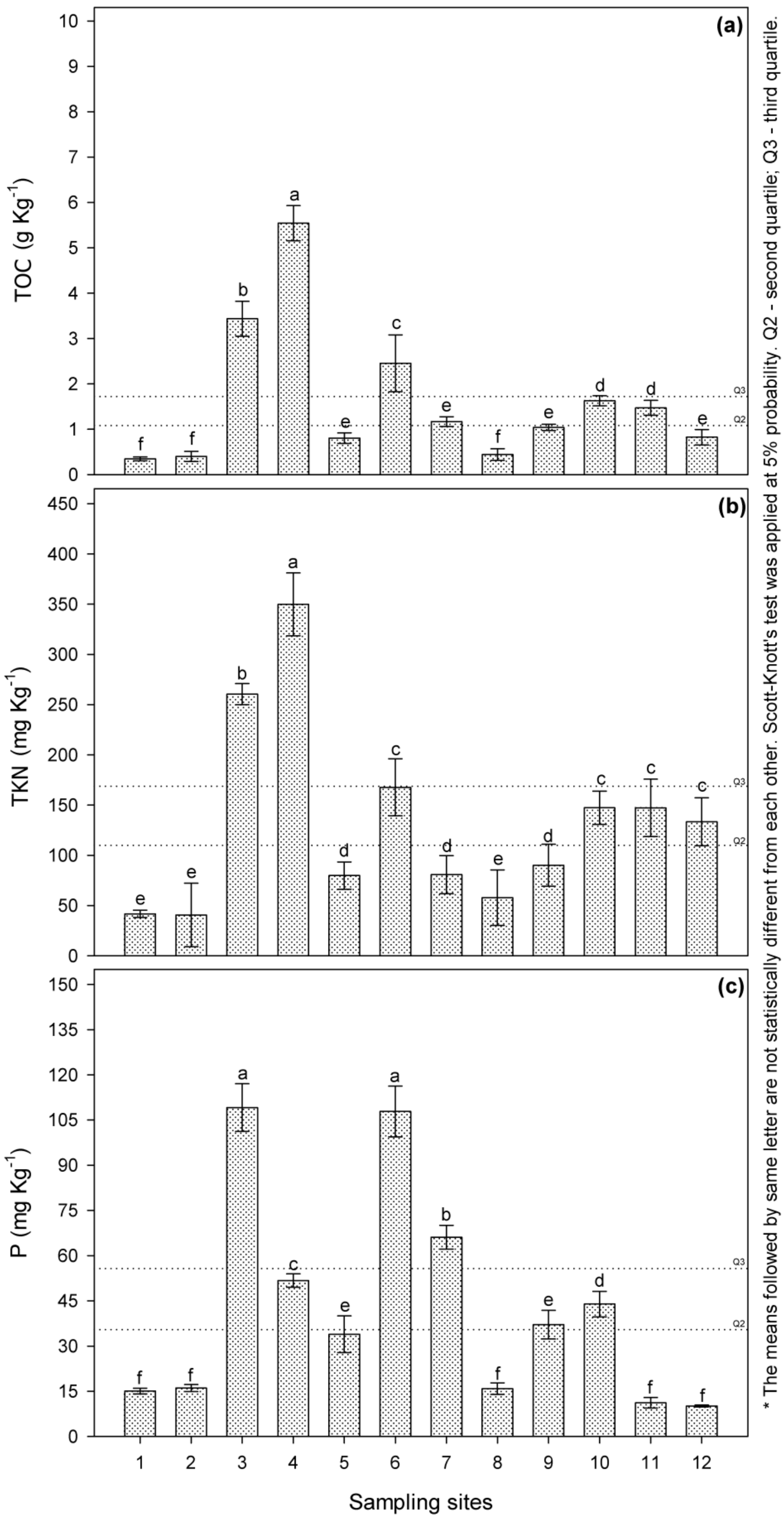

Fig. 4-3. Values of (a) organic carbon, (b) nitrogen, and (c) phosphorus of surface sediment in margins of the Lake Guaíba.

Tab. 4-3. Grain size fractions (%), densities, electrical conductivity (EC), and pH of surface sediment in margins of the Lake Guaíba.

sites	gravel	c. sand	f. sand	silt	clay	Ds	Dss	Pt	EC	pH	pH	pH	Δ pH
	-2 to -1	0 to 2	3 to 4	5 to 8	φ >9	g/cm³	g/cm³	cm³/cm³	µS/cm	H_2O	KCl	$CaCl_2$	
1	11.5 [d*]	79.9 [b]	7.5 [d]	0.4 [f]	0.7 [c]	1.63 [a]	2.61 [a]	0.38 [c]	24.0 [d*]	7.1 [c]	6.8 [d]	6.4 [e]	+0.3 [a]
2	14.0 [d]	77.2 [c]	7.8 [d]	0.3 [g]	0.8 [c]	1.58 [b]	2.63 [a]	0.40 [b]	45.9 [c]	7.0 [c]	6.8 [d]	6.3 [f]	+0.2 [b]
3	8.6 [e]	66.7 [e]	20.6 [b]	2.3 [b]	1.8 [a]	1.46 [e]	2.56 [b]	0.43 [a]	187 [a]	6.7 [d]	6.8 [d]	6.3 [f]	-0.1 [d]
4	12.6 [d]	65.3 [e]	18.4 [b]	1.7 [c]	2.0 [a]	1.53 [c]	2.57 [b]	0.41 [b]	195 [a]	6.6 [e]	6.5 [f]	6.3 [e]	+0.0 [c]
5	7.0 [e]	79.2 [b]	12.0 [c]	0.8 [e]	1.0 [b]	1.57 [b]	2.62 [a]	0.40 [b]	75.5 [b]	7.6 [a]	7.7 [a]	7.0 [a]	-0.1 [d]
6	24.3 [a]	61.8 [f]	11.7 [c]	1.0 [e]	1.2 [b]	1.52 [c]	2.55 [b]	0.40 [b]	83.0 [b]	6.4 [e]	6.4 [g]	5.9 [g]	+0.0 [c]
7	21.5 [b]	69.1 [d]	8.0 [d]	0.6 [f]	0.8 [c]	1.56 [b]	2.61 [a]	0.40 [b]	53.4 [c]	7.0 [c]	6.8 [d]	6.3 [f]	+0.2 [b]
8	9.4 [e]	76.2 [c]	12.8 [c]	1.3 [d]	0.3 [d]	1.57 [b]	2.61 [a]	0.40 [b]	30.2 [d]	7.3 [b]	7.4 [b]	6.7 [c]	-0.1 [d]
9	16.6 [c]	76.2 [c]	6.2 [d]	0.2 [g]	0.8 [c]	1.56 [b]	2.57 [b]	0.39 [b]	57.3 [c]	6.7 [d]	6.6 [e]	6.2 [f]	+0.1 [c]
10	8.4 [e]	85.0 [a]	5.8 [d]	0.1 [g]	0.8 [c]	1.55 [b]	2.59 [a]	0.40 [b]	47.0 [c]	7.1 [c]	7.2 [c]	6.5 [d]	-0.1 [d]
11	7.3 [e]	48.8 [h]	42.7 [a]	0.3 [f]	0.9 [c]	1.49 [d]	2.58 [b]	0.42 [a]	66.6 [b]	7.3 [b]	7.1 [c]	7.0 [a]	+0.2 [b]
12	0.0 [f]	51.6 [g]	44.3 [a]	3.4 [a]	0.8 [c]	1.57 [b]	2.62 [a]	0.40 [b]	49.6 [c]	7.3 [b]	6.9 [d]	6.8 [b]	+0.4 [a]

*Means followed by same letter are not statistically different from each other. Scott-Knott's test was applied at 5 % probability. Fraction <2 mm. Phi (φ): Krumbein's particle size scale. Ds - bulk density; Dss - particle density; Pt - total porosity; EC (1:5); pH (1:2.5). Δ pH - difference between H_2O and KCl values.

Tab. 4-4. Levels of macro elements of surface sediment in margins of the Lake Guaíba.

sites	Fe	Al	Ca	Mg	K	Na	Mn	Ba	V
	.... %		.... g/kg				....	……... mg/kg	……...
1	0.33 [c]	0.09 [f]	0.17 [e]	0.09 [g]	0.07 [c]	0.23 [b]	0.12 [c]	25.38 [d]	8.85 [c]
2	0.41 [c]	0.07 [f]	0.16 [e]	0.09 [g]	0.07 [c]	0.22 [b]	0.15 [c]	28.18 [d]	8.24 [c]
3	0.45 [c]	0.24 [b]	0.48 [b]	0.47 [b]	0.25 [a]	0.28 [b]	0.04 [c]	38.39 [c]	8.29 [c]
4	0.61 [b]	0.39 [a]	0.87 [a]	0.41 [c]	0.23 [a]	0.33 [a]	0.06 [c]	62.75 [b]	13.97 [a]
5	0.65 [b]	0.16 [d]	0.40 [c]	0.30 [d]	0.15 [b]	0.24 [b]	0.27 [b]	48.17 [c]	11.13 [b]
6	0.39 [c]	0.22 [b]	0.49 [c]	0.56 [a]	0.21 [a]	0.27 [b]	0.03 [c]	29.75 [d]	7.35 [c]
7	0.63 [b]	0.20 [c]	0.54 [b]	0.57 [a]	0.23 [a]	0.30 [a]	0.08 [c]	38.21 [c]	10.72 [b]
8	0.41 [c]	0.10 [f]	0.27 [d]	0.35 [d]	0.08 [c]	0.33 [a]	0.11 [c]	32.81 [d]	6.02 [d]
9	0.36 [c]	0.13 [e]	0.25 [d]	0.30 [d]	0.17 [b]	0.30 [a]	0.06 [c]	24.46 [d]	6.38 [d]
10	0.36 [c]	0.13 [e]	0.41 [c]	0.23 [e]	0.16 [b]	0.37 [a]	0.09 [c]	29.58 [d]	6.44 [d]
11	1.22 [a]	0.20 [c]	0.85 [a]	0.56 [a]	0.26 [a]	0.33 [a]	0.60 [a]	84.39 [a]	12.44 [a]
12	0.41 [c]	0.10 [f]	0.29 [d]	0.16 [f]	0.06 [c]	0.29 [b]	0.10 [c]	25.13 [d]	4.31 [e]
Q3	0.61	0.21	0.53	0.50	0.23	0.32	0.14	43.87	11.16
Q2	0.44	0.14	0.41	0.35	0.17	0.29	0.09	31.02	8.06

*Means followed by same letter are not statistically different from each other by Scott-Knott's test at 95 % of confidence. Fraction <2 mm. Q3 - third quartile; Q2 - second quartile.

Tab. 4-5. Levels of zinc, chromium and cadmium of surface sediment in margins of the Lake Guaíba and reference values.

sites	Zn	Pb	Cu	Cr	Ni	Cd
	………………………………… mg/kg …………………………………					
1	9.27 f*	3.12 e	1.79 d	3.63 d	0.97 e	0.30 a
2	13.01 e	2.24 e	1.74 d	2.71 e	0.56 f	0.36 a
3	34.48 a	14.60 a	10.88 a	4.54 c	1.43 d	0.36 a
4	28.64 b	9.15 b	8.26 b	5.73 a	2.97 b	0.32 a
5	26.29 b	8.08 b	4.84 c	3.28 d	1.20 e	0.27 b
6	27.73 b	6.24 c	10.39 a	5.10 b	3.42 a	0.25 b
7	23.38 c	6.13 c	4.12 c	3.64 d	2.01 c	<LD
8	24.33 c	3.47 e	1.79 d	1.52 g	1.39 d	0.23 b
9	11.85 e	4.29 e	1.78 d	2.73 e	0.51 f	0.22 b
10	17.78 d	3.56 e	2.06 d	2.11 f	1.07 e	<LD
11	33.57 a	4.69 d	1.85 d	3.38 d	1.76 c	<LD
12	8.08 f	3.02 e	0.85 d	2.12 f	0.18 g	<LD
LD	2	2	0.6	0.4	0.4	0.2
Q3	27.84	7.15	5.90	4.21	1.82	0.31
Q2	23.87	4.47	2.11	3.16	1.28	0.24
RV (1)	36.03	8.85	6.77	4.96	-	0.10
RV (2)	14.78	5.02	2.32	1.84	2.67	0.06
GV (3)	123	35	35.7	37.3	18	0.6

*Means followed by same letter are not statistically different from each other by Scott-Knott's test at 95 % of confidence. <2 mm fraction. LD - Limit of Detection; ND - Not Detected; Q3 - third quartile; Q2 - second quartile. (1) RV - Reference values to sediments (Studies on Lake Guaíba Watershed): Bendati (2000);(2) Fontoura (2014) – Q3.(3) GV - Guiding values to dredged sediments: CONAMA Resolution 454/2012 (Level 1).

Sediment on marginal areas of the Lake Guaíba are predominantly composed by sandy fraction, with deposition of fractions of silt, clay and organic matter especially in deep parts (NICOLODI; TOLDO JR; FARINA, 2013). According to Carranza-Edwards et al. (2009), beaches are exposed to different physical processes (such as level changes, wave movements, winds and other factors), which lead to removal the fine fractions. The effect of wave turbulence occurs also on Lake Guaíba (NICOLODI; TOLDO JR; FARINA, 2013), defining the composition of the sediment in the lacustrine beaches. With the weathering of the rocks, primary and secondary minerals remain in the sediments, charged from various sources due to the rivers that supply the Lake Guaíba. Mineralogy found less altered clay minerals such as pyroxenes and 2:1, as well as more weathered clay minerals such as quartz and feldspars.

Tab. 4-6. Pearson correlation coefficients (r) on surface sediment in margins of the Lake Guaíba.

	clay	**TOC**	**Al**	**TKN**	**P**
clay	-	0.86**	0.79**	0.83**	0.58**
TOC	0.86**	-	0.93**	0.94**	0.56**
Al	0.79**	0.93**	-	0.86**	0.53**
Zn	0.53**	0.55**	0.69**	0.54**	0.53**
Pb	0.78**	0.68**	0.68**	0.67**	0.72**
Cu	0.75**	0.75**	0.73**	0.68**	0.89**
Cr	0.79**	0.77**	0.81**	0.67**	0.65**
Ni	0.49**	0.65**	0.77**	0.55**	0.60**

*significant at 0.05 level; **significant at 0.01 level. n = 36.

Compared to the other sampling, the sites 3, 4, and 6 (next to Dilúvio and Cavalhada streams outflows) present lower pH and particle density (Dss), and higher electrical conductivity (EC), total organic carbon (TOC), and concentration of macronutrients (N, P, K, Ca, Mg) and metals (Al, Zn, V, Cu, Ni and Pb), indicating a possible organic interference from these water bodies with notorious sewage pollution.

Environmental changes occurred especially in places near to Dilúvio stream (with outflow near to the sites 3 and 4), which flows over 15 km in regions with high population density and areas with industry and service companies. The Dilúvio stream is a canalized small river with wastewater and sewage illegal launches along the water course, causing multiple possibilities of organic and metal pollution. Similar situation occurs at Cavalhada (site 6), as well as other streams flowing into the lake. Concentrations of metals are the highest in streams draining urban areas with industrial use (LANDRE et al., 2011).

Indicators of low water quality on Lake Guaíba were found in a monitoring study (2000-2009) evaluated by Andrade et al. (2012), with the worst quality at north-left margin (near to central Porto Alegre). Despite multiple lake pollution potential, the major liability on Guaíba derives directly from organic load originated by domestic sewage from Porto Alegre City, becoming more critical in areas with high population density (ANDRADE et al., 2012; BASSO, 2012). Total organic carbon (TOC) showed the highest levels at the sites 3 and 4, near to the Dilúvio stream outflow, and at the site 6, near to the Cavalhada stream outflow (Fig. 4-3); this support the hypothesis of organic pollution in surface sediments in margins of the Lake Guaíba (Tab. 4-5). The TOC showed a linear correlation ($R^2 = 0.87$; $p<0.01$) with TKN contents, suggesting that the N was a constituent of sediment organic matter (LUCAS; LIBER; DOIG, 2015).

Sediments act as a "black box", recording the memory of the lake environmental changes. Chemical elements form bonds in the sediment (mainly in the fine fraction) increasing the environmental persistence. Labile forms can migrate to water, while insoluble forms tend to remain adsorbed on particles; nevertheless, allowing the transport of elements in case of sediment movement (CAVALCANTI et al., 2014; COTTA; REZENDE; PIOVANI, 2006). With a predominant sandy profile in a large part of the Lake Guaíba Watershed, there are sediment extraction (for construction uses), as well as dredging to navigability maintaining. These extractive processes have environmental risks associated with movement of stable sediments, which can destabilize the environment, enabling the contaminants in the water column (BEVILACQUA et al., 2009). Sediment is a critical source and reservoir of nutrients in lake ecosystems. Exchanges and diffusions of P occurs between the sediment and water, with potential availability and release risk to the overlying water (WANG; LIANG, 2016). Nutrient increases in lakes generally are result from human pressures on surrounding, especially in urban areas (JANSSEN et al., 2014).

Phosphorus (P) is an element with re-disposal risk in case of sediment disturbance. According to Andrade and Giroldo (2014), sediment is probably the main source of P in the Lake Guaíba, especially in high hydraulic retention times. P is one of the key factors that influence primary productivity in lake ecosystems and an essential element to photosynthetic autotrophic organisms, but its excess (usually caused by sewage disposal) modifies water and sediment quality, stimulating eutrophication and interfering on trophic processes system (WANG; LIANG, 2016). Nitrogen and phosphorus are the major nutrients with potential to cause eutrophication in water bodies (JANSSEN et al., 2014).

Studies have evaluated metal bioaccumulation on aquatic biota in the Lake Guaíba. Bendati (2000) found concentrations of Cd, Cu, and Zn between 3 to 4 times higher in bivalve mollusks than in the sediment (with less accumulation for Cr and Pb). Costa and Hartz (2009) found Cd concentrations up to 15 times higher in fishes than in the sediment (with less accumulation for Cr, Cu, and Zn). Biologically non-essential metal contents (Cd, Cr, and Pb) tend to be smaller than the essential metals (such as Cu and Zn); however, both heavy metals can result in damage to biota at certain levels (COSTA; HARTZ, 2009; COTTA; REZENDE; PIOVANI, 2006). According to Landre et al. (2011), Cu, Pb, and Zn are the most prevalent metals found in urban runoff. It corroborates with our results, indicating that sediments from Lake Guaíba have been received urban pollution for a long time.

Elements can enter on sediment by weathering (lithogenic), atmospheric deposition, organisms decomposing, as well as anthropogenic amendments (COTTA; REZENDE; PIOVANI, 2006). Nevertheless, due to industrial uses on the Lake Guaíba region, element concentrations can be found above the tolerable limits to organisms. The use of Quartiles 2 and 3 (Tab. 4-4 and Tab. 4-5) was adequate for determination of no apparent contamination limits (<Q2) and presumptively polluted (>Q3), at the evaluated sites in this study, being more evident on cases where there were notable site pollutions. Comparing to CONAMA Resolution No. 454 (BRASIL, 2012) no element evaluated exceeded the proposed limits (guiding values) to dredge sediments. Elements such as Fe, Al, Ca, Mg, Na, K, Mn, and Zn are naturally found in large concentrations in regional soil and mineral sediments, while metals such as Pb, Cu, Cr, Ni, and Cd are usually found only in trace concentrations in these environmental (CARRANZA-EDWARDS et al., 2009; JIRSA et al., 2013).

High levels of metals and other elements in the sediment samples of northern Lake Guaíba were expected given the high population density and consequent water pollution at surroundings (ANDRADE et al., 2012; COSTA; HARTZ, 2009). However, levels at the site 11 (Ponta dos Coatis) were unexpected, due to small population in this rural region of Porto Alegre. This site presented the highest values ($p<0.05$) of Fe, Ca, Mg, Mn, K, Na, Ba, V (Tab. 4-4) and Zn (Tab. 4-5). Nevertheless, these results did not prove that site suffered direct anthropic damages (like deriving of fertilizers or pesticides), being able to those elements accumulates from natural deposits or indirect effects. The Lake Guaíba has a dynamic flow controlled by the level of fluctuations of Patos Lagoon and wind direction and intensity, being able to have flows as much as towards the south to the north (MENEGAT; CARRARO, 2009). This dynamic (from the Patos Lagoon) can influence grain size fractions in the southern part of the Lake Guaíba, changing fine sand values on the sites 11 and 12 (as well as silt on site 12), influencing element levels at these sites.

Clusters analysis (Fig. 4-4a) demonstrate features interrelationships, positioning on the left side the places with more evident pollution (sites 4, 6, and 3) and in the right-side places with lower anthropic pressure (sites 1, 2, and 8). This evaluation even ordered the sites (right to left) from the north to the south, showing alterations with the distance. Principal components (Fig. 4-4b and Tab. 4-7) also corroborated with some arguments, as the relationship between TOC and clay fraction with potential toxic elements (Cu, Cr, Ni, and Pb), as well as P and TKN, distancing from other variables (such Fe, Mn, Mg, and Zn) possibly linked to sediment mineral fractions (Tab. 4-7). Sites 3, 4, and 6 were well related to clay fraction, TOC, TKN, P, EC, Al, Cu, Cr, Ni, Pb, and Zn (Tab. 4-7 e Fig. 4-4). Other sites appear to be less contaminated with metals, carbon, nitrogen, and phosphorus, and had more coarse sand fraction (explaining those values).

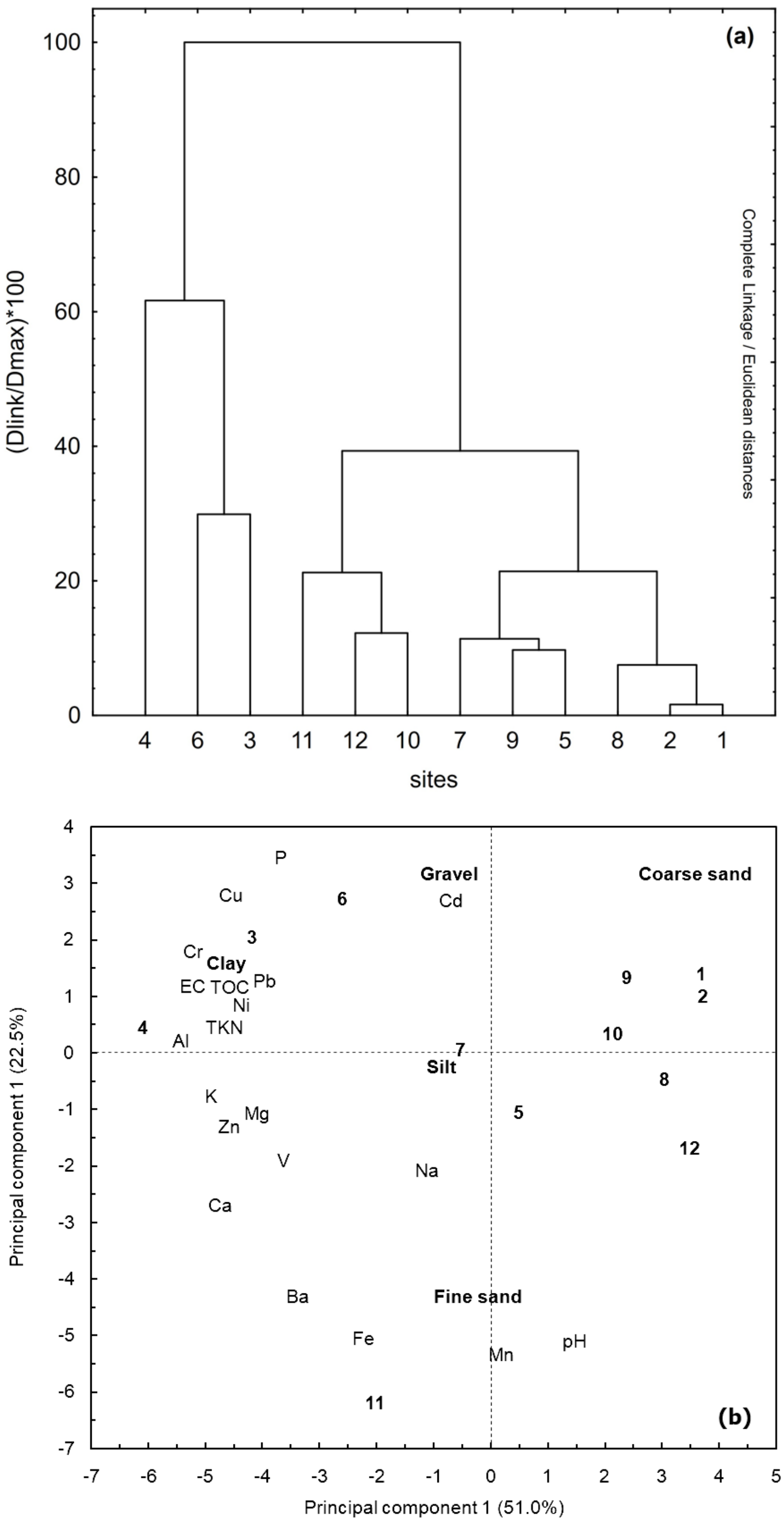

Fig. 4-4. Multivariate analysis of (a) clusters to sampling sites and (b) principal components to surface sediment in margins of the Lake Guaíba.

Tab. 4-7. Percentage explained by each principal component and percentage explained by each variable in each principal component.

Variable	Principal component 1	Principal component 2
pH	0.3	**14.4**
CE	**7.2**	1.7
TOC	**7.6**	1.3
TKN	**6.9**	0.7
P	4.3	7.5
Fe	2.0	**16.5**
Al	**9.0**	0.0
Ca	**7.3**	4.4
Mg	5.8	0.9
Na	0.7	2.8
K	**7.6**	0.6
Mn	0.0	**18.4**
Ba	4.0	11.9
Zn	**7.0**	1.2
V	4.4	3.8
Pb	6.0	1.8
Cu	**6.5**	5.5
Cr	**6.9**	1.9
Ni	6.2	0.2
Cd	0.3	4.6
Variance explained (%)	**51.0**	**22.5**

*Bold numbers >|7|.

4.5 Conclusions

Surface sediment in margins of the Lake Guaíba presented a predominant sandy particle size. The sites with more heavy metals (Zn, Cu, Ni, and Pb), carbon, nitrogen, and phosphorus concentrations were the places near to polluted urban streams outflows. Due to the sandy nature in the Lake Guaíba, the recorded levels of metals (and others parameters) would be considered lightly high and then reflected a real human impact.

The pollution of the Lake Guaíba is public and notorious, being linked to the collective consciousness of local population - and it will persist even the reversal of environmental issue. Several projects had aimed to control the Guaíba pollution; however, without definitive results. In order to solve these environmental liabilities, public actions should not focus only on Guaíba, but also in water bodies (such as the streams) that flow into the lake.

The improvement of environmental conditions of the Guaíba, plus the possibility of increasing on diversity of Lake uses (such as the return of bathing beaches) links directly to increase the life quality of regional population and must be constantly targeted by governmental agencies. Our results demonstrated that the Lake Guaíba is wide impacted by pollutants and it is necessary control the disposal of industrial and urban waste in the water bodies of the region.

5. CAPÍTULO IV – GEO-ACCUMULATION OF HEAVY METALS IN THE SEDIMENT OF LAKE GUAÍBA TRANSITIONAL WATERS, SOUTHERN BRAZIL

5.1 Introduction

High population densities in the metropolitan areas and the associated industrial and agricultural activities impact local water resources that often serve as a source of water to the same population. Metals are natural elements found in the soil and mineral matrix; however, they can be accumulated in the environment through anthropic pollution. Chemicals entering water bodies, bind to suspended particles and are deposited in bottom sediments where they accumulate in concentrations many times greater than natural concentrations (SHARLEY et al., 2016; ZHOU et al., 2017). These sediments formed by deposition of organic and inorganic particles that originate in metropolitan areas play an important role in aquatic ecosystems, affecting biogeochemical cycles, nutrients redistribution, and maintenance of environmental quality (LIU et al., 2016; SHARLEY et al., 2016).

Lake Guaíba is an urban shallow open lake located in the metropolitan region of Porto Alegre, the capital of Rio Grande do Sul State (RS), southern Brazil (Fig. 5-1). It has served as the main water source for the capital since its foundation in the 18th century. Currently, the water of the Lake Guaíba has multiple uses such as water supply, wastewater dilution, recreation, fishing, and navigation. Lake Guaíba has an area (A) of 496 km^2, volume (V) of 1.44 km^3, mean depth (V/A) of 3 m, average discharge (Q) of 1,193 m^3/s, water residence time (V/Q) of 14 days, and short-term average sedimentation rate (^{14}C and ^{210}Pb) of 6 mm/year (LAYBAUER, 2002). The lake is fed by the tributaries rivers “Jacuí” (almost 85 % of the water), “dos Sinos”, “Caí”, and

“Gravataí”. Those rivers meet at the Jacuí’s Delta, forming a transitional environment (from riverine to lacustrine), and this water flows through the Lake until reaching Patos Lagoon. The lake acts as a reservoir that receives significant water and sediment load and cannot be seen merely as an extension of its branch of rivers (LAYBAUER, 2002).

The sediment in Lake Guaíba transitional waters has physical and chemical diversity influenced by its tributaries. The objectives of this study were to characterize the physico-chemical diversity of bottom sediments in this transitional water and to determine the influence of tributaries on sediment characteristics. Specifically, we determined the extent to which metal concentrations of bottom sediments were controlled by distance from tributaries versus sediment characteristics within the lake.

5.2 Material and methods

Surface bottom sediment (0-5 cm) composite samples (with three sub-samples) were collected at six locations in Lake Guaíba during June 2016 with a drag bucket sampler. Sampling locations (Fig. 5-1) were geo-located (*Garmin GPSMAP®78s and GPS TrackMaker®v13*) and Side Scan Sonar (SSS) images (*Humminbird Side Imaging®*) were registered. The average bottom water temperature during sampling was 14.5 °C.

Sediment samples were returned to the laboratory, dried (45 °C), and sieved (2 mm; with no presence of gravels). Sieved samples were analyzed for pH in $CaCl_2$ (ratio 1:2.5, v/v), bulk density (Ds), particle density (Dss), particle size (pipette method), electrical conductivity (1:5, v/v), total organic carbon (TOC; Walkley-Black), total Kjeldahl nitrogen (TKN), and bioavailable phosphorus (P; Melich-1). Element concentrations (Fe, Al, Ca, Mg, K, Mn, Na, Ba, V, Zn, Cu, Cr, Co, Ni, Pb, As, Cd, Mo, and Se) were assessed by digestion (HNO_3–H_2O_2–HCl) according to the method EPA-3050B (USEPA 1996) and quantification was performed in ICP-OES (*PerkinElmer® Optima™ 8300*) using internal control standards of LAS-UFRGS (PSJ, PSJ-1, PSJ-2 and PM) to verify the quality. All analyzes were performed in laboratory quadruplicates.

Fig. 5-1. Map location of sediment samples on Lake Guaíba transitional waters. Darkest area in state map represents the lake drainage basin.

X-ray diffraction (XRD) analyses were made on powder blades (*Bruker*®*D2-phaser*) over CuKα radiation [λ = 1.54 Å], steps 0.020º and range 4 to 70 º2θ. Halite (H) was used as an internal indicator at 0.282 nm to characterize the Lake Guaíba sample set. The identification of minerals was performed according to Brindley and Brown (1980).

The geo-accumulation index (I_{geo}) is an indicator used as an empirical relationship of the degree of metal pollution. The index was determined following the equation (MULLER, 1969):

$$I_{geo} = log_2\left(\frac{Cn}{1.5 \times Bn}\right)$$

where *Cn* is the measured value of the metal in the sediment sample, *Bn* is the geochemical background level of element, and *1.5* is the background matrix correction factor to lithogenic effects (CHAHARLANG et al., 2016; LIU et al., 2016). The background (*Bn)* values were obtained from Laybauer (2002): Zn – 110; Cu – 27; Cr – 21; Ni – 32; Pb – 27 µg/g ($HCl\text{-}HNO_3\text{-}HF$).

The standardization by Aluminum (/Al) was used to compensate the variations in metals concentrations due to different particle sizes; the Al is the metal most presented in the earth's crust.

Results were submitted to analysis of variance (ANOVA) and, when significant differences were indicated, means were compared by Tukey test with a 95 % confidence interval ($p<0.05$). Relationships among sediment characteristics and physical attributes of the lake were evaluated by Pearson Correlation. All graphics and statistical analyses were development at software *Statistica® v13*.

5.3 Results and discussion

As a river enters a lacustrine water body, the water velocity decreases and sediments settle out forming a delta. As the hydrological character transitions from riverine to lacustrine: coarser materials (such as sand) tend to settle first, followed by lighter materials, such as silt and clay (LUCAS; LIBER; DOIG, 2015). Thus, a spatial gradient of particle size distribution was expected in the lake. The particle size of the bottom sediment varied along the 12 km that was evaluated (Tab. 5-1). Particle size decreased from G1 to G6, along the course from Jacuí's Delta to Lake Guaíba (Fig. 5-1 and Fig. 5-2). Coarse sand (φ 0–2) content decreased from 68 to less than 1 % along the water flow line while silt (φ 5–8) content increased from 3 to 46 %. Fine sand (φ 3–4) accumulated in intermediate sections (71 % at G3). Clay (φ> 9) occurred in higher concentrations in the lower half section, ranging from 4 to 10 % (Fig. 5-2). The silt/clay ratio of the bottom sediment into the Lake Guaíba transitional waters was very similar (*p*<0.05) among sections G1, G2, G3, and G4, with greater values at G5 and G6 (Fig. 5-2).

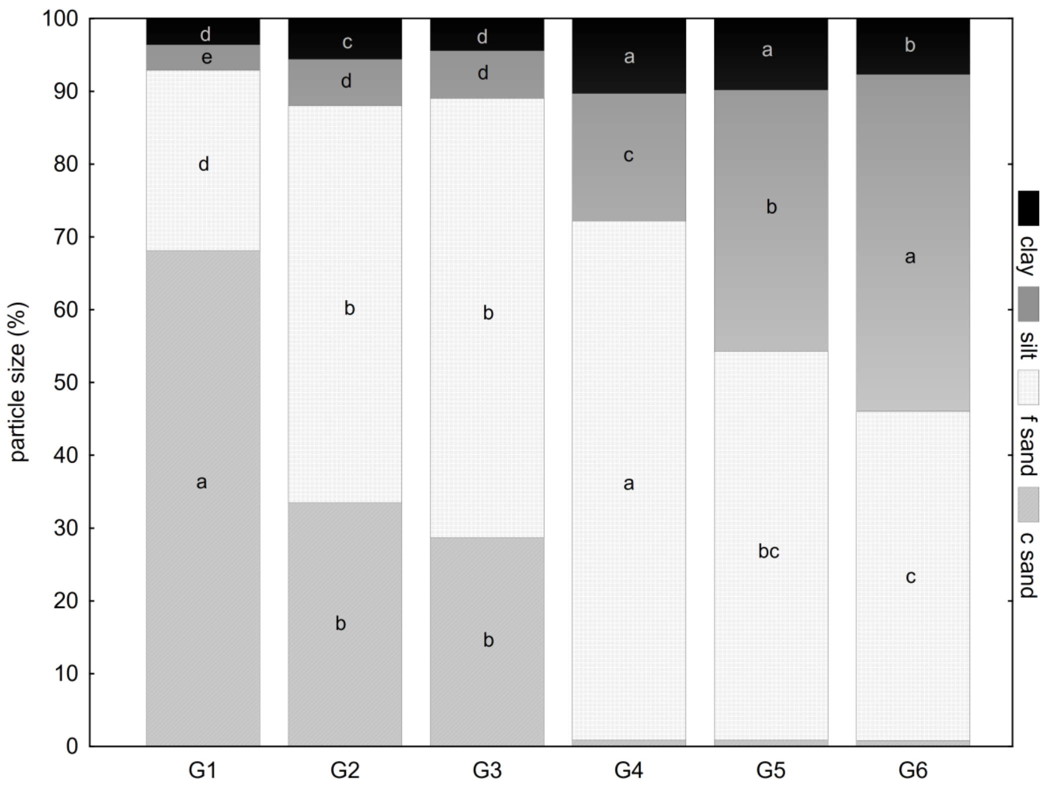

Fig. 5-2. Particle size (clay, silt, fine sand, and coarse sand) in bottom sediment at Lake Guaíba transitional waters. Means followed by the same letter are not statistically different (comparing the sites) from each other by Tukey's test at 95 % confidence.

Bedform is related to the sediment particle size, water depth and flow velocity (STAUDT et al., 2017; WANG et al., 2016). Coarse sediments deposited by flowing water entering a calm water body produce characteristic ripples in the bottom, as shown in the section G1 and, to a lesser extent, in the section G2. These ripples are absent in other sections (Fig. 5-3). This pattern was consistent with reductions in sand content and increased fine particle (silt and clay) within the sections (Fig. 5-2) as well as the reduced water depth at G3 (Tab. 5-1). The occurrence of fine particles in sections G4 to G6 indicate more stable conditions (STAUDT et al., 2017). According to Laybauer (2002), there is a relationship between Lake Guaíba bathymetry and sediment particle size (finer particles in deeper parts); however, it is less significant in the transitional waters given the different hydrodynamics in the region.

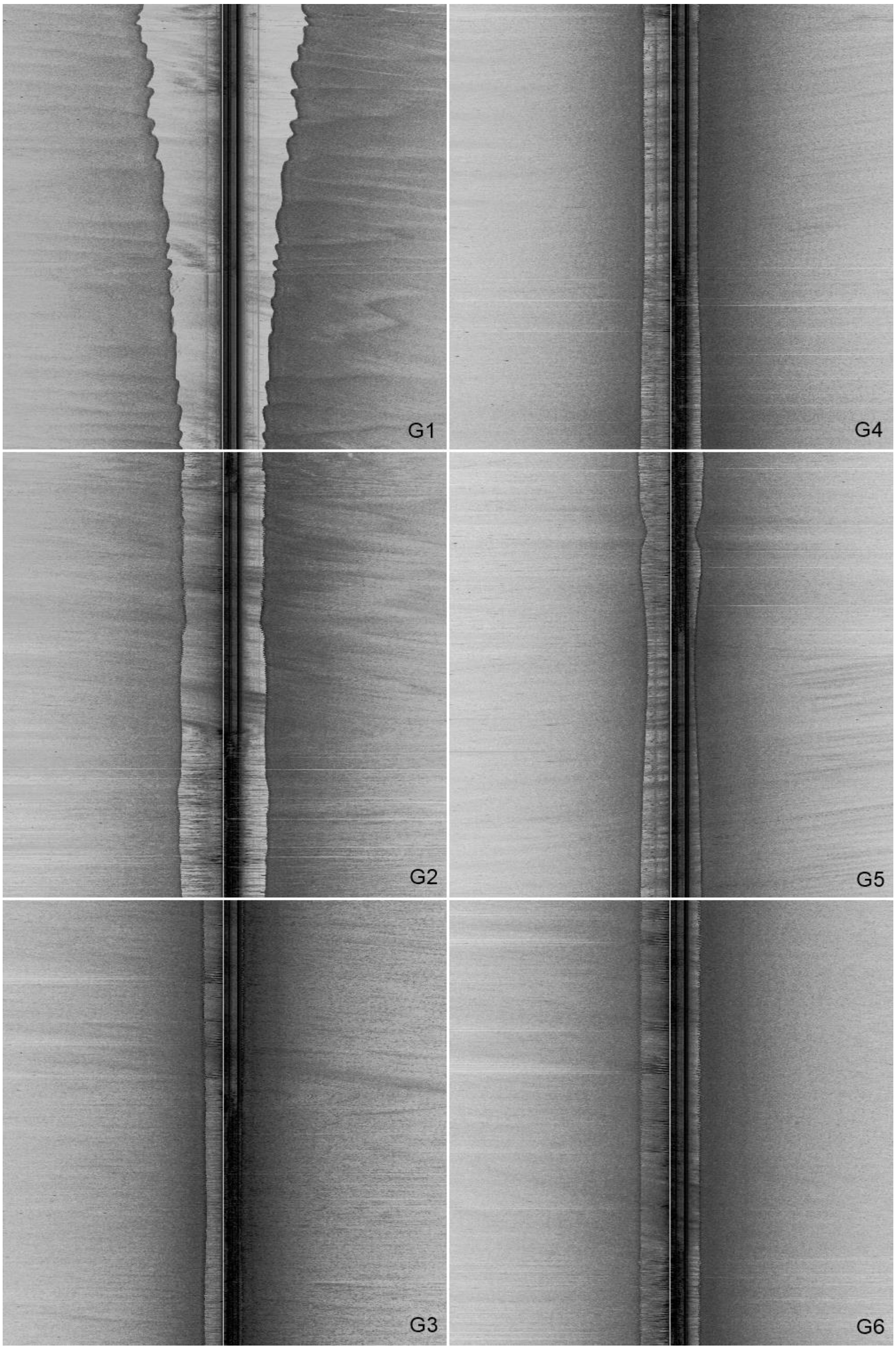

Fig. 5-3. Side Scan Sonar (SSS) images at sediment sampling sections on Lake Guaíba.

Tab. 5-1. Physical and chemical values in bottom sediment at Lake Guaíba transitional waters.

Sections	**G1**	**G2**	**G3**	**G4**	**G5**	**G6**
coordinates (°)	-51,25262	-51,25994	-51,27034	-51,28000	-51,28994	-51,27743
	-30,04657	-30,06655	-30,08790	-30,09367	-30,12465	-30,14286
distance (Km)[1]	0.0	2.3	4.9	6.0	9.6	11.9
depth (m)[2]	4.9	3.9	2.2	2.7	3.2	2.9
pH ($CaCl_2$)[3]	6.4 [c]	6.7 [b]	7.3 [a]	6.5 [c]	6.0 [d]	6.1 [d*]
EC (µS/cm)[4]	35.9 [d]	49.5 [c]	92.8 [a]	84.0 [b]	96.2 [a]	84.5 [b]
Ds (g/cm^3)	1.29 [a]	1.21 [b]	1.22 [b]	1.01 [c]	0.94 [d]	0.89 [e]
Dss (g/cm^3)	2.57 [a]	2.58 [a]	2.57 [ab]	2.54 [abc]	2.52 [bc]	2.49 [c]
Pt (cm^3/cm^3)	0.50 [e]	0.53 [d]	0.52 [d]	0.60 [c]	0.63 [b]	0.64 [a]
TOC (mg/g)	1.91 [c]	2.71 [c]	2.73 [c]	8.35 [b]	11.73 [a]	11.89 [a]
TKN (µg/g)	172.3 [c]	312.9 [c]	302.1 [c]	721.1 [b]	928.9 [a]	972.9 [a]
P (µg/g)	8.02 [b]	8.62 [b]	7.58 [b]	9.53 [b]	12.17 [a]	14.14 [a]
C:N	11.5 [ab]	8.8 [b]	9.4 [ab]	12.0 [ab]	13.2 [a]	12.3 [ab]
Fe (mg/g)	7.11 [e]	11.68 [d]	14.15 [c]	26.66 [b]	29.36 [a]	30.33 [a]
Al (mg/g)	4.75 [d]	7.89 [c]	8.52 [c]	22.16 [b]	28.37 [a]	27.31 [a]
Ca (µg/cg)	4.50 [d]	9.26 [c]	13.12 [c]	27.53 [b]	30.52 [b]	34.86 [a]
Mg (µg/cg)	4.16 [d]	7.31 [c]	8.53 [c]	23.54 [b]	29.01 [a]	30.42 [a]
K (µg/cg)	2.69 [d]	4.22 [cd]	5.23 [c]	13.00 [b]	15.48 [a]	14.29 [ab]
Mn (µg/cg)	2.01 [c]	4.54 [b]	4.55 [b]	10.60 [a]	9.92 [a]	10.02 [a]
Na (µg/cg)	0.97 [c]	1.34 [c]	1.29 [c]	3.37 [b]	4.11 [a]	4.03 [a]
Ba (µg/g)	52.94 [d]	87.20 [c]	110.13 [c]	225.34 [b]	260.20 [a]	264.40 [a]
V (µg/g)	18.64 [e]	30.79 [d]	33.62 [d]	100.09 [c]	117.50 [b]	133.18 [a]
Co (µg/g)	4.37 [e]	7.73 [d]	10.67 [c]	23.31 [b]	27.54 [a]	28.21 [a]
As (µg/g)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Mo (µg/g)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Se (µg/g)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Means followed by the same letter are not statistically different from each other by Tukey's test at 95 % confidence. (1) Cumulative distance between points; (2) Bathymetry; (3) pH $CaCl_2$ (1:2.5); (4) EC - electrical conductivity (1:5). Ds - bulk density; Dss - particle density; Pt - total porosity. LOD – Limit Of Detection: As – 2.0; Mo – 0.2; Se – 4.0 µg/g.

Clay fraction contents were relatively low in all evaluated sites (Fig. 5-2), as most of the suspended clays entering the Lake Guaíba are exported downstream to the Patos Lagoon as suggested by Laybauer (2002). This is supported by results from the X-ray diffraction (XRD) that indicated that quartz was the predominant mineral. All XRD samples also had peaks at 0.389 and

0.377 nm for potassium feldspar (Ft K), with more intense reflections of calcium feldspars (Ft Ca) in the sites G2 and G3. Sampling sites G5 and G6 showed low intensity reflections relative to minerals of the mica group at 0.90 nm (Fig. 5-4). The presence of kaolinite, the most common clay mineral in this region (identified at 0.717nm) was observed only at sample site G2.

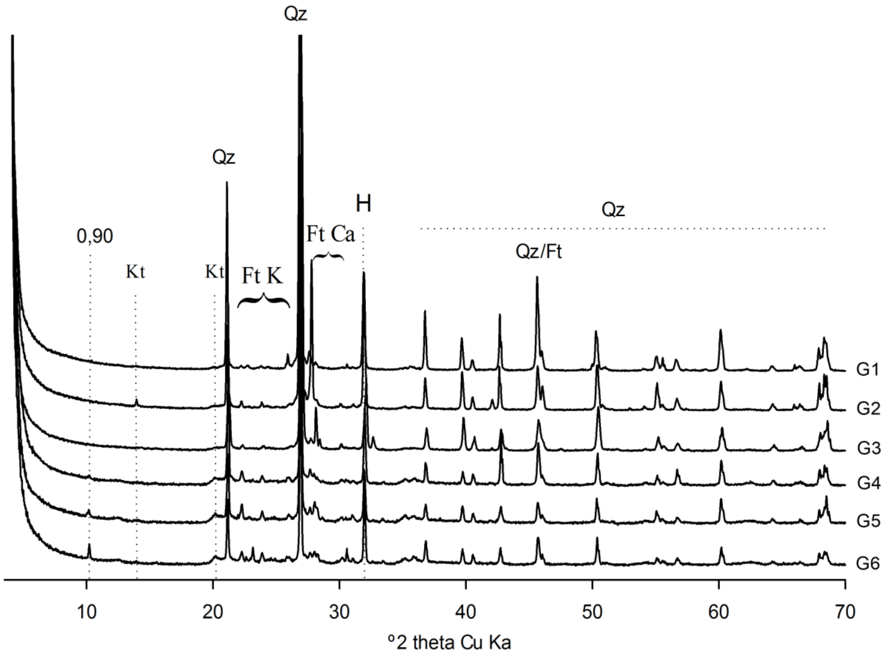

Fig. 5-4. X-ray diffraction (XRD) in bottom sediment of Lake Guaíba transitional waters. Micas (0.90 nm); Kt - kaolinite (0.649 nm); Ft - potassium and calcium feldspars (0.404 - 0.402 nm and 0.321 - 0.299); H - halite (0.282 nm); Qz - quartz (0.334 nm).

Particle size has a strong influence on sorption potential of elements and compounds. Finer grains have greater surface areas (adsorbing sites) and, consequently, concentration of pollutants tend to be greater in finer-textured sediments (HE; BARTHOLDY; CHRISTIANSEN, 2012; SANGSTER et al., 2015; TANSEL; RAFIUDDIN, 2016). These smaller particles also have a greater tendency to be re-suspended and move with the water column. Therefore, compounds associated with these particles are more likely to travel greater distances (SANGSTER et al., 2015).

Carbon concentrations are also affected by the particle size (LIU et al., 2016). Total organic carbon (TOC) increased 600 %, from 1.91 (G1) to 11.89 mg/g (G6), and had a strong correlation with clay plus silt contents (R^2 = 0.94; p<0.01), as well as the distance from Jacuí's Delta (r = 0.92; p<0.01). The C/N ratio ranged from 8.8 (G2) to 13.2 (G5) in Lake Guaíba transitional waters

(Tab. 5-1). The C/N is an indicator of organic matter sources (LUCAS; LIBER; DOIG, 2015); however, the C/N does not had any strong correlation with other parameters (Tab. 5-3). Phosphorus (P) concentrations, and most of the metals, also rose with clay plus silt contents, increasing with the distance from Jacuí's Delta (Tab. 5-1 and Tab. 5-2).

Tab. 5-2. Concentrations of zinc, copper, chromium, nickel, lead and cadmium on bottom sediment of Guaíba transitional waters, reference values and standardized values by aluminum.

Sections	Zn	Cu	Cr	Ni	Pb	Cd
	……………………………… µg/g ………………………………					
G1	11.61 e	4.91 e	4.90 e	2.44 e	3.03 c	<LOD
G2	21.05 d	10.14 d	8.12 d	4.49 d	4.83 c	<LOD
G3	26.39 d	9.90 d	8.56 d	5.07 d	5.23 c	<LOD
G4	61.79 c	31.96 c	21.58 c	15.48 c	12.79 b	<LOD
G5	72.78 b	41.39 b	26.71 b	18.88 b	14.99 ab	<LOD
G6	82.10 a	46.36 a	30.17 a	21.31 a	15.66 a	<LOD
RV (1)	155.3	46.4	38.9	35.4	33.6	0.54
RV (2)	14.78	2.32	1.84	2.67	5.02	0.06
BG (3)	110	27	21	32	27	0.3
GV (4)	123	35.7	37.3	18	35	0.6
	Zn/Al	**Cu/Al**	**Cr/Al**	**Ni/Al**	**Pb/Al**	**Cd/Al**
G1	2.45 c	1.03 e	1.03 ab	0.51 e	0.64 a	<LOD
G2	2.69 abc	1.29 c	1.03 ab	0.57 de	0.62 a	<LOD
G3	3.10 a	1.16 d	1.01 ab	0.60 cd	0.62 a	<LOD
G4	2.80 abc	1.44 b	0.98 ab	0.70 b	0.58 a	<LOD
G5	2.57 bc	1.46 b	0.94 b	0.67 bc	0.53 a	<LOD
G6	3.01 ab	1.70 a	1.11 a	0.78 a	0.57 a	<LOD

Means followed by the same letter are not statistically different from each other by Tukey's test at 95 % confidence. ND - Not Detected. RV - Reference Values to sediments on Guaíba: (1) Laybauer (2002); (2) Fontoura (2014). (3) BG – Background values to Lake Guaíba bottom bulk sediment (LAYBAUER, 2002).(4) GV – Guiding Values to dredged sediments: CONAMA Resolution No. 454 (BRASIL, 2012), Level 1. Standardized values (metals/Al) multiplied by 1,000. LOD – Limit Of Detection: Zn - 2; Cu - 0.6; Cr - 0.4; Ni - 0.4; Pb - 2; Cd - 0.2 µg/g.

Tab. 5-3. Pearson correlation coefficients (r) on bottom sediment of Lake Guaíba transitional waters.

	distance	clay	silt	f sand	c sand	TOC
distance	-	0,67**	0,95**	0,30	-0,87**	0,92**
depth	-0,62**	-0,44*	-0,35	-0,77**	0,73**	-0,40
pH	-0,49*	-0,55**	-0,71**	0,31	0,34	-0,72**
EC	0,79**	0,62**	0,59**	0,63**	-0,82**	0,66**
Ds	-0,94**	-0,84**	-0,94**	-0,32	0,89**	-0,97**
Dss	-0,80**	-0,59**	-0,81**	-0,08	0,64**	-0,80**
Pt	0,94**	0,85**	0,94**	0,33	-0,90**	0,97**
TOC	0,92**	0,82**	0,94**	0,23	-0,84**	-
N	0,92**	0,83**	0,92**	0,29	-0,86**	0,96**
C/N	0,43*	0,43*	0,53**	-0,06	-0,36	0,62**
P	0,83**	0,57**	0,90**	-0,02	-0,64**	0,84**
Fe	0,93**	0,88**	0,89**	0,43*	-0,93**	0,95**
Al	0,92**	0,87**	0,92**	0,33	-0,89**	0,98**
Ca	0,94**	0,83**	0,91**	0,39	-0,92**	0,95**
Mg	0,93**	0,85**	0,93**	0,32	-0,89**	0,98**
K	0,89**	0,89**	0,88**	0,38	-0,90**	0,96**
Mn	0,85**	0,93**	0,80**	0,54**	-0,94**	0,91**
Na	0,89**	0,86**	0,90**	0,31	-0,87**	0,97**
Ba	0,93**	0,87**	0,90**	0,39	-0,92**	0,96**
V	0,93**	0,84**	0,94**	0,30	-0,88**	0,97**
Zn	0,94**	0,83**	0,93**	0,33	-0,90**	0,97**
Cu	0,94**	0,82**	0,95**	0,27	-0,87**	0,98**
Co	0,94**	0,86**	0,91**	0,38	-0,91**	0,97**
Cr	0,94**	0,82**	0,95**	0,28	-0,88**	0,98**
Ni	0,94**	0,83**	0,94**	0,29	-0,88**	0,98**
Pb	0,92**	0,86**	0,91**	0,33	-0,89**	0,96**

N = 24. *significant at 0.05 level; **significant at 0.01 level.

Relative concentrations of metals (at mean magnitude) were ordered: Fe > Al > Ca > Mg > K > Mn > Na > Ba > V > Zn > Cu > Cr > Co > Ni > Pb (without detection to As, Cd, Mo, and Se). Concentrations of Zn, Cu, Cr, Ni and Pb increased substantially (500-700 %) from the G1 to G6 sections following the general pattern of increased clay plus silt in sediments (Tab. 5-2). Both Cu and Ni concentrations exceeded the proposed Brazilian guiding values (level 1) for sediments (BRASIL, 2012) at the G5 and G6 sections; however, the concentration of Ni in the background in Lake Guaíba is higher than the guiding value. Both Cu and Cr were also greater than background levels at sections G4 to G6. Generally, no differences occurred between the G5 and G6 sections and only a few differences between G2 and G3 sections were observed, being similar to the patterns observed for sand.

Our results (Tab. 5-2) differ from results of previous studies (FONTOURA, 2014; LAYBAUER, 2002) of Lake Guaíba sediments. This variation appears to be largely a consequence of the differences in the particle sizes examined. When results with similar particles sizes are compared, the concentrations are similar. For example, Fontoura (2014) reported concentrations of Cu and Cr that were lower than the mean concentrations we observed, but this author worked with samples from areas of the lake dominated by sand-sized particles (>95 %), which we showed to have lower concentrations in Lake Guaíba. Laybauer (2002) analyzed samples with more fine particles (almost 50 % silt plus clay). In Laybauer's study, samples with a large percentage of sand (20–40 %) had similar concentrations of some heavy metals to those in fine fractions (<63 µm), probably due to organic coatings and/or Fe and Mn oxi-hydroxides on the surface of the sandy grains. This distinction is significant as Brazilian regulatory statues are written for bulk sediment samples and these samples should represent the particle distribution within the lake.

The lowest metal/Al ratios occurred at sample point G1 for Zn, Cu, and Ni and differences among sample locations was statistically significant for these metals. No statistically significant differences among sample locations occurred for Pb/Al, and minor to Cr/Al ratios (Tab. 5-2). The geo-accumulation index, which standardizes metal accumulation against background concentrations, indicates some increase of Cu and Cr in sediments. Together these results indicate a major influence of particle size on the concentrations of metals in the bottom sediment. Although, the geo-accumulation Index (I_{geo}) compensates the natural concentrations, showing values of Cu and Cr surpassing a bit the “natural quality” (Fig. 5-5). These results present a minor (or absent) metal enrichment (CHAHARLANG et al., 2016; LIU et al., 2016); however, it raises the possibility of punctual pollution in Lake Guaíba.

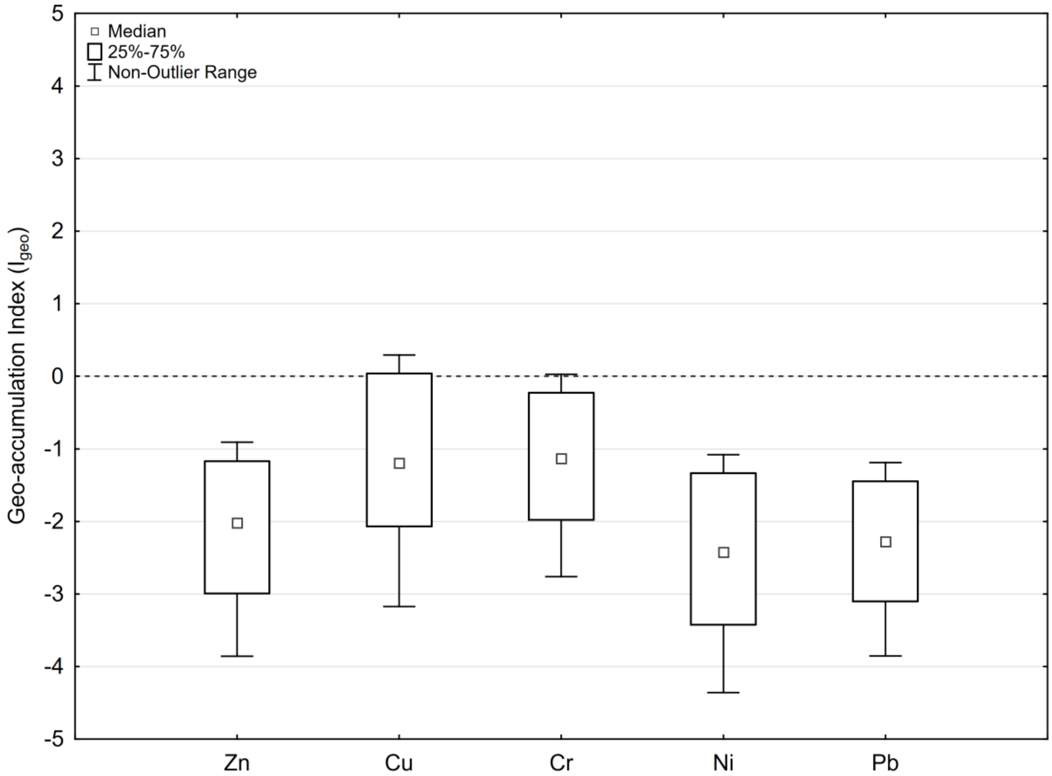

Fig. 5-5. Geo-accumulation Index (I_{geo}) boxplots of metals zinc, copper, chromium, nickel, and lead in bottom sediment of Lake Guaíba transitional waters.

5.4 Conclusions

Lake Guaíba transitional waters had a strong correlation between particle size deposited and the distance from the entering tributaries (Jacuí's Delta). Both distance from entering tributaries as well as the particle size and carbon are highly correlated with metal concentrations. The concentrations of metals (especially Zn, Cu, Cr, Ni, and Pb) are largely controlled by sediment particle size. Silt and total organic carbon presented higher correlation with the metals than clay; but this may occur by the exportation of clay to the south part of the lake and to the Patos Lagoon.

6. CAPÍTULO V – SEDIMENT POLLUTION IN AN URBAN WATER SUPPLY LAKE IN SOUTHERN BRAZIL

6.1 Introduction

Pollution is an environmental crisis that accompanies rapid economic development in many countries around the world (ZHOU et al., 2017). Urbanization typically results in impacts at freshwater systems, caused by diffuse (nonpoint) and punctual sources (SHARLEY et al., 2016).

Sediments are a major sink for hydrophobic pollutants such as metals and organic compounds in lotic aquatic ecosystem (SHARLEY et al., 2016). Those chemicals enter in lake waters naturally through a variety of sources (weathering and anthropogenic) and ways, as stormwater runoff, groundwater inflow, sewage and wastewater disposal, high vehicle traffic, and atmospheric deposition (BING et al., 2016; SMOL, 2008). Once in the water column, those chemicals typically bind or adsorb in suspended particles and deposit at bottom sediment, accumulating in concentrations several times higher than the overlying water (SHARLEY et al., 2016; SMOL, 2008; ZHOU et al., 2017).

Sediment quality monitoring is globally used to access anthropogenic impacts on aquatic ecosystems, providing an ideal component to assess pollution trends over long periods (SHARLEY et al., 2016). The transport and fate of potentially toxic elements (such Zn, Pb, and Cd) are a critical contamination issue for aquatic ecosystems where can be bioaccumulated in food webs (BING et al., 2016). These metals with highly residence time and bioavailability pose a risk to organisms in lake systems, and potentially to human health (SHARLEY et al., 2016).

Urbanization and anthropogenic activities creates many environmental issues in urban water supply reservoirs, especially in metropolitan regions. Thus, this study was carried out aiming to evaluate the variance in the physical-chemical characteristics of bottom sediment along the Lake Guaíba, southern Brazil. Specifically, we seek to find the sources of sediment contamination sources in the lake.

6.2 Materials and methods

Surface sediment (0-10 cm) was sampled, in January 2017, in 27 sites of Lake Guaíba, southern Brazil, covering all the regions of the lake.

6.2.1 Study Area

Lake Guaíba is a freshwater lake situated in the metropolitan region of Porto Alegre City (state's capital), southern Brazil (Fig. 6-1). It's a open urban shallow lake with an area (A) of 496 km^2, volume of 1.44 km^3, mean depth of 3 m, average discharge of 1,193 m^3/s, water residence time of 14 days, and sedimentation rate of 6 mm/year (LAYBAUER, 2002). Lake Guaíba is part of interconnected freshwater lakes, together with the Patos Lagoon (with outflow in the Atlantic Ocean), Lagoon of Casamento, and Lagoon Mirim.

The lake's name (from the original "*Guahyba*") comes from the indigenous language *Tupi-Guarani* (Brazilians natives) meaning "meeting of the waters", due to the Jacuí's Delta where are the outflow of rivers “Jacuí”, “dos Sinos”, “Caí”, and “Gravataí”. The Lake Guaíba's drainage region covers 84,751 km^2 (with 2,523 km^2 of specific watershed), covering 251 municipalities: 1/3 of the area, 50 % of the municipality, and more than 60 % of the inhabitants of the state (DE ANDRADE et al., 2018). The region has many industries and service companies (Petrochemical, Leather and Footwear, Food and Beverage, Landfills and Wastewater Treatment, Mining and Metallurgy, Pulp and Paper), creating many pollution possibilities.

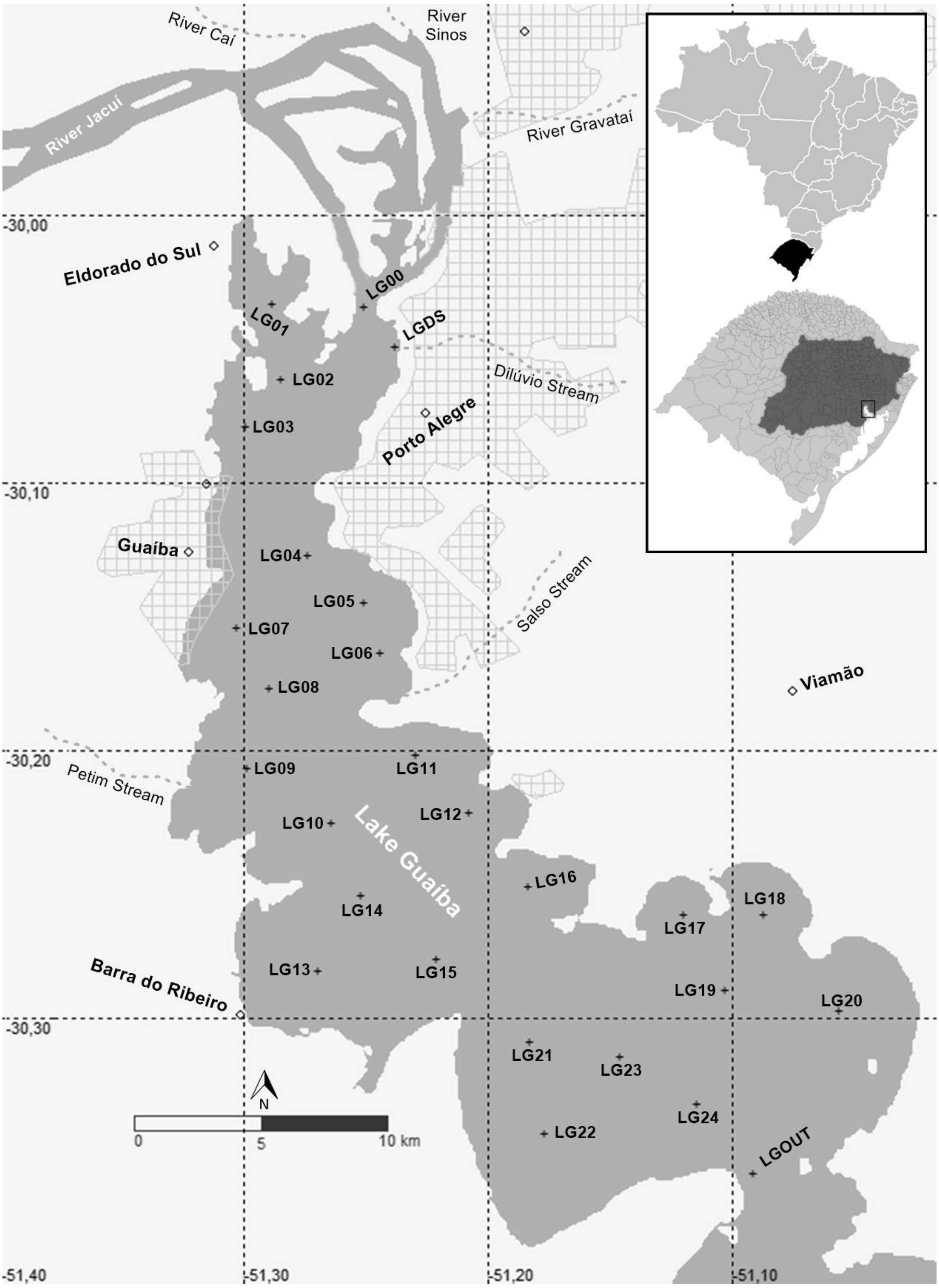

Fig. 6-1. Map location of sediment samples on Lake Guaíba. Darkest area in state map represents Lake Guaíba drainage region.

The Lake Guaíba is the main water supply to the capital since its foundation in the early 18th century, with historical, economic, and cultural importance to region. Currently, the Lake Guaíba have multiple uses such as water source, sewage and wastewater dilution, navigation, recreation, fishing, and it's an important part of the visual identity of Porto Alegre and region (DE ANDRADE et al., 2018).

6.2.2 Sediment sample and preparation

Surface bottom sediment (0-10 cm) composite samples (with three sub-samples) were collected between 18th and 19th January 2017 in Lake Guaíba (Porto Alegre, Brazil) with an Ekman Bottom Grab (dredge) sampler. During those days Guaíba had 0.51 m of water level (being 0.47 m the historical average for January) and 25.1±0.1 °C of average air temperature (CEIC, 2017). Sampling sections (Fig. 6-1) were geo-located (*GPS TrackMaker®v13*). Depth and water temperatures (Tab. 6-2) were measured with an echobathymeter (*Eagle® Cuda 300*). Sediment samples were dried (45 °C) and sieved (2 mm) to perform the analysis.

6.2.3 Physicochemical analysis

The sediment samples were evaluated to: pH in $CaCl_2$ (ratio 1:2.5, v/v); electrical conductivity (1:5, v/v); bulk density (Ds); and particle-size (pipette method). Total organic carbon (TOC) and total nitrogen (TN) were evaluated with an Organic Elemental Analyzer (OEA; *Thermo Scientific™ Flash™ 2000 NC Soil Analyzer*); Sulphanilamide was used as a standard to verify the process quality.

Inorganic elements (Fe, Al, Ca, Ba, Sr, Co, Tl, Zn, Cu, Cr, Ni, Pb, Cd, and Hg) were assessed via microwave assisted acid extraction, method EPA 3051A (USEPA 2007). The sediment samples (0.2 g) had an overnight with 5 mL of concentrated nitric acid (HNO_3; *Fisher® Trace Metal Grade*) before the microwave extraction. Dilution (1:100) was made with ultrapure water (*Barnstead®*). Certified standard reference materials (NIST2711 – Montana, NIST2709 - San Joaquin, and EPA CRM020-50 – Metals #2) were used to verify the process quality (Tab. 6-1). All process was done in triplicate. The quantification was performed with an Inductively Coupled Plasma Mass Spectrometry (ICP-MS, *PerkinElmer ELAN® 9000*).

Tab. 6-1. Evaluation of certified standard reference materials.

Samples	Zn	Cu	Cr	Ni	Pb	Cd
			.... µg/g			
CRM1	414	140.0	52.3	21.7	1400.0	54.10
mv±se	355±15	169.2±9.8	29.7±4.9	21.8±2.0	1631±26	50.9±0.4
Recovery %	**86**	**121**	**57**	**100**	**117**	**94**
CRM2	103	33.9	130.0	85.0	17.3	0.37
mv±se	95±4	46.6±4.3	93.0±1.7	88.1±2.3	20.8±2.0	0.34±0.01
Recovery %	**92**	**138**	**72**	**104**	**120**	**92**
CRM3	3011	729.0	13.6	16.9	5111.0	15.40
mv±se	3208±57	1286±32	18.2±0.3	25.1±3.4	3943±60	19.5±0.2
Recovery %	**107**	**176**	**134**	**148**	**77**	**126**

Certified Reference Materials (CRM): 1 - NIST2711 – Montana; 2 - NIST2709 - San Joaquin; 3 - EPA20-50 – Metals #2. mv – measured value; se - standard error.

Metals were compared with the Brazilian sediment guidelines, Conama No. 454 (BRASIL, 2012), based from the Canadian Environmental Quality Guidelines (CEQGs) - Sediment Quality Guidelines for the Protection of Aquatic Life (Freshwater), where: the “Level 1” of Brazilian guideline is equivalent to Interim Sediment Quality Guideline (ISQG), as the Threshold Effect Level (TEL); and the “Level 2” equivalent to Probable Effect Level (PEL).

The Geo-accumulation Index (I_{geo}) was determined following the equation (MULLER, 1969): $I_{geo}=\log_2 (Cn/1.5\times Bn)$; where *Cn* is the measured value of the metal in the sediment sample, *Bn* is the geochemical background level of element (LAYBAUER, 2002), and *1.5* is the background matrix correction factor to lithogenic effects (CHAHARLANG et al., 2016; LIU et al., 2016; MULLER, 1969). Although, the background analysis from Laybauer`s was assessed with a total extraction (HCl-HNO_3-HF).

6.2.4 Organic compounds

The extraction of organic compounds was made transferring 5 g of the dry sediment, into 50 mL polypropylene centrifuge tubes followed by 10 mL of a mixture (1:1 v/v) of HPLC grade acetone and dichloromethane (*Fisher Scientific*). The tubes were placed for 30 min in ultrasonic bath, and then centrifuged for 20 min at 3500 rpm. The supernatants were transferred to glass evaporation tubes, and the residues were re-extracted by adding the solvent mixture and repeating the extraction process two more times. The collected extracts were evaporated in an evaporator workstation (*TurboVap*®) almost to dryness at a temperature not exceeding 45 ºC. The residues in the evaporation tube were dissolved by adding 0.9 mL of methanol, vortexed for 30 seconds and its content was transferred to 1 mL volumetric tube and made up to volume with methanol. The methanol extracts were transferred to 2 mL GC vials for analysis.

Non-target screening GC-MS analyses (semiquantitative) were performed with a gas chromatograph *Hewlett Packard 6890* connected to a mass selective detector *HP 5973*. A *HP-5MS* capillary column (30 m × 0.25 mm × 0.50 µm) containing 5 % phenyl methyl siloxane (*HP 19091J-133*) was programmed to start at 40 ºC (2 min), followed by an increase to 280 ºC (6 ºC/min) holding this temperature for 5 min (total run time of 47 min; maximum temperature of 325 ºC). Helium was used as the carrier gas at a flow rate of 1.0 mL/min with 7.15 psi pressure and 36 cm/sec. Samples were injected in split mode (with ratio 3.679:1; split flow 3.7 mL/min; total flow 6.9 mL/min; electron energy of 70 eV). The whole system was controlled by a *ChemStation* which included a version of the *Wiley HP Mass Spectral Libraries* containing more than 275,000 entries.

6.2.5 Statistical analysis and geoprocessing

Results were submitted to analysis of variance (ANOVA) and, when significant, means were compared by Tukey test with a 95 % confidence interval ($p<0.05$). All graphics and statistical analyses were developed with software *TIBCO Statistica*® v13.

The geoprocessing database was designed with geographic information system (GIS) software (*Esri, ArcGIS*® v10.4), performed using an inverse distance weighted (IDW) technique. The IDW interpolation uses a linearly weighted combination of a set of sample points. In this study 27 neighboring sediment sample points were used for interpolation. The weight is a function of inverse distance. The spatial resolution at which the output raster was created was 30 meters. A Python script was written for interpolation evaluation and systematization.

6.3 Results

The sediments in the Lake Guaíba (Fig. 6-1) show a wide range in the physical-chemical characteristics. Depth ranged from 1.8 (LG02) to 5.1 (LG21 and LG23) meters (Tab. 6-2); no significant correlations ($r<0.5$; $p>0.05$) appears with the depth. Depth increase (Fig. 6-2) from the north (inflow in Jacuí's Delta) to south (emissary to Patos Lagoon). Clay ranged from 1.9 (LG08) to 41.7 % (LG21); silt ranged from 1.6 (LG08) to 77.5 % (LG03); total sand (fine, coarse, and gravel) ranged from 0.5 (LG01) to 96.5 % (LG08). Clay plus Silt (C+S) was high in the central and southern Guaíba, as in the "curve" (LG02 and LG03) in north area, following the natural settling of particle size (Fig. 6-2).

The pH ($CaCl_2$ 1:2.5) in the surface sediments of Lake Guaíba had a median of 5.4, ranging from 4.6 (LG06) to 6.7 (LGOUT). The electrical conductivity (EC) ranged from 43 (LG08) to 410 μS/cm (LG16), with a median of 115 μS/cm (Tab. 6-3). The pH had a negative correlation with the clay plus silt ($r = -0.76$); EC does not show any strong correlation with other parameters.

Carbon (TOC) and nitrogen (TN) ranged, respectively, from 1.0 and 0.0 (LG08) to 55.7 and 14.7 (LG12) mg/g (Tab. 6-3), with a very high correlation between both ($r = 0.99$). TOC was higher near to the margins of southern Porto Alegre, and also near to the cities of Guaíba and Eldorado do Sul (Fig. 6-2), with a tendency to increase from north to south, where are more clay and silt.

Metals in Lake Guaíba sediments show a wide range between the evaluated sites (Tab. 6-4). Comparing all the places, sites LG00, LG04, LG08, LG13, LG14, LG22, and LGOUT (Fig. 6-1) shows all the metals below the average values. However, some sites had metals above the average and/or the guideline values: LG05 and LG06 (Zn, Cu, Cr, and Ni); LG09 (Fe, Ca, Ba, Sr, Co, and Zn); LG11 and LG12 (Cu, Cr, Ni, Pb, and Cd); LG15 (Ni); LG16 (Zn and Cr); LG23 (Cu); and LG24 (Pb and Hg). Although LGDS (Dilúvio Stream outflow) had most of the elements below the average, shows values of Zn and Cd above (Tab. 6-4) and higher values of Zn, Cu, and Cd standardized by Al

(Tab. 6-5). The standardization tends to compensate the particle size's differences between the sites.

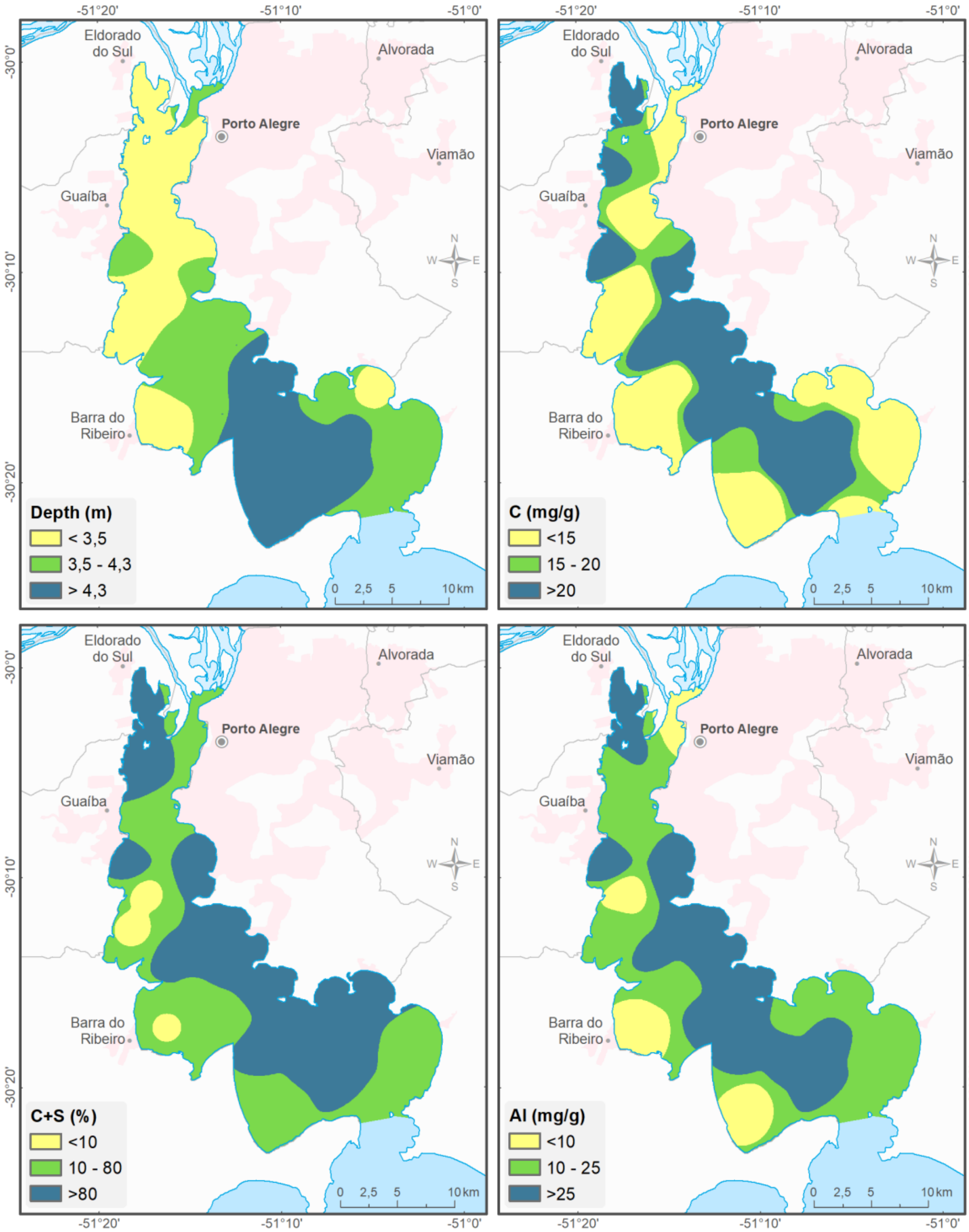

Fig. 6-2. Geoprocessed maps of depth, carbon (TOC), clay plus silt (C+S), and aluminum (Al) in bed sediments of Lake Guaíba.

Tab. 6-2. Geographic localization of sampling sites, depth, bulk density, and particle size of sediment of Lake Guaíba.

Sites	latitude	longitude	margin	zone	reference	depth	density	clay	silt	f sand	c sand	gravel	clay/silt
						m	g/cm³	……………..……….. % ………...…..…..					
LG00	-30.0363190	-51.2499111	W	N	Jacuí's Delta	4.1	1.3	6.5	4.0	10.5	79.0	0	1,6
LGDS	-30.0514225	-51.2376303	E	N	Dilúvio Stream	3.3	1.3	7.5	9.1	44.0	35.8	3.6	0,8
LG01	-30.0355211	-51.2876890	W	N	Eldorado do Sul	2.5	0.9	34.3	65.2	0.4	0.1	0	0,5
LG02	-30.0636839	-51.2841680	W	N	-	1.8	0.9	22.2	72.2	5.3	0.3	0	0,3
LG03	-30.0809827	-51.2989838	W	N	-	2.3	0.8	19.4	77.5	2.8	0.3	0	0,3
LG04	-30.1293107	-51.2735179	E	N	-	2.9	1.1	8.5	8.9	64.0	18.7	0	1,0
LG05	-30.1467343	-51.2503922	E	N	Ipanema	3.0	0.9	22.6	66.6	10.6	0.2	0	0,3
LG06	-30.1655963	-51.2435432	E	N	Salso Stream (WWTP)	3.7	0.9	32.4	66.7	0.7	0.1	0	0,5
LG07	-30.1563240	-51.3022836	W	N	Guaíba	3.9	0.8	30.7	67.2	1.6	0.5	0	0,5
LG08	-30.1786947	-51.2892246	W	N	Coroa da Figueira	2.3	1.4	1.9	1.6	5.9	87.4	3.2	1,2
LG09	-30.2086114	-51.2982998	W	C	Petim Stream	3.0	1.0	4.7	2.4	49.0	43.8	0	1,9
LG10	-30.2288165	-51.2634978	W	C	Ponta do Jacaré	3.9	0.9	37.6	61.7	0.6	0.1	0	0,6
LG11	-30.2038094	-51.2286573	E	C	Ponta Grossa	3.7	0.9	30.9	67.8	1.2	0.1	0	0,5
LG12	-30.2250496	-51.2073636	E	C	Belém Novo (WWTP)	4.3	0.9	24.9	70.9	3.9	0.3	0	0,4
LG13	-30.2840736	-51.2688244	W	C	Barra do Ribeiro	3.1	1.3	4.4	4.2	38.6	52.7	0	1,1
LG14	-30.2560079	-51.2512670	W	C	-	3.7	1.1	19.5	59.9	18.0	2.6	0	0,3
LG15	-30.2797318	-51.2203220	W	C	Ponta do Salgado	4.3	1.0	35.4	39.7	14.0	10.9	0	0,9
LG16	-30.2529519	-51.1825786	E	C	Arado Velho	4.9	0.9	33.7	50.8	12.9	2.6	0	0,7
LG17	-30.2633943	-51.1190083	E	S	Saco do Cego	3.8	0.9	19.9	73.4	5.8	0.9	0	0,3
LG18	-30.2633152	-51.0861995	E	S	Lami (WWTP)	3.4	1.0	22.5	75.2	2.2	0.1	0	0,3
LG19	-30.2912602	-51.1022052	E	S	-	4.4	0.9	23.9	74.3	1.4	0.4	0	0,3
LG20	-30.2990871	-51.0552867	E	S	Itapuã	4.1	1.0	22.2	47.3	22.0	8.5	0	0,5
LG21	-30.3107174	-51.1823184	W	S	-	5.1	0.9	41.7	51.9	5.3	1.1	0	0,8
LG22	-30.3446676	-51.1762855	W	S	-	4.4	1.2	5.1	6.6	78.7	9.6	0	0,8
LG23	-30.3162638	-51.1449740	W	S	-	5.1	0.8	35.9	62.4	1.5	0.2	0	0,6
LG24	-30.3337417	-51.1136519	W	S	-	4.6	0.9	35.3	61.9	2.4	0.5	0	0,6
LGOUT	-30.3598773	-51.0903975	W	S	Outflow	3.6	1.1	16.1	10.8	18.3	54.7	0	1,5

Margin (W – west; E – east); Zone (N – north; C – central; S – south); WWTP - Wastewater (sewage) Treatment Plant; Sand (fine and coarse).

Tab. 6-3. Electrical conductivity (EC), pH, Total Organic Carbon (TOC), and Total Nitrogen (TN) in the sediment of Lake Guaíba.

Samples	EC	pH ($CaCl_2$)	TOC	TN	C:N
	µS/cm	1:2.5	mg/g	mg/g	
LG00	58.3	5.5	3.71	0.31	12
LGDS	190	5.7	6.78	0.61	12
LG01	122	5.4	27.00	2.61	10
LG02	90.5	5.0	17.48	1.44	12
LG03	72.8	4.8	20.85	1.57	13
LG04	68.3	5.7	5.27	0.45	12
LG05	110	4.9	19.26	1.64	12
LG06	143	4.6	26.18	2.27	12
LG07	216	5.1	32.84	3.04	11
LG08	43.1	6.0	1.04	0.00	-
LG09	107	6.5	5.01	0.57	9
LG10	116	5.0	28.30	2.66	11
LG11	197	5.0	23.77	2.11	11
LG12	171	5.0	55.69	14.70	4
LG13	81	6.2	2.37	0.25	10
LG14	68	5.5	6.91	0.67	10
LG15	117	5.0	21.76	2.21	10
LG16	410	6.2	22.44	2.24	10
LG17	114	5.5	14.64	1.46	10
LG18	53.3	5.4	9.83	0.98	10
LG19	205	5.4	24.41	2.31	11
LG20	73.7	5.5	10.94	1.06	10
LG21	152	5.1	19.47	1.98	10
LG22	92.9	6.3	2.91	0.33	9
LG23	171	5.1	26.09	2.62	10
LG24	215	5.2	29.30	2.74	11
LGOUT	188	6.7	13.49	1.10	12
Median	115	5.4	19.26	1.57	10
RV	-	-	16.70	3.00	**-**

ND – Not Detected; EC – 1:5; RV – Reference Value (LAYBAUER, 2002).

Tab. 6-4. Metals (pseudo-total) in the sediment of Lake Guaíba and quality guideline values.

Samples	Fe	Al	Ca	Ba	Sr	Co	Tl	Zn	Cu	Cr	Ni	Pb	Cd	Hg
	....	mg/g	....	....	....	....	....	....	µg/g	....	....	....	....	....
LG00	15.3	6.9	0.6	139	21.5	6.4	0.01	99	13.8	10.3	9.0	9.2	0.11	0.02
LGDS	23.7	7.9	1.4	378	32.8	13.8	0.02	231	74.4	14.9	9.9	19.3	0.51	0.04
LG01	86.2	34.1	2.4	625	90.1	39.1	0.04	141	95.6	50.0	31.3	41.1	0.41	0.06
LG02	76.2	26.4	2.9	412	83.3	32.7	0.03	117	96.4	39.4	28.4	28.7	0.32	0.06
LG03	71.2	22.7	2.4	475	79.9	34.7	0.03	117	80.8	40.0	26.7	26.7	0.14	0.06
LG04	39.8	10.9	2.2	235	49.2	17.9	0.01	68	37.1	20.0	11.9	12.3	0.03	0.03
LG05	80.7	27.5	2.9	452	82.8	36.5	0.03	200	115.4	56.8	34.7	34.0	0.24	0.07
LG06	85.9	34.6	2.5	547	82.4	47.2	0.06	196	116.2	72.7	37.7	34.2	0.32	0.07
LG07	83.0	32.1	2.5	637	85.6	38.9	0.04	119	88.9	45.4	28.1	38.8	0.35	0.08
LG08	37.8	3.4	1.5	231	21.9	15.1	0.01	67	29.5	5.7	7.8	7.9	0.09	0.02
LG09	191.3	13.7	6.1	1,448	142.8	97.6	0.03	261	75.9	31.7	31.0	29.5	0.22	0.06
LG10	80.8	27.7	2.7	632	81.3	41.9	0.04	176	99.0	41.9	37.7	41.7	0.40	0.09
LG11	85.6	34.9	2.9	583	85.3	43.7	0.04	161	132.1	68.3	43.4	41.6	0.44	0.08
LG12	84.9	33.0	3.0	578	81.1	44.3	0.04	163	114.4	63.4	38.4	37.7	0.33	0.08
LG13	57.1	4.6	0.7	275	22.2	24.1	0.02	47	20.6	10.9	12.6	19.8	0.05	0.04
LG14	50.0	13.0	2.1	424	48.4	24.5	0.02	49	28.3	24.7	13.9	19.2	0.05	0.04
LG15	78.0	27.6	2.4	696	80.2	37.6	0.04	110	77.9	46.8	37.2	43.1	0.35	0.09
LG16	91.6	31.7	4.0	586	81.6	45.5	0.04	181	98.4	58.9	33.5	39.5	0.31	0.08
LG17	66.5	12.8	2.6	524	69.2	36.5	0.04	139	74.4	42.4	31.1	35.3	0.27	0.07
LG18	55.6	16.6	5.6	465	61.8	29.4	0.03	125	78.4	34.2	23.9	28.0	0.26	0.06
LG19	80.9	27.9	2.8	606	84.5	41.0	0.04	114	99.3	53.6	35.2	41.1	0.39	0.08
LG20	139.3	19.1	3.2	545	81.7	58.4	0.03	166	75.8	42.8	25.7	33.2	0.44	0.07
LG21	81.7	27.6	2.6	688	80.1	39.9	0.04	125	74.4	47.9	25.4	38.6	0.30	0.08
LG22	34.3	6.0	1.1	217	23.1	14.8	0.01	32	25.4	10.6	10.2	9.6	0.06	0.02
LG23	78.6	27.5	2.9	672	86.3	38.9	0.04	148	108.9	47.3	30.7	40.6	0.39	0.08
LG24	81.6	29.5	3.0	728	89.1	39.8	0.05	140	82.1	48.9	34.8	53.0	0.23	0.10
LGOUT	38.5	12.3	11.1	282	61.5	16.0	0.02	46	34.7	17.4	13.8	16.2	0.06	0.03
Median	77	23	2.5	540	80	38	0.03	132	78	42	28	33	0.3	0.07
RV	-	-	-	-	-	-	-	155	46	39	35	34	0.5	0.06
BG	-	-	-	-	-	-	-	110	27	21	32	27	0.3	0.03
ISQG	-	-	-	-	-	-	-	123	35.7	37.3	18	35	0.6	0.17
PEL	-	-	-	-	-	-	-	315	197	90	35.9	91.3	3.5	0.49

Reference values (RV) from 1998-1999 and Background values (BG) to Lake Guaíba bottom bulk sediment (LAYBAUER, 2002). Sediment Quality Guidelines for the Protection of Aquatic Life (Freshwater): Interim Sediment Quality Guideline (ISQG) - Conama No. 454, Level 1; Probable Effect Level (PEL) – Conama No. 454, Level 2 (BRASIL, 2012).

Tab. 6-5. Normalized values of zinc, copper, chromium, nickel, lead, and cadmium standardized by Aluminium in Lake Guaíba sediments.

Samples	Zn/Al		Cu/Al		Cr/Al		Ni/Al		Pb/Al		Cd/Al	
LG00	1.01	cb	-1.11	e	-0.91	b	-0.16	bcde	-0.39	bc	0.12	bcdef
LGDS	3.41	a	2.92	a	0.02	b	-0.26	cde	0.91	bc	4.32	a
LG01	-0.60	f	-0.64	cde	-0.87	b	-0.80	e	-0.48	bc	-0.17	cdefg
LG02	-0.56	ef	-0.20	bcde	-0.77	b	-0.50	e	-0.62	bc	-0.16	cdefg
LG03	-0.45	def	-0.21	bcde	-0.17	b	-0.33	cde	-0.56	bc	-0.69	efg
LG04	-0.29	def	-0.32	bcde	-0.17	b	-0.50	e	-0.59	bc	-0.98	g
LG05	-0.11	def	0.09	bcde	0.38	b	-0.22	cde	-0.49	bc	-0.47	efg
LG06	-0.37	def	-0.35	bcde	0.43	b	-0.51	e	-0.77	c	-0.42	efg
LG07	-0.66	f	-0.62	cde	-0.82	b	-0.82	e	-0.45	bc	-0.23	cdefg
LG08	1.92	b	2.55	a	-0.46	b	1.66	abc	0.80	bc	1.00	b
LG09	1.78	b	0.83	bc	0.96	ab	1.58	abcd	0.57	bc	0.18	bcde
LG10	-0.26	def	-0.22	bcde	-0.78	b	-0.01	bcde	-0.16	bc	0.03	cdefg
LG11	-0.54	ef	-0.08	bcde	0.18	b	-0.18	bcde	-0.53	bc	-0.13	cdefg
LG12	-0.46	def	-0.20	bcde	0.20	b	-0.37	de	-0.54	bc	-0.33	defg
LG13	0.50	cd	0.47	bcd	1.16	ab	2.51	a	3.62	a	-0.12	cdefg
LG14	-0.68	f	-1.02	de	0.02	b	-0.56	e	-0.22	bc	-0.88	fg
LG15	-0.64	f	-0.66	cde	-0.42	b	-0.08	bcde	-0.12	bc	-0.16	cdefg
LG16	-0.37	def	-0.49	bcde	-0.06	b	-0.57	e	-0.47	bc	-0.38	defg
LG17	0.45	cde	0.96	b	3.06	a	1.80	ab	1.25	b	0.60	bcd
LG18	-0.05	def	0.46	bcd	0.40	b	0.11	bcde	0.07	bc	0.13	bcde
LG19	-0.63	f	-0.26	bcde	0.06	b	-0.22	cde	-0.22	bc	-0.03	cdefg
LG20	0.11	cdef	-0.04	bcde	0.74	b	-0.07	bcde	0.09	bc	0.75	bc
LG21	-0.55	ef	-0.71	de	-0.29	b	-0.82	e	-0.30	bc	-0.29	defg
LG22	-0.41	def	0.10	bcde	-0.23	b	0.54	abcde	-0.07	bc	-0.41	efg
LG23	-0.38	def	0.05	bcde	-0.28	b	-0.41	de	-0.14	bc	0.07	bcdef
LG24	-0.51	def	-0.67	de	-0.41	b	-0.37	de	0.21	bc	-0.55	efg
LGOUT	-0.68	f	-0.63	cde	-0.99	b	-0.44	e	-0.39	bc	-0.81	efg

Means followed by the same letter are not statistically different from each other by Tukey's test at 95 % confidence.

In many sites metals Zn, Cu, Cr, Ni, and Pb had values above the Interim Sediment Quality Guideline (ISQG), "level 1" in Brazilian sediment quality guidelines (BRASIL, 2012); however, only Ni had values above the Probable Effect Level (PEL) in some sites (LG06, LG10, LG11, LG12, and LG15). Comparing the median values of the sites (Tab. 6-4) with the ISQG, reference values (RV) and background values (BG) of the Lake Guaíba (LAYBAUER, 2002): Cu and Cr were above all (ISQG, RV, and BG); Zn above the ISQG and BG, but below the RV (samples from 1998-1999); Ni above the ISQG and below the RV and BG; Pb above the BG and below the ISQG and RV; Hg above the RV and BG and below the ISQG; and Cd below or near all (ISQG, RV, and BG).

Geo-accumulation index (I_{geo}) of Zn surpasses the unpolluted values (zero line) only in sites LG05, LG06, LG09, LG16, and LGDS (Fig. 6-3); Pb surpasses only in site LG24, and Cd only to site LGDS. Means of Cu, Cr, and Hg surpass the "unpolluted" value; the sites where no one metal surpasses the unpolluted value was: LG00, LG04, LG08, LG13, LG14, LG22, and LGOUT. Most part of the sites with higher I_{geo} was near to east margin (Porto Alegre's), and with lowest (or no one surpassing value) near to west margin (Fig. 6-1).

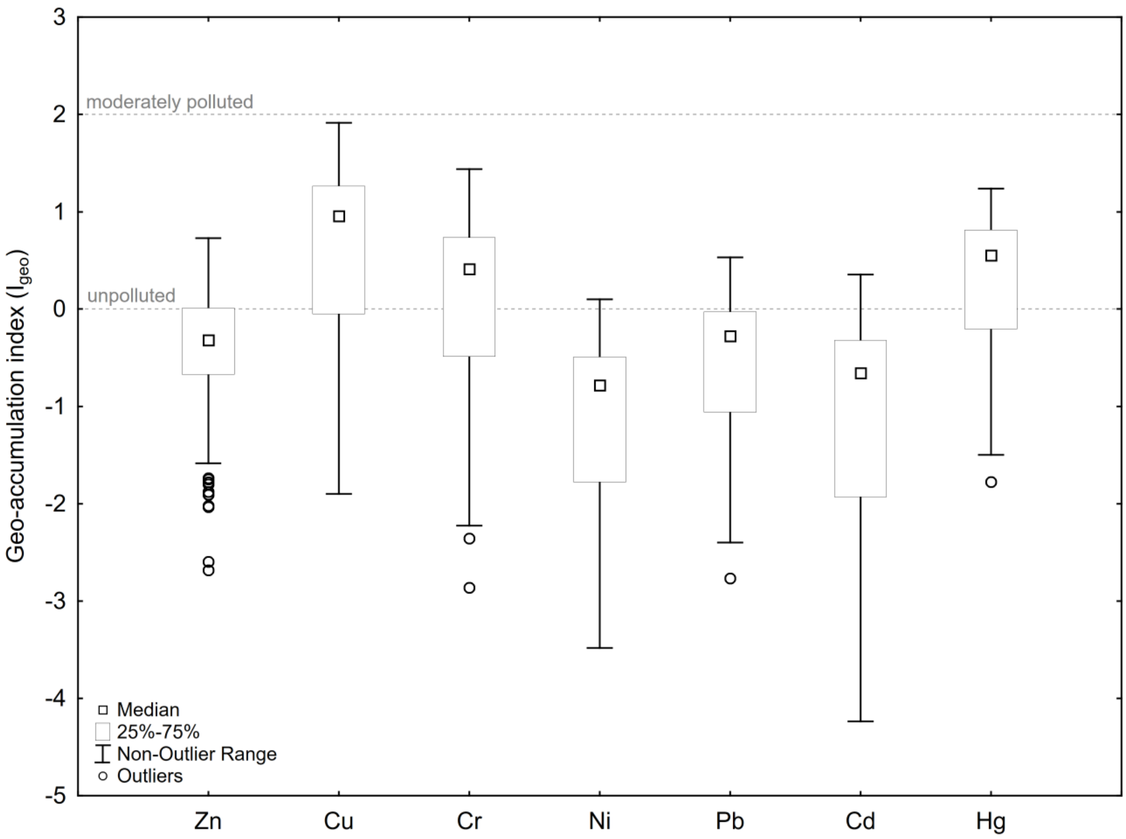

Fig. 6-3. Geo-accumulation Index (I_{geo}) of zinc, copper, chromium, nickel, lead, cadmium, and mercury in Lake Guaíba sediments.

Principal component analysis (PCA) showed a relationship between metals (Al, Cr, Pb, Tl, Hg, Cu, Ni, and Cd) with clay, silt, and carbon (TOC); distant from the first group was another relationship between the metals Fe, Co, Ba, Zn, and Sr (Fig. 6-4).

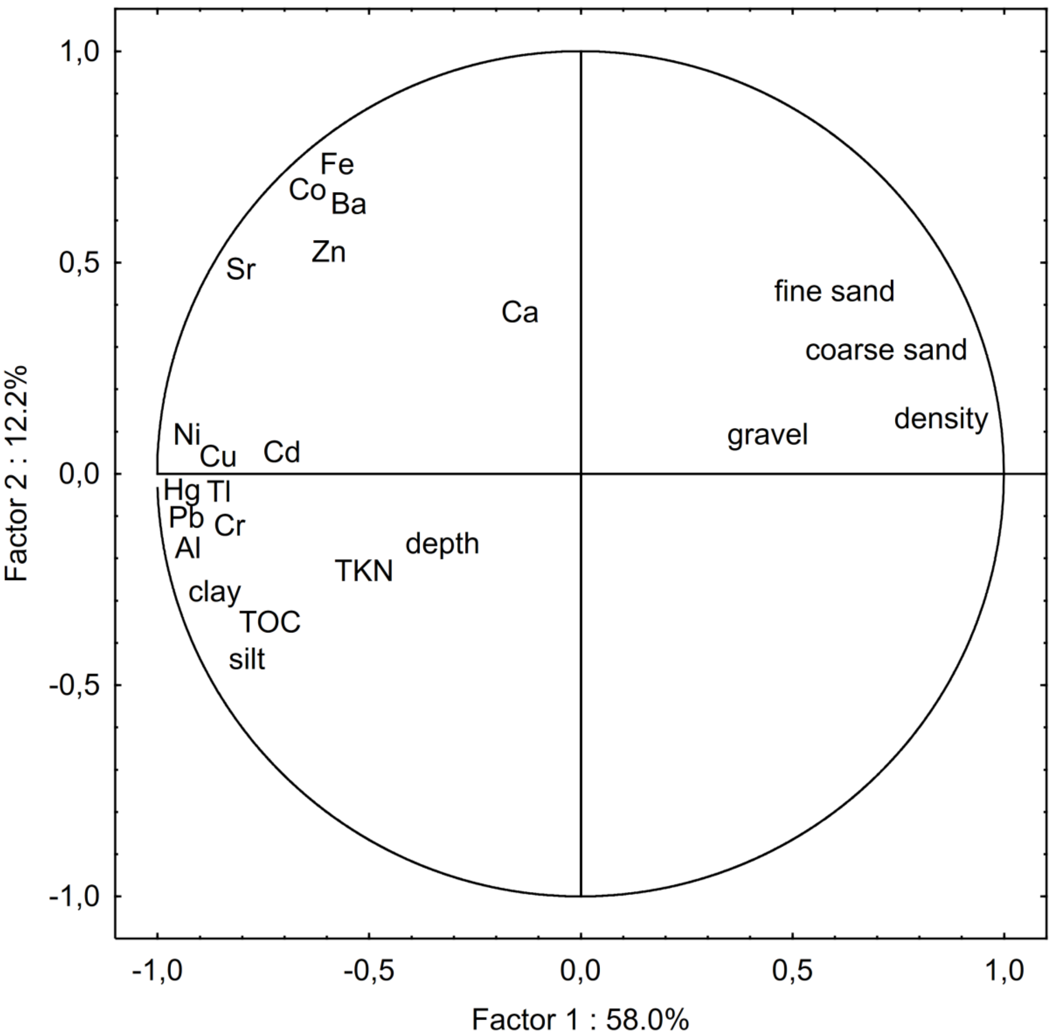

Fig. 6-4. Principal component analysis (PCA) in Lake Guaíba sediments.

A screening in the sediment of Lake Guaíba found four principal groups and more nineteen organic compounds (Tab. 6-6). Some compounds (found in the most sites) were pooled: Aliphatic hydrocarbons (HC) – alkanes (from 10 to 44 carbons); Non-Aliphatic HC (mixed); Cycloaliphatic & derivatives; and Benzene & derivatives. Four organic compounds were found in all the sites evaluated: “14-Beta-H-Pregna”; “Diacetone Alcohol” (4-hydroxy-4-methyl-2-pentanone); “Phenol, 2,4-bis TMS” [phenol, 2,4-bis(1,1-dimethylethyl)]; “Nonahexacontanoic acid”.

Tab. 6-6. Organic compounds (%; non-target screening) found in the sediment of Lake Guaíba.

Library/ID	LG00	LGDS	LG01	LG02	LG03	LG04	LG05	LG06	LG07	LG08	LG09	LG10	LG11	LG12	LG13	LG14	LG15	LG16	LG17	LG18	LG19	LG20	LG21	LG22	LG23	LG24	LGOUT
Aliphatic HC (alkanes) [a]	4.9	3.8	9.3	13.0	8.7	9.9	8.7	13.5	6.6	5.8	6.6	19.4	31.3	3.4	3.1	6.9	13.2	3.8	3.0	11.7	7.1	8.2	4.2	9.2	8.3	6.0	4.1
Non-Aliphatic HC (mixed) [a]	5.6	1.2	4.5	1.1	0.7	3.5	2.0	-	0.6	2.1	3.9	5.3	-	-	1.9	5.8	2.7	1.0	1.3	1.1	0.1	5.3	1.2	5.4	4.7	1.5	2.0
Cycloaliphatic & derivatives	-	8.1	-	-	-	-	0.4	-	1.5	-	-	1.0	-	-	-	-	-	-	-	-	-	-	2.1	-	0.2	-	0.1
Benzene & derivatives	1.2	-	0.4	22.8	21.2	0.7	0.7	0.3	0.7	0.5	1.0	0.4	-	-	0.7	0.3	0.2	20.2	17.2	24.9	0.6	6.7	2.1	0.2	0.5	0.7	0.1
14-Beta-H-Pregna	2.2	4.3	6.8	5.4	4.5	1.5	7.2	7.7	9.7	0.3	1.9	13	11	7.7	1.7	0.1	6.8	11	6.7	2.9	9.8	8.2	5.5	2.0	8.8	9.3	8.7
Diacetone Alcohol [b]	12.8	1.5	1.0	2.0	0.2	2.1	2.7	0.9	2.8	2.7	1.0	1.9	0.2	0.1	23.8	2.3	0.7	0.8	0.2	0.8	0.4	2.7	33.6	0.7	2.0	2.3	0.1
Phenol, 2,4-bis (TMS) [c]	2.7	5.0	3.1	4.5	3.8	4.1	1.9	3.0	2.3	3.5	3.1	2.2	1.9	3.4	5.1	2.8	2.9	3.2	3.6	2.9	2.1	3.4	2.2	2.1	2.8	2.5	2.1
Nonahexacontanoic acid	0.5	0.4	1.1	2.3	2.1	1.5	2.3	2.6	2.6	0.3	0.9	0.2	1.2	5.7	1.5	1.9	3.3	3.7	1.0	0.5	3.0	2.0	1.6	4.5	3.4	3.4	2.7
Phthalic acid- [d]	-	6.3	-	2.6	-	-	-	5.8	-	-	-	-	-	10.4	-	-	-	-	6.0	5.8	10.6	9.1	4.7	-	-	5.7	-
Carbamic acid- [e]	0.5	-	0.1	-	-	0.1	-	-	1.0	0.3	0.3	0.6	-	-	0.3	0.5	-	-	-	-	-	-	-	0.5	-	0.3	1.1
Tetradecanoic acid	-	-	1.1	-	-	-	0.7	-	4.9	-	-	7.2	5.6	5.7	-	-	-	-	-	-	5.4	-	4.3	-	6.8	4.6	0.4
Dodecanoic acid	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Atrazine-desisopropyl [f]	-	-	-	0.0	-	-	-	0.1	0.2	-	-	-	0.1	0.3	-	-	-	-	-	0.1	-	-	-	-	-	-	-
Fluoranthene	-	0.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Bergamotane	-	-	-	0.1	0.1	-	-	0.6	0.3	-	-	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Citronellal	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	0.5
Coumarin- [g]	-	-	-	-	-	-	-	3.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dibenzoxazepine-*met* [h]	-	-	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dihydrophytol [i]	-	-	-	-	-	-	-	-	-	-	0.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Hexyl-1-decanol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.9
Dimethyl 3-thiahexanedioate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.2	-	2.1	-	-	-	-	-
2-Undecanone, 6,10-dimethyl-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.6	-	-
8-Methyloctahydrocoumarin	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3	-	-	-	-	-	-	-	-	-	-

[a] HC - HidroCarbons; [b] 4-hydroxy-4-methyl-2-pentanone; [c] phenol, 2,4-bis(1,1-dimethylethyl); [d] diisooctyl ester; [e] (2-hydroxy-1-methyl-4,6-tridecadienyl)-, ethyl ester; [f] 1,3,5-triazine-2,4-diamine, 6-chloro-N-ethyl-; [g] 3-hydroxymethyl-6,8-dimethoxycoumarin; [h] 4-hydroxydibenz[b,f][1,4]oxazepin-11(10h)-one; [i] 1-hexadecanol, 3,7,11,15-tetramethyl-.

6.1 Discussion

The bed sediments in Lake Guaíba have predominant fine particle sizes (silt and clay). However, some sites present a high amount (>70 %) of total sand (sum of fine, coarse, and gravel); this sites were in “sandy point’s” (LG04 and LG08), sand deposition regions (LG09, LG13, and LG22) and areas with large water flow (LG00 – Jacuí’s Delta outflow; LGDS – Dilúvio Stream outflow; LGOUT – connection with Patos Lagoon). Depth did not show significant correlations ($r<0.5$) with the particle size. Most part of those sandy sites was in the west margin of the lake (right side of the predominant water flow), the opposite of occurs in rivers (MENEGAT; CARRARO, 2009). The Lake Guaíba presents characteristics of “fluvial lakes” (SMOL, 2008), with the sediment deposition being dependent of the water flows and velocity.

Aluminum (Al) had the highest values in the sites LG01, LG06, LG07, LG11, LG12, LG16, and LG24 (Tab. 6-4); all those sites had high values of clay plus silt (>85 %). The Al (most abundant metal of lithosphere) has a high correlation with Clay ($r = 0.88$; $R^2 = 0.78$; Fig. 6-5a) and Silt ($r = 0.76$). Aluminum (Al) follows the same tendency of clay plus silt (C+S), with higher values in the central and southern zones of Lake Guaíba, as in the "curve" in north area (Fig. 6-2), due to the high correlation. These sites also show higher values of Total Organic Carbon (TOC), that has a strong correlation with the Al ($r = 0.93$). All sites with more than 25 % of Clay had also high values (>20 mg/g) of TOC (Tab. 6-2 and Tab. 6-3). However, despite the expected relationship between particle size and carbon (LIU et al., 2016), the correlation of Clay and TOC was reduced due to the site LG12 getting out of the trend line (Fig. 6-5b).

The electrical conductivity (EC) had higher values in the margin of Porto Alegre, major in the sites LGDS, LG05, LG06, LG11, LG12, and LG16 (Tab. 6-3), creating a plume to the south Guaíba (Fig. 6-1). High values appear also in the site LG07 (216 µS/cm), near to Guaíba city.

Site LG12 had the highest carbon (TOC) and nitrogen (TN) concentrations, and the lowest relation C:N (3.8), in an average of 10 (Tab. 6-3). The C:N ratio is an indicator about the organic matter sources and fate and reflect changes in the nutrient status (LUCAS; LIBER; DOIG, 2015). Site LG12 was near of Belém Novo neighborhood, with large presence of residences near the lake shore and a Wastewater Treatment Plant (WWTP). This site had higher values of Zn, Cu, Cr, Ni, Pb, and Cd (Tab. 6-4).

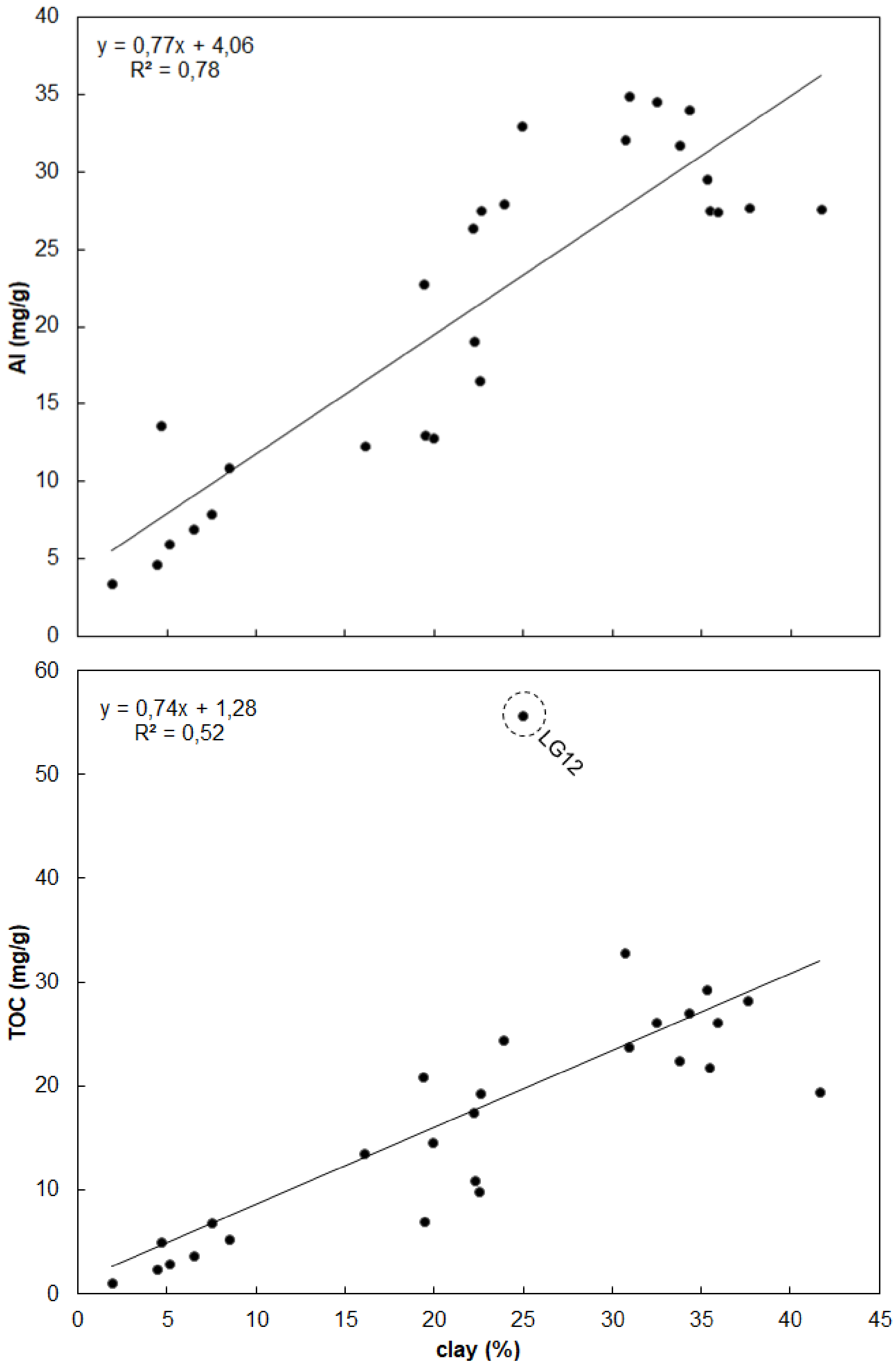

Fig. 6-5. Linear correlation of clay versus (a) Aluminum and (b) Total Organic Carbon (TOC) in Lake Guaíba sediments.

Metals in bed sediments of Lake Guaíba have a strong relationship most with clay fractions, but direct or indirect also with the silt fraction and TOC (Fig. 6-4). Thus, metals and organic matters can entry on Lake Guaíba by many ways (Fig. 6-6). Metals Zn, Cu, Cr, and Ni appears in higher concentrations near to the margin of southern Porto Alegre (Fig. 6-7), where was more clay plus silt (Fig. 6-2). It's not possible to say if those metals came directly from Porto Alegre or if those metals just accumulate in these areas due to the occurrence of clay and silt fraction.

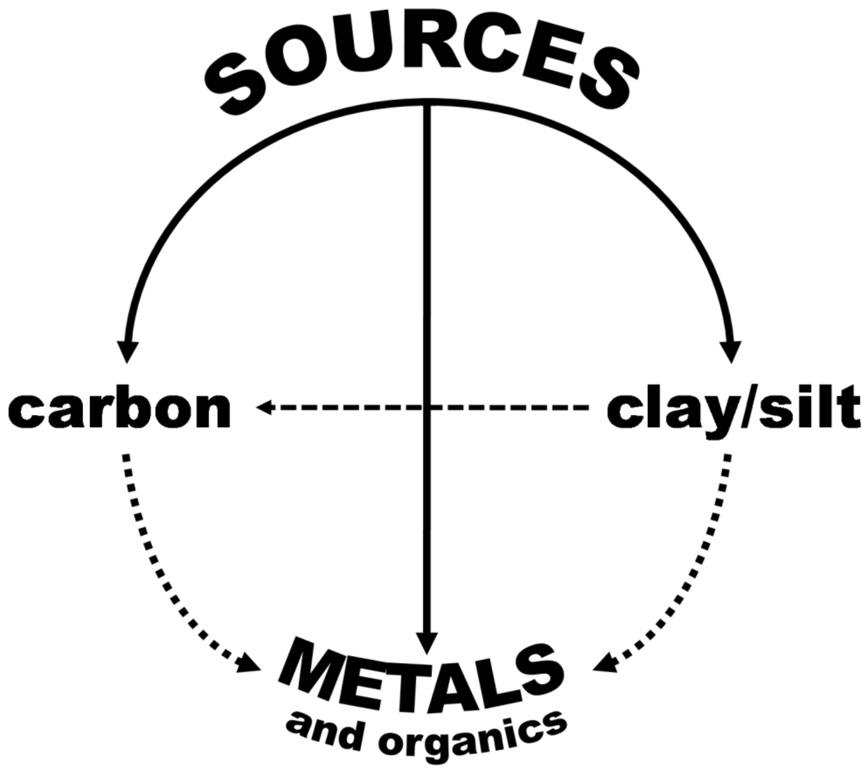

Fig. 6-6. Graphical abstract about the metal and organic pollution sources and ways in Lake Guaíba sediments.

Due the strong relation between clay and aluminum, the standardization (subdivision) of metals by Al can compensate the variability of particle sizes. Despite the high values of some standardized metals (Tab. 6-5) in sites LG08, LG09, and LG13, these values may are overestimated due the low clay plus silt (<10 %) or due to the high clay/silt (Tab. 6-2). Site LG17 show high standardized values to some metals (Cu, Cr, Ni, and Pb), although the low bulk average concentrations (Tab. 6-4).

Site LGDS (Dilúvio Stream outflow) had very high standardized values to metals Zn, Cu, and Cd (Tab. 6-5), confirming the high bulk concentrations of the same metals (Tab. 6-4). The LGDS had the highest concentration of Cd (0.51 µg/g) and the second highest of Zn (231 µg/g). Metals Zn and Cd have visible concentrations near to the outflow of the stream (Fig. 6-7). Dilúvio Stream have a watershed of 83.7 km² , with a high population density (6,400 hab/km²), and a length of 17.6 km (MENEGAT et al., 2006); the stream is a well-known polluted water body that flows over Porto Alegre with outflow in the Lake Guaíba, polluting the sediments in the margins with TOC, TN, Zn, Cu, Pb, Cr, and Ni (DE ANDRADE et al., 2018). Due to the outflow, the site LGDS accumulates more fine and coarse sand and gravel (Tab. 6-2), carrying out the silt and clay (and, consequently, the pollution).

Site LG06 (with high values of Zn, Cu, Cr, and Ni) is near to the outflow of Salso Stream. Similar to Dilúvio Stream (LGDS), the Salso suffers the effects in a region with high population density (626 hab/km²) and unlawful discharges of raw sewage. Salso Stream have length 16.7 km and a drainage basin of 93 km² (MENEGAT et al., 2006). Despite the coverage of treatment systems in the region, many households do not make proper connection to the system. Salso Stream have high average amounts of clay plus silt (75 %) and organic matter (8 %) near to the outflow, as metals Zn (134), Cu (35), Cr (33), Pb (32), and Ni (11 µg/g); previous studies reported indicatives of contamination with Zn, Cu, and Ni in the Salso Stream (SOARES et al., 2004). Site LG11 is near to the outflow of Guabiroba Stream (with a watershed of 10 km² and popular density of 426 hab/km²), but this local may accumulate the water flows from LG06.

The sediment particle size is inversely proportional to their sorption capacity of metals and compounds; in the meantime, smaller particles can be re-suspended in and moving with the water column (SANGSTER et al., 2015; TANSEL; RAFIUDDIN, 2016; ZHOU et al., 2017). Thus, polluted sediments may act as a potential release source of those elements and compounds (ZHOU et al., 2017).

The Geo-accumulation Index (I_{geo}) indicate an empirical relationship of metal enrichment degree, comparing to the natural (background) concentrations (CHAHARLANG et al., 2016; LIU et al., 2016; MULLER, 1969). However, I_{geo} (Fig. 6-2) do not compensate the variability of particle size (Tab. 6-2) or TOC (Tab. 6-3); comparing those values, all the sites with positive I_{geo}

had high values of clay plus silt and TOC, unless LGDS (Zn = 0.49; Cu = 0.88; and Cd = 0.18) and LG09 (Zn = 0.66; Cu = 0.91; and Hg = 0.46). Sites LG00, LG04, and LGOUT (other sites with minor clay plus silt and TOC) did not show any positive I_{geo}.

Major part of the locals with lowest (negative) I_{geo} was in the west margin of the lake, and most part of the sites with higher was near to east margin (close to Porto Alegre City). Some of the sites with high metals concentrations (Tab. 6-4) were in the central area of the lake and east margin (near to Porto Alegre City): LG05 and LG06 (Zn, Cu, Cr, and Ni); LG11 and LG12 (Cu, Cr, Ni, Pb, and Cd); LG16 (Zn and Cr). Sites LG05, LG06, LG11, and LG12 had the highest I_{geo} of Cu (>1.5) and Cr (>0.85). Metals Cu, Cr, and Hg surpass the “unpolluted” value in the average (Fig. 6-3).

In site LG00 (Lake Guaíba water inflow, from Jacuí’s Delta) there was not any bulk concentrations of metal above the average (Tab. 6-4), and the local shows low values of clay, silt and carbon (Tab. 6-2 and Tab. 6-3); however, the site had positive values of Zn/Al and Cd/Al (Tab. 6-5). Major part of the pollution of the Lake Guaíba came from the polluted water bodies that flow to the lake (ANDRADE; ANDRADE; CAMARGO, 2018), as the rivers Sinos, Caí, and Gravataí (in Jacuí’s Delta) and the urban streams. In order to solve these environmental liabilities, public actions should not focus only on Guaíba, but also in those water bodies (DE ANDRADE et al., 2018).

The sediment in site LG09 had the highest concentrations of Fe (191 mg/g), Ba (1.45 mg/g), Sr (143 µg/g), Co (98 µg/g), and Zn (261 µg/g), and a high Ca (6.1 mg/g). Calcium (Ca), Barium (Ba), and Strontium (Sr) are alkaline earth metals. LG09 and LGDS (Dilúvio Stream outflow) were the only places with low clay plus silt and TOC, but high I_{geo} (Zn – 0.66, Cu – 0.91, and Hg – 0.46). LG09 was near to the outflow of Petim Stream, close to Guaíba City (in the west margin). In the drainage basin of the stream there are many land uses: natural areas; production of eucalyptus, rice, and other grains; and historic coal mining areas.

Site LG24 had the highest concentration of Hg (0.10 µg/g; I_{geo}=1.19) and Pb (53 µg/g; I_{geo}=0.39) in Lake Guaíba; this high contamination may come from the deposition along the time, the same in site LG15 (Ni) and LG23 (Cu). Differently, the high value of Ca in LGOUT occurred due to the large presence of shells of native bivalves in the place. Pb had higher concentrations in the south part of Lake Guaíba and where was more clay plus silt (Fig. 6-7). Lead (Pb) is predominantly a legacy contaminant, with significantly reducing across the world over time (SHARLEY et al., 2016); sources of Pb include coal combustion, leaded gasoline, ore smelting, and re-suspension of soil, sediment, and road dust (WAN et al., 2016). The phasing out of Pb pollution was correlated with the abolition of leaded fuels in many countries during the 1970s (SHARLEY et al., 2016).

Generally, there is a risk of pollution by Zn, Cu, Cr, and Ni in the sediments of Lake Guaíba. Metals Zn and Ni reduced the concentrations along the time, but it is still high comparing to ISQG; Cu and Cr increased the concentrations. Metals Pb, Cd, and Hg are more controlled, below the guideline; however, Pb shows values above the BG and ISQG, and Hg above BG and RV, in many sites (Tab. 6-4). Despite that Zinc (Zn) and Copper (Cu) may be naturally found in high concentrations in some soils in the Lake Guaíba drainage region (FEPAM, 2014), they can pose in risks the organisms in freshwater ecosystems (FU et al., 2016). Cooper (Cu) had century-old use in the southern Brazil as Cu-based pesticides in vineyards (PATINHA et al., 2018).

According to Laybauer (2002), the balance of metals in the Lake Guaíba had a constant trend between the beginning of the 20th century and the 1960s, with a strong increase (2-3x in the contents of Cr, Ni, and Zn) between the 1980s and 1990s due to the increase in industrial activities in the region (like the Leather and Footwear industry). After this time period, concentrations were reduced and were probably linked to improvements at environmental processes and public oversight. Considering the short-term average sedimentation rate of sediments in Lake Guaíba (6 mm/year) and the collected layer (0-10 cm), the samples could represent a history of about 15 years.

The Industrial Revolution generated increases in global pollution; although, late development countries show this same pattern with a certain delay. China had a second high pollution trend from the 1980s and stabilizing in the 2000s, caused by the political reform in the country (BING et al., 2016; WAN et al., 2016). Toxic metal pollution is usually related to industrial development and its subsequent reduction is generally related to prevention laws and consequent investment in emission control (WAN et al., 2016).

Sediment material is divided into two broad categories based on its sources: “allochthonous”, from outside; and “autochthonous”, from inside (SMOL, 2008). The sediments (and consequently the pollution) that get in the Lake Guaíba came from the water bodies that flow to the lake, from the urban dust, from the runoff, and other sources (Fig. 6-6). Lake sediments accumulated significant fractions of organic matter (increasing oxygen demand and nutrient regeneration), that came from external inputs (from the catchment), internal biota (phytoplankton, macrophytes, bacterias), as well from pollution sources (ZHANG et al., 2017).

In Porto Alegre the concentrations of Zn, Cr, Cu, Ni, and Pb in urban dust were high in comparison with background values for southern Brazil; the means (± standard deviation) values were: Zn - 256±128; Cr - 157±53; Cu - 114±46; Ni - 62±24; and Pb - 52±31 µg/g (POLETO et al., 2009). In this same region, higher metal concentrations (Zn, Pb, Ni, and Cd) were found (in order) in areas with predominant commercial, residential, and industrial activities; this occurs due to the higher vehicular traffic in the commercial and residential areas (MARTÍNEZ; POLETO, 2014). Atmospheric deposition reflects the regional anthropogenic metal emissions; although, xenobiotics can be found even in remote alpine lakes, as in the Tibetan Plateau (BING et al., 2016). Chromium (Cr) pollution is most often associated with industrial activity and processes such as metal finishing or electroplating, and is not considered a diffuse pollutant (SHARLEY et al., 2016).

A variation in urban dust between cities reflects differences in land use, such as the degree of industrialization and patterns of traffic movements (POLETO et al., 2009). Urban and motorway road dust are highly contaminated with potential toxic metals (as Zn, Cu, Cr, Ni, and Pb) than non-urban regions; high vehicular traffic have been reported as a major source of metal diffuse pollution around the world (ADAMIEC; JAROSZ-KRZEMIŃSKA; WIESZAŁA, 2016; SHARLEY et al., 2016; ZHANG et al., 2016). The wear and tear of vehicles pieces (emission, brake pads, tires, oil, grease, rust), as well the pavement paint and degradation, release dust and debris that are carried by stormwater runoff to roadside soils and waterbodies, accumulating in the sediments (SHARLEY et al., 2016; ZHANG et al., 2016). Braking system and tires are exposed to frictions, emitting particles. Brake pads and linings presents several metals in addiction to Iron (Zn, Cu, Cd, Fe, Ni, and Pb); tires present large amounts of Zn, due to ZnO and ZnS added to activate vulcanization in the tire tread (ADAMIEC; JAROSZ-KRZEMIŃSKA; WIESZAŁA, 2016; SHARLEY et al., 2016; ZHANG et al., 2016).

Persistent organic pollutants (POPs) is a generic name to a group of organic chemicals with characteristics of long half-life times, present in the environment even without current use and remaining very long in sediment (SAKAN; OSTOJIĆ; ĐORĐEVIĆ, 2017). Examples of POPs are: Polychlorinated biphenyls (PCBs); Polyaromatic hydrocarbons (PAHs); Organochlorine pesticides (OCPs). Generally POPs are hydrophobic, binding to the particle fraction in the water bodies and depositing in the basin bed. Those organic micro-pollutants have multiple sources, as: industry, agriculture, traffic, domestic sewage, industrial wastewater, and runoff from nonpoint sources (SAKAN; OSTOJIĆ; ĐORĐEVIĆ, 2017).

Aliphatic Hydrocarbons (alkanes) were found in higher values in sites LG02, LG06, LG10, LG11, LG15, and LG18. Site LG11 had the highest amount of Aliphatic Hydrocarbons (31 %). Benzene & derivatives were found in higher values in sites LG02, LG03, LG16, LG17, and LG18 (Tab. 6-6). Site LG00 (Dilúvio Stream outflow) had higher values of organic compounds: Cycloaliphatic & derivatives; Phenol, 2,4-bis (TMS); Phthalic acid; and Fluoranthene. Fluoranthene is a PAH found in many combustion products, being a marker of pyrogenic sources (SAKAN; OSTOJIĆ; ĐORĐEVIĆ, 2017). Hydrocarbons (HC) and derivatives (aliphatic, benzene, PAH) are commonly found in petroleum products (as vehicular fuels); those entering in the aquatic ecosystems by surface runoff, urban sewage, industrial discharges and dry or wet air deposition, accumulating in the sediments due to the hydrophobicity (NASCIMENTO et al., 2017).

The Phenol, 2,4-bis(1,1-dimethylethyl) is an alkyl phenol formed in the degradation of pesticides and agricultural products (being commonly found in the sediment and water), presenting characteristics of POPs (as high toxicity, persistence, and bioaccumulation) and acting as endocrine disruptor (KEE; MUKHERJEE; PARIATAMBY, 2015). Endocrine disrupting chemicals (EDCs) are exogenous agents that can alter endocrine system functions, being found in personal care products, fuels, pharmaceuticals, and other chemicals

(SCOGNAMIGLIO et al., 2016; WIRBISKY et al., 2016). Phenol, 2,4-bis (TMS) was found in all the evaluated sites (Tab. 6-6). Previous studies reported the presence of Phenol in toxicity analysis in Lake Guaíba watershed (GONÇALVES et al., 2012; TERRA; GONÇALVES, 2013).

Esters of phthalic acid, also known as phthalates, are commonly used as additives or plasticizers in a wide range of industrial applications (SCOGNAMIGLIO et al., 2016).The Phthalic Acid Esters (PAEs) have been widely used in common products as plasticizers (as in PVC), being easily released and accumulated in the environment (due to their hydrophobicity) and transferred to organisms (TAN et al., 2017). PAEs are also considered to be EDCs (SCOGNAMIGLIO et al., 2016; TAN et al., 2017).

Site LG07 (near to a historical Cellulose Factory, in Guaíba City) had higher amounts of the follows organic compounds: 14-Beta-H-Pregna; Carbamic acid-; and Atrazine-desisopropyl (Tab. 6-6). The "14-Beta-H-Pregna" is naturally found in plants (KOLDAŞ et al., 2015); TOC had a high correlation ($r = 0.86$) with the phytochemical, and a linear correlation ($R^2 = 0.71$), when excluded the site LG12 (highest TOC). Carbamic acids are sub-products of many compounds, as pesticides or polymers (WANG et al., 2003).

The Atrazine-desisopropyl (1,3,5-triazine-2,4-diamine, 6-chloro-N-ethyl-) is a degradation product of the herbicide Atrazine (a pre-emergent herbicide to control broadleaf and grassy weeds), and also a EDC (WIRBISKY et al., 2016). Atrazine runs off with soil in rainfall or irrigation water to aquatic ecosystems, and there degradation products can cause ecological damage (QU et al., 2017). In a survey about the presence of emerging contaminants in Brazilian's drinking water sources, Atrazine was detected in the Lake Guaíba in concentration of 3 ng/L (MACHADO et al., 2016).

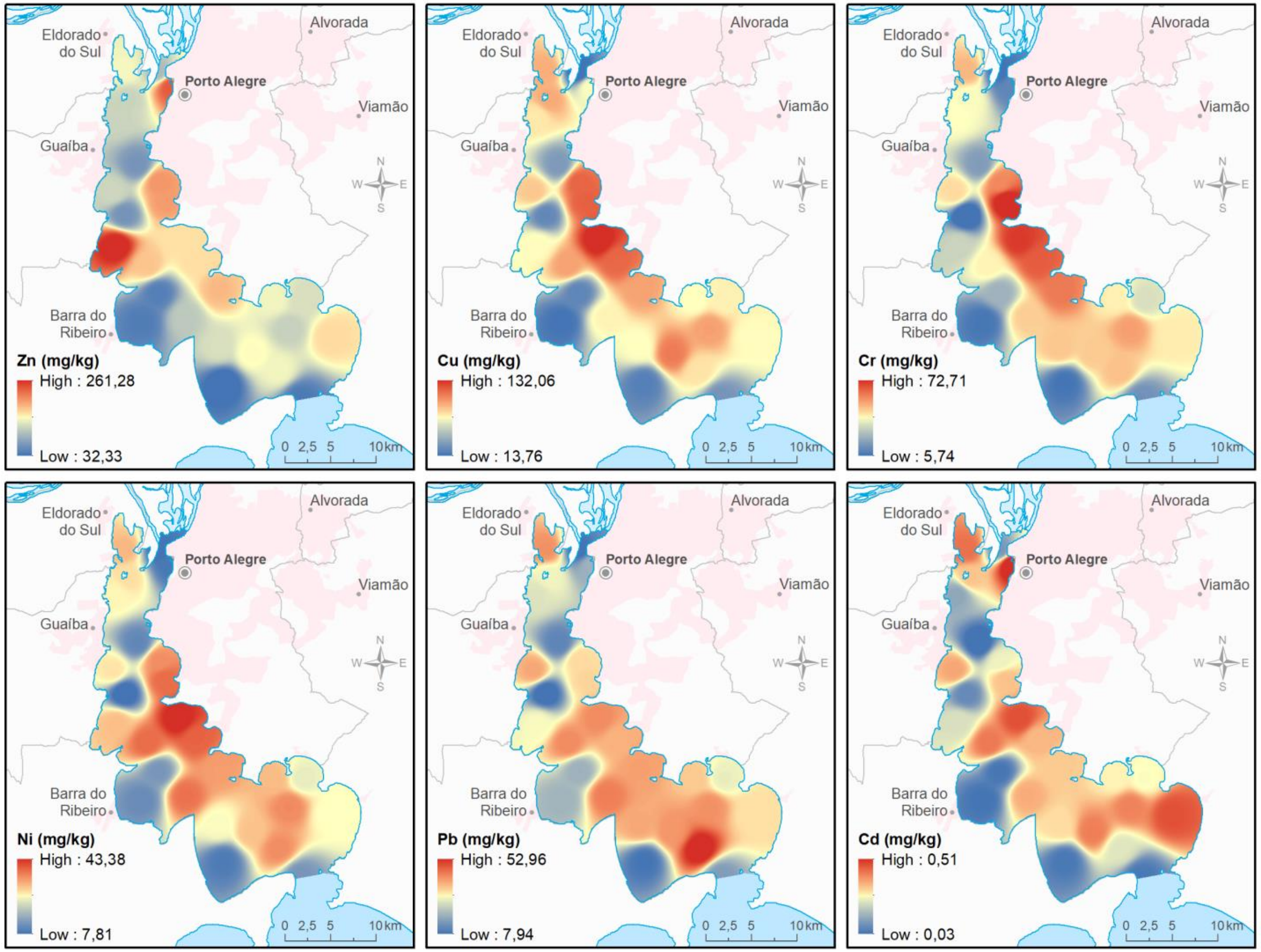

Fig. 6-7. Geoprocessed maps of Zn, Cu, Cr, Ni, Pb, and Cd in bed sediments of Lake Guaíba.

6.2 Conclusions

Sediments of Lake Guaíba have physical-chemical variability by the settle tendency and water flow from the riverine to lacustrine areas. The particle sizes have a high correlation with the metal concentrations. Bed sediments of Lake Guaíba are polluted with Zn, Cu, Cr, and Ni, major in the east margin (near to Porto Alegre). The potential toxic metals and organic compounds found in Lake Guaíba are commonly reported in urban regions around the world. Those elements and compounds derive from many anthropic activities, as industries, sewage, and vehicles. With diffuse sources in the region, the pollution control in Lake Guaíba is very complex.

7. CONCLUSÕES GERAIS

A poluição do Lago Guaíba reduziu ao longo do tempo em função do maior controle ambiental derivado as políticas e legislações ambientais, similar ao ocorrido ao redor do mundo. Entretanto, o lago ainda sofre passivos ambientais decorrentes da falta de adequado saneamento que não acompanhou o crescimento populacional regional.

Os sedimentos do Lago Guaíba possuem grande variedade físico-química em função dos fluxos de seus afluentes e hidrosedimentologia do lago. A concentração dos metais nos sedimentos possui ligação direta com sua granulometria, sendo inversamente proporcional ao tamanho das partículas.

A contaminação e poluição dos sedimentos do Lago Guaíba ocorre principalmente em função de seus corpos hídricos afluentes, sofrendo o efeito de seus fluxos predominantes.

Os sedimentos do Lago Guaíba apresentam alterações nas concentrações de carbono, fósforo e nitrogênio, decorrentes potencialmente de esgotos não tratados, assim como alterações históricas dos metais Zn, Pb, Cu, Cr, Ni, Cd e Hg, ligados principalmente a indústrias e usos antrópicos diversos.

O controle da poluição do Lago Guaíba é complexo em função de que suas fontes são diversas e perpassam o território de diversas cidades da região metropolitana de Porto Alegre, tornando-se um problema de nível estadual.

A poluição do Lago Guaíba foi inicialmente documentada ainda no século XIX, seguindo ao longo das décadas com maior ou menor intensidade. Atualmente, em pleno século XXI, as populações de Porto Alegre e região ainda sofrem de tempos em tempos os efeitos destas alterações ambientais.

A melhoria da qualidade ambiental do lago teria impactos diretos na qualidade de vida da população regional e deveria ser foco constante dos órgãos públicos. Em função do uso do lago como fonte de abastecimento hídrico para milhões de habitantes, o controle da poluição do lago deveria ser ampliado. Entretanto, os diversos usos de suas águas e interesses econômicos envolvidos dificultam uma adequada proteção ambiental no Lago Guaíba.

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9. RESUMO BIOGRÁFICO

Leonardo Capeleto de Andrade, filho de Carmen Capeleto e Paulo Sérgio de Andrade, nasceu em 17 de outubro de 1987, em Carazinho, Rio Grande do Sul (RS), Brasil. Estudou o ensino fundamental no Colégio La Salle e o ensino médio na EEEM Cônego João Batista Sorg, ambas em sua cidade natal. Entre 2005 e 2010 cursou graduação em Engenharia Ambiental, na Universidade de Passo Fundo (UPF), desenvolvendo atividades de Iniciação Científica na área de monitoramento ambiental de um antigo aterro de resíduos sólidos urbanos de Passo Fundo. Entre 2010 e 2012 atuou como pesquisador de Desenvolvimento Tecnológico e Industrial (DTI), com bolsa CNPq, em Canoas (RS), na área de remediação de solos contaminados com hidrocarbonetos de petróleo. Entre 2012 e 2014 desenvolveu seu mestrado no Programa de Pós-Graduação em Ciência do Solo (PPGCS), da Universidade Federal do Rio Grande do Sul (UFRGS). Entre 2014 e 2018 desenvolveu seu doutorado, no mesmo programa (PPGCS/UFRGS), com período de doutorado sanduíche (2017) na University of Georgia (UGA).