UNIVERSIDADE FEDERAL DE SANTA MARIA
CENTRO DE CIÊNCIAS NATURAIS E EXATAS
PROGRAMA DE PÓS-GRADUAÇÃO EM BIODIVERSIDADE ANIMAL

METAIS EM ÁGUA, SEDIMENTO E DUAS ESPÉCIES DE PEIXES COM DIFERENTES NÍVEIS TRÓFICOS EM UM RIO SUBTROPICAL BRASILEIRO

DISSERTAÇÃO DE MESTRADO

PAULA DAMIÃO WEBER

SANTA MARIA, RS, BRASIL

2011

METAIS EM ÁGUA, SEDIMENTO E DUAS ESPÉCIES DE PEIXES COM DIFERENTES NÍVEIS TRÓFICOS EM UM RIO SUBTROPICAL BRASILEIRO

PAULA DAMIÃO WEBER

Dissertação apresentada ao Curso de Mestrado do Programa de Pós-Graduação em Biodiversidade Animal, da Universidade Federal de Santa Maria(UFSM, RS), como requisito parcial para obtenção do grau de **Mestre em Biodiversidade Animal**

Orientador: Prof. Dr. Bernardo Baldisserotto

Santa Maria, RS, Brasil

2011

Universidade Federal de Santa Maria
Centro de Ciências Naturais e Exatas
Programa de Pós-Graduação em Biodiversidade Animal

A Comissão Examinadora, abaixo assinada,
aprova a Dissertação de Mestrado

METAIS EM ÁGUA, SEDIMENTO E DUAS ESPÉCIES DE PEIXES COM DIFERENTES NÍVEIS TRÓFICOS EM UM RIO SUBTROPICAL BRASILEIRO

elaborada por
Paula Damião Weber

como requisito parcial para obtenção do grau de
Mestre em Biodiversidade Animal

COMISSÃO EXAMINADORA:

Dr. Bernardo Baldisserotto (UFSM)
(Presidente/Orientador)

Cláudia Martinez, Dra. (UEL)

Vania Lúcia Loro, Dra. (UFSM)

Santa Maria, 16 de dezembro de 2011

AGRADECIMENTOS

Agradeço, especialmente, ao meu orientador Dr. Bernardo Baldisserotto, pela confiança em mim depositada, pelos inúmeros ensinamentos e oportunidades que tem me proporcionado desde a graduação, por ter aceitado orientar um tema com o qual pouco trabalha, enfim, por estar sempre presente, por toda compreensão, paciência, ajuda e amizade em todos estes anos. Muito obrigada!

Ao meu co-orientador, Dr. Everton Behr, pelas idas a campo, por toda ajuda, parceria, conversas, risadas, ecléticos ensinamentos. Muito obrigada pela amizade!

Ao Daniel, por todas as idas a campo, por estar sempre pronto para amarrar as redes em lugares improváveis, por toda ajuda, parceria e gargalhadas.

Ao meu namorado Daniel Rangel, por todos estes anos de amizade, carinho e amor, e por ter dirigido, todas às vezes, até os locais de coleta, pela parceria, pela ajuda em campo, pelas conversas, risadas e por ter muita paciência. Muito obrigada por tudo!

A minha mãe, minha irmã e meu pai, que sempre me apoiaram em tudo! Principalmente a minha mãe, Eliane Weber, que carregou o barco comigo, inúmeras vezes! Que me ajudou com todos os preparativos antes e depois do campo, inclusive fechando buracos nas redes, que me manteve centrada e confiante e que por fim, sem ela eu não teria conseguido.

Ao Maurício Daut que amostrou os peixes em São Leopoldo e sempre foi muito atencioso e compreensivo. Muito obrigada!

Aos colegas do PPG Biodiversidade Animal, em especial ao Francesco Della Flora e a Lucele Zanini e também aos colegas do LAFIPE, pelo apoio e convivência repleta de conversas e risadas.

A coordenadora do PPG, Sonia Cechin pela dedicação e por ser tão prestativa.

Aos membros da banca, Vania Lúcia Loro e Cláudia Martinez por aceitarem o convite, pelas críticas e sugestões.

"…There is a pleasure in the pathless woods;
There is rapture on the lonely shore;
There is society, where none intrudes,
By the deep sea, and music in its roar:
I love not man the less, but Nature more..."
(Lord Byron)

RESUMO

Dissertação de Mestrado
Programa de Pós-Graduação em Biodiversidade Animal
Universidade Federal de Santa Maria

METAIS EM ÁGUA, SEDIMENTO E DUAS ESPÉCIES DE PEIXES COM DIFERENTES NÍVEIS TRÓFICOS EM UM RIO SUBTROPICAL BRASILEIRO

AUTORA: PAULA DAMIÃO WEBER
ORIENTADOR: BERNARDO BALDISSEROTTO
Data e Local de Defesa: Santa Maria, 16 de dezembro de 2011.

Em ambientes aquáticos, metais pesados são produzidos a partir de fontes naturais e antropogênicas e o grau de contaminação nos tecidos dos peixes depende do tipo de poluente, da espécie de peixe, do local da amostragem, do nível trófico e seu modo de alimentação. A concentração de metais pesados (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Zn e Pb) na água, sedimento e fígado de duas espécies de peixes (*Oligosarcus* spp - carnívoro e *Chyphocarax voga* - detritívoro) foram analisados em dois pontos do Rio do Sinos, Brasil, durante as quatro estações do ano. O objetivo foi testar as hipóteses que o nível trófico e a proximidade com áreas impactadas influenciam o nível de contaminação por metais. As maiores concentrações de metais pesados foram observadas no sedimento, seguidas pela água e menores nos peixes. Como o sedimento foi o maior dreno para poluição por metais neste rio, provavelmente desempenhou um importante papel na captação destes metais pela espécie detritívora, a qual acumulou mais metais no fígado que a espécie carnívora. Além disso, o potencial risco ambiental foi baixo para os dois pontos amostrados, demonstrando a baixa contaminação por metais na área.

Palavras-chave: Rio dos Sinos. Peixes. Detritívoro. Carnívoro. Metais. Poluentes. Sedimento. Nível trófico.

ABSTRACT

Master Dissertation
Post-Graduation in Animal Biodiversity
Universidade Federal de Santa Maria

METALS IN WATER, SEDIMENT AND TISSUES OF TWO SPECIES FROM DIFFERENT TROPHIC LEVELS IN A SUBTROPICAL BRAZILIAN RIVER

AUTHOR: PAULA DAMIÃO WEBER
ADVISOR: BERNARDO BALDISSEROTTO

In aquatic environments, heavy metals are produced from natural and anthropogenic sources and the degree of contamination in fish tissues depend on pollutant type, fish species, sampling site, trophic level and their mode of feeding. The heavy metal concentration (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Zn and Pb) in water, sediment and liver of two fish species (*Oligosarcus* spp - carnivore and *Chyphocarax voga* - detritovore) was analyzed at two sampling sites in Sinos River, Brazil, during the four seasons. The highest heavy metals concentration was observed in the sediment, followed by water and lowest in fish. As the sediment was the major sink for pollution by metals in this river, it probably played an important role in the uptake of these metals by the detritivore species, which accumulated more metals in the liver than the carnivore species. Furthermore, potential ecological risk was low for both sampling sites, showing the low metal contamination in this area.

Keywords: Sinos River. Fish. Detritivore. Carnivore. Metals. Pollutants. Sediment. Trophic level.

LISTA DE FIGURAS

LISTA DE TABELAS

SUMÁRIO

INTRODUÇÃO

Poluição por metais pesados em rios tem se tornado um assunto de grande interesse nas últimas décadas, não somente pela ameaça ao abastecimento público de água, mas também devido aos riscos pelo consumo humano dos recursos pesqueiros. Metais pesados são produzidos a partir de várias fontes naturais ou antropogênicas como deposição atmosférica, desgaste geológico, atividades agrícolas e resíduos residenciais e industriais (JABEEN & CHAUDHRY, 2010). Por serem continuamente liberados nos rios são ameaças sérias, devido a sua toxicidade, longa persistência, bioacumulação e biomagnificação na cadeia trófica aquática (TERRA et al., 2008).

A bacia hidrográfica do Rio dos Sinos está situada a nordeste do Estado do Rio Grande do Sul, com uma área de 3.820 km^2, correspondendo a 4,5% da bacia hidrográfica do Guaíba e 1,5% da área total do Estado, com uma população aproximada de 975.000 habitantes, sendo que 90,6 % ocupam áreas urbanas e 9,4 % áreas rurais. Suas nascentes estão localizadas na Serra Geral, no município de Caraá, a cerca de 600 metros de altitude, correndo no sentido leste-oeste até a cidade de São Leopoldo onde muda para a direção norte-sul, desembocando no delta do Rio Jacuí, a uma altitude de 12 metros. Seus principais formadores são o Rio Rolante e Paranhana, além de diversos arroios. A cobertura vegetal da bacia está muito reduzida e os remanescentes localizam-se, predominantemente, nas nascentes do Rio dos Sinos e seus formadores.

A porção superior do Rio dos Sinos (de Caraá até Rolante) apresenta vegetação ciliar e pequenos banhados. São áreas de baixa densidade populacional, com pequenas propriedades rurais cuja agricultura é diversificada (culturas de arroz, cana de açúcar e hortaliças, etc). A pecuária também é pouco desenvolvida, mas existem pequenas criações. Na porção média do Rio dos Sinos (entre Taquara e Sapiranga) a densidade populacional aumenta, mas as duas grandes cidades (Sapiranga e Taquara) não estão localizadas próximas às margens. Esta porção do rio não apresenta uma característica tão rural como a porção superior. O trecho inferior, de Campo Bom até a foz no delta do Jacuí é de grande concentração populacional e industrial, onde os principais arroios formadores drenam grandes centros urbanos, como Campo Bom (Arroio Schmidt), Novo Hamburgo (Arroio Pampa e Arroio Luiz Rau), São Leopoldo (Arroio Peão), Estância Velha e Portão (Arroio Portão/Estância Velha), Sapucaia do Sul (Arroio José Joaquim) e Esteio e zona norte de Canoas (Arroio Sapucaia) (FEPAM, 2010) (Figura 1).

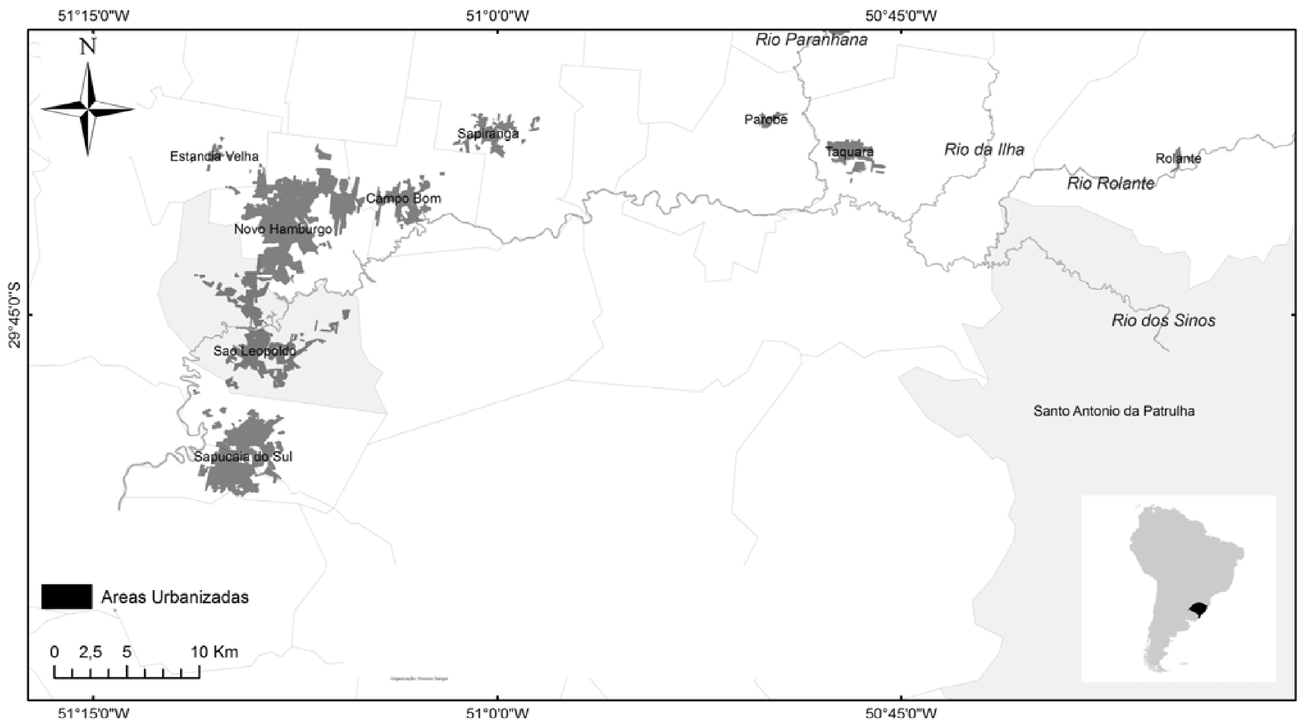

Figura 1 – Mapa do Rio dos Sinos sinalizando os dois pontos de coleta

O programa de identificação de fontes emissoras da Fundação Estadual de Proteção Ambiental (FEPAM) estimava que, aproximadamente, 35 toneladas de metais pesados (Cu, Zn, Cr, Cd e Pb) são liberadas no Rio dos Sinos por atividades humanas. Além disso, as rochas basálticas, o tipo de rocha predominante na bacia hidrográfica do Sinos, e os solos originados delas liberam quantidades significativas de metais pesados no Rio. As concentrações naturais de metais no fundo do Rio dos Sinos são várias vezes superiores aos fundos naturais dos rios ao redor do globo (HATJE et al.,1998).

O monitoramento da contaminação por metais pesados em sistemas fluviais usando tecidos de peixes contribui para avaliar a qualidade dos ecossistemas aquáticos, sendo seu grau de contaminação dependente do tipo de poluente, da espécie de peixe, da localização da amostragem, do nível trófico e seu modo de alimentação. Nesse sentido, amostras de peixes são consideradas como um dos fatores mais indicativos para a estimativa de vestígios de poluição por metais em sistemas de água doce (TERRA et al., 2008).

Espécies em níveis tróficos relativamente baixos estão expostas, comparativamente, a níveis de contaminação menores, portanto, peixes em posição superior na teia alimentar são mais propensos a acumular metais (TERRA et al., 2008). Nesse sentido, escolhemos uma espécie e um gênero que, segundo Petry & Schulz (2001) foram amostradas ao longo de todo o curso do rio, *Oligosarcus* spp, da família Characidae de nome popular tambicu ou branca, com distribuição no estado no Sistema da Laguna dos Patos e Sistema Lagunar Costeiro (KOCH et al., 2000). É um carnívoro, com tendência a piscivoria (NUNES & HARTZ, 2006). *Cyphocharax voga* da família Curimatidae, nome popular biru, quando jovem, possui diminutos dentes cônicos com os quais se alimenta de algas; na fase adulta, perde esses dentes e passa a nutrir-se do conteúdo orgânico existente no lodo (KOCH et al., 2000).

O objetivo geral do presente estudo foi determinar a acumulação de metais pesados na água, sedimento e fígado de duas espécies de peixes com diferentes hábitos alimentares em dois locais de amostragem no Rio dos Sinos, pois segundo Costa & Hartz (2009), estudos realizados com diferentes espécies de peixes tem demonstrado que os metais se acumulam principalmente em órgãos do metabolismo, como o fígado, para desintoxicação através da produção de metalotioneínas. E, segundo corrobora Shinn et al. (2009), o fígado é o principal sítio de acumulação, metabolismo e excreção de poluentes em peixes. Portanto, foram amostradas uma espécie e um gênero de peixes em diferentes níveis tróficos, sendo *Oligosarcus* spp, carnívoro e *Cyphocharax voga,* detritívoro, durante as quatro estações do ano em duas áreas do rio, uma com baixo e outra com alto impacto antrópico.

Os objetivos específicos foram:

-verificar se peixes em níveis tróficos superiores são mais propensos a acumular metais;

- verificar se a proximidade com o ponto poluído (São Leopoldo) aumenta a bioacumulação de metais no fígado de peixes;

- verificar se *Oligosarcus* spp e *Cyphocharax voga* podem ser utilizados como biomonitores na avaliação da qualidade de ecossistemas aquáticos.

A presente Dissertação está estruturada de acordo com as normas da Universidade Federal de Santa Maria (MDT), sendo composta por dois manuscritos relacionados com a contaminação por metais pesados em rios e suas implicações, a saber:

- Manuscrito 1: fornece uma revisão da literatura atual sobre metais pesados, suas fontes e acumulação em peixes de água doce.

- Manuscrito 2: descreve um estudo realizado no Rio dos Sinos com o objetivo de determinar a acumulação de metais pesados na água, sedimento e fígado de duas espécies de peixes com diferentes hábitos alimentares amostrados em dois locais com diferente nível de antropização.

ARTIGO 1 – HEAVY METAL BIOACCUMULATION IN FRESHWATER FISH: REVIEW

Paula Weber[1] & Bernardo Baldisserotto[1]

[(1)]Departamento de Fisiologia e Farmacologia, Universidade Federal de Santa Maria – UFSM, Av. Roraima, 1000, Santa Maria, RS, Brazil

Corresponding author: paulaweberbio@gmail.com

RESUMO

Utilizado como meio de transporte, como fonte de água ou, como um coletor de resíduos, o ambiente aquático, sem dúvida, sofre as conseqüências das atividades antrópicas. Metais provenientes de fontes naturais ou antropogênicas continuamente entram nos ecossistemas aquáticos representando uma séria ameaça devido à sua toxicidade, longo tempo de persistência, bioacumulação e biomagnificação na cadeia alimentar. As principais fontes de metais provem de impurezas em fertilizantes, pesticidas e lodo oriundo do esgoto. Metais em minerais e rochas são, geralmente, inofensivos e só se tornam potencialmente tóxicos quando dissolvidos em água. As concentrações da maioria dos metais pesados são maiores no sedimento em relação à água. Análises da distribuição de metais pesados em sedimentos adjacentes a áreas populosas podem ser utilizados para investigar impactos antropogênicos em ecossistemas sendo úteis na avaliação dos riscos decorrentes de descargas de resíduos humanos. Peixes são considerados como um dos organismos aquáticos mais suscetíveis a substâncias tóxicas presentes no ambiente aquático, tendo seus tecidos utilizados para avaliação da qualidade desses ecossistemas. Diferentes tecidos têm capacidades de acumulação de metais variáveis, devido aos diferentes papéis metabólicos dos metais e as diferentes funções dos órgãos, contudo o fígado desempenha um papel importante na acumulação e desintoxicação de metais pesados. Peixes que vivem próximos ao fundo dos rios e se alimentam de invertebrados bentônicos tem maiores concentrações de metais quando comparados com aqueles que vivem na superfície ou coluna d´água. A maioria dos metais pesados é transferida pela cadeia alimentar através da rota: sedimentos – zoobentos – carnívoros bentônicos – humanos.

Palavras-chave: Metais; Água; Sedimento; Peixe; Fígado; Cadeia alimentar

ABSTRACT

Used either as a means of transportation, as a source of water, or as a sink for waste, the aquatic environment no doubt suffers the consequences of anthropic activities. Metals from natural and anthropogenic sources continuously enter the aquatic ecosystem and pose a serious threat because of their toxicity, long time persistence, bioaccumulation, and biomagnification in the food chain. The metal main sources are impurities in fertilizers, pesticides and sewage sludge. Metals in minerals and rocks are generally harmless and only become potentially toxic when they dissolve in water. Most heavy metals concentrations are higher in sediment than in water. Analysis of the distribution of heavy metals in sediments adjacent to populated areas could be used to investigate anthropogenic impacts on ecosystems and can assist in the assessment of risks posed by human waste discharges. Fish are considered as one of the most susceptible aquatic organisms to toxic substances present in aquatic environment, having their tissues used for assessing the quality of these ecosystems. Different tissues vary their accumulation capacities of metals, which may be due to the different metabolic roles of metals and organs functions but liver plays an important role in accumulation and detoxification of heavy metals. Fish that live near the river bed and feeds on benthic invertebrates have higher concentrations of metals when compared with those who live in the upper or middle water column. Most heavy metals are transferred through the food chain via the route: sediment – zoobenthos – benthic carnivores – human.

Keywords: Metals; Water; Sediment; Fish; Liver; Food chain.

1. INTRODUCTION

1.1 Heavy metal sources

Used either as a means of transportation, as a source or water, or as a sink for waste, the aquatic environment no doubt suffers the consequences of anthropic activities. A river system naturally drains all areas surrounding it, washing into the aquatic environment many harmful substances (SHINN et al., 2009). The ever growing list of chemical contaminants released into the environment on a large scale includes numerous aliphatic and aromatic compounds, heavy metals and radionucleotides (KAMALA- KANNAN et al., 2008).

Environmental contamination of natural waters by heavy metal residues is of great concern. Metals from natural and anthropogenic sources continuously enter the aquatic ecosystem and pose a serious threat because of their toxicity, long time persistence, bioaccumulation, and biomagnification in the food chain (PAPAGIANNIS et al., 2004). Metal toxicity can be influenced by various abiotic environmental factors such as oxygen, hardness, pH, alkalinity and temperature (MALIK, 2010).

Increased industrialization and agricultural activities contribute to their elevated levels in natural waters (WAHLBERG et al., 2001). The most frequently found heavy metal contaminants include Pb, Cr, Cd, Fe and Cu. Trace concentrations of metals like Cd, Cr, Cu, Ni, Pb, Fe and Zn are commonly found in many organic wastes, particularly from industrial and municipal sources (MALHAT, 2011).

Heavy metals are originated from aerosols in the atmosphere and direct effluent discharges into waters. Agriculture constitutes one of the very important non-point sources of metals pollutants from impurities in fertilizers, pesticides and sewage sludge (MALHAT, 2011). Metals in minerals and rocks are generally harmless and only become potentially toxic when they dissolve in water. They enter the environment naturally by weathering of rocks, leaching of soils, vegetation, and volcanic activity (AL-SAAD et al., 1997). Human activities also introduce metals to the environment by mining, smelting, combustion of fossil fuel, and industrial wastes disposal. Most of metal loads are transported by water in a dissolved or particulate phase and most of it reaches water via land runoff. In addition, rainwater carries significant Cd, Cu, Zn and especially Pb from the atmosphere to the water (MALHAT, 2011).

Most heavy metals concentrations are higher in sediment than in water (Tables 1,2,3).

Table 1 - Metal concentration in water (μg L^{-1}) from rivers/lakes throughout the world

Locality	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn	Reference
Bozyazi (Turkey)	N.D.	N.D.	N.D.	25	N.D.	62	4.1	15.4	N.D.	64	Karadede & Ünlü, 2000
Akpinar (Turkey)	N.D.	N.D.	N.D.	220	N.D.	N.D.	3.9	11	N.D.	197	
Lake Manzala (Egypt)	N.D.	N.D.	20	55	N.D.	N.D.	N.D.	N.D.	22	311	Bahnasawy et al., 2008
Upper lake of Bophal (India)	N.D.	N.D.	9.7	12	50	N.D.	N.D.	170	31.9	290	Malik et al., 2008
Yangtze River (China)	N.D.	0.9	<1	2.8	1.2	N.D.	N.D.	N.D.	2	3	YI et al., 2008
Epe Lagoon (Nigeria)	N.D.	N.D.	N.D.	N.D.	N.D.	7300	N.D.	600	N.D.	420	Olowu et al., 2009
Badagry Lagoon (Nigeria)	N.D.	N.D.	N.D.	N.D.	N.D.	650	N.D.	100	N.D.	540	
River Lot (France)	N.D.	N.D.	0.5	3.22	N.D.	N.D.	N.D.	N.D.	4.33	19.38	Shinn et al., 2009
Buriganga River (Bangladesh)	N.D.	N.D.	9.34	163.09	587.20	N.D.	N.D.	8.80	65.45	N.D.	Ahmad et al., 2010
Yellow River (China)	N.D.	N.D.	0.45	2.9	N.D.	N.D.	N.D.	N.D.	8.1	8.3	Wang et al., 2010
Delice River (Turkey)	158.63	9.25	0.36	N.D.	N.D.	303.33	42	7.47	N.D.	N.D.	Akbulut & Tuncer, 2011

Table 2 - Metal concentration in water (μg L^{-1}) from rivers/lakes from Brazil

Locality	Al	As	Cd	Co	Cu	Cr	Fe	Mn	Ni	Pb	Zn	Reference
Class I, II River	100	10	1	50	9	50	300	100	25	10	180	CONAMA Resolution N° 357/2005
Class III, IV River	200	33	10	200	13	50	5000	500	25	33	5000	
Butuí River	590	N.D.	N.D.	N.D.	328.3	95	N.D.	1150	N.D.	N.D.	10	Porto & Ethur, 2009
Icamaquã River	64	N.D.	N.D.	N.D.	278.3	68.3	N.D.	850	N.D.	N.D.	0	
Uruguai River	50	N.D.	N.D.	N.D.	170.0	108.3	N.D.	816.7	N.D.	N.D.	0	
Das Velhas River (Unpolluted)	207	0.3	N.D.	0.10	1.4	2.1	640	620	N.D.	N.D.	N.D.	Veado et al., 2006
Das Velhas River (Mining Region)	12100	2.3	N.D.	63	37	15	5900	860	N.D.	N.D.	N.D.	
Das velhas River (Farming Region)	10200	1.4	N.D.	52	26	10	4300	6400	N.D.	N.D.	N.D.	

Table 3 - Metal concentration in sediment (μg g^{-1}) from rivers/lakes throughout the world

Locality	Al	As	Cd	Co	Cu	Cr	Fe	Mn	Pb	Ni	Zn	Reference
Bozyazi (Turkey)	N.D.	N.D.	N.D.	N.D.	14570	N.D.	12587000	73600	N.D.	43690	60790	Karadede & Ünlü, 2000
Akpinar (Turkey)	N.D.	N.D.	N.D.	N.D.	22700	N.D.	19265000	514070	N.D.	139690	59140	
Das Velhas River – Unpolluted (Brazil)	52000	56	N.D.	23	47	63	55000	960	N.D.	N.D.	N.D.	Schulz & Martins-Junior, 2000
Das Velhas River - Mining Region	70000	560	N.D.	28	58	330	160000	1460	N.D.	N.D.	N.D.	
Das velhas River - Farming Region	4000	650	N.D.	15	60	260	115000	1030	N.D.	N.D.	N.D.	
Nasser Lake (Egypt)	N.D.	N.D.	N.D.	89.5	109	79	51500	1000	N.D.	122	143	Rashed, 2001
Yangtze River (China)	N.D.	N.D.	0.205	N.D.	41.4	64.2	N.D.	N.D.	38.2	N.D.	108.1	Yi et al., 2008
River Lot (France)	N.D.	N.D.	14.75	N.D.	24.35	N.D.	N.D.	N.D.	57.5	N.D.	692	Shinn et al., 2009
Yellow River (China)	N.D.	N.D.	0.586	N.D.	18.485	N.D.	N.D.	N.D.	16.125	N.D.	78.531	Wang et al., 2010
Delice River (Turkey)	4450.7	40.98	0.598	N.D.	N.D.	N.D.	718	681.9	N.D.	110.38	N.D.	Akbulut & Tuncer 2011

The Brazilian National Environmental Council (CONAMA) is responsible for the classification for rivers water quality in Brazil and the Resolution No. 357/2005 presents four freshwater classes: class I river with the best parameters, such as dissolved oxygen (DO) not less than 6 mg L^{-1} O_2 and low metal levels and the worst parameters such as DO not higher than 4 mg L^{-1} O_2 and the highest metal levels for class IV river (Table 2).

Sediments represent an important sink for metals in aquatic systems, and their concentrations in sediment can be several orders of magnitude greater than in the water (MENDIL et al., 2010). Heavy metals are inert in the sediment, although they may be released into the water column in response to certain disturbances causing potential threat to ecosystems because provide habitats and a food source for benthic fauna (YI et al., 2011) and may also represent a long-term sources of contamination to higher tropic levels (MENDIL et al., 2010).

Consequently, analysis of the distribution of heavy metals in sediments adjacent to populated areas could be used to investigate anthropogenic impacts on ecosystems and would assist in the assessment of risks posed by human waste discharges (YI et al., 2011).

1.2 Fish as biomonitor of environmental quality

Biomonitors are defined as organisms which accumulate trace metals in its tissues, the accumulated metal concentration of which may be analyzed to provide a relative measure of the total amount metal taken up by all routes by that organism, integrated over a preceding time period (RAINBOW, 2006). Organisms that inhabit an aquatic environment are useful indicators of the impact of the presence toxic heavy metals (SHINN et al., 2009).

Fish are at the top of the aquatic food chain and may accumulate large amounts of certain metals from water, food or sediment (YILMAZ et al., 2010). Fish are also considered as one of the most susceptible aquatic organisms to toxic substances present in water (JARIC et al., 2011).

Species in relatively low trophic levels are exposed to comparatively lower contamination. On the other hand, fish in the upper food web position are prone to accumulate metals (TERRA et al., 2008).

Table 4 Heavy metal concentration (μg g^{-1}) in different fish liver with different feeding habits

Specie	Feeding habit	Cd	Cu	Cr	Ni	Pb	Zn	Reference
Prochilodus lineatus	Detritivore	18.3	81	<0.5	N.D.	5.0	175	Villar et al., 2001
Pterodoras granulosus	Omnivore	<0.03	253	<0.5	N.D.	<0.5	110	
Labeo dyocheilus	Omnivore	72.3	1644.0	643.7	111.7	377.0	1175.7	Yousafzai et al., 2010
Wallago attu	Carnivore	64.3	136.0	513.0	108.0	623.3	509.7	

The hypothesis of higher metal concentration in the highest trophic levels was met for the examined species in Paraíba do Sul River since the carnivore showed the highest Cr, Pb and Zn concentration than the omnivore and detritivore specie (TERRA et al., 2008). However, species in the lower trophic levels in very impacted sites can present higher metal accumulation, with the local playing a more important role than the trophic web fish position, like the omnivorous *Labeo dyocheilus* that accumulated a considerably high amount of heavy metals when compared with the carnivorous *Wallago attu* (YOUSAFZAI et al., 2010). Fish that live near the river bed and feeds on benthic invertebrates had higher concentrations of metals when compared with those who live in the upper or middle water column. Most heavy metals are transferred through the food chain via the route: sediment – zoobenthos – benthic carnivores – human (YI et al., 2011).

1.3 Heavy metal bioaccumulation

Heavy metals like Cu, Zn and Fe are essential for fish metabolism while some others such as Hg, Cd and Pb have no known role in biological systems (CANLI & ATLI, 2003). For normal metabolism the essential metals must be taken up from water, food or sediment but excessive intake of the essential metals can produce toxic effects (YOUSAFZAI et al., 2010). However, similar to the route of essential metals, non-essential ones are also taken up by fish and accumulate in their tissues (CANLI & ATLI, 2003).

Cu and Zn are essential elements for growth and development and their uptake from the environment is regulated according to nutritional demand through homeostatic control. However, Cu and Zn become toxic at concentrations above the limits of homeostatic control (SHINN et al. 2009). Cu accumulates by several means, depending on environmental conditions and species habits, most in phytoplankton due to Cu great capacity for precipitation. This metal is essential for animals and plants, as it takes part in enzyme formation and participates in respiratory processes (DE SOUZA LIMA JUNIOR et al., 2002).

Cd and Pb are non-essential heavy metals that do not have dedicated regulatory mechanisms and are therefore more toxic to organisms (SHINN et al., 2009). Generally Pb occurs in very low concentrations in the biota, even when there are high concentrations in the abiotic environment (DE SOUZA LIMA JUNIOR et al., 2002).

Pollutants enter aquatic organisms through five main routes (food or non-food particles, gills, water and skin), absorbed into blood and then carried to either a storage point or to the liver for its transformation or storage. Metals that are transformed and not stored in the liver are excreted in bile or transported to other excretory organs such as gills or kidneys for elimination or stored in fat or, when metals cannot be regulated by fish, bioaccumulation can occur (JABEEN & CHAUDLHRY, 2010).

In general, significant positive correlations could be observed between the level of heavy metal accumulated in the organs of fish and the pollutant load of the water (FARKAS et al., 2002; FARKAS et al., 2003).

Studies showed that accumulation of heavy metals in a tissue is mainly dependent upon water concentrations of metals and exposure period, although some other environmental factors such as salinity, pH, hardness and temperature play significant roles in metal accumulation (CANLI & ATLI, 2003). In most studies liver is the organ having higher metal accumulation. Different tissues have varied accumulating capacities of metals, which may be due to the different metabolic roles of metals and organs functions (WANG et al., 2010). The liver plays an important role in accumulation and detoxification of heavy metals (YOUSAFZAI, 2004), probably by this reason has been recommended by many authors as the best environmental indicator of both water pollution and chronic exposure to heavy metals (JARIC et al., 2011).

Exposure of fish to elevated levels of heavy metals induces the synthesis of metallothioneine proteins, which are metal binding proteins that regulate and concentrate these metals in the liver (CARPENE & VASÁK, 1989). The high accumulation in liver may alter the levels of various biochemical parameters in this organ which may also cause severe liver damage (NAYARANAN & VINODHINI, 2008). The presence of heavy metals at high concentrations does not necessarily present a threat to the exposed organisms as they may not be uptaken by the organism at all or, if uptaken, its metabolism can deal with the load (FERNANDES et al., 2008).

Several countries have legislation concerning heavy metals for human consumption of fish. The Brazilian legislation determined as maximum allowed levels 0.1 μg g^{-1} for Cr, 30 μg g^{-1} for Cu, 100 μg g^{-1} for Zn, 2 μg g^{-1} for Pb (ANVISA 2003). According to European Commission Regulation (1881/2006/EC), the maximum acceptable concentrations for Cd and Pb in fish meat are 0.05 μg g^{-1} and 0.3 μg g^{-1} wet weight, respectively. National regulation of Republic Serbia prescribed 1.0, 0.1 and 2 μg g^{-1} wet weight for Pb, Cd and As in fresh fish meat, respectively (VISNJIC-JEFTIC, 2010). Limits recommended by Food and Agriculture Organization for both Cu and Zn are 30 μg g^{-1} and 0.5 μg g^{-1} wet weight for both Pb and Cd (FAO, 1983).

2. CONCLUSION

Coupling the concentration of pollutants in tissues of exposed organisms to the concentrations found in the environment, while taking into consideration relevant abiotic factors as well as the tolerance capacity of the organisms, are key processes in environmental risk assessment.

3. REFERENCES

AHMAD, M. K.; ISLAM, S.; RAHMAN, S.; HAQUE, M. R.; ISLAM, M.M. Heavy metals in water, sediment and some fishes of Buriganga River, Bangladesh. **Int. J. Environ**. **Res.** n. 4(2), p. 321 – 332, 2010.

AHMAD, A. K. & SHUHAIMI-OTHMAN. Heavy metal concentrations in sediments and fishes from Lake Chini, Pahang, Malaysia. **J. Biol. Sci**. n. 10(2), p. 93 – 100, 2010.

AKBULUT, N. E. & TUNCER, A. M. Accumulation of heavy metals with water quality parameters in Kizilirmak River Basin (Delice River) in Turkey. **Environ. Monit. Assess**. n. 173, p. 387 – 395, 2011.

AL-SAAD, H.; MUSTAFA, Y.; AL-IMARAH, F. Distribution of trace metals in tissues of fish from Shall Al-Arab estuary, Iraq. **Mar Meso**. n. 11, p. 15 – 25. 1997.

ANVISA. Legislação específica para a area de alimentos – contaminantes inorgânicos (metais pesados) em peixes e produtos de pesca. Available on line:<http://www.anvisa.gov.br>. 2003.

BAHNASAWY, M.; KHIDR, A.; DHEINA, N. Assessment of heavy metal concentrations in water, plankton and fish of Lake Manzala, Egypt. **Turk. J. Zool**. n. 35(2), p. 271 – 280, 2011.

CANLI, M. & ATLI, G. The relationship between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species. **Environ. Pollut.** n. 121, p. 129 – 136, 2003.

CARPENE, M. & VASÁK, M. Hepatic Metallothionin from Goldfish (*Carassius auratus*). **Comp. Biochem. Physiol**. n. 92B, p. 463 – 468. 1989.

CONAMA - Brazilian National Environmental Council. Resolution No. 357/2005

DE SOUZA LIMA JUNIOR, R. G.; ARAÚJO, F. G.; MAIA, M. F.; PINTO, A. S. S. B. Evaluation of heavy metal in fish of Sepetiba and ilha Grande Bays, Rio de Janeiro, Brazil. **Environ. Res. Sec. A**. n. 89, p. 171 – 179, 2002.

EBRAHIMPOUR, M. & MUSHRIFAH, I. Seasonal Variation of Cadmium, Copper, and Lead Concentrations in Fish from a Freshwater lake. **Biol. Trace Elem. Res**. n. 138, p. 190 – 201, 2010.

European Commission, Commission Regulation (EC) No. 629/2008 of 2 July 2008, Amending Regulation (EC) No. 1881/2006 setting maximum levels for certain contaminants in foodstuffs. J. Europ. Union L173. p. 6 – 9, 2008.

FAO. Compilation of legal limits for hazardous substances in fish and fishery products. **FAO Fishery Circular**. n. 464. 1983.

FARKAS, A.; SALÁNKI, J.; SPECZIÁR, A. Relation between growth and the heavy metal concentration in organs of bream *Abramis brama* L. populating Lake Balaton. **Arch. Environ. Contam. Toxicol**. n. 43. p. 236 – 243, 2002.

FARKAS, A.; SALÁNKI, J.; SPECZIÁR, A. Age- and size-specific patterns of heavy metals in the organs of freshwater fish *Abramis brama* L. populating a low-contaminated site. **Water Res**. n. 37, p. 959 – 964, 2003.

FERNANDES, C.; FONTAINHAS-FERNANDES, A.; CABRAL, D.; SALGADO, M. A. Heavy metals in water, sediment and tissues of Liza saliens from Esmoriz-Paramos lagoon, Portugal. **Environ. Monit. Assess**. n. 136. p. 267 – 275, 2008.

HATJE, V.; BIDONE, E. D.; MADDOCK, J. L. 1998. Estimation of the natural and anthropogenic components of heavy metal fluxes in fresh water Sinos River, Rio Grande do Sul State, South Brazil. **Environ. Technol**. n.19, p. 483 – 487, 1998.

JABEEN, F. & CHAUDHRY, A. S. Environmental impacts of anthropogenic activities on the mineral uptake in *Oreochromis mossambicus* from Indus River in Pakistan. **Environ. Monit. Assess**. n.166, p. 641 – 651, 2010.

JARIC, I.; VISNJIC-JEFTIC, Z.; CVIJANOVIC, G.; GACIC, Z.; JOVANOVIC, L.; SKORIC, S.; LENHARDT, M. Determination of differential heavy metal and trace element accumulation in liver, gills, intestine and muscle of sterlet (Acipenser ruthenus) from Danube River in Serbia by ICP-OES. **Microchem. J**. n. 98, p. 77 – 81, 2011.

KAMALA – KANNAN, S.; DRABHO, D. B. B.; JAE, L. K.; KANNAN, N.; KRISHNAMOORTHY, R.; SHANTHI, K.; JAYAPRAKASH, M. Assessment of heavy metals (Cd, Cr and Pb) in water, sediment and seaweed (*Ulva lactuca*) in the Pulicat Lake, south East India. **Chemosphere**. n. 71, p.1233 - 1240, 2008.

KARADEDE, H. & ÜNLÜ, E. Concentrations of some heavy metals in water, sediment and fish species from the Atatürk Dam Lake (Euphrates), Turkey. **Chemosphere**. n. 41, p. 1371 – 1376, 2000.

KOCH, W. R.; MILANI, P. C.; GROSSER, K. M. Guia ilustrado Peixes Parque Delta do Jacuí. Porto Alegre: Publicação editada pela Fundação Zoobotânica do Rio Grande do Sul. p.19 – 45, 2000.

LÜ, C.; HE, J.; FAN, Q.; XUE, H. Accumulation of heavy metals in wild commercial fish from the Baotou Urban Section of the Yellow River, China. **Environ. Earth Sci**. n. 62, p. 679 – 696, 2011.

MALHAT, F. Distribution of Heavy Metal Residues in Fish from the River Nile Tributaries in Egypt. **Bull. Environ. Contam. Toxicol**. n. 83, p. 163 – 165, 2011.

MALIK, N.; BISWAS, A. K.; QURESHI, T. A.; BORANA, K.; VIRHA, R. Bioaccumulation of heavy metals in fish tissues of freshwater lake of Bophal. **Environ. Monit. Assess**. n. 160, p. 267 – 276, 2010.

MENDIL, D.; DEMIRCI, Z.; TÜZEN, M.; SOYLAK, M. Seasonal investigation of trace element contents in commercially valuable fish species from the Black Sea, Turkey. **Food Chem. Tox.** n. 48, p. 865 - 870, 2010.

OLOWU, R. A.; AYEJUYO, O.O.; ADEWUYI, G. O., ADEJORO, I. A.; DENLOYE, A. A. B.; BABATUNDE, A. O.; OGUNDAJO, A. L. Determination of heavy metals in fish tissues, water and sediment from Epe and Badagry Lagoons, Lagos, Nigeria. **E-journal of Chemistry.** n. 7(1), p. 215 – 221, 2010.

PAPAGIANNIS,I.; KAGALOU,I.; LEONARDOS, J.; PETRIDIS, D.; KALFAKAKOU, V. Copper and zinc in four freshwater fish species from Lake Pamvotis (Greece). **Environ. International**. n. 30, p. 357-362, 2004.

PETRY, A. C. & SCHULZ, U. H. Levantamento da comunidade de peixes do Rio dos Sinos. **Acta Biológica Leopoldensia**. n. 23, p. 49 – 58, 2001.

PETRY, A. C. & SCHULZ, U. H. Longitudinal changes and indicator species of the fish fauna in the subtropical Sinos River, Brazil. **J. Fish Bio**. n. 69, p. 272 – 290, 2006.

PORTO, L. C. S. & ETHUR, E. M. Elementos traço na água e em vísceras de peixes da bacia Hidrográfica Butuí-Icamaquã, Rio Grande do Sul, Brasil. **Ciência Rural**. v. 39, n. 9, p. 2512 - 2518, 2009.

RAINBOW, P. S. Biomonitoring of trace metals in estuarine and marine environments. **Australian. J. Ecotoxi**. v. 12, p. 107-122, 2006.

SHINN, C.A.; DAUBA, F.; GRENOUILLET, G.; GUENARD, G.; LEK, S. Temporal variation of heavy metal contamination in fish of the river lot in southern France. **Ecotoxi. Environ. Safety**. n.72, p.1957 – 1965, 2009.

SCHULZ, U. H. & MARTINS-JUNIOR, H. Astyanax fasciatus as bioindicator of water pollution of Rio dos Sinos, RS, Brazil. **Braz. J. Biol.** n. 61(4), p. 615 – 622, 2001.

TERRA, B. F.; ARAÚJO, F. G.; CALZA, C. F.; LOPES, R. T.; TEIXEIRA, T. P. Heavy Metal in Tissues of Three Fish Species from Different Trophic Levels in a Tropical Brazilian River. **Water Air Soil Pollut.** n. 187, p. 275 – 284, 2008.

VEADO, M. A. R. V.; ARANTES, I. A.; OLIVEIRA, A. H.; ALMEIDA, M. R. M. G.; MIGUEL, R. A.; SEVERO, M. I.; CABALEIRO, H. L. Metal pollution in the environment of Minas Gerais State – Brazil. **Environ. Monit. Assess**. n. 117, p. 157 – 172, 2006.

VINODHINI, R. & NAYARANAN, M. Bioaccumulation of heavy metals in organs of fresh water fish *Cyprinus carpio* (Common carp). **Int J. Environ. Sci. Tech**. n. 5 (2), p. 179 – 182. 2008.

VILLAR, C.; STRIPEIKIS, J.; COLAUTTI, D.; D'HUICQUE, L.; TUDINO, M.; BONETTO, C. Metals contents in two fishes of different feeding behavior in the Lower Paraná River and Río de la Plata Estuary. **Hydrobiologia.** n. 457, p. 225 – 233, 2001.

VISNJIC-JEFTIC, Z.; JARIC, I.; JOVANOVIC, L.; SKORIC, S.; SMEDEREVAC-LALIC, M.; NIKCEVIC, M.; LENHARDT, M. Heavy metal and trace element accumulation in muscle, liver and gills of the Pontic shad (*Alosa immaculate* Bennet 1835) from the Danube River (Serbia). **Microchem. J**. n. 95, p. 341 – 344, 2010.

WAHLBERG, N. H.; FLACHIER, A.; LANE, S. N.; SANGFORS, O. Environmental impact and metal exposure of aquatic ecosystems of rivers contaminated by small scale gold mining: the Puyango river basin, southern Ecuador. **Sci. Total Environ**. n. 278, p. 239 – 261, 2001.

WANG, Y.; CHEN, P.; CUI, R.; SI, W.; ZHANG, Y.; JI, W. Heavy metal concentrations in water, sediment, and tissues of two fish species (*Triplohysa pappenheimi, Gobio hwanghensis*) from the Lanzhou section of Yellow River, China. **Environ. Monit. Assess**. n. 165, p. 97 – 102, 2010.

YI, Y.; YANG. Z.; ZHANG, S. Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. **Environ. Pollution**. n. xxx. p. 1 – 11. 2011.

YILMAZ, F.; OZDEMIR, N.; DEMIREK, A.; TUNA, L. A. Heavy metal levels in two species *Leuciscus cephalus* and *Lepomis gibosus*. **Food Chem**. n.100, p. 830 – 835, 2007.

YOUSAFZAI, A. M.; CHIVERS, D. P.; KHAN, A. R.; AHMAD, I.; SIRAJ, M. Comparison of Heavy Metals Burden in Two Freshwater Fishes *Wallago attu* and *Labeo dyocheilus* With Regard to Their Feeding Habits in Natural Ecosystem. **Pakistan J. Zool**. n. 42(5), p. 537 – 544, 2010.

RASHED, M. N. Monitoring of environmental heavy metals in fish from Nasser Lake. **Environ. International**. n. 27, p. 27 – 33, 2001.

WANG, Y.; CHEN, P.; CUI, R.; SI, W.; ZHANG, Y.; JI, W. Heavy metal concentrations in water, sediment, and tissues of two fish species (*Triplohysa pappenheimi, Gobio hwanghensis*) from the Lanzhou section of Yellow River, China. **Environ. Monit. Assess**. n. 165, p. 97 – 102, 2010.

ARTIGO 2 - METAL IN WATER, SEDIMENT AND TISSUES OF TWO SPECIES FROM DIFFERENT TROPHIC LEVELS IN A SUBTROPICAL BRAZILIAN RIVER

Paula Weber[1], Everton Rodolfo Behr[2], Daniel Secretti Vendruscolo[2], Érico Flores[3], Valderi Dressler[3], Bernardo Baldisserotto[1]

(1)Departamento de Fisiologia e Farmacologia, Universidade Federal de Santa Maria – UFSM, Av. Roraima, 1000, Santa Maria, RS, Brazil.

(2)Unidade Descentralizada de Educação Superior da UFSM em Silveira Martins, RS, Brazil – everton_behr@hotmail.com

(3)Departamento de Química, Universidade Federal de Santa Maria

Corresponding author: Bernardo Baldisserotto

Departamento de Fisiologia e Farmacologia,

UFSM - 97105.900 - Santa Maria – RS, Brazil.

bbaldisserotto@hotmail.com

phone 55 55 3220-9382 / fax 55 55 3220-8241

RESUMO

Em ambientes aquáticos, metais pesados são produzidos a partir de fontes naturais e antropogênicas e o grau de contaminação depende do tipo de poluente, da espécie de peixe, do local da amostragem, do nível trófico e seu modo de alimentação. A concentração de metais pesados (Al, Cd, Co, Cr, Cu, Fe, Mn, Zn e Pb) na água, sedimento e fígado de duas espécies de peixes (*Oligosarcus* spp.- carnívoro e *Chyphocarax voga* – detritívoro) com níveis tróficos diferentes foram analisados em dois pontos do Rio do Sinos, Brasil, durante as quatro estações do ano. O objetivo foi testar as hipóteses de que o nível trófico e a proximidade com áreas impactadas influenciam o nível de contaminação por metais. As maiores concentrações de metais pesados foram observadas no sedimento, seguido pelos peixes e menores na água. Como o sedimento foi o maior dreno para poluição por metais neste rio, provavelmente desempenhou um importante papel na captação destes metais pela espécie detritívora, a qual acumulou mais metais no fígado que a espécie carnívora. Além disso, o potencial risco ambiental foi baixo para os dois pontos amostrados, demonstrando a baixa contaminação por metais na área e o seguro consumo dos peixes do Rio dos Sinos pela população humana.

Palavras- chave: Rio dos Sinos. Metais. Peixes de água doce. Fígado. Sedimento. Detritívoro. Carnívoro. Risco ecológico.

ABSTRACT

In aquatic environments, heavy metals are produced from natural and anthropogenic sources and the degree of contamination depend on pollutant type, fish species, sampling site, trophic level and their mode of feeding. The heavy metal concentration (Al, Cd, Co, Cr, Cu, Fe, Mn, Zn and Pb) in water, sediment and liver of two fish species (*Oligosarcus* spp- carnivore and *Chyphocarax voga* – detritivore) with different trophic levels was analyzed at two sampling sites in the Sinos River, Brazil, during the four seasons. The highest heavy metals concentration was observed in the sediment, followed by fish and lowest in water. As the sediment was the major sink for pollution by metals in this river, it probably played an important role in the uptake of these metals by the detritivore species, which accumulated more metals in the liver than the carnivore species. Furthermore, potential ecological risk was low for both sampling sites, showing the low contamination in the area and safe consumption of fish from Sinos River for human population.

Keywords: Sinos River. Liver. Sediment. Detritivore. Carnivore. Ecological risk.

1. INTRODUCTION

In the fluvial environments, heavy metals are originated from various natural and anthropogenic sources, such as atmospheric deposition, geologic weathering, agricultural activities and residential and industrial products [1,2]. Albeit efforts – to a greater or lesser extent – to contain waste and reduce environmental impacts, a river system will naturally drain all areas surrounding it, washing into the aquatic environment many harmful substances [3].

In Rio Grande do Sul State, Southern Brazil, the Sinos River is an example of a heavily impacted, multiple use watercourse, which provides drinking water for 1.6 million inhabitants [4]. Severe environmental modifications exist in the medium and lower parts of the basin. In these regions, the streams that compose the hydrological network of the basin pass through urban centers with high populations and industrial density [5]. The main disturbances that degrade the Sinos River tributaries are pollution originating from domestic and industrial sewage in urban areas, eutrophication, erosion and elimination of the riparian buffer strips in agricultural areas. The Source Emission Identification Program of the State Foundation for Environment Protection (FEPAM) estimates that ~35 ton yr^{-1} of heavy metals (Cu, Zn, Cr, Cd and Pb) are released by human activities into the Sinos river. Furthermore the basalt rocks, the predominant rock type in the Sinos drainage basin, and the soils originated from them, released significant amounts of heavy metals into the river [6]. Discharges of toxic industrial sewage occur sporadically, causing fish kills in the river main stem. During the most severe registered fish kill, more than 100 t died in October 2006 [5].

Heavy metals, including both essential and non-essential elements, have a particular significance in ecotoxicology [7] because of their toxicity, long persistence, bioaccumulation and bio-magnification in the food chain [8]. The degree of contamination depend on pollutant type, fish species, sampling location, trophic level and their mode of feeding [9].

Monitoring heavy metal contamination in river systems by using fish tissues helps to assess the quality of aquatic ecosystems [10]. Heavy metals enter fish through five main routes (food or non-food particles, gills, water and skin), follow into blood and are carried to either a storage point or to the liver for its transformation or storage [2]. The liver is the main site of accumulation, biotransformation and excretion of pollutants in fish [3].

Species in relatively low trophic levels are exposed to comparatively lower contamination. On the other hand, fish in the upper food web position are prone to accumulate metals [11]. In this sense, we selected *Oligosarcus* spp, a carnivorous gender of Characidae which use the water column [12], and *Cyphocharax voga,* a detritivore Curimatidae closely related to sediment and benthopelagic in natural habitat [13].

The aim of this study is to determine the heavy metal accumulation in water, sediment and in the liver of two freshwater fish species occupying different feeding habits in two sampling sites along the Sinos River and therefore to test the hypothesis that fish in upper web food position are prone to accumulate more metals and that the proximity of polluted site is more likely to have contaminated fish. Furthermore, it was also verified if these species could be used as environmental indicators of large-scale aquatic ecosystems quality.

2. MATERIAL AND METHODS

2.1.Study area

The hydrographic basin of Sinos River is located in the northeastern region of Rio Grande do Sul state, Brazil. The river main stem is 190 km long and drains an area of approximately 3.820 km^2, relative to 1.5% of the total area of the state [5]. The Sinos basin belongs to the phytogeographic region classified as Semidecidual Seasonal Forest, which today only exists on the slopes of the Serra Geral. The climate is subtropical with four well-defined seasons [14].

The upper region of the Sinos River basin, near the source of the river and originally covered by forest, is now characterized by plantations of sugarcane and rice paddies. In the middle section of the basin, large areas are used for rice cultivation and cattle ranching. The lower region is densely urbanized with a high concentration of industries. This area is impacted by water withdrawal for domestic and industrial use, domestic and industrial sewage as well as huge amounts of domestic garbage [5].

2.2. Sample collection

The fish were caught in winter and spring 2010 and summer and autumn 2011 at two locations (Figure 1): one polluted site, in the lower section and one supposed unpolluted by the absence of industrialization, in the upper region. Benthopelagic fish with detritivorous habit, *Cyphocharax voga* [13] and pelagic fishes with carnivorous habit from *Oligosarcus* gender [12] were collected at each station using multimesh gill nets for 1-2 days until a sufficient number of individuals, at least 7-9 fish were caught. After the capture, fish were immediately frozen individually at – 20°C. Sediment and water samples were collect with polyethylene bottles from the same localities.

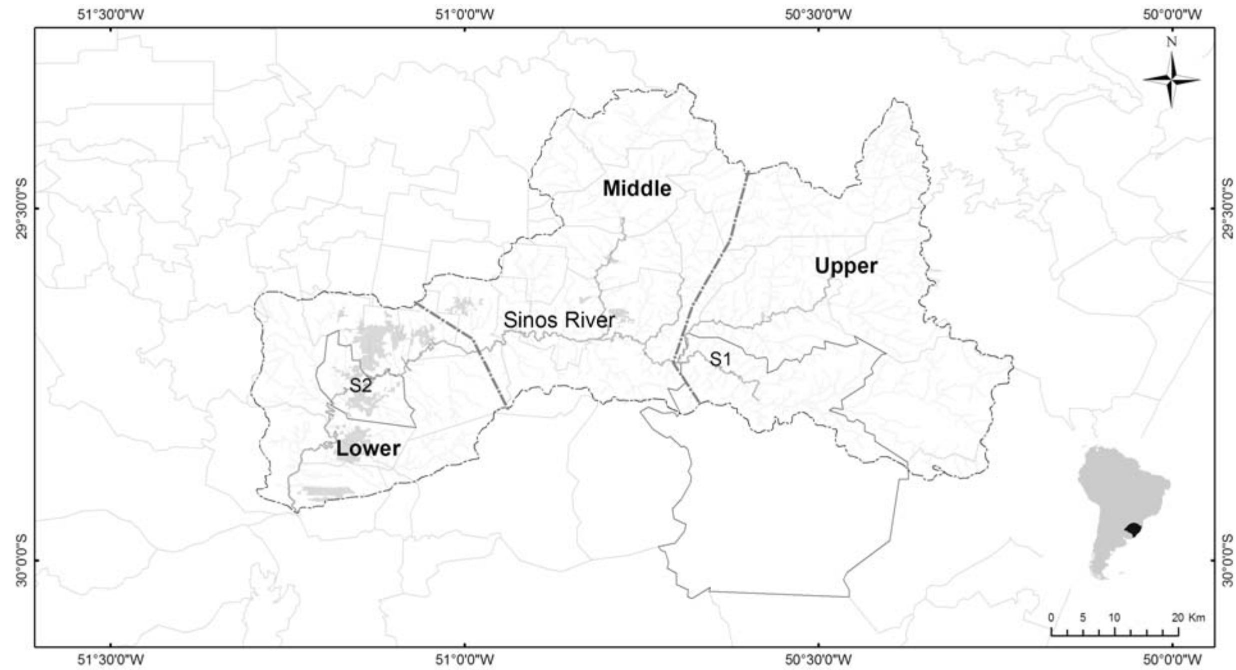

Figure 1 – Map of the sampling sites in the Sinos River. S1 = Sampling site one located in upper Sinos River; S2 = sampling site two located in lower Sinos River.

Some physico-chemical parameters from the two sampling sites are in Table 1.

Table 1 – Water Physico-chemical properties in Sinos River

Physico-chemical parameters	Site 1	Site 2
Temperature (°C)	17.3	19.4
pH	7.5 ± 0.67	6.9 ± 0.27
Hardness ($CaCO_3$)	18 ± 1.01	16 ± 1.2
Dissolved oxygen (mg L^{-1})	8.1 ± 1.07	4.5 ± 2.89

2.3. Sample preparation

The samples were transported to the laboratory on the next day of sampling and stored (- 20°C) prior to analysis. The length and weight of fish were recorded. *Oligosarcus* spp ranged from 135 to 305 mm and *C. voga* from 116 to 227 mm. The whole liver was removed and kept in polyethylene tubes till analysis. Water, liver and sediment samples were digested by using a heating block equipped with glass tubes. Amounts of 250 mg of sample were weighed and transferred to the glass tubes. After that, 5 mL of concentrated high purity nitric acid was added and heated for 3 h at 120 ºC. After cooling, solutions were transferred to polypropylene flask and the volume completed to 30 mL with high purity water. Certified reference materials (CRM - NIST 1640: Trace Elements in Natural Water; HISS-1: Marine Sediments; DOLT-3: Dogfish liver) were used for accuracy evaluation, and the recovered values (in %) are as described in Table 2.

Table 2 – Recovered values (in %) for all analyzed metals in water, sediment and tissue. N.D. – non determined.

	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn
water	105	89	105	103	95	102	105	101	104	101
sediment	102	123	204	84	105	117	96	102	92	97
tissue	N.D.	110	108	N.D.	N.D.	103	99	N.D.	406	102

2.4. Sample analysis

An inductively coupled plasma optical spectrometer (Spectro, Model Ciros CCD, Kleve, Germany) equipped with a cross flow nebulizer (Spectro), a glass double pass spray chamber (Spectro) and a quartz torch with a quartz injector tube (2 mm i.d.) was used. Instrumental performance optimization, including nebulizer gas flow rate, torch alignment and RF power was carried out following the instructions of the manufacturer (Table 3).

2.4.1. Reagents

Water was distilled/deionized and further purified using a Milli-Q system (18.2 MΩ cm, Millipore, Billerica, USA) and used to prepare all reagents and standard solutions. Analytical grade nitric acid (Merck, Darmstadt, Germany) was doubly distilled in a model duoPUR 2.01E sub-boiling system (Milestone, Bergamo, Italy). Diluted nitric acid was used for analytical solutions preparation and for sample dilution. All other reagents used were of analytical grade. A multielement stock standard solutions containing 10 mg L^{-1} of analytes (SCP33MS, SCP Science, Quebec, Canada) was used. Analytical standards were prepared by sequential dilution in 5% (v/v) HNO_3 in the range of 2.5 to 200 mg L^{-1} for ICP- MS.

Table 3 - Instrumental parameters for elements determination by ICP - OES

Parameter	Condition
RF power (W)	1400
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	1.00
Nebulizer gas flow rate (L min^{-1})	1.10
Nebulization chamber	Doubble pass (type Scott)
Nebulizer	Crossflow
Wavelength (nm)	
Al I	396.153
As I	189.042
Cd II	226.502
Co II	228.616
Cr II	267.716
Cu I	324.754
Fe II	238.204
Mn II	259.373
Pb II	220.353
Zn I	213.856

2.5. Statistical analysis

Homocedasticity of variances was assessed with Levene´s test. Some data were log transformed to meet the parametric assumptions prior to statistical analysis. Two-way analysis of variance and Tukey HSD multiple comparison test were used to compare river sampling sites, species, sediment or water at each season. Minimum significance level was $p < 0.05$ and software Statistica 7.0 was used. The correlation analysis between metal accumulation in the liver and fish length was performed with the software Sigma Plot 11.0.

2.6. Potential ecological risk

Potential ecological risk was calculated using Hakanson (1980) [15] methodology in which the sensitivity of the aquatic system depends on its productivity. The potential ecological risk index (RI) was introduced to assess the degree of heavy metal pollution in sediments, according to the toxicity of heavy metal pollution and the response of the environment:

$RI = \sum E^i_r$ (1)

$E^i_r = T^i_r C^i_f$ (2)

$C^i_f = C^i_o / C^i_n$ (3)

where RI is calculated as the sum of all risk factors for heavy metals in sediment, E^i_r is the monomial potential ecological risk factor, T^i_r is the toxic-response factor for a given substance, which accounts for a given substance, which accounts for the toxic requirement and the sensitivity requirement. C^i_f is the contamination factor, C^i_o is the concentration of metals in sediment, and C^i_n is a reference value for metals (Table 4).

Table 4 – Reference values (C^i_n) and toxicity coefficients (T^i_r) of heavy metals in sediments

Heavy metals	As	Cu	Cd	Cr	Pb	Zn
C^i_n (μg g^{-1})	15	30	0.5	60	25	80
T^i_r	10	5	30	2	5	1

The risk factor RI proposed by Hakanson (1980) [15] was based on eight parameters (PCB, Hg, Cd, As, Pb, Cu, Cr and Zn) but in this study we excluded PCB and Hg. Using equations (1) – (3) and parameters listed in table 5, the potential ecological risk indices E^i_r and R_1 for each sampling site were calculated.

The potential ecological risk for single regulator (E^i_r) follows a ranking with: low risk ($E^i_r < 40$), moderate ($40 \leq E^i_r < 80$), considerable ($80 \leq E^i_r < 160$), high ($160 \leq E^i_r < 320$) and very high ($E^i_r \geq 320$). RI is the total heavy metal potential ecological risk index and represents the sensitivity of various biological communities to toxic substances [16] and follows the terminology: low ecological risk for all factors (RI < 95), moderate (95 ≤ RI < 190), considerable (190 ≤ RI < 380) and very high (RI ≥ 380).

3. RESULTS

No difference between seasons was observed for all analyzed parameters. The concentrations of heavy metals were highest in the sediment, intermediate in water and lowest in fish liver, except for Zn and Fe that were higher in fish liver than in water for both sampling sites (Table 5).

Waterborne and sediment heavy metals levels showed no difference between sampling sites, except Co ($P < 0.05$), Fe ($P < 0.05$) and Mn ($P < 0.05$) that were higher in the sediment of sampling site one (Table 5). There was no difference in fish metal accumulation between sampling sites, except for Mn ($P < 0.05$) and Co ($P < 0.05$) that showed higher accumulation in the liver of *C. voga* at sample site one (Table 5).

C. voga presented higher values for all metals in the liver than *Oligosarcus* spp. The mean concentration of the tested elements for *C. voga* followed the sequence Fe>Al>Mn>Zn>Cu>Pb>Co>Cd>Cr and for *Oligosarcus* spp Fe>Zn>Al>Mn>Cu>Pb>Cd>Cr>Co. There was no significant correlation between heavy metals accumulation in the liver and fish length for *C. voga* and *Oligosarcus* spp (Table 5).

Table 5 – Waterborne As, Al, Cd, Co, Cr, Cu, Fe, Mn, Zn, and Pb concentration (µg L^{-1} total concentration), sediment (µg g^{-1} dry weight) and *Oligosarcus* spp and *C. voga* liver (µg g^{-1} wet weight) from sampling sites 1 and 2 (mean ± SEM). * indicates a significant difference from site 1.

	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Zn	Pb
					Site 1					
Water	35.7±7.06	13.4±1.2	0.9	2.3±0.61	1.40	5.5±1.5	36.2±8.65	48.7±22.3	3.3±1.4	8.5±0.7
Sediment	12878.4±3424.23	2.06±1.9	1.05±0.42	17.6±1.50	23.1±2.02	15.1±1.4	24868.1±3147.1	620.5±91.1	29.1±19.6	13.4±4.4
Oligosarcus	6.4±0.65	5.17±2.1	0.3±0.08	0.2±0.05	0.2±0.08	2.1±0.1	329.9±40.2	2.9±1.2	27.6±1.8	1.5±0.1
C. voga	65.3±32.6	8.094±0.7	0.7±0.1	1.6±0.2	0.6±0.1	4.8±0.6	1593.0±301.8	65.3±8.2	30.9±3.7	2.1±0.4
					Site 2					
Water	107.1±54.5	13.8±1.8	0.9	1.9±0.4	1.4±0.02	12.1±5.3	120.8±57.9	60.7±20.6	10.5±8.4	9.9
Sediment	8528.7±2416.8	2.09±2.3	0.4±0.16	5.2±1.1*	23.5±0.45	8.6±1.8	7182.8±2395.1*	136.9±36.2*	22.5±14.5	7.3±1.01
Oligosarcus	8.1±3.7	1.51±0.04	0.1±0.03	0.1±0.008	0.1±0.01	1.5±0.07	167.1±25.1	1.06±0.06	25.3±2.9	1.3±0.008
C. voga	38.8±9.09	1.76±0.5	0.3±0.04	0.8±0.2*	0.3±0.08	4.5±0.7	1081±156.1	24.2±7.3*	26.4±2.09	1.4±0.2

3.1. Potential ecological risk

All metals have low potential ecological risk at both sampling sites in the Sinos River, except Cd in site one that had moderate potential ecological risk. The total heavy metal potential ecological risk index also leads to the conclusion that both sampling sites are of low ecological risk (Table 6).

Table 6 – Heavy metal potential risk indexes of the Sinos River two sampling sites

	E^i_r						RI
Sites	As	Cu	Cd	Cr	Pb	Zn	
1	1.37	2.51	63.13	0.77	0.798	0.364	68.94
2	1.39	1.44	27.9	0.78	1.475	0.282	33.27

4.1. Metals in water samples

Waterborne metal levels in sampling site one were below maximum values allowed by Resolution No. 357/2005 of the Brazilian National Environment Council (CONAMA) [17] for class I river intended for human supply after simplified treatment. However, in sampling site two Al and Cu values were in agreement with class III river in a ranking of IV river classes, where class IV is intended only for navigation and harmony landscape. FEPAM (1999) [5] classified the water quality from the sampling site one as two (on a scale from one, indicating pristine conditions, to four, indicating heavily polluted) with minimum DO 6.6 mg L^{-1} and sampling site two as 4 with minimum DO 0.2 mg L^{-1}.

4.2. Metals in sediment samples

In the sediment samples, there was no difference between sampling sites for most analyzed metals, except for Co, Fe and Mn. Fe followed by Al had the highest accumulation values for both sites which correspond to a classical weathering product in tropical areas where the sediments are mainly composed of Al and Fe [18].

Suspended sediments adsorb pollutants from the water, thus lowering their concentration in the water column [16]. In this sense, the levels of metal accumulation in the sediment were high at both sampling sites of the Sinos River. Sampling site one presents strong agriculture activity whose main metals source are impurities from fertilizers, pesticides and sewage sludge [19]. Furthermore the soil of Sinos River is originated from basalt rocks that may release significant amount of metals in sediment [6]. The highest Mn and Co sediment concentrations in site one is in agreement with another study in Sinos River that showed that Mn is strongly adsorbed by clay minerals, being in or out of soil crystalline structure and Co, Ni, Cu and Zn owe their accumulation to the clayey soil components [20]. Moreover highest Co level in Sinos River was 17.62 µg g^{-1}d.w. which is lower than reported for unpolluted freshwater sediment, 20 µg g^{-1}d.w. [21].

The sampling site two draws domestic and industrial sewage as well as huge amounts of domestic garbage due to the dense urbanization with a high concentration of industries in this area [5] which could accumulate organic matter and reduce the amount of dissolved oxygen, as demonstrated by the ratings of FEPAM for this area, but is not interfering in heavy metal accumulation.

4.3. Metals concentration in fish liver

When fish are exposed to elevated waterborne metals, they can absorb and then bioaccumulate these metals through gills and skin or ingesting contaminated water and food. Consequently metals in fish tissues can be several folds higher than their corresponding waterborne values [2]. In fish liver there was no difference in metal accumulation between sampling sites, except for Mn and Co that had higher accumulation in the liver of *C. voga* at sampling site one. Mn is an essential element for both animal and plant [22] and is possibly homeostatically controlled and relatively nontoxic to aquatic biota and is seldom a problem in freshwaters [23]. Co is also an essential element, component of B_{12} vitamin [24] and, as a rule, Zn and Co accumulate in fish liver, where active metabolic processes take place [26]. Then, the Co amount found in the liver fish from Sinos River is probably a reflection of the functions of this tissue in Co metabolism.

Cu is an essential element because of its important role in biological systems [24] and the low levels found in the present study (2.12 – 4.8 μg g^{-1} w.w.) are in agreement with its homeostatic control below 50 μg g^{-1} d.w. [27].

Highest liver Zn concentrations occurred in fish associated with substrata or those which feed on it and may characterize recent incorporation through the digestive tract [28]. Higher Zn accumulation values than in the species collected in the present study (25.3 – 30.9 μg g^{-1} w.w.) were found in the liver of the omnivorous *Labeo dyocheilus* (1175.7 μg g^{-1} w.w.) [8] and similar values occurred in another omnivorous fish *Leporinus obtusidens* collected in the Guaíba Lake, from the same Sinos River basin and where a lot of organic waste is discharged [29].

Cr is a non essential element used in the leather industry, in inks, and in processing of steel, among other uses [28]. The levels of this metal in the liver of fish collected in Sinos River were safe for human consumption. Higher Cr levels occurred in the fish specie himri (*Carasobarbus luteus* - 1.22 – 2.57 μg g^{-1} w.w) from Orontes River, Turkey, where even suffering with domestic sewage, industrial wastes and agricultural activities, fishes were ascertain to be safe in view of the limits for consumption by humans [30].

Similar values of *Oligosarcus* spp (167.1 – 329.9 μg g^{-1} w.w.) Fe accumulation were found in *Chondrostoma regium* (185.36 μg g^{-1} w.w.) collected from the Atatürk Dam Lake, a non polluted site [31] and in the liver of *Carasobarbus luteus* (150.51 – 354.12 μg g^{-1} w.w.) in a polluted site [30]. The high Fe values found in *C. voga* (1081 – 1593.0 μg g^{-1} w.w.) may result from its feeding habit because this metal accumulate in the sediment of the Sinos River since the soil of this region contains a significant amount of this metal [6].

Cd and Pb are toxic metals that can be assimilated, stored and concentrated by organisms through food chain. Cd is not part of natural biochemical processes and is an extremely toxic and very hazardous heavy metal [32]. A study realized in Manchar Lake, Pakistan, a polluted place especially due to waste water of agricultural land and domestic wastes of urban areas, showed higher Cd (9.3 ± 1.44 μg g^{-1} d.w.) and Pb (8.4 ± 0.60 μg g^{-1} d.w.) values for *Oreochromis mossambicus* [33], a ominovorous fish with detritivore tendency, than in *C. voga* liver (1.44 – 2.19 μg g^{-1} w.w. Pb and 0.3 – 0.75 μg g^{-1} w.w. Cd).

Numerous studies analyzed heavy metal accumulation in the muscle since it is the main fish part that is consumed by humans [11,34,16]. However, muscle is not always a good indicator of the whole body fish contamination like liver is, due to the fact the liver is an organ of continuous accumulation, biotransformation and detoxification providing a more immediate assessment of the current environmental level of pollutants [3,35]. Overall, fishes from the Sinos River are safe to human consumption considering heavy metal accumulation.

The hypothesis that fish on upper web food position are prone to accumulate more metals was not observed in the present study because the higher metal concentration levels were found in the detritivore species. This is in agreement with the fact that in low contaminated waters the metal uptake in fish takes place mainly by feeding [36]. Yousafzai et al. (2010) [8] showed that omnivore fishes accumulated 65.2% more metal burden than carnivore fishes. Different concentration of heavy metals in different fish species might be a result of different ecological needs, metabolism and feeding patterns [37].

The hypothesis that the sediment is the major sink for metal pollution and plays an important role in heavy metal uptake by fish [16] was confirmed in the present study. Therefore controlling the sources of contamination of water and sediment in the river system is the key for fish protection. The higher metal accumulation occurred in detritivore species that could be used as a biomonitor for monitoring metal pollution.

The most severe registered fish kill in Sinos River occurred in October 2006, with more than 100 t of dead fishes [5]. Our results agree with the study performed by the State Foundation for Environment Protection (FEPAM) [5] which states that the event was punctual and the deaths occurred due to a sum of factors such as dry weather, discharge of organic matter and therefore low levels of dissolved oxygen in water and not due to the high levels of pollutants such as heavy metals accumulated in fish tissues.

4.4. Potential ecological risk

A risk index provide a fast and simple quantitative value on the potential ecological risk of a given contamination situation in a given lake or fresh water system [15]. Potential ecological risk for single regulator indexes for Sinos River at both sampling sites showed low potential ecological risk for all analyzed metals, except for Cd that had moderate potential ecological risk in site one. In other studies in lakes and rivers, Cd also presented higher ecological risk than any other metal which is due to the higher Cd toxicity coefficient despite of its lower concentration [38,39,40].

Cadmium ecological risk in Sinos River could also be due to the addition of fertilizers, especially phosphate, because of the natural occurrence of various heavy metals in phosphate rock which are not eliminated in the manufacturing process [41]. Furthermore, the construction and maintenance crop removes the soil originated from basalt rocks that may release significant amount of metals in sediment [6]. The low total heavy metal potential risk in the Sinos River reveals the low danger of metals to resident aquatic organisms of this river.

5. CONCLUSION

On the basis of investigations at two sites, metal concentration was highest in sediment, middle in water and lower in the fish liver, with the sediment the major sink for metal pollution in Sinos River. Site one, that is considered cleaner, showed a higher metal concentration for all analyzed parameters, then could be considered most polluted site regarding waterborne metals. The detritivore species, *C. voga*, presented the highest concentration for all analyzed metals from the two collect sites and may therefore be used as biomonitor of the aquatic environment where it lives.

6. ACKNOLEDGEMENTS

B. Baldisserotto received CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico -Brazil) research grant and P. Weber a MSc grant from CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil).

7. REFERENCES

[1] A.F. Demirak, A.L. Yilmaz, T. Ozdemir, N. Ozdemir. Heavy metals in water, sediment and tissues of *Leuciscus cephalus* from a stream in southwestern Turkey, Chemosphere. 63 (2006) 1451-1458.

[2] F. Jabeen, A.S. Chaudhry. Environmental impacts of anthropogenic activities on the mineral uptake in *Oreochromis mossambicus* from Indus River in Pakista, Environ. Monit. Assess. 166 (2010) 641 – 651.

[3] C.A. Shinn, F. Dauba, G. Grenouillet, G. Guenard, S. Lek. Temporal variation of heavy metal contamination in fish of the river lot in southern France, Ecot. Environ. Safety. 72 (2009) 1957 – 1965.

[4] A.C. Petry, U.H. Schulz. Longitudinal changes and indicator species of the fish fauna in the subtropical Sinos River, Brazil, J. Fish Biol. 69 (2006) 272 – 290.

[5] FEPAM - Fundação Estadual de Proteção Estadual Henrique Luis Roessler. 2009. Available from: <http://www.fepam.rs.gov.br>, Access in: jan 2011.

[6] V. Hatje, E.D. Bidone, J.L. Maddock. Estimation of the natural and anthropogenic components of heavy metal fluxes in fresh water Sinos River, Rio Grande do Sul State, South Brazil, Environ. Technol. 19 (1998) 483 – 487.

[7] M. Ebrahimpour, I. Mushrifah. Seasonal variation of cadmium, copper, and lead concentrations in fish from a freshwater lake, Biol. Trace. Elem. Res. 138 (2010) 190 – 201.

[8] A.M. Yousafzai, D.P. Chivers, A.R. Khan, I. Ahmad, M. Siraj. Comparison of heavy metals burden in two freshwater fishes *Wallago attu* and *Labeo dyocheilus* with regard to their feeding habits in natural ecosystem, Pakistan J. Zool. 42 (5) (2010) 537 – 544.

[9] F.E. Asuquo, I. A Ewa-Oboho, E.F. Asuquo, P.J. Udoh. Fish species used as biomarkers for heavy metals and hydrocarbon contaminations for the cross river, Nigeria, Environmentalist. 24 (2004) 29 – 37.

[10] S.M. Adam. Biological indicators of aquatic ecosystem stress. Bethesda, MD: American Fisheries Society. 656 (2002).

[11] B.F. Terra, F.G. Araújo, C.F. Calza, R.T. Lopes, T.P. Teixeira. Heavy metal in tissues of three fish species from different trophic levels in a tropical Brazilian river, Water Air Soil Pollut. 187 (2008) 275 – 284.

[12] D.M.C. Nunes, S.M. Hartz. Feeding dynamics and ecomorphology of *Oligosarcus jenynsii* (Gunther, 1864) and *Oligosarcus robustus* (Menezes, 1969) in the Lagoa Fortaleza, Southern Brazil, Braz. J. Biol. 66 (1A) (2006) 121 – 132.

[13] F. Corrêa, S.R.N. Piedras. Alimentação de *Cyphocharax voga* (Hensel, 1869) (Characiformes, Curimatidae) no arroio Corrientes, Pelotas, Rio Grande do Sul, Brasil, Biotemas. 21 (4) (2008) 117 – 122.

[14] P.F. Costa, U.H. Schulz. The fish community as an indicator of biotic integrity of the streams in the Sinos River basin, Braz. J. Biol. 70 (4) (2010) 1195 – 1205.

[15] L. Hakanson. An ecological risk index for aquatic pollution control of sediment ecological approach, Water Res. 14 (1980) 975 – 1000.

[16] Y. Yi, Z. Yang, S. Zhang. Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin, Environ. Pollut. 159 (2011) 2575-2585.

[17] CONAMA - Resolution N_0. 357 of the Brazilian National Environment Council. DOU N_0. 53 (2005) Section 1, 58-63.

[18] F. Sondag, J.L. Guyot, J.S. Moquet, A. Laraque, G. Adele, G. Cochonneau, J.C. Dodou, C. Laganei, P. Vauchel. Suspended sediment and dissolved load budgets of two Amazonian rivers from the Guiana Shield: Maroni River at Langa Tabiki and Oyapock Riverat Saut Maripa (French Guiana), Hydrol. Process. 24 (2010) 1433 – 1445.

[19] F. Malhat. Distribution of heavy metal residues in fish from the River Nile tributaries in Egypt, Bull. Environ. Contam. Toxicol. 83 (2011) 163 – 165.

[20] M.T.G. Oliveira, S.B.A. Rolim, P.C. Mello-Farias, A. Meneguzzi, C. Lutckmeier. Industrial pollution of environmental compartments in the Sinos River Valley, RS, Brazil: geochemical– biogeochemical characterization and remote sensing, Water Air Soil Pollut. 192 (2008) 183 – 198.

[21] I.C. Smith, B.L. Carson. Trace metals in the environment. Ann Arbor: Ann Arbor Science Publishers. (1981).

[22] A.K. Anim, E.K. Ahialey, G.O. Duodu, M. Ackah, N.O. Bentil. Accumulation profile of heavy metals in fish samples from Nsawam, along the Densu River, Ghana, Res. J. Environ. Eart. Sci. 3 (1) (2011) 56 – 60.

[23] J.G. Wiener, J.P. Giesy Jr. Concentrations of Cd, Cu, Mn, Pb and Zn in fishes in a highly organic softwater, pond. J. Fish. Res. Board. Can. 36 (1979) 270 – 279.

[24] A.A. Fallah, S.S. Saei-Dehkordi, A. Nematollahi, T. Jafari. Comparative study of heavy metal and trace element accumulation in edible tissues of farmed and wild rainbow trout (*Oncorhynchus mykiss*) using ICP-OES technique, Microchem. J. 98 (2011) 275 – 279.

[25] T.I. Moiseenko, N.A. Gashkina, Y.N. Sharova, L.P. Kudryavstseva. Ecotoxicological assessment of water quality and ecosystem health: A case study of the Volga River, Ecotox. Environ. Saf. 71 (3) (2008) 837 – 850.

[26] C.V. Nolan, S.W. Fowler, J. Teyssie. Cobalt speciation and bioavailability in marine organisms, Marine Ecol. Progr. Series. 88 (1992) 105 – 116.

[27] G.G. Pyle, J.W. Rajotte, P. Couture. Effect of industrial metals on wild fish population along a metal contamination gradient, Ecotoxicol. Environ. 61 (2005) 287 – 312.

[28] R.G. De Souza Lima Junior, F.G. Araújo, M.F. Maia, A.S.S.B. Pinto. Evaluation of heavy metal in fish of Sepetiba and Ilha Grande Bays, Rio de Janeiro, Brazil, Environ. Res. Sec. A. 89 (2002) 171 – 179.

[29] S.C. Costa, S.M. Hartz. Evaluation of trace metals (cadmium, chromium, copper and zinc) in tissues of a commercially important fish (*Leporinus obtusidens*) from Guaíba Lake, Southern Brazil, Braz. Archiv. Biol. Tech. 52 (1) (2009) 241 – 250.

[30] A.B. Yilmaz, M. Dogan. Heavy metals in water and in tissues of himri (*Carasobarbus luteus*) from Orontes (Asi) River, Turkey, Environ. Monit. Assess. 144 (2008) 437–444.

[31] H. Karadede, E. Ünlü. Concentrations of some heavy metals in water, sediment and fish species from the Atatürk Dam Lake (Euphrates), Turkey, Chemosphere. 41 (2000) 1371 – 1376.

[32] M. Kosanovic, M.Y. Hasan, D. Subramanian, A.A.F. Al Ahbabi, O.A.A. Al Kathiri, E.M.A.A. Aleassa, A. Adem. Influence of urbanization of the western coast of the United Arab Emirates on trace metal content in muscle and liver of wild Red-spot emperor (*Lethrinus lentjan*), Food Chem. Toxicol. 45 (2007) 2261 – 2266.

[33] M.B. Arain, T.G. Kazi, M.K. Jamali, N. Jalbani, H.I., Afridi, A. Shan. Total dissolved and bioavailable elements in water and sediment samples and their accumulation in *Oreochromis mossambicus* of polluted Manchar Lake, Chemosphere. 70 (2008) 1845 – 1856.

[34] A. Meche, M.C. Martins, B.E.S.N. Lofrano, C.J. Hardaway, M. Merchant, L. Verdade. Determination of heavy metals by inductively coupled plasma-optical emission spectrometry in fish from the Piracicaba River in Southern Brazil, Microchem. J. 94 (2010) 171 – 174.

[35] I. Jaric, Z. Visnjic-Jeftic, G. Cvijanovic, Z. Gacic, L. Jovanovic, S. Skoric, M. Lenhardt. Determination of differential heavy metal and trace element accumulation in liver, gills, intestine and muscle of sterlet (*Acipenser ruthenus*) from Danube River in Serbia by ICP-OES, Microchem. J. 98 (2011) 77 – 81.

[36] A. Farkas, J. Salánki, A. Specziár. Age- and size-specific patterns of heavy metals in the organs of freshwater fish *Abramis brama* L. populating a low-contaminated site, Water Res. 37 (2003) 959 – 964.

[37] S.M. Allen-Gil, V.G. Martynov. Heavy metals burdens in nine species of freshwater and anadromous fish from the Pechora River, northern Russia, Sci. Tot. Environ. 160 – 161 (1995) 653 – 659.

[38] H. Yin, Y. Gao, C. Fan. Distribution, sources and ecological risk assessment of heavy metals in surface sediments from Lake Taihu, China, Environ. Res. Lett. 6 (2011).

[39] L. Zheng, G. Liu, Y. Kang, R. Yang. Some potential hazardous trace elements contamination and their ecological risk in sediments of western Chaohu Lake, China, Environ. Monit. Assess. 166 (2010) 379 – 386.

[40] C. Fu, J. Guo, J. Pan, J. Qi, W. Zhou. Potential ecological risk assessment of heavy metal pollution in sediments of the Yangtze River within the Wanzhou Section, China, Biol. Trace. Elem. Res. 129 (2009) 270 – 277.

[41] M.S.C. Camargo, A.R.M. dos Anjos, C. Rossi, E. Malavolta. Adubação fosfatada e metais pesados em latossolo cultivado com arroz, Sci Agric. 57 (3) (2000) 513 – 518.

CONCLUSÕES FINAIS

- As concentrações de metais foram maiores no sedimento, intermediárias na água e menores nos peixes.

- A espécie detritívora apresentou maiores concentrações para todos os metais analisados nos dois pontos de coleta e, provavelmente, pode ser utilizada como biomonitor da qualidade do ambiente aquático em que vive.

- O sedimento é o maior dreno para poluição por metais.

REFERÊNCIAS

COSTA, S. C. & HARTZ, S. M. Evaluation of trace metals (cadmium, chromium, copper and zinc) in tissues of a commercially important fish (*Leporinus obtusidens*) from Guaíba Lake, Southern Brazil. **Brazilian Archives of Biology and Technology**. n. 52, p. 241 – 250, 2009.

CORRÊA. F. & PIEDRAS, S. R. N. Alimentação de *Cyphocharax voga* (Hensel, 1869) (Characiformes, Curimatidae) no arroio Corrientes, Pelotas, Rio Grande do Sul, Brasil. **Biotemas**. n. 21 (4), p. 117 - 122, 2008.

FEPAM (disponível em <http:// www.fepam.rs.gov.br> Acesso em janeiro 2011)

HATJE, V.; BIDONE, E. D.; MADDOCK, J. L. 1998. Estimation of the natural and anthropogenic components of heavy metal fluxes in fresh water Sinos River, Rio Grande do Sul State, South Brazil. **Environmental Technology**. n.19, p. 483 – 487, 1998.

JABEEN, F. & CHAUDHRY, A. S. Environmental impacts of anthropogenic activities on the mineral uptake in *Oreochromis mossambicus* from Indus River in Pakistan. **Environ Monit Assess**. n.166, p. 641 – 651, 2010.

KOCH, W. R.; MILANI, P. C.; GROSSER, K. M. Guia ilustrado Peixes Parque Delta do Jacuí. Porto Alegre: Publicação editada pela Fundação Zoobotânica do Rio Grande do Sul. p.19 – 45, 2000.

NUNES, D. M. C. & HARTZ, S. M. Feeding dynamics and ecomorphology of *Oligosarcus jenynsii* (Gunther, 1864) and *Oligosarcus robustus* (Menezes, 1969) in the Lagoa Fortaleza, Southern Brasil. **Braz. J. Biol**. n. 66 (1A), p. 121 – 132, 2006.

PETRY, A. C. & SCHULZ, U. H. Levantamento da comunidade de peixes do Rio dos Sinos. **Acta Biológica Leopoldensia**. n. 23, p. 49 – 58, 2001.

PETRY, A. C. & SCHULZ, U. H. Longitudinal changes and indicator species of the fish fauna in the subtropical Sinos River, Brazil. **Journal of Fish Biology**. n. 69, p. 272 – 290, 2006.

SHINN, C.A.; DAUBA, F.; GRENOUILLET, G.; GUENARD, G.; LEK, S. Temporal variation of heavy metal contamination in fish of the river lot in southern France. **Ecotoxicology and Environmental Safety**. n.72, p.1957 – 1965, 2009.

TERRA, B. F.; ARAÚJO, F. G.; CALZA, C. F.; LOPES, R. T.; TEIXEIRA, T. P. Heavy Metal in Tissues of Three Fish Species from Different Trophic Levels in a Tropical Brazilian River. **Water Air Soil Pollut.** n. 187, p. 275 – 284, 2008.