Microchemical Journal 106 (2013) 61–66

Contents lists available at SciVerse ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Metals in the water, sediment, and tissues of two fish species from different trophic levels in a subtropical Brazilian river

Paula Weber [a], Everton Rodolfo Behr [b], Camila De Lellis Knorr [c], Daniel Secretti Vendruscolo [b], Erico M.M. Flores [c], Valderi L. Dressler [c], Bernardo Baldisserotto [a,*]

[a] Departamento de Fisiologia e Farmacologia, Universidade Federal de Santa Maria – UFSM, Av. Roraima, 1000, Santa Maria, RS, Brazil
[b] Unidade Descentralizada de Educação Superior da UFSM em Silveira Martins, RS, Brazil
[c] Departamento de Química, Universidade Federal de Santa Maria, Brazil

ARTICLE INFO

Article history:
Received 9 May 2012
Accepted 14 May 2012
Available online 23 May 2012

Keywords:
Sinos River
Liver
Sediment
Detritivore
Carnivore
Ecological risk

ABSTRACT

In aquatic environments, heavy metals are produced from natural and anthropogenic sources and the degree of contamination in fish tissues depend on the pollutant type, fish species, sampling site, trophic level, and their mode of feeding. The heavy metal concentration (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Zn, and Pb) in the water, sediment, and liver of two fish species (*Oligosarcus* spp. – carnivore and *Chyphocarax voga* – detritivore) 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 water, and the 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, the potential ecological risk was low for both sampling sites, showing the low metal contamination in this area.

1. Introduction

In fluvial environments, heavy metals originate from various natural and anthropogenic sources, such as atmospheric deposition, geologic weathering, agricultural activities, and residential and industrial products [1,2]. Efforts – to a greater or lesser extent – to contain waste and reduce environmental impacts are widely hindered because a river system naturally drains all areas surrounding it, thereby washing many harmful substances into the aquatic environment [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 the elimination of the riparian buffer strips in agricultural areas. The Source Emission Identification Program of the State Foundation for Environment Protection (FEPAM) estimates that around 35 tons per year 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, release 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 depends on the 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 the 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 that use the water column [12], and *Cyphocharax voga*, a detritivore Curimatidae closely related to sediment and benthopelagic in the 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

* Corresponding author at: Departamento de Fisiologia e Farmacologia, UFSM, 97105.900, Santa Maria, RS, Brazil. Tel.: +55 55 3220 9382; fax: +55 55 3220 8241.
E-mail address: bbaldisserotto@hotmail.com (B. Baldisserotto).

0026-265X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.microc.2012.05.004

Sinos River and, therefore, to test the hypothesis that fish in the upper web food position are prone to accumulate more metals and that the proximity of the polluted site is more likely to have contaminated fish. Furthermore, it was also verified as to whether 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 the Sinos River is located in the northeastern region of Rio Grande do Sul state, Brazil. The river's 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 Semideciduous 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 the winter and spring of 2010 and the summer and autumn of 2011 at two locations (Fig. 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 at least 7–9 fish were caught. After the capture, the fish were immediately frozen individually at −20 °C. Sediment and water samples were collected with polyethylene bottles from the same localities. Some physico-chemical parameters from the two sampling sites are shown in Table 1.

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 the 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 until analysis. Water, liver, and sediment samples were digested by using a heating block equipped with glass tubes. 250 mg samples was 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 °C. After cooling, the solutions were transferred to a polypropylene flask and the volume completed to 30 mL with high purity water. All the results were expressed on dry mass. 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.

2.4. Sample analysis

An inductively coupled plasma optical emission 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.) were used. Instrumental performance optimization, including the 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, MA, USA) and used to prepare all the 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 solution 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}.

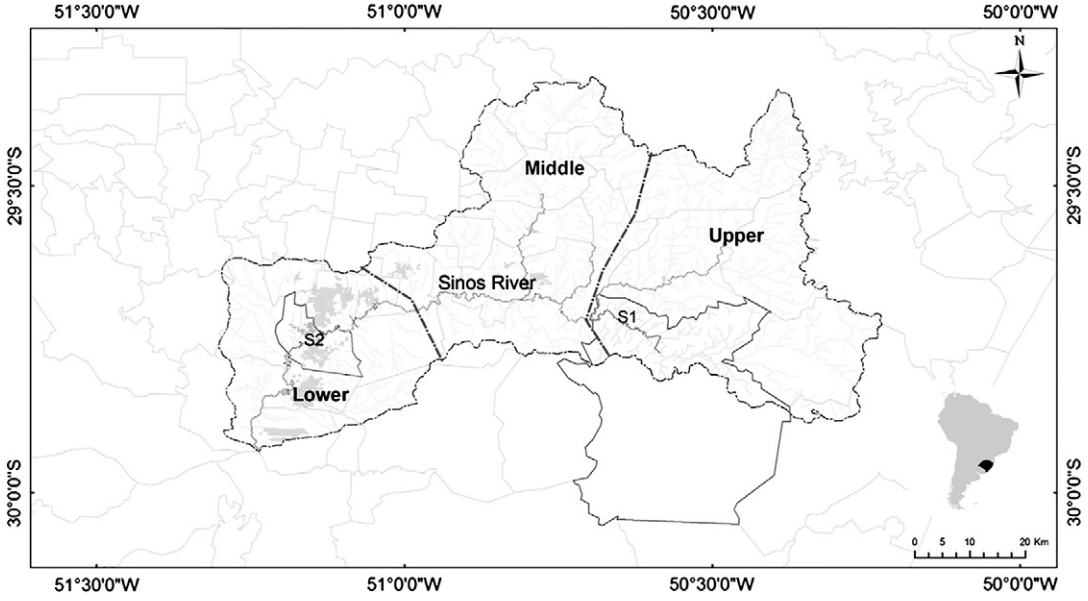

Fig. 1. Sampling sites in the Sinos River. S1 = Sampling site one located in upper Sinos River; S2 = sampling site two located in lower Sinos River.