Ecotoxicology and Environmental Safety 98 (2013) 179–186

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Integrated ecotoxicological assessment of bottom sediments from the Paraná basin, Argentina

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ARTICLE INFO

Article history:
Received 26 April 2013
Received in revised form
19 August 2013
Accepted 2 September 2013
Available online 23 September 2013

Keywords:
Bottom sediments
Toxicity assessment
Hyalella curvispina
Benthic community
Sediment matrix composition

ABSTRACT

Paraná River, the six largest in the world, is receptor of pollution loads from tributaries traversing urban and industrialized areas, and extensive agriculture, particularly in its middle and low stretch along the Argentinean sector, where most of the productive activities of the country develop. Within the frame of monitoring surveys, the quality of bottom sediments from distal positions of twenty tributaries and three of the main course was evaluated. The assessment covered testing lethal and sublethal effects with the *Hyalella curvispina* based toxicity test, a benthic macrofauna survey and physicochemical variables of sediment matrix composition. A multivariate statistical analysis approach permitted integrating the obtained data from the different survey lines of evidence, explaining potential causes of the measured biological effects. The main perturbations detected were associated to tributaries in the middle sector of the basin, where anoxic conditions with high sulfide contents prevail mostly related to organic matter inputs of diverse combined activities, where sediments induce high lethality, and a consequent strong reduction of the benthic community population and diversity. The integrated survey approach proved being a robust tool in the assessment of causative–adverse effects relationships.

1. Introduction

The del Plata Basin is the second largest in South America and comprises Argentina, Uruguay, Brazil, Bolivia and Paraguay, with three large sub-basins, corresponding to the Paraná (2600,000 km^2), Paraguay (1000,000 km^2) and Uruguay Rivers (365,000 km^2). The annual discharge reaching the Atlantic Ocean is 23,000 m^3/s (Berbery and Barros, 2002). The Paraná River is the sixth largest river of the world, a mean annual discharge of 17,000 m^3/s and suspended load of 118.7 million tons/yr (Orfeo and Stevaux, 2002). The basin traverses a variety of geological units, like the Andes Mountains, the Chaco-Pampean Plains, the Eastern Plains, the Jurassic–Cretaceous Area and the Brazilian Shield (Iriondo, 1988). These well differentiated geologic and climatic environments are controlling factors in the sedimentology, clay mineralogy and matrix composition of the basin (Bertolino and Depetris, 1992). The grain size of sediments is dominated by silt and clay sizes (Iriondo, 2004; Manassero et al., 2008; Orfeo, 1999), with vast amounts of colloids and clay aggregates circulating in the basin (Konta, 1985). Most of the Argentinean productive activities and population settlements are associated to this basin. Previous monitoring campaigns have shown multiple sources of pollution along the basin. The middle and low Paraná receive heavily polluted inputs from tributaries traversing across urban and industrialized areas, added of extensive agriculture (Marino and Ronco, 2005; Peluso et al., 2013; Ronco et al., 2008, 2011; SAyDS- PNA- UNLP, 2007). Although transport of polluted mud favor mixing and recycling of particles it was possible to identify anoxic water and sediments with high sulfide and organic matter contents, changes in the composition of major matrix components and heavy metals (Ronco et al., 2011).

The dynamics of fine bottom sediments play an important role in environmental studies as they act as transporting agents and sinks of pollutants (Burton and Landrum, 2003; Camilión et al., 2003; Horowitz, 1985; Lee et al., 2000; Ronco et al., 2001). The capacity of adaptation of benthic organisms in relation to changes of environmental parameters and available food determines their distribution, growth and reproduction. Distribution and abundance are related to factors such as organic matter presence and content, substrate type and occurrence of contaminants (Wetzel and Likens, 1991). Since the bottom sediment provides nutrients and habitat to a large variety of benthic organisms, the assessment of sediment quality becomes relevant for the protection of aquatic life (Paixão et al., 2011).

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0147-6513/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.ecoenv.2013.09.001

Within the frame of monitoring surveys of the Argentinean Paraguay–Paraná basin sector (between 25°21′and 34°18′ latitude), the objective of the present study is to analyze and discuss results of quality assessment of bottom sediments from distal positions of the major tributaries and the main river course, testing lethal and sublethal effects with an amphipod based toxicity test, correlating with measured physicochemical variables by means of multivariate analysis, and finally integrating the information with the screening of benthic community.

2. Materials and methods

2.1. Study area and sample collection

The sampling campaign was done in the scientific vessel SPA-1 "Dr. Leloir" of the Prefectura Naval Argentina (PNA) between June and July of 2011. Grab sediment samples were taken from a total 23 sampling points of the Paraguay and Paraná rivers (see Fig. 1) using an Eckman dredge (to an approximate depth of 10 cm). Each composite sample was obtained from at least 15 discrete grab samples per site. Twenty of the samples were taken in the confluence of the principal tributaries with the Paraná River and the rest within the main Paraná water course. Table 1 shows the sampling sites identification, corresponding abbreviations and a brief description. Also, in situ measured parameters in the water column are given.

Sediment samples were kept in a cooler at 4 °C while transferred to the laboratory. Upon arrival they were manually homogenized and sub-samples were obtained for chemical analysis and for toxicity testing. For this last case were held at 4 °C in the dark for no more than 2 weeks before the start of the toxicity tests (ASTM, 2002). A separate composite sample prepared from two sub-samples was used for the analysis of the community structure, which was previously sieved through a certified 400 mesh, and the material was fixed in 10 percent formaldehyde in the field.

2.2. Physical–chemical analysis

Physical and chemical variables of the water column from each sampling site (conductivity, transparency, pH, temperature and dissolved oxygen), were measured in situ in each sampling station (multi-parameter water quality monitor HORIBA U-52). Biological Oxygen Demand (BOD5) was also determined in the laboratory according Method 5210 D (APHA (American Public Health Association), 1998). Physical characteristics of sediments samples included grain size and organic matter. Sieving and settling velocity technique, with previous cement removal (Day, 1965) was performed for grain size analysis; sediments were sieved trough a set of Standard Sieves larger than 63 μm to separate the sands. Grain size of the fraction smaller than the 63 μm was determined by the standard pipette technique (Folk, 1954). Organic matter content in the sediment was obtained by calcination (loss on ignition) in a muffle furnace at 550 °C. Sulfides were analyzed according to Method 9030 (USEPA (United States Environmental Protection Agency), 1996); nitrogen (Bremner, 1965) and phosphorus (Andersen, 1979) contents were done by colorimetric methods. Analysis of metal content (Cd, Cu, Cr, Ni, Pb and Zn) was done by atomic absorption spectrophotometry (direct flame) following acid digestion of samples according to Method 3050 (USEPA (United States Environmental Protection Agency), 1996). Mercury was extracted according Method 7471B (USEPA (United States Environmental Protection Agency), 1996) and concentration was determined by cold vapor spectrophotometry (CV-AAS). Detection limits (mg/kg) varied depending on the metal: 0.03 Hg; 0.3 Cd; 1.0 Cu; 2.0 Ni; 3.0 Pb and Zn; 10.0 Fe and Mn). Quality controls included reagent blanks, duplicate samples and certified reference material analysis (Pond Sediment 2, National Institute for Environmental Studies, Yatabe, Tsukuba Ibaraki, Japan). Reference materials analysis provided results with accuracy ranging between 80 and 95 percent. Chemicals for sample treatments or analysis of major matrix components were analytical grade. Certified standards of metals were from AccuStandard, Inc. (1000 mg/l standard stock solutions, traceable to the National Institute of Standards and Technology, USA).

2.3. Toxicity testing

Toxicity of each of the sediment samples were assessed using the amphipod *Hyalella curvispina*. In recent years, this amphipod species has been used as test organism in ecotoxicological assessments. Its easiness in breeding under laboratory conditions, sensitivity to toxicants (García et al., 2010; Peluso et al., 2011), and being part of the native fauna lead to using it in field and laboratory testing of aquatic environments of Argentina (Giusto and Ferrari, 2008; Jergentz et al., 2004). Test organisms were obtained by sieving from laboratory cultures maintained in dechlorinated tap water (hardness 220 mg/l $CaCO_3$, pH 8.2, conductivity1.10 mS/cm) (Peluso et al., 2011). Ten-day whole-sediment tests were conducted following USEPA (United States Environmental Protection Agency) (2000) standardized protocol with modifications. Toxicity test procedure was previously described by Peluso et al. (2013). Reference sediment used in testing was obtained in S2 since according to information from previous monitoring campaigns did not exhibit detectable levels of pollution (Ronco et al., 2011). Measured endpoints were survival and growth (length). Performance criteria for the control sediment required 80 percent survival. Amphipods survival higher than 50 percent in each of replicate was set for carrying out the analysis with the variable length.

2.4. Benthic community analysis

The separation and taxonomic identification of sample material was done in the laboratory under stereoscopic microscope. All taxa were categorized into functional feeding groups based on available information (Merrit and Cummins, 1996; Cummins et al., 2005). The calculated benthic index (Cornet, 1986)

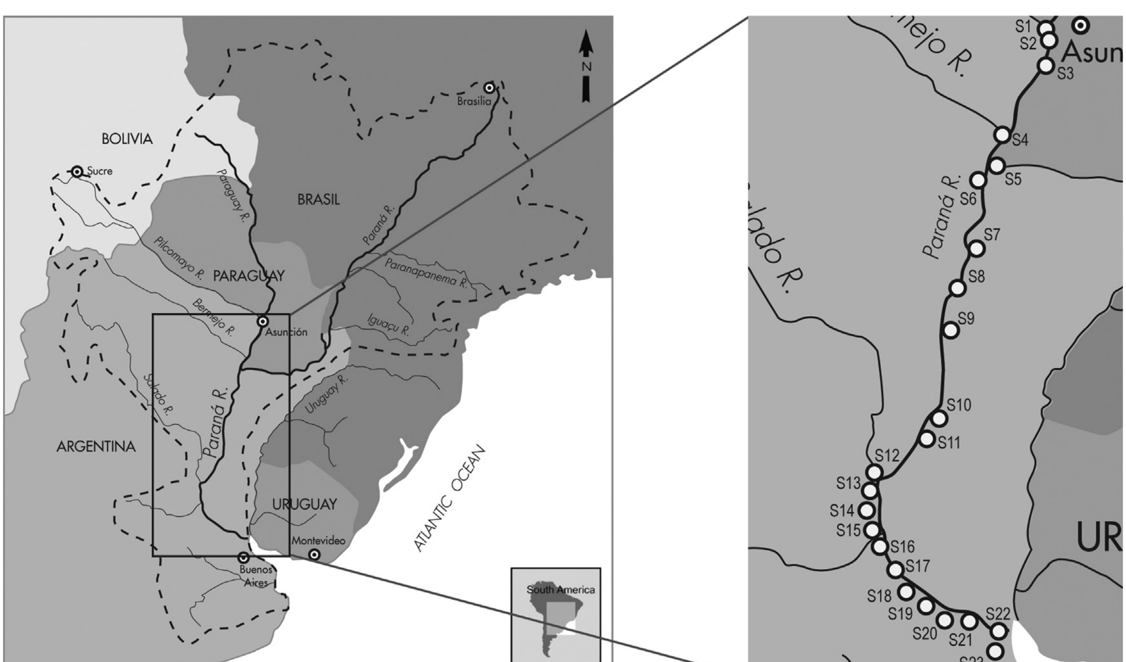

Fig. 1. Area of the study with the location of the 23 sampling sites.