Ecotoxicology and Environmental Safety 107 (2014) 154–161

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Trace metal concentration and fish size: Variation among fish species in a Mediterranean river

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ARTICLE INFO

Article history:
Received 17 December 2013
Received in revised form
29 April 2014
Accepted 12 May 2014
Available online 17 June 2014

Keywords:
Bioaccumulation
Heavy metals
Llobregat River
Mediterranean
Cyprinid fish

ABSTRACT

Concentration of trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and As) in the muscle of six fish species was analyzed to determine the variation with fish size and fish species in an Iberian river with moderate metal pollution. Al, Fe and Zn were the most abundant metals across sites. Fish size and sampling site explained more variation than fish species, and a high intraspecific variability (among individuals) in metal loads was also observed. Considering the most spread species, concentrations were highest in bleak (*Alburnus alburnus*) and lowest in gudgeon (*Gobio occitaniae*) for all the elements. Metal loads were comparable with literature data from contaminated sites, often exceeding recommended European Environmental Quality Standards. The relationships between metal concentration and fish size varied markedly among sites, elements, and fish species. The slopes of these relationships were often significantly heterogeneous, a fact barely acknowledged in the literature, and were often negative, probably due to size-specific metabolic rates related to fish growth.

1. Introduction

Trace metals in aquatic environments may be of natural origin from rocks and soil or from human activities, e.g. industry, urban and agricultural discharge, mine runoff, solid waste disposal and atmospheric deposition (Bradl, 2005). Unlike other pollutants of organic origin, metals are not degraded or eliminated from the ecosystem (Rajkowska and Protasowicki, 2013) and accumulate in sediments and organisms (Zoumis et al., 2001; Ikem et al., 2003; Mendil and Dogan Uluozlü, 2007). Certain metals like manganese, zinc, copper, iron and nickel are essential (i.e. elements with recognized role in biological systems) in low concentrations for the aquatic organisms metabolism (Clark, 2001). Others, such as cadmium, lead and arsenic, are among the most toxic nonessential metals (Goyer et al., 1995; Canli and Atli, 2003). Even essential metals may be toxic for biological activities of organisms at certain concentrations (Pérez-Cid et al., 2001; Kucuksezgin et al., 2006).

Fish normally occupy high positions in aquatic trophic webs, accumulating several kinds of contaminants in their tissues, including trace elements (Bervoets and Blust, 2003; Noël et al., 2013). Heavy metals in fish represent a potential risk, not only to the fish themselves but also to piscivorous birds, mammals and even humans (Grimanis et al., 1978; Adams et al., 1992). Metal concentrations measured in fish are directly or indirectly influenced by a large set of abiotic and biotic factors. Fish can uptake trace metals by two main routes (Farkas et al., 2003; Terra et al., 2008; Rozon-Ramilo et al., 2011), either by adsorption from water through the gills, and from food absorbed through the digestive tract. The predominant pathways for heavy metal uptake appear to be highly variable over the range of metals, fish species and levels of contamination. Dietborne uptake is generally believed to be predominant in low-contaminated waters (Williams & Giesy, 1978; Dallinger et al., 1987; Farkas et al., 2003). The bioavailability, and so the bioaccumulation of trace metals in fish, depends thus on the concentrations in water and the rest of the ecosystem, e.g. algae, invertebrates and sediment, the latter being ingested with food by bottom feeders. Nevertheless, direct proportionality does not necessarily exist between water concentrations and bioaccumulation levels in aquatic organisms (Andres et al., 2000; Yi and Zhang, 2012).

Metals present in water show different bioavailabilities, both for fish and their prey. Water chemistry features such as dissolved and suspended organic carbon, pH, hardness and alkalinity are important modifiers of metal bioavailability and toxicity to aquatic organisms (Paquin et al., 2002; Niyogi and Wood, 2004). In addition, metals present in water show different bioavailabilities depending on whether they are in dissolved phase or bound to suspended matter (Bryan and Langston, 1992). Feeding behavior,

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http://dx.doi.org/10.1016/j.ecoenv.2014.05.006
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Table 1
Trace metal concentrations in water (μg l^{-1}), sediments (mg kg^{-1}) and fish (mg kg^{-1}) of Llobregat River. The data shown are average monthly observations for water concentrations (2003–2011) and average yearly observations for sediments (2004–2011) and fish (2010–2011). Minimum and maximum values are displayed between parentheses. Data provided by the Catalan Water Agency.

	Al	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Water										
LL1	84.75 (30–520)	13.47 (2.5–55)	30.85 (10–230)	2.695 (0.5–5)	6.158 (2.5–10)	4.305 (1.5–13)	20.61 (6–76)	2.341 (2–6)	1.4 (0.3–2.5)	5.244 (5–10)
LL2	84.87 (30–390)	15.34 (2.5–41)	30 (10–210)	2.775 (0.5–5)	6.4 (2.5–10)	4.3 (1.5–15)	23.07 (9–65)	2.346 (2–6)	1.405 (0.3–2.5)	5.375 (5–10)
LL3	117.7 (30–700)	40.94 (2.5–144)	32.25 (10–250)	2.8 (0.5–5)	6.25 (2.5–10)	4.425 (1.5–10)	31.85 (10–102)	2.295 (2–4)	1.4 (0.3–2.5)	5.375 (5–10)
LL4	120.8 (50–354)	50.3 (20–110)	70.25 (30–210)	11 (5–12.5)	11 (4–18)	5.98 (4.5–8.7)	23.5 (22–91)	2.5 (2–3)	0.7 (0.25–2.5)	1.8 (0.5–5)
Sediments										
LL1	25,979 (16149–38748)	401.4 (322.7–475.3)	19790 (16478–24554)	8 (7.1–9.8)	22.06 (16.6–27.5)	31.03 (20.5–42.6)	99.07 (73–125.1)	10.01 (7.3–15.1)	1.2 (0.4–1.8)	21.3 (17.6–27.4)
LL3	29,879 (15656–46763)	559.4 (404.3–920.8)	24518 (16482–39685)	10.03 (6.5–16.3)	26.34 (16.3–46.7)	35.1 (22.4–71.4)	105.3 (66–205.7)	14.2 (8.7–22.8)	1.371 (0.5–3.3)	25.9 (16.1–51)
Fish										
LL1	233.8 (3.24–753.7)	0.324 (0.137–0.5)	19.91 (4–46.59)	0.076 (0.005–0.25)	0.242 (0.062–0.679)	0.785 (0.427–1.5)	9.586 (3.301–12.61)	0.092 (0.04–0.25)	0.0275 (0.0025–0.1)	0.19 (0.03–0.43)

habitat, fish size and age, sex, physiological conditions, spawning status or migration, even in the same area, can affect bioaccumulation beyond environmental concentrations (Andres et al., 2000; Canli and Atli, 2003; Farkas et al., 2003). Body size, in particular, has been shown to have a potentially strong effect on concentrations in muscle and other fish tissues and organs (e.g. Canli and Atli, 2003; Farkas et al., 2003; Yi and Zhang, 2012; Noël et al., 2013).

This study was undertaken to determine the trace metal contamination in fish from the Llobregat River, a good example of human-impacted watercourse, characterized by Mediterranean regime, regulated by three large dams located in its upper basin. Contaminants of urban, industrial and agricultural origin occur in the lower course of the Llobregat, when the river flows through the Barcelona conurbation. While being characterized by moderate metal pollution in all sites investigated, a slight upstream–downstream heavy-metal pollution gradient was found, based on water and sediment concentrations (Table 1). Aluminum, arsenic, cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc were the target of our research because of their extensive presence in the Llobregat (Guasch et al., 2010) The sampling sites (Fig. 1) have been studied previously (e.g. Muñoz et al., 2009; Ginebreda et al., 2010; Ricart et al., 2010; Sabater et al., 2012). Site LL1 (Pont de Vilomara) is the least contaminated, situated upstream of the confluence with the Cardener river; site LL2 (Castellbell i el Vilar) receives some industrial effluents and surface runoff from agricultural areas; sites LL3 (Abrera) and LL4 (Martorell) are located in a densely inhabited area and receive urban and industrial wastewater inputs.

We analyzed the relative contribution of fish size and species, on muscle trace metal concentrations, in order to test whether the concentration–fish size relationship was consistent among sites and species. Negative relationships between fish size and muscle metal burden have been described (e.g. Canli and Atli, 2003; Farkas et al., 2003; McKinley et al., 2012) even though these relationships may be affected by the seasonal variation of fat content in the fish muscle (Farkas et al., 2003). We hypothesized that the environmental concentrations of heavy metals would affect the heavy metal concentrations in fish tissues. Since differences in heavy metal concentration between sites were low (Table 1), similar muscle loads were expected for each species along the river course, particularly for essential metals, whose excretion should be more efficient. We also expected higher

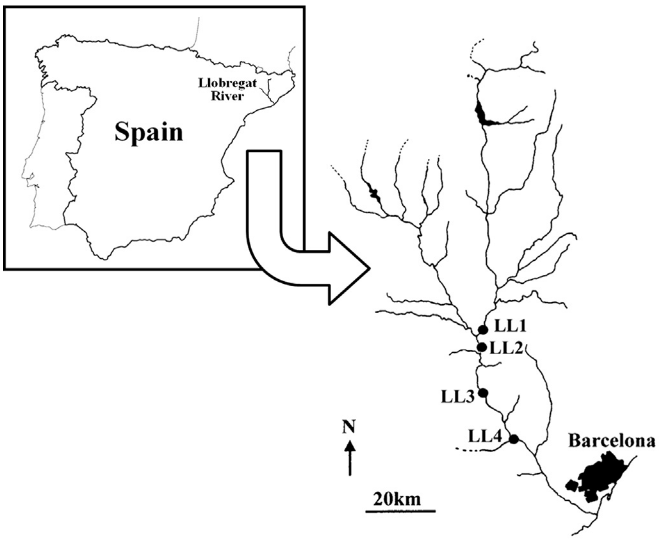

Fig. 1. Study area and sampling sites (LL1–LL4) in the Llobregat River basin, NE Spain (see text for further details).