Preliminary assessment and biological impact of trace metal pollution in Piles River (Spain)

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ABSTRACT

We have analyzed the contents of copper, lead and cadmium in water, sediments and eel populations of Piles river in an upstream rural area and a downstream urban area. All heavy metals were determined by an electrochemical method (PSA). Sediment analyses showed that concentrations of these heavy metals in the samples from rural upstream were higher than those from urban downstream, suggesting that the main source of metal pollution in Piles river was originated by agricultural activities. There were significant correlations between copper, lead and cadmium concentrations in eel livers and sediments. For those metals, eels have proven to be a good indicator of aquatic environment pollution.

1. INTRODUCTION

Heavy metals today have a great ecological significance due to their toxicity and accumulative behaviour (Purves[1]). These elements, contrary to most pollutants, are not bio-degradable and undergo a global eco-biological cycle

(Nurnberg[2]) in which natural waters are the main pathways. They are a serious problem because, as opposed to other pollutants (particularly organic), they do not decompose or get eliminated from ecosystems. Elevated levels of trace metals in natural systems can be derived from a number of sources and pose a severe threat to the local aquatic environment (Forstner and Wittmann[3]). Although there is a need for source assessments of trace metal pollutants entering local river systems, they have not been sufficiently addressed to date.
In this work we try to illustrate the effects that agricultural and urban activities can have on a freshwater system by studying Piles river at an agricultural area located upstream and an urban area located downstream. Concentrations of copper, lead and cadmium in water and sediments were determined. Concentrations of those heavy metals in eel populations from Piles river were also analyzed. Correlations between concentrations of copper, lead and cadmium in these organisms, water and sediments are discussed.

2. MATERIAL AND METHODS

Piles river was sampled at two different sites. Caldones site, located upstream in an agriculture area; and Viesques site, located downstream in an urban area. Two samples of water and sediments were taken at each of the two points of Piles river during July of 1994. Twelve fishes (*Anguilla anguilla*) were caught at each site by electric fishing. Copper, lead and cadmium concentrations were determined in every case by means of Potentiometric Stripping Analysis (PSA).

2.1 Determination of metals in river water

Water samples were taken 10 cm below the river surface. Temperature, conductivity and dissolved oxygen were determined in the field. Upon return to the laboratory, pH was determined and water samples were filtered under vacuum through Whatman nylon filters of 0.45 μm pore. Filtered river waters were acidified with concentrated nitric acid to pH 2 and stored until analyzed.

2.2 Determination of metals in sediments

Sediment samples were collected using a core sampler to a depth of approx. 10 cm. At each site, two replicate samples of sediments were collected and kept frozen until analysis. Core sediment samples were separated into two fractions: top layer (0-3 cm) and bottom layer (7-10 cm). 20 g of each fraction were dried at 105°C for 24 hours. Particles larger than 2 mm were eliminated and fractions were disaggregated in a glass mortar and pestle. Fractions were finely ground, taken to dryness and 1 g was digested in Teflon reactors with 5 ml of concentrated nitric acid/perchloric acid (3:1) for 7 minutes using a microwave oven. Once cooled, the solution was transferred to a 20 ml flask. The flask was levelled off and the mineralized residue, which does not interfere in the determination of the metals was allowed to settle.

2.3 Determination of metals in eels

Caught eels were weighed and standard lengths were recorded. Eel livers were removed, weighed and dried at 105°C for 24 hours. Dried livers were weighed and digested in Teflon reactors with 5 ml of concentrated nitric acid/perchloric acid (5:1) for 7 minutes using a microwave oven. The contents of the reactor were transferred to a volumetric flask and levelling off at 20 ml for subsequent analysis.

3. RESULTS AND DISCUSSION

3.1 Metals in Piles river water

Piles river flows through the town of Gijón and is polluted by agricultural and municipal effluents. Samples were collected at two different sites: Caldones site, located upstream in an agricultural area; and Viesques site, located downstream in an urban area. The sampling sites were selected to provide information on the relative contribution of agricultural activities and urban activities to the heavy metal pollution of the river. As can be seen in figure 1, the concentrations of copper, lead and cadmium in Piles river water do not indicate significant pollution, being close to unpolluted rivers found in the literature (Herbert L. et al.[4]). Copper concentrations were below 3.5 μg/l with almost the same concentration in both sampling sites. Lead concentrations were below 4.5 μg/l, the downstream site, Viesques, showed a higher concentration than the upstream site, Caldones. Cadmium concentrations were below 1.0μg/l, being higher in the upstream site. The cadmium concentrations obtained may be considered very low which confirm the non-pollution by cadmium of the river. Water analysis showed minor differences between the urban and agricultural areas of Piles river.

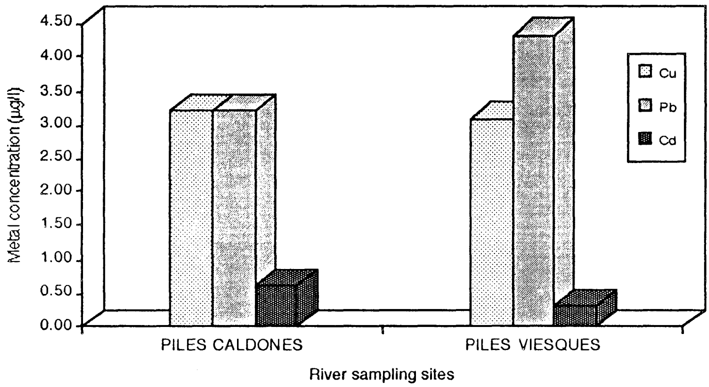

Figure 1. Copper, lead and cadmium concentrations in Piles river water.

3.2. Metals in river sediments

It has been reported that sediment analysis can be very useful for identifying sources of water pollution (Forstner and Wittman[3]). Figure 2 shows the concentrations of copper, lead and cadmium found in the analysis of sediments from the two river sampling sites. Copper concentrations were below 12 μg/g dry wt, lead concentrations below 28 μg/g dry wt and cadmium concentrations below 0.3 μg/g dry wt. Trace metal concentrations in sediments from the upstream sampling site were higher than those from the downstream sampling site. The analysis of sediments showed that the concentration of copper, lead and cadmium in samples from the rural upstream area, which is affected by agricultural effluents, are higher than those from urban downstream. The main source of heavy metal pollution in Piles river seems to be rural. Urban water discharges, which appear to have less concentration of heavy metals, occur

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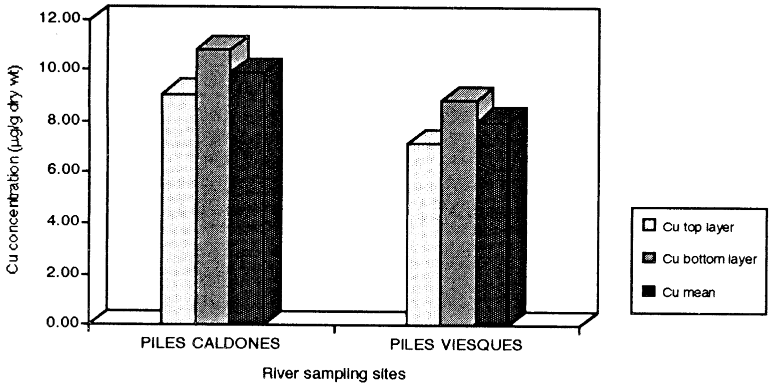

Figure 2a. Copper concentrations in top and bottom sediment layers from Piles river.

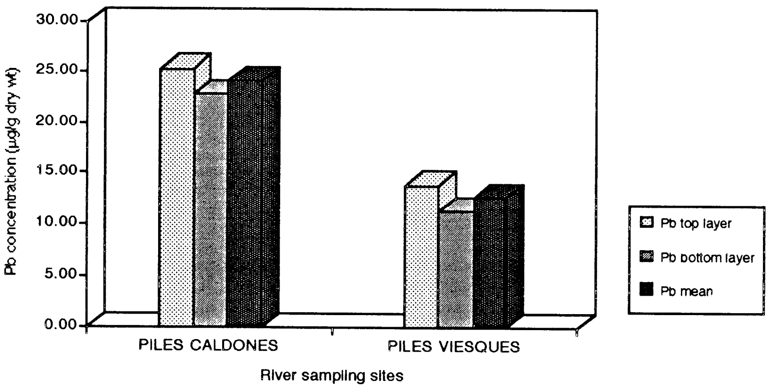

Figure 2b. Lead concentrations in top and bottom sediment layers from Piles river.

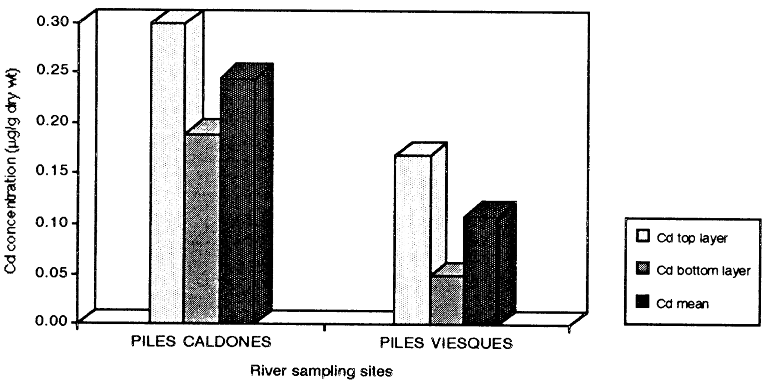

Figure 2c. Cadmium concentrations in top and bottom sediment layers from Piles river.

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between the upstream and donwstream sampling sites, thus lowering the concentration of heavy metals downstream as it is reflected in the sediment analyses. Sediment analysis hase provided a better tool for monitoring metal pollution in freshwater systems than water analysis, as it is widely reported in the literature (Forstner and Salomons[5]).

Vertical sediment profiles (core) also are useful, because they often uniquely preserve the historical sequences of pollution intensities, and at the same time they enable a reasonable estimation of the background level (Salomons and Forster[6]). Both sampling sites showed the same vertical sediment (core) profile. As expected, the top sediment layer (0-3 cm) contained higher levels of cadmium and lead than the bottom sediment layer (7-10 cm); however copper was more concentrated in the bottom sediment layer than in the top sediment layer. The geochemical behaviour of copper appears to be different, leading to a different sediment profile in the sediment fractions.

3.3 Metals in eel livers

This study was undertaken to determine the relationship between river metal content and its effects in fish populations. Eels were chosen because they are the most abundant fishes in Piles river. Analyses were carried out in livers because this tissue has proven to be the best indicator of exposure to heavy metals (Miller P.A. et al.[7]).

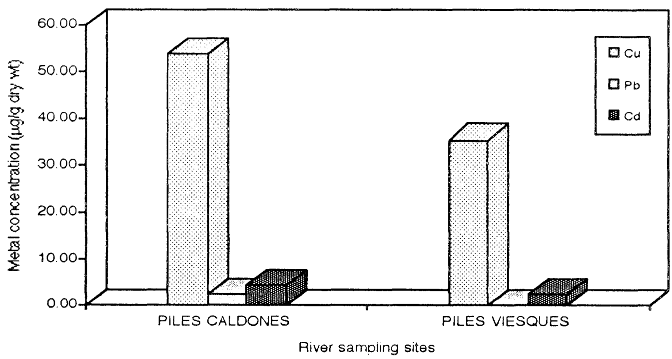

Figure 3. Average copper, lead and cadmium concentrations in eel livers from Piles river.

Average copper, lead and cadmium concentrations in eel livers from Piles river are shown in figure 3. Copper was the highest concentrated metal in eel livers, average copper concentrations were 53 µg/g dry wt (eels from the upstream site) and 36 µg/g dry wt (eels from the downstream site). Lead and cadmium concentrations were much lower, below 5 µg/g dry wt. Eel livers from the upstream site had higher copper, lead and cadmium concentrations (1.6 times higher) than eel livers from the downstream site. Water quality objectives use waterborne metal concentrations as indicator of impacts in aquatic life. Sediments, however, represent the most concentrated pool of metals in aquatic environments, metals that can be assimilated by the aquatic organisms (Luoma[8]). From the analysis of sediments we have found that the level of heavy metal pollution was higher upstream than downstream in Piles river. In the same fashion, eel livers from the upstream site contained higher heavy metal concentrations than eel livers from the downstream site. Therefore, results from the analysis of eel populations showed a remarkable correlation with sediment analysis. The concentrations of copper, lead and cadmium in eel livers were reliable indicators of chronic copper, lead and cadmium exposure. The analysis of eel populations has proven to be a good predictor and bioindicator of heavy metal environmental exposure, enabling a reasonable estimation of metal pollution gradients.

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