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Remediation of a watershed contaminated by heavy metals: A 2-year field biomonitoring of periphytic biofilms

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ABSTRACT

This study focuses on an industrial contamination site subjected to remediation processes since 2007 in the Riou-Mort watershed (southwest France). The purpose was to assess the first impacts of remediation on periphytic biofilms, and was performed during two years of biomonitoring. Periphytic biofilms were collected on glass slides immersed 24 days at different sites along the contamination gradient for 12 colonisation cycles. Metal contaminations (Cd and Zn) were analysed in biofilms and the evolution of diatom communities was assessed, integrating teratology quantifications. Despite remediation work initiated at the industrial site, this study demonstrated the persistence of metal contamination in water, as well as in biofilms. In addition, our data, showed that the remediation process was initially marked by an increase in metal contamination in the river, with increasing diatom community shifts. Metal-contaminated biofilms presented decreasing species diversities and were dominated by metal-resistant species such as *Eolimna minima*, whom abundances increased in 2010 reaching $57.2 \pm 10\%$. No significant decrease in metal accumulation was observed and total Cd content in biofilms collected downstream the industrial site ranged from 772.7 ± 88 in July 2009 to 636.9 ± 20 μg/gDW in July 2010. Results obtained on artificial substrates were compared with those of natural substrates and showed similar diatom communities and abundances of deformed diatoms but lower diversities. This ensured that glass slide subtrates gave a good representation of periphytic biofilm health. Finally, results were compared to studies performed before the remediation process and this did not reveal a decrease of metal accumulation in biofilms nor shifts in taxonomic composition of the communities, rather the remaining dominance of metal resistant species such as *E. minima* was confirmed.

1. Introduction

Lot River contamination was highlighted early in the 1970s by the National Observation Network. It revealed very high cadmium (Cd) concentrations in bivalves collected downstream in the Gironde estuary, which proved in fact to be the most contaminated along the European coastline. The main source of Cd was identified in the upper part of the Lot River (Latouche, 1992), in a small Lot tributary (the Riou-Mort River) draining a waste area of a now-abandoned factory previously specialised in zinc (Zn) ore treatment, which had been active for over a century, from 1842 to 1987. A first attempt at remediation was undertaken in 1971, by collecting and treating the water drained from the slag heap. This process was completed in 1987 by confining a part of the waste deposits in storage basins with underlying and overlying mud (Audry et al., 2004). Thus, flux of dissolved Cd emitted from the industrial site declined from 25 to 30 t/year in the early 80s to 0.6 to 1.5 t/year in 2007, according to self-monitoring by the industry. Nevertheless, large parts of metal wastes were still insufficiently confined and exposed to erosion and leaching (Audry et al., 2004; Coynel et al., 2007), and the metal contamination remained very high. Several studies have already focussed on the impact of metals on periphytic biofilms in this field site before remediation (Duong et al., 2008; Gold et al., 2002; Morin et al., 2008a). They demonstrated strong bioaccumulation and diatom community shifts induced by metal discharges into the Riou-Mort River and its tributary the Riou-Viou River.

Biofilm consists of attached algae, bacteria, and associated detrital material that adheres to substrates in water (Horne and Goldman, 1994). Their benthic position favours the integration of local environmental conditions and their short life cycle enables them to respond more rapidly to environmental changes than higher level organisms (Gold et al., 2002). Since many compounds can be bioaccumulated by biofilm components, they are considered good bioindicators of freshwater quality at the community scale (Coste et al., 2008; Duong et al., 2008; Lavoie et al., 2006). In addition, diatoms respond

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to perturbation both at the community level and at the individual level, with alterations of frustule morphology that have often been associated with high metal concentrations (Cattaneo et al., 2004b; Falasco et al., 2009a; Morin et al., 2008b).

The Water Framework Directive has classified Cd among the priority substances for which no release should exist by 2015. However, natural recovery process can take years (Keller et al., 1998) and thus more human intervention may be necessary to restore this habitat. In this context, in 2007 major remediation processes were initiated around the industrial watershed. The current industrial operator has proposed to excavate metal residues and to store them on a site compliant with the environmental requirements for hazardous waste storage. This remediation process requires monitoring studies to evaluate progress in remediation efforts and to identify potential environmental benefits of remediation.

The purpose of this study was to follow metal contaminations (Cd and Zn) in biofilms and to study the evolution of diatom communities over two years, to assess the first impacts of this major remediation on periphytic biofilms. Periphytic biofilms were used as models because they are widely distributed and they occupy an essential position at the base of the aquatic food web in many freshwater environments; thus they are an indicator of metal transfer through the food web (Farag et al., 2004; Rhea et al., 2006). Biofilms were collected after 24 days of colonisation on bare glass slides immersed in the rivers. The process was renewed every 48 days for 12 periods in 2009 and 2010. Metal accumulation in the biofilms as well as diatom community structure were characterised, in order to i) assess spatio-temporal variability over the two-year survey, ii) compare these results with previously recorded data and assess the impacts of the remediation process. Glass slides provided inert substrates for biofilm growth and allowed between-site comparisons due to standardised substrate area and colonisation duration. Additionally, we compared the results from biofilms collected on glass slides with those from natural substrates to validate their use in bioassessment.

2. Material and methods

2.1. Study sites along the contamination gradient

Four sites were studied in the industrial basin of Decazeville (watershed area: 155 km²), located in South-West France (44°N/2°E). This industrial area is characterised by high Cd and Zn contamination originating from a factory which has treated Zn ore for over a century. Contaminated discharges directly percolated into the Riou-Viou River, where it crosses the industrial site, until the end of the 1980s. Although industrial activity stopped in 1987, the waters are still Cd- and Zn-enriched leading to a decreasing contamination gradient downstream from the Riou-Mort River to the Lot River (Fig. 1).

The four biomonitoring sites were located along the contamination gradient and biomonitoring was conducted here for two years (2008–2010). The reference site (Firmi) was located in the upstream zone of the Riou-Mort River and was characterised by very low background metal contamination. The second site was also considered unimpacted (Decazeville); it was located on the Riou-Mort River just upstream from the industrial zone and was slightly impacted by metal discharges but subject to urban wastes. The third site was on the Riou-Viou River (Moulin), a few kilometres upstream from the factory, and presenting concentrations in the water column close to lithology-dependent background concentrations (Coynel et al., 2009). The most contaminated site (Joany) was located downstream from the factory, about 3 km from its confluence with the Riou-Viou River, and was characterised by high average concentrations of Cd and Zn, 90–95% originating from industrial components (Coynel et al., 2009), and subjected to urban waste discharges.

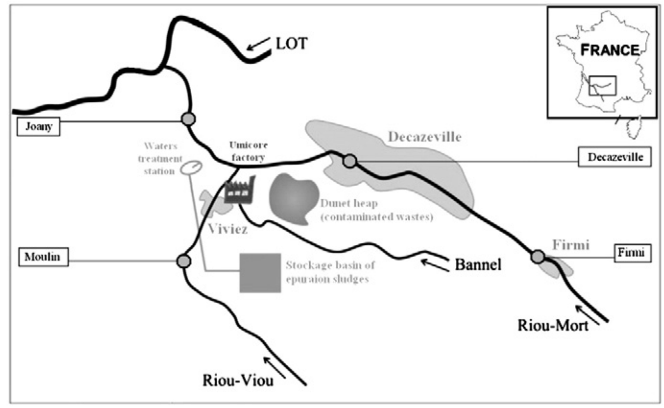

Fig. 1. Location of the rivers and of the four sampling sites along the pollution gradient.

2.2. Colonisation and sampling of periphytic biofilms

The biomonitoring lasted two years. The first year (November 2008 to October 2009) consisted of consecutive cycles of 24-day colonisation periods: 24 days after each biofilm sampling, a new colonisation cycle was launched leading to consecutive colonisation cycles every 48 days. Then, after a break of six months, during winter when effects were expected to be less marked, the monitoring started again from April until October 2010. Therefore, the first year contained eight and the second year four colonisation cycles, but because of vandalism, glass slides could not be sampled for one cycle: July 2010.

For each colonisation cycle, plastic racks containing 12 slides were immersed in the water column at each site for 24 days as described in Arini et al. (2011). The glass slides were used as artificial substrates for biofilm growth (total surface area reaching 450 cm²). After the 24-day immersion, the racks were removed from the rivers. At each site, three replicates of two slides were collected randomly and biofilm scraped using a cutter blade. Each biofilm replicate was then suspended in 200 mL of mineral water. A biofilm fraction from each site (5 mL) was preserved with 1 mL of formalin solution (Formaldehyde 37%, Prolabo, France) for diatom counting and identification. The rest of biofilm suspensions was kept at 4 °C in the dark before metal analyses.

In parallel, natural substrates were collected at each sampling time. A total of five independent substrates chosen randomly were scraped and pooled as one sample per site. Like biofilms from artificial substrates, samples were preserved with 1 mL of formalin solution before analyses.

Hydrological data were available for the Joany station at www.hydro.eaufrance.fr.

2.3. Measurements of physicochemical parameters

2.3.1. Environmental variables and nutrient concentrations

On each occasion (installation and collection of the racks), water temperature, pH, conductivity and dissolved oxygen were measured at the four sites using a multi-probe analyser (WTW, Weilheim, Germany).

One litre of river water was collected at the end of each colonisation cycle to analyse phosphorus, ammonium, nitrite and nitrate concentrations in the laboratory. Nitrogen forms were measured by a continuous flow analyser, and phosphorus by colorimetric assay read by a spectrophotometer. Protocols followed French and international standards (NF T90-023, NF T90-007, NF EN ISO 11732 and NF EN ISO 13395, respectively).

2.3.2. Metal concentrations in the rivers

Trace metal analyses were performed with water samples acidified with 10% ultrapure HNO_3 (Merck, Darmstadt, Germany). Total-Zn concentrations were measured using flame atomic absorption spectrometry (Varian, AA20, Australia), with a detection limit of 10 µg Zn/L. Total-Cd concentrations were measured by atomic absorption spectrometry