Pollution in Mediterranean river ecosystems of the Iberian Peninsula: effects on benthic communities

Mélange de contaminants dans les écosystèmes lotiques méditerranéens dans la Péninsule Ibérique : effets sur les communautés benthiques (biofilms).

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RÉSUMÉ

Nous avons examiné la présence de produits pharmaceutiques et métaux lourds, et leurs effets sur les communautés de biofilms dans quatre grands bassins fluviaux méditerranéens (Llobregat, Ebre, Júcar et Guadalquivir) dans la Péninsule Ibérique. Cinq sites ont été sélectionnés dans chaque rivière. Dans tous les sites, nous avons analysé l'occurrence de 81 composés pharmaceutiques (dans l'eau et les sédiments) ainsi que des métaux lourds dans l'eau et les communautés de biofilms). Plusieurs indicateurs ont été mesurés sur les composantes algales et bactériennes des biofilms fluviaux. La teneur en métaux lourds (Mn, Fe, Co, Ni, Cu, Zn, As et Pb) dans l'eau et le biofilm (bioaccumulation) indique un gradient amont-aval dans tous les systèmes fluviaux. Le Guadalquivir et Llobregat ont les plus fortes concentrations de métaux lourds, suivie par l'Ebre et le Júcar. Les plus fortes concentrations de produits pharmaceutiques dans l'eau ont été détectées dans le Llobregat, suivi par l'Ebre, Júcar et du Guadalquivir. Les produits pharmaceutiques avec les plus fortes concentrations sont les agents de contraste aux rayons X, les composés pour traiter l'hypertension, des analgésiques et des anti-inflammatoires. Les analyses multivariées reliant variables biologiques et polluants ont révélé une interaction potentielle entre les métaux (As et la bioaccumulation de Cu) et des métriques biologiques. Certains effets des produits pharmaceutiques dans les aspects structuraux et fonctionnels de la communauté de biofilm pourraient être déduits de ces relations.

ABSTRACT

We examined the presence of pharmaceutical products and metals, and their effects on biofilm communities in four Mediterranean large river basins (Llobregat, Ebro, Júcar and Guadalquivir) in the Iberian Peninsula. Five sites were selected in each river. In all the sites we analysed the occurrence of 81 pharmaceutical compounds (in water and sediment) as well as heavy metals (in water and biofilm communities). Several metrics were measured related to both the algal and bacterial components of fluvial biofilms. Heavy metal content (Mn, Fe, Co, Ni, Cu, Zn, As and Pb) in water and biofilm (bioaccumulated) showed an upstream-downstream gradient in all the river systems. The Guadalquivir and Llobregat had the highest concentrations of heavy metals, followed by Ebro and Júcar. The highest concentrations of pharmaceuticals in water were detected in the Llobregat, followed by Ebro, Júcar and Guadalquivir. The pharmaceutical with the highest concentrations were the x-ray contrast media, the compounds to treat hypertension and analgesics and anti-inflammatory products Multivariate analyses using the biological and pollutant variables revealed a potential relationship between metals (As and bioaccumulation of Cu) and the biofilm metrics. Certain effects of the pharmaceutical compounds in both structural and functional aspects of the biofilm community could be inferred from these relationships.

KEYWORDS

Biofilm communities, metals, multivariate analyses, pharmaceutical compounds.

INTRODUCTION

The levels of organic compounds found in surface waters have increased in the recent decades as a result of human activities. Of these compounds, pharmaceuticals are one of the most commonly detected in flowing waters, and particularly in the lower sections of large rivers. These compounds reach river waters as a result of an incomplete removal during wastewater treatment processes (Farré et al., 2008). Aquatic environments are also often exposed to the presence of heavy metals, from a variety of anthropogenic sources (urban, industrial and agricultural) (Corcoll et al., 2011). Biofilm communities in rivers are exposed to varying environmental conditions, which become mixed with chemical stressors and difficult assigning the specific effects of pollutants (Ricart et al., 2010).

The Llobregat River is one of Barcelona's major water resources, but polluted by industrial, agricultural and urban wastewaters. The Ebro River is the most important Mediterranean river in the Iberian Peninsula, with the highest discharge volume. It has been largely regulated by dams and channels. The regulation, irrigation and industrial activities around the main cities have deteriorated soil and water quality, where pollution is relevant. The Jucar River is located in a semiarid zone with an intensive water use that has lead to an overregulation of the system. Urban, industrial and agricultural pressure increases (and water quality decreases) downstream. The Guadalquivir river receives many inputs, from both natural and anthropogenic origin, that cause deterioration of water quality. The lower part of the river is also impacted by reservoirs and dams and its regime is rather artificial. Several pharmaceutical products and metals have been reported in the lower parts of Mediterranean river systems, which could represent a threat to biofilm communities.

Toxic effects on biofilms in Mediterranean river are associated to water scarcity (that leads to low dilution capacity and higher concentrations of pollutants). Our objectives were to identify the effects of pharmaceutical products and metals in four typical Mediterranean basins using biofilm communities, as well as to identify relevant community metrics indicative of these stressors.

1 METHODS

Five sites were selected in each river, where we analysed the occurrence of pharmaceuticals (in water and sediment) and metals (in water and bioaccumulated in biofilm communities). 81 pharmaceutical compounds were analysed. These were analgesics and anti-inflammatories, antibiotics, anticoagulants, lipid regulators, histamine H1 and H2 receptor antagonists, β-blockers, to treat hypertension, diuretics, anti-diabetics, x-ray contrast media, psychiatric drugs and veterinary pharmaceuticals. Metals analysed were Mn, Fe, Co, Ni, Cu, Zn, As and Pb.

Biofilm samples were collected and several metrics related to both the algal and bacterial components of the community were measured: photosynthetic parameters (Photosynthetic efficiency, photosynthetic capacity, photochemical quenching and non-photochemical quenching), algal biomass (measured as chlorophyll-a content), antioxidant enzyme activities (catalase, ascorbate peroxidase, superoxide dismutase and glutathione reductase), extracellular enzyme activities (β-Glucosidase and phosphatase) and bacterial abundance.

2 RESULTS AND DISCUSSION

Water metal content showed an upstream-downstream gradient in all the river systems. The Guadalquivir and Llobregat rivers were the most polluted, followed by Ebro and Júcar. Metal bioaccumulation in the biofilm followed the same pattern (Fig. 1).

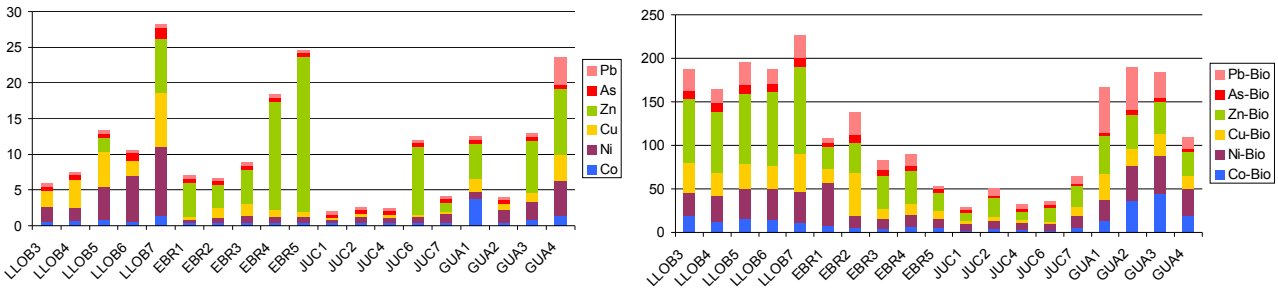

Fig. 1. Metals dissolved in water (µg/L) and bioaccumulation of metals on biofilm communities (µg/g DW)

The highest concentrations of pharmaceuticals in water were detected in the Llobregat River, especially at the mouth of the river. The x-ray contrast media and the compounds to treat hypertension had the highest values. The Ebro River also had very high concentrations of compounds. X-ray contrast media and analgesics and anti-inflamatories were the most abundant. The Júcar and Guadalquivir were the rivers showing the lowest concentrations of pharmaceuticals. Veterinary pharmaceuticals and psychiatric drugs were the families with highest values in the Júcar River, whereas compounds to treat hypertension and analgesics and anti-inflamatories registered the highest values in the Guadalquivir River (Table 1).

Table 1. Maximum and minimum values of the families of pharmaceutical products analysed in water (ng/L): bdl: below detection limit

	Llobregat		Ebro		Júcar		Guadalquivir	
	Max	Min	Max	Min	Max	Min	Max	Min
Analgesics and anti-inflammatories	486.8	76.9	106.8	16.8	10.2	5.3	34.8	8.3
Antibiotics	254.8	24.4	32.5	13.2	3.6	2.7	15.3	3.2
Anticoagulants	18.6	4.9	3.8	0.2	0.9	0.7	1.4	0.7
Lipid regulators	335.7	25.6	28.4	1.5	6.9	4.6	12.9	3.8
Histamine H1 and H2 receptor antagonists	24.2	3.9	6.4	3.7	5.2	4.9	5.3	4.9
B-blockers	415.7	10.2	23.7	15.9	5.1	4.7	5.9	4.7
To treat hypertension	664.4	95.8	177.1	38.4	14.8	12.9	79.2	14.1
Diuretic	136.9	38.7	41.2	15.6	1.6	1.5	31.4	0.4
Anti-diabetic	50.5	1.1	1.1	0.7	1.9	1.8	1.8	0.7
X-ray contrast media	1370.4	0.5	69.3	0.2	1.3	bdl	1.4	bdl
Psychiatric drugs	416.9	80.6	41.6	11.4	10.8	9.1	22.1	10.7
Veterinary pharmaceuticals	41.4	7.6	10.6	3.2	19.9	6.9	9.6	4.1

Multivariate analyses revealed that both physical and chemical parameters and metal pollution were influencing the biofilm community. The total variance explained was 80%. In terms of physical and chemical variables, soluble reactive phosphorus and conductivity had a significant effect on the biofilm responses, explaining a 9.2% of the variance. Metals alone accounted for 22.7% of the explained variation, with the bioaccumulation of copper and the presence of arsenic in water being the two statistically significant variables. Shared variance represented 48.1%.

Soluble reactive phosphate and conductivity described a downstream gradient of eutrophication for all the rivers. Downstream sites were also characterised by high algal and bacterial biomass, as well as high values of photosynthetic efficiency. Metal pollution described a gradient in which the sites with high content of metals had lower algal biomass and photosynthetic efficiencies but high detoxification capacity (increase of catalase antioxidant enzyme activity).

3 CONCLUSION

Several pharmaceuticals and metals were found at higher concentrations in the studied rivers than in others reported in the literature. Our results reveal a potential causal relationship between pollutants and several biofilm community metrics. Although our assessment has been based on field data and needs to be complemented with laboratory experiments in order to assign causality, it provides evidence on how metals and pharmaceutical products disrupt biological communities in large Mediterranean rivers.

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