Journal of Hydrology 383 (2010) 52–61

Contents lists available at ScienceDirect

Journal of Hydrology

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

Primary and complex stressors in polluted mediterranean rivers: Pesticide effects on biological communities

Marta Ricart [a,c,*], Helena Guasch [a], Damià Barceló [b,c], Rikke Brix [b], Maria H. Conceição [d], Anita Geiszinger [a], Maria José López de Alda [b], Julio C. López-Doval [e], Isabel Muñoz [e], Cristina Postigo [b], Anna M. Romaní [a], Marta Villagrasa [b,c], Sergi Sabater [a,c]

[a] Institute of Aquatic Ecology, University of Girona, Campus Montilivi, 17071 Girona, Spain
[b] Department of Environmental Chemistry, IDAEA, CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain
[c] Catalan Institute for Water Research (ICRA), Parc Científic i Tecnològic de la Universitat de Girona, Edifici Jaume Casademont, C/ Pic de Peguera, 15, 17003 Girona, Spain
[d] Faculdade UnB-Ceilândia, Universidade de Brasília, QNN 14 Area Especial, Guariroba, 71906-500 Brasilia, DF, Brazil
[e] Department of Ecology, University of Barcelona, Av. Diagonal 645, 08028 Barcelona, Spain

ARTICLE INFO

Keywords:
Llobregat river
Pesticides
Diatoms
Invertebrates
Biofilm metrics
Multivariate analysis

SUMMARY

We examined the presence of pesticides in the Llobregat river basin (Barcelona, Spain) and their effects on benthic biological communities (invertebrates and diatoms). The Llobregat river is one of Barcelona's major drinking water resources. It has been highly polluted by industrial, agricultural, and urban wastewaters, and—as a typical Mediterranean river—is regularly subjected to periodic floods and droughts. Water scarcity periods result in reduced water flow and dilution capacity, increasing the potential environmental risk of pollutants. Seven sites were selected, where we analysed the occurrence of 22 pesticides (belonging to the classes of triazines, organophosphates, phenylureas, anilides, chloroacetanilides, acidic herbicides and thiocarbamates) in the water and sediment, and the benthic community structure. Biofilm samples were taken to measure several metrics related to both the algal and bacterial components of fluvial biofilms.

Multivariate analyses revealed a potential relationship between triazine-type herbicides and the distribution of the diatom community, although no evidence of disruption in the invertebrate community distribution was found. Biofilm metrics were used as response variables rather than abundances of individual species to identify possible cause-effect relationships between pesticide pollution and biotic responses. Certain effects of organophosphates and phenylureas in both structural and functional aspects of the biofilm community were suggested, but the sensitivity of each metric to particular stressors must be assessed before we can confidently assign causality. Complemented with laboratory experiments, which are needed to confirm causality, this approach could be successfully incorporated into environmental risk assessments to better summarise biotic integrity and improve the ecological management.

Introduction

The levels of organic compounds found in surface waters have increased in the recent decades as a result of human activities. Of these organic compounds, pesticides are most commonly detected in flowing waters (Azevedo et al., 2000; Quintana et al., 2001; Nakamura and Daishima, 2005; Sáenz and Di Marzio, 2009). These compounds (insecticides, herbicides, fungicides, etc.) are mainly used for agricultural purposes. They enter the aquatic environment via runoff after being sprayed in agricultural fields and can potentially reach groundwater. They are also used in non-agricultural applications, such as weed control on railways, roads and golf courses (Planas et al., 1997), algaecides in paints, and protective agents in flat roof sealing (Rodríguez-Mozaz et al., 2004).

The contamination of water resources by pesticides has resulted in the publication of several regulatory documents. For example, the European Water Framework Directive, WFD, (Directive 2000/60/EC) requires a good ecological status for all European river systems by 2015. To achieve this goal, aquatic communities must be protected from chemical stress, which at the very least will require a progressive reduction in the influx of priority substances into European river systems.

Various pesticides are currently included in the list of priority substances (Decision 2455/2001/EC) and the European Union has recently established environmental quality standards (EQS),

* Corresponding author. Address: University of Girona, Faculty of Sciences, Avinguda Montilivi s/n, 17071 Girona, Spain. Tel.: +34 972 418 811; fax: +34 972 418 153.
E-mail address: martarivi@gmail.com (M. Ricart).

0022-1694/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhydrol.2009.08.014

annual average (AA), and maximum allowable concentrations (MAC) for various priority pesticides (and other contaminants) in surface waters (European Parliament and Council, 2008). These EQS are very low for some compounds such as endosulfan (AA concentration of 5 ng L^{-1} in inland surface waters and 500 pg L^{-1} in other surface waters) but are less restrictive for other compounds such as alachlor, atrazine, diuron, and simazine, with AA concentrations of 0.3, 0.6, 0.2, and 1 g L^{-1}, respectively, in both inland and other surface waters (Directive 2008/105/CE).

The WFD also stipulates that biological assessment must be an integral part both of water quality monitoring and of the evaluation of ecosystem health.

Benthic communities in rivers are continuously exposed to varying environmental conditions, which affect both community structure and function (Sabater et al., 2007). However, the diversity of the substances potentially affecting these communities (e.g. nutrients, dissolved organic matter, and hazardous toxicants) and the variability of environmental conditions make it difficult to monitor the specific effects of certain toxicants and to differentiate them from the potential influences of other environmental parameters. Moreover, any disturbance in the river ecosystem might be buffered or enhanced by complex biological interactions (Geiszinger et al., 2009).

The Llobregat river is one of Barcelona's major drinking water resources (Catalonia, NE Spain). The major land use types in the study area (middle and lower sections of the river) are urban and industrial activities (38%) and farmlands (13%) (Muñoz et al., 2009). The Llobregat is highly polluted by industrial and urban wastewaters as well as by surface runoff from agricultural areas (Rodríguez-Mozaz et al., 2004). Nowadays, it receives inputs from various sewage treatment plants, which may be relevant during periods of water scarcity (Kuster et al., 2008a). These events result in reduced water flow and dilution capacity, increasing the potential environmental risk of pollutants to the immediate environment and potentially to the functioning of the entire ecosystem.

There has been a lot of research in recent decades aimed at developing methodological tools for bioassessment. Multivariate techniques (ter Braak and Verdonschot, 1995) have been widely used to assess the effects of pollution in aquatic ecosystems (Fore et al., 1996). These tools have been used to assess disturbance in the Llobregat and its tributary, the Anoia river, to determine potential relationships between the presence of pharmaceuticals and the structural composition of the biological communities (Muñoz et al., 2009).

The objective of the present work was to analyse the relevance of pesticides in the biological communities (benthic algae and invertebrate fauna) of a Mediterranean river basin, using multivariate analyses. Physical and chemical parameters were included in the data set, as well as the concentrations of 22 pesticides from seven chemical families found in water and sediment; both water and sediment can be sources of stress for benthic communities (Muñoz et al., 2009).

Several herbicides have been reported in the lower part of the Llobregat river (Planas et al., 1997; Lacorte et al., 1998; Kuster et al., 2008a), which could represent a toxicity threat to photosynthetic organisms. As micro-algae comprise the largest fraction of biofilm biomass in rivers (Stevenson, 1996), we hypothesised that biofilms would be affected by herbicides. However, whether the pesticides can affect other biological groups, and to which degree, remains unknown. This question is particularly relevant in Mediterranean river systems due to their high hydrological and chemical variability. The respective effects of the environmental factors and pollutants in the community structure may be reflected in changes in the abundance of different taxa. Currently, this is assessed using multivariate techniques and various community metrics. Each metric represents a unique ecosystem attribute that responds to stress in a predictable way (Karr, 1993). The ecological condition of a site is assessed by considering different metrics (Plafkin et al., 1989). Both approaches have been followed in this study.

Our objectives were: (i) to identify the effects of pesticides in a typical Mediterranean basin, in this case the Llobregat, using invertebrate and diatom abundances as indicators; (ii) to identify indicative community metrics of these stressors; and finally, (iii) to compare the sensitivity of these two approaches with the aim of contributing to the improvement of ecological management systems.

Materials and methods

Study site and survey design

The Llobregat river is 156.5 km long (Tomàs and Sabater, 1985) and drains a catchment area of 4948 km^2. It has two main tributaries, the Cardener and the Anoia. The geological substratum of this river is mainly calcareous (Sabater et al., 1987). The mean annual discharge in the Llobregat river is 14 $m^3\ s^{-1}$, though monthly values range from <2 to 130 $m^3\ s^{-1}$. In dry years, the number of days below the average water flow ranges from 70–85%. Mostly in autumn, the torrential rain events can derive in catastrophic floods (exceptionally accounting for up to 1500–2000 $m^3\ s^{-1}$; Llasat et al., 2001).

Periodic floods and droughts have led to frequent morphological disturbances in the river bed and its banks. This is particularly true in the lower part of the Llobregat where the riparian vegetation has disappeared. The aquifers located in the lower part of the basin are overexploited and since the river dries out every summer marine intrusion occurs into the aquifer. The ecological status of the Llobregat is also affected by the salt inputs deriving from the ancient salt mines of the Cardener watershed. This adds up to the high nutrient concentration and to the industrial and urban pollution reaching the river and the main tributary Anoia, causing a poor condition in the low part of the river.

There were seven sampling points selected along the watershed of the Llobregat. Four sites were established along the main course of the river (from its mid-to-lower part) and three sites from its tributary, the Anoia river (Fig. 1). The sites were selected in order to include a downstream pollution gradient. There were four samplings, which took place during two significant hydrological periods in the river system (spring and autumn 2005 and 2006). Water flow is usually low in spring (monthly average of 2.8–3.2 $m^3\ s^{-1}$ during the study period) and higher in autumn (monthly average of 5.7–6.6 $m^3\ s^{-1}$).

Physical and chemical parameters

Sampling parameters measured included oxygen (%), pH, conductivity, and temperature (WTW Meters, Weilheim, Germany), which were measured in the field during each sampling period. Water samples were collected in triplicate for nutrient analysis. Samples were filtered (Nylon Membrane Filters 0.2 μm, Whatman, Maidstone, UK) and frozen in the laboratory until analysis. Nitrate, sulphate, and chloride were determined by ion-chromatography (761 Compact IC, Metrohm, Herisau, Switzerland). Soluble reactive phosphorus (SRP) was determined according to Murphy-Riley's protocol (1992), while ammonium was measured following standard procedures (APHA, 1989).

Pesticides in water and sediment

A total of 22 pesticide compounds from seven chemical families were analysed in water and sediment. These families were triazines (deisopropylatrazine, desethylatrazine, simazine, cyanazine,