Science of the Total Environment 503–504 (2015) 58–68

Contents lists available at ScienceDirect

Science of the Total Environment

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

Pesticide monitoring in the basin of Llobregat River (Catalonia, Spain) and comparison with historical data

Ana Masiá [a,*], Julián Campo [a], Alícia Navarro-Ortega [b], Damià Barceló [b,c], Yolanda Picó [a]

[a] Food and Environmental Safety Research Group, Department of Medicine Preventive, Faculty of Pharmacy, University of Valencia, Av. Vicent Andrés Estellés s/n, 46100 Burjassot, Valencia, Spain
[b] Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research, IDAEA-CSIC, C/ Jordi Girona 18-26, 08034 Barcelona, Spain
[c] Catalan Institute for Water Research (ICRA), C/ Emili Grahit, 101, Edifici H2O, Parc Científic i Tecnològic de la Universitat de Girona, 17003 Girona, Spain

HIGHLIGHTS

- Occurrence of currently used pesticides was detected in the Llobregat River basin.
- Benzimidazoles, organophosphorus and ureas appeared frequently at high levels.
- Sediments and biota were contaminated primarily by organophosphorus (higher K_{ow}).
- Risk evaluation showed low chronic risk to algae and fish from pesticide residues.
- Historical data confirmed a background contamination in the last 20 years.

ARTICLE INFO

Article history:
Received 16 April 2014
Received in revised form 17 June 2014
Accepted 20 June 2014
Available online 14 July 2014

Keywords:
Water
Sediment
Fish
Spatial distribution
Temporal distribution

ABSTRACT

Through an extensive sampling in the Llobregat River basin, the presence of 50 currently used pesticides in water, sediment, and biota was assessed. Pesticides were detected primarily in water (up to 56% of the analytes), whereas their presence in sediments was more intermittent, and in biota was scarce. Those at high concentrations in water were the benzimidazoles (carbendazim in 22% of the samples up to 697 ng L^{-1}), the organophosphorus (malathion in 54% of the samples up to 320 ng L^{-1}), and the ureas (diuron in 54% of the samples up to 159 ng L^{-1}). However, this pattern differed in sediments and biota, which were contaminated primarily with organophosphorus (higher K_{ow}) (chlorpyrifos 93% of sediments up to 131 ng g^{-1}). According to the results of this study, pesticide residues in the Llobregat River basin do not seem to represent a high risk to biota, even though some algae and fish can be affected. Nevertheless, the monitoring program can be very useful to control the contamination of the river basin, as the availability of historical data on the basin confirmed background contamination in the last 20 years.

1. Introduction

The application of pesticides and other plant protection products can maintain high product quality by controlling insects and other plant pathogens that harm crops (Cooper and Dobson, 2007). On the other hand, water catchments are highly susceptible to contamination, because these chemicals have high potential to reach the aquatic environment after application, via runoff, agricultural storm-water discharges, and return flows from irrigated fields (Campo et al., 2013; Damasio et al., 2011). As a result, pesticides can remain in water, accumulate in sediment or bioaccumulate in biota, depending on their solubility, with potential to cause adverse effects on human health and the environment, even at low concentrations (Kuster et al., 2008).

To improve this situation, the European Union (EU) Water Framework Directive (briefly WFD) (Directive 2000/60/EC) establishes the bases to regulate the water resources with the objective of preserving, protecting, and improving their quality and sustainable use. The adopted Decision No 2001/2455/EC, sets up a list of 33 priority substances to be controlled, the third part of which are pesticides. Directive 2008/105/EC defines environmental quality standards (EQS), annual average (AA), and maximum allowable concentrations (MAC) in surface waters. Although various pesticides are currently included in the list of priority substances in the EU regulations, many others are still unregulated (Proia et al., 2013).

The Llobregat River is subjected to extensive urban, industrial, and agricultural activities, becoming a damaged river basin, where relevant concentrations of a broad range of organic pollutants occur in surface water and related compartments (Gonzalez et al., 2012; Koeck-Schulmeyer et al., 2011). At the same time, this river is also one of the most important sources of water in the area, serving several million inhabitants living in

* Corresponding author. Tel.: +34 963544118; fax: +34 963544954.
E-mail address: Ana.Masia@uv.es (A. Masiá).

http://dx.doi.org/10.1016/j.scitotenv.2014.06.095

Barcelona and in the metropolitan area (Paune et al., 1998). The Llobregat River basin has been the object of many published studies. According to a search carried out in ISI Web of Science, using the keyword 'Llobregat', there are more than 600 publications in the past year (2013). Most of these articles focused on surface and groundwater of the lower and medium parts of the river, which are the areas with the worst water quality. Many of them reveal the presence of organic micro-pollutants in wastewaters, surface and groundwater, and ultimately drinking water (Cespedes et al., 2005; Ginebreda et al., 2010; Guerra et al., 2010; Koeck-Schulmeyer et al., 2011, 2012; Kuster et al., 2008; Proia et al., 2013).

An extensive monitoring (including 50 pesticides) has been developed in two consecutive campaigns (2010–2011) in surface water, wastewater effluents, sediment, and biota samples along the entire course of the Llobregat River and its tributaries, with the purpose of establishing pesticide occurrence and distribution. The results obtained by this monitoring were compared with historical data gathered during other monitoring programs in this river basin to describe trends in water quality status and determine potential risks for human health. The added values of this study are the following: (i) although data on the occurrence of some of the studied pesticides in the Llobregat River are available, this is the first time that a so extensive number of pesticides (i.e. 50 active ingredients) is determined in the basin; (ii) three environmental compartments (i.e. water/sediment/biota) were studied for the first time, because most of the previous studies were restricted to water, and (iii) the contamination levels of the Llobregat River were reviewed only once, dealing with the presence and biological effects of any type of emerging contaminants (Gonzalez et al., 2012). Thus, it is also the first time that data related to pesticide occurrence in this river have been assembled and compared in a detailed way.

Furthermore, the results of this study can be widely applicable to other basins that follow the hydrological pattern of the Mediterranean rivers and suffer the increasing effect of climate change. The most representative areas with typical characteristics of the Mediterranean climate are countries bordering the Mediterranean Sea (Spain, Greece, Turkey, Morocco, Algeria, and Italy) as well as countries that have similar climate, such as South Africa, Chile, California, and Australia (Oliver et al., 2012; Delmotte et al., 2011; Daam et al., 2011; Kookana et al., 2010).

2. Material and methods

2.1. Site description

The Llobregat River (northeast of Catalonia, Spain), emerges in the pre-Pyrenees mountains at an altitude of 1400 m a.s.l. and flows along 150 km until its mouth in the Mediterranean Sea, 10 km south of Barcelona, draining an area of 4948 km^2 (Gonzalez et al., 2012). As a Mediterranean river, it presents flow fluctuations highly dependent on climatic conditions, including periodic floods and droughts related to seasons, in which the flow can range from several $m^3\ s^{-1}$ in periods of storms (i.e. normally in spring and autumn) to few $m^3\ s^{-1}$ during summer (dry period). It is also subjected to discharges from more than 30 wastewater treatment plants (WWTPs), which increase the flow river in dry periods, but reduce the dilution factor, compromising clearly water quality (Gonzalez et al., 2012). The river has around 40 tributaries, but the main ones are the Cardener (CAR) and Anoia (ANO) rivers. Both constitute a focus of pollution because of the important agricultural area (mainly vineyards in the Anoia River) and dense population with important demands of water (Gonzalez et al., 2012; Cespedes et al., 2005; Gonzalez et al., 2012; Proia et al., 2013). Close to its mouth, the Llobregat Delta, considered internationally important by the EU, represents the most valuable area from an ecological point of view because it constitutes the migratory route between Europe and Africa of more than 300 species of birds. The Delta is also a fertile area with an important agricultural activity focused on the cultivation of crops such as artichokes, lettuce, and tomatoes (Koeck-Schulmeyer et al., 2012).

2.2. Sampling and sample analysis

The sampling campaign was performed during 15 days in September/October 2010 and October/November 2011. For this purpose, a group of pesticides (as well as some of their common transformation products), from different chemical families were selected according to their extent of use in the studied area, water solubility, and amenability to liquid chromatography–mass spectrometry (LC–MS) analysis (see Table S-1). In the first campaign, 42 pesticides were determined, while in the second, 50. The pesticides added in the second campaign were frequently detected in some non-target analysis of water samples, revealing their constant presence (Masiá et al., 2013a).

Water and sediments were collected at 14 selected sites along the Llobregat River and its tributaries Anoia and Cardener (Fig. 1). Grab water samples (2 L) were collected in clean amber glass bottles, from the middle of the river width. Sediment samples (approx. 250 g) were taken in the same point as the water samples using a Van Veen grab sampler (0.5 L capacity); they were transferred and wrapped into an aluminum foil. Additionally, pesticides were analyzed in influent, effluent, and sludge samples from three waste water treatment plants (WWTPs), which flow into the river, to study the influence of the effluent discharges in the final water quality of the studied rivers. The selected WWTPs were Igualada (located in the Anoia River), Manresa (located in the Cardener River, close to its confluence with the Llobregat River) and Abrera (located in the lower part of the Llobregat River). WWTP samples were 24 h composite samples provided by the plant operators. Georeferences of all sampling points are shown in Table S-2.

Fish samples were taken only in 2010, according to the EQS (Directive, 2008/105/EC) at five selected sites of the river course: LLO3, LLO4, LLO5, LLO6, and LLO7. Fish samples were collected using electro-fishing by the personnel of Institute of Environmental Assessment and Water Research (IDAEA) in Barcelona, Spain and Catalan Institute for Water Research (ICRA) in Girona, Spain. The collected fish included adult and young barbus (*Barbus guiraonis*) taken at LLO3, LLO4 and LLO6 sites; black bass (*Mycropterus salmoides*) adult taken at LLO3 and common carp (*Cyprinus carpus*) taken in each biota sampling point. Concerning the extraction techniques, an already published SPE method (Oasis HLB SPE cartridge 200 mg sorbent/6 mL cartridge, Waters, Milford, MA, USA) was used for water samples (Masiá et al., 2013a). QuEChERS method (Anastassiades et al., 2003), also described in the literature, was applied in the sediment (Campo et al., 2013) and biota (Belenguer et al., 2014) samples. Detailed information on the methods is provided in Figs. S-1 and S-2 of the Supplementary material. Pesticides were determined by liquid chromatography–tandem mass spectrometry, using an HP1200 series LC system, equipped with automatic injector, degasser, quaternary pump and column oven, which was interfaced to an Agilent 6410 triple Quad (QQQ) mass spectrometer, with an electrospray ionization (ESI) interface (Agilent Technologies, Waldbronn, Germany) operating in positive ionization mode. Data were processed using a MassHunter Workstation Software for qualitative and quantitative analyses (A GL Sciences, Tokyo, Japan). Detailed instrumental and dynamic MRM conditions are provided in Tables S-3 and S-4 of the Supplementary material. The validation of the method is also fully described in the Supplementary material (see validation of the method and Table S-5). The limits of detection ranged from 0.01 to 2 ng L^{-1} for water, 0.03 to 1.67 ng g^{-1} for sediment, and 0.08 to 3.75 ng g^{-1} for fish. Recoveries at different concentrations were between 49 and 112% and RSDs $<$25%.

2.3. Quality control (QC)

Regarding the QC procedures, parameters such as laboratory and field blanks, matrix spikes, and triplicate samples were evaluated. Blank contamination is the most common problem observed in the determination of pesticides at trace levels. Thus, precautions were taken to prevent contamination from personnel, organic solvents, equipment,