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Pesticides in the Ebro River basin: Occurrence and risk assessment☆

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ABSTRACT

In this study, 50 pesticides were analyzed in the Ebro River basin in 2010 and 2011 to assess their impact in water, sediment and biota. A special emphasis was placed on the potential effects of both, individual pesticides and their mixtures, in three trophic levels (algae, daphnia and fish) using Risk Quotients (RQs) and Toxic Units (TUs) for water and sediments. Chlorpyrifos, diazinon and carbendazim were the most frequent in water (95, 95 and 70% of the samples, respectively). Imazalil (409.73 ng/L) and diuron (150 ng/L) were at the highest concentrations. Sediment and biota were less contaminated. Chlorpyrifos, diazinon and diclofenthion were the most frequent in sediments (82, 45 and 21% of the samples, respectively). The only pesticide detected in biota was chlorpyrifos (up to 840.2 ng g^{-1}). Ecotoxicological risk assessment through RQs showed that organophosphorus and azol presented high risk for algae; organophosphorus, benzimidazoles, carbamates, juvenile hormone mimic and other pesticides for daphnia, and organophosphorus, azol and juvenile hormone mimics for fish. The sum TU_{site} for water and sediments showed values < 1 for the three bioassays. In both matrices, daphnia and fish were more sensitive to the mixture of pesticide residues present.

1. Introduction

Pesticides are a widespread group of chemical substances used to improve agricultural production. However, these substances could be persistent in water, accumulative in sediment or bioaccumulative in biota, depending on their solubility and Log K_{ow}. They are hazardous for living organisms, human health or environment, even at low concentrations (Campo et al., 2013; Claver et al., 2006; Damásio et al., 2011; Giordano et al., 2009; Masiá et al., 2015a). Furthermore, physical, chemical and biological processes degrade pesticides into one or more transformation products that could be more toxic or persistent than the parent one. There is a need of data on the real occurrence of pesticide residues in environmental matrices (De Gerónimo et al., 2014; Köck-Schulmeyer et al., 2014; Palma et al., 2014a; Bruzzoniti et al., 2014; Martínez-Domínguez et al., 2015; Masiá et al., 2014, 2015b; Wei et al., 2015).

The potential ecotoxicological risks associated with pesticide residue contamination are addressed through toxic units (TUs) and/or risk quotients (RQs) (EC, 2003; Ginebreda et al., 2014; Kökc et al., 2010). Their application in most studies is restricted to water samples (Ginebreda et al., 2014; Kuzmanović et al., 2016). However, pesticide residues can also be adsorbed into sediments (Masiá et al., 2015b). WFD (EC, 2000) and environmental quality standards (EQS) (EC, 2008; EU, 2013) unquestionably support to include sediments in the risk assessment. A variety of methods were proposed but only scarcely applied to evaluate the potential toxicity of sediments (e.g., toxic equivalent factor approach, TUs summation, hazard index) (Schwarzenbach and Westall, 1981; Booij et al., 2015; de Castro-Catalá et al., 2016).

Another problem caused by pesticides contamination is the simultaneous occurrence of several of them and the need to establish the real impact of these mixtures on biota (Cedergreen,

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2014; Roig et al., 2015), which can be predicted by independent action (IA) or concentration addition (CA). The former assumes that the components have different mechanisms of action —ignoring synergies/antagonisms and effect summation and therefore underestimating the effect— and the latter that have a similar one —overestimating the effects. (Cedergreen, 2014; Ginebreda et al., 2014; Kuzmanović et al., 2016). CA is often the recommended first step on a tiered process because presents the worst case scenario (even that synergies are not considered) (de Castro-Catalá et al., 2016).

Mediterranean area is one of the most affected by climatic fluctuations that alter hydrological conditions and originate the great wavering on concentrations of the cocktail of pesticide residues present in water (Batalla et al., 2004). Ebro River is the second largest river of the Iberian Peninsula and the first one that flows into the Mediterranean area of Spain. Previous studies performed in the Ebro River linking occurrence of pollutants, concentrations and toxicity, but most of them have focused on a single chemical family or select one environmental matrix (water, soils, sediments or biota) (Claver et al., 2006; Damásio et al., 2010; Köck-Schulmeyer et al., 2013; Köck et al., 2010; Navarro et al., 2010; Silva et al., 2011).

The objective of this study was to establish pesticide's occurrence, spatial distribution and transport and to evaluate the ecotoxicological risk in three trophic levels (Algae, daphnia and fish), using RQs for each pesticide and sumTUs for each sampling site. The partial objectives of this study were to (i) monitor the concentration of 50 pesticides and transformation products in the surface waters, sediments and biota of the Ebro River basin in two consecutive campaigns (2010–2011) (ii) compare the concentration of the pesticides found in the present study with those detected since 2001 and with the EQS values of the pesticides included in the Directive 2013/39/EU (EU, 2013), and (iii) perform an environmental risk assessment not only for water concentrations but also sediments based on the RQs and TUs methods.

2. Experimental design

2.1. Physical setting and sampling

The Ebro River is located at the northeast of Spain and drains an area of approximately 85,000 km^2. It has 928 km in length and receives waters from several tributaries, which altogether represent 12,000 km of waterway network, ending into Mediterranean Sea and forms a delta of more than 300 km^2 (Lacorte et al., 2006; Navarro et al., 2010; Roig et al., 2015). The basin is characterized by a Mediterranean valley, which forms a triangular morphological unit, surrounded by mountains. Mean annual precipitation and temperature vary with altitude, ranging respectively from 1800 mm to 8 °C in the Pyrenees to 320 mm and 18 °C in the Ebro valley. Traditionally, the Ebro River basin is agricultural land, but lately industry has been a growing sector. In 2008, one third of the total surface of the basin was agricultural and it is still the most irrigated area in Spain (906.000 ha) (Herrero-Hernández et al., 2013), the most important crops are herbaceous plants (all over the basin), grapes for wine production (La Rioja), fruit trees (Lleida) and rice (Ebro Delta) (Silva et al., 2011). The Spanish statistics estimated that ca. 14,000 T of pesticides were used in 2010 and ca. 13,500 T in 2011. The monitoring in this study comprised two sampling campaigns, 2010 and 2011, including 24 sampling stations for water and sediments covering the whole River Basin (see Fig. S-1 and S-2) and finally five for biota sampling in 2010. These sites are representative of the whole basin (geo – references are in Table S-2).

Samples were taken in October in both years. Grab water samples (2 L) were collected in clean amber glass bottles, from the middle of the river width. Each bottle was thoroughly rinsed with MilliQ water at the laboratory and with the river water at the sampling point before collection. Sediment samples (approx. 250 g) were taken in the same point as the water ones using a Van Veen grab sampler (0.5 L capacity). They were transferred and wrapped into an aluminum foil (previously washed with methanol and dried in oven at 100 °C) that was put inside an aluminum box. Fish samples were only collected in 2010 at five selected sites of the River course: EBR2, EBR3, EBR4, EBR5 and OCA using electro-fishing because the complexity of the basin, the difficulties to perform electrofishing and the small sample sizes obtained.

All samples were transported in hermetic boxes refrigerated with ice upon arrival at the laboratory. There, the water samples were kept at 4°°C and pre-treated and processed in a period not exceeding 5 days. Before the analysis, water samples were vacuum filtered through 1 μm glass fiber filters followed by 0.45 μm nylon membrane filters (VWR, Barcelona, Spain). Sediment and fish samples were frozen, lyophilized (Hetosicc CD4, Birkerod, Denmark), pulverized, thoroughly mixed, passed through a 2 mm Ø sieve and kept at −20 °C until the analysis that was performed within 3 months.

2.2. Extraction procedures and instrumental analysis: water, sediment and fish samples

For this study, 42 pesticides including some of their transformation products were determined in the 2010 campaign. Carbendazim, thiabendazole, terbumeton, terbumeton deethyl, terbuthylazine, terbuthylazine deethyl, terbuthylazine-2-hydroxy and tebuconazole were added in the next year. These pesticides belong to different chemical families, with a variety of uses as well as different physicochemical characteristics and toxicity (see Table S-1).

The water extraction was carried out according to Masiá et al. (2013b). Very briefly, water samples (200 mL) were extracted using an Oasis HLB solid-phase extraction (SPE) cartridge (200 mg sorbent/6 mL cartridge, Waters, Milford, MA, USA). The cartridge was dried under vacuum for 10 min and the analytes eluted with 10 mL of dichloromethane–methanol (50:50, v/v). The extract was evaporated to dryness and reconstituted with 1 mL of methanol. The fish and sediment samples were extracted using the QuEChERS method as described by Masiá et al. (2015b). Lyophilized sediment (1 g) or fish (2 g) were extracted with 8 ml of H_2O MilliQ, 15 ml of acetonitrile, 6 g of $MgSO_4$ and 1.5 g of NaCl. Then, 2 mL of the resulting supernatant were cleaned-up by dispersive SPE with 0.3 g of $MgSO_4$, 0.1 g of PSA, 0.1 g of C_{18} and 0.015 g of GCB. All samples were analyzed in triplicate. The results presented are the average of the three values.

The chromatographic instrument was an HP1200 series LC – automatic injector, degasser, quaternary pump and column oven – combined with an Agilent 6410 triple quadrupole (QQQ) mass spectrometer, equipped with an electrospray ionization interface (Agilent Technologies, Waldbronn, Germany). Data were processed using a MassHunter Workstation Software for qualitative and quantitative analysis (A GL Sciences, Tokyo, Japan). The detailed conditions are in the Supplementary material Tables S-3 and S-4).

2.3. Quality assurance and quality control

The analytical methods validation was detailed in the SM Table S-5. The method's limits of detection (MLDs) and quantification (MLQs) ranged from 0.01 to 2 ng L^{-1} for water, from 0.03 to 1.67 ng g^{-1} for sediment and from 0.08 to 3.75 ng g^{-1} for biota. Recovery tests were carried out in quintuplicate in order to evaluate the precision of the method. In water samples, recoveries varied