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Spatio-temporal patterns of pesticide residues in the Turia and Júcar Rivers (Spain)

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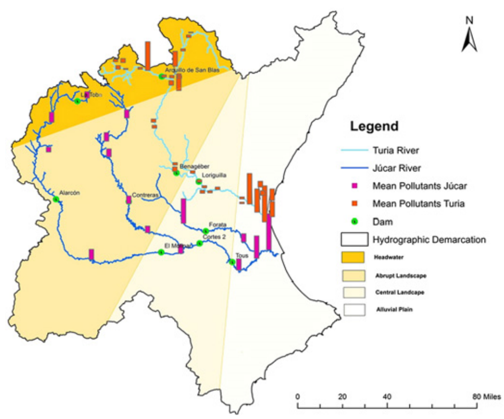
HIGHLIGHTS

- Occurrence of the same pesticides was detected in both river basins.
- Mouth was the most contaminated area.
- Chlorpyrifos, hexythiazox and diazinon were the most frequent pesticides.
- Sediments were less contaminated than water, mostly by organophosphorus (higher K_{ow}).
- 7 pesticides were detected at concentrations higher than 100 ng L^{-1}.

GRAPHICAL ABSTRACT

Spatio-temporal patterns of pesticide residues in the Turia and Júcar Rivers 2010–2013 (Spain).



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ABSTRACT

A study was conducted on the occurrence of 50 pesticides in water and sediments of Turia and Júcar Rivers (Valencian Community, Eastern Spain) for a period of two consecutive years each, 2010/2011 and 2012/2013, respectively to assess the contribution of agriculture and urban activities on pesticide pollution. The results showed that mean concentrations of pesticides ranged from <LOQ up to 200 ng/L. Chlorpyrifos was the most frequent pesticide whereas imazalil, thiabendazole, tolclofos methyl, ethion and carbofuran were those found at higher concentrations. Ubiquitous pesticides are those with long half-lives. The most polluted parts of the rivers were the headwaters and the mouth, which could be related to the agricultural practices and rainfall. Contrarily, in the abrupt part of the rivers of difficult access the contamination is low. Other quality parameters monitored in this study also corroborate the worst water quality in the alluvial plains that coincides with higher anthropic pressure. The temporal variations also indicated a strong relation of pesticide concentrations with hydrology, the higher the river flow, the higher number and frequency of pesticides but at lower concentrations. On the contrary, at lower river flows higher pesticide concentrations were detected. The risk assessment for aquatic biota pointed out that organophosphorus and fungicides are a threat to fish and daphnia and herbicides and fungicides are hazards for algae. Thus, the strict control of pesticide concentrations is important to preserve the aquatic ecosystems health.

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1. Introduction

Pesticide is a broad term that includes insecticides, herbicides, fungicides and other compounds considered by both, the EU Water Framework Directive 2000/60/EC and the US Environmental Protection Agency (EPA) as priority pollutants (EC, 2000; EPA, 2012). As a result of massive global uses, pesticides and their degradation products spread through the environment and contaminate water, soil and atmosphere, leading to a consequent potential risk to humans and the environment. Their presence in the aquatic ecosystems is actually linked to diffuse pollution from run-off of agricultural fields and urban gardening areas. In addition, due to the input of urban run-off into the sewer lines, their presence in wastewaters cannot be underestimated (Campo et al., 2013; Giordano et al., 2009; Köck-Schulmeyer et al., 2013; Singer et al., 2010). Surface waters located in intensive agriculture areas, densely populated, are more vulnerable to pesticides (Köck-Schulmeyer et al., 2014; Masiá et al., 2015a). Apart from the toxicity data, the risk assessment is based on the concentrations determined by chemical analysis (Kuzmanović et al., 2015; Rose et al., 2015).

The presence of pesticides and their metabolites in surface water, sediments, biota and groundwater has been reported at low ng/L to several μg/L range in areas of intensive agricultural activity (De Gerónimo et al., 2014; Masiá et al., 2015a, 2013a; Page et al., 2014). These studies are mainly based on the collection and the analysis of samples for one punctual campaign because only this implies the analysis of a relatively large number of samples from different locations (Bonansea et al., 2013; De Gerónimo et al., 2014; Gómez et al., 2012; Phong et al., 2012). Several characteristics that change over the time, such as proximity of crop fields to surface waters, water body characteristics (surface area, depth and flow), and climatic conditions (temperature, humidity, wind and precipitation) affect the transport of pesticides and their transfer to other environmental compartments. These pesticide variations over the time are not taken into account when only one punctual campaign is carried out. However, they are of utmost importance in cases, such as the Mediterranean area, severely affected by water scarcity and characterized by alternative periods of torrential floods and severe droughts (Köck-Schulmeyer et al., 2014; Masiá et al., 2013a; Palma et al., 2014). The collection of long-term data (survey monitoring) is essential for the assessment of global changes in fluvial systems.

The Turia and Júcar rivers — located in the SE of Spain — are two important rivers draining their waters in the Mediterranean Sea. Both belong to the Júcar Hydrographic Demarcation. The human population living in the basin (5,162,163 inhabitants in 2009) makes an intensive use of the available water. In fact, the demand of water exceeds supply. The irrigated and rainfed agriculture is the economic activity that occupies about half of the territorial scope of the Júcar Hydrographic Demarcation with an approximate total irrigated area of 350,000 ha, mainly concentrated in the lower part of both rivers (CHJ, 2014). Nowadays, agriculture accounts for nearly 80% of water demand (1394 hm^3 $y-^1$), but this appears to be stabilized or reduced, whereas urban/industrial demand is forecasted to rise.

This study is aimed at monitoring 50 currently used pesticides in water and sediments of the Júcar and Turia Rivers in two consecutive periods of time 2010–2011 and 2012–2013, respectively (see Supplementary material, Table S-1 for detailed list, physico-chemical properties and half-lives). The relation among physico-chemical water parameters, temperature, flow and the occurrence concentrations of pesticides was studied along both rivers. This is the first extensive pilot study undertaken (44 sampling points) in the Júcar Hydrographic Demarcation. It intends to improve the knowledge of these pesticides' occurrence in the aquatic environment. The selection of the target pesticides and metabolites was based on the extent of use, water solubility and amenability to LC–MS analysis.

2. Experimental

2.1. Site description

The two rivers flow into the Mediterranean Sea near the city of Valencia, Spain. The Júcar River Basin has a total drainage area of 22,123 km^2 and its main river, the Júcar, is 498 km long and has an average flow of 49.22 m^3 s^{-1}. The most important tributaries are the Cabriel (with 220 km length, 4754 km^2 of drainage area and 20.92 m^3 $s-^1$ of average flow) and Magro (130 km, 1544 km^2 and 0.96 m^3 $s-^1$). The Turia River is a 280 km length with an average flow rate of 10.43 m^3 $s-^1$ and its basin has a total drainage area of 6393.6 km^2 and receives as the most important tributary the river Alfambra (with 60 km, 1398 km^2 and 1.5 m^3 $s-^1$).

In both rivers, the climate is typically Mediterranean with warm and dry summers (from July to August) and relatively wet and mild winters. The rainy season is from September to May, with maximum rainfall in October (autumn) and April (spring), and a mean annual precipitation of 500 mm, but there is a large spatial variation. The annual thermal oscillation presents continental characteristics, with cold and long winters not surpassing 4.5 °C as average temperature, and short and mild summers with an average of 21.2 °C. Periodically, the hydrological regime is affected by flood and drought events. Hydrology has been deeply altered due to human activities, and water resources are under increasing pressure (Hooke, 2006). The Júcar and Turia flows are regulated by large dams, smaller structures and weirs, and the channelization of some reaches (Lobera et al., 2015). Fig. 1 shows the location of the different sampling points (geo-references are in Table S-2). Methodologically, the area was classified into four zones according to their morphology, landscape, land use and degree of human pressure (some photos illustrating the landscape in the different zones are in Fig. S-1). These four zones are:

(i) Zone 1 or headwaters cover the headwaters of the Turia and Júcar Rivers. In the case of the Turia River, it comprises from the Sierra de Albarracín to the limits of the Teruel province, including the area and surroundings of Teruel city. The upper part of the river Júcar covers the eastern flank of the Montes Universales in the province of Cuenca where river crosses mountainous lands with a north–south direction in an area that crosses the city of Cuenca. This area shows hilly landscapes, with a very low population density.
(ii) Zone 2 or abrupt landscapes include the Rincon of Ademuz and the region of the Serranos, which are characterized by a rough and steep morphology that makes difficult the use of the river waters for agriculture. This zone also supports a low density of population, although slightly higher than the previous one.
(iii) Zone 3 or central landscapes are areas of hills and plains that involve the transition from the mountainous part of the basin to the more populated and exploited one. It is characterized by a gradual increase in the urban areas along with extensive agriculture, and
(iv) Zona 4 or alluvial plains comprise the regions of L'horta and Valencia city that make up the coastal area, which corresponds to the final phase of the Turia and Júcar River Basins. This final area includes the Natural Park of the Albufera of Valencia surrounded by the Turia River in the North and the Júcar in the South. Paradoxically, this flat area displays the highest density of growing areas, industries, infrastructure, and urban areas.

2.2. Sampling and sample analysis

The sampling was designed to perform large-scale and long-term (both complete basins, two consecutive years) monitoring to assess temporal trends of pollutants. The influence of seasonal variability was