Monitoring spatial distribution of PPCPs using chromatographic methods and Geographical Information Systems

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Abstract The present study combines the chromatographic analysis of Pharmaceuticals, Personal Care Products (PPCPs) and Geographical Information System. (GIS). These PPCPs were at concentrations ranging from 5ng L^{-1} to 1µg L^{-1}, emphasizing Ibuprofen (until 400 ng L^{-1}) or Bisphenol A (until 50 0ng L^{-1}). The second part of the study is divided in two steps. Information required was integrated into a common Geographical Information System (GIS) framework. For this, location of the sampling points, population data (number of inhabitants, inhabitants ranged by age and sex) and the results of the chromatographic analysis were incorporated into the geo-referenced system (reference system ETRS-1989) established in the GIS structure, according to official standards, following the Spanish Spatial Data Infrastructure. The second step was a spatial analysis of the PPCPs, establishing a descriptive model of territorial presence of contaminants by combination of their location at a particular place with population densities. As remarkable results a high concentration of anti-inflammatories in the big cities or the detection of THC metabolites closed to the youngest populations were observed.

Keywords: Monitoring, Turia River, HPLC-MS/MS, GIS, PPCPs.

1. Introduction

Nowadays the quality of the freshwater has been deteriorated (Mattikalli *et al*. 1996) by the continuous pollution. Emerging contaminants in natural water sources is growing. Studies on these contaminants are based on both develop new methods to analyse them (Comtois-Marotte *et al*. 2017, Carmona *et al*. 2014, Andrés-Costa *et al*. 2016, Gago-Ferrero *et al*. 2012, Bletsou *et al*. 2015), and monitor their spatial distribution (Valcarcel *et al*. 2013, Vazquez-Roig *et al*. 2015, (Alygizakis *et al*. 2016).

The pollutants sometimes are residues of some important compounds, as medicines, which are vital tools to maintain and improve the health (Hardon *et al*. 2004). The pharmaceutical progress and the increase of the health care have increase the consumption of medicines (Khetan *et al*. 2007). According to OECD, Spain spent 436€ per capita in medicines during the year 2014 (OECD 2016). Some diseases are correlated to habits, environment and age of the people (Garcia *et al*. 2012; Vega Quiroga *et al*. 1996), as heart medicines, for example, which we can expect that will be used by the people with older age. The same could happen with illicit drugs, personal care products and related substances.

Geographical Information Systems (GIS) had been used for multiple studies. A classical usage for this system was the study of the land changes (Xiao *et al*. 2006), (Bhaduri *et al*. 2000) but also is used to monitor the pollution (Briggs *et al*. 2005, Evans *et al*. 1990, Kourgialas *et al*. 2017).

The aim of this study is monitor PPCPs and other contaminants through Turia River (Spain) using a chromatographic method for the compond analysis and a Geographical Information System for monitoring the pollution and try to know the correlations with the population.

2. Methods

2.1. Sampling

Freshwater samples were collected in different points across Turia River (East of Spain) as shown Figure 1. Turia River is a Mediterranean River, that origins in Teruel province (Aragón, Spain) and flows at Mediterranean Sea in Valencia City (Spain), passing through Cuenca (Castilla-La Mancha, Spain). This Mediterranean River has an average flow rate of 10.43m^3 s^{-1} (Carmona and Ruiz 2011) and is of the rivers of the representative Mediterranean.

WWTP samples were taken in three different wastewater treatment plants, Pinedo I (PI) and II (PII) that receive residual water from Valencia City (Spain). PI receives a flow around 101 674 m3/day and PII 219 774 m^3 day^{-1} (Bhaduri *et al*. 2000).

Turia River samples were daily collected yearly in September of 2013 and September of 2012. WWTP were sampled daily for one week in March of 2013 and March 2014. These were putted inside a portable freezer at 4 °C. Once at laboratory were frozen (−20 °C) in the dark until the extraction. All water samples analysed in this study were filtered with a 0.50 µm GC-50 glass fiber filter of 90mm by Advantec (Minato-ku, Tokyo, Japan) with vacuum.

2.2.Chromatographic analysis

Chromatographic analysis was performed with a 1260 Infinity Ultra High-Performance Liquid Chromatograph (UHPLC) tandem with a 6410 Triple Quad Mass Spectrometry (MS/MS) from Agilent Technologies (Santa Clara, CA, USA), which were used in Negative (NI) and Positive (PI) ionization modes. PPCPs and illicit drugs were separated using a Kinetex XB-C18 100A analytical column, 50 x 2.10mm with a particle size of 1.7µm, from Phenomenex (Torrance, CA, USA).

A mobile phase made of 2.5mM NH4F in methanol (A) and 2.5mM NH4F in water (B) for negative ion mode and 2.5mM NH4F in methanol (A) and 2.5mM NH4F in water (B) with 0.1% of formic acid in both solutions for positive mode were used. The gradient used for both ionization modes starts with 30% of A and finished with 95% of B in 12 minutes that was maintained during 8 minutes more. After that, the system is stabilizing 12 minutes more to arrive to the initial conditions. Flow rate of mobile phase is of 0.2mL min-1 and have an injection volume of 5µL each.

The ESI ionization source parameters were: drying gas (nitrogen) flow of 10L min-1, temperature of 300ºC (573.15K), nebuliser pressure of 15 psi (1034.2 mbar) and capillarity voltage of 4000V. The mass spectrometer worked in MRM and a delta of Electron Multiplier Voltage (EMV) of 600V for both ion modes.

2.3.Spatial analysis

The spatial analysis on this study was divided in two steps. In the first one, the information required was integrated into a common Geographical Information System (GIS) framework, using ArcGIS 10.2.2 from Esri (Redlands, CA, USA). For this, location of the sampling points, population data (number of inhabitants, inhabitants ranged by age and sex) obtained from the database of the Spanish Statistics Institute (INE) and the results of the chromatographic analysis were incorporated into the geo-referenced system (reference system ETRS-1989) established in the GIS structure, according to official standards, following the Spanish Spatial Data Infrastructure. The second step consisted in a spatial analysis of the PPCPs and prescribed drugs, establishing a descriptive model of territorial presence of contaminants

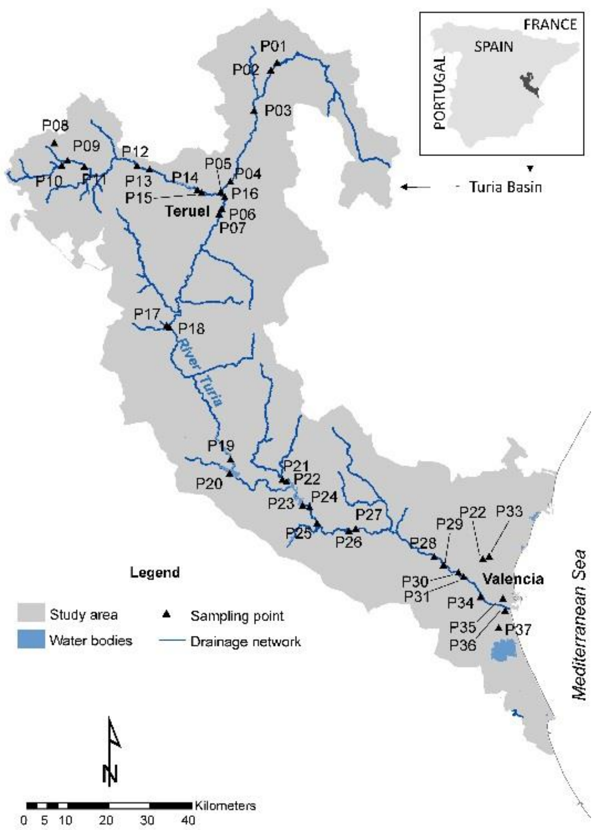

Figure 1. Sampling points

Compound	River Water 2012 (*n=22*)		River Water 2013 (*n=29*)	
	Conc. ng L^{-1}	Freq *n*	Conc. ng L^{-1}	Freq *n*
Bezafibrate	27	8	7	1
Bisphenol A	496	9	41	25
Butylparaben	39	10	5	2
Chlorfibric Acid	67	21	n.d.	--
Cloroamphenicol	40	7	68	3
Diclofenac	83	11	33	9
Ethylparaben	55	13	6	1
Flufenamic Acid	97	9	22	2
Gemfibrozil	43	22	34	20
Ibuprofen	402	18	153	27
Indomethacin	21	14	n.d.	--
Methylparaben	488	17	24	15
Naproxen	1483	11	36	24
Propylparaben	216	18	12	9
Salicylic Acid	321	17	22	3
THC	n.d.	--	32	29
THCCOOH	23	4	23	29
Thiamphenicol	31	15	10	1
Trichlocarban	86	3	n.d.	1
Triclosan	64	1	n.d	--
Warfarin	32	3	54	22

Table 1. Average concentrations and frequency of detection of the PPCP.

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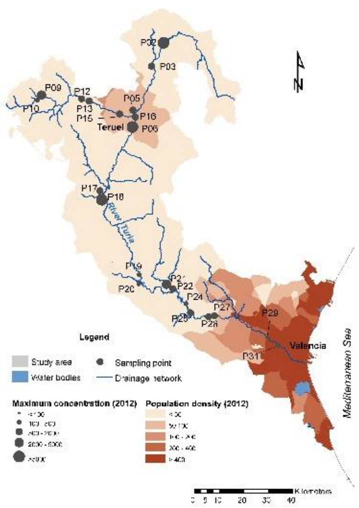

Figure 2. PPCPs and population distribution in 2012.

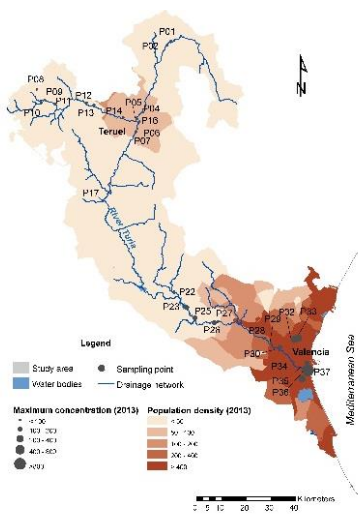

Figure 3. PPCPs and population distribution in 2013.

by combination of their location at a particular place with population densities.

3. Results

Table 1 shows the average concentration and the frequency of detection of the different pharmaceuticals. In 2012 Naproxen was found at high concentration (1483 ng L^{-1}) but next year the concentration is reduced until 36 ng $L^{-1.}$ On the contrary. .the frequency was higher in 2013, from 11 to 24. Same happen with Biphenol A or Ibuprofen reducing more than 91% and around 62% respectively the concentrations from one year to the other.

In **Figure 2** and **Figure 3** the spatial distribution of the PPCPs throughout the course of the Turia River according to the population is illustrated. There is no correlation between population and the concentration of PPCP for the first sampling campaign. However, positive correlation between the two variables was clear in the second campaign. The highest concentrations are in the largest cities like Teruel or Valencia

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