The Albufera Natural Park (Valencia, Spain): the impact of Pharmaceutical and Personal Care compounds

Daniele Sadutto*, Rodrigo Alvarez-Ruiz, Marta Ballester, Yolanda Picó
Food and Environmental Safety Research Group (SAMA-UV), Desertification Research Centre (CIDE-UV, GV, CSIC), Faculty of Pharmacy, University of Valencia, Av. Vicent Andrés Estellés s/n, 46100, Burjassot, Valencia, Spain.
* sadutto@uv.es

In the last years, the interest in detecting environmental contaminants in different matrices (mostly sediment, soil and water) is increasing because their more relevant impact on the global ecosystem [1]. In this study, we focused on determination of Pharmaceutical Compounds and Personal Care Products. The study was conducted on about 30 compounds, including acid, basic and neutral (**Table 1**). The selected compounds constitute an important block of organic contaminants frequently found for many reasons, such as industrial waste, expired or unused medicinal product not disposed in the right way, and excretion of drugs and their metabolites derived from therapeutic treatments [2].
This field study is intended to propose an analytical methodology to assess and monitor the occurrence of emerging contaminants (EC) of the Albufera Natural Park. Has an area of 21120 hectares and it is located 10 km to the South of Valencia City. It consists of a highly eutrophic coastal lagoon surrounded mainly by rice fields that occupy the primitive marshland. The Turia River, to the north, the Jucar River, to the South, and a network of irrigation channels bring fresh water to the Albufera system.
Different analytical methods to determine ca. 30 EC were developed and optimized to obtain the best efficiency and sensitivity. Samples analysed included 35 water samples and 20 sediment samples for L'Albufera Lake and its surrounding area. **Fig. 1** shows the location of the sampling points. The extraction is based on solid-phase extraction (SPE) using two different stationary phases of cartridges Reversed Phase and Polymeric Weak Cation Phase, provided suitable recoveries to extract this compounds from water or to clean up the sediment extracts. The determination was carried out by liquid chromatography-tandem mass spectrometry (LC-MS/MS) with a triple-quad using two precursor → product ion transitions for each compound in the multiple selected reaction monitoring mode (MRM).
The results evidenced the presence of many of the selected EC both in water and sediment. All selected pharmaceuticals were detected in water samples. The highest concentration was for thiamphenicol (up to 2 µg/L). In sediments, twenty-three pharmaceuticals were found, the most frequently detected (> half of the samples) were salicylic acid, buthylparaben, caffeine, clofibric acid, diclofenac, flufenamic acid, furosemide, thiamphenicol, tramadol, triclosan and warfarine. However, amoxicillin and ibuprofen were those at the highest concentrations, 84.8 and 100.1 ng/g dry weight (d.w.). The most abundant ones are analgesic and anti-inflammatory drugs (salicylic acid, diclofenac), antihypertensive (furosemide), anticoagulant (warfarin), stimulants (caffeine) and preservatives (parabens).

Table 1- List of compounds and therapeutic category. For each substance is specified the electrospray ionization mode: positive (+) or negative (-). Substances that ionized in positive mode are basic or neutral whereas the other are acid.

Compound	Therapeutic category	Ionization mode	Compound	Therapeutic category	Ionization mode
Acetylsalicylic Acid	Analgesic/Anticoagulant	-	**Ibuprofen**	Analgesic	-
Alprazolam	Anxiolytic	+	**Indomethacin**	Antibiotic	-
Amoxicillin	Antibiotic	+	**Lorazepam**	Anxiolytic	+
Atenolol	Antihypertensive	+	**Metformin**	Antidiabetic	+
Atorvastatin	Lipid regulador	+	**Metylparaben**	Preservative	-
Bezafibrate	Lipid regulador	-	**Naproxen**	Analgesic	-
Bisphenol A	Plastic additive	-	**Norfloxacin**	Antibiotic	+
Butylparaben	Preservative	-	**Ofloxacin**	Antibiotic	+
Caffeine	CNS stimulant	+	**Omeprazol**	Gastrointestinal	+
Cloramphenicol	Antibiotic	-	**Paracetamol**	Analgesic	+
Clofibric Acid	Lipid regulador	-	**Propylparaben**	Preservative	-
Codeine	Analgesic	+	**Simvastatin**	Lipid regulador	+
Diclofenac	Analgesic	-	**Thiamphenicol**	Antibiotic	-
Enalapril	Antihypertensive	+	**Tramadol**	Analgesic	+
Etoricoxib	Analgesic	+	**Triclocarban**	Antibacterial	-
Etylparaben	Preservative	-	**Triclosan**	Antibacterial	-
Flufenamic Acid	Analgesic	-	**Warfarin**	Anticoagulant	-
Furosemide	Antihypertensive	-			

These data pointed out that is important to optimize removal treatments and to create new barriers to avoid the discharges of EC to these sensitive environments. Overall, this methodology produced an accurate outlook of a basal state for the Albufera Natural Park and could be developed in the context of a chronic monitoring of this site. Furthermore, the results pinpointed the need of further studies on the short and long term ecotoxicological impact in animal and vegetal species.

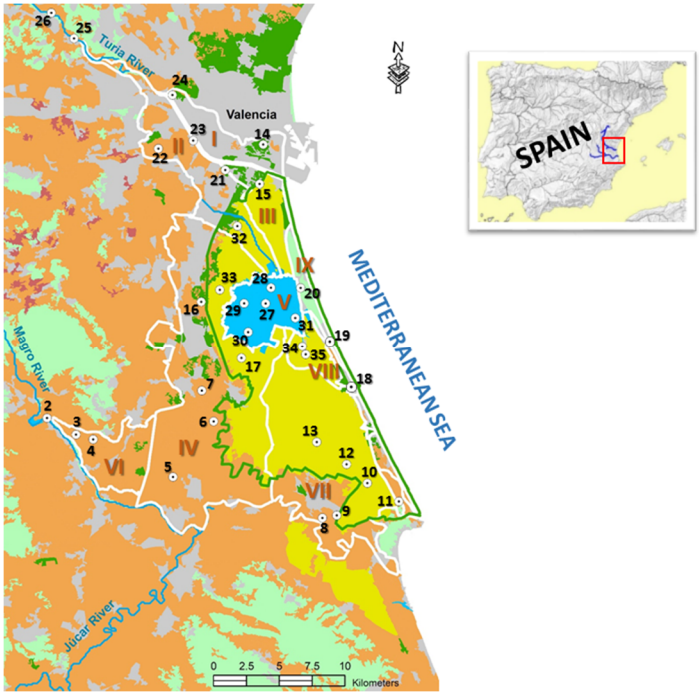

Fig. 1. Location of the sampling points

Acknowledgment

This work has been supported by the Spanish Ministry of Economy and Competitiveness and the ERDF (European Regional Development Fund) through the project CGL2015-64454-C2-1 and by the Generalitat Valenciana through the project ANTROPOCEN@ (PROMETEO/2018/155). D. Sadutto knowledges the Generalitat Valenciana for his "Santiago Grisolía" grant "GRISOLIAP/2018/102, Ref CPI-18-118". R. Álvarez-Ruiz also acknowledges the Spanish Ministry of Economy and Competitiveness and the ERDF (European Regional Development Fund) for his FPI grant BES-2016-078612.

References.

[1] Blasco (2008), Impact of emergent contaminants in the environment: environmental risk assessment. Handbook of Environmental Chemistry Vol. 5, pp. 169e188.

[2] Anekwe J.Ebele (2017), "Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment". Emerging Contaminants , Vol. 3, Issue 1, Pag. 1-16.