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An environmental forensic procedure to analyse anthropogenic pressures of urban origin on surface water of protected coastal agro-environmental wetlands (L'Albufera de Valencia Natural Park, Spain)

Juan Pascual-Aguilar[a,*], Vicente Andreu[a], Yolanda Picó[b]

[a] Centro de Investigaciones sobre Desertificación-CSIC-UV-GV, Departamento de Degradación y Conservación de Suelos, Carretera de Moncada-Náquera km 4.5, 46115 Moncada, Valencia, Spain
[b] Laboratori de Nutrició i Bromatologia, Facultat de Farmàcia, Universitar de València, Av. Vicent Andrés Estellés s/n, 46100 Burjassot, València, Spain

HIGHLIGHTS

- Carbamazepine was the pharmaceutical substance most detected with concentrations up to 31.0 ng/L.
- Cocainics were found in higher concentrations (maximum of 67.8 ng/L in sample PM6) and in more sites.
- Connectivity is strong between municipalities with high population, SWTPs and irrigation areas.

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ABSTRACT

Detection and spatial distribution of 14 drugs of abuse and 17 pharmaceuticals in surface waters was investigated to determine transport hydrological connectivity between urban, agriculture and natural environments. Solid-phase extraction and liquid chromatography tandem mass spectrometry was applied to all samples. To determine spatial incidence of contaminants, analytical results of target compounds were georeferenced and integrated into a geographical information systems structure together with layers of municipal population, location of sewage water treatment plants and irrigation channels and sectors. The methodology was applied to L'Albufera Natural Park in Valencia (Spain). A total of 9 drugs of abuse were detected at 16 points (76% of the sample sites). Cocaine and its metabolite, benzoylecgonine, were the most detected substances, being found in 12 and 16 samples, respectively. Maximum concentrations were found in benzoylecgonine (78.71 ng/L) and codeine (51.60 ng/L). Thirteen pharmaceuticals were found at 16 points. The most detected compounds were carbamazepine (15 samples) and ibuprofen (11 samples). Maximum concentrations were detected in acetaminophen (17,699.4 ng/L), ibuprofen (3913.7 ng/L) and codeine (434.0 ng/L). Spatial distribution of pharmaceuticals showed a clear relationship between irrigation areas, high population densities municipalities (above 1000 h/km^2) and sewage water treatment plants.

1. Introduction

Emerging contaminants are any synthetic or naturally occurring chemicals or microorganisms not commonly monitored in the environment. Due to persistency and potential for harming the environment, biota and humans, their identification and quantification in environmental compartments is of research concern. Of the many emerging contaminants that might be detected [1], pharmaceuticals and drugs of abuse can be seen as mainly originated in urban environments. Many of them are also identified in aquatic environments after treatment in sewage water treatment plants (SWPTs) [2,3], which in turn pose major threats to other environments through hydrological connectivity of landscapes.

Research has addressed the development of methods to determine the occurrence of illicit drugs and their metabolites in either inflow or treated wastewaters. Most recent works focused on the use of liquid chromatography separation (LC) coupled with mass spectrometry (MS) detection [4]. Gas chromatography (GC) separation coupled with MS has also been used [5].

The environmental implications of emerging contaminants might also be considered. After treatment, sewage water will enter the water system again and subsequently be used for human

* Corresponding author. Tel.: +34 963 42 41 62; fax: +34 963 42 41 60.
E-mail addresses: juan.a.pascual@uv.es, juanantonio.pascual@imdea.org (J. Pascual-Aguilar), Vicente.andreu-perez@uv.es (V. Andreu), Yolanda.pico@uv.es (Y. Picó).

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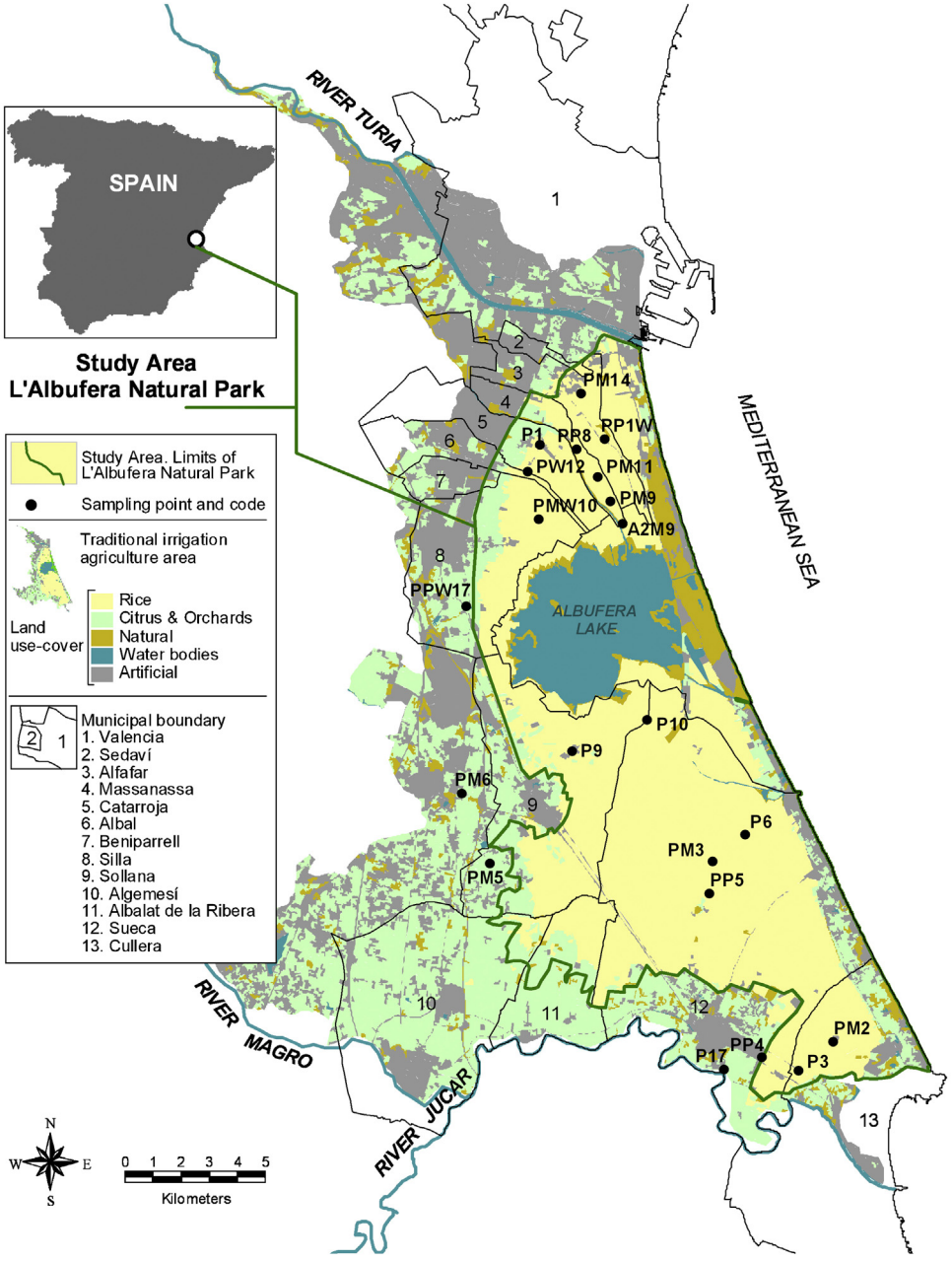

Fig. 1. Location of the study area and sampling points setting. The study area, line in green, is located between two coastal alluvial plains (Rivers Turia and Júcar) on which a traditional irrigation system was constructed (larger area with land use-cover background map). Municipalities are depicted in dark grey, with numbers for name identification in the map legend. Black dots with their respective codes (PM14, P3, etc.) refer to sampling points for surface water collection and analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

consumption or in productive activities including farming, before finally circulating as surface water and even continuing the water cycle underground. Although some works have studied the presence of both pharmaceuticals and illicit substances in rivers and open water systems after passing through urban agglomerations and sewage treatment plants [6], little research has analysed flow paths and water incorporation into permanent water bodies such as coastal lagoons.

Despite the successful development of analytical methods to detect emerging contaminants and their identification in different environmental compartments such as surface waters [7], soils [8] and underground waters [9], little progress has been made in identifying transmission mechanisms between environments, particularly between those landscapes and water deposits connected by hydrological flows, either natural (rivers) or artificial (irrigation canals and ditches).

The aim of this work is the development of an integral methodology to evaluate the presence and spatial distribution of illicit drugs in surface waters. Mediterranean coastal wetlands are of great interest for their rich biodiversity, but they are also fragile and exposed to various human pressures such as farming systems [10] and urban sprawl [11] that alter their ecological and environmental conditions. The methodology was thus applied in the Natural Park of L'Albufera de Valencia to obtain background on how these substances travel from urban and agricultural systems to the protected area.

The working hypothesis considers that there is continuity of water flows. Therefore, connectivity between different