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Presence of pharmaceuticals and heavy metals in the waters of a Mediterranean coastal wetland: Potential interactions and the influence of the environment

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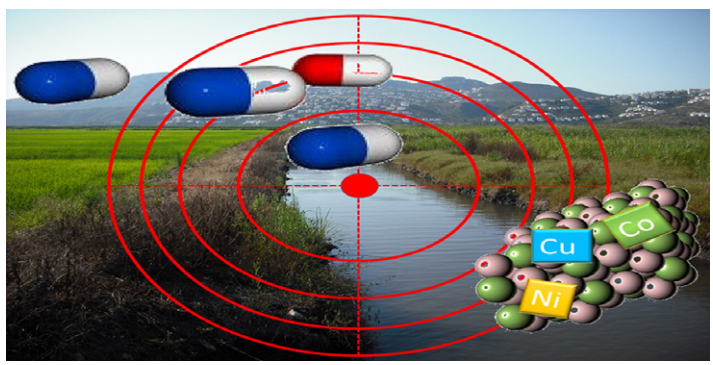
HIGHLIGHTS

- 17 pharmaceuticals and 7 heavy metals were studied in waters of a coastal wetland.
- Codeine, ibuprofen, and acetaminophen showed the higher frequency of detection.
- Potential interactions of Ni, Co and Cu with different pharmaceuticals were observed.
- Rivers and irrigation channels showed the highest values of pharmaceuticals.
- The studied compounds presented differences regarding water sources and land uses.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence of 17 relevant pharmaceuticals and 7 heavy metals in the waters of the Pego–Oliva Marsh Natural Park (Valencia Community, Spain) were monitored. Thirty four zones (including the lagoon and the most important irrigation channels), covering the main land uses and water sources, were selected for sampling. Thirty three of them were contaminated with at least one pharmaceutical. Ibuprofen and codeine were the pharmaceuticals more frequently detected, in concentrations between 4.8 and 1.2 ng/L and a maximum of 59 ng/L and 63 ng/L, respectively. Regarding metals, Zn showed values under the detection limit in all the samples, while Cd, Co, Cr, Cu, Ni and Pb were detected at concentrations lower than the WHO and EU maximum levels for drinking waters. Ni showed significant direct correlations with diazepam, norfloxacin, ofloxacin and fenofibrate, and inverse relationships with ibuprofen, at 99 and 95% of significance. Cu, Co and Cr also showed significant correlations with some of the pharmaceuticals. These interactions could favor the synergistic/antagonistic interactions among pharmaceuticals and metals in the marsh, which can affect its aquatic fauna and flora or even human health. The influences of the water sources, land uses and spatial distribution of both types of contaminants were also studied.
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1. Introduction

Wetlands are among the Earth's most productive ecosystems. They provide a diverse array of important ecosystem services, are fundamental in the maintenance of the water cycle, as well as act controlling floods and flows, in the recharge of aquifers, in carbon sequestration, etc. (Melendez-Pastor et al., 2010; Kagalou et al., 2008). Furthermore, these areas are unique in biological diversity, constituting a great reserve of waters for the planet and producing biomass and nutrients for the trophic chain (Carletti et al., 2006; Berberoglu, 2003). Among these ecosystems, the coastal wetlands present the greatest dynamism and biodiversity. They are open structures, usually eutrophics and rich in nutrients (Vazquez-Roig et al., 2011), which show an intense relationship with the surrounding environment. At the same time, these ecosystems show a great fragility, being particularly sensitive to alterations in their water quality.

During the last 50 years, the increasing human pressure and the socio-economic development have caused serious damages to these ecosystems. In particular, in the Southern region of the Mediterranean, 65% of the population (around 120 million inhabitants) is concentrated in coastal hydrological basins, where environmental pressures have increased (EEA, 2015). The Mediterranean coast of Spain has the fastest growing population in Europe, which increased up to 50% in the past decade, with around 1.7 million houses (Cundy et al., 2006; Dimopoulos et al., 2005). This scenario has resulted in land use changes and the related hydrological alterations, with increasing problems in the management and treatment of very different type of residues (urban, agricultural, industrial, etc.).

In this sense, pharmaceuticals and heavy metals are considered as potential indicators of human development in the different environmental media, and mainly in natural waters (Vystavna et al., 2013; Dickenson et al., 2011). Pharmaceuticals have been also considered as anthropogenic markers of social activity (Kasprzyk-Hordern et al., 2009); meanwhile, heavy metals have been more related to industrial activities. The presence of pharmaceuticals has become an increasing problem for environmental sustainability, and also for human health, with consequences very scarcely known. Recent investigations show their global presence in surface waters at low concentration levels (in the ng/L range) (Matamoros et al., 2012; Chen et al., 2011; Andreu et al., 2009). In fact, urban wastewaters are usually the greatest source of these emerging pollutants. However, animal feeding operations, industrial waste effluents and uncontrolled landfills are other sources that should not be underestimated. Although some pharmaceuticals are designed as bioactive compounds, there are others that also shown a clear environmental toxicity to bacteria, algae, invertebrates, fish and other aquatic fauna (Lolic et al., 2015; Nallani et al., 2011).

In the same way, heavy metals can be considered as other aspect of the human fingerprint as well. Although all of them are present in the earth crust, their wide presence in waters, soils and atmosphere is mainly due to human activities (industries, traffic, urbanization, etc.). Their effects on environmental and human health are well known, representing a constant threat to be controlled. However, their sources in the environment are also difficult to identify, as they could be a combination of natural and anthropogenic, both diffuse and point sources (Bayen, 2012). Even pharmaceuticals can contain heavy metals as inorganic impurities, being characteristic of the synthetic route of the manufacturing process (Rao and Talluri, 2007) or can present synergies with them (Lu et al., 2014; Chen et al., 2013). The effects of all these compounds could be magnified in the wetlands.

This study is focused on the Pego–Oliva Marsh Natural Park (Valencia Community, Spain), which is characterized by a long history of human pressures, such as marsh transformations for agricultural uses, urbanization, etc. In this area, the levels of 17 relevant pharmaceuticals, covering some of the most important therapeutic classes, and 7 heavy metals were evaluated together with the possible interrelationships between them. Their geo-spatial distribution and the possible influence of environmental factors (land uses, water sources, and distance to the seashore) were also studied. Synergies between contaminants, such as pharmaceuticals and heavy metals are, until now, scarcely studied and can be relevant because of their widespread distribution in the environment.

2. Material and methods

2.1. Study area

The Pego–Oliva marsh Natural Park has a surface of 1273 ha, and is located at the extreme South of the Gulf of Valencia in the boundary between two municipalities, Oliva and Pego (Valencia Community, Spain, 38° 52′ N and 00° 03′ W). The population of these towns are 39,236 inhabitants (in year 2012), and can increase in more than 75,000 people during summer. The marsh is an old silted lagoon delimited, by north and south by two rivers (Racons and Bullent/Molinell) and two mountain chains (Mustalla and Segaria ridges) of karst characteristics that contribute to its water charge, and furrowed by numerous irrigation channels and ditches. At the East, a sand barrier of 9 km long separates the marsh from the sea. This marsh experiences a huge variability on the rains regime, with periodic floods especially in spring and autumn, and an annual average precipitation of 900 mm (Cantora-Uiza and Aboal-Sanjur, 2012).

The Pego–Oliva marsh has a high biodiversity and is a key point in the route of migratory birds. Because of this, it has been included in the Life program of the European Union, the Natura 2000 Network and in the RAMSAR Convention. Nevertheless, and besides their character of natural protected area, in the last decades it has undergone serious changes mainly due to the human expansion and the associated need of resources and services. Therefore, parts of the marsh were drained for rice and citrus farming, and urban development, mainly in the coastal strip and the surrounding ridges. These alterations, which have affected around 70% of the wetland, have caused a remarkable decrease in the nesting of numerous species of interest. Since 1994, when it was declared Natural Park by the Regional Government, several and continuous programs of environmental protection measures have been applied. Nowadays, the Park is considered by the environmental authorities to be close to its optimal state. In addition, to minimize the human impact, four wastewater treatment plants (WWTPs) were built in the limits of the marsh. The characteristics of the WWTPs are provided in the Supplementary material, Table S1.

2.2. Sampling

Water samples were collected in 34 points of the Natural Park area (Fig. 1) in June 11th of 2013. See Supplementary material (Table S2) for georeferences. Samples were picked up in the most important water channels and rivers covering the study zone. Some samples were taken from spring/wells to have also an idea of the ground water quality of the area regarding these compounds.

Before sampling, polyethylene bottles (2.5 L) were washed successively with detergent, tap water, distilled water and, finally, the sample water. Samples were collected as grab samples. Polyethylene bottles where used instead of glass ones because some pharmaceuticals are adsorbed to glass. The bottles were filled to the top with the water to eliminate air bubbles and maintained at 4 ° C until their arrival at the laboratory. Once in it, samples were filtered through glass microfiber GF/A filters (0.7 μm diameter) prior to extraction, acidified at pH < 2 and stored in dark bottles at −20 °C until the analysis. Samples were analyzed within 1 week.

2.3. Chemicals and materials

Pharmaceuticals were selected covering an important and wide variety of different therapeutic classes: β-blockers (metoprolol MPL and

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