CEST 2025

19th International Conference on Environmental Science and Technology

Kos, Greece, 3 to 6 September 2025

The Anthropocene and the wetlands: Pharmaceuticals and trace elements interactions in a Mediterranean wetland (L'Albufera, Spain).

Andreu V., Gimeno-García E., Picó Y., Campo J.

SAMA Reasearch Group, Desertification Research Center-CIDE (UV-GV-CSIC), Carretera CV-315 Km 10.7, 46113 Moncada (València), SPAIN.

*corresponding author: Vicente Andreu
e-mail: vicente.andreu-perez@uv.es

Abstract Trace elements and pharmaceutical products can affect the fragile balance in which Mediterranean wetlands are sustained. A clear example of that is L'Albufera Natural Park (Valencia, Spain), which shows constant pressure derived from high human and industrial occupation. In it, 14 areas were sampled to determine the levels of pharmaceuticals (PHs) and trace elements (HMs) in the soils. 17 drugs were selected, covering the most commonly used, and 12 trace elements of concern. The determination of the organic compounds was performed by Solid Phase Extraction (SPE), the extracts were analyzed by HPLC-MS/MS. The total content of 12 trace elements (As, B, Cd, Co, Li, Ni, Pb, Rb, Se, Sr, Ti and Tl) were extracted by microwave acid digestion, and the extractable fraction was obtained with EDTA, both were determined by ICP-OES. The highest average values were for Ti (518.62 mg/kg) and Sr (379.19 mg/kg), with maximum values of 807.37 and 724.43, respectively.
Thirteen of the pharmaceuticals analyzed were detected in soils, in at least one sample. Carbamazepine was the most frequently detected. The highest concentrations correspond to acetaminophen (17.70 µg/kg). The northern area is the most polluted in all cases. Some interactions have been found between HMs and PHs.
Keywords: Emerging contaminants, Mediterranean wetland, Pharmaceuticals, heavy metals, environmental interactions.

1. Introduction

Since the Industrial Revolution, two of the most important parameters in the fingerprint of human development on earth have been the presence of HMs and PHs in the environment. Some organic compounds have been called "emerging contaminants". Among them, PHs represent a group of growing concern around the world due to their potential effects on wildlife through soils, waters, and sediments, because the large number of compounds used in human and veterinary medicine. The number of these substances detected in the environment has increased in recent years, covering a broad spectrum of almost all therapeutic classes. These compounds typically reach the soil through treated wastewaters used in agricultural irrigation, or by the use of sewage sludge as organic amendment. In the same way, a new group of inorganic elements called "hazardous elements or "elements of concern" has been included in the EU's list of "emerging pollutants", including B, Bi, Rb, Sr, Se, Ti, Tl, V, etc.

In this work, the presence of twelve HMs of concern (As, B, Cd, Co, Li, Ni, Pb, Rb, Se, Sr, Ti and Tl) and 17 PHs, in soils of the L'Albufera Natural Park (Valencia, Spain) have been studied. The possible interactions between heavy metals (total and extractable fractions) and pharmaceuticals were evaluated, as well as the influence of the intrinsic characteristics of soils.

2. Materials and Methods

The selected area (486 km^2) is the alluvial plain delimited by the Turia (to the North) and Júcar (to the South) rivers, which flow into the sea along a wide coastal plain (Figure 1). This landscape structure has a dense network of canals and irrigation ditches. Agriculture is the main activity in the area, mainly rice. There is also a high population density, with industrial and urban development representing an important source of pollution hotspots.

Soil samples from the arable layer, from 0 to 50 cm deep, were collected. From each of the 20 sampling areas, of 25 m2 (5x5 m), 5 subsamples were taken. Once in the lab, the samples were dried and passed through a 2 mm Ø sieve, and then the subsamples from each sampling point were homogenized to create a composite sample. Samples were then stored in sealed plastic bags at 4 ºC. Those intended to measure PHs were stored in darkness at -20 ºC until analysis.

Standard laboratory analytical methods were applied to measure the physical and chemical properties of soils.

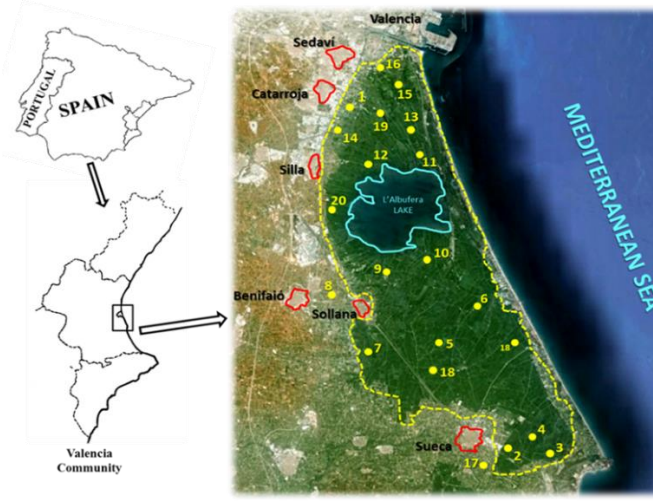

Figure 1. Study area and location of the sampling zones.

The PHs extraction was performed by Solid Phase Extraction (SPE), the extracts were analyzed by HPLC-QqQ-MS/MS. 12 trace elements were selected covering both widely known metals (Cd, Co, Ni and Pb) and elements included in the list of "hazardous elements" (As, B, Li, Rb, Se, Sr, Ti and Tl). The total content of them was extracted by microwave acid digestion, and the extractable fraction was obtained with EDTA 0.05M at pH 7, both were determined by ICP-OES.

3. Results and Discussion

All the elements studied were detected in all analysed samples. The highest average values were for Ti (518.62 mg/kg) in paddy areas and Sr (379.19 mg/kg) in citrus areas, with maximum values of 807.37 and 724.43 mg/kg, respectively. It is necessary to consider the scarcity of existing information on the group of "hazardous elements", as there is no data on toxicity, regulations or legal recommendations for many of them. In this sense, elements such as B, Li, Rb, Sr and Tl exceed the limits observed in the literature in their total values.

Regarding the extractable content of the elements, a distribution pattern similar to that of the total contents in the study area. The highest values were for Sr (724.43 mg/kg) and Ti (807.37 mg/kg) in the north of the Park. From the study of the extractable/total ratio of the studied elements, it was observed that some areas showed very high levels of availability in toxic metals such as Sr (52.13 %, zone 16) and Pb (75.31 %, zone 4), or Cd (43.81%, zone 11). It could indicate a potential toxicity status of these soils.

Among soil characteristics, electrical conductivity (EC) and organic matter (OM) are those that have the greatest influence on the dynamics of the HMs total contents, except for Cd and Ti, which are more significantly related to pH. Regarding the extractable fraction, it is still the EC and OM that show highly significant correlations with most of the elements, although the mineral N presents important negative correlations with Cd and Pb.

Of the 17 pharmaceuticals analyzed, 13 were detected, in at least one sample, at MDL concentrations at 13.2 µg/g. The presence of pharmaceutical products in soils was widespread, probably due to the continuous contributions of water treated by wastewater treatment plants that do not completely eliminate them (Verlicchi et al. 2012). Carbamazepine is the only compound to appear at all sampling points, followed by acetaminophen (14), sulfamethoxazole (12) and diclofenac (10). The lowest appearance has been ofloxacin and chlorfibric acid, which only appear in four points in both cases. The highest mean levels were for acetaminophen (1290.05 µg/g) and Paracetamol (306.44 µg/g). In the northern area of the lagoon, higher levels and frequency of PHs were observed, which is justified by the higher concentration of population and the influence of the wastewater treatment plants of the city of Valencia. Maximum values of sulfamethoxazole (144.01 µg/kg) were also found in this area. However, the most contaminated sampling zone was P6, located in the Northwest of the lagoon. This point is set in the middle of an agricultural area but surrounded by several tourist and leisure places. Organic matter and available phosphorus are the soil parameters most significantly related to pharmaceuticals. However, above all, it is pH that had the greatest influence on them, in particular with Ciprofloxacin, Ibuprofen, Ofloxazin and Trimetroprim. In general, for both PHs and HMs, the northern area of the Natural Park, in the rice fields, concentrates the highest values of the compounds studied, together with the citrus areas in the southeast of the area.

4. Conclusions

Pharmaceuticals and emergent elements in soils of the L'Albufera Natural Park in Valencia have been established. The northern area of the Park showed the presence of a greater number of the compounds and metals studied, which coincides with a higher population density and the presence of important WWTPs. In this area, the sampling zones closest to the coast had higher concentrations of metals. B, Li, Rb, Sr and Tl that exceed the maximum levels recommended by the literature. Of the 17 pharmaceuticals studied, 13 appeared in at least one sample. Ni, B and Co have highly significant correlations with different compounds. Organic matter and electrical conductivity are the soil parameters most closely related to both inorganic elements and pharmaceuticals.

Acknowledgements

This work has been supported by the Spanish Ministry of Science and Innovation through the project CIPROM/2021/032 of the Generalitat Valenciana (Spain).

References

Verlicchi P., Al Aukidy M., Zambello E. (2012), Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment-A review, *Science of the Total Environment*, 429, 123–155