The pollution before the flood: Microplastics and PAHs in water, sediment and fish from Júcar River basin (E Spain)

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Abstract. In October 2024, Júcar River and its tributary, Magro, were responsible for the fatal floods in the south of the province of Valencia. There is general concern about the environmental pollution by microplastics (MPs) due to their possible adverse effects on organisms and their ability to accumulate various types of contaminants, such as polycyclic aromatic hydrocarbons (PAHs). Thus, the co-occurrence of MPs and PAHs was investigated in superficial water, sediment and fish samples from the Júcar River basin (E Spain) to set the benchmark of pollution before the flood. Extraction protocols were optimized according to matrix and analyte type. MPs were determined by micro-FTIR (μFTIR) and Pyrolysis coupled with Gas Chromatography-Mass Spectrometry (Py-GC-MS), while PAHs were quantified using GC-MS. Ecological and human health risk was, also, estimated by different indexes. Both MPs and PAHs were detected in the majority of samples with higher concentrations near the river mouth that coincides with the metropolitan area of Valencia and an industrialized zone. A potential ecological and cancer risk would be possible due to exposure to MPs and PAHs. This study provides helpful insight into pollutants and their associated risk a few months before the rivers overflowed.

1. Introduction

In 2024, Júcar river and its tributary, Magro, overflowed due to torrential rain causing multiple casualties and extensive property damages in the south of the province of Valencia (1). Júcar river flows through three different provinces (Cuenca, Albacete, Valencia), being one of the most important rivers in eastern Spain with over one million people living in the basin. It has been selected as European Pilot River Basin for the implementation of the Water Framework Directive (Directive 2000/60/EC). An aspect of the environmental pollution by MPs, which requires further investigation concerns their ability to accumulate various types of contaminants on their surface and act as their vectors (2). These contaminants include PAHs, which are known for their carcinogenic effect on humans and, therefore, some of them are regulated with the aim of decreasing their release to the environment (2,3). For this reason, the co-occurrence and risk of MPs and PAHs was determined PAHs in water, sediment and fish samples from the Júcar River basin. The results of this study could provide an insight on the pollution levels of the river, set the benchmark values of MPs and PAHs before the flood, assess of the potential risk to animals and people exposed to river water and sediment and, finally, be compared to future studies to fully understand the impact of the river overflow.

2. Materials & Methods

Water, sediment and fish samples from the Júcar River and its tributaries, Cabriel and Magro Rivers, were collected during May and June 2024. Water and sediments were collected from 15 points, while fish samples were collected from 6 points and included species like *Micropterus salmoides* (black bass), *Barbus guiraonis* (barbel) and *Alburnus alburnus* (bleak).

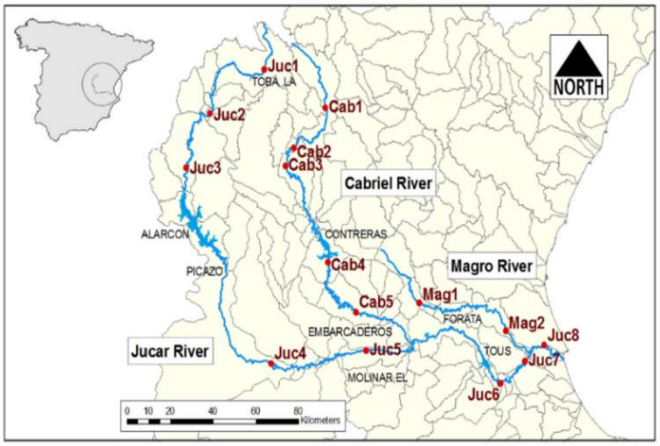

Figure 1. Map of the sampling points along the Júcar River basin.

Extraction protocols were optimized according to the matrix and the contaminant type. Density separation and digestion (H_2O_2, persulfate) were combined for MPs extraction from water and sediment, while for fish, a microwave-assisted digestion was performed using a combination of acid and base to obtain the MPs present in their gastrointestinal track. For the determination of PAHs, solid-phase extraction (SPE) and microwave-assisted extraction (MAE) were adapted for each matrix. For MPs, μFTIR and Py-GC-MS were utilized, while the identification and quantification of PAHs was done using GC-MS. Ecological risk assessment was based on the Pollution Load Index (PLI), Hazard Index (HI), pollution risk index (PRI) and Risk Quotient (RQ) approaches, while cancer risk was estimated by the

estimated daily intake (EDI) and the lifetime carcinogenic risk model (ILCR).

3. Results & Discussion

As far as the water samples are concerned, μFTIR analysis indicated the presence of MPs in all water samples (100%) with concentrations ranging from 0.1 to 6.9 MPs L^{-1}. The main polymer types identified were polyethylene (PE), and halogenated polystyrene (PS)/polypropylene (PP). Chrysene was detected in all the samples from Cabriel River and one sample from Júcar River (JUC1) at a concentration of 0.7±0.1-10.9±2.4 μg L^{-1}, while the samples collected near the river mouth showed the highest total PAHs concentrations. Anthropogenic activity is the primary source of PAHs to river water and, thus, the sampling points closest to the metropolitan area of Valencia and an industrial area (JUC8 and MAG2, respectively) were characterised by the highest concentrations in this study. In the case of sediments and fish, samples were extracted twice and analysed both by μFTIR and Py-GC-MS. According to μFTIR, 73% of the sediment samples and 66% of the fish samples were polluted by MPs (sediments: 20-140 MPs Kg^{-1}, fish: 6.7-26.7 MPs g^{-1}), and the most abundant polymers were PE and nylon. On the other hand, fish samples analyses by Py-GC-MS showed the presence of PP only in the bleak from Júcar River, as well as, PVC in 46.6% of the samples with quantities up to 152.5-705.3 μg g^{-1}. However, an overestimation of the PVC quantity is inevitable due to the indicators used for its quantification, which include aromatic compounds that can be pyrolysis products of the organic fraction of the matrix. Since different parts of the same sample were processed and analysed by the two methods, the results of μFTIR and Py-GC-MS should be combined and not compared. Sediments act as pollutant ¨sinks¨ and GC-MS results indicated the presence of at least nine PAHs in each sample. 2-methylnaphthalene presented the highest concentration that reached 1054.7±44.3 ng g^{-1}. 2-methylnaphthalene, acenaphthene, anthracene, phenanthrene and fluoranthene were detected and quantified in all fish samples, with 2-methylnaphthalene and fluoranthene having the highest concentrations. The bleak from Júcar River was characterised by the occurrence of 11 PAHs and it was the only sample that showed contamination by benzo[a]pyrene.

Water and sediments are indicators of the pollution at specific points of the river, while fish samples provide an indication of the contaminant levels along the entire river basin. Ecological risk assessment indexes of water and sediment suggest potential high risk to the environment due to the plastic polymer types and PAHs detected at the final part of the river, near the mouth. However, there seems to be low risk for the fish due to exposure to MPs, while there could be potential risk to the fish due to PAHs occurrence but these results should be interpreted with caution since background concentrations for PAHs in fish tissues are not available. Cancer risk assessment for PAHs present in water and fish, that could be consumed, showed ILCR values were > 10^{-6} for all water samples where PAHs were detected and for the bleak from the river, indicating potential cancer risk.

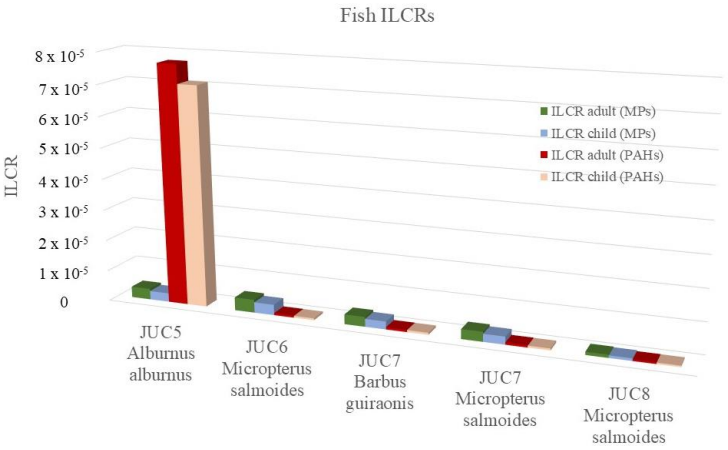

Figure 2. ILCR for adults and children due to MPs and PAHs exposure through fish consumption

4. Conclusions

In this study, benchmark levels of MPs and PAHs before the floods were estimated. MPs occurrence was the largest in the water samples from JUC8 (near the river mouth, close to Valencian metropolitan area) and CAB5 (last sampling point of Cabriel River, upstream of Jucar River confluence), with concentrations of 6.9 MPs L^{-1} and 6.8 MPs L^{-1}, respectively. PAHs were found in higher abundance in sediments and fish because of their hydrophobicity, and their sources seem to be mostly petrogenic but, also, pyrogenic near the river source that could be due to forest fires in the area. Ecological and human health risk was identified as a result of the occurrence of these pollutants in the river system, suggesting the importance of close monitoring in order to better understand and control the pollution levels of an important river basin of the south of the province of Valencia that is characterized by flood risk.

References

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