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Research Paper

Co-occurrence of microplastics and polycyclic aromatic hydrocarbons in the Júcar River basin (E Spain): The benchmark before 2024's floods

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ABSTRACT

The south of the province of Valencia (Spain) is characterised by high flood risk and, in October 2024, Júcar River tributaries were partially responsible for catastrophic floods in the area related to the influence of global warming. The floods carried large amounts of water and sediment and, with them, many pollutants such as microplastics (MPs) and polycyclic aromatic hydrocarbons (PAHs). Co-occurrence of MPs and PAHs was investigated in water, sediment and fish samples from the Júcar River basin to set a benchmark of pollution in this flood susceptible area, only four months before the October 2024 catastrophe. Extractions were optimized based on matrix and compound type. Analyses were performed by micro-FTIR, Pyrolysis coupled with Gas Chromatography-Mass Spectrometry (Py-GC–MS) and GC–MS/MS, and ecological and human health risks were, also, estimated for the determined pollutants. Both MPs and PAHs were detected in the majority of samples, with higher concentrations near the river mouth (up to 100 ± 3.8 MPs Kg $^{-1}$ and 2017.4 ± 107.8 ng g^{-1} of total PAHs), located close to the metropolitan area of Valencia and its industrial zone. One fish sample (*A. alburnus*) presented a concentration of 19.97 ± 1.1 μg g^{-1} of polypropylene (PP) and was contaminated by 11 PAHs, including benzo[*a*]pyrene (14.2 ± 1.2 ng g^{-1}). Incremental life cancer risk values for MPs and PAHs ranged from 1.7×10^{-6} to 3.1×10^{-4} for all water samples where PAHs were detected, and for the highly polluted fish sample (14.5×10^{-3} and 7.7×10^{-5}), indicating potential risk. Principal component analysis (PCA) suggested positive correlation between PP, benzo[*a*]pyrene and potential cancer risk. This is the first study that provides data on both MPs and PAHs ecological and human health risk assessment in the same environmental samples from a river catchment and establish a benchmark for these pollutants before flooding.

1. Introduction

The occurrence of microplastics (MPs) in the aquatic environment has been widely reported and it is considered a serious health and ecological issue [1]. The main source of these pollutants is the inadequate management of plastic waste, that leads to plastic pollution spreading through air and land runoff [2]. Such runoff effect is facilitated by creeks and rivers, and allows plastic particles to reach other freshwater systems and the marine environment [1]. The low density of MPs, which are polymeric particles of a size ≤5 mm [3], permits them to float in the water column and to be transported [4]. Accumulation of biofilm or suspended clay can increase their density and, consequently, deposition into the sediments [5]. For this reason, river sediments are considered sinks for MPs and are important indicators of the actual pollution levels of ecosystems [6]. Plastic particles pose a serious threat to aquatic organisms that mistake them for food [7]. Ingestion of MPs by approximately 150 fish individuals in freshwater and marine systems has been reported [8] and their adverse effects on these organisms include oxidative stress, neurotoxicity and behavioural abnormalities [9]. Furthermore, several studies suggest that smaller MPs and nanoplastics (NPs) are able to cross biological barriers (skin, tissues), and accumulate in different organs, not only in the gastrointestinal tract [10,11]. The presence of these particles in river water and organisms proves that MPs can enter the food chain and affect human health [12]. Another aspect of MPs' behaviour that causes concern is the potential sorption of organic contaminants on their surfaces, i.e., polycyclic

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aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), that could increase their toxicity [13–15].

PAHs are a category of organic compounds featuring at least two aromatic rings with lipophilic properties [14]. The two main categories of PAHs are the low molecular weight (LMW) ones, that consist of 2–3 aromatic rings, and the high molecular weight (HMW) PAHs with >3 aromatic rings [16]. The main source of PAHs contamination is the incomplete combustion of fossil fuels, biomass, and other organic and inorganic materials [2]. Forest fires, garbage and oil burning are processes that can generate PAHs [14]. Moreover, urban runoff and atmospheric deposition of PAHs leads to their widespread distribution in various environmental compartments [2]. Once in the environment, PAHs tend to accumulate in sediments and in the tissues of biota, while their concentrations are lower in water, due to their hydrophobic nature [17]. The occurrence of PAHs in aquatic organisms has been investigated and toxic effects that include reproduction and growth impairment, as well as, endocrine disruption and mutations have been reported [2,17]. Their presence in different tissues and organs indicates a way of entry for these pollutants to the food web [2]. PAHs are known for their carcinogenic effect on humans and, therefore, some of them are regulated with the aim of decreasing their release into the environment [18]. Regulatory measures in place mainly focus on the control of emissions and wastewater treatment, while remediation strategies for the removal of PAHs from water and sediment after oil spills focus on the containment, and subsequent cleaning of the affected area [16].

Due to their high hydrophobicity and high surface area to volume ratio, MPs show an increased affinity to organic pollutants such as PAHs and can act as their vectors [15]. The adsorption usually follows second-order kinetics, suggesting chemical affinity between the polymer and the pollutant [19]. Apart from the adsorption of PAHs present in the environment on MPs, these organic contaminants can, also, leach from plastics, along with other additives [20]. The majority of scientific studies reports the abundance of MPs or PAHs in environmental matrices, while information about their co-occurrence and the quantity of PAHs extracted from MPs found in the environment has only recently received attention [14]. Extracting organic compounds from MPs present in water, sediment and biota can be challenging due to their low quantity and, sometimes, the destruction of the sample in MP identification and quantification, specifically when Py-GC–MS is employed [14]. For this reason, MPs and PAHs from the same matrix are, usually, extracted and analysed separately. The determination of the co-occurrence of MPs and PAHs in environmental samples allows the better understanding of their combined toxic effects on organisms [21]. Tien et al. (2020) observed a positive correlation between MPs and PAHs in fish samples from the Fengshan River in Taiwan [21], and exposure experiments indicated that the presence of MPs and NPs seems to increase the bioavailability of PAHs to *Daphnia magna* [22]. However, another study reported that sorption of PAHs on MPs reduces their availability to zebrafish (*Dario reno*) [23]. There are polymer- and species- dependent parameters that define the adverse effects of MPs and PAHs, and those additional data are needed for a more realistic risk assessment of the combination of these pollutants in the ecosystem [24].

The pollution of rivers by MPs and PAHs affects the quality of both freshwater and marine environments, and knowledge of their actual pollution status facilitates the development and management of inland, coastal and marine areas [25]. MPs presence is far more investigated in seawater than in freshwater [26]. In Spain, there are several studies that determine the presence of MPs [27,28] or PAHs [29,30] in river water, sediment and fish. A study of benthic sediments and river water from the Ebro River reported elevated MPs concentration in the sediments, most of them fibres, supporting the evidence that this matrix acts as a s̈ink for these pollutants [27]. Another study in rivers from the NW Spain, also, identified MPs in river sediment and water, showing a negative impact to the most sensitive benthic macroinvertebrate taxa [28]. Some PAHs levels in Spanish river sediments and waters are controlled either by hydrographical confederations or by water agencies and are within the acceptable environmental limits [31]. However, to the authors'knowledge, no study to date provides information on the co- occurrence of both MPs and PAHs, using concentration levels to assess their ecological and human health risk. The Júcar River catchment was selected as study area since it is one of the most important in eastern Spain. In October 2024, the final part of the Júcar River basin (after Magro River confluence) was flooded due to torrential rains associated to an upper-level low pressure system phenomenon, and caused multiple casualties and extensive property damages [32]. The flood carried large amounts of water and sediment, and with them significant amounts of pollutants have been likely transported [33]. Thus, the ultimate objectives of this study include: (1) the identification and quantification of MPs present in water, sediment and fish samples of the Júcar River catchment using two different analytical approaches, namely micro-FTIR (μFTIR) and Py-GC–MS, (2) the estimation of the level of 19 PAHs in the same samples by GC–MS/MS, (3) the setting of a pollution benchmark related to MPs and PAHs in the basin before the 2024 flooding and, finally, (4) the use of ecological and human health risk assessment approaches to estimate the potential toxicity of MPs and PAHs. This is the first study that investigates the MP- and PAH-contamination and their associated risks, simultaneously, providing an insight on the pollution levels of the river before the flood, and allowing the assessment of the potential risk of both pollutants to animals and people exposed to river water, sediment and fish, due to the flood or through consumption.

2. Materials and methods

2.1. Chemicals

Sodium chloride (NaCl), hydrogen peroxide (H_2O_2) and persulfate were purchased from Epica S. L. (Valencia, Spain). Sodium hydroxide (NaOH) and nitric acid (HNO_3) were obtained from Merck (Darmstadt, Germany), while methanol (MeOH), acetonitrile (ACN), dichloromethane (DCM), hexane (Hex) and isooctane, all with purity >99 %, were purchased from Avantor (Pennsylvania, USA). Water was purified by an Elix Milli-Q system (Millipore, Massachusetts, USA). For the calibration curve of PAHs, the L429-PAR mixture was purchased from Wellington Laboratories (Ontario, Canada). The Microplastic calibration standard MPs-SiO_2 (Frontier Laboratories, Japan) was used, containing the following polymers: polyethylene (PE), polypropylene (PP), polystyrene (PS), acrylonitrile butadiene styrene (ABS), styrene-butadiene rubber (SBR), poly(methyl methacrylate) (PMMA), polycarbonate (PC), polyvinyl chloride (PVC), polyethylene terephthalate (PET), nylon 6 (N6), and nylon 6,6 (N66) diluted in silicon dioxide (SiO_2).

2.2. Study area and sampling

The Júcar River, with a length of 498 km, flows through three different provinces (Cuenca, Albacete, Valencia) and is characterised as one of the most important rivers in eastern Spain, with over one million people living in its Mediterranean catchment. The Júcar River's source is located at 1700 m a.s.l. in the Iberian System (Montes Universales), and its mouth in the Mediterranean Sea (40 km south of Valencia city). The river area is characterised by periods of floods and droughts [32]. The watershed of 21,578 km^2 is mountainous and well preserved in its upper part, but water quality problems appear in the medium and lower parts where agriculture accounts for nearly 80 % of water demand. Júcar River receives wastewater discharges from more than 20 urban and industrial wastewater treatment plants (WWTPs), including those of large cities such as Cuenca and Teruel. In its lower part, after the confluence of Cabriel and Magro Rivers, Júcar River drains to L'Albufera of Valencia, a large coastal lagoon and marshy area with protected wetlands (L'Albufera Natural Park), and agricultural lands. This basin was selected as European Pilot River Basin for the implementation of the Water

Framework Directive [34]. Water demand from this river is, also, for human consumption, irrigation and production of hydropower [35].

The sampling campaign was carried out during May and June 2024. The specific period was selected after consideration of the weather conditions (lack of rainfall at least two weeks before the start of the sampling campaign and throughout) and the rivers flow. A total of 15 sampling points were selected, eight along Júcar River starting near the source (JUC1) and finishing near the mouth (JUC8), five along Cabriel River (CAB1–5) and two points from Magro River (MAG1–2) (Fig. 1). The sampling points were divided into three different zones, namely Zone 1 that includes the area near the source of the rivers (JUC1–3, CAB1–3, MAG1), Zone 2 corresponding to the middle part of the basin (JUC4–7, CAB4, MAG2), and Zone 3, at the final part of the rivers near the mouths (JUC8, CAB5). The location of the sampling points, together with the types of samples taken from each point can be found in Table S1 (Supplementary Material). As for river water, a total of 11 L were collected using glass bottles to avoid plastic contamination: 10 L were used for MPs analysis, while 1 L was stored for PAHs determination. Composite sediment (1 Kg) was collected from the rivers bank (depth of 0–0.5 m). The sediments were freeze dried prior to extraction to remove the water without affecting the possible pollutants present. Fish samples were obtained by electrofishing, using a voltage of 140 V during 35–60 min. A total of 39 samples, 15 of water, 15 of sediment, and 9 fish were analysed. Water and sediment were obtained from all sampling locations, while fish was obtained from 6 points of Júcar River, namely JUC1, JUC2, JUC5, JUC6, JUC7 and JUC8 (Table S1). The fish included the endemic species Iberian barbel (*Barbus guiraonis*), common bleak (*Alburnus alburnus*) and the invasive species black bass (*Mycropterus salmoides*).

2.3. Extraction of microplastics

Different extraction procedures were optimized in order to extract MPs from the three matrices: water, sediment and fish. For the water, a volume of 10 L was passed through a 5 mm metallic sieve to remove bigger particles and, then, through a 5 μm metallic sieve to retain MPs (5 μm $\leq$ size $\leq$5 mm). All retained particles were transferred from the sieve into a Sediment Microplastic Isolation Unit (SMI) that was built with PVC, and conditioned with saturated NaCl solution (1.2 g cm^{-3}), as described elsewhere [7,36]. Briefly, the SMI was cleaned, conditioned and, after adding the particles from the sieve, it was filled using 700 mL of saturated NaCl solution. After stirring for 15 min, the solution was left for 4 h to settle and to allow the MPs to float to the surface. Then, the SMI valve was closed and the floating fraction was filtered employing a vacuum-assisted filtration system (KG13A, Advantec) onto silicone filters (Smart Membranes, MakroPor12M5–350: 1.2 × 1.2 cm square, 5 μm pore size) for micro-FTIR (μFTIR). The quantity of particles after sieving was low and, thus, it did not permit multiple analysis. The μFTIR was selected for the determination since it provides information about exact particle size (when compared to Py-GC–MS) although, once the particles are on the silicone filters, their recovery for further processing is quite challenging.

Fig. 1. Map of sampling points from Júcar (JUC1–8), Magro (MAG1–2) and Cabriel (CAB1–5) Rivers. The three river bodies (blue) and the Júcar River catchment (red) are represented. Major cities near the basin and the industrial area of Carlet are highlighted in the map, while the tributary confluence points near JUC5 and JUC7 are circled in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Sediment extraction was similar to the water one at the beginning, but it required oxidation steps due to high organic matter content. Specifically, after sieving of the sediments using a 5 mm sieve for the removal of rocks and other bigger particles, 40 g of the sample was placed in the SMI for density separation, as described above. After flotation, the solution was filtered onto cellulose nitrate filters and the filters were left to dry at room temperature. Then, the particles on the filter were placed in a glass beaker and 50 mL of H_2O_2 were added. An incubation of 2 h at 45 °C followed and, after that, the solution was filtered again. If there was still high organic matter content, the filtration was done using cellulose nitrate filters and after drying, the particles were, once again, placed in a glass beaker with 100 mL of persulfate solution (1 mol L^{-1}), and incubated for 2 h at 45 °C. Final solutions were filtered onto silicone filters for μFTIR analysis. Same density separation and oxidation steps were followed for Py-GC–MS analysis, with the only difference being the use of quartz filters for the final filtration.

Fish samples were dissected upon arrival at the laboratory. For MPs determination, the entire gastrointestinal track (GIT) was separated, homogenized and stored at -20 °C prior to analysis. Part of the homogenized GIT was digested (0.3 g) employing an Ethos X Microwave Extraction System (Milestone, Italy). Fish GIT was placed in teflon cells with 4 mL of NaOH (4 M) and 6 mL of HNO_3 (2 M) for digestion. The digestion lasted 20 min and the temperature was 120 °C with agitation active throughout the entire procedure. After digestion, the solutions were filtered onto silicone filters for μFTIR analysis. Once more, same digestion steps were followed for Py-GC–MS with quartz filters for the final filtration.

2.4. Extraction of polycyclic aromatic hydrocarbons

The remaining 1 L of river water from all the sampling points was filtered using 90 mm glass fibre filters (Advantec, Japan) to remove floating particles prior to PAHs determination. Solid-phase extraction (SPE) was used to extract 250 mL of water, using ACN as a dispersive solvent [37]. Briefly, each river water sample was mixed with ACN at a 75:25 *v*/v H_2O:ACN ratio and was, then, extracted using Strata™ -X 33 μm Polymeric Reversed Phase (200 mg/ 6 mL) cartridges (Phenomenex, Torrance, Ca, USA), and a 12-port vacuum manifold Supelco Visiprep 57,030-U system (Sigma-Aldrich). Samples were passed through the cartridges with a flow of 10 mL min^{-1} under vacuum and, subsequently, the cartridges were cleaned using 6 mL of ultrapure water and left to dry for 30 min. The elution of the analytes was performed with 5 mL of DCM at gravity flow. Finally, the eluents were concentrated to 1 mL at 40 °C using a sample concentrator and heating plate (Nitrogen generator ZEFIRO 35 from CINEL S.R.L) before GC–MS/MS analyses.

Sediment and fish samples were extracted inside the Ethos X Microwave Extraction System. For sediments, 5 g were extracted using 20 mL of a solution of Hex:DCM (1:1 *v*/v) as the extraction solvent. The microwave-assisted extraction lasted for 15 min at 110 °C. Subsequently, the solvent was centrifuged at 3000 rpm for 5 min and filtered using nylon filters. Then, it was concentrated to 1 mL by a rotary evaporator (Buchi R-100 Rotavap System), and a SPE clean-up was performed using Strata PAH cartridges (Phenomenex, USA). The elution of the analytes of interest was done by 40 mL of Hex and 8 mL of Hex: DCM (2:1 *v*/v). Extracts were concentrated to 1 mL and stored before GC–MS/MS. The concentrations of PAHs are expressed in ng g^{-1}

sediment dry weight (dw). PAHs were also determined in fish muscle samples. Microwave Assisted Extraction (MAE) was used for the extraction of 0.5 g of homogenized fish muscle, using 6 mL of DCM. MAE lasted for 1 h at 80 °C with agitation throughout the entire procedure. After extraction, the samples were passed to falcon tubes and they were centrifuged at 3000 rpm. Then, they were passed to new falcon tubes, to remove the solid particles of the fish muscle, and they were concentrated to 1 mL. A clean-up step was, then, performed by SPE using silica Bond Elut SI (1 g, 6 mL, particle size 40 um) cartridges (Agilent Technologies, USA) and the elution was done by DCM and Hex:DCM (2:1 *v*/v), same as the sediments. Then, concentration to 2 mL was achieved under nitrogen flow. Samples were analysed to investigate the presence of 19 PAHs of environmental interest and concentrations in fish are presented in ng g^{-1} fish wet weight (ww).

2.5. Determination of microplastics

The determination of MPs present in all the samples was performed by μFTIR. The Nicolet iN10MX microscope has two different detectors, the Deuterated Triglycine Sulphate thermal detector (DTGS) that functions at room temperature and the Mercury Cadmium Telluride A band (MCT-A) that requires liquid nitrogen to achieve low temperature. The liquid nitrogen-cooled MCT detector was employed, since it provides higher resolution and allows the detection of MPs with minimal sizes near 10 μm. Approximately, 1 L of liquid nitrogen (Air Liquide, France) is consumed per day. The software employed for spectra analysis was the OMNIC Picta (version 1.8.1.259). Scanning of the entire filter was performed and spectra from all the particles present were collected. For whole filter analysis, the collection of a mosaic is necessary. The IR spectra of the entire filter (1.2 × 1.2 cm) were recorded in transmission mode, performing 16 scans (time: 3 s) and the resolution and scan speed were set to normal. The width of the aperture was 150 × 150 μm and the detector spectral range was set from 4000 to 675 cm^{-1}. The Blackman-Harris signal filter was selected as recommended by the manufacturing company. Once the filter mosaic was captured, the Particles Wizard software was utilized to determine the number of particles, the size of each particle, and the spectrum of each particle on the filter. A background was set, which spectrum was subtracted from the particle ones. Polymer search was performed using several libraries (e.g., the HR Sprouse Polymers by Transmission and the Wizard Library). In the final report, the results with the highest match score appeared in a list, and if a score > 70 % was achieved, the identification was considered acceptable.

Moreover, Py-GC–MS was performed for the quantitative determination of the mass of polymers in sediment and fish samples. An EGA/PY-3030D pyrolyzer (Frontier Laboratories) coupled to an 8890 Gas Chromatograph combined with a Mass Selective Detector 5977B (Agilent Technologies), and equipped with an Auto-Shot Sampler AS-1020E (Frontier Laboratories) was employed. The GC was equipped with a split/splitless injector and a HP-5MS capillary column (5 % diphenyl-95 % dimethylpolysiloxane, 30 m × 0.25 mm × 0.25 μm, Agilent Technologies). The quartz fibre filters were punched and directly transferred in pyrolysis cups. Samples were pyrolyzed at 600 °C for 0.2 min. Py-GC interface temperature was set at 280 °C. The pyrolysis products were eluted in constant flow (1 mL min^{-1}) of helium with a 30:1 split ratio. The transfer line was kept at 280 °C. The GC temperature programme was: 40 °C for 6 min, 20 °C min^{-1} to 310 °C for 40 min. The MS operated in EI positive mode (70 eV, *m/z* 35–550). The temperature of the ion source and quadrupole analyser were 230 °C and 150 °C, respectively. The characteristic pyrolysis products of all the polymers that were included in the analysis can be seen in Table S2.

2.6. Determination of polycyclic aromatic hydrocarbons

PAHs determination in the extracts was done by GC–MS/MS. The instrument used was an Agilent GC 7890B coupled with a MS 7010 triple quadrupole mass spectrometer, equipped with an Agilent ALS autosampler, and a Multi Mode Injector port used in the pulsed splitless mode (Temperature injector = 280 °C, 60 psi; Temperature transfer line = 300 °C). The column used was an HP-5MS UI (95 % dimethyl – 5 % phenylpolysiloxane, 30 m × 0.250 mm, film thickness 0.25 μm). The mobile phase was helium, with a flow of 1.2 mL min^{-1}, a pressure of 11.05 psi. For the collision cell, helium was used with a flow of 4.0 mL min^{-1}, while nitrogen was used with a flow of 1.5 mL min^{-1} with a pressure of 10 psi. The GC oven temperature programme was: 40 °C for 6 min, then 20 °C min^{-1} to 55 °C, 50 °C min^{-1} to 120 °C, 20 °C min^{-1} to 200 °C and, finally, 8 °C min^{-1} to 310 °C for 3 min (solvent delay = 6 min). The list of the 19 PAHs that were analysed together with their transitions and retention times can be found in Table S3.

2.7. Risk assessment

2.7.1. Ecological risk assessment

An ecological risk assessment approach was employed to estimate the potential environmental risk of the occurrence of MPs and PAHs in river water, sediment and fish. For the MPs, four different factors were calculated, namely: (i) the Hazard Index (HI), based on the chemical toxicity of each polymer type, (ii) the Pollution Load Index (PLI), determined by the amount of MPs present, (iii) the Pollution Risk Index (PRI) and (iv) the Risk Quotient (RQ), determined by both amount and polymer toxicity of MPs to specific organisms. All these factors were calculated using the Eqs. (1)–(6).

$$HI = \sum Pn \times Sn \tag{1}$$

For HI estimation, P_n is the percentage of plastic polymers identified at each sample, and Sn is the hazard score of each polymer as obtained from Linther et al. (2011) [38].

$$CFi = \frac{Ci}{C0i} \tag{2}$$

$$PLI = \sqrt[n]{CFi} = CFi \tag{3}$$

$$PLI_{zone} = \sqrt[n]{PLI1 \times PLI2 \times \ldots \times PLIn} \tag{4}$$

$$PRIi = HIi \times PLIi \tag{5}$$

PLI was proposed for heavy metals [39]. CFi is the quotient of the number of MPs (Ci) and the minimum MPs concentration (C0i), which is the minimum concentration of MPs found per sampling point and analytical tool in the present study. As it is shown in Eq. (3), PLI at each sampling site is equal to CFi since the MPs are considered as a whole, since $n = 1$ [7,40]. Aiming to compare and combine both indexes, the HI and PLI values were classified into four categories (I–IV) of increasing hazard according to the criteria outlined in Table S4, which is based on the UN Globally Harmonized System (GHS). PRI is the combination of HI and PLI per sampling point and matrix [41].

$$RQ = \frac{MEC}{PNEC} \tag{6}$$

RQ is the ratio of the measured environmental concentration (MEC) over the predicted no effect concentration (PNEC) [42]. PNEC refers to an endpoint obtained from species susceptibility distribution (SSD) analysis. In the present study, it was adapted from Koelmans et al. (2020) [43], for the river water, who determined a PNEC value of 75.6 MPs L^{-1} as HC_5 in freshwater systems, and from Yang et al. (2023) [44], for river sediment, who estimated a PNEC of 539 MPs Kg^{-1} in the Yangtze River Basin. If RQ < 1 there is no immediate risk for the environment since the concentrations are lower than the one that can cause adverse effects, while RQ > 1 indicates risk to the environment.

For the estimation of the ecological risk associated with PAHs present in the Júcar River basin, the risk quotient (RQ_{PAHs}) was calculated according to the following equation:

$$RQ = \frac{CPAHs}{CQV} \quad (7)$$

The C_{PAHs} represents the PAH concentrations in the sample, while C_{QV} is the quality value of PAHs. The negligible concentrations (NCs) and the maximum permissible concentrations (MPCs) of individual PAHs in water and in sediment represent the quality values, respectively. Hence, the RQ_{NCs} and RQ_{MPCs} were calculated according to the Eqs. (8) and (9), respectively:

$$RQ = \frac{CPAHs}{NCs} \quad (8)$$

$$RQ = \frac{CPAHs}{MPCs} \quad (9)$$

NCs and MPCs for water and sediments are taken from Cao et al. (2010) [45]. For the fish samples, only RQ_{MPCs} were calculated using the environmental quality standard value of 0.0085 μg Kg^{-1} for benzo[*a*] pyrene proposed by the European Union Directive 2013/39/EU [46]. For individual PAHs, $RQ_{NCs} \sim 0$ indicate very low risk, while $RQ_{NCs} \geq 1$ and $RQ_{MPCs} \leq 1$ indicate medium risk, and $RQ_{MPCs} \geq 1$ indicates high risk [47]. For total PAHs, $RQ_{NCs} < 800$ and $RQ_{MPCs} \sim 0$ describe low risk, $RQ_{NCs} > 800$ and $RQ_{MPCs} \leq 1$ show medium risk, while $RQ_{NCs} \geq 800$ and $RQ_{MPCs} \geq 1$indicates high risk [47].

2.7.2. Human health risk assessment

The risk of consuming MPs- and PAHs-polluted water or fish was estimated using the results of this study. The estimated daily intake (EDI) of plastic particles found in water (particles per liter per day) and in fish (particles per Kg per day) was calculated for adults and children with respect to body weight [48]. The following Eq. (10) was used to estimate the total expected daily intake of MP-contaminated water and fish, consumed through the oral channel:

$$EDI = \frac{Mc \times Rc}{Mw} \quad (10)$$

where M_c was the mean concentration of each plastic polymer found in each water or fish sample, R_c was the consumption rate of water (adults: 2.4 L day^{-1}, children: 1.5 L day^{-1}) or fish (adults: 0.050 Kg day^{-1}, children: 0.029 Kg day^{-1}) and M_w was the mean bodyweight for an adult (70 Kg) and a child (35 Kg). The daily consumption rates of water and fish were chosen using up-to-date data available about seafood and fish consumption in Spain [49], and were in accordance with rates used in similar studies [48,50].

Risk associated with PAHs contamination of river water and fish was also calculated. Several parameters were evaluated, including the potency equivalent concentration (PEC), exposure daily intake (EDI) and lifetime carcinogenic risk model (ILCR) [50–52]. Toxic equivalency factors (TEFs) proposed by Nisbet et al. (1992) [52] were applied for the determination of the Benzo[*a*]pyrene (BaP)-equivalent concentrations in order to compare detected PAHs' carcinogenicity to that of BaP.

The PEC of the total PAHs per sample was calculated using the following Eq. (11):

$$PEC = \sum Ci \times TEFi \quad (11)$$

where C_i refers to the corresponding concentration of each individual PAH and TEF is the toxicity equivalent factor of each PAH relative to BaP [51,52].

Similar to the MPs, the EDI was calculated according to the Eq. (10) using the total PAHs concentration per water or fish sample. However, in order to consider the PAHs' carcinogenicity, EDI was determined using the BaP-equivalent concentrations as well.

Finally, ILCR of adults and children was estimated for both MPs and PAHs as follows:

$$C_{mass} = C_{No} \times \alpha^3 \times \rho \times 1000 \quad (12)$$

$$ILCR = \frac{C \times CSF \times IR \times EF \times ED}{Bw \times AT} \quad (13)$$

where IR is the R_c and B_w is the M_w (used for the EDI calculations), both for fish and for water. For MPs, C is the C_{mass} in mg L^{-1} or mg Kg^{-1} as calculated by the Eq. (12), where C_{No} is the polymer concentration in MPs L^{-1} or MPs Kg^{-1}, α^3 is the average size of one side in cm and ρ is the density of each polymer [53]. For PAHs, C is the BaP-equivalent concentration of PAHs. CSF is the available cancer slope factor of each polymer for MPs, while for PAHs is the one of BaP (7.3 kg d^{-1} mg^{-1}). EF is the exposure frequency (365 d $year^{-1}$), ED is the continuous exposure duration (70 years), and AT is the mean age of people (70 years) [51,53]. If ILCR $<10^{-6}$ then the cancer risk is characterised as negligible, when $10^{-6} <$ ILCR $<10^{-4}$ there is potential low risk, when $10^{-4} <$ ILCR $<10^{-3}$ there is moderate risk, while ILCR$>10^{-3}$ indicates potential high risk [54].

2.8. Quality control / quality assurance

To avoid external contamination, the use of plastic material was limited. Only metallic shovels and aluminium boxes were employed during sampling and transportation, respectively. Sample preparation and extraction were performed in a closed and isolated fume hood, while wearing laboratory cotton coats and using glass and metallic materials that were previously cleaned with MeOH and ultrapure MilliQ® water. Procedural blanks and positive controls (spiked samples) were utilized during the extraction to ensure the lack of external contamination and interference. PAHs were not detected in any of the procedural blanks. All samples were treated and extracted using three replicates. Relative standard deviations (RSD) were < 10 %. The EPA PAHs method 8270 internal standards mixture (1,4-dioxane-d_8, 1,4-dichlorobenzene-d_4, naphthañene-d8, acenapthene-d10, phenanthrene-d10, chrysene-d10 and perylene-d12) was added as recovery indicator for the samples. The limit of detection (LOD) of PAHs was determined 3× the signal/noise ratio.

2.9. Statistical analysis

Statistical analysis was performed using Python (version 3.13.2) in the Visual Code Studio integrated development environment (version 1.98.2). Principal component analysis (PCA) was employed to treat the complex multivariate dataset in this study. Kaiser Meyer Olkin (KMO) and Bartlett's tests were utilized to evaluate the suitability of the data for factor analysis since they indicate whether variables are adequate or inadequate within the model. Moreover, the Pearson correlation approach was used to assess the linear relationship between the variables and complement the PCA.

3. Results and discussion

3.1. Occurrence of microplastics in water, sediment and fish from the Júcar River basin

According to μFTIR results, MPs were present in water from all sampling points. Concentrations of the plastic particles in water varied from 0.1 ± 0.02 to 6.9 ± 0.7 MPs L^{-1}, with JUC8 (Sueca, near the mouth of the river) and CAB5 (Villatoya, Upstream Júcar confluence) being the most polluted samples (6.9 ± 0.7 MPs L^{-1} and 6.8 ± 0.4 MPs L^{-1}, respectively). A variety of different polymers (i.e., PE, PP, nylon 6, halogenated PP and PS, cellulose and viscose fibres) was identified, with PE and PP being the most abundant polymer types (62.9 % and 10.4 % of the particles respectively). The use of μFTIR allowed the determination of the precise size of each plastic particle present in a sample. In the case of the water, MPs length ranged from 23.7 to 523.9 μm, while their width ranged from 8.6 to 214.1 μm. All polymer types, sizes and concentrations per sampling point are reported in Table S5. The MPs

quantity in the river water detected in this study was similar to the one reported in the Llobregat River basin (Barcelona, Spain) that reached a maximum concentration of 3.6 MPs L^{-1} [55], while it was higher than the ones observed in the Henares River catchment (Central Spain), ranging from 0.001 to 0.23 MPs L^{-1} [56], and in the Ebro River Delta (Catalonia, Spain) that showed a MPs concentration of 0.0035 ± 0.0014 MPs L^{-1} [27]. However, the number of particles determined in the present study is significantly lower than the quantities reported in two rivers in Portugal, namely Douro River and Antuã River, which had a mean concentration of 231 MPs L^{-1} (fragments) and 46 fibres L^{-1} (Douro River), and concentrations between 58 and 193 MPs L^{-1} (March) and 1–1265 MPs L^{-1} (October) (Antuã) [57,58]. This difference could be attributed to the fact that the sampling points in Portugal were in close proximity to heavily affected industrial areas. The main polymers identified in the water samples from Douro and Antuã Rivers included PES, PE and PP, which were also detected in the Júcar River basin. Synthetic clothes, packaging industries and fishing activities are the main sources of these plastic types [27,55].

As for the sediment samples, MPs were detected in 11 out of the 15 samples analysed by μFTIR (Table S6). In the sediment of JUC4, JUC7, CAB1 and CAB3 there were no MPs present. The most polluted sampling points were JUC8 (80 ± 3.8 MPs Kg^{-1}) and CAB5 (75 ± 5.3 MPs Kg^{-1}). 45 % of the polymers in sediments were PE, while 25 % were PP and 15 % were PES. N6 and chlorinated PS (Cl-PS) were also detected. MPs length was between 30.2 and 525.4 μm, and width was between 17.1 and 421.2 μm. As mentioned in Sections 2.3 and 2.4, MPs were extracted from sediments in order to be analysed by Py-GC–MS as well. Since different fractions of the sample were employed for each analytical tool, the results of these techniques should be combined, and not compared. According to Py-GC–MS analysis, plastic polymers were present in 14 samples out of 15, with CAB1 and CAB3 being the only samples without MPs as it was, also, proven by μFTIR. The most abundant polymers were PE and PMMA, with concentrations reaching 3.46 ± 0.2 μg g^{-1} in MAG2 (Carlet, industrialised area) and 0.06 ± 0.002 μg g^{-1} in CAB5, respectively. PP followed with concentrations up to 0.24 ± 0.02 μg g^{-1} and it was present in four samples. The Py-GC–MS determines the mass of each polymer in the sample, and it does not provide information about the size of the plastic particles detected. For this reason, the two techniques employed are considered complementary. Results from both methods indicate the abundance of PE in sediments from the Júcar River basin. The μFTIR analysis of the sediments from this study showed similar MPs concentrations as the ones found in sediments from Rías Baixas and Miño River (Galicia, Spain), with an average of 70.2 ± 74.2 MPs Kg^{-1} [59]. MPs concentration of sediments from the Henares River catchment (0–2630 MPs Kg^{-1}) [55], the Ebro River Delta (mean: 2052 ± 746 MPs Kg^{-1}) [27], and the Antuã River (March: 100–629 MPs Kg^{-1}, October: 18–514 MPs Kg^{-1}) [58] were higher than the ones reported in this study. The most abundant plastic polymer types in sediment from the Júcar River basin were PE and PP (μFTIR), two polymers that have been previously reported in river sediments in Spain [27,59]. PMMA was, also, detected in sediments by Py-GC–MS. Its presence has been already reported in river sediment, with building and construction activities being the most likely sources [27,60].

In this study, the GIT of different fish species was isolated, homogenized and extracted in order to determine the presence of MPs. Samples included Iberian barbel (*Barbus guiraonis*), common bleak (*Alburnus alburnus*) and black bass (*Mycropterus salmoides*) from six out of the eight sampling points along the Júcar River. The μFTIR analyses showed absence of MPs in barbels from JUC1 and JUC2 (headstream), as well as in the barbel from JUC5 (Table S7). Six fish samples were polluted by plastic particles, with all the black bass individuals presenting polymer concentrations from 13.4 ± 0.4 to 30 ± 2.3 MPs Kg^{-1}. Similar to the water and sediment samples, the most abundant polymer type identified in fish by μFTIR was PE (80.9 %). N6 and Cl-PS were also identified in black bass samples (4 % and 4.3 %, respectively). MPs size ranged from 19.7 to 254.6 μm (length and width). Py-GC–MS results indicated the presence of PVC markers, namely naphthalene, methyl-naphthalene, indene and methyl-indene in four fish samples (Table S8). Only when all four markers were detected, PVC was quantified, using naphthalene as marker pyrolysis product. PVC concentrations were 152.5 ± 15.3–437.35 ± 42.33 μg g^{-1} with the highest being found in the black bass from JUC6 (Cotes, Bypass to the "Royal Júcar Irrigation Chanel"). Quantification of PVC in fish by Py-GC–MS is challenging since the markers of PVC can also occur from the pyrolysis of the organic fraction of the sample [61]. Thus, an overestimation of the PVC quantity cannot be excluded. Moreover, GIT of the common bleak from JUC5 contained 19.97 μg g^{-1} of PP. After digestion and filtration onto a quartz filter of this sample, the filter was observed under a stereomicroscope and a small light blue particle was identified. For the Py-GC–MS, the part of the filter where this particle was located was selected and placed in a cup for analysis, and the results confirmed that it was indeed a plastic polymer (PP). The presence of PP in the common bleak from JUC5 was confirmed by both analytical tools employed in this study. Literature data on the presence of MPs in river fish from Spain is scarce, and more data about the actual MP pollution levels are needed, since fish from freshwater systems are commonly consumed, offering a way for MPs to enter the food chain. The findings of this study show higher MPs concentration in fish GIT, when compared to results reported in commercial fish GIT from Orontes River (Turkey), where a mean concentration of 5.1 ± 2 MPs Kg^{-1} has been reported [62], but lower than the concentrations reported in fish GIT from Dafeng River (China) (8 10^2 -5.7 10^3 MPs Kg^{-1}) [63]. PE, N6, PS and PP are polymer types that have already been identified in river fish samples [60,62,64]. Since these polymers were also present in river water and sediment from the Júcar River basin, the fishes from this study were seemingly directly exposed to them, and can have ingested the plastic particles by accident [65].The concentration of the polymers found in sediments and fish by Py-GC–MS can be seen in Table S8, while polymer type percentages in all matrices from Júcar River catchment are shown in Fig. S1.

3.2. *Occurrence of PAHs in water, sediment and fish from the Júcar River basin*

The occurrence of PAHs was investigated by GC–MS/MS. In river water, chrysene was detected in all the samples from Cabriel River and one sample from Júcar River (JUC1). Concentration range was 0.7 ± 0.1–10.9 ± 2.4 μg L^{-1} with an average of 5.8 ± 1.2 μg L^{-1} (Table S9). Acenaphthene was quantified in four samples with concentrations ranging between 1.9 ± 0.2 and 8.6 ± 0.1 μg L^{-1}, while fluorene was present only in JUC8 (41.3 ± 0.3 μg L^{-1}), and acenaphthylene in MAG2 with a concentration of 45.6 ± 4.1 3 μg L^{-1}. River water from JUC2, JUC3, JUC5, JUC6 and MAG1 did not contain any of the PAHs analysed. Data from the Júcar River Basin Confederation from the last 10 years show PAHs concentrations below the quantification limits in sampling points close to the ones from this study [66]. These limits range from 1 to 167 μg L^{-1}, substantially higher than the ones calculated in this study. Only in JUC5 in 2021, anthracene, phenanthrene and pyrene were detected in the river water with concentrations of 17 μg L^{-1}, 18 μg L^{-1} and 15 μg L^{-1}, respectively. The PAHs concentrations detected in this study were higher than the ones reported in the Llobrergat River basin (Catalonia, Spain), determined after forest fire incidents, which ranged from 2 to 336 ng L^{-1} [67], the ones in Guadalquivir River (Andalusia Spain,) that were also at ng L^{-1} levels [68], and in Douro River (Portugal) that had a total mean PAHs concentration of 55 ng L^{-1} [69]. Pyrene has been reported in river water samples as a result of forest fires, but it was not present in the water samples from the Júcar River basin in the study of Llamas et al. (2023) [70]. Moreover, acenaphthene levels in the water samples analysed were lower than the ones reported in Guadalhorce River (Andalusia, Spain) that reached up to 0.8 mg L^{-1} [71]. Total PAHs concentrations observed in Júcar River water samples were similar to the ones of Shitalakshya River (mean: 5.5 ± 0.3 μg L^{-1}) [72] with the exception of JUC8 and MAG2. In general, a tendency of higher

total PAH concentrations near the final part of the river was observed in the cases of the Júcar and Magro rivers (Table S9), indicating a transportation of these contaminants from the source to the mouth of the rivers. Anthropogenic activity is the primary source of PAHs to river water [71] and, accordingly, the sampling points closest to the metropolitan area of Valencia and the industrial area of Carlet (JUC8 and MAG2, respectively) featured the highest concentrations in this study.

Sediments can act as sïnks of organic contaminants such as PAHs. In the case of the Júcar River basin, GC–MS/MS results indicated the presence of at least nine PAHs in each sample (Table S10). Napththalene, 2-methylnaphthalene, fluorene, anthracene, phenanthrene, fluoranthene and pyrene were detected and quantified in all sediment samples. The 2-methylnaphthalene presented the highest concentration that reached 1054.7 ± 44.3 ng g^{-1} in sediment from JUC5, followed by naphthalene (highest concentration: 446.9 ± 25.8 ng g^{-1} -JUC5) and fluorene (maximum concentration of 511.5 ± 11.6 ng g^{-1} in JUC1). Ten PAHs were detected in the sediment from JUC5 and the total PAHs concentration of this sample was the highest (2322.7 ± 167.6 3 ng g^{-1}). PAHs detected in the water at this part of the river in 2021 [66] could have been subsequently deposited in the sediment, which is a well-known reservoir for pollutants. The sediment sample collected at CAB5 contained 11 out of the 19 PAHs that were studied and showed high concentrations of 2-methylnaphthalene (665.9 ± 17.3 ng g^{-1}), pyrene (499.5 ± 24.5 ng g^{-1}) and chrysene (254.1 ± 16.2 ng g^{-1}). Total PAHs concentrations from this study were lower compared to the levels from a study in Douro River with an average concentration of 5200 ng g^{-1} [69], and one study in the Ebro River basin that reached up 4931 ng g^{-1} [73]. They were higher than the ones from another study in the Ebro River with total PAHs concentration range between 11.2 and 407 ng g^{-1} [74]. Sediment concentrations from the Júcar River basin were in a similar range as the ones measured in Ría de Arousa (Galicia, Spain), which were from 44.8 to 7901 ng g^{-1} [30], and in Odiel and Tinto Rivers as well as Santo Padre Canal (Andalusia, Spain), with concentrations of 680, 820 and 1810 ng g^{-1}, respectively [75].

Furthermore, PAHs concentrations were estimated in fish muscle samples by GC–MS/MS as well. Fish in freshwater systems can come into contact with PAHs mostly through particulate matter in the water or through the sediments, and their level of contamination depends on their trophic level and their water column position [76]. As it can be observed in Table S11, the nine fish from the Júcar River basin that were analysed in this study presented at least five PAHs. 2-methylnaphthalene, acenaphthene, anthracene, phenanthrene and fluoranthene were detected and quantified in all fish samples, with 2-methylnaphthalene and fluoranthene having the highest concentrations when compared to the other PAHs. Muscle tissue of the common bleak from JUC5 was characterised by the occurrence of 11 PAHs. This sample showed elevated concentrations of naphthalene (71.1 ± 0.1 ng g^{-1}), 2-methylnaphthalene (203.3 ± 1.1 ng g^{-1}) and fluoranthene (118.2 ± 2.4 ng g^{-1}). Moreover, in this specific fish sample, chrysene and BaP were present at a concentration of 2.5 ± 0.01 ng g^{-1} and 14.4 ± 1.2 ng g^{-1}, respectively. In the present study, PAHs were detected and quantified in fish muscle while in the Ebro River basin, PAHs were not reported in the fish analysed [74]. Fish muscle total PAHs concentrations in the Júcar River basin were lower than the ones found in fish muscle samples from 30 river ecosystems in Taiwan that reached up to 5510 ng g^{-1} and were, also, extracted by MAE [77]. Studies that have investigated the occurrence of PAHs in fish samples tend to focus on the four PAHs that are considered carcinogenic, namely BaP, chrysene, benzo[*b*]fluoranthene and benzo[*a*]anthracene, as well as their sum (PAH4), and have shown concentrations within the allowed limits set by the European Commission in muscle meat of fish [76,78,79]. BaP was identified only in the common bleak sample from JUC5 at a concentration higher than 2 ng g^{-1} that is considered the allowed limit for fish consumption [76]. The PAH4 was below the allowed limit (12 ng g^{-1}) in all fish samples from the Júcar River basin, except the common bleak (JUC5) (Table S11). High concentration of BaP in this specific sample could be due to the high PP content since this type of polymer presents high affinity to BaP and it could act as its vector, binding substantial amounts of PAHs [19,80]. PAH adsorption capacities of approximately 46–236 μg PAH per gram of MPs have been reported in water within 45 min, demonstrating an uptake that is both fast and significant [81]. Diffusive absorption into the polymer matrix is another possible mechanism, mostly for rubbery polymers such as PE and PP [82]. Even though the plastic particle was found in the GIT and the PAHs were measured in muscle, internal transportation of BaP is the most likely scenario since neither water nor sediment samples were contaminated by this specific PAH. The different PAH concentrations in all matrices from Júcar River catchment can be found in Fig. S2.

With the aim of understanding the origin of PAHs, various ratios have been employed in the bibliography, such as the LMW/HMW ratio, fluoranthene (Fluo)/ fluoranthene + pyrene (Fluo+Pyr) ratio, and anthracene (Ant)/ anthracene + phenanthrene (Ant+Phe) ratio [83]. A ratio of LMW/MHW <1 indicates pyrogenic source of PAHs while a ratio > 1 a petrogenic one (crude oil and its products) [83]. A Fluo/ (Fluo + Pyr) ratio from 0.4 to 0.5 points to fossil fuel combustion, whereas <0.4 to petrogenic sources, and > 0.5 grass, wood or coal combustion [84]. An Ant/(Ant+Phe) ratio value <0.1 suggests a petrogenic source, and > 0.1 a pyrogenic one (combustion) [85]. To establish the PAHs sources in the three zones of the Júcar River basin, the LMW/HMW was the only one that could be calculated in all different zones and matrices. In general, PAH levels are expected to be lower in the river water when compared to the sediments and fish due to their low hydrophilicity. Only four of the PAHs that were investigated in this study were detected in the water. Three of the identified PAHs were LMW PAHs (acenaphthene, acenaphthylene and fluorene), while only one HMW PAH, namely chrysene, was present. Thus, from the proposed ratios, only the LMW/HMW could be applied to the water samples and the results were 0.3, 3 and 2 in zone 1, 2 and 3, respectively, indicating pyrogenic source of PAHs near the source of the river and petrogenic source in the middle and final part, near the mouth. These results could be due to forest fires near the river source, while in the middle and final part of the river, petroleum discharges and terrestrial run-off could be identified as sources [86]. However, without more data on PAHs occurrence in the water from the Júcar River basin, these results should be interpreted with caution, since the rest of the ratios could not be calculated. In the case of the sediments, the LMW/HMW ratios were 2.8, 2.7 and 2.8 in zone 1, 2 and 3, respectively, suggesting a petrogenic source of PAHs along the entire Júcar River basin. Moreover, in the case of the fish, the LMW/HMW ratio was 3.2, indicating petrogenic sources that could be explained when compared to the water (middle/ final part of the river) and sediment values. Nevertheless, interpretation of these results should be done cautiously since PAHs levels in fish can be influenced by fish metabolism and their ability to absorb these substances.

Even though official PAHs emissions data in the province of Valencia show a decrease in atmospheric emission from 0.49 t $year^{-1}$ in 2015 to 0.058 t $year^{-1}$ in 2023 (most recent available data), these pollutants should be closely monitored due to their toxicity [87]. The reports indicate that crude and refined oil products are the main contributors to these emissions [87]. In general, proximity to highways, industrial and residential centres can explain the prevalence of petrogenic sources of PAHs [88]. In Spain, national PAHs emission data show that total PAHs concentrations are a few hundred tonnes per year, with residential wood burning contributing over half of that, and road transport accounting to 10–20 % [89]. In 2021, all industrial PAHs emissions in Valencia region summed to roughly a few hundred kilograms, with the refinery, chemical plants, and ceramics kilns as notable contributors [87]. All the aforementioned sources could affect the PAHs levels detected in the Júcar River basin. For example, the industrial area of Carlet (Fig. 1) contributes to high PAHs concentrations in sampling points MAG2, JUC7 and JUC8 due to industrial waste disposal. Moreover, in the case of CAB5, the sampling was performed in the village of Villatoya near the

WWTP. Inadequate elimination of PAHs from wastewater could be the cause of the total PAHs concentration of 6.9 ± 0.2 μg L^{-1} in the water, and 2017.4 ± 107.8 ng g^{-1} in the sediment of this specific point [90].

3.3. Risk assessment

3.3.1. Estimation of the ecological risk associated with MPs occurrence

HI, PLI, PRI and RQ factors were calculated for all sample types and sampling points. As it can be seen in Table S12, PLI values of river water from JUC6, JUC7, CAB1, CAB2 and CAB4 were between 10 and 20, thus belonging to the risk category level II, while those of CAB3, MAG1 and MAG2 were between 20 and 30 (risk category level III), and the ones from JUC8 and CAB5 were > 30 (risk category level IV). PLIs of the three zones (Section 2.6) showed higher values near the river mouth (Zone 3) for water and sediment using μFTIR ($PLI_{Zone3\ WATER} = 68$, $PLI_{Zone3\ SED} = 4$), while a $PLI_{Zone2\ SED}$ of 14 was the highest when the Py-GC–MS results for sediments were used. The $PLI_{Zone3\ WATER}$ was the only value that belonged to the risk category level III, indicating high potential ecological risk in this zone. HI values of the water samples from JUC4-JUC8, CAB5, and MAG1-MAG2 were > 1000, indicating potential high risk to the environment due to the polymer types detected. JUC2 had a HI value of 0 because the only type of polymer present in the water sample was polylactic acid (PLA), that is a biopolymer and is not considered toxic. PRI values of all water samples, except JUC2, were > 1200 indicating very high potential risk due to high HI values. However, RQ results calculated using PNEC values, which were estimated by SDD approaches and take into consideration toxicity data, were below 1 in all sampling points showing low risk.

Sediment samples from the river were analysed by both μFTIR and Py-GC–MS, therefore all the ecological risk assessment indexes were calculated using the results from both techniques (Table S12). Using those of μFTIR, PLI values of all sediments were below 10, indicating very low risk due to MP quantity, while HI values from JUC1, JUC5, JUC6, JUC8, CAB2, CAB5, MAG1 and MAG2 were > 1000 and belonged to the risk level category IV. PRI values of sediments showed high potential risk in JUC3 and very high potential risk in JUC1, JUC2, JUC5, JUC6, JUC8, CAB2, CAB5, MAG1 and MAG2. As it was observed for the river water, the RQ values of all sediments were lower than 1 indicating low ecological risk. The Py-GC–MS results indicated that JUC1 and CAB2 belonged to the risk level category II, JUC4 to the category III, while JUC2, JUC5 and MAG2 to the category IV. Once again, HI values were higher than 1000, placing all samples in the Risk level category IV, except JUC8 as well as CAB1 and CAB3 where no MPs were detected by this analytical method.

In Table S13, the PLI, HI, PRI and RQ values for the fish samples collected in different points along the Júcar River are presented. Fish GIT samples had lower MPs quantities when compared to the water and sediment samples. All PLI values belonged to the risk level category I, indicating low ecological risk. HI and PRI values were elevated due to polymer toxicity in the common bleak sample from JUC5, and in the three black bass individuals that were collected in JUC7 and JUC8. For RQ calculations, the values were lower than 1 for both freshwater and sediment PNEC values used in this study. Thus, there seems to be low risk for the fish whether their exposure to the MPs comes from the water or the sediment. As mentioned in Section 3.1, the main polymer detected in fish samples by Py-GC–MS was PVC, and its source could be the organic fraction of the sample. For this reason, these results were excluded from the risk assessment estimations in order to avoid overestimation of the risk and provide more reliable models. Moreover, due to lack of PVC in river water and sediment analysed in this study, because of the flotation density for MPs extraction, it cannot be confirmed that the fish were exposed to PVC in this environment.

3.3.2. Estimation of the ecological risk associated with PAHs occurrence

For the ecological risk assessment of PAHs in all matrices analysed, the RQ approach was followed. Both RQ_{NCs} and RQ_{MPCs} were calculated in the present study. Table S14 contains the RQ values of both the individual and the total PAHs that were detected in the river water samples. Five samples, namely JUC2, JUC3, JUC5, JUC6 and MAG1, were not contaminated by PAHs and so the RQ values were 0. For individual PAHs, RQ_{NCs} and RQ_{MPCs} were > 1 in all the polluted samples indicating high potential risk. As far as the RQ of the total MPs per water sample is concerned, $RQ_{JUC8\ Water}$ and $RQ_{MAG2\ Water}$ values showed high risk in these two sampling points, while $RQ_{JUC1\ Water}$, $RQ_{JUC7\ Water}$, $RQ_{CAB1\ Water}$ - $RQ_{CAB5Water}$ indicate medium environmental risk. Only $RQ_{JUC4\ Water}$ showed low risk.

Sediment samples were characterised by RQ_{NCs} and RQ_{MPCs} > 1 for naphthalene and 2-methylnaphthalene, while fluorene had both values >1 in JUC1, JUC3 and JUC5 and pyrene showed both values ≥1 in the sediments from JUC4 - JUC6, CAB4 and CAB5. However, RQ_{NCs} and RQ_{MPCs} values of total PAHs indicated low risk in all sediment samples from the Júcar River basin (Table S15). For fish muscle samples, only RQ_{MPCs} were calculated due to lack of data of negligible concentrations (NCs) in fish. MPCs were adapted from the European Directive 2013/39/EU [46], which mentions an EQS of 5 ng g^{-1} for BaP. RQ_{MPCs} of individual PAHs were ≥ 1 for naphthalene, 2-methylnaphthalene and phenanthrene in all fish where these contaminants were detected (Table S16). The Iberian barbel from JUC1 and the common bleak from JUC5 presented RQ_{MPCs} ≥ 1 for acenaphthene, anthracene, phenanthrene, fluoranthene and pyrene. The RQ_{MPCs} of total PAHs in fish were ≥ 1 for seven out of the nine samples analysed in this study, specifically for the Iberian barbell form JUC1, JUC2 and JUC7, for the common bleak from JUC5, and for all black bass individuals from JUC6 and JUC7. Since RQ_{NCs} were not calculated, these results should be interpreted with caution to avoid overestimation of the ecological risk.

3.3.3. Estimation of the human health risk associated with MPs and PAHs occurrence

Human health risk linked to the presence of MPs and PAHs in river water and fish was estimated in this study. EDI results for adults and children showed that the highest values in water samples were for both PE and PP polymers in CAB5 (Table S17). PES was detected only in MAG2 and presented an EDI of 0.013 MPs Kg^{-1} body weight per day (bwd) and 0.017 MPs Kg^{-1} bwd for adults and children, respectively. Children presented higher EDIs than adults (Table S17). EDIs for fish samples were also estimated, as it can be seen in Table S18. Only PE and PP were considered for EDI calculations in fish, with PP in the common bleak sample from JUC5 presenting the highest EDI using the Py-GC–MS results ($EDI_{adult} = 0.014$ MPs Kg^{-1} bwd, $EDI_{child} = 0.16$ MPs Kg^{-1} bwd). Moreover, for PE, the highest EDIs were found in the black bass from JUC8 ($EDI_{adult} = 0.015$ MPs Kg^{-1} bwd, $EDI_{child} = 0.018$ MPs Kg^{-1} bwd). As far as the ILCR is concerned, ILCR values higher than 10^{-6} but lower than the priority risk level (10^{-4}) imply potential carcinogenic risk and require actions [51]. In this study, ILCRs for MPs- polluted water and fish were estimated using C_{mass} to convert the μFTIR results (MPs Kg^{-1}) for each polymer to a standardized mass per liter (water) or per Kg (fish) measurement [53]. ILCRs for water ranged between 0 and 3.9×10^{-4} and were higher for PE than PP (Table S17). ILCR values for children were higher than those for adults in all sampling points. These results indicated moderate to low cancer risks to humans through ingestion. ILCRs of fish can be found in Table S18. When calculated using C_{mass}, values were in the range of $x10^{-7}$- $x10^{-6}$ indicating low cancer risk in both adults and children. The ILCR value calculated for the PP detected in the common bleak from JUC5 was higher ($ILCR_{adult} = 14.5 \times 10^{-3}$, $ILCR_{child} = 11.6 \times 10^{-3}$), suggesting potential high cancer risk.

In the case of PAHs, EDI and ILCR values can be seen in Tables S19 and S20 for water and fish, respectively. Firstly, PECs were calculated to take into account the BaP-equivalent value of each PAH. For EDI and ILCR estimations, the BaP_{eq} concentrations for each sample was employed in order to have a more accurate approach regarding carcinogenicity. EDI values ranged from 2.3×10^{-8} to 1.1×10^{-5} and were higher for adults when compared to the ones for children. The highest

EDI was observed for the common bleak sample. ILCRs for adults were slightly higher than for children in both PAHs-contaminated water and fish samples. The acceptable risk level is 10^{-6} as established by the USEPA [51]. For water, ILCR values were between 10^{-5} and 10^{-6} for all samples where PAHs were detected, indicating low potential cancer risk. The results for PAHs from the Júcar River basin are slightly higher than those reported in eight rivers in Germany in terms of ingestion ILCR, where ILCRs were $< 10^{-6}$, indicating negligible risk [54]. In the case of fish from the Júcar River basin, only the Iberian barbel from JUC1 and the common bleak from JUC5 were characterised by ILCRs $>10^{-6}$, which are values higher than the guideline one and suggest low to moderate cancer risk [51]. Even though the rest of the fish samples showed negligible risk potential, the risk estimated for the barbel and the bleak from the Júcar River basin provide proof of potential cancer risk to humans through fish consumption and should be monitored for risk management. The presence of BaP in the bleak from JUC5 should be highlighted since this PAH is known as an endocrine disrupting pollutant, and its carcinogenicity has been demonstrated in human and animal toxicity studies [91]. It was recently linked to breast and lung cancer [92,93].

3.4. Principal component and correlation analyses

PCA was characterised as a useful tool for the simplification of the complex dataset in this study, which included MPs and PAHs concentrations as well as ecological and cancer risk assessment factors. The Kaiser Meyer Olkin (KMO) value of 0.6 was higher than the acceptable threshold (0.5), and the proof of sphericity by the Bartlett's test yielded a significant result (< 0.05) proving that PCA was an appropriate technique for data treatment in this study. The PCA was carried out on the correlation matrix of the data set (39 samples and 20 variables) with more than half of the variation (57.1 %) being explained by the first two principal components (PCs) (Fig. S3). They presented high eigenvalues and described most of the variation in the data associated with the different MPs, PAHs types and their associated risk in all matrices analysed. The biplot of the PCA can be seen in Fig. 2. PC1 could be related to MPs and PAHs concentrations in the matrices, while PC2 can be associated with ecological and cancer risk factors (Table S21). The plot, also, suggest that the cancer risk could be closely related to the concentrations of PP and BaP, while the influence of other MPs and PAHs on the ILCRs seems to be negligible. This assumption is further supported by the known carcinogenicity of benzo[*a*]anthracene and the co-occurrence of PP and BaP in high concentrations in a fish sample. Since high affinity of PP for BaP has been reported [80], it can be hypothesized that this specific PAH, found in the sample with the highest PP concentration, could have leached from the PP particle inside the fish GIT and passed to other tissues. According to the PCA, their co-occurrence could be related to increased cancer risk. As it was mentioned in Section 3.3.3, BaP carcinogenicity has been thoroughly established using in vivo studies and BaP-equivalent concentrations are widely used for the determination of other PAHs toxicity [94]. MPs exposure studies have shown that these pollutants could cause genotoxicity, strongly predicting possible carcinogenicity [95,96]. Moreover, PP has been linked to carcinogenicity in cell lines, enhancing the metastasis-related gene expression in breast cancer cells [97]. Thus, the correlation between PP, BaP and cancer risk demonstrated by the PCA in this study could be supported by the separate effects of these contaminants, as well as by the evidence that prove the ability of MPs to accumulate pollutants like PAHs on their surface [98]. Last but not least, it has been reported that BaP adhered to PP particles can more readily reach and enter cells, inducing DNA damage, even though there is no human study that directly tests PP and BaP exposure [99].

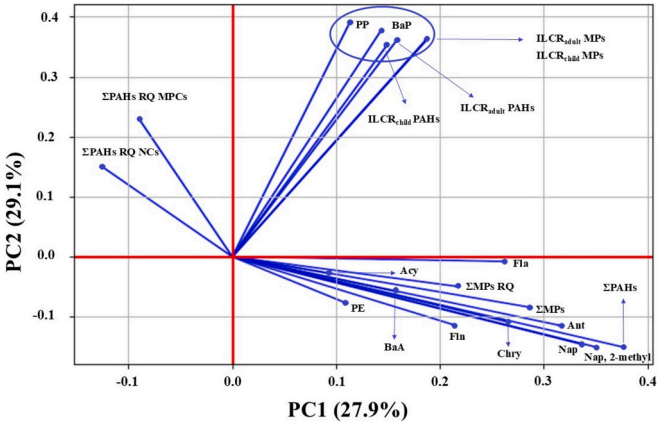

Fig. 2. Biplot of the PCA of the MPs and PAHs concentrations and associated risk dataset.

Furthermore, Pearson correlation analysis of the dataset was utilized to further check correlations and to support the PCA results. The heatmap of the Pearson correlation matrix between all the variables analysed is presented in Fig. 3, with the red colour representing positive correlations and blue colour negative correlations between each pair of variables. The correlation map confirmed PCA results indicating strong positive correlations between PP, BaP and the incremental life cancer risk of both PAHs and MPs in adults and children. This could be a result of the proven carcinogenicity of this specific PAH. Their combination in a fish sample suggests that a close monitoring and possible actions are needed to avoid the access of these pollutants to the food web, and to minimize their toxic effects on organisms. Also, fluoranthene (Fla) and naphthalene (Nap) concentrations in the samples from Júcar River basin seem to be positively correlated to potential cancer risk. However, these results should be interpreted carefully since there was no positive correlation of these variables when analysed by PCA.

3.5. Limitations

Limitations of this study mostly include the risk assessment approaches of both MPs and PAHs. In the case of the ecological risk assessment of PAHs, the RQ_{NCs} could not be calculated for the fish samples due to lack of NCs data. For this reason, these results should be interpreted with caution to avoid overestimation of the ecological risk. Furthermore, the ILCR model is not optimized for MPs. Conversion of the MPs concentration from MPs L^{-1} or MPs Kg^{-1} to C_{mass} (mg L^{-1} or mg Kg^{-1}) was necessary for ILCR estimation, as explained in Section 2.7.2. It

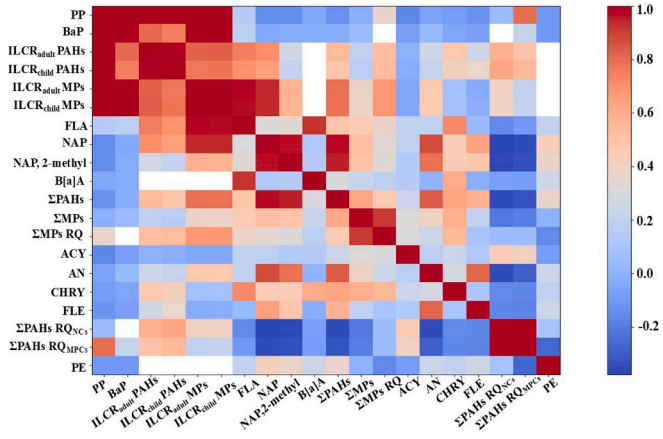

Fig. 3. Heatmap of the Pearson correlation matrix. The colour depth represents the strength of the correlation between each pair of parameters considered, with red representing positive correlation and blue representing negative correlation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is important to highlight that the MPs present in this study, were all detected in the fish GIT that is not normally consumed by humans. Also, the particles analysed in this study were bigger than 5 μm and, thus, plastic particles <5 μm that could be present in all samples were not detected due to technique resolution limitations. These smaller particles could pass through the membranes of the GIT to other edible fish tissues [100]. Careful consideration of the ILCRs values calculated by C_{mass} is required since the most important limitation of this model is the assumption that all MPs are uniformly shaped in a cubic form, with an average weight derived from size and density, something that is not accurate in the environment [53].

3.6. Júcar River basin as a high flood risk area

As it was previously mentioned, parts of the Júcar River catchment suffered the impact of torrential rain and overflowed in October 2024 [32,33] In general, Mediterranean Spain is characterised as a high flood risk area, mostly due to heavy precipitation episodes that can cause flash floods [101]. Hydrometeorological extremes in flood susceptible areas are one of the results of climate change, which can lead to instability because of the early entrance of mid-level cold disturbances during periods, like early autumn, when the sea surface temperature is relatively high [101,102]. The use of CMIP5 models for the projection of precipitation changes that could affect the Júcar and Segura River basins in the future demonstrated that, even though the precipitation showed a tendency of decrease near the source of the rivers, it was predicted that torrential rainfalls will increase near coastal areas, thus, increasing the hazard of intense flooding incidents [103]. These incidents could facilitate the transportation of a variety of contaminants from urban and agricultural soils to freshwater and marine ecosystems [103]. It has been reported that during an extreme flooding event of the Rhone River (France), 77 % of the total annual load of particulate PAHs was discharged in a single flood in November 1994 [104]. Moreover, a study of the Tet River (Gulf of Lion) showed that a large quantity of plastics (approx. 247,000 items $year^{-1}$) was transported to the ocean through the river during floods caused by torrential rain phenomena [105]. All in all, climate change seems to increase the probability of extreme torrential rain events, which subsequently lead to strong flooding incidents, especially near coastal areas. As a result, the Júcar River catchment is prone to such type of events as proved by the catastrophic flood of 2024, and the pollutants detected in this study could have been discharged to residential areas in a similar way as presented elsewhere [104,105].

4. Conclusions

In this study, the benchmark levels of MPs and 19 PAHs before the catastrophic floods of the 29th of October 2024 in the province of Valencia were estimated. This is the first study that reports the actual pollution levels of Júcar and Magro Rivers only four months before such overflow which caused over 220 fatalities and extensive property damage. Furthermore, it is the first one that offers a comprehensive ecological and cancer risk assessment approach for both MPs and PAHs found in environmental samples. MPs occurrence was the highest in the water collected in the final part of the river, near its mouth and the metropolitan area of Valencia, with maximum concentration of 6.9 MPs L^{-1}. PAHs were found in higher abundance in sediments (up to 2017.4 ± 107.8 ng g^{-1} of total PAHs in CAB5) and fish (up to 478.5 ± 25.8 in *A. alburnus* from JUC5) because of their hydrophobicity, while MPs were also higher in the solid matrices when compared to the water. PAHs sources in the Júcar River basin seem to be mainly crude petroleum or refined products, most likely due to terrestrial run-off from the highways and the industry near the middle and final parts of the rivers. Moreover, RQ values indicated low ecological risk due to MPs, while PAHs' RQ values suggested potential risk near the metropolitan area of Valencia and its industrial area. Last but not least, cancer risk assessment for MPs and PAHs showed that ILCR values suggest potential cancer risk in matrices that can be consumed. Also, PCA and Pearson correlation of the dataset point to a possible positive correlation between PP, benzo[*a*] pyrene, and the potential cancer risk for adults and children exposed to polluted water, sediment and fish during the flood. Thus, this is the first study that provides data on the co-occurrence and the associated ecological and cancer risk of both MPs and PAHs in three different environmental matrices and highlights the importance of close monitoring in order to understand and control more adequately the pollution levels in high flood risk areas.

CRediT authorship contribution statement

Vasiliki Soursou: Writing – original draft, Validation, Methodology, Funding acquisition, Formal analysis, Data curation. **Francesca Modugno:** Writing – review & editing, Supervision, Resources, Funding acquisition, Formal analysis. **Jacopo La Nasa:** Writing – review & editing, Visualization, Supervision, Resources, Formal analysis. **Stefania Giannarelli:** Writing – review & editing, Visualization, Supervision, Resources, Formal analysis. **Vicente Andreu:** Writing – review & editing, Visualization, Supervision, Resources. **Julián Campo:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.enceco.2025.07.013.

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