Article

A Snapshot on the Occurrence and Risk Assessment of Organic Pollutants in an Urban River

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Abstract: A snapshot screening was carried out in an urban river at the end of a dry period in the water and sediments to assess the presence and environmental risk for the following CECs: paracetamol, ibuprofen, diclofenac, clofibric acid, carbamazepine, ofloxacin, caffeine, tonalide, galaxolide, and bisphenol-A. Concomitantly, the occurrence and environmental risk of sixteen PAHs congeners, six indicator PCBs, and twelve dioxin-like PCBs were evaluated in sediments. The most abundant and ubiquitous CECs were bisphenol A (BPA) and caffeine, and the total contents in the surface water varied between 90.95–212.18 and 3.17–167.38 ng L⁻¹, respectively. The concentrations found in lixiviates ranged from 134.94–772.85 (BPA) and 14.43–92.60 ng L⁻¹ (caffeine). Other CECs were detected in lower concentrations, and their presence varied between sampled sites. Values of total PAHs congeners in sediment varied between 10.39–52.91 ng g⁻¹ dw. The majority of the detected PAHs seem to have a pyrolitic origin with a small petrogenic contribution. Total PCBs' concentrations ranged from 5.06 to 6.13 ng g⁻¹ dw. Despite the relatively low concentration of most of the detected compounds, the overall environmental risk, considering the screened compounds altogether, cannot be considered negligible. The obtained results are discussed in terms of other data available (though highly dispersed) in the literature. A four-color alert system is included to inform about the level of risk associated with the amount of each CEC, PAH, and PCB.

Keywords: urban river; water and surface sediments; CECs; PAHs; PCBs; risk evaluation

1. Introduction

Freshwater aquatic ecosystems have high levels of biodiversity and offer a wide range of ecosystem services, including water supply and purification as well as cultural and recreational services [1]. However, despite the Water Framework Directive (WFD- Directive 2000/60/EC of 23 October) and a set of “satellite legislation” [2], establishing that aquatic systems should achieve good ecological status, water and sediment anthropogenic contamination continue to be a reality, jeopardizing the services provided by these systems. Indeed, one of the major global threats that these ecosystems face is exposure to contamination resulting from the inputs of complex mixtures of compounds from several sources (e.g., atmospheric deposition of substances originated from wildfires, vehicle exhaustion and industrial facilities, outflow from wastewater treatment plants (WWTP) and other non-point sources) [3,4]. Even the most remote aquatic ecosystems are affected by contamination [5,6]. Among the most worrying pollutants are contaminants of emerging concern (CECs), polyaromatic hydrocarbons (PAHs) and polychloro biphenys (PCBs). CECs include a broad range of substances such as pharmaceuticals, pesticides, plasticizers, and fragrances. These compounds are not commonly monitored and when dumped into the environment, from point and diffuse sources, many still have biological activity and undergo...
transformation into other compounds that may cause undesired effects on ecosystems and health and, therefore, become hazardous, persistent, or semi-persistent and ubiquitous contaminants [7–16].

PAHs are generally persistent, semi-volatile, and hydrophobic, with low water solubility and, despite being widely distributed in the environment, their concentrations are usually very low in water, with a clear tendency to be adsorbed onto sediments [17]. Most PAHs are generated by pyrolysis or an incomplete combustion of organic material [18,19], being toxic, mutagenic, carcinogenic, teratogenic, and very bioaccumulative compounds [19–24]. PCBs are a group of chlorinated persistent organic pollutants. Like PAHs, PCBs are hydrophobic with low water solubility, persistent, ubiquitous, and bioaccumulative [25]. PCBs were widely spread during the last century through many industrial processes, as undesired reaction products. Due to their persistent nature and harmful impacts on organisms and environment, PCBs have been banned in different countries since the 1970s. Because of their long half-life, they can still be detected long after the ban [18,26–32]. More than 700 substances included in 20 classes have been identified in European aquatic ecosystems (NORMAN network, 2016, [33]). Despite this vast number, the legal control over their discharge and environmental levels has not been set up yet from many of them. Indeed, only 33 substances or compound classes are considered priority substances by WFD and EC Directive, 2013/39/EU. The management of these substances in freshwater aquatic environments faces two challenges: the consequences of chronic exposure to these mixtures are mostly unknown [34], and there is a serious lack of information concerning most aquatic ecosystems’ chemical and ecological status [2,35]. Despite the many references that focus on monitoring the occurrence of CECs in surface water in European freshwater ecosystems, monitoring of these compounds in surface waters is still not routinely carried out in (Table S1) and PAHs’ and PCBs’ monitoring in European riverine sediments is even scarcer (Table S2). After an extensive review, the only existing approaches, scanning for CECs in Portuguese freshwaters, were the references [36–46] in superficial waters and WWTP. PAHs and PCBs have been mainly monitored in estuarine and marine ecosystems [47–50], except for the evaluation of the presence of PCBs performed by [51] in a small intermittent urban stream. To our knowledge, this study is the first approach to CECs, PAHs, and PCB(s) carried out in the upper Portuguese part of the Douro basin (NE Portugal). For this purpose, the Fervença river was used as an example of a stressed urban river in a low-density region. Therefore, the objectives of this exploratory study were: (a) to determine the occurrence and environmental risk of paracetamol, ibuprofen, diclofenac, clofibric acid, carbamazepine, ofloxacin, caffeine, HHCB, AHTN, and BPA both in water and sediment lixiviates; (b) to estimate the occurrence and environmental risk of PCBs (IPCBs: 28, 52, 101, 138, 153, and 180; DLPCBs: 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189) and PAHs in sediments; (c) to assess in a relatively simple and straightforward form the environmental risk posed by the different studied substances, following a procedure that is easily adapted for other substances not studied here. Additionally, the obtained results were compared with dispersed studies on these contaminants, carried out previously in other European countries, and gathered in Tables S1 and S2. We would like to stress the relevance of this preliminary information for river managers and decision-makers. A four-color alert system is included to inform about the level of risk associated with the amount of each CEC, PAH, and PCB.

2. Materials and Methods

2.1. Study Site

The Fervença River (River Douro Basin—Figure 1) runs for about 25 km, flowing through Bragança, NE Portugal, the major city located in this region (41°48′20″ N; 6°45′25″ W—24,078 inhabitants [52]). The Fervença is a tributary of the Sabor River, that is, itself, a tributary of the Douro River, showing three distinct sections: (1) upstream the city, a rural area, where the main sources of diffuse contamination are associated with extensive agriculture and farming; (2) within the city, where diffuse contamination is generated from
storm water and runoff from constructed areas, and point contamination sources originated mainly from illegal sewage discharges and (3) downstream the city and the wastewater treatment plant (WWTP) flowing throughout a rural area.

![Figure 1](image_url)  
**Figure 1.** (A): Location of Fervença River, Bragança city, sampling sites and WWTP and (B): Riverbed conditions F1, F2, and F3.

Bragança WWTP planned for a population of 41,955 inhabitants, intended for domestic and industrial wastewater (WW) treatment, and located downstream of the city, is the most important contamination source herein. After secondary treatment, WW is disposed directly into the river. The climate in NE Portugal is continental, with a Mediterranean influence. Therefore, this permanent river has a torrential hydrological regime, with large flow variations, in line with rainfall amounts. However, the river flow was low due to the precipitation below the average values from the end of spring 2017 until March 2018 (Figure S1).

### 2.2. Water and Sediment Samples and Contaminant Determination

The concentrations of pollutants tend to increase during dry periods. The occurrence of such periods has become more frequent due to the climate change situation in which we are living, and this was the case with the sampling campaign for this piece of research that took place by the end of the mentioned dry period, on 12 February 2018. The most representative sampling site was selected at each riverine section: F1, F2, and F3. The selection of the pollutants to be assessed was based on the following criteria: (i) they are present in the EU’s watch list for emerging water pollutants, or (ii) they are candidates to follow-up EU’s watch lists, or (iii) they may have a relevant potential impact on human and environmental health.

To characterize each sample site, several environmental parameters—temperature, pH, dissolved oxygen (DO), conductivity, and total dissolved solids (TDS)—were measured at each point. In addition, total phosphorus (TP) and phosphate (SRP) were determined in the lab according to [53]. In addition, the degree of fine interstitial sediments’ deposition and the disturbance of riparian wood was visually evaluated in each sampling site (Figure 1).

Concerning the analysis of contaminants, three replicated 150 mL of water were sampled at 0.2 m depth, in the middle of the river, onto glass bottles previously rinsed with 10% nitric acid and acetone. Bottle caps were Teflon-laminated on the inner part that might be in contact with the sample. Surface sediments were randomly sampled in triplicate, from the top 5 to 10 cm depth, using a core sampler, and pooled and mixed together. Immediately after collection, the sediment samples were stored in acid-rinsed sterilized polyethylene bags. Sediments lixiviates were prepared [54] by stirring 4 parts of milli-Q water and 1 part of sediment during 24 h. The resulting fluid was allowed to decant for ca. 1 h. The supernatant fluid was filtered through paper with a pore size ca.
20–25 µm that had been previously washed with distilled water and then dried. The first 10 mL of supernatant liquid were rejected to reduce the amount of impurities. Both water and sediment samples were stored in the dark in a refrigerated container and then frozen at −20 °C until analysis.

Extraction of CECs was carried out by SPE with polymeric cartridges of Waters Oasis HLB and elution with methanol. Samples were concentrated on a rotary evaporator under N2 and the obtained concentrate was redissolved in methanol or in the mobile phase according to the analytical technique. CECs analysis was carried out by HPLC/MS for all compounds except galaxolide and tonalide, using a Thermo Aquasil 3 mm, 150 mm × 4.6 mm column. Elution was performed in gradient, as follows: A = water + 5 mM ammonium acetate, B = methanol + 5 mM ammonium acetate, T = 50 °C, injection volume 20 µL, and 1 mL·min⁻¹. Detection was carried out in ESI+ and ESI− modes by HRMS.

Galaxolide and tonalide were analysed by GC/MS using a J&W, DB-XLB 60 m × 0.25 mm × 0.25 mm column. Injection was performed on PTV mode; vol. of injection 9 µL, T = 50 °C, splitless time 0.20 min, splitless flux 20 mL·min⁻¹, transfer velocity 3 °C·s⁻¹, and final temperature 300 °C (15 min). Elution was carried out as follows: 40 °C (5 min) to 200 °C at 10 °C·min⁻¹, to 300 °C at 30 °C·min⁻¹, to 300 °C (10 min). Constant flux at 1 mL·min⁻¹, transfer line 290 °C. Detection was performed by EI+ in tandem MS-MS.

PAHs and PCBs were extracted by SPE with C18 J disks. Elution was carried out with ethyl acetate. Concentration was carried out in a rotary evaporator under N2, redissolving the concentrate in ethyl acetate. Analysis was performed by GC-MS on a J&W, DB-XLB 60 m × 0.25 mm × 0.25 mm column. Injection was made on PTV mode, initial T = 50 °C, split flux 50 mL·min⁻¹, splitless time 5 min, injection time 0.5 min, transfer rate 4 °C/min, final T 290 °C, and injection volume 9 mL. Elution was made as follows: 50 °C (2 min) to 150 °C at 10 °C·min⁻¹, to 300 °C (5 min) at 3 °C/min. Constant flux: 1 mL·min⁻¹. Transfer line: 290°C. Detection was made in SIR (Selected Ion Recording) mode.

2.3. Quality Assurance/Quality Control

Special care was taken to prevent potential contaminations during sampling and analysis. The absence of contamination was assessed by pouring LC-MS grade water into collection bottles and carrying out the whole analytical procedure. To prevent cross-contamination, both the sample loop and the extraction column were flushed at a 2 mL min⁻¹ flow with 98% of methanol after every extraction and conditioned with the appropriate eluent before analyzing the next sample.

Calibration curves (0.1–500 ng·L⁻¹) were generated using linear regression analysis. Calibration curves were injected at the beginning and the end of each sequence. Blanks (Mili-Q water, 5 mL) were injected in every 2 vials to prevent carryover. Standards of known concentration were measured through the sequence to test background levels and to check for signal stability. Where samples showed concentrations above the linearity range, the samples were diluted and reinjected. Quality controls were carried out by blank analysis, as well as reproducibility and repeatability tests.

2.4. Environmental Risk Assessment

The Hazard Quotient (HQ) was calculated to evaluate the potential ecological risk. HQ is the ratio between the measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC) [55–57]. When the measured environmental concentrations were below LOQ, their values were considered as being LOQ/2 [58]. PNEC value is a ratio between a benchmark concentration selected as the lowest toxicity value from the available experimental data for aquatic organisms from different trophic levels (e.g., algae, crustacean, aquatic insect larvae, fish) and an assessment factor (AF) that varies between 1000 (if there is only acute toxicity data for at least one of the evaluated trophic levels) and 10 (when there is chronic toxicity data for all trophic levels). Therefore, an exhaustive bibliographic search was performed in order to compile a list of published PNEC, derived preferentially from chronic toxicity values, for the compounds evaluated in the present
research (Table S3). Reference [59] recommends using PNEC values derived from chronic toxicity, because these compounds generally induce most likely chronic rather than acute toxic effects. Moreover, the lowest value for PNEC for each compound was chosen to maximize the protective threshold. If HQ < 0.1, the risk is negligible; if the 0.1 < HQ < 1, the risk is low; however, a probable adverse effect should be considered; when 1 < HQ < 10, the risk is moderate and, finally, when HQ > 10, the risk is high. Toxic Units (TUs) for each group of compounds were determined by adding the respective HQs [13,60].

Because of the scarcity or lack of toxicity data for PAHs in sediments, PNEC values for sediments were derived from PNEC values for water using the equilibrium partitioning method expressed as the simplified formula suggested in [61]. The PNEC values used in this approach are presented in Table S4. Complementarily, the classification of PAHs’ contamination, proposed by [62], was used. ΣPAHs were categorized into four groups: low (0–100 ng·g⁻¹), moderate (100–1000 ng·g⁻¹), high (1000–5000 ng·g⁻¹), and very high (>5000 ng·g⁻¹). Depending on PAHs composition, it is possible to identify different sources of these compounds by carrying out the diagnostic determination ratios—the ratios of defined pairs of individual compounds [20,22,30,63–66]. In the present study, the following ratios were determined: F/(F + Pyr), Ant/(Ant + P), BaA/(BaA + Chr), IcdP/(IcdP + BghiPer) and ΣLPAHs (low molecular weight: 2 and 3 ring)/ΣHPAHs (high molecular weight: 4 to 6 ring). To overcome the shortage related to the identified discrepancy among the values of diagnostic ratios [66,67], the use of the total index calculated was suggested as:

$$\text{Total Index} = \frac{\text{An}}{\text{An} + \text{P}}/0.1 + \frac{\text{F}}{\text{F} + \text{Pyr}}/0.4 + \frac{\text{BaA}}{\text{BaA} + \text{Chr}}/0.2 + \frac{\text{IcdP}}{\text{IcdP} + \text{BghiPer}}/0.5$$

Similarly to PAHs, PCBs’ PNECs determination for sediment were derived from PNEC for water (Table S5). However, the available PNEC are considered to be merely indicative values [68] and were only available for PCBs indicators. These PCBs have no or only one chlorine atom at the ortho-position. Mixtures of the non-dioxin-like PCBs are generally assessed on the basis of a chemical analysis of the sum of the seven so-called ‘indicator PCBs’; these were selected as suitable representatives for all PCBs because they are predominantly present in biotic and abiotic matrices [69]. So far, there is still no uniform standard available to assess the biological effects of PCBs [26,70]. Therefore, and also due to the lack of PNEC water values for most of the dioxin-like PCBs, their potential toxicity was also estimated by using the values of the Toxic Equivalence Factors (TEFs). The TEF value for each PCBs was multiplied by its environmental concentration in order to calculate Toxic Equivalents (TEQs) (Table S5). The sum of all TEQs allowed the determination of the total PCB TEQ [71]. The obtained PCB TEQ was compared with interim sediment quality guideline (ISQGs) of 0.85 pg TEQ·g⁻¹ dw and the probable effect levels (PELs) of 21.5 pg TEQ/g as recommended by [72].

3. Results and Discussion
3.1. Physicochemical Parameters

Conductivity, TDS, total phosphorus, and phosphate showed increasing values from F1 to F3 (Table 1). The values obtained are higher than those found in other rivers of the region and are higher than expected for the time of the year. These can be explained not only by the anthropogenic impacts that the Fervença is subjected to but also to the low flow after a long absence of precipitation [73]. The deposition of fine interstitial sediments showed the same pattern: in F1, riverbed > 50% of the material consists of small pebbles and coarse sand (0.5 cm); in F2, 30–50% of the material is more abundant larger than coarse sand (0.5 cm); and the rest is formed by silt and sand. In F3, the riverbed is only composed of silt and fine sand (Figure 1). This pattern indicates an increasing gradient of eutrophication and anthropogenic disturbance from F1 to F3.
Table 1. Location, channel and riparian indexes, macroinvertebrate community structure and some water parameters (mean values) in F1, F2, and F3 at the time of the present study.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location and height over sea level</td>
<td>41.79454 N</td>
<td>41.7985 N</td>
<td>41.7716 N</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>−6.8008 W</td>
<td>−6.7645 W</td>
<td>−6.7136 W</td>
</tr>
<tr>
<td>Dissolved oxygen (mg·L⁻¹)</td>
<td>9.8 (83) *</td>
<td>10.3 (85) *</td>
<td>9.0 (74) * 1</td>
</tr>
<tr>
<td>Conductivity (µS·cm⁻¹)</td>
<td>149</td>
<td>209</td>
<td>290</td>
</tr>
<tr>
<td>Total dissolved solids (mg·L⁻¹)</td>
<td>75</td>
<td>105</td>
<td>145</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
<td>6.5</td>
<td>7.2</td>
</tr>
<tr>
<td>PO₄³⁻ (mg·L⁻¹)</td>
<td>0.03</td>
<td>0.04</td>
<td>0.42</td>
</tr>
<tr>
<td>Total phosphorus (mg·L⁻¹)</td>
<td>0.08</td>
<td>0.23</td>
<td>1.10</td>
</tr>
<tr>
<td>Riparian Quality</td>
<td>Some disturbance</td>
<td>Some disturbance</td>
<td>Disturbance</td>
</tr>
<tr>
<td></td>
<td>Good quality</td>
<td>Good quality</td>
<td>Fair quality</td>
</tr>
</tbody>
</table>

* (DO%); 1 in summer months, dissolved oxygen can reach 2.3 mg·L⁻¹ [73].

3.2. CECs Monitoring in Water

All the targeted CECs were found in the Fervença river, and the results are summarized in Table 2 and Figure 2. A four-color alert system is included to inform about the level of risk associated with the amount of each CEC. Paracetamol and chlorofibric acid concentrations found in the present study were near or below the LOQ. As expected, the highest diversity and compound abundance was detected in F3 (the sampling site downstream Bragança city and its WWTP). The most abundant compounds were diclofenac (398.35 ng·L⁻¹), ofloxacin (376.16 ng·L⁻¹), tonalide (231.43 ng·L⁻¹), galaxolide (224.36 ng·L⁻¹), BPA (212.18 ng·L⁻¹), caffeine (167.38 ng·L⁻¹), carbamazepine (52.10 ng·L⁻¹), and ibuprofen (21.81 ng·L⁻¹). The assumption that WWTP effluents are the main sources of superficial water contamination has been proven in several studies: [39,40] observed that the diclofenac and ibuprofen concentrations ranged between 79–380 and 370–3600 ng·L⁻¹, respectively, in Bragança WWTP effluent samples obtained in summer and autumn; Ref. [74] analyzed several Portuguese WWTP effluents and despite the effluent concentrations of carbamazepine, chlorofibric acid, diclofenac, ibuprofen, caffeine, HHCB, and AHTN were generally much lower than the influent concentrations (chlorofibric acid and diclofenac demonstrated a high level of adsorption to the sludge), none of these compounds were totally removed in the WW treatment process. Other international approaches [13,15,75–77] also demonstrate that the conventional WWTPs are neither specifically designed nor operated to remove residual concentrations of organic pollutants, causing the potential accumulation of such pollutants in the receiving water bodies. Nevertheless, in the sampling points located upstream the WWTP, ibuprofen ranged between 7.65 (F1) and 6.94 ng·L⁻¹ (F2), and caffeine ranged between 3.17–10.23 ng·L⁻¹ in F1 and F2, respectively. AHTN in F2 showed a similar concentration to F3 (207.92 ng·L⁻¹). The highest BPA concentration observed in the Fervença river was achieved in F1 (642.69 ng·L⁻¹). The concentrations achieved in F1 and F2 indicate the occurrence of non-point pollution sources [78].
Table 2. Measured mean environmental concentrations (MEC) and Hazard Quotient (HQ) for CECs dissolved in water and lixiviates from sediments in F1, F2, and F3.

<table>
<thead>
<tr>
<th>Pharmaceuticals</th>
<th>F1</th>
<th>HQ</th>
<th>F2</th>
<th>HQ</th>
<th>F3</th>
<th>HQ</th>
<th>L-F1</th>
<th>HQ</th>
<th>L-F2</th>
<th>HQ</th>
<th>L-F3</th>
<th>HQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paracetamol</td>
<td>0.05</td>
<td>0.002</td>
<td>0.05</td>
<td>0.002</td>
<td>0.05</td>
<td>0.002</td>
<td>0.05</td>
<td>0.002</td>
<td>0.05</td>
<td>0.002</td>
<td>0.05</td>
<td>0.002</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>7.56</td>
<td>0.756</td>
<td>6.94</td>
<td>0.694</td>
<td>21.81</td>
<td>2.181</td>
<td>10.36</td>
<td>1.036</td>
<td>18.80</td>
<td>1.880</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>0.05</td>
<td>0.001</td>
<td>0.05</td>
<td>0.001</td>
<td>398.35</td>
<td>7.967</td>
<td>92.63</td>
<td>0.142</td>
<td>0.005</td>
<td>0.01</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Clofibric Acid</td>
<td>0.05</td>
<td>0.000</td>
<td>0.05</td>
<td>0.000</td>
<td>0.05</td>
<td>0.000</td>
<td>21.47</td>
<td>2.147</td>
<td>0.05</td>
<td>0.000</td>
<td>0.05</td>
<td>0.000</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>0.05</td>
<td>0.000</td>
<td>0.05</td>
<td>0.000</td>
<td>52.10</td>
<td>0.521</td>
<td>0.05</td>
<td>0.000</td>
<td>0.05</td>
<td>0.000</td>
<td>47.10</td>
<td>0.471</td>
</tr>
<tr>
<td>Ofloxacin</td>
<td>0.05</td>
<td>0.002</td>
<td>0.05</td>
<td>0.002</td>
<td>376.16</td>
<td>3.762</td>
<td>0.05</td>
<td>0.002</td>
<td>0.05</td>
<td>0.002</td>
<td>0.05</td>
<td>0.002</td>
</tr>
</tbody>
</table>

| Stimulant alkoid | Caffeine | 3.17| 0.063| 10.23| 0.205| 167.38| 3.348| 14.43| 0.030| 92.60| 0.191| 20.41| 0.042|
| Musk fragrances  |          |     |      |       |       |       |      |     |       |      |       |     |
| Galaxolide (HHCB)| 0.05| 0.000| 0.05| 0.000| 224.36| 0.224| 0.05| 0.000| 0.05| 0.000| 0.05| 0.000|
| Tonalide (AHTN)  | 0.05| 0.000| 0.05| 0.000| 231.45| 0.231| 0.05| 0.000| 0.05| 0.000| 0.05| 0.000|

| Plasticizers     | Bisphenol A (BPA) | 642.69| 64.27| 90.95| 9.095| 212.18| 21.218| 134.92| 0.957| 149.27| 1.059| 772.85| 5.484|
| Toxic units (without BPA) | 0.824| 0.964| 26.175| 0.185| 0.207| 0.071|
| Total Toxic units | 65.09| 10.06| 47.393| 1.142| 1.266| 5.555|

Limit of quantification (LOQ) = 0.1 ng·L⁻¹ (concentrations below LOQ were considered as LOQ/2); Green: Negligible risk; Yellow: Low risk; Orange: Moderate risk and Red: High risk.

Figure 2. Relative percentage of CECs found in water (A) and in sediment (B) in F1, F2, and F3.

3.3. CECs Monitoring in Sediment Lixiviates

The results seem to indicate that the presence of CECs in sediments might be independent of the distance and discharge from WWTP (Table 2; Figure 2). Ibuprofen, diclofenac, clorofibric acid, carbamazepine, caffeine, and BPA were trapped in the sediments (lixiviates). In F1 and F3 an accentuated divergence in concentrations between water and sediment. [79] also observed that sites with higher concentrations of CECs in sediment generally exhibit lower concentrations in water and vice-versa. Ibuprofen was found in F1 (10.36 ng·L⁻¹) and in F2 (18.80 ng·L⁻¹). Diclofenac and clorofibric acid were detected only in the F1 sediment. Ibuprofen was found both in F1 (10.36 ng·L⁻¹) and F2 (18.80 ng·L⁻¹). The observed concentrations for diclofenac and ibuprofen in F1 can be related with the sandy nature of the sediments, as [80] demonstrated that diclofenac and ibuprofen exhibit significant sorption to sandy sediments. Carbamazepine was found in similar concentrations to those
found in water in F3. Reference [79] also observed that carbamazepine was in elevated concentrations in sediments located downstream from WWTP, probably with high sorption and low migration rates [81].

Similarly to surface water, the most ubiquitous compounds found in sediments were caffeine and BPA. It is not surprising that BPA is the most abundant compound found in the river. Indeed, it is one of the most widely produced plasticizers used massively in the formulation of polycarbonate and epoxy resins. Polycarbonate is used in reusable plastics, food packages, drinking water bottles, dental sealants, and in many other products. Epoxy resins are generally coated in food contact surfactants and electrical coils [8,82]. BPA release probably originated from the degradation of the polymer structure of plastics in the environment and the wastewaters [83,84]. Reference [85] verified that BPA was found in higher concentrations in suspended matter than in sediments because of the affinity of BPA for small organic particles. Reference [84] corroborated the results obtained by [85], observing that BPA is mostly present in water and suspended solids (52%), soil (25%) and sediments (23%). This behavior might be due to its moderate hydrophobicity ($\log K_{ow} = 3.32$: Table S6). The results obtained for F1 are in line with these assumptions. In F2 and F3, the higher levels of BPA associated with sediments, and eventually to suspended solids, can be explained by the gradual increasing predominance of fine particles in the riverbed (Figure 1). Caffeine was also found in F1, F2, and in F3. This compound is considered an indicator of anthropogenic disturbance because it is present in all ecosystem compartments (water, sediment, and biota) including in rainwater [9,86]. As expected, in the Fervença river, it was detected both in water and sediments, with increasing concentrations in water from F1 to F3. Nevertheless, in F1 and F2 the caffeine concentration was higher in sediments than in water. The ability of the studied compounds to sorb to the sediments is influenced by their octanol-water partitioning coefficient ($K_{ow}$: Table S6): The higher log $K_{ow}$ values, the greater is the tendency for a given compound to be sorbed into the sediment [60,87]. However, this correlation is not always consistent with the concentrations in sediments for all the detected compounds. As shown by [78,79], for small rivers, the ratio of the measured concentrations between water and sediment is not only influenced by the solubility of CECs but also by the polar and ionic nature of the compounds [60,80,81,87]. Indeed, this ratio depends on other local characteristics such as: sediment mineral composition and grain size [81]; temporal contamination fluctuations [78], river bed morphology [88,89]; the degree of shading in the riverbed promoted by riparian vegetation [90], which influences photochemical degradation rates of many CECs [91]; and the river ecosystem complexity and associated biodiversity [4,92–94]. These characteristics have an influence on the CECs’ sorption and desorption behavior and ultimately on water and sediment concentrations’ ratio.

3.4. Comparative Analysis of CECs in Relation to Previously Available Data

The literature published after 2008 in Portugal and Europe in freshwater ecosystems was searched considering the CECs included in the current approach. Extensive data were found for water in Europe and less for Portugal. For sediments, the existing research is much less abundant (Table S1). Due to the general data lack for sediments, this analysis is mainly centered on water. Contrarily to River Liz (Portugal) and other European rivers, the paracetamol concentrations were $\leq 0.05$ ng·L$^{-1}$ in the Fervença river. In several surveyed European rivers, the concentrations of ibuprofen exceed 1 µg·L$^{-1}$ in water. Even in the monitored Portuguese rivers, the observed concentrations exceeded those detected in the Fervença waters, except the Douro tributaries Tinhela, Rabaçal, and Cabrum, which flow throughout natural areas with almost no human occupation. Ibuprofen has a high ubiquity in surface water because it is one of the most prescribed drugs in Europe [95,96] and Portugal [37], and together with diclofenac, it is considered to be ‘pseudo-persistent’, as their constant use results in their continuous replenishment within receiving environments [97]. Similarly, diclofenac seems to have a high ubiquity both in water and sediment in Fervença. The same range concentrations to those found in F3 (398.35 ng·L$^{-1}$) were detected
in Kalamas river (Greece), Thames river, and several German streams (Table S1). Similar concentrations were found in the Ave river (Portugal) in autumn [98]. However, unlike the Ave and some other European rivers that flow through densely urbanized, industrialized areas and where very intensive agriculture is practiced, the Fervença flows through areas with low population density, being non-industrialized and with more extensive agriculture. Thus, one would expect to always find lower concentrations in the Fervença even in F3 (located downstream of the WWTP). Nevertheless, it should be noted that although our results were obtained in February, the river had flow values similar to those of late summer due to the lack of precipitation, which allows us to assume that the concentrations observed for diclofenac and the other contaminants are concentrations typically observed in late summer before the first rains. Concerning carbamazepine, the obtained concentrations (higher in F3: 52.10 ng L\(^{-1}\)) are in line with those obtained in other rivers such as river Ouse (UK). Ofloxacin, in F3, showed one of the highest concentrations when compared with other similar studies (Table S1). Caffeine concentrations ranged from 3.17 (F1) to 167.38 ng L\(^{-1}\) in F3. Regarding the observed concentrations, it is verified that they are of an identical order of magnitude to those found in other Portuguese and European rivers located in more densely urbanized and industrialized areas (Table S1). For HHCB, the observed concentrations in F3 are in line with the highest concentrations reported for river Prut (Romania) and Leça River (Portugal). The observed concentrations for AHTN are of the same magnitude as those reported for river Molgora (Italy) (Table S1). However, contrarily to what we observe in the Fervença, most authors (Table S1 and [99]) have found that the HHCB/AHTN ratio is always greater than one in the environment. According to [100], the larger concentrations of HHCB are explained by the higher photodegradation rates of AHTN in the natural environment. However, in Fervença, this ratio is lower than one at the sampling period. AHTN concentrations in Fervença are one of the highest found in literature. BPA also demonstrated relatively high concentrations when compared to other European rivers (Table S1).

3.5. PAHs and PCBs Presence in Surface Sediments

PAHs were categorized in three groups: (1) 2–3 ring; (2) 4 ring; and (3) 5–6 ring (Table 3). A four-color system, indicating risk, has been adopted, as described above. In F1, the three groups demonstrated very similar total concentrations: 2–3 rings (15.75 ng g\(^{-1}\) dry weight (dw)); 4 rings (14.98 ng g\(^{-1}\) dw); and 5–6 rings (12.82 ng g\(^{-1}\) dw). In F2, the highest concentrations were observed for 2–3 ring PAHs (18.88 ng g\(^{-1}\) dw) and 4 ring PAHs (28.11 ng g\(^{-1}\) dw), and for 5–6 ring PAHs, the total concentrations were 5.93 ng g\(^{-1}\) dw. In F3, the highest concentrations were observed for 2–3 ring PAHs (18.88 ng g\(^{-1}\) dw) and 4 ring PAHs (28.11 ng g\(^{-1}\) dw), and for 5–6 ring PAHs, the total concentrations were 5.93 ng g\(^{-1}\) dw. F3 presented the lowest concentrations for all groups. The most abundant PAHs in this sampling site were 2–3 rings (5.25 ng g\(^{-1}\) dw). Indeed, the highest Σ PAHs were observed in F2 (52.92 ng g\(^{-1}\) dw), followed by F1 (43.55 ng g\(^{-1}\) dw). The lowest Σ PAHs (10.39 ng g\(^{-1}\) dw) were detected in F3. Nevertheless, in F1 and F2, the higher weight molecular PAHs (HPAHs) were predominant. A similar pattern was observed for Tiber River (Italy) and Danube (Serbia). Nevertheless, the contamination level due to PAHs can be considered low compared to other European river sediments (Table S2). Indeed, the observed concentrations in the Fervença were similar to the lowest concentrations observed in the European rivers. These concentrations can be explained by the fact that the Fervença River is located in a region with low population density and little industrialization.
Table 3. Measured environmental concentrations (MEC) and Hazard Quotient (HQ) for the analyzed PAHs in sediments in F1, F2, and F3. Compound name abbreviations are in brackets.

<table>
<thead>
<tr>
<th></th>
<th>F1 MEC ng g⁻¹ dw</th>
<th>HQ</th>
<th>F2 MEC ng g⁻¹ dw</th>
<th>HQ</th>
<th>F3 MEC ng g⁻¹ dw</th>
<th>HQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2–3 rings</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene (N)</td>
<td>0.05</td>
<td>0.001</td>
<td>0.05</td>
<td>0.001</td>
<td>0.05</td>
<td>0.001</td>
</tr>
<tr>
<td>Acenaphthylene (Acy)</td>
<td>0.05</td>
<td>0.005</td>
<td>0.05</td>
<td>0.005</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>Acenaphthene (Ace)</td>
<td>0.05</td>
<td>0.001</td>
<td>0.05</td>
<td>0.001</td>
<td>0.05</td>
<td>0.001</td>
</tr>
<tr>
<td>Fluorene (F)</td>
<td>2.63</td>
<td>0.035</td>
<td>1.07</td>
<td>0.014</td>
<td>1.07</td>
<td>0.08</td>
</tr>
<tr>
<td>Phenanthrene (P)</td>
<td>8.08</td>
<td>0.019</td>
<td>10.13</td>
<td>0.024</td>
<td>10.13</td>
<td>2.95</td>
</tr>
<tr>
<td>Anthracene (Ant)</td>
<td>4.89</td>
<td>0.076</td>
<td>7.53</td>
<td>0.118</td>
<td>7.53</td>
<td>2.07</td>
</tr>
<tr>
<td>Σ</td>
<td>15.75</td>
<td>0.076</td>
<td>18.88</td>
<td>0.088</td>
<td>18.88</td>
<td>5.25</td>
</tr>
<tr>
<td>4 rings</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoranthene (Flu)</td>
<td>2.48</td>
<td>0.165</td>
<td>6.28</td>
<td>0.418</td>
<td>6.28</td>
<td>1.31</td>
</tr>
<tr>
<td>Pyrene (Pyr)</td>
<td>6.97</td>
<td>0.134</td>
<td>9.25</td>
<td>0.178</td>
<td>9.25</td>
<td>0.35</td>
</tr>
<tr>
<td>Benz(a)anthracene (BaA)</td>
<td>2.81</td>
<td>0.281</td>
<td>9.40</td>
<td>0.940</td>
<td>9.40</td>
<td>1.31</td>
</tr>
<tr>
<td>Chrysene (Chr)</td>
<td>2.72</td>
<td>0.045</td>
<td>3.18</td>
<td>0.053</td>
<td>3.18</td>
<td>0.49</td>
</tr>
<tr>
<td>Σ</td>
<td>14.98</td>
<td>0.017</td>
<td>28.11</td>
<td>0.054</td>
<td>28.11</td>
<td>3.46</td>
</tr>
<tr>
<td>5–6 rings</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(b + j)fluoranthene (BbjF)</td>
<td>2.79</td>
<td></td>
<td>2.70</td>
<td></td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>Benzo(k)fluoranthene (BkF)</td>
<td>4.77</td>
<td>0.954</td>
<td>1.80</td>
<td>0.359</td>
<td>1.80</td>
<td>0.49</td>
</tr>
<tr>
<td>Benzo(a) pyrene (BaP)</td>
<td>1.21</td>
<td>0.302</td>
<td>0.05</td>
<td>0.013</td>
<td>0.05</td>
<td>0.17</td>
</tr>
<tr>
<td>Dibenz (a.h)anthracene (DBA)</td>
<td>0.05</td>
<td>0.004</td>
<td>0.05</td>
<td>0.004</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Benzo(ghi)perylenne (BghiPer)</td>
<td>2.21</td>
<td>0.737</td>
<td>0.05</td>
<td>0.017</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Indeno(1.2.3-cd) pyrene (IcdP)</td>
<td>1.79</td>
<td>0.138</td>
<td>1.28</td>
<td>0.099</td>
<td>1.28</td>
<td>0.23</td>
</tr>
<tr>
<td>Σ</td>
<td>12.82</td>
<td>5.93</td>
<td>1.68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΣTotal ≥ 4 rings</td>
<td>27.80</td>
<td>34.04</td>
<td>5.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toxic units</td>
<td>2.897</td>
<td></td>
<td>2.244</td>
<td></td>
<td>0.460</td>
<td></td>
</tr>
</tbody>
</table>

Limit of quantification (LOQ) = 0.1 ng L⁻¹ (concentrations below LOQ were considered as LOQ/2); Green: Negligible risk; Yellow: Low risk; Orange: Moderate risk and Red: High risk.

The diagnostic ratio indicated the dominance of PAHs with pyrolitic origin with a small petrogenic contribution. The mixed combustion of biomass and fossil fuels seems to be the primary source of pyrogenic PAHs (Table 4).

Table 4. PAH diagnostic ratios calculated for the analyzed samples and their limit values, indicating pyrogenic/petrogenic sources.

<table>
<thead>
<tr>
<th>Ratios</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>Limit Values for Petrogenic Source</th>
<th>Limit Values for Pyrogenic Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ant/(Ant + P)</td>
<td>0.38</td>
<td>0.43</td>
<td>0.59</td>
<td>&lt;0.1</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>F/(F + Pyr)</td>
<td>0.26</td>
<td>0.40</td>
<td>0.78</td>
<td>&lt;0.4</td>
<td>&gt;0.5 a</td>
</tr>
<tr>
<td>BaA/(BaA + Chr)</td>
<td>0.39</td>
<td>0.75</td>
<td>0.73</td>
<td>&lt;0.2</td>
<td>&gt;0.35 b</td>
</tr>
<tr>
<td>IcdP/IcdP + BghiPer</td>
<td>0.48</td>
<td>0.96</td>
<td>0.82</td>
<td>&lt;0.2</td>
<td>&gt;0.5 c</td>
</tr>
<tr>
<td>LMW/HMW</td>
<td>0.57</td>
<td>0.55</td>
<td>1.02</td>
<td>&gt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Total Index</td>
<td>8.01</td>
<td>14.72</td>
<td>20.69</td>
<td>&lt;4</td>
<td>&gt;4</td>
</tr>
</tbody>
</table>

a 0.4–0.6 petroleum (liquid fossil fuels, crude oil) combustion and >0.6 biomass and coal combustion. b 0.2–0.35 petroleum combustion and >0.35 biomass and coal combustion. c 0.2–0.5 petroleum combustion and >0.5 biomass and coal.
The observed trends in PAHs’ concentrations in the Fervença might be explained based on a multiplicity of factors: from those intrinsic to chemical properties of PAHs to those concerning riverine ecosystem functioning, biota composition (which, as mentioned in the previous section, can decisively influence their biodegradation rates [27,92] and environmental disturbance such as coarse riverbed clogging and atmospheric deposition rates [20,22,24]. The highest concentrations of PAHs found in F1 and F2 might be related to the dominance of HPAHs which, according to [24], have a higher tendency to accumulate in the sediments, since they are less soluble in water than LPAHs (higher log Kow—Table S7). Since HPAHs are released during the incomplete combustion (pyrolysis) of organic material, the main sources of these compounds in Portugal are, according to [101], forest fires, agricultural wastes and industrial waste incineration, and residential wood combustion (RWC). The mentioned authors estimated that the total emissions of PAHs due to RWC in Portugal is about 9 Tm·y⁻¹ (Bragança district contribution is about 0.3 Tm·y⁻¹; Figure 3). Indeed, RWC is higher in Portuguese inland rural areas, such as Bragança, where winters are more severely cold. Figure 3 shows that most PAHs emitted from RWC are present in samples from F1 to F3, indicating that sediment contamination might have partially resulted from local and/or regional atmospheric dust deposition [102]. Concerning LPAHs, (petrogenic origin), it is plausible to hypothesize that their main sources might be the rainwater runoff from urbanized areas and roads (F1 and F3 are located near a regional road) discharged directly into the river or into a sewage network. Indeed, it is known that rainwater runoff is one of the most important sources of organic pollution [102–104].

![Figure 3](image-url)

**Figure 3.** (A): PAHs’ relative abundances in sediments in F1, F2, and F3; (B): PAHs’ emissions from RWC (T y⁻¹) in Bragança district (source: [101]). The name of the compounds and respective abbreviations are presented in Table 3.

Concentrations of PCBs’ congeners and relative abundance are presented on Table 5 and Figure 4, respectively. Both in F1 and F2, PCB 101 congener was the most abundant
(1.32 and 1.56 ng·g⁻¹ dw, respectively). Conversely, in F3, PCB 138 showed the highest concentration (1.63 ng·g⁻¹ dw). The Σ(IPCBs) was higher in F3 (4.22 ng·g⁻¹ dw) and lower in F2 (2.65 ng·g⁻¹ dw). Concerning Σ(DLPCBs), the highest values were found both in F1 and F2 (4.11 and 3.42 ng·g⁻¹ dw, respectively). The DLPCBs that contributed more for these observed values were PCB 105 and PCB 118 in both F1 (0.99 and 0.97 ng·g⁻¹ dw, respectively) and F2 (2.16 and 1.45 ng·g⁻¹ dw, respectively). Similarly to PAHs, PCBs have a high bioaccumulation potential (Kow in Table S8). The flow regime, the sediment characteristics and the number of Cl atoms are crucial factors to explain the distribution and mobility of PCBs in sediments and from the sediments into the water and particulate organic matter [26,26,27,29,29,31]. The lack of heavy industry in the region where the Fervença River is located, suggests the concentrations found in the present study might have resulted from atmospheric inputs and from deposition through rain wash [105]. According to [106,107], about 20 to 30% of the total amounts of PCBs discharged into municipal WWTPs originated from the surface runoff. This assumption could help explain the higher concentrations of IPCBs observed in F3. Besides, past dumping in domestic sewage or directly in the river of dyes, inks and other substances containing PCBs might be another explanation for the observed concentrations.

Table 5. Measured mean environmental concentrations (MEC) and Hazard Quotient (HQ) and TEQ (toxic equivalents) for the analyzed PCBs in sediments in F1, F2, and F3.

<table>
<thead>
<tr>
<th>PCBs indicators</th>
<th>F1 ng g⁻¹ dw</th>
<th>HQ</th>
<th>ng TEQ g⁻¹</th>
<th>F2 ng g⁻¹ dw</th>
<th>HQ</th>
<th>ng TEQ g⁻¹</th>
<th>F3 ng g⁻¹ dw</th>
<th>HQ</th>
<th>ng TEQ g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB28</td>
<td>0.05</td>
<td>0.581</td>
<td></td>
<td>0.05</td>
<td>0.581</td>
<td></td>
<td>1.16</td>
<td>13.488</td>
<td></td>
</tr>
<tr>
<td>PCB52</td>
<td>1.19</td>
<td>74.375</td>
<td></td>
<td>0.05</td>
<td>3.125</td>
<td></td>
<td>1.28</td>
<td>80.0</td>
<td></td>
</tr>
<tr>
<td>PCB101</td>
<td>1.32</td>
<td>6.471</td>
<td>1.56</td>
<td>7.647</td>
<td>0.05</td>
<td>0.245</td>
<td>0.05</td>
<td>0.245</td>
<td></td>
</tr>
<tr>
<td>PCB138</td>
<td>0.05</td>
<td>1.612</td>
<td>0.05</td>
<td>1.613</td>
<td>1.63</td>
<td>22.381</td>
<td>0.05</td>
<td>0.245</td>
<td></td>
</tr>
<tr>
<td>PCB153</td>
<td>0.05</td>
<td>1.852</td>
<td>0.05</td>
<td>1.852</td>
<td>0.05</td>
<td>1.852</td>
<td>0.05</td>
<td>1.852</td>
<td></td>
</tr>
<tr>
<td>PCB180</td>
<td>0.05</td>
<td>1.471</td>
<td>0.89</td>
<td>26.176</td>
<td>0.05</td>
<td>31.176</td>
<td>0.05</td>
<td>31.176</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2.71</td>
<td>2.65</td>
<td>4.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PCBs “dioxin-like”

| PCB81           | 0.05         | 1.50 × 10⁻⁵ | 0.05 | 1.50 × 10⁻⁵ | 0.05 | 1.50 × 10⁻⁵ | 0.05 | 1.50 × 10⁻⁵ | 0.05 | 1.50 × 10⁻⁵ |
| PCB77           | 0.05         | 6.250   | 0.05 | 6.250        | 0.05 | 6.250        | 0.05 | 6.250        | 0.05 | 6.250        |
| PCB118          | 0.05         | 1.50 × 10⁻⁶ | 0.05 | 1.50 × 10⁻⁶ | 0.05 | 1.50 × 10⁻⁶ | 0.05 | 1.50 × 10⁻⁶ | 0.05 | 1.50 × 10⁻⁶ |
| PCB120          | 0.05         | 5.00 × 10⁻⁶ | 0.05 | 5.00 × 10⁻⁶ | 0.05 | 5.00 × 10⁻⁶ | 0.05 | 5.00 × 10⁻⁶ | 0.05 | 5.00 × 10⁻⁶ |
| PCB167          | 0.05         | 1.50 × 10⁻⁶ | 0.05 | 1.50 × 10⁻⁶ | 0.05 | 1.50 × 10⁻⁶ | 0.05 | 1.50 × 10⁻⁶ | 0.05 | 1.50 × 10⁻⁶ |
| PCB156          | 0.05         | 1.50 × 10⁻³ | 0.05 | 1.50 × 10⁻³ | 0.05 | 1.50 × 10⁻³ | 0.05 | 1.50 × 10⁻³ | 0.05 | 1.50 × 10⁻³ |
| PCB157          | 0.05         | 1.50 × 10⁻⁵ | 0.05 | 1.50 × 10⁻⁵ | 0.05 | 1.50 × 10⁻⁵ | 0.05 | 1.50 × 10⁻⁵ | 0.05 | 1.50 × 10⁻⁵ |
| PCB189          | 0.05         | 1.50 × 10⁻³ | 0.05 | 1.50 × 10⁻³ | 0.05 | 1.50 × 10⁻³ | 0.05 | 1.50 × 10⁻³ | 0.05 | 1.50 × 10⁻³ |
| Total           | 3.42         | 4.11   | 0.84       |              |      |            |              |        |            |

Limit of quantification (LOQ) = 0.1 ng·L⁻¹ (concentrations below LOQ were considered as LOQ/2); * TEQ with the same value F1, F2 and F3; Green: Negligible risk; Yellow: Low risk; Orange: Moderate risk and Red: High risk.
Most studies (Table S2) only evaluate the presence of IPCBs (the most common PCBs across the compositional range of the most common technical mixtures), whereas the DLPCB used to assess human health risks are scarcely approached [107]. Therefore, in the present study, only IPCBs concentrations were compared with other European studies. Fervença showed one of the lowest concentrations (Table S2).

### 3.6. Environmental Risk Assessment

Table 2 shows the HQs’ values, determined for each evaluated compound from the selected PNEC values presented on Table S1. In water, the main concerns for aquatic organisms were: BPA (in F1 and F3 HQ > 10) and ofloxacin in F3 (HQ > 10). Moreover, in F3, the obtained HQs for ibuprofen and diclofenac were between 1 and 10, indicating a moderate risk. Despite the very high contribution of BPA for overall environmental risk as shown by TU, the remaining compounds together were not negligible: even without considering BPA in TU, the environmental risk lay between low and high, both in water and in lixiviates. PAHs’ HQs are presented in Table 3. The HQs were compatible with the assumption that in all sampling sites, the sediment contamination by PAHs is low. Indeed, considering each compound, the environmental risk varied between negligible and low.
When considering TU values, the risk rose to moderate (F1 and F2) and was still considered low in F3.

The results of risk assessment for PCBs are presented in Table 5 (derived from the PNEC and TFEs-Table S5). HQs values were compatible with the assumption that the environmental risk caused by the presence of PCBs was very high. Nine of the analyzed PCBs exceeded PNEC values and their global risk were high in all sampling sites. Nevertheless, in the case of some DLPCBs, when there were simultaneously available HQs and TEQ, they demonstrated important discrepancies (Table 4).

Despite the limitations of the environmental risk assessment methodology, such as (1) PNEC values based on toxicity tests using model organisms or systems not taking into account the high complexity of ecosystems and species interactions [4,83,93,108]; (2) the neglect of the behavior of compounds and their mixtures in the environment [2,11,75,109]; and (3) the absence of ecotoxicological data for some compounds, this study has provided the very first perspective of the contamination scenario for the Fervença river and the Portuguese part of river Douro Basin, indicating the potential exposures, which might result in adverse effects for environmental health. This river is contaminated with a mixture of substances: (1) pharmaceuticals and probably their metabolites [110–113], and some, such as ofloxacin, with bactericidal activity even after being excreted [114]; (2) HHCB and AHTN and probably with their transformation products [12,115]; (3) caffeine, that perhaps might need more attention, when associated with other contaminants such as paracetamol [15], which is present herein; (4) endocrine disruptors (BPA and some PCBs) and (5) those with toxic, mutagenic, carcinogenic, and teratogenic potential (PAHs and PCBs).

It is expected that the measured concentrations and HQ values have been influenced by the extended dry period. It is general knowledge that the contaminants’ concentrations can increase several times more than the average mean values during the low flow periods. Nevertheless, considering the climate change scenario, low flow periods are expected to be more frequent [116]. Therefore, the concentrations and HQ obtained during these low flow periods can be more relevant for implementing decision-maker tools for promoting preventive river management measures, such as habitat restoration and the improvement of WWTP efficiency.

4. Conclusions

We have determined and quantified a variety of compounds and evaluated their potential environmental risk, thus generating the first picture of the Fervença chemical status and contributing new relevant information on the occurrence of several compounds in freshwater sediments, since the available data concerning these issues is still fragmented, dispersed, and almost non-existent. The obtained data suggest the potential existence of the environmental risk for freshwater organisms. Nevertheless, further information of the impact of these substances on autochthonous biota is needed to develop more accurate methodologies of risk assessment. Therefore, future approaches allowing one to understand the real environmental effects should include the use of environmental, community, molecular, and cellular markers. Moreover, surveys should be extended in a regularly way, in the future, to other aquatic ecosystems located both in Portuguese and Spanish sides of the International River Douro Basin to broaden the available information for an efficient implementation of Basin Management Plans, leading to the achievement of the Good Ecological Status (“sensu” WFD) of these aquatic ecosystems, either considering regional, national, or global levels.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app13010146/s1, Refs. [117–176] are cited in Supplementary file. Table S1: CECs’ concentrations reported in surface waters and sediments in different European countries; Table S2: PAHs’ and PCBs’ concentrations reported in sediments in different European countries; Table S3: Toxicological data ng L$^{-1}$ in literature and values of Predicted non Observed Effect Concentrations (PNEC) for the selected CECs dissolved in freshwater; Table S4: PAHs’ PNEC freshwater, Koc values, and PNEC sediment; Table S5: PNEC freshwater, Koc values used to derived
PNEC sediment of PCBs and TEF values; Table S6: CAS number and main physical–chemical properties of CECs analyzed, in the present study of water and in lixiviates from sediment; Table S7: CAS number and main physical–chemical properties of the PAHs analyzed in the sediments of the sampling sites; Table S8: CAS number and main physical–chemical properties of the PCBs analyzed in the sediments of the sampling sites; Figure S1: Precipitation during the hydrological years 2016/2017 and 2017/2018 in Bragança.

**Author Contributions:** Conceptualization, M.C. and A.M.A.-G.; methodology, M.C. and A.M.A.-G.; validation M.C. and A.M.A.-G.; formal analysis, M.C. and A.M.A.-G.; investigation, M.C. and A.M.A.-G.; data curation, M.C. and A.M.A.-G.; writing—original draft preparation, M.C. and A.M.A.-G.; writing—review and editing, M.C. and A.M.A.-G.; visualization, M.C. and A.M.A.-G. All authors have read and agreed to the published version of the manuscript.

**Funding:** IACOBUS program (Euroregion Galicia-North Portugal), through grants for inter-institutional research-supported visits in 2018 (MC) and 2019 (AMAG). Foundation for Science and Technology (FCT, Portugal), FCT/MCTES to CIMO (UIDB/00690/2020 and e UIDB/00690) and SusTEC (LA/P/0007/2020). Xunta de Galicia (Spain), GPC ED431B 2020/52.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** A.M.A.-G. is grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES PIDDAC) to CIMO (UIDB/00690/2020) and UIDB/00690/2020 and SusTEC (LA/P/0007/2020). M.C. acknowledges funding by the Xunta de Galicia (GPC ED431B 2020/52). The authors are grateful to the IACOBUS program (Euroregion Galicia-North Portugal) for financial support for exchange visits of M.C. to IPB (2018) and A.M.A.-G. to UDC (2019).

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


45. Homem, V.; Llompart, M.; Vila, M.; Ribeiro, A.R.L.; Garcia-Jares, C.; Ratola, N.; Celeiro, M. Gone with the Flow—Assessment of Personal Care Products in Portuguese Rivers. *Chemosphere* 2022, 293, 133552. [CrossRef]


53. Geraldes, A.M.; Boavida, M.J. Distinct Age and Landscape Influence on Two Reservoirs under the Same Climate. *Hydrobiologia* 2003, 504, 277–288. [CrossRef]


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