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RESEARCH ARTICLE

Environmental exposure of anthropogenic micropollutants in the Prut River at the Romanian-Moldavian border: a snapshot in the lower Danube river basin

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Abstract

The Prut River, the second longest tributary of the Danube river, was investigated for a wide range of anthropogenic organic pollutants to fill the data gap on environmental contamination in eastern European surface waters. In this study, the occurrence of a wide range of organic pollutants was measured along the transboundary Prut River, between Sculeni and Branza in 2010–2012. Using two different analytical methods, gas chromatography coupled to mass spectrometry and liquid chromatography coupled to high-resolution mass spectrometry, over 300 compounds were screened for and 88 compounds were determined in the Prut River. In general, the chemicals occurred at low levels. At the last sampling site upstream of the confluence with the Danube river at Branza, the highest average concentrations (≥ 100 ng L^{-1}) were determined for the artificial sweetener acesulfame, the pharmaceuticals metformin, 4-acetamidoantipyrene, and 4,4,5,8-tetramethylchroman-2-ol, the antioxidants 2,4-di-tert-butylphenol, 3-tert-butyl-4-hydroxyanisol, and 3,5-di-tert-butyl-4-hydroxy-toluene, the personal care products HHCB (galaxolide), 4-phenyl-benzophenone, and octyl dimethyl-p-aminobenzoic acid, the industrial chemical diphenylsulfone, and the sterol cholesterol. Low concentrations of agricultural pesticides occurred in the catchment. At Branza, the total accumulated load of all measured compounds was calculated to be almost 19 kg day^{-1}. In comparison to the Rhine River, the loads in the Prut, determined with same LC-HRMS method for the same set of analytes, were two orders of magnitude lower. Discharge of wastewater without proper treatment from the city of Iasi in the Jijia catchment (Romania) as well as from the city of Cahul (Moldova) revealed a distinct increase in concentrations and loads in the Prut at Frasinesti and Branza. Thus, an implementation of wastewater treatment capacities in the Prut River basin would considerably reduce the loads of micropollutants from urban point sources.

Keywords Prut River catchment · Target screening · Organic pollutants · River monitoring · GC-MS · LC-HRMS

Introduction

The available information concerning the exposure of surface waters to anthropogenic organic micropollutants in Eastern Europe is still relatively scarce (e.g., Antic et al. 2015; Chitescu et al. 2015; Loos et al. 2010; Moldovan et al. 2009; Moldovan et al. 2007; Roots and Roose 2013; Sapozhnikova et al. 2005). An EU-wide survey investigated the occurrence of polar organic persistent pollutants in European rivers from 27 countries for 35 selected compounds (Loos et al. 2009b). In a Joint Danube Survey, most relevant micropollutants in water samples from the Danube river and tributaries were benzotriazoles, pharmaceuticals, organophosphorous compounds, PFOS, and PFOA (Liška et al. 2015; Loos et al. 2017). The nearly ubiquitous occurrence of anthropogenic

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organic chemicals in surface waters may be of toxicological and ecotoxicological concerns, particularly when present as components of complex mixtures (Schwarzenbach et al. 2003).

Therefore, the Prut River, as the second longest tributary of the Danube river, was investigated for a wide range of anthropogenic organic pollutants to provide comparable and reliable data on the environmental contamination of eastern European surface waters. The transboundary Prut River basin, with a confluence 150 km upstream of the Danube Delta, expands over a total area of 27,500 km^2, of which 9500 km^2 is in the territory of Ukraine, 9760 km^2 in Romania, and 8240 km^2 in Moldova (Rusu et al. 2012). The catchment of the Prut is intensively used for agriculture and vineyards, with 53% used as arable land. In Moldova, about 77% is used for agriculture (EPIRB 2015). The Prut River and its tributaries are affected by urban wastewater discharge, waste disposal, and outdated industrial production modes. A main problem is the lack of exposure data of organic micropollutants in the Prut River and data for calculating pollution loading from diffuse sources. Therefore, there is a strong need to improve current knowledge regarding the occurrence and fate of hazardous substances in this transboundary river.

In the present work, a comprehensive target analysis was performed in the Prut River using gas chromatography coupled to mass spectrometry (GC-MS) and liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS) to increase the analytical spectrum and thus enabling the simultaneous screening of a large number of substances.

The objectives of our investigation were as follows: (i) to present the occurrence and concentration ranges of micropollutants using grab samples; (ii) to make first load estimations; (iii) to study the contribution of urban and agricultural sources of organic micropollutants in the Prut River basin; and (iv) to improve the database on the water quality for the assessment of inadequately represented catchments in Europe.

Materials and methods

Details on the suppliers of solvents, reagents, and reference standards are provided in the Supporting Information (SI).

River system

The 967-km-long Prut River originates in the Chernogora Mountains in the southwestern Ukrainian Carpathians. It flows first eastwards in Ukraine, then forms the border between Ukraine and Romania (31 km) and later between Romania and Moldova (695 km) before discharging into the Danube river just upstream of the Danube Delta (Rusu et al. 2012). Main tributaries in the studied stretch are the rivers Jijia (275 km), Elanu (73 km), and Horincea (35 km) in Romania, and Lapusna (74 km) and Camenca (20 km) in Moldova. During the autumn and winter periods, several minor tributaries run dry and only flow intermittently during rain events; therefore, the flow of the Prut varies depending on the season (EPIRB 2015).

Along the studied river stretch, the Prut River itself receives effluents from three municipal WWTPs. The WWTP in Iasi serves a population of around 475,000 inhabitants and treats on average 180,000 m^3 wastewater per day. The WWTP consists of mechanical treatment, activated sludge treatment, and secondary settling. The wastewater is discharged into the Bahlui River, a tributary to the Jijia which flows into the Prut. The catchment area of the WWTP at Ungheni includes roughly 30,000 inhabitants and the capacity of the WWTP is 15,000 m^3 day^{-1}. Sewage treatment includes mechanical, biological, and secondary treatment. The treated wastewater is discharged directly to the Prut River. The catchment area of the WWTP in Cahul includes about 40,000 inhabitants and, although it has a treatment capacity of 17,400 m^3 day^{-1}, only 2500–3000 m^3 day^{-1} (14–17%) wastewater is treated. The WWTP consisted of decanters, a biological filter, and secondary decanters.

The Prut basin is estimated to be inhabited by approximately 3 million people (Shepherd 2011), with 0.89 million in Ukraine and 0.80 in Moldova (http://blacksea-riverbasins.net/en/pilot-basins/prut-basin). Main cities are Chernivtsi (240,000 inhabitants) in Ukraine, Ungheni (40,000 inhabitants), Leova (more than 10,000 inhabitants), and Cahul (41,000 inhabitants) in Moldova, and Iasi (320,000 inhabitants) in Romania, a main industrial complex located on the Bahlui River, a tributary to the Jijia. The industrial manufacturing sector comprises automotive and pharmaceutical industries, metallurgical production, textiles and clothing, building materials, and food. Additionally, vineyards are located in the region.The Jijia River contains a significant share of wastewater from several villages in the catchment and discharges to the Prut upstream of Frasinesti.

Sampling

Three sampling campaigns were performed along the 250-km-long stretch of the Prut River, from Sculeni to Branza in May and November 2011, and June 2012. Sampling sites in the river system were selected in order to reflect different urban and agricultural settings. The samples consisted of grab samples at six locations along the Prut River: Sculeni, Ungheni, Frasinesti, Leova, Stoianovca, and Branza (Fig. 1), and were analyzed by GC-MS.

For two sampling campaigns in November 2011 and June 2012 at three sites (Ungheni, Frasinesti, and Branza), samples were screened by liquid chromatography followed by electrospray ionization (ESI) coupled to high-resolution mass spectrometry (Orbitrap).

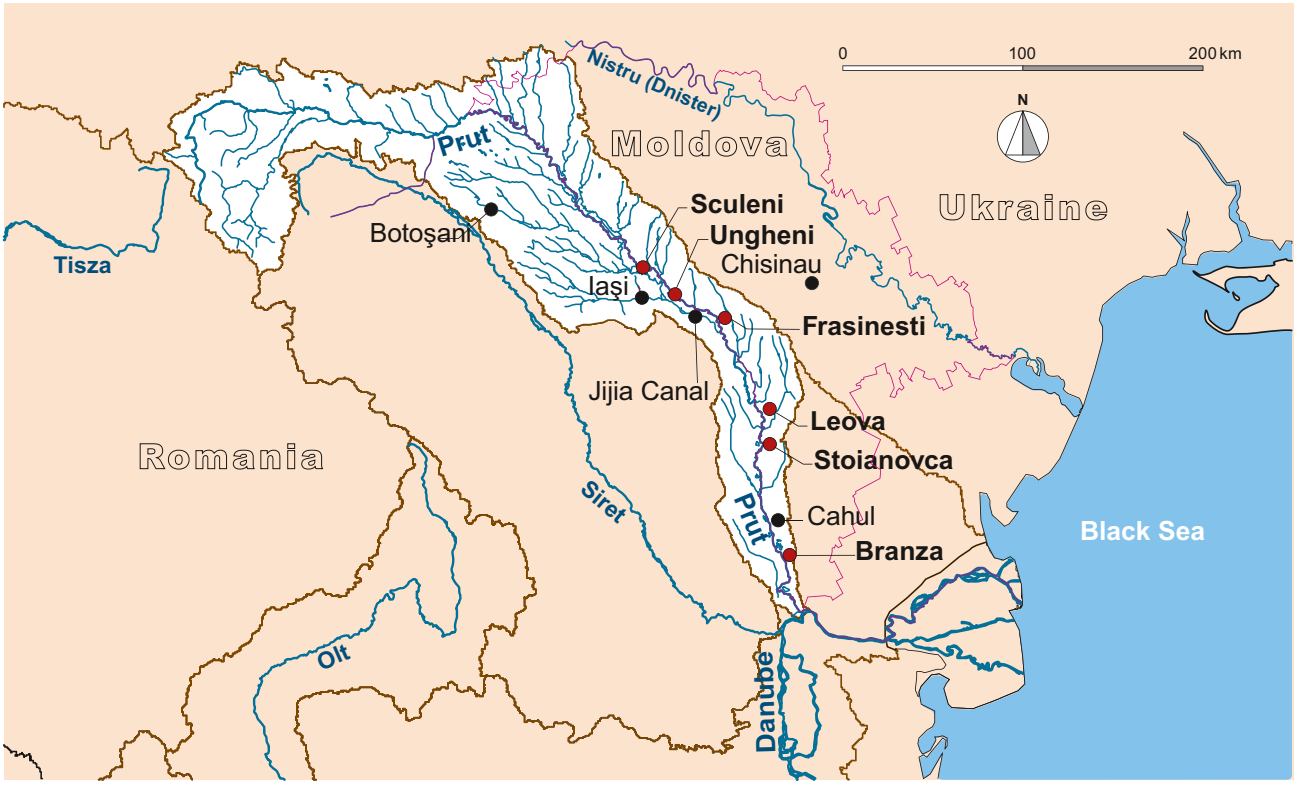

Fig. 1 Map of the Prut River basin. The sampling locations in bold are marked with a red dot

All sampling sites were at least 5 km up- or downstream of villages, the WWTP of Ungheni, or tributary inflows into the Prut, to achieve complete mixing at the sampling site.

Grab samples (1.0 L) were taken below the surface, collected in glass bottles, stabilized on-site by acidifying to pH 3 with 2 N HCL, and stored at 5 °C for maximum 1 week until analysis in Cluj (Romania). It should be noted that, because of the low pH, degradation processes of hydrolytically labile compounds may have occurred. For the LC-HRMS analysis, water samples were transported to Eawag in Switzerland, where they were stored at − 20 °C until analysis.

Water flows were provided by the State Hydrometeorological Service of Moldova (http://www.meteo.md/index.php/en) and added up with an estimated contribution of tributaries for Sculeni, Ungheni, Frasinesti, Leova/Stoianovca, and Branza which were 66, 71, 79, 84, and 89 m^3 sec^{-1} (May 2011), 30, 34, 42, 47, and 52 m^3 sec^{-1} (November 2011), and 51, 55, 64, 69, and 74 m^3 sec^{-1} (June 2012), respectively.

Analytical methods

GC-MS

Samples were analyzed by GC-MS for 12 antioxidants, 4 phosphorous flame retardants, 5 personal care products, 3 industrial chemicals, 4 agricultural chemicals, 2 pharmaceuticals, and caffeine.

The solid-phase extraction (SPE) procedure has been described in detail in earlier publications in Moldovan et al. (2009) and Moldovan et al. (2007). Briefly, the samples (500 mL) were filtered through glass-fiber filters (0.45 μm, Whatman, Maidstone, England) and spiked with internal standards. Quantification was carried out with the internal standards AHTN-D3 (tonalide d3) and PCB 30. Limits of quantification (LOQs) of ≥ 10 ng L^{-1} were obtained from the linear range of the calibration curve of a spiked drinking water sample and calculated for a signal-to-noise (S/N) ratio of 10. Analytes were concentrated by SPE on OASIS HLB sorbent cartridges (60 mg, Waters).

The GC-MS analyses were performed using a GC-ITMS system (Thermo Electron Polaris Q Mass Spectrometer) operated in EI mode at 70 eV. The source temperature was 250 °C and emission current 300 μA. The gas chromatograph was equipped with a capillary column HP-5MS (length of 30 m and internal diameter of 0.25 mm) with 0.25 μm film thickness. The temperature was programmed from 90 °C (1 min) to 120 °C at 10 °C min^{-1} and then to 200 °C at 3.5 °C min^{-1} and then to 315 °C at 5 °C min^{-1}, finally holding at this temperature for 11 min.

All analyses were performed in duplicate. The average standard deviations were < 12%. The recoveries were determined by using river water spiked with different amounts of analytes and the calculated amount compared with the spiked concentration. The recoveries varied between 62 and 106%.

All standards showed a linear range from 10 to 1000 ng L^{-1}. Results were corrected with the corresponding relative recoveries. Blank samples were regularly checked for the absence of background contamination and carry over.

LC-high-resolution tandem MS

Samples were screened by LC-ESI-HRMS for 302 pharmaceuticals, personal care products, pesticides, biocides, corrosion inhibitors, industrial chemicals, and associated metabolites and transformation products (Heeb et al. 2012; Kern et al. 2009; Ruff et al. 2015). Quantification was carried out with 113 isotope-labeled internal standards (IS) (suppliers are provided in the SI). LOQs (S/N ≥ 10) were between 0.1 and 100 ng L^{-1}.

To achieve sufficient enrichment for the broad range of compounds, manually filled SPE cartridges containing Oasis HLB, Strata-X-AW (weak anionic exchanger), Strata-X-CW (weak cationic exchanger), and Isolute ENV+ were used (Kern et al. 2009). The analytical method was the same as described in Ruff et al. (2015). Briefly, LC was performed by injecting 20 μL extract on a XBridge (Waters, Milford, MA, USA) reversed-phase C18 column (2.1 mm × 50 mm, particle size 3.5 μm) with pre-column (2.1 mm × 10 mm) of the same material.

Mobile phases consisted of (A) water and (B) methanol, both acidified with 0.1% formic acid (99%, Merck, Darmstadt, Germany). A 200 μL min^{-1} solvent gradient was: 0 min 10% B, 0–4 min linear gradient to 50% B, 4–17 min linear gradient to 95% B, 17–25 min kept at 95% B, 25–25.1 min switch to 10% B, and 25.1–29 min kept at 10% B. For detection, an Orbitrap LTQ mass spectrometer (Thermo Scientific, San Jose, CA (USA)) with ESI was used.

Full-scan MS detection (*m*/*z* 115 to 1000) was performed with resolution of 60,000 (at *m*/*z* 400) in positive and negative modes, with a spray voltage of + 4 and − 4 kV, respectively, and a capillary temperature of 300 °C. Data-dependent acquisition was used to record five MS/MS scans using a 1.5 Da isolation window between each full scan.

Results and discussion

In the Prut, 31 compounds comprising antioxidants, phosphorous flame retardants, personal care products, pharmaceuticals, industrial and agricultural chemicals were detected by GC-MS at all sample locations during the three sampling campaigns (Fig. 2, Table SI 1). Additionally, the LC-HRMS analytical screening allowed to extend the exposure assessment to pharmaceuticals, biocides, pesticides, household, and industrial chemicals used in this region (Fig. 3, Table SI 2). In this screening, 57 target compounds were determined at Ungheni, Frasinesti, and Branza in May 2011 and June 2012.

Household sources

Antioxidants

A large variety of chemically diverse antioxidants are used as additives in polymer materials, such as in packaging materials, polyethylene pipes, plastics but also in cosmetics and personal care products, as well as in motor oils, and can thus be released into the aquatic environment (del Nogal Sánchez et al. 2010; Jenke 2003).

Twelve antioxidants and transformation products were determined in aqueous samples from the Prut River at average concentrations varying between 11 and 357 ng L^{-1}. The highest levels were determined for 2,4-di-tert-butylphenol (2,4-DBP) at average concentrations of 226 ng L^{-1} (range 119–404 ng L^{-1}). This compound has been reported as possible hydrolysis product or impurity of phenolic antioxidants like Irganox 1010 (pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) and Irganox 1076 (octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) used in polyethylene and polyvinyl chloride pipelines in water supply systems (Jenke 2003; Loschner et al. 2011; Lutzhoft et al. 2013; Skjevrak et al. 2003; Skjevrak et al. 2005). Irganox 1076 was present in the Prut at average concentrations of 61 ng L^{-1} (range < LOQ–95 ng L^{-1}), and a transformation product of Irganox 1010, 7,9-di-tert-butyl-1-oxaspiro[4.5] deca-6,9-diene-2,8-dione (7,9-DBOSDDD) (Loschner et al. 2011) occurred at average levels of 25 ng L^{-1} (range < LOQ–54 ng L^{-1}).

Further phenolic antioxidants present in the Prut were the following: 3-tert-butyl-4-hydroxyanisol (BHA, average 134 ng L^{-1}, range 110–179 ng L^{-1}), 3,5-di-tert-butyl-4-hydroxytoluene (BHT, average 89 ng L^{-1}, range 44–139 ng L^{-1}), its oxidation products 3,5-di-tert-butyl-4-hydroxybenzaldehyde (BHT-CHO, average 24 ng L^{-1}, range 10–41 ng L^{-1}) and 3,5-di-t-butyl-4-hydroxybenzyl alcohol (BHT-CH_2OH, up to 27 ng L^{-1} in few samples). Additional to their use as additives in food, packaging, and cosmetics, BHT and BHA are also added to commercial diesel and lubricant oils to improve resistance to oxidation (del Nogal Sánchez et al. 2010). Antioxidants are key additives that protect lubricants from degradation and conventional motor oil may contain up to 10% of them. This indicates that motor fuel could thus be a major potential source of antioxidants in the Prut River.

BHT and BHT-CHO occurred in the Prut at similar concentrations as in Spain (Rodil et al. 2010), but at significantly lower levels than in earlier studies in Germany (Fries and Puttmann 2002) and Sweden (Bendz et al. 2005), where they were determined up to 791 and 840 ng L^{-1}, respectively.

Decreasing concentrations in the aquatic environment may be due to a temporal trend in usage of these additives.

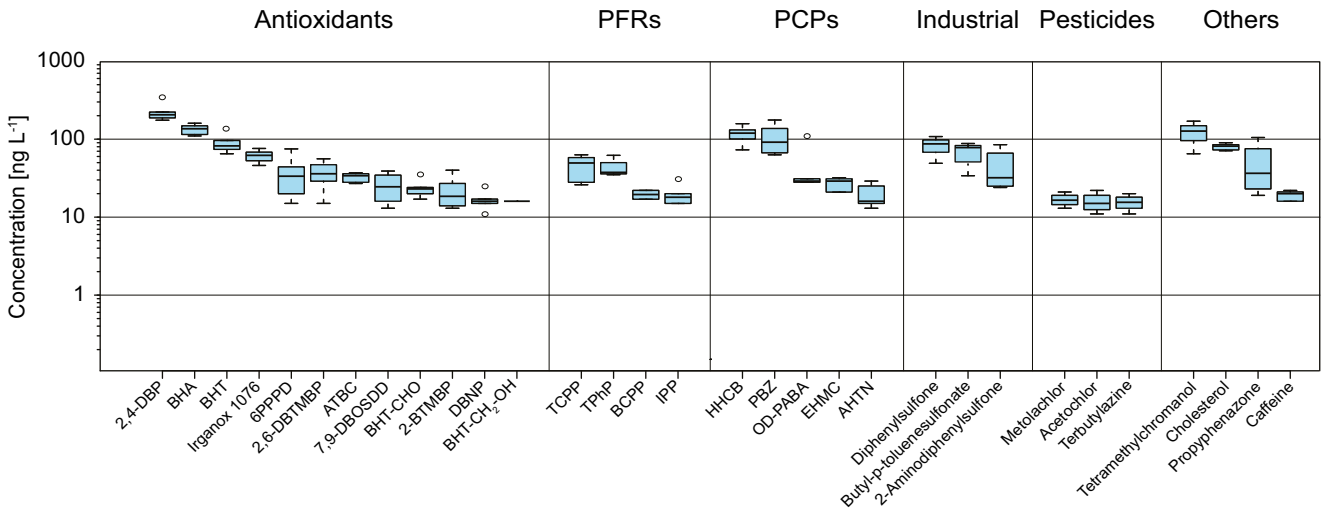

Fig. 2 Concentration ranges of antioxidants, phosphorous flame retardants (PFRs), personal care products (PCPs), pesticides, and others determined by GC-MS. Three sampling campaigns at all sites of the Prut River in May and November 2011, and June 2012. The solid bar marks the median. The box denotes the 0.25 and 0.75 percentiles. The whiskers mark the last value within a range of 1.5 times the 0.25 and 0.75 percentiles

The antioxidant derivative 2,6-di-tert-butyl-4-nitrophenol (DPNP), which has been reported to be formed during combustion of diesel fuel spiked with the antioxidant BHT (Jensen et al. 2014), was present at low levels (average 17 ng L^{-1}, range < LOQ–55 ng L^{-1}).

The aromatic amine N-(1,3-dimethylbutyl)-N′-phenyl-1,4-phenylenediamine (6PPD), which is used in high production volumes as an anti-ozonant and anti-oxidant agent mainly in the rubber industry (Cerna et al. 2012; OSPAR Commission 2006), occurred at average levels of 37 ng L^{-1} (range < LOQ–140 ng L^{-1}). The main pathway to the environment is through tire abrasion (OSPAR Comission 2008; OSPAR Commission 2006). Additionally, emission from tire deposits in landfills may also be a possible entry path into the aquatic environment. Although 6PPD is reported to have a low stability in water, it has a strong tendency to adsorb to organic matter and thus potentially fulfills the criteria on persistence (OSPAR Commission 2006).

The alkylated phenols with antioxidant activity 2,6-di-tert-butyl-4-(2,4,6-trimethylbenzyl)phenol (2,6-DBTMBP) and 2-tert-butyl-4-(1,1,3,3-tetramethylbutyl)phenol (2-BTMBP) were determined at average concentrations of 37 ng L^{-1} (range 10–78 ng L^{-1}) and 22 ng L^{-1} (range < LOQ–74 ng L^{-1}), respectively. 2-Tert-butyl-4-(1,1,3,3-tetramethylbutyl)phenol

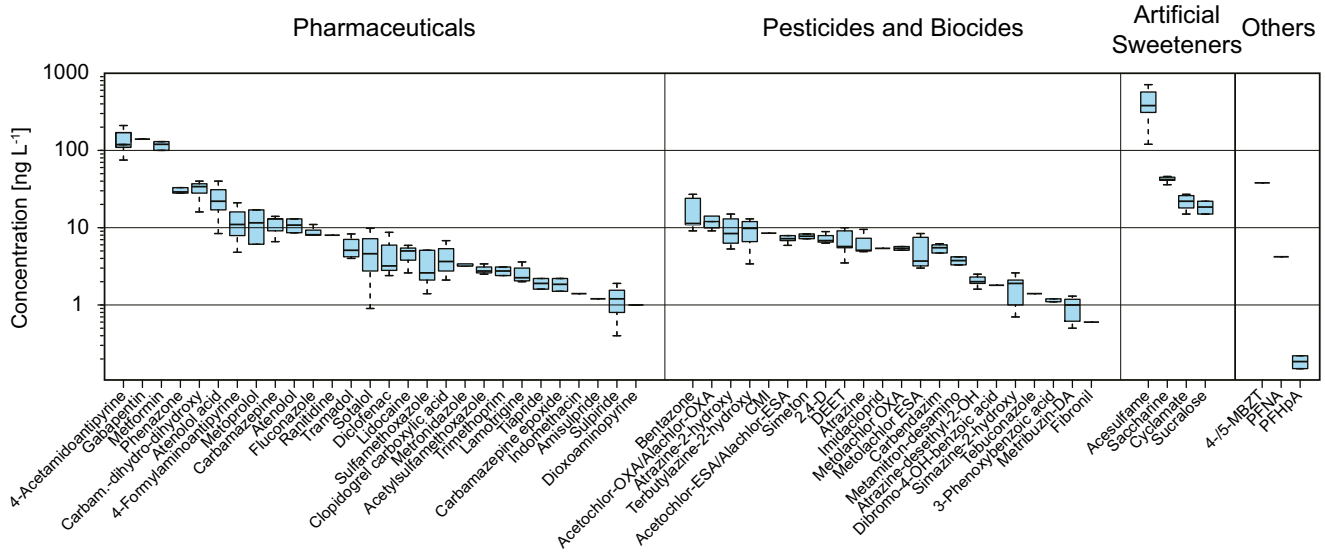

Fig. 3 Concentration ranges of pharmaceuticals, pesticides, biocides, artificial sweeteners, and others, determined by LC-HRMS. Two sampling campaigns comprising the sites Branza and Frasinesti (November 2011 and June 2012), and Ungheni (June 2012). The solid bar marks the median. The box denotes the 0.25 and 0.75 percentiles. The whiskers mark the last value within a range of 1.5 times the 0.25 and 0.75 percentiles

has been reported in wastewaters in China at one order of magnitude higher levels (Zhang et al. 2007). Alkylated phenols like 4-(1,1,3,3-tetrametylbutyl)-phenol are also used for manufacturing of antioxidants and fuel stabilizers (Krymkin et al. 2016; OECD 1995) and thus 2-BTMBP and 2,6-DBTMBP may also occur in lubricant additives and enter the aquatic environment during rain events as important traffic roads run alongside the Prut.

Furthermore, acetyl tributyl citrate (ATBC), a widely used plasticizer in PVC films for food contact application (up to 30% *w/w*) (Jenke 2003; Zygoura et al. 2011), was present in the Prut at average concentrations of 33 ng L^{-1} (range < LOQ–52 ng L^{-1}).

Phosphorous flame retardants

Organophosphates used as flame retardants, plasticisers, and lubricants can enter the aqueous environment after use in private households, industry, and from drainage of streets (Andresen et al. 2004; van der Veen and de Boer 2012; Wei et al. 2015). Three phosphorous flame retardants (PFRs) were present along the Prut, namely the halogenated tris-(2-chloro-1-propyl)phosphate (TCPP, average 46 ng L^{-1}, range < LOQ–110 ng L^{-1}), the non-halogenated triphenyl phosphate (TPhP, average 43 ng L^{-1}, range 13–118 ng L^{-1}) and the isopropylphenyl diphenyl phosphate (IPP, average 20 ng L^{-1}, range < LOQ–36 ng L^{-1}). An isomer of TCPP, bis(1-chloro-2-propyl)-2-chloropropyl phosphate (BCPP), was determined only at Branza (average 20 ng L^{-1}, range < LOQ–33 ng L^{-1}).

Comparable levels were determined for TCPP in a Joint Danube Survey (JDS3) in the year 2013 at average concentrations of 115 ng L^{-1} (maximum 603 ng L^{-1}) (Liška et al. 2015; Loos et al. 2017). The concentrations in the Prut River were also in the same order of magnitude, although at lower maxima than those measured in other European rivers, where levels ranged from 20 to 2900 ng L^{-1} in Austria (Martinez-Carballo et al. 2007), Germany (Andresen et al. 2004; Bollmann et al. 2012; Quednow and Puttmann 2009; Regnery and Puettmann 2010; Wolschke et al. 2015), Italy (Bacaloni et al. 2007), and Spain (Cristale et al. 2013b; Rodil et al. 2012). The TPhP levels in the Prut River were slightly higher when compared to the JDS3 (Liška et al. 2015; Loos et al. 2017), but in a similar range as measured in Germany (Andresen et al. 2004), in Catalonia, Spain (Cristale et al. 2013b), in the UK (Cristale et al. 2013a), and in Austria (Martinez-Carballo et al. 2007).

Personal care products

The two polycyclic musks HHCB (galaxolide) and AHTN (tonalide), used as fragrance ingredients in a wide range of products including cosmetics and detergents, occurred at average concentrations of 117 ng L^{-1} (range 59–280 ng L^{-1}) and 19 ng L^{-1} (range 10–38 ng L^{-1}), respectively. These synthetic musks have often been determined in surface waters, with levels of HHCB and AHTN ranging from 64 to 12,470 ng L^{-1} and from 52 to 6780 ng L^{-1}, respectively (Brausch and Rand 2011; Lange et al. 2015). The HHCB concentrations in the Prut were comparable to the levels in the Somes (Romania), whereas the AHTN levels were significantly lower (Moldovan et al. 2009; Moldovan et al. 2007).

Two UV filters used in sunscreens and cosmetics for skin (Brooke et al. 2008; Ramos et al. 2015) were determined in summer: ethylhexyl methoxycinnamate (EHMC, average 27 ng L^{-1}, range < LOQ–62 ng L^{-1}) and octyl dimethyl-p-aminobenzoic acid (OD-PABA, average 45 ng L^{-1}, range < LOQ–196 ng L^{-1}).

Several studies have reported the ubiquitous occurrence of UV filters in surface waters at nanograms per liter to low micrograms per liter levels (e.g., Brausch and Rand 2011; Ekpeghere et al. 2016; Ramos et al. 2015; Sánchez-Quiles and Tovar-Sánchez 2015; Tsui et al. 2014). In the River Kolpa in Slovenia, EHMC and OD-PABA occurred at comparable levels of 88 and 47 ng L^{-1}, respectively (Cuderman and Heath 2007). Although the photostability of EHMC and OD-PABA in aqueous solution was assessed to be low (Rodil et al. 2009), the presence of dissolved organic matter retards the photolysis reaction (Sakkas et al. 2003).

Additionally, 4-phenylbenzophenone (PBZ), a UV ink photoinitiator used in packaging materials such as plastics, cardboard, and paper (Bentayeb et al. 2013; Gallart-Ayala et al. 2011), was present at an average concentration of 104 ng L^{-1} (range < LOQ–323 ng L^{-1}). To our knowledge, it is the first time that this compound was determined in the aquatic environment (Ramos et al. 2015).

Pharmaceuticals

Generally, the concentrations of pharmaceuticals were below 20 ng L^{-1}, except metformin (100–240 ng L^{-1}), 4-acetamidantipyrine (75–210 ng L^{-1}), gabapentin (140 ng L^{-1}), propyphenazone (< LOQ–117 ng L^{-1}), phenazone (antipyrine) (15–73 ng L^{-1}), carbamazepine-10,11-dihydro-10,11-dihydroxy (16–40 ng L^{-1}), and atenolol acid (8.4–40 ng L^{-1}). A phytochemical with an anti-inflammatory activity, 4,4,5,8-tetramethylchroman-2-ol (tetramethylchromanol) (Gunalan et al. 2014), occurred at levels between < LOQ and 362 ng L^{-1} (average 121 ng L^{-1}). Chromane derivatives may be used together with chemotherapeutic agents as they show an anti-inflammatory activity (Rial et al. 2011).

Compared to other river systems in Europe, the levels determined in the Prut were low. Higher levels were determined in the Danube river, e.g., for carbamazepine (average 26 ng L^{-1}, maximum 68 ng L^{-1}) and carbamazepine-10,11-

dihydro-10,11-dihydroxy (average 53 ng L^{-1}, maximum 161 ng L^{-1}), and diclofenac (average 10 ng L^{-1}, maximum 255 ng L^{-1}) (Chitescu et al. 2015; Loos et al. 2017). In the Rhine River, higher levels were reported for metformin (172–1314 ng L^{-1}), gabapentin (25–536 ng L^{-1}), atenolol acid (20–213 ng L^{-1}), and carbamazepine-10,11-dihydro-10,11-dihydroxy (12–99 ng L^{-1}), and lower levels for phenazone (-antipyrine) (1–14 ng L^{-1}) (Ruff et al. 2015).

Artificial sweeteners

Several artificial sweeteners were determined along the Prut River: acesulfame (120–750 ng L^{-1}), cyclamate (15–27 ng L^{-1}), saccharine (36–46 ng L^{-1}), and sucralose (15–22 ng L^{-1}). The sucralose levels in the Prut were comparable to the ones determined in Eastern Europe in an earlier study (Loos et al. 2009a). In the Rhine River, higher levels for acesulfame (379–3044 ng L^{-1}), cyclamate (14–106 ng L^{-1}), saccharine (14–241 ng L^{-1}), and sucralose (18–175 ng L^{-1}) were reported (Ruff et al. 2015).

Corrosion inhibitors and caffeine

The corrosion inhibitor 4-/5-methylbenzotriazole (4/5MBZ) was determined detected once at Frasinesti at 38 ng L^{-1}, whereas caffeine occurred at concentrations between < LOQ and 46 ng L^{-1}, which was significantly lower than levels determined in the rivers Danube (up to 1467 ng L^{-1}; Loos et al. 2010), Rhine (42–1068 ng L^{-1}; Ruff et al. 2015), and Somes (27–332 ng L^{-1}; Moldovan et al. 2007). In the Danube river, 4/5MBZ occurred at significant higher levels (average 67 ng L^{-1}, maximum 290 ng L^{-1}) (Liška et al. 2015; Loos et al. 2017).

Industrial chemicals

The spatial sampling along the Prut allowed identification of several compounds as industrial point source chemicals. Downstream of Ungheni, butyl-p-toluenesulfonate and 2-aminodiphenylsulfone occurred at average levels of 65 ng L^{-1} (range < LOQ–244 ng L^{-1}) and 46 ng L^{-1} (range < LOQ–208 ng L^{-1}), respectively. These chemicals are presumably used as intermediates in textile industries in Ungheni and Iasi as well in the catchment of the Jijia River, e.g., in Botosani at the Sitna tributary. A yarn manufacturer, as well as fiber preparation, spinning, and rugs, exists in the district of Ungheni.

A similar situation was observed for diphenylsulfone, a solvent used in the polymeric industry, which was determined at average levels of 81 ng L^{-1} (range < LOQ–240 ng L^{-1}) after the junction of the Jijia River at Frasinesti.

Agricultural sources

Pesticides

For the years 2010–2012, the FAO estimated an average consumption in Romania and the Republic of Moldova of 6750 and 2400 tons of pesticides and 3650 and 1050 tons of herbicides, respectively (http://www.fao.org/faostat/en/#compare).

Because of relatively dry periods before the sampling campaigns in November 2011 and June 2012, only low levels of pesticides (< 10 ng L^{-1}) originating from surface runoff from agricultural fields were determined in the Prut River basin. Few herbicides occurred at slightly higher concentrations: bentazone (11–27 ng L^{-1}), terbutlyazine (< LOQ–41 ng L^{-1}), acetochlor (< LOQ–28 ng L^{-1}), and metolachlor (< LOQ–33 ng L^{-1}).

The bentazone and metolachlor levels in the Prut were in the same range of the average concentrations in the Danube river and tributaries (Liška et al. 2015; Loos et al. 2010; Loos et al. 2017), whereas concentrations of other pesticides were significantly lower compared to the high concentrations determined in the Danube river basin in Serbia of terbutylazine (up to 200 ng L^{-1}), acetochlor (110 ng L^{-1}), and metolachlor (150 ng L^{-1}), where the amount of pesticides used is significantly higher (Antic et al. 2015).

Cholesterol

Cholesterol, a plant and animal sterol, enters the environment mainly after excretion in urine and feces. For pasture animals, this leads to direct input onto soils and surface waters. Cholesterol was determined in the Prut at average concentrations of 80 ng L^{-1} (range 22–150 ng L^{-1}). The environmental concentrations are rather lower compared to other countries, probably because of the extensive character of livestock farming in the region Moldova and Romania. Significant higher levels have been reported to occur in ambient waters, e.g., in the USA at concentrations up to 4300 ng L^{-1} (Kolpin et al. 2004; Singh et al. 2010) and also in the Pearl River Delta in China with average levels up to 540 ng L^{-1}, although with significant temporal and spatial variability (Wang et al. 2010).

Total concentrations

Following the flow of the Prut, the total average concentrations of micropollutants determined by GC-MS increased, particularly at the last sampling site: from 1071 ng L^{-1} at Sculeni, to 1438 ng L^{-1} at Ungheni, to 1502 ng L^{-1} at Frasinesti, to 1271 ng L^{-1} at Leova, to 1385 ng L^{-1} at Stoianovca, and to 2154 ng L^{-1} at Branza. The total average concentrations determined by LC-HRMS were 587 ng L^{-1} at Ungheni, 1428 ng L^{-1} at Frasinesti, and 1091 ng L^{-1} at Branza.

Where Environmental Quality Standards (EQS), as defined by the European Union (EU 2013) and the Swiss Centre for Applied Ecotoxicology (Oekotoxzentrum 2016) were available, the micropollutant concentrations did not exceed levels of ecotoxicological concern in the Prut. Nevertheless, for tributaries with low dilution like the Jijia, higher local and temporal concentration peaks may be expected and may therefore lead to a potential risk for the ecosystem.

Mass fluxes

Although grab samples are susceptible to over-interpretation because local, short-term inputs may be overrepresented, contaminant loads were calculated for a first estimation. The average load of micropollutants determined by GC-MS increased from 4.56 kg day^{-1} at Sculeni, to 6.63 kg day^{-1} at Ungheni, to 8.10 kg day^{-1} at Frasinesti, to 7.42 kg day^{-1} at Leova, to 8.04 kg day^{-1} at Stoianovca, and to 13.40 kg day^{-1} at Branza (Table SI 1). The total average loads determined by LC-HRMS were 2.28 kg day^{-1} at Ungheni, 5.86 kg day^{-1} at Frasinesti, and 5.39 kg day^{-1} at Branza (Table SI 2).

At Branza, the total average loads consisted of antioxidants 5.51 kg day^{-1}, personal care products 3.12 kg day^{-1}, phosphorous flame retardants 1.17 kg day^{-1}, pharmaceuticals 3.52 kg day^{-1}, artificial sweeteners 2.64 kg day^{-1}, industrial chemicals 1.36 kg day^{-1}, pesticides and biocides 0.87 kg day^{-1}, and others (caffeine and cholesterol) 0.66 kg day^{-1} (Fig. 4).

A strong increase of the total loads occurred between Ungheni and Frasinesti (56%), triggered by the inputs of pharmaceuticals (+ 140%), artificial sweeteners (+ 223%), industrial chemicals (+ 67%), pesticides and biocides (+ 58%), and PFRs (+ 29%) originating from the Jijia catchment. Between Frasinesti and Branza, with the city of Cahul located in this catchment area, the loads increased by 36%, mainly triggered by antioxidants (+ 60%), PCPs (+ 124%), PFRs (+ 80%), and pesticides and biocides (+ 57%).

At Branza, average loads above 0.5 kg day^{-1} were determined for acesulfame (2.27 kg day^{-1}, 82% of the total sweeteners), 2,4-DBP (2.22 kg day^{-1}), BHT (0.85 kg day^{-1}), BHA (0.72 kg day^{-1}), PBZ (1.10 kg day^{-1}), HHCB (0.98 kg day^{-1}), OD-PABA (0.68 kg day^{-1}), metformin (0.61 kg day^{-1}), 4-acetamidoantipyrene (0.82 kg day^{-1}), tetramethylchromanol (1.06 kg day^{-1}), diphenylsulfone (0.67 kg day^{-1}), and cholesterol (0.56 kg day^{-1}).

Recalcitrant chemicals are suitable as chemical markers for estimating the impact of municipal wastewaters. Wastewater tracers, e.g., artificial sweeteners, atenolol acid, and carbamazepine, have been suggested as chemical markers due to a pronounced persistence in the aquatic environment (Buerge et al. 2009; Clara et al. 2004; Radjenovic et al. 2008; Scheurer et al. 2009; Scheurer et al. 2011; Tran et al. 2014; Yang et al. 2017) and thus may be used to estimate the impact on the Prut River by the Jijia tributary.

However, a significant and highly variable removal of acesulfame was observed in WWTPs in Germany, and thus, this chemical may not be an appropriate wastewater tracer in WWTPs (Castronovo et al. 2017; Kahl et al. 2018). Nevertheless, its transformation after discharge to surface waters has not been reported yet. At Frasineti and Brinza, the ratio of the averaged acesulfame loads to the ones of atenolol acid, carbamazepine, and carbamazepine-10,11-dihydro-10,11-dihydroxy remained constant. This indicates that acesulfame is rather stable in the Prut River.

The loads of the conservative markers acesulfame, atenolol acid, carbamazepine, and carbamazepine-10,11-dihydro-10,11-dihydroxy increased between Ungheni and Frasinesti by a factor of 4.5, 3.6, 2.1, and 2.3, respectively, and subsequently remained relatively constant until Branza. Thus, emission sources in the region of Iasi play a major role with regard to the substantial use and release of micropollutants via the tributary Jijia in the receiving Prut River.

Nevertheless, the average total daily load determined by LC-HRMS of 5.39 kg at Branza is more than two orders of magnitude lower than the daily load of 1 ton determined in the Rhine at

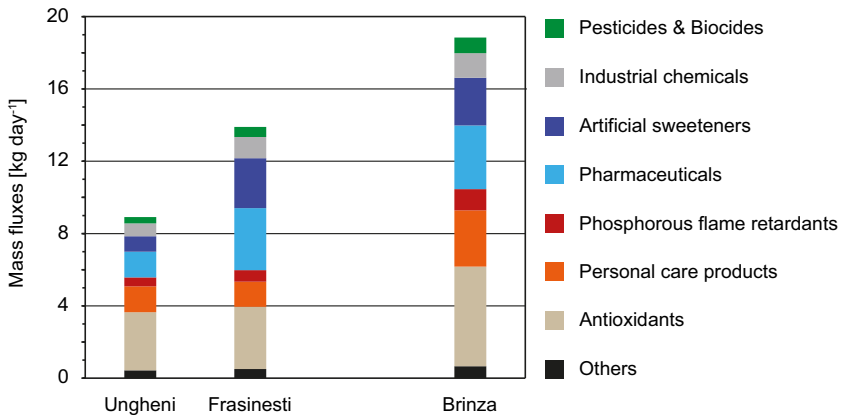

Fig. 4 Average of specific daily mass fluxes (kg day^{-1}) of organic micropollutants measured at the sites Ungheni, Frasinesti, and Branza on the Prut River

the Dutch-German border when analyzing the same set of analytes with the same screening method (Ruff et al. 2015).

The comparison to other studies showed significant lower per-capita consumption of several chemicals in the Prut catchment. While a per-capita consumption of acesulfame and sucralose in the catchment of the Rhine River (at the monitoring station in Bimmen-Lobith) of 8.21 and 0.47 mg capita^{-1} day^{-1}, respectively, were calculated (Ruff et al. 2015), a one order of magnitude lower values of 0.76 and 0.02 mg capita^{-1} day^{-1}, respectively, was estimated for the Prut catchment downstream of Branza, assuming a population of 3 million inhabitants living in the Prut basin.

For carbamazepine, the levels in the Prut (0.02 mg capita^{-1} day^{-1}) were one order of magnitude lower than in the Rhine (0.23 mg capita^{-1} day^{-1}) (Ruff et al. 2015) and in the Danube at Arges upstream the delta (0.17 mg capita^{-1} day^{-1}) (Loos et al. 2010). Additionally, low per-capita loads of 0.20 and 0.27 mg capita^{-1} day^{-1} were also observed in the Prut for metformin and 4-acetamidoantipyrene, respectively.

Conclusions

This study fills a data gap on eastern European surface waters regarding the contamination with organic micropollutants. The number of compounds determined by GC-MS and LC-HRMS in the Prut River was up to 88 substances, which in general occurred at low concentrations. Most prominent findings at concentrations ≈ 100 ng L^{-1} and above occurred for the artificial sweetener acesulfame, the pharmaceuticals metformin, 4,4,5,8-tetramethylchroman-2-ol and 4-acetamidoantipyrene, the antioxidants 2,4-di-tert-butylphenol (2,4-DBP), 3-tert-butyl-4-hydroxyanisol (BHA), and 3,5-di-tert-butyl-4-hydroxy-toluene (BHT), the personal care products HHCB, 4-phenylbenzophenone (PBZ), and octyl dimethyl-p-aminobenzoic acid (OD-PABA), the industrial chemical diphenysulfone, and the sterol cholesterol. Low concentrations of agricultural pesticides occurred in the catchment. At the last sampling site upstream the confluence with the Danube, the accumulated daily load of all determined substances was estimated to be almost 19 kg day^{-1}.

Discharge of wastewater without proper treatment from the Jijia catchment as well from the city of Cahul revealed a distinct increase in concentrations and loads in the Prut at Frasinesti and Branza. Thus, implementation of wastewater treatment capacities in the Prut River basin would considerably reduce the loads of micropollutants from urban point sources.

Where Environmental Quality Standards (EQS) were available, the micropollutant concentrations did not exceed levels of ecotoxicological concern in the Prut. However, for tributaries with low dilution like the Jijia River, higher local and temporal concentration peaks may be expected and may therefore lead to a potential risk for the ecosystem.

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