

Article

# Behavior of Organic Micropollutants During River Bank Filtration in Budapest, Hungary

Zsuzsanna Nagy-Kovács <sup>1,\*</sup>, Balázs László <sup>1</sup>, Ernő Fleit <sup>1</sup>, Katalin Czihat-Mártonné <sup>1</sup>, Gábor Till <sup>1</sup>, Hilmar Börnick <sup>2</sup>, Yasmin Adomat <sup>3</sup> and Thomas Grischek <sup>3</sup> 

<sup>1</sup> Budapest Waterworks Ltd, Váci út 23-27, 1134 Budapest, Hungary; balazs.laszlo@vizmuvek.hu (B.L.); erno.fleit@vizmuvek.hu (E.F.); katalin.martonne@vizmuvek.hu (K.C.-M.); gabor.till@vizmuvek.hu (G.T.)

<sup>2</sup> Institute for Water Chemistry, Technische Universität Dresden, 01062 Dresden, Germany; Hilmar.boernick@tu-dresden.de

<sup>3</sup> Division of Water Sciences, University of Applied Sciences Dresden, Friedrich-List-Platz 1, 01069 Dresden, Germany; yasmin.adomat@htw-dresden.de (Y.A.); thomas.grischek@htw-dresden.de (T.G.)

\* Correspondence: zsuzsanna.nagy-kovacs@vizmuvek.hu; Tel.: +36-30-439-4566

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**Abstract:** This paper summarizes results from a half-year sampling campaign in Budapest, when Danube River water and bank filtrate were analyzed for 36 emerging micropollutants. Twelve micropollutants were detected regularly in both river water and bank filtrate. Bisphenol A, carbamazepine, and sulfamethoxazole showed low removal (<20%) during bank filtration on Szentendre Island and Csepel island, whereas 1H-benzotriazole, tolyltriazole, diclofenac, cefepime, iomeprol, metazachlor, and acesulfame showed medium to high removal rates of up to 78%. The concentration range in bank filtrate was much lower compared to river water, proving the equilibration effect of bank filtration for water quality.

**Keywords:** river bank filtration; attenuation; organic micropollutants; pharmaceuticals

## 1. Introduction

Organic micropollutants from various sources are present in most European surface water bodies [1,2]. Not all micropollutants can be completely removed during drinking water treatment using common techniques such as flocculation, filtration, and activated carbon filtration [3]. River bank filtration (RBF) is known to have a high efficiency in removing organic micropollutants, mainly depending on their biodegradability and adsorption properties [4,5]. Furthermore, attenuation of organic micropollutants is dependent on redox conditions during RBF. Whereas many compounds are better degraded under oxic conditions, there are other compounds which are only (partly) attenuated under anoxic conditions [6]. Authors even suggest operating sequential RBF systems to take advantage of both redox conditions [7,8].

Additionally, an important aspect is that the removal rates of different micropollutants cannot be transferred from one site to another, therefore, it is important to investigate site specific characteristics [9] for a river bank filtration site.

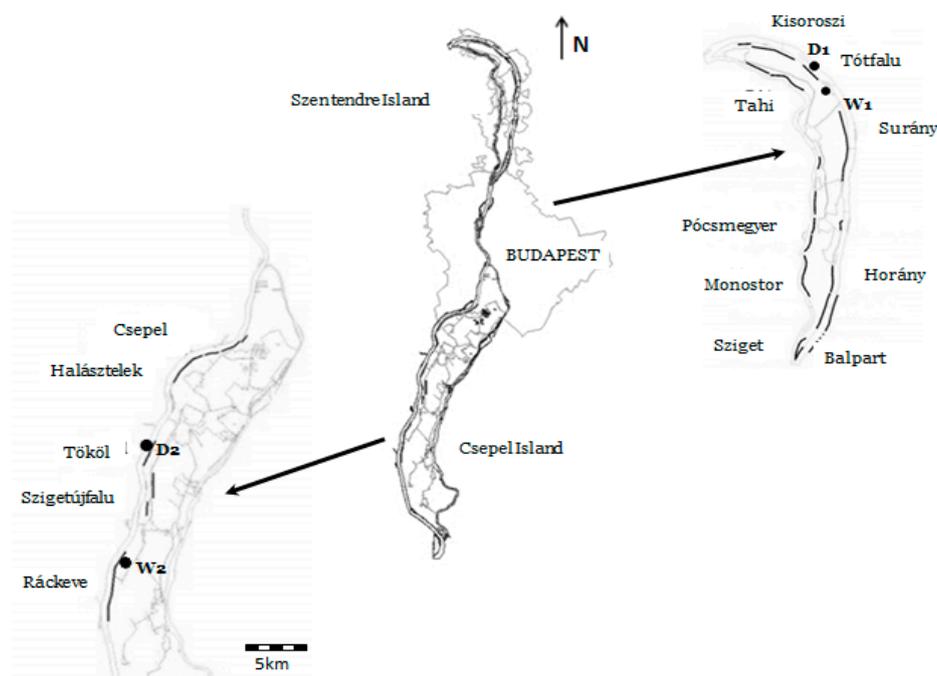
Due to the development of analytical methods, the number of compounds identified in source water is continuously increasing. Some of these compounds are defined as emerging pollutants, which are potentially hazardous compounds with limited available information about their possible effects on humans and aquatic organisms. They comprise of pharmaceuticals, hormones, perfluorinated compounds (PFCs), corrosion inhibitors, algal toxins, or pesticide transformation products [2,10]. It is of major interest to a water company to identify relevant micropollutants and indicators to assess the water quality, taking into account cost issues for regular monitoring.

As there are no defined limit values for many emerging pollutants in the Hungarian and German drinking water guidelines, the water companies themselves have to define parameters, which should be included in their water quality monitoring programs. Additionally, knowledge about the behavior of emerging pollutants during RBF is a pre-requisite to eventually adjust the post-treatment accordingly. Recently, the combination of bank filtration and engineered post-treatment systems (e.g., ultrafiltration, nanofiltration, reverse osmosis, electro chlorination) has been investigated in the EU project AquaNES [11].

On one hand, the aim of the presented study was to improve knowledge on the occurrence, range, and behavior of typical emerging pollutants in the Danube River and RBF wells upstream and downstream of the Hungarian capital Budapest. It was also an important aspect to identify relevant pollutants to be included in future monitoring of the wells operated by Budapest Waterworks.

## 2. Materials and Methods

Budapest Waterworks supply 1.89 million inhabitants based on two large and several small RBF systems. For the study, sampling was focused on the two large RBF systems along the Danube River, on Szentendre Island upstream of the city and Csepel Island downstream of the city (Figure 1). The Danube River has been sampled from the shores at both sites to see the impact of the city on source water quality. The location of the wells on the islands is favorable for RBF, resulting in high portions of bank filtrate [12]. The sampling point upstream of Budapest ( $W_1$ ) is fed by two separate well groups, Kisoroszi and Tótfalu (Figure 1), and the sampling point downstream of Budapest ( $W_2$ ) is fed by the Ráckeve well group. For the Kisoroszi well group, the average pumping rate is  $80.696 \text{ m}^3/\text{day}$  and the ratio of bank filtrate is 70%; for the Tótfalu well group these values are  $13.090 \text{ m}^3/\text{day}$  and 91%; and for the Ráckeve well group  $90.925 \text{ m}^3/\text{day}$  and 70%.



**Figure 1.** Danube River water and bank filtrate sampling points with the names of well groups on Szentendre Island and Csepel Island in Budapest.  $D_1$ : Danube River water sampling point upstream of Budapest.  $W_1$ : Bank filtrate sampling point upstream of Budapest.  $D_2$ : Danube River water sampling point downstream of Budapest.  $W_2$ : Bank filtrate sampling point downstream of Budapest.

On Szentendre Island, samples were taken from a collecting point as a mixture of bank filtrate from two different well groups. On Csepel Island, the collector pipe fed by several horizontal collector

wells was selected for sampling. The bank filtrates were untreated at both locations. Samples of Danube River water and bank filtrate were taken from October 2017 until March 2018. Sampling on Szentendre Island was performed monthly and sampling on Csepel Island was performed weekly, as downstream of the city water quality was expected to be more prone to pollution.

Sampling was done wearing single-use rubber gloves to prevent any contamination of the sample. Glass vial 1 (30 mL) was rinsed with the sampling water three times and emptied. A second glass vial, vial 2 (30 mL), was rinsed two times and half-filled. From vial 2, a volume of 5 mL was taken and transferred to vial 1. Next, 250  $\mu$ L of an internal standard was added using a Hamilton microsyringe. The vial was closed and shaken. The spiked sample was taken with a one-way syringe and filtered through a 0.2  $\mu$ m membrane filter (Chromafil Xtra RC-20/25, Macherey-Nagel Germany) and filled into a vial (ND 13) after the first 1 mL was wasted. Internal standards were stored at 2 °C–6 °C until usage and samples were stored at –18 °C until analysis. Before analysis, the samples were defrosted and analyzed without further preparation.

The analysis of 36 target compounds was carried out at the Institute for Water Chemistry, TU Dresden, using a UHPLC Shimadzu Nexera X2 coupled with a Sciex Q6500+ mass detector. Separation was realized on a porous silica column Phenomenex Luna Omega polar C18 (100  $\times$  2.1 mm) with a particle size of 1.6  $\mu$ m. For all determinations, the UHPLC was operated in gradient mode with a flow rate of 0.60 mL/min and a mobile phase of (A) water and (B) acetonitrile, both acidified with 0.02% formic acid. After an isocratic step for 1 min, a linear gradient was applied from 5% B to 98% B within 9 min. An isocratic step followed for 0.2 min, then, within 1.1 min, a linear gradient was applied again from 98% to 5% B. The column temperature was 40 °C. The mass spectrometer was operated in both positive and negative ion, multiple reaction-monitoring mode (MRM) using nitrogen as the collision gas. Quantification was accomplished using an internal standard method. In the case of compounds without an appropriate isotope-labelled internal standard, an external calibration method was applied. Instrument calibration was performed by analyzing standards at 0.1, 0.5, 1, 5, 10, 50, 100, 500, 1000, 5000, and 10,000 ng/L. The limit of quantification (LOQ) was set at a signal-to-rate ratio (S/N)  $\geq$  10. To prove that the instrument was properly calibrated throughout the analysis, a calibration verification standard was analyzed every 10 samples. Also, blank samples were analyzed between each compound to verify that the measured levels were not an artefact. Data acquisition was accomplished by MultiQuant™ Software (Sciex, version 1.62). Table 1 shows the list of compounds, including their range of quantification.

**Table 1.** List of analyzed emerging pollutants with range of quantification and MRM transitions.

Analyte	Range of Quantification in LOQ–10,000 ng/L	Quantifier MRM Transition Q <sub>1</sub> →Q <sub>3</sub> (m/z)	Qualifier MRM Transition Q <sub>1</sub> →Q <sub>3</sub> (m/z)
<b>Industrial Chemicals</b>			
1H-benzotriazole	50–10000	120→65	120→92
Bisphenol A	5–10000	233→138	233→215
Tolyltriazole	10–10000	134→77	134→79
<b>Herbicides, Pesticides and Transformation Products</b>			
Dimethachlor-ESA	1–10000	300→120	300→80
Dimethachlor-OA	10–10000	250→178	250→130
Dimethoate	10–10000	230→199	230→125
Diuron	10–10000	230→199	230→125
Imidacloprid	5–10000	256→209	256→175
Irgarol	1–10000	254→198	254→108
Isoproturon	1–10000	208→72	208→175
Metazachlor-ESA	5–10000	322→121	322→148
Metazachlor-OA	1–10000	271→67	271→65
Metolachlor-ESA	5–10000	328→120	328→80
Metolachlor-OA	5–10000	278→206	278→174
Nicosulfuron	5–10000	410→182	410→213
Terbutylazine-2-hydroxy	1–10000	210→97	210→154
Terbutryn	5–10000	142→186	142→91

Table 1. Cont.

Analyte	Range of Quantification in LOQ–10,000 ng/L	Quantifier MRM Transition Q <sub>1</sub> →Q <sub>3</sub> (m/z)	Qualifier MRM Transition Q <sub>1</sub> →Q <sub>3</sub> (m/z)
<b>Food Additives</b>			
Acesulfame	1–10000	162→82	162→78
<b>Pharmaceuticals and X-ray Contrast Agents</b>			
Bezafibrate	10–10000	362→316	362→139
Carbamazepine	1–10000	237→194	237→179
Cefepime	50–10000	481→396	481→324
Cefotaxime	50–10000	456→396	456→167
Cefuroxime	50–10000	447→386	447→342
Clarithromycin	10–10000	748→590	748→158
Clindamycin	5–10000	425→126	427→126
Diclofenac	50–10000	294→250	294→252
Erythromycin	5–10000	734→576	734→158
Fluoxetine	10–10000	310→148	310→44
Gabapentin	50–10000	172→154	172→137
Ibuprofen	5–10000	205→161	205→159
Iomeprol	50–10000	778→687	778→405
Metoprolol	5–10000	268→116	268→133
Naproxen	10–10000	229→185	229→169
Paracetamol	5–10000	152→110	152→93
Roxithromycin	50–10000	837→679	837→158
Sulfamethoxazole	1–10000	254→156	154→108

### 3. Results

Out of the comprehensive list given in Table 1, 12 micropollutants representing each group were detected nearly regularly. The micropollutants bezafibrate, clarithromycin, clindamycin, erythromycin, gabapentin, ibuprofen, metoprolol, naproxen, paracetamol, dimethachlor-ESA, dimethachlor-OA, igarol, imidacloprid, isoproturon, nicosulfuron, metazachlor-OA, terbutylazine-2-hydroxy, and terbutryn were only found in Danube River water but either not found, or found at very low levels, in bank filtrate, thus the attenuation rate is nearly 100%. Azithromycin, cefotaxime, cefuroxime, dimethoate, diuron, fluoxetine, and roxithromycin were not detected in any samples.

The minimum, median, and maximum concentrations of these 12 compounds found in Danube River water and in bank filtrate (BF) are comprised in Tables 2 and 3, respectively.

**Table 2.** Minimum, median, and maximum concentrations in ng/L of most prominent compounds in the Danube River Water at sampling points on Szentendre Island and Csepel Island.

Compound	Danube River Water (Szentendre) <i>n</i> = 6			Danube River Water (Csepel) <i>n</i> = 24		
	Minimum	Median	Maximum	Minimum	Median	Maximum
1H-Benzotriazole	181	272	345	183	256	338
Bisphenol A	15	33	124	14	86	990
Tolyltriazole	84	121	172	86	142	255
Carbamazepine	19	30	40	19	31	54
Cefepime	194	358	532	135	394	680
Diclofenac	70	153	442	59	154	418
Iomeprol	106	131	161	68	122	272
Sulfamethoxazole	6	14	17	7	13	45
Metolachlor-ESA	33	113	162	24	85	163
Metolachlor-OA	6	31	49	7	23	53
Metazachlor-ESA	52	180	359	31	152	1142
Acesulfame	102	219	343	115	266	512

**Table 3.** Minimum, median, and maximum concentrations in ng/L of most prominent compounds in bank filtrate at sampling points on Szentendre Island and Csepel Island.

Compound	Bank Filtrate (Szentendre)			Bank Filtrate (Csepel)		
	n = 6			n = 24		
	Minimum	Median	Maximum	Minimum	Median	Maximum
1H-Benzotriazole	70	85	92	125	146	200
Bisphenol A	19	51	98	30	105	2381
Tolyltriazole	32	63	73	64	88	118
Carbamazepine	18	24	24	20	29	43
Cefepime	57	193	301	123	248	546
Diclofenac	36	103	144	13	87	231
Iomeprol	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Sulfamethoxazole	9	13	18	6	9	16
Metolachlor-ESA	29	43	70	34	57	83
Metolachlor-OA	11	38	88	9	17	26
Metazachlor-ESA	25	40	273	28	125	686
Acesulfame	112	131	134	145	195	258

value lower than limit of quantification (LOQ).

It can be seen from the mean results of the Danube River water samples that the two locations have no considerable differences.

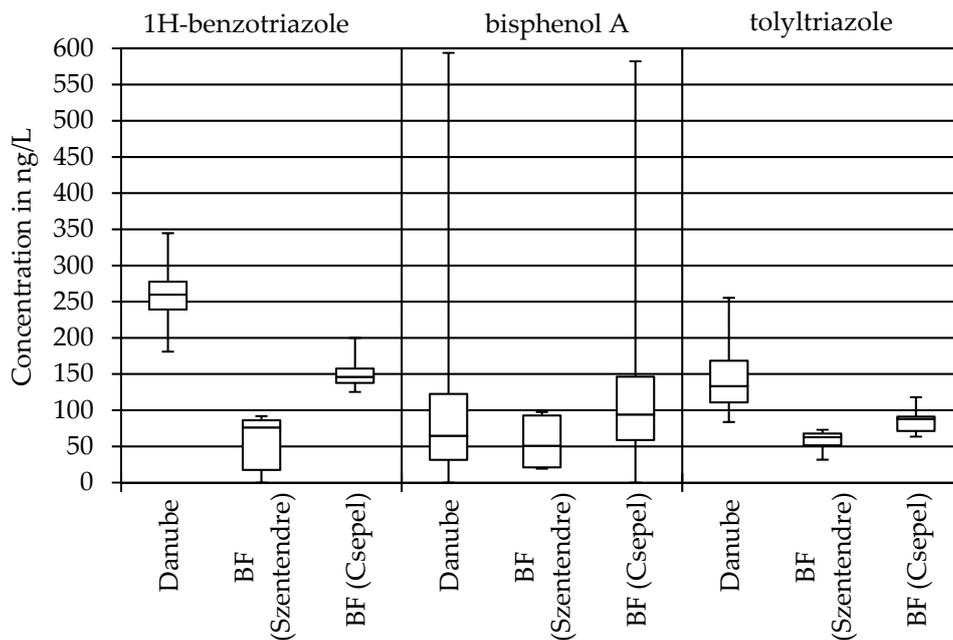
For each compound, only a mean removal rate has been determined, based on median concentrations for river water and bank filtrate for each site (Table 4). Data pairs were not suitable for this case, considering that well water samples are mixed samples of bank filtrate with different travel times. Samples from river water and bank filtrate taken on the same day are not related to each other. Thus, calculated negative removal rates could result from a higher concentration of a micropollutant before the start of the sampling campaign or on certain days during the sampling campaign, or when river water was not sampled or was sampled from another source (e.g. land-side groundwater).

**Table 4.** Median removal rates of the most prominent compounds in the River Danube water and bank filtrate at sampling points on Szentendre Island and Csepel Island.

Compound	Removal Rates in % (Szentendre)	Removal Rates in % (Csepel)
1H-benzotriazole	69	43
bisphenol A	−54	−22
tolyltriazole	48	38
carbamazepine	20	4
cefepime	46	37
diclofenac	32	44
iomeprol	bank filtrate concentrations below LOQ	
sulfamethoxazole	9	30
metolachlor-ESA	62	33
metolachlor-OA	−20	25
metazachlor-ESA	78	18
acesulfame	40	27

### 3.1. Industrial Products

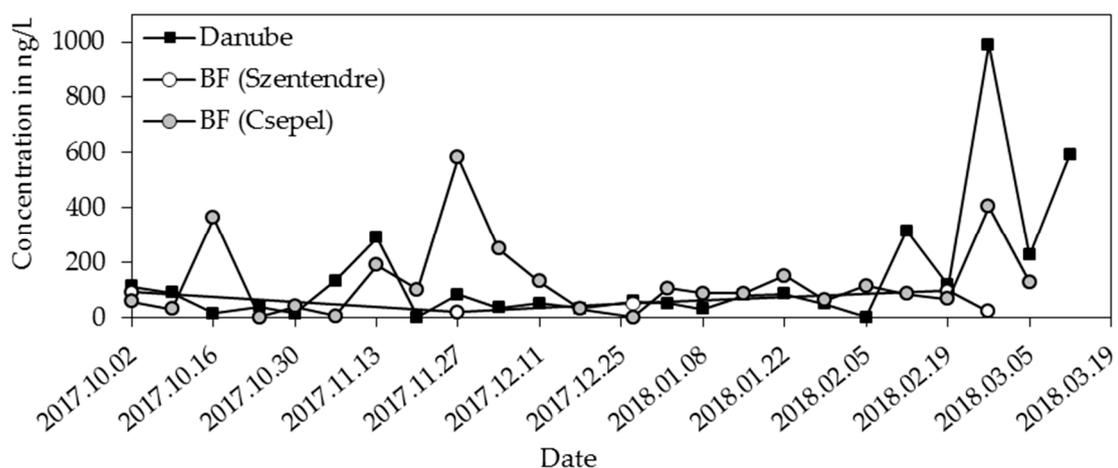
All three compounds of the group of industrial chemicals were detected in river water and bank filtrate. The highest median values were found for 1H-benzotriazole followed by tolyltriazole and bisphenol A in both river water and bank filtrate (Figure 2).



**Figure 2.** Boxplots representing concentrations of industrial chemicals in the Danube River water and bank filtrate.

For better visibility, two outliers for bisphenol A are not shown in Figure 2: 989 ng/L in Danube River water at Csepel (26 February 2018) and 2381 ng/L in bank filtrate at Csepel (12 March 2018). Concentrations were similar in river water samples at both sites, thus data for the Danube have been combined to have a higher number of samples ( $n = 30$ ) as input concentration.

During the sampling campaign, bisphenol A was detected in all water samples (Figure 3). The obtained bisphenol A levels varied from 4 to 2381 ng/L. The highest concentrations were observed during spring season on Szentendre Island and differed significantly from the determined bisphenol A levels in autumn and winter. These variations may result from environmental factors such as precipitation and temperature or different usage patterns of bisphenol A related products.

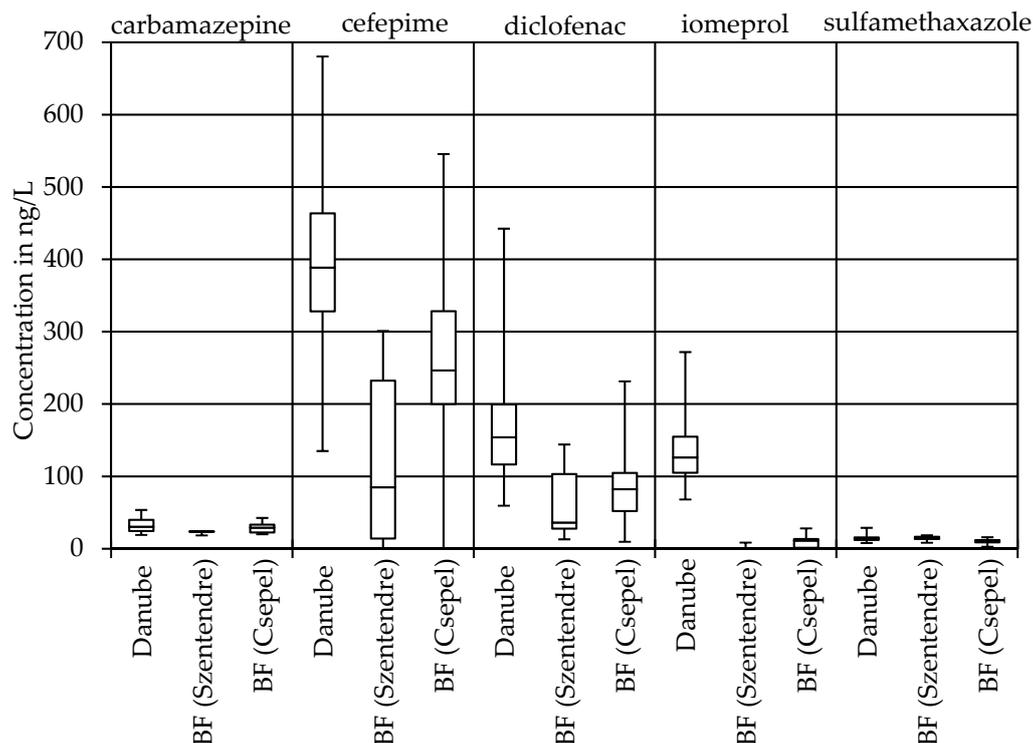


**Figure 3.** Seasonal fluctuation of bisphenol A concentration in Danube River water (squares) and bank filtrate (circles) (outlier of 2381 ng/L in BF (Csepel) on 26 February 2018, not shown).

### 3.2. Pharmaceuticals and X-ray Contrast Agents

Out of 19 monitored pharmaceuticals, five compounds were found to be regularly present in both Danube River water and bank filtrate. The cephalosporin antibiotic cefepime and the analgesic

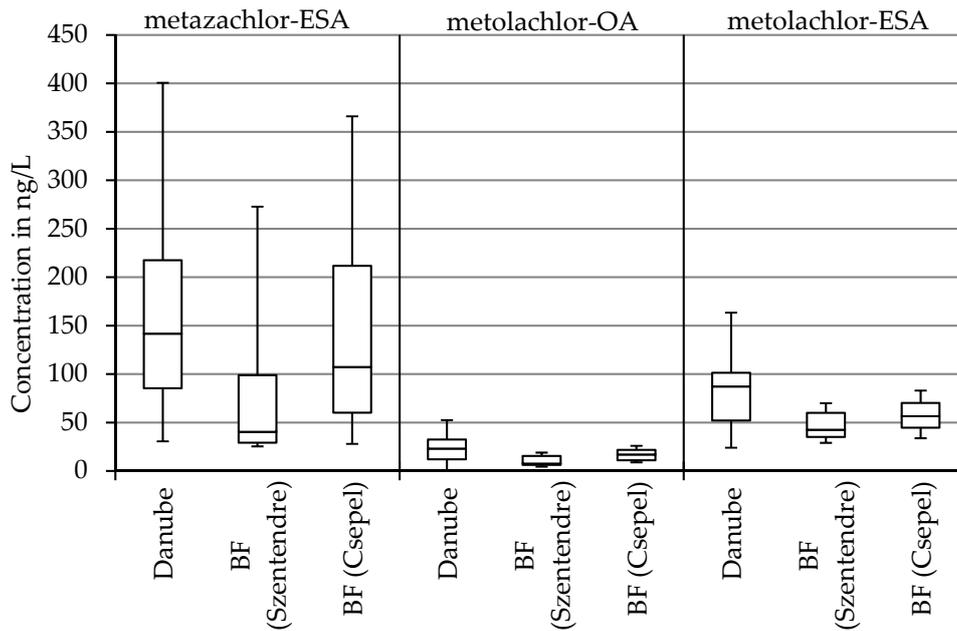
diclofenac were the most frequently detected pharmaceuticals, followed by the X-ray contrast agent iomeprol, the antiepileptic carbamazepine, and the antibiotic sulfamethoxazole (Figure 4). The median concentration of cefepime from all 30 Danube River water samples was 376 ng/L, of diclofenac was 154 ng/L, and of iomeprol was 126 ng/L. The levels of pharmaceutical residue in the bank filtrate were in all cases lower than those detected in the river water. Cefepime, diclofenac, and iomeprol concentrations decreased by 57%, 62%, and 96%, respectively. Iomeprol was found at much lower concentrations in river water compared to other European rivers with RBF sites, such as the Elbe River, with median concentrations from 500 to 800 ng/L since 2015 [13].



**Figure 4.** Boxplots representing concentrations of pharmaceuticals and X-ray contrast media in the Danube River water and bank filtrate.

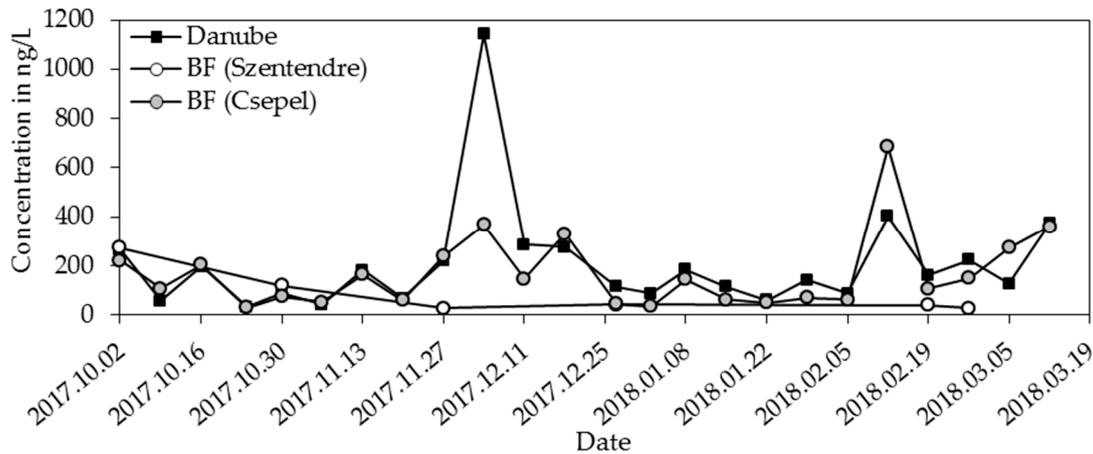
### 3.3. Herbicides, Pesticides, and Transformation Products

Out of the 14 analyzed herbicides, pesticides, and transformation products, the metabolites of metazachlor and metolachlor were most frequently measured. The highest concentrations were determined for metazachlor ethane sulfonic acid (ESA), metolachlor oxanilic acid (OA), and metolachlor-ESA (Figure 5).



**Figure 5.** Boxplots representing concentrations of herbicides, pesticides, and transformation products in the Danube River water and bank filtrate.

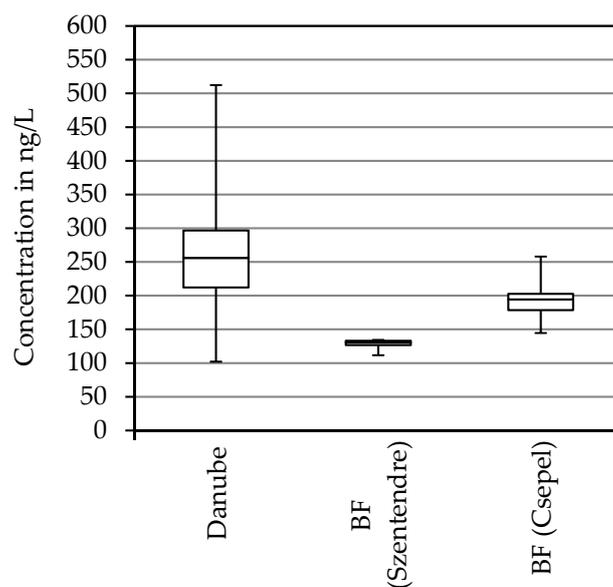
The two highest levels of metazachlor-ESA are not shown in Figure 5. They were detected in December 2017 (1141 ng/L) in the Danube River water and in February 2018 (685 ng/L) in the bank filtrate on Csepel Island (Figure 6).



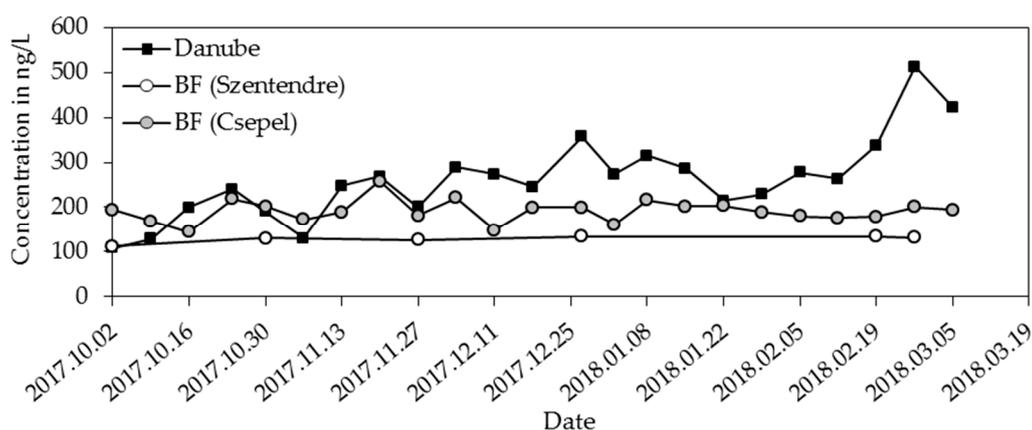
**Figure 6.** Seasonal fluctuation of metazachlor-ESA concentrations in the Danube River water (squares) and bank filtrate (circles).

### 3.4. Food Additives

The artificial sweetener acesulfame was detected in all water samples (Figure 7). The concentration in river water ranged from 102 to 512 ng/L ( $n = 30$ ) and in bank filtrate from 112 to 258 ng/L ( $n = 30$ ). The highest concentrations in river water were found after Christmas 2017 and during the low flow period starting end of February 2018 (Figure 8).



**Figure 7.** Boxplots representing concentrations of acesulfame in the Danube River water and bank filtrate.



**Figure 8.** Seasonal fluctuation of acesulfame concentration in the Danube River water (squares) and bank filtrate (circles).

#### 4. Discussion

The levels of 1H-benzotriazole and tolyltriazole are used as complexing agents (e.g., corrosion inhibitors) or for silver protection in dishwashing agents. Benzotriazoles can undergo several processes during RBF, such as biodegradation and retardation [14]. The concentration range of benzotriazoles in the Danube was determined to be between 130–300 ng/L [2]. During the demonstrated measurement campaign, they were present in the Danube River water at considerably higher concentrations than in the bank filtrate. Mean removal rates for the Szentendre and Csepel sites were 68% and 43% for 1H-benzotriazole and 48% and 37% for tolyltriazole, respectively.

Bisphenol A is used as an intermediate in the production of polycarbonate plastics and epoxy resins, unsaturated polyester-styrene resins, and as flame retardants in products like food and drink storage containers or protective coatings for metal cans [14–17]. Microbiological biodegradation has been investigated and according to the findings, bisphenol A is eliminated during bank filtration [18]. That is in contradiction with the results of the present study, where negative removal rates have been obtained. To exclude the effect of temporary spills of bisphenol A in the river on bank filtrate quality, preparation of mixed river water samples based on hourly sampling over at least one week would be an option.

Pharmaceuticals and X-ray contrast agents belong to the most predominant group of compounds in the aquatic environment, due to the high input quantities, their resistance to degradation (persistence or pseudo-persistence), and polar character-limiting attenuation by adsorption. Pharmaceuticals and their metabolites are mainly released into waterbodies via waste water effluents because they are not well attenuated in the human body and in the sewage treatment plant [2,19,20]. Considering the fact that most pharmaceuticals are very polar, they are hardly removed in conventional wastewater treatment plants. These properties also hinder the removal in drinking water treatment processes. As a result, residual concentrations are often found even in drinking water [9].

Carbamazepine is a medication used primarily in the treatment of epilepsy and neuropathic pain. It is reported that carbamazepine is a persistent compound, with relatively stable concentrations throughout bank filtration [21]. Measurement results are similar, with removal rates 20% and 4% for the sites upstream and downstream from the capital, respectively.

Cefepime is a fourth-generation cephalosporin antibiotic that has a broad spectrum of activity against both Gram-negative and Gram-positive bacteria. Cefepime was found to be partly removed by 46% and 37% during RBF at Budapest.

Diclofenac is a potent nonsteroidal anti-inflammatory drug (NSAID), taken or applied to reduce inflammation and as an analgesic reducing pain. Due to its wide use, it is a well observed pharmaceutical micropollutant. High concentrations were found in river waters but not in groundwater, suggesting that it is eliminated effectively. Also, it has been described that even in wells with relatively short travel times, its concentration decreased sharply [21]. At 32% and 43% removal rates, diclofenac can be considered to be relatively degradable.

Iomeprol is an iodinated X-ray contrast agent. According to Schittko et al., iomeprol was significantly removed during BF under anoxic conditions [22]. This was also the case at both sites in Budapest, where concentrations of iomeprol in bank filtrate were below LOQ.

Sulfamethoxazole is an antibiotic, effective in the treatment against Gram-negative and Gram-positive bacterial infections. It is considered to be a rather persistent pollutant, showing relatively stable concentrations through the subsurface water passage. [21] With removal rates at 9% and 30%, it proved to be fairly persistent in the present study as well.

The removal rates for sulfamethoxazole and diclofenac were higher on Csepel Island, which is assumed to be a result of longer flow paths and travel times. On average, the distance between the wells on Szentendre Island from the bank of the Danube River is 103 m, whereas it is 156 m on Csepel Island. From the data of this study, it is not yet possible to assess if the distance between the wells and the river bank or the travel time is more responsible for the attenuation, because the wells have different pumping rates and are not all continuously operated.

The concentration range of cefepime, diclofenac, and iomeprol was less than a factor of 2, whereas the discharge of the Danube River has been changing by a factor of 3.33 during the sampling period. For diclofenac and iomeprol, much lower fluctuations were found in bank filtrate, proving the buffering effect of RBF.

The median concentration of cefepime in Danube River water was calculated to 376 ng/L, which is low compared to findings from the Somes River, Romania [23].

Metazachlor and metolachlor are widely used herbicides, applied predominantly to maize crops and rape. Depending on their stability, they undergo decomposition processes. Therefore, not only active ingredients but their metabolites also occur as emerging contaminants. Metazachlor and metolachlor also have short half-lives in soils (5–30 days), therefore, they quickly degrade to oxanilic acid (OA), ethane sulfonic acid (ESA), and derivatives [24,25]. Those transformation products are only weakly adsorbed onto soil, resulting in a high mobility. As a consequence, the OA and ESA metazachlor and metolachlor derivatives are among the most frequent and concentrated water pollutants [25]. The maximum concentrations of metazachlor-ESA were determined during winter months. This may indicate a more frequent agricultural usage of parent herbicides during winter [26] but is not supported by results from common monitoring of herbicides, for which no peaks were observed in winter. As of

metolachlor-ESA and metazachlor-ESA removal rates were higher at Szentendre with 62% and 78%, respectively, while for the Csepel site lower values were determined, at 33% and 18%, respectively. For metolachlor-OA results were inconclusive at the Szentendre site with a negative removal rate, while at Csepel it was 25%.

Acesulfame is one of the most used artificial sweeteners. It is passing in wastewater treatment plants and thus typically found in waste water affected river water. Other sweeteners, such as cyclamate or saccharine, are usually degraded during wastewater treatment [27]. Therefore, acesulfame is a favorable indicator for human sewage and could be used to estimate the portion of bank filtrate in the abstracted water from the RBF wells. Assuming no attenuation during RBF and no occurrence in natural groundwater, the median concentration of 143 ng/L in the wells on Csepel Island and 266 ng/L in the Danube River water at Csepel would indicate a portion of bank filtrate of 73%, which is within the range found from groundwater flow modeling [12].

## 5. Summary

Out of the 36 micropollutants that have been analyzed, 12 were present in almost all the samples. In the case of eight compounds, the median concentrations were lower in the Szentendre Island bank filtrate samples. Diclofenac, sulfamethoxazole, and metolachlor-OA results were lower in the Csepel Island bank filtrate samples. The results of bisphenol A showed considerable seasonal variations.

The median concentrations of iomeprol were below the limit of detection for both sites.

The results for the herbicides, pesticides, and transformation product groups showed considerable differences between the results originating from Szentendre Island and Csepel Island. It would be interesting to further investigate the concentration of micropollutants in the ground water [21].

This study presents the first measurement campaign of the Budapest Waterworks within the AquaNES project. Results give an overview about the occurrence of micropollutants, which are not yet monitored regularly, in the Danube River water and its bank filtrate at Budapest. Most of the analyzed micropollutants have no determined method nor defined limits in any Hungarian or European regulation. The applied methods are not yet accredited, and accordingly, measurement results are of an informative nature. In general, it can be declared that persistent micropollutants in the river water and bank filtrate are well below the concentrations of contaminants found in other alimentations. Nevertheless, this issue is of high priority for all waterworks that are operating RBF systems to assure safe drinking water.

**Author Contributions:** Z.N.-K., B.L., E.F., Y.A. and T.G. reviewed previous literature and prepared the article draft. K.C.-M. was responsible for the sampling. H.B. performed the analyses and researched the use of the compounds. G.T. participated in project coordination. All co-authors reviewed and edited the article draft.

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