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GREY WATER FOOTPRINT OF CONTAMINANTS OF EMERGING CONCERN FROM WASTEWATER IN THE SAVA RIVER BASIN

SIVI VODNI ODTIS NOVODOBNIH ONESNAŽEVAL IZ ODPADNIH VOD V POREČJU SAVE

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Abstract

Water pollution by contaminants of emerging concern (CECs) causes risks to both the environment and human health. We assessed water pollution by CECs in the Sava River basin in two monitoring campaigns carried out in May and July 2017. The grey water footprint (GWF) is a tool that converts the level of pollution by particular substances into the volume of water needed for dilution to a harmless level. Therefore, it can serve as an indicator for comparing various pollutants. The results show that substances that determine the GWF differ in individual locations. The highest value of the GWF was associated with 17β-estradiol, however, found only in one wastewater sample. The study showed that the value of the GWF in individual locations fluctuates and does not depend on the size of the wastewater treatment plant from which the wastewater is discharged. At selected wastewater treatment plants, a sustainability assessment was carried out using the Water Pollution Level indicator. The values in all cases were below the level of 1.0, indicating sustainable discharge; only in two cases did values reach the defined threshold to question the potential of non-sustainable discharge. The study contributes to earlier studies on the GWF and enlarges knowledge regarding the GWF of CECs.

Keywords: Contaminants of emerging concern, grey water footprint, micropollutants, Sava River basin, wastewater treatment plant.

Izvleček

Prisotnost novodobnih onesnaževal (NO) v vodi povzroča tveganje za okolje in zdravje ljudi. Onesnaženost vode z NO v porečju reke Save smo ocenjevali na podlagi dveh vzorčenj v okviru monitoringa, izvedenega maja in julija 2017. Sivi vodni odtis pretvori onesnaženost s posameznimi snovmi v količino vode, ki je potrebna za njihovo razredčenje, na neškodljivo raven. Zato lahko služi kot kazalnik za primerjavo različnih onesnaževal. Rezultati meritev kažejo, da se snovi, ki določajo sivi vodni odtis, razlikujejo od lokacije do lokacije. Najvišja vrednost sivega vodnega odtisa je bila povezana s snovjo 17β-estradiol, ki pa je bila ugotovljena le v enem vzorcu odpadne vode. Študija je pokazala, da se vrednosti sivega vodnega odtisa zelo razlikujejo od lokacije do lokacije in niso odvisne od velikosti čistilnih naprav. Za izbrane čistilne naprave je

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bila izvedena ocena trajnostnosti z uporabo kazalnika stopnje onesnaženosti vode. Vrednosti so bile v vseh primerih pod ravnjo 1,0, ki pomeni trajnostni izpust onesnaženja, v dveh primerih pa sta vrednosti že spadali v območje negotovosti. Študija prispeva k prejšnjim študijam o sivem vodnem odtisu in povečuje znanje o sivem vodnem odtisu pri tej vrsti onesnaženja.

Ključne besede: Novodobna onesnaževala, sivi vodni odtis, mikroonesnaževala, reka Sava, čistilna naprava.

1. Introduction

The rapid development of analytical methods in recent years has facilitated the search for new pollutants in aquatic environments. The presence of these pollutants in wastewater, surface water, groundwater, and marine water, as well as in soil and sludge has been well documented (Patel et al., 2019). These substances have been detected in many countries around the world, on all continents, and even in Antarctica (Balakrishna et al., 2023); but especially in North America and Europe (Wilkinson et al., 2022). In the case of contaminants of emerging concern (CECs), it is not clear what effects they can have on the environment. Legal requirements for the regulation of their discharge into surface water bodies have not yet been established. An exception here is for example Switzerland, where the Waters Protection Act was revised in 2014 to further improve wastewater treatment for the removal of CECs. These are mainly active pharmaceutical agents, personal care products, lifestyle compounds (e.g. caffeine), industrial micropollutants, pesticides, etc. CECs appear in the environment as a result of human activity and have the potential to harm ecosystems and humans (Sauvé and Desrosiers, 2014). They can enter the environment in many ways, but one of the most important is considered to be the discharge of wastewater (Astuti et al., 2023; Lapworth et al., 2012; Saidulu et al., 2021). Current wastewater treatment technologies are not designed for CECs removal, therefore some of these substances can more or less pass via wastewater treatment plants (WWTPs) and spread further into the environment. The removal efficiency of CECs at WWTPs varies a considerably, ranging from negative efficiency values (when, due to metabolization processes, some substances are formed during the wastewater treatment process) to very efficient removals approaching 100%. The removal rate depends on many factors (Rapp-Wright et al., 2023). Different wastewater treatment technologies have different removal efficiencies for particular groups of CECs (Samal et al., 2022). Also in the environment, the fate of CECs is influenced by many processes, depending on both i) their physicochemical properties and ii) the extant environmental characteristics. Some CECs are very stable and are detected many kilometers downstream from discharge points. Some CECs (e.g. anti-cancer drugs) can take many months or even years to break down in the environment (Castellano-Hinojosa et al., 2023).

This study uses the grey water footprint (GWF) concept to assess water pollution by CECs. The GWF indicates the volume of water needed to assimilate the pollutant load to acceptable concentrations (Hoekstra et al., 2011). Although the water footprint was introduced in 2002 (Hoekstra and Hung, 2002), the GWF was included in the concept couple of years later, in the period of 2005-2008 (Ansorge and Stejskalová, 2023). The water footprint is an environmental indicator of freshwater use that assesses both direct and indirect water consumption. The GWF of pollution discharged from WWTPs has been studied in several countries around the world, e.g. in Romania (Ene and Teodosiu, 2011; Teodosiu et al., 2016), Spain (Gómez-Llanos et al., 2020, 2018; Morera et al., 2016), the Czech Republic (Ansorge et al., 2020a, 2020b), China (Gu et al., 2016; Li et al., 2016; Qin et al., 2019), Iran (Rezaee and Tabesh, 2022), Canada (Johnson and Mehrvar, 2019), and Turkey (Kalya and Alver, 2022; Yapıcıoğlu, 2020).

Most of the studies dealing with the GWF assessment of WWTPs were focused mostly on the standardly monitored pollutants (organic, and nutrient pollution). Research on GWFs in relation to CECs discharged from WWTPs is still incipient; only a few studies have been published dealing with

CECs, especially pharmaceuticals. Martínez-Alcalá et al. (2018) studied the GWF of four of the most common pharmaceuticals carbamazepine (CBZ), diclofenac (DF), ketoprofen (KP), and naproxene (NP) in wastewater in southern Spain. Wöhler et al. (2020) modelled the GWF of human and veterinary pharmaceuticals based on the total consumption of these pharmaceuticals in Germany and the Netherlands, and carried out a sustainability assessment in the Vecht River basin. In another study, Wöhler et al. (2021) presented approaches for more detailed modelling of the potential burden of the aquatic environment by veterinary antibiotics (Stejskalová et al., 2022).

Researchers dealing with water footprint issues usually find it difficult to obtain funds for in-situ monitoring. However, for the GWF analyses, data sets obtained as part of other legislative or research activities could be used. This creates new specific data sets, which researchers can use for their water footprint studies, such as the GWF dataset of pollution discharged from WWTPs in the Czech Republic (Ansorge et al., 2021).

This study aims to determine the GWF of CECs monitored as part of the survey carried out by Slovenian and Croatian researchers who mapped the occurrence of CECs in discharged wastewater from WWTPs in the Sava River basin. According to our best knowledge, apart from the four studies mentioned above, no one has dealt with the issue of the GWF of pharmaceuticals and CECs yet. This study uses monitored data from 6 WWTPs in the Sava River basin, concerning not only pharmaceuticals but also other micropollutants, and thus enlarges our knowledge about the GWF of CECs.

2. Material and methods

In May and July 2017, researchers from the Jožef Stefan Institute (Ljubljana, Slovenia) and the Ruđer Bošković Institute (Zagreb, Croatia) carried out two sampling campaigns on wastewater discharges at 6 WWTPs in the Sava River basin (Česen et al., 2019). The Slovenia study monitored the WWTPs in Ljubljana (LJ), Domžale-Kamnik (DK), and Novo Mesto (NM). In Croatia, the WWTPs in Zaprešić (ZP), Zagreb (ZG), and Velika Gorica (VG) were monitored. The monitoring focused on 23 substances, especially on pharmaceuticals and personal care products (PPCPs), lifestyle compounds, and endocrine-disrupting industrial chemicals. The list of monitored substances is presented in Table 1. The mass load of discharged pollution from particular WWTPs was determined from measured concentrations and flow rates at the effluents from monitored WWTPs (Table 2 and 3).

***Preglednica 1:** Novodobna onesnaževala, vključena v monitoring.*

***Table 1:** List of monitored contaminants of emerging concern.*

Abbr.	Name	CAS
BePB	Benzyl-paraben	94-18-8
BIS2	2,2′-Methylenediphenol	2467-02-9
BPA	Bisphenol A	80-05-7
BPAF	Bisphenol AF	1478-61-1
BPB	Bisphenol B	77-40-7
BPE	Bisphenol E	2081-08-5
BPF	Bisphenol F	620-92-8
BPS	Bisphenol S	80-09-1
CAF	Caffeine	58-08-2
CBZ	Carbamazepine	298-46-4
DF	Diclofenac as sodium salt	15307-79-6
DFtp1	DF transformation product	---
DH-BP	2,4-Dihydroxybenzophenone	131-56-6
E1	Estrone	53-16-7
E2	17β-Estradiol	50-28-2
H-BP	4-Hydroxybenzophenone	1137-42-4
HM-BP	Oxybenzone	131-57-7
HPP	4-Cumylphenol	599-64-4
IB	Ibuprofen	15687-27-1
KP	Ketoprofen	22071-15-4
MEC	Mecoprop	93-65-2
MePB	Methyl paraben	99-76-3
NP	Naproxene	22204-53-1

Preglednica 2: *Masna obremenitev [g/dan] novodobnih onesnaževal v maju (N.C. – ni izračunana, ker NO v odpadni vodi niso bila zaznana).*

Table 2: *Mass load [g/day] of contaminants of emerging concern in May (N.C. – not calculated since EC was not detected in wastewater).*

May	LJ	DK	NM	ZP	ZG	VG
BePB	38	N.C.	N.C.	N.C.	N.C.	2.45
BIS2	N.C.	0.639	N.C.	N.C.	2.72	0.135
BPA	2.97	3.19	1.46	N.C.	N.C.	17.3
BPAF	N.C.	0.000659	N.C.	N.C.	0.509	0.0224
BPB	N.C.	N.C.	N.C.	N.C.	N.C.	0.179
BPE	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
BPF	N.C.	N.C.	N.C.	N.C.	N.C.	0.253
BPS	N.C.	N.C.	N.C.	N.C.	N.C.	2.67
CAF	43.6	4.14	0.615	331	110	22.5
CBZ	26.1	5.16	1.92	0.575	108	3.95
DF	44.8	8.73	2.73	0.756	41.6	3.91
DFtp1	N.C.	N.C.	N.C.	N.C.	N.C.	37.8
DH-BP	N.C.	N.C.	N.C.	N.C.	N.C.	2.2
E1	23.3	N.C.	N.C.	N.C.	N.C.	13.1
E2	N.C.	N.C.	N.C.	4.75	N.C.	N.C.
H-BP	1.23	0.262	0.0708	199	2.7	0.232
HM-BP	0.165	N.C.	N.C.	N.C.	1.88	N.C.
HPP	N.C.	0.93	N.C.	N.C.	N.C.	N.C.
IB	N.C.	N.C.	N.C.	35.8	N.C.	36.5
KP	N.C.	N.C.	N.C.	10.9	14	16.3
MEC	N.C.	N.C.	0.0373	N.C.	N.C.	N.C.
MePB	1.35	0.455	N.C.	12.8	3.09	0.272
NP	N.C.	N.C.	N.C.	3.5	21.3	14.5

Preglednica 3: *Masna obremenitev [g/dan] novodobnih onesnaževal v juliju (N.C. – ni izračunana, ker NO v odpadni vodi niso bila zaznana).*

Table 3: *Mass load [g/day] of contaminants of emerging concern in July (N.C. – not calculated since EC was not detected in wastewater).*

July	LJ	DK	NM	ZP	ZG	VG
BePB	N.C.	N.C.	N.C.	3.91	N.C.	0.14
BIS2	0.649	0.664	N.C.	N.C.	1.16	0.154
BPA	N.C.	1.5	9.04	0.585	N.C.	13.9
BPAF	N.C.	N.C.	0.000209	N.C.	N.C.	0.0115
BPB	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
BPE	N.C.	N.C.	N.C.	2.76	N.C.	N.C.
BPF	N.C.	0.0914	0.011	0.675	N.C.	0.349
BPS	N.C.	N.C.	N.C.	0.625	N.C.	2.58
CAF	29.2	8.74	0.598	103	165	144
CBZ	25.3	6.11	2.08	30.8	87.8	3.82
DF	56.8	11.1	2.12	2.24	27.6	4.34
DFtp1	N.C.	N.C.	N.C.	N.C.	N.C.	4.63
DH-BP	N.C.	0.658	N.C.	1.69	N.C.	3.33
E1	10.9	1.61	N.C.	N.C.	N.C.	9.64
E2	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.

July	**LJ**	**DK**	**NM**	**ZP**	**ZG**	**VG**
H-BP	1.04	N.C.	0.092	N.C.	1.76	0.227
HM-BP	0.741	0.0758	N.C.	N.C.	4.09	0.288
HPP	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
IB	N.C.	N.C.	N.C.	25.1	N.C.	36.3
KP	5.91	N.C.	N.C.	11.6	23	12.8
MEC	N.C.	N.C.	0.294	N.C.	N.C.	N.C.
MePB	1.66	N.C.	N.C.	5.48	N.C.	0.278
NP	N.C.	N.C.	N.C.	3.63	58.7	12.6

From the mass load of CECs discharged into the receiving water body, the GWF can be calculated according to the Equation:

$$\mathrm{GWF} = max\{GWF_1, GWF_2, \dots, GWF_n\} \qquad (1)$$

The GWF of the WWTP is determined by the substance with the highest value of the GWF. That is determined as the ratio between the mass load of substance *i* (*Li*) and the assimilation capacity of the receiving water body (i.e. the difference between the maximum permitted concentration of the substance *i* in the receiving water body ($C_{max,i}$) and the natural concentration of the substance *i* in the receiving water body ($C_{nat,i}$):

$$\mathrm{GWF}_i = \frac{L_i}{C_{max,i} - C_{nat,i}} \qquad \text{[volume/time]} \qquad (2)$$

For artificial substances that are not present in nature we consider $C_{nat,i} = 0$ (Hoekstra et al., 2011). Since CECs do not have the $C_{max,i}$ values determined yet, *Predicted No Effects Concentration* (PNEC) values are used in the GWF calculation. The PNEC indicates the concentration of a chemical substance below which no adverse effects of exposure in the ecosystem were spotted. (Martínez-Alcalá et al., 2018). The PNEC values listed in the NORMAN Ecotoxicology Database were used for this study. The database presents PNEC values agreed upon the basis of pan-European expert consultations (Dulio et al., 2020). PNEC values for diclofenac as sodium salt (CAS 15307-79-6) and transformation products of diclofenac are not listed in the NORMAN Ecotoxicology Database. Therefore, PNEC = 0.05 µg/l was used for both cases, which corresponds with the PNEC of diclofenac (CAS 15307-86-5).

The PNEC values used for the GWF calculation are presented in Table 4.

Preglednica 4: *Vrednosti predvidene koncentracije brez učinka [µg/l].*

Table 4: Predicted No Effects Concentration values *[µg/l].*

Abbr.	**Lowest PNEC** (in freshwater)	**Last Update**
BePB	2.94743	26 Mar 2018
BIS2	4.89838	26 Mar 2018
BPA	0.24	27 Nov 2022
BPAF	1.01908	26 Mar 2018
BPB	1.35007	26 Mar 2018
BPE	2.1516	26 Mar 2018
BPF	5.44092	26 Mar 2018
BPS	12.88093	26 Mar 2018
CAF	0.1	03 Oct 2018
CBZ	2	27 Nov 2022
DF	0.05	
DFtp1	0.05	
DH-BP	1.71313	26 Mar 2018
E1	0.0036	27 Nov 2022
E2	0.0004	27 Nov 2022
H-BP	2.77269	26 Mar 2018
HM-BP	1.5411	26 Mar 2018
HPP	0.78665	26 Mar 2018
IB	0.011	27 Nov 2022
KP	2.09574	26 Mar 2018
MEC	0.1	03 Oct 2018
MePB	5	03 Oct 2018
NP	1.7	27 Nov 2022

For discharges from WWTPs in Ljubljana, Domžale-Kamnik, Zaprešić, and Zagreb, the sustainability assessment was carried out using the Water Pollution Level (WPL). The WPL indicator (Hoekstra et al., 2011) is calculated as the ratio of the GWF to the actual runoff from the river basin (R_{act}):

$$WPL = \frac{GWF}{R_{act}} \qquad [---] \qquad (3)$$

For the WWTP in Ljubljana, run-off in the Jevnica profile station was used. For the WWTP in Domžale-Kamnik, run-off in the Ljubljana profile station was used. For the WWTP in Zagreb WWTP, run-off in the Oborovo profile station was used. For the WWTP in Zaprešić, run-off in the Jankomir profile station was used. For the WWTPs in Novo Mesto and Velika Gorica, no relevant profiles could be added.

Data were provided by the Slovenian Environment Agency (ARSO) and by the Croatian Meteorological and Hydrological Service (Table 5). Considering the uncertainties associated with the GWF calculated using PNEC, an uncertainty interval of ±30% was set (Ansorge et al., 2019):

WPL < 70 % ... sustainable discharge

70 % ≤ WPL ≤ 130 % ... potentially non-sustainable discharge

WPL > 130 % ... unsustainable discharge

Preglednica 5: *Vrednosti pretoka [m^3/dan].*

Table 5: *Run-off values [m^3/day].*

Station on Sava River	Run-off	
	23 May 2017	**12 Jul 2017**
Jevnica	7 456 320	6 376 320
Ljubljana	4 959 360	4 976 640
Jankomir	14 256 000	8 493 120
Oborovo	14 169 600	8 026 560

3. Results

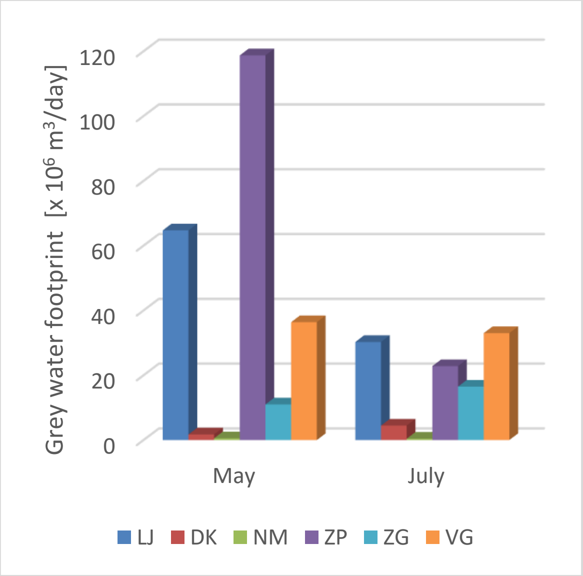
The overview of the GWF values reached in May and July is presented in Tables 6 and 7, respectively. The highest GWF value (11.875 mil. m^3/day) was detected in May, at the WWTP in Zaprešić, and was caused by 17β-estradiol hormone, which has the lowest PNEC value among all monitored substances. Estrone (also female hormone) was the determining pollution according to Equation 1, at WWTPs in Ljubljana (in May and July), Velka Gorica (in May), and Domžale-Kamnik (in July). Stimulant caffeine was the determining pollutant at the WWTP in Zagreb (in May and July). Diclofenac (nonsteroidal anti-inflammatory drug, NSAID) was the determining pollutant at WWTPs in Domžale-Kamnik (in May), and in Novo Mesto (in May and July). Another NSAID, ibuprofen, was the determining pollutant at WWTPs in Zaprešić (in July) and Velka Gorica (in July). A comparison of GWF values at individual WWTPs is shown in Figure 1.

The Water Pollution Level caused by CECs discharges from monitored WWTPs is presented in Table 8. In all cases, the WPL is <1. However, in the Jevnica profile station (downstream of the WWTP Ljubljana) and Jankomir profile station (downstream of the WWTP Zaprešić), the uncertainty value of ±30% was exceeded in May.

Preglednica 8: *Stopnja onesnaženosti vode.*

Table 8: *Water Pollution Level.*

Station on Sava River (WWTP)	WPL	
	23 May 2017	**12 Jul 2017**
Jevnica (LJ)	0.87	0.47
Ljubljana (DK)	0.04	0.09
Jankomir (ZP)	0.83	0.27
Oborovo (ZG)	0.08	0.21



Slika 1: *Primerjava vrednosti sivega vodnega odtisa na posameznih čistilnih napravah.*

Figure 1: *Comparison of grey water footprint values at the individual wastewater treatment plants.*

Preglednica 6: *Sivi vodni odtis [m^3/dan] novodobnih onesnaževal v maju (N.C. – ni izračunan, ker NO v odpadni vodi niso bila zaznana; najvišja vrednost je označena s krepkim tiskom).*

Table 6: *GWF [m^3/day] of contaminants of emerging concern in May (N.C. – not calculated since EC was not detected in wastewater; highest values are in bold).*

May	LJ	DK	NM	ZP	ZG	VG
BePB	12 892	N.C.	N.C.	N.C.	N.C.	831
BIS2	N.C.	130	N.C.	N.C.	555	28
BPA	12 375	13 292	6 083	N.C.	N.C.	72 083
BPAF	N.C.	1	N.C.	N.C.	499	22
BPB	N.C.	N.C.	N.C.	N.C.	N.C.	133
BPE	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
BPF	N.C.	N.C.	N.C.	N.C.	N.C.	47
BPS	N.C.	N.C.	N.C.	N.C.	N.C.	207
CAF	436 000	41 400	6 150	3 310 000	**1 100 000**	225 000
CBZ	13 050	2 580	960	288	54 000	1 975
DF	896 000	**174 600**	**54 600**	15 120	832 000	78 200
DFtp1	N.C.	N.C.	N.C.	N.C.	N.C.	756 000
DH-BP	N.C.	N.C.	N.C.	N.C.	N.C.	1 284
E1	**6 472 222**	N.C.	N.C.	N.C.	N.C.	**3 638 889**
E2	N.C.	N.C.	N.C.	**11 875 000**	N.C.	N.C.
H-BP	444	94	26	71 771	974	84
HM-BP	107	N.C.	N.C.	N.C.	1 220	N.C.
HPP	N.C.	1 182	N.C.	N.C.	N.C.	N.C.
IB	N.C.	N.C.	N.C.	3 254 545	N.C.	3 318 182
KP	N.C.	N.C.	N.C.	5 201	6 680	7 778
MEC	N.C.	N.C.	373	N.C.	N.C.	N.C.
MePB	270	91	N.C.	2 560	618	54
NP	N.C.	N.C.	N.C.	2 059	12 529	8 529

Preglednica 7: *Sivi vidni odtis [m^3/dan] novodobnih onesnaževal v juliju (N.C. – ni izračunan, ker NO v odpadni vodi niso bila zaznana; najvišja vrednost je označena s krepkim tiskom).*

Table 7: *Grey water footprint [m^3/day] of contaminants of emerging concern in July (N.C. – not calculated since EC was not detected in wastewater; highest values are in bold).*

July	LJ	DK	NM	ZP	ZG	VG
BePB	N.C.	N.C.	N.C.	1 327	N.C.	48
BIS2	132	136	N.C.	N.C.	237	31
BPA	N.C.	6 250	37 667	2 438	N.C.	57 917
BPAF	N.C.	N.C.	0.21	N.C.	N.C.	11
BPB	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
BPE	N.C.	N.C.	N.C.	1 288	N.C.	N.C.
BPF	N.C.	17	2	124	N.C.	64
BPS	N.C.	N.C.	N.C.	49	N.C.	200
CAF	292 000	87 400	5 980	1 030 000	**1 650 000**	1 440 000
CBZ	12 650	3 055	1 040	15 400	43 900	1 910
DF	1 136 000	222 000	**42 400**	44 800	552 000	86 800
DFtp1	N.C.	N.C.	N.C.	N.C.	N.C.	92 600
DH-BP	N.C.	384	N.C.	987	N.C.	1 944
E1	**3 027 778**	**447 222**	N.C.	N.C.	N.C.	2 677 778
E2	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.

July	**LJ**	**DK**	**NM**	**ZP**	**ZG**	**VG**
H-BP	375	N.C.	33	N.C.	635	82
HM-BP	481	49	N.C.	N.C.	2 654	187
HPP	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
IB	N.C.	N.C.	N.C.	**2 281 818**	N.C.	**3 300 000**
KP	2 820	N.C.	N.C.	5 535	10 975	6 108
MEC	N.C.	N.C.	2 940	N.C.	N.C.	N.C.
MePB	332	N.C.	N.C.	1 096	N.C.	56
NP	N.C.	N.C.	N.C.	2 135	34 529	7 412

4. Discussion and Conclusion

Although different types of CECs were monitored within this study, the determining pollution causing the GWF were (apart from caffeine) only pharmaceuticals. Estrone and 17β-estradiol (both, estrogen steroid female sex hormones) were detected in wastewater 6 times, of which 5 times as determining pollution causing the GWF. Ibuprofen was detected in wastewater 4 times, of which 2 times as determining pollution causing the GWF at a particular WWTP. In the remaining two cases, the decisive contaminant causing the GWF were again estrone or 17β-estradiol. These hormones have set very low PNEC values, compared to other evaluated CECs, about 1-3 orders of magnitude lower. 17β-estradiol has one order of magnitude more stringent PNEC (0.0004 µg/l) than estrone, with the second-lowest PNEC value (0.003 µg/l) among all monitored substances. Ibuprofen has the third-lowest PNEC value (0.011 µg/l) among the monitored substances. Diclofenac and caffeine, which have the fourth- and sixth-lowest PNEC values, were other substances helping the determination of (in some cases) the GWF at particular WWTPs. It can be summarized that diclofenac and caffeine were decisive for the GWF only in cases when the above-mentioned estrogen hormones or ibuprofen (with much lower PNEC values) were not detected in wastewater. This highlights the importance of knowing the environmental impacts of CECs, which are reflected in PNEC values and also in the forthcoming environmental quality standard values.

The sustainability assessment using the WPL indicator applied in this study does not reflect the overall status of pollution in the receiving water body. Therefore, even a situation where the discharge is marked as non-risky may actually exceed the available assimilation capacity of the receiving water body in the given profile. To describe the real situation in the watercourse, it is necessary to include in the WPL calculation all sources of all pollutants in the watershed, as envisaged by the Water Footprint Assessment Manual (Hoekstra et al., 2011, p. 87). However, not all the necessary inputs for this study were present. It should be also noted that the calculation of the river basin pollution load in the form of a simple summing up of all GWFs of pollution sources in the watershed, as assumed by the Water Footprint Assessment Manual (Hoekstra et al., 2011, p. 87) neglects the self-purification processes of natural water systems and has other limitations, such as the practical impossibility of summing up all the various pollution sources emitting different pollutants and focusing on just one main pollutant in the river basin (Ansorge et al., 2022).

While some CECs degrade relatively quickly in the watershed, other CECs are resistant in the environment. For example, a study focused on the Czech part of the Elbe River basin shows that the amount of pharmaceuticals in individual profiles is in direct proportion to the number of inhabitants living in the river basin upstream the evaluated profile, because the PPCP consumption is, more or less, uniform within the population (Fuksa and Smetanová, 2022). However, the variability of the occurrence of pharmaceuticals in wastewater is high, as demonstrated by this study, as well as many others, from Slovenia (Česen et al., 2018), India (Praveenkumarreddy et al., 2021), South Africa (Mhuka et al., 2020), etc.

One of the potential weaknesses of assessing CECs using the GWF may be the cross-interactions of individual substances. Discharged wastewater is a mixture of substances and the GWF assesses them separately. The GWF calculation is based on PNEC values, which represent, from an ecotoxicological point of view, concentrations without toxic effects of the given substance, determined with a certain probability. However, in ecotoxicology, the effects of various mixtures of these substances and the determination of their PNEC are discussed in the form of various model approaches (Coors et al., 2018; Ginebreda et al., 2014).

The conclusions of this study can be applied to the Central European region, as according to Hrkal et al. (2023), the homogeneity of PPCP detected in Central European waters testifies both to a similar level of medical care and the health status of the population, as well as to similar consumption habits and lifestyles.

Author Contributions

Conceptualization L.A.; methodology L.A. and P.S.; validation L.S. and P.S.; data curation L.A. and L.S.; writing—original draft preparation L.A.; writing—review and editing L.A., L.S., and P.S.; funding acquisition L.S.

All authors have read and agreed to the published version of the manuscript.

Data Availability Statement

All data needed to replicate the study are included in this article. Source data for Tables 2 and 3 are published as Supplement Data to the article by Česen et al. (2019).

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