Monitoring organic micropollutants in stormwater runoff with the method of fingerprinting

Langeveld, Jeroen G.; Post, Johan; Makris, Konstantinos F.; Palsma, Bert; Kuiper, Melanie; Liefting, Erik

DOI
10.1016/j.watres.2023.119883

Publication date
2023

Document Version
Final published version

Published in
Water Research

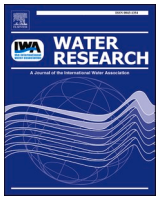
Citation (APA)
Langeveld, J. G., Post, J., Makris, K. F., Palsma, B., Kuiper, M., & Liefting, E. (2023). Monitoring organic micropollutants in stormwater runoff with the method of fingerprinting. *Water Research*, *235*, Article 119883. https://doi.org/10.1016/j.watres.2023.119883

Water Research 235 (2023) 119883

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres



Monitoring organic micropollutants in stormwater runoff with the method of fingerprinting

Jeroen G. Langeveld [a,b], Johan Post [a], Konstantinos F. Makris [a,b,*], Bert Palsma [d], Melanie Kuiper [c], Erik Liefting [a]

[a] Partners4UrbanWater, Nijmegen, the Netherlands
[b] Department of Watermanagement, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, the Netherlands
[c] Waterschap Drents Overijsselse Delta, Dokter van Deenweg 186, Zwolle 8025 BM, the Netherlands
[d] Stichting Toegepast Onderzoek Waterbeheer (Stowa), Postbus 2180, Amersfoort 3800 CD, the Netherlands

ARTICLE INFO

Original content: Concentration of micropollutants during wet weather flow in the influent of 5 WWTPs in The Netherlands (Original data).

Keywords:
Pesticides
Priority substance
Stormwater
Micropollutants

ABSTRACT

The ecological state of receiving water bodies can be significantly influenced by organic micropollutants that are emitted via stormwater runoff. Reported efforts to quantify the emission of micropollutants mainly focus on sampling at combined sewer overflows and storm sewer outfalls, which can be challenging. An alternative method, called fingerprinting, was developed and tested in this study. The fingerprinting method utilizes wastewater treatment plant (WWTP) influent samples and derives the proportion of stormwater in a sample. This is achieved by comparing the wet weather vs dry weather concentrations of substances-tracers which are present only in wastewater. It is then possible to estimate the concentration of organic micropollutants in stormwater runoff from measurements in the influent of a WWTP based on a mass balance. In this research, the fingerprinting method was applied in influent samples obtained in five WWTPs in the Netherlands. In total, 28 DWF and 22 WWF samples were used. The chosen tracers were ibuprofen, 2-hydroxyibuprofen, naproxen and diclofenac. Subsequently, the concentration in stormwater runoff of 403 organic micropollutants was estimated via the WWF samples. The substances that were present and analyzed included glyphosate and AMPA, 24 out of 254 pesticides, 6 out of 28 organochlorine pesticides, 45 out of 63 pharmaceuticals, 15 out of 15 PAHs, 2 of the 7 PCBs, and 20 of 33 other substances (e.g. bisphenol-A). A comparison with findings from other studies suggested that the fingerprinting method yields trustworthy results. It was also noted that a representative and stable dry weather flow reference concentration is a strict requirement for the successful application of the proposed method.

1. Introduction

The ecological quality of receiving water bodies can be negatively affected by organic micropollutants, such as pharmaceuticals, pesticides and biocides (Beckers et al., 2018), as urban wet weather discharges (UWWDs) are one of the main emission pathways (Becouze et al., 2016). UWWDs comprise discharges via the wastewater treatment plant (WWTP) effluent, storm sewer outfalls (SSOs) and combined sewer overflows (CSOs). Hence, the relative contribution of emissions via SSOs, CSOs and WWTPs differs per substance and depends on the removal efficiency at the WWTP, the origin of the substance (wastewater or stormwater) and the characteristics of the sewer systems (e.g. combined or separated) (Launay et al., 2013). The Water Framework Directive (2000/60/EC) and subsequent Directives/Decisions (2008/105/EC, 2013/39/EC) enforce the EU countries to improve and protect the aquatic ecology by explicitly referring to specific groups of pollutants and their maximum allowable concentration. Additionally, a new proposal (2022/0345) was published lately by the European Commission for an update of the "Urban Wastewater Directive" (91/271/EEC), focusing among others on new micropollutants that can be harmful even at very low concentrations and new limit values for micropollutants that require additional treatment. Consequently, exploration of the sources and concentrations of organic micropollutants in SSOs and CSOs should receive significant attention. However, only sparse relative literature is found, probably due to the high sampling and analysis costs.

* Corresponding author at: Partners4UrbanWater, Nijmegen, the Netherlands.
E-mail address: kostas.makris@urbanwater.nl (K.F. Makris).

https://doi.org/10.1016/j.watres.2023.119883
Received 19 December 2022; Received in revised form 1 March 2023; Accepted 13 March 2023
Available online 20 March 2023

Monitoring projects aiming at detecting the occurrence of specific micropollutants at UWWDs have taken place in France (Zgheib et al., 2010; Granger et al., 2016), Germany (Launay et al., 2016; Wicke et al., 2016, 2021), Switzerland (Burkhardt et al., 2007; Wittmer et al., 2010), Denmark (Birch et al., 2011; Bollmann et al., 2014),Sweden (Bendz et al., 2005) and the United States (Burant et al., 2018; Masoner et al., 2019). Results revealed that stormwater can contain a wide range of organic micropollutants and it can be a more dominant source of emission than WWTPs for certain substances. However, the main pollutants may differ per country. For example, in Denmark the pollutant terbutryn (paint on exterior of buildings) is found (Bollmann et al., 2019), whereas in Germany the pollutant carbendazim (fungicide in paint on exterior of buildings) is abundant (Wicke et al., 2016). Consequently, there is a need to monitor organic micropollutants in stormwater also in other countries in order to establish effective protection measures.

The established way to obtain the necessary information on emission routes of micropollutants is to perform measurements at combined sewer overflows and stormwater outfalls (e.g. Birch et al., 2011; Gasperi et al., 2012; Launey et al., 2016; Beckers et al., 2018). However, many organic micropollutants are used infrequently. This implies that the catchment discharging to the CSO/SSO should be reasonably large in order to have a fair chance of capturing the pollutants from individual discharges. Monitoring CSOs has another drawback, as the CSO frequency can be very low, resulting in very long monitoring periods before any statistically significant results are obtained. These challenges can have an enormous impact on the monitoring programs of countries that share such characteristics. For instance, in the Netherlands, most of the SSOs only serve a small subcatchment of 1 ha on average due to the small gradients of the ground surfaces, while the spilling frequency of CSOs is approximately 4 times per year.

To overcome the mentioned difficulties of sampling during SSO or CSO events, an alternative approach, called fingerprinting, has been developed, which allows for the use only of WWTP influent. Performing measurements at a WWTP is advantageous as the necessary sampling equipment is standard available. The fingerprinting method was inspired by the findings of Launay et al. (2016) who demonstrated that the proportion of stormwater in a sample taken at a CSO can be determined by calculating the dilution rate based on specific substances. Hence, the fingerprinting method is based on certain tracers which are found only in wastewater and can be used to estimate the concentration of compounds in stormwater runoff via a mass balance. The method was deployed at five WWTPs in the Netherlands, aiming at the analysis of a large number (403) of micropollutants. The combination of such an extensive analysis with the demonstration of the fingerprinting method is expected to provide the knowledge and the tools for the quantification of micropollutants in stormwater runoff in a cost-efficient and technically feasible way.

2. Materials and methods

2.1. Sampling locations

The samples were collected at the influent of 5 different WWTPs in The Netherlands. The WWTPs are located in relatively rural areas. Each WWTP processes the wastewater that is drained by a combination of combined, separated and improved separated (the first flush is directed towards the WWTP) sewer systems. The main characteristics of the WWTPs, sewer systems and catchments are given in Table 1.

2.2. Sampling procedure and chemical analysis

The first step of this study was to select the appropriate tracers that can be used in order to determine the proportion of stormwater in a sample taken at the influent of a WWTP during a rain event. A substance has to meet certain requirements so as to qualify as a tracer. In terms of physicochemical properties, it should be inert and demonstrate no adsorption to organic matter. In terms of operational characteristics, it should have a temporally constant load (no weekly profile), be used by a large proportion of population, have no occurrence in runoff and be detected during both dry weather flow (DWF) and wet weather flow (WWF) in concentration levels that exceed the level of quantification (LOQ). Ibuprofen and its breakdown product 2-hydroxyibuprofen, diclofenac, and naproxen are considered to meet all the mentioned requirements according to the findings of Launay et al. (2016). The concentrations of all the analyzed substances during DWF, including the selected tracers, had already been measured during a preceding DWF monitoring campaign, see Schuman et al. (2019). For each WWTP, five to six DWF samples of the influent were available on the basis of 48 h flow proportional sampling with an autosampler, leading to a total of 28 DWF samples.

Concerning the WWF samples, a protocol was developed in order to ensure that the analysis is performed on samples with a sufficient mixture of wastewater and stormwater. Sampling was scheduled based on weather forecasts (one day in advance) that predicted high chances of rainfall that would lead to significant runoff. Analysis followed a two-step procedure. First, an analysis was based on BOD, COD, nitrogen (ammonia and ammonium), phosphorous and suspended solids. If the results provided sufficient evidence of significant dilution (i.e. high proportion of rain in the WWF sample), the (expensive) second step was conducted to analyze the concentration of organic compounds. 24 h flow proportional samples were taken via an autosampler at the WWTPs during storm events in the summer of 2018 (May-September) and 2019 (June). The specific sampling periods were selected in order to gain insight into the contribution of pesticides. Two additional WWF samples were taken during events in the winter of 2018/2019 to serve as control measurements for a period where pesticides are likely absent in the runoff. In total, 35 WWF samples were collected. Nonetheless, only 22 samples were finally used in the analysis, mainly due to inconsistent primary results. Further details are given in Section 3.2.

The complete analysis package for approved samples consisted of 403 substances including: glyphosate/ amino methyl phosphonic acid (AMPA)/ glyfosinate, 254 pesticides, 28 organochlorine pesticides, 7 polychlorinated biphenyls (PCBs), 15 polycyclic aromatic hydrocarbons (PAHs), 33 other substances (e.g. bisphenol-A and triclosan), and 63

Table 1
Characteristics of measurement locations.

Location	Design capacity	System characteristics	Catchment characteristics
Raalte	2.500 m^3/h (81.270 p. e.[a])	228 ha CSS[b], 54 ha improved SS[c], and 13,5 ha SS[c]	DWF[d] 688 m^3/h (390 m^3/h domestic, 26 m^3/h recreational and 273 m^3/h industrial wastewater)
Heino	670 m^3/h (11.250 p.e.)	54 ha CSS, and 20 ha improved SS	DWF 125 m^3/h (96 m^3/h domestic, 19 m^3/h recreational and 10 m^3/h industrial wastewater)
Steenwijk	2.400 m^3/h (60.000 p.e.)	161 ha CSS, and 125 ha improved SS	DWF 851 m^3/h (501 m^3/h domestic, 87 m^3/h recreational and 263 m^3/h industrial wastewater)
Echten	4.553 m^3/h (186.200 p. e.)	462 ha CSS, 62 ha improved SS, and 181 ha SS.	DWF 1630 m^3/h (964 m^3/h domestic, 121 m^3/h recreational and 545 m^3/h industrial wastewater)
Beilen	2004 m^3/h (123.000 p. e.)	141 ha CSS, and 33 ha improved SS	DWF 750 m^3/h (297 m^3/h domestic, 103 m^3/h recreational and 350 m^3/h industrial wastewater)

[a] p.e.: population equivalent
[b] CSS: combined sewer system
[c] SS: separate system (only foul water is transported to the WWTP; improved SS: also first flush)
[d] DWF: dry weather flow

pharmaceuticals. An additional package of 32 heavy metals was analyzed in order to only test the efficiency of the method also to inorganic substances. Therefore, the effect of heavy metals on water quality is not discussed. An overview of the applied analysis per substance is given in the Supplementary Material.

2.3. Estimation of the concentration of micropollutants in stormwater

2.3.1. The Kaplan-Meier method

Following the chemical analysis, the data analysis had two objectives: (i) determining the number of observations above the LOQ, which provided insight into the presence of substances, and (ii) determining the mean concentration per substance for the obtained samples. The latter involves the challenges when chemical analysis yields concentrations lower than the LOQ and that the LOQ may vary depending on the different techniques/patents applied to make the estimation feasible (e.g. dilution of the sample). This implies that common handling methods, such as substituting values below LOQ with zero (Stein et al., 2006), are not applicable. In this study, an alternative method was utilized; the Kaplan-Meier method (Kaplan and Meier, 1958). This method was originally developed for the analysis of survival rates as a function of time ("survival functions"), but has also proven useful to compute summary statistics when some observations are below the LOQ (Helsel, 2010). The advantages of using the Kaplan-Meier method are that the underlying distribution function of concentrations does not need to be known and that it considers all measured concentrations (i.e. both above and below the LOQ). The only precondition for applying the Kaplan-Meier method is that at least two measured concentrations are above the LOQ.

The Kaplan-Meier method is applied in steps. Initially, the measured concentrations (c_i) of a substance are sorted from higher to lower, including values < LOQ. The following statistical term is then defined for every concentration:

$$F = 1 - \frac{d}{n} \tag{1}$$

where d is the number of times a unique concentration has been measured above LOQ, and n is the number of times a substance has been measured with this unique or lower concentration.

Subsequently, the cumulative distribution function (CDF) is estimated for every unique concentration based on the following equation:

$$CDF_i = CDF_{i-1}\ F_{i-1}, \text{fori} > 1 \tag{2}$$

and $CDF_i = 1$, for i=1.

The mean concentration of a substance x, adjusted for observations below LOQ, is given by the area under the curve of the CDF with respect to unique concentrations. This relation is given in the following formula:

$$c_x = \sum_{i=1}^{N} c_i\ (CDF_i - CDF_{i+1}) \tag{3}$$

where N is the number of unique concentrations.

2.3.2. The fingerprinting method

The fingerprinting method was applied in two steps: (i) finding the proportion of stormwater in each sample, (ii) using a mass balance to estimate the concentration of every targeted substance in stormwater.

The proportion of stormwater per tracer (p_{rain}) was calculated in each sample for every WWF event at each WWTP, based on the degree of dilution of each tracer:

$$p_{rain} = 1 - \frac{c_{t,WWF}}{\overline{c}_{t,DWF}} \tag{4}$$

where $c_{t,WWF}$ is the concentration of every tracer in each WWF sample, and $\overline{c}_{t,DWF}$ is the mean concentration of every tracer in the DWF samples estimated via the Kaplan Meier method.

For the second part of the method, the proportion of rain per WWF sample was considered to be the mean of the p_{rain} values, averaged over the four used tracers in order to compensate for any random variability of the DWF background reference ($\overline{c}_{t,DWF}$) of each tracer.

The concentration per substance in stormwater ($c_{x,stormwater}$) was then estimated in each WWF sample on the basis of a mass balance:

$$c_{x,stormwater} = \frac{c_{x,\ WWF} - (1 - \overline{p}_{rain})\ \overline{c}_{x,DWF}}{\overline{p}_{rain}} \tag{5}$$

where $c_{x,\ WWF}$ is the concentration of substance x in the considered sample, $\overline{p}_{rain}$ is the proportion of rain in each WWF sample (Eq. (4)) averaged over the selected tracers, and $\overline{c}_{x,DWF}$ is the mean concentration of substance x in DWF estimated via the Kaplan Meier method.

Eventually, the concentration of a substance in stormwater was estimated by applying the Kaplan-Meier method on the determined $c_{x,stormwater}$ values per substance.

3. Results

3.1. Reference concentrations of the fingerprints

Table 2 shows results regarding the DWF samples, including the basic parameters and the mean concentrations of the selected tracers. The characterization of wastewater proved indeed to be more sensitive to the tracers than the basic parameters, since the deviations between the drug concentrations of the WWTPs are clearer. The concentrations of drugs were highest at the WWTP of Heino, which is the WWTP with the relatively largest share of domestic wastewater (77%).

The measured values of the tracers are normalized according to the ibuprofen concentration (Table 2, in parenthesis), in order to track the relative contribution of the tracers in the wastewater received by every WWTP. The results revealed that the ratio between the various pharmaceuticals does not differ much per WWTP. Comparing with respective ratios from German measurements (Launay et al., 2016), the ratios of the current study prove to be very different. An obvious explanation is the different policy of prescribing painkillers between the Netherlands and Germany.

3.2. Estimated proportion of stormwater

Fig. 1 shows the results of the estimated proportion of stormwater for the WWTP of Raalte after implementation of Eq. (5) and considering the measured background concentrations of the tracers (Table 2). The degree of dilution proved to be very consistent for the majority of the rain events, which means that the proportion of stormwater can be determined with great certainty. In the event of the 9th of August, the variability is higher mainly due to a relatively lower value of diclofenac, but the proportion of stormwater can still be determined within a reasonable margin. Further, it is clear that no real share of stormwater can be determined during the storm on the 6th of September. This was already apparent based on the results of the standard parameters and the laboratory was informed not to perform the full analysis on organic micropollutants. However, due to internal communication issues the samples have been analyzed in full. Additional analysis showed that on that date the predicted precipitation had hardly fallen and the sample therefore simply contained hardly any stormwater. The observed variation on that date can be attributed to the variability in the mean DWF concentration of the tracers. Similar results were found in measurements at all WWTPs on the 6th of September. Results for the rest of the WWTPs are presented in Tables S1–S5 (Supplementary Material).

In total, 33 samples were fully analyzed. The results of fingerprinting proved inconsistent for eight samples due to low precipitation on the 31st May and 6th September. Additionally, a minimum threshold (25%) for the calculated proportion of stormwater was maintained as the

Table 2
Mean values of measured parameters in DWF samples. The normalized ratio between the concentration of the used tracers with respect to the concentration of ibuprofen is given in parenthesis.

Parameter	Location of WTTP					Germany (Launay, et al., 2016)
	Raalte (n=5)	Heino (n=6)	Steenwijk (n=6)	Echten (n=6)	Beilen (n=5)	
General parameters (mg/L)						
COD	872	958	945	688	790	
Ammonia & Ammonium	84	97	87	63	68	
Phosphorous	11	13	11	14	11	
TSS (total suspended solids)	298	353	353	356	364	
Drugs used as tracers for fingerprinting – Mean DWF concentration (µg/L)						
Ibuprofen	8.0 (1)	11.2 (1)	9.6 (1)	4.8 (1)	3.7 (1)	8.6 (1)
2-hydroxyibuprofen	12.9 (1.61)	18.6 (1.66)	17.5 (1.82)	7.8 (1.63)	5.6 (1.51)	-
Diclofenac	0.5 (0.06)	0.5 (0.05)	0.6 (0.06)	0.3 (0.06)	0.3 (0.08)	1.7 (0.20)
Naproxen	5.9 (0.74)	5.6 (0.50)	7.7 (0.80)	3.7 (0.77)	3.5 (0.95)	1 (0.12)

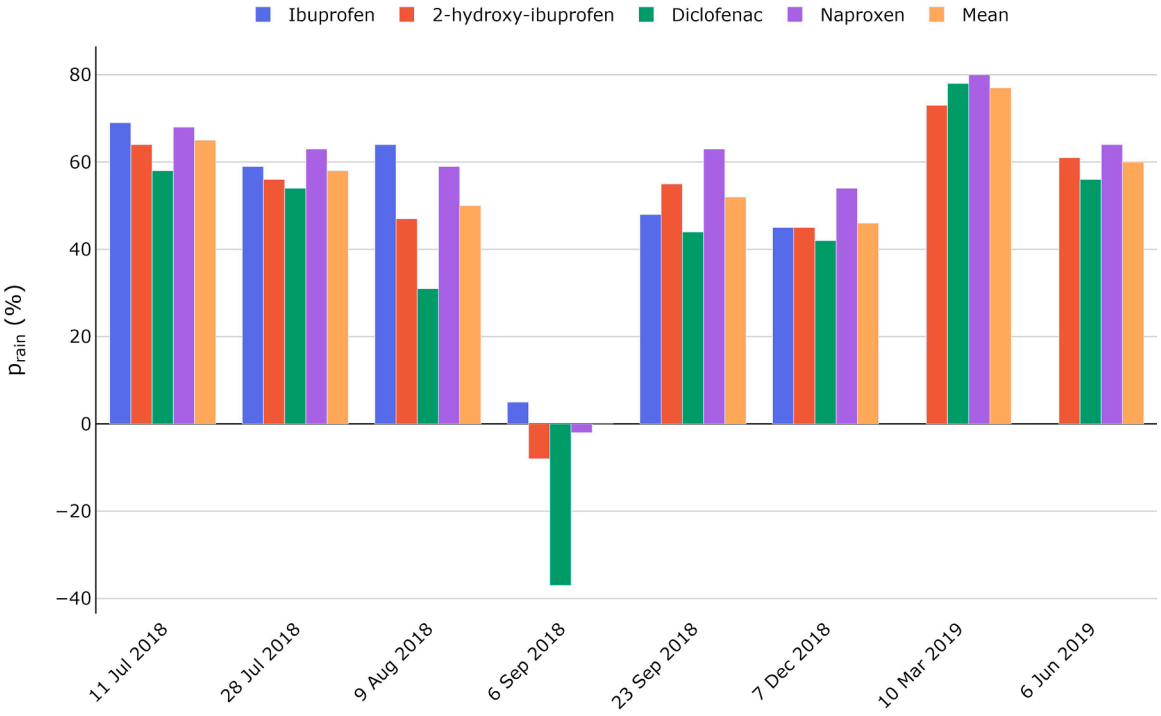


Fig. 1. Estimated proportion of stormwater (p_{rain}) per rain event at WWTP of Raalte based on the selected tracers.

uncertainty of estimated concentrations increases rapidly for lower values (see Eq. (S1) in Supplementary Material). This roughly corresponded to storm events with less than 0.5 mm per day precipitation (Fig. S1(a)–(g) in Supplementary Material). Consequently, three more samples were discarded, resulting in 22 useful WWF samples. Table 3 gives an overview of the storm events that were sampled, indicating the events that were discarded and events that were used for further application of the fingerprinting method.

3.3. *Detected micropollutants and their estimated concentration in stormwater*

An analysis was initially performed to identify the present micropollutants based on the available samples (28 DWF and 22 WWF). The number of substances found in any of the WWF samples were: Glyphosate/AMPA from the set of Glyphosate/AMPA/Glyphosate, 24 out of 254 pesticides, 6 out of 28 organochlorine pesticides, 45 out of 63 pharmaceuticals, 15 out of 15 PAHs, 2 of the 7 PCBs, and 20 of the 33 other substances. Fig. 2 gives the detection frequency of selected substances that were found per substance group. Tables S6–S12 in Supplementary Material provide an overview of the detection frequency of all substances found in both DWF and WWF samples.

Furthermore, the concentrations of micropollutants in stormwater runoff have been calculated using the fingerprinting method, as described in Section 2.3.2. By considering the estimated proportion of stormwater in each sample based on the mean concentrations of the tracers (Tables S1–S5) and applying Eq. (5), the concentration of each analyzed substance in stormwater runoff was estimated. For substances that also occur in DWF, it was noted that Eq. (5) yields a negative concentration in stormwater runoff if the concentration in the sample is higher than in the DWF. This issue occurs partly because the DWF concentration for such substances is not constant, and partly because some substances, including X-ray contrast agents, exist only incidentally in high concentrations in samples taken during a storm event. In this study, if a negative concentration was calculated, it was replaced by zero. For substances with concentrations lower than the LOQ, the Kaplan-Meier method was used for the estimation of the mean concentration. Fig. 3 presents the mean concentrations of several organic micropollutants in both DWF and stormwater runoff. Tables S6–S12 show the mean concentrations for all detected substances along with their respective LOQ values.

3.3.1. *Glyphosate / AMPA*

Glyphosate, a herbicide, was found in 12 WWF samples, of which 11

Table 3
Overview of sampled storm events for every WWTP.

Storm events	Beilen	Echten	Heino	Raalte	Steenwijk
Discarded due to basic parameters	31-5-2018			31-5-2018	
Discarded due to low p_{rain} (<25%)	7-12-2018	28-7-2018 23-9-2018			
Discarded due to inconsistent p_{rain} (<0%)	6-9-2018 23-9-2018 6-6-2019	31-5-2018 6-9-2018		6-9-2018	31-5-2018 6-9-2018
Used for further analysis	10-3-2019	23-7-2018 7-12-2018 10-3-2019 6-6-2019	28-7-2018 9-8-2018 7-12-2018 10-3-2019 6-6-2019	11-7-2018 28-7-2018 9-8-2018 23-9-2018 7-12-2018 10-3-2019 6-6-2019	9-8-2018 23-9-2018 7-12-2018 10-3-2019 6-6-2019

were taken in the summer, and in 3 DWF samples (Table S6). AMPA, a degradation product of glyphosate, was traced in 8 WWF samples (6 in summer) and 3 times in DWF samples. This trend corresponds well with the use of glyphosate, since herbicides are used during the growing season to control weeds on paved surfaces. Fig. 3 presents the estimated concentrations of glyphosate and AMPA via the fingerprinting method. The estimated concentration of glyphosate in stormwater was 4.7 µg/L, almost twice the mean concentration found in the DWF samples. This implies that stormwater runoff is an important emission route for glyphosate. Concentrations of the same order of magnitude have been found in another study in the Netherlands (Withagen et al., 2004), as well as in studies in Belgium (Tang et al., 2015), France (Botta et al., 2009), Switzerland (Hanke et al., 2010) and the UK (Ramwell et al., 2014). Although the DWF concentration of AMPA was similar to that of glyphosate, the estimated stormwater concentration was 0.49 µg/L. Similar patterns were also observed in Botta et al. (2009), Ramwell et al. (2014). A possible reason could be that the conditions in the urban environment do not favor the degradation to AMPA, therefore the lower concentration is the result of dilution due to stormwater.

3.3.2. *Pesticides*

The most commonly encountered pesticides were found in both DWF and WWF samples (Fig. 2). Such substances are fipronil (insecticide/biocide against fleas, mites and ticks), phthalimide (component of fungicides), DEET (insect repellent) and permethrin (insecticide against mosquitoes, ticks and woodworm). This means that many of these substances are at least partly released via the wastewater emission route. 14 of the analyzed substances seem to be released only via the stormwater route and only at the beginning of the growing season (May/June), including diuron (pesticide against weed), and desethylterbutylazine (herbicide in agriculture). This pattern corresponds to agricultural use and agrees with international literature (Launay et al., 2016; Wittmer et al., 2010), which shows that agricultural pesticides are discharged via stormwater sewers. Some substances, such as fipronil, are found in both summer and winter, while others (e.g. Permethrin), are

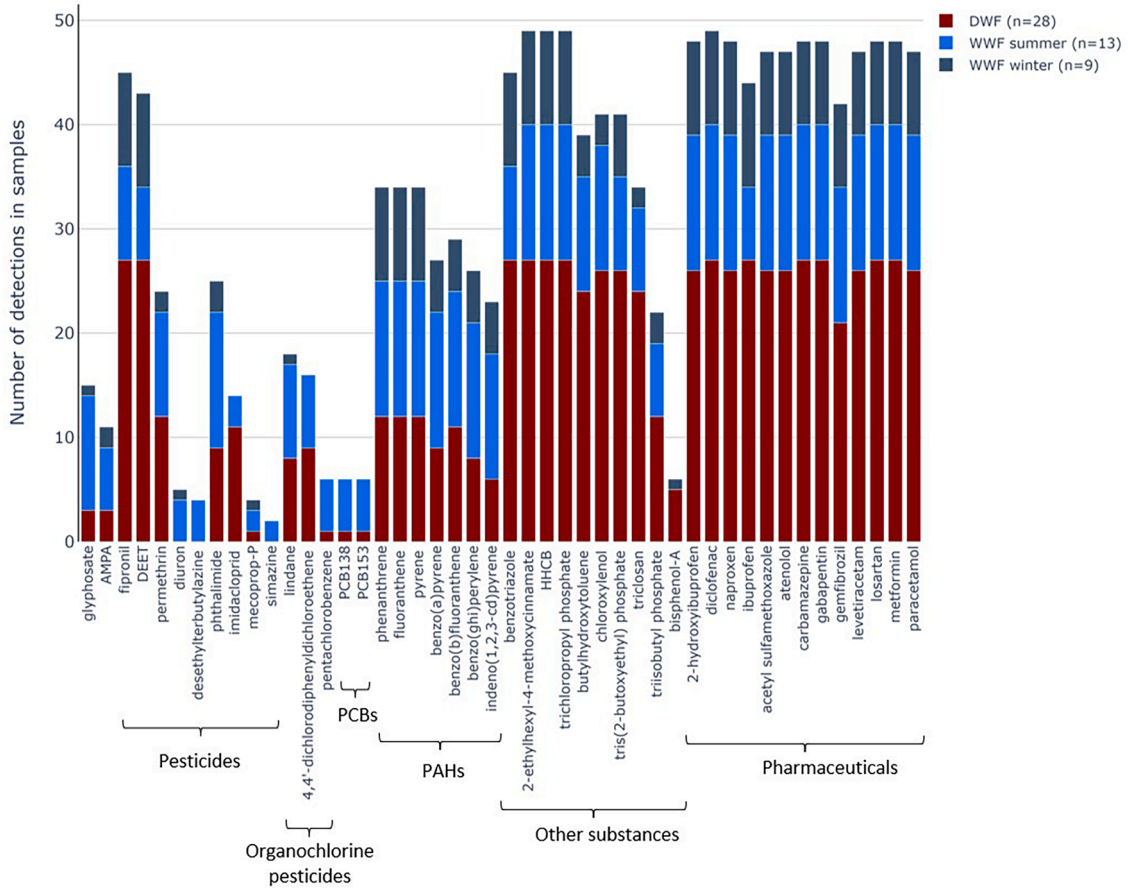


Fig. 2. Number of samples with detected organic micropollutants during DWF and WWF. The whole dataset is given in Tables S6–S12.

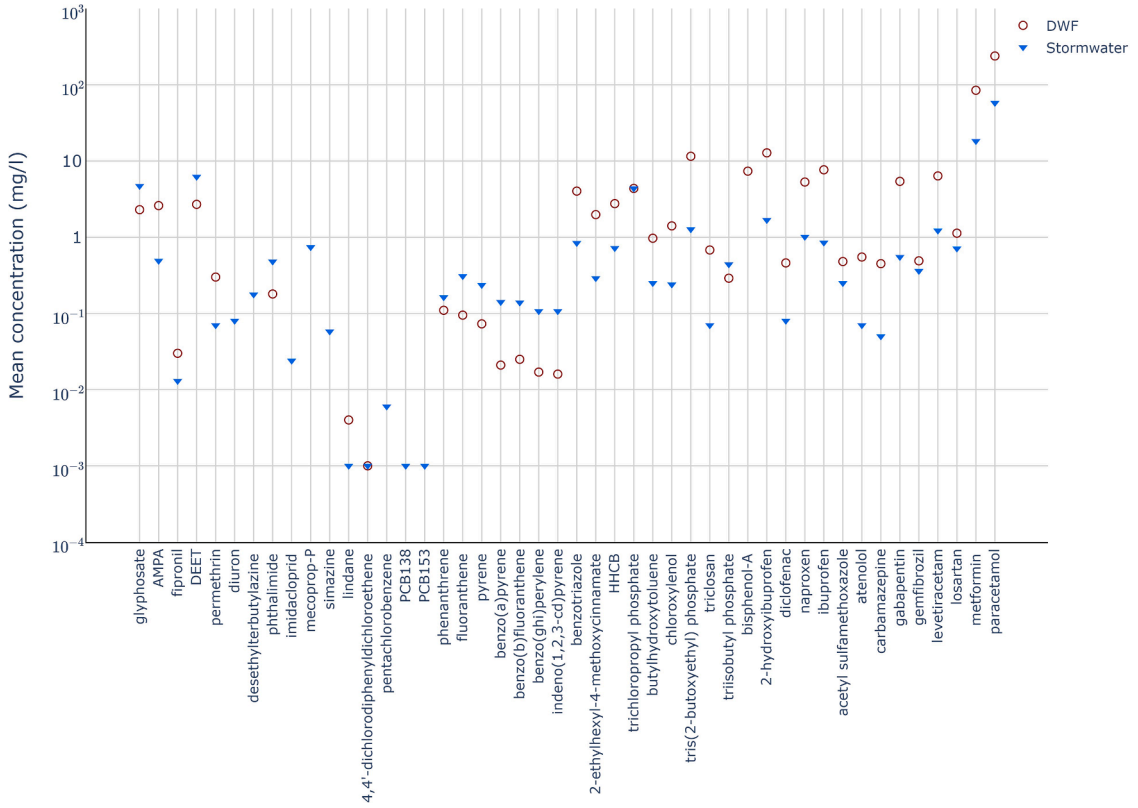


Fig. 3. Mean concentrations of detected organic micropollutants in DWF and stormwater runoff. The whole dataset is given in Tables S6–S12.

mainly found in summer.

Fig. 3 provides an overview of the estimated concentrations for the pesticides found. DEET is the pesticide with a higher concentration in stormwater (6.2 µg/L), implying that the stormwater pathway should receive more attention for this substance. Fipronil and permethrin were found predominantly in DWF. Since the partition coefficient ($\log K_{ow}$) is quite high for both substances (4.0 and 4.67 respectively), it is quite possible that the calculated concentration in stormwater is caused by the contribution of the sediment and biofilm in the sewer. It should be stressed that micropollutants which adsorb to organic material in the sewer may be released during a storm event (Hajj-Mohamad et al., 2014). The contribution of organic material from the combined sewer that is released during a storm can vary in a range between 20% and 80% (Schilperoort et al., 2012). Since this share cannot be determined retrospectively, the results indicate the substances for which the sewer may have had an influence via the so-called 'in-sewer stocks'.

Further, phthalimide was found in both DWF and WWF samples, but in higher concentrations in stormwater (0.48 µg/L). Imidacloprid has only been detected in 3 WWF samples and on average occurs in low concentrations. Mecoprop-P (root repellent in roofing material) has only been measured a few times, but the estimated stormwater concentration (0.74 µg/L) is well above the LOQ (0.25 µg/L). Simazine, a priority substance, was also estimated at a concentration (0.07 µg/L) well above the LOQ (0.04 µg/L).

3.3.3. Organochlorine pesticides

Six organochlorine pesticides were found out of the 28 examined. The most detected substance in the WWF samples was Lindane, which used to be a widely used pesticide in agriculture but currently is used in products against scabies and head lice. Lindane and 4,4′-dichlorodiphenyldichloroethene (degradation product of insecticides) were found at similar rates in both DWF and WWF. Other substances, such as pentachlorobenzene (fire retardant) and Hexachlorobenzene (fungicide), were only found in WWF samples taken during summer. Table S8 gives a detailed overview of the detected organochlorine pesticides. Three of these were found only once or twice, which is insufficient to calculate an average concentration. Therefore, Fig. 3 contains the calculated concentrations for only three substances.

Lindane was found in high concentrations in DWF (0.004 µg/L) and at significantly lower concentrations in stormwater (0.001 µg/L). Stormwater runoff is clearly not an emission route of Lindane. Based on a $\log K_{OW}$ of 3.8, the concentration in the WWF samples could be influenced by the sewer stocks. This could also be the result of variation in the background concentration in DWF.

3.3.4. Polychlorinated biphenyls (PCBs)

Two of the 7 PCBs examined, PCB138 and PCB153, were regularly found in WWF samples and only during summer. These were found only once in DWF samples (Fig. 2). The detected PCBs have been used in the past as an insulating agent, and currently are used as coolants and hydraulic fluid. Table S9 indicates that the estimated stormwater concentrations are in the order of magnitude of the LOQ (0.001 µg/L). It is likely that both substances have been released after historical use. Zgheib et al. (2012) and Wicke et al. (2021) found all seven of the investigated PCBs in their WWF samples in France and Germany, respectively, while PCB 138 and PCB 153 were the most found PCBs. Additionally, the mean estimated concentration in Zgheib et al. (2012) was considerable higher for both congeners (0.048 µg/L).

3.3.5. Polycyclic aromatic hydrocarbons (PAHs)

PAHs have been detected in all WWF samples over the year and also in most of the DWF samples. PAHs are mainly released during the combustion of organic material and fossil fuels and are therefore ubiquitous in the environment. The presence of PAHs in WWF and DWF samples is therefore in line with expectations. Phenanthrene, fluoranthene and pyrene are hydrocarbons that were found in all analyzed samples (Fig. 2). The estimated concentrations via the fingerprinting method are within the ranges found in other studies (Göbel et al., 2007;

Birch et al., 2011).

3.3.6. Other substances

Most of the samples included other substances, such as two variants of benzotriazole (pharmaceutical and cleaning agent), 2-ethylhexyl-4-methoxycinnamate (UV filter cosmetics), HHCB (fragrance) and trichloropropyl phosphate (flame retardant). Other substances were found mainly in DWF samples but with occurrence also in the WWF samples, such as butylhydroxytoluene (antioxidant), chloroxylenol (bactericidal and fungicidal agent), tris(2-butoxyethyl) phosphate (plasticizer with flame retardant properties), triclosan (cosmetic products, antibacterial and antifungal agent) and triisobutyl phosphate (plasticizer and solvent). The industrial chemical Bisphenol-A (used in food packaging and thermal paper) has been detected a limited number of times, mostly in DWF samples (once in a winter WWF sample and five times in DWF samples).

After applying the fingerprinting method, the estimated concentrations in stormwater are for most of these substances lower than in the DWF samples, and are most likely affected by the variability in the DWF reference concentration ($\overline{c}_{t,DWF}$). The exceptions are the substances trichloropropyl phosphate and triisobutyl phosphate. The estimated stormwater concentration of these substances is at least at the same level with the average concentration in DWF, indicating that the route via stormwater runoff can be considered important. Given the expected use of the substances, e.g. flame retardants and plasticizers, it is probable that they are released via the stormwater route.

Bisphenol-A was found in the DWF samples at an average concentration of 7.37 μg/L, while it was found only once in the WWF samples. This corresponds well to another study in the Netherlands (Vethaak et al., 2002), in which bisphenol-A was found in 2 out of 5 stormwater sample at a concentration of 0.06 μg/L. Research in Germany (Wicke et al., 2016) shows comparable values (0.09 μg/L), while research in France (Gasperi et al., 2014) demonstrates an order of magnitude higher concentrations (0.6 μg/L). Comparing these values is challenging as a different LOQ is established depending on the lab method used. It is obvious, nonetheless, that DWF is the dominant source for this substance and that the contribution of stormwater runoff is minimal. Nonetheless, bisphenol-A was found in stormwater in the USA, yielding concentrations between 0.0019 and 0.158 μg/L (Boyd et al., 2004).

3.3.7. Pharmaceuticals

Several pharmaceutical substances have been found in many samples irrespectively of the type of influent (DWF/WWF) and season (summer/winter). 31 substances are present in at least 80% of the samples, which confirms that pharmaceuticals are ubiquitous in the influent of WWTPs. Some of the substances that were frequently detected are 2-hydroxyibuprofen, diclofenac, naproxen, acetyl sulfamethoxazole, atenolol, carbamazepine, gabapentin, gemfibrozil, levetiracetam, iosartan, metformin and paracetamol. The whole range of detected pharmaceuticals is presented in Table S12.

Table S12 also shows the high magnitudes of the estimated concentrations for iomeprol, ioxitalamic acid and iopromide. These substances are X-ray contrast media, which are known to be found in the influent occasionally. Their presence depends on the days on which such medical examinations are conducted in hospitals and on the coincidence that such patients live in the studied catchment area. Therefore, the DWF concentration for these substances is not stable, resulting in overestimated concentrations in the stormwater runoff. In the case of clarithromycin, lidocaine and candesartan, the estimated stormwater concentrations are similar to the DWF. Unstable DWF reference measurements seem to be again the obvious cause of such observed irregularities.

4. Discussion

4.1. Impact of detected substances on water quality

In this section, the emphasis lies on priority substances according to Directive 2008/105/EC. Table 4 shows the substances that were found to be above the annual average concentration (AA-EQS) or maximum acceptable concentration (MAC-EQS). Six out of seven substances in Table 4 belong to the PAHs group, indicating that restricting the amount of PAHs that are driven to receiving surface waters is essential for preserving high water quality. Especially Benzo(a)pyrene demonstrated a concentration also higher than the MAC-EQS limit. Pentachlorobenzene, an organochlorine pesticide, is a priority substance that was not released via DWF, but with a significant concentration in stormwater runoff, above the AA-EQS. Additionally, except for fluoranthene, all the substances in Table 4 are considered as hazardous substances (2013/39/EU). Anthracene, dieldrin, diuron, hexachlorobenzene, naphthalene and simazine are detected substances with concentrations lower than the respective EQS values, with anthracene and hexachlorobenzene also being marked as hazardous priority substances. Glyphosate and mecoprop demonstrated concentrations well above their LOQs, while they are defined as substances subject to review for possible identification as priority substances (2008/105/EC). Furthermore, the detected substances diclofenac, ciprofloxacin, oxadiazon and methiocarb are in the watch list of substances (2015/495/EU, 2018/840/EU).

It is evident that the number and type of present substances have an impact on the ecology and biodiversity of the receiving water bodies. In an effort to estimate the ecological risks of these substances, the open-access model of multi substance Potentially Affected Fraction (msPAF) was used (www.sleutelfactortoxiciteit.nl). The msPAF of species expresses the mixture toxic pressure calculated with a mixed model, using a sequence of concentration addition for substances with same Toxic Mode of Action (TMoA) and response additivity for substances with dissimilar TMoA. The model is explained in detail in de Zwart and Posthuma (2005). In the current study, the default chemical properties were used as given in de Zwart (2002). The msPAF for the present organic micropollutants in stormwater runoff was estimated to be 3.9%. According to the Dutch guidelines (Posthuma et al., 2016), this value implies that the detected substances demonstrate a toxic impact but at a limited extent. The substances with a determining effect on the outcome were benzo(ghi)perylene, permethrin, diazinon and benzo(b)fluoranthene. Nonetheless, further research is necessary to confirm whether the calculated concentration in stormwater runoff of permethrin, an insecticide, was an artefact of the fingerprinting method or whether this substance was actually released via stormwater.

4.2. Evaluation of the fingerprinting method

Performance assessment of the fingerprinting method is achieved via a comparison with results from other studies which include the analysis of several micropollutant groups at the outlet of storm sewer outfalls with conventional techniques (LC-MS, GC-MS). The comparison is depicted in Fig. 4. Irrespectively of the analyzed micropollutant group,

Table 4
Concentration (μg/L) of substances above the AA-EQS or MAC-EQS.

Substance	AA-EQS*	MAC-EQS*	Stormwater**
benzo(a)pyrene	0.05	0.1	0.141
benzo(b)fluoranthene	0.03	n/a	0.139
benzo(k)fluoranthene	0.03	n/a	0.072
benzo(ghi)perylene	0.002	n/a	0.107
indeno(1,2,3-cd)pyrene	0.002	n/a	0.107
fluoranthene	0.1	1	0.308
pentachlorobenzene	0.0007	n/a	0.006

* Values obtained from 2008/105/EC
** Values obtained via the fingerprinting method

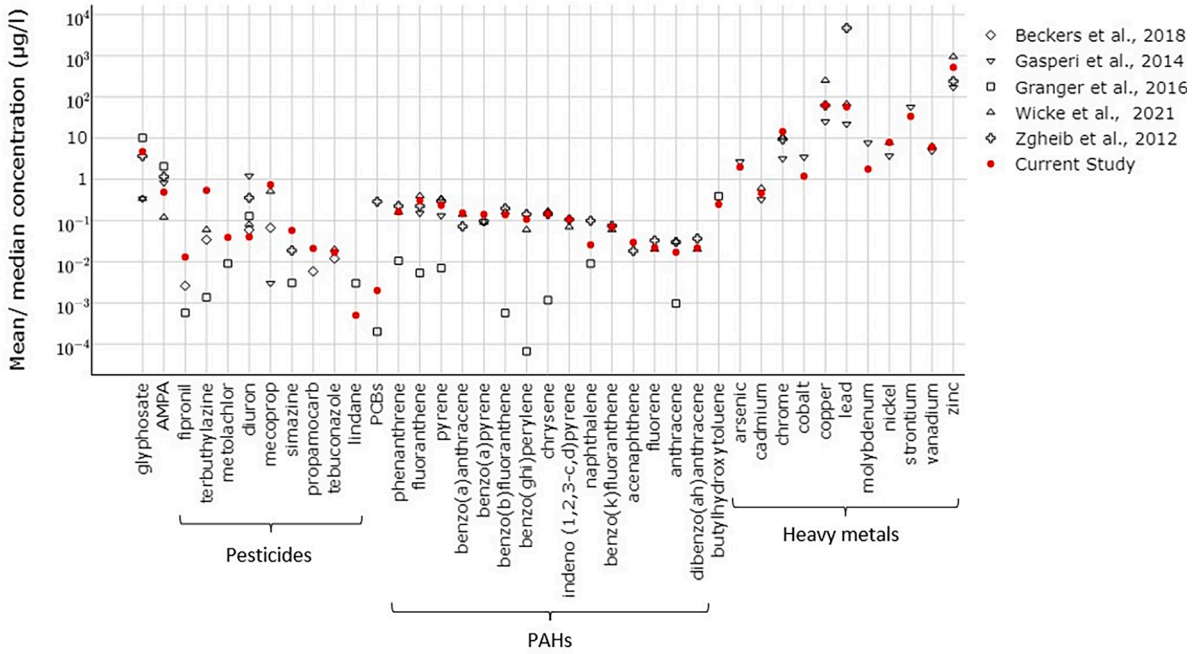


Fig. 4. Comparison between the results of the fingerprinting method (Current Study) and findings in the international literature.

the fingerprinting method yields results which are in line with the findings of other researchers. Especially in the case of PAHs group, which is of great interest for directives, fingerprinting seems to provide similar results. Promising results are also found by estimating the concentration of heavy metals in stormwater with the fingerprinting method, which are used here only as an additional comparison reference.

Furthermore, ibuprofen, diclofenac, 2-hydroibuprofen and naproxen were used as fingerprints to determine the proportion of stormwater in the WWF samples. These substances were chosen because they are not released via the stormwater route and do occur in high concentrations in the WWTP influent during both WWF and DWF. It would be expected that the estimated concentrations in stormwater of these substances would be negligible (ideally equal to zero). However, a noticeable deviation from zero was observed (Fig. 3). In order to explore the possible reasons for this deviation, the theoretical framework of the uncertainty analysis on the fingerprinting method is given in the Supplementary Material. Based on this analysis, two main sources of uncertainty are identified: (i) the measuring error of the applied analytical methods, and (ii) the standard deviation of the DWF reference. The second source is considered to be the major source of the overall uncertainty as it affects both the estimation of rain proportion in a sample and the stormwater concentration of the targeted substance. In particular, Eq. (S1) indicates that the uncertainty becomes considerably lower as the proportion of rain in the sample increases. Additionally, the variability in the DWF concentrations stems from the inconsistent or occasional use of substances. In this study, the practical application of the uncertainty analysis would require more measurements in order to estimate the individual uncertainties of the parameters. Repeated measurements of the same samples could reveal the measuring error per substance in the applied analytical methods. Weighted averaging, based on minimizing the uncertainty of the result, could then be used to further improve estimates. The analysis of additional DWF samples could also lead to a more consistent DWF reference, to which the fingerprinting method seems to be highly sensitive.

Moreover, the fingerprinting method is only dedicated to estimating the concentration of micropollutants in stormwater runoff. Since sampling occurs only at the influent of WWTPs, it is not possible to differentiate among specific emission routes (e.g. CSOs and SSOs), and the actual micropollutant load on the receiving water bodies may differ. During significant precipitation events, sewer overflows could be triggered in combined sewer systems, leading to the discharge of untreated sewage which contains micropollutants expected to be present only in the DWF (e.g. pharmaceuticals). Moreover, illicit connections and cross-flows are known issues in separate systems which constitute potential source for micropollutants emitted via stormwater outlets. Therefore, exploring the actual emission routes and pressure on the aquatic environment for a specific location due to overflows prior to the WWTP requires complementary sampling also at other sewer outlets. Furthermore, although the emission routes cannot be explored, the fingerprinting method remains robust for estimating the micropollutants' concentrations in stormwater even if the function of SSOs and CSOs leads to a substantial amount of storm and wastewater being discharged before the WWTP. This is achieved by taking into account the dilution rate in every sample, which is expressed via the proportion of rain in the sample (Eq. (5)). As a result, the considered mass balance can still quantify the concentration of substances, given that even a small fraction reaches the WWTP.

5. Conclusions

Analysis of 403 micropollutants in the influent of five wastewater treatment plants (WWTPs) revealed the concentrations in stormwater runoff of the detected substances based on a new method, called fingerprinting. The findings of this study show that the proposed fingerprinting method yields meaningful results in most cases which are in agreement with monitoring results from international literature, even with just 5 DWF (Dry Weather Flow) and 5–7 WWF (Wet Weather Flow) sampling days. It was possible to estimate the proportion of stormwater in the sample on the basis of the selected tracers: ibuprofen, its breakdown product 2-hydroxyibuprofen, naproxen and diclofenac. The fingerprinting method led to inconsistent results concerning rain events with a low proportion of stormwater in the samples ($< 25\%$), which is equivalent to a storm event with less than 0.5 mm per day. At such low proportions of stormwater, the errors in the estimation of the mean WWF concentrations became dominant. It was noticed that a representative and stable DWF background concentration is a strict requirement for the successful application of the fingerprinting method.

The chemical analysis offered an overview of the present organic micropollutants in stormwater runoff. All (15) examined polycyclic aromatic hydrocarbons (PAHs) were found. Of the 63 pharmaceuticals investigated, 45 were traced, while 24 of the 254 examined organic pesticides were found at least once. In addition, 6 of the 28 examined organochlorine pesticides and 2 of the 7 investigated polychlorinated biphenyl (PCBs) were detected.

Application of the fingerprinting method revealed substances with a significant concentration in stormwater runoff. The seasonal pattern of glyphosate was clear with abundance in stormwater. DEET was released via both wastewater and stormwater runoff in significant concentrations. Phthalimide was frequently found in stormwater well above the limit of quantification. Mecoprop was also found in high concentration in stormwater.

The other detected pesticides can be divided into 2 groups. The first group includes agricultural pesticides, such as the regularly encountered herbicides terbuthylazine, dimethenamid-P, chlorpropham and S-metolachlor, which were mainly found at the beginning of the growing season. In addition, there are about 20 substances that were found only once or a few times. The second group concerns insecticides such as imidacloprid, fipronil, permethrin and lindane, which were frequently found in DWF and not significantly in stormwater runoff.

PAHs were found in higher concentrations in stormwater runoff, while the concentrations for specific PAHs (benzo(a)pyrene, benzo(b) fluoranthene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene), and fluoranthene) were above the environmental quality requirements (AA-EQS/ MAC-EQS) for priority substances. Other examined substances (e.g. 1,2,3 benzotriazole) were frequently found, but only three of them (trichloropropyl phosphate, pentachlorobenzene, and triisobutyl phosphate) with significant concentration in stormwater.

In general, the concentrations of substances in stormwater vary, for instance among measured pesticides from agricultural use and pesticides related to construction materials typically found in different prevalence in different countries. Knowing the concentrations of micropollutants in stormwater is an important prerequisite when developing storm water policies. The fingerprinting method could be a useful tool in this effort, with significant advantages over sampling at stormwater outlets, where sampling is difficult and/or the catchment area is quite small. Nonetheless, sampling at such outlets is still required when the objective is a detailed mapping of the emission routes.

Declaration of Competing Interest

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

Acknowledgements

The authors would like to thank STOWA for the funding of this research, the Drent Overijsselse Delta Waterboard for their help with sampling at the WWTPs, and Aqualysis waterlaboratorium for the chemical analyses.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2023.119883.

References

Beckers, L.M., Busch, W., Krauss, M., Schulze, T., Brack, W., 2018. Characterization and risk assessment of seasonal and weather dynamics in organic pollutant mixtures from discharge of a separate sewer system. Water Res. 135, 122–133. https://doi.org/10.1016/j.watres.2018.02.002.

Becouze-Lareure, C., Dembélé, A., Coquery, M., Cren-Olivé, C., Barillon, B., Bertrand-Krajewski, J.L., 2016. Source characterisation and loads of metals and pesticides in urban wet weather discharges. Urban Water J. 13 (6), 600–617m. https://doi.org/10.1080/1573062X.2015.1011670.

Bendz, D., Paxéus, N.A., Ginn, T.R., Loge, F.J., 2005. Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Höje River in Sweden. J. Hazard. Mater. 122 (3), 195–204. https://doi.org/10.1016/j.jhazmat.2005.03.012.

Birch, H., Mikkelsen, P.S., Jensen, J.K., Lützhøft, H.C.H., 2011. Micropollutants in stormwater runoff and combined sewer overflow in the Copenhagen area, Denmark. Water Sci. Technol. 64 (2), 485–493. https://doi.org/10.2166/wst.2011.687.

Bollmann, U.E., Tang, C., Eriksson, E., Jönsson, K., Vollertsen, J., Bester, K., 2014. Biocides in urban wastewater treatment plant influent at dry and wet weather: concentrations, mass flows and possible sources. Water Res. 60, 64–74. https://doi.org/10.1016/j.watres.2014.04.014.

Bollmann, U.E., Simon, M., Vollertsen, J., Bester, K., 2019. Assessment of input of organic micropollutants and microplastics into the Baltic Sea by urban waters. Mar. Pollut. Bull. 148, 149–155. https://doi.org/10.1016/j.marpolbul.2019.07.014.

Botta, F., Lavison, G., Couturier, G., Alliot, F., Moreau-Guigon, E., Fauchon, N., Blanchoud, H., 2009. Transfer of glyphosate and its degradate AMPA to surface waters through urban sewerage systems. Chemosphere 77 (1), 133–139. https://doi.org/10.1016/j.chemosphere.2009.05.008.

Boyd, G.R., Palmeri, J.M., Zhang, S., Grimm, D.A., 2004. Pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) in stormwater canals and Bayou St. John in New Orleans, Louisiana, USA. Sci. Total Environ. 333 (1-3), 137–148. https://doi.org/10.1016/j.scitotenv.2004.03.018.

Burant, A., Selbig, W., Furlong, E.T., Higgins, C.P., 2018. Trace organic contaminants in urban runoff: associations with urban land-use. Environ. Pollut. 242, 2068–2077. https://doi.org/10.1016/j.envpol.2018.06.066.

Burkhardt, M., Kupper, T., Hean, S., Haag, R., Schmid, P., Kohler, M., Boller, M., 2007. Biocides used in building materials and their leaching behavior to sewer systems. Water Sci. Technol. 56 (12), 63–67. https://doi.org/10.2166/wst.2007.807.

De Zwart, D., 2002. Observed regularities in SSDs for aquatic species. In: Posthuma, L., Suter, G.W.I., Traas, T.P. (Eds.), Species Sensitivity Distributions in Ecotoxicology. CRC press.

De Zwart, D., Posthuma, L., 2005. Complex mixture toxicity for single and multiple species: proposed methodologies. Environ. Toxicol. Chem. An Int. J. 24 (10), 2665–2676. https://doi.org/10.1897/04-639R.1.

Gasperi, J., Zgheib, S., Cladière, M., Rocher, V., Moilleron, R., Chebbo, G., 2012. Priority pollutants in urban stormwater: part 2–case of combined sewers. Water Res. 46 (20), 6693–6703. https://doi.org/10.1016/j.watres.2011.09.041.

Gasperi, J., Sebastian, C., Ruban, V., Delamain, M., Percot, S., Wiest, L., Gromaire, M.C., 2014. Micropollutants in urban stormwater: occurrence, concentrations, and atmospheric contributions for a wide range of contaminants in three French catchments. Environ. Sci. Pollut. Res. 21 (8), 5267–5281. https://doi.org/10.1007/s11356-013-2396-0.

Granger, D., Capdeville, M.J., Dumora, C., Dufour, V., Polard, T., Gonthier, A., Budzinski, H., 2016. Micropollutants reduction strategy at the scale of an urban area: comparison between effluents from stormwater overflows and from wastewater treatment plant. In: Proceedings of the 9th International Conference on planning and technologies for sustainable management of Water in the City. GRAIE, Lyon, France.

Göbel, P., Dierkes, C., Coldewey, W.G., 2007. Storm water runoff concentration matrix for urban areas. J. Contam. Hydrol. 91 (1-2), 26–42. https://doi.org/10.1016/j.jconhyd.2006.08.008.

Hajj-Mohamad, M., Aboulfadl, K., Darwano, H., Madoux-Humery, A.S., Guérineau, H., Sauvé, S., Dorner, S., 2014. Wastewater micropollutants as tracers of sewage contamination: analysis of combined sewer overflow and stream sediments. Environ. Sci. Process. Impacts 16 (10), 2442–2450. https://doi.org/10.1039/C4EM00314D.

Hanke, I., Wittmer, I., Bischofberger, S., Stamm, C., Singer, H., 2010. Relevance of urban glyphosate use for surface water quality. Chemosphere 81 (3), 422–429. https://doi.org/10.1016/j.chemosphere.2010.06.067.

Helsel, D., 2010. Much ado about next to nothing: incorporating nondetects in science. Ann. Occup. Hyg. 54 (3), 257–262. https://doi.org/10.1093/annhyg/mep092.

Kaplan, E.L., Meier, P., 1958. Nonparametric estimation from incomplete observations. J. Am. Stat. Assoc. 53 (282), 457–481. https://doi.org/10.1080/01621459.1958.10501452.

Launay, M.A., Dittmer, U., Steinmetz, H., 2016. Organic micropollutants discharged by combined sewer overflows–characterisation of pollutant sources and stormwater-related processes. Water Res. 104, 82–92. https://doi.org/10.1016/j.watres.2016.07.068.

Launay, M., Dittmer, U., Steinmetz, H., Kuch, B., 2013. Temporal variations of organic pollutants levels during storm events in an urban receiving water body. In: 8ème Proceedings of the Conférence Internationale Sur les Techniques et Stratégies Durables pour la Gestion des eaux Urbaines par temps de pluie/8th International Conference on Planning and Technologies for Sustainable Management of Water in the City. GRAIE, Lyon, France.

Masoner, J.R., Kolpin, D.W., Cozzarelli, I.M., Barber, L.B., Burden, D.S., Foreman, W.T., Bradley, P.M., 2019. Urban stormwater: an overlooked pathway of extensive mixed contaminants to surface and groundwaters in the United States. Environ. Sci. Technol. 53 (17), 10070–10081. https://doi.org/10.1021/acs.est.9b02867.

Posthuma, L., de Zwart, D., Osté, L., van der Oost, R., Postma, J., 2016. Ecological key factor toxicity. Part 1. Method for mapping the effects of toxic substances in surface water (Ecologische sleutelfactor toxiciteit. Deel 1. Methode voor het in beeld brengen van de effecten van giftige stoffen in oppervlaktewater). STOWA 2016-15A. Foundation for Applied Water Research STOWA.

Ramwell, C.T., Kah, M., Johnson, P.D., 2014. Contribution of household herbicide usage to glyphosate and its degradate aminomethylphosphonic acid in surface water drains. Pest Manage. Sci. 70 (12), 1823–1830. https://doi.org/10.1002/ps.3724.

Schilperoort, R.P.S., Dirksen, J., Langeveld, J.G., Clemens, F.H.L.R., 2012. Assessing characteristic time and space scales of in-sewer processes by analysis of one year of continuous in-sewer monitoring data. Water Sci. Technol. 66 (8), p1614–p1620. https://doi.org/10.2166/wst.2012.115.

Schuman, E., Evenblij, H., Verhoek, T., 2019. Removal efficiencies of micropollutants at WWTPs in the Rhine-East region (Verwijderingsrendementen microverontreinigingen op RWZI's in regio Rijn-Oost). Royal HaskoningDHV.

Stein, E.D., Tiefenthaler, L.L., Schiff, K., 2006. Watershed-based sources of polycyclic aromatic hydrocarbons in urban storm water. Environ. Toxicol. Chem. An Int. J. 25 (2), 373–385. https://doi.org/10.1897/05-285R.1.

Tang, T., Boënne, W., Desmet, N., Seuntjens, P., Bronders, J., Van Griensven, A., 2015. Quantification and characterization of glyphosate use and loss in a residential area. Sci. Total Environ. 517, 207–214. https://doi.org/10.1016/j.scitotenv.2015.02.040.

Vethaak, A.D., Rijs, G.B.J., Schrap, S.M., Ruiter, H., Gerritsen, A., Lahr, J. (2002). Estrogens and xeno-estrogens in the aquatic environment of the Netherlands: occurrence, potency and biological effects. Rapportnr.: 2002.001. Rijkswaterstaat, RIKZ. http://resolver.tudelft.nl/uuid:0f06dad4-ff1c-4007-a337-386aa5446e28.

Wicke, D., Matzinger, A., Caradot, N., Sonnenberg, H., Schubert, R.L., von Seggern, D., Rouault, P., 2016. Extent and dynamics of classic and emerging contaminants in stormwater of urban catchment types. In: Proceedings of the 9th International Conference on planning and technologies for sustainable management of Water in the City. GRAIE, Lyon, France.

Wicke, D., Matzinger, A., Sonnenberg, H., Caradot, N., Schubert, R.L., Dick, R., Rouault, P., 2021. Micropollutants in urban stormwater runoff of different land uses. Water 13 (9), 1312. https://doi.org/10.3390/w13091312.

Withagen, J.C.M., van der Horst, C.L.M., Beltman, W.H.J., Kempenaar, C., 2004. Results of Glyphosate and AMPA Run-off Monitoring and Observations of Weeds in Seven test Municipalities (spring and autumn 2003): Report in the Context of the Project Sustainable weed Management on pavements (*Resultaten monitoring afspoeling glyfosaat en AMPA en Waarnemingen van Onkruidbeelden in Zeven proefgemeenten (voorjaar en najaar 2003): Rapportage in het kader van het project Duurzaam Onkruidbeheer op Verhardingen) (DOB-project* (No. 297). Plant Research.

Wittmer, I.K., Bader, H.P., Scheidegger, R., Singer, H., Lück, A., Hanke, I., Stamm, C., 2010. Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. Water Res. 44 (9), 2850–2862. https://doi.org/10.1016/j.watres.2010.01.030.

Zgheib, S., Moilleron, R., Chebbo, G., 2010. What priority pollutants occur in stormwater and wastewater? WIT Trans. Ecol. Environ. 135, 3–13. https://doi.org/10.2495/WP100011.

Zgheib, S., Moilleron, R., Chebbo, G., 2012. Priority pollutants in urban stormwater: part 1–case of separate storm sewers. Water Res. 46 (20), 6683–6692. https://doi.org/10.1016/j.watres.2011.12.012.