Fingerprinting: a cost effective method for monitoring organic micropollutants in stormwater

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Highlights

- Construction materials and public behaviour strongly affect micropollutant levels in stormwater
- Fingerprinting is a straightforward method to explore micropollutant levels
- Storm water is less toxic than WWTP effluent or CSO discharges

Introduction

Organic micropollutants, including medicines, pesticides and biocides, discharged via urban wet weather discharges (Becouze et al., 2019) (UWWDs) negatively affect the ecological quality of receiving water bodies (Beckers et al., 2018). UWWDs comprise discharges via wastewater treatment plant (WWTP) effluent, storm sewer outfalls (SSO) and combined sewer overflows (CSO). In Europe, the Water Framework Directive (WFD) enforces member states to improve and protect the aquatic ecology. There is only sparse literature available on the concentrations of organic micropollutants in SSOs and CSOs. A literature survey revealed (based on monitoring projects in France, Germany, Switzerland and Denmark) that stormwater may contain a range of organic micropollutants. The main pollutants do, however, differ per country. For instance, in Denmark the pollutant terbutryn (paint on exterior of buildings) is found (Bollmann et al., 2019), while in Germany the pollutants carbendazim (fungicide in paint on exterior of buildings) is abundant (Wicke et al., 2015). Consequently, there was a need to monitor organic micropollutants in Dutch stormwater. Based on literature, it is to be expected that many of the organic micropollutants may seldomly be used. This means that the catchment discharging to the CSO/SSO should be reasonably large (e.g. > 10 ha) to have a fair change of capturing the pollutants from individual discharges. As most of the SSOs in the Netherlands only serve a small subcatchment of on average 1 ha, selection of a suitable monitoring location is cumbersome. Monitoring CSOs has another drawback, as the CSO frequency in the Netherlands is approximately 4 times annually, resulting in very long monitoring periods before any statistically significant results can be obtained. To overcome the difficulties of sampling SSO or CSO events, an alternative approach has been developed, inspired by research findings of Launay et al, 2016, to cost effectively monitor the organic pollutants in storm water discharges.

Methodology

Method of fingerprinting

Launay et al., 2016 demonstrated that the proportion of stormwater in a sample taken at a CSO can be determined by calculating the dilution rate based on wastewater tracers. Launay et al., 2016 used conductivity as a proxy, but indicated that some medicines could potentially act as perfect wastewater tracer. The method of fingerprinting used in this research continues on this line of thinking and consists of the following steps:

- Select appropriate tracers to determine the proportion of stormwater in a sample taken at the influent of a WWTP during a storm event. The tracer substance has to meet the following requirements: being inert, no adsorption to organic matter (so a low log K_{ow}), constant load (no weekly profile, like for röntgen contrast agents), being used by a large proportion of population, no occurrence in runoff and being detected during DWF and WWF in concentration levels >> level of detection. In agreement with Launay et al., 2016, diclofenac, ibuprofen (and its degradation product 2-hydroxyibuprofen, and naproxen were found to be ‘perfect’ wastewater tracers.

- Determine the reference level of the 4 tracers in wastewater by monitoring at least 5 times 48 hour flow proportional composite samples of influent during DWF.
- Sample during 7 wet weather days (WWF) the influent of the WWTP in a 24 hour flow proportional composite sample and determine concentration level of tracers in the sample
- Determine proportion of stormwater in the WWF sample per tracer by means of a mass balance
- Compare/check storm water proportion determined per tracer. Remove outliers if necessary and calculate the storm water proportion as the average of the accepted tracers
- Recalculate the concentration of the analysed substances taking into account the reference level at DWF

The statistics of storm water concentrations have been calculated using the Kaplan-Meier approach for dealing with the left censored monitoring data (Kaplan and Meier, 1958).
Subsequently, the toxicity of storm water discharged via SSOs and CSOs has been calculated.

Materials
The method has been applied to 5 WWTPs, ranging in capacity from 11.000 to 186.000 p.e.. For each WWTP, 5 DWF 48 hour composite samples have been taken and between 4 and 7 WWF 24 hour composite samples. 2 of the WWF samples per WWTP were taken in winter, the other during the growing season.
For each sample, 450 analysed substances were analysed, comprising 33 metals, 15 PAHs, glyfosaat/AMPA, 254 organic pesticides, 28 organochloor pesticides, 63 medicines, 7 PCBs and 27 other organic micropollutants in stormwater. This abstract only gives a sneak preview of the results for organic pesticides, at the ICUD, all compounds will be presented.

Results and discussion

The fingerprinting method resulted in 22 samples where more than 25% of the volume consisted of storm water and where the storm water proportion could be calculated with a reasonable accuracy (±10%).
Results from Figure 2 show that only 31 of the 254 tested organic pesticides were detected in at least 1 of the 22 WWF samples. Terbutryn and Carbendazim, being significant in Denmark and Germany, were not detected, illustrating the need for more monitoring on a national level.

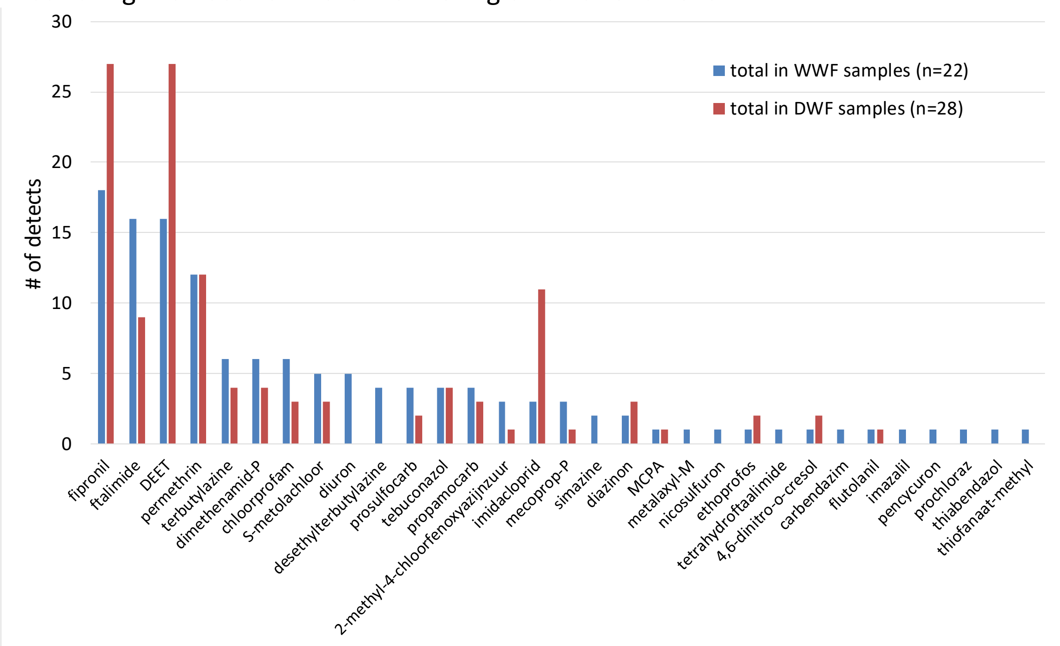

Figure 2. # of detects for organic pesticides in dry weather (DWF) and wet weather

Some pesticides, like DEET (insect repellent), fipronil (pesticide against bugs for dogs/cats) and permethrin (similar use as fipronil plus woodworm prevention) are also very frequently detected in the DWF samples, indicating that wastewater often contains pesticides from indoor usage.
The next step was to calculate the apparent concentration levels in storm water, using the Kaplan-Meier method when concentrations where found to be lower than the detection limit. Table 1 summarises the statistics for a small number of relevant substances. The red cells in table 1 indicate that the contribution of

storm water is significant (at least 2 times the reported detection limit + higher than the concentration in DWF).

Table 1. Calculated average concentrations in DWF (average of DWF samples, applying Kaplan-Meier) and in storm water (applying fingerprinting + Kaplan-Meier).

Parameter	DWF (µg/l)	stormwater (µg/l)	Remarks (typical use + problem for WFD or drinking water production
fipronil	0,03	0,0066	insecticide, biocide (fleas, mite, ticks). WFD problem
DEET	2,7	5,3	insect repellent. WFD problem + problem for drinking water production
permethrin	0,30	0,013	insecticide (mosquitos, ticks, woodworm). WFD problem
terbutylazine	0,05	0,53	weed control at cornfields. WFD + drinking water problem
diuron	0,00	0,11	weed control + several usages (anti-algal, antifungal)
imidacloprid	0,057	0,024	insecticide (fleas, ants, cockroaches). WFD problem
mecoprop-P	0,00	0,91	prevention of damage of bituminous roofs by roots.

DEET shows a strong annual profile with a rather high annual average. Both the wastewater flow and the storm water flow contribute to the overall pollutant load. The average concentrations of the insecticides fipronil, permethrin and imidacloprid in DWF is (much) higher than in storm water. This indicates that the dominant route of these substances coincides with known usage patterns inside the houses. For permethrin, additional research on the prevalence in storm water is required, as even at the low concentrations in storm water as mentioned in table 1, the toxicity of the stormwater is determined to a large extent by this compound only. Terbutylazine, and a few other pesticides that can be solely related to agriculture, where detected in the storm water at the beginning of the growth season (end of May/early June). This corresponds to results of Launay et al., 2016, although the type of pesticide differs. The emission route is still unclear, ranging from collected wastewater from cleaning of equipment to diffuse pollution via dust particles blown from the agricultural field to the urban areas. Roof runoff was reported by Wicke et al., 2016, Wittmer et al., 2010 and Burkhardt et al., 2007 to be the main contributor of mecoprop-P. This was confirmed at 2 out of 5 monitoring sites.

Conclusions and future work

The fingerprinting method was shown to be a cost effective method for collecting storm water samples for analyses of organic micropollutants. The method allows for the collection of a reasonable number of samples within one year. Results show that 'Dutch' stormwater differs from 'German' or 'Danish' stormwater by the types of measured pesticides from agricultural use as well as the types of pesticides related to construction materials typically found in the different countries, which need to be taken into account when developing storm water policies.

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