Extent and dynamics of classic and emerging contaminants in stormwater of urban catchment types

Quantité et dynamique des contaminants conventionnels et émergents dans les eaux pluviales de bassins versants types

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RÉSUMÉ

Le ruissellement des eaux pluviales est une source majeure de polluants pour les milieux aquatiques. Une campagne d'un an d'échantillonnage des effluents de réseaux séparatifs pluviaux a été mise en place à Berlin afin de mieux caractériser la présence de micropolluants dans les eaux pluviales. Les points de contrôle ont été sélectionnés dans cinq bassins versants de structure urbaine relativement homogène de manière à étudier l'influence de l'occupation des sols sur les concentrations en micropolluants. Des échantillons moyens représentatifs, proportionnels au volume écoulé (un échantillon moyen par évènement pluvieux) ont été analysés pour une large gamme de micropolluants (phtalates, biocides, pesticides, retardateurs de flamme, HAP et métaux lourds) ainsi que pour les paramètres standards (MES, P, phosphate, NH4, DCO, DBO). Pour une sélection d'évènements pluvieux, des échantillons instantanés ont été prélevés pendant la durée de l´évènement pour caractériser la dynamique des polluants et analyser la présence d'un éventuel "first flush". L'analyse des concentrations moyennes révèlent des différences de concentrations significatives entre les bassins versants pour la majorité des micropolluants détectés. Les résultats des échantillons instantanés indiquent que la plupart des paramètres ne subissent pas d'effet de "first flush", les concentrations de plusieurs micropolluants restant même constantes au cours des évènements pluvieux (par exemple mécoprop, carbendazime, TBEP).

ABSTRACT

Untreated stormwater runoff can be an important source of pollutants affecting urban surface waters. To investigate the relevance of micropollutants in urban stormwater runoff for the city of Berlin, an event-based, one-year monitoring program for sampling of separate storm sewers was conducted. Monitoring points were selected in five homogeneous catchments of different urban structure types to consider catchment-specific differences. Volume proportional samples (one composite sample per event) were analysed for a comprehensive set of ~100 micropollutants determined from literature review (e.g. plasticisers [phthalates], biocides/pesticides, flame retardants [organophosphates, polybrominated diphenylethers], PAH, heavy metals) as well as standard parameters (TSS, total P, phosphate, ammonium, COD, BOD). For selected storm events, time resolved samples were analysed to investigate the concentration dynamics and evaluate first flush characteristics. Results of event mean concentrations show catchment-specific differences for the majority of detected micropollutants. Furthermore, results of time-resolved samples indicate that most parameters do not show clear first flush effects with concentrations of several micropollutants even remaining constant during the course of the storm event (e.g. mecoprop, carbendazim, TBEP).

KEYWORDS

Catchment differences, emerging pollutants, pollution dynamics, stormwater

1 INTRODUCTION

In cities in which stormwater drainage is dominated by separated sewer systems, stormwater runoff can be an important source of diffuse pollution affecting urban surface waters. In Berlin, each year 70% or 48 million m³ of stormwater are discharged mostly untreated into Berlin's surface waters via the separated sewer system. Beside "classic" stormwater pollutants (e.g. suspended solids, COD, phosphorous or heavy metals), emerging substances such as biocides, plasticizers, flame retardants and traffic related micropollutants started to come into focus in recent years (Zgheib et al. 2012, Gasperi et al. 2014, Burkhardt et al. 2012). To evaluate the relevance of these trace organic substances entering urban surface waters through stormwater discharge, a one-year, quantitative monitoring program was set up in the city of Berlin.

2 METHODS

Monitoring points were selected in five homogenous catchments of different urban structures typical for Berlin to be able to consider catchment-specific differences and estimate annual loads: old building areas (mostly perimeter block structure) <1930 [OLD], newer building areas (newer multi-storey buildings) >1950 [NEW], one-family houses with gardens [OFH], highly frequented streets >7500 vehicles per day [STR] and commercial areas [COM]. These catchment types represent the majority (>80%) of the connected impervious area of Berlin. Automatic sampling and flow measuring devices were installed in separate storm sewers of selected catchments (one sampling point per catchment). Details of the selection process and monitoring strategy can be found in Wicke et al. (2014).

For each storm event and site, one volume proportional composite sample was analysed for a comprehensive set of ~100 micropollutants (see Table 1) as well as standard parameters (TSS, total P, phosphate, ammonium, COD and BOD) to determine event mean concentrations (EMC). Samples were selected to cover a wide range of rain event characteristics (e.g. high and low intensity) and different seasons. In total, 93 composite samples were analysed for micropollutants. In addition, for 26 events each sampling bottle was analysed for standard parameters (26) or micropollutants (3) to investigate concentration dynamics.

Table 1: Groups of analysed substances with examples and application.

Substance groups (# compounds)	**Examples**	**Application**
Phthalates (8)	DEHP	Plasticizer (e.g. PVC)
Organophosphates (6)	TCPP, TBEP	Flame retardants, plasticizer
Biocides / Pesticides (20)	Glyphosate, carbendazim, mecoprop	Gardens, exterior paints, wall conservation
Industrial chemicals (15) benzothiazoles (3) benzotriazoles (3) alkyl phenols (4) others (5)	 benzothiazole benzotriazole nonylphenol MTBE, bisphenol A, PFOS	 Vulcanising accelerator (tires) Corrosion inhibitors Synthetics, tire abrasion
Polycyclic Aromatic Hydrocarbons PAH (16)	Fluoranthene, Benzo[a]pyrene	Combustion processes, tire wear
Polybrominated Diphenylether (9)	PBDE	Flame retardants
Organotin compounds (5)	Mono-,di-, tributyltin	Wood preservative, antifouling
Polychlorinated Biphenyls (PCB) (7)	PCB 153	coolant and insulating fluid
Heavy metals (8)	Copper, zinc, titanium	Brake and tyre wear, building materials
Miscellaneous	Nicotine	Littered cigarette butts

3 RESULTS AND DISCUSSION

Results of the monitoring programme show that 69 of the 95 analyzed micropollutants (Table 1) were detected in stormwater runoff. For 15 contaminants average concentrations >1 µg/L were determined, especially in the group of phthalates, organophosphates, PAHs and heavy metals, whereas organotin compounds, PBDE and PCB were not detected (Fig 1). Fig 1 also indicates that the sum of all trace organic compounds is around 10 µg/L at median and can be significantly higher for single events.

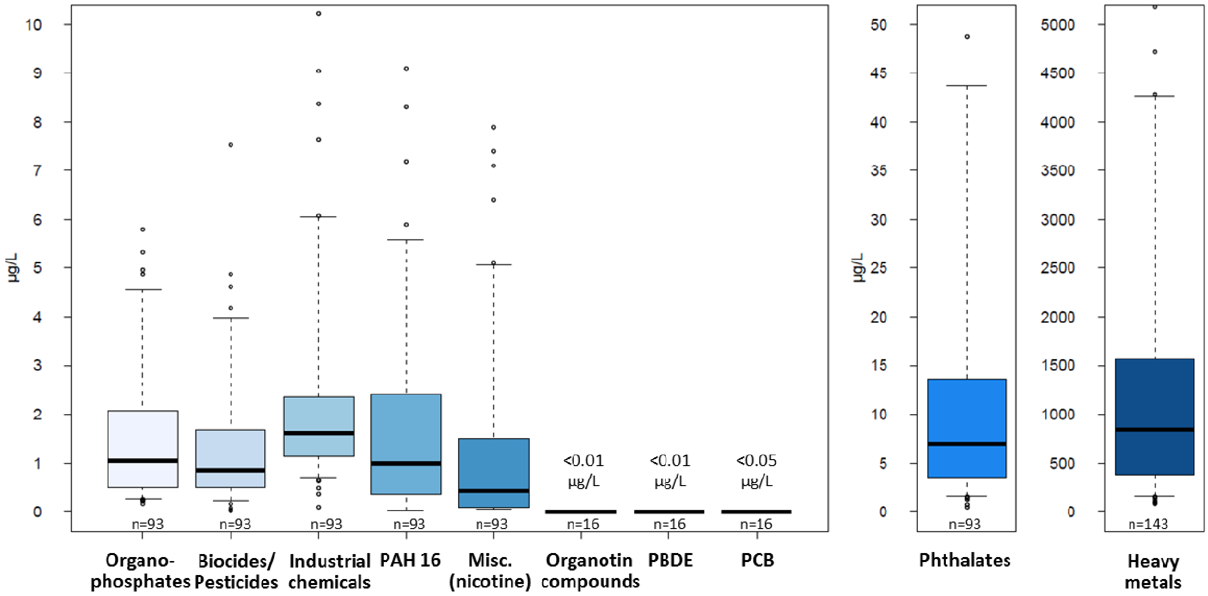

Figure 1: Concentrations of micropollutant groups (sum of all micropollutants per group, see Table 1) in stormwater of 5 different catchment types.

3.1 Catchment-specific differences

For most investigated parameters catchment specific differences in concentrations were found (Fig 2). For instance, concentrations for traffic-borne benzothiazoles (vulcanizing accelerators used for production of tires) and PAH (sum of EPA 16 PAHs) are highest in road runoff (STR), although also present at the other catchment types that also contain smaller roads <7500 vehicles per day. DEHP also seems to be related to traffic. Organophosphates (flame retardants) are highest in the old building areas, potentially due to application of insulation materials during extensive renovations in recent years. For biocides, catchment specificity depends on individual compounds. Whereas mecoprop (contained in bituminous sealing membranes for roofs, Bucheli et al. 1998) can be found in all catchments with roof runoff, carbendazim (fungicide, in urban context applied in exterior paints and silicone sealants) is mostly found at monitoring station OLD, probably also due to recent renovation efforts. On the other hand, concentrations of nicotine show no significant differences between catchment types but seem to be related to roads, probably because littering of cigarette butts on roads and sidewalks takes place ubiquitous in the city (see Fig 2).

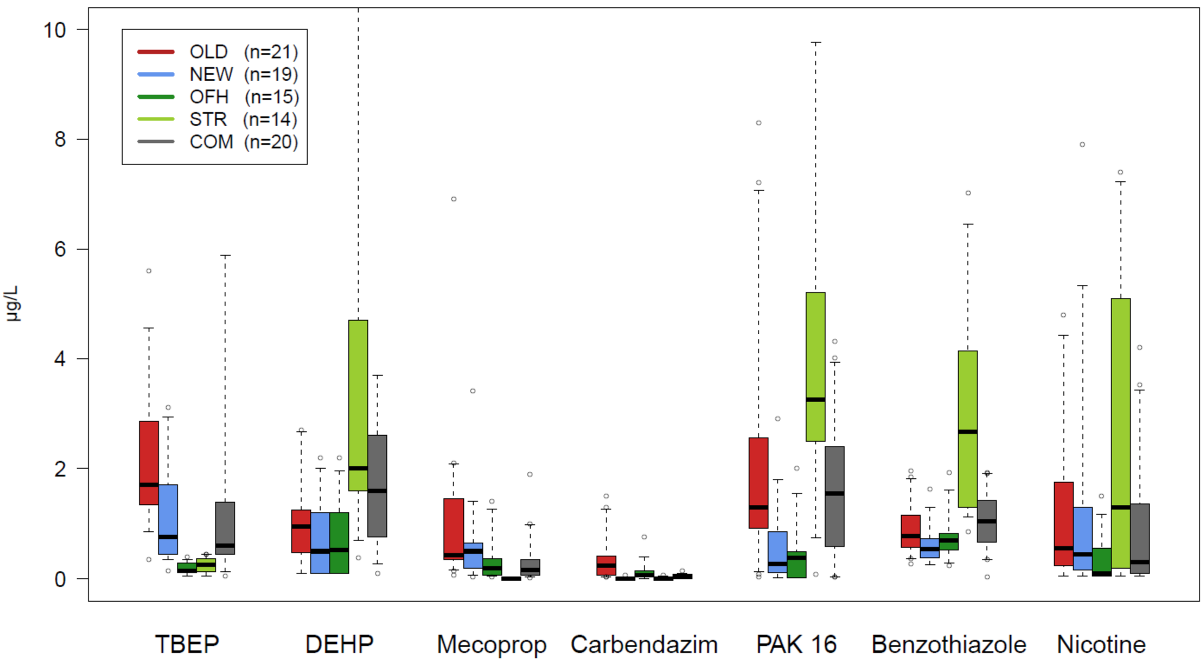

Figure 2: Concentrations of selected micropollutants in stormwater of 5 different catchment types.

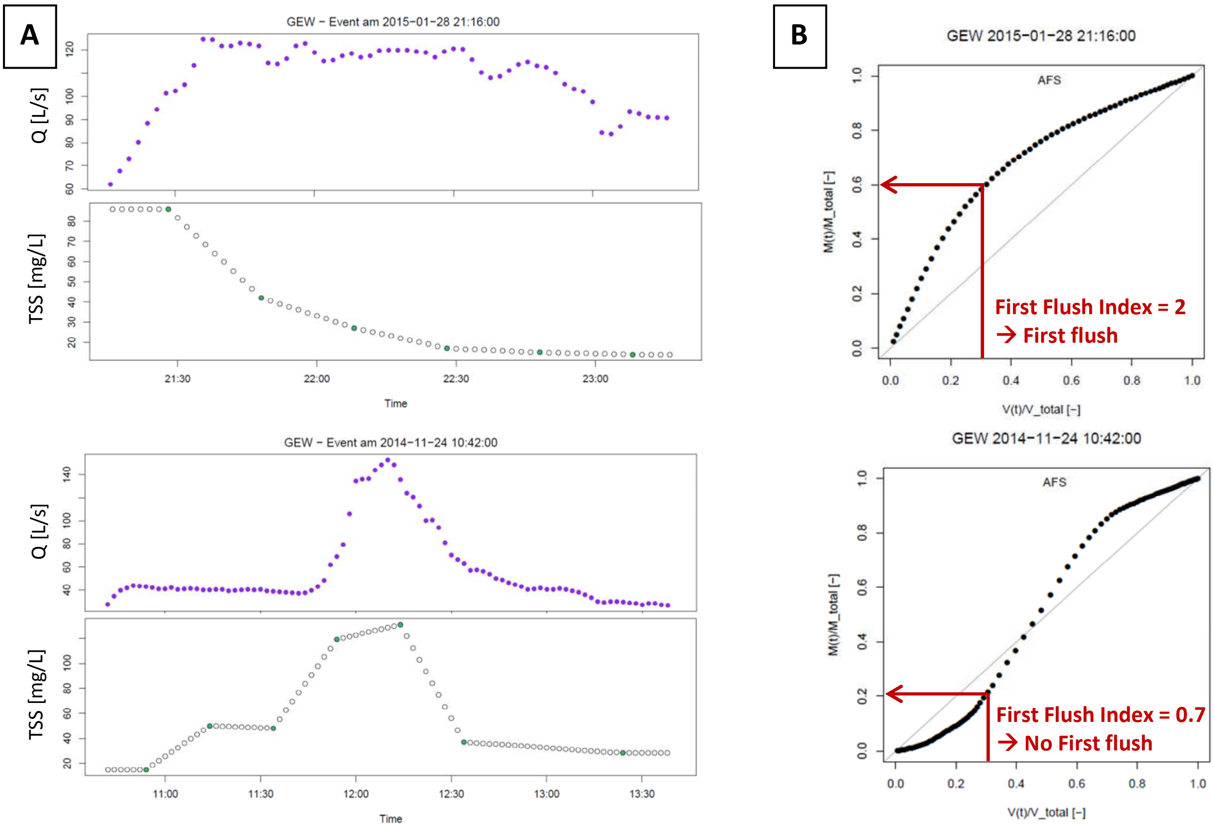

Figure 3: A – flow and concentration dynamics of TSS for 2 events of different behaviour at commercial catchment. B – corresponding first flush plots showing relative cumulated load over relative cumulated volume.

3.2 Concentration dynamics

Figure 3 exemplarily shows the concentration dynamics of total suspended solids (TSS) for 2 different storm events of the commercial catchment (COM). It can be seen that for the upper event highest concentrations were detected at the beginning of the storm event with exponential decrease until the end of the storm event, commonly referred as first flush behaviour. On the other hand, the second event shows a different behaviour with concentrations following the flow course without first flush. To quantify the extent of first flush, M(V)-curves were plotted that show the relative cumulated load over the relative cumulated volume as described in Bertrand-Krajewski et al. (1998) (see Figure 3, right). From this, the first flush index (FFI) was calculated for each event and pollutant, representing the ratio between the relative cumulated load and 0.3 (relative cumulated volume of 30%, see Figure 3B). Although there is no exact definition at which FFI the concentration dynamics represents a first flush, an FFI ≥ 2 is often considered as first flush (Diaz-Fierros et al. 2002). FFI were determined for all 26 events and analysed parameters (TSS, COD, total P, zinc, copper, lead and titanium). Results are displayed as boxplots exemplarily for the old housing catchment (OLD) and commercial catchment (COM) in Figure 4. As can be seen, median FFI is around 1 for all compounds indicating no overall first flush behaviour. However, box span and whisker show that for most compounds single events reach values close to and above 2, especially for TSS, COD and lead (Pb).

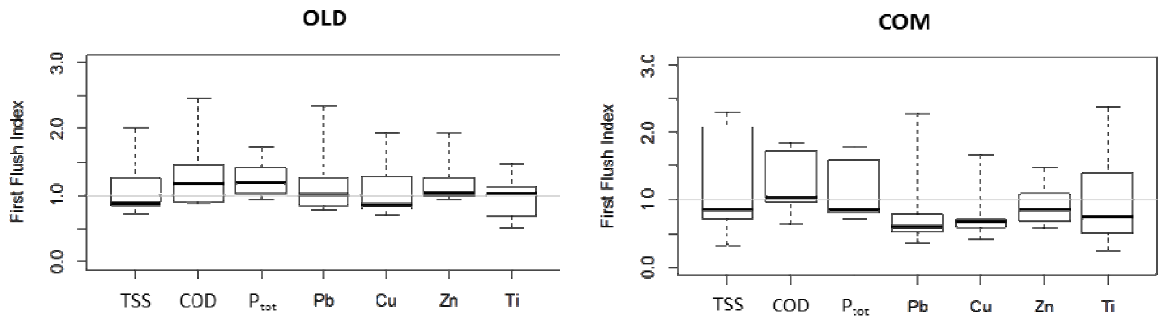

Figure 4: First flush indices (FFI, ratio between relative cumulated load and relative cumulated volume at 30%) for time-resolves events at catchments OLD (n=7) and COM (n=9). First flush is considered when FFI ≥ 2.

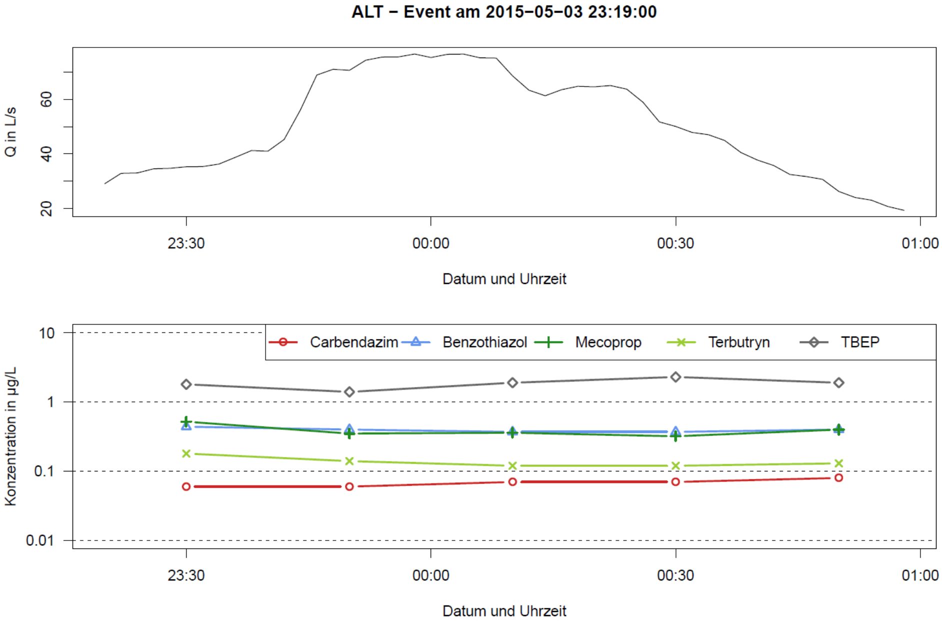

Figure 5: Concentration dynamics of selected micropollutants during storm event at monitoring station OLD.

Concentration dynamics of micropollutants shows that for several micropollutants such as biocides (carbendazim, mecoprop and terbutryn), organophosphates (TBEP) or benzothiazoles the concentration level remains constant over the whole course of the storm event (Fig. 5) demonstrating the relevance of micropollutant release during storm events.

4 CONCLUSIONS

All in all, results show that stormwater discharge may be a relevant source of micropollutants in urban streams, particularly in cities dominated by separate sewer systems. Catchment-specific differences need to be considered to understand micropollutant patterns in urban stormwater and potentially prevent loads at the source. Concentration dynamics indicates that release on catchment scale does often not follow a first flush behaviour especially for leaching micropollutants, indicating that treatment strategies targeting only the first part of runoff volume may not be successful.

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