

## Temporal variations of organic pollutants levels during storm events in an urban receiving water body

Variations temporelles des teneurs en polluants organiques lors d'évènements pluvieux dans un milieu récepteur urbain

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### RÉSUMÉ

Le bassin versant de la rivière Schwippe est caractérisé par un fort taux d'urbanisation et d'industries et la qualité de l'eau est fortement influencée par les eaux de ruissellement urbain. En juillet 2011, une station de surveillance de la qualité de l'eau a été mise en place dans la rivière en amont des rejets de stations de traitement des eaux usées. L'objectif fut de décrire les variations temporelles des concentrations en polluants organiques dans le milieu récepteur sous forte pression urbaine et d'améliorer la compréhension concernant les dynamiques de pollution pour les bassins versants urbains. Les résultats montrent que pour un même évènement pluvieux, les pics de concentration de chaque micropolluant sont décalés dans le temps. Cela peut être expliqué par leur origine différente (eaux usées, ruissellement urbain) et par leurs propriétés physico-chimiques. Lors d'évènements pluvieux, la qualité de l'eau du milieu récepteur est hautement variable et dépend des caractéristiques de la pluie, telles que l'intensité et la durée de la pluie, la période sèche antérieure et de l'activité des déversoirs d'orage. La turbidité ou les matières en suspension représentent des paramètres indicateurs appropriés pour la détermination des concentrations en micropolluants liés aux particules lors d'évènements pluvieux.

### ABSTRACT

The catchment of the river Schwippe is characterized by a high degree of urbanization and industry and the surface water quality is strongly influenced by urban runoff. In July 2011 a water quality monitoring station was installed in the river upstream of the wastewater treatment plant (WWTP). The aim was to describe temporal variations of organic pollutants concentrations in the urban receiving water body and to improve the understanding of pollution dynamics in the urban catchment. The results show that in the course of a storm event the peaks of different micropollutants are shifted in time. This can be explained by their different origin (wastewater, street runoff) and by their physico-chemical properties. River water quality during rain events is highly variable and depends on rainfall characteristics, such as rainfall intensity and duration, antecedent dry period and on combined sewer overflow (CSO) activity. Turbidity or total suspended solids are suitable indicator parameters for the assessment of concentrations of particle-bound micropollutants during storm events.

### KEYWORDS

Micropollutants, Receiving water quality, Storm event, Urban areas

## 1 INTRODUCTION

The occurrence of micropollutants in the aquatic environment is an important contemporary issue. Principal sources of micropollutants in surface waters are wastewater treatment plant (WWTP) discharges (Zuccato et al., 2010), storm runoff and combined sewer overflows (CSO) (Phillips et al., 2012). Several studies showed that for organic pollutants effectively removed through wastewater treatment, inputs from CSO are of greater magnitude as inputs from WWTP (Buerge et al., 2006; Phillips and Chalmers, 2009). Furthermore, CSO represent short peaks with high levels of micropollutants in surface waters (Musloff et al., 2009). In order to better understand this process, a high sampling and analytical effort has to be performed. Moreover, the continuous monitoring of water quality and data collection would allow a more accurate description of the impact of rainfall events on the water quality (Lawler et al., 2006) and would represent suitable information for the assessment of organic pollutants levels in surface waters.

The study presented in this paper aims at (1) describing the temporal variations of organic trace pollutants concentrations in urban receiving water bodies during storm events, (2) improving comprehension of pollution dynamics in urban catchments and (3) testing possible substitute parameters for the assessment of the behaviour of organic trace pollutants in surface waters during storm events. On this end, a continuous water quality monitoring program combined with a sampling program was started in July 2011.

## 2 MATERIAL AND METHODS

### 2.1 Study site

This study was conducted in an urban catchment (area 86 km<sup>2</sup>) in the south-west of the city of Stuttgart, Germany. At the sampling point in the Schwippe, the catchment includes the entire cities of Böblingen and Sindelfingen that compose about 40% of the total area (see Figure. 1). The average baseflow is approximately 100 L/s. The urbanized areas are mainly drained by a combined sewer system. Only a commercial and industrial zone of 120 ha is drained by a separate system. Upstream of the sampling location the river Schwippe receives discharges from 30 CSO structures. All of these structures are combined with storage tanks.

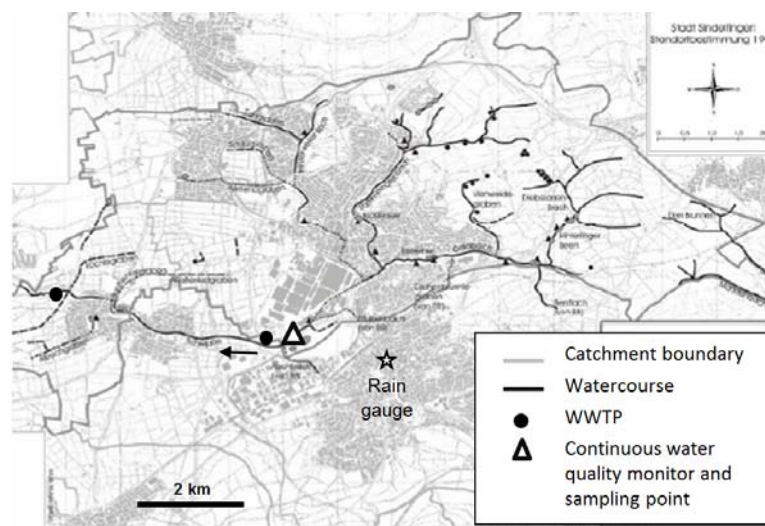


Figure 1. Map of the Schwippe catchment showing the location of the monitoring station (WWTP=wastewater treatment plant effluent)

### 2.2 Sampling strategy

This study attempts to analyse the fate of micropollutants during wet weather from the catchment area upstream of the WWTP discharges. Since July 2011, continuous water quality monitoring allowed to observe the influence of multiple storm events on the river Schwippe. Six storm events were analysed for organic pollutants. The characteristics of each storm are summarized in Table 1. The location of the rain gauge is shown on Figure 1.

Table 1. Characteristics of the rain events sampled

Rain event	Depth (mm)	Rain start	Rain duration (h:min)	Mean intensity (mm/h)	Max intensity (mm/h)	Antecedent dry weather duration	Number of CSO structures with overflow
06/10/2011	10.6	20:12	3:13	3.3	12	17 days	6
07/10/2011	2.1	7:42	5:36	0.4	6	8h17min	0
08/10/2011	3	4:51	3:12	0.9	3	14h33min	0
12/10/2012	1.8	6:00	0:55	2	3.6	66h05min	0
12/10/2012	8.4	8:00	2:25	3.5	7.2	1h05min	0
12/10/2012	12.9	15:00	0:55	14	26.4	4h35min	4

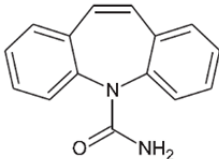
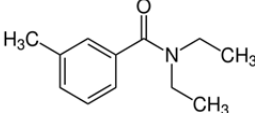
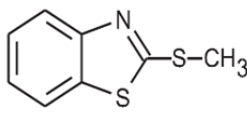
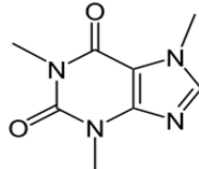
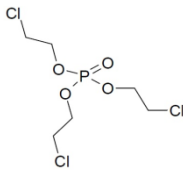
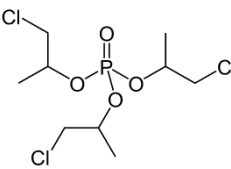
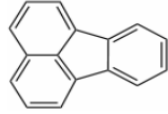

On-line surface water analysis (collection of 1-minute data for turbidity, electrical conductivity, dissolved oxygen, pH and water temperature) was installed upstream of the effluent discharge. This on-line station permits the analysis of the dynamics of solids transport during storm events and to find possible surrogate parameters for the assessment of micropollutants behavior in surface waters. Samples were taken at the same location in the river Schuppe. This sampling location permits the evaluation of pollution levels from the catchment area, including the emissions from rainwater and combined sewer overflows. For the storm events in October 2011, a refrigerated (4 °C) automatic sampler was used and allowed to collect time-proportional samples (2h-composite samples). Due to technical problems, samples for the storm event in October 2012 were taken as grab samples.

## 2.3 Analysis

Each sample was analyzed for pH, electrical conductivity, total suspended solids (TSS), chemical oxygen demand (COD),  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ , total phosphorous and phosphate ( $\text{PO}_4^{3-}$ ), in accordance with standard European methods.

Based on literature review, the following micropollutants were chosen for chemical analysis: carbamazepine, caffeine, the insect repellent N,N-diethyl-m-toluamide (DEET), 2-methylthiobenzothiazole (MTBT), Tris(2-chloroethyl)phosphate (TCEP), Tris(2-chloropropyl)phosphate (TCPP), fluoranthene and pyrene. These compounds are characterized in Table 2. Several criteria were taken into account: the origin of the pollutants, their potential threat for the aquatic environment and their physico-chemical properties. After adding the internal standards (16 perdeuterated PAH according to US-EPA, Carbamazepine- $\text{d}^{10}$ , Caffeine- $^{13}\text{C}_3$ ) the samples (2 L non filtrated and 2 L filtrated using cellulose nitrate membranes 0.45  $\mu\text{m}$ ) were liquid-liquid extracted with dichloromethane (2 x 40 mL). The organic extract was rotavaporated to 1 mL and dried with sodium sulphate (granulated, anhydrous). Prior to Gas Chromatography/Mass Spectrometry (GC/MS)-analysis the extracts were reduced to 100  $\mu\text{L}$  using a gentle nitrogen stream (40 °C). High Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)-analysis was performed using a GC HP 5890 Series II directly coupled with a mass selective detector HP 5972 in single ion monitoring mode (column agilent DB-5ms, 30 m x 0.250 mm x 0.25  $\mu\text{m}$ ). Quantification was done directly via isotope dilution method (native and labeled compound pairs) or external calibration.

Table 2. List of selected analyzed micropollutants

Micropollutant	Application	Structure	Characteristics
<b>Carbamazepine</b>	Anticonvulsant		Little degradation in sewage treatment plants, water-persistent in the environment, potential ecotoxicity, demonstrated chronic effects (Zhang et al., 2008)
<b>N,N-Diethyl-m-toluamide (DEET)</b>	Insect Repellent		Persistent in the environment, little data for the detection of aquatic toxicity, slightly toxic to birds, fish and freshwater invertebrates (Costanzo et al., 2007)
<b>2-Methylthio-benzothiazole (MTBT)</b>	Fungicide or stabilizer in the rubber production		Main sources in the environment are industrial plants, tire debris (street runoff)
<b>Caffeine</b>	Psychomotor stimulant		High soluble in water, negligible volatile, stable under variable environmental conditions
<b>Tris(2-chlorethyl) phosphate (TCEP)</b>	Plasticizers and flame retardants		Classified in the European Union as potential human carcinogen, hazardous, non-biodegradable, toxic effects to aquatic organisms
<b>Tris-(chloropropyl)-phosphate (TCPP)</b>	Flame retardants (especially in foams in automotive applications, furniture and mattresses)		Bioaccumulation potential, hazardous, readily biodegradable
<b>Fluoranthene</b>	Fluoranthene and pyrene, like other PAHs, are formed during combustion processes and are as contained in exhaust gases (diesel gas, etc.)		Among the PAHs, persistent organic pollutants, environmental degradation proceeds very slowly, toxicity, bioaccumulation potential, priority substances, practically insoluble in water
<b>Pyrene</b>			

### 3 RESULTS AND DISCUSSION

#### 3.1 Storm events on October 2011

As shown in Figure 2, from all the selected micropollutants, MTBT is the compound which has the highest concentrations in the river due to storm events (from 330 until 1260 ng/L). These values are much higher than the values found in the literature (Zeng et al., 2004; Kloepper et al., 2005).

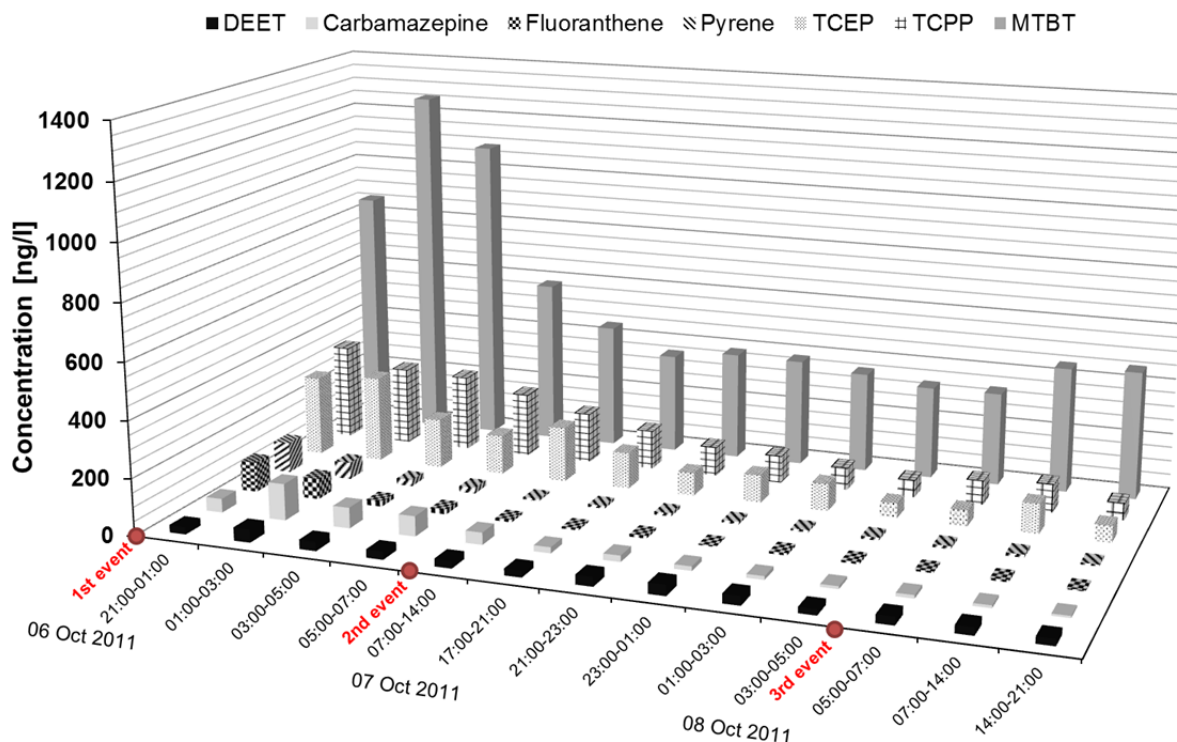


Figure 2. Temporal course of concentrations for seven selected organic pollutants in the river Schwippe during storm events between 06 October and 08 October 2011

MTBT belongs to benzothiazoles and is used as a vulcanization accelerator in tire and rubber manufacturing processes (Zeng et al., 2004). The catchment is high urbanized and includes a large automobile production site. This can explain the very high MTBT concentrations in the river Schwippe during the storm event on 06 October 2011 after 17 dry days: this compound is deposited on the road surface through traffic and industrial activities and washed into surface waters during the storm event.

To describe the temporal variations of polycyclic aromatic hydrocarbons (PAHs) in surface waters during storm events, the two compounds fluoranthene and pyrene were chosen, as they are two of the main PAHs contributing to pollution in the aquatic environment (Birch et al., 2011; Zgheib et al., 2011). Their concentrations ranged from 4 ng/L to 110 ng/L. The same trend was observed for both of the compounds: the concentrations are highest at the beginning of the first rain event, and the other smaller events have no influence on the concentrations. Gasperi et al. (2008) showed that the PAHs levels during storm events in a Parisian urban catchment originated predominantly from in-sewer erosion and from runoff. Furthermore, due to extremely low water solubility, fluoranthene and pyrene are mainly associated with particles in the aquatic environment. So at the beginning of the rain event, the particle-bound pollution is remobilised in sewers or washed directly to surface waters and represents a larger influence on surface water quality as the soluble pollution.

The TCEP and TCPP concentrations ranged from 50 ng/L to 340 ng/L, which are similar to the results described by Regnery and Püttmann (2010). As their concentrations follow the same trend as the two selected PAHs concentrations, it can be deduced that these compounds are more particle-bound.

Carbamazepine and DEET, because of their application, can only be found in wastewater and not in rainwater. The sampling location is not influenced by the WWTP discharges, so increases of concentrations of these compounds are due to CSO events. In fact, there was overflow at six CSO structures in the catchment area. The peak concentrations arrived four hours after the rainfall start, so after the peak concentrations of fluoranthene, pyrene, TCEP and TCPP. The maximal concentrations for carbamazepine and DEET were 130 ng/L and 50 ng/L respectively.

### 3.2 Storm events on October 2012

On 12 October 2012, three rain events occurred (see Table 1). The last one has the highest rain intensity and only for this event, four CSO events were detected in the catchment above the sampling location. It can explain the different variations of concentrations for the eight selected pollutants (see Figure 3). The concentrations of the typical wastewater pollutants carbamazepine and DEET increased in the river Schwippe only during this event, because of the CSO events. The maximal concentrations for carbamazepine and DEET were 90 ng/L and 40 ng/L respectively.

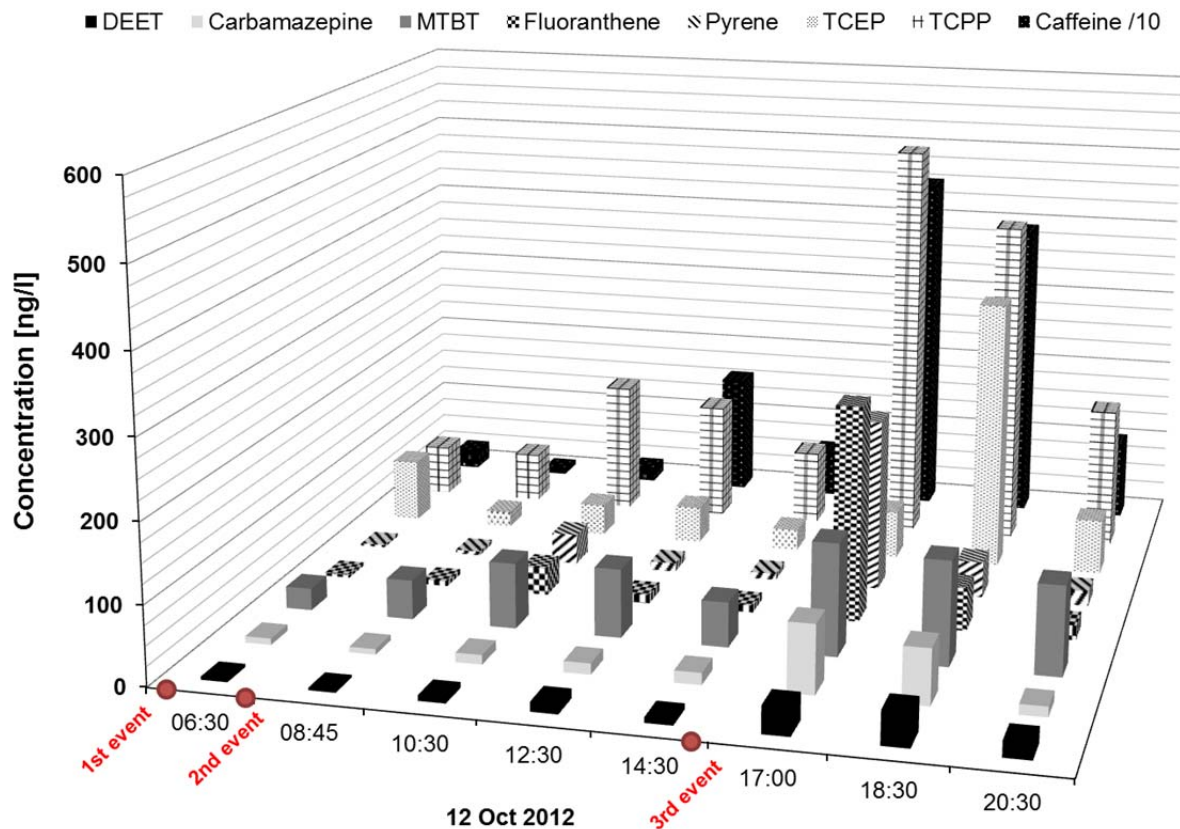


Figure 3. Temporal course of concentrations for eight selected organic pollutants in the river Schwippe during storm events on 12 October 2012

The two first events permitted the description of the influence of urban runoff, as no CSO events occurred. The first event affected only the concentrations of TCEP and TCPP. The second rain event is more intense and longer. Concentrations increased in surface waters for MTBT, fluoranthene, pyrene, TCEP and TCPP. These compounds, present in street dust, were transported to the river with urban runoff.

On 12 October 2012, the highest concentrations for the selected pollutants occurred when the rain intensity was very high, resulting CSO events. The maximal concentrations for fluoranthene and pyrene were 275 ng/L and 220 ng/L respectively, double the highest concentrations as for the storm event in October 2011. Concerning the compounds TCEP and TCPP, their concentrations ranged from 20 ng/L to 425 ng/L, so the results as similar to the results of the storm event in 2011. The highest MTBT concentration was 140 ng/L, ten times less than the highest concentration during the storm event in October 2011. As MTBT is predominantly present in road debris, the antecedent dry period seems to be the most important factor to explain such high concentrations in rivers during storm events.

From all the selected micropollutants, caffeine is the compound which has the highest concentrations in the river due to storm events (from 70 until 4515 ng/L). For reasons of clarity, the caffeine concentrations were divided by 10 in Figure 3. Like carbamazepine and DEET, because of his application, caffeine can only be found in wastewater. The sampling location is not influenced by the WWTP discharges, so increases of concentrations of this compound are due to CSO events. Furthermore, Buerge et al. (2006) showed that caffeine is a suitable marker for CSO to surface waters.

### 3.3 On-line data analysis

Figure 4 shows the parameters of turbidity, electrical conductivity (EC) and dissolved oxygen (DO) content, which were measured on-line in the Schwippe, above the discharge of the wastewater treatment plants in August 2011 (1-minute data). For reasons of clarity, the dissolved oxygen concentrations and the cumulative rainfall were increased by a factor of 10.

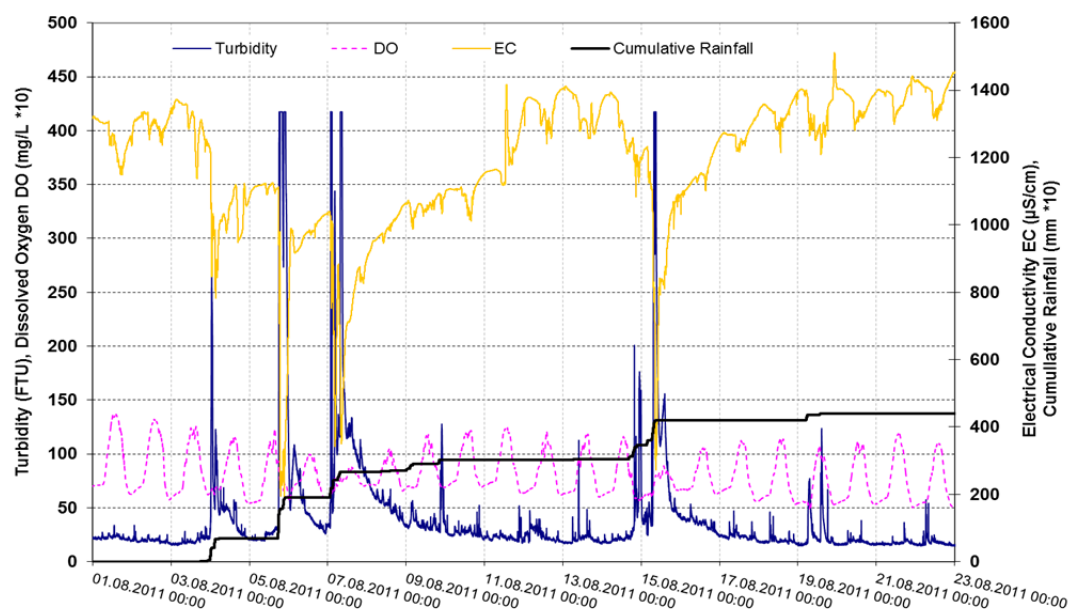


Figure 4. Water quality time series of the River Schwippe during successive storm events

The oxygen concentrations ranged from 5 mg/L to 14 mg/L and showed daily fluctuations. Due to the photosynthetic activity of algae and macrophytes the oxygen concentration increased during the day. The strong daily variations show that the Schwippe is a eutrophic and polluted water body (Wetzel, 2001). For nutrient-based water balance the daily variations are less pronounced. Similarly, the electrical conductivity in the Schwippe showed daily fluctuations.

Rain events affected all three presented parameters, however the effects on the turbidity and conductivity were most pronounced. The turbidity increased suddenly and sharply, while the conductivity decreases sharply. Several factors can explain the suddenly increases in turbidity: the remobilisation of in-sewer sediments or river sediments, CSO events and urban runoff. Moreover for all the storm events, secondary turbidity peaks could be observed. They may represent the later arrival of turbid waters from more distant sources at the top of the catchment area (Lawler et al., 2006). Therefore, these two parameters are suitable to illustrate the influence of rain events on surface waters. Furthermore, it is important to have at least two parameters as a control, as the plausibility check is increased.

### 3.4 Correlation analysis

The cost of the organic contaminants analysis is very high. Therefore, another objective of this study was to determine a replacement parameter to reduce the extent of organic micropollutants analysis required. For example, other studies showed that on-line turbidity measurements could be used to estimate urban stormwater pollutant concentrations and loads (Métadier and Bertrand-Krajewski, 2012).

#### 3.4.1 Correlation between TSS and two selected PAHs

Correlations between standard parameters and trace elements were established for the storm events described above. For the storm events, it was determined whether a correlation between TSS and PAH concentrations exists. The scatter plots of the data points show a good correlation between TSS and pyrene concentrations and between TSS and fluoranthene concentrations (see Figure 5). Moreover, the same trend can be observed for the different storm events. These results should be interpreted with caution, since insufficient data was available to demonstrate this with clear evidence. Another second measurement period, from January 2013, will allow sampling several storm events in order to increase the quantity of data and to verify if the same trend is observed, especially for very

high values as only one sample could be analysed until yet.

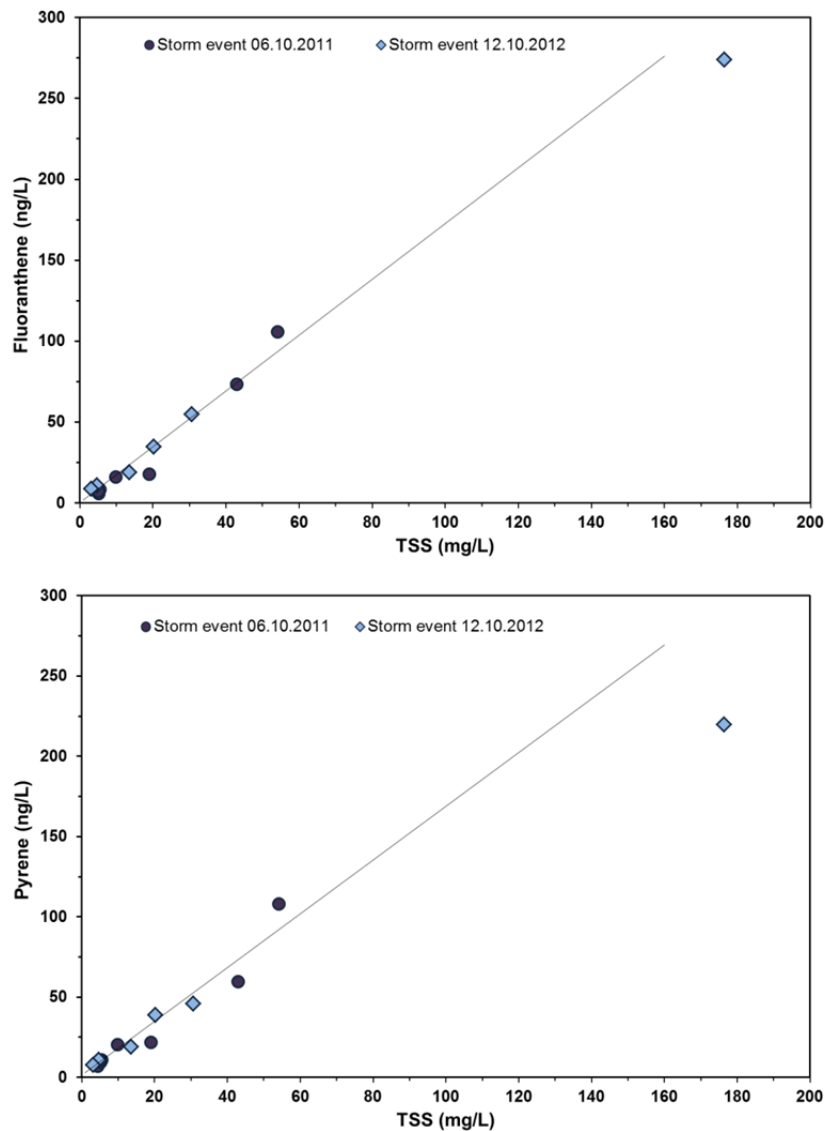


Figure 5: Scatter plots of the comparative measurements fluoranthene, pyrene and TSS

### 3.4.2 Correlation between turbidity and MTBT

For this study it was investigated whether online measured turbidity values are suitable for the assessment of MTBT concentrations for wet weather. Figure 6 illustrates the relationship between the on-line turbidity measurements and the laboratory determined MTBT concentrations for the rain event on the 06.10.2011. A good correlation could be found between turbidity and MTBT concentration.



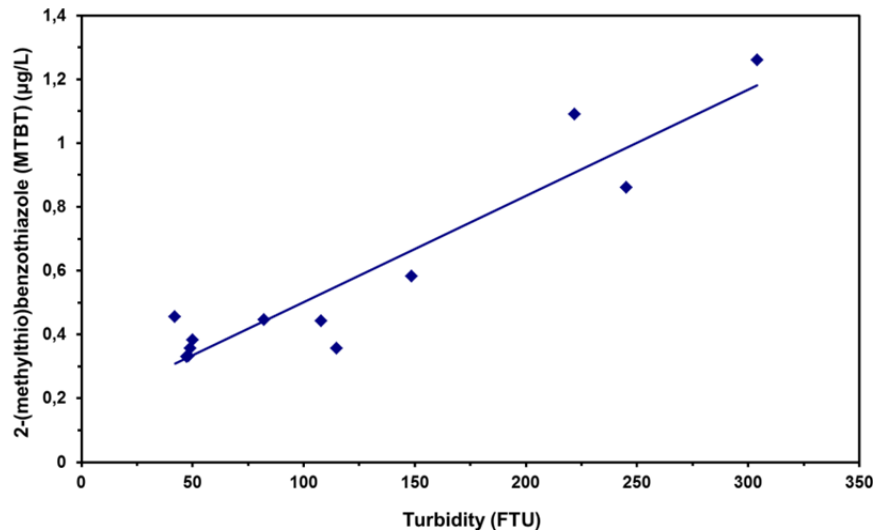


Figure 6: Scatter plot of comparison measurements MTBT and turbidity

The results can be currently seen as a trend. For validation, a number of other events must be considered. In another phase of the project, several rain events will be sampled to confirm the observed trend.

#### 4 CONCLUSIONS

Storm events can have a significant influence of organic pollutants levels in the surface water and should be taken into account when assessing the occurrence of pollutants in surface waters. CSO events represent short peaks in discharge with high loads of micropollutants.

But for a same storm event, the peaks with the highest concentrations for each micropollutant are temporally shifted, due mainly to their origin (wastewater, street runoff) and to their physico-chemical properties: particle-bound micropollutants such as polycyclic aromatic hydrocarbons have the highest concentrations at first and the peaks for the water-soluble pollutants arrive at a later time.

Results of this study indicate that surface water quality changes during storms are highly variable and depend on rainfall characteristics, such as rainfall intensity and duration, antecedent dry period and the number of CSO structures with overflow. In the high urbanized catchment of the river Schwippe, the antecedent dry period and the rain intensity seem to be essential factors to explain the very high concentrations of organic pollutants in surface waters during storm events, as industrial and urban pollution can accumulate in the catchment and are only transported into surface waters due to storm events.

Turbidity or suspended solids can represent suitable indicator parameters for the assessment of particle-bound micropollutants in rivers during storm events. Once more events are monitored, data analysis for correlation will be extended to general conclusions. But these results are specific to the study site, and more research is required to validate this fact and to extend it to other urban catchments.

**LIST OF REFERENCES**

- Birch, H., Mikkelsen, P.S., Jensen, J.K. and Lützhof, H. (2011). *Micropollutants in stormwater runoff and combined sewer overflow in the Copenhagen area, Denmark*. Water Science and technology, 64(2), 485-493
- Buerge, I.J., Poiger, T., Müller, M.D. and Buser H.-R. (2006). *Combined sewer overflows to surface waters detected by the anthropogenic marker caffeine*. Environ. Sci. Technol. 40, 4096-4102
- Costanzo, S.D., Watkinson, A.J., Murby, E.J., Kolpin, D.W. and Sandstrom, M.W. (2007). *Is there a risk associated with the insect repellent DEET (N,N-diethyl-m-toluamide) commonly found in aquatic environments?* Science of the Total Environment 384: 214-220
- Gasperi J., Garnaud, S., Rocher, V. and Moilleron, R. (2008). *Priority pollutants in wastewater and combined sewer overflow*. Science of the Total environment 407, 263-272
- Kloepfer, A., Jekel, M. and Reemtsma, T. (2005). *Occurrence, sources, and fate of benzothiazoles in municipal wastewater treatment plants*. Environ. Sci. Technol., 39(10), 3792-3798
- Lawler, D.M., Petts, G.E., Foster, I.D.L. and Harper, S. (2006). *Turbidity dynamics during spring storm events in an urban headwater river system: The Upper Tame, West Midlands, UK*. Science of the Total Environment 360, 109-126
- Métadier, M. and Bertrand-Krajewski, J-L. (2012). *The use of long-term on-line turbidity measurements for the calculation of urban stormwater pollutant concentrations, loads, pollutographs and intra-event fluxes*. Water Research 46, 6836-6856
- Musolff, A., Leschik, S., Möder, M., Strauch, G., Reinstorf, F. and Schirmer, M. (2009). *Temporal and spatial patterns of micropollutants in urban receiving waters*. Environmental Pollution 157, 3069-3077
- Phillips, P. and Chalmers, A. (2009). *Wastewater effluent, combined sewer overflows, and other sources of organic compounds to Lake Champlain*. Journal of the American Water Resources Association, 45(1), 45-57
- Phillips, P.J., Chalmers, A.T., Gray, J.L., Kolpin, D.W., Foreman, W.T. and Wall, G.R. (2012). *Combined sewer overflows: an environmental source of hormones and wastewater pollutants*. Environ. Sci. Technol. 46, 5336-5343
- Regnery, J. and Püttmann, W. (2010). *Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany*. Water Research 44, 4097-4104
- Wetzel, R.G. (2001). *Limnology – Lake and River Ecosystems*. Elsevier Academic Press, 1006 p.
- Zeng, E.Y., Tran, K. and Young, D. (2004). *Evaluation of potential molecular markers for urban stormwater runoff*. Environmental Monitoring and Assessment 90, 23-43.
- Zgheib, S., Moilleron, R., Saad, M. and Chebbo, G. (2011). *Partition of pollution between dissolved and particulate phases: What about emerging substances in urban stormwater catchments?* Water Research 45, 913-925
- Zhang, Y., Geißen S-U. and Gal, C. (2008). *Carbamazepine and diclofenac: Removal in wastewater treatment plants and occurrence in water bodies*. Chemosphere 73: 1151-1161
- Zuccato, E., Castiglioni, S., Bagnati, R. Melis, M. and Fanelli, R. (2010). *Source, occurrence and fate of antibiotics in the Italian aquatic environment*. Journal of Hazardous Materials 179, 1042-1048