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Concentrations of dissolved herbicides and pharmaceuticals in a small river in Luxembourg

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Abstract Urban and agricultural areas affect the hydraulic patterns as well as the water quality of receiving drainage systems, especially of catchments smaller than 50 km^2. Urban runoff is prone to contamination due to pollutants like pesticides or pharmaceuticals. Agricultural areas are possible sources of nutrient and herbicide contamination for receiving water bodies. The pollution is derived from leaching by subsurface flow, as well as wash-off and erosion caused by surface runoff. In the Luxembourgish Mess River catchment, the pharmaceutical and pesticide concentrations are comparable with those detected by other authors in different river systems worldwide. Some investigated pesticide concentrations infringe current regulations. The maximum allowable concentration for diuron of 1.8 $\mu g\ l^{-1}$ is exceeded fourfold by measured 7.41 $\mu g\ l^{-1}$ in a flood event. The load of dissolved pesticides reaching the stream gauge is primarily determined by the amount applied to the surfaces within the catchment area. Storm water runoff from urban areas causes short-lived but high-pollutant concentrations and moderate loads, whereas moderate concentrations and high loads are representative for agricultural inputs to the drainage system. Dissolved herbicides, sulfonamides, tetracyclines, analgesics and hormones can be used as indicators to investigate runoff generation processes, including inputs from anthropogenic sources. The measurements prove that the influence of kinematic wave effects on the relationship between hydrograph and chemographs should not be neglected in smaller basins. The time lag shows that it is not possible to connect analysed substances of defined samples to the corresponding section of the hydrograph.

Keywords Flood events · Luxembourg · Pesticides · Pharmaceuticals · Surface water · Water pollution

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Introduction and objectives

Different flows originating from agricultural land, settlement areas and affiliated infrastructures negatively affect especially the storm water runoff of receiving water bodies. The hydraulic and chemical consequences depend on specific source and regional catchment conditions. In this context,

the ever-increasing amount of impervious and compacted surfaces in central Europe leads to faster runoff and larger storm water discharges in affected drainage systems. Especially catchments smaller than 50 km^2 are influenced by anthropogenic activities and contamination from different pollutant sources. Primarily urban and agricultural areas affect the hydraulic patterns, as well as the water quality, of receiving drainage systems. Urban runoff is prone to contamination due to wash-off from urban surfaces (e.g., facades/roof protection pesticides, garden/roadside weed removal herbicides, pharmaceuticals), as well as erosion in the sewer system. Furthermore, agricultural areas are possible sources of contamination for receiving water bodies (nutrients, pesticides, etc.). The pollution is derived from leaching by subsurface flow, as well as wash-off and erosion caused by surface runoff. Hydro-meteorological conditions, agricultural activities, rainwater management practices, as well as affiliated manmade structures induce differences in the sequences of discharge (hydrographs) and chemical composition (chemographs) of storm water runoff, as do relocation and erosion within the watercourse, exchanges and solution processes (e.g., with near groundwater) and the kinematic wave effect. The interactions of varying sources and processes within the watershed are intricated within flood events and always result in different hydro- and chemographs.

On one hand, this study investigates a multitude of pharmaceuticals and pesticides, with the objective of obtaining an overview of average and top-level pollution concentrations at the small Mess catchment in Southwestern Luxembourg. In this context, the observation of flood events is important, because analyses carried out during baseflow conditions can lead to a strong underestimation of real concentrations and related fluxes. On the other hand, dissolved pesticides and pharmaceuticals are used as indicators to investigate runoff generation processes, including inputs from anthropogenic sources. For the final investigation of the structure and composition of flood events, with regard to discharge components in a high temporal resolution, further effects of channel processes such as first flush and kinematic wave effects are discussed.

State of the art

Urban storm waters are mostly characterised by short, quick and high discharges (Chang 2007; Diaz-Fierros et al. 2002; White and Greer 2006). Rainwater management practices differentiate between combined and separated sewer systems, both of which can be completed by retention measures. In consideration of discharge limitations, especially in combined sewer systems, the precipitation intensity is a key factor for combined sewer overflows (CSO). Generally, directly connected systems have a strong impact on the receiving water body (Hatt et al. 2004; Lee and Bang 2000; Marsalek et al. 1993).

During the last years, the analytical techniques have been significantly improved so that xenobiotics can now be detected in surface water, drinking water reservoirs, or in groundwater in the range of some nanogram per liter. The input pathways of those substances into our environment vary, but in most cases, dissolved pharmaceuticals reach the surface water via treated or untreated sewage discharge either. A large number of xenobiotics, including sulfonamides (sulfathiazole, sulfamethoxazole, sulfadimethoxine, sulfamethazine), tetracyclines (chlortetracycline, oxytetracycline, tetracycline), analgesics (ibuprofen, diclofenac), alkylphenolic compounds (4-nonylphenol, 4-tert-octylphenol, nonylphenol monoethoxylate, nonylphenol diethoxylate) and hormones (estrone, 17β-estradiol, 17α-ethinylestradiol) is detected (Davi and Gnudi 1999; Hernández et al. 2007; Kolpin et al. 2002; Renew and Huang 2004). Pesticides are also known to be present in many environmental compartments, including sediments, groundwater and surface water. Besides agricultural applications, various herbicides are used in the urban environment e.g. facades and roof protection, garden and roadside weed removal (Blanchoud et al. 2004; Botta et al. 2009; Leu et al. 2005; Skark et al. 2004; Wittmer et al. 2010). Sometimes the diffuse pesticides input from urban areas via CSO exceeds the annual load of point source emissions by water treatment plants (Taebi and Droste 2004).

The main sources contributing to contamination of urban storm water runoff are the application of plant protectants on urban surfaces, wet

and dry deposition of contaminants from the atmosphere and pollutant allocation from road traffic (Gilbert and Clausen 2006; Greenstein et al. 2004; Kim et al. 2006; Leu et al. 2005). The wash-off effect from contaminated surfaces and the following runoff concentration and in most cases its direct discharging by channels or pipes often leads to high concentrations in urban storm water runoff (Gnecco et al. 2005; Krein et al. 2007; Van Metre and Mahler 2003). Moreover, event-based and seasonal first flush effects intensify the pollutant concentrations significantly (Barco et al. 2008; Deletic 1998; Lee et al. 2004; Robson et al. 2006; Tiefenthaler et al. 2008; Wittmer et al. 2010). The impact of event-based first flush effects is grave especially for receiving waters, which are influenced by rainwater management systems without retention measures. Further contamination results from the erosion of deposits inside of pipes. This process, as well as mixing with domestic wastewater, is crucial for the additional contamination of rainwater runoff in combined sewers (Gromaire et al. 2001; Kafi-Benyahia et al. 2005; Schriewer et al. 2008). The urban storm water runoff impacts from several sources differ due to the varying discharge generation and affiliated area's structure. The composition of urban storm water however is lesser affected by general land-use type, excluding industrial areas (Asaf et al. 2004; Lee and Bang 2000).

In contrast to urban areas, the water pathways of agricultural land are mostly characterised by subsurface runoff, deep percolation and evaporation. The formation of surface runoff within storm events is possible as well and depends on the runoff connection to the drainage system as well as surface and bedrock conditions (Chapman et al. 2001; Deasy et al. 2009; Elrashidi et al. 2005). The greater proportion of ground and soil water, of flood waves from agricultural areas, lead to elongated peaks, with a lower maximum and smaller event discharge.

Due to the usage of pharmaceuticals in animal husbandry and the application of pesticides and fertilisers, these compounds are often present in agricultural areas. These substances and their metabolites could affect natural drainage systems. The leaching is a possible pathway under dry weather conditions, whereas wash-off and erosion effects occur only under wet weather conditions. The increase of subsurface flow and the occurrence of surface runoff within storm events could lead to a relevant concentration increase of pesticides, nutrients and pharmaceuticals in the receiving water body (Freitas et al. 2008; Heberer 2002; Kay et al. 2004; Li et al. 2008; Ng et al. 1995; Pailler et al. 2009a, b; Poor and McDonnell 2007).

Processes occurring within the watercourse, such as relocation and erosion, as well as exchange and solution processes (e.g. with near groundwater), represent further diffuse sources of chemicals. The kinematic wave effect influences the relationship between discharge and chemical load, leading to important time lags between hydro- and chemographs, as well as suspended sediments, even in small catchments (Chapman et al. 1993; Krein and DeSutter 2001; Kurtenbach et al. 2006). Antecedent conditions, as well as sources and processes mentioned above inside the watershed are intricate within flood events and induce differences in the sequence of discharge and in chemical composition of storm water.

Area under investigation

Luxembourg is divided into two natural regions, the Oesling in the north (225–559 m above sea level) and the Gutland in the south (140–440 m above sea level). Hydrological measurements are conducted in the small Mess catchment in the southwestern part of Luxembourg. It is located in the Gutland region, which is characterised by a cuesta landscape where large gentile sloped valleys occur on marly substrates, contrasting with the deeply cut Luxembourg sandstone. The basin has a total surface area of 32.5 km^2 at the stream gauge. Marls and sandy marls of the sedimentary Paris basin dominate the lithology (93% Lias bedrock, 7% alluvials near the stream network). The marly bedrock is considered as being mostly impermeable. Luvisoils, pelosoils, planosoils, fluvisoils and gleysoils are dominating, with a silty–clayey to clayey texture. The land use in the basin consists of grassland (58%) and arable land (22.7%); forest is about 9.7%, urban and industrial areas amount to 8.7%, 2.3% contain the road and rail network (Fig. 1). The most

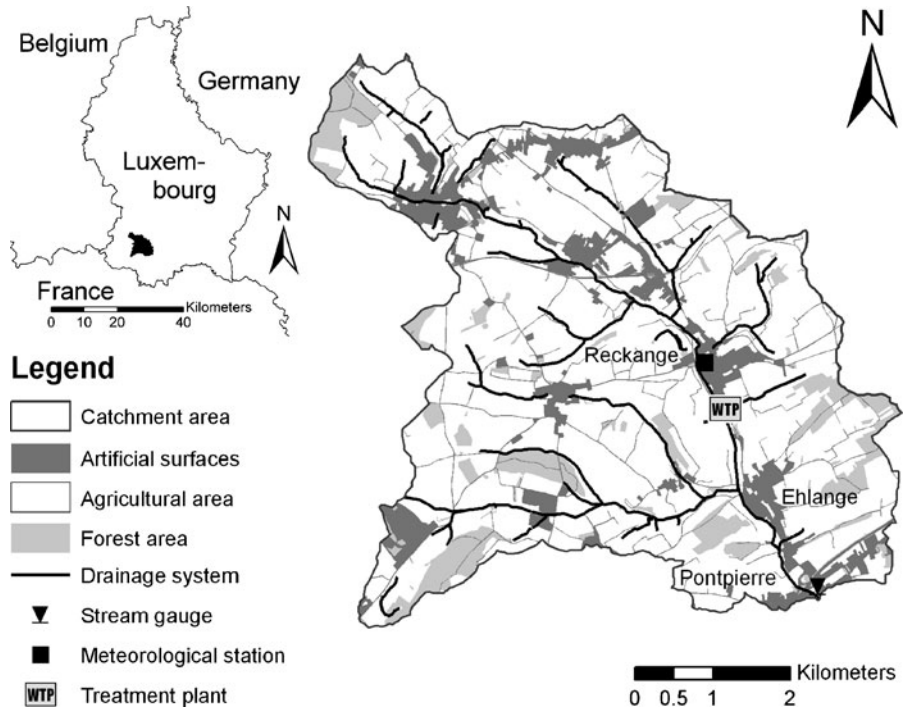

Fig. 1 Area under investigation

widespread crops are maize, colza and winter wheat. Runoff from several roads, effluents from small industries and untreated wastewaters from solitary farms and storm drainages of the combined sewer system influence river water quality. A mechanical–biological sewage water treatment plant is located in the small village of Reckange. This purification plant is connected with 3,500 inhabitants (340,000 m^3 sewage per year). Housing areas are drained by a combined sewage water system with several storm-control reservoirs.

By passing above the Ardennes massif, the dominating westerly atmospheric fluxes cause annual rainfall totals in Luxembourg exceeding 900 mm. December, January and February are the wettest months (more than 100 mm), while April, August and September are the driest months (less than 70 mm) on average. January is the coldest month (0°C) and July the warmest month (16.9°C). Monthly potential evapotranspiration values vary from 81.8 mm in July to 13.5 mm in December (Local station, 1971–2000). The runoff regime is of pluvial oceanic unimodal type, with high runoff occurring during winter (maximum runoff in February) and low runoff occurring in summer (minimum runoff in September). A meteorological station of the 'Administration des services techniques de l'Agriculture' (Agriculture Administration) is recording the most important hydro-climatological parameters, such as air temperature and humidity (both in 2 m above ground). Rainfall (1 m above ground) is measured in ten minutes intervals with a heated tipping bucket rain gauge (Lambrecht 15188). This station is located about three kilometres north of our stream gauge in the center of the catchment area.

The stream gauge (ISCO 4120 flow logger, pressure probe) in the village of Pontpierre registers 15-minute average water levels. Discharge is obtained with level-to-flow conversions applying the Manning equation. In parallel, conductivity is automatically registered in 10-min intervals (WTW 3310). The mean discharge of the Mess was of 261 l s^{-1} in the year 2008, with a specific runoff of 8 l s^{-1} km^{-2}. During the same year a total of 253 of 804 mm rainfall had been transformed into discharge. In summer, multi-peaked flood waves, which can be traced to consecutive contributions of tributaries and the rainfall patterns, are characteristic in the catchment. Especially

thunderstorms produce runoff events characteristic of a steep gradient and a relatively short outlet. Precipitation events of very small intensities and amount are indicated by small discharge peaks, which result predominantly from the runoff from impervious surface areas. The long-lasting, low intensity winter precipitation events cause singular broad discharge maxima, which are primarily composed of laterally flowing soil water and groundwater. In the Mess basin, during winter runoff events, the largest dilution mostly occurs some hours before the discharge maximum. This dilution is mainly induced by rainwater runoff from paved surface areas like streets or roofage. Furthermore, the spillways of the sewage system storm water retention basins and the sewage water treatment plant deliver larger volumes of rainwater and high quantities of diluted sewerage water.

Sampling

Two ISCO autosamplers with 2-l glass bottles (24 bottles, non-cooled) were connected to the flow logger in order to trigger the sampling after a fixed water level is reached. Subsequently, sampling is performed at different intervals throughout the duration of the investigated events. Every sample is a spot sample and not a composite one, collected during a certain time span. A representative selection of samples has been chosen for analysis selected according to discharge and electrical conductivity (WTW 197i conductivity meter) or water colour. In total, between October 2006 and January 2010, 29 flood events were analysed with respect to nitrate–nitrogen (NO_3–N), nitrite–nitrogen (NO_2–N), chloride (Cl^-) and sulphate (SO_4^{2-}). Fourteen of these floods were additionally investigated concerning dissolved pharmaceuticals or pesticides. During base-flow conditions, grab samples were taken by hand in brown glass bottles to investigate low flow conditions before and after the flood events under investigation. In addition to the sampling described above, during March 2007 and January 2010, 36 samples were taken from the outflow of the local sewage water treatment plant of Reckange. All samples were stored at 4°C in the dark and processed immediately as described below. Concentrations of Cl^-, NO_2–N, SO_4^{2-} and NO_3–N were determined by ion chromatography (Dionex DX-500).

This investigation focuses on the analysis of four classes of veterinary and human pharmaceuticals (sulfonamides, tetracyclines, analgesics and hormones). The 12 selected pharmaceuticals include four sulfonamides (sulfathiazole, sulfamethoxazole, sulfadimethoxine and sulfamethazine), three tetracyclines (chlortetracycline, tetracycline and oxytetracycline), two analgesics (ibuprofen and diclofenac) and three hormones (estrone, ß-estradiol and 17-α-ethinylestradiol). In addition, the two degradation compounds sulfamethazine-N4-acetyl and 4′-hydroxy-diclofenac are under investigation. Furthermore, 19 herbicides belonging to various chemical classes (phenylureas, chlorotriazines, triazinones, organophosphorus and chloroacetanilides) were analysed. The phenylureas are isoproturon, diuron, linuron, metoxuron, chlorotoluron, monolinuron, metabenzthiazuron and metobromuron. From the triazines group atrazine, simazine, desethylatrazine (DEA), terbutylazine, cyanazine and sebutylazine were investigated. Considered organophosphorus herbicides are glyphosate and its main metabolite aminomethylphosphonic acid (AMPA). Metazachlor and metolachlor were chosen from the chloroacetanilide herbicide group.

Sample preparation and extraction

Surface water and wastewater were successively filtered through 3- and 1-µm glass fibre filters (Pall Corporation, Ann Arbor, USA) to eliminate the coarse suspended matter and then filtered through 0.45 µm cellulose acetate filters (Sartorius, Göttingen, Germany). For the extraction of the pharmaceuticals, the 2 l samples were acidified to pH 4 with diluted sulphuric acid solution (25%). Afterwards, 3 ml of Na_2-EDTA 0.5 M were added per liter of water and extracted in the following 24 to 48 h to minimise degradation (Choi et al. 2007; Verma et al. 2007). All target compounds were concentrated by Solid-Phase Extraction (SPE) on polymeric cartridges (Waters Oasis® HLB, 200 mg, 6 mL) using an automated SPE workstation (Caliper Autotrace, Teralfene,

Belgium). One liter of the samples was loaded on 200 mg–6 ml HLB at 10 ml min^{-1}. The sorbents were previously conditioned using 5 ml of methanol and 5 ml of Milli-Q water at pH 4. After sample loading, the cartridges were rinsed with 5% of methanol in water (5 ml) and dried with a stream of N_2 for 15 min. The selected compounds were eluted using methanol (2 × 5 ml). Extracts were concentrated with a gentle stream of N_2 and redissolved in 1 ml of a water/acetonitrile 75/25 (v/v) mixtures before HPLC injection.

With the exception of glyphosate and AMPA, all of the above-mentioned pesticides were analysed by on-line solid-phase extraction coupled with liquid chromatography and tandem mass spectrometry. Filtered water samples were acidified by 0.1% formic acid and spiked with labelled atrazine as an internal standard. The pre-concentration of pesticides was obtained by pumping 10 ml of sample through a Dionex NG1 guard cartridge at a flow rate of 1 ml min^{-1}, with a Dionex AS-HV high-volume autosampler and an LPG 3000 gradient pump. The analytes were then eluted and separated by reverse-phase HPLC on a Dionex Ultimate 3000 system with an HPG-3200 binary high-pressure gradient pump, a WPS-3000 autosampler and a TCC-3100 thermal compartment.

Due to their specific chemical properties, glyphosate and its main metabolite AMPA were analysed by derivatisation with Fluorenylmethyloxycarbonyl chloride (FMOC-Cl), off-line SPE and LC-MS/MS. The derivatisation was obtained by adding 5 ml of Borate buffer (120 mM) and 7 ml of FMOC-Cl solution (2.5 mM in acetonitrile) to 50 ml of filtered sample in a 100-ml glass bottle. The mixture was left to react overnight at room temperature, then the derivatisation was stopped by adding 0.5 ml of concentrated phosphoric acid. After a dilution with DI-water, the derivatised analytes were extracted by automated off-line SPE on Waters Oasis HLB cartridges, using the above-mentioned Caliper Autotrace SPE Workstation.

LC/MS–MS analysis

The chromatographic system consisted of an Ultimate 3000 Intelligent LC system (Dionex, Sunnyvale, USA) with a binary high-pressure gradient pump HPG-3200, an automatic injector WPS-3000 and a column oven TCC-3100. For the analysis of the pharmaceuticals and hormones, the chromatographic column was a NUCLEODUR C18 GRAVITY column, 125 × 2 mm internal diameter, 3 μm particle size (Macherey Nagel, Düren, Germany). The MS–MS analyser consisted of a triple quadrupole mass spectrometer API 3200 (Applied Biosystem/MDS Sciex, Rotterdam, The Netherlands) equipped with a Turbo Ion Spray interface (Electrospray). N_2 was used as nebuliser, curtain and collision gas. Sulfonamides, tetracyclines and diclofenac were analysed in positive electrospray ionisation mode (+ESI) while estrogens and ibuprofen were analysed separately in negative electrospray ionisation mode (−ESI). The API 3200 triple quadrupole mass spectrometer was running under Multiple Reaction Monitoring mode (MRM) for increased sensitivity, with two MRM transitions for each molecule for improved selectivity. Optimal conditions were chosen in each mode. Each compound was analysed separately by flow injection analysis, in positive and negative mode, to find the optimum parameters (voltages and gas flows) for maximum intensities. Calibration curves ranging from 1 to 100 ng ml^{-1} were used to quantify the xenobiotics. After the final calculation the majority of the substances were successfully quantified at 1 ng l^{-1} except for E2 (3 ng l^{-1}) and EE2 (6 ng l^{-1}). The choice of a single extraction method on HLB cartridges was a compromise between recovery of extraction and the ease of the method. Our method led to efficient recoveries for sulfonamides (75–85%), analgesics (80–95%) and hormones (80–90%). The recovery of tetracycline group was sufficient. For the pesticides, the analytical column was a Dionex Acclaim C18 (2 × 100 mm, 3 μm particle size) and the mobile phase was a gradient of water and acetonitrile, both containing 0.1% formic acid. The column temperature was 40°C and the flow rate was 250 μl min^{-1}. The detection and quantification were achieved by positive electrospray MS/MS in Multiple Reaction Monitoring (MRM) mode. Each compound was detected and confirmed by two MRM transitions. The FMOC derivatives were quantified by reverse-phase chromatography

coupled to a triple quadrupole. The analytical column was a Macherey-Nagel Nucleodur Gravity C18 and the mobile phase was a gradient of ACN and 10 mM ammonium acetate. The oven temperature was set at 40°C, and the flow rate was 250 µl min^{-1}. The detection was achieved in negative electrospray mode, using two transitions for each compound. For the pesticides, the limit of quantification is 1 ng l^{-1}.

Results

Concentrations of dissolved pharmaceuticals and herbicides

The development of risk assessment methods in order to propose management tools demands detailed understanding of contaminant concentrations and fluxes. Table 1 illustrates the concentrations of the dissolved veterinary and human pharmaceuticals measured in 14 flood events between May 2007 and October 2009 in the Mess River catchment. The pharmaceutical concentrations are comparable with those detected by other authors in different river systems. In the Mess River, the highest concentrations are measured for ibuprofen (2,383 ng l^{-1}), sulfamethoxazole (118 ng l^{-1}), estrone (89 ng l^{-1}) and diclofenac (45 ng l^{-1}) with its metabolite 4′-hydroxy-diclofenac (49 ng l^{-1}). From the tetracycline group, chlortetracycline (25 ng l^{-1}), tetracycline (17 ng l^{-1}) and oxytetracycline (9 ng l^{-1}) are of relevance.

Despite usage restrictions and the banishment of different toxic compounds, pesticides still represent an issue in water pollution. For the EU-wide banned atrazine, the measured maximum is 118 ng l^{-1} (Table 2). All samples had atrazine concentrations well above the LOQ of 1 ng l^{-1} indicating recent use of this herbicide. Due to their broad application fields, determining the main origin of pesticides found in water streams is not always easy. Glyphosate (6,220 ng l^{-1}), AMPA (1,118 ng l^{-1}), diuron (7,410 ng l^{-1}), terbutylazine (4,038 ng l^{-1}) and metolachlor (1,140 ng l^{-1}) were the pesticides found in the highest concentrations during flood events in the Mess River. Metoxuron, cyanazine, hexazinone, sebutylazine and monolinuron have not been detected in the investigated flood events. According to Skark et al. (2004) the occurrence of herbicides such as chlortoluron, isoproturon and terbutylazine in surface water is due to agricultural application. In Luxembourg, terbutylazine and metolachlor are used in the production of maize, rape, turnip and cabbage. Isoproturon is mainly applied in the cultivation of grain. The occurrence of diuron (house paint and antifouling) and glyphosate (fruit, vegetable, not cultivated land, private gardens, parks and public areas) primarily results from their use in settlement areas. A snapshot sampling in different catchments all over the country supports these assumptions (results not shown, Guignard et al. 2009). Corresponding distribution patterns appeared to be significantly different depending on the land-use of the river catchments. Glyphosate and AMPA were found in higher concentrations in urban basins, whereas terbutylazine, metolachlor, atrazine and DEA were prominent in rural zones. In addition, Table 2 illustrates that the pesticide concentrations in the Mess are in the same range than those detected in other river systems.

Chemographs of dissolved pharmaceuticals during flood events

Chemographs display the concentrations of different variables as a function of time. The time series of xenobiotic concentrations are plotted in parallel to the hydrograph and the precipitation data. This aims to classify the chemographs and hydrographs based on their structure. Krein and Symader (2000) as well as Kurtenbach and Krein (2007) or Pailler et al. (2009a, b) illustrate different examples of this technique. Figure 2 shows the hydrograph and chemographs of selected dissolved pharmaceuticals during the flood event on August 25th 2009 in the Mess River basin. The first discharge peak at 8 A.M. consists of runoff from the area at the vicinity of the stream gauge mainly from the major roads and from the local combined sewer system. Wastewater components are activated but the concentrations of dissolved pharmaceuticals stay comparatively low. The main discharge peak at 9 A.M. originates from the village of Reckange, its combined sewer

Table 1 Measured concentrations of selected dissolved pharmaceuticals in 14 flood events between May 2007 and October 2009 in comparison to other studies, detection limits and limits of quantification

Substance	*n*	*n* (>LOQ)	Maximum value ($ng\,l^{-1}$)	Mean (n > LOQ) ($ng\,l^{-1}$)	St. dev. (n > LOQ) ($ng\,l^{-1}$)	Detection limit ($ng\,l^{-1}$)	Limit of quantification ($ng\,l^{-1}$)	Maximum values of other surface water studies ($ng\,l^{-1}$)
Ibuprofen	87	87	2,383	89	259	0.3	1	2,010[i], 370[e], 150[c], 200[d]
Estrone	99	55	89	8	13	0.3	1	12[h], 4[g], 3[a]
Diclofenac	75	51	45	7	9	0.3	1	8[i], 60[c], 380[d]
Sulfamethoxazole	75	45	118	24	31	0.3	1	20[i], 2[e], 5[c], 0[k], 80[f]
Tetracycline	75	40	17	4	3	0.3	1	20[f]
4′-hydroxy-diclofenac	33	31	49	21	14	0.3	1	800[j]
Sulfamethazine	75	25	19	8	4	0.3	1	0[f]
Oxytetracycline	75	22	9	4	2	0.3	1	10[f]
β-Estradiol	99	9	6	4	1	1	3	6[h], 6[b], 4[g], 3[a]
Sulfathiazole	75	7	5	2	1	0.3	1	10[f]
Chlortetracycline	75	6	25	11	10	0.3	1	40[f]
17-α-Ethinylestradiol	99	1	6	6	–	2	6	1[h], 0[k], 5[g], 3[a]
Sulfamethazine-N4-acetyl	33	0	–	–	–	0.3	1	
Sulfadimethoxine	75	0	–	–	–	0.3	1	40[f]

LOQ limit of quantification

[a]Vonbank et al. (2004), Seine, France

[b]Dorabawila and Gupta (2005), Maryland Rivers, USA

[c]Gros et al. (2006), Ebro River, Spain

[d]Heberer (2002), Berlin groundwater next to polluted surface water, Germany

[e]Kasprzyk-Hordern et al. (2008), Taff River, UK

[f]Kim and Carlson (2007), Cache la Poudre River, Colorado, USA

[g]Kuch and Ballschmiter (2001), River Water South Germany

[h]Laganà et al. (2004), Tiber River, Italy

[i]Roberts et al. (2006), Tyne River, UK

[j]Scheurell et al. (2009), Karachi river water, Pakistan

[k]Zuccato et al. (2005), Po River, Italy

Table 2 Measured concentrations of selected dissolved herbicides in three flood events from May/June 2008 in comparison to other studies, detection limits and limits of quantification

Substance	*n*	*n* (>LOQ)	Maximum value ($ng\ l^{-1}$)	Mean (n > LOQ) ($ng\ l^{-1}$)	St. dev. (n > LOQ) ($ng\ l^{-1}$)	Detection limit ($ng\ l^{-1}$)	Limit of quantification ($ng\ l^{-1}$)	Maximum values of other surface water studies ($ng\ l^{-1}$)
Glyphosate	28	28	6,220	1,650	1,638	0.5	1	820[c]
Diuron	19	19	7,410	683	1,652	0.5	1	310[a], 1,600[b]
AMPA	28	28	1,118	599	293	0.5	1	1,423[c]
Terbutylazine	28	28	4,038	519	1,073	0.5	1	570[a], 2000[d], 240[g]
Metolachlor	28	28	1,140	251	340	0.5	1	6,700[f], 270[g]
Metabenzthiazuron	28	28	990	96	222	0.5	1	
Isoproturon	28	28	1,040	74	195	0.5	1	7,800[a], 0[b], 2,000[d]
Atrazine	28	28	118	9	22	0.5	1	10,100[a], 0[b], 9,300[d], 630[e], 14,170[f], 410[g]
Linuron	28	10	20	9	6	0.5	1	1,800[d]
Simazine	28	17	38	9	11	0.5	1	0[b],300[d], 294[e], 310[g]
Metazachlor	28	27	35	7	7	0.5	1	5,100[d]
DEA	28	28	6	3	1	0.5	1	600[g]
Chlortoluron	28	4	3	2	1	0.5	1	
Metobromuron	28	1	2	2	–	0.5	1	
Cyanazine	28	0	–	–	–	0.5	1	2,800[d]
Hexazinon	28	0	–	–	–	0.5	1	
Metoxuron	28	0	–	–	–	0.5	1	
Monolinuron	28	0	–	–	–	0.5	1	
Sebutylazine	28	0	–	–	–	0.5	1	

LOQ limit of quantification

[a]Wittmer et al. (2010), Headwater catchment, Switzerland

[b]Gasperi et al. (2008), Combined sewer Paris, France

[c]Botta et al. (2009), Boële, France

[d]Kreuger (1999), Vemmenhög, Sweden

[e]Cerejeira et al. (2003), Tejo, Portugal

[f]Ng et al. (1995), Nissouri Creek, Canada

[g]Hildebrandt et al. (2008), Ebro basin, Spain

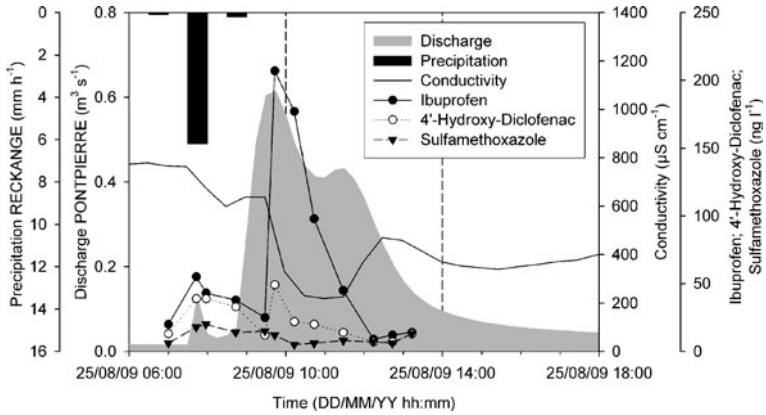

Fig. 2 Dissolved ibuprofen, 4′-hydroxy-diclofenac, sulfamethoxazole (all ng l^{-1}) and conductivity (µS cm^{-1}) measured during the flood event in the Mess River catchment on August 25th 2009

overflows and the local sewage water treatment plant. It appears that this section 3 km upstream of the gauging station flushes untreated wastewater (10 A.M.) via combined sewer overflows into the brook, contaminated with 4′-hydroxy-diclofenac (50 ng l^{-1}) and ibuprofen (200 ng l^{-1}). In parallel, the concentrations of the natural hormone estrone rise up to 10 ng l^{-1} (chemograph not shown). The 1-h lag time between the discharge maximum and the corresponding ibuprofen peak or the associated decline of electrical conductivity identify a kinematic wave effect.

Figure 3 shows the hydrograph and chemographs of selected dissolved pharmaceuticals during the flood event on August 2nd 2007 in the Mess River basin. At this point in time, due to higher precipitation intensities (max. 3.5 mm 10 min^{-1}) and rainfall amounts (8.4 mm), the first flush mobilises dissolved pharmaceuticals—mainly ibuprofen (70 ng l^{-1})—from the combined sewer system in the vicinity of the gauging station. The estrone peak (7 ng l^{-1}) and the first peak of NO_3–N (4 mg l^{-1}) in the rising limb at noon mark the inflow of water from the area of the village of Ehlange 2 km upstream of the stream gauge, its rural surroundings and from the western tributary of the Mess River. The second peak of ibuprofen (110 ng l^{-1}) 1 h after discharge maximum highlights the chemical signal from the settlement areas of the municipality of Reckange, similar to the signal in Fig. 2. In the falling limb at 6 P.M., stream water is primarily composed of laterally inflowing soil water with higher NO_3–N content (5 mg l^{-1}) (Elrashidi et al. 2005; Poor and McDonnell 2007) and higher concentrations of dissolved sulfamethoxazole and oxytetracycline (Pailler et al. 2009a). The environment may be exposed to veterinary medicines administered to livestock through the application of organic fertilisers, especially by slurry that is applied to the

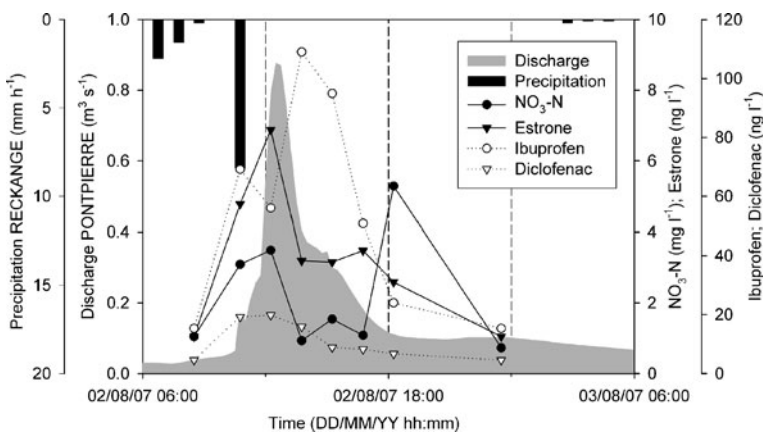

Fig. 3 Dissolved NO_3–N, estrone, ibuprofen and diclofenac measured during the flood event in the Mess River catchment on August 2nd 2007

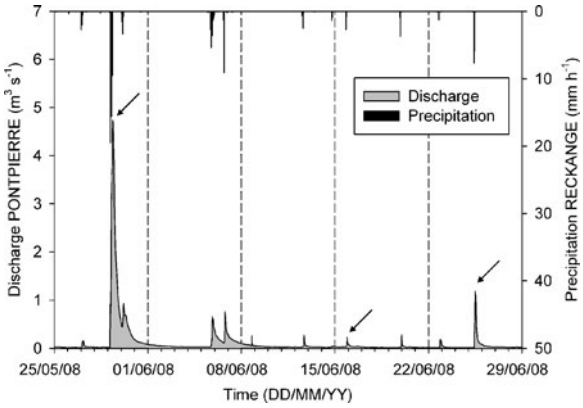

Fig. 4 Mess River hydrograph May/June 2008, three selected flood events marked with arrows

arable land. In this context, the drainage of clay soils—also characteristic for the Mess basin—has been identified as an important mechanism by which pollution of surface waters with oxytetracycline can occur (Kay et al. 2004; Li et al. 2008; Pailler et al. 2009a). The 1.5-h time lag between discharge maximum from the area of Reckange and its corresponding ibuprofen peak or the associated decline of NO_3–N illustrate a distinct kinematic wave effect.

Chemographs of dissolved herbicides during flood events

Several flood waves with different precipitation intensities and runoff ratios have been investigated and sampled in early summer 2008, a main application period of herbicides in the area under investigation. Three events have been selected according to different precipitation intensities for a further thorough analysis (Fig. 4). The following results in Figs. 5, 6 and 7 are presented in the order of increasing flood intensity.

The flood event of June 15th 2008 is characterised by low rainfall (3.5 mm), low precipitation intensities (max. 1.2 mm 10 min^{-1}) and a small

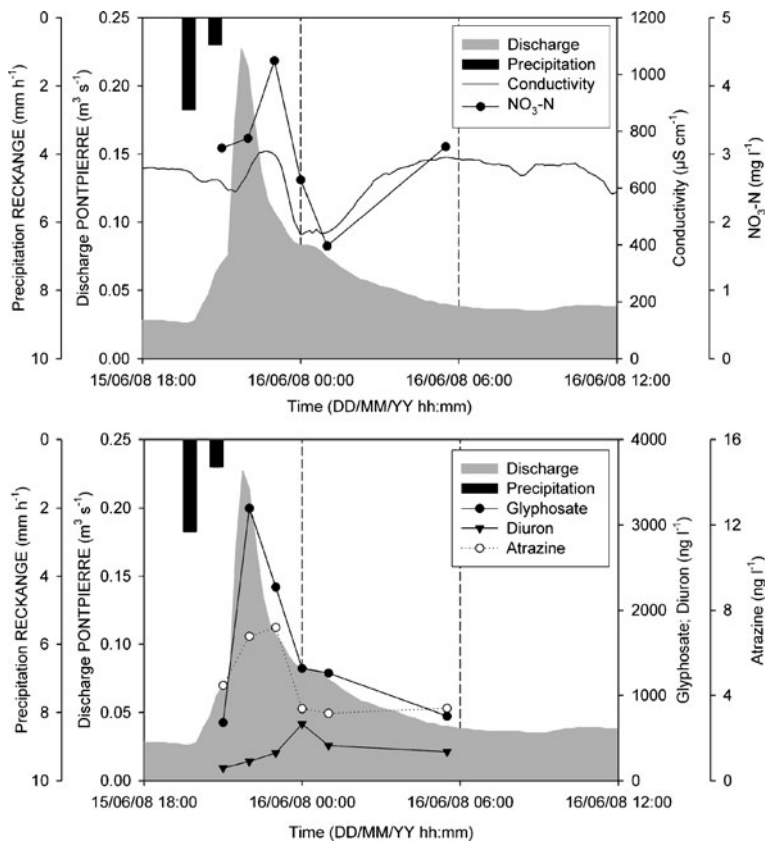

Fig. 5 Dissolved NO_3–N, glyphosate, diuron, atrazine and conductivity measured during the flood event in the Mess River catchment on June 15th 2008

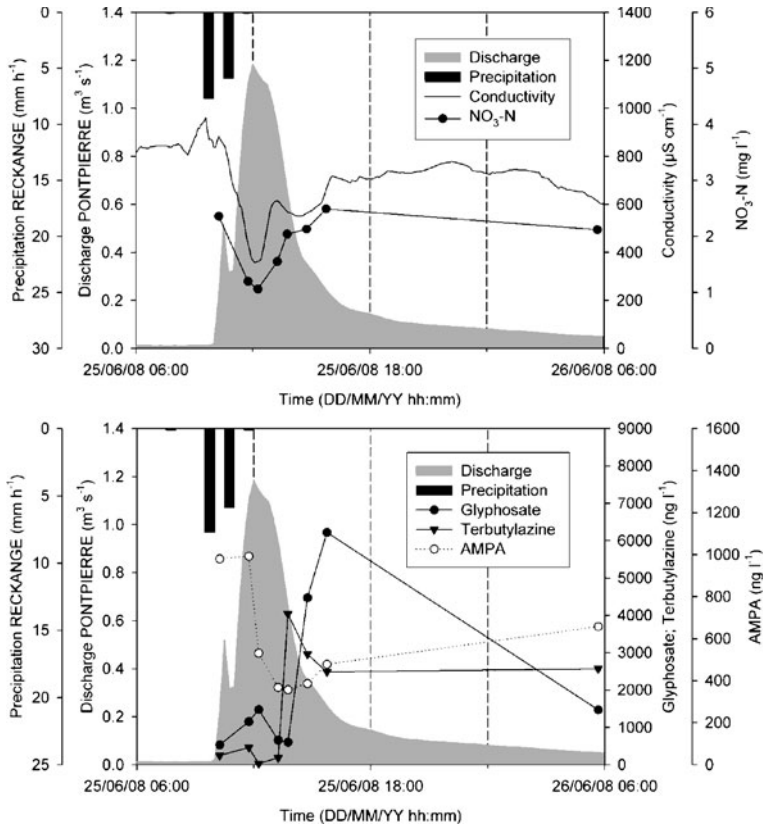

Fig. 6 Dissolved NO_3–N, glyphosate, terbuthylazine, AMPA and conductivity measured during the flood event in the Mess River catchment on June 25th 2008

runoff ratio (2.4%; Fig. 5). At 10 P.M., a single peak of dissolved glyphosate (3,000 ng l^{-1}) is observed, originating from the vicinity of the gauging station, including the motorway crossing the Mess River approximately 150 m upstream and the village of Pontpierre. The local department of highways, the municipal administrations and private house owners apply this herbicide for weed removal at roadsides. A peak of atrazine (8 ng l^{-1}) is registered 1 h later together with increasing NO_3–N (4.5 mg l^{-1}) and the maximum of a small conductivity peak. This runoff component from agricultural sources is followed by peaking diuron concentrations (700 ng l^{-1}) originating from runoff from the settlement area of Reckange. This peak goes in parallel with declining conductivity, indicating dilution with low mineralised rainwater, which is supposed to be flushed from impervious surfaces in the relevant village.

The flood event of June 25th 2008 (Fig. 6) is characterised by a higher rainfall (13.7 mm), higher precipitation intensities (4.3 mm 10 min^{-1}) and a higher runoff ratio (3.7%) than the first flood event on June 15th 2008. The first concentration peak of glyphosate (1,500 ng l^{-1}) at 12 A.M. originates from the vicinity of the stream gauge mainly from the town of Ehlange. Between the flood events on June 15th (Fig. 5) and June 25th (Fig. 6), pesticides have again been applied in the catchment area, which is indicated by a late distinct glyphosate peak (6,000 ng l^{-1}) in the falling limb (3 P.M.). AMPA shows a dilution curve in parallel to peaking discharge, but this concentration decrease is shifted 2 h after the discharge peak. The highest concentrations of terbutylazine (4,000 ng l^{-1}) are measured when AMPA exhibits the biggest dilution; this water mainly originates from the agricultural surroundings of Reckange.

The flood event of May 29th 2008 (Fig. 7) is characterised by the highest rainfall intensities (10.1 mm 10 min^{-1}) and the highest runoff ratio (9.6%) from the selected flood events. It shows a

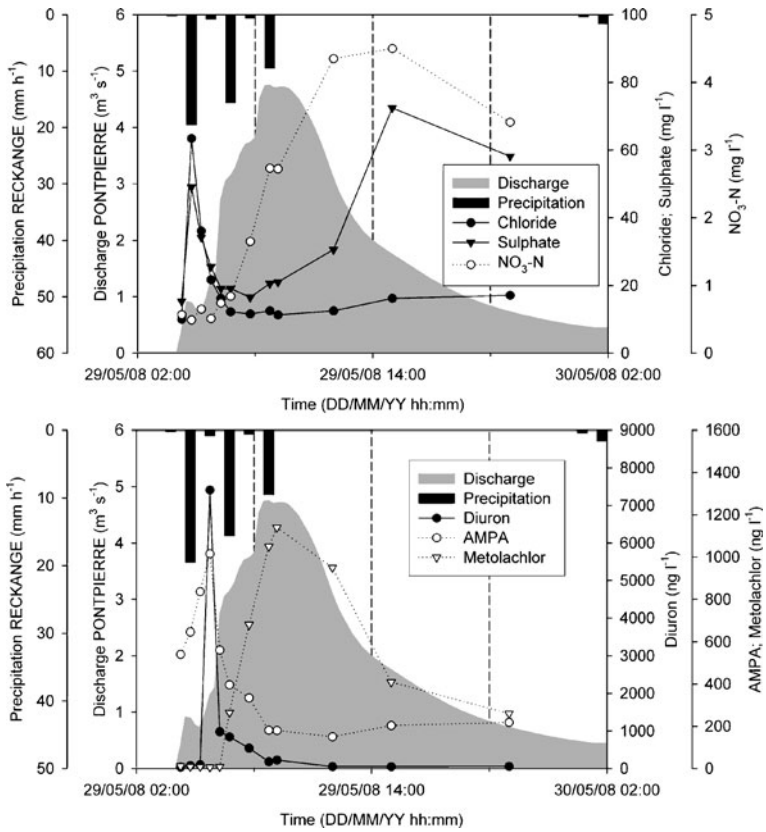

Fig. 7 Dissolved chloride, sulphate, NO_3–N, diuron, AMPA and metolachlor measured during a flood event in the Mess River catchment on May 29th 2008

clear succession of different runoff components. The first discharge originates from impervious areas near the stream gauge, shown by a first small discharge peak with high concentrations of dissolved chloride (flushed atmospheric deposition material), sulphate (weathering material) and glyphosate (5,075 ng l^{-1}, not shown). In the following rising limb, the sewer overflows of Reckange leads to high AMPA (1,100 ng l^{-1}) and diuron (7,000 ng l^{-1}) concentration peaks, which are diluted afterward by the main discharge peak. Simultaneously, isoproturon (1,040 ng l^{-1}) and atrazine (118 ng l^{-1}) concentrations rise. Some hours later, a further runoff component contains surface runoff from arable land highlighted by an increase of the metolachlor concentration up to 1,200 ng l^{-1}. A distinct NO_3–N curve indicates the soil water component followed by a late peak of dissolved sulphate representing the final groundwater component. Sulphate originates from gypsum layers and gypsum pockets incorporated in the local bedrock.

Substance loads and event mean concentrations

The load of different substances has been calculated by multiplying substance concentrations with corresponding discharge values. The load of a single flood is the total of these products and equals the area of the time series plotted against the multiplication results between discharge and substance concentration. The Event Mean Concentration (EMC) is a flow-weighted average of the constituent concentration. For an individual storm runoff event, it is defined as the total pollutant load divided by total runoff volume. Table 3 shows the loads and the EMC of different compounds calculated for the three flood events described in Fig 4. With increasing precipitation amount and intensity, the runoff ratio increases (2.4%, 3.6%, 9.8%). Nutrient loads and loads of sulphate and chloride exhibit a strong relationship to discharged volume. The EMC of chloride decreases with rising runoff ratios, which is an indication of the lower importance of surface

Table 3 Hydro-climatological characterisation, chemical loads and corresponding event-mean concentrations of three flood events in the Mess River catchment from May/June 2008

	15.6.2008		25.6.2008		29.5.2008	
Precipitation	Rainfall (mm)	Maximum intensity (mm 10 min^{-1})	Rainfall (mm)	Maximum intensity (mm 10 min^{-1})	Rainfall (mm)	Maximum intensity (mm 10 min^{-1})
	3.5	1.2	13.7	4.3	46.2	10.1
Discharge	Runoff (m^3)	Runoff ratio (%)	Runoff (m^3)	Runoff ratio (%)	Runoff (m^3)	Runoff ratio (%)
	2,700	2.4	15,000	3.6	147,000	9.8
Anions	Load (kg)	EMC (g m^{-3})	Load (kg)	EMC (g m^{-3})	Load (kg)	EMC (g m^{-3})
SO_4	134	50	606	40	6,063	41
Cl	97	36	350	23	2,149	15
NO_3-N	8	2.9	28	2	483	3
NO_2-N	0.4	0.1	2.6	0.2	12	0.1
Pesticides	Load (mg)	EMC (μg m^{-3})	Load (mg)	EMC (μg m^{-3})	Load (mg)	EMC (μg m^{-3})
Glyphosate	4,038	1,496	37,668	2,502	68,741	467
AMPA	2,068	764	9,182	610	33,792	230
Diuron	897	331	Not meas.	Not meas.	34,004	231
Metabenzthiazuron	261	96	569	38	57,711	392
Terbutylazine	258	95	23,277	1,546	2,658	18
Metolachlor	213	79	4,073	271	91,284	621
Isoproturon	56	21	253	17	7,951	54
Atrazine	12	4	84	6	949	6
Metazachlor	8	3	135	9	1,291	9
AMPA/Glyphosate ratio	0.51		0.24		0.49	

runoff from paved areas like rooftops or streets in stronger rainfall runoff events. On the contrary, NO_3–N exhibits the highest EMC in the biggest flood just as the EMC of metolachlor or isoproturon. This indicates a higher proportion of surface runoff from arable land and higher proportions of soil water in general. The EMCs for glyphosate and AMPA are elevated in smaller floods originating mainly from urban storm water runoff, running directly into the brook. High EMC values in this flood event of June 25th are caused by repeated applications of terbutylazine and glyphosate before the event. Furthermore, a smaller AMPA/glyphosate ratio is an indication for "fresh glyphosate sources" with only a small amount of AMPA as the relevant degradation compound. However, the study of Botta et al. (2009) suggests that sewage from domestic activities with cleaning agents are likely to be another source of AMPA. Here, further investigations are necessary. In total, the herbicide loads confirm the outcome of investigations by Skark et al. (2004) who concluded that non-agricultural pesticide use contributed more than two thirds of the whole observed pesticide load in the tributaries and at least one third in the River Ruhr.

Discussion

The results show that comparable to other studies (Wittmer et al. 2010; Pailler et al. 2009a), a distinct relationship between discharge and pollutant concentrations does not exist for pharmaceuticals or for pesticides. The variable dependence of xenobiotic concentrations to event specific conditions and processes is discussed in the following sections. Many studies have described the first flush phenomenon as a relatively high load of pollutants in the first part of runoff events (Hatt et al. 2004; Lee et al. 2002). In contrast, the kinematic wave effect (Chapman et al. 1993; Krein and DeSutter 2001; Kurtenbach et al. 2006) results in a postponement of pollutant loads in comparison to associated discharge. Lee and Bang (2000) concluded that the pollutant concentration peak occurs before the flow peak in watersheds with areas smaller than 100 ha, and the pollutant concentration peak is followed by the flow peak in the watersheds with areas larger than 100 ha. The investigation of first flush effects and kinematic wave effects is done by drawing the curve (Fig. 8) that gives the variation of the cumulative pollutant mass divided by the total pollutant mass (dimensionless cumulative pollutant mass) in relation to the cumulative volume divided by the total

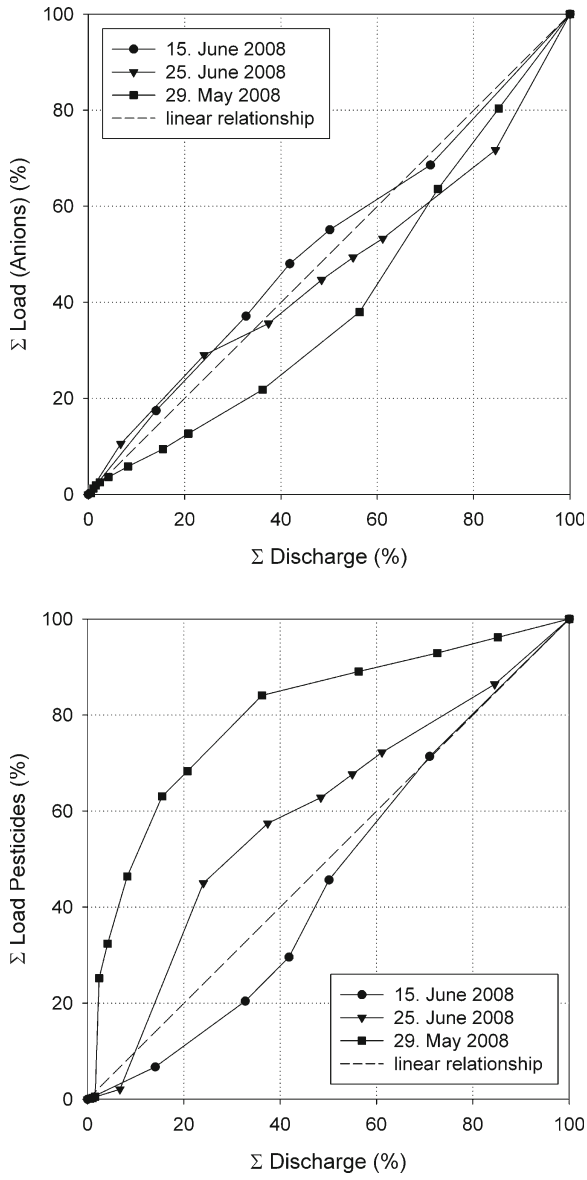

Fig. 8 Dimensionless cumulative runoff volume and runoff mass curves for measured anions (Chloride, NO_3–N, NO_2–N, Sulphate) and selected pesticides (isoproturon, atrazine and diuron) supposed to be flushed from impervious surfaces

volume (dimensionless cumulative runoff volume) (Bertrand-Krajewski et al. 1998).

If the concentration remains constant during the storm event, the pollutant mass is proportional to the volume and the double frequency cumulating curve follows the line of origin with a gradient of one (Line of Identity). If the data for a particular storm lies above this, a first flush is suggested. If the curve falls below the Line of Identity, the main substance load is observed coming after the discharge peak. This can be caused by the kinematic wave effect, the later arrival of compounds originating farer away from the gauging station or a late reaction of deeper soil or groundwater components. Figure 8 highlights that in the flood event with the lowest precipitation intensity, measured anions are not important and the curve goes along the Line of Identity. In the bigger events, the late soil water component with measured anions is more important. Therefore this line lies under the Line of Identity. In contrast, the cumulative load curves of the selected pesticides lay about this line. The maximum divergence was used as a measure of the magnitude of the first flush. A significant first flush was considered to have occurred in the biggest event on May 29th 2008. The presence of accumulated materials on the surfaces tends to be responsible for the first flush phenomenon of herbicides.

The results confirm the investigations by Skark et al. (2004), who concluded that pathways for pesticide input to the receiving waters were related to both, surface runoff and underground passage. Two thirds of the observed diuron load in the surface water resulted from an input by direct runoff. The corresponding spills cause high but short-lived concentration peaks. The authors interpreted this as a result of total pesticide application to impervious surfaces. As a consequence, the high corresponding concentrations in the tributary infringe current regulations and recommendations. The directive 2008/105/EC of the European Parliament and of the Council on Environmental Quality Standards in the field of water policy contains environmental quality standard parameters. The maximum allowable concentration for diuron of 1.8 $\mu g\ l^{-1}$ is exceeded fourfold by measured 7.41 $\mu g\, l^{-1}$ in the flood event of May 29th 2008. The determination of the impact of storm water runoff from settlement areas can greatly increase the predictive power of models of urban effects on water quality. In addition, the results show that like Hatt et al. (2004) demonstrated, very small proportions of impervious area are capable of increasing pollutant concentrations, as long as there is a direct connection between the impervious area and the corresponding stream. Consequently, the aim must be to break the direct linkage between the impervious areas and the receiving water.

Furthermore, it seems that for some compounds the antecedent conditions before flood events, such as precipitation quantities, results in an exhaustion of potential sources, so that less material is available to be washed off in subsequent events. Kim et al. (2006) and Krein and Schorer (2000) show similar results for dissolved and particle bound pollutants. An example is the short succession of the three thunderstorms with high precipitation amounts, which induced the flood event in the Mess River on May 29th 2008 (Fig. 7). Areas directly connected to the Mess River are flushed by the first event and the second and the third thunderstorms do not mobilise further dissolved diuron, AMPA or chloride. These compounds show distinct peaks after the first rainfall event and no reaction thereafter.

Conclusions

Overall, the pharmaceutical and pesticide concentrations in the Mess are comparable with those detected by other authors in different river systems. Some investigated pesticide concentrations in the tributary temporarily infringe current regulations.

The analysis of flood events using rainfall pattern, hydrograph and dissolved xenobiotic chemographs can provide a detailed insight into the temporal structure of flood events. However, the corresponding anthropogenic sources show a temporal and spatial variability, caused by different rainfall patterns and distributions as well as different characteristics (e.g. retention capacities) of the sewer systems. The discharge increase from anthropogenic sources is mainly brought about by overlandflow, the influx of surface water

from the road network, as well as from residential areas. It is difficult to postulate that recurring characteristics of the processes control the xenobiotics chemographs, due to highly variable anthropogenic factors. These are the changing amount of pharmaceutical consumption, sewage water treatment plant control programs, pesticide application dates and amounts, or the heterogeneous urban storm water runoff generation. Furthermore, hydraulic processes within current flood waves like kinematic wave effects influence the event structure e.g. time lags between discharge and dissolved loads. The load of dissolved pesticides reaching the stream gauge is primarily determined by the amount applied to the surfaces within the catchment area. In the Mess River catchment, a characteristic difference between urban and agricultural induced pollution by pesticides exists in the concentration/load relationship. Storm water runoff from urban areas causes short-lived but high-pollutant concentrations and moderate loads in the Mess River, whereas moderate concentrations and high loads are representative for agricultural inputs to the drainage system. Non-agricultural pesticides contribute to a large part to the observed pesticide loads in the Mess.

Generally, kinematic wave effect, accumulation, exchange, dilution and mixture processes modify the flood wave and its composition within the watercourse. The measurements prove that the influence of kinematic wave effects on the relationship between hydrograph and chemographs should not be neglected in smaller basins. The time lag shows that it is not always possible to connect analysed substances of defined samples to the corresponding section of the hydrograph. The different velocities indicate that after the substances have been transported over several hundred meters, there is no relationship between those parameters. Consequently, classification between discharge component and dissolved substances at the sampling points is impeded. These results highlight that simple rating curves between discharge and pollutant loads intended to calculate the total load by hydrographs are overly simple. At the Mess River, even the position of the gauging station is important, because the time lag between chemical signal and discharge increases over distance.

However, every flood event is unique due to variable rainfall characteristics, changing catchment conditions, as well as anthropogenic activities. The next step is the investigation of long lasting, low intensity winter precipitation events that cause singular broad discharge maxima, which are primarily composed of laterally flowing soil water and groundwater.

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References

Asaf, L., Nativ, R., Shain, D., Hassan, M., & Geyer, S. (2004). Controls on the chemical and isotopic compositions of urban stormwater in a semiarid zone. *Journal of Hydrology, 294*, 270–293.

Barco, J., Papiri, S., & Stenstrom, M. K. (2008). First flush in a combined sewer system. *Chemosphere, 71*, 827–833.

Bertrand-Krajewski, J. L., Chebbo, G., & Saget, A. (1998). Distribution of pollutant mass vs. volume in stormwater discharges and the first flush phenomenon. *Water Research, 32*, 2341–2356.

Blanchoud, H., Farrugia, F., & Mouchel, J. M. (2004). Pesticide uses and transfers in urbanised catchments. *Chemosphere, 55*, 905–913.

Botta, F., Lavison, G., Couturier, G., Alliot, F., Moreau-Guigon, E., Fauchon, N., et al. (2009). Transfer of glyphosate and its degradate AMPA to surface waters through urban sewerage systems. *Chemosphere, 77*, 133–139.

Cerejeira, M. J., Viana, P., Batista, S., Pereira, T., Silva, E., Valério, M. J., et al. (2003). Pesticides in Portuguese surface and ground waters. *Water Research, 37*, 1055–1063.

Chang, H. (2007). Comparative streamflow characteristics in urbanizing basins in the Portland metropolitan area, Oregon, USA. *Hydrological Processes, 21*, 211–222.

Chapman, A. S., Fostera, I. D. L., Leesa, J. A., Hodgkinson, R. A., & Jackson, R. H. (2001). Particulate phosphorus transport by sub-surface drainage from agricultural land in the UK. Environmental significance at the catchment and national scale. *The Science of the Total Environment, 266*, 95–102.

Chapman, P. J., Wheater, H. S., & Reynolds, B. (1993). The effect of geochemical reactions along flowpath on storm water chemistry in headwater catchments. In N. E. Peters, E. Hoehn, C. Leibundgut, N. Tase, & D. E. Walling (Eds.), *Tracers in hydrology* (pp. 11–35). Chichester: IAHS. IAHS 215.

Choi, K. J., Kim, S. G., Kim, C. W., & Kim, S. H. (2007). Determination of antibiotic compounds in water by on-line SPE-LC/MSD. *Chemosphere, 66*, 977–984.

Davi, M. L., & Gnudi, F. (1999). Phenolic compounds in surface water. *Water Research, 33*, 3213–3219.

Deasy, C., Brazier, R. E., Heathwaite, A. L., & Hodgkinson, R. (2009). Pathways of runoff and sediment transfer in small agricultural catchments. *Hydrological Processes, 23*, 1349–1358.

Deletic, A. (1998). The first flush load of urban surface runoff. *Water Research, 32*, 2462–2470.

Diaz-Fierros, F. T., Puerta, J., Suarez, J., & Diaz-Fierros, F. V. (2002). Contaminant loads of CSOs at the wastewater treatment plant of a city in NW Spain. *Urban Water, 4*, 291–299.

Dorabawila, N., & Gupta, G. (2005). Endocrine disrupter – estradiol – in Chesapeake Bay tributaries. *Journal of Hazardous Materials, A120*, 67–71.

Elrashidi, M. A., Mays, M. D., Peaslee, S. D., & Hooper, D. G. (2005). A technique to estimate nitrate-nitrogen loss by runoff and leaching for agricultural land, Lancaster County, Nebraska. *Communications in Soil Science and Plant Analysis, 35*, 2593–2615.

Freitas, L. G., Singer, H., Müller, S. R., Schwarzenbach, R. P., & Stamm, C. (2008). Source area effects on herbicide losses to surface waters—A case study in the Swiss Plateau. *Agriculture, Ecosystems & Environment, 128*, 177–184.

Gasperi, J., Garnaud, S., Rocher, V., & Moilleron, R. (2008). Priority pollutants in wastewater and combined sewer overflow. *Science of the Total Environment, 407*, 263–272.

Gilbert, J. K., & Clausen, J. C. (2006). Stormwater runoff quality and quantity from asphalt, paver, and crushed stone driveways in Connecticut. *Water Research, 40*, 826–832.

Gnecco, I., Berretta, C., Lanza, L. G., & La Babera, P. (2005). Storm water pollution in the urban environment of Genoa, Italy. *Atmospheric Research, 77*, 60–73.

Greenstein, D., Tiefenthaler, L., & Bay, S. (2004). Toxicity of parking lot runoff after application of simulated rainfall. *Archives of Environmental Contamination and Toxicology, 47*, 199–206.

Gromaire, M. C., Garnaud, S., Saad, M., & Chebbo, G. (2001). Contribution of different sources to the pollution of wet weather flows in combined sewers. *Water Research, 35*, 521–533.

Gros, M., Petrovic, M., & Barceló, D. (2006). Development of a multi-residue analytical methodology based on liquid chromatography-tandem mass spectrometry (LC-MS/MS) for screening and trace level determination of pharmaceuticals in surface and wastewaters. *Talanta, 70*, 678–690.

Guignard, C., Manfroi, L., Ziebel, J., Krein, A., & Hoffmann, L. (2009). Impact of land use on the occurrence and mobilisation of pesticides in surface water. In *12th international conference on chemistry and the environment, Poster contribution, Org P82*.

Hatt, B. E., Fletcher, T. D., Walch, C. J., & Taylor, S. L. (2004). The influence of urban density and drainage infrastructure on the concentrations and loads of pollutants in small streams. *Environmental Management, 34*, 112–124.

Heberer, T. (2002). Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data. *Toxicological Letters, 131*, 5–17.

Hernández, F., Sancho, J. V., Ibáñez, M., & Guerrero, C. (2007). Antibiotic residue determination in environmental waters by LC-MS. *Trends in Analytical Chemistry, 26*, 466–485.

Hildebrandt, A., Guillamón, M., Lacorte, S., Tauler, R., & Barcelo, D. (2008). Impact of pesticides used in agriculture and vineyards to surface and groundwater quality (North Spain). *Water Research, 42*, 3315–3326.

Kafi-Benyahia, M., Gromaire, M. G., & Chebbo, G. (2005). Spatial variability of characteristics and origins of urban wet weather pollution in combined sewers. *Water Science and Technology, 52*, 53–62.

Kasprzyk-Hordern, B., Dinsdale, R. M., & Guwy, A. J. (2008). The effect of signal suppression and mobile phase composition on the simultaneous analysis of multiple classes of acidic/neutral pharmaceuticals and personal care products in surface water by solid-phase extraction and ultra performance liquid chromatography - negative electrospray tandem mass spectrometry. *Talanta, 74*, 1299–1312.

Kay, P., Blackwell, P. A., & Boxall, A. B. A. (2004). Fate of veterinary antibiotics in a macroporous tile drained clay soil. *Environmental Toxicology and Chemistry, 23*, 1136–1144.

Kim, L.-H., Zoh, K.-D., Joeng, S.-M., Kayhananian, M., & Stenstrom, M. K. (2006). Estimating pollutant mass accumulation on highways during dry periods. *Journal of Environmental Engineering, 132*, 985–993.

Kim, S.-C., & Carlson, K. (2007). Quantification of human and veterinary antibiotics in water and sediment using SPE/LC/MS/MS. *Analytical and Bioanalytical Chemistry, 387*, 1301–1315.

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., et al. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance. *Environmental Science & Technology, 36*, 1202–1211.

Krein, A., & DeSutter, R. (2001). Use of artificial flood events to demonstrate the invalidity of simple mixing models. *Hydrological Sciences Journal, 46*, 611–622.

Krein, A., Salvia-Castellvi, M., Iffly, J. F., Pfister, L., & Hoffmann, L. (2007). The importance of precedent hydro-climatological conditions for the mass transfer of pollutants in separated sewer systems and corresponding tributaries during flood events. *Water, Air and Soil Pollution, 182*, 357–368.

Krein, A., & Schorer, M. (2000). Road runoff pollution and its contribution to river sediments. *Water Research, 34*, 4110–4115.

Krein, A., & Symader, W. (2000). Pollutant sources and transport patterns during natural and artificial flood events in the Olewiger Bach and Kartelbornsbach basins, Germany. In M. Stone (Ed.), *Proceedings of the IAHS symposium on the role of erosion and sediment transport in nutrient and contaminant transfer* (pp. 167–173). Wallingford: IAHS.

Kreuger, J. (1999). Pesticides in stream water within an agricultural catchment in southern Sweden, 1990–1996. *The Science of the Total Environment, 216*, 227–251.

Kuch, H. M., & Ballschmiter, K. (2001). Determination of endocrine-disrupting phenolic compounds and estrogens in surface and drinking water by HRGC-(NCI)-MS in the picogram per liter range. *Environmental Science & Technology, 35*, 3201–3206.

Kurtenbach, A., & Krein, A. (2007). Pre-event hydrological conditions as determinants for sediment and pollutant transport during artificial and natural floods. In B. Westrich & U. Förstner (Eds.), *Sediment dynamics and pollutant mobility in rivers—an interdisciplinary approach* (pp. 279–287). Heidelberg: Springer.

Kurtenbach, A., Möller, S., Krein, A., & Symader, W. (2006). On the relationship between hydrographs and chemographs. *Hydrological Processes, 20*, 2921–2934.

Laganà, A., Bacaloni, A., De Leva, I., Faberi, A., Fago, G., & Marino, A. (2004). Analytical methodologies for determining the occurrence of endocrine disrupting chemicals in sewage treatment plants and natural waters. *Analytica Chimica Acta, 501*, 79–88.

Lee, J. H., & Bang, K. W. (2000). Characterization of urban stormwater runoff. *Water Research, 34*, 1773–1780.

Lee, J. H., Bang, K. W., Ketchum, L. H., Choe, J. S., & Yu, M. J. (2002). First flush analysis of urban storm runoff. *The Science of the Total Environment, 293*, 163–175.

Lee, H., Lau, S.-L., Kayhanian, M., & Stenstrom, M. K. (2004). Seasonal first flush phenomenon of urban stormwater discharges. *Water Research, 38*, 4153–4163.

Leu, C., Singer, H., Müller, S. R., Schwarzenbach, R. P., & Stamm, C. (2005). Comparison of atrazine losses in three small headwater catchments. *Journal of Environmental Quality, 34*, 1873–1882.

Li, D., Yang, M., Hu, J., Ren, L., Zhang, Y., & Li, K. (2008). Determination and fate of oxytetracycline production wastewater and the receiving river. *Environmental Toxicology and Chemistry, 27*, 80–86.

Marsalek, J., Barnwell, T. O., Geiger, W., Grottker, M., Huber, W. C., Saul, A. J., et al. (1993). Urban drainage systems: Design and operation. *Water Science and Technology, 27*, 31–70.

Ng, H. Y. F., Gaynor, J. D., Tan, C. S., & Drury, C. F. (1995). Dissipation and loss of atrazine and metolachlor in surface and subsurface drain water: A case study. *Water Research, 29*, 2309–2317.

Pailler, J.-Y., Guignard, C., Meyer, B., Iffly, J.-F., Pfister, L., Hoffmann, L., et al. (2009a). Behaviour and fluxes of dissolved antibiotics, analgesics and hormones during flood events in a small heterogeneous catchment in the Grand Duchy of Luxembourg. *Water, Air and Soil Pollution, 203*, 79–98.

Pailler, J.-Y., Krein, A., Pfister, L., Hoffmann, L., & Guignard, C. (2009b). Solid phase extraction coupled to liquid chromatography-tandem mass spectrometry analysis of sulfonamides, tetracyclines, analgesics and hormones in surface water and wastewater in Luxembourg. *Science of the Total Environment, 407*, 4736–4743.

Poor, C. J., & McDonnell, J. J. (2007). The effects of land use on stream nitrate dynamics. *Journal of Hydrology, 332*, 54–68.

Renew, J. E., & Huang, C. H. (2004). Simultaneous determination of fluoroquinolone, sulfonamide, and trimethoprim antibiotics in wastewater using tandem solid phase extraction and liquid chromatography-electrospray mass spectrometry. *Journal of Chromatography A, 1042*, 113–121.

Roberts, P. H., & Thomas, K. V. (2006). The occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment. *The Science of the Total Environment, 356*, 143–153.

Robson, M., Spence, K., & Beech, L. (2006). Stream quality in small urbanised catchment. *The Science of the Total Environment, 357*, 194–207.

Scheurell, M., Franke, S., Shah, R. M., & Hühnerfuss, H. (2009). Occurrence of diclofenac and its metabolites in surface water and effluent samples from Karachi, Pakistan. *Chemosphere, 77*, 870–876.

Schriewer, A., Horn, H., & Helmreich, B. (2008). Time focused measurements of roof runoff quality. *Corrosion Science, 50*, 384–391.

Skark, C., Zullei-Seibert, N., Willme, U., Gatzemann, U., & Schlett, C. (2004). Contribution of non-agricultural pesticides to pesticide load in surface water. *Pest Management Science, 60*, 525–530.

Taebi, A., & Droste, R. L. (2004). Pollution loads in urban runoff and sanitary wastewater. *The Science of the Total Environment, 327*, 175–184.

Tiefenthaler, L. L., Stein, E. D., & Schiff, K. C. (2008). Watershed and land use-based sources of trace metals in urban storm water. *Environmental Toxicology and Chemistry, 27*, 277–287.

Van Metre, P. C., & Mahler, B. J. (2003). The contribution of particles washed from rooftops to contaminant loading to urban streams. *Chemosphere, 52*, 1727–1741.

Verma, B., Headley, J. V., & Robarts, R. D. (2007). Behaviour and fate of tetracycline in river and wetland waters on the Canadian Northern Great Plains. *Journal of Environmetal Science and Health Part A, 42*, 109–117.

Vonbank, R., Hans Simmler, H., Boller Cargouët, M., Perdiz, D., Mouatassim-Souali, A., Tamisier-Karolak, S., et al. (2004). Assessment of river contamination by estrogenic compounds in Paris areas (France). *The Science of the Total Environment, 324*, 55–66.

White, M. D., & Greer, K. A. (2006). The effects of watershed urbanization on the stream hydrology and riparian vegetation of Los Peñasquitos Creek, California. *Landscape and Urban Planning, 74*, 125–138.

Wittmer, I. K. , Bader, H.-P., Scheidegger, R., Singer, H., Lück, A., Hanke, I., et al. (2010). Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. *Water Research, 44*, 2850–2862.

Zuccato, E., Castiglioni, S., & Fanelli, R. (2005). Identification of the pharmaceuticals for human use contaminating the Italian aquatic environment. *Journal of Hazardous Materials, 122*, 205–209.