Accepted Manuscript

Hysteresis and parent-metabolite analyses unravel characteristic pesticide transport mechanisms in a mixed land use catchment

Ting Tang, Christian Stamm, Ann van Griensven, Piet Seuntjens, Jan Bronders

PII: S0043-1354(17)30669-3
DOI: 10.1016/j.watres.2017.08.016
Reference: WR 13139
To appear in: *Water Research*
Received Date: 04 April 2017
Revised Date: 18 July 2017
Accepted Date: 07 August 2017

Please cite this article as: Ting Tang, Christian Stamm, Ann van Griensven, Piet Seuntjens, Jan Bronders, Hysteresis and parent-metabolite analyses unravel characteristic pesticide transport mechanisms in a mixed land use catchment, *Water Research* (2017), doi: 10.1016/j.watres.2017.08.016

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

This manuscript version is made available under the CC-BY-NC-ND 4.0 license
<http://creativecommons.org/licenses/by-nc-nd/4.0/>

Hysteresis and parent-metabolite analyses unravel characteristic pesticide transport mechanisms in a mixed land use catchment

Ting Tang^{a,b,c,*}, Christian Stamm^d, Ann van Griensven^{b,e}, Piet Seuntjens^{a,c,f}, Jan Bronders^a

^aFlemish Institute for Technological Research, Boeretang 200, 2400 Mol, Belgium

^bVrije Universiteit Brussel, Dept. Hydrology and Hydraulic Engineering, Pleinlaan 2, 1050 Brussels, Belgium

^cUniversity of Antwerp, Dept. Bioscience Engineering, Groenenborgerlaan 171, 2000 Antwerp, Belgium

^dEAWAG, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

^eUNESCO-IHE, Westvest 7, 2611 AX Delft, Netherlands

^fGhent University, Dept. Soil Management, Coupure Links 653, 9000 Gent, Belgium

*Corresponding author: Email: ting.tang@vito.be

Phone: +32 1433 6763

Revised manuscript submission to *Water Research*

Abstract

To properly estimate and manage pesticide occurrence in urban rivers, it is essential, but often highly challenging, to identify the key pesticide transport pathways in association to the main sources. This study examined the concentration-discharge hysteresis behaviour (hysteresis analysis) for three pesticides and the parent-metabolite concentration dynamics for two metabolites at sites with different levels of urban influence in a mixed land use catchment (25 km²) within the Swiss Greifensee area, aiming to identify the dominant pesticide transport pathways. Combining an adapted hysteresis classification framework with prior knowledge of the field conditions and pesticide usage, we demonstrated the possibility of using hysteresis analysis to qualitatively infer the dominant pesticide transport pathway in mixed land-use catchments. The analysis showed that hysteresis types, and therefore the dominant transport pathway, vary among pesticides, sites and rainfall events. Hysteresis loops mostly correspond to dominant transport by flow components with intermediate response time, although pesticide sources indicate that fast transport pathways are responsible in most cases (e.g. urban runoff and combined sewer overflows). The discrepancy suggests the fast transport pathways can be slowed down due to catchment storages, such as topographic depressions in agricultural areas, a wastewater treatment plant (WWTP) and other artificial storage units (e.g. retention basins) in urban areas. Moreover, the WWTP was identified as an importance factor modifying the parent-metabolite concentration dynamics during rainfall events. To properly predict and manage pesticide occurrence in catchments of mixed land uses, the hydrological delaying effects and chemical processes within artificial structures needs to be accounted for, in addition to the catchment hydrology and the diversity of pesticide sources. This study demonstrates that in catchments with diverse pesticide sources and complex transport mechanisms, the adapted hysteresis analysis can help to improve our understanding on pesticide transport behaviours and provide a basis for effective management strategies.

46

47 **Keywords:** urban pollutant; biocide; transport pathway; runoff; WWTP; urbanised catchment

48

ACCEPTED MANUSCRIPT

1. Introduction

In urban areas, pesticide sources are highly diverse, due to uses on lawns, gardens, pets, building materials and occasionally on impervious surfaces for pest control (Jiang and Gan, 2016; Wittmer et al., 2010). Urbanised catchments are also highly complex in terms of possible pesticide transport pathways. In addition to the modified runoff behaviour due to impervious surfaces, artificial structures, such as wastewater treatment plant (WWTP), urban drainage systems and combined sewer overflow (CSO), redirect and/or retain water and pollutants in urban areas (Botta et al., 2009; Wittmer et al., 2010). At the catchment scale, artificial structures in agricultural areas, such as roadside drains and subsurface tile drains, have similar functionalities to alter the transport pathways for water and pollutants (Doppler et al., 2012; Tediosi et al., 2012). The highly diversified sources of urban pesticides, together with the strongly altered hydrological behaviour, make it particularly challenging to characterise the mechanisms underlying the mobilisation and transport of pesticides and their metabolites, and to determine the key transport pathways. Yet, knowledge on pesticide use, mobilisation and transport mechanisms is essential for proper estimation and prediction of pesticide loss into urban waters, the associated risk assessment and pesticide management practises.

Hydrological processes are the key drivers for mobilisation and transport of pollutants into surface water (Klaus et al., 2014; Tang et al., 2015). Understanding the concentration (C) and discharge (Q) dynamics at the (sub-)catchment outlet can thus help us to identify the key transport mechanisms in the (sub-)catchment in association to land use (e.g. urban, agriculture) and pesticide sources. Pesticide concentration-discharge (C/Q) dynamics are typically studied in the form of event-based time series of discharge and concentration at given instream sites (Blanchoud et al., 2004; Botta et al., 2009; Wittmer et al., 2010) for investigating the intra-

event variations or identifying key sources. An alternative method is the event-based hysteresis analysis, as C/Q plot. Hysteresis patterns have been frequently observed and investigated for conventional water quality parameters, such as suspended sediment, nutrients, turbidity and major ions (Gellis, 2013; Lloyd et al., 2016; Rose, 2003; Williams, 1989), but also for new applications, such as bacteriophages (Fauvel et al., 2016). Hysteresis analysis has been increasingly used, thanks to the developments of in-situ continuous monitoring of conventional water quality parameters. The technique is regarded as a valuable tool to infer the source areas, transport mechanisms, storage and mobilisation capacity of pollutants during given storm events in a catchment (Lloyd et al., 2016; Williams, 1989).

Equally important, but much less studied, are the transport mechanisms of biologically-active pesticide metabolites. As the dominant route for environmental pesticide degradation (Fenner et al., 2013), biodegradation generally produces metabolites that are more polar and more water soluble than the parent compounds, resulting in different transport behaviours between the parent and metabolite compounds (Boxall et al., 2004). For example, Boxall et al. (2004) found that the organic carbon absorption coefficient (K_{oc}) of about one-third of the investigated pesticide metabolites was at least one order of magnitude lower than that of the parent compound, meaning that a larger fraction of the metabolites are expected to be transported into surface water and groundwater. It is therefore of interest to investigate the differences in the transport behaviour of parent and metabolite compounds, especially for biologically-active and risk-relevant metabolites.

This study aims to identify the dominant transport pathways of pesticides and their metabolites in a catchment of mixed land uses, where an intensive field monitoring study was conducted (Wittmer et al., 2010). Several papers have been published on this field study (Hanke et al., 2010; Wittmer et al., 2011a, 2010), mainly on the concentration dynamics, load

101 and loss rate of pesticides in the catchment. However, little attention was paid to characterise
102 how transport pathways differed among different pesticides. As pointed out by Gupta et al.
103 (2008), *information* is obtained by viewing and analysing *data* in *context*. In this paper, we
104 add to the existing information by abstracting information in the context of pesticide transport
105 mechanisms, using hysteresis analysis and parent-metabolite concentration analysis. Few
106 studies involving hysteresis analyses for pesticides (Taghavi et al., 2010) have been found by
107 the authors so far, despite that hysteresis analysis is frequently used to infer flow mixing
108 processes for water quality parameters. Therefore, the second objective of this study is to
109 examine the applicability of hysteresis analysis for pesticide transport in catchments with
110 mixed land uses and complex transport mechanisms.

2. Methods and materials

This study uses the dataset collected by a comprehensive field study on pesticide and biocide dynamics in surface water, which was carried out in a sub-catchment (about 25 km²) of the Greifensee catchment on the Swiss Plateau (**Fig.1a**) from March to November, 2007 (Hanke et al., 2010; Wittmer et al., 2011a, 2010). The most relevant aspects of the study area and the monitoring dataset are briefly described below, followed by the data analysis techniques used in this paper. For more details on catchment characteristics, the field campaign and chemical analytical procedure, the reader is referred to Wittmer et al. (2011b, 2010) and Hanke et al. (2010).

2.1 Study area

The study area has a typical mixed land use (**Fig.1b**) for the Swiss Plateau, with roughly 65% of agricultural area (46% pasture, 19% arable farming), 14% of forests, 20% of urban area (10% sealed area, 7% of lawns and gardens, and 3% roofs), and 1% of water (including impoundment, wetland and river networks). The most widespread arable crops are maize, winter wheat, and barley. The urban area consists mainly of two villages of approximately 10,000 and 2,000 inhabitants, respectively.

The contributing area of the urban drainage system (outline of **Fig. 1b**) roughly lies within the elevation-defined hydrological catchment boundary (outline of **Fig. 1d**). The drainage system consists of both combined (70% of artificially drained urban areas) and separate systems for wastewater and storm runoff (**Fig. 1c**). The storm sewers for separate systems collect only surface runoff and route the flow directly into surface water, whereas the pure wastewater pipes for separate systems collect wastewater from households and discharge to the only

WWTP in the catchment for treatment. The combined systems are equipped with CSOs with or without retention basins (**Fig. 1c**). They collect both wastewater and surface runoff, and direct the flow to the WWTP. However, during heavy rainfall events, the combined systems discharge excess water directly to surface water through the CSOs. The agricultural areas in the catchment are characterised by a large fraction of artificially drained soils by tile drains (total length similar to that of the storm sewers) and a rather dense network of roads, which are sometimes linked to storm sewers. In the sub-catchment to the southeast (*Urban_{South}*), for instance, roughly 30% of agricultural areas are tile drained. These structures are potential shortcuts, which intercept overland flow and pesticide runoff, and transfer water and pesticides quickly to the surface water (Doppler et al., 2012; Leu et al., 2004).

The catchment was hydrologically divided into four sub-catchments of distinct land use compositions (**Fig. 1d**). *Urban_{North}* is the most heavily urbanised sub-catchment (5.8 km²). It hosts the village with 10,000 inhabitants, the WWTP that serves the whole catchment and three CSOs with a total basin volume of 450 m³ (**Fig. 1c**, Wittmer et al., 2010). Three sampling sites are located in *Urban_{North}*: 1) the outlet of a storm sewer (site 6-StS), which collects storm runoff from roughly 5.7 ha of residential area; 2) the effluent of the WWTP (site 5 -WWTP), which serves the whole catchment; and 3) the sub-catchment outlet (site 2 - *Urban_{north}*), which is less than 500 m downstream of the effluent of WWTP and is thus heavily influenced by this effluent. *Urban_{South}* is a sub-catchment with mixed land uses and the other village of 2,000 inhabitants (11 km²). Except for the sub-catchment outlet (site 4 -*Urban_{south}*), one CSO with a retention basin (300 m³) was also selected as a sampling site (site 7 - CSO) in this sub-catchment. Sub-catchment *Agri* (4 km²) is agriculture-dominated with one sampling site at its outlet (site 3 - AGR). *Agri_{drain}* (4.2 km²) is the agriculture-dominated downstream sub-catchment. It is flat, heavily tile-drained and at the outlet of the entire catchment (site 1 - Total).

2.2 Monitoring dataset

The discharge and pesticide measurements at the seven sampling sites yield a dataset representative for various sources of pesticides. This monitoring dataset contains data of 5-minute interval on rainfall from 3 stations and discharge at the seven sampling sites. The temporal resolution of pesticide concentration data was either 15 min or 1 hour depending on the sampling frequency and analysis priority. Overall, roughly half of the rainfall events were sampled, mostly in May and June. Additional grab samples were taken during dry periods when discharge at the instream sites was not influenced by rainfall events. For the WWTP effluent, volume-proportional daily composite samples were collected. In total, six hundred samples were analysed, by online solid-phase extraction coupled to liquid chromatography and a triple quadrupole mass spectrometer after filtration with glass-fibre filters (GF/F, 0.7 mm, Whatman). The reader is referred to Wittmer et al. (2010) for details.

Of the 25 substances available in the dataset, including pesticides, biocides and wastewater tracers, we focused on four substances of different origins (**Fig. 2**) and two metabolites. Three substances (atrazine, diuron and mecoprop) were used for the hysteresis analysis and two substances (diuron and glyphosate) were used for the parent-metabolite analysis together with their main metabolites 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU) and aminomethylphosphonic acid (AMPA), respectively. To associate the measured concentrations with the sources of the substances, we also made use of substance consumption data, including survey data on agricultural uses by farmers, estimated urban uses by professional and private users based on survey data, and estimated biocide uses on building materials from local or national statistical data (**Fig. 2**). The application data and the estimation procedures are available in Wittmer et al. (2011a) and Hanke et al. (2010).

2.3 Data analysis

Hysteresis analysis on pesticide event concentrations

During an individual storm event, concentrations of water quality parameters at the same discharge are typically different on the rising (stage from base flow discharge to peak discharge) and falling limb (the recession stage after peak discharge) of a hydrograph, resulting in a cyclical shape on the C/Q plot, known as the hysteresis loop (Gellis, 2013; Lloyd et al., 2016 and references therein). Such hysteresis occurs whenever there is a difference in the relative timing or the form of substance and discharge responses (Evans and Davies, 1998). The difference can result from variable mixing processes among flow components with different travel time to the sampling sites. For example, urban runoff is a typical fast flow component. Pollutants mobilised and transported via this pathway would have increasing instream concentration on the rising limb with peak concentration coincident with peak surface runoff, resulting in a clockwise loop with positive trend. Another example is substances (e.g. salt) originating and transported by base flow, which is typically a slow flow component. Due to the dilution effect of storm water, the concentration decreases during the storm event, especially on the rising limb of hydrographs, resulting in an anticlockwise loop with negative trend. **Fig. 3** illustrates an artificially-constructed example on the derivation of a hysteresis loop from typical event-based discharge and concentration measurements, which can further be classified and associated to substance transport pathways, as shown in **Fig. 4**. Since minimum four points are required to define an ellipse, we consider five measurements as a minimum requirement to derive an identifiable hysteresis loop. In our dataset, only a limited number of rainfall events have sufficient data to derive such a plot for a few pesticides. Therefore, we derived and examined hysteresis loops for two events with the

most measurements available for three substances at six sampling sites (#1 in **Fig. 4**, except for the WWTP effluent). The three pesticides (atrazine, diuron and mecoprop) represent sources from agricultural fields, urban buildings and mixed sources, respectively (**Fig. 2**).

Equally important to the derivation of hysteresis loops from observations is the classification and interpretation of hysteresis loops. Herein, we adapted the classification system proposed by Evans and Davies (1998), who linked loop types to flow mixing processes. In our classification process (#2 in **Fig. 4**), two diagnostics were used, namely the rotation pattern (clockwise or anticlockwise) and trend (positive, negative or no trend) of the hysteresis loops (**Table 1**). The trend of a hysteresis loop refers to the discharge-concentration correlation of all available data points, describing whether the concentration increases or decreases with discharge. The nonparametric Kendall's rank correlation test (Hipel and McLeod, 1994) was employed to detect whether a statistically-sound monotonic trend (with significance level $p < 0.1$) exist for each hysteresis loop. The diagnostic curvature pattern (concave or convex), also proposed in Evans and Davies (1998), was not taken into account, because 1) the rotation pattern and trend of a given loop were sufficient for the classification, and 2) the hysteresis loops derived in our study did not allow for appropriate classification of the curvature due to the limited number of points (< 10 measurements in general).

Direct interpretation of the hysteresis based on the 3-component model (groundwater, soil lateral flow and surface runoff) in Evans and Davies (1998) was not feasible, given the limited measurements per event and the high number of possible pesticide transport pathways in the catchment. Therefore, we associated the hysteresis types to the response time of the dominant flow component for substance transport during rainfall events (**Table 1**, last column, #3 in **Fig. 4**). The response time herein refers to the relative time lag of pesticide transport via a given pathway and is given in three categories (fast, intermediate and slow) for

simplification. The three categories are relative terms that can be roughly estimated from the hydrograph. Typically, the fast response coincides with a concentration peak on the rising limb (i.e. positive trend), slow response coincides with a concentration peak at the beginning and end of an event (i.e. negative trend), and intermediate response coincides with a concentration peak at similar timing of the discharge peak or early stage of the falling limb. To determine the dominant transport pathway from the three categories, we identified the possible pesticide transport pathways at a given site and the response time for each pathway based on the potential pesticide sources, previous studies on the pathways and the catchment characteristics (#4 in **Fig. 4**). The dominant pathway in this manner refers to the pathway with highest load contribution in a given event (#5 in **Fig. 4**). For example, the artificial example in **Fig. 3** gives an A1 loop (anticlockwise loop with no significant trend), which corresponds to intermediate-flow dominated substance transport, namely highest load contribution from flow paths of intermediate response time.

Table 1 Classification of hysteresis loops in association to flow components and the response time of the dominant flow component (adapted from Evans and Davies, 1998)

Hysteresis type	Rotation pattern	Trend	3-component ranking of substance concentration ^a	Relative response time of the dominant flow component ^b
C1	clockwise	No trend	$C_{sr} > C_{bf} > C_{if}$	Fast
C2	clockwise	positive	$C_{sr} > C_{if} > C_{bf}$	Fast
C3	clockwise	negative	$C_{bf} > C_{sr} > C_{if}$	Slow
A1	anticlockwise	No trend	$C_{if} > C_{bf} > C_{sr}$	Intermediate

A2	anticlockwise	positive	$C_{if} > C_{sf} > C_{bf}$	Intermediate
A3	anticlockwise	negative	$C_{bf} > C_{if} > C_{sr}$	Slow

Note: ^a sr: surface runoff (event-driven fast flow component); if: soil interflow (event-driven intermediate flow component); bf: base flow (slow flow or non-event driven flow component).

^b the classification is based on the relative response time of the component with highest concentration (first rank in the 4th column), with no distinction for the 2nd and 3rd rank.

Relationship between the concentrations of pesticide parent and metabolite substances

Apart from hysteresis analysis, parent-metabolite concentration relationships help to determine the differences in the transport behaviour of the parent and metabolite compounds related to residence time in the urban water system and additional sources of metabolites. Such analysis is particularly useful for pesticide metabolites that are transformation products of multiple compounds, such as AMPA. AMPA is the principal metabolite of the widely-used herbicide glyphosate and a degradation product of several household phosphoric detergents, including ethylene diamine tetramethylene phosphonate (EDTMP) and diethylenetriamine–penta-methylene phosphonic acid (DTPMP) (Nowack, 2003). AMPA and DCPMU were used in the analysis, as metabolites of glyphosate and diuron, respectively. The two metabolites were selected because both metabolites have alternative sources, with the former from wastewater and the latter from another herbicide linuron. Correlation analysis was employed using data of the four substances from all sites during the study period, except for measurements below detection limits (mainly for DCPMU). The Spearman's ρ for paired samples and associated significance level were calculated to test the significance of the correlation in a site-based manner to differentiate the dominant transport pathways among sites. Lastly, the parent-metabolite concentration ratio was compared among sites to further infer the metabolite sources at different sites.

3. Results and discussion

Based on the catchment hydrology, eight possible pathways are identified for pesticide transport from the point of origin to the streams (**Table 2**). Other rainfall-independent pathways, such as atmospheric deposition and wind drift during pesticide spray were not included due to their limited contribution during rainfall events (de Snoo and de Wit, 1998; Wittmer et al., 2016). To determine the dominant pathway, the response time of the pathways was again classified into three categories, based on prior knowledge of the catchment and response time of pathways reported in literature (#4 in **Fig. 4**, Doppler et al., 2012; Klaus et al., 2014; Wittmer et al., 2016).

Table 2 Possible transport pathways and the corresponding response time in light of the catchment characteristics

No.	Flow component	Relative response time
<i>P1</i>	urban runoff subsequently transported in storm sewers	Fast
<i>P2</i>	urban runoff subsequently transported in combined sewers and discharged via CSOs	Fast or Intermediate
<i>P3</i>	urban runoff directly discharged to adjacent streams	Fast
<i>P4</i>	urban runoff subsequently transported in combined sewers and discharged via WWTP	Intermediate
<i>P5</i>	agricultural surface runoff discharged to the streams via shortcuts, such as roads and farmyards	Fast
<i>P6</i>	agricultural subsurface lateral flow from unsaturated zone directly discharged to the streams	Intermediate

- agricultural overland water infiltrated and collected by tile drains
P7 via preferential, matrix and lateral flow Intermediate
- P8* base flow directly discharged to streams Slow

Note: *P1*- *P4*: urban runoff is generally considered as the fastest flow pathway (Wittmer et al., 2010).

Nevertheless, depending on the rainfall intensity, retention basin for CSOs and the WWTP (hydrological retention time of roughly 10 hours) can detain the flow and result in slower transport for *P2* and *P4* (Wittmer et al., 2016). *P8*: rainfall independent, characterized by low pesticide concentration (Doppler et al., 2012)

3.1 Hysteresis analysis for selected events

The selected rainfall events for hysteresis analysis are relatively short (**Table 3**, < 30 hours), compared to those defined in Wittmer et al. (2010, > 60 hours). The rationale is to select distinguishable events with minimum number of discharge peaks (≤ 3 peaks) and maximum number of measurements (≥ 5 measurements), so that the hysteresis loops can be properly identified. The two selected events were both moderate events (intensity around 2 mm/h) with a higher total rainfall amount and considerably shorter antecedent dry period for *Event 1*. Classification of the hysteresis loops (**Table 4**) demonstrates that pesticide hysteretic behaviours vary not only amongst substances, but also among rainfall events and sampling sites.

Table 3 Properties of the two selected rainfall events for hysteresis analysis

	<i>Event 1</i>	<i>Event 2</i>
Event Date	5-6/May/2007	28/May/2007
Rainfall amount, mm	48	27
Rainfall duration, h	28.3	13.3
Rainfall intensity, mm/h	1.69	2.04

Antecedent dry period, d	0.375	4.14
Peak rainfall intensity^a, mm/h	8	4
Rain-driven discharge at WWTP^b, m³	11790 (1.0%) ^c	8599 (1.3%)

Note: ^a the maximum value of the hourly moving average rainfall amount; ^b The dry weather discharge of 3000 m³/d (Wittmer et al., 2016) is abstracted from the total discharge to obtain the rainfall-drive discharge at WWTP effluent. ^c Discharge as a percentage of the total catchment rainfall amount is given in brackets.

Table 4 Classification for the relative response time for the dominant transport pathway(s) and hysteresis loops of the three pesticides for the two events, based on the adapted method of Evans and Davies (1998, **Table 1**)

Substance	Sampling site	Hysteresis type	
		Event 1	Event 2
Atrazine	StS	(a)	Fast [C2, Fig. 9a]
	Urban _{north}	Slow [A3, Fig. 5a]	Fast [C2] ^e
	CSO	Fast [C1]	(b)
	Urban _{south}	Slow [A3]	(c)
	AGR	Intermediate [A1, Fig. 8a]	Intermediate [A1]
	Total	Intermediate [A1, Fig. 5b]	(b)
Diuron	StS	(a)	Fast [C1, Fig. 9b]
	Urban _{north}	Intermediate [A1, Fig. 6a]	Intermediate [A1]
	CSO	Intermediate [A1]	(b)
	Urban _{south}	Fast [C1] ^e	Intermediate [A1]
	AGR	(b)	(b)
	Total	Intermediate [A1, Fig. 6b]	(d)
Mecoprop	StS	(a)	(d)
	Urban _{north}	Fast [C1, Fig. 7a]	Intermediate [A2, Fig. 7b]
	CSO	(b)	Intermediate [A1]
	Urban _{south}	Fast [C1]	Intermediate [A2]
	AGR	Intermediate [A1, Fig. 8b]	Intermediate [A1]
	Total	Fast [C1]	(b)

^a Hysteresis loops could not be derived due to limited number of (<5) measurements for the event.

^b The rotation pattern could not be identified and no significant trend ($p \geq 0.1$) can be detected.

^c The rotation pattern could not be identified, but with a significant negative trend ($p < 0.1$).

^d The rotation pattern could not be identified, but with a significant positive trend ($p < 0.1$).

^c A figure-8 type of loop was obtained where the loop crosses near median discharge.

Hysteresis loops amongst substances

Atrazine

Atrazine was used in agricultural fields in all the four sub-catchments, mainly in May between the two rainfall events under consideration. Under the Swiss conditions, pesticide transport to groundwater and subsequent in base flow is of limited importance (Doppler et al., 2012; Wittmer et al., 2016). Given the wide presence of agricultural tile drains in the catchment, we hypothesise that the dominant transport pathways for atrazine were lateral subsurface flow (*P6*) and preferential flow to tile drains (*P7*, Wittmer et al., 2016) with contribution from *P5* (surface runoff via shortcuts) at early stage of the event, resulting in anticlockwise loops (A1 or A2).

The majority of hysteresis loops for atrazine at instream sites were anticlockwise (**Table 4**), with no or negative trend (A1 or A3 loops, **Fig. 5** and **Fig. 8a**), meaning that atrazine was primarily transported by either an intermediate-flow (*P6* or *P7*) or slow-flow component (*P8*). The dominance of intermediate-flow component agrees with the aforementioned expectation. Interestingly, three instream sites demonstrated stable atrazine concentration on the rising limb of the hydrograph, but significant increase on the falling limb during *Event 1* (e.g. **Figs. 5b & 8a**), which strongly indicates retarded atrazine transport via *P6* and *P7*. Similar atrazine C/Q dynamics can be observed in Wittmer et al. (2010, Fig. 4 therein), and Doppler et al. (2012, Figs. 5&6 therein). The most likely reason herein is the retention of atrazine in overland flow by surface depressions, primarily due to the short antecedent dry period of *Event 1* (**Table 3**) and the resultant high soil moisture prior to the event. Owing to the relatively high moisture, soil reaches saturation easily during the event and ponding of

overland runoff thereafter occurs at the topographic depressions that are not immediately connected to manholes of the tile drainage system. On the other hand, the stable concentration at the rising limb indicated that rainfall did result in increasing atrazine transport, potentially due to agricultural runoff via shortcuts (*P5*), but the increase was counterbalanced by the dilution effect of urban runoff (*P1-P3*). The slow-flow component for **Fig. 5a** (A3 loop) is base flow, indicated by relatively low concentrations during the entire rainfall event (Doppler et al., 2012). Atrazine is known for its relatively high leachability and moderate persistence in soil (Gassmann et al., 2013; PPDB, 2013). Therefore, its transport via base flow acts as a constant source of instream atrazine (Squillace et al., 1993) and can be the dominant pathway only when the other pathways are less likely to occur, for example, before the application season and during long dry periods (Gomides Freitas, 2005).

Diuron

In the study area, diuron was mainly used as a biocide in construction paints and renders for façades and roofs (**Fig. 2**, Gerecke et al., 2002; Wittmer et al., 2010). The substance was no longer registered for use as a pesticide for private or professional gardeners in Switzerland and its agricultural use was negligible during the study period. Load calculation for diuron by Wittmer et al. (2011a, Fig. 2 therein) indicated major contribution by sub-catchment *Urban_{North}*, particularly the WWTP (60%), and diuron transport was urban rain driven. Therefore, we hypothesise that its transport to urban sites is fast- or intermediate- flow dominated (*P1-P4*), depending on the delaying capacity of the WWTP and the retention basins of the CSOs (**Fig. 1b**).

Overall, hysteresis patterns for diuron were dominated by A1 loops (**Table 4, Fig. 6**), indicating pesticide transport via an intermediate-flow component. As aforementioned, the associated dominant pathways, *P2* and *P4*, respectively for *Urban_{north}* and *Urban_{south}*, are

affected by the delaying effect of the artificial storage units in the catchment. In our study area, 70% of the artificially-drained urban areas were connected to the combined sewer system (**Fig. 1c**), which either directed the flow to the WWTP (roughly 1% of total rainfall, **Table 3**) or discharged via the CSOs. With a minimum hydrological retention time of approximately 7.5 hours during the events (duration: 28.3 and 13.3 hours, **Table 3**), the WWTP evidently had a strong delaying effect and modified the C/Q dynamics. Additionally, the four retention basins of the CSOs, with capacity of 450 m³ and 300 m³ in *Urban_{North}* and *Urban_{South}*, respectively (**Fig. 1c**), also acted as delaying factors. The influence of the storage units extended to the catchment outlet (A1 loop, **Fig. 6b**), despite the storage units mainly present in sub-catchments *Urban_{North}* and *Urban_{South}*, and the flow components from sealed and non-sealed areas were no longer distinguishable at the catchment outlet (Wittmer et al., 2010). Lastly, increase of diuron concentration was observed on the rising limb of most loops (**Fig. 6**), indicating the contribution of fast-flow (*P1* & *P3*) triggered transport.

Mecoprop

Mecoprop was used as a protection agent in flat roof sealing and as a herbicide on lawns and roadsides (Gerecke et al., 2002; Wittmer et al., 2010). In agricultural areas, roughly 10 kg was used in early April, mostly in sub-catchments *Urban_{North}* and *Urban_{South}*. Surveys of mecoprop use in the catchment showed it had mixed sources with the main use in urban areas (**Fig. 2**). Load calculation by Wittmer et al. (2011a) indicated major contribution by urban runoff via sub-catchment *Urban_{North}*, particularly the WWTP (41%). Therefore, we hypothesise that its transport to urban sites is similar to that of diuron, namely dominated by fast- or intermediate-flow components (*P1-P4*).

An evident difference was observed for mecoprop between the two rainfall events (**Table 4**), where *Event 1* and *Event 2* are fast-flow (C1, **Fig. 7a**) and intermediate-flow (A1&A2, **Fig.**

7b) dominated transport, respectively, except for site AGR (Fig. 8b), which exhibited delayed intermediate-flow dominated transport. The difference suggests mecoprop transport is more dependent on rainfall characteristics than diuron and atrazine. For *Event 2*, the dominant pathways in urban sites, similar to diuron, were *P2* and *P4* with the delaying effect by the storage units. However, the delaying effect for mecoprop was less pronounced than for diuron, as demonstrated by the positive trend for mecoprop. One plausible explanation for this phenomenon is the lower adsorption of mecoprop than diuron (K_{oc} : 20-43 mL/g verse 998-1358 mL/g, PPDB, 2013), which potentially leads to a higher fraction of mecoprop in the dissolved phase (Stasinakis et al., 2009). Due to the higher fraction of dissolved mecoprop, it bypasses the WWTP and CSOs more easily and its transport is more dependent on these storage units, which in turn depends on rainfall intensity and rainfall amount. The fast-flow pathways for *Event 1* include urban runoff that was collected by the storm sewer (*P1*) and the mecoprop-rich CSOs (*P2*). More than 40% of total applied mecoprop (Fig. 2) was used as urban pesticide in lawns and roadsides. Pesticides on such surfaces, if directly connected to storm sewers, can be efficiently transported into surface water and result in high concentrations (Ramwell et al., 2002; Wittmer et al., 2010). At site AGR, the hysteresis loop for mecoprop (Fig. 8b) resembled that of atrazine, indicating dominant transport via overland water infiltrated and discharged as lateral subsurface flow (*P6*), or collected and discharged via the tile drains (*P7*).

Hysteresis loops amongst rainfall events and sites

The dominant transport pathway is closely related to the main source for a given sampling site, as reflected by the difference in hysteresis amongst sites. At sites with single sources and limited influence of urban storage units (StS and AGR), higher consistency was observed among events and substances than other sites. Hysteresis loops at the storm sewer outlet (C1

and C2, **Fig. 9**) suggests fast-flow dominated transport, consistent with the expected pathway, namely storm runoff and subsequent transport in storm sewers (*PI*). At site AGR, where only agricultural sources are present, A1 loops were obtained for all events and substances with agricultural uses (atrazine and mecoprop, **Fig. 8**). Available hysteresis loops at the catchment outlet (site Total, **Figs. 5b&6b**) all had a double loop pattern with an outer and an inner hysteresis, corresponding to multiple discharge peaks due to the superposition of flow components with distinct response time (Wittmer et al., 2010). Consequently, the relative location of the inner loop on the concentration-axis can give additional information on substance transport behaviours. For example, although A1 loops were obtained for both diuron (**Fig. 6b**) and atrazine (**Fig. 5b**), the flow component contributing to atrazine was clearly a lot slower than that of diuron, given that the inner loop for atrazine was located at the lower concentration range. Lastly, rainfall characteristics had the strongest influence on mecoprop (**Fig. 7**), while its influence on atrazine and diuron was also visible from the hysteresis loops, particularly for urbanised sites (**Table 4**).

In summary, the hysteresis analysis demonstrated that the dominant transport pathways are affected by the sources, chemical properties, rainfall properties and hydrological processes. Moreover, the topographic depressions in agricultural areas and storage units in urban areas can delay the presumably fast transport (Doppler et al., 2012; Launay et al., 2016) of pesticides, and considerably modify the short-term concentration dynamics, which would not be evident without analysis of intra-event C/Q dynamics. From a modelling perspective, pesticide transport process cannot be easily generalised. Not only substance transformation in the depression and storage units, but also the hydrological delaying effect and pesticide distribution therein should be properly represented for high-resolution or small spatial-scale simulation of pesticide transport, in both urban and agricultural areas. From a management perspective, given the importance of runoff-driven transport, delayed or not, pesticide source

control measures are of fundamental importance in urban outdoor environments. Moreover, one should make better use of urban storage units to enhance pesticide removal efficiency, especially for pesticides and metabolites that easily bypass the storage units.

3.2 Relationship between pesticide parent and metabolite substances

Hypothetically, if a metabolite is originated from one parent substance and the two substances have similar transport behaviours, the parent-metabolite concentration ratio shall remain stable, regardless of sites or rainfall characteristics. With additional sources or different transport mechanisms, the concentration ratio may vary among different sites or rainfall events. Therefore, we examined the parent-metabolite in light of the different sites and rainfall events (**Fig. 10**). In total, 75 and 60 pairs of concentration data were used for glyphosate-AMPA and diuron-DCPMU relationship, respectively.

Diuron-DCPMU

DCPMU (3-(3,4-dichlorophenyl)-1-methylurea) can be a metabolite of mainly three herbicides: diuron, linuron and methazole (Suzuki and Casida, 1981). Methazole has been banned in Europe and diuron was mainly used as a biocide in urban areas during the study period (**Fig. 2**). Linuron can be used for a wide range of crops in Switzerland, such as carrot, celery, potato, cereals and parsley. However, it is unclear whether or how much linuron was used in the catchment. Nevertheless, both diuron and linuron are amongst the frequently detected pesticides in Swiss waters (BAFU, 2008).

Besides the Spearman's rank correlation test for each site, linear regression was applied to sites with a significant monotonic trend ($p < 0.05$, solid lines in **Fig. 10**). Mixed trends were

obtained at different sites for the diuron-DCPMU relationship (**Fig. 10a**). Positive correlations ($p < 0.05$) were obtained for sites CSO, Urban_{north} and Total, while no significant trend was obtained for the rest, though a weak negative correlation ($p < 0.15$) was obtained for site WWTP. The hysteresis analysis showed that diuron was mainly transported via CSOs (*P2*), WWTP (*P3*), and at the early stage of rainfall event, via the storm sewers (*P1*). The significant positive correlation at site CSO indicates *P2* as a dominant pathway for DCPMU. However, it is unclear whether WWTP (*P3*) and storm sewers (*P1*) are also important pathways for DCPMU transport, given the considerably different trends and concentration ranges at the two sites. Nevertheless, we can safely conclude that the WWTP plays an important role in modifying the diuron-DCPMU concentration dynamics, which is evident from the different trends and the diuron-DCPMU concentration ratios. The median diuron-DCPMU ratio of the seven sites is ranked as follows: WWTP > Urban_{north} > Total > Urban_{south} > CSO > StS > AGR. This ranking demonstrates a general decreasing trend as the influence of urban wastewater decreases, rather than the expected influence of urban storm runoff. The exceptionally high diuron-DCPMU ratios at WWTP likely resulted from faster degradation of DCPMU than diuron in the WWTP, as experimentally demonstrated by Stasinakis et al. (2009).

Glyphosate-AMPA

AMPA is the principal metabolite of glyphosate in water and soil. It is also a transformation product of household phosphoric detergents, such as EDTMP and DTPMP (Nowack, 2003). In urban environments, the main source of AMPA is likely household detergents in domestic wastewater (Botta et al., 2009).

Significant positive correlations ($p < 0.05$) on glyphosate-AMPA concentration were obtained for five sites (**Fig. 10b**). For the remaining two sites (Urban_{north} and CSO), positive relationships were also obtained, though not at a statistically significant level ($p > 0.05$). Given that wastewater is a relatively stable source of AMPA (Botta et al., 2009), for sites strongly influenced by wastewater (CSO and WWTP), the dilution effect should result in reduced AMPA concentration with increased glyphosate concentration, leading to negative correlations. The positive correlations at wastewater-influenced sites therefore imply additional sources of AMPA other than the constant source from wastewater. Additionally, the high AMPA concentrations (> 400 ng/L, **Fig. 10b**) were mostly obtained during the three consecutive rainfall events between 26 May and 5 June, suggesting rainfall-driven additional sources of AMPA. Two additional sources of AMPA are possible in the catchment: 1) the degradation of glyphosate applied in the urban areas; 2) the resuspension or desorption of AMPA that was previously trapped in the drainage system and the storage units. In WWTP sludge samples, AMPA content can be up to 20 times that of glyphosate (Ghanem et al., 2007) due to the slower degradation and stronger sorption of AMPA (PPDB, 2013). The resuspension of in-sewer deposits and active sludge and the subsequent desorption of AMPA from the suspended solid therein (Gasperi et al., 2012; Launay et al., 2016) results in higher AMPA content in the flow. For sites with less or no influence by wastewater (e.g. AGR), the positive correlations indicate similar transport mechanisms for glyphosate and AMPA. The median glyphosate-AMPA ratio of the seven sites is ranked as follows: AGR $>$ Total $>$ CSO $>$ StS $>$ Urban_{north} $>$ Urban_{south} $>$ WWTP. The rank demonstrated a general decrease of the ratio as the influence of urban wastewater increases, confirming the significant contribution of AMPA by wastewater.

4. Conclusions

To facilitate the classification and interpretation of hysteresis patterns with complex flow-mixing processes, we adapted an existing classification system based on a 3-component model by relating to the relative response time for a given pathway, and associated the hysteresis loops to the dominant transport pathways. The adapted method provides a reference methodology to interpret hysteresis patterns in catchments with diverse pollutant sources and complex transport mechanisms. The hysteresis analysis demonstrated that hysteresis patterns, and therefore the dominant pesticide transport pathway, vary among pesticides, sampling sites and rainfall events. The commonly-known fast transport pathways of pesticides can be slowed down in both urban and agricultural areas, which may easily be overlooked without intra-event *C/Q* analysis. In agricultural areas, topographic depressions can potentially detain atrazine and mecoprop transport via subsurface lateral flow and tile flow, which were the two dominant transport pathways for the two substances. In urban areas, WWTPs and other storage units (e.g. drainage systems and retention basins of CSOs) are important factors in modifying the *C/Q* dynamics of pesticides in the catchment. They can effectively delay diuron and mecoprop transport, mainly due to the retention time. Overall, diuron transport was dominated by runoff that subsequently transported in combined sewers and discharged via the CSOs or WWTP, whereas mecoprop transport was more rainfall dependent and runoff discharged via CSOs, WWTP or separate sewers may be the dominant transport pathways. Parent-metabolite analysis revealed an additional functionality of the storage units, namely as an active reactor due to various physiochemical processes and contributing to unexpected metabolite concentration dynamics. Although the functionalities of urban artificial structures seem to depend on chemical properties, the delaying effect was general among all substances. To properly simulate the intra-event pesticide dynamics, modelling tools should take into account the above-mentioned effects of urban storage units and agricultural depressions,

554 especially the WWTP. The complexity of pesticide transport mechanisms suggests that the
555 processes cannot be easily generalised or simplified, and there is hence a need for dynamic
556 mechanistic modelling to understand and predict pesticide transport in urbanised catchments.

Acknowledgements

The work was performed in the framework of the joint doctoral program of Ting Tang at the Flemish Institute for Technological Research (Grant No. 1310105), Free University of Brussels and University of Antwerp. Additional funding by Research Foundation – Flanders (FWO, Grant No. V403716N) is also gratefully acknowledged for part of the work carried out at the Swiss Federal Institute of Aquatic Science and Technology (EAWAG). The authors wish to thanks Dr. Irene Wittmer for her effort to make it easy to access and understand the monitoring dataset.

References

- AWEL, 2007. Sewage system of canton Zurich; reproduced with permission.
- BAFU, 2008. Pflanzenschutzmittel im gewerblichen Gartenbau (Pesticides in commercial horticulture). Bundesamt für Umwelt BAFU, Bern.
- Blanchoud, H., Farrugia, F., Mouchel, J.M., 2004. Pesticide uses and transfers in urbanised catchments. *Chemosphere* 55, 905–913. doi:10.1016/j.chemosphere.2003.11.061
- Botta, F., Lavison, G., Couturier, G., Alliot, F., Moreau-Guigon, E., Fauchon, N., Guery, B., Chevreuil, M., Blanchoud, H., 2009. Transfer of glyphosate and its degradate AMPA to surface waters through urban sewerage systems. *Chemosphere* 77, 133–139. doi:10.1016/j.chemosphere.2009.05.008
- Boxall, A.B.A., Sinclair, C.J., Fenner, K., Kolpin, D., Maund, S.J., 2004. When synthetic chemicals degrade in the environment. *Environ. Sci. Technol.* 38, 368A–375A. doi:10.1021/es040624v
- de Snoo, G.R., de Wit, P.J., 1998. Buffer Zones for Reducing Pesticide Drift to Ditches and Risks to Aquatic Organisms. *Ecotoxicol. Environ. Saf.* 41, 112–118. doi:10.1006/eesa.1998.1678
- Doppler, T., Camenzuli, L., Hirzel, G., Krauss, M., Lück, A., Stamm, C., 2012. Spatial variability of herbicide mobilisation and transport at catchment scale: insights from a field experiment. *Hydrol. Earth Syst. Sci.* 16, 1947–1967. doi:10.5194/hess-16-1947-2012
- Evans, C., Davies, T.D., 1998. Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry. *Water Resour. Res.* 34, 129–137. doi:10.1029/97WR01881
- Fauvel, B., Cauchie, H.-M., Gantzer, C., Ogorzaly, L., 2016. Contribution of hydrological data to the understanding of the spatio-temporal dynamics of F-specific RNA bacteriophages in river water during rainfall-runoff events. *Water Res.* 94, 328–40.

doi:10.1016/j.watres.2016.02.057

Fenner, K., Canonica, S., Wackett, L.P., Elsner, M., 2013. Evaluating pesticide degradation in the environment: blind spots and emerging opportunities. *Science* 341, 752–8.

doi:10.1126/science.1236281

Gasperi, J., Zgheib, S., Cladière, M., Rocher, V., Moilleron, R., Chebbo, G., 2012. Priority pollutants in urban stormwater: Part 2 – Case of combined sewers. *Water Res.* 46, 6693–6703. doi:10.1016/j.watres.2011.09.041

Gassmann, M., Stamm, C., Olsson, O., Lange, J., Kümmerer, K., Weiler, M., 2013. Model-based estimation of pesticides and transformation products and their export pathways in a headwater catchment. *Hydrol. Earth Syst. Sci.* 17, 5213–5228. doi:10.5194/hess-17-5213-2013

Gellis, A.C., 2013. Factors influencing storm-generated suspended-sediment concentrations and loads in four basins of contrasting land use, humid-tropical Puerto Rico. *CATENA* 104, 39–57. doi:10.1016/j.catena.2012.10.018

Gerecke, A.C., Schärer, M., Singer, H.P., Müller, S.R., Schwarzenbach, R.P., Sägesser, M., Ochsenein, U., Popow, G., 2002. Sources of pesticides in surface waters in Switzerland: pesticide load through waste water treatment plants—current situation and reduction potential. *Chemosphere* 48, 307–315. doi:10.1016/S0045-6535(02)00080-2

Ghanem, A., Bados, P., Estaun, A.R., de Alencastro, L.F., Taibi, S., Einhorn, J., Mougin, C., 2007. Concentrations and specific loads of glyphosate, diuron, atrazine, nonylphenol and metabolites thereof in French urban sewage sludge. *Chemosphere* 69, 1368–1373. doi:10.1016/j.chemosphere.2007.05.022

Gomides Freitas, L., 2005. Herbicide losses to surface waters in a small agricultural catchment, Spatial and temporal variability and influence of substance properties. *ETH* 16076. doi:10.3929/ETHZ-A-005048055

Gupta, H. V., Wagener, T., Liu, Y., 2008. Reconciling theory with observations: Elements of

a diagnostic approach to model evaluation. *Hydrol. Process.* 22, 3802–3813.

doi:10.1002/hyp.6989

Hanke, I., Wittmer, I., Bischofberger, S., Stamm, C., Singer, H., 2010. Relevance of urban glyphosate use for surface water quality. *Chemosphere* 81, 422–429.

doi:10.1016/j.chemosphere.2010.06.067

Hipel, K., McLeod, A., 1994. Time Series Modelling of Water Resources and Environmental Systems. *Dev. Water Sci.* 45, 255–256. doi:10.1016/S0167-5648(08)70658-0

Jiang, W., Gan, J., 2016. Conversion of pesticides to biologically active products on urban hard surfaces. *Sci. Total Environ.* 556, 63–69. doi:10.1016/j.scitotenv.2016.02.165

Klaus, J., Zehe, E., Elsner, M., Palm, J., Schneider, D., Schröder, B., Steinbeiss, S., van Schaik, L., West, S., 2014. Controls of event-based pesticide leaching in natural soils: A systematic study based on replicated field scale irrigation experiments. *J. Hydrol.* 512, 528–539. doi:10.1016/j.jhydrol.2014.03.020

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

Leu, C., Singer, H., Stamm, C., Müller, S.R., Schwarzenbach, R.P., 2004. Variability of Herbicide Losses from 13 Fields to Surface Water within a Small Catchment after a Controlled Herbicide Application. *Environ. Sci. Technol.* 38, 3835–3841.

doi:10.1021/es0499593

Lloyd, C.E.M., Freer, J.E., Johnes, P.J., Collins, A.L., 2016. Using hysteresis analysis of high-resolution water quality monitoring data, including uncertainty, to infer controls on nutrient and sediment transfer in catchments. *Sci. Total Environ.* 543, 388–404.

doi:10.1016/j.scitotenv.2015.11.028

Nowack, B., 2003. Environmental chemistry of phosphonates. *Water Res.* 37, 2533–2546.

doi:10.1016/S0043-1354(03)00079-4

- 645 PPDB, 2013. The Pesticide Properties DataBase (PPDB). UK: University of Hertfordshire
 646 [WWW Document]. URL <http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm> (accessed
 647 2.28.14).
- 648 Ramwell, C.T., Heather, A.I.J., Shepherd, A.J., 2002. Herbicide loss following application to
 649 a roadside. *Pest Manag. Sci.* 58, 695–701. doi:10.1002/ps.506
- 650 Rose, S., 2003. Comparative solute–discharge hysteresis analysis for an urbanized and a
 651 “control basin” in the Georgia (USA) Piedmont. *J. Hydrol.* 284, 45–56.
 652 doi:10.1016/j.jhydrol.2003.07.001
- 653 Squillace, P.J., Thurman, E.M., Furlong, E.T., 1993. Groundwater as a nonpoint source of
 654 atrazine and deethylatrazine in a river during base flow conditions. *Water Resour. Res.*
 655 29, 1719–1729. doi:10.1029/93WR00290
- 656 Stasinakis, A.S., Kotsifa, S., Gatidou, G., Mamais, D., 2009. Diuron biodegradation in
 657 activated sludge batch reactors under aerobic and anoxic conditions. *Water Res.* 43,
 658 1471–9. doi:10.1016/j.watres.2008.12.040
- 659 Suzuki, T., Casida, J.E., 1981. Metabolites of diuron, linuron, and methazole formed by liver
 660 microsomal enzymes and spinach plants. *J. Agric. Food Chem.* 29, 1027–1033.
 661 doi:10.1021/jf00107a035
- 662 Swisstopo, 2009. Swiss Geodata; reproduced with permission of Swisstopo (JA082266).
- 663 Taghavi, L., Probst, J.-L., Merlina, G., Marchand, A.-L., Durbe, G., Probst, A., 2010. Flood
 664 event impact on pesticide transfer in a small agricultural catchment (Montoussé at
 665 Auradé, south west France). *Int. J. Environ. Anal. Chem.* 90, 390–405.
 666 doi:10.1080/03067310903195045
- 667 Tang, T., Boëne, W., Desmet, N., Seuntjens, P., Bronders, J., van Griensven, A., 2015.
 668 Quantification and characterization of glyphosate use and loss in a residential area. *Sci.*
 669 *Total Environ.* 517C, 207–214. doi:10.1016/j.scitotenv.2015.02.040
- 670 Tediosi, A., Whelan, M.J., Rushton, K.R., Thompson, T.R.E., Gandolfi, C., Pullan, S.P., 2012.

- Measurement and conceptual modelling of herbicide transport to field drains in a heavy clay soil with implications for catchment-scale water quality management. *Sci. Total Environ.* 438, 103–112. doi:10.1016/j.scitotenv.2012.08.042
- Williams, G.P., 1989. Sediment concentration versus water discharge during single hydrologic events in rivers. *J. Hydrol.* 111, 89–106. doi:10.1016/0022-1694(89)90254-0
- Wittmer, I.K., Bader, H.P., Scheidegger, R., Singer, H., Lück, A., Hanke, I., Carlsson, C., Stamm, C., 2010. Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. *Water Res.* 44, 2850–2862. doi:10.1016/j.watres.2010.01.030
- Wittmer, I.K., Bader, H.P., Scheidegger, R., Stamm, C., 2016. REXPO: A catchment model designed to understand and simulate the loss dynamics of plant protection products and biocides from agricultural and urban areas. *J. Hydrol.* 533, 486–514. doi:10.1016/j.jhydrol.2015.11.046
- Wittmer, I.K., Scheidegger, R., Bader, H.-P., Singer, H., Stamm, C., 2011a. Loss rates of biocides can exceed those of pesticides. *Sci. Total Environ.* 13, 2648. doi:10.1016/j.scitotenv.2010.11.031
- Wittmer, I.K., Scheidegger, R., Stamm, C., Gujer, W., Bader, H.-P., 2011b. Modelling biocide leaching from facades. *Water Res.* 45, 3453–60. doi:10.1016/j.watres.2011.04.003

List of figures

Fig. 1 The study area is a subbasin of the Greifensee catchment in northeast Switzerland (a) and has a typical land use composition for the Swiss Plateau (b). The urban areas are equipped with both combined and separate sewer systems (c). The area is divided into four sub-catchments of different land use features, each with a sampling site at the river outlet (site 1-4), together with three sampling sites for effluents of the WWTP, one CSO and one storm sewer, respectively (d). Data sources: AWEL (2007) and Swisstopo (2009) [Please refer to the web version for references to colours in this figure]

Fig. 2 Estimated substance consumption in the catchment for different purposes during the measurement period (March to November, 2007, 256 days). Error bars indicate the 5% and 95% uncertainty level based on 100,000 Monte Carlo simulations implemented in SIMBOX (see Wittmer et al., 2011a for details). The figure is reproduced based on data from Wittmer et al. (2011a) and Hanke et al. (2010). Note: *Atrazine was still registered in Switzerland as a corn herbicide at the time of the field study.

Fig. 3 An artificially-constructed example illustrating how a hysteresis loop (b, an A1 loop with intermediate-flow dominated substance transport, see **Table 1** for the classification and interpretation) is derived from typical event-based discharge and concentration measurements (a). In the example, the total discharge is the superposition of three flow components of the same flow volume with different response time (fast, intermediate and slow) and different substance concentration ($C_{interm} = 5 * C_{slow} = 10 * C_{fast}$).

Fig. 4 Schematic overview of the procedure to identify the dominant pesticide transport pathways based on the hysteresis plot of time-series data (#1) and prior knowledge on the field conditions (#4).

Fig. 5 Hysteresis loops for atrazine at sites Urban_{north} (a, A3 loop) and Total (b, A1 loop) during *Event 1*, demonstrating slow-flow and intermediate-flow dominated atrazine transport, respectively.

Fig. 6 Hysteresis loops for diuron at sites Urban_{north} and Total (A1 loops) during *Event 1*, demonstrating intermediate-flow dominated transport.

Fig. 7 Different hysteresis patterns for mecoprop during *Event 1* (a, C1 loop) and *Event 2* (b, A2 loop) at site Urban_{north}, indicating influence of rainfall properties on the dominant mecoprop transport pathway.

Fig. 8 The A1 loops at site AGR with considerable concentration increase on the falling limb of the hydrograph indicate delayed intermediate-flow dominated transport of atrazine (a) and mecoprop (b) for *Event 1* from the agricultural fields.

Fig. 9 Hysteresis patterns at site StS for atrazine and diuron during *Event 2* (C2 and C1, respectively) confirm the expected single source transport via urban runoff and subsequently storm sewer (*PI*).

Fig. 10 Correlations between the concentrations (in ng/L) of diuron-DCPMU (a) and glyphosate-AMPA (b), indicating site-based linear regression lines. Note: solid and dotted lines represent sites with significant ($P < 0.05$) and non-significant monotonic correlations, respectively; different shapes represent different rainfall events, with ∇ represents dry weather samples or unlabelled event samples. [Please refer to the web version for references to colours in this figure]

Hysteresis and parent-metabolite analyses unravel characteristic pesticide transport mechanisms in a mixed land use catchment

Ting **Tang**, Christian **Stamm**, Ann van **Griensven**, Piet **Seuntjens**, Jan **Bronders**

Highlights

- Hysteresis analysis was used to infer the dominant pesticide transport pathway.
- We adapted a hysteresis classification method to account for various flow paths.
- Some fast pesticide transport pathways can be slowed down for various reasons.
- Topographic depressions and artificial storage units may delay pesticide transport.

Estimated consumption (kg) during the measurement period

a

Concentration (ng/L)

b

Concentration (ng/L)

Normalised discharge

1. Derive the hysteresis loop

2. Classification

(Table 1)

- Rotation pattern
- Trend

C1 C2 C3 A1 A2 A3

3. Response time of the dominant flow path (Table 1)

Fast Intermediate Slow

4. Field Conditions:

- Pesticide sources
- Possible flow paths
- Response time of each path (Table 2)

P1	Fast
P2	Fast
...	...
P8	Slow

5. Identify the dominant flow path(s), P