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

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A B S T R A C T

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 km^2) 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 important 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 effect and chemical processes within the artificial structures need 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.

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; Ramwell et al., 2002; Tang et al., 2015; Wittmer et al., 2011a). 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

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(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 the 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 plots. Hysteresis patterns have been frequently observed and investigated not only 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 with 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 and loss rate of pesticides in the catchment. However, little attention was paid to characterise how transport pathways differed among different pesticides. As pointed out by Gupta et al. (2008), *information* is obtained by viewing and analysing *data* in *context*. In this paper, we add to the existing information by abstracting information in the context of pesticide transport mechanisms using hysteresis analysis and parent-metabolite concentration analysis. Few studies involving hysteresis analyses for pesticides (Taghavi et al., 2010) have been found by the authors so far, despite that hysteresis analysis is frequently used to infer flow mixing processes for water quality parameters. Therefore, the second objective of this study is to examine the applicability of hysteresis analysis for pesticide transport in catchments with 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 km^2) 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. The reader is referred to Wittmer et al. (2011b, 2010) and Hanke et al. (2010) for more details on catchment characteristics, the field campaign and chemical analytical procedure.

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. 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 km^2). 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 m^3 (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: $\mathrm{Urban_{north}}$), 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 has the other village of 2,000 inhabitants (11 km^2). Except for the sub-catchment outlet (site 4: $\mathrm{Urban_{south}}$), one CSO with a retention basin (300 m^3) was