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Lentic small water bodies: Variability of pesticide transport and transformation patterns

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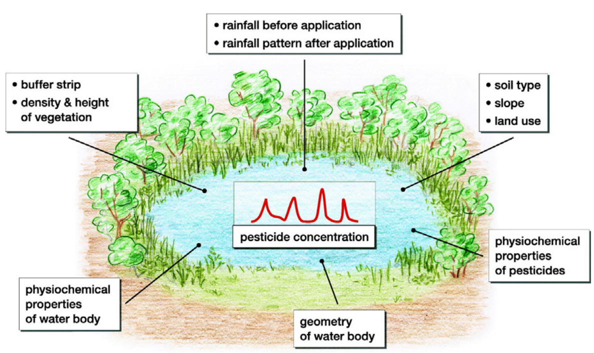
HIGHLIGHTS

- Transformation products of applied in the previous year were clearly detected in the following year.
- Parent compounds were measured in the year of application only.
- Consistent concentration patterns were observed for metazachlor and for the transformation products but not for flufenacet.
- Positives of a pesticide probably present a snapshot, they may originate from former applications at larger distance.
- Subsurface inputs are a crucial entry path for pesticides into lentic small water bodies and are not well understood, yet.

GRAPHICAL ABSTRACT



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ABSTRACT

Lentic small water bodies have a high ecological potential as they fulfill several ecosystem services such as the retention of water and pollutants. They serve as a hot spot of biodiversity. Due to their location in or adjacent to agricultural fields, they can be influenced by inputs of pesticides and their transformation products. Since small water bodies have rarely been part of monitorings/campaigns up to now, their current exposure and processes guiding the pesticide input are not understood, yet. This study presents results of a sampling campaign of 10 lentic small water bodies from 2015 to 2016. They were sampled once after the spring application for a pesticide target screening, before autumn application and three times after rainfall events following the application. The autumn sampling focused on the herbicides metazachlor, flufenacet and their transformation products - oxalic acid and - sulfonic acid as representatives for common pesticides in the study region. The concentrations were associated with rainfall before and after application, characteristics of the site and the water bodies, physicochemical parameters and the applied amount of pesticides. The key results of the pesticide screening in spring indicate positive detections of pesticides which have not been applied for years to the single fields. The autumn sampling showed frequent occurrences of the transformation products, which are formed in soil, from 39% to 94% of all samples (n = 71). Discharge patterns were observed for metazachlor with highest concentrations in the first sample after application and then decreasing, but not for flufenacet. The concentrations of the

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transformation products increased over time and revealed highest values mainly in the last sample. Besides rainfall patterns right after application, the spatial and temporal dissemination of the pesticides to the water bodies seems to play a major role to understand the exposure of lentic small water bodies.

1. Introduction

The environmental fate of pesticides and their effects on non-target areas and organisms has been investigated for many decades (among others Kreuger, 1998; Leu et al., 2004). Due to the European Water Framework Directive (WFD) (2009/128/EC, 2009), a monitoring of pesticide concentrations in rivers with a catchment > 10 km^2, in lakes with a surface area >50 ha and groundwater has been obligatory in the European member states since 2000. Surface water bodies below these surface/catchment sizes are not considered within the EU-WFD. These so called small water bodies (SWB) are often located in rural areas with intensive agricultural use and have a considerable potential to be harmed by agrochemicals since they are adjacent and in direct contact with agricultural fields (Schäfer et al., 2007; Liess et al., 2008; Bunzel et al., 2014). Potential input pathways are by air and water. Water related transport pathways are by surface runoff, lateral flow in the unsaturated zone or shallow groundwater in the saturated zone (Du et al., 2016; Fares, 2016). However, SWB should receive more attention since they perform important hydro-ecological functions: they collect storm water directly by tile drainages and surface runoff or indirectly by subsurface flow and can interact with groundwater (EPCN, 2010; Céréghino et al., 2014; Golus and Bajkiewicz-Grabowska, 2016). Furthermore, SWB retain pollutants by sorption/sedimentation processes, support microbiological degradation and plant uptake (Steidl et al., 2008; Das Gupta et al., 2016; Ma et al., 2016). Due to the changing physicochemical environment in SWB (Lischeid and Kalettka, 2012), they provide a variety of different habitats which leads to a high biodiversity in these ecosystems (Downing, 2010; Biggs et al., 2016; Hill et al., 2016). Especially for amphibians, lentic SWB are of importance since they enable the change between aquatic and terrestrial habitat according to the current life cycle. If SWB are located in an appropriate setting, they act as step stones for migrating species and support genetic exchange as well as meta-populations in habitats (Roe and Georges, 2007; Jeliazkov et al., 2014). Such a patchy spatial arrangement of SWB allows species to migrate to favored habitats when climate change alters environmental conditions (Rosset and Oertli, 2011). According to their high number at global scale, SWB are assessed to be a relevant part of the carbon cycle and contribute significantly to carbon sequestration (Gilbert et al., 2016; Holgerson and Raymond, 2016).

So far, SWB have just been protected by the Council Directive 92/43/EEC on the conservation of natural habitats and of wild fauna and flora (92/43/EEC, 1992). Since authorities/researchers are aware of the importance of SWB, they attract more attention by selected monitoring programs (Brinke et al., 2015; Tamis et al., 2017) or legal instruments such as National Action Plans for the sustainable use of Pesticides (NAP). The mentions of SWB s in NAPs of other European states are listed in (Table 1).

Considerable pesticide contaminations have been found in lotic SWB with maximum concentrations up to 130 μg L^{-1} for prosulfocarb, 129 μg L^{-1} for ethofumesat and 92 μg L^{-1} for metamitron and several exceedances of environmental quality standards were reported (Neumann et al., 2003; Brinke et al., 2015; Szöcs et al., 2017). However, these studies demonstrate that the data base for SWB is too small to give a representative status of contamination, especially for lentic SWB (LSWB). The collected data are inconsistent in sampling procedure, strategy, amount and selection of the active compound and solely demonstrate the current status at the date of sampling (Schreiner et al., 2016; Ulrich et al., 2015; Brinke et al., 2015). Besides, driving factors of pesticide transport into LSWB and of their transformation processes have not been investigated and are not understood, yet.

To better understand pesticide fate at sites with lentic SWB and to protect valuable functions of these water bodies, the objectives of our study are (i) to improve and enhance the data base for pesticide contamination in lentic SWB, (ii) to observe the spatial and temporal heterogeneity of pesticide input into these water bodies within one catchment, (iii) to record transformation patterns of the mother compounds into their transformation products and (iv) to relate physicochemical characteristics of the target compounds, hydrological parameters and site characteristics to the findings.

Despite of several definitions of SWB in terms of size or water levels, the authors refer to perennial rivers/lotic water bodies with catchments <10 km^2 and lakes/lentic water bodies with a surface area <50 ha based on the EU Water Framework Directive.

2. Material and methods

In our study, 10 LSWB were monitored in autumns 2015 and 2016 after pesticide application. Event-based grab samples were analyzed for the applied herbicides flufenacet and metazachlor as well as their transformation products - oxalic acid (OA) and - sulfonic acid (ESA).

2.1. Description of the study site and sampling points

The catchment of the lowland river Kielstau is located in the North of Germany, Federal State Schleswig-Holstein (Fig. 1). Briefly summarized, it is a catchment with an area of 50 km^2 and the river Kielstau has a length of 17 km. The region with plain topography is intensively used for agriculture (63% of catchment area). Due to the lowland character, hydraulic gradients are low and there is a high potential for water retention in the landscape (Kiesel et al., 2010). The groundwater levels are high and the shallow groundwater is in close interaction with surface water (Pfannerstill et al., 2014). Approximately 38% of the agricultural fields are drained to improve management practices and plant growth (Fohrer et al., 2007). The prevalent soil types are Planosols and Luvisols and Gleysols and Histosols in the depressions. The average annual temperature is 8.9 °C, the annual precipitation is 885 mm and the annual sunshine duration is 1631 h (data from 1990 to 2016; DWD, 2017a). The Kielstau catchment was appointed as Unesco demosite in 2010 (Fohrer and Schmalz, 2012).

Within the catchment, 10 LSWB were selected which are located in agricultural fields, hence, pesticides were sprayed on all sides of the

Table 1
Consideration of SWB in National Action Plans of selected EU Member States (National Action Plans - European Commission, 2017).

EU Member State	Content
Belgium	SWB not mentioned
Denmark	Pesticide contaminations can affect lakes
France	SWB not mentioned
Germany	Focus on SWB, especially on lentic ones due to poor data base, targets defined for 2015 and 2023
Italy	Lentic water bodies and natural dystrophic lakes are considered; Mediterranean temporary ponds are of high priority
Poland	Particular aspect on lakes
United Kingdom	Buffer strips are defined/required for ponds