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Controls of event-based pesticide leaching in natural soils: A systematic study based on replicated field scale irrigation experiments

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SUMMARY

Tile drains strongly influence the water cycle in agricultural catchment in terms of water quantity and quality. The connectivity of preferential flow to tile drains can create shortcuts for rapid transport of solutes into surface waters. The leaching of pesticides can be linked to a set of main factors including, rainfall characteristics, soil moisture, chemical properties of the pesticides, soil properties, and preferential flow paths. The connectivity of the macropore system to the tile drain is crucial for pesticide leaching. Concurring influences of the main factors, threshold responses and the role of flow paths are still poorly understood. The objective of this study is to investigate these influences by a replica series of three irrigation experiments on a tile drain field site using natural and artificial tracers together with applied pesticides. We found a clear threshold behavior in the initialization of pesticide transport that was different between the replica experiments. Pre-event soil water contributed significantly to the tile drain flow, and creates a flow path for stored pesticides from the soil matrix to the tile drain. This threshold is controlled by antecedent soil moisture and precipitation characteristics, and the interaction between the soil matrix and preferential flow system. Fast transport of pesticides without retardation and the remobilization could be attributed to this threshold and the interaction between the soil matrix and the preferential flow system. Thus, understanding of the detailed preferential flow processes clearly enhances the understanding of pesticide leaching on event and long term scale, and can further improve risk assessment and modeling approaches.

1. Introduction

Tile drained systems regulate the moisture content of agricultural field sites and affect the hydrology and water quality of cultivated catchments (Schilling and Helmers, 2008; Li et al., 2010; Kennedy et al., 2012). The connectivity of preferential flow paths to tile drains controls quality of the surface water bodies, creating shortcuts for transport of water and solutes to the drains and subsequently into surface waters (Vereecken, 2005; Algoazany et al., 2007; Schilling and Helmers, 2008). Rapid transport of many different solutes into surface waters has thus been reported for tile drained sites: anions (Flury et al., 1995; Villholth et al., 1998; Lennartz et al., 1999; Köhne et al., 2006; Stone and Wilson, 2006), nitrate (Mohanty et al., 1998; Kennedy et al., 2012), strongly adsorbing phosphates (Stamm et al., 1998, 2002), hormons (Gall et al., 2011, 2014), and pesticides (Kladivko et al., 1991, 2001; Czapar et al., 1992; Flury, 1996; Zehe and Flühler, 2001a). Different studies have shown the long-term effect of tile drains on pesticide leaching (Gärdenäs et al., 2006; Rupp et al., 2006). Kladivko et al. (1999) showed that pesticide leaching on a tile drained field site was event driven; peak concentration of pesticides decreased with time since application, although there are exceptions. Preferential flow may lead to simultaneous early appearance and time to peak of reactive, i.e. non-conservative, and conservative solutes in the

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tile drain (Everts et al., 1989; Kung et al., 2000b; Fortin et al., 2002). Numerous recent studies have tried to quantify the total amount of pesticides that leach into surface waters after their applications (Donald et al., 1998; Gaynor et al., 2001; Leu et al., 2004); the annual pesticide loss rates can range from 0.1% to several percent (Flury, 1996). Even small proportions of pesticides leaching to ground or surface water have a significant effect on the ecosystem or human health. Small concentrations in surface water can harm the ecosystem (Jarvis, 2007), safe limits for drinking water (Jarvis, 2007) and target values of water quality (Dabrowski et al., 2002) can be exceeded. Generally, controls on short-term and long-term leaching behavior of pesticides can be subdivided into four different categories:

1. *Event driven factors:* Irrigation/rainfall amount and intensity, and antecedent soil moisture.
2. *Chemical properties of the pesticide:* Adsorption and degradation.
3. *Structural characteristics of the site:* Type and amount of surface connected macropores, macropore network, depth and density of the tile drain network.
4. *Soil characteristics:* Soil matrix properties and soil layering that can effect dispersion and exchange between soil matrix and soil macropores.

Various studies have shown that precipitation characteristics have an important role on triggering preferential flow and contaminant leaching (Malone et al., 2004; McGrath et al., 2007; Nolan et al., 2008). Based on a lysimeter study, McGrath et al. (2010) showed that pesticide transport was a capacity-controlled threshold process, depending on the precipitation amount. They identified 19 mm of precipitation as the threshold for their lysimeter site and found that 38% and 56% of the total transport of two pesticides was attributed to rainfall events exceeding 19 mm, compared to only about 1% to 10% of total bromide mass. In addition, McGrath et al. (2010) showed that the highest amount of pesticide leached 208 days after the pesticide application, during a heavy rainstorm. The complex interaction of antecedent soil moisture and precipitation characteristics is an important control on pesticide leaching (Jarvis, 2008). A modeling study using MACRO (Jarvis, 1994) identified both antecedent conditions and precipitation characteristics as crucial parameters for pesticide leaching (Lewan et al., 2009). The study also demonstrated that there are different leaching behaviors between spring and fall applications. The combination of wet soils and large rainfall events was found to trigger glyphosate leaching (Vereecken, 2005). The effect of soil moisture on pesticide leaching was investigated by Flury et al. (1995), who showed that movement of Atrazine was less pronounced in dry than in wet soil. In line with these findings, Ng et al. (1995) showed that the loss of Atrazine and Metolachlor to surface waters is positively correlated to soil moisture. Jarvis (2007) noted that pesticide application to wet soils increases the risk of pesticide leaching due to the faster triggering of preferential flow.

The total mass losses are also controlled by the sorption properties of the solutes, like K_{oc} – the organic carbon sorption constant (Kladivko et al., 1999). McGrath et al. (2008) showed that the use of the retardation coefficient *R* as a measure of the mobility of resident solutes depends on the flow pathway considered. McGrath et al. (2010) also stated that the characterization of fluxes in soils based on weakly sorbing resident tracers, may underestimate the potential for rapid transport of sorbing solutes under natural variations in rainfall. Pesticides, which were found to be rather immobile in laboratory columns, can be very mobile in field soils (Jury et al., 1986; Flury, 1996). Therefore, parameterizations from lab experiments are not transferable to field situations. Doppler et al. (2012) suggested that mobilization of pesticides at catchment scale "may be less affected by sorption than expected" (Doppler et al., 2012, p. 1965). This raises the question which method may be appropriate to determine transport behavior of reactive solutes in natural soils for better evaluating potential risk. Methods applied in the past to determine the transport parameters of solutes are soil column experiments (Young and Ball, 2000), soil profile excavation (Zehe and Flühler, 2001a), and solute breakthrough curves of tile drained field sites (Kung et al., 2000b; Zehe and Flühler, 2001a) or springs (Wienhöfer et al., 2009). High pesticide sorption can also increase particle bound transport. This particle bound transport may facilitate transport of pesticides or other strongly sorbing solutes (de Jonge et al., 1998, 2004) through the soil. Vilholth et al. (2000) found that 6% of total pesticide leaching of Prochlaroz at a 5 m $\times$ 5 m field plot could be attributed to particle bound transport. De Jonge et al. (1998) found, for the same pesticide, between 2.5% and 13.1% particle bound transport in column experiments.

The degree of pesticide leaching may also be influenced by different site-specific factors. Allaire et al. (2002) outlined the role of continuity and tortuosity of the preferential flow system on solute leaching, and Klaus and Zehe (2010, 2011) showed the pivotal role of macropore density and connectivity to the tile drain system with model simulations. Alletto et al. (2010) gave a detailed review on the effect of tillage on pesticide leaching and stated that conservation tillage systems increase macropore connectivity and thus pesticide leaching; the detailed understanding of the processes and interactions remain unclear (Alletto et al., 2010). Flury (1996) summarized that the effect of soil preparation is more pronounced in finer textured soils. Kladivko et al. (1999) investigated the effect of tile drain spacing on long term pesticide leaching and showed that smaller spacing lead to higher pesticide losses into surface waters, consistent with work for more mobile solutes (e.g. Skaggs et al., 2005; Nangia et al., 2010). Contrary, Southwick et al. (1992) found, for one season, more Atrazine losses at a field site with wider tile drain spacing than at a site with smaller spacing.

The above listed studies agree on the fact that connectivity of the macropore system to the tile drain determines whether rapid pesticide leaching occurs or not. Concurring influences of other event dependent characteristics, adsorption characteristics, characteristics of the site, and hydrological flow paths are still poorly understood. The objective of the present study is to investigate these influences in a systematic manner by a replica series of three irrigation experiments on a tile drained field site with two pesticides, natural and artificial tracers to investigate subsurface flow processes and their link to contaminant transport in the Weiherbach catchment. Klaus et al. (2013) showed, based on the same three experiments that tile drain discharge during irrigation experiments consisted largely of pre-event water from the soil matrix (>80%) entering the preferential flow paths after exceedance of a storage threshold. They used stable isotopes of the water molecule (^{18}O and ^{2}H) in tile drain discharge, irrigation water, and the soil water to determine the origin of the water. Most of the water in the tile drain system was sourced in a depth of 20–40 cm.

Here we use a thorough analysis of the pesticide transport together with the knowledge about the water sources of the tile drain discharge to better link understanding of flow path and pesticide transport to address the following questions:

- What is an appropriate sampling scheme to evaluate pesticide leaching of structured soils?
- How do macropore-matrix interaction and hydrological thresholds influence field scale pesticide transport?
- How do chemical properties and antecedent conditions and precipitation characteristics control the pesticide leaching?
- How important is particle bound pesticide leaching?