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Variability of glyphosate and diuron sorption capacities of ditch beds determined using new indicator-based methods

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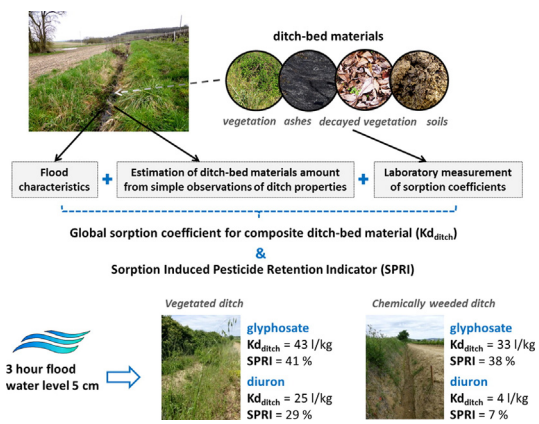
HIGHLIGHTS

- Kd_{ditch} is an indicator of the global ditch-bed pesticide sorption capacity.
- *SPRI* is an indicator of pesticide retention associated to sorption in ditch-beds.
- Pesticide sorption capacity varies with ditch material abundance and flood type.
- A water level increase from 0.5 to 15 cm results in a 90% drop of *SPRI*.
- Soil and ash are mainly responsible for diuron and glyphosate adsorption in ditches.

GRAPHICAL ABSTRACT



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ABSTRACT

Pesticide sorption to ditch-bed materials can efficiently decrease pesticide concentrations in the flowing water. Pesticide sorption depends on flood characteristics and the nature and abundance of ditch-bed materials, such as soils, living and decaying vegetation and ash. However, the affinities of pesticides for various ditch-bed materials have rarely been investigated, and variations in the global sorption capacity of ditch beds resulting from their heterogeneous compositions and variable flood characteristics have not been determined. Thus, we studied the variability of sorption capacities of ditch-bed materials for glyphosate and diuron in three catchments in France and propose a method for calculating global sorption processes in heterogeneous ditch beds. The methodology consists in estimating a global sorption coefficient for the composite ditch-bed materials (Kd_{ditch}) and an indicator of the amount of pesticide potentially retained by sorption during a flood event (*SPRI*). Furthermore, we computed the Kd_{ditch} and *SPRI* of glyphosate and diuron for 8 ditches subjected to 3 h flood events with water levels varying from 0.5 to 15 cm. Our results show that increasing the water level from 0.5 to 15 cm resulted in a 90% decrease in the sorption capacities of the ditch beds for both pesticides. At a medium water depth of 5 cm, *SPRI* varied from 25 to 51% and from 7 to 35% among the ditches for glyphosate and diuron, respectively. The variabilities of the glyphosate and diuron sorption capacities among the ditches were mainly driven by the nature and abundance of soil and ash. As the management of farm ditches, performed to maintain their hydraulic performance, modifies the abundances of various ditch-bed materials, it constitutes a potential lever of action for

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water quality improvement. Thus, Kd_{ditch} and *SPRI* could serve as rapid and cost-effective tools for optimizing ditch network management strategies to improve water quality in cropped catchments.

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1. Introduction

Farm ditch networks are engineered landscape features that are designed and managed to perform a variety of ecosystem services, including waterlogging control, soil erosion prevention, biodiversity conservation or water purification (Dollinger et al., 2015a; Herzon and Helenius, 2008; Levavasseur et al., 2016). The water purification potential of ditches has raised interests among institutions that are tasked with protecting water quality. Indeed, farm ditch networks play an important role in the fates of pesticides within cropped catchments.

Ditches collect drainage and runoff fluxes potentially loaded with pesticides and rout them downstream towards receiving water bodies or groundwater (e.g., Louchart et al., 2001). Despite constituting contaminants dispersal pathways because they link cropped fields with water bodies, ditches may have buffering effect for attenuating water pollution by pesticides according to their composition and hydraulic properties (Dollinger et al., 2015a; Herzon and Helenius, 2008; Needelman et al., 2007a). The high pesticide retention capacities reported for ditches have been attributed so far mainly to the sorption of pesticides to the various materials in the ditch beds although other biogeochemical processes e.g., biotic- and abiotic degradation or sedimentation of pesticides-loaded particles may, to some extent, also contribute to mitigate pesticides in ditches (Dollinger et al., 2015a; Stehle et al., 2011). Consequently, the buffering capacity of ditches is closely linked with the nature and profusion of the ditch-bed materials.

The main endogenous materials that provide efficient sorption sites for pesticides include soils and decaying and living vegetation. Ditch soils are formed from the accumulation of both field eroded particles and humified plant or algae residues and are structured due to root activity and drying/wetting cycles (Needelman et al., 2007b; Ruppert et al., 2014; Vaughan et al., 2008). Thus, the soil texture, structure and chemical composition in ditches are very site specific. Moreover, these nutrient-rich soils combined with particular hydrologic conditions provide ideal growth conditions for a variety of terrestrial and wetland plants (Herzon and Helenius, 2008; Needelman et al., 2007b). Consequently, ditches can be densely vegetated, and the natural decay of ditch plants and the input of dead leaves from surrounding trees and perennial crops (e.g., vineyards, orchards) may result in the formation of consequent litter layers (Levavasseur et al., 2014).

Managing farm ditches to maintain ecosystem services will modify the properties of the ditches, particularly the abundances of various bed materials in the ditches. Ditch management operations, i.e., dredging, chemical weeding, mowing and burning, impact the properties of ditches in contrasting ways (Dollinger et al., 2015a). Although dredging removes most materials from ditch beds, mowing and burning provide additional materials (e.g., hay and ash) that can have high sorption capacities (Dollinger et al., 2015a). Thus, farm ditch management can be used as an efficient method for protecting water quality in cropped catchments. Performing a diagnosis of farm ditch networks and designing appropriate management strategies requires good knowledge of the factors that drive pesticide adsorption and desorption in ditch beds.

The sorption capacities of ditch beds depend on 3 factors, the abundances and characteristics of the various bed materials, the relative affinity of a given pesticide for the available bed materials, and the hydraulic regime (Dollinger et al., 2015a). Adsorption and desorption coefficients measured in the laboratory using small samples are important but insufficient for characterizing the pesticide sorption capacities of ditch beds because they only provide information regarding the relative affinities of given pesticides to the various materials. Few studies have reported sorption coefficients for ditch soils, litter and wetland plants (e.g., Crum et al., 1999; Passeport et al., 2011; Rogers and Stringfellow, 2009; Vallée et al., 2014). Moreover, to our knowledge, the global sorption capacity of ditches resulting from their heterogeneous ditch-bed compositions has not been determined. Indeed, no methods are currently available for assessing the global sorption capacities of ditch beds with contrasting properties under varying hydraulic regimes based on operational, cost-effective and easily reproducible observations of ditch properties.

In this study, we therefore aimed at estimating the variations of the sorption capacities of ditch beds for glyphosate and diuron of catchments with different management, hydrological and pedological features. The specific objectives of this study were to i) identify the main drivers of the pesticide sorption capacity of ditch beds and ii) develop indicator-based methods suitable for analysing the ranking of sorption capacities of farmed ditches with contrasting properties and under varying hydraulic regimes. Three case studies are considered in the present study in three head-water catchments in France.

2. Materials and methods

2.1. Physico-chemical properties of studied pesticides

The herbicides glyphosate and diuron were selected for their potential contrasting sorption behaviours to ditch materials based on their physico-chemical properties (Table S1). Moreover, both herbicides are among the 15 pesticides that are most widely detected in surface water bodies and groundwater in France (SOeS, Ministère de l'Écologie, du Développement Durable et de l'énergie, 2013). Glyphosate [*N*-(phosphomethyl)glycine] is a zwitterionic molecule with strong hydrophilicity and very high water solubility (Table S1). The speciation of glyphosate varies with the pH of the surrounding environment (Dollinger et al., 2015b). Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is a hydrophobic molecule with moderate water solubility and remains neutral under environmental conditions (Table S1).

2.2. Sampling and measurement methods used to determine the properties of the ditch-bed materials

2.2.1. Sampled ditches and ditch bed materials

2.2.1.1. Selected ditches, soils and ash. Soils were sampled from ditch surface layers at different locations along ditch networks from 3 head-water catchments in different agricultural, climatic and pedological settings. Soils RO-D1-S through RO-D9-S (Table S2) were sampled from the Roujan catchment located south of France, which has a semi-arid Mediterranean climate and contains loamy soils and mainly vine crops (Andrieux et al., 1993). Soils RU-D1-S and RU-D2-S were sampled from the Ruiné catchment located west of France, which has an oceanic climate and contains clay soils and chalky soils on the plateaus and in the depressions (Vernier and Dubernet, 1997), respectively, and sunflower, corn, and vine crops. Soils M-D1-S and M-D2-S were sampled from the Morcille catchment located east of France, which is characterized by a continental temperate climate and contains sandy-loam soils and mainly vine crops (Rabiet et al., 2010). Ash samples were collected just after a burning event from the Roujan catchment.

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