



Seepage patterns of Diuron in a ditch bed during a sequence of flood events



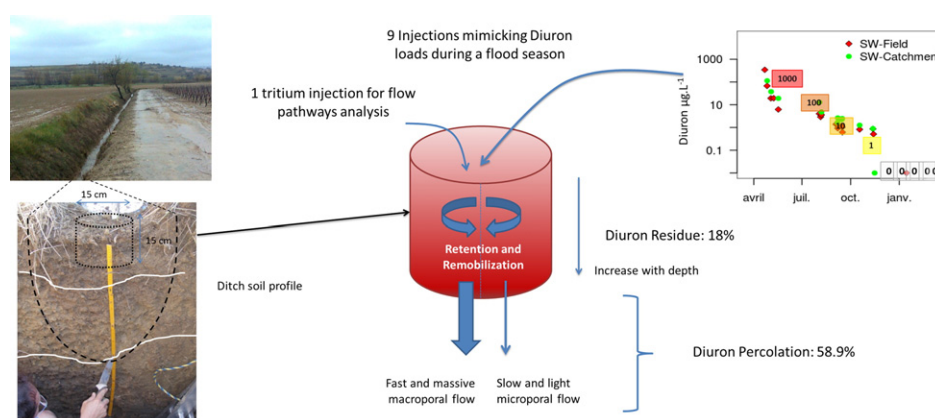
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HIGHLIGHTS

- Diuron percolation in a ditch bed during flood events was mimicked in a column setup.
- Diuron percolation can represent up to 50% of the infiltrated Diuron.
- The ditch bed exhibits a high buffering capacity due to its high sorption properties.
- Contamination period of percolation water lasts longer than that of infiltrating water.
- Diuron residues stored in ditch bed do move deeper than in field topsoils.

GRAPHICAL ABSTRACT



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ABSTRACT

Although ditches limit surface water contamination, groundwater recharge through ditches in Mediterranean catchments may result in groundwater contamination. We analysed the dynamics of pesticide percolation in ditches by conducting an original lab experiment that mimicked the successive percolation processes that occur during a flood season. Nine successive percolation events were operated on an undisturbed soil column collected from a ditch bed. The infiltrating water was doped with ^{14}C -Diuron at concentrations that were chosen to decrease between the events so as to correspond to values observed during actual flood events. The water and solute fluxes were monitored during each event, and the final extractable and non-extractable Diuron residues in the column were determined. Two main observations were made. First, a high leaching potential was observed through the ditch bed over a succession of infiltrating flood events, with 58.9% of the infiltrated Diuron and its metabolites leaching. Second, compared with the contamination of surface water circulating in the ditches, the contamination of seepage water exhibited smaller peak values and persisted much longer because of the desorption of Diuron residues stored in the ditch bed. Thus, ditches serve as buffering zones between surface and groundwater. However, compared with field plots, ditches appear to be a preferential location for the percolation of pesticides into groundwater at the catchment scale.

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1. Introduction

Groundwater contamination by pesticides used for agriculture has been recorded in several countries (Meffe and de Bustamante, 2014; Herrero-Hernández et al., 2013; Barbash et al., 2001; Kolpin et al., 2000). Pesticides may directly reach groundwater from fields by infiltrating with rainfall or irrigation water (Guzzella et al., 2006; Vonberg et al., 2014), by moving through natural or human-made channels that collect water flowing overland, and/or by entering shallow water tables (Burkart et al., 1999; Field et al., 2003). In the last case, groundwater contamination arises if seepage occurs in the channel beds.

In cultivated watersheds, ditches are specific types of channels that are constructed as networks, are often involved in controlling waterlogging, and are potential vectors for contaminants. Nevertheless, regarding surface water contamination, ditches are also considered as buffer zones (Stehle et al., 2011) because they can retain 3 to 99% of the loads of pesticides in the surface water, depending on the molecule and soil type (Dollinger et al., 2015). For drainage ditches under humid conditions, sorption is the main process that explains this high clean up capacity. Drainage ditches have also been shown to limit the spread of contaminants into the groundwater by exfiltrating pesticides (Zheng et al., 1988; Chambers and Bahr, 1992). However, under sub-humid to arid conditions, infiltration generally occurs from ditches; therefore, part of the clean up effect of ditches may result from the percolation of pesticides to deeper soil layers. Moreover, because transmission losses through ditches can represent a significant source of groundwater recharge (e.g., Dages et al., 2009; Ponce et al., 1999), the clean-up of surface waters by infiltrating ditches may lead to groundwater contamination.

Groundwater contamination due to the seepage of contaminated water through ditches or intermittent streams has already been observed (Burkart et al., 1999; Field et al., 2003). For example, Field et al. (2003) measured Diuron in a shallow water table below a field that was never treated with Diuron and suggested that its presence resulted from the infiltration of Diuron-contaminated surface water from a nearby stream. Groundwater contamination fluxes from ditches may be higher than field percolation fluxes for several reasons: (i) transmission fluxes in ditches are larger than field infiltration fluxes (Ponce et al., 1999; Izbicki et al., 2000; Flint et al., 2002; Dages et al., 2009); (ii) infiltration occurs under ponding conditions that favour preferential fluxes (Allaire et al., 2002; Jarvis, 2007), which are known to significantly contribute to groundwater contamination (Flury, 1996); and (iii) the percolation distance to the groundwater is smaller because the ditch bed is located well below the surface of the field soil. In addition, percolation across ditch beds may differ from percolation in field soils because the soil in the ditch beds is different from agricultural soils. The former often exhibit larger organic carbon contents than their neighbouring field soils (Vaughan et al., 2008) and larger adsorption properties (e.g., Cooper et al., 2004; Margoum et al., 2006). The porous structure and infiltration properties of soils in ditch beds are specific because ditch beds are often formed from layered fine sediments deposited by surface flow and support different types of vegetation with specific rooting patterns (Vaughan et al., 2008). To our knowledge, observations of the transport patterns of pesticides in ditch beds are unavailable in the scientific literature.

Therefore, this paper presents an experimental analysis of the percolation patterns and fate of the Diuron herbicide in a ditch bed within the Roujan semi-arid vineyard catchment, the surface waters of which are largely contaminated by herbicides all year (see Louchart et al., 2001). The specific objectives of this study were to i) analyse whether the ditch bed exerts a buffering effect on the contamination of seepage water and ii) evaluate the contamination patterns of percolated water across the ditch bed under the influence of a succession of flood events after herbicide application over the catchment. This experiment consisted of a set of infiltration tests with a ^{14}C -labelled pesticide, Diuron, on an undisturbed soil core collected from a ditch bed. The

contamination levels of the infiltrating water by Diuron were fixed to mimic those observed in the Roujan catchment during a vine-cropping season.

2. Materials and methods

2.1. Soil and core sampling

The study site is a ditch near the outlet of the Roujan catchment (43.3°N, 3.19°E) that is located 60 km west of Montpellier (Hérault, France). The soil in the ditch bed is classified as an endogleyic calcisol according to the Food and Agriculture Organization of the United Nations (FAO)-United Nations Educational, Scientific and Cultural Organization (UNESCO) (1989). A pedological description of the soil profile indicated the presence of three horizons, two clay loam organic-rich horizons (0–17 cm and 17–45 cm) and one silty clay loam horizon (45–80 cm). The two upper soil horizons formed from recent sedimentation layers and the third horizon below 45 cm consisted of an old ditch bed. A granular structure with high porosity and few very coarse fragments occurred in each horizon. The particle size distribution, organic carbon content, organic matter, nitrogen content, cation exchange capacity (CEC), CaCO_3 content and pH (H_2O) were determined for each soil horizon and are reported in Table 1.

In this study, an undisturbed soil core was extracted in May 2013 from the ditch bed, and sampling was limited to the first horizon (0–17 cm) to focus on the interface between the surface and subsurface waters, which was assumed to exhibit the largest sorption processes because of its large organic matter content. During sampling, moderate vegetation mainly composed of horsetails (*Equisetum*) was present in the ditch, and worms and ants were present in the soil profile near the sampling site. Moreover, the volumetric soil moisture content was $0.3 \text{ m}^3 \cdot \text{m}^{-3}$, which was near field capacity and was suitable for limiting soil structural deformation during core extraction. To extract the soil core, a 20 cm tall and 15.2 cm diameter PVC cylinder was gently pushed into the upper 15.5 cm of the ditch bed. After extraction, this core was stored in the laboratory at 4 °C until the infiltration experiments. Near the core, bulk soil samples and 4 additional cores with known volumes were collected to determine the classical soil pedological parameters (Table 1) and bulk density (ρ_b) at the site. The ρ_b was determined as the ratio between the dry soil mass and the total core sampling volume. The soil porosity was estimated based on the bulk density by using the classical formula $1 - \rho_b/\sigma_g$, where the specific density of the solid phase of a typical mineral soil (σ_g) was set to $2.65 \text{ g} \cdot \text{cm}^{-3}$. The saturated water content was estimated to occur when 95% of the pores were filled. The mean bulk density, porosity and saturated water content obtained from the four replicates at a depth of 0–17 cm were $1.28 \text{ g} \cdot \text{cm}^{-3}$, $0.51 \text{ m}^3 \cdot \text{m}^{-3}$ and $0.49 \text{ m}^3 \cdot \text{m}^{-3}$, respectively.

2.2. Selected herbicide

Diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea) was used in the column experiment; it is a well-known and pre-emergent systemic herbicide that has been widely used to selectively control the germination of weeds. In addition, Diuron is slightly toxic, and it was previously one of the most frequently detected pesticides in surface waters in France (SOEs, 2013). It was therefore banned in 2008. It is however still detected in surface waters, especially in southern areas of France according to recent surveys (Agence de l'eau Rhône Méditerranée and Corse, 2010; SOEs, 2013). Diuron has been monitored in the outflow of the Roujan catchment since 1994. The physical–chemical properties of Diuron included a water solubility of $36.4 \text{ mg} \cdot \text{L}^{-1}$ and a Henry's law constant of $2 \times 10^{-6} \text{ Pa m}^3 \text{ mol}^{-1}$. In addition, the typical DT_{50} (half-life) is 75.5 days but ranges from 20 to 119 (PPDB, University of Hertfordshire, 2013).

The sorption characteristics of Diuron were determined according to the Organisation for Economic Co-operation and Development (OECD)

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