WATER RESEARCH 47 (2013) 1123–1135

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Herbicide mitigation in microcosms simulating stormwater basins subject to polluted water inputs

P. Bois [a,b], D. Huguenot [a,c], K. Jézéquel [a], M. Lollier [a], J.Y. Cornu [a,d], T. Lebeau [a,e,*]

[a] Université de Haute Alsace, EA 3991, LVBE (Laboratoire Vigne Biotechnologies et Environnement), Equipe Dépollution Biologique des Sols, 33 rue de Herrlisheim, BP 50568, 68008 Colmar Cedex, France

[b] Institut de Mécanique des Fluides et des Solides de Strasbourg UdS/CNRS/ENGEES/INSA, 2 rue Boussingault, 67 000 Strasbourg, France

[c] Université Paris-Est, Laboratoire Géomatériaux et Environnement, EA 4508, 5 bd Descartes, 77454 Marne la Vallée Cedex 2, France

[d] UMR 1220 TCEM (Transfert sol-plante et Cycle des Eléments Minéraux dans les écosystèmes cultivés), 71 rue E. Bourlaux, F-33883 Villenave d'Ornon, France

[e] LUNAM Université, UMR 6112 LPGN (Laboratoire de Planétologie et Géodynamique de Nantes), 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France

ARTICLE INFO

Article history:
Received 5 September 2012
Received in revised form
16 November 2012
Accepted 18 November 2012
Available online 3 December 2012

Keywords:
Bioremediation
Diuron
Ecological engineering
Glyphosate
Phytoremediation
Sediment

ABSTRACT

Non-point source pollution as a result of wine-growing activity is of high concern. Stormwater basins (SWB) found downstream of vineyard watersheds could show a potential for the mitigation of runoff water containing herbicides. In this study, mitigation of vinery-used herbicides was studied in microcosms with a very similar functioning to that recorded in SWB. Mitigation efficiency of glyphosate, diuron and 3,4-dichloroaniline (3,4-DCA) was investigated by taking into account hydraulic flow rate, mitigation duration, bioaugmentation and plant addition. Mitigation efficiency measured in water ranged from 63.0% for diuron to 84.2% for 3,4-DCA and to 99.8% for glyphosate. Water-storage duration in the SWB and time between water supplies were shown to be the most influential factors on the mitigation efficiency. Six hours water-storage duration allowed an efficient sorption of herbicides and their degradation by indigenous microorganisms in 5 weeks. Neither bioaugmentation nor plant addition had a significant effect on herbicide mitigation. Our results show that this type of SWB are potentially relevant for the mitigation of these herbicides stemming from wine-growing activity, providing a long enough hydraulic retention time.

1. Introduction

Land devoted to wine-growing represents only 1.6% of the total agricultural area in France (Agreste, 2006). Pesticides used in this practice account however for approximately 20% of total marketed pesticides. Besides, the pronounced slope of numerous vineyard watersheds favours runoff water and erosion of soil particles carrying pesticides. At the watershed scale, pesticide losses *via* surface runoff most frequently represent less than 1% of the applied active substance, rarely exceeding 10% (Aubertot et al., 2005; Carter, 2000). Yet pesticide runoff from agricultural fields remains a significant

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[*] *Corresponding author*. LUNAM Université, UMR 6112 LPGN (Laboratoire de Planétologie et Géodynamique de Nantes), 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France. Tel.: +33 276645158.

E-mail address: Thierry.Lebeau@univ-Nantes.fr (T. Lebeau).

0043-1354/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2012.11.029

source of water pollution (Brady et al., 2006; Leu et al., 2004) with amounts and concentrations high enough to cause detrimental biological effects (Schulz, 2004).

Stormwater basins (SWB) often found downstream of agricultural watersheds are built to prevent flooding, to ensure runoff water temporary storage and to retain dissolved and particle-bound contaminants (Meyer, 1985). Growing attention has recently been paid to these features that make SWB relevant for pollution control (Grégoire et al., 2009). They are specific types of constructed wetlands also defined as event-driven wetlands, increasingly considered as cost-effective wastewater treatment devices (Schröder et al., 2007). By design, SWB are exposed to highly variable environmental conditions, resulting in variable hydraulic and chemical retention times. Short retention times are usually associated with low removal rates as a result of short time contacts between the pollutant and the catalyser (biotic or not).

Most of the time pesticide retention times are not long enough for SWB to retain all pesticides (Moore et al., 2002), without being mentioned their complete biodegradation. The supply of sorbents in pesticide-mitigation devices is then promising, e.g., sand and sugar beet pulp for glyphosate, diuron and 3,4-dichloroaniline (3,4-DCA), the main metabolite of diuron (Huguenot et al., 2010), and only if their localization is relevant, i.e., it do not impair SWB hydraulic performances.

Microbial degradation and plant uptake are generally assumed to be the processes most responsible for contaminant removal in constructed wetlands (Stottmeister et al., 2003; Matamoros et al., 2007) especially *via* associated rhizospheric microflora, along with sorption processes (Wanko et al., 2009). We recently reported (Bois et al., 2011) on bacterial populations recovered from the sediment of a stormwater basin (SWB) located downstream of vineyard hills near Rouffach (France) and described by Wanko et al. (2009). In this SWB, glyphosate (respectively diuron) concentrations were around 0.07–4.1 μg L^{-1} (0.01–0.16 μg L^{-1}) in water and 11.8 μg kg^{-1} (2.1 μg kg^{-1}) in sediment (Maillard et al., 2011). The rhizospheric mixed culture '106' consisting of *Arthrobacter* sp., *Pseudomonas putida*, *Delftia acidovorans* and *Brevundimonas* sp. strains was selected for its high capacity in degrading glyphosate, diuron and 3,4-DCA at concentrations far above those recorded in Rouffach SWB.

In constructed wetlands, most mitigation systems are based on bioattenuation (natural biological dissipation) rather than on *in situ* bioaugmentation (biological dissipation carried out by microorganisms precultivated *ex situ*). Yet bioaugmentation of soil or sediment, assisted or not by plants may be a relevant technology (Lebeau, 2011).

This work aimed at studying the effects of bioaugmentation by the mixed bacterial culture '106', plants (*Phragmites australis*) and hydraulic regime on pollutant dissipation, in order to enhance glyphosate, diuron and 3,4-DCA removal in both runoff water (transiting through SWB) and sediment (accumulating into the basins). As pesticides are rarely applied alone, Cu was added to the mixture of glyphosate, diuron and 3,4-DCA supplied to the microcosms. Cu is indeed applied in vineyards until 120 years as Copper Bordeaux mixture to control powdery mildew. The study was performed in small-scale devices. These microcosms were by aspects (hydraulic regime, sand–sediment mix) close to the aforementioned vineyard SWB.

2. Material and methods

2.1. Sediments sampling sites

Sediments were sampled in a SWB located at the outflow of a vineyard watershed (Rouffach, France). Wine-growing activity uses there glyphosate, diuron – outlawed since December 2008 in Europe but grace periods for using up stocks was approved, not to mention that diuron is always found in vineyard soils – and copper (Gregoire et al., 2010).

2.2. General settings

Microcosm experiments were performed in an air-conditioned chamber (20 °C) equipped with Osram S36W/965 Biolux neon lights (France). These lights delivered 147 μmol photons m^2 s^{-1} at 555 nm (Biolux 36W/965, Osram, France) in a programmable way (photoperiod: 16 h light, 8 h dark). HDPE (High Density Polyethylene) rectangular boxes (Garhin, France) were used as microcosms (Fig. 1) with a 6.55 L ($l \times w \times h$: 39 cm × 24 cm × 10 cm) working volume corresponding to the SWB usable volume at the 1:150 000 scale. Batch sorption experiments were performed on this material using all studied compounds at 10 mg L^{-1} concentration range. No sorption was detected. Water inflow/outflow was enabled by holes (5 mm diameter) at the microcosm entrance and exit, respectively at 8.0 cm and 0.5 cm from the bottom. Microcosms were filled with a sand–sediment mix (SS, 80:20 w/w) whose composition was close to that of the SWB: rolled washed sand (0–4 mm) purchased from Holcim granulats (Herrlisheim, France) and sediment coming from the aforementioned SWB. SWB sand filter indeed became in time a sand–sediment (SS) mixture as sediment is carried in the runoff water at the time of rain events. This mixture was stored in sealed flasks (humidity, *ca.* 11%) to ensure constant mixture characteristics over the experiments. Sand–sediment (SS) mix was coarse sand, 69%, fine sand, 9%, silt, 15% and clay, 7%, with organic carbon content 1.3%, pH (H_2O), 8.0, cation exchange capacity, 0.092 meq g^{-1}, carbonate content, 19%, and C:N ratio, 13.8.

2.3. Plants

P. australis was planted in some microcosms (see the experimental design section for more details), as it was the

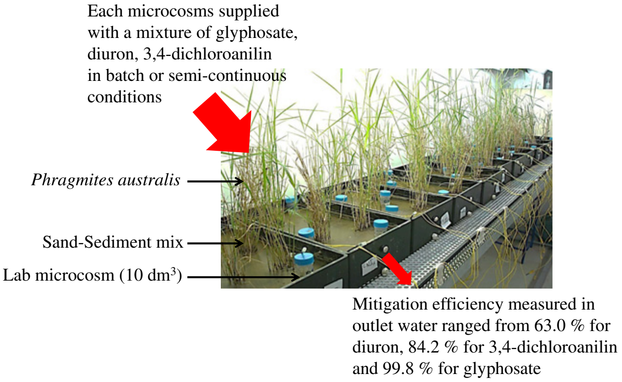

Fig. 1 – Microcosms experimental device.