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Transport and degradation of pesticides in a biopurification system under variable flux, part I: A microcosm study

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Retention and degradation of pesticides in microcosms liable to different fluxes.

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ABSTRACT

The efficiency of a biopurification system, developed to treat pesticide contaminated water, is to a large extent determined by the chemical and hydraulic load. Insight into the behaviour of pesticides under different fluxes is necessary. The behaviour of metalaxyl, bentazone, linuron, isoproturon and metamitron was studied under three different fluxes with or without the presence of pesticide-primed soil in column experiments. Due to the time-dependent sorption process, retention of the pesticides with intermediate mobility was significantly influenced by the flux. The higher the flux, the slower pesticides will be sorbed, which resulted in a lower retention. Degradation of the intermediate mobile pesticides was also submissive to variations in flux. An increase in flux, led to a decrease in retention, which in turn decreased the opportunity time for biodegradation. Finally, the presence of pesticide-primed soil was only beneficial for the degradation of metalaxyl.

1. Introduction

Point source pollution of ground and surface water by pesticides can be caused by spills during filling operations, leakages of spray equipment, spray leftovers, spills of rinsing water from internal and external cleaning of the spraying equipment (Isensee and Sadeghi, 1996; Torstensson and Castillo, 1997; Shepherd and Heather, 1999; Ramwell et al., 2004; Jaeken and Debaer, 2005). This on-farm contamination can be reduced by the use of a biopurification system (*e.g.* biobed, phytobac and biofilter) (De Wilde et al., 2007). Basically, these systems consist of a biological active matrix that retains pesticides into the organic matter and enhances their microbial degradation.

As the efficiency of the system is largely determined by the chemical and hydraulic load, insight into the expected fraction coming onto the system is crucial for the control and management of the biopurification system. This load depends on the type of crop, spraying scheme, behaviour of the operator, the type of spraying machine, type of biopurification system and the period of the season (De Wilde et al., 2007). Firstly, the type of crop might determine the spraying frequency. Crops which are very submissive to pests and diseases (*e.g.* potatoes) should be regularly treated and thus generate a higher hydraulic load. Secondly, depending on the spraying scheme, a farmer treating different crops with different pesticides will need to rinse often (and thus generates more contaminated water) to avoid contamination of the following crop with a remnant of the previous treatment. Thirdly, the attitude of the operator has to be taken into account. An operator not rinsing in the field will generate contaminated water with a much higher chemical load than an operator rinsing in the field. A fourth important parameter is the spraying machine. According to the type of spraying machine (*e.g.* orchard sprayer or field sprayer), the internal (dead volume of the sprayer) and external chemical and hydraulic load will be different. The internal chemical and hydraulic load is higher in field sprayers as the booms and hoses are much longer compared to an orchard sprayer. However, the external contamination on the field sprayer is much smaller than on orchard sprayers due to the vertical spraying direction (Debaer et al., 2008). A fifth point of attention is the period of the season, which determines for a big extent how much contaminated water will be brought on the system. During winter, spraying of the crop is hardly performed, thus during late fall and winter no water will be generated. Finally, the type of biopurification system might also

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determine how much water can be processed. For example, a phytobac, can treat a larger amount of water compared to a biofilter because the dimensions of the phytobac are generally much bigger and thus more substrate is present (De Wilde et al., 2007). An average hydraulic load on a biofilter is 20 L d^{-1} m^{-3}. However, a biofilter without the presence of a buffer tank (a tank where all the contaminated water is collected) will receive the load at once. This can mount up to 100 to 200 L d^{-1} m^{-3}, which is very pernicious for the efficiency of the system (Debaer, C., Personal communication)

To optimize the biopurification system, a flow range should be studied to determine its influence on the leaching of the pesticides. A high flow will probably decrease retention of the pesticide, which decreases the residence time and hence decreases the exposure time to biodegradation. On the other hand, a low flow does not permit to treat a high amount of pesticide contaminated water. The identification of a suitable flow per m^3 matrix will allow adjustments of the dimensions of the system according to the needs irrespective of the type or design of the biopurification system.

Therefore, the first goal of this study was to test the influence of three different flows (low, intermediate and high flow) on transport and degradation of metamitron, bentazone, metalaxyl, isoproturon and linuron. The second goal was to confirm previous findings described in De Wilde et al. (2010). In this study, an increase in metalaxyl degradation could be observed when the organic matrix was inoculated with pesticide-primed material (i.e. previously exposed to the contaminant). Therefore, the organic matrix used in the current study was inoculated with a mixture of five pesticide-primed soils. The efficiency of the inoculated microcosms was than compared with microcosms containing a soil which was not previously treated.

2. Materials and methods

2.1. Selected pesticides, matrix description and column set-up

The pesticides used in this study were linuron (K_{oc} = 620 L kg^{-1}), metalaxyl (K_{oc} = 165 L kg^{-1}), isoproturon (K_{oc} = 36–241 L kg^{-1}), bentazone (K_{oc} = 51 L kg^{-1}), and metamitron(K_{oc} = 77–132 L kg^{-1}) (www.eu-footprint.org). Analytical standard grades (99%) of metalaxyl, isoproturon, linuron, metamitron, and bentazone were purchased from Riedel-de Haen, Seelze, Germany. Technical grade metalaxyl (95.5% purity) was kindly supplied by Syngenta (Basel, Switzerland), technical grade linuron (97.7% purity) by Dupont de Nemours (Hamburg, Germany), technical grade isoproturon (98% purity) by Bayer Crop Science (Monheim, Germany), technical grade bentazone (98,4% purity) by BASF (Limburgerhof, Germany), and technical grade metamitron (99% purity) by Agrichem B.V. (Oosterhout, the Netherlands). Methanol, acetonitrile, and water were of A.R. grade (VWR, Leuven, Belgium).

The organic substrates (characterized in De Wilde et al., 2009b) included in the columns were peat mix (Peltracom, Overpelt, Belgium) (particle size: 0.50–0.71 mm), straw (Zulte, Belgium) (Particle size: 12–37 mm), dried cow manure (Viano, Aalst, Belgium) (particle size: 5–6 mm), coco chips (Peltracom, Overpelt, Belgium) (particle size: 13–26 mm) combined with, on the one hand a mixture of pesticide-primed soils and on the other hand a reference soil. The mixture of pesticide-primed soils consisted of a linuron-primed soil originating from a potato field in Halen, Belgium. The field was last treated in 2008. The isoproturon-primed soil was obtained from a wheat and oat field in Tielt-Winge, Belgium. This was last sprayed in 2005. The metamitron-primed soil originated from a sugarbeet field in Tielt-Winge (Belgium) and was last sprayed in 2006. The bentazone-primed soil came from a maize field in Leefdaal (Belgium) and was last sprayed in 2008. Finally, the metalaxyl-primed soil came from a potato field in Halen, Belgium. The final spraying date was not recorded.

Column microcosms were packed in triplicate with the same mixture of air dried organic substrates for all treatments, namely 5% (w/w) dried cow manure, 25% (w/w) coco chips, 35% (w/w) peat mix, 25% (w/w) straw and 10% (w/w) soil. The composition of the biomix was based on previous results (De Wilde et al., 2009a,c) and appeared to be fairly efficient in retaining and degrading pesticides. The soil fraction was the reference soil which had no pesticide treatment history or consisted of a mixture of a 2% (of the total amount of susbtrate) metalaxyl, 2% isoproturon, 2% linuron, 2% metamitron and 2% bentazone-primed soil. The organic matrix composition with pesticide-primed soil was used in the columns with low, intermediate and high flow. The reference soil was only incorporated in the columns which were irrigated at intermediate flow. Thus, for the intermediate flow six columns were set-up. Below, columns will be referred to as low, intermediate, high flow for the columns inoculated with pesticide-primed soil and as intermediate flow with the statement 'with reference soil' to indicate the difference with the pesticide-primed matrix.

Substrate amounts were weighed, manually mixed in a bucket for about 5–10 min to form homogeneous mixes, and then packed into the glass columns. Compaction of the matrix was carried out by placing a weight of 5 kg on top of the column. The glass columns had the following dimension: 15 cm × 10 cm (l × d).

2.2. Displacement experiments

Displacement experiments were conducted under unsaturated, steady-state flow conditions. Steady-state water flow conditions were established prior to the application of the solute step input. A $CaCl_2$ solution (0.001 M $CaCl_2$) was supplied to the column surface using PTFE (Polytetrafluoroethylene) tubes. A peristaltic pump (Type 205S/CA, Watson Marlow, Zwijnaarde, Belgium) delivered a constant Darcy flux of 0.84 cm d^{-1}, 1.45 cm d^{-1} and 2.40 cm d^{-1} for respectively the low, intermediate and high flow. Calculating the flow in function of the volume of the column leads to the following flows for the microcosms: 56.3 L d^{-1} m^{-3}, 95.6 L d^{-1} m^{-3}, and 160.1 L d^{-1} m^{-3}. For the sake of simplicity, the following notation will be used for the highest, intermediate and lowest flow, respectively, q_{max}, q_{mid} and q_{min}. To differentiate between intermediate flow in the columns with pesticide-primed soil and with the reference soil, the notation of the columns with reference soil will be expanded to $q_{mid+ref}$.

It was assumed that steady-state conditions were reached once the mass of the column remained constant in time. When steady-state conditions were achieved, pesticides were, initially together with a bromide solution (1 mM Br^-), applied to the column. Bromide in the form of KBr was used as a non-reactive tracer to determine physical transport parameters. The pesticide solution pumped onto the columns contained 0.001 M $CaCl_2$ and 10 mg L^{-1} of each pesticide mentioned above. The pesticide solution was added continuously as a step input, the bromide solution was applied as a pulse with a duration of 320 h. The effluent was collected in a fraction collector at the bottom every 2–3 days, outflow volumes and pesticide concentrations were measured. The lower boundary condition was free drainage (zero potential). The substrate was retained in the column by a glass filter (porosity no 2) at the bottom of the column. The experiment lasted for about 180 d until the effluent concentrations of most pesticides reached a constant value. Pesticide effluent concentrations were determined after filtration by HPLC-DAD UV analysis performed on a Finnigan Surveyor HPLC (Thermo Electron Corporation; Waltham, MA, USA) equipped with a gradient pump, a degasser, an autosampler, a diode array detector (DAD) and an Alltima HP C18 EPS 3 μm 150 mm × 3.0 mm column (Alltech Associates Inc. Deerfield, IL, USA), as described by De Wilde et al. (2008). Bromide concentrations were determined by means of ion chromatography (Dionex ICS 2000), containing an AS15 column and KOH elluent. Bromide detection was performed by conductivity with a detection limit of 0.001 mM.

2.3. Transport model

The transport model used is similar to the model elaborated in De Wilde et al. (2009a) for breakthrough curves (BTCs) where equilibrium sorption prevailed. However, non-equilibrium sorption of pesticides could be observed. Transport of pesticides where the sorption reaction is a rate-limited process can be described with the one kinetic site model (Simunek and Van Genuchten, 2008). Transport of a pesticide for steady-state water flow conditions can be written as:

$$\frac{\partial C_1}{\partial t} = D\frac{\partial^2 C_1}{\partial z^2} - \nu\frac{\partial C_1}{\partial t} - \frac{\rho_b}{\theta}\frac{\partial C_s}{\partial t} - \mu_1 C_1 \quad (1)$$

where D is the dispersion coefficient [cm^2 h^{-1}], ν is the pore water velocity [cm h^{-1}], $\nu = q/\theta$, in which q is the Darcian water flux [cm h^{-1}] and θ is the volumetric water content [cm^3_{water} cm^{-3}_{pores}], ρ_b is the bulk density [g mL^{-1}], μ_l is the first-order degradation constant for the solute in the liquid phase [h^{-1}], C_l is the concentration in the liquid phase [mg L^{-1}], C_s is the sorbed concentration [mg kg^{-1}] and t [h] and z [cm] are the temporal and spatial coordinates, respectively. The change in the sorbed concentration with non-equilibrium can be written as follows:

$$\frac{\rho}{\theta}\frac{\partial C_s}{\partial t} = \alpha\frac{\rho_b}{\theta}(C_{s,eq} - C_s) \quad (2)$$

$$C_{s,eq} = K_f C_1^n \quad (3)$$

where α is a first-order kinetic constant describing the kinetics of the sorption process [h^{-1}] and $C_{s,eq}$ the sorbed concentration at equilibrium [mg kg^{-1}], C_s is the sorbed concentration of the kinetic sorption sites [mg kg^{-1}], K_f the Freundlich coefficient [L kg^{-1}], and n the Freundlich exponent [–].

Finally, incorporating (2) and (3) into (1) leads to:

$$\frac{\partial C_1}{\partial t} = D\frac{\partial^2 C_1}{\partial z^2} - \nu\frac{\partial C_1}{\partial t} - \frac{\rho_b}{\theta}\alpha\left(K_f C_1^n - C_s\right) - \mu_1 C_1 \quad (4)$$

The model described above (referred to below as one kinetic site model) is described here as a first-order process depending only on pesticide concentration.