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Characterizing pesticide sorption and degradation in macro scale biopurification systems using column displacement experiments

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Transport of pesticides in macrocosm containing organic substrates.

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ABSTRACT

The efficiency of biopurification systems to treat pesticide-contaminated water was previously studied in microcosms. To validate the obtained results, macrocosm systems were set-up. Four pesticides (linuron, isoproturon, bentazone, and metalaxyl) were continuously applied to ten different organic substrate mixes. Retention of the pesticides was similar and in some cases slightly lower in the macrocosms compared to the microcosms. Differences in retention between the different mixes were however minimal. Moreover, the classification of the retention strength of the pesticides was identical to that observed in microcosms: linuron > isoproturon > metalaxyl > bentazone. Monod kinetics were used to describe delayed degradation, which occurred for isoproturon, metalaxyl and bentazone. No breakthrough of linuron was observed, thus, this pesticide was appointed as the most retained and/or degraded pesticide, followed by isoproturon, metalaxyl and bentazone. Finally, most of the matrix mixes efficient in degrading or retaining pesticides were mixes containing dried cow manure.

1. Introduction

The increasing use of pesticides in agriculture has given rise to a situation in which countries now have to cope with the problem of residues of these compounds in ground and surface water. 40–90% of ground and surface water contamination is caused by direct losses (e.g. 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; Jaeken and Debaer, 2005; Ramwell et al., 2004; Shepherd and Heather, 1999; Torstensson and Castillo, 1997) on hard surfaces where there is minimal opportunity for pesticide sorption and/or degradation. Considering the cost of treating water to remove pesticides, contamination should be treated at the source, more in particular on the farm before discharging. On-farm biopurification systems, developed to treat pesticide-contaminated water, consist of a biologically active matrix that retains pesticides into the organic matter and enhances their microbial degradation. In order to optimize the efficiency of these systems, the fate of pesticides and the contribution of degradation and retention processes inside these systems need to be well characterized. At present, research on a laboratory scale with small columns has been carried out to understand retention and degradation processes taking place inside these systems (De Wilde et al., 2009). The current paper aims at validating the results obtained on a small scale, by up scaling. The up scaling of the column displacement experiments was performed in barrels of ±75 L fed with a pesticide mix. The objectives of this study were (1) to model the transport of pesticides in the system with HYDRUS-1D (Simunek et al., 2005) using theoretical and experimental data in order to evaluate the influence of the organic matrix composition on sorption and degradation of the studied pesticides. (2) To evaluate the degradation capacity of certain mixes using batch experiments in order to obtain information about the degradation efficiency of the mix and the location in the biopurification system where degradation is taking place. (3) To perform a follow-up of the residual concentrations in the mixes with time after the pesticide application was stopped.

2. Materials and methods

2.1. Pesticide properties

The pesticides used in this study were identical to the ones used in the micro scale columns (De Wilde et al., 2008) and were: linuron (3-3,4

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dichlorophenyl-1-methoxy-1-methyl-urea) ($K_{oc} = 410$ L kg^{-1}), metalaxyl (methyl *N*-(2,6-dimethylphenyl)-*N*-(methoxyacethyl)-DL-alaninate) ($K_{oc} = 47$ L kg^{-1}), isoproturon (*N*,*N*-dimethyl-*N*'-[4-(1-methylethyl)phenyl]urea) ($K_{oc} = 36$ L kg^{-1}), and bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide) ($K_{oc} = 13$ L kg^{-1}). Analytical standard grades (99%) of metalaxyl, isoproturon, linuron 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), and technical grade bentazone (98.4 % purity) by BASF (Limburgerhof, Germany). Methanol, acetonitrile, and water were of A.R. grade (VWR, Leuven, Belgium).

2.2. Matrix substrate description

The organic substrates included in the matrix of the barrels were peat mix, garden waste compost, straw, sandy loam soil, cow manure, willow chopping and/or coco chips. The characteristics and the main physicochemical properties of these substrates were reported previously by De Wilde et al. (De Wilde et al., 2008, in press, 2009).

2.3. Macro scale column set-up

Barrels (polyethylene) with a height of 50 cm and inner diameter of 45 cm were packed in duplicate with ten different mixes of air-dried organic substrates and sandy loam soil as reported in Table 1. Substrate amounts were measured gravimetrically, mixed with a concrete mixer to form homogeneous mixes, and then packed into the plastic barrels till a height of 45 cm. A temperature USB data logger (EL-USB-LITE, Lascar, Switzerland) which records temperature every 30 min was positioned at a height of about 22.5 cm in the organic matrix. Barrels were stored at room temperature. A silicone tube was connected to a hole in the bottom of the barrel to collect effluents. The hole was covered with gauze to prevent blockage of the tube and to allow free drainage. The bottom of the barrel was filled with Taunus quartz covered with anti-root foil to prevent migration of small parts of the organic matrix. Batch sorption experiments were performed to assess sorption of the studied pesticides on the silicone tubes, Taunus quartz, and anti-root foil, but no significant sorption was observed (data not shown).

2.4. 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 0.90 cm d^{-1}. Droplets fell on a paper filter placed on the organic substrates in order to provide a fairly homogenous distribution of the solution. The large-scale columns were covered with a plastic lid with a small opening for the inlet to avoid evaporation. It was assumed that steady-state conditions had been reached once the mass of the column remained constant in time. When steady-state conditions were achieved, pesticides were applied to the column, initially together with bromide solution (0.1 mM Br^-). The pesticide solution pumped onto the column contained 0.001 M $CaCl_2$ and 10 mg L^{-1} linuron, isoproturon, metalaxyl and bentazone. The pesticide solution was added continuously as a step input, the bromide solution was applied as a pulse with a duration of 44.5 h. The effluent was collected in a fraction collector at the bottom every 2–3 d, outflow volumes, pH and pesticide concentrations were measured. Bromide in the form of KBr was used as a non-reactive tracer to determine physical transport parameters. Bromide concentrations were determined using ion chromatography (Dionex ICS 2000), containing an AS15 column and KOH effluent. Bromide detection was performed by conductivity with a detection limit of 0.001 mM. The experiments lasted for about 150 d until the effluent concentrations of most pesticides reached a constant value.

Pesticide effluent concentrations were determined using solid-phase extraction followed 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. (De Wilde et al., 2008).

Table 1
Composition of the substrate matrices as applied in the macrocosm system (kg).

	MIX 1	MIX 2	MIX 3	MIX 4	MIX 5	MIX 6	MIX 7	MIX 8	MIX 9	MIX 10
Garden waste compost						8.17	14.71			6.54
Cow manure								3.23	1.29	3.23
Coco chips			2.57	5.13			10.5		5.13	2.05
Peat mix	5.36	9.44	5.25	9.44	5.25			4	8.4	4.2
Straw	1.41	1.35	0.68		0.68	1.36		1.36		0.68
Willow chopping					6.31					1.262
Sandy loam soil	30.24	6.04	30.27	6.04	30.23	30.15	6.04	30.18	6.04	6.04

2.5. Transport models

The HYDRUS-1D model for simulating one-dimensional water flow and transport of solutes in soils was used to describe the transport of pesticides in the column (Simunek et al., 2005). Identical to the microcosm experiment, it was assumed that experimental breakthrough curves (BTCs) could be described using the classical convection-dispersion transport model (CDE) that neglects both physical and chemical non-equilibrium and non-linear sorption (Lapidus and Amundson, 1952):

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - \nu\frac{\partial c}{\partial z} - \mu_l c \tag{1}$$

where R is the retardation factor [-]:

$$R = 1 + \frac{\rho}{\theta}K_f n c^{n-1} \tag{2}$$

where D is the dispersion coefficient [L^2 T^{-1}], ν is the pore water velocity [LT^{-1}], $\nu = q/\theta$, in which q is the Darcian water flux [LT^{-1}] and θ is the volumetric water content [L^3 L^{-3}], ρ_b is the bulk density [M L^{-3}], μ_l is the first-order degradation constant for the solute in the liquid phase [T^{-1}], and t [T] and z [L] are the temporal and spatial coordinates, respectively. However, as previously described in the microcosm experiment, degradation is not always a first-order process. A lag phase which is commonly observed in laboratory mineralization experiments (Mertens et al., submitted for publication) was also present in the BTCs of the pesticide in column displacement experiments (De Wilde et al., 2009). Therefore, the simplified version of the Monod kinetics (Guimont et al., 2005; De Wilde et al., 2009) was incorporated into HYDRUS-1D to describe BTCs where a lag phase was clearly present. The change in pesticide concentration (when neglecting the effect of transport) and the bacterial growth can be described as:

$$\frac{dc}{dt} = -\left(\frac{\mu_m}{YK_s}X\right)c = -\left(\mu^* X\right)c \tag{3}$$

$$\frac{dX}{dt} = -\left(\frac{\mu_m}{K_s}c\right)X - k_{decay}X = \left(\mu_m^* c\right)X - k_{decay}X$$

where c is the liquid pesticide concentration [$M_p L_w^{-3}$], X is the pesticide-degrading biomass concentration [$M_b L_w^{-3}$], μ_m is the mass growth rate [T^{-1}], K_s is the half saturation constant [$M_p L_w^{-3}$], k_{decay} is the decay rate [T^{-1}] (subscripts b, p and w refer to biomass, pesticide and water, respectively), Y is a mass ratio of the organisms formed per pesticide utilized [$M_b M_p^{-1}$], μ_m/K_s is the modified mass growth rate [$L_w^3 M_p^{-1} T^{-1}$], and μ^* has units of [$L_w^3 M_b^{-1} T^{-1}$]. Incorporating equation (3) into the one-dimensional transport equation (1), results in:

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - \nu\frac{\partial c}{\partial z} - \left(\mu^* X\right)c \tag{5}$$

These equations (referred to below as the Monod model) have been implemented in HYDRUS-1D. The fitting parameters for this model are μ^*, μ_m^* (yield Y) and k_{decay}.

2.6. Batch degradation experiments

After the displacement experiment was ended, the organic matrix was removed from the barrels and divided into three parts, i.e. lower (0–15 cm), middle (15–30 cm) and upper (30–45 cm) part. 0.5 ± 0.001 g of matrix of the upper and lower layer of mixes 3, 4, 9, and 10 and of fresh material with the same composition as mix 9 were transferred into an autoclaved Erlenmeyer. Experiments were carried out in triplicate for each mix and layer. 50 mL of MMO medium containing 20 mg L^{-1} of linuron, isoproturon, bentazone, and metalaxyl, which was prepared as described by Dejonghe et al. (Dejonghe et al., 2003), was added to the Erlenmeyer which was incubated on a shaker at 150 rpm at room temperature. A sterile control, to check for abiotic losses, was prepared for each mix-layer combination through the addition of 8% chloroform to the MMO solution. Every 2–3 d, 800 μL of the solution was sampled and filtered with a syringe filter with a PVDF membrane with a pore size of 0.22 μm (Carl Roth, Karlsruhe-Rheinhafen, Germany). The aliquot was injected into the HPLC-DAD.

2.7. Pesticide extraction from the organic matrix

The three fractions of the organic matrix (0–15 cm, 15–30 cm, and 30–45 cm) were analyzed to quantify the residual pesticides. Samples were homogenized with a concrete mixer after quantification and stored during three months at room temperature in a closed container. After three months, samples were taken and analyzed to determine the residual pesticide concentrations. Extraction of the pesticides was carried out on 50 ± 0.001 g organic matrix of which the dry matter content was determined gravimetrically after drying at 105 °C during 24 h. 200 mL of methanol was added to the organic matrix and shaken during 1 h at 150 rpm. The