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

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ABSTRACT

Biopurification systems treating pesticide contaminated water are very efficient, however they operate as a black box. Processes inside the system are not yet characterized. To optimize the performance, knowledge of degradation and retention processes needs to be generated. Therefore, displacement experiments were carried out for four pesticides (isoproturon, bentazone, metalaxyl, linuron) in columns containing different organic mixtures. Bromide, isoproturon and bentazone breakthrough curves (BTCs) were well described using the convection–dispersion equation (CDE) and a first-order degradation kinetic approach. Metalaxyl and linuron BTCs were well described using the CDE model expanded with Monod-type kinetics. Freundlich sorption, first-order degradation and Monod kinetics coefficients were fitted to the BTCs. Fitted values of the distribution coefficient $K_{f,column}$ were much lower than those determined from batch experiments. Based on mobility, pesticides were ranked as: bentazone > metalaxyl – isoproturon > linuron. Based on degradability, pesticides were ranked as: linuron > metalaxyl – isoproturon > bentazone.

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1. Introduction

Organic contaminants in general, and organic pesticides in particular, are widespread in both surface and ground waters (Dousset et al., 2007; Kamra et al., 2001; Rodriguez-Cruz et al., 2007; Shaw et al., 2000). Several field surveys and measurement campaigns have demonstrated that 40–90% of surface water contamination is attributable to point sources or direct losses (Carter, 2000; Decoin, 2003; Kreuger and Nilsson, 2001; Mason et al., 1999). Point source pollution results, for example, from spills at 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). These practices occur mainly at the filling and cleaning areas of farms, where the ground is often covered with concrete, gravel or sand and where the ability to adsorb and degrade pesticides is relatively low, creating high risk for contamination (Helweg et al., 1998; Wiren-Lehr et al., 2001). Even small quantities of the concentrated spray solution may present a serious contamination risk. To meet European standards for drinking water (98/93/EEC), efforts are required to improve water treatment and prevent contamination. On-farm water treatment systems for treatment of pesticide contaminated waste water need to be cheap, reliable, and labor efficient, with low waste disposal costs.

On-farm biopurification systems, introduced by Torstensson and Castillo (1997) in 1997 in Sweden, have been developed for this purpose. Typical overall clean-up efficiency exceeds 95%, often removing more than 99% of the pesticide contamination (De Wilde et al., 2007). These systems consist of a biologically active matrix that retains pesticides into the organic matter and enhances their microbial degradation. The composition and the type of the organic material present in the biobed are crucial for retention of chemicals, as well as for the amount and activity of microorganisms responsible for their degradation (Castillo and Torstensson, 2007).

Retention of pesticides in these systems does not depend solely on the structure and composition of the organic substrates, but also on the physicochemical characteristics of the pesticide. The efficiency of these systems is expected to be much lower in retaining and degrading mobile pesticides, such as bentazone ($K_{oc} = 13$ L kg^{-1}), metsulfuron-methyl ($K_{oc} = 39.5$ L kg^{-1}), and mecoprop ($K_{oc} = 31.5$ L kg^{-1}), than less mobile pesticides such as linuron ($K_{oc} = 410$ L kg^{-1}) (De Wilde et al., 2007). However, at present, biopurification systems operate as a black box, since the research carried out to sufficiently understand processes taking place inside of these systems is limited. In order to optimize the efficiency of these systems for a broad range of pesticides and organic substrates, the fate of pesticides and the effects of degradation and retention processes inside these systems need to be well characterized.

This study focuses on the fate of four pesticides, i.e., linuron, bentazone, metalaxyl and isoproturon, in small-scale bio-purification systems, focusing mainly on degradation and retention (sorption) processes. A comparison is carried out between sorption in batch experiments and in column displacement experiments. Degradation of pesticides is evaluated using the first-order or Monod kinetics, the latter to describe the possible occurrence of delayed degradation. While the transport of pesticides has been frequently evaluated in soil columns, this study uses different mixtures of organic materials, which have not previously been characterized in detail. The one-dimensional transport model HYDRUS-1D (Simunek et al., 2005) was used to identify and quantify solute transport and hydraulic parameters.

2. Materials and methods

2.1. Experimental

2.1.1. Pesticide properties

The pesticides used in this study were selected based on their physicochemical characteristics, solubility, frequency of detection in surface and ground waters, and frequency of use. The mobility of a pesticide, which we assumed to be characterized by the organic carbon partition coefficient K_{oc}, was an important selection parameter, as it largely determines pesticide retention. Linuron (3,3,4 dichlorophenyl-1-methoxy-1-methyl-urea) ($K_{oc} = 410$ L kg^{-1}) was selected as a rather immobile pesticide, metalaxyl (methyl N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-DL-alaninate) ($K_{oc} = 47$ L kg^{-1}) and isoproturon (N,N-dimethyl-N'-[4-(1-methyl-ethyl)phenyl]urea) ($K_{oc} = 36$ L kg^{-1}) as intermediately mobile pesticides, and bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide) ($K_{oc} = 13$ L kg^{-1}) as a mobile pesticide. None of the four selected pesticides was highly persistent, because their DT50$_{soil}$ values (time, during which the pesticide concentration decreases by 50%) were lower than 50 days (Vercruysse and Steurbaut, 2002). 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).

The sorption properties of the four pesticides on various organic substrates used in the column microcosm experiments (described below) were previously determined by De Wilde et al. (2008b) in batch experiments conducted according to the OECD guideline 106. The Freundlich sorption parameters (i.e., K_f – the distribution coefficient, and n – the exponent) calculated in that study for all pesticide–substrate combinations are presented in Table 1.

2.1.2. Matrix substrate description

The following organic substrates were selected for inclusion in the matrix of the laboratory columns: peat mix, garden waste compost, straw, sandy loam soil, dried cow manure and coco chips. The characteristics of these substrates were discussed in detail by De Wilde et al. (2008a). Their main physicochemical properties are presented in Table 2. The substrates peat mix, garden waste compost, dried cow manure and coco chips were used in the form which is commercially available. Straw was cut to obtain fractions of 3–6 cm. Before its use, the sandy loam soil (33% sand, 56% loam and 11% clay) was first air-dried and crushed to pass a 2 mm sieve. Only the fraction smaller than 2 mm was used.

Table 1
Freundlich sorption parameters for various combinations of pesticides and organic substrates determined in batch experiments.

Substrate	Sorption parameter	Metalaxyl	Isoproturon	Linuron	Bentazone
Coco chips	$K_{f,batch}$ (L kg^{-1})	10.66	9.22	51.01	7.08
	n_{batch}	0.98	1.17	0.85	0.79
Garden waste compost	$K_{f,batch}$ (L kg^{-1})	16.59	27.08	80.55	2.45
	n_{batch}	0.81	0.61	0.58	0.78
Sandy loam soil	$K_{f,batch}$ (L kg^{-1})	6.91	2.12	2.86	0.57
	n_{batch}	0.74	1.09	0.86	0.91
Cow manure	$K_{f,batch}$ (L kg^{-1})	4.25	34.87	47.67	4.36
	n_{batch}	1.20	0.71	0.60	0.79
Peat mix	$K_{f,batch}$ (L kg^{-1})	58.83	57.27	192.57	9.27
	n_{batch}	0.74	0.77	0.63	0.76
Straw	$K_{f,batch}$ (L kg^{-1})	6.58	7.91	95.28	2.54
	n_{batch}	1.01	1.08	0.81	0.89

2.1.3. Column microcosm set-up

Column microcosms were packed in triplicates with five different mixtures of air-dried organic substrates and sandy loam soil as indicated in Table 3. Substrate amounts were measured volumetrically, manually mixed in a bucket for about 5–10 min to form homogeneous mixtures, and then packed into glass columns. Compaction of the matrix was carried out by placing a weight of 5 kg on top of the column. The columns were 15 cm high and had an inner diameter of 10 cm. The bottom of the columns was lined with a glass filter, so that seepage face conditions could develop there.

2.1.4. 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 1.74 cm d^{-1}. Droplets fell on a paper filter placed on the organic substrates in order to provide a homogenous distribution of the solution. The top of each column was covered with parafilm to avoid evaporation. It was assumed that steady-state conditions had been reached once the mass of the soil 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. While pesticides were added continuously as a step input, the bromide solution was applied as a pulse with duration of 18.3 h. The effluent was collected in a fraction collector at the bottom every 2–3 days (the effluent was the total amount of solution eluted during two consecutive sampling days) and both outflow volumes and pesticide concentrations were measured. Bromide in the form of KBr was used as a non-reactive tracer in the column experiments 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 100 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, and a diode array detector (DAD), as described in detail by De Wilde et al. (2008a). The analytical column used in the analysis was an Alltima HP C18 EPS 3 µm 150 mm × 3.0 mm (Alltech Associates Inc. Deerfield, IL, USA).

2.2. 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). It was assumed that experimental breakthrough curves (BTCs) could be described using the classical convection–dispersion transport model that neglects both physical and chemical non-equilibrium (Lapidus and Amundson, 1952). Chemical non-equilibrium (Cameron and Klute, 1977) was not considered since the sorption process for the pesticide–substrate combinations was sufficiently fast under the applied low flow rates to establish local equilibrium (De Wilde et al., 2008a).

Assuming that decay is only active in the liquid phase, and since a nonlinear relationship between liquid and solid-phase concentrations can be described using the Freundlich adsorption isotherm: $s = K_f c^n$, where c [M L^{-3}] and s [M M^{-1}] are

Table 2
Physicochemical characteristics of the substrates used in the matrix of the column experiment.

	pH	OC[a] (%)	P$_2$O$_5$ (%)	K$_2$O (%)	CaO (%)	MgO (%)	Na (mg 100 g^{-1})	CEC[c] (meq 100 g^{-1})	Specific density ($\times 10^6$ g m^{-3})
Garden waste compost	7.7	27.84	ND[b]	ND	ND	ND	ND	ND	1.84
Straw	6.6	42.34	0.69	7.72	0.38	0.36	0.57	25.21	1.56
Coco chips	6.7	44.69	0.98	12.39	0.08	0.1	2.52	58.98	1.67
Peat mix	6.4	47.61	0.45	0.8	67	0.79	0.42	129.42	1.58
Sandy loam soil	6.9	0.91	0.03	0.42	0.19	0.08	0.21	13.87	2.81
Cow manure	6.9	37.59	9.87	11.37	1.8	4.92	1.41	53.22	1.68

[a] OC – organic carbon.
[b] ND – not determined.
[c] CEC – cation exchange capacity.

concentrations in the liquid and solid phases, respectively, and K_f and n are Freundlich parameters, the transport of a reactive solute for steady-state water flow conditions can be written as

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} - \frac{\rho_b}{\theta}\frac{\partial s}{\partial t} - \mu_1 c \tag{1}$$

where D is the dispersion coefficient [L^{2}T^{-1}], v is the pore water velocity [LT^{-1}], $v = q/\theta$, 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 [ML^{-3}], μ_1 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. The change in the sorbed concentration can be written as follows

$$\frac{\rho_b}{\theta}\frac{\partial s}{\partial t} = \frac{\rho_b}{\theta}\frac{ds}{dc}\frac{\partial c}{\partial t} = \frac{\rho_b}{\theta}K_f n c^{n-1}\frac{\partial c}{\partial t} \tag{2}$$

Finally, incorporating (2) into (1) leads to

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} - \mu_1 c \tag{3}$$

where R is the retardation factor (−):

$$R = 1 + \frac{\rho_b}{\theta}K_f n c^{n-1} \tag{4}$$

In the model described above (referred to below as the CDE model), pesticide degradation is assumed to be a first-order process depending only on pesticide concentration. However, this is in contrast with a lag phase (a start-up period, during which degradation is not detected) commonly observed in laboratory mineralization experiments (Mertens et al., 2008). Therefore, we incorporated the simplified version of the Monod kinetics (Guimont et al., 2005) to describe BTCs where a lag phase was clearly present (e.g., metalaxyl BTCs) into HYDRUS-1D. In such a model, bacterial growth can be described using the following Monod kinetics:

$$\frac{dX}{dt} = \left(\mu_{m,b}\frac{c}{K_s + c}\right)X - k_{decay,b}X \tag{5}$$

where X is the pesticide-degrading biomass concentration [M$_b$L$_w^{-3}$], c is the liquid pesticide concentration [M$_p$L$_w^{-3}$], $\mu_{m,b}$ is the mass growth rate [T^{-1}], K_s is the half saturation constant [M$_p$L$_w^{-3}$], and $k_{decay,b}$ is the decay rate [T^{-1}] (subscripts b, p and w refer to biomass, pesticide and water, respectively). The bacterial Monod growth function can be related to the pesticide consumption utilizing a yield coefficient, Y, defined as a mass ratio of the organisms formed per pesticide utilized [M$_b$M$_p^{-1}$]. The local change in pesticide concentration when neglecting the effects of the transport can then be expressed as follows

$$\frac{dc}{dt} = -\frac{1}{Y}\left(\mu_{m,b}\frac{c}{K_s + c}\right)X \tag{6}$$

If we assume that the pesticide concentration (c) is significantly lower than the half saturation constant ($c \ll K_s$), then Eqs. (5) and (6) simplify as follows

$$\frac{dX}{dt} = \left(\frac{\mu_{m,b}}{K_s}c\right)X - k_{decay,b}X = \left(\mu_{m,b}^*c\right)X - k_{decay,b}X \tag{7}$$

$$\frac{dc}{dt} = -\left(\frac{\mu_{m,b}}{YK_s}X\right)c = -\left(\mu_b^*X\right)c \tag{8}$$

where $\mu_{m,b}/K_s$ is the modified mass growth rate [L$_w^3$M$_p^{-1}$T^{-1}], and μ_b^* has units of [L$_w^3$M$_p^{-1}$T^{-1}]. Incorporating Eq. (8) into the one-dimensional transport Eq. (3), results in

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} - \left(\mu_b^*X\right)c \tag{9}$$

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

3. Results and discussion

Physical transport was first evaluated by analyzing the bromide BTCs. The volumetric water content, θ, and the longitudinal dispersivity, λ ($D = \lambda \cdot v$), were fitted to the observed Br$^-$ BTCs. Once the physical transport was fully characterized using bromide BTCs, chemical processes for isoproturon, metalaxyl, linuron, and bentazone were analyzed by inverting the pesticide BTCs with the Levenberg–Marquardt algorithm in HYDRUS-1D, using the physical transport parameters estimated for bromide transport. In all inversions of the pesticide BTCs, the soil water content, θ, the water flux, q, the bulk density, ρ, and the dispersivity, λ, were fixed. Estimated reaction parameters included the Freundlich parameters $K_{f,column}$ and n_{column}, and the liquid degradation constant μ_1.

3.1. Bromide BTCs

BTCs are plotted in Fig. 1 as Br$^-$ concentrations versus the number of pore volumes (PV) eluted (one pore volume represents time needed for the volume of water that fills the voids of the column to be eluted: PV = $qt/(\theta L)$). The HYDRUS-1D model fitted the experimental data well with R^2 varying between 0.70 and 0.92. However, the fit to the Br$^-$ BTCs of mixtures 5A and B is poorer due to the presence of a plateau in the experimental data. High values before and after the peak could be caused by analytical errors. The experimental BTCs did not show any significant asymmetry or long-tailing that would indicate physical non-equilibrium. The mass balance of the amount of Br$^-$ entering and leaving the column showed an overall average mass recovery of 96%, therefore it could be concluded that physical equilibrium prevailed. Fitted transport parameters are presented in Table 4, together with bulk densities of the column microcosm. High water contents (in comparison to soils), likely caused by the high water sorbing capacity of organic substrates such as peat mix and coco chips, were found for all columns. The dispersivity length was quite similar for all mixtures, with a slightly higher dispersion for mixtures 3 and 4. Only slight
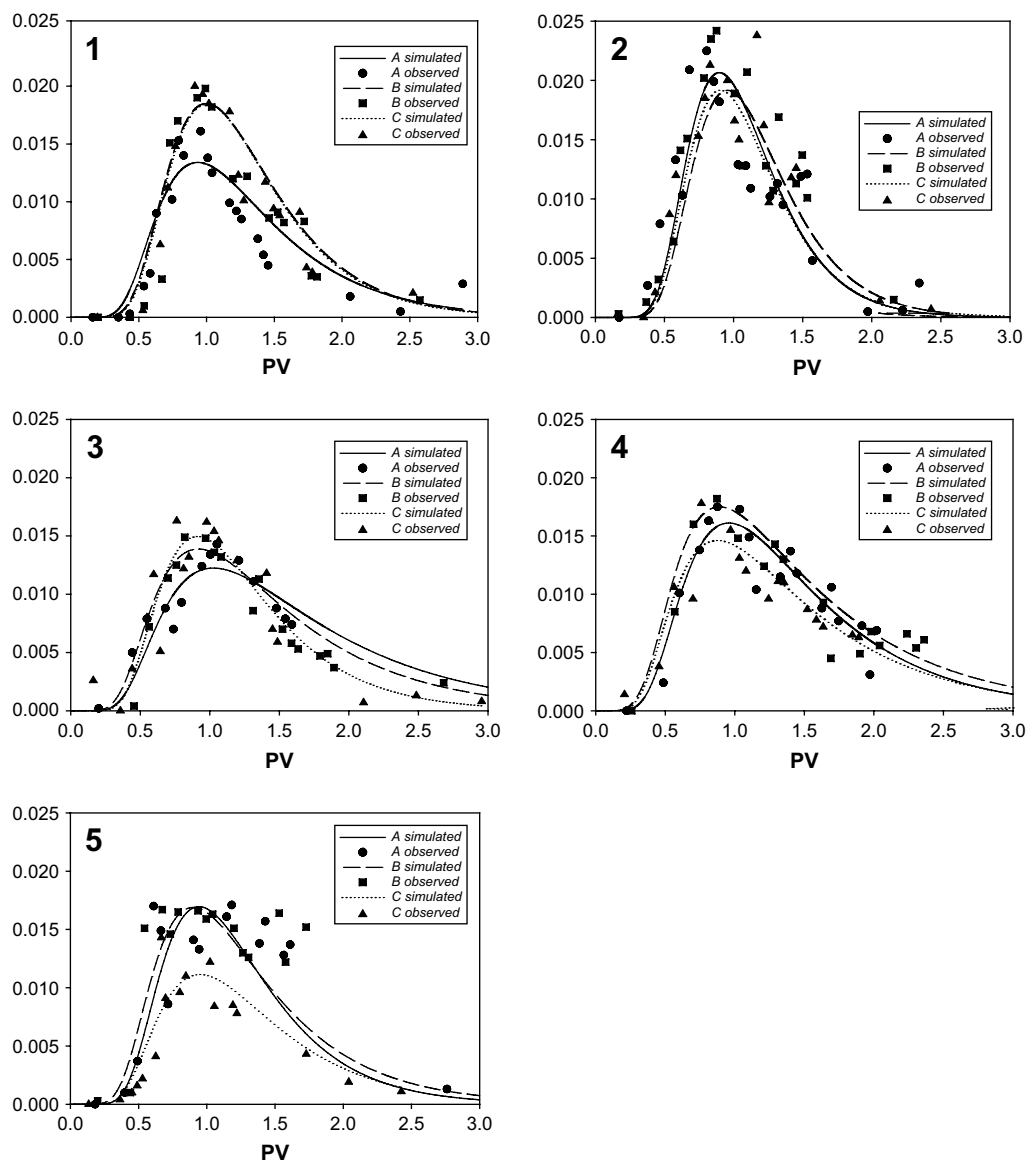
Table 3
Composition of the matrix in the column microcosms set-up (g).

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
Garden waste compost	–	159.93	–	–	–
Straw	27.33	28.43	27.27	12.97	13.00
Coco chips	–	–	–	52.43	52.57
Peat mix	105.20	–	87.03	104.77	83.87
Sandy loam soil	641.07	643.27	640.63	642.33	639.67
Cow manure	–	–	64.27	–	64.27

Fig. 1. Observed and simulated BTCs of Br⁻ in 5 experimental column set-ups (replicates A, B, and C) containing different types of organic substrate. (1) Mixture 1, (2) mixture 2, (3) mixture 3, (4) mixture 4 and (5) mixture 5. Symbols represent the observed data, full, dashed and dotted lines the model fits. Absolute concentrations are plotted against the number of pore volumes (PV).

Table 4
Estimated physical transport parameters for Br⁻ in the 5 microcosms using the CDE transport model (±95% confidence interval).

Mix	θ	λ (cm)	R^2	ρ (g cm⁻³)
1A	0.68 ± 0.03	2.20 ± 0.34	0.86	0.66
1B	0.53 ± 0.02	1.61 ± 0.28	0.87	0.66
1C	0.54 ± 0.02	1.56 ± 0.20	0.91	0.66
2A	0.51 ± 0.02	1.88 ± 0.31	0.81	0.70
2B	0.52 ± 0.02	1.14 ± 1.14	0.85	0.70
2C	0.55 ± 0.02	1.12 ± 0.23	0.78	0.71
3A	0.69 ± 0.03	3.04 ± 0.51	0.84	0.69
3B	0.57 ± 0.04	3.33 ± 0.76	0.91	0.70
3C	0.63 ± 0.02	1.97 ± 0.29	0.87	0.70
4A	0.53 ± 0.05	2.99 ± 0.36	0.90	0.69
4B	0.47 ± 0.02	4.28 ± 0.72	0.87	0.69
4C	0.57 ± 0.02	3.82 ± 0.49	0.87	0.69
5A	0.57 ± 0.04	1.86 ± 0.56	0.70	0.73
5B	0.53 ± 0.03	2.50 ± 0.55	0.75	0.72
5C	0.83 ± 0.04	2.13 ± 0.42	0.80	0.72

differences existed in transport parameters between replicated columns. These differences could be explained by the spatial heterogeneity of the structure of the organic substrates and packing of the columns.

3.2. Isoproturon BTCs

Isoproturon BTCs are shown in Fig. 2 in terms of relative concentrations (i.e., measured concentrations relative to the inlet concentration) versus the number of pore volumes (PV) eluted. The fitted solute reaction parameters are presented in Table 5. The CDE model described the isoproturon BTCs well, as reflected in high values of the determination coefficient R^2 (0.95–1.00) (Table 5). The BTCs shifted significantly more to the right than bromide (Fig. 1), which indicates that the pesticide is strongly adsorbed into the organic substrates, which is also reflected by the retardation coefficient R (Table 5). However, R which is calculated using the initial concentration as input concentration, is slightly overestimated if degradation occurs and if $n > 1$. Mixtures 1 and 2 retained isoproturon the most, with averages R of 12 and 15, respectively.
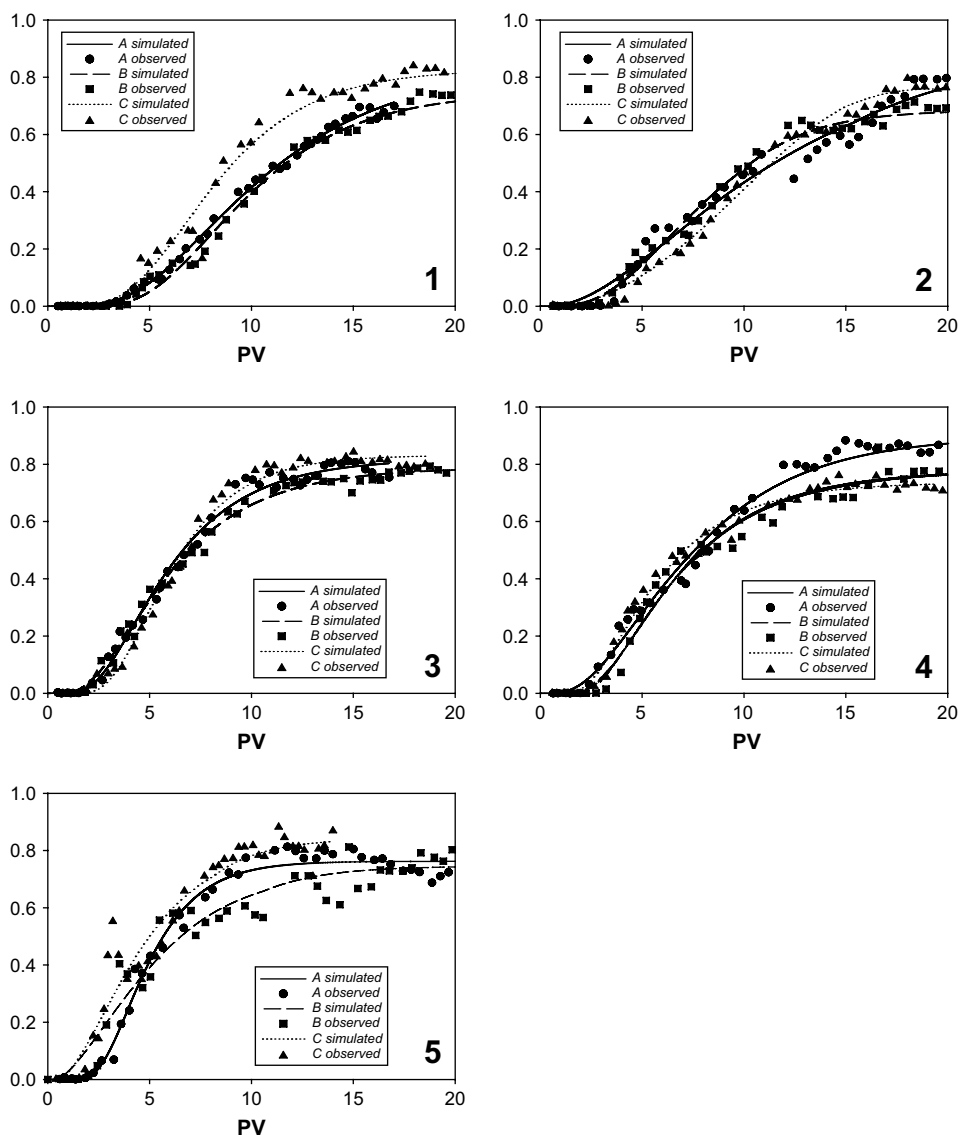
Fig. 2. Observed and simulated BTCs of isoproturon in 5 experimental column set-ups (replicates A, B, and C) containing different types of organic substrate. (1) Mixture 1, (2) mixture 2, (3) mixture 3, (4) mixture 4 and (5) mixture 5. Symbols represent the observed data, full, dashed and dotted lines the model fits. Relative concentrations are plotted against the number of pore volumes (PV).

Mixtures 3, 4 and 5 retained isoproturon in a similar way, with averages R of 7, 8 and 7, respectively. This indicates that the classical biomix composition as in mixtures 1 and 2 with peat mix or garden waste compost retains isoproturon the most. Decreasing the amount of peat or straw appears to decrease the retention of this pesticide. The value of the Freundlich exponent n_{column} is an indicator of the curvature of the sorption isotherm. Most sorption isotherms are of the S-type ($n > 1$), which indicates a strong competition by water molecules for adsorption sites at low pesticide concentrations (Giles et al., 1960). However, the sorption of isoproturon on mixtures 1, 3 and, 4 was almost linear. Also note that the uncertainty of this parameter was relatively low (i.e., narrow confidence intervals, see Table 5). However, this was true only when sorption was almost linear. Notice below that when sorption was nonlinear, the uncertainty increased significantly (Table 6). A comparison of the Freundlich parameters obtained using column transport experiments with those obtained in batch experiments (Table 5) showed that $K_{f,column}$ values were about 2.4–6.9 times smaller for the column experiments. This means that isoproturon is more strongly sorbed by organic substrates in batch experiments,

and that using coefficients based on such studies in transport models would overestimate sorption. This was reported previously by Meyer-Windel et al. (1999) for atrazine and isoproturon, and Kookana et al. (1992) for fenamiphos, linuron and simazine. In the present study initial analysis of the BTCs were performed with the Freundlich parameters obtained in batch experiments, nonetheless optimizations with chemical equilibrium and non-equilibrium assumptions did not improve the fit of the BTC. Batch sorption experiments are not always representative of the sorption process occurring in column studies or in the field, since the solid/liquid ratio is much higher in percolate column experiments than in batch experiments, there could also be an increase in surface area resulting from the disaggregation of clusters during shaking and moreover, the pesticide–substrate solution is continuously shaken, which improves contact between pesticide and substrate, which could enhance sorption (Fesch et al., 1998). However, there also exist an alternative opinion that is supported by a number of experiments and resulting publications that show that results from batch experiments can be used to describe the transport behaviour of pesticides in soil columns and outdoor if the essential processes

Table 5
Solute reaction parameters fitted to isoproturon BTCs (±95% confidence interval).

Mix	$K_{f,column}$ (L kg^{-1})	n_{column}	$K_{f,batch}$ (L kg^{-1})	n_{batch}	μ_l ($\times 10^{-3}$) (h^{-1})	R^2	R	DT50 (d)
1A	9.30 ± 0.39	1.12 ± 0.02	18.28	0.89	1.24 ± 0.18	1.00	14.19	331
1B	7.81 ± 0.44	1.03 ± 0.04			2.74 ± 0.18	0.99	11.84	125
1C	5.60 ± 0.63	1.09 ± 0.05			1.75 ± 0.38	0.98	10.18	168
2A	3.27 ± 0.40	1.43 ± 0.07	11.72	0.81	1.15 ± 0.17	0.98	18.06	452
2B	3.47 ± 0.29	1.26 ± 0.04			3.64 ± 0.12	0.99	11.60	92
2C	2.11 ± 0.10	1.56 ± 0.02			2.43 ± 0.12	0.99	16.50	196
3A	5.93 ± 0.31	1.01 ± 0.05	17.15	0.90	1.45 ± 0.09	0.99	7.09	141
3B	4.32 ± 0.38	1.09 ± 0.05			2.10 ± 0.09	0.99	8.10	112
3C	5.65 ± 0.59	0.95 ± 0.06			1.46 ± 0.16	0.99	6.40	126
4A	3.98 ± 0.40	1.17 ± 0.05	18.37	0.93	0.98 ± 0.04	0.99	9.87	292
4B	6.19 ± 0.07	0.90 ± 0.01			2.72 ± 0.12	0.98	7.52	80
4C	5.89 ± 0.49	0.92 ± 0.05			2.76 ± 0.10	0.99	6.53	68,3
5A	4.07 ± 0.43	0.94 ± 0.05	17.25	0.93	2.37 ± 0.28	0.99	5.26	64
5B	1.44 ± 0.43	1.47 ± 0.16			2.78 ± 0.19	0.95	9.53	99
5C	1.98 ± 0.45	1.41 ± 0.12			1.03 ± 0.00	0.95	7.30	205

such as non-equilibrium sorption are considered (e.g., Boesten et al., 1989; Streck et al., 1995; Streck and Richter, 1999; Altfelder et al., 2001; Ma and Selim, 2005).

Since the inlet concentration of isoproturon is not reached at the outlet, degradation needs to occur inside the columns, as is also reflected by the positive values of the first-order degradation rate μ_l (Table 5). Differences in degradation potential between the mixtures were minimal, all degradation constants (μ_l) were of the same magnitude. Thus, the composition of the matrix appears to have little influence on degradation of isoproturon. As degradation is only considered in the liquid phase, half-life values (DT50) need to be calculated instead of from μ_l from μ_l/R for sorbing chemicals. Half-life (DT50) values of isoproturon were calculated and presented in Table 5. According to the DT50 value, degradation was slightly higher in mixtures 3, 4 and 5, while it was lower in mixtures 1 and 2. This is much higher than the reported values in literature (DT50$_{soil}$ = 6–20 days) (Roberts, 1998; Tomlin, 2006). Sorption to organic substrates can decrease the bioavailability and therefore decrease biodegradation.

3.3. Bentazone BTCs

Experimental bentazone BTCs were also analyzed using the CDE model (Fig. 3, Table 6). The determination coefficient R^2 ranged from 0.51 to 0.91. The arrival of bentazone, which is a very mobile

pesticide, was very similar to that of the inert tracer bromide, showing that this pesticide is hardly retained in the organic substrates. Since the value of the Freundlich exponent n_{column} has been proven to be highly uncertain (high standard deviations in Table 6), the retardation factor was calculated assuming linear adsorption ($n = 1$). Reported retardation factors are therefore underestimated because the n exponent is larger than 1. In general, the retardation factors R were close to 1, indicating that hardly any retention occurred for all mixtures, and confirming Gaston and Locke's (1996) results in columns of Dundee silty clay loam soil. The fitted n_{column} values for most mixtures were relatively high, as compared to n values for bentazone reported in the literature, which ranged from 0.88 to 1.061 for Mississippi and coastal plain soils (Gaston et al., 1996; Grey et al., 1996). However, as discussed above, these values are highly uncertain. The n_{column} values are determined by the changing slope of the part of the BTC curve where C/C_0 increases from 0 to equilibrium conditions. Since bentazone breakthrough occurs very fast, the number of data points in this part of the curve is limited. This results in a poor estimation of the n value. Calculated $K_{f,column}$ values for bentazone are much smaller than those obtained from the batch experiments (Table 6), which confirms the similar results obtained for isoproturon. While bentazone $K_{f,column}$ values were much lower than for isoproturon, the ratio of K_{oc} (isoproturon)/K_{oc} (bentazone) was much smaller than $K_{f,column}$ (isoproturon)/$K_{f,column}$ (bentazone). This could

Table 6
Solute reaction parameters fitted to bentazone BTCs (±95% confidence interval).

Mix	$K_{f,column}$ (L kg^{-1})	n_{column}	$K_{f,batch}$ (L kg^{-1})	n_{batch}	μ_l ($\times 10^{-3}$) (h^{-1})	R^2	R[a]	DT50 (d)
1A	$1.35 \times 10^{-3} \pm 2.95 \times 10^{-3}$	3.62 ± 0.96	3.42	0.81	3.51 ± 1.02	0.92	1.00	14,032
1B	$1.41 \times 10^{-1} \pm 1.06 \times 10^{-1}$	1.66 ± 0.31			4.84 ± 0.54	0.90	1.29	10,516
1C	$1.75 \times 10^{-5} \pm 6.03 \times 10^{-2}$	5.86 ± 1.57			2.79 ± 0.00	0.71	1.00	18,932
2A	$5.45 \times 10^{-6} \pm 1.26 \times 10^{-5}$	6.12 ± 0.99	2.93	0.80	3.45 ± 1.28	0.88	1.00	14,427
2B	$1.42 \times 10^{-4} \pm 1.83 \times 10^{-4}$	4.74 ± 0.57			5.67 ± 1.11	0.92	1.00	8398
2C	$9.07 \times 10^{-2} \pm 1.13 \times 10^{+1}$	0.00 ± 4.55			6.21 ± 1.07	0.81	1.00	7828
3A	$6.11 \times 10^{-3} \pm 1.48 \times 10^{-2}$	3.39 ± 1.12	3.40	0.81	1.02 ± 0.54	0.70	1.02	55,619
3B	$2.70 \times 10^{-3} \pm 7.03 \times 10^{-3}$	3.79 ± 1.22			1.61 ± 1.07	0.69	1.01	28,849
3C	$1.54 \times 10^{-2} \pm 4.10 \times 10^{-2}$	2.84 ± 1.15			3.55 ± 0.91	0.53	1.05	14,028
4A	1.00 ± 1.03	0.12 ± 0.26	4.10	0.81	4.10 ± 1.25	0.82	1.16	49,892
4B	1.31 ± 1.34	0.33 ± 0.55			6.12 ± 2.54	0.51	1.64	31,518
4C	$4.75 \times 10^{-3} \pm 8.59 \times 10^{-3}$	3.23 ± 0.82			3.76 ± 1.62	0.85	1.02	51,749
5A	$3.12 \times 10^{-6} \pm 9.91 \times 10^{-6}$	6.28 ± 1.39	4.08	0.81	1.96 ± 1.71	0.84	1.00	24,249
5B	$5.84 \times 10^{-2} \pm 5.75 \times 10^{-2}$	2.15 ± 0.42			0	0.91	1.17	–
5C	$2.92 \times 10^{-4} \pm 1.04 \times 10^{-3}$	4.25 ± 1.51			0	0.87	1.00	–

[a] Retardation coefficient was calculated assuming linear sorption ($n = 1$).
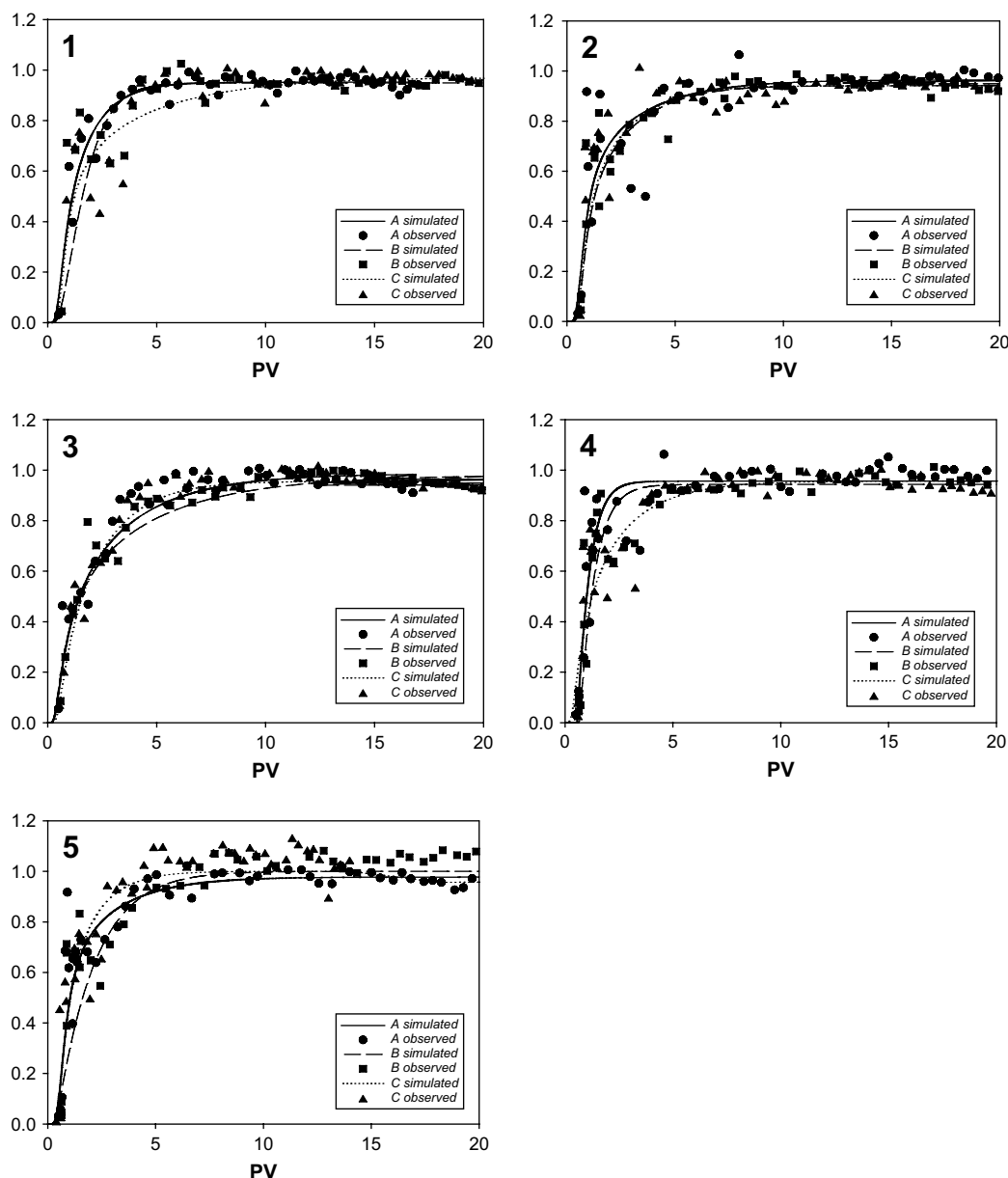
Fig. 3. Observed and simulated BTCs of bentazone in 5 experimental column set-ups (replicates A, B, and C) containing different types of organic substrate. (1) Mixture 1, (2) mixture 2, (3) mixture 3, (4) mixture 4 and (5) mixture 5. Symbols represent the observed data, full, dashed and dotted lines the model fits. Relative concentrations are plotted against the number of pore volumes (PV).

indicate that bentazone is sorbed to an even lesser extent than isoproturon in column experiments compared to batch experiments. However, it should be noted that $K_{f,column}$ and n_{column} values were also very uncertain as a result of the limited number of data points in the early part of BTCs. Correlations between the two sorption parameters were as high as −0.99. Note that the uncertainty of sorption parameters and their correlation is reflected in the relatively large confidence intervals. Because of this uncertainty, it is difficult to compare various mixtures with respect to their bentazone retention capacity.

Degradation of bentazone was about one magnitude lower than degradation of isoproturon, making it almost negligible. Outflow bentazone concentrations quickly approached the input concentration, which indicated very limited degradation. This is also confirmed by the values of the half-life of bentazone which were very high (>7828 days). This is in contrast to the literature, where bentazone was described as a very low persistent molecule with

a half-life in soil of less than two weeks (Wauchope et al., 1992). However, low degradation of bentazone in our column studies could be expected because of the very short residence time in the columns. Finally, as for isoproturon, composition of the matrix was of little importance because small differences in degradation efficiency between the organic mixtures were present and values were of the same order of magnitude.

3.4. Metalaxyl BTCs

Transport of metalaxyl (both observed, as well as simulated using the CDE model) through the experimental columns is shown in Fig. 4. Collected experimental metalaxyl BTCs for mixtures 2, 3, and 5 have a very different pattern than those obtained for isoproturon and bentazone. Although a step input was applied, the BTCs for mixtures 2, 3, and 5 showed a pattern that is characteristic for a pulse input (Fig. 4). Effluent concentrations increased up to
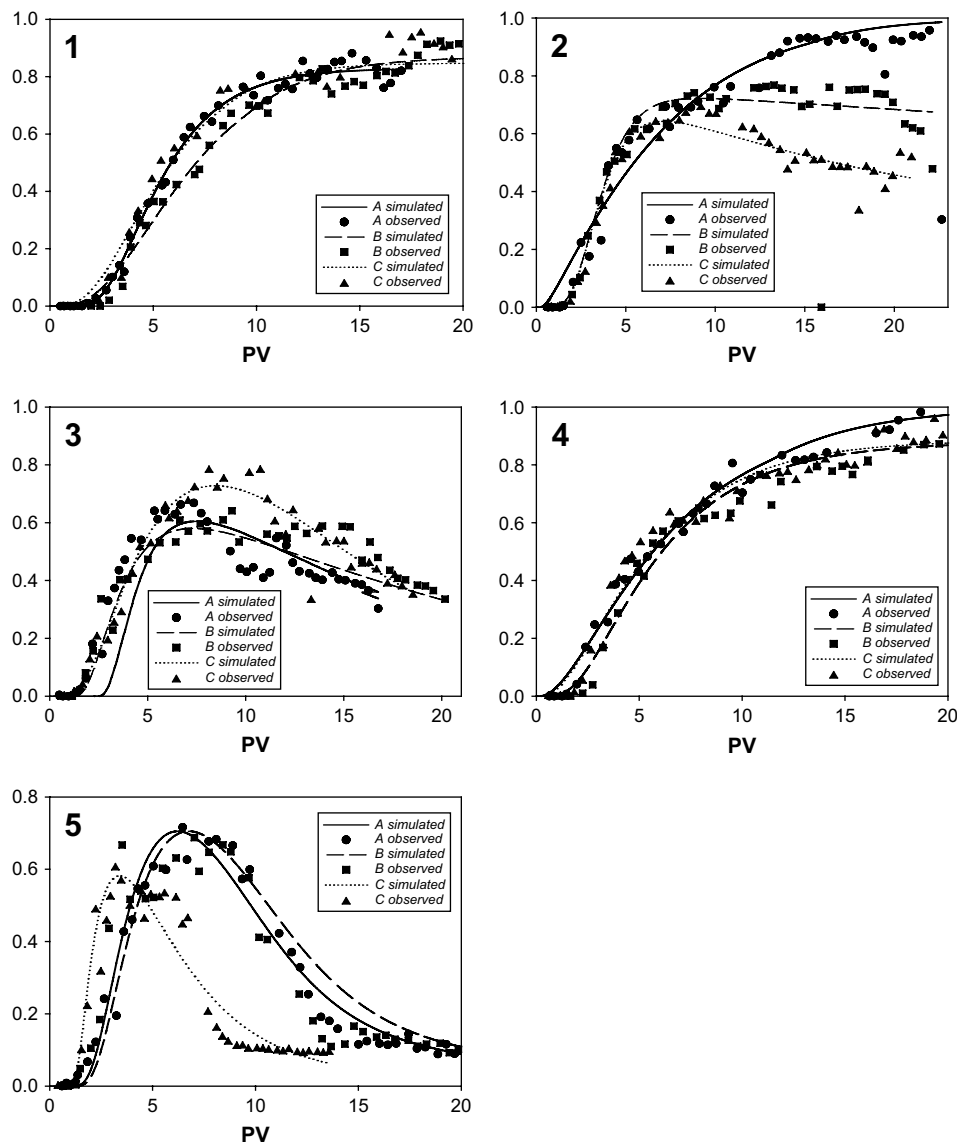
Fig. 4. Observed and simulated BTCs of metalaxyl in 5 experimental column set-ups (replicates A, B, and C) containing different types of organic substrate. (1) Mixture 1, (2) mixture 2, (3) mixture 3, (4) mixture 4 and (5) mixture 5. Symbols represent the observed data, full, dashed and dotted lines the model fits. Relative concentrations are plotted against the number of pore volumes (PV).

a certain value, and then began decreasing. A first-order degradation process could not be used to describe the observed effluent metalaxyl concentrations in these mixtures. It was hypothesized that these BTCs could be described using a Monod-type degradation model (Eqs. (7) and (9)) that considers bacterial growth and decay.

The classical CDE model (3) was first used to fit the first part of the BTCs up to the maximum effluent concentration for mixtures 2, 3, and 5, in order to obtain the Freundlich parameters of this initial part of the BTCs. Although we realize that the Monod-type degradation is involved already during this first part of the BTC, its effects are relatively limited, and in this way we can obtain initial estimates of these reaction parameters. The determination coefficient R^2 for the CDE model ranged from 0.64 to 0.99 (Table 7). Since the retardation coefficient R for metalaxyl is higher than one, retention of this pesticide into the organic matrix occurs (Table 7). Retention of metalaxyl (average $R = 8.51$) is similar to that of isoproturon (average $R = 7.97$) in mixture 4, but is slightly lower in mixtures 1, 2, 3, and 5. This is in agreement with more or less similar K_{oc} values of metalaxyl ($K_{oc} = 47$ L kg^{-1}) and isoproturon ($K_{oc} = 36$ L kg^{-1}).

Retardation factors of 2.3–3.8 were observed by Fernandes et al. (2003) for agricultural soils with a lower organic matter content than in the mixtures evaluated in this study. This likely explains the higher retention found in our experiments.

The $K_{f,column}$ values of metalaxyl (Table 7) (average $K_{f,column} = 2.84$ L kg^{-1}) were very similar to those of isoproturon (Table 4) (average $K_{f,column} = 4.74$ L kg^{-1}). However, these values were again much lower than those obtained from batch experiments ($K_{f,batch} = 15.39$ L kg^{-1}) (Table 7). This confirms that values obtained from batch experiments cannot be used directly in transport models as they would lead to a significant underestimation of the leaching potential of the pesticide.

First-order degradation constants for metalaxyl in mixtures 1 and 4 are presented in Table 7. The obtained values were of the same magnitude as those recorded for isoproturon, and close to those reported by Kookana et al. (1992). Overall, the lowest first-order degradation was found in mixtures 1 and 4. These are also the mixtures in which no delayed degradation occurred (Fig. 4). The DT50 values are very high for mix 2A and 4A because the effluent concentration in these mixtures reached the inlet concentration.

Table 7
Predicted solute parameters for metalaxyl (±95% confidence interval).

Mix	$K_{f,column}$ (L kg^{-1})	n_{column}	$K_{f,batch}$ (L kg^{-1})	n_{batch}	μ_l ($\times 10^{-3}$) (h^{-1})	R^2	R	DT50 (d)
1A	5.83 ± 0.48	0.95 ± 0.04	17.54	0.85	1.36 ± 0.08	0.99	5.75	122
1B	2.86 ± 0.33	1.26 ± 0.06			1.31 ± 0.14	0.98	9.27	204
1C	2.22 ± 0.59	1.28 ± 0.13			1.53 ± 0.26	0.94	7.60	144
2A	0.69 ± 0.25	1.78 ± 0.16	9.46	0.89	0.01 ± 0.09	0.90	11.10	22,607
2B	1.88 ± 0.40	1.08 ± 0.10			–	0.96	4.27	–
2C	1.94 ± 0.32	1.07 ± 0.08			–	0.97	4.19	–
3A	4.58 ± 0.47	0.77 ± 0.06	15.17	0.87	–	0.92	3.09	–
3B	2.68 ± 0.55	0.94 ± 0.07			–	0.96	3.68	–
3C	2.95 ± 0.30	1.00 ± 0.07			–	0.92	4.29	–
4A	1.62 ± 0.36	1.47 ± 0.10	18.58	0.85	0	0.96	10.15	1,006,514
4B	3.74 ± 1.09	1.04 ± 0.14			1.36 ± 0.32	0.96	7.25	154
4C	2.39 ± 0.46	1.28 ± 0.10			1.06 ± 0.21	0.97	8.12	220
5A	3.11 ± 0.61	0.89 ± 0.11	16.20	0.87	–	0.64	3.72	–
5B	2.77 ± 0.57	0.76 ± 0.12			–	0.68	2.70	–
5C	3.22 ± 0.26	0.67 ± 0.05			–	0.93	1.87	–

Nonetheless, the overall DT50 value in the organic mixtures is similar or slightly lower to the values described in literature (DT50 > 200 days) (Tomlin, 2006). Evidence of delayed degradation can be clearly seen in mixtures 2, 3, and 5 (Fig. 4). Two out of three replicated BTCs for mixture 2 (B and C) showed a slight decrease of pesticide concentrations after reaching a maximum value. The decrease of metalaxyl concentrations, compared to the maximum value, was about 20% for replicate B and 31% for replicate C. However, a much more pronounced decrease in effluent concentrations was observed in mixtures 3 and 5. The decrease of effluent concentrations in mixture 3 was between 45% and 50% for different replicates, and in mixture 5 it was about 85%. The presence of cow manure is the only difference in the composition of mixtures 3 and 5, compared to mixtures 1, 2, and 4. Cow manure represents a source of nitrogen, which could stimulate the growth of metalaxyl degrading bacteria. Although no specific results have been reported in the literature on the influence of manure on metalaxyl degradation, the effects of manure on degradation of other pesticides are well documented. For example, Dolaptsoglou et al. (2007) found that the incorporation of composted animal manure accelerated the degradation of 1,3-D. Moreover, atrazine, metolachlor, and trifluralin degradation also improved in the presence of manure (Moorman et al., 2001). Finally, the dealkylation reactions of s-triazines and phenylureas were also enhanced by manure (Doyle et al., 1978).

The Monod kinetic parameters and the yield coefficients determined by fitting the entire experimental data curves are presented in Table 8. Determination coefficients of the fit using the CDE model (9) with the Monod kinetics (7) ranged between 0.86 and 0.96, indicating that the model described the experimental data very well. Since reaction coefficients of Eq. (7) are the same

whether (7) was formulated in absolute or relative biomass concentrations, and the biomass concentration (X) in Eq. (8) is divided by the yield (Y), the actual absolute values of biomass cannot be determined from the pesticide (c) breakthrough curve alone. To determine the biomass, at least one measured value of the biomass concentration is needed (e.g., initial, final, or any other). This is because the biomass concentration and yield are fully correlated. Higher values of biomass concentrations and the correspondingly lower yield will produce identical results. For that reason, we carried out simulations in relative biomass concentrations with the initial value being equal to one. The yield coefficient Y was then calculated as the ratio between $\mu_{m,b}^*/\mu_b^*$. This yield coefficient showed high values for mixture 5, indicating that more biomass was generated in this mixture per unit of degraded pesticide compared to mixtures 2 and 3. Parameters $\mu_{m,b}^*$ and $k_{decay,b}$ are strongly related, and determine the amount of biomass in the system. Although similar values of $\mu_{m,b}^*$ were observed for mixtures 3 and 5, much lower values of $k_{decay,b}$ were obtained for mixture 5. This means that the biomass will reside longer in mixture 5 and will be less susceptible to decay, which may lead to a higher pesticide degradation capacity of this mixture. Mixture 5 contains 25% less straw than mixture 3, however in mixture 5 straw
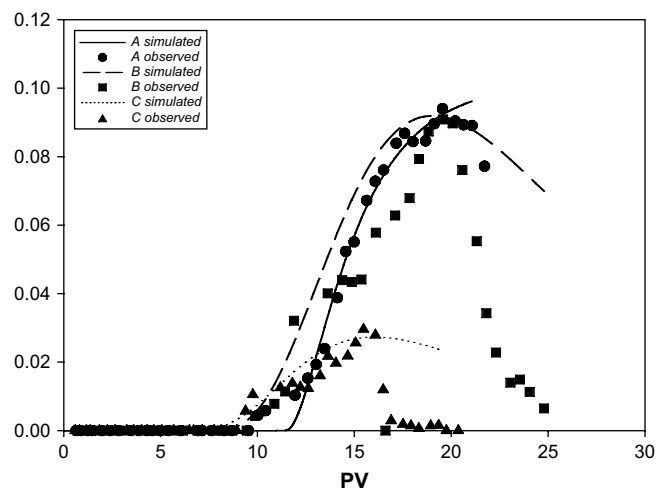
Table 8
Monod kinetic parameters and the yield coefficient for the degradation of metalaxyl (±95% confidence interval).

Mix	μ_b^* ($\times 10^{-7}$) (L kg^{-1} h^{-1})	$\mu_{m,b}^*$ ($\times 10^{-4}$) (L kg^{-1} h^{-1})	$k_{decay,b}$ (h^{-1})	R^2	Y (−)
2B	9.15 ± 14.02	-0.18 ± 8.21	$3.15 \times 10^{-6} \pm 7.01 \times 10^{-3}$	0.96	20.20
2C	13.43 ± 2.92	-2.11 ± 1.93	$1.08 \times 10^{-3} \pm 1.37 \times 10^{-3}$	0.96	156.89
3A	9.99 ± 0.89	-5.27 ± 1.09	$2.57 \times 10^{-3} \pm 6.22 \times 10^{-4}$	0.96	527.39
3B	10.95 ± 3.96	-0.98 ± 3.23	$2.30 \times 10^{-5} \pm 2.01 \times 10^{-3}$	0.86	89.66
3C	4.62 ± 0.95	-2.42 ± 1.41	$6.26 \times 10^{-4} \pm 1.06 \times 10^{-3}$	0.98	524.84
5A	3.38 ± 0.65	-3.95 ± 0.99	$5.27 \times 10^{-4} \pm 4.88 \times 10^{-4}$	0.93	1168.18
5B	4.43 ± 0.70	-2.69 ± 0.54	$4.90 \times 10^{-8} \pm 2.14 \times 10^{-4}$	0.91	607.71
5C	1.99 ± 0.25	-2.51 ± 0.93	$1.12 \times 10^{-7} \pm 4.30 \times 10^{-4}$	0.90	1266.12

Fig. 5. Observed and simulated BTC of linuron for mixture 4 (in triplicate: A, B, C) containing 25% sandy loam soil, 25% peat mix, 25% coco chips, 25% straw. Symbols are the observed data, full, dashed and dotted lines the model fits given by the convection–dispersion equation. Relative concentrations are presented against the number of pore volumes (PV).

Table 9
Predicted solute parameters of linuron ($\pm$95% confidence interval).

Mix	$K_{f,column}$ (L kg^{-1})	n_{column}	$K_{f,batch}$ (L kg^{-1})	n_{batch}	μ_l ($\times 10^{-2}$) (h^{-1})	R^2	R	DT50 (d)
4A	29.52 ± 0.42	0.46 ± 0.03	88.35	0.75	2.98 ± 0.03	0.93	6.12	142
4B	27.85 ± 0.72	0.78 ± 0.07			–	0.91	20.15	–
4A	28.05 ± 2.18	0.83 ± 0.09			–	0.90	20.10	–

is replaced by coco chips, which is slower mineralized than straw and thus could provide nutrients longer which could decrease the decay of the biomass.

3.5. Linuron BTCs

Linuron is a pesticide with a higher K_{oc} value than isoproturon, metalaxyl, and bentazone, thus classifying it as immobile. This low mobility was previously reported by Guzzella et al. (2006), Hance (1965) and MacNamar and Toth (1970). No breakthrough of this pesticide was observed in 4 mixtures (out of 5), even after about 20 pore volumes. Breakthrough occurred only in mixture 4 (Fig. 5). Replicate A did not show clear evidence of the delayed degradation, which was apparent for replicates B and C. However, from the final point of the BTC there was an indication that linuron effluent concentrations will also decrease for replicate A. As for metalaxyl, the CDE model was used for the first part (up to the maximum effluent concentration) of the BTCs to determine the Freundlich parameters (Table 9) ($R^2 = 0.90$–0.93). The $K_{f,column}$ constants were much higher than for the other pesticides, which was expected because of the late arrival and the high K_{oc} value of linuron. Again, $K_{f,column}$ values obtained from column experiments (average $K_{f,column} = 29.08$ L kg^{-1}) were lower than those from the batch experiments (average $K_{f,batch} = 88.35$ L kg^{-1}) (Table 9). The retardation coefficient R confirms the high retention of linuron on the organic substrate. However, a lower retardation coefficient could be observed for replicate A due to the very low n value, which led to a decrease in sorption with increasing concentration. First-order degradation constant of mix 4A is one order of magnitude higher than those for metalaxyl and isoproturon, likely explaining why no breakthrough occurred in the other mixtures (Table 9). The DT50 value of mix A was 142 days which is much higher than the value reported by Fava et al. (2006) of 14 days in soil. A combination of the strong adsorption, and a correspondingly long resident time of linuron in the column, along with high degradation probably resulted into a complete degradation of linuron before it reached the bottom of the column. Linuron has previously been reported as a substrate for bacterial growth by Cullington and Walker (1999) and by Widehem et al. (2002).

The BTCs of replicates B and C were fitted with the CDE model combined with the Monod kinetics (Table 10). However, very low effluent concentrations and incomplete breakthrough prevented us from obtaining fitted parameters with sufficient confidence. Also, model fits were relatively poor with R^2 ranging from 0.47 to 0.50.

4. Summary and conclusions

Pesticide displacement experiments were carried out for isoproturon, bentazone, metalaxyl, and linuron on columns filled with five different types of organic mixtures. The experimental bromide, isoproturon, and bentazone BTCs were well described using the transport model based on the convection–dispersion equation and first-order degradation. The transport model had to be enhanced with the Monod kinetics to describe experimental BTCs of metalaxyl and linuron that displayed a decrease of outflow concentrations after reaching an intermediate maximum. Freundlich adsorption parameters and first-order degradation constants were fitted to the observed BTCs. $K_{f,column}$ values fitted to transport experiments were much lower than those determined by previous batch studies, confirming the idea that sorption coefficients obtained from batch experiments are often not suitable for describing solute transport at the column or field scale. The K_{oc} value is a very good indicator of the mobility of the pesticide. Bentazone was the most mobile pesticide, followed by metalaxyl, isoproturon, and linuron. From the point of view of their degradability, pesticides can be ranked as follows: linuron > metalaxyl – isoproturon > bentazone. In the case of linuron, a combination of a strong sorbing capacity with a high degradation rate led to no breakthrough for 4 out of 5 mixtures. Finally, the composition of the organic matrix had a minor influence on retention and degradation of isoproturon, bentazone and linuron. However, it did appear to have an influence on the degradation of metalaxyl, where the presence of cow manure stimulated degradation.

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Table 10
Monod kinetic parameters and the yield coefficient for the degradation of linuron ($\pm$95% confidence interval).

Mix	μ_b^* ($\times 10^{-7}$) (L kg^{-1} h^{-1})	$\mu_{m,b}^*$ ($\times 10^{-4}$) (L kg^{-1} h^{-1})	$k_{decay,b}$ (h^{-1})	R^2	Y (–)
4B	2.04 ± 18.36	-6.65 ± 1.39	$5.80 \times 10^{-7} \pm 1.52 \times 10^{-5}$	0.50	32.67
4C	4.15 ± 21.71	-7.04 ± 26.4	$6.65 \times 10^{-7} \pm 1.90 \times 10^{-5}$	0.47	16.96

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