



## Transport and degradation of pesticides in a biopurification system under variable flux Part II: A macrocosm study

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

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### ABSTRACT

Transport of bentazone, isoproturon, linuron, metamitron and metalaxyl were studied under three different flows in macrocosms. The aim was to verify the observations from Part I of the accompanying paper, with an increase in column volume and decrease in chemical and hydraulic load. Very limited breakthrough occurred in the macrocosms for all pesticides, except bentazone, at all flows.

From batch degradation experiments, it was observed that the lag time of metamitron and linuron decreased drastically in time for all flows, indicating a growth in the pesticide degrading population. This in contrast to isoproturon and metalaxyl, where an increase in lag time could be observed in time for all flows. From the batch degradation experiments, it could be concluded that the influence of flow on the lag time was minimal and that the inoculation of the pesticide-primed soil had a little surplus value on degradation.

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### 1. Introduction

A microcosm solute transport study designed to gain insight in the influence of a variable hydraulic and chemical load on transport of pesticides in a biopurification system was described in the first paper of these companion papers. In brief, the behaviour of metalaxyl, bentazone, linuron, isoproturon and metamitron was studied under three different flows (0.84 cm d<sup>-1</sup>, 1.45 cm d<sup>-1</sup> and 2.40 cm d<sup>-1</sup>) with or without the presence of pesticide-primed soil in microcosms ( $l \times d$ : 15 cm  $\times$  10 cm). Retention of the pesticides with intermediate mobility (metalaxyl, metamitron and isoproturon) was significantly influenced by the flux, in contrast to bentazone and linuron, respectively, a very mobile and immobile pesticide. 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. The presence of pesticide-primed soil was only beneficial for the degradation of metalaxyl.

The purpose of this paper was to validate the obtained results on a larger scale and to decrease the chemical and hydraulic load.

The load applied on the microcosms was fairly high (56.3 L d<sup>-1</sup> m<sup>-3</sup>, 95.6 L d<sup>-1</sup> m<sup>-3</sup>, and 160.1 L d<sup>-1</sup> m<sup>-3</sup>) and could be considered as worst case scenario as the average hydraulic load on a biofilter is 20 L d<sup>-1</sup> m<sup>-3</sup>. The high load applied in the microcosms resulted in breakthrough of most of the pesticides, except linuron. Therefore, the aim was to reduce the load close to the value applied in practice, to increase the efficiency of the biopurification system. Furthermore, compared to the microcosms, batch degradation experiments were performed in order to gain some knowledge on the evolution of the pesticide degrading population in time and on the influence of the hydraulic and chemical load on the development of the population.

### 2. Materials and methods

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

The selected pesticides were identical to the ones used in the microcosm study (De Wilde et al., 2009b) and were bentazone, isoproturon, linuron, metalaxyl and metamitron. Methanol, acetonitrile, and water were of A.R. grade (VWR, Leuven, Belgium).

The composition of the organic matrix used in the macrocosms was identical to the composition described in detail in Part I of this study. Substrate amounts were weighed and mixed with a concrete mixer to form homogeneous mixes, and then packed into the plastic barrels (polyethylene barrels, height: 50 cm, inner diameter: 45 cm) till a height of 45 cm, without compaction of the materials. Barrels were stored at room temperature. A silicone tube was connected to a hole in the bottom of

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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.

## 2.2. Displacement experiments

Displacement experiments were conducted under similar conditions described in Part I of this series. A  $\text{CaCl}_2$  solution (0.001 M  $\text{CaCl}_2$ ) was supplied to the barrel surface using PTFE (polytetrafluoroethylene) tubes. The inlet consisted of one tube, which dripped the solution on to a filter paper (Whatman n° 1, 50 cm, Schleicher & Schuel) on top of the organic matrix. In this study, a constant Darcy flux of  $0.56 \text{ cm d}^{-1}$ ,  $1.56 \text{ cm d}^{-1}$  and  $2.54 \text{ cm d}^{-1}$  was applied for respectively the low, intermediate and high flow. This corresponds to  $12.5 \text{ L d}^{-1} \text{ m}^{-3}$ ,  $34.6 \text{ L d}^{-1} \text{ m}^{-3}$ , and  $56.4 \text{ L d}^{-1} \text{ m}^{-3}$ . Hence, with the same fluxes but an increase in diameter and column length, a decrease in the chemical and hydraulic load is achieved. For the sake of simplicity, the following notation will be used for the highest, intermediate and lowest flow, respectively,  $q_{\text{max}}$ ,  $q_{\text{mid}}$  and  $q_{\text{min}}$ . 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  $q_{\text{mid+ref}}$ . Macrocosms were set-up in triplicate for each flow, thus in total 12 barrels.

It was assumed that steady-state conditions with the  $\text{CaCl}_2$  solution 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  $\text{Br}^-$ ), 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  $\text{CaCl}_2$  and  $10 \text{ mg L}^{-1}$  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 380 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). Pesticide and bromide analysis have been described in Part I. The experiments lasted for about 165 d until the effluent concentrations of most pesticides reached a constant value.

## 2.3. Transport model

The transport model used is identical to the model described in Part I. Physical transport was first evaluated by analyzing the bromide BTCs. The volumetric water content,  $\theta$ , and the longitudinal dispersivity,  $\lambda$ , were fitted to the observed  $\text{Br}^-$  BTCs. Once the physical transport was fully characterized using bromide BTCs, chemical processes (sorption and degradation) for bentazone, isotroturon, linuron, metalaxyl and metamitron were analyzed by inverting the pesticide BTCs with the transport code HYDRUS-1D (Simunek et al., 2005), using the physical transport parameters estimated for bromide transport. Similar to Part I, the one kinetic site sorption model was used with a fixed Freundlich exponent (metalaxyl,  $n = 0.934$ ; bentazone,  $n = 0.828$ ).

## 2.4. Pesticide extraction from the matrix

At the end of the macrocosms displacement experiment, the 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). These three parts were separately mixed and from each part an aliquot of  $\pm 100 \text{ g}$  was sampled. These three samples were than mixed and this mix was used to quantify the extractable residues. Extraction of the pesticides was carried out on  $50 \pm 0.001 \text{ g}$  organic matrix of which the dry matter was determined gravimetrically after drying at  $105 \text{ }^\circ\text{C}$  during 24 h. 200 mL of methanol was added to the organic matrix and shaken during 1 h at 150 rpm. The liquid phase was separated from the solid phase with a Buchner filter. These steps were repeated three times after which the liquid phases were collected and evaporated with a rotavapor. The pesticides were re-dissolved in 10 mL 90:10 (v/v) methanol – 0.1%  $\text{H}_3\text{PO}_4$  water solution and analyzed with HPLC–DAD.

## 2.5. Batch degradation experiments

Five samples of the matrix ( $\pm 5 \text{ g}$ ) were collected from the top layer of one replicate of each mix at different moments in time, more in particular, 12, 60 and 123 days after the start of the macrocosm experiment. This in order to evaluate lag time and half-life of pesticide degradation in time. At each point in time, the subsamples were mixed and  $0.5 \pm 0.001 \text{ g}$  was transferred into an autoclaved Erlenmeyer flask. Experiments were carried out in triplicate for each mix. 50 mL of MMO medium (mineral medium without any carbon source but with nitrogen containing salts) containing  $20 \text{ mg L}^{-1}$  of the studied pesticides, which was prepared as described by Dejonghe et al. (2003), was added to the Erlenmeyer flasks. This mix was incubated on a shaker at 150 rpm at room temperature. A sterile control, to check for abiotic losses, was included for each mix through the addition of 8% chloroform to the MMO solution. Every 2–3 days 800  $\mu\text{L}$  of the solution was sampled and filtered with a syringe filter containing a PVDF membrane with a pore size of  $0.22 \mu\text{m}$  (Carl Roth, Karlsruhe–Rheinhafen, Germany). The experiments lasted for 35, 45 and 53 days for

respectively samples taken after 12, 60 and 123 days. The aliquots were injected into the HPLC–DAD for pesticide concentration measurements.

## 3. Results and discussion

### 3.1. Bromide BTCs

The experimental and fitted BTCs of the inert tracer  $\text{Br}^-$  during transport in macrocosms at different fluxes are presented in Fig. 1. The CDE model fitted the observed data well, with  $R^2$  ranging from 0.91 to 0.98 (Table 1).

The fitted transport parameters and bulk densities are presented in Table 1. An increase of the flow rate, resulted in an increased water content of the organic matrix, which is in line with the observations of the microcosms in Part I. The dispersivity  $\lambda$  is higher than in Part I (Table 1) due to an increase in the displacement length (from 15 to 45 cm) or to an increase in system diameter. As expected, the value of the dispersivity  $\lambda$  is in the same range as the values obtained in the macrocosms studied in De Wilde et al. (2009b). Differences in dispersivity between the different flows is insignificant, which is in contrast to the observations on a small scale in Part I where dispersivities differed by a factor 2. An invariant  $\lambda$ , pointed out that physical equilibrium prevailed. The variation in the bulk density  $\rho$  was slightly higher in the macrocosms. Due to the larger volumes, heterogeneity in the packing could increase.

### 3.2. Bentazone, isotroturon, linuron, metalaxyl and metamitron BTCs

Observed and fitted transport of bentazone and metalaxyl in macrocosms subjected to three different input flows are shown in Figs. 2 and 3, respectively. Breakthrough of isotroturon, linuron and metamitron was low or did not occur. Breakthrough of isotroturon at  $q_{\text{max}}$  occurred after about 7.9 PV, and reached a maximum relative concentration ( $C/C_0$ ) of 0.09. After about 11.6 PV, the relative concentration decreased again to 0.02. At a lower flow  $q_{\text{mid+ref}}$ , breakthrough occurred at 7.8 PV and increased up to a maximum relative concentration of 0.07, which decreased to 0 after 11.4 PV. For linuron, breakthrough only occurred at a flow  $q_{\text{max}}$  with an increase in relative concentration to 0.02 after 8.92 PV, this concentration decreased to 0 after 10.85 PV. Breakthrough of metamitron occurred at  $q_{\text{max}}$  and  $q_{\text{mid+ref}}$  after respectively, 6.8 and

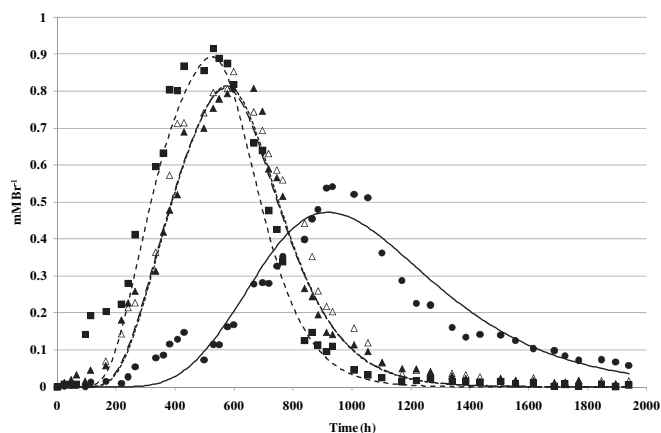


Fig. 1. Observed and simulated BTCs of  $\text{Br}^-$  in 4 experimental macrocosm set-ups with variable water flux. Observed BTCs are presented with the following symbols: ●,  $q_{\text{min}}$ ; ▲,  $q_{\text{mid}}$ ; △,  $q_{\text{mid+ref}}$ ; ■,  $q_{\text{max}}$ . Simulated BTCs are presented as: —,  $q_{\text{min}}$ ; ·····,  $q_{\text{mid}}$ ; - - -,  $q_{\text{mid+ref}}$ ; - · - ·,  $q_{\text{max}}$ . Absolute concentrations are plotted against time (h) (error bars are  $\pm$ standard deviation ( $P < 0.05$ ) ( $n = 3$ )).

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