

# Temporal distribution of pyrimethanil and dimethomorph fungicides on an Andisol under cut rose production in Colombia

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## Summary

Colombia is one of the world's foremost producers of flowers (80% is exported to the EEUU and Canada, ca. 20% to Europe). Cut rose production is produced under greenhouse in clay, loam, sandy soils mainly in Cundinamarca region (79 %), with daily irrigation and pesticides applied twice per week. Though it is known that tropical soils are able to degrade and immobilize agrochemicals due to higher levels of organic matter and microorganisms, some leaching models for tropical soils are calibrated with parameters derived from temperate regions. Thus, the aim of the current study was to assess actual fungicide temporal distribution of commonly used fungicides, detected in the groundwater, i.e. pyrimethanil and dimethomorph through one lysimeter of 100 cm depth. However, no significant concentrations were detected (every 20 cm). Using soil columns of 20 cm, fungicide concentrations were obtained in some leachates during 90 days. We found that both fungicides were dissipated faster than in temperate soils in the first soil layer, posing lower risk of lixiviation. The 20 cm column was advised against the 100 cm lysimeter due to the fast dissipation of the fungicides.

*Keywords:* lixiviation, lysimeter, tropical soils

## Introduction

Pesticides are substances used to control insects or endemic diseases in order to enhance food production and to protect plantations (Mosquera-Vivas et al. 2016a, Mosquera-Vivas et al. 2016b). However, these chemicals are found off-site of application due to the diffusion in the soil and air (Carter 2000, Ward et al. 2006, Dalvie et al. 2014, Maillard et al. 2011). The fate of pesticides in the atmosphere-plant-soil system depends on their behavior in the soil, where the soil columns under laboratory conditions are very useful for understanding the dissipation rates and temporal distribution of substances, because of under field conditions cost and difficulty are higher, particularly for medium- and long-term studies (Kruger et al. 1996, López-Piñeiro et al. 2014). The dissipation of pesticides is owed to volatilization, bio-degradation, chemical degradation and leaching throughout the macropores, mesopores and micropores of the soil (Barra-Caracciolo et al. 2010). For instance, the degradation

process is critically important to know the off-site impact of chemicals applied to field crops in order to protect the surface and groundwater sources (Gebremariam et al. 2012); besides, it can be controlled the temporal distribution and transport of pesticides in the vadose zone (Mosquera-Vivas et al. 2016a, Mosquera-Vivas et al. 2016b).

The fungicides dimethomorph and pyrimethanil are pesticides used to control fungi in many crops worldwide (Capri et al. 2001, Liang et al. 2011, Liu et al. 2012). Water solubility of dimethomorph is 28.5 mg L<sup>-1</sup>, and it is quite resistant to hydrolysis (Lunn 2007). The degradation rate of dimethomorph in soil is dependent on its concentration (Wang et al. 2017) and it is considered moderately persistent in soil with half-lives of between 11.5 and 480 days in laboratory aerobic studies and between 10 and 61 days in field studies (Beigel 2001, Liu et al. 2012, Liang et al. 2011, Wang et al. 2017, Footprint 2017, FAO 2017a). Field dissipation studies in UK, France and Spain reported that dimethomorph residues were only found in the first 20 cm of the soils with trace amounts only during the first 2 months of the study. Initial residues of dimethomorph were about 0.3–0.4 mg kg<sup>-1</sup>, decreasing to < 0.05 mg kg<sup>-1</sup> after 7 months (FAO 2017a). The fungicide was found in surface waters and ground waters in several countries (Maillard et al. 2011, Herrero-Hernández et al. 2013, Avetta et al. 2014), with a GUS index of 2.56 is considered moderately leachable in soil. Jimin et al. (2010) studied the adsorption of dimethomorph in three different soils, and found that the adsorption isotherms fit well to the Freundlich equation. The  $K_f$  values found for the fungicide varied between 2.72 - 8.51 mL g<sup>-1</sup>, and the  $K_{foc}$  values ranged between 316-515 mL g<sup>-1</sup> (Footprint 2017). Pyrimethanil has relatively high water solubility when compared to other pesticides (121 mg L<sup>-1</sup>) and its half-life in soil has been reported between 30 – 55 days (Wightwick et al. 2010, Footprint 2017), indicating moderate persistence in the soil. In soil columns experiments (16.5 cm in diameter and 40 cm in length) with different rainfall intensities, pyrimethanil residues in the soil after two weeks fungicide application (recommended dose) were lower than 0,2 µg kg<sup>-1</sup> (Ng et al. 2014). Fenoll et al (2010) reported that only 6% of pyrimethanil were found in leachates in disturbed clay-loam soil columns, exhibiting higher retention on the upper layer of soil. The leachability of pyrimethanil was markedly higher (40%) in a soil with similar texture but less organic matter OM content (Fenoll et al. 2011). Furthermore, the fungicide is often detected worldwide in sediments and surface waters (Müller et al. 2012, Gregoire et al. 2010, Schäfer et al. 2011,

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Reilly et al. 2012). Several studies reported sorption parameters for pyrimethanil in soil, with  $K_d$  values between 2.51-7.83 mL g<sup>-1</sup> and  $K_{oc}$  values varied between 75-500 mL g<sup>-1</sup> (Yu et al. 2010, Mukherjee et al. 2016, Footprint 2017). However, how these fungicides move in the vadose zone of tropical soils is unknown. Thus, the aim of this study is to investigate the dissipation and transport through soil profile of dimethomorph and pyrimethanil in undisturbed tropical Andisol columns and a lysimeter under laboratory controlled conditions.

## Materials and methods

### Pesticides

Pyrimethanil [N-(4,6-dimethylpyrimidin-2-yl)aniline] and dimethomorph [(EZ)-4-[3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloyl]morpholine] are fungicides used for controlling botrytis and downy mildew in the cut rose crops, respectively. The analytical fungicides ( $\geq 98\%$  purity) were provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany); whereas Forum® (500 g L<sup>-1</sup> dimethomorph) and Scala® (408 g L<sup>-1</sup> pyrimethanil) were acquired from BASF (Ludwigshafen am Rhein, Germany) and Bayer Crop-Science (Monheim am Rhein, Germany). Forum® and Scala® were the non-conservative tracers; meanwhile, bromide of potassium, KBr, was the conservative tracer in the soil columns at depth of 0-20 cm.

### Soil and soil columns experiments

The studied soils are Andisols, classified as a Thaptic Hapludands with more than 3% OC, an udic regime, a melanic epipedon with haploidization processes, and a cation exchange capacity (CEC) higher than 50% in the horizon A1 and A2. More details about physical and chemical soil properties of the Andisol are given in Mosquera-Vivas et al. (2016a). The soil columns were sampled at 2,595 m above sea level in the Tenjo-Cundinamarca region.

The temporal distribution of pyrimethanil and dimethomorph under laboratory conditions was carried out in one (column A) at a depth 0-100 cm and 20 soil columns (0-20 cm). The undisturbed soil column A was collected into the greenhouse cultivated with cut rose using an acrylic tube of 100 cm in length and 30 cm in diameter. It was transported to the laboratory and four effluent sampling points were located over the length of the soil column at different heights (20 cm, 40 cm, 60 cm and 80 cm). Two porous capsules were installed on the opposite side of the acrylic column at the same heights of the sampling points. A square base of 50 cm x 50 cm supported the acrylic column with a final outlet sampling point. The undisturbed soil column held at average temperature of 17.0 °C  $\pm$  2.0 °C and at average relative humidity of 66.0%  $\pm$  9.0%. The soil temperature ranged from 12 °C to 24 °C and the water content at depth of 50 cm varied from 0.400 m<sup>3</sup> m<sup>-3</sup> to 0.419 m<sup>3</sup> m<sup>-3</sup>. A solution of CaCl<sub>2</sub> 0.01 M was applied to the top of the column until steady-state flow was achieved and then a pulse input of pyrimethanil (515 mg L<sup>-1</sup>) and dimethomorph (329 mg L<sup>-1</sup>) was applied (4.0 mm). After a pulse input of 0, 1, 3, 7, 14, 34, 45, 60, 75 and 95 days, soil solution was collected in each sampling point and the both fungicides pyrimethanil and dimethomorph were extracted with ethyl acetate by liquid-liquid extraction and the organic phase was injected into an

Agilent Technologies (Santa Clara, CA) Model 7890A Gas Chromatography (GC) coupled to a 5975C Mass Selective Detector (MSD) for quantifying the pesticides.

The 20 undisturbed soil columns were sampled on the inner of 25 m<sup>2</sup> of the greenhouse with PVC tubes with 11 cm in diameter and 20 cm in length (Pore Volume, PV, equal to 1441 mL). It was transported to the laboratory, hermetic sealed and held at average temperature of 18.8 °C  $\pm$  0.6 °C. We provided water pulses on the top; besides, a geotextile and output of water were put in the bottom of the column. A solution of CaCl<sub>2</sub> 0.01 M was applied to the top of the column until steady-state flow was achieved (0.17 VP) and then a pulse input of KBr (5321 mg L<sup>-1</sup>). Pyrimethanil (515 mg L<sup>-1</sup>) and dimethomorph (329 mg L<sup>-1</sup>) were applied (4.0 mm) to eighteen of twenty soil columns (Martínez-Cordón et al. 2015). After a pulse input of 0, 1, 3, 7, 14, 30, 45, 60 and 90 days, two soil columns were cut in three layers of 0-5 cm, 5-10 cm and 10-20 cm and the soil was dried at room temperature (18.8 °C). Ten grams of dry soil was extracted with ethyl acetate by solid-liquid and the organic phase was injected into the GC-MSD system for quantifying the both fungicides dimethomorph and pyrimethanil. Details of the extraction and quantification of pesticides are given in Mosquera-Vivas et al. (2016a) and Mosquera-Vivas et al. (2016b). Moreover, 10 g of dry soil was extracted with water and the supernatant was filtered (0.22  $\mu$ m) and injected into an Agilent Technologies (Santa Clara, CA) Model 1100 High Performance Liquid Chromatography (HPLC) coupled to Diode Array Detector (DAD) for quantifying the bromide. Before the destruction of the soil columns, we applied a solution of CaCl<sub>2</sub> 0.01 M (2.8 mm) six days per week and the leachates were collected, filtered (0.22  $\mu$ m) and injected into the HPLC-DAD system; as well, the fungicides were extracted by solid phase extraction methodology and the organic phase was injected into the GC-MSD system.

### Data analysis

The dissipation rate ( $k$ ) and the half-life ( $t_{1/2}$ ) of dimethomorph were calculated assuming a first-order kinetic model as,

$$C_t = C_0 e^{-kt} \quad (\text{Equation 1})$$

$$t_{1/2} = \frac{\ln(0.5)}{-k} \quad (\text{Equation 2})$$

Meanwhile, the  $k$  and  $t_{1/2}$  of pyrimethanil were obtained assuming a power model as,

$$C_t = C_0 t^{-k} \quad (\text{Equation 3})$$

$$t_{1/2} = \left(\frac{1}{2}\right)^{1/k} \quad (\text{Equation 4})$$

where  $C_0$  is the initial concentration of the fungicides. Bromide breakthrough curves (BTC's) in the columns at depth of 0-20 cm were described with the convection-dispersion equation (CDE) as follows

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (\text{Equation 5})$$

where  $\frac{\partial C}{\partial t}$  is the change of the concentration of bromide in the time,  $\frac{\partial C}{\partial x}$  is the change of the concentration of bromide

in the distance,  $v$  is the average pore-water velocity (L/T) and  $D$  is the dispersion coefficient (L<sup>2</sup>/T). The  $v$  and  $D$  were calculated using the software STANMOD 2.0 with CXFITM code in equilibrium and non-equilibrium (Šimůnek et al. 1999). Also, we estimated de Péclet number (Equation 6) to know whether transport by advection should be considered. When the Péclet number is smaller than 1, diffusion is considered as the dominant transport mechanism of the solutes in the soil (Huysmans & Dassargues 2004),

$$P_e = \frac{v}{D} \times L \quad (\text{Equation 6})$$

where  $P_e$  is the Péclet number and  $L$  is the length of the column.

The recovery of the conservative tracer (% *Rec Br*<sup>-</sup>) in the soil columns at depth of 0-20 cm was calculated as

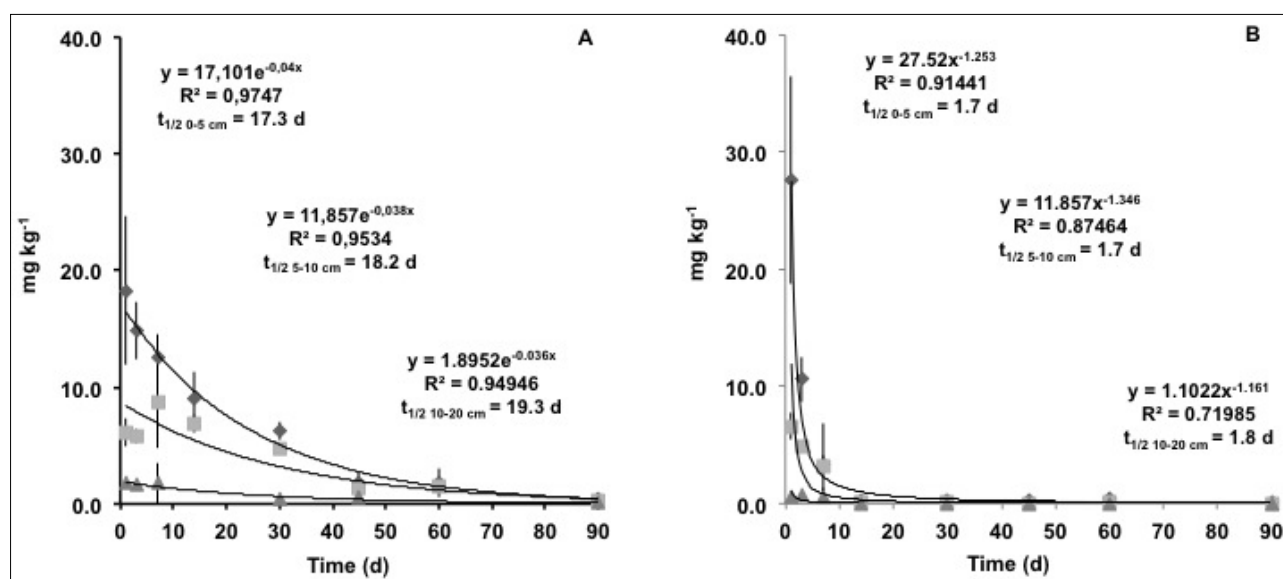
$$\% \text{ Rec Br}^- = \frac{\text{Br}^- \text{ Recovered}}{\text{Br}^- \text{ Added}} \times 100\% \quad (\text{Equation 7})$$

## Results

The dissipation rate ( $k$ ) and the half-life ( $t_{1/2}$ ) obtained by fitting a first-order kinetic model to dimethomorph and power model to pyrimethanil data from the soil columns at depth of 0-20 cm are given in *Figure 1*. The models performed well, with coefficient of determination ( $R^2$ ) values between 0.72 and 0.97. The  $k$  values of dimethomorph were similar throughout the first 20 cm of the Andisol; therefore, 19.3 days (range = 16.2 d – 23.9 d) was the half-life of the fungicide. The same behavior showed the pyrimethanil, but its dissipation was faster with  $t_{1/2}$  equal to 1.7 days (range = 1.5 d – 2.3 d). The  $v$ ,  $D$ ,  $R^2$  values and the Mean Square of Error (MSE) obtained by fitting a CDE to conservative tracer data from the soil columns are summarized in *Table 1*. Besides, the Péclet number ( $P_e$ ) is given in *Table 1*.

One bromide breakthrough curve (BTC) and the recovery of the conservative tracer are shown in *Figure 2*. Bromide was not found in the leachate or in soil from columns 1 and 2. In columns 3, 4, 5, 6, and 8 the anion was not found in the leachates, but more than 80 % of the bromide applied was recovered in the extracted soil samples. In columns 7 and 9 the bromide began to elute at 4 d and 1 d after application, respectively. In columns 11 through 16, the bromide eluted between 3 and 6 d after application and the maximum concentration was reached between 15 and 19 d. In columns 17 through 20, bromide eluted at 4 d and the maximum concentration of the anion was obtained between 16 and 21 d. The percentages of recovery of the bromide applied were between 77.45 and 101.04 %, and on average 92.17 % of the anion was recovered, with a coefficient of variation of 7.36 %. In general, the effluent curves were shifted slightly to the left compared to the theoretical curve, and all curves presented the same shape. The BTC's for columns 15 through 20 were fit to CDE in equilibrium with an  $R^2 > 0.97$ , MSE between 67 and 252, and a retention factor of 1. The  $v$  and  $D$  coefficients were  $0.64 \text{ cm d}^{-1} \pm 0.05 \text{ cm d}^{-1}$  y  $2.85 \text{ cm}^2 \text{ d}^{-1} \pm 0.71 \text{ cm}^2 \text{ d}^{-1}$ , respectively. The BTC's in columns 15, 16, 19, and 20, were also fit to CDE in non-equilibrium, with an  $R^2 > 0.98$ , MSE between 41 and 126, and a retention factor of 1. The  $v$  and  $D$  coefficients were  $0.71 \text{ cm d}^{-1} \pm 0.07 \text{ cm d}^{-1}$  and  $2.44 \text{ cm}^2 \text{ d}^{-1} \pm 0.45 \text{ cm}^2 \text{ d}^{-1}$ , respectively. When comparing the BTC's of the anion at physical equilibrium and non-equilibrium, the MSE was found to be lower in the non-equilibrium condition; as such, the non-equilibrium model better fit the experimental data. Statistically, the  $v$  and  $D$  coefficients did not differ for the process at physical equilibrium and non-equilibrium.

The adimensional  $\beta$  parameter is a partitioning coefficient between the mobile and immobile liquid phase, and the parameter  $\omega$  is the transfer of mass between the two zones (mobile and immobile) (Toride et al. 1995). According to the  $\beta$  values, 60 %, 50 %, 40 %, and 41 % of the water present in the soil resided in the matrix for columns 15, 16, 19, and 20, respectively. The smaller the  $\beta$  parameter,



*Figure 1.* Dissipation of dimethomorph (A) and pyrimethanil (B) in the soil columns at depth of 0-20 cm. Soil layers: 0-5 cm (diamond), 5-10 cm (square) and 10-20 cm (triangle). Error bars indicate standard deviation.

Table 1. Transport parameters of the Andisol in equilibrium and non-equilibrium.

Column number	Equilibrium					Non-equilibrium						
	$\nu$ cm d <sup>-1</sup>	$D$ cm <sup>2</sup> d <sup>-1</sup>	R <sup>2</sup>	MSE	$P_e$	$\nu$ cm d <sup>-1</sup>	$D$ cm <sup>2</sup> d <sup>-1</sup>	$\beta$	$\omega$	R <sup>2</sup>	MSE	$P_e$
15 (0-20 cm)	0.63 ± 0.02	3.30 ± 0.12	0.97	252	3.82	0.72 ± 0.01	2.22 ± 0.16	0.40 ± 0.06	1.00 ± 0.30	0.99	53	6.50
16 (0-20 cm)	0.61 ± 0.02	4.00 ± 0.14	0.97	220	3.05	0.72 ± 0.01	2.91 ± 0.18	0.50 ± 0.06	9.21 ± 3.05	0.99	59	4.95
17 (0-20 cm)	0.64 ± 0.006	2.24 ± 0.04	0.99	67	5.71	-----	-----	-----	-----	-----	-----	-----
18 (0-20 cm)	0.63 ± 0.006	2.08 ± 0.04	0.99	96	6.06	-----	-----	-----	-----	-----	-----	-----
19 (0-20 cm)	0.60 ± 0.01	2.87 ± 0.07	0.98	131	4.18	0.61 ± 0.01	2.70 ± 0.14	0.60 ± 0.93	25.05 ± 125	0.98	126	4.52
20 (0-20 cm)	0.73 ± 0.008	2.61 ± 0.05	0.99	105	5.59	0.77 ± 0.006	1.93 ± 0.13	0.59 ± 0.04	6.39 ± 1.92	0.99	41	7.98

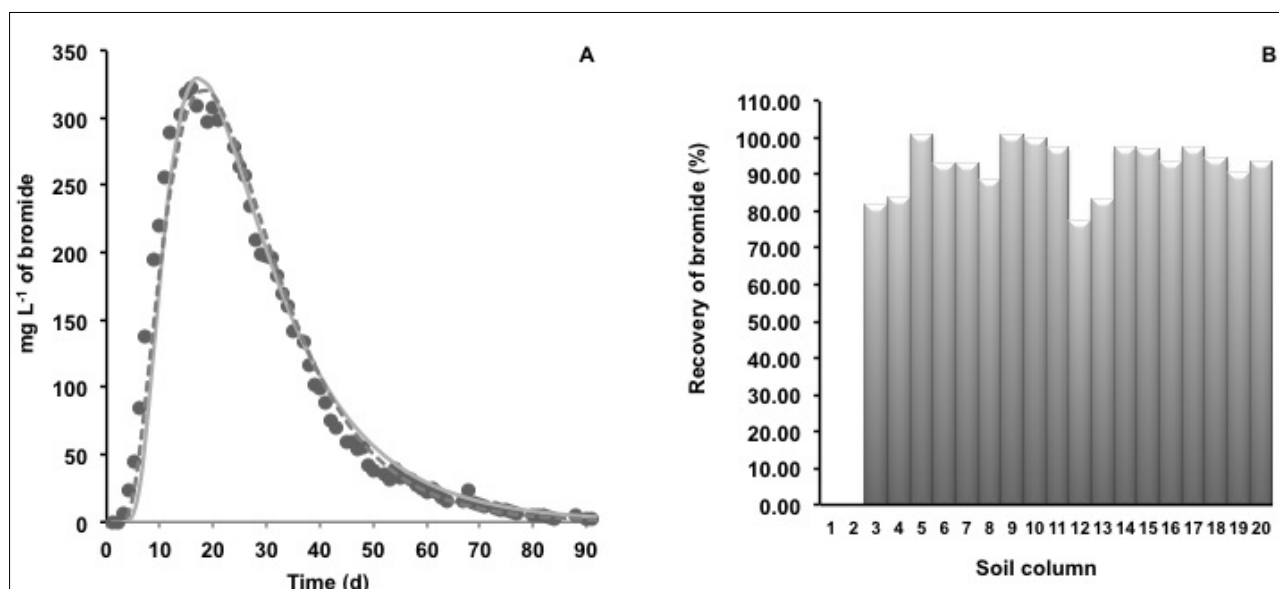


Figure 2. Bromide breakthrough curve of column number twenty (A) and recovery of bromide (B) at depth of 0-20 cm. Experimental data (circles), CXFITM code in equilibrium (line continued) and CXFITM code in non-equilibrium (line discontinued).

the larger the degree of physical non-equilibrium in the porous medium. Dousset et al. (2007) found a  $\beta$  value for undisturbed columns of 0.44, in other words, 56 % of the water resides in the matrix or slow zone of the soil. With the  $\omega$  (t) parameter, it is possible to calculate the average transfer time of mass from the macropores to the matrix or micropores in the soil ( $1/\omega$ ). If this time is longer than the average travel time of solutes ( $L/\nu$ ), the transfer of mass from the macropores to the soil matrix is predominant, but if the average travel time of solutes is much larger than the average mass transfer time, solutes travel with the mass of water (convective flow). The average travel time of the bromide was between 26 and 33 d, while the average mass transfer time presented a range of 0.04 to 1 d.

Dimethomorph and pyrimethanil were not detected at 20 cm, 40 cm, 60 cm, 80 cm or 100 cm in the lysimeter (column A). But in the 0-20 cm columns, dimethomorph (0.12 %) was found in the leachate during the pulse application from column 9, and in this same column dimethomorph was quantified in the leachates from days 2 through 10 (0.03 %). In column 16, dimethomorph was found in leachates from days 25 through 49 (0.02 %).

## Discussion

Fast dissipation of dimethomorph might be explained due to biotic soil processes, which are considered to play a fundamental role in its degradation. This is explained by its stability under sterile conditions (FAO 2017a). The rapid dissipation of pyrimethanil might be due to hydrolysis, producing 2-hydroxy-4,6-dimethylpyrimidine and aniline (FAO 2017b). When results are compared to temperate soils, dissipation of dimethomorph and pyrimethanil in the Andisol was found to be faster than in some temperate soils (Capri et al. 2001, Vanni et al. 2006, FAO 2017a); Fenoll et al. 2011, Piao et al. 2011, PPDB 2017). These differences may be explained due to the soil type, type and amount of soil microorganisms, applied dose, and water content factors, which control the degradation of pesticides in soil (Chai et al. 2013, Kah et al. 2007) and differed among the studies. However, the dissipation of the dimethomorph was close to that established by Liang et al. (2011) and was higher than that found by Liu et al. (2012) for a soil from Beijing, China. This demonstrates the importance of obtaining the half-life of pesticides under specific conditions to explain the movement of solutes through the soil. The longer the

half-life of the solute in soil, the higher the risk of leaching and therefore of diffuse pollution.

The average bromide recovery percentage shows that the conservative tracer does not degrade, not volatilizes, and not retained permanently in the soil; therefore it is useful for obtaining the transport parameters of the porous medium. Dousset et al. (2007) and Lennartz & Kamra (1998) found bromide recovery percentages in undisturbed and disturbed soil columns between 87 and 97.5%. The left shift of the effluent curves and the detection of bromide in the first leachates (1-6 d) suggested the existence of a preferential flow in the first 20 cm of the soil profile. This flow was generated by the movement of the water through the macropores present in the medium and allowed the solutes to leach rapidly in the unsaturated zone. The presence of macropores in the 0-20 cm deep soil layer was confirmed in the field.

The BTC's were slightly asymmetrical (tails at the end of the curves), which showed the presence of stagnant or immobile water in the blind pores of the system (Rao & Bhabani 2007). The asymmetry indicated that the solutes were transported in a non-physical equilibrium system and that the water flow regime in the soil was heterogeneous (Dousset et al. 2007, Gamedinger et al. 1990, Toride et al. 1995). In a system in non-physical equilibrium two zones of movement are differentiated in the movement of water and solutes: the mobile zone (flow) and the immobile zone (stagnant), and the transfer of mass between the two zones modeled by a first-order process controlled by diffusion. The differences in the travel and transfer times of the bromide indicated that in the first 20 cm of the Andisol, solutes were transported with the mass of the water through the porous medium. This aspect was further verified by the values of the Péclet numbers. Values greater than 1 meant that convective flow played an important role in the transport of solutes compared to diffusive flow, though the presence of diffusive flow can not be ruled out. This diffusive flow was observed in the tails of the bromide elution curves. In the immobile zone, the transport of solutes is due to diffusion alone, which responds to concentration differences between the mobile and immobile regions (Rao & Bhabani 2007).

The dimethomorph found in some of the leachates from columns of 0-20 cm depth was due to: i) rates of dissipation, ii) convective flow, and iii) preferential flow. This fungicide was more stable than pyrimethanil, convective flow transported it along with the mass of the water, and the preferential flow could be responsible for moving it in column 9 during the application of the pulse. The preferential flow was generated by the presence of macropores in the soil, in which gravity and velocity could be high, allowing the flow to be transitional to turbulent (thick layer flow). In addition, the macroporosity of the soil has dead zones that affect the continuity of the flow of water in the vadose zone and the transport of solutes (Jarvis 2007).

Dimethomorph and pyrimethanil were not detected at 20 cm, 40 cm, 60 cm, 80 cm or 100 cm in the lysimeter (column A), which can be explained due to the fast dissipation of the fungicides.

## Conclusions

Lysimeters and small columns combine various aspects of the field and laboratory work to evaluate environmental

fate of pesticides. Properly dimensioning the size of the soil container saves not only resources but also avoid misleading results. We were unable to detect dimethomorph and pyrimethanil in Andisol in the lysimeter of 100 cm depth. However, when the experiments were conducted in small 20 cm depth columns, fungicides were found. The failure of the column of 100 cm was due to the faster dissipation of the studied active ingredients in high organic tropical soils as compared to temperate soils. Thus, the high organic topsoil layers posed lower risk of lixiviation. However, presence of preferential flows on soil columns and under natural conditions enabled the chemicals to reach further soil depths and presumably explain the contamination of the groundwater.

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