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ABSTRACT

Chlorpyrifos (O, O-diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate) and carbaryl (1-naphthyl methylcarbamate) are often applied concurrently as insecticides in food production. The aim of this study was to research their migration behavior in a real environment. We researched the leaching of both pesticides by setting up field lysimeters on a farm with the typical soil used in fruit production today. In order to analyze the variables involved in this process, we performed complementary adsorption studies, we performed complementary adsorption studies using batches and undisturbed soil laboratory columns for both compounds. The results for pesticide transport through the lysimeters showed that less than 1% of chlorpyrifos was recovered in the leachates, while almost 17% was recovered for carbaryl. Having completed the experiment in undisturbed laboratory columns, soil analysis showed that chlorpyrifos mainly remained in the first 5 cm, while carbaryl moved down to the lower sections. These results can be explained in view of the sorption coefficient values (K_D) obtained in horizons A and B for chlorpyrifos (393 and 184 L kg^{-1}) and carbaryl (3.1 and 4.2 L kg^{-1}), respectively. By integrating the results obtained in the different approaches, we were able to characterize the percolation modes of these pesticides in the soil matrix, thus contributing to the sustainable use of resources.

Introduction

Pesticides are commonly used in association with agricultural production and represent one of the major environmental risks to the quality of surface and ground water resources. Once pesticides have been introduced to the environment, degradation and sorption are key processes affecting the fate and transport of organic chemicals. Sorption of organic pollutants to soils is an environmentally significant process to control the advective-dispersive transport of compounds, transformation and bioaccumulation processes,[1] bioavailability, ecotoxicity, degradation rate, and mobility.[2,3] In particular, leaching parameters define the pesticide's capacity to reach groundwater[4–6] and this capacity is influenced by the unsaturated soil zone, land use, irrigation, and weather characteristics, among other factors.[7,8]

The environmental fate of chemicals can be addressed at different levels involving the use of methodologies of varied complexity: in the laboratory with batch experiments and undisturbed soil columns, in the field with soil enclosure lysimeters,[9–11] and also through the application of indices and prediction models.[12–14] The parameters used most often as indicators of a given soil's sorption capacity and pesticide mobility are the sorption coefficient (K_D) and desorption coefficient (K_{DES}); the greater the K_D value, the greater the sorption. Mobility in soil is also affected by the ability of the sorbed chemicals to desorb from the soil. Various herbicides have exhibited desorption hysteresis; that

is, once a compound is sorbed it is not readily desorbed.[15] Specifically, Azcarate[16] analyzed the sorption, desorption and leaching potential of herbicides in soil, suggesting that factors such as landscape position, soil depth and rate of decomposition should be taken into account when characterizing pesticides as leachers. Undisturbed laboratory columns are often used to assess the mobility behavior of different chemicals. Gupta et al.[17] analyzed the leaching magnitude of thifluzamide under laboratory conditions and revealed that this chemical was moderately mobile in alluvial soil; only small amounts (<1%) were recovered from leachate aliquots whereas a major portion remained in the 0–15 cm soil depth. Maszkowska et al.[18] studied the leaching behavior of sulfonamides using column and batch sorption tests in soils with different particle size distribution, organic matter content, and pH; and they found that results from the two methodologies were comparable to a large extent. Lysimeters have been used for a variety of purposes in recent decades. Although laboratory columns are useful to profile the mobility potential of a given pesticide in soil, field lysimeters provide a more reliable approach to reflect field behavior.[19,20] This is mainly because the structure of natural soils differs both vertically and laterally, affecting the complex flow of water through the soil profile. Furthermore, there are macropores in soil which adds to the complexity of how water flow occurs.[21] In the Danish Pesticide Leaching Assessment Programme, Rosenbom[14] found that rapid

preferential transport that bypasses the retardation of the plow layer seems to dominate leaching in a number of scenarios. Moreover, in the same region as our study, Dufilho et al.[22] simulated different factors that could affect leaching by applying a mathematical model of unsaturated flow and dual porosity, MACRO 5.0. They concluded that the combination of some specific suitable agricultural practices with soil factors and phreatic depth could be used to define the conditions recommended for pesticide use in fixed areas.

Organophosphate and carbamate pesticides are two classes of cholinesterase inhibiting insecticides, several of which are highly toxic. Until the 21st century, they were among the most widely used insecticides available. Nowadays, some of them have been banned and others have been restricted to specific uses. These compounds are applied in a wide variety of habitats including agricultural lands, forests, rangelands, wetlands, residential areas, and commercial sites. For this study we selected chlorpyrifos (O, O-diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate) and carbaryl (1-naphthyl methylcarbamate), both WHO (World Health Organization) class II (moderately hazardous) pesticides. They have contrasting physicochemical properties and are commonly used in the region.[23,24] Chlorpyrifos has very limited water solubility, a high n-octanol/water partition coefficient value (K_{ow}), and a Groundwater Ubiquity Score (GUS) value of 0.17; while carbaryl has higher solubility, a lower K_{ow} value and a GUS value of 2.02.[12] Therefore, according to these characteristics, an extremely low mobility potential would be expected for chlorpyrifos, while a low mobility potential would be expected for carbaryl.[25,26] These pesticides have been detected in several environmental compartments, air, rain water, sediments, surface water, and, to a lesser extent, in shallow groundwater, and their sorption capacity has been documented.[27–32]

In the region where this study was performed, fruit production is one of the major economic activities. At the same time, groundwater is very near to the surface, making it a compartment vulnerable to pesticide residues. Therefore, knowing the migration potential of any pesticides applied concurrently acquires particular significance. The aim of this paper is to investigate the migration behavior of chlorpyrifos and carbaryl through an integrated approach including undisturbed soil columns, batch sorption studies, and field lysimeters.

Material and methods

Chemicals

The insecticides used in this study were chlorpyrifos and carbaryl. Some specific properties of these compounds are listed in Table S1 and their chemical structures are shown in Figure S1.

We used pure analytical standards, carbaryl 99% and chlorpyrifos 99.5%, both from Chem Service (660 Tower Ln, West Chester, PA 19380, USA). Formulated pesticides used in the field were: Lorsban® 75% WP and Sevin® 85% WP.

Soils

Two horizons of one soil profile from an agricultural production farm were used for the studies performed. The first 15 cm represented horizon A (SA), while horizon B (SB) went from 15 to 40 cm. Table 1 shows the physicochemical properties of the soil.

Sorption isotherms

Sorption isotherms were determined by conducting batch equilibrium experiments. The initial concentration values for chlorpyrifos ranged from 0.130 to 0.840 mg L^{-1}, while for carbaryl they ranged from 0.230 to 3.860 mg L^{-1}. The aqueous solution/soil ratio was 20:1; shaking time for chlorpyrifos was 16 h and for carbaryl it was 3 h, both in the dark at 20°C and at a centrifuge rate of 3000 rpm (30 min). The equilibrium concentration of chlorpyrifos was measured by LLE/GC-μECD (liquid–liquid extraction coupled with gas chromatography—microelectron capture detector) and the equilibrium concentration of carbaryl was measured by HPLC-UV (high performance liquid chromatography-ultraviolet detector, $\lambda = 220$ nm). In this study, carbaryl working solutions were maintained at pH = 6, to prevent degradation during the sorption process.[33] The concentration of pesticides (C_s) sorbed to the soil was calculated as the difference between the initial concentration (C_i) and the equilibrium concentration (C_e) in the supernatant, after incubation.[32] The K_D values were obtained as the ratio between the concentration sorbed in the solid phase and the equilibrium concentration in the solution from the linear region of the isotherms. Blanks without soil were analyzed to evaluate pesticide degradation under experimental conditions and blanks containing soil and a 0.01 M CaCl$_2$ solution, without pesticides, were treated in the same way as laboratory method blanks for quality control.[34] After the sorption processes reached equilibrium, desorption experiments were conducted using tubes that contained an initial pesticide concentration selected from the middle of the concentration range studied, for each pesticide. A volume of 8 mL of 0.01 M CaCl$_2$ was added to the solid phase contained in the selected tubes; this solution was then agitated in a shaker until equilibrium was reached (16 h for chlorpyrifos and 3 h for carbaryl). The tubes were then centrifuged and the supernatant was used for quantitation, as described at the beginning of this section. All experiments were carried out in duplicate.

Table 1. Soil physicochemical properties and sorption coefficients (K_D).

Soils	pH	% OC	% Clay	% Silt	% Sand	CEC[c] (cmol kg^{-1})	Chlorpyrifos K_D[a] (L kg^{-1})	R^2	Carbaryl K_D[b] (L kg^{-1})	R^2
SA	7.80	3.03	17.5	32.8	49.7	14.7	393	0.95	3.1	0.85
SB	8.30	1.50	23.8	50.7	25.5	12.7	184	0.94	4.2	0.94

[a]$n = 12$, Typical Error $_{SA}$: 29, Typical Error $_{SB}$: 14; [b]$n = 6$, Typical Error $_{SA}$: 0.68, Typical Error $_{SB}$: 0.5; [c]CEC: Cation exchange capacity.

Freundlich [Eq. (1)] and Langmuir [Eq. (2)] equations were employed to describe the sorption behavior of pesticides. These equations are written as

$$C_s = K_F \times C_e^{nF} \tag{1}$$

$$\frac{C_e}{C_s} = \frac{1}{C_{max}K_L} + \frac{C_e}{C_s} \tag{2}$$

where C_s is the amount of pesticide sorbed, C_e is the equilibrium concentration of pesticide and C_{max} represents the maximum sorption capacity; n_F is the sorption intensity constant; K_F is the Freundlich sorption coefficient while K_L is the Langmuir sorption constant.

Lysimeter

The lysimeter devices were placed at a depth of 30 cm, in duplicate, in the soil of a farm with current fruit production. The soil enclosure lysimeters were prepared by pounding a 40 cm i.d. (internal diameter) metal tube into the soil using a heavy hammer. The soil was undermined from the side of the lysimeter, and a funnel was placed immediately below the soil column studied in order to collect the leaching water under gravity. The mass of pesticide that reached the lysimeter area, while the pesticide was being applied, was measured by placing Petri dishes ($n = 6$), which were randomly distributed throughout the experimental plot. Petri dishes were collected at the end of the treatment and rinsed three times with methylene chloride, gathering the extracts. Flood irrigation was simulated 24 h after an actual pesticide application and the water leached was collected and extracted using methylene chloride. Pesticide quantitation was performed from the extracts using GC-NPD (gas chromatography with nitrogen phosphorus detector). The amount of pesticide leached was calculated as a percentage of the mass of active ingredient reaching the soil surface. The pesticides used in this experiment were formulated commercial products.

Laboratory columns

The soil columns used in this study were prepared in metallic tubes with a length of 25 cm and an internal diameter of 7.5 cm, in triplicate. Undisturbed soil columns near to where the field lysimeters were located were obtained in situ by introducing the tubes from the ground surface. Soil samples were collected during the non-application period and analyzed in order to ensure the absence of pesticide residues. Columns were arranged in a wood stand, the leaching fractions were collected through a canvas filter and a glass funnel converging into glass bottles. Before applying the compounds, the columns were conditioned at room temperature, avoiding direct light, with 0.01 M CaCl$_2$ in distilled water to their maximal water holding capacity and then allowed to drain for 24 h. The soil in the columns was spiked with 2 mL of a standard pesticide solution in acetone containing carbaryl and chlorpyrifos (126.7 and 97.5 mg L^{-1}, respectively). The concentration applied was the same as the mass of pesticide reaching the soil during the actual field application. Once the solvent had dissolved,

an irrigation event similar to the lysimeter experiment was simulated in atmospheric conditions. Four pore volumes were lixiviated and collected in separate containers. The pore volume was calculated from the soil porosity and the total soil volume inside the column. A degradation control was performed simultaneously. At the end of the leaching experiment, the column soil was divided horizontally into 3 cores measuring 5 cm each. The moisture content of each soil segment was determined and extraction was performed by SAESC (sonication-assisted extraction in small columns) with ethyl acetate. Leached solutions were extracted by LLE using hexane as an extracting solvent.

Although formulated pesticides were used in the lysimeters while active ingredients were used in the columns, it has often been argued that active substances become independent from any coformulates upon entering the soil and that pesticide fate in soil is unchanged when compared to that of the pure active ingredient.[35]

Analytical methodology

The soil analytical methodology (SAESC) was previously validated by recovery tests carried out at three concentrations: 0.2 μg g^{-1}, 0.5 μg g^{-1} and 1 μg g^{-1} (7 replicates/concentration). Soil samples were sieved (2 mm) and stored at room temperature until fortification. Polypropylene columns (20 mL) were prepared with two glass fiber filters without binder circles (AP40 EM), 2 g Na$_2$SO$_4$ and 5 g fortified soil. Extraction was performed twice with 4 mL ethyl acetate each time, for 15 min in an ultrasonic water bath (150 W, 35 kHz, room temperature). The soil samples were washed with 2 mL ethyl acetate and the combined extracts were concentrated to 1 mL under a nitrogen stream. The recovery percentages were between 80% and 97% for carbaryl and between 83% and 93% for chlorpyrifos. The coefficients of variation (CV) were less than 8% for both pesticides. The limits of quantitation (LOQ) were 34 μg kg^{-1} and 24 μg kg^{-1} for carbaryl and chlorpyrifos, respectively. In the validation of the water sample methodology (LLE) the recovery percentages ranged from 70% to 110%, and the CVs were less than 12% for both pesticides. Each set of samples was analyzed in duplicate, simultaneously with a laboratory blank. The LOQ was 0.10 μg L^{-1} for chlorpyrifos and 0.40 μg L^{-1} for carbaryl. Carbaryl and chlorpyrifos extracted from both matrices (water and soil) were analyzed using an Agilent 6890 gas chromatograph equipped with an Agilent 7683 autosampler, split/splitless injector and an HP-1 capillary column, (30 m in length, 0.25 mm i.d., 0.25 μm film thickness). A nitrogen phosphorous detector (GC/NPD) was used for the quantitation of the compounds studied (NPD temperature: 300°C, oven temperature program: 70°C; 20°C min^{-1}→160°C; 4°C min^{-1}→240°C; injection volume: 1 μL). Quantitation was performed using the internal standard method.

Results and discussion

Batch sorption experiments

The insecticide chlorpyrifos is applied as part of the phytosanitary program, sometimes alone and often in conjunction with carbaryl. The sorption behavior was assessed for both pesticides. Sorption isotherms for horizons A (SA) and B (SB) are
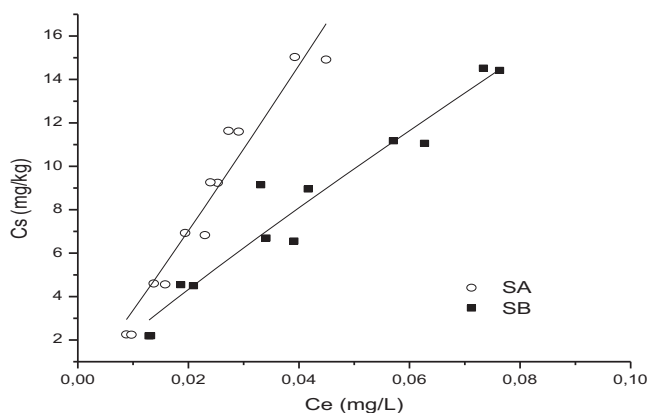
Figure 1. Sorption isotherms of chlorpyrifos in soil. Conditions: initial concentration = 0.130–0.840 mg L^{-1}; aqueous solution/soil ratio = 20:1; Contact time = 16 h. All experiments were performed at 20°C and pH = 6. The solid line corresponds to the Freundlich sorption isotherm (R^2_{SA} = 0.93; R^2_{SB} = 0.94).

shown for chlorpyrifos and carbaryl in Figures 1 and 2, respectively. An increase in sorbed pesticide amount (C_s) was observed with an increase in pesticide concentration. A linear response is shown for chlorpyrifos, while for carbaryl nonlinear behavior and a saturation zone can be seen in the concentration range studied. Experimental data for chlorpyrifos were well described by the Freundlich equation (Fig. 1). The highest K_F sorption coefficient was obtained for horizon A, with higher organic matter content (K_F = 445, n_F = 1.06, R^2 = 0.94) in contrast to horizon B (K_F = 146, n_F = 0.90, R^2 = 0.94). This behavior is typical of a hydrophobic compound interacting mainly with organic soil components.[32]

Carbaryl sorption isotherms for SA and SB are shown in Figure 2. The L-shaped isotherms obtained mean that surface adsorption was the dominant mechanism, rather than soil partitioning.[36] The maximum sorption capacity, calculated by fitting the experimental data to the Langmuir isotherm, is similar in both horizons (C_{maxA} = 7.15 mg kg^{-1}, C_{maxB} = 6.65 mg kg^{-1}). However, when comparing Langmuir sorption constants, the K_L from horizon B (1.28 L mg^{-1}) is greater than the K_L from horizon A (0.43 L mg^{-1}).

The differences in K_L could be explained by this insecticide's greater affinity for soil mineral components. Horizon B reveals
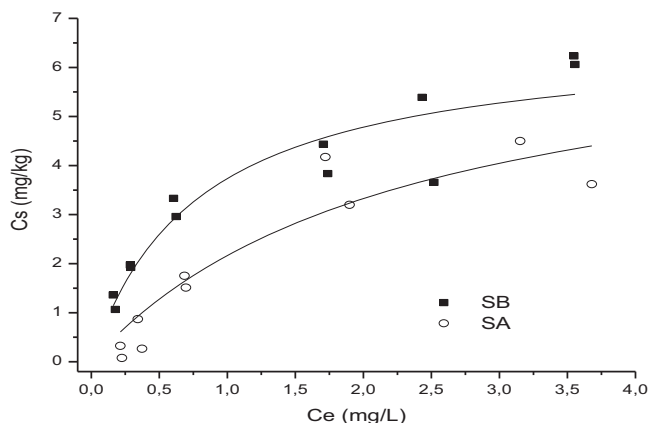
a lower carbon content with a significantly higher clay content (Table 1), which could result in more hydrophilic mineral sites available to retain this pesticide (K_{ow} = 2.69).[37,38] The behavior of carbaryl may be explained by soil sorption capacity which is proportional to the number of active sites, showing saturation at higher pesticide concentrations, probably involving specific interactions as hydrogen bonds. Previous studies have shown that inorganic soil components are involved in carbaryl retention. For example, Fernandes De Oliveira et al.[33] reported site-specific interactions between the carbamate functional group of the adsorbate and exchangeable cations of clay minerals; and Yang and Sheng[39] previously reported that silica components contribute slightly to pesticide sorption because of the strong hydrophilic nature of the adsorbent.

Table 1 presents sorption coefficients (K_D) for chlorpyrifos and carbaryl calculated from the initial linear section of the isotherm curves. The sorption of chlorpyrifos was higher than that of carbaryl for the two soil horizons studied, which is consistent with the hydrophobicities of the two pesticides. These values were similar to those reported in recent studies for these pesticides in farm soils.[31,40,41]

In the soil studied, a higher K_D value was registered for chlorpyrifos in horizon A (393 L kg^{-1}) than in horizon B (184 L kg^{-1}). These results can be attributed to the %OC (organic carbon percentage) in horizon A which is twice the percentage of horizon B, suggesting that chlorpyrifos distributes between the aqueous and solid phases as a function of hydrophobic interactions with the soil organic matter. Conversely, the differences between %OC in the two horizons did not seem to affect carbaryl sorption, for which there were no significant differences in the two K_D values (SA: 3.1 L kg^{-1} and SB: 4.2 L kg^{-1}). Beyond the sorption process, desorption plays an important role in the assessment of mobility. Desorption percentages were markedly different for the two pesticides; carbaryl showed a desorption of 60%, one order of magnitude higher than chlorpyrifos (2.2%), values determined in SA. This was expected taking into account the experimental K_D values obtained and also the K_{OW} and water solubility values for the chemicals studied (Table S1). Chlorpyrifos has a closer affinity to the solid phase, its desorption percentage is low compared to carbaryl, which shows opposite behavior that further substantiates the hypothesis of a higher migration potential for the latter pesticide.

Field lysimeters

Pesticides that enter the unsaturated soil profile are transported downwards by the water flux and can be adsorbed, desorbed and/or degraded as they pass through the soil. The rate by which a pesticide passes through the soil depends on the pesticide properties, the soil properties and the prevailing environmental conditions. Lysimeters, placed in the area studied, reliably reflect natural conditions, including the agricultural practices applied. The percentages leached for the two pesticides studied were very different (Table 2); a priori, this behavior could be related to their physicochemical properties.

Less than 0.5% of chlorpyrifos leached from the lysimeter, exhibiting extremely low mobility that matches its low GUS value and high K_D (Table 1), while an average of 17% of

Figure 2. Sorption isotherms of carbaryl in soil. Conditions: initial concentration = 0.230–3.860 mg L^{-1}; aqueous solution/soil ratio = 20:1; Contact time = 3 h. All experiments were performed at 20°C and pH = 6. The solid line corresponds to the Langmuir sorption isotherm (R^2_{SA} = 0.87; R^2_{SB} = 0.87).

Table 2. Total leaching percentage of carbaryl and chlorpyrifos in field lysimeters (Lys).

Compound	Mass applied to the Lys surface[a] (mg)	Average mass leached (%)±SD	GUS[b]
Carbaryl	1.21	17.6 ± 1.6	2.02
Chlorpyrifos	4.83	0.38 ± 0.08	0.17

[a]Data obtained from Petri dishes ($n = 6$), [b]GUS: Groundwater ubiquity score.

Table 3. Total leaching percentage of carbaryl and chlorpyrifos.

Compound	Lysimeters (%)		Columns (%)	
	Mean	SD	Mean	SD
Carbaryl	17.6	1.6	9.6	1.0
Chlorpyrifos	0.38	0.08	0.31	0.01

The mass of pesticide applied and water volume were equivalent in lysimeters and columns.

carbaryl leached from the lysimeter under the same conditions. Martins,[20] who worked with lysimeters in Brazilian soil using seven pesticides including chlorpyrifos, also found the lowest mobility for this pesticide. However, the amount of pesticides leaching from the bottom of lysimeters is determined by both matrix transport and preferential flow transport in soil. Preferential flow through macropores is likely to occur, where pesticides could be transported rapidly via desiccation cracks and worm channels regardless of their sorptive properties.[19] Also, the prevalent form of transport depends on the irrigation mode, among other factors; Starrett et al.[42] found that if a given volume of irrigation water was applied weekly there were greater pesticide leaching losses than for small daily applications of the same cumulative total. Kazemi et al.[43] reported that delaying irrigation by 24 h after pesticide application increased sorption to the soil, thus reducing leaching accordingly. This effect may be more remarkable for hydrophobic pesticides, such as chlorpyrifos. Thus, under our experimental conditions, where irrigation was performed 24 h after pesticide application, leaching could have been lower and preferential flow may not have affected it, especially for chlorpyrifos, which was strongly adsorbed to the soil. In previous studies by our working group we found carbaryl and chlorpyrifos residues in groundwater monitoring wells and their rate of detection was similar, although the concentration measured was higher for carbaryl (most of the values were greater than 0.1 μg L^{-1}) than for chlorpyrifos (most of the values were less than 0.1 μg L^{-1}). Said behavior may be justified by their chemical properties, long-term use, and varied agricultural practices.[13,28]

Undisturbed laboratory columns

The procedure for utilizing soil laboratory columns is simple, and useful to profile the soil mobility potential of a pesticide. Intact columns in the laboratory represent a suitable methodology to simulate field conditions, in a controlled setting. The leaching behavior measured using the mass contained in the pore volumes (V1, V2, V3 and V4) is consistent with the physicochemical properties of the compounds. Figure 3 shows the mass percentage eluted per pore volume for the two pesticides. An extremely low mass was obtained for chlorpyrifos over the course of the four pore volumes while carbaryl behavior was remarkably different.

Previous column studies suggest that chemical transport in the soil column is mainly influenced by sorption capacity.[11] In our study, the most weakly adsorbed pesticide, carbaryl, had a higher recovery rate (9.6%) in the leachate, while the recovery rate of chlorpyrifos was only 0.31% (Table 3). Figure 4 shows the distribution of pesticides in the first soil horizon, which was measured every 5 cm. Chlorpyrifos exhibited stronger retaining capacity in the first 5 cm whereas carbaryl moved down slightly over the course of the three segments.

It has been demonstrated that the undisturbed column test is a good predictive tool for assessing groundwater pollution. Using laboratory columns, Grondona et al.[7] showed that endosulfan and the sulfate metabolite would be able to reach shallow groundwater as would other pesticides with similar characteristics.

By comparing leaching percentage values between columns and lysimeters for the two chemicals (Table 3), we can see the greatest differences for carbaryl, which could be explained by the greater probability of preferential flow occurring in the field. For chlorpyrifos there were no differences found between the two systems studied. Since more than 24 h passed between pesticide application and irrigation, we assume that chlorpyrifos bound strongly to the soil matrix, thereby reducing its capacity to travel in the aqueous phase, and flow through preferential paths did not have the same influence as it did for carbaryl.

Figure 3. Column mass leached according to pore volume. Pore volume: 275 mL, $n = 3$.
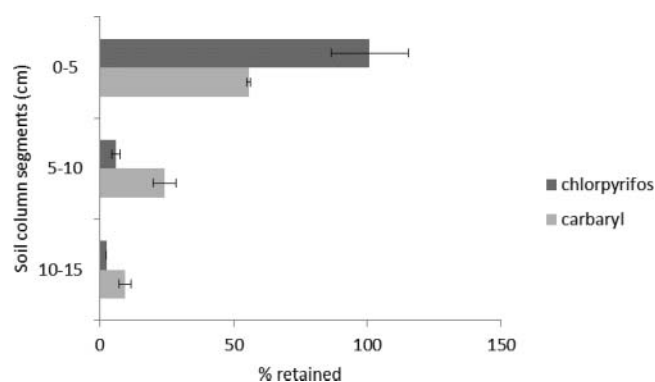
Figure 4. Soil column distribution of chlorpyrifos and carbaryl in the first horizon, $n = 3$.

We conducted a comparative study on the behavior of two pesticides with distinct characteristics, using an integrated approach. We found that the column study outcomes are consistent with the findings from batch sorption studies, and they also support the results seen in the field experiments performed on the same set of soil. Nevertheless, it has to be taken into account that sorption/desorption processes for organic chemicals in batch experiments are conducted in equilibrium conditions while column and lysimeter processes occur in non-equilibrium conditions.[10,18]

Conclusions

This study confirmed that sorption to soil reduces pesticide mobility, according to soil composition and pesticide physico-chemical properties: the batch experiments showed that chlorpyrifos was more strongly sorbed to the soil than carbaryl. Chlorpyrifos can be characterized as non-percolator, while carbaryl is moderately percolator. The magnitude of real field leaching is highly dependent on natural soil conditions and the agricultural practices applied. By comparing the leaching results from intact laboratory columns with those from leaching in field lysimeters we were able to infer the occurrence of preferential paths for carbaryl. An integrated approach including batch experiments, laboratory columns and field lysimeters allows us to understand the behavior of pesticides in agricultural and natural soils, which is essential to define strategies for sustainable development of ground-water resources.

Acknowledgments

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Supplementary Materials

Table S1. Some selected properties of chlorpyrifos and carbaryl.[25,26]

Compound	Chemical formula	Chemical family	DT50[a] (days)	Koc[b] (L kg^{-1})	pKow[c]	Sw[d] (mg L^{-1})
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	Organophosphate	Soil (aerobic): 50 Aqueous photolysis: 29.6 Aqueous hydrolysis: 23	8151	4.7	1.05
Carbaryl	$C_{12}H_{11}NO_2$	Carbamate	Soil (aerobic): 16 Aqueous photolysis: 10 Aqueous hydrolysis: 3	300	2.36	9.1

[a]DT50: 50% dissipation time; [b]K_{OC}:Organic-carbon normalized partition coefficient; [c]pK$_{OW}$: Octanol-water partition coefficient (log K_{OW}); [d]Sw: water solubility.
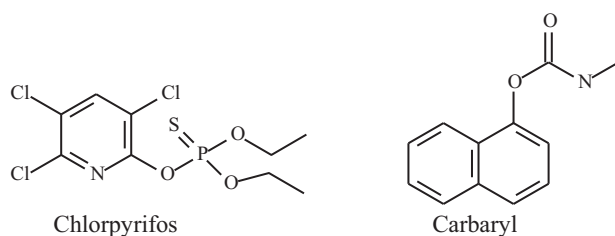

Figure S1. Chemical structures of the pesticides chosen for the study.