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Abstract

The main goals of conservation agriculture are to enhance soil fertility and to reduce soil degradation especially through erosion. However, conservation agriculture practices can exhibit a higher risk of contamination through vertical flows. The objectives of this study were to (i) characterise water and pesticide transfers in two different soils both managed under conventional and conservation agriculture and (ii) assess the effects of pesticide properties, soil type and agricultural system on pesticide fate. We studied the behaviour of two herbicides (nicosulfuron and mesotrione) and a molluscicide (metaldehyde) in percolation experiments in undisturbed soil columns. A series of two rain events (one with a high, the other with a low intensity) separated by a two-day flow interruption was applied three days after the pesticides and bromide application. Batch sorption coefficients, K_d, were also measured. While the Pesticides Properties Data Base (2020) indicated a decrease of sorption in the order mesotrione > metaldehyde > nicosulfuron, the measured K_d, decreased in the order mesotrione (2.3 ± 1.4 L.kg^{-1}) > nicosulfuron (0.7 ± 0.4 L.kg^{-1}) > metaldehyde (0.1 ± 0.1 L.kg^{-1}). We highlighted distinct behaviour of pesticide leaching depending mainly on soil type, agricultural practices and pesticide properties. For low degree of preferential flow, pesticide leaching can be related to the sorption properties of pesticides. Nicosulfuron and mesotrione delays are more pronounced under conservation management while metaldehyde always arrived with no delay. During the high intensity rain event, on one soil type, high degree of preferential flow masked sorption effect on leaching since every pesticide arrived at the same time as the tracer and amounted to up to 21 % of pesticide recovery compared to 4% on the other soil type. Conservation agriculture was found to improve the vertical transfers of water and pesticides while, on one of the studied soil type, the presence of a low conductive plough pan significantly limits water drainage.

Keywords: pesticides, leaching, agricultural management, sorption, preferential flow, non-equilibrium transport

1. Introduction

Due to their degraded soil structure, soils cultivated under conventional tillage practices, such as mouldboard ploughing, are generally more sensitive to surface runoff and soil loss by water and wind erosion (Holland, 2004). In this context, the contamination of neighbouring surface waters by agrochemicals is often increased (Alletto et al., 2010). In order to enhance the sustainability of agricultural systems and reduce the drawbacks of conventional agriculture, alternative cultivation practices such as conservation agriculture have been developed. The main goals of conservation agriculture are to reduce soil degradation through erosion but also the contamination of surface water by agrochemicals due to runoff or transfer of sorbed solutes on eroded soil particles (Holland, 2004; Hobbs et al., 2008). Conservation agriculture is defined as a combination of three main interlinked soil conservation techniques: (i) minimal or no soil disturbance, (ii) permanent soil cover by crop residues and/or cover crops and (iii) diversification of plant species in the crop rotation (FAO, 2016). The interaction between these three principles leads to complex and interlinked changes in soil physical, chemical and biological properties that remain poorly characterized. Taking into account these changes is crucial to properly assess the performance of such agricultural systems. However, contradictory published results especially on soil hydraulic processes and pesticide transfers are reported (Green et al., 2003; Strudley et al., 2008; Alletto et al., 2010; Verhulst et al., 2010).

Tillage decreases soil compaction in the tilled layer but in the same time it disrupts pore connectivity between the tilled layer and deeper soil horizons thus limiting deep water movements (Cameira et al., 2003; Fuentes et al., 2004). In addition, the destruction of low stability aggregates by raindrop impacts may lead to the sealing of soil surface thus reducing soil infiltration and enhancing the risk of erosion (Holland, 2004). On the contrary, in no-tilled soils, because of less disturbance of the topsoil, total porosity is, in most cases, reduced while, in the same time, a greater continuity of vertically oriented macropores is generally observed leading to higher hydraulic conductivity in untilled than in tilled soils (Wahl et al., 2004; Soto-Gómez et al., 2019). In addition, in conservation agriculture, the faunal activity is enhanced, especially earthworms, resulting in a dense biomacropore network (Shipitalo et al., 2000). Introducing cover crops can also improve water conductivity in no-tillage systems, by creating stable biomacropore network through root development during crop growing season (Abdollahi and Munkholm, 2014; Williams and Weil, 2004). Maintaining crop residues at the soil surface progressively leads to an accumulation of soil organic matter in topsoil layers

(Kay and VandenBygaart, 2002) and improves aggregate stability (Devine et al., 2014). Moreover, the dead residues form a mulch that physically protects soil surface from crusting (Baumhardt and Lascano, 1999).

Due to this higher proportion of (bio)macropores, preferential transport of water and solutes is expected to be enhanced in conservation agriculture, thus increasing the risk of contamination of groundwater (Isensee and Sadeghi, 1997). However, field studies reported either higher (Elliott et al., 2000), lower (Gish et al., 1995) or no differences (Fortin et al., 2002) in pesticide losses between no tillage and tillage practices. Laboratory leaching studies on undisturbed soil columns also brought mixed results with higher (Levanon et al., 1993), lower (Sigua et al., 1995) or equivalent (Porfiri et al., 2015; Okada et al., 2016) leaching in tilled compared to untilled soils.

Field and laboratory studies have permitted to identify several factors influencing leaching (Alletto et al., 2010). Rainfall parameters such as arrival time of the first rain after application, the duration and intensity of the rain event were indeed reported as crucial to determine the fate of pesticides in soils (Sigua et al., 1993; Isensee and Sadeghi, 1997). In the meantime, pesticide properties also determine the fate of the compounds into the soil. When comparing the movement of two different pesticides, Fermanich and Daniel (1991) attributed leaching differences to the chemical characteristics (soil adsorption and water solubility) of the compounds. However, despite these advances in knowledge, understanding of the effects of agricultural practices on the fate of pesticides remains unsatisfactory, limiting our ability to assess and predict the environmental impacts of cropping systems (Alletto et al., 2010; Marín-Benito et al., 2018). A possible origin of these contradictory effects observed in the literature may be that most of the studies are based on analytical approach and has thus attempted to isolate the effects of the different agronomic levers mobilized in cropping systems management (e.g. most of studies have focused on tillage effects, or on cover crop effects,

…), whereas a systemic approach (i.e. assessing the effects of interactions between levers) would be more appropriate to evaluate pesticide environmental behaviour. In this study, we therefore chose to characterize the behaviour of water and pesticides in two soils managed under two different agricultural systems evaluated as a whole (i.e. including a combination of management practices), one in conventional agriculture (tillage, bare soil, monoculture), the other in conservation agriculture using the three levers (no tillage, cover crops and crop rotations) for more than 10 years. We assume that a better understanding of the interactions between the various components of a cropping system is needed to reveal its advantages and disadvantages, and that the study of long-differentiated cropping systems can assist in the decision-making process.

Three pesticides, widely used by farmers for maize production, and for which little information is available in the literature, were chosen for the laboratory percolation experiment on undisturbed soil columns. Metaldehyde is a molluscicide generally spread in autumn and winter as baits pellets to protect all types of crops. In a recent review, Castle et al. (2017) reported that metaldehyde is highly mobile in soil and can hence contaminate water resources. Nicosulfuron is a post-emergence herbicide used to control grass species in maize. Because of their anionic character, sulfonylurea herbicides are highly mobile in soil and could contaminate ground waters (Gonzalez and Ukrainczyk, 1996). Regarding the effect of cropping practices on the fate of nicosulfuron, Afyuni et al. (1997) found that conventional tillage generally resulted in more runoff but lower herbicide losses by runoff than no-tillage. Mesotrione is an herbicide that provides pre-emergence and post-emergence control of all the important broad-leaved weeds in maize and some of the annual grass weeds. Very little has been published on mesotrione transfer in soils. Rouchaud et al. (2001) found no movement of mesotrione lower than 20 cm in soil that was attributed to a combination of its low mobility and degradation rate.

The laboratory percolation experiments performed on undisturbed soil columns aimed to (i) characterise water and pesticides transfers in two different soils both managed under conventional and conservation agriculture and (ii) assess the effects of pesticide properties, soil type and agricultural system on the leaching risk of the studied pesticides.

2. Materials and Methods

2.1 Sites and agricultural managements

The two sites of this study are located in the South West of France, in the Pyrénées-Atlantiques and in the Gers French departments. According to the Köppen climate classification, both sites have an altered oceanic climate.

The soil on the Pyrénées-Atlantiques site is a thick humic acid soil developed from Quaternary silty alluvial deposits, classified, according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2007) as a Vermic Umbrisol, and according to the French Soil Classification (AFES, 2008), as a veracrisol, locally called “Touyas”. It has a rich, deep (from 50 to 80 cm-depth) well-structured organic horizon (Table 1). Soil texture is mainly formed by fine silt (> 450-500 $g.kg^{-1}$) with a low proportion of sand (< 100-120 $g.kg^{-1}$). This soil type has a high agronomic potential, especially for maize (average yield ≈ 13-15 $t.ha^{-1}$) and soybean (average yield ≈ 3.7-4.2 $t.ha^{-1}$) productions (mainly conducted without irrigation). This site will be referred to as VER (veracrisol) site in the rest of the paper.

The soil on the Gers site is classified as a Stagnic Luvisol according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2007), corresponding to a luvisol redoxisol in the French Soil Classification (AFES, 2008), locally called “Boulbènes”. It has a loamy surface layer (fine + coarse silt ≈ 450-500 $g.kg^{-1}$) and an illuvial clay horizon appearing between 45 and 55 cm. The substratum is a low-permeability alluvial pebbly layer appearing at around 60-80 cm. With low organic carbon contents in the soil surface horizon (in most cases < 7-8 $g.kg^{-1}$) and high silt contents, these soils are strongly sensitive to crusting. Due to these properties (especially hydromorphic conditions at low depth), this soil type has a moderate agronomic potential with mainly irrigated crops (average maize yields ≈ 10-12 $t.ha^{-1}$). This site will be referred to as LUV (luvisol) site in the rest of the paper.

Each site consists of two adjacent plots managed under conventional (TILL) and conservation (CONS) practices. The conventional plots (TILL) are cultivated under maize monoculture (for more than 40 years) and soil is left bare in winter. Tillage depth with a mouldboard plough is about 22-23 cm on VER site and 30 cm on LUV site. In both conservation plots (VER and LUV), agricultural management consists of (i) a diversified crop rotation (including maize, soybean, cereals and sometimes intercrops of cereals and legumes), (ii) a permanent soil surface cover by mulch and cover crops sown during the fallow periods (on VER site, cover crop is composed by a mix of phacelia and faba bean, while on LUV site, it is composed by a mix of two cereals and faba bean), and (iii) no-tillage practices. Such conservation agriculture practices are performed since 2006 and 2000 respectively for VER and LUV sites.

2.2 Soil core sampling

Three replicated (called area a, area b and area c) undisturbed soil cores (30 cm length; 14 cm internal diameter; ≈ 4 618 cm^3 volume) were sampled at the soil surface of the TILL and CONS plots of each site. They were collected in polycarbonate columns inserted in a steel cylinder of the same size pushed slowly into the soil by using mechanical shovel. The surrounding soil was progressively removed to facilitate the extraction of the core and avoid the compaction of the soil. To minimise spatial variability in soil properties as much as possible, the replicates were sampled at a distance of 20 m from the adjoining edge of the plots by following a transect parallel to this edge and with a distance of 20 m between replicates of the same plot. Sampling was performed in November 2017 in VER site, after maize crop on both plots (corresponding to 6 months after tillage operations on TILL plot), and in January 2018 in LUV site, after soybean crop on the conservation plot (corresponding to 8 months after tillage operations on TILL plot). Mulch located at the soil surface of each CONS plot was kept at the top of the columns. Quantities of mulch were 1400 ± 700 $g.m^{-2}$ and 630 ± 220 $g.m^{-2}$ on the LUV site and VER site respectively. Mulch was absent from the TILL plots columns. The columns were sealed and stored in a cold room (4°C) until the experiment.

2.3 Batch sorption experiments

The three pesticides adsorption coefficients, K_d [$mg.L^{-1}$], were measured on soil samples, collected during the sampling of soil columns, at two depths (0-10 cm and 10-30 cm) for each plot. A solution of metaldehyde [49.9 $\mu g.L^{-1}$], nicosulfuron [19.8 $\mu g.L^{-1}$] and mesotrione [20.1 $\mu g.L^{-1}$] was prepared by dilution in a calcium chloride solution (0.01 M $CaCl_2$). Pesticides were purchased from CIL (Cluzeau Info Labo, Ste Foy, France) with purity > 97% (metaldehyde 97%, nicosulfuron 98.4%, mesotrione 99%). Samples of air-dried soil (3 g) were weighed into Falcon centrifuge tubes (50 mL) and a 9 mL aliquot of herbicide solution was added to each. For each plot and depth, three replicates were made corresponding to the three locations of the replicates of undisturbed soil cores. The tubes containing treated soil were left for 24 h in an end-over-end shaker to reach equilibrium at room temperature, and then centrifuged at 9000 rpm for 10 min. Each pesticide concentration was determined by UHPLC-MS/MS (described in section 2.5). The quantity of sorbed pesticide was calculated as the difference between the amount initially added and the amount measured in the supernatant after equilibrium. The equilibrium sorption distribution coefficients, K_d, were calculated using the equation:

$$K_d = \frac{S}{C_{eq}}$$

where S is the quantity of pesticide sorbed on the soil at equilibrium (mg.kg^{-1} soil) and C_{eq} is the concentration of pesticide in the solution at equilibrium (mg.L^{-1}).

The sorption coefficient K_d was normalised to soil organic carbon content using the equation:

$$K_{OC} = \frac{K_d}{C_{org}}$$

where C_{org} is the organic carbon content of the soil sample (g.kg^{-1} soil).

The measurement of carbon content was done according to the ISO 10694 standard. Carbon content is measured by the CO_2 emission of the sample following a dry combustion. A correction for carbonates present in the sample is applied.

2.4 Leaching experiments

The percolation experiments were conducted under unsaturated water flow in laboratory conditions. A $CaCl_2$ solution (1.8 10^{-4} M $CaCl_2$) was applied at the soil surface by a rainfall simulator. The rainfall simulator was placed a few centimetres above the soil surface and consisted of 45 hypodermic needles (0.33 mm diameter) at 12.5 mm spacing and connected to a membrane pump controlling the flow. To maintain unsaturated conditions, a negative pressure of −80 cm was applied at the soil column base by placing a stainless steel mesh (20 µm pore size) and a 0.5 cm layer of glass beads (diameter < 0.45 µm) at the soil bottom and connecting the column base to a vacuum pump applying constant pressure. The layer of glass beads provided a homogeneous contact between the soil and the mesh. To monitor water content and water pressure, the columns were equipped with two TDR probes and three tensiometers.

The experiments were designed to study the mobility of three pesticides under two rainfall regimes. Before the pesticides application, the soil columns were equilibrated to similar hydration conditions by receiving a constant rainfall of 2 mm.h^{-1} for a duration of 1 day until steady state was reached. We checked that none of the three pesticides were detected in the column effluents during this equilibration period. For only two columns of the LUV site, we detected residual concentrations (9 to 51 times lower for nicosulfuron and 24 to 69 times lower for mesotrione than the concentrations in the first sample collected after the pesticide application). Then a 7.7-mL volume pulse containing the three pesticides and bromide, an anionic water tracer, was manually applied at the mulch (CONS plots) or soil (TILL plots) surface with a pipette. Little drops were applied on the whole column surface in order to obtain a repartition as homogenous as possible. The concentrations of each pesticide in the mixture reflects realist application dose on the field (Table 2). A series of two rain events separated by a two-day flow interruption was applied three days after the pesticides and bromide application to approximate field conditions. The first rain event lasted 4 h with a high flow intensity of 10 mm.h^{-1} to evaluate the behaviour of pesticides under a high risk of preferential flow. The second rain event lasted 10 to 15 days depending of the experimental series with a low flow intensity of 2 mm.h^{-1} maintained until most of the pesticides were eluted. Effluents were collected at regular time steps (every 12 min during the first rain; every 60 min for about 36 h at the beginning of the second rain and then every 90 min) and stored at 4 °C in darkness, and analysed within the next four days to avoid pesticide degradation.

During the pre-saturation phase of the columns, the presence of a very low conductive plow pan (not higher than 0.6 mm.h^{-1} of hydraulic conductivity) in the TILL plot of LUV site prevented the establishment of a steady state. According to field observations of soil structure, its thickness was about 7-8 cm, we therefore removed the 10-cm bottom layer of the three replicates and applied the same procedure. This experimental issue limited the comparison between sites and treatments and no statistical analysis were performed but provided useful information to interpret water movement in this soil type under a conventional soil tillage management.

At the end of the leaching experiment, columns were left to drainage during two days before disassembly of the system. Four soil layers (0-3, 3-5, 5-10 and 10-20/30 cm) were sliced to extract the remaining pesticides and bromide in soil. For each layer, soil was homogenised and a single composite sample was collected and analysed. Mulches were also collected for CONS plots. Samples were stored at -20°C before analysis.

2.5 Bromide and pesticides quantification in leachates, soil and mulch

Bromide concentration in effluents was measured by a bromide ion selective electrode (HI 4102, HANNA instruments) connected to a multimeter meter. The measure was done on a 15 mL aliquot after adding a ionic strength adjuster (HI-4000-00) and converted to concentration ($mg.L^{-1}$) with a calibration curve previously determined.

Pesticide concentrations in effluents were measured by online solid phase extraction (SPE) and ultra-performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS Acquity-TQD, Waters Corp., Milford, MA, USA). The chromatographic separation was carried out with a Waters Acquity BEH C18 column, with a gradient profile between water and acetonitrile both containing 0.1% acetic acid, with a flow rate of 0.4 $mL.min^{-1}$. Sample injection volume was 1 mL. The detailed parameters for chromatography and mass spectrometry are given in supplementary information (Appendix Methods A.1).

Deuterated-labelled standards of metaldehyde (D16), nicosulfuron (D6) and mesotrione (D4) were added to each sample prior to analysis to correct under- or overestimations of the concentrations due to MS matrix effects. Isotope-dilution quantification was performed with calibration curves containing the three pesticides and their deuterated analogues.

Soil and mulch bromide extractions were made using a 2:1 deionised water:soil (v:m) and 10:1 deionised water/mulch (v:m) ratio, respectively. Samples were shaken for 24 h, and then centrifuged 10 min at 10 000 rpm. Bromide concentration was measured by HPLC with a Dionex IonPac AS9-HC Analytical Column (250 mm). The chromatographic separation was carried out with 8.0 mM Carbonate + 1.5 mM NaOH solution with a flow rate of 0.8 $mL.min^{-1}$. Sample injection volume was 0.25 µL. The detection was done by suppressed conductivity detection.

Soil and mulch pesticide extractions were made using a 5:1 solvent:soil (v:m) and 8:1 solvent:mulch (v:m) ratio, respectively. Deuterated labelled standards of metaldehyde (D16), nicosulfuron (D6) and mesotrione (D4) were added to the solid samples 24 h before extractions to correct losses during extraction, purification and MS ionisation. Two successive extractions were done on 5 g of fresh soil or 3 g fresh mulch using methanol:McIlvaine buffer:disodium ethylenediaminetetraacetate in 60:20:20 volumetric proportions. The extracts were purified on SPE cartridges (Macherey Nagel Oasis HLB 6cc; 500 mg) after dilution in ultrapure water. SPE cartridges were eluted using 6 mL methanol. Thereafter, the eluates were evaporated to dryness under a nitrogen flow and dissolved in 4 mL of water:acetonitrile (90:10, v:v) prior to UHPLC-MS/MS analysis.

2.6 Breakthrough curves (BTC) analysis

In order to compare the results between the different plots and sites, the breakthrough curves were plotted as the measured relative concentration, i.e. the ratio of the effluent concentration, C (mg.L^{-1}), to the initial pulse concentration, C_0 (mg.L^{-1}), versus the number of pore volume eluted i.e., the ratio of the cumulated volume of leachates, V (mL) to the column pore volume, V_0 (mL).

To identify preferential flow, we calculated two early arrival times, the arrival time of the first breakthrough of the solutes, T_b (-) and the 5% solute arrival time, $T_{5\%}$ (-). $T_{5\%}$ is defined as the number of pore volumes eluted when 5% of the applied solute has arrived in the effluents (Knudby and Carrera, 2005; Norgaard et al., 2013). The arrival time of the maximal peak concentration, T_p (-) and the relative maximum concentration of the peaks, C_p (-) were also used to quantify the leaching of the solutes.

Expected retardation factors (R_e) for each pesticide during the percolation experiments were calculated from the measured K_d of the batch sorption experiments, as follows:

$$R_e = 1 + \rho \frac{K_d}{\theta}$$

where ρ is the bulk density of soil (g.cm^{-3}) and θ is soil volumetric water content (cm^3.cm^{-3}). Due to the intermittent flow conditions of the column experiments, a range of minimal and maximal values of R_e was calculated to take into account the θ variation throughout the leaching periods.

2.7 Statistical analysis

Analysis of variance (ANOVA) was performed to reveal the effect of sampling depth (only for K_d), agricultural system and solute nature on K_d, T_b, $T_{5\%}$, T_p, C_p, and leached, soil, mulch quantities recovered. Shapiro-Wilk normality test and Bartlett's homoscedasticity test were applied to the residues of the ANOVA to verify application condition. Where the conditions were not met, a Kruskal-Wallis test was carried out.

3. Results

3.1 Batch sorption experiments

Whatever the agricultural management or the sites, mesotrione sorption was the highest while metaldehyde sorption was the weakest with no adsorption of metaldehyde on LUV site, except for one replicate having a K_d coefficient very close to 0 (on TILL plot at the 10-25 cm-depth, Table 1). Mesotrione was significantly ($^{***}P < 0.001$) more adsorbed in CONS soils than in TILL soils for both sites whereas no significant differences could be observed for metaldehyde and nicosulfuron. No clear trend was also observed for the differences in K_d between the 0-10 and 10-25 cm-depth, even in the case of conservation agriculture for which, on LUV site, mesotrione K_d was found to be slightly higher for the 10-25 cm than in the 0-10 cm-depth horizon, despite a higher amount of organic carbon in the topsoil layer but a smaller clay content.

No correlation was found between organic carbon content and sorption of the three studied pesticides. Correlation with clay content was only found for mesotrione K_d (r = 0.97, $^{***}P < 0.001$) on the LUV site. Smaller significant correlations were found between mesotrione K_d and soil pH on both sites (r= -0.66, $^{*}P < 0.05$ on VER site and r= -0.71, $^{**}P < 0.01$ on LUV site). No other correlations were found for the other pesticides.

3.2 Water and pesticides transfers

3.2.1 Water and pesticides transfers on VER site

Fig.1a displays the breakthrough curves (BTCs) of bromide for both plots of VER site. No noticeable difference regarding the time to first breakthrough was observed (Table 3). After the flow interruption, the concentrations of bromide in the resumed effluents did not differ much from the concentration of the last effluent, so that globally the overall BTCs displayed a single peak. Generally bromide peaks of the TILL plot arrived earlier with higher maximum relative concentrations, C_p, than those of CONS plot but these differences were not significant. The 5% tracer arrival time reached low values of 0.28 ± 0.05 and 0.31 ± 0.03 on the TILL plot and the CONS plot respectively, which is an indication of non-equilibrium transport (Table 3). These results indicate low differences in the degree of preferential flow between both plots. After about 2.6 pore volumes (last detection of bromide), recovery rates of leached bromide ranged from 79.4% ± 5.3 in CONS plot to 87.3% ± 7.4 in TILL plot (Appendix Table A.2), with no significant difference. The extraction performed on soil after the end of the experiment revealed that very high quantities of bromide (an average of 17.5 ± 1.2 % of the applied mass of bromide) remained in the soil for both agricultural systems (Fig. 2a). Less than 1% of the applied mass of bromide was found in the mulch in the CONS plot.

Pesticides BTCs presented different behaviours (Fig. 3). Metaldehyde was the most rapidly displaced pesticide through the columns under both agricultural systems. Its breakthrough time was very close to the breakthrough time of bromide. Although the retardation factor indicated that metaldehyde should be delayed as compared with bromide under both plots (Appendix Table A.1), metaldehyde T_p was lower than bromide T_p (Table 3). As for bromide, mean metaldehyde T_p was globally lower in TILL plot and C_p was higher. However, none of the differences observed were statistically significant.

Nicosulfuron and mesotrione were however significantly delayed compared to bromide and their peaks appeared about respectively 0.54 ± 0.07 and 0.75 ± 0.12 pore volume later than those of bromide in the TILL plot. In the CONS plot, nicosulfuron and mesotrione peaks appeared about 0.81 ± 0.16 and 1.36 ± 0.14 pore volume later than bromide peaks. Mesotrione was thus more delayed than nicosulfuron and even more under conservation agriculture which is in accordance with the trend expected from the calculated retardation factors (Appendix Table A.1). Differences according to agricultural systems were both significant for nicosulfuron (*$P < 0.05$) and mesotrione (***$P < 0.001$).

The mass recovery of leached metaldehyde was highly variable and low (Fig. 2a; Appendix Table A.2), reaching a maximum of 27.9% of the initial input. The recovery of leached mesotrione was also low (less than 20.8 %) while nicosulfuron reached at least 47.5 % of recovery of its initial applied mass. Because of extremely poor extraction-purification yields, metaldehyde could not be quantified in soils. Extractable nicosulfuron and mesotrione in soils represented at most 4.7% and 3.8% of the initial mass with most of the pesticides found in the upper layer (0-3 cm) of soil whatever the cultural system (Appendix Fig. A.1a). Finally, less than 2% of the initially applied mass of nicosulfuron and mesotrione were found in mulch in CONS plot. For this soil type, even if delays in nicosulfuron and mesotrione leaching were observed between TILL and CONS plots, no effect of the agricultural system were found on cumulated pesticide mass transferred by leaching through the columns after 6.5 ± 0.5 pore volumes were eluted, nor on the residual soil pesticide quantities.

3.2.2 Water and pesticides transfers in LUV site

We remind that for LUV site the columns length of the TILL plot was reduced to 20 cm since the very low conductive plow pan layer (< 0.6 $mm.h^{-1}$) was removed to allow percolation of water during the rainfall simulation. Fig. 1b displays the BTCs of bromide for both plots of LUV site. They showed strong evidences of a high degree of preferential flow. They exhibited two distinct peaks for both plots, with a higher variability in the TILL plot. Both peaks arrived before one pore volume was eluted. The first one had the highest maximum relative bromide concentration and occurred during the first rain event. In both plots, the relative amount of bromide leached was more than 20% whereas less than 10% of the applied bromide was leached in the VER site during the first rain event (Appendix Table A.2). The second peak occurred during the second rain event and displayed a long elution tail. The 5% tracer arrival times were globally similar for both plots and lower than the ones of the VER site (Table 3). When outflow resumed after the first rain event, the relative concentration of bromide was always lower suggesting that during the two-day interruption flow bromide migrated in regions of immobile or low-flow water. Only one replicate (area b) in the TILL plot did not display a clear second peak but rather a decrease of concentrations after outflow resumed. Lower quantities of bromide were found in the soils of LUV site (with an average of 6.6 ± 1.7 % of the applied mass of bromide) compared to VER site. Less than 1 % of the initial amount of bromide applied was found in mulch in CONS plot. On average, slightly more bromide was recovered in the CONS plot leachates and soils than in TILL plot (Fig. 2b).

The three pesticides were displaced rapidly through the columns of LUV site (Fig. 4). Their leaching pattern was similar to that of bromide during the first rain event. First breakthrough of the pesticides appeared at the same time as bromide, and generally no difference in the 5% arrival times of pesticides was observed with the 5% arrival time of bromide (except for mesotrione on the CONS plot). For both agricultural managements, no statistical differences regarding the arrival times of the maximal concentration of the first peak, T_{p1}, between the solutes was found (Table 3). This is in disagreement with the calculated retardation factors which indicated that nicosulfuron and mesotrione should be more delayed (Appendix Table A.1). These results confirmed thus the existence of a high degree of preferential flow. For both plots, 17.2 ± 1.0 %, 15.8 ± 3.7 % and 11.6 ± 3.0 % of the initially applied metaldehyde, nicosulfuron and mesotrione respectively, were recovered from the leachates of the first rain whereas less than 3% of the applied pesticides was leached in the VER site during the first rain event (Appendix Table A.2). Except for metaldehyde, pesticide mass recovery was lower for CONS than for TILL plot. During the second rainfall event, the three pesticides followed bromide pattern on the TILL plot. On the CONS plot, metaldehyde generally occurred at the same time as bromide while nicosulfuron and mesotrione were delayed. However, no statistical differences were found except between T_{p2} of metaldehyde and mesotrione.

At the end of the experiment, higher amounts of nicosulfuron were recovered in the leachates of TILL plot than CONS plot (with a recovery rate of 76.2 ± 2.2% of its initially applied mass in TILL plot against 66.5 ± 0.4 % in CONS plot). We did not perform a statistical comparison of these leaching results between agricultural systems because the TILL soil columns were 10 cm shorter than the CONS soil columns to remove the plough pan identified as impermeable. However, we will discuss the consequences of soil physical properties differences due to agricultural system on pesticide environmental risk in Section 4.3. Nicosulfuron amounts recovered in leachates were higher than those measured for the two other pesticides (with average recovery rates of 40.4 ± 11.3 % and 39.2 ± 8.6 % for metaldehyde and mesotrione respectively in both plots, with no difference between the agricultural systems). Higher nicosulfuron and mesotrione amounts were found in soils and mulches of LUV site than those observed in VER site (Appendix Table A.2). In total, comparable amounts of nicosulfuron were recovered between TILL and CONS whereas a higher amount of mesotrione was recovered in TILL (Fig. 2b; Appendix Table A.2).

4. Discussion

4.1 Influence of pesticide properties on pesticide leaching

The molluscicide metaldehyde was found to be the most rapidly transferred pesticide through the soil columns among the three studied pesticides, with a similar behaviour to the bromide anionic tracer used to mimic water movement. Such differences in leaching dynamics are not consistent with their pesticide properties found in the Pesticides Properties Data Base (PPDB, 2020). According to solubility in water and sorption coefficient mentioned in this base for these three molecules (Table 2), nicosulfuron should indeed be the more mobile pesticide among the three studied, and, according to its low water solubility and its affinity for organic carbon, metaldehyde should be the least mobile. However, leaching results are consistent with the sorption coefficient values measured in the soil studied. Metaldehyde was indeed found to be not retained in the batch experiments, even with the most organic soil studied (VER site). To our current knowledge, very few data dealing with metaldehyde retention in soils are available in the literature. However, our results indicate that this molecule can be subject to very rapid transfer and therefore contamination of water resources, partly due to very weak retention in soil. Finally, even though co-transport to dissolved or colloidal organic matter was not quantified, and dissolved organic carbon was found throughout the soil column experiments (data not shown), we suspect that these processes may be relatively minor regarding the low adsorption affinity of the three molecules observed in the batch sorption experiment study.

Cumulated nicosulfuron losses by leaching were the highest among the three molecules, ranging from 47.5 to 78.8 % according to soil type and agricultural system. Retention of nicosulfuron is weak (Olivera et al., 2001; PPDB, 2020), as found in our soil samples. It seems not to be influenced by organic carbon (Gonzalez and Ukrainczyk, 1996), but rather by clay minerals content, especially smectites on which it is rapidly and strongly sorbed (Ukrainczyk and Rashid, 1995). For some authors, such a rapid sorption on clay minerals would strongly limit nicosulfuron leaching to groundwater (Gonzalez and Ukrainczyk, 1999). Our study highlights the high potential risks of leaching of this molecule on alluvial soils with low clay content (< 150 $g.kg^{-1}$) that could lead to groundwater contamination.

Mesotrione leaching was found to be the slowest in coherence with the higher sorption coefficient values (compared to the two other studied pesticides) measured in the studied soils, reaching a maximum of 6.4 $L.kg^{-1}$ (replicate area c of the CONS plot on VER site). Such values were among the highest found in the literature for this compound (Mendes et al., 2016), and its sorption behaviour was in agreement with others works: positively correlated to clay content and negatively correlated to pH (Dyson et al., 2002; Alekseeva et al., 2014; Mendes et al., 2016; Carles et al., 2017). Despite no correlation was found with soil organic carbon content, these higher sorption values for mesotrione could be explained by its affinity to organic constituents, especially fulvic acids (Dyson et al., 2002). In a recent study Mendes et al. (2018), showed that mesotrione leaching could reach 80 % of initial applied mass in some soils. In our study, cumulated loss of mesotrione by leaching ranged from 10.1 to 50.8 % of initial applied mass. Considering an applied agronomic dose of 150 $g.ha^{-1}$, the presence of mesotrione in groundwater with concentration above the fixed limit by the European Water Framework directive is likely to occur.

As mentioned in the results section, all pesticides studied had a default in mass balance ranging from 17 to up to 88 % that could be due to their (relatively rapid) degradation in soils. For metaldehyde, with the highest mass balance default, it is likely that part of it was degraded before the first rainfall was applied. Its degradation half-life in soils is indeed short, from less than 1 day (Zhang et al., 2011) to a few days (PPDB, 2020), and metaldehyde is also supposed to be highly volatile. Both dissipation processes may explain the low recovery rate of metaldehyde in our column experiments. Furthermore, during leaching, its rapid degradation rate could explain why metaldehyde T_p were always lower that bromide T_p. Indeed, rapid degradation rates can reduce the effluent concentrations leading to a truncated peak and so an apparent early peak (van Genuchten and Wagenet, 1989; Brusseau, 1992). For nicosulfuron and mesotrione, default in mass balance may not be explained by volatilisation, both of these herbicide families (sulfonylurea and triketone) being considered as non-volatile (Russell et al., 2002; Dumas et al., 2017). For nicosulfuron, bound residue formation could explain the difference in mass balance. In a degradation study performed with ^{14}C-nicosulfuron on the same soils (data not shown), bound residues were found to represent from 25 to 40 % of applied herbicide after only 7 days of incubation. For mesotrione however, it has been suggested that due to their triketonate function, triketones have a pronounced ability to form extremely stable complex with transition metals (Dumas et al., 2017). On another side, Cherrier et al. (2005) reported that sulcotrione (identical to mesotrione except for one group on the benzene cycle) undergoes a fast transformation that results in a small amount of non-extractable residues of around 12.5% after 65 days.

4.2 Influence of soil type on pesticide leaching

Two soil types, both with an alluvial origin, were used to study pesticide leaching. Significant differences in pesticide behaviour were observed and attributed to differences in soil properties. On the well-structured organic loamy soil (VER site), the rain simulations were carried out without any limitation in water infiltration. For this soil, field measurements of hydraulic conductivity (data not shown) were in agreement with these laboratory observations and no hydraulic discontinuity has been observed between the surface and the bottom of the soil columns (30 cm-depth). On this soil of VER site, preferential flow of water and solutes was identified as indicated by the low 5% bromide arrival time and the very high amounts of bromide recovered from the soils (≈ 18 % of applied dose). This indeed suggests that the tracer was probably trapped into immobile regions (Casey et al., 1997; Miller et al., 2000; Ilsemann et al., 2002; Alletto et al., 2006), adsorption on solid phase being unlikely due to the anionic nature of the tracer. However, the degree of preferential flow found in the VER site was lower than that observed in the LUV site as indicated by the absence of an early peak during the first rain event. On the low-organic soil surface horizon with unstable structure of LUV site, a high degree of preferential flow of solutes and water occurred in both agricultural systems. This is supported by the concomitant arrival of bromide and pesticides during the first rain event. Differences in the degree of preferential transport found between the two sites also resulted in differences in the pesticide mass balances and cumulated mass of pesticide in leachates. Whatever the agricultural systems, higher amounts of pesticides were indeed found in leachates of LUV site compared to VER site (leached quantities of metaldehyde and mesotrione were more than double),

4.3 Influence of agricultural systems on pesticide leaching

Conservation agriculture is known to modify pesticide retention in soil compared to conventionally-tilled soil due to an increase in organic carbon content at the soil surface (Locke and Bryson, 1997; Alletto et al., 2010) and the presence of crop residues, forming a mulch, that could intercept and retain pesticides. In our study, we have chosen soils that have experienced conservation agriculture for many years (since 2006 for VER site and 2000 for LUV site). This time duration should promote a high contrast in the physical, chemical and biological properties of the soils compared to the same soil managed under tillage. However, no clear trend in pesticide retention between the two agricultural systems has been observed, probably due to the poor affinity of the studied pesticides with organic carbon. Differences in pesticide retention in the mulches from VER and LUV sites measured at the end of the percolation experiments have nevertheless been observed, with a greater amounts of pesticides retained in the mulch of the LUV site (Fig. 2). This could be due to differences in the cover crop composition between the two conservation agriculture systems (Cassigneul et al., 2015, 2016). In a complementary study, biodegradation of nicosulfuron has been studied for these two agricultural managements on both sites and no significant difference has been found in the topsoil layers despite a greater microbiological activity in conservation agriculture plots (data not shown). Consequently, it is therefore unlikely that, for these types of soil, there will be a significant reduction in the amount of pesticides available for leaching by a significant improvement of the retention and/or degradation of molecules in conservation agriculture systems.

Regarding the water dynamics, on VER site, the natural structure of this soil, in relation to its high organic carbon content, did not lead to a significant differentiation of infiltration capacities of the surface horizon between the annually ploughed plot and the conservation agriculture plot. These lab results are confirmed by field hydraulic conductivity measurements between 0-25 cm-depth giving saturated conductivity values ranging from 46 to 97 $mm.h^{-1}$ without any difference between tilled and untilled plot (data not shown). On LUV site, however, ploughing resulted in the formation of an impermeable layer (with a hydraulic conductivity < 0.6 $mm.h^{-1}$), which did not allow water to percolate sufficiently rapidly to maintain the targeted water pressure (- 80 cm) at the bottom of the soil column and resulted in a progressive saturation of the soil column. Such a low conductivity of the plough pan has previously been described on a similar soil type and agricultural management (Alletto et al., 2010), and could therefore be considered a representative physical property for this cropping system (*ie* soil type x agricultural management). The removal of this compact zone made these percolations feasible. This result provided us with important information on the water regime of this plot. As a consequence on the field, during rainfall or irrigation on this soil type managed with regular deep soil tillage, the ploughed horizon is very rapidly saturated due to a too low infiltration rate below 20 cm, the water then runs off by lateral subsurface flow (and probably also by surface runoff) dragging the compounds present into solution such as pesticides or nitrates. When the combination of the three agronomical levers of conservation agriculture are applied, significant changes in the physical properties of LUV soil occur and lead to an improvement of water infiltration by a greater connectivity of mesopores and macropores. This soil functioning, which becomes close to that of soils with high agronomic potential such as those on VER site, has the advantage of no longer generating subsurface runoff, but can lead to high degree of preferential flow (Shipitalo et al., 2000; Cameira et al., 2003; Jarvis, 2007).

5. Conclusions

We evaluated pesticide leaching in agricultural systems combining the three levers of conservation agriculture (no tillage, cover crops and crop rotation) and in conventional agriculture systems (mouldboard ploughing). Pesticide percolation on undisturbed soil columns sampled in two adjacent plots cultivated under conservation and conventional agriculture were performed in two different sites. The study revealed the influence of pesticide properties, soil type and agricultural systems on pesticide leaching. The main results are the following:

i. Pesticide properties partly determined their leaching. Pesticide properties are known to play a major role in their environmental fate. Databases exist to inform them, but we have seen through the use of information from the PPDB (2020) that caution should be exercised in their use. Ideally, when possible, it is preferable to carry out measurements directly on the soils studied to get more accurate values of their properties. In this study, the measured K_d were in better agreement with the delay of pesticides in undisturbed soil columns experiments than PPDB (2020) values which were less reliable in view of our leaching results. However, in the presence of high degree of preferential flow, potential retention of pesticides can be masked, as illustrated by the differences between ‘expected’ retardation factors calculated from the batch sorption coefficients K_d and the delays in pesticide leaching in the undisturbed soil columns.

ii. Soil type strongly influenced pesticide leaching by conditioning the transport mechanisms. While the two soils studied had an alluvial origin and a low clay content, their own structure generates a different degree of preferential flow that translated into 9 to 19% of the pesticide mass leached during the first intensive rain event in the LUV site of this study, whereas less than 3% of the pesticide mass were leached in the VER site of this study during the first rain event.

iii. The agricultural practices diversely influenced pesticide leaching on the two sites. In the case of the Stagnic Luvisol, the role of agricultural systems on the soil water dynamics and, consequently, on the fate of pesticides become more important. As observed in this study, in ploughed soil of alluvial valley (LUV site), transfers by drainage are strongly limited by a hydraulic discontinuity due to tillage operations. This severe limitation of water drainage could trigger lateral subsurface flows in the field. Conservation agriculture (for several years), improved the pore network connectivity and the water flow became predominantly vertical. In such a situation, the main risk is that preferential flows in the macroporosity occur and generate pesticide transfers.

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Title: Laparoscopic right partial adrenalectomy (with video)
Titre: Surrénalectomie partielle droite laparoscopique (avec vidéo)

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Table 1

Batch sorption coefficient on soil, K_d (L.kg^{-1}), organic-carbon sorption coefficient, K_{oc} (L.kg^{-1}OC), organic carbon content, clay content and soil pH. Values correspond to the mean value of the three spatial replicates (a, b, c).

Site	Plot	Depth	Organic carbon	Clay content	Soil pH	Metaldehyde		Nicosulfuron		Mesotrione	
		cm	g.kg^{-1}	g.kg^{-1}		K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
VER	TILL	0-10	17.4 ± 2.2	163.7 ± 11.8	6.5 ± 0.3	0.2 ± 0.1	9.8 ± 5.7	0.6 ± 0.1	34.1 ± 11.1	2.0 ± 0.6	111.9 ± 19.6
		10-30	17.4 ± 2.0	158.3 ± 11.9	6.8 ± 0.3	0.2 ± 0.1	13.8 ± 4.1	0.6 ± 0.1	32.9 ± 8.1	1.5 ± 0.2	84.3 ± 12.1
	CONS	0-10	19.0 ± 0.6	155.7 ± 8.3	6.3 ± 0.0	0.2 ± 0.3	13.2 ± 14.1	1.0 ± 0.3	53.8 ± 16.3	4.5 ± 1.7	234.2 ± 91.3
		10-30	18.4 ± 0.5	155.0 ± 10.5	6.4 ± 0.1	0.3 ± 0.1	15.5 ± 6.5	0.6 ± 0.2	30.9 ± 8.5	2.7 ± 1.3	146.8 ± 73.3
LUV	TILL	0-10	7.5 ± 1.7	123.0 ± 14.2	6.8 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	1.3 ± 2.0	186.2 ± 296.8	0.8 ± 0.4	104.1 ± 45.6
		10-30	7.6 ± 1.6	120.7 ± 8.6	6.8 ± 0.2	0.0 ± 0.0	1.0 ± 1.7	0.2 ± 0.1	28.2 ± 13.1	0.7 ± 0.4	91.4 ± 49.9
	CONS	0-10	11.4 ± 1.8	163.7 ± 22.0	5.8 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	0.5 ± 0.3	41.0 ± 26.9	2.8 ± 0.9	237.1 ± 49.0
		10-30	8.7 ± 1.1	180.3 ± 11.0	6.0 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	0.8 ± 0.2	99.9 ± 30.4	4.0 ± 0.8	477.1 ± 164.5

Table 2

Properties of metaldehyde, nicosulfuron and mesotrione (Pesticide Properties DataBase, 2020) and the applied dose. K_d and K_f are linear and Freundlich sorption coefficient respectively ($L.kg^{-1}$). n is the exponent from the equation of the Freundlich model. K_{oc} is the organic-carbon sorption coefficient ($L.kg^{-1}OC$). DT50 is the half-life of the pesticide.

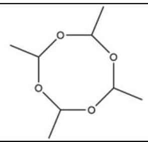
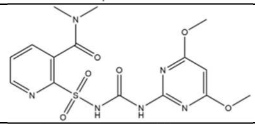
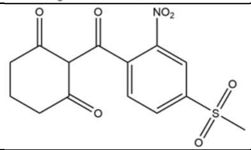
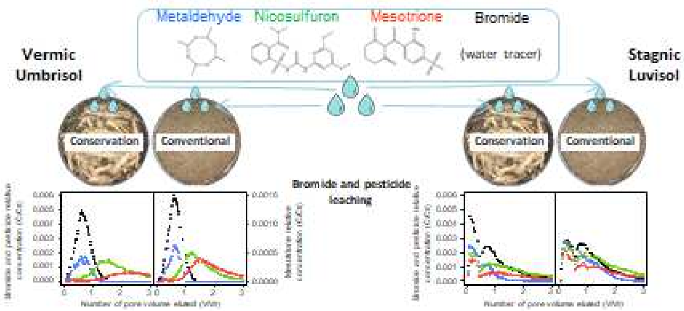
Nature	Pesticide	Molecule structure	Solubility in water at 20°C ($mg.l^{-1}$)	K_f	1/n	K_d	K_{oc}	DT50 (lab 20°C)	Volatility	Field application ($g.ha^{-1}$)	Column application (µg)
Molluscicide	Metaldehyde		188	0.63	0.93	-	240	5.1	Highly volatile	125-500	453 ± 75
Herbicide	Nicosulfuron		7500	0.29	0.93	-	30	16.4	Low volatility	30-100	53 ± 5
Herbicide	Mesotrione		1500	0.89	0.94	1.62	122	19.6	Low volatility	120-160	285 ± 60

Table 3

Arrival time of first breakthrough, T_b, the 5% solute arrival time, $T_{5\%}$, the arrival time of maximal peak concentration, T_{pi} and relative maximum concentration of the peaks, C_{pi}, with i={1,2} the number of peaks. Values correspond to the mean value of the three spatial replicates (a, b, c).

Site	Plot	Solute	T_b [-]	$T_{5\%}$ [-]	T_{p1} [-]	C_{p1} [-]	T_{p2} [-]	C_{p2} [-]
VER	TILL	Bromide	0.08 ± 0.03	0.28 ± 0.05	0.61 ± 0.03	$6.8\ 10^{-3} \pm 1.7\ 10^{-3}$	-	-
		Metaldehyde	0.11 ± 0.05	0.35 ±0.08	0.40 ± 0.20	$1.6\ 10^{-3} \pm 1.0\ 10^{-3}$	-	-
		Nicosulfuron	0.28 ± 0.36	0.81 ±0.23	1.14 ± 0.07	$2.0\ 10^{-3} \pm 2.2\ 10^{-4}$	-	-
		Mesotrione	0.15 ± 0.08	1.40 ± 0.18	1.36 ± 0.13	$5.1\ 10^{-4} \pm 1.7\ 10^{-4}$	-	-
	CONS	Bromide	0.08 ± 0.02	0.31 ± 0.03	0.76 ± 0.14	$4.6\ 10^{-3} \pm 4.5\ 10^{-4}$	-	-
		Metaldehyde	0.09 ± 0.03	0.52 ± 0.20	0.53 ± 0.13	$8.9\ 10^{-4} \pm 7.9\ 10^{-4}$	-	-
		Nicosulfuron	0.07 ± 0.04	0.95 ± 0.05	1.57 ± 0.17	$1.7\ 10^{-3} \pm 1.3\ 10^{-4}$	-	-
		Mesotrione	0.09 ± 0.03	2.58 ± 0.28	2.12 ± 0.05	$1.9\ 10^{-4} \pm 3.8\ 10^{-5}$	-	-
LUV	TILL	Bromide	0.05 ± 0.01	0.15 ± 0.04	0.19 ± 0.08	$3.8\ 10^{-3} \pm 8.9\ 10^{-4}$	0.72 ± 0.08	$2.9\ 10^{-3} \pm 1.1\ 10^{-3}$
		Metaldehyde	0.05 ± 0.01	0.16 ±0.04	0.14 ± 0.06	$3.1\ 10^{-3} \pm 3.6\ 10^{-4}$	0.63 ± 0.10	$1.6\ 10^{-3} \pm 4.1\ 10^{-4}$
		Nicosulfuron	0.05 ± 0.01	0.16 ±0.06	0.19 ± 0.06	$3.4\ 10^{-3} \pm 8.0\ 10^{-4}$	0.76 ± 0.15	$2.0\ 10^{-3} \pm 4.2\ 10^{-5}$
		Mesotrione	0.05 ± 0.01	0.18 ±0.05	0.17 ± 0.06	$2.6\ 10^{-3} \pm 5.5\ 10^{-4}$	0.78 ± 0.15	$1.2\ 10^{-3} \pm 1.2\ 10^{-4}$
	CONS	Bromide	0.04 ± 0.02	0.12 ± 0.05	0.15 ± 0.07	$4.1\ 10^{-3} \pm 7.5\ 10^{-4}$	0.71 ± 0.03	$2.4\ 10^{-3} \pm 4.8\ 10^{-5}$
		Metaldehyde	0.03 ± 0.00	0.13 ± 0.01	0.12 ± 0.04	$2.7\ 10^{-3} \pm 2.7\ 10^{-4}$	0.66 ± 0.07	$1.4\ 10^{-3} \pm 2.3\ 10^{-4}$
		Nicosulfuron	0.03 ± 0.00	0.16 ± 0.02	0.16 ± 0.05	$2.1\ 10^{-3} \pm 3.4\ 10^{-4}$	1.05 ± 0.26	$1.2\ 10^{-3} \pm 1.1\ 10^{-4}$
		Mesotrione	0.03 ± 0.00	0.21 ± 0.03	0.15 ± 0.05	$1.4\ 10^{-3} \pm 1.5\ 10^{-4}$	1.10 ± 0.15	$4.7\ 10^{-4} \pm 1.7\ 10^{-4}$


Metaldehyde
Nicosulfuron
Mesotrione
Bromide
(water tracer)
Vermic Umbrisol
Stagnic Luvisol
Conservation
Conventional
Conservation
Conventional
Bromide and pesticide leaching
Number of pore volume eluted (V/V0)
Number of pore volume eluted (V/V0)