



HAL
open science

Water and pesticide transfers in undisturbed soil columns sampled from a Stagnic Luvisol and a Vermic Umbrisol both cultivated under conventional and conservation agriculture

Sixtine Cueff, Lionel Alletto, Marjolaine Bourdat-Deschamps, Pierre Benoit, Valérie Pot

► To cite this version:

Sixtine Cueff, Lionel Alletto, Marjolaine Bourdat-Deschamps, Pierre Benoit, Valérie Pot. Water and pesticide transfers in undisturbed soil columns sampled from a Stagnic Luvisol and a Vermic Umbrisol both cultivated under conventional and conservation agriculture. *Geoderma*, 2020, 377, 10.1016/j.geoderma.2020.114590 . hal-02935076

HAL Id: hal-02935076

<https://hal.inrae.fr/hal-02935076>

Submitted on 22 Aug 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial | 4.0 International License

1 **Water and pesticide transfers in undisturbed soil columns sampled from a Stagnic**
2 **Luvisol and a Vermic Umbrisol both cultivated under conventional and conservation**
3 **agriculture**

4

5 Sixtine Cueff ^{a,b,*}, Lionel Alletto ^a, Marjolaine Bourdat-Deschamps ^b, Pierre Benoit ^b, Valérie
6 Pot ^{b,*}

7

8 ^a Université de Toulouse, INRAE, UMR AGIR, F-31326, Castanet-Tolosan, France

9 ^b Université Paris-Saclay, INRAE, AgroParisTech, UMR ECOSYS, 78850, Thiverval-
10 Grignon, France

11 * corresponding authors: Valérie Pot, valerie.pot@inrae.fr; Sixtine Cueff,
12 sixtine.cueff@gmail.com

13

14 **Abstract**

15 The main goals of conservation agriculture are to enhance soil fertility and to reduce soil
16 degradation especially through erosion. However, conservation agriculture practices can
17 exhibit a higher risk of contamination through vertical flows. The objectives of this study
18 were to (i) characterise water and pesticide transfers in two different soils both managed
19 under conventional and conservation agriculture and (ii) assess the effects of pesticide
20 properties, soil type and agricultural system on pesticide fate. We studied the behaviour of
21 two herbicides (nicosulfuron and mesotrione) and a molluscicide (metaldehyde) in percolation
22 experiments in undisturbed soil columns. A series of two rain events (one with a high, the
23 other with a low intensity) separated by a two-day flow interruption was applied three days
24 after the pesticides and bromide application. Batch sorption coefficients, K_d , were also
25 measured. While the Pesticides Properties Data Base (2020) indicated a decrease of sorption

26 in the order mesotrione > metaldehyde > nicosulfuron, the measured K_d , decreased in the
27 order mesotrione ($2.3 \pm 1.4 \text{ L.kg}^{-1}$) > nicosulfuron ($0.7 \pm 0.4 \text{ L.kg}^{-1}$) > metaldehyde (0.1 ± 0.1
28 L.kg^{-1}). We highlighted distinct behaviour of pesticide leaching depending mainly on soil
29 type, agricultural practices and pesticide properties. For low degree of preferential flow,
30 pesticide leaching can be related to the sorption properties of pesticides. Nicosulfuron and
31 mesotrione delays are more pronounced under conservation management while metaldehyde
32 always arrived with no delay. During the high intensity rain event, on one soil type, high
33 degree of preferential flow masked sorption effect on leaching since every pesticide arrived at
34 the same time as the tracer and amounted to up to 21 % of pesticide recovery compared to 4%
35 on the other soil type. Conservation agriculture was found to improve the vertical transfers of
36 water and pesticides while, on one of the studied soil type, the presence of a low conductive
37 plough pan significantly limits water drainage.

38

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

41

42 1. Introduction

43

44 Due to their degraded soil structure, soils cultivated under conventional tillage practices,
45 such as mouldboard ploughing, are generally more sensitive to surface runoff and soil loss by
46 water and wind erosion (Holland, 2004). In this context, the contamination of neighbouring
47 surface waters by agrochemicals is often increased (Alletto et al., 2010). In order to enhance
48 the sustainability of agricultural systems and reduce the drawbacks of conventional
49 agriculture, alternative cultivation practices such as conservation agriculture have been
50 developed. The main goals of conservation agriculture are to reduce soil degradation through

51 erosion but also the contamination of surface water by agrochemicals due to runoff or transfer
52 of sorbed solutes on eroded soil particles (Holland, 2004; Hobbs et al., 2008). Conservation
53 agriculture is defined as a combination of three main interlinked soil conservation techniques:
54 (i) minimal or no soil disturbance, (ii) permanent soil cover by crop residues and/or cover
55 crops and (iii) diversification of plant species in the crop rotation (FAO, 2016). The
56 interaction between these three principles leads to complex and interlinked changes in soil
57 physical, chemical and biological properties that remain poorly characterized. Taking into
58 account these changes is crucial to properly assess the performance of such agricultural
59 systems. However, contradictory published results especially on soil hydraulic processes and
60 pesticide transfers are reported (Green et al., 2003; Strudley et al., 2008; Alletto et al., 2010;
61 Verhulst et al., 2010).

62 Tillage decreases soil compaction in the tilled layer but in the same time it disrupts pore
63 connectivity between the tilled layer and deeper soil horizons thus limiting deep water
64 movements (Cameira et al., 2003; Fuentes et al., 2004). In addition, the destruction of low
65 stability aggregates by raindrop impacts may lead to the sealing of soil surface thus reducing
66 soil infiltration and enhancing the risk of erosion (Holland, 2004). On the contrary, in no-
67 tilled soils, because of less disturbance of the topsoil, total porosity is, in most cases, reduced
68 while, in the same time, a greater continuity of vertically oriented macropores is generally
69 observed leading to higher hydraulic conductivity in untilled than in tilled soils (Wahl et al.,
70 2004; Soto-Gómez et al., 2019). In addition, in conservation agriculture, the faunal activity is
71 enhanced, especially earthworms, resulting in a dense bioturbation network (Shipitalo et al.,
72 2000). Introducing cover crops can also improve water conductivity in no-tillage systems, by
73 creating stable bioturbation network through root development during crop growing season
74 (Abdollahi and Munkholm, 2014; Williams and Weil, 2004). Maintaining crop residues at the
75 soil surface progressively leads to an accumulation of soil organic matter in topsoil layers

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

79 Due to this higher proportion of (bio)macropores, preferential transport of water and
80 solutes is expected to be enhanced in conservation agriculture, thus increasing the risk of
81 contamination of groundwater (Isensee and Sadeghi, 1997). However, field studies reported
82 either higher (Elliott et al., 2000), lower (Gish et al., 1995) or no differences (Fortin et al.,
83 2002) in pesticide losses between no tillage and tillage practices. Laboratory leaching studies
84 on undisturbed soil columns also brought mixed results with higher (Levanon et al., 1993),
85 lower (Sigua et al., 1995) or equivalent (Porfiri et al., 2015; Okada et al., 2016) leaching in
86 tilled compared to untilled soils.

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

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

111 Three pesticides, widely used by farmers for maize production, and for which little
112 information is available in the literature, were chosen for the laboratory percolation
113 experiment on undisturbed soil columns. Metaldehyde is a molluscicide generally spread in
114 autumn and winter as baits pellets to protect all types of crops. In a recent review, Castle et al.
115 (2017) reported that metaldehyde is highly mobile in soil and can hence contaminate water
116 resources. Nicosulfuron is a post-emergence herbicide used to control grass species in maize.
117 Because of their anionic character, sulfonylurea herbicides are highly mobile in soil and could
118 contaminate ground waters (Gonzalez and Ukrainczyk, 1996). Regarding the effect of
119 cropping practices on the fate of nicosulfuron, Afyuni et al. (1997) found that conventional
120 tillage generally resulted in more runoff but lower herbicide losses by runoff than no-tillage.
121 Mesotrione is an herbicide that provides pre-emergence and post-emergence control of all the
122 important broad-leaved weeds in maize and some of the annual grass weeds. Very little has
123 been published on mesotrione transfer in soils. Rouchaud et al. (2001) found no movement of
124 mesotrione lower than 20 cm in soil that was attributed to a combination of its low mobility
125 and degradation rate.

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

130

131 **2. Materials and Methods**

132

133 2.1 Sites and agricultural managements

134

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

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

147 The soil on the Gers site is classified as a Stagnic Luvisol according to the World
148 Reference Base for Soil Resources (IUSS Working Group WRB, 2007), corresponding to a
149 luvisol redoxisol in the French Soil Classification (AFES, 2008), locally called “Boulbènes”.
150 It has a loamy surface layer (fine + coarse silt $\approx 450\text{-}500\text{ g.kg}^{-1}$) and an illuvial clay horizon

151 appearing between 45 and 55 cm. The substratum is a low-permeability alluvial pebbly layer
152 appearing at around 60-80 cm. With low organic carbon contents in the soil surface horizon
153 (in most cases $< 7-8 \text{ g.kg}^{-1}$) and high silt contents, these soils are strongly sensitive to
154 crusting. Due to these properties (especially hydromorphic conditions at low depth), this soil
155 type has a moderate agronomic potential with mainly irrigated crops (average maize yields \approx
156 $10-12 \text{ t.ha}^{-1}$). This site will be referred to as LUV (luvisol) site in the rest of the paper.

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

168

169 2.2 Soil core sampling

170

171 Three replicated (called area a, area b and area c) undisturbed soil cores (30 cm length; 14
172 cm internal diameter; $\approx 4 \text{ 618 cm}^3$ volume) were sampled at the soil surface of the TILL and
173 CONS plots of each site. They were collected in polycarbonate columns inserted in a steel
174 cylinder of the same size pushed slowly into the soil by using mechanical shovel. The
175 surrounding soil was progressively removed to facilitate the extraction of the core and avoid

176 the compaction of the soil. To minimise spatial variability in soil properties as much as
177 possible, the replicates were sampled at a distance of 20 m from the adjoining edge of the
178 plots by following a transect parallel to this edge and with a distance of 20 m between
179 replicates of the same plot. Sampling was performed in November 2017 in VER site, after
180 maize crop on both plots (corresponding to 6 months after tillage operations on TILL plot),
181 and in January 2018 in LUV site, after soybean crop on the conservation plot (corresponding
182 to 8 months after tillage operations on TILL plot). Mulch located at the soil surface of each
183 CONS plot was kept at the top of the columns. Quantities of mulch were $1400 \pm 700 \text{ g.m}^{-2}$
184 and $630 \pm 220 \text{ g.m}^{-2}$ on the LUV site and VER site respectively. Mulch was absent from the
185 TILL plots columns. The columns were sealed and stored in a cold room (4°C) until the
186 experiment.

187 2.3 Batch sorption experiments

188

189 The three pesticides adsorption coefficients, K_d [mg.L^{-1}], were measured on soil samples,
190 collected during the sampling of soil columns, at two depths (0-10 cm and 10-30 cm) for each
191 plot. A solution of metaldehyde [$49.9 \mu\text{g.L}^{-1}$], nicosulfuron [$19.8 \mu\text{g.L}^{-1}$] and mesotrione [20.1
192 $\mu\text{g.L}^{-1}$] was prepared by dilution in a calcium chloride solution (0.01 M CaCl_2). Pesticides
193 were purchased from CIL (Cluzeau Info Labo, Ste Foy, France) with purity $> 97\%$
194 (metaldehyde 97%, nicosulfuron 98.4%, mesotrione 99%). Samples of air-dried soil (3 g)
195 were weighed into Falcon centrifuge tubes (50 mL) and a 9 mL aliquot of herbicide solution
196 was added to each. For each plot and depth, three replicates were made corresponding to the
197 three locations of the replicates of undisturbed soil cores. The tubes containing treated soil
198 were left for 24 h in an end-over-end shaker to reach equilibrium at room temperature, and
199 then centrifuged at 9000 rpm for 10 min. Each pesticide concentration was determined by
200 UHPLC-MS/MS (described in section 2.5). The quantity of sorbed pesticide was calculated as

201 the difference between the amount initially added and the amount measured in the supernatant
202 after equilibrium. The equilibrium sorption distribution coefficients, K_d , were calculated using
203 the equation:

$$204 \quad K_d = \frac{S}{C_{eq}}$$

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

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

$$209 \quad K_{OC} = \frac{K_d}{C_{org}}$$

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

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

214

215 2.4 Leaching experiments

216

217 The percolation experiments were conducted under unsaturated water flow in laboratory
218 conditions. A CaCl_2 solution ($1.8 \cdot 10^{-4}$ M CaCl_2) was applied at the soil surface by a rainfall
219 simulator. The rainfall simulator was placed a few centimetres above the soil surface and
220 consisted of 45 hypodermic needles (0.33 mm diameter) at 12.5 mm spacing and connected to
221 a membrane pump controlling the flow. To maintain unsaturated conditions, a negative
222 pressure of -80 cm was applied at the soil column base by placing a stainless steel mesh (20
223 μm pore size) and a 0.5 cm layer of glass beads (diameter $< 0.45 \mu\text{m}$) at the soil bottom and
224 connecting the column base to a vacuum pump applying constant pressure. The layer of glass

225 beads provided a homogeneous contact between the soil and the mesh. To monitor water
226 content and water pressure, the columns were equipped with two TDR probes and three
227 tensiometers.

228 The experiments were designed to study the mobility of three pesticides under two rainfall
229 regimes. Before the pesticides application, the soil columns were equilibrated to similar
230 hydration conditions by receiving a constant rainfall of 2 mm.h^{-1} for a duration of 1 day until
231 steady state was reached. We checked that none of the three pesticides were detected in the
232 column effluents during this equilibration period. For only two columns of the LUV site, we
233 detected residual concentrations (9 to 51 times lower for nicosulfuron and 24 to 69 times
234 lower for mesotrione than the concentrations in the first sample collected after the pesticide
235 application). Then a 7.7-mL volume pulse containing the three pesticides and bromide, an
236 anionic water tracer, was manually applied at the mulch (CONS plots) or soil (TILL plots)
237 surface with a pipette. Little drops were applied on the whole column surface in order to
238 obtain a repartition as homogenous as possible. The concentrations of each pesticide in the
239 mixture reflects realist application dose on the field (Table 2). A series of two rain events
240 separated by a two-day flow interruption was applied three days after the pesticides and
241 bromide application to approximate field conditions. The first rain event lasted 4 h with a high
242 flow intensity of 10 mm.h^{-1} to evaluate the behaviour of pesticides under a high risk of
243 preferential flow. The second rain event lasted 10 to 15 days depending of the experimental
244 series with a low flow intensity of 2 mm.h^{-1} maintained until most of the pesticides were
245 eluted. Effluents were collected at regular time steps (every 12 min during the first rain; every
246 60 min for about 36 h at the beginning of the second rain and then every 90 min) and stored at
247 $4 \text{ }^{\circ}\text{C}$ in darkness, and analysed within the next four days to avoid pesticide degradation.

248 During the pre-saturation phase of the columns, the presence of a very low conductive
249 plow pan (not higher than 0.6 mm.h^{-1} of hydraulic conductivity) in the TILL plot of LUV site

250 prevented the establishment of a steady state. According to field observations of soil structure,
251 its thickness was about 7-8 cm, we therefore removed the 10-cm bottom layer of the three
252 replicates and applied the same procedure. This experimental issue limited the comparison
253 between sites and treatments and no statistical analysis were performed but provided useful
254 information to interpret water movement in this soil type under a conventional soil tillage
255 management.

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

261

262 2.5 Bromide and pesticides quantification in leachates, soil and mulch

263

264 Bromide concentration in effluents was measured by a bromide ion selective electrode (HI
265 4102, HANNA instruments) connected to a multimeter meter. The measure was done on a 15
266 mL aliquot after adding a ionic strength adjuster (HI-4000-00) and converted to concentration
267 (mg.L^{-1}) with a calibration curve previously determined.

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

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

279 Soil and mulch bromide extractions were made using a 2:1 deionised water:soil (v:m) and
280 10:1 deionised water/mulch (v:m) ratio, respectively. Samples were shaken for 24 h, and then
281 centrifuged 10 min at 10 000 rpm. Bromide concentration was measured by HPLC with a
282 Dionex IonPac AS9-HC Analytical Column (250 mm). The chromatographic separation was
283 carried out with 8.0 mM Carbonate + 1.5 mM NaOH solution with a flow rate of 0.8 mL.min⁻¹
284 ¹. Sample injection volume was 0.25 µL. The detection was done by suppressed conductivity
285 detection.

286 Soil and mulch pesticide extractions were made using a 5:1 solvent:soil (v:m) and 8:1
287 solvent:mulch (v:m) ratio, respectively. Deuterated labelled standards of metaldehyde (D16),
288 nicosulfuron (D6) and mesotrione (D4) were added to the solid samples 24 h before
289 extractions to correct losses during extraction, purification and MS ionisation. Two successive
290 extractions were done on 5 g of fresh soil or 3 g fresh mulch using methanol:McIlvaine
291 buffer:disodium ethylenediaminetetraacetate in 60:20:20 volumetric proportions. The extracts
292 were purified on SPE cartridges (Macherey Nagel Oasis HLB 6cc; 500 mg) after dilution in
293 ultrapure water. SPE cartridges were eluted using 6 mL methanol. Thereafter, the eluates were
294 evaporated to dryness under a nitrogen flow and dissolved in 4 mL of water:acetonitrile
295 (90:10, v:v) prior to UHPLC-MS/MS analysis.

296

297 2.6 Breakthrough curves (BTC) analysis

298

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

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

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

$$313 \quad R_e = 1 + \rho \frac{K_d}{\theta}$$

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

318

319 2.7 Statistical analysis

320

321 Analysis of variance (ANOVA) was performed to reveal the effect of sampling depth
322 (only for K_d), agricultural system and solute nature on K_d , T_b , $T_{5\%}$, T_p , C_p , and leached, soil,
323 mulch quantities recovered. Shapiro-Wilk normality test and Bartlett's homoscedasticity test

324 were applied to the residues of the ANOVA to verify application condition. Where the
325 conditions were not met, a Kruskal-Wallis test was carried out.

326

327 **3. Results**

328

329 3.1 Batch sorption experiments

330

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

341 No correlation was found between organic carbon content and sorption of the three
342 studied pesticides. Correlation with clay content was only found for mesotrione K_d ($r = 0.97$,
343 $***P < 0.001$) on the LUV site. Smaller significant correlations were found between
344 mesotrione K_d and soil pH on both sites ($r = -0.66$, $*P < 0.05$ on VER site and $r = -0.71$, $**P <$
345 0.01 on LUV site). No other correlations were found for the other pesticides.

346

347 3.2 Water and pesticides transfers

348

349 3.2.1 Water and pesticides transfers on VER site

350

351 Fig.1a displays the breakthrough curves (BTCs) of bromide for both plots of VER site. No
352 noticeable difference regarding the time to first breakthrough was observed (Table 3). After
353 the flow interruption, the concentrations of bromide in the resumed effluents did not differ
354 much from the concentration of the last effluent, so that globally the overall BTCs displayed a
355 single peak. Generally bromide peaks of the TILL plot arrived earlier with higher maximum
356 relative concentrations, C_p , than those of CONS plot but these differences were not
357 significant. The 5% tracer arrival time reached low values of 0.28 ± 0.05 and 0.31 ± 0.03 on
358 the TILL plot and the CONS plot respectively, which is an indication of non-equilibrium
359 transport (Table 3). These results indicate low differences in the degree of preferential flow
360 between both plots. After about 2.6 pore volumes (last detection of bromide), recovery rates
361 of leached bromide ranged from $79.4\% \pm 5.3$ in CONS plot to $87.3\% \pm 7.4$ in TILL plot
362 (Appendix Table A.2), with no significant difference. The extraction performed on soil after
363 the end of the experiment revealed that very high quantities of bromide (an average of $17.5 \pm$
364 1.2% of the applied mass of bromide) remained in the soil for both agricultural systems (Fig.
365 2a). Less than 1% of the applied mass of bromide was found in the mulch in the CONS plot.

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

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

381 The mass recovery of leached metaldehyde was highly variable and low (Fig. 2a;
382 Appendix Table A.2), reaching a maximum of 27.9% of the initial input. The recovery of
383 leached mesotrione was also low (less than 20.8 %) while nicosulfuron reached at least 47.5
384 % of recovery of its initial applied mass. Because of extremely poor extraction-purification
385 yields, metaldehyde could not be quantified in soils. Extractable nicosulfuron and mesotrione
386 in soils represented at most 4.7% and 3.8% of the initial mass with most of the pesticides
387 found in the upper layer (0-3 cm) of soil whatever the cultural system (Appendix Fig. A.1a).
388 Finally, less than 2% of the initially applied mass of nicosulfuron and mesotrione were found
389 in mulch in CONS plot. For this soil type, even if delays in nicosulfuron and mesotrione
390 leaching were observed between TILL and CONS plots, no effect of the agricultural system
391 were found on cumulated pesticide mass transferred by leaching through the columns after 6.5
392 ± 0.5 pore volumes were eluted, nor on the residual soil pesticide quantities.

393

394 3.2.2 Water and pesticides transfers in LUV site

395

396 We remind that for LUV site the columns length of the TILL plot was reduced to 20 cm
397 since the very low conductive plow pan layer ($< 0.6 \text{ mm.h}^{-1}$) was removed to allow

398 percolation of water during the rainfall simulation. Fig. 1b displays the BTCs of bromide for
399 both plots of LUV site. They showed strong evidences of a high degree of preferential flow.
400 They exhibited two distinct peaks for both plots, with a higher variability in the TILL plot.
401 Both peaks arrived before one pore volume was eluted. The first one had the highest
402 maximum relative bromide concentration and occurred during the first rain event. In both
403 plots, the relative amount of bromide leached was more than 20% whereas less than 10% of
404 the applied bromide was leached in the VER site during the first rain event (Appendix Table
405 A.2). The second peak occurred during the second rain event and displayed a long elution tail.
406 The 5% tracer arrival times were globally similar for both plots and lower than the ones of the
407 VER site (Table 3). When outflow resumed after the first rain event, the relative concentration
408 of bromide was always lower suggesting that during the two-day interruption flow bromide
409 migrated in regions of immobile or low-flow water. Only one replicate (area b) in the TILL
410 plot did not display a clear second peak but rather a decrease of concentrations after outflow
411 resumed. Lower quantities of bromide were found in the soils of LUV site (with an average of
412 6.6 ± 1.7 % of the applied mass of bromide) compared to VER site. Less than 1 % of the
413 initial amount of bromide applied was found in mulch in CONS plot. On average, slightly
414 more bromide was recovered in the CONS plot leachates and soils than in TILL plot (Fig. 2b).

415 The three pesticides were displaced rapidly through the columns of LUV site (Fig. 4).
416 Their leaching pattern was similar to that of bromide during the first rain event. First
417 breakthrough of the pesticides appeared at the same time as bromide, and generally no
418 difference in the 5% arrival times of pesticides was observed with the 5% arrival time of
419 bromide (except for mesotrione on the CONS plot). For both agricultural managements, no
420 statistical differences regarding the arrival times of the maximal concentration of the first
421 peak, T_{p1} , between the solutes was found (Table 3). This is in disagreement with the
422 calculated retardation factors which indicated that nicosulfuron and mesotrione should be

423 more delayed (Appendix Table A.1). These results confirmed thus the existence of a high
424 degree of preferential flow. For both plots, $17.2 \pm 1.0 \%$, $15.8 \pm 3.7 \%$ and $11.6 \pm 3.0 \%$ of the
425 initially applied metaldehyde, nicosulfuron and mesotrione respectively, were recovered from
426 the leachates of the first rain whereas less than 3% of the applied pesticides was leached in the
427 VER site during the first rain event (Appendix Table A.2). Except for metaldehyde, pesticide
428 mass recovery was lower for CONS than for TILL plot. During the second rainfall event, the
429 three pesticides followed bromide pattern on the TILL plot. On the CONS plot, metaldehyde
430 generally occurred at the same time as bromide while nicosulfuron and mesotrione were
431 delayed. However, no statistical differences were found except between T_{p2} of metaldehyde
432 and mesotrione.

433 At the end of the experiment, higher amounts of nicosulfuron were recovered in the
434 leachates of TILL plot than CONS plot (with a recovery rate of $76.2 \pm 2.2\%$ of its initially
435 applied mass in TILL plot against $66.5 \pm 0.4 \%$ in CONS plot). We did not perform a
436 statistical comparison of these leaching results between agricultural systems because the TILL
437 soil columns were 10 cm shorter than the CONS soil columns to remove the plough pan
438 identified as impermeable. However, we will discuss the consequences of soil physical
439 properties differences due to agricultural system on pesticide environmental risk in Section
440 4.3. Nicosulfuron amounts recovered in leachates were higher than those measured for the
441 two other pesticides (with average recovery rates of $40.4 \pm 11.3 \%$ and $39.2 \pm 8.6 \%$ for
442 metaldehyde and mesotrione respectively in both plots, with no difference between the
443 agricultural systems). Higher nicosulfuron and mesotrione amounts were found in soils and
444 mulches of LUV site than those observed in VER site (Appendix Table A.2). In total,
445 comparable amounts of nicosulfuron were recovered between TILL and CONS whereas a
446 higher amount of mesotrione was recovered in TILL (Fig. 2b; Appendix Table A.2).

447

448 **4. Discussion**

449

450 4.1 Influence of pesticide properties on pesticide leaching

451

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

470 Cumulated nicosulfuron losses by leaching were the highest among the three molecules,
471 ranging from 47.5 to 78.8 % according to soil type and agricultural system. Retention of
472 nicosulfuron is weak (Olivera et al., 2001; PPDB, 2020), as found in our soil samples. It

473 seems not to be influenced by organic carbon (Gonzalez and Ukrainczyk, 1996), but rather by
474 clay minerals content, especially smectites on which it is rapidly and strongly sorbed
475 (Ukrainczyk and Rashid, 1995). For some authors, such a rapid sorption on clay minerals
476 would strongly limit nicosulfuron leaching to groundwater (Gonzalez and Ukrainczyk, 1999).
477 Our study highlights the high potential risks of leaching of this molecule on alluvial soils with
478 low clay content ($< 150 \text{ g.kg}^{-1}$) that could lead to groundwater contamination.

479 Mesotrione leaching was found to be the slowest in coherence with the higher sorption
480 coefficient values (compared to the two other studied pesticides) measured in the studied
481 soils, reaching a maximum of 6.4 L.kg^{-1} (replicate area c of the CONS plot on VER site).
482 Such values were among the highest found in the literature for this compound (Mendes et al.,
483 2016), and its sorption behaviour was in agreement with others works: positively correlated to
484 clay content and negatively correlated to pH (Dyson et al., 2002; Alekseeva et al., 2014;
485 Mendes et al., 2016; Carles et al., 2017). Despite no correlation was found with soil organic
486 carbon content, these higher sorption values for mesotrione could be explained by its affinity
487 to organic constituents, especially fulvic acids (Dyson et al., 2002). In a recent study Mendes
488 et al. (2018), showed that mesotrione leaching could reach 80 % of initial applied mass in
489 some soils. In our study, cumulated loss of mesotrione by leaching ranged from 10.1 to 50.8
490 % of initial applied mass. Considering an applied agronomic dose of 150 g.ha^{-1} , the presence
491 of mesotrione in groundwater with concentration above the fixed limit by the European Water
492 Framework directive is likely to occur.

493 As mentioned in the results section, all pesticides studied had a default in mass balance
494 ranging from 17 to up to 88 % that could be due to their (relatively rapid) degradation in soils.
495 For metaldehyde, with the highest mass balance default, it is likely that part of it was
496 degraded before the first rainfall was applied. Its degradation half-life in soils is indeed short,
497 from less than 1 day (Zhang et al., 2011) to a few days (PPDB, 2020), and metaldehyde is

498 also supposed to be highly volatile. Both dissipation processes may explain the low recovery
499 rate of metaldehyde in our column experiments. Furthermore, during leaching, its rapid
500 degradation rate could explain why metaldehyde T_p were always lower than bromide T_p .
501 Indeed, rapid degradation rates can reduce the effluent concentrations leading to a truncated
502 peak and so an apparent early peak (van Genuchten and Wagenet, 1989; Brusseau, 1992). For
503 nicosulfuron and mesotrione, default in mass balance may not be explained by volatilisation,
504 both of these herbicide families (sulfonylurea and triketone) being considered as non-volatile
505 (Russell et al., 2002; Dumas et al., 2017). For nicosulfuron, bound residue formation could
506 explain the difference in mass balance. In a degradation study performed with ^{14}C -
507 nicosulfuron on the same soils (data not shown), bound residues were found to represent from
508 25 to 40 % of applied herbicide after only 7 days of incubation. For mesotrione however, it
509 has been suggested that due to their triketonate function, triketones have a pronounced ability
510 to form extremely stable complex with transition metals (Dumas et al., 2017). On another
511 side, Cherrier et al. (2005) reported that sulcotrione (identical to mesotrione except for one
512 group on the benzene cycle) undergoes a fast transformation that results in a small amount of
513 non-extractable residues of around 12.5% after 65 days.

514

515 4.2 Influence of soil type on pesticide leaching

516

517 Two soil types, both with an alluvial origin, were used to study pesticide leaching.
518 Significant differences in pesticide behaviour were observed and attributed to differences in
519 soil properties. On the well-structured organic loamy soil (VER site), the rain simulations
520 were carried out without any limitation in water infiltration. For this soil, field measurements
521 of hydraulic conductivity (data not shown) were in agreement with these laboratory
522 observations and no hydraulic discontinuity has been observed between the surface and the

523 bottom of the soil columns (30 cm-depth). On this soil of VER site, preferential flow of water
524 and solutes was identified as indicated by the low 5% bromide arrival time and the very high
525 amounts of bromide recovered from the soils ($\approx 18\%$ of applied dose). This indeed suggests
526 that the tracer was probably trapped into immobile regions (Casey et al., 1997; Miller et al.,
527 2000; Ilsemann et al., 2002; Alletto et al., 2006), adsorption on solid phase being unlikely due
528 to the anionic nature of the tracer. However, the degree of preferential flow found in the VER
529 site was lower than that observed in the LUV site as indicated by the absence of an early peak
530 during the first rain event. On the low-organic soil surface horizon with unstable structure of
531 LUV site, a high degree of preferential flow of solutes and water occurred in both agricultural
532 systems. This is supported by the concomitant arrival of bromide and pesticides during the
533 first rain event. Differences in the degree of preferential transport found between the two sites
534 also resulted in differences in the pesticide mass balances and cumulated mass of pesticide in
535 leachates. Whatever the agricultural systems, higher amounts of pesticides were indeed found
536 in leachates of LUV site compared to VER site (leached quantities of metaldehyde and
537 mesotrione were more than double),

538

539 4.3 Influence of agricultural systems on pesticide leaching

540

541 Conservation agriculture is known to modify pesticide retention in soil compared to
542 conventionally-tilled soil due to an increase in organic carbon content at the soil surface
543 (Locke and Bryson, 1997; Alletto et al., 2010) and the presence of crop residues, forming a
544 mulch, that could intercept and retain pesticides. In our study, we have chosen soils that have
545 experienced conservation agriculture for many years (since 2006 for VER site and 2000 for
546 LUV site). This time duration should promote a high contrast in the physical, chemical and
547 biological properties of the soils compared to the same soil managed under tillage. However,

548 no clear trend in pesticide retention between the two agricultural systems has been observed,
549 probably due to the poor affinity of the studied pesticides with organic carbon. Differences in
550 pesticide retention in the mulches from VER and LUV sites measured at the end of the
551 percolation experiments have nevertheless been observed, with a greater amounts of
552 pesticides retained in the mulch of the LUV site (Fig. 2). This could be due to differences in
553 the cover crop composition between the two conservation agriculture systems (Cassigneul et
554 al., 2015, 2016). In a complementary study, biodegradation of nicosulfuron has been studied
555 for these two agricultural managements on both sites and no significant difference has been
556 found in the topsoil layers despite a greater microbiological activity in conservation
557 agriculture plots (data not shown). Consequently, it is therefore unlikely that, for these types
558 of soil, there will be a significant reduction in the amount of pesticides available for leaching
559 by a significant improvement of the retention and/or degradation of molecules in conservation
560 agriculture systems.

561 Regarding the water dynamics, on VER site, the natural structure of this soil, in relation to
562 its high organic carbon content, did not lead to a significant differentiation of infiltration
563 capacities of the surface horizon between the annually ploughed plot and the conservation
564 agriculture plot. These lab results are confirmed by field hydraulic conductivity measurements
565 between 0-25 cm-depth giving saturated conductivity values ranging from 46 to 97 mm.h⁻¹
566 without any difference between tilled and untilled plot (data not shown). On LUV site,
567 however, ploughing resulted in the formation of an impermeable layer (with a hydraulic
568 conductivity < 0.6 mm.h⁻¹), which did not allow water to percolate sufficiently rapidly to
569 maintain the targeted water pressure (- 80 cm) at the bottom of the soil column and resulted in
570 a progressive saturation of the soil column. Such a low conductivity of the plough pan has
571 previously been described on a similar soil type and agricultural management (Alletto et al.,
572 2010), and could therefore be considered a representative physical property for this cropping

573 system (*ie* soil type x agricultural management). The removal of this compact zone made
574 these percolations feasible. This result provided us with important information on the water
575 regime of this plot. As a consequence on the field, during rainfall or irrigation on this soil type
576 managed with regular deep soil tillage, the ploughed horizon is very rapidly saturated due to a
577 too low infiltration rate below 20 cm, the water then runs off by lateral subsurface flow (and
578 probably also by surface runoff) dragging the compounds present into solution such as
579 pesticides or nitrates. When the combination of the three agronomical levers of conservation
580 agriculture are applied, significant changes in the physical properties of LUV soil occur and
581 lead to an improvement of water infiltration by a greater connectivity of mesopores and
582 macropores. This soil functioning, which becomes close to that of soils with high agronomic
583 potential such as those on VER site, has the advantage of no longer generating subsurface
584 runoff, but can lead to high degree of preferential flow (Shipitalo et al., 2000; Cameira et al.,
585 2003; Jarvis, 2007).

586

587 **5. Conclusions**

588

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

596 i. Pesticide properties partly determined their leaching. Pesticide properties are known to
597 play a major role in their environmental fate. Databases exist to inform them, but we have

598 seen through the use of information from the PPDB (2020) that caution should be exercised in
599 their use. Ideally, when possible, it is preferable to carry out measurements directly on the
600 soils studied to get more accurate values of their properties. In this study, the measured K_d
601 were in better agreement with the delay of pesticides in undisturbed soil columns experiments
602 than PPDB (2020) values which were less reliable in view of our leaching results. However,
603 in the presence of high degree of preferential flow, potential retention of pesticides can be
604 masked, as illustrated by the differences between ‘expected’ retardation factors calculated
605 from the batch sorption coefficients K_d and the delays in pesticide leaching in the undisturbed
606 soil columns.

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

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

622

623 **Acknowledgement**

624 This study was performed with data obtained in the framework of the BAG'AGES and
625 BAG'AGES CISOL projects and financed by Agence de l'Eau Adour-Garonne and Occitanie
626 Region. We would like to thank Nathalie Bernet, Valentin Serre, Christophe Labat, Ghislaine
627 Delarue, Valérie Dumeny and Leonore Flipo who participated to the acquisition of data in this
628 experiment. We would also like to thank Eric Michel and Line Capowiez (INRA UMR
629 EMMAH, France) for measuring the concentration of bromide in soils.

630

631 **References**

- 632 Abdollahi, L., Munkholm, L.J., 2014. Tillage System and Cover Crop Effects on Soil Quality:
633 I. Chemical, Mechanical, and Biological Properties. *Soil Sci. Soc. Am. J.* 78, 262–270.
634 <https://doi.org/10.2136/sssaj>
- 635 Afyuni, M.M., Waggoner, M.G., Leidy, R.B., 1997. Runoff of Two Sulfonylurea Herbicides in
636 Relation to Tillage System and Rainfall Intensity. *J. Environ. Qual.* 26, 1318–1326.
- 637 Alekseeva, T., Kolyagin, Y., Sancelme, M., Besse-hoggan, P., 2014. Effect of soil properties
638 on pure and formulated mesotrione adsorption onto vertisol (Limagne plane, Puy-de-
639 Dôme, France). *Chemosphere* 111, 177–183.
640 <https://doi.org/10.1016/j.chemosphere.2014.03.061>
- 641 Alletto, L., Coquet, Y., Benoit, P., Heddadj, D., Barriuso, E., 2010. Tillage management
642 effects on pesticide fate in soils. A review. *Agron. Sustain. Dev.* 30, 367–400.
- 643 Alletto, L., Coquet, Y., Vachier, P., Labat, C., 2006. Hydraulic Conductivity, Immobile Water
644 Content, and Exchange Coefficient in Three Soil Profiles. *Soil Sci. Soc. Am. J.* 70,
645 1272–1280. <https://doi.org/10.2136/sssaj2005.0291>
- 646 Baumhardt, R.L., Lascano, R.J., 1999. Water Budget and Yield of Dryland Cotton
647 Intercropped with Terminated Winter Wheat. *Agron. J.* 91, 922–927.

648 Brusseau, M.L., 1992. Modeling Solute Transport Influenced by Multiprocess
649 Nonequilibrium and Transformation Reactions. *Water Resour. Res.* 28, 175–182.

650 Cameira, M.R., Fernando, R.M., Pereira, L.S., 2003. Soil macropore dynamics affected by
651 tillage and irrigation for a silty loam alluvial soil in southern Portugal. *Soil Tillage Res.*
652 70, 131–140. [https://doi.org/10.1016/S0167-1987\(02\)00154-X](https://doi.org/10.1016/S0167-1987(02)00154-X)

653 Carles, L., Joly, M., Bonnemoy, F., Lereboure, M., Batisson, I., Besse-Hoggan, P., 2017.
654 Identification of sulfonylurea biodegradation pathways enabled by a novel nicosulfuron-
655 transforming strain *Pseudomonas fluorescens* SG-1: Toxicity assessment and effect of
656 formulation. *J. Hazard. Mater.* 324, 184–193.
657 <https://doi.org/10.1016/j.jhazmat.2016.10.048>

658 Casey, F.X.M., Logsdon, S.D., Horton, R., Jaynes, D.B., 1997. Immobile Water Content and
659 Mass Exchange Coefficient of a Field Soil. *Soil Sci. Soc. Am. J.* 61, 1030–1036.
660 <https://doi.org/10.2136/sssaj1997.03615995006100040006x>

661 Cassigneul, A., Alletto, L., Benoit, P., Bergheaud, V., Etiévant, V., Dumény, V., Le Gac,
662 A.L., Chuette, D., Rumpel, C., Justes, E., 2015. Nature and decomposition degree of
663 cover crops influence pesticide sorption : Quantification and modelling. *Chemosphere*
664 119, 1007–1014. <https://doi.org/10.1016/j.chemosphere.2014.08.082>

665 Cassigneul, A., Benoit, P., Bergheaud, V., Dumény, V., Etiévant, V., Goubard, Y., Maylin,
666 A., Justes, E., Alletto, L., 2016. Fate of glyphosate and degradates in cover crop residues
667 and underlying soil : A laboratory study. *Sci. Total Environ.* 545–546, 582–590.
668 <https://doi.org/10.1016/j.scitotenv.2015.12.052>

669 Castle, G.D., Mills, G.A., Gravell, A., Jones, L., Townsend, I., Cameron, D.G., Fones, G.R.,
670 2017. Review of the molluscicide metaldehyde in the environment. *Environ. Sci. Water*
671 *Res. Technol.* 3, 415–428. <https://doi.org/10.1039/c7ew00039a>

672 Cherrier, R., Boivin, A., Perrin-ganier, C., Schiavon, M., 2005. Sulcotrione versus atrazine

673 transport and degradation in soil columns. *Pest Manag. Sci.* 61, 899–904.
674 <https://doi.org/10.1002/ps.1105>

675 Devine, S., Markewitz, D., Hendrix, P., Coleman, D., 2014. Soil Aggregates and Associated
676 Organic Matter under Conventional Tillage , No-Tillage , and Forest Succession after
677 Three Decades. *PLoS One* 9, 1–12. <https://doi.org/10.1371/journal.pone.0084988>

678 Dumas, E., Giraud, M., Goujon, E., Halma, M., Knhili, E., Stauffert, M., Batissonc, I.,
679 Besse-Hoggan, P., Bohatier, J., Bouchard, P., Celle-Jeanton, H., Costa Gomes, M.,
680 Delbac, F., Forano, C., Goupil, P., Guix, N., Husson, P., Ledoigt, G., Mallet, C., Mousty,
681 C., Prévot, V., Richard, C., Sarraute, S., 2017. Fate and ecotoxicological impact of new
682 generation herbicides from the triketone family : An overview to assess the
683 environmental risks. *J. Hazard. Mater.* 325, 136–156.
684 <https://doi.org/10.1016/j.jhazmat.2016.11.059>

685 Dyson, J.S., Beulke, S., Brown, C.D., Lane, M.C.G., 2002. Adsorption and Degradation of the
686 Weak Acid Mesotrione in Soil and Environmental Fate Implications. *J. Environ. Qual.*
687 31, 613–618.

688 Elliott, J.A., Cessna, A.J., Nicholaichuk, W., Tollefson, L.C., 2000. Leaching Rates and
689 Preferential Flow of Selected Herbicides through Tilled and Untilled Soil. *J. Environ.*
690 *Qual.* 29, 1650–1656.

691 FAO, 2016. Conservation Agriculture, in: *Save and Grow in Practice: Maize, Rice and*
692 *Wheat.*

693 Fermanich, K.J., Daniel, T.C., 1991. Pesticide Mobility and Persistence in Microlysimeter
694 Soil Columns from a Tilled and No-Tilled Plot. *J. Environ. Qual.* 20, 195–202.

695 Fortin, J., Gagnon-Bertrand, E., Vézina, L., Rompré, M., 2002. Preferential Bromide and
696 Pesticide Movement to Tile Drains under Different Cropping Practices. *J. Environ. Qual.*
697 31, 1940–1952.

698 Fuentes, J.P., Flury, M., Bezdicek, D.F., 2004. Hydraulic Properties in a Silt Loam Soil under
699 Natural Prairie, Conventional Till, and No-Till. *Soil Sci. Soc. Am. J.* 68, 1679–1688.

700 Gish, T.J., Shirmohammadi, A., Vyrvipillai, R., Wienhold, B.J., 1995. Herbicide Leaching
701 under Tilled and No-Tillage Fields. *Soil Sci. Soc. Am. J.* 59, 895–901.

702 Gonzalez, J., Ukrainczyk, L., 1999. Transport of Nicosulfuron in Soil Columns. *J. Environ.*
703 *Qual.* 28, 101–107. <https://doi.org/10.2134/jeq1999.00472425002800010011x>

704 Gonzalez, J.M., Ukrainczyk, L., 1996. Adsorption and Desorption of Nicosulfuron in Soils. *J.*
705 *Environ. Qual.* 25, 1186–1192.
706 <https://doi.org/10.2134/jeq1996.00472425002500060003x>

707 Green, T.R., Ahuja, L.R., Benjamin, J.G., 2003. Advances and challenges in predicting
708 agricultural management effects on soil hydraulic properties. *Geoderma* 116, 3–27.
709 [https://doi.org/10.1016/S0016-7061\(03\)00091-0](https://doi.org/10.1016/S0016-7061(03)00091-0)

710 Hobbs, P.R., Sayre, K., Gupta, R., 2008. The role of conservation agriculture in sustainable
711 agriculture. *Philos. Trans. R. Soc. B Biol. Sci.* 363, 543–555.
712 <https://doi.org/10.1098/rstb.2007.2169>

713 Holland, J.M., 2004. The environmental consequences of adopting conservation tillage in
714 Europe : reviewing the evidence. *Agric. Ecosyst. Environ.* 103, 1–25.
715 <https://doi.org/10.1016/j.agee.2003.12.018>

716 Ilsemann, J., van der Ploeg, R.R., Horton, R., Bachmann, J., 2002. Laboratory method for
717 determining immobile soil water content and mass exchange coefficient. *J. Plant Nutr.*
718 *Soil Sci.* 165, 332–338.

719 Isensee, A.R., Sadeghi, A.M., 1997. Interactions of tillage and rainfall on atrazine leaching
720 under field and laboratory conditions. *Chemosphere* 34, 2715–2723.

721 IUSS Working Group WRB, 2007. World Reference Base For Soil Resources 2006, first
722 update. A framework for international classification, correlation and communication.

723 Rome: FAO, Food and Agriculture Organization of the United Nations.

724 Jarvis, N.J., 2007. A review of non-equilibrium water flow and solute transport in soil
725 macropores : principles , controlling factors and consequences for water quality. *Eur. J.*
726 *Soil Sci.* 58, 523–546. <https://doi.org/10.1111/j.1365-2389.2007.00915.x>

727 Kay, B.D., VandenBygaart, A.J., 2002. Conservation tillage and depth stratification of
728 porosity and soil organic matter. *Soil Tillage Res.* 66, 107–118.

729 Knudby, C., Carrera, J., 2005. On the relationship between indicators of geostatistical , flow
730 and transport connectivity. *Adv. Water Resour.* 28, 405–421.
731 <https://doi.org/10.1016/j.advwatres.2004.09.001>

732 Levanon, D., Codling, E.E., Meisinger, J.J., Starr, J.L., 1993. Mobility of Agrochemicals
733 through Soil from Two Tillage Systems. *J. Environ. Qual.* 22, 155–161.

734 Locke, M.A., Bryson, C.T., 1997. Herbicide-soil interactions in reduced tillage and plant
735 residue management systems. *Weed Sci.* 45, 307–320.
736 <https://doi.org/https://doi.org/10.1017/S0043174500092882>

737 Marín-Benito, J.M., Alletto, L., Barriuso, E., Bedos, C., Benoit, P., Pot, V., Mamy, L., 2018.
738 Pesticide fate modelling in conservation tillage : Simulating the effect of mulch and
739 cover crop on S-metolachlor leaching. *Sci. Total Environ.* 628–629, 1508–1517.
740 <https://doi.org/10.1016/j.scitotenv.2018.02.144>

741 Mendes, K.F., Hall, K.E., Takeshita, V., Lanzoni Rossi, M., Tornisielo, V.L., 2018. Animal
742 bonechar increases sorption and decreases leaching potential of aminocyclopyrachlor and
743 mesotrione in a tropical soil. *Geoderma* 316, 11–18.
744 <https://doi.org/10.1016/j.geoderma.2017.12.017>

745 Mendes, K.F., Rodrigues dos Reis, M., Inoue, M.H., Pimpinato, R.F., Tornisielo, V.L., 2016.
746 Sorption and desorption of mesotrione alone and mixed with S -metolachlor +
747 terbuthylazine in Brazilian soils. *Geoderma* 280, 22–28.

748 <https://doi.org/10.1016/j.geoderma.2016.06.014>

749 Miller, J.J., Lamond, B.J., Sweetland, N.J., Larney, F.J., 2000. Preferential Leaching of Water
750 and Chloride in a Clay Loam Soil as Affected by Tillage and Rainfall Intensity. *Water*
751 *Qual. Res. J.* 35, 711–734.

752 Norgaard, T., Moldrup, P., Olsen, P., Vendelboe, A.L., Iversen, B. V., Greve, M.H., Kjaer, J.,
753 de Jonge, L.W., 2013. Comparative Mapping of Soil Physical–Chemical and Structural
754 Parameters at Field Scale to Identify Zones of Enhanced Leaching Risk. *J. Environ.*
755 *Qual.* 42, 271–283. <https://doi.org/10.2134/jeq2012.0105>

756 Okada, E., Luis, J., Bedmar, F., 2016. Adsorption and mobility of glyphosate in different soils
757 under no-till and conventional tillage. *Geoderma* 263, 78–85.
758 <https://doi.org/10.1016/j.geoderma.2015.09.009>

759 Olivera, R.S., Koskinen, W.C., Ferreira, F.A., 2001. Sorption and leaching potential of
760 herbicides on Brazilian soils. *Weed Res.* 41, 97–110.

761 Porfiri, C., Montoya, J.C., Koskinen, W.C., Azcarate, M.P., 2015. Adsorption and transport of
762 imazapyr through intact soil columns taken from two soils under two tillage systems.
763 *Geoderma* 252, 1–9. <https://doi.org/10.1016/j.geoderma.2015.03.016>

764 PPDB, 2020. PPDB - An international database for pesticide risk assessments and
765 management. *Hum. Ecol. Risk Assess. An Int. J.* 22, 1050–064.
766 <https://doi.org/10.1080/10807039.2015.1133242>

767 Rouchaud, J., Neus, O., Eelen, H., Bulcke, R., 2001. Mobility and adsorption of the triketone
768 herbicide mesotrione in the soil of corn crops. *Toxicol. Environ. Chem.* 79, 211–222.
769 <https://doi.org/10.1080/02772240109358989>

770 Russell, M.H., Saladini, J.L., Lichtner, F., 2002. Sulfonylurea Herbicides. *Pestic. Outlook* 13,
771 166–173. <https://doi.org/10.1039/b206509f>

772 Shipitalo, M.J., Dick, W.A., Edwards, W.M., 2000. Conservation tillage and macropore

773 factors that affect water movement and the fate of chemicals. *Soil Tillage Res.* 53, 167–
774 183.

775 Sigua, G.C., Isensee, A.R., Sadeghi, A.M., 1993. Influence of rainfall intensity and crop
776 residue on leaching of atrazine through intact no-till soil cores. *Soil Sci.* 156, 225–232.

777 Sigua, G.C., Isensee, A.R., Sadeghi, A.M., Im, G.J., 1995. Distribution and transport of
778 atrazine as influenced by surface cultivation, earthworm population and rainfall pattern.
779 *Chemosphere* 31, 4237–4242.

780 Soto-Gómez, D., Pérez-rodríguez, P., Vázquez Juiz, L., López- Periago, J.E., Paradelo, M.,
781 2019. A new method to trace colloid transport pathways in macroporous soils using X-
782 ray computed tomography and fluorescence macrophotography. *Eur. J. Soil Sci.* 70,
783 431–442.

784 Strudley, M.W., Green, T.R., Ascough II, J.C., 2008. Tillage effects on soil hydraulic
785 properties in space and time : State of the science. *Soil Tillage Res.* 99, 4–48.
786 <https://doi.org/10.1016/j.still.2008.01.007>

787 Ukrainczyk, L., Rashid, N., 1995. Irreversible Sorption of Nicosulfuron on Clay Minerals.
788 *Journal of Agric. Food Chem.* 43, 855–857. <https://doi.org/10.1021/jf00052a001>

789 van Genuchten, M.T., Wagenet, R.J., 1989. Two-Site/Two-Region Models for Pesticide
790 Transport and Degradation: Theoretical Development and Analytical Solutions. *Soil Sci.*
791 *Soc. Am. J.* 53, 1303–1310.

792 Verhulst, N., François, I., Govaerts, B., 2010. Conservation agriculture, improving soil quality
793 for sustainable production systems? *Adv. soil Sci. food Secur. soil Qual.* 1799267585,
794 137–208.

795 Wahl, N.A., Bens, O., Buczko, U., Hangen, E., Hüttl, R.F., 2004. Effects of conventional and
796 conservation tillage on soil hydraulic properties of a silty-loamy soil. *Phys. Chem. Earth*
797 29, 821–829. <https://doi.org/10.1016/j.pce.2004.05.009>

798 Williams, S.M., Weil, R.R., 2004. Crop Cover Root Channels May Alleviate Soil Compaction
799 Effects On Soybean Crop. *Soil Sci. Soc. Am. J.* 68, 1403–1409.

800 Zhang, H., Wang, C., Lu, H., Guan, W., Ma, Y., 2011. Residues and dissipation dynamics of
801 molluscicide metaldehyde in cabbage and soil. *Ecotoxicol. Environ. Saf.* 74, 1653–1658.
802 <https://doi.org/10.1016/j.ecoenv.2011.05.004>
803

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

Authors: A. Cubisino, MD^{1, 2*}; F. Guillon MD¹; J.M. Fabre MD, PhD¹

¹ Digestive and Mini-invasive Surgery unit, Department of digestive surgery and transplantation, St Eloi Hospital, 80 avenue Augustin Fliche, 34295, Montpellier, France; Université de Montpellier-Nîmes, 641, avenue du Doyen-Gaston-Giraud, 34090 Montpellier, France.

² Division of General Surgery, Department of Medical and Surgical Sciences, Hospital of Cattinara, University of Trieste, Strada di Fiume 447, 34149, Trieste, Italy.

***Corresponding author:**

Antonio Cubisino

Digestive and Mini-invasive Surgery unit,
Department of Digestive Surgery and Transplantation,
Saint-Eloi Hospital, University of Montpellier.
80 avenue Augustin Fliche, 34295, Montpellier, France.
Tel: +33769402104.
Mail: antoniocubisino@gmail.com

Table 1

Batch sorption coefficient on soil, K_d (L.kg⁻¹), organic-carbon sorption coefficient, K_{oc} (L.kg⁻¹OC), 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 cm	Organic carbon g.kg ⁻¹	Clay content g.kg ⁻¹	Soil pH	Metaldehyde		Nicosulfuron		Mesotrione	
						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.


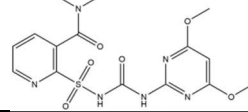
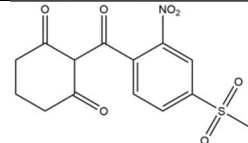
Nature	Pesticide	Molecule structure	Solubility in water at 20°C ($mg.l^{-1}$)	K_f	1/n	K_d	K_{oc}	DT50 (lab 20°C)	Volatility	Field application ($g.ha^{-1}$)	Column application (μg)
Molluscicide	Metaldehyde		188	0.63	0.93	-	240	5.1	Highly volatile	125-500	453 ± 75
Herbicide	Nicosulfuron		7500	0.29	0.93	-	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_{p1} 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	$6.8 \cdot 10^{-3} \pm 1.7 \cdot 10^{-3}$	-	-
		Metaldehyde	0.11 ± 0.05	0.35 ± 0.08	0.40 ± 0.20	$1.6 \cdot 10^{-3} \pm 1.0 \cdot 10^{-3}$	-	-
		Nicosulfuron	0.28 ± 0.36	0.81 ± 0.23	1.14 ± 0.07	$2.0 \cdot 10^{-3} \pm 2.2 \cdot 10^{-4}$	-	-
		Mesotrione	0.15 ± 0.08	1.40 ± 0.18	1.36 ± 0.13	$5.1 \cdot 10^{-4} \pm 1.7 \cdot 10^{-4}$	-	-
	CONS	Bromide	0.08 ± 0.02	0.31 ± 0.03	0.76 ± 0.14	$4.6 \cdot 10^{-3} \pm 4.5 \cdot 10^{-4}$	-	-
		Metaldehyde	0.09 ± 0.03	0.52 ± 0.20	0.53 ± 0.13	$8.9 \cdot 10^{-4} \pm 7.9 \cdot 10^{-4}$	-	-
		Nicosulfuron	0.07 ± 0.04	0.95 ± 0.05	1.57 ± 0.17	$1.7 \cdot 10^{-3} \pm 1.3 \cdot 10^{-4}$	-	-
		Mesotrione	0.09 ± 0.03	2.58 ± 0.28	2.12 ± 0.05	$1.9 \cdot 10^{-4} \pm 3.8 \cdot 10^{-5}$	-	-
LUV	TILL	Bromide	0.05 ± 0.01	0.15 ± 0.04	0.19 ± 0.08	$3.8 \cdot 10^{-3} \pm 8.9 \cdot 10^{-4}$	0.72 ± 0.08	$2.9 \cdot 10^{-3} \pm 1.1 \cdot 10^{-3}$
		Metaldehyde	0.05 ± 0.01	0.16 ± 0.04	0.14 ± 0.06	$3.1 \cdot 10^{-3} \pm 3.6 \cdot 10^{-4}$	0.63 ± 0.10	$1.6 \cdot 10^{-3} \pm 4.1 \cdot 10^{-4}$
		Nicosulfuron	0.05 ± 0.01	0.16 ± 0.06	0.19 ± 0.06	$3.4 \cdot 10^{-3} \pm 8.0 \cdot 10^{-4}$	0.76 ± 0.15	$2.0 \cdot 10^{-3} \pm 4.2 \cdot 10^{-5}$
		Mesotrione	0.05 ± 0.01	0.18 ± 0.05	0.17 ± 0.06	$2.6 \cdot 10^{-3} \pm 5.5 \cdot 10^{-4}$	0.78 ± 0.15	$1.2 \cdot 10^{-3} \pm 1.2 \cdot 10^{-4}$
	CONS	Bromide	0.04 ± 0.02	0.12 ± 0.05	0.15 ± 0.07	$4.1 \cdot 10^{-3} \pm 7.5 \cdot 10^{-4}$	0.71 ± 0.03	$2.4 \cdot 10^{-3} \pm 4.8 \cdot 10^{-5}$
		Metaldehyde	0.03 ± 0.00	0.13 ± 0.01	0.12 ± 0.04	$2.7 \cdot 10^{-3} \pm 2.7 \cdot 10^{-4}$	0.66 ± 0.07	$1.4 \cdot 10^{-3} \pm 2.3 \cdot 10^{-4}$
		Nicosulfuron	0.03 ± 0.00	0.16 ± 0.02	0.16 ± 0.05	$2.1 \cdot 10^{-3} \pm 3.4 \cdot 10^{-4}$	1.05 ± 0.26	$1.2 \cdot 10^{-3} \pm 1.1 \cdot 10^{-4}$
		Mesotrione	0.03 ± 0.00	0.21 ± 0.03	0.15 ± 0.05	$1.4 \cdot 10^{-3} \pm 1.5 \cdot 10^{-4}$	1.10 ± 0.15	$4.7 \cdot 10^{-4} \pm 1.7 \cdot 10^{-4}$

