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- 1 Influence of agroforestry plant species on the infiltration of S-Metolachlor in buffer soils
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13 Abstract:

Agroforestry practices have been acknowledged for reducing pesticide losses while maintaining land productivity. Pesticide removal from overland flow results from great infiltration capacities of the buffer soils. This can in turn threaten the quality of groundwater in case of poor pesticide sorption and degradation in the root-influenced zone. These mechanisms and their balance are likely to be influenced by plant species. However, little is known about the role of agroforestry species in the infiltration of herbicides. The aim of this study was thereby to evaluate how popular agroforestry species modulate the infiltration of water and of a widely used herbicide. We established large buffer 21 microcosms by planting Brome grass, Black walnut, Pin oak and Poplar trees in repacked soil columns. After a growth season of 4 months, we performed ponded infiltration experiments with 22 bromide and S-Metolachlor. We used then the HYDRUS 1D model to compare the hydrodynamic 23 24 properties and S-Metolachlor transport patterns between the microcosms. In addition, we compared 25 the sorption properties of the rhizosphere and bulk soils. We found that the tree species increased 26 the sorption of S-Metolachlor in soil with Kd being 3 times greater than in the un-vegetated and 27 Brome grass microcosms. Poplar trees increased the hydraulic conductivity (Ksat) compared to the 28 control and was associated to a low retardation of S-metolachlor, which increases the risk of 29 groundwater contamination. With slightly reduced Ksat and retardation factor in the root zone, 1.6 30 to 1.8 times greater than in the control treatment, Black walnut appears as an optimal species for 31 mitigating S-Metolachlor. The Brome grass and oak microcosms had the lowest Ksat of all treatments 32 and S-Metolachlor retardation factors were equal and slightly increased compared to the control, 33 respectively. These results show that agroforestry buffer's efficiency can be optimized by selecting 34 appropriate species.

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36 Keywords: Agroforestry; Herbicide; Leaching; Non-point Source Pollution; Plant; Soil

37

38 1 Introduction

Pesticides losses from croplands via runoff or drainage constitute up to 10% of pesticides sprayed to protect crops from pests and weeds (Louchart et al., 2001; Tang et al., 2012; Voltz and Louchart, 2001). This non-point source pollution (NPSP) threatens the quality and ecological health of both surface water bodies and groundwater thereby restricting specific usages such as drinking water supply and engendering significant remedial cost worldwide (Li and Jennings, 2018; Reichenberger et al., 2007; Schultz et al., 1995). Pesticides losses from croplands to surrounding surface and subsurface water bodies is closely linked to landscape organization and land management (Louchart et

al., 2001; Tang et al., 2012; Udeigwe et al., 2015; Voltz and Louchart, 2001). Non-cropped elements 46 47 of landscapes such as vegetated ditches, hedgerows or vegetated riparian zones reduce overland 48 runoff, filter shallow groundwater and mitigate pesticides thanks to an array of hydrological and 49 biochemical processes (Dosskey, 2001, 2010; Lacas et al., 2005; Needelman et al., 2007; 50 Reichenberger et al., 2007). However, despite the financial and technical support for buffer's 51 implementation, farmers remain reluctant to convert croplands into non-productive buffer zones 52 (Lovell and Sullivan, 2006). Agroforestry practices such as in-field agroforestry buffers or alley 53 cropping, by combining intensively cropped areas with economically viable non-cropped buffer 54 zones, may offer an optimal landscape setting for both maintaining land productivity and reducing pesticide losses (Jose, 2009; Nair, 2007). In alley cropping agroforestry systems, high value hardwood 55 56 trees are planted in rows, between which, crops are established in allay ways (Kremer and Kussman, 57 2011). Agroforestry buffers refer to in-field, edge-of-field or riparian buffers planted with both grass 58 and wooded species (Caron et al., 2010; Udawatta et al., 2011).

59 Evidence on efficiency of agroforestry systems in reducing NPSP from overland flow has been 60 provided by several studies across North America and Europe. Pesticides abatements rates varying 61 between 58 and 90%, have been measured between the inlet and outlet of edge-of-field and in-field agroforestry buffers (Borin et al., 2010; Caron et al., 2010; Lin et al., 2011). The pesticide abatements 62 63 in those studies were attributed to significant runoff reduction and sediment trapping. Indeed, buffer vegetation provides roughness that slows overland flow and increases infiltration duration (Caron et 64 65 al., 2010a; Dosskey, 2001; Dosskey et al., 2010). In addition, enhanced evapotranspiration by buffer 66 vegetation with deeper root systems induces drier soil moisture conditions than for adjacent row 67 crop soils thereby enhancing infiltration and water storage capacities in the buffers (Anderson et al., 68 2008; Dosskey et al., 2010; Lin et al., 2011; Sahin et al., 2016; Schultz et al., 1995). Moreover, roots and biological activity increase the soil macroporosity in vegetated buffers creating preferential flow 69 70 pathways. While the pesticide reduction from overland flow in agroforestry buffers has been fairly well described, the fate of pesticide in buffer soils and the risk for groundwater contamination
remains to be documented.

Preferential flow in soils leads to rapid leaching of pollutants and consequently to non-equilibrium sorption which increases the risk of groundwater contamination (Dages et al., 2015; Pot et al., 2005; Vanderborght et al., 2002). However, the vicinity of root channels, which are major conducting macropores, might be enriched in specific soil organic carbon and microbial biomass enhancing sorption and degradation potentials. Efficiency of agroforestry buffer zones depend on a balance of these mechanisms.

79 The magnitude of water and pesticide infiltration fluxes is assumed to be mainly dependent on 80 vegetation type because of contrasted root biomass distribution along the soil profile (Lin et al., 81 2011; Schultz et al., 1995), diverse composition of soil organic carbon and microbial activities (Chu et 82 al., 2013; Lin et al., 2004, 2010) and differing soil structure and moisture modification (Anderson et 83 al., 2008; Sahin et al., 2016; Schultz et al., 1995; Seobi et al., 2005). Pesticide retention patterns 84 would then be contrasted among plant species and between the rhizosphere and the soil matrix (Chu et al., 2013; Lin et al., 2010, Rodríguez-Cruz et al., 2012). Water and pesticide transport and retention 85 86 in the root zone of a few herbaceous species have been evaluated and compared (Belden and Coats, 87 2009; Lin et al., 2004, 2011) but there is, to our knowledge, no study investigating the influence of 88 temperate agroforestry species on those mechanisms. Accordingly, the objectives of this study were 89 i) to compare the influence of popular agroforestry buffer trees and herbaceous species on the 90 mechanisms of water and herbicide fluxes and ii) to compare soil textural, chemical and sorption 91 properties between the bulk soil and rhizosphere of the tested species.

92 In order to isolate the effect of the plant species from pedo-climatic effects that can be locally highly 93 variable and difficult to monitor precisely, we chose to implement a large microcosm approach. The 94 water and herbicide infiltration parameters obtained from microcosm approaches might not be 95 directly transferable to all field situations. However, the differential in water and herbicide 96 infiltration parameters measured between microcosms planted with various species indicates if a
97 given species has the ability to increase or decrease the hydraulic conductivity or herbicide sorption
98 in the root influenced zone. This information is useful for designing agroforestry buffers with
99 optimized herbicide mitigation capacity.

100

101 2 Materials and Methods

102 2.1 Microcosm design

Five treatments consisting of large (25.4 cm diameter, 30 cm height) packed soil columns were designed. Three treatments were planted each with a respective tree species, 1 treatment was planted with an herbaceous species and the final treatment remained un-vegetated. Each treatment was established in triplicate for a total of 15 columns.

107

108 2.1.1 Plant species

The herbaceous species selected was smooth brome grass (*Bromus* sp.), a cold season grass widely
used in agroforestry buffers strips because of its great performance under shade (Lin et al., 2004,
2007). Smooth brome grass seeds were purchased from Stock Seed Farm (Murdock, Nebraska, USA).

The tree species selected were poplar (*Populus* sp.), oak (*Quercus* sp.) and walnut (*Juglans* sp.). Poplar tree is probably the most popular tree species in agroforestry buffer design (Caron et al., 2010; Chu et al., 2010). This fast growing species is used all over the world in diverse agroforestry systems. Oak and walnut trees are also widely used (Cardinael et al., 2015; Garrett et al., 1991; Pinto-Correia et al., 2011). Pin oak (*Quercus palustris*) and black walnut (*Juglans nigra*) are species well acclimated to the Midwestern USA and often locally grown in agroforestry systems. Bare-root dormant tree seedlings, 30 to 40 cm tall, were used to establish the tree buffer microcosms. Hybrid poplar seedlings (*Populus deltoides x Populus nigra*) were purchased from the Arbor Day Foundation
 Nursery (Lincoln, Nebraska, USA). Pin oak and black walnut seedlings were purchased from the Cold
 Stream Farm Nursery (Michigan, USA).

122

123 2.1.2 Soil collection and columns preparation

The soil used to build the buffer microcosms was sampled in a permanent prairie plot at the Horticulture and Agroforestry Research Center in New Franklin, Missouri, USA (39°0.2' Nord, 92°46' West). The plot has no history of pesticide or herbicide use. The soil at the site is a Menfro silt loam (fine-silty, mixed superactive, mesic Typic Hapludalf) (Udawatta et al., 2010). About 350 kg soil was collected from the upper, organic matter-rich, horizon (0-30 cm depth). The soil was stored in a walkin growth chamber where it was air dried at 30°C then sieved at 2 mm.

PVC cylinders, 25.4 cm ID and 30 cm length were sealed at the bottom with a PVC sheet and packed with the dry sieved soil at a 1.2 g cm⁻³ density. To ensure the homogeneity of the soil density over the column's height, the columns were packed progressively by 1 cm layer increments. For each layer, the mass of soil required to reach a density of 1.2 g cm⁻³ was precisely weighed, then homogeneously spread over the surface and manually compacted to reach 1 cm height.

For the un-vegetated controls and smooth brome grass microcosms, the columns were packed directly at the final height of 23 cm. The soil in the columns was humidified with a rainfall simulator to reach 50% of the water holding capacity and for the brome grass treatment, 10 seeds per columns were dispersed to the surface and gently buried at 1-2 mm depth. The columns were covered with aluminum foil for 10 days until the seeds germinated.

For the tree treatments, the columns were first packed by 1 cm increments as described earlier over a height of 8 cm. Each seedling, previously soaked in clear tap water to remove the hydroponic gel from the roots, was positioned in a column so that the taproot was centered and the collar positioned at 23 cm above the bottom of the column. The lateral roots were distributed around the tap root and maintained in their natural orientation while packing the columns as previously described to reach a final height of 23 cm at a 1.2 g cm⁻³ density. The natural architecture of the root system was thus preserved and the soil density was homogeneous along the column. The soil was then humidified to reach 50% of the water holding capacity as previously described.

148

149 2.1.3 Vegetation growth period

150 After the tree seedlings were planted and the brome grass was seeded, all of the microcosms were 151 incubated for 4 months in a walk-in environmental growth chamber (Environmental Growth 152 Chambers GC72 walk-in unit, Chagrin Falls, Ohio) under constant and controlled climatic conditions. 153 During the growth period, a 12-h day and 12h-night cycle was imposed. During the day, the temperature was set to 25°C, humidity to 25 % and the total light intensity was 3.95 10⁵ lumens 154 composed of 97 % fluorescent light and 3 % halogen lights providing the blue and red light range for 155 156 plant growth, respectively. During the night, the temperature was set to 19°C, humidity to 40 % and 157 the complete darkness was maintained. Irrigation was designed to simulate rainfall events with 158 cumulative amount, intensity and frequency representative of the mid-Missourian climate. Each 159 microcosm received a cumulated amount of 100 mm/month, which corresponds to the average 160 monthly rainfall over the April to August period. Two major rainfall events of 10 mm each and a minor event of 5 mm were performed weekly. All of the microcosms including the un-vegetated ones 161 were subjected to the same climatic conditions for 4 months. At the end of the growth period, 2 out 162 of 3 trees of each treatment had grown well. Thereby, the infiltration experiments were conducted in 163 duplicates for all of the treatments. 164

165

166 2.2 Characterization of the water and solute infiltration fluxes

167 2.2.1 Selected herbicide and conservative tracer

168 Bromide was selected as a conservative tracer to characterize the hydrodynamic properties in the 169 microcosms because it rarely sorbs to soil particles and is only present as trace element in the 170 environment (Flury and Wai, 2003). S-Metolachlor was selected as a model herbicide to characterize 171 the transfer and retention mechanisms. S-Metolachlor, is from the Chloroacetamide family, is 172 hydrophobic (log Kow = 3.05). It's water solubility is relatively low, 480 mg l^{-1} , its soil sorption affinity 173 is moderate and it's degradation half-life in soil varies between 15 and 92 days (PPDB, 2018). S-174 Metolachlor is widely used across the world for selective weeding in a variety of crops including 175 maize, rapeseed, cotton etc. (e.g., O'Connell et al., 1998). Being moderately sorbed by soils and 176 despite a relatively low persistence (a few weeks), this compound is classified as moderately mobile 177 (PPDB, 2018). Indeed, it has been frequently detected in surface and groundwater in the USA and EU 178 (e.g., Toccalino et al., 2014).

179

180 2.2.2 Transport experiments

For the transport experiments the PVC sheets at the bottom of the columns were replaced by metal with 3 to 4 mm pore size to prevent soil loss without restricting the water flow in the columns. Columns were progressively saturated by capillarity rise 48h prior to the infiltration experiments to minimize trapping of gas bubbles in the soil pores.

Bromide tracer experiments were performed in duplicates and S-Metolachlor transport experiments on a single series. Two series of infiltration experiment were thus performed; the first evaluating only bromide transport and the second both bromide and S-Metolachlor transport. The injection solutions used for the first series of displacement experiments contained 500 mg l⁻¹ of bromide (Br⁻). This series was performed on a set of columns including one from each treatment; control (Cl), smooth brome grass (BGI), black walnut (BWI), pin oak (OI) and poplar (PI). The injection solution used for the 191 second series of transport experiments contained 500 mg l⁻¹ bromide and 300 μg l⁻¹ S-Metolachlor. 192 This series was performed on a second set of columns including the second replicate from each 193 treatment; control (CII), smooth brome grass (BGII), black walnut (BWII), pin oak (OII) and poplar 194 (PII). Thereby, the bromide transport experiments were performed in duplicates while the S-195 Metolachlor transport experiments were performed only once for each treatment. Indeed, one series 196 had to remain uncontaminated by S-Metolachlor for further characterization of the textural, 197 chemical and sorption properties (see section 2.3).

198 At the beginning of the transport experiments, the saturated columns were manually ponded with a 199 10-mm water height of the injection solution. The water height was maintained constant during the 200 infiltration by adjusting the supply of the injection solution. A total volume of 118 mm (6000 cm³) of 201 solution was supplied to each column. Among the 10 columns, the pore volumes ranged from 119 202 (6030 cm³) to 129 (6537 cm³) mm as estimated with pedotransfer functions from the density and 203 volume of the soil cylinders (Schaap et al., 2001). Therefore, the volume of tracer solution supplied 204 during the displacement experiment was always approximately equal, or slightly lower than the 205 column pore volume. When the solution supply stopped, the decrease in water head was monitored 206 during the remaining period of ponded water infiltration. Just after all the ponded solution had 207 infiltrated, the columns were ponded again with a constant head of 10 mm tracer free water, and the 208 columns were eluted with 118 mm of degassed tap water, following the same procedure. During the 209 infiltration and elution periods, 100 ml fractions of the effluents were collected in polypropylene (PP) 210 containers at the outlets of the columns. The sampling frequency varied from 50 s to about 2 min, 211 depending on the columns drainage rate. The outlet flowrates were monitored using the timing of 212 sample collection and the measured weights. The recovery of each solute was calculated by dividing 213 the mass of the solute collected in the effluent by the mass injected (C_{out}/C_{in}) (Belden and Coats, 214 2009; Dollinger et al., 2018).

216 2.2.3 Determination of the hydrodynamic properties by inverse modelling

217 As described in Dollinger et al. (2018), the bromide tracer experiments were simulated using 218 HYDRUS-1D (Šimůnek et al., 2008; Šimůnek et al., 2003) that solves the Richards and convection-219 dispersion equations. The classical formalism of the Richards equation assuming homogeneous flow 220 pathways and the dual-permeability model considering two mobile compartments, a fast macroporal 221 compartment and the slow matrix, were successively used to simulate the experiments. Although the 222 single porosity model gave acceptable results for most columns (Fig. S1 and S2), the dual 223 permeability model was more effective for all of the columns (Fig. S3 and S4) and was thus used to 224 determine the hydrodynamic properties. Equations of the dual-permeability model are briefly 225 described in the supplementary material (Eq. S1a and S1b). For more details on the equilibrium and 226 non-equilibrium formalisms, please refer to Šimůnek et al., (2008) or Köhne et al. (2009). The water 227 retention curve $\theta(h)$ and the unsaturated hydraulic function K(h) are defined for both compartments 228 using the van Genuchten model (Van Genuchten, 1980). K(h) is described as the product of the 229 relative hydraulic conductivity function Kr (dimensionless) and the saturated hydraulic conductivity 230 Ks [L.T⁻¹]. The transport equations associated with dual-permeability formulation for water flow (Eq. 231 S2a to S2c) are based on the classical convection-dispersion equation for both the fast compartment 232 and the slow compartment completed with an exchange term between the two compartments 233 (Šimůnek et al., 2008; Köhne et al., 2009).

234 An inverse modeling approach was implemented to reproduce both the bromide breakthrough 235 curves and percolation outfluxes of the 2 series of transport experiments. The 0.23 m-soil profiles 236 were densely discretized with 150 nodes to facilitate numerical convergence. An initial hydrostatic 237 equilibrium with a zero-pressure was considered and a variable head corresponding to the water 238 level fluctuation at the top of the soil column was imposed as top boundary condition. The eight 239 following parameters were fitted against total soil column porosity, cumulative water outflows 240 heights bromide concentrations at the outlet of the soil column: and

241 $\theta r_m, \theta s_m, \theta s_f, K s_m, K s_f, \omega, D i s p_m, D i s p_f$ with θs and θr respectively the saturated and residual soil 242 water content and *D i s p*, the dispersion coefficient [L]. To avoid local minimum, the stability of the 243 fitted parameter set estimated was evaluated using different sets of initial parameters, including the 244 estimated sets themselves. The other hydrodynamic parameters were set according to their textural 245 composition and their bulk density using Rosetta (Schaap et al., 2001), except θr_f that was set to 246 zero. The Bromide diffusion coefficient was fixed to 2 10⁻⁹ m².s⁻¹ (Köhne et al., 2006).

247

248 2.2.4 Modelling of the S-Metolachlor breakthrough curves

249 To simulate the breakthrough curves of S-Metolachlor, we used the dual-permeability formalism for 250 the water flow coupled to the convection-dispersion equation for the solute transport with an 251 additional term for sorption. We assumed the degradation processes to be negligible given the short 252 duration of the experiments varying between 2 and 6 h compared to the half-life of 15 to 92 days of 253 this molecule (section 2.2.1). A linear sorption equilibrium model with no desorption hysteresis was 254 considered. First, we used the sorption coefficients measured in the batch studies (section 2.3.2). We 255 implemented in the model the "rhizosphere" sorption coefficient for the macroporal compartment 256 and the "bulk" sorption coefficient for the slow matrix compartment. Then, to account for potential 257 reduced sorption mechanisms that might occur especially in the macroporal compartment due to 258 reduced contact duration, we implemented an inverse modelling approach. Therefore, the sorption coefficients Kd_f and Kd_m were fitted against the S-Metolachlor breakthrough curves. The retardation 259 260 factors (Schaffer and Licha, 2015) were calculated for both the matrix and macroporal compartments 261 for the 2 sets of sorption coefficients (measured and optimized).

262

264 2.3 Measurement of the physico-chemical and sorption properties in the rhizosphere and bulk soil

265 from the different microcosms

266 2.3.1 Soil sampling and analysis

267 Soil from the first series that did not receive S-Metolachlor during the transport experiment was 268 collected from each treatment (CI, BGI, BWI, OI and PI). For the vegetated treatments, bulk and 269 rhizosphere soil were collected separately. Rhizosphere soil was defined as soil attached to the root 270 system. To sample the rhizosphere soil, roots were gently shaken to remove un-attached particles 271 then brushed to collect the attached fraction. Bulk soil was collected in areas not or poorly colonized 272 by roots. Very fine roots (diameter <1mm) had colonized most of the soil profiles in the vegetated 273 treatments so the bulk soil collected aren't totally un-affected by the root systems. We hypothesized 274 that the bulk and rhizosphere soils were homogeneous along the soil profile of a given column as the 275 columns were packed with homogeneous soil.

The soil samples were then sieved at 2 mm and sent to the Soil and Plant Testing Laboratory at the University of Missouri for analysis of texture, pH, organic matter content (OM) and cationic exchange capacity (CEC).

After soil sampling, the root and aerial biomass from the CI, BGI, BWI, OI and PI treatments were separately collected and oven dried at 105 °C for 24h.

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282 2.3.2 Adsorption isotherms

The adsorption parameters were measured according to a procedure adapted from the OECD Guideline 106 (OECD, 2000) with equilibrium conditions and solid-to-liquid ratio chosen to mimic the soil solution conditions as much as possible given the analytical constraints. Prior to the experiments, the sieved soils were air dried to a target humidity of 10 % which was precisely measured by oven 287 drying at 105°C for 24h. Then, 4 ml of the S-Metolachlor solutions with concentration ranging from 50 to 1000 μ g l⁻¹ (50, 100, 250, 500 and 1000 μ g l⁻¹) prepared in an electrolyte solution composed of 288 CaCl₂ 0.01 M and NaN₃ 200 mg l⁻¹ were equilibrated with 2 g of soil in polypropylen (PP) centrifuge 289 290 tubes. CaCl₂ was added in the electrolyte solution to minimize the soil aggregate breakdown and 291 NaN₃ to prevent microbial degradation during the incubation periods. The tubes were equilibrated 292 for 48 h without shaking and then centrifuged at 3000 rpm for 10 minutes. Aliquots of the 293 supernatants were collected and filtered at 0.2 µm prior to S-Metolachlor analysis. S-Metolachlor 294 concentration in soils was assessed by mass balance between initial and equilibrium concentrations. 295 Both linear (Eq. 1a) and Freundlich models (Eq. 1b) were fitted to the experimental data.

296 Cs = Kd Cw

(Equation 1b)

(Equation 1a)

where Cs is the amount of sorbed pesticides in the soil at equilibrium (μ g kg⁻¹), Cw is the equilibrium concentration in the supernatant (μ g l⁻¹), Kd is the linear sorption coefficient (l kg⁻¹), Kf (μ g⁽¹⁻ⁿ⁾ lⁿ kg⁻¹) and n are the Freundlich coefficients with n the non-linearity parameter of the Freundlich model.

Adsorption of S-Metolachlor to the PP tubes and membrane filters were evaluated before the sorption experiments and found to be negligible. All of the batch experiments were conducted in triplicates.

304

305 2.4 Chemical analyses

Bromide was quantified in the leachate samples using an ion-specific electrode (Hanna Instruments, HI4102, USA). A previous study has proven the accuracy of this electrode when compared to ionic chromatography (Dollinger et al., 2018). For the measurement, 15 ml sample aliquots were mixed with 500 µl of the HI4000-00 reactive solution (Hanna Instruments, USA) and stirred for 2 minutes
before the electrode measurement. The limit of quantification of this method was 1 mg l⁻¹.

311 The quantification of S-Metolachlor was performed using a Waters Acquity TQ triple quadrupole 312 mass spectrometer (Waters, USA) with an electrospray ionization interface operated in positive 313 mode (ESI+) coupled to a Waters Alliance 2695 HPLC system (Waters, USA). The separation was 314 performed at 40°C on a 4.6 ID and 100 mm length C18 column (Kinetex) under gradient mode. The 2 315 solvents constituting the mobile phase were acetonitrile (A) and MilliQ H₂O with 10 mM ammonium 316 acetate and 0.1 % formic acid (B). The gradient was initiated with 2 % of A and 98 % B for 0.3 min 317 then the relative proportion of solvent A was risen from 2 to 80 % between 0.3 and 7.27 min, risen 318 again from 80 to 98 % between 7.27 and 7.37 then maintained until 9 min run. Between 9 and 10 319 min run, the relative proportion of A was lowered from 98 to 2 % than maintained until the end of the 15 min run. The flowrate of the mobile phase was 0.5 ml min⁻¹ all along the run. The data 320 321 acquisition was performed with the multiple reaction monitoring (MRM) mode by monitoring the 322 dissociation of the m/z 284 precursor ion to the m/z 252 product ions for a cone voltage and a 323 collision energy of 30 and 16 volts respectively. Prior to the analysis all of the samples were filtered 324 at 0.2 µm on inorganic membrane filters (Whatman Anotop 10). The limit of quantification was 0.05 µg l⁻¹. 325

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327

328 3 Results and discussion

329 3.1 Root system architecture and plant growth

At the end of the 4 months growth period, the plants of the vegetated microcosms had grown well in two replicates out of the three initially established. The aerial biomass structure and height was visually very similar among the two replicates for a given species exception made of the poplar trees. The two poplar trees revealed to be different hybrids. The PI hybrid had triangle leaves' shape and dark red shoots while the PII hybrid had more elongated leaves' shape and green shoots. The PII hybrid was also taller than the PI hybrid. The height of the three tree species had almost doubled during the growth period and the collar circumference reached 3.3 to 3.6 cm. The global biomass recorded was from far the greatest for brome grass followed by poplar trees (Fig. 1). Oak and walnut trees had equivalent biomasses which were lower than those of poplar trees. For all species, the root biomass was 2 to 10 times greater than the aerial biomass.

340 The smooth brome grass had developed a very dense root system that had colonized the entire 341 column profile with similar densities at the different depths. The root development didn't seem to be 342 constrained by the cylinder wall. The roots had all similar diameters (about 1 mm) and were greatly 343 interwoven with no dominant orientation angle. For the tree species, the architecture of the root 344 system didn't evolve much during the 4 months growth (Fig. 2). The end part of the tape roots from 345 the oak and black walnut seedlings had degenerated and few lateral roots were created but the 346 diameter of tape roots and lateral roots almost doubled. In addition, branching from the lateral roots 347 had generated a dense network of very fine roots (< 1 mm diameter). The structure of the black 348 walnut root system was characterized by a large tap root and 10-20 large lateral roots evenly 349 distributed along the tape root with orientation angles varying from 40 to 60° from the tape root axis 350 and a dense fine to very fine root system. The root system architecture was rather similar for oak 351 trees but the lateral roots were more horizontal. The tape root and lateral roots were also finer than 352 those from the black walnut seedlings. Lateral roots' elongation was also not constrained by the 353 cylinder walls for both species. The architecture of the poplar root systems was greatly contrasted. 354 Few lateral roots were generated at the high end of the tape root but most of them were located at 355 the bottom end. The lateral roots' elongation was greatly constrained by the cylinder size so when 356 the roots reached the walls, new branching were created and those branched roots circled several 357 times the soil cylinder at the edge with the PVC walls. Thereby, contrastingly with the other tree 358 species, the root density was very high on the edges and low in the center of the soil profile.

359 Root system architecture is dependent on the soil compaction heterogeneity, contrasted water and 360 nutrient availability but also on the slope of the plot, the wind and other climatic conditions (Di Iorio 361 et al., 2005; Hodge et al., 2009; Pregitzer et al., 2002; Zanetti et al., 2015). The homogeneous soil 362 density, humidity and nutrient availability provided by the microcosms allows almost un-constraint 363 development of the root systems. Only the size of the cylinders could constrain the natural 364 development of the lateral root as observed for the poplar trees (Fig. 2). The root systems 365 architecture from the plant grown in the large microcosms should not differ much from those of the 366 same species established in field buffers with low constraint level environments like some riparian 367 buffers with shallow water table collecting runoff loaded with nutrients from surrounding crop plots. 368 Under more constrained field conditions like some alley cropping systems, the morphology of the 369 root system could differ according to the pedo-climatic factors (Malamy, 2005).

370

371 3.2 Influence of plant species on water and solutes infiltration fluxes

372 The bromide breakthrough curves and outflow patterns monitored during the infiltration 373 experiments allow comparing the water fluxes and hydrodynamic properties between the different 374 treatments. The bromide breakthrough curves were relatively well repeatable between the 375 duplicates of the smooth brome grass, black walnut and oak treatments (Fig. 3). For those 376 treatments the outflow patterns were also similar and constant between the injection and elution 377 phases (Fig. 3). For the poplar treatment, the outflow was greater for the second replicate (PII), the 378 bromide concentration rise was sharper during the injection phase and the concentration dropped 379 faster during the elution phase, which resulted in an earlier bromide peak. This could be either due 380 to the fact that the 2 poplar hybrids had different phenotypical characteristics or to the fact that 381 roots had circled the soil profile and may have induced contrasted sidewall flow paths in both replicates (section 3.1). The patterns also greatly differed between the 2 replicates of the control 382 383 treatment with an outflow 2 times greater for the first replicate accompanied by an accelerated

384 bromide transport. The outflow decreased for the CI replicate all along the infiltration experiment. Being un-vegetated, the controls had lower evaporation rates during the growth period and a 385 386 biological crust composed of algae and moss formed at the surface of the columns. This poorly 387 permeable crust covered almost the entire surface of the CII replicate but only half of it for the CI 388 replicate which could explain the different patterns. Moreover, desiccation cracks that formed 389 between the irrigation events at the early stage of the growth periods were set by these crusts. 390 Under field condition, soils un-protected by vegetation and especially soils with high silt and clay 391 contents, are also exposed to crusting and to the formation of drying cracks that modify the 392 infiltration rates (e.g., Chamizo et al., 2012; Dunne et al., 1991; Eldridge et al., 2000).

393

Despite some significant variability between the control and poplar replicates contrasted patterns of 394 395 hydrodynamic properties between the treatments could be highlighted (Table 1). The macroporal 396 flow contribution to the global outflow was found to be higher for the vegetated treatments than for 397 the un-vegetated controls, exception made of the PII microcosms. For the un-vegetated treatments, 398 the macroporal fraction of the soil porosity (ω) was significant but the hydraulic conductivity and 399 dispersion of the macroporal compartment were only slightly greater than those of the matrix 400 compartment. The high hydraulic conductivity and dispersion in both compartments resulted in the 401 fast leaching of bromide with concentration greater than the LOD measured already in the first 402 collected samples. Contrastingly, the hydraulic conductivity and dispersion of the matrix 403 compartment were significantly lower in the vegetated treatment while those of the macroporal 404 compartment were equivalent to those of the un-vegetated treatments. Accordingly, the overall 405 hydraulic conductivities were reduced and the transport of bromide was slower. The breakthrough 406 time reached up to 18 minutes in the oak treatments. The greatest global Ksat were recorded for the 407 control and poplar treatments and the lowest for the smooth brome grass and oak treatments. Black 408 walnut treatments had intermediate Ksat. The hydraulic conductivity conditions the amount of water 409 infiltrated during a runoff event. Thereby, among the different plant species tested, poplar trees
410 would be the most efficient in reducing overland flow followed by black walnut then oak trees and
411 smooth brome grass.

412

413 For most of the treatments, S-Metolachlor transport had patterns contrasting with those of bromide 414 (Fig. 4). For the control treatment, S-Metolachlor breakthrough was not significantly delayed 415 compared to bromide but the concentration rise during the injection phase was slower. However, 416 the concentration drop during the elution phase was similar to that of bromide. For this CII 417 treatment, the bromide recovery was about 10 % greater than that of S-Metolachlor at the end of 418 the transport experiment but the model extrapolation suggests a 2% difference after eluting with 10 419 pore volumes (Table 2). As the transport pattern of S-Metolachlor was measured on the CII replicate 420 having the slowest Ksat, it represents the best case scenario. For the brome grass treatment, S-421 Metolachlor breakthrough was slightly delayed compared to bromide. The concentration rise during 422 the injection phase was slower and so was the concentration drop during the elution phase (Fig. 4). A 423 second small peak for both bromide and S-Metolachlor was observed (Fig. 4). This second peak 424 corresponds to the fraction of the solute fluxes transported in the slow matrix compartment. For the 425 other treatments, only the peak corresponding to the fraction of solutes transported through the 426 fracture was observed and the second peak was probably too low to be distinguished as suggested 427 by the greater macroporal fractions in these cases (Table 1). As for the control, the difference in 428 recovery rate between bromide and S-Metolachlor was about 10% at the end of the experiment for 429 the brome grass treatment but the values simulated for an elution period of 10 pore volumes were 430 equal. Contrastingly, for the black walnut and oak treatments, the S-Metolachlor breakthrough was 431 so delayed that the concentration didn't even started to drop during the elution phase (Fig. 4). The 432 difference in recovery rates between bromide and S-Metolahclor reached 30% for those treatments 433 at the end of the experiment and was still of 10% after a simulated elution period of 10 pore

volumes. Last, for the poplar treatment, the bromide and S-Metolachlor breakthrough curves were
relatively similar for the first part of the curve and except for a slightly faster concentration drop
during the elution phase for S-Metolachlor (Fig. 4). Accordingly, the difference in recovery rates
between bromide and S-Metolachlor was only 5% at the end of the experiment. For the poplar
treatment, S-Metolachlor transport was assessed on the PII replicate having the greatest Ksat.
Thereby, it represents the worst-case scenario.

440 Except for the poplar treatment, the direct implementation in the model of the Kd measured in the 441 batch experiments allowed rather good reproduction of the S-Metolachlor breakthrough curves (Fig. 442 4). However the optimization of the sorption parameters improved the predictions especially for the 443 control, brome grass and poplar treatments (Fig.4 and Table 2). Therefore, the extrapolation of the S-444 Metolachlor recovery rates to 10 pore volumes was calculated using the optimized sorption 445 coefficients in the transport model (section 2.2.4). Except for the poplar treatment, the very large 446 confidence interval on the optimized Kd for the matrix compartments (up to ± 10³) suggest that this 447 parameter is not sensitive. This is in accordance with the great contribution of the macroporal flow 448 (Table 1) and the fast S-Metolachlor breakthrough (Fig. 3). The Kd measured for the bulk fraction 449 were thereby used to parameterize the matrix compartment of the control, smooth brome grass, 450 black walnut and oak treatments. The Kd optimized for the fracture compartment differed from the 451 Kd values measured for the "rhizosphere" soils and this parameter was sensitive for all treatments. 452 For the Poplar treatment, the optimized Kd values were zero for both compartments. Accordingly, S-453 Metolachlor was not retarded compared to bromide. The optimized Kd for the black walnut and oak 454 treatments were the highest resulting in overall high retardation factors compared to the control and 455 brome grass treatments (Table 2).

456 Under the studied flooding conditions, the risk of groundwater contamination by S-Metolachlor was 457 the lowest for the black walnut and oak treatments followed by the brome grass and the un-458 vegetated treatment. The poplar treatment recorded the highest contamination risk among all treatments. More generally, in the case of successive drying/wetting cycles as for buffer soils submitted to successions of flood events, retardation of herbicides gives a chance for degradation processes to take place and may also generate non-reversible sorption mechanisms. Therefore, as the transport model considered neglects desorption hysteresis and degradation processes, the extrapolation of S-Metolachlor breakthrough to 10 pore volumes and more or to a succession of flood events, might overestimate the recovery rates.

465

466 3.3 Influence of the root systems on the soil properties

467 The soil analyses of the vegetated microcosms show that the textural and chemical properties and 468 especially the texture class and organic matter content were very similar in the rhizosphere and bulk 469 soils for a given species (Table 3). However, when comparing treatments, it appears that the organic 470 matter content was slightly greater in the tree microcosms than in the smooth brome grass and 471 control treatments. The smooth brome grass treatment was equivalent in terms of organic matter 472 content to the un-vegetated control. Moreover, the texture was slightly finer in the smooth brome 473 grass treatment than in the others and the CEC slightly higher in the control and poplar treatments. 474 In sum, root systems of the different species contrastingly affected the soil textural and chemical 475 properties. However, this action of the root systems was not restricted to the close vicinity of the 476 root system but extended to most of the profile. This might be due to the dense colonization of the 477 soil profiles by the very fine root systems but also to root exudation and diffusion of dissolved 478 organic carbon in the soil columns (section 3.1).

The sorption of S-Metolachlor on the rhizosphere and bulk soil from all treatments were best fitted by linear isotherms (Fig. 5, Table 3). As many other hydrophobic and non-ionic herbicides, S-Metolachlor has a great affinity for the organic matter fraction of soils and its sorption rate is mainly driven by the organic matter content (Weber et al., 2004). Accordingly, the linear sorption coefficients (Kd) were about 3 times greater for the oak, poplar and walnut treatments having 484 greater organic matter content (Table 3) than for the control and brome grass treatments. Moreover, 485 the difference in Kd between the rhizosphere and bulk soils in the vegetated microcosms was 486 negligible (Table 3). The Kd and Kf measured are in the range of sorption coefficients reported in the 487 literature for soil with similar properties (e.g., Alletto et al., 2013; Krutz et al., 2004; Shaner et al., 488 2006). The greater Kd in soils from the oak and black walnut treatments could explain, along with low 489 hydraulic conductivities, the greater retention capacity of S-Metolachlor.

490 Except for smooth brome grass, the optimized parameters were slightly lower for the macroporal 491 compartment (0.13, 0.72, 0.77 and 0.00 l/kg for C, BW, O and P, respectively) than the coefficients 492 measured in the rhizosphere of the different species (Table 3), which suggests that the higher flow 493 velocities resulted in a reduced contact time for sorption for this compartment. For the matrix 494 compartment, the optimized sorption coefficients were found to be poorly sensitive in accordance to 495 the limited contribution of the matrix to the global outflow. For the poplar treatment, the high 496 measured sorption is counterbalanced by faster infiltration, which limits the time for equilibrium 497 sorption. Indeed, the estimated sorption coefficients for both compartments are null.

498

499 4 Conclusion

500 Designing agroforestry buffers for multipurpose use including herbicide retention is limited by 501 consequent gaps of knowledge concerning the influence of plant species composition on the 502 infiltration of water and herbicides. Therefore, the influence of various tree or herbaceous species, 503 commonly used in agroforestry buffers, on the water and S-Metolachlor infiltration fluxes in buffer 504 soil and how these plant species modify the soil textural, chemical and sorption properties were 505 tested in large microcosms. The results highlight the advantage of introducing wooded species in 506 vegetated buffers. Indeed for the 3 tree species tested, the hydraulic conductivity of the soil was 507 equivalent or significantly higher than that of brome grass which guaranties a greater reduction of 508 overland flow and associated herbicide fluxes. For the oak and black walnut, this increased

509 infiltration was not associated with greater S-Metolachlor transport, which would have threatened 510 the groundwater quality. With a medium hydraulic conductivity, low macroporal flow and high S-511 Metolachlor retardation, black walnut appears to be the most interesting species. Future research 512 should investigate the transfer mechanisms of different categories of pesticides and under 513 contrasted pedoclimatic contexts. This would improve the genericity of the present results and allow 514 designing buffers adapted to local contexts.

515

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523 References

- 524 Alletto, L., Benoit, P., Bolognési, B., Couffignal, M., Bergheaud, V., Dumény, V., Longueval, C.,
- 525 Barriuso, E., 2013. Sorption and mineralisation of S-metolachlor in soils from fields cultivated with
- 526 different conservation tillage systems. Soil Tillage Res. 128, 97–103.
- 527 https://doi.org/10.1016/j.still.2012.11.005
- Anderson, S.H., Udawatta, R.P., Seobi, T., Garrett, H.E., 2008. Soil water content and infiltration in
 agroforestry buffer strips. Agrofor. Syst. 75, 5–16. https://doi.org/10.1007/s10457-008-9128-3
- 530 Belden Jason B., Coats Joel R., 2009. Effect of grasses on herbicide fate in the soil column: Infiltration
- of runoff, movement, and degradation. Environ. Toxicol. Chem. 23, 2251–2258.
- 532 https://doi.org/10.1897/03-422
- 533 Borin, M., Passoni, M., Thiene, M., Tempesta, T., 2010. Multiple functions of buffer strips in farming
- areas. Eur. J. Agron., Cropping Systems Design: new methods for new challenges 32, 103–111.
- 535 https://doi.org/10.1016/j.eja.2009.05.003

- 536 Cardinael, R., Mao, Z., Prieto, I., Stokes, A., Dupraz, C., Kim, J.H., Jourdan, C., 2015. Competition with
- 537 winter crops induces deeper rooting of walnut trees in a Mediterranean alley cropping agroforestry
- 538 system. Plant Soil 391, 219–235. https://doi.org/10.1007/s11104-015-2422-8
- 539 Caron, E., Lafrance, P., Auclair, J.-C., Duchemin, M., 2010a. Impact of Grass and Grass with Poplar
- 540 Buffer Strips on Atrazine and Metolachlor Losses in Surface Runoff and Subsurface Infiltration from
- 541 Agricultural Plots. J. Environ. Qual. 39, 617–629. https://doi.org/10.2134/jeq2009.0041
- 542 Caron, E., Lafrance, P., Auclair, J.-C., Duchemin, M., 2010b. Impact of Grass and Grass with Poplar
- 543 Buffer Strips on Atrazine and Metolachlor Losses in Surface Runoff and Subsurface Infiltration from
- Agricultural Plots. J. Environ. Qual. 39, 617–629. https://doi.org/10.2134/jeq2009.0041
- 545 Chamizo, S., Cantón, Y., Lázaro, R., Solé-Benet, A., Domingo, F., 2012. Crust Composition and
- 546 Disturbance Drive Infiltration Through Biological Soil Crusts in Semiarid Ecosystems. Ecosystems 15,
 547 148–161. https://doi.org/10.1007/s10021-011-9499-6
- 548 Chu, B., Anderson, S.H., Goyne, K.W., Lin, C.-H., Lerch, R.N., 2013. Sulfamethazine Transport in
 549 Agroforestry and Cropland Soils. Vadose Zone J. 12. https://doi.org/10.2136/vzj2012.0124
- 550 Chu, B., Goyne, K.W., Anderson, S.H., Lin, C.-H., Udawatta, R.P., 2010. Veterinary antibiotic sorption
- to agroforestry buffer, grass buffer and cropland soils. Agrofor. Syst. 79, 67–80.
- 552 https://doi.org/10.1007/s10457-009-9273-3
- 553 Dages, C., Samouëlian, A., Negro, S., Storck, V., Huttel, O., Voltz, M., 2015. Seepage patterns of
- 554 Diuron in a ditch bed during a sequence of flood events. Sci. Total Environ. 537, 120–128.
 555 https://doi.org/10.1016/j.scitotenv.2015.07.130
- 556 Di Iorio, A., Lasserre, B., Scippa, G.S., Chiatante, D., 2005. Root System Architecture of Quercus
- pubescens Trees Growing on Different Sloping Conditions. Ann. Bot. 95, 351–361.
 https://doi.org/10.1093/aob/mci033
- 559 Dollinger, J., Dagès, C., Samouelian, A., Coulouma, G., Lanoix, M., Blanca, Y., Voltz, M., 2018.
- 560 Contrasting soil property patterns between ditch bed and neighbouring field profiles evidence the
- 561 need of specific approaches when assessing water and pesticide fate in farmed landscapes.
- 562 Geoderma 309, 50–59. https://doi.org/10.1016/j.geoderma.2017.09.006
- Dosskey, M.G., 2001. Toward Quantifying Water Pollution Abatement in Response to Installing
 Buffers on Crop Land. Environ. Manage. 28, 577–598. https://doi.org/10.1007/s002670010245
- 565 Dosskey, M.G., Vidon, P., Gurwick, N.P., Allan, C.J., Duval, T.P., Lowrance, R., 2010. The Role of
- 566 Riparian Vegetation in Protecting and Improving Chemical Water Quality in Streams1. JAWRA J. Am.
- 567 Water Resour. Assoc. 46, 261–277. https://doi.org/10.1111/j.1752-1688.2010.00419.x
- Dunne, T., Zhang, W., Aubry, B.F., 1991. Effects of Rainfall, Vegetation, and Microtopography on
 Infiltration and Runoff. Water Resour. Res. 27, 2271–2285. https://doi.org/10.1029/91WR01585
- 570 Eldridge, D.J., Zaady, E., Shachak, M., 2000. Infiltration through three contrasting biological soil crusts
- 571 in patterned landscapes in the Negev, Israel. CATENA 40, 323–336. https://doi.org/10.1016/S0341-
- 572 8162(00)00082-5

- 573 Flury Markus, Wai Nu Nu, 2003. Dyes as tracers for vadose zone hydrology. Rev. Geophys. 41.
- 574 https://doi.org/10.1029/2001RG000109
- 575 Garrett, H.E., Jones, J.E., Kurtz, W.B., Slusher, J.P., 1991. Black Walnut (Juglans nigra L.) Agroforestry –
- 576 Its Design and Potential as a Land-use Alternative. For. Chron. 67, 213–218.
- 577 https://doi.org/10.5558/tfc67213-3
- 578 Hodge, A., Berta, G., Doussan, C., Merchan, F., Crespi, M., 2009. Plant root growth, architecture and
- 579 function. Plant Soil 321, 153–187. https://doi.org/10.1007/s11104-009-9929-9
- Jose, S., 2009. Agroforestry for ecosystem services and environmental benefits: an overview. Agrofor.
 Syst. 76, 1–10. https://doi.org/10.1007/s10457-009-9229-7
- 582 Köhne, J.M., Köhne, S., Šimůnek, J., 2009. A review of model applications for structured soils: a)
- 583 Water flow and tracer transport. J. Contam. Hydrol. 104, 4–35.
- 584 https://doi.org/10.1016/j.jconhyd.2008.10.002
- 585 Köhne, S., Lennartz, B., Köhne, J.M., Šimůnek, J., 2006. Bromide transport at a tile-drained field site:
- 586 experiment, and one- and two-dimensional equilibrium and non-equilibrium numerical modeling. J.
- 587 Hydrol. 321, 390–408. https://doi.org/10.1016/j.jhydrol.2005.08.010
- 588 Kremer, R.J., Kussman, R.D., 2011. Soil quality in a pecan–kura clover alley cropping system in the
 589 Midwestern USA. Agrofor. Syst. 83, 213–223. https://doi.org/10.1007/s10457-011-9370-y
- 590 Krutz, L.J., Senseman, S.A., McInnes, K.J., Hoffman, D.W., Tierney, D.P., 2004. Adsorption and
- 591 Desorption of Metolachlor and Metolachlor Metabolites in Vegetated Filter Strip and Cultivated Soil.
- 592 J. Environ. Qual. 33, 939–945. https://doi.org/10.2134/jeq2004.0939
- Lacas, J.-G., Voltz, M., Gouy, V., Carluer, N., Gril, J.-J., 2005. Using grassed strips to limit pesticide
 transfer to surface water: a review. Agron. Sustain. Dev. 25, 253–266.
- 595 Li, Z., Jennings, A., 2018. Global variations in pesticide regulations and health risk assessment of
- 596 maximum concentration levels in drinking water. J. Environ. Manage. 212, 384–394.
- 597 https://doi.org/10.1016/j.jenvman.2017.12.083
- Lin, C.-H., Goyne, K.W., Kremer, R.J., Lerch, R.N., Garrett, H.E., 2010. Dissipation of Sulfamethazine
- and Tetracycline in the Root Zone of Grass and Tree Species. J. Environ. Qual. 39, 1269–1278.
 https://doi.org/10.2134/jeq2009.0346
- Lin, C.H., Lerch, R.N., Garrett, H.E., George, M.F., 2004. Incorporating forage grasses in riparian
- buffers for bioremediation of atrazine, isoxaflutole and nitrate in Missouri. Agrofor. Syst. 63, 91–99.
 https://doi.org/10.1023/B:AGFO.0000049437.70313.ef
- Lin, C.-H., Lerch, R.N., Garrett, H.E., Jordan, D., George, M.F., 2007. Ability of Forage Grasses Exposed
 to Atrazine and Isoxaflutole to Reduce Nutrient Levels in Soils and Shallow Groundwater. Commun.
 Soil Sci. Plant Anal. 38, 1119–1136. https://doi.org/10.1080/00103620701327976
- Lin, C.-H., Lerch, R.N., Goyne, K.W., Garrett, H.E., 2011. Reducing Herbicides and Veterinary
- 608 Antibiotics Losses from Agroecosystems Using Vegetative Buffers. J. Environ. Qual. 40, 791–799.
- 609 https://doi.org/10.2134/jeq2010.0141

- Louchart, X., Voltz, M., Andrieux, P., Moussa, R., 2001. Herbicide Transport to Surface Waters at Field
 and Watershed Scales in a Mediterranean Vineyard Area. J. Environ. Qual. 30, 982–991.
- Lovell, S.T., Sullivan, W.C., 2006. Environmental benefits of conservation buffers in the United States:
- 613 Evidence, promise, and open questions. Agric. Ecosyst. Environ. 112, 249–260.
- 614 https://doi.org/10.1016/j.agee.2005.08.002
- 615 Malamy, J.E., 2005. Intrinsic and environmental response pathways that regulate root system
- 616 architecture. Plant Cell Environ. 28, 67–77. https://doi.org/10.1111/j.1365-3040.2005.01306.x
- Nair, P.R., 2007. The coming of age of agroforestry. J. Sci. Food Agric. 87, 1613–1619.
 https://doi.org/10.1002/jsfa.2897
- 619 Needelman, B.A., Kleinman, P.J.A., Strock, J.S., Allen, A.L., 2007. Improved management of
- agricultural drainage ditches for water quality protection: An overview. J. Soil Water Conserv. 62,171–178.
- 622 O'Connell, P.J., Harms, C.T., Allen, J.R.F., 1998. Metolachlor, S-metolachlor and their role within
- 623 sustainable weed-management. Crop Prot. 17, 207–212. https://doi.org/10.1016/S0261-
- 624 2194(98)80011-2
- 625 OECD, 2000. OECD Guidelines for testing chemicals n°106.
- 626 Pinto-Correia, T., Ribeiro, N., Sá-Sousa, P., 2011. Introducing the <Emphasis
- 627 Type="Italic">montado</Emphasis>, the cork and holm oak agroforestry system of Southern
- 628 Portugal. Agrofor. Syst. 82, 99. https://doi.org/10.1007/s10457-011-9388-1
- 629 Pot, V., Simůnek, J., Benoit, P., Coquet, Y., Yra, A., Martínez-Cordón, M.-J., 2005. Impact of rainfall
- 630 intensity on the transport of two herbicides in undisturbed grassed filter strip soil cores. J. Contam.
- 631 Hydrol. 81, 63–88. https://doi.org/10.1016/j.jconhyd.2005.06.013
- 632 PPDB, 2018. Footprint Pesticides Properties Database database.
- Pregitzer, K.S., DeForest, J.L., Burton, A.J., Allen, M.F., Ruess, R.W., Hendrick, R.L., 2002. Fine root
 architecture of nine North American trees. Ecol. Monogr. 722 293-309.
- 635 Reichenberger, S., Bach, M., Skitschak, A., Frede, H.-G., 2007. Mitigation strategies to reduce
- 636 pesticide inputs into ground- and surface water and their effectiveness; A review. Sci. Total Environ.
- 637 384, 1–35. https://doi.org/10.1016/j.scitotenv.2007.04.046
- 638 Rodríguez-Cruz, M.S., Marín-Benito, J.M., Ordax, J.M., Azejjel, H., Sánchez-Martín, M.J., 2012.
- 639 Influence of pine or oak wood on the degradation of alachlor and metalaxyl in soil. J. Environ.
- 640 Manage., Environmental Risks and Problems, Strategies to reduce them through Biotechnology and
- 641 Engineering 95, S228–S232. https://doi.org/10.1016/j.jenvman.2010.10.043
- 642 Sahin, H., Anderson, S.H., Udawatta, R.P., 2016. Water infiltration and soil water content in claypan
- 643 soils influenced by agroforestry and grass buffers compared to row crop management. Agrofor. Syst.
- 644 1–22. https://doi.org/10.1007/s10457-016-9899-x

- 645 Schaap, M.G., Leij, F.J., van Genuchten, M.T., 2001. rosetta: a computer program for estimating soil
- 646 hydraulic parameters with hierarchical pedotransfer functions. J. Hydrol. 251, 163–176.
- 647 https://doi.org/10.1016/S0022-1694(01)00466-8
- 648 Schaffer, M., Licha, T., 2015. A framework for assessing the retardation of organic molecules in
- 649 groundwater: Implications of the species distribution for the sorption-influenced transport. Sci. Total
 650 Environ. 524–525, 187–194. https://doi.org/10.1016/j.scitotenv.2015.04.006
- 651 Schultz, R.C., Collettil, J.P., Isenhart, T.M., Simpkins, W.W., Mize, C.W., Thompson, M.L., 1995. Design
- and placement of a multi-species riparian buffer strip system. Agrofor. Syst. 29, 201–226.
- 653 https://doi.org/10.1007/BF00704869
- 654 Seobi, T., Anderson, S.H., Udawatta, R.P., Gantzer, C.J., 2005. Influence of Grass and Agroforestry
- Buffer Strips on Soil Hydraulic Properties for an Albaqualf. Soil Sci. Soc. Am. J. 69, 893–901.
- 656 https://doi.org/10.2136/sssaj2004.0280
- 657 Shaner, D.L., Brunk, G., Belles, D., Westra, P., Nissen, S., 2006. Soil dissipation and biological activity
- of metolachlor and S-metolachlor in five soils. Pest Manag. Sci. 62, 617–623.
- 659 https://doi.org/10.1002/ps.1215
- Šimůnek, J., Genuchten, V., Th, M., 2008. Modeling Nonequilibrium Flow and Transport Processes
 Using HYDRUS. Vadose Zone J. 7, 782–797. https://doi.org/10.2136/vzj2007.0074
- 662 Šimůnek, J., Jarvis, N.J., van Genuchten, M.T., Gärdenäs, A., 2003. Review and comparison of models
- 663 for describing non-equilibrium and preferential flow and transport in the vadose zone. J. Hydrol., Soil
- 664 Hydrological Properties and Processes and their Variability in Space and Time 272, 14–35.
- 665 https://doi.org/10.1016/S0022-1694(02)00252-4
- 666 Tang, X., Zhu, B., Katou, H., 2012. A review of rapid transport of pesticides from sloping farmland to
- 667 surface waters: Processes and mitigation strategies. J. Environ. Sci. 24, 351–361.
- 668 https://doi.org/10.1016/S1001-0742(11)60753-5
- 669 Toccalino, P.L., Gilliom, R.J., Lindsey, B.D., Rupert, M.G., 2014. Pesticides in Groundwater of the
- 670 United States: Decadal-Scale Changes, 1993–2011. Groundwater 52, 112–125.
- 671 https://doi.org/10.1111/gwat.12176
- 672 Udawatta, R.P., Garrett, H.E., Kallenbach, R., 2011. Agroforestry Buffers for Nonpoint Source
- 673 Pollution Reductions from Agricultural Watersheds. J. Environ. Qual. 40, 800–806.
- 674 https://doi.org/10.2134/jeq2010.0168
- Udawatta, R.P., Garrett, H.E., Kallenbach, R.L., 2010. Agroforestry and grass buffer effects on water
 quality in grazed pastures. Agrofor. Syst. 79, 81–87. https://doi.org/10.1007/s10457-010-9288-9
- 677 Udeigwe, T.K., Teboh, J.M., Eze, P.N., Hashem Stietiya, M., Kumar, V., Hendrix, J., Mascagni, H.J., Ying,
- T., Kandakji, T., 2015. Implications of leading crop production practices on environmental quality and
- 679 human health. J. Environ. Manage. 151, 267–279. https://doi.org/10.1016/j.jenvman.2014.11.024

- 680 Van Genuchten, T., 1980. A closed-form equation for predicting the hydraulic conductivity of
- unsaturated soils. Soil Sci Soc Am J 44, 892–898. http://dx.doi.org/10.
- 682 2136/sssaj1980.03615995004400050002x
- Vanderborght, J., Gähwiller, P., Flühler, H., 2002. Identification of Transport Processes in Soil Cores
- Using Fluorescent Tracers. Soil Sci. Soc. Am. J. 66, 774–787. https://doi.org/10.2136/sssaj2002.7740
- 685 Voltz, M., Louchart, X., 2001. Les facteurs-clés de transfert des produits phytosanitaires vers les eaux686 de surface.
- 687 Weber, J.B., Wilkerson, G.G., Reinhardt, C.F., 2004. Calculating pesticide sorption coefficients (Kd)
- using selected soil properties. Chemosphere 55, 157–166.
- 689 https://doi.org/10.1016/j.chemosphere.2003.10.049
- 690 Zanetti, C., Vennetier, M., Mériaux, P., Provansal, M., 2015. Plasticity of tree root system structure in
- 691 contrasting soil materials and environmental conditions. Plant Soil 387, 21–35.
- 692 https://doi.org/10.1007/s11104-014-2253-z





Fig 1: Plant biomass repartition after 4 months growth in a walk-in environmental growth chamber.

The brown bars represent the root biomass and the green bars the shoot biomass. The grey barsrepresent the plant height.





Fig 2: Evolution of the root system's architecture of the 3 tree species after 4 months growth in loess
soil microcosms incubated in the walk-in environmental growth chamber. The architecture of the root
systems did not evolve a lot as few new lateral roots were created but existent lateral roots elongated
and thickened significantly.





Fig 3: Repeatability of the water fluxes and conservative tracer transport patterns in the buffer microcosms. The water outflow (left) and bromide breakthrough (right) measured during the ponded leaching experiments in duplicates of brome grass, black walnut and pin oak microcosms exhibited a good repeatability. For the un-vegetated control (top) and poplar (bottom) microcosms, the measurements on the two replicates were less repeatable.



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Fig 4: Bromide and S-Metolachlor breakthrough curves. The graphs represent the evolution of the 720 721 measured bromide (black dots) and S-Metolachlor (red dots) concentration normalized by the 722 injection concentration value (C/C0) of each molecule as a function of the cumulated outflow volume 723 expressed as the cumulated volume normalized by the nominal pore volume (V/V0). The graphs on 724 the right are zooms from those on the left for the duration of the experiments only. The plain lines 725 represent the simulated breakthrough curves in black for bromide and in red for S-Metolachlor. The 726 light red lines represent the S-metolachlor breakthrough curves simulated with the sorption 727 parameters from the batch tests and the darkred lines are the S-Metolachlor breakthrough curves 728 simulated with optimized sorption coefficients. Bromide and S-Metolachlor breakthrough was 729 simulated for a period of 10 pore volumes and plotted for 8 pore volumes because of minor 730 differences between 8 and 10 pore volumes.



Fig 5: Linear sorption isotherms of S-Metolachlor on the rhizosphere and bulk soil from the different
buffer microcosms. The error bars represent the standard deviations (n=3).

Microcosm	^a K _{sat}	° Øs	^ь Өтот	b Ors	^b ∂s₅	^b Kss	[▶]	^b Ks _f	b W	^b Disp _s	^b Disp _f	^a BT	^b Pref. flow	R²	RMSE
	m s ⁻¹	m ³ m ⁻³	m s ⁻¹	m ³ m ⁻³	m s ⁻¹	%	т	т	S	%	-	mg l⁻¹			
CI	3.35 10 ⁻⁵	0.52	0.61	0.01	0.65	1.78 10 ⁻⁵	0.51	8.32 10 ⁻⁵	0.26	6.11 10 ⁻²	6.85 10 ⁻²	0	62.34	1.00	7.06
CII	1.57 10 ⁻⁵	0.52	0.45	0.03	0.70	1.22 10 ⁻⁵	0.13	2.03 10 ⁻⁵	0.44	1.00 10-1	1.44 10 ⁻¹	0	56.66	1.00	5.64
BGI	1.35 10 ⁻⁵	0.52	0.54	0.10	0.41	4.21 10 ⁻⁶	0.84	3.53 10 ⁻⁵	0.29	3.51 10 ⁻³	6.22 10 ⁻²	563	77.40	1.00	3.03
BGII	1.39 10 ⁻⁵	0.52	0.64	0.07	0.57	5.50 10 ⁻⁶	0.83	3.72 10 ⁻⁵	0.26	9.84 10 ⁻³	9.59 10 ⁻²	442	69.96	0.99	7.02
BWI	2.21 10 ⁻⁵	0.52	0.57	0.09	0.48	8.96 10 ⁻⁶	0.78	5.19 10 ⁻⁵	0.32	1.19 10 ⁻²	3.80 10-2	644	73.17	1.00	2.83
BWII	2.00 10 ⁻⁵	0.53	0.53	0.03	0.36	5.26 10 ⁻⁶	0.79	4.16 10 ⁻⁵	0.41	1.63 10 ⁻²	3.56 10 ⁻²	371	84.60	1.00	5.49
OI	1.35 10-5	0.53	0.50	0.10	0.22	3.23 10 ⁻⁶	0.90	3.16 10 ⁻⁵	0.42	9.70 10 ⁻⁴	2.73 10 ⁻²	762	87.63	1.00	3.41
OII	1.33 10 ⁻⁵	0.53	0.58	0.03	0.38	3.19 10 ⁻⁶	0.90	2.95 10 ⁻⁵	0.39	1.58 10 ⁻²	5.03 10 ⁻²	1077	85.53	1.00	2.49
PI	2.43 10 ⁻⁵	0.52	0.51	0.10	0.35	7.39 10 ⁻⁶	0.77	5.02 10 ⁻⁵	0.39	1.55 10 ⁻³	3.76 10 ⁻²	494	81.29	1.00	4.19
PII	3.18 10 ⁻⁵	0.52	0.54	0.002	0.77	2.40 10 ⁻⁵	0.38	4.30 10 ⁻⁵	0.45	8.52 10 ⁻²	1.92 10 ⁻¹	0	59.45	0.98	9.86

Table 1: Hydrodynamic properties of the vegetated and un-vegetated buffer microcosms

a: parameters derived from the experimental measurements. *b*: parameters estimated by inverse modelling of the bromide breakthrough curves with a dual permeability model implemented in HYDRUS 1D. **BT**: breakthrough time. **Pref. flow**: contribution of the preferential flow relative to the global outflow. The R² and RMSE values reflect the performance of the model in reproducing the bromide breakthrough curves.

Table 2: Transport characteristics of bromide and S-Metolachlor

Microcosm	Method	Bromide recovery rate	S-Metolachlor recovery rate	R_f of the matrix compartment	R _f of the macroporal compartment	R ² for the S-Metolachlor transport model
		%	%	[-]	[-]	[-]
Control	measured	71.32 – 79.19	65.52	1.90	1.90	0.50
Control	simulated	72.37 (96.29) – 78.85 (98.04)	66.73 (96.67)	1.90	1.31	acroporal tment R² for the S-Metolachlo transport model [-] [-] 0 0.50 1 0.96 8 0.81 4 0.94 7 0.99 6 0.99 9 0.98 5 0.07
	measured	77.55 – 71.33	62.86	1.81	1.78	0.81
Brome Grass	simulated	73.95 (99.97) – 69.71 (103.19)	54.80 (103.08)	1.81	1.31 0.96 1.78 0.81 2.34 0.94 3.37 0.99 2.62 0.98	0.94
Die els sue las d	measured	74.09 – 80.75	48.85	3.08	3.37	0.99
Black walnut	simulated	75.78 (99.48) – 80.70 (99.88)	47.73 (91.69)	3.08	2.62	0.98
	measured	84.27 – 78.91	50.93	3.04	3.06	0.99
PIN Oak	simulated	83.77 (102.27) – 76.75 (100.40)	43.69 (90.81)	3.04	2.69	0.98
Denler	measured	79.87 – 75.35	70.21	3.30	3.35	0.07
Popiar	simulated	80.15 (100.84) – 79.03 (100.12)	79.03 (100.19)	1.00	1.00	0.89

For the bromide recovery rates, the 2 values are those of the 2 replicates (e.g. CI and CII) measured or calculated for the duration of the experiment. For the simulated recovery rates of bromide and S-Metolachlor, the values in brackets are the values extrapolated for a volume injected being approximately 10 times the value of the pore volume. R_f is the retardation factor. For each treatment the R^2 for the S-Metolachlor transport model are given for the set of measured Kd (measured) and the set of optimized Kd (simulated).

	рН _{н20}	\mathbf{pH}_{salt}	ОМ	CEC	Sand	Silt	Clay	Texture class	Freundlich model		Linear model		
Soil			%	meq/100g	%	%	%		Kf μg ⁽¹⁻ⁿ⁾ l ⁿ kg ⁻¹	n	R²	Kd I kg⁻¹	R²
Un-vegetated control	7.2	6.6	1.3	10.1	10.0	72.5	17.5	Silt loam	3.63	0.66	0.99	0.39	0.99
Brome grass - Rhizosphere	7.7	7.1	1.3	8.1	7.5	75.0	17.5	Silt loam	2.30	0.70	0.93	0.34	0.95
Brome grass - Bulk	6.4	5.9	1.3	9.1	7.5	75.0	17.5	Silt loam	1.99	0.73	0.98	0.35	0.99
Black walnut - Rhizosphere	7.0	6.3	1.6	9.1	10.0	72.5	17.5	Silt loam	1.27	0.97	0.98	1.05	0.99
Black walnut - Bulk	6.9	6.2	1.5	8.4	10.0	72.5	17.5	Silt loam	0.79	1.04	0.95	0.92	0.99
Oak - Rhizosphere	6.8	6.1	1.5	9.0	10.0	72.5	17.5	Silt loam	0.41	1.14	0.93	0.93	0.99
Oak - Bulk	7.4	6.7	1.6	7.8	10.0	72.5	17.5	Silt loam	1.23	0.96	0.97	0.92	1.00
Poplar - Rhizosphere	7.1	6.4	1.6	10.4	10.0	72.5	17.5	Silt loam	2.24	0.88	1.00	1.03	1.00
Poplar - Bulk	7.2	6.4	1.6	10.2	10.0	72.5	17.5	Silt loam	2.50	0.84	0.98	0.99	0.97

Table 3: Comparison of the textural, chemical and sorption properties between the rhizosphere and bulk soils in the vegetated microcosms

The R² values reflect the performance of the models (linear and Freundlich) in reproducing the experimental sorption isotherms.