

Supplementary information

Plants affect the dissipation and leaching of anilide pesticides in soil mesocosms: insights from compound-specific isotope analysis (CSIA)

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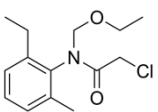
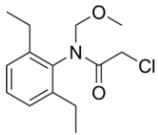
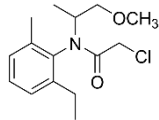
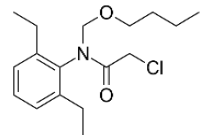
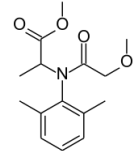
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48 **A. Physico-chemical properties of acetochlor, alachlor, S-metolachlor, butachlor and metalaxyl.**

	Acetochlor	Alachlor	S-metolachlor	Butachlor	Metalaxyl
Chemical structure					
Molecular formula ^a	C ₁₄ H ₂₀ ClNO ₂	C ₁₄ H ₂₀ ClNO ₂	C ₁₅ H ₂₂ ClNO ₂	C ₁₇ H ₂₆ ClNO ₂	C ₁₅ H ₂₁ NO ₄
Number of carbon atoms of alkoxy chain	2	1	1	4	1
Molar mass [g·mol ⁻¹] ^a	269.77	269.77	283.79	311.9	279.33
Solubility (water) [mg·L ⁻¹] ^a	282	240	480	20	8400
Bulk density [g·mL ⁻¹] ^a	1.12	1.13	1.12	1.08	1.2
Log K _{ow} ^a	4.14	3.09	3.05	4.5	1.75
K _{oc} [mL·g ⁻¹] ^a	156	335	185	700	162
Vapor pressure (25 °C) [mPa] ^a	2.2×10 ⁻²	2.9	3.7	0.24	0.75
H _{cc} 20 °C [dimensionless] ^a	2.1×10 ⁻³	3.2×10 ⁻³	8.98×10 ⁻⁷	1.54×10 ⁻⁶	1.6×10 ⁻⁵
DT ₅₀ - soil (Typical) [d] ^a	14	14	15	56	36

49 ^a Values from IUPAC <https://iupac.org/>

50 **B. Characteristics of vineyard and forest soils**

51 *1. Soil analysis*

52 Water content was measured by drying soil aliquots at 105 °C (ISO 11465). Soil
53 physicochemical parameters were determined following standard analytical procedure
54 on dried soil sieved at 2-mm. pH was measured in a 1:5 v/v soil/water (pH_w) and in 1:5
55 v/v soil/0.1N KCl solution (pH_k) (ISO 10390). Cation exchange capacity was measured
56 by the cobalt-hexamine chloride extraction method (ISO 23470). Total carbon and total
57 organic carbon (TOC) were measured by combustion on a CHN elementary analyzer
58 (ISO 10694). Prior to organic carbon measurement, the vineyard soil was decarbonized
59 using an acid fumigation. The carbonate content of the forest soil was negligible and
60 decarbonization was not necessary. The difference between total carbon and organic
61 carbon was considered to quantify carbonate content. Particle size distribution was
62 measured continuously using a laser granulometer (Beckmann Coulter LS230) and
63 converted into three classes of texture content following the WRB: <2 µm clay, 2-50
64 µm silt, 50-2000 µm sand. Major and minor elements were measured following the
65 alkaline soil fusion method (ISO 14869-2:2002) by ICP-AES and ICP-MS.
66 Mineralogical analysis was performed using X-Ray diffraction (D8 Advance Eco
67 Diffractometer).

Soil type	Vineyard soil (V)	Forest soil (F)	
Origin	Rouffach (Alsace, France)	Strengbach (Alsace, France)	
Soil sieving	< 2 mm	< 2 mm	
Treatment	Air-dried	Air-dried	
Clay (< 2 μ m) [%]	24.4	6.8	
Silt (2 - 50 μ m) [%]	61.1	31.6	
Sand (50 - 2000 μ m) [%]	14.5	61.6	
Soil texture (USDA system)	Silt Loam	Sandy Loam	
Total carbon (TC) [%]	4.0	4.5	
Total nitrogen (TN) [%]	0.3	0.2	
Organic matter (OM; loss on ignition) [%]	1.4	5.3	
pH (water)	8.0	3.4	
pH (KCl)	7.3	2.6	
Cation exchange capacity (CEC) [cmol ⁺ kg ⁻¹]	18.0	14.3	
CaCO ₃ [%]	2.9	-	
Crystalline composition	Calcite	Smectite (2:1)	
	Albite	Vermiculite (2:1)	
	Chlorite	Illite-mica (2:1)	
	Illite-mica (2:1)	Kaolinite (1:1)	
	Kaolinite (1:1)	Montmorillonite (2:1)	
Water content [%]	18.2	46.9	
Organic carbon (OC) [%]	1.1	4.5	
Bulk density (at field) [g cm ⁻³]	1.4	1.0	
Major elements [% dry soil] (ICP-AES)	SiO ₂	52.7	61.3
	Al ₂ O ₃	7.7	14.9
	MgO	1.4	0.6
	CaO	15.1	0.0
	Fe ₂ O ₃	3.2	2.6
	MnO	0.1	0.0
	TiO ₂	0.5	0.0
	Na ₂ O	0.8	0.6
	K ₂ O	1.8	4.3
P ₂ O ₅	0.4	0.2	
Trace elements [ppm] (ICP-AES)	Sr	204	71
	Ba	401	230
	Cr	74	29
	Ni	30	2
	Sc	7	5
	V	58	29

	Soil type	Vineyard soil (V)	Forest soil (F)
	Origin	Rouffach (Alsace, France)	Strengbach (Alsace, France)
	Soil size	< 2 mm	< 2 mm
	Treatment	Air-dried	Air-dried
Trace elements [ppm] (ICP-MS)	Co	9	2
	Cu	75	10
	Zn	23	10
	As	9	9
	Rb	102	411
	Y	27	10
	Zr	268	116
	Nb	11	23
	Mo	0.4	0.4
	Cd	1.3	0.5
	Sn	5.2	17.5
	Sb	1.4	3.1
	Cs	10.4	37.3
	La	29.9	25.1
	Ce	62.1	51.1
	Pr	7.2	5.8
	Nd	28.2	21.0
	Sm	6.0	3.9
	Eu	1.1	0.4
	Gd	4.7	2.5
	Tb	0.8	0.4
	Dy	4.5	1.9
	Ho	1.0	0.4
	Er	2.5	1.0
	Tm	0.2	0.2
	Yb	2.5	1.0
	Lu	0.4	0.2
	Hf	7.5	3.8
	Ta	0.9	3.9
	W	8.0	21.0
	Pb	28.3	39.5
	Th	11.0	11.3
U	2.6	3.3	

73 **C. Water holding capacity (WHC)**

74 WHC was determined by saturating soil and pressurizing them at -33kPa for 24h (Rai et
75 al., 2017). WHC for V was $34 \pm 3.5\%$ and $48 \pm 0.8\%$ for F. To homogenize water content
76 throughout the experiments, the final water content was set at 50% (W/W) in all
77 mesocosms. This corresponds to 300 mL per dry weight soil per mesocosm.

78

79 **D. Spiking mesocosms**

80 A stock solution of the pesticides mix (acetochlor, alachlor, *S*-metolachlor, butachlor,
81 metalaxyl) at 1 g/L (200 mg each compound in 200 mL) was prepared in
82 dichloromethane (DCM). An aliquot of pesticide stock solution in DCM was dissolved
83 in 100 mL of ultra-pure water (obtained from a MilliQ device) to reach the target soil
84 concentration (25 mg/kg) of the pesticide mix. The solution was stirred several hours
85 until total evaporation of DCM to achieve a homogeneous pesticides contaminated water
86 solution. The aqueous pesticide solution was used to adjust the soil water content (field
87 capacity) of each mesocosms. 100 mL of aqueous pesticide solution (150 mg/L) were
88 added per spiked mesocosms. Additionally, 200 mL of ultra-pure water were used to
89 rinse the glass-beakers and the remaining amount of pesticides was transferred by
90 capillarity from the bottom of the soil mesocosms (final amount of 180 mg of
91 pesticides).

92

93 **E. Preparation and application of artificial rainfalls**

94 The artificial rainwater was prepared according to the ERMCA408 reference material
95 (ERM certification report, 2010) with sterile ultra-pure water and targeted a pH of 6.3
96 ± 0.6 . Artificial rainfalls were applied by pumping rainwater using a five-holes tube

97 peristaltic pump. Rainfall characteristics are shown in Table S1. Rainfall covered the
98 whole surface of each mesocosms (201 cm²).

99 **Table S1.** Characteristics of rainfalls applied on days 45, 60 and 75 across the experiment.

Pattern description	Duration (min)	Intensity (mm/h)	Rate (mL/min)	Volume (mL)
Mid-lasting pattern with intermediate intensity	12	62	25	300

100

101 **F. Samples collection and preparation**

102 *Bulk soil:* Bulk soil samples consisted in mesocosms soil from unplanted
103 mesocosms. In planted mesocosms, bulk soil consisted in the easily detached soil
104 fraction after manually shaking plants.

105 *Rhizosphere:* The rhizosphere fraction was obtained from planted mesocosms. An
106 adapted protocol from Barillot et al., (2013) was used to collect rhizosphere soil
107 attached to the roots. Briefly, roots and rhizosphere soil were shaken vigorously in ultra-
108 pure water. Ultra-pure water was replaced until water remained clean (at least three
109 times), so that rhizosphere soil is detached from the roots. Remaining rhizosphere was
110 obtained as a suspension, centrifuged (4000 rpm at 4°C for 20 min) to separate solid
111 from liquid phase and pooled all aliquots. Concentration of pesticides was determined in
112 both phases and results were pooled for the whole rhizosphere. In bulk soil and
113 rhizosphere samples, determination of pH and CEC was done following methods
114 explained in SI-B1.

115 *Roots:* Roots were ultrasonicated for 30 min and collected using a 1 mm-sieve.
116 They were rinsed again with ultra-pure water and when clean, they were dried (60 °C, 1
117 week). Roots were considered clean when adhering soil particles were removed. The

118 presence of soil on roots was checked with binoculars. When particles were found on
119 roots, a brush was used to discard them.

120 *Aerial part:* One sample per planted mesocosms was obtained at day 75 by cutting
121 the green part from the stem basis. Samples were washed separately with ultrapure
122 water.

123 *Leachates:* Leachates were collected after each rainfall (L1 on day 45, L2 on day
124 60 and L3 on day 75) in a collector below the mesocosms. Each mesocosms was left for
125 12h in the climate chamber to allow complete rain leaching. Pesticides and chemical
126 characterization (pH, DOC, major cations and anions and minor elements) were
127 determined in the leachates separately for each mesocosm. Pesticides were determined
128 by GC-MS and major and minor elements were determined by ICP-AES, and ICP-MS
129 and ionic chromatography (ICS5000- Thermo-Fisher). pH determination was carried
130 out using a calibrated pH-electrode.

131

132 **G. Pesticides extraction**

133 1. *Extraction from soils/rhizosphere*

134 Soil extraction and cleaning procedure were adapted from methods described by Ivdra
135 et al. (2014). Soil samples (around 5 g dry soil) were put into a 15 mL centrifuge tubes,
136 mixed with 3 mL of the extraction solvent (DCM:Pentane 3:1) and vortexed 5 s
137 followed by 5 min into ultrasonic bath (Branson 5510, 40 kHz) to homogenize it. In
138 order to increase extraction efficiency, Millipore ultra-pure water was added to reach
139 50% (W/W) when necessary. Samples were then vortexed for 1 min and centrifuged for
140 5 min at 5000 rpm. The supernatant was transferred to amber glass vials and the
141 extraction procedure was repeated twice without further addition of water. The resulting

142 supernatants from the three extraction cycles were combined and concentrated under a
143 gentle nitrogen stream at room temperature to the last drop and adjusted to 1 mL of
144 acetonitrile. The extracts were dried over anhydrous MgSO₄, and cleaned up using 12.5
145 mg PSA and 75 mg MgSO₄. After vortexing the mixture for 30 s and centrifuging at
146 5000 rpm for 90 s, the supernatant was transferred to clean GC vials and stored in the
147 dark at -20°C until quantification and carbon isotopic analysis.

148 2. *Extraction from leachates*

149 Extraction cartridges were washed successively with 5 mL ethanol, rinsed with ACN (5
150 mL), and conditioned with deionized water (10 mL). Up to 6 samples were loaded on
151 parallel cartridges which was then dried under nitrogen flux for 10 min. The pesticides
152 were eluted by 5 mL of EtOAc followed by 5 mL of ACN. The extracts were
153 subsequently concentrated under nitrogen flux to 1 droplet, and adjusted to 1 mL with
154 of ACN for quantification and carbon isotopic composition analyses. Validity of the
155 method was previously developed by Elsayed et al., (2014).

156

157 **H. Pesticides quantification by GC-MS**

158 All pesticides were analyzed by gas chromatography (GC, Trace 1300, Thermo Fisher
159 Scientific) coupled with a mass spectrometer (MS, ISQ™, Thermo Fisher Scientific).
160 Metolachlor-*d*₁₁ was automatically added to each sample as an internal standard at a
161 constant concentration using a TriPlus RSH™ system (Thermo Fisher Scientific).
162 Samples (1.5 µL volume) and internal standard (1 µL at 1000 µg/L) were injected into a
163 split/splitless injector operated in split mode with a split flow at 6.0 mL/min and held at
164 280°C. Separation was performed on a TG-5MS column (30 m × 0.25 mm ID, 0.25 µm
165 film thickness), with helium as carrier gas at a 1.5 mL/min flow rate. The GC oven

166 program was held at 50°C for 1 min, ramped to 160°C at 30°C/min, then to 220°C at 4
 167 °C/min, and finally, to 300°C at 30 °C/min held for 1 min. The MS transfer line and
 168 source were heated at 320°C. Each sample was measured in triplicate. Characteristics of
 169 GC-MS measurements for all pesticides are provided below (Table S2).

170 **Table S2** Environmental limits of detection (LOD), limits of quantification (LOQ), and
 171 accuracy of GC-MS measurements of ACE, ALA, SM, BUT and MTY in samples.

Compound	GC-MS		
	LOD [$\mu\text{g/L}$]	LOQ [$\mu\text{g/L}$]	Accuracy [%]
Acetochlor	7.5	22.7	100.0 \pm 7.5
Alachlor	7.6	23.0	98.5 \pm 6.6
S-Metolachlor	6.5	19.6	98.7 \pm 5.5
Butachlor	5.7	17.4	98.6 \pm 5.4
Metalaxyl	7.1	21.4	99.7 \pm 7.8

172
 173 Recoveries of the extraction method were evaluated by spiking a stock solution of all
 174 pesticides in soil samples in a concentration ranged from 0.5 to 150 $\mu\text{g/g}$. Pesticides
 175 extraction was performed one day after spiking while samples were storage in the fridge
 176 (24h, 4 °C). Recoveries are provided in Table S3.

177

178 **Table S3** Recovery rate of ACE, ALA, SM, BUT and MTY from soil samples.

	Vineyard soil ^a	Forest soil ^a
	Recovery [%]	Recovery [%]
ACE	59.5 \pm 2.2	49.8 \pm 3.5
ALA	59.5 \pm 2.0	47.9 \pm 3.0
SM	63.9 \pm 1.9	49.2 \pm 2.9
BUT	39.0 \pm 1.7	30.8 \pm 2.2
MTY	67.8 \pm 2.6	57.8 \pm 2.9

179 ^a Means of measurements ($n = 3$) of 12 soil extraction experiments with a concentration rage from 0.5 to 150 $\mu\text{g/g}$ of
 180 the pesticide mix.

181 **I. EA-IRMS and GC-C-IRMS methods for pesticides analysis**

182 The carbon/nitrogen isotope compositions were determined using a GC-C-IRMS system
 183 consisting of a TRACE™ Ultra Gas Chromatograph (ThermoFisher Scientific) coupled via a
 184 GC IsoLink/Conflow IV interface to an isotope ratio mass spectrometer (DeltaV plus,
 185 ThermoFisher Scientific). The oxidation furnace of the interface consisted of a Ni/Cu/Pt
 186 reactor and was set to a temperature of 1000°C. A TG-5MS column (60 m × 0.25 mm ID,
 187 0.25 µm film thickness) was used for chromatographic separation, with helium as the carrier
 188 gas at a flow rate of 1.5 mL min⁻¹. For carbon analysis, the column was held at 50 °C for 1
 189 min, heated at a rate of 15°C·min⁻¹ to 150 °C, then up to 250 °C at 2°C·min⁻¹ and then
 190 heated at 20°C·min⁻¹ to 300 °C and held for 3 min. For nitrogen analysis, the column was
 191 held at 50°C for 1 min, heated at a rate of 20 °C·min⁻¹ to 150 °C, then up to 270 °C at
 192 10°C·min⁻¹ and then heated at 30°C·min⁻¹ to 300 °C and held for 3 min. Samples and
 193 standards (0.5 to 3.5 µL volume) were injected into a split/splitless injector operated in
 194 splitless mode and held at 250°C.

195 **EA-IRMS and GC-C-IRMS instrumental parameters for pesticides analysis**

Compound	EA-IRMS		GC-C-IRMS		MDL				Linearity ranges	
	$\delta^{13}\text{C}$ [‰ vs. VPDB] ^a (n = 2) external (SD)	$\delta^{13}\text{C}$ [‰ vs. VPDB] (n = 2) EA-IRMS (our lab) (SD)	$\delta^{13}\text{C}$ [‰ vs. VPDB] ^b (n = 12) (SD)	$\Delta\delta^{13}\text{C}$ [‰ vs. VPDB] ^c (SD)	Amount of C injected on column		Amount of compound injected		Ampl m/z 44 at MDL	Amount of compound injected
					[ng]	[nmol]	[pmol] on column	[mg/L] in solution	[mV]	[mg/L] in solution
ACE	-29.3 (<0.1)	-28.6 (<0.1)	-29.6 (0.2)	-0.4 (0.1)	17.2	1.5	106	9.5	1264	10 - 200
ALA	-29.4 (<0.1)	n.d.	-29.6 (0.3)	-0.3 (0.1)	17.0	1.4	103	9.3	767	10 - 200
SM	-30.9 (<0.1)	-30.2 (0.2)	-30.6 (0.6)	-0.6 (0.1)	18.8	1.6	95	9.8	1044	10 - 200
BUT	-26.8 (<0.1)	-26.5 (<0.1)	-27.0 (0.4)	-0.8 (0.1)	15.7	1.3	76	7.2	1322	10 - 200
MTY	-31.5 (<0.1)	-31.3 (<0.1)	-31.9 (0.3)	-0.4 (0.2)	16.1	1.4	93	9.6	874	10 - 200

196 ^a For comparison, the same standards were also measured at OEA laboratories. UK. on an EA-IRMS (EuroVector.
197 Milan. Italy) coupled via a ConFlo III (open split. Thermo Fisher Scientific. Bremen. Germany) to a MAT 253
198 isotope ratio mass spectrometer (Thermo Fisher Scientific)
199 ^b Reported $\delta^{13}\text{C}$ errors correspond to the standard deviation (1σ) calculated from triplicate measurements of duplicate
200 tests.
201 ^c The error associated with $\Delta\delta^{13}\text{C}$ values was calculated via error propagation based on ± 1 SD of mean $\delta^{13}\text{C}$ value.
202 $\Delta\delta^{13}\text{C}$ values were determined as the difference between the measured $\delta^{13}\text{C}$ value of each compound standard
203 obtained by EA-IRMS and the mean $\delta^{13}\text{C}$ value of the corresponding standards, obtained by replicate injections in
204 GC-C-IRMS systems under optimal conditions.
205 SD: Standard deviation. MDL: method detection limit. N.d.: not detected.

206 **J. Carbon stable isotope fractionation ($\Delta\delta^{13}\text{C}$) for soil extraction procedure**

207 The effect of the pesticide extraction procedure on $\delta^{13}\text{C}$ values of ACE, ALA, SM, BUT
208 and MTY was evaluated by spiking into ultra-pure water a DCM stock solution of ACE,
209 ALA, SM, BUT and MTY standards with known isotope signature to determine the
210 offset generated by the extraction procedure. ACE, ALA, SM, BUT and MTY
211 concentrations in the soil of ranged from 0.5 up to 150 mg/kg. Solutions were stirred for
212 1 h until evaporation of the solvent to achieve a homogeneous, pesticide-contaminated
213 water solution. Each soil (about 5 g) was then spiked with a pesticide mixture. Water
214 content of soil samples was adjusted to 50% (W/W) for both vineyard and forest soils.
215 Samples were stirred vigorously for 1 h for homogenization, and incubated one day in
216 the dark at 4°C prior to extraction. Each condition was tested in duplicate. Extraction
217 was performed using the procedures described above (section G.1).

218 The impact of the extraction of ACE, ALA, SM, BUT and MTY from soil matrices on
219 efficiency and isotope fractionation varied among compounds and soil types. The study
220 confirmed the absence of significant fractionation effects for all pesticides ($\Delta\delta^{13}\text{C} <$
221 1‰), even at low concentrations outside the previously established linearity range (Table
222 S4).

223

224 **Table S4** Carbon isotopic fractionation ($\Delta\delta^{13}\text{C}$) associated with the extraction of ACE, ALA,
225 SM, BUT and MTY for the vineyard and the forest soils. The offset generated by the soil
226 extraction did not significantly change regardless the initial amount of pesticides.

Pesticide	Vineyard ^a	Forest ^a
	$\Delta\delta^{13}\text{C}^{\text{b}}$ [‰ vs VPDB] \pm SD	
Acetochlor	-0.1 \pm 0	0 \pm 0.1
Alachlor	-0.2 \pm 0	-0.1 \pm 0.1
S-metolachlor	-0.7 \pm 0.1	-0.5 \pm 0

Butachlor	-1 ± 0.1	-0.8 ± 0.1
Metalaxyl	0.1 ± 0.2	-0.2 ± 0.2

227 ^a Means of measurements ($n > 3$) of 12 individual soil extraction experiments with different concentrations of ACE,
 228 ALA, SM, BUT and MTY.

229 ^b The error given for the $\Delta\delta^{13}\text{C}$ values was calculated *via* error propagation based on ± 1 SD of mean ^{13}C values from
 230 $n = 3$ measurements for each sample. $\Delta\delta^{13}\text{C}$ values were determined as the difference between the measured $\delta^{13}\text{C}$
 231 value of a given compound in the extract and the mean $\delta^{13}\text{C}$ value of the corresponding standard obtained by replicate
 232 injections in the GC-C-IRMS.

233

234 **K. Nitrogen stable isotope fractionation ($\Delta\delta^{15}\text{N}$) for leachate extraction procedure**
 235 **with SPE of *S*-metolachlor (SM)**

236 Pesticides were extracted from leachates following a protocol adapted from US EPA
 237 method 525.2 and described by Elsayed et al. (2014). Briefly, a SPE (solid phase
 238 extraction) procedure was followed, using SolEx C18 cartridges (1 g, Dionex®, CA,
 239 USA) on an AutoTrace 280 SPE system (Dionex®, CA, USA).

240

241 EA-IRMS and GC-C-IRMS instrumental parameters for N-CSIA of SM

242

Compound	EA-IRMS		GC-C-IRMS			$\Delta\delta^{15}\text{N}$ associated with SPE extraction
	$\delta^{15}\text{N}$ [‰ vs. AIR] ^a ($n = 2$) internal (SD)	$\Delta\delta^{15}\text{N}$ [‰ vs. AIR] ^b (SD)	MDL			$\Delta\delta^{15}\text{N}$ [‰ vs. AIR] (SD)
			Amount of N injected on column [ng]	Amount of compound injected [mg/L] in solution	Ampl m/z 28 at MDL [mV]	
SM	0.5 (<0.1)	0.1 (0.7)	17	113	150	0.0 (0.5)

243 ^a For comparison, the same standards were also measured using an EA-IRMS ((Flash EA IsoLinkTMCN IRMS,
 244 Thermo Fisher Scientific, Bremen, Germany).

245 ^b The error given for $\Delta\delta^{15}\text{N}$ values was calculated *via* error propagation based on ± 1 SD of mean ^{15}N values. $\Delta\delta^{15}\text{N}$
 246 values were determined as the difference between the measured $\delta^{15}\text{N}$ value of a given compound in the extract and
 247 the mean $\delta^{15}\text{N}$ value of the corresponding standard obtained by replicate injections in the GC-C-IRMS systems
 248 optimal conditions.

249 SD: Standard deviation. MDL: method detection limit. N.d.: not detected.

250 **L. Water mass budget**

251 Overall water budget of the mesocosms throughout the experiment.

	Soil	Initial soil water content	Rainfall per application ^a	L45	L60	L75	ETP
Total water volume leached [mL]		300	300	217.4 ± 19.5	235.0 ± 21.1	228.9 ± 19.4	5.7 ± 5.6
Rainfall volume leached out [%]	vineyard	planted		72.5 ± 6.5	78.3 ± 7.0	76.3 ± 6.5	
Rainfall volume retained in mesocosms [%]		unplanted		35.1 ± 3.0	35.5 ± 6.3	34.4 ± 3.0	
	vineyard	300	300	240.4 ± 4.7	254.4 ± 1.6	240.9 ± 8.7	
		unplanted		80.1 ± 1.6	84.8 ± 0.5	80.3 ± 2.9	
	forest	300	300	30.3 ± 1.5	29.3 ± 1.2	30.3 ± 2.3	
		planted		115.6 ± 13.4	115.3 ± 28.2	76.6 ± 9.3	10.6 ± 5.0
	forest	300	300	38.5 ± 4.5	38.4 ± 9.4	25.5 ± 3.2	
		unplanted		61.4 ± 3.0	68.4 ± 5.1	64.1 ± 0.7	
	forest	300	300	101.4 ± 23.9	132.3 ± 43.3	74.0 ± 6.7	
		unplanted		33.8 ± 8.0	44.1 ± 14.4	24.7 ± 1.2	
	forest	300	300	58.6 ± 1.9	61.1 ± 8.0	58.2 ± 1.1	

252 L45 (n=3), 60 (n=2) and L75 (n=2) represent leachates collected at those times. ETP: average potential evapotranspiration throughout the incubation.

253 ^a Three rainfalls applied. Uncertainty corresponds to mean standard deviation (SD).

254 **M. Pesticide mass budget**

255 Pesticides loads in leachates (t45, 60 and 75) and mass budget in soil and rhizosphere (t1, 45 and 75) throughout the experiment.

Soil type	Incubation [days]	ACE		ALA		SM		BUT		MTY		
		Leachate pesticide loads [µg]	Pesticide in soil/rhizosphere [µg]	Leachate pesticide loads [µg]	Pesticide in soil/rhizosphere [µg]	Leachate pesticide loads [µg]	Pesticide in soil/rhizosphere [µg]	Leachate pesticide loads [µg]	Pesticide in soil/rhizosphere [µg]	Leachate pesticide loads [µg]	Pesticide in soil/rhizosphere [µg]	
Vineyard	Planted	1	-	14945±144	-	14492±160	-	14945±353	-	10237±248	-	14953±565
		45		483±3/8.3±2.								
		60	195±13	1	295±7	641±3/0	362±41	900±18/10.8±3.0	505±6	485±0/3.3±4.7	979±47	2470±69/11±7
		75	1.2±1.0	-	2.9±0.4	-	31±21	-	1.8±0.2	-	156±11	-
	Unplanted	1		120±0/3.9±1.5	0.5±0.0	167±6/3.5±5.0	21±5	190±29/12.1±7.7	12±1	126±0/2.0±2.2	118±25	433±187/13±8
		45	0.7±0.5									
		60	-	14946±505	-	14492±405	-	14946±544	-	10237.3±76.6	-	14953±751
		75	326±124	496±5	387±101	658±3	813±135	1520±79	597±24	478.7±1.1	1719±243	1626±74
Forest	Planted	1	-	14946±128	-	14953±698	-	14946±493	-	12264.7±154.1	-	14954±779
		45		2887±300/37.8±1.0								
		60	102±7	.8±1.0	204±92	3450±38/52±0	210±92	7349±829/63±0	91±8	3518±364/42±1	420±143	11380±984/100±2
		75	0.6±0.0	-	1.0±0.1	-	4.6±0.7	-	1.7±0.2	-	14±7	-
	Unplanted	1		544±278/3.9±0.8	0.9±0.2	660±367/3.5±1.5	1.9±0.7	2368±1330/12±3	21±5	356±269/4.3±1.4	15±6	6228±1185/14±17
		45	0.4±0									
		60	-	14946±68	-	14954±63	-	14946±55	-	12265±722	-	14954±192
		75	109±28	2191±164	161±35	2395±192	167±38	3726±632	127±48	1746±153	361±101	6355±1291
Unplanted	1											
	45	6.2±6.0	-	7.7±7.0	-	12±6	-	2.8±0.7	-	50±31	-	
	60	0.9±0.2	1047±319	1.4±0.2	1350±498	3.0±0.5	3666±675	15±9	549±393	20±7	6179±20	
	75											

- Not applicable

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258 **N. Dissipation kinetics calculations**

259 Single First-Order Rate Model (SFO) was applied to the dataset:

260 $C_t = C_0 e^{-k \cdot t}$ Equation S1

261 The linear form of the single first-order equation is:

262 $\ln \frac{C_t}{C_0} = -k \cdot t$ Equation S2

263 Where, C_t = concentration at time t, C_0 = initial concentration, k = rate constant of decline 1/days, t = time

264 The half-life or time needed for the degradation of 50% of initial pesticide concentration (DT_{50} or $T_{1/2}$, days) was estimated from equation:

265 $DT_{50} = T_{1/2} = \frac{\ln \left[\frac{C_0}{\frac{C_0}{2}} \right]}{k} = \frac{0.693}{k}$ Equation S3

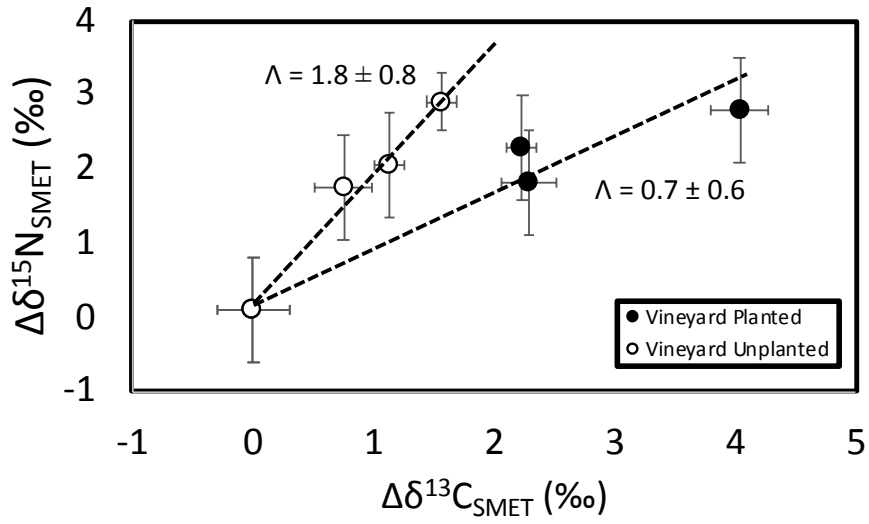
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267 **Table S5.** Summary of k and $T_{1/2}$ values obtained for acetochlor, alachlor, *S*-metolachlor, butachlor and metalaxyl in soil mesocosms

Soil		k (days ⁻¹)					T _{1/2} (days)					
		ACE	ALA	SM	BUT	MTY	ACE	ALA	SM	BUT	MTY	
Vineyard	Planted	0.069	0.054 ± 0.018	0.058	0.176 ± 0.179	0.042	10.1	14.0 ± 5.4	12.0	7.0 ± 4.5	16.6	
	Unplanted	0.069	0.054 ± 0.017	0.047	0.171 ± 0.183	0.050	10.1	14.0 ± 5.4	14.8	10.7 ± 2.1	13.8	
Forest	Planted	0.037	0.033	0.017	0.092 ± 0.095	0.013	19.5	21.8	51.5	20.5 ± 9.1	54.3	
	Unplanted	0.035	0.032	0.022	0.095 ± 0.092	0.013	19.8	21.5	33.1	16.6 ± 0.8	56.9	
268	Uncertainty	not	given	for	ACE,	ALA,	SM,	MTY,	when	n	<	3.

269 **O. Dual isotope plots and Lambda (Λ) values**

270 Dual isotope plot ($\delta^{15}\text{N}$ vs. $\delta^{13}\text{C}$) of data for SM in the vineyard planted and unplanted
271 mesocosms.



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