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Supplement of

Pesticide fate on catchment scale: conceptual modelling of stream CSIA data

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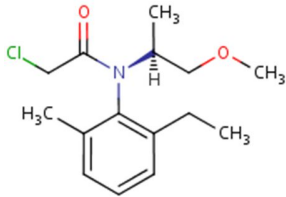
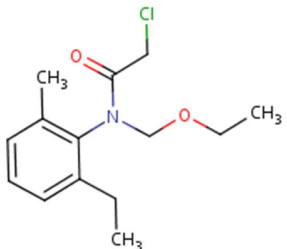
1 **S1. Compound properties**

2 Metolachlor consists of four stable stereoisomers; S-metolachlor (Table S1) denotes the two
 3 herbicidally active stereoisomers of metolachlor. S-metolachlor is classified as moderately
 4 water-soluble (480 mg L⁻¹) and moderately mobile in soil (Log K_{oc} between 1.79 and 2.57).

5 Acetochlor has a moderate solubility (282 mg L⁻¹) and mobility in soil (Log K_{oc} of 2.19).

6 The current commercial formulations of metolachlor have been enriched to contain more than
 7 80% of the herbicidally active S-enantiomer (S-metolachlor), and progressively replaced racemic
 8 metolachlor in the 2000s (Buser et al., 2000).

9 **Table S1.** Compound properties of the two study compounds.^a

	S-metolachlor	Acetochlor
		
Chemical formula	C ₁₅ H ₂₂ ClNO ₂	C ₁₄ H ₂₀ ClNO ₂
Molecular mass [g mol ⁻¹]	283.8	269.8
Solubility in water at 20°C [mg L ⁻¹]	480	282
Henry's law constant at 25°C [Pa·m ³ mol ⁻¹]	2.2·10 ⁻³	2.1·10 ⁻³
Log K _{OC} ^b	1.79 - 2.57 ^c	2.19
Soil half-life [d]	15 - 54 ^d	14
Half-life for hydrolysis in water [d]	stable	stable

^a Source: University of Hertfordshire (2013); TOXNET database (U.S. National Library of Medicine; <http://toxnet.nlm.nih.gov>).

^b Soil organic carbon-water partition coefficient

^c Alletto et al., 2013

^d Lefrancq, 2014

10

11

12 **S2. Formulation of the storage selection (SAS) function**
 13

14 The SAS function was approximated by a beta distribution defined by the mixing parameter
 15 $m_Q(t)$ (cf. van der Velde et al., 2015). The latter depends on the model parameters α_Q and β_Q :

$$m_Q(t) = \alpha_Q \left(1 - \beta_Q \frac{S(t) - S_{min}}{S_{max} - S_{min}} \right) \quad (S1)$$

16 where S_{min} and S_{max} are the minimum and maximum transport zone storage, respectively. The
 17 parameter α_Q ranges between 0.2 and 1.9, and β_Q ranges between 0 and 0.95 (see Table 3). Under
 18 dry conditions, $m_Q(t)$ approaches α_Q and will primarily lead to old water discharge, whereas,
 19 under wet conditions, $m_Q(t)$ approaches $\alpha_Q(1-\beta_Q)$ and will primarily lead to young water
 20 discharge. Hence, the SAS function results in preference for young water if $m_Q(t) < 1$, preference
 21 for old water if $m_Q(t) > 1$, and a uniform distribution if $m_Q(t) = 1$ (i.e., “random sampling” of
 22 outflow from storage; see Fig. 1 in van der Velde et al., 2015).

23 **S3. Measured concentrations and $\delta^{13}C$ -values at the plot, drain, and catchment outlet**
 24 **for S-metolachlor and acetochlor**
 25

26 **Table S2.** Concentrations and $\delta^{13}C$ -values at the plot (\pm standard deviation)

Sample name	Date	S-metolachlor		Acetochlor	
		Concentration [$\mu\text{g L}^{-1}$]	$\delta^{13}C$ [‰]	Concentration [$\mu\text{g L}^{-1}$]	$\delta^{13}C$ [‰]
Application tank			-31.9 \pm 0.31		
PW4	10.04.12	0.36 \pm 0.01	n.d. ^a	0.00	0.00
PW5	17.04.12	64.10 \pm 8.59	n.d.	1.75 \pm 0.15	
PW7	02.05.12	36.16 \pm 2.39	-31.60 \pm 0.28	0.00	0.00
PW9	15.05.12	48.73 \pm 1.50	n.d.	0.00	0.00
PW10	22.05.12	40.85 \pm 1.37	-32.20 \pm 0.14	0.48 \pm 0.08	-33.20 \pm 0.19
PW11	29.05.12	27.12 \pm 0.75	-32.10 \pm 0.29	0.30 \pm 0.11	-34.20 \pm 0.07
PW13	12.06.12	19.08 \pm 0.75	n.d.	0.00	n.d.
PW14	19.06.12	7.80 \pm 0.55	-30.70 \pm 0.29	0.23 \pm 0.00	-29.90 \pm 0.32
PW17	10.07.12	10.75 \pm 0.17	-29.60 \pm 0.12	0.00	n.d.
PW18	16.07.12	14.90 \pm 0.04	n.d.	0.00	n.d.

a not determined

27

28 **Table S3.** Concentrations at the drain outlet (\pm standard deviation)

Sample name	Date	S-metolachlor [$\mu\text{g L}^{-1}$]	Acetochlor [$\mu\text{g L}^{-1}$]
DW1	20.03.12	0.000	0.000
DW3	03.04.12	0.000	0.226 \pm 0.009
DW4	10.04.12	0.000	0.000
DW5	17.04.12	0.097 \pm 0.003	0.000
DW6	24.04.12	0.000	0.501 \pm 0.007
DW7	02.05.12	0.314 \pm 0.092	0.226 \pm 0.005
DW8	09.05.12	0.000	0.234 \pm 0.002
DW9	15.05.12	0.000	0.000
DW10	22.05.12	2.208 \pm 1.319	0.853 \pm 0.054
DW11	29.05.12	0.284 \pm 0.161	0.000
DW12	05.06.12	0.207 \pm 0.007	0.000
DW13	12.06.12	0.363 \pm 0.027	0.000
DW14	19.06.12	0.187 \pm 0.007	0.330 \pm 0.002
DW15	26.06.12	0.341 \pm 0.354	0.000
DW16	03.07.12	0.338 \pm 0.049	0.000
DW17	10.07.12	0.161 \pm 0.052	0.000

29

30 **Table S4.** Concentrations and $\delta^{13}\text{C}$ -values at the catchment outlet (\pm standard deviation)

Sample name	Date	S-metolachlor		Acetochlor	
		Concentration [$\mu\text{g L}^{-1}$]	$\delta^{13}\text{C}$ [‰]	Concentration [$\mu\text{g L}^{-1}$]	$\delta^{13}\text{C}$ [‰]
CW1	20.03.12	0.07 \pm 0.01	n.d. ^a	0.00	n.d.
CW2	27.03.12	0.00	n.d.	0.20 \pm 0.01	n.d.
CW3	03.04.12	0.00	n.d.	0.21 \pm 0.00	n.d.
CW4	10.04.12	0.00	n.d.	0.00	n.d.
CW5	17.04.12	0.00	n.d.	0.00	n.d.
CW6	24.04.12	0.00	n.d.	0.00	n.d.
CW7- α	02.05.12	0.00	n.d.	0.00	n.d.
CW7- β	02.05.12	1.06 \pm 0.00	n.d.	0.00	n.d.
CW8	09.05.12	0.00	n.d.	0.24 \pm 0.01	n.d.
CW9	15.05.12	0.00	n.d.	0.00	n.d.
CW10- α	21.05.12	62.09 \pm 1.63	-32.20 \pm 0.18	59.33 \pm 0.84	-28.99 \pm 0.24
CW10- β	21.05.12	40.23 \pm 2.70	-32.39 \pm 0.18	29.18 \pm 0.28	-29.65 \pm 0.15

CW10- γ	21.05.12	16.38±0.53	-31.59±0.70	31.09±0.54	-29.68±0.16
CW11	29.05.12	6.46±0.54	-31.81±0.31	1.08±0.16	-29.76±0.29
CW12	05.06.12	1.21±0.27	n.d.	0.31±0.00	n.d.
CW13- α	07.06.12	0.45±0.03	n.d.	0.49±0.06	n.d.
CW13- β	07.06.12	2.79±0.32	n.d.	1.07±0.02	n.d.
CW13- γ	09.06.12	1.67±0.05	n.d.	0.54±0.02	n.d.
CW14	19.06.12	1.69±0.20	-30.59±0.12	0.40±0.05	-25.61±0.87
CW15	26.06.12	0.04±0.00	n.d.	0.00	n.d.
CW16- α	28.06.12	0.28±0.03	n.d.	0.00	n.d.
CW16- β	28.06.12	0.19±0.01	n.d.	0.00	n.d.
CW16- γ	03.07.12	0.17±0.01	n.d.	0.00	n.d.
CW17- α	06.07.12	0.58±0.01	n.d.	0.00	n.d.
CW17- β	07.07.12	0.24±0.01	n.d.	0.22±0.00	n.d.
CW17- γ	07.07.12	0.68±0.02	n.d.	0.00	n.d.
CW17- χ	07.07.12	0.33±0.00	n.d.	0.00	n.d.
CW18	17.07.12	0.28±0.01	-29.74±0.79	0.00	n.d.
CW19	24.07.12	0.17±0.07	n.d.	0.00	n.d.
CW20	31.07.12	0.14±0.00	n.d.	1.89±0.00	n.d.
CW21	08.08.12	0.14±0.00	n.d.	0.00	n.d.
CW22	14.08.12	0.11±0.00	n.d.	1.19±0.00	n.d.
CW23	21.08.12	0.00	n.d.	0.00	n.d.
CW24	20.11.12	0.10±0.00	n.d.	0.00	n.d.

a not determined

31

32

33 **S4. Calculation of the extent of degradation for a sample at the catchment outlet**

34 A conservative estimate of the extent of degradation for some environmental sample can be

35 obtained from the Rayleigh equation approach (Elsner and Imfeld, 2016; Mariotti et al., 1981;

36 Rayleigh, 1896):

$$f_{deg} = \left(\frac{R_S}{R_0}\right)^{\frac{1}{\alpha-1}} \quad (S2)$$

37 where R_0 is the isotope ratio (e.g., $^{13}\text{C}/^{12}\text{C}$) of the contaminant at the contamination source, R_S is

38 the isotope ratio of the contaminant in an environmental sample at some distance from the

39 source, f_{deg} represents the remaining fraction of the contaminant in the sample relative to the

40 source, and α is the kinetic isotope fractionation factor (commonly reported in per mil (‰) as the
41 kinetic isotopic enrichment factor; $\varepsilon = (\alpha - 1)$, where $\alpha < 1$). In this study, we applied Eq. (S2) to
42 the simulated CSIA data at the catchment outlet, and calculated the extent of degradation based
43 on the Rayleigh equation approach as:

$$D_{Rayleigh}[\%] = (1 - f_{deg}) \cdot 100 \quad (S3)$$

44 In order to evaluate the potential use of the Rayleigh equation approach for catchment-scale
45 applications, we compared $D_{Rayleigh}$ to the “true” extent of degradation at the catchment outlet
46 (D_{Sample}), which is given by the ratio between the simulated outlet concentrations of S-
47 metolachlor (C_{met} ; the sum of its light and heavy carbon isotopes) and a conservative tracer
48 (C_{trac}):

$$D_{Sample}[\%] = \left(1 - \frac{C_{met}}{C_{trac}}\right) \cdot 100 \quad (S4)$$

49

50 **S5. Objective functions for optimization and parameter identifiability via optimization**

51 Parameters were optimized against the N_C , N_Q and $N_{\delta 13C}$ coefficients simultaneously by using the
 52 combined objective function $N_{comb} = (N_Q/6 + N_C + N_{\delta 13C}) / (13/6)$. The factor 1/6 for N_Q , which
 53 was determined via prior test calibration runs, ensures that all three terms contribute
 54 approximately evenly during the optimization process.

55 N_Q compares measured to modelled discharge at the catchment outlet, considering the best fit
 56 in a window of plus or minus one day to account for potential time lags of measured discharge in
 57 response to rainfall events:

$$N_Q = 1 - \left(\frac{\min(\sum_{t=1}^n (Q_{t,mod} - Q_{t,meas})^2, \sum_{t=1}^n (Q_{t-1,mod} - Q_{t,meas})^2, \sum_{t=1}^n (Q_{t+1,mod} - Q_{t,meas})^2)}{\sum_{t=1}^n (Q_{t,meas} - \overline{Q_{meas}})^2} + 0.03 \cdot f \right) \quad (S5)$$

58 where n is the total number of days with discharge measurements, $Q_{t,mod}$ and $Q_{t,meas}$ are the
 59 modelled and measured discharge on day t , respectively, $Q_{t-1,mod}$ and $Q_{t+1,mod}$ are the modelled
 60 discharge one day before and after day t , respectively, $\overline{Q_{meas}}$ is the mean of the measured
 61 discharge values, and f counts the number of days where the modelled discharge is zero while the
 62 measured discharge is not, or vice versa (weighted by a factor of 0.03).

63 N_C considers errors in normal and ln-transformed concentration values, with the latter
 64 emphasizing deviations at low concentrations:

$$N_C = 1 - 0.5 \cdot \left(\frac{\sum_{i=1}^n tw_i \cdot (C_{i,mod} - C_{i,meas})^2}{\sum_{i=1}^n tw_i \cdot (C_{i,meas} - \overline{C_{meas}})^2} + \frac{\sum_{i=1}^n tw_i \cdot (\ln(C_{i,mod}) - \ln(C_{i,meas}))^2}{\sum_{i=1}^n tw_i \cdot (\ln(C_{i,meas}) - \overline{\ln(C_{meas})})^2} \right) \quad (S6)$$

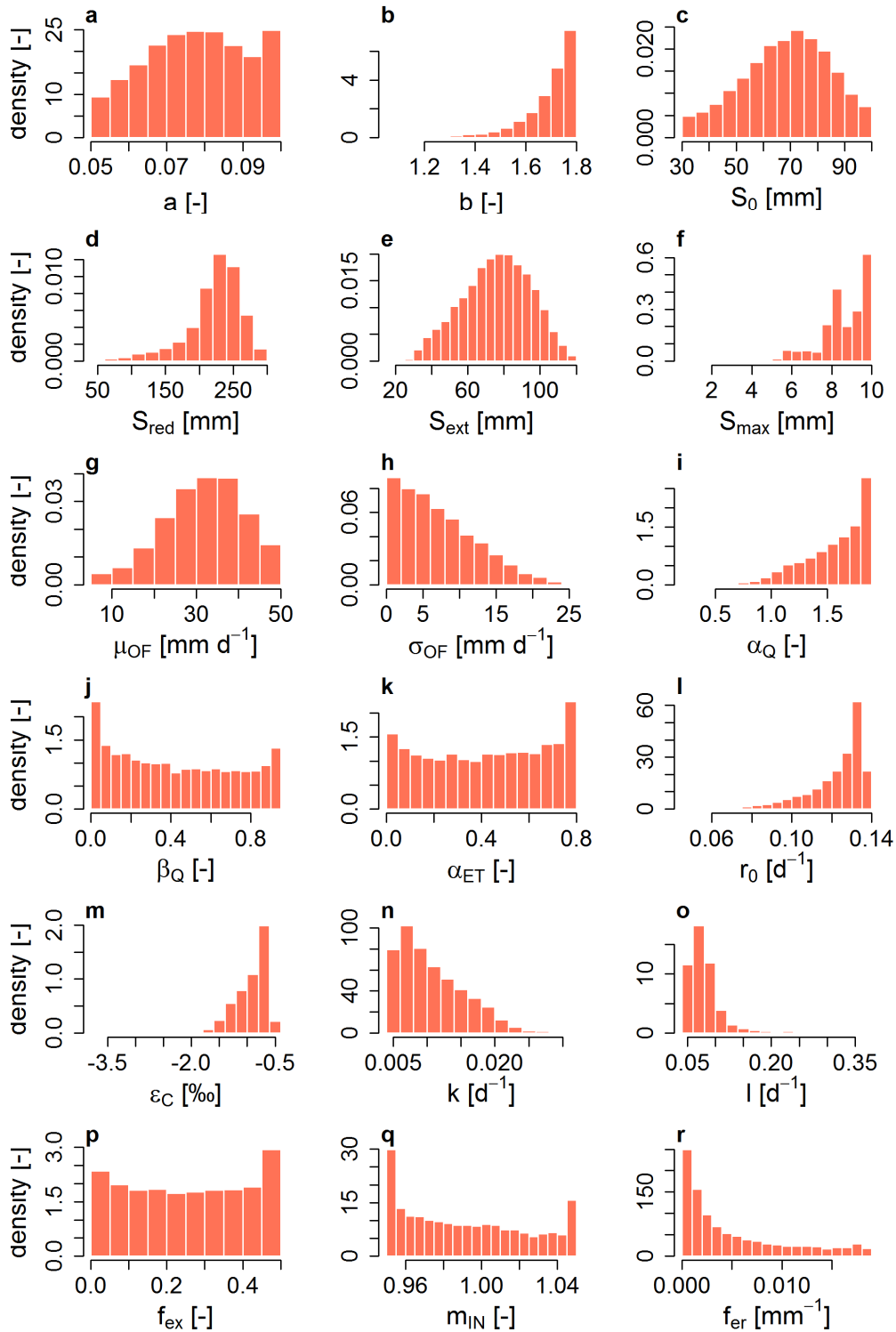
65 where n is the total number of concentration samples, $C_{i,meas}$ is the concentration of sample i ,
 66 $C_{i,mod}$ is the flow-weighted average concentration over all days comprised in sample i , $\overline{C_{meas}}$ and
 67 $\overline{\ln(C_{meas})}$ are the mean of the measured and ln-transformed measured concentrations,

68 respectively, and tw_i is the time-proportional weight of sample i (with flow-proportional samples
 69 spanning more than a day considered as a daily sample). Note that the grab sample in November
 70 was considered as a daily value. The same tw_i is also used in the calculation of $N_{\delta^{13}\text{C}}$, which
 71 gives the deviations of the flow-proportionally weighted modelled ($\delta^{13}\text{C}_{i,\text{mod}}$) from the measured
 72 carbon isotope ratios ($\delta^{13}\text{C}_{i,\text{meas}}$):

$$N_{\delta^{13}\text{C}} = 1 - \frac{\sum_{i=1}^n tw_i \cdot (\delta^{13}\text{C}_{i,\text{mod}} - \delta^{13}\text{C}_{i,\text{meas}})^2}{\sum_{i=1}^n tw_i \cdot (\delta^{13}\text{C}_{i,\text{meas}} - \overline{\delta^{13}\text{C}_{\text{meas}}})^2} \quad (\text{S7})$$

73 where n is the total number of $\delta^{13}\text{C}$ -samples, and $\overline{\delta^{13}\text{C}_{\text{meas}}}$ is the mean of the measured $\delta^{13}\text{C}$ -
 74 values.

75 Figure S1 shows the histograms of the 18 calibrated parameters from all 10,000 behavioural
 76 simulations. Most histograms have one clear maximum and thus indicate identifiability of the
 77 respective parameter. However, a few parameters exhibit flat histograms; these are β_{Q} and α_{ET}
 78 for the flow-related parameters, and f_{ex} and m_{IN} for the parameters of the pesticide model. As β_{Q}
 79 determines the preference of old water in discharge from the transport zone and α_{ET} defines the
 80 preference for young water in evapotranspiration, it was not possible to distinguish between the
 81 effects of evapotranspiration (ET) and old water discharge on pesticide concentrations in the
 82 study catchment. Accordingly, the amount of pesticide transfer in plant exudation following
 83 transport via ET, defined by f_{ex} , shows little parameter identifiability. Finally, the flat frequency
 84 distribution of m_{IN} indicates no clear tendency towards more or less pesticide input than assessed
 85 by the survey of pesticide applications.

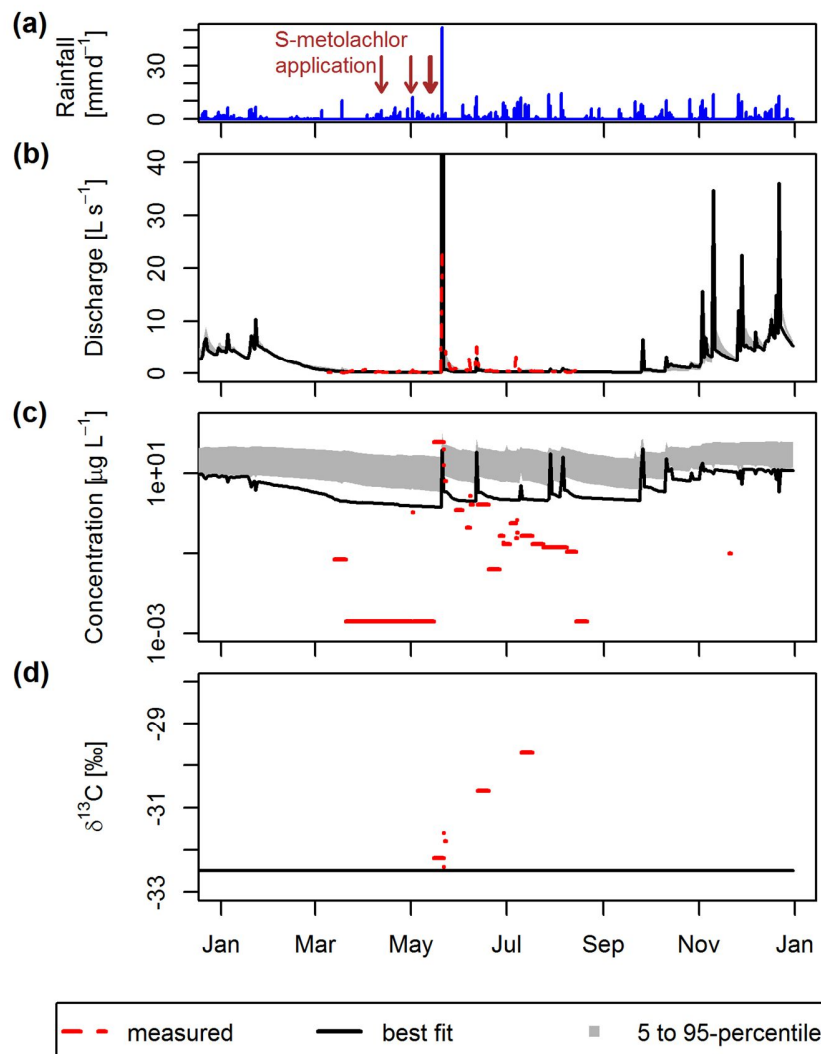


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87 **Figure S 1:** Histograms (frequency distributions) of the 18 calibrated model parameters from the
 88 10,000 behavioural model simulations.

89 **S6. Simulation results for the model without degradation**

90 The model was run without pesticide degradation and calibrated against measured discharge and
91 concentrations in 1000 simulations. Figure S2 shows that this model setup fails to reproduce the
92 measured concentrations (Fig. S2c), even though erosion increased relative to the original model.



93

94 **Figure S 2:** Measured (red lines) and modelled time series for discharge (b), S-metolachlor
95 concentrations (c; note the log-scaling) and $\delta^{13}\text{C}$ -values (d) at the catchment outlet in 2012 for
96 the model without degradation (1000 calibration runs). The black line indicates the results of the
97 calibration run with the best fit in terms of the mean of $N_Q/6$, N_C , and $N_{\delta^{13}\text{C}}$. Shaded areas show
98 the range between the 5- and 95-percentiles of all simulation results. Blue bars in (a) indicate
99 daily precipitation and brown arrows indicate the dates of pesticide application.

100

101 **References**

102 1. Alletto, L.; Benoit, P.; Bolognesi, B.; Couffignal, M.; Bergheaud, V.; Dumény, V.;
103 Longueval, C.; Barriuso, E., Sorption and mineralisation of S-metolachlor in soils from fields
104 cultivated with different conservation tillage systems. *Soil and Tillage Research* 2013, 128, (0),
105 97-103, doi: 10.1016/j.still.2012.11.005.

106 2. Buser, H.-R.; Poiger, T.; Müller, M. D., Changed Enantiomer Composition of
107 Metolachlor in Surface Water Following the Introduction of the Enantiomerically Enriched
108 Product to the Market. *Environ. Sci. Technol.* 2000, 34, (13), 2690-2696, doi:
109 10.1021/es0000201.

110 3. Lefrancq, M. Transport and attenuation of pesticides in runoff from agricultural
111 headwater catchments: from field characterisation to modelling. Université de Strasbourg,
112 Strasbourg, 2014.

113 4. Elsner, M.; Imfeld, G., Compound-specific isotope analysis (CSIA) of micropollutants in
114 the environment — current developments and future challenges. *Current Opinion in*
115 *Biotechnology* 2016, 41, 60-72, doi:10.1016/j.copbio.2016.04.014.

116 5. Mariotti, A.; Germon, J. C.; Hubert, P.; Kaiser, P.; Letolle, R.; Tardieux, A.; Tardieux, P.,
117 Experimental determination of nitrogen kinetic isotope fractionation: Some principles;
118 illustration for the denitrification and nitrification processes. *Plant Soil* 1981, 62, (3), 413–430,
119 doi: 10.1007/BF02374138.

- 120 6. Rayleigh, L. Theoretical considerations respecting the separation of gases by diffusion
121 and similar processes. *Philosophical Magazine Series 5* 1896, 42, (259), 493-498, doi:
122 10.1080/14786449608620944.
- 123 7. University of Hertfordshire, The Pesticide Properties DataBase (PPDB) developed by the
124 Agriculture & Environment Research Unit (AERU), University of Hertfordshire, 2013.
- 125 8. van der Velde, Y.; Heidbüchel, I.; Lyon, S. W.; Nyberg, L.; Rodhe, A.; Bishop, K.;
126 Troch, P. A., Consequences of mixing assumptions for time-variable travel time distributions.
127 *Hydrological Processes* 2015, 29, (16), 1099-1085, doi:10.1002/hyp.10372.