Supplementary material

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

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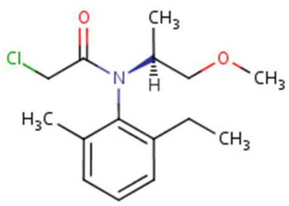
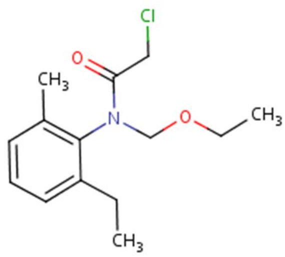
S1. Compound properties

Metolachlor consists of four stable stereoisomers; S-metolachlor (Table S1) denotes the two herbicidally active stereoisomers of metolachlor. S-metolachlor is classified as moderately water-soluble (480 mg L^{-1}) and moderately mobile in soil (Log K_{oc} between 1.79 and 2.57). Acetochlor has a moderate solubility (282 mg L^{-1}) and mobility in soil (Log K_{oc} of 2.19).

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

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}]	$2.2 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$
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

S2. Measured concentrations and $\delta^{13}C$-values at the plot, drain, and catchment outlet for S-metolachlor and acetochlor

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

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

a not determined

Table S3. Concentrations at the drain outlet (±standard deviation)

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

Table S4. Concentrations and δ^{13}C-values at the catchment outlet (±standard deviation)

Sample name	Date	S-metolachlor		Acetochlor	
		Concentration [µg L^{-1}]	**δ^{13}C [‰]**	**Concentration [µg L^{-1}]**	**δ^{13}C [‰]**
CW1	20.03.12	0.07±0.01	n.d.[a]	0.00	n.d.
CW2	27.03.12	0.00	n.d.	0.20±0.01	n.d.
CW3	03.04.12	0.00	n.d.	0.21±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±0.00	n.d.	0.00	n.d.
CW8	09.05.12	0.00	n.d.	0.24±0.01	n.d.
CW9	15.05.12	0.00	n.d.	0.00	n.d.
CW10-α	21.05.12	62.09±1.63	-32.20±0.18	59.33±0.84	-28.99±0.24
CW10-β	21.05.12	40.23±2.70	-32.39±0.18	29.18±0.28	-29.65±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

S3. Calculation of the extent of degradation for a sample at the catchment outlet

A conservative estimate of the extent of degradation for some environmental sample can be obtained from the Rayleigh equation approach (Elsner and Imfeld, 2016; Mariotti et al., 1981; Rayleigh, 1896):

$$f_{deg} = \left(\frac{R_S}{R_0}\right)^{\frac{1}{(\alpha-1)}} \tag{S1}$$

where R_0 is the isotope ratio (e.g., $^{13}C/^{12}C$) of the contaminant at the contamination source, R_S is the isotope ratio of the contaminant in an environmental sample at some distance from the source, f_{deg} represents the remaining fraction of the contaminant in the sample relative to the source, and α is the kinetic isotope fractionation factor (commonly reported in per mil (‰) as the kinetic isotopic enrichment factor; $\varepsilon = (\alpha - 1)$, where $\alpha<1$). In this study, we applied Eq. (S1) to the simulated CSIA data at the catchment outlet, and calculated the extent of degradation based on the Rayleigh equation approach as:

$$ED_{Rayleigh}[\%] = \left(1 - f_{deg}\right) \cdot 100 \tag{S2}$$

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

$$ED_{Sample}[\%] = \left(1 - \frac{C_{met}}{C_{trac}}\right) \cdot 100 \tag{S3}$$

S4. Equations of the flow and pesticide transport model

Table S5. Equations of the hydrological model. See also explanation of parameters in Table S7.

Hydrological model	
Source zone	
Storage	$\frac{dS_{sz}(t)}{dt} = P(t) - ET_{sz}(t) - Q_{sz}(t)$
Evapotranspiration	$ET_{sz}(t) = \begin{cases} ET_{pot}(t) \text{ } if \text{ } ET_{pot}(t) \leq \frac{S_{sz}(t)}{dt} \\ \frac{S_{sz}(t)}{dt} \text{ } if \text{ } ET_{pot}(t) > \frac{S_{sz}(t)}{dt} \end{cases}$
Discharge	$Q_{sz}(t) = \begin{cases} 0 \text{ } if \text{ } P(t) - ET_{sz}(t) - \left(\frac{d(S_{max} - S_{sz}(t))}{dt}\right) \leq 0 \\ P(t) - ET_{sz}(t) - \left(\frac{d(S_{max} - S_{sz}(t))}{dt}\right) \text{ } otherwise \end{cases}$
Overland flow[a]	$OF(t) = \frac{\int_0^{Q_{sz}(t)} N(x \mid \mu_{OF}, \sigma_{OF})(Q_{sz}(t) - x)dx}{\int_0^{\infty} N(x \mid \mu_{OF}, \sigma_{OF})\, dx}$
Transport zone	
Storage	$\frac{dS_{tz}(t)}{dt} = R_{tz}(t) - ET_{tz}(t) - Q_{tz}(t)$
Recharge	$R_{tz}(t) = \begin{cases} Q_{sz}(t) \text{ } if \text{ } Q_{sz}(t) \leq R_{max} \\ R_{max} \text{ } if \text{ } Q_{sz}(t) > R_{max} \end{cases}$
Evapotranspiration	$ET_{tz}(t) = \begin{cases} min\left(ET_{pot}(t) - ET_{sz}(t), \frac{dS_{tz}(t)}{dt}\right) if \text{ } S_{tz}(t) \geq S_{red} \\ min\left(\frac{S_{tz}(t) - S_{red}}{S_{ext} - S_{red}}\left(ET_{pot}(t) - ET_{sz}(t)\right), \frac{dS_{tz}(t)}{dt}\right) \text{ } if \text{ } S_{ext} < S_{tz}(t) < S_{red} \\ 0 \text{ } if \text{ } S_{tz}(t) \leq S_{ext} \end{cases}$
Discharge	$Q_{tz}(t) = [(2-b)a(S_{tz}(t) - S_0)]^{\frac{1}{(2-b)}}$

a $N(x \mid \mu_{OF}, \sigma_{OF})$ denotes the normal distribution with mean μ_{OF} and standard deviation σ_{OF} evaluated at x (cf. Table S7).

Table S6. Equations of the pesticide model. See also explanation of parameters in Table S7.

Pesticide model		
Source zone		
	Parameter	Equation
Storage	Change of pesticide mass	$\frac{dM_{sz}(t)}{dt} = \phi_{inp}(t) - \phi_{sz}(t) + \phi_{ex}(t) - \phi_{er}(t) - D_{sz}(t)$
Fluxes	Application	$\phi_{inp}(t)$
	Via discharge	$\phi_{sz}(t) = Q_{sz}(t)C_{sz}(t)$
	Via plant exudation	$\phi_{ex}(t) = f_{ex}ET_{tz}(t)C_{ET}(t)$
	Via erosion	$\phi_{er}(t) = f_{er}OF(t)M_{sz}(t)$
	Degradation	$D_{sz}(t) = r_0 M_{sz}(t)$
Concentration	Average concentration	$C_0(t) = \frac{M_{sz}(t)}{S_{sz}(t)}$
	In discharge (Q_{sz})	$C_{sz}(t) = \int_0^\infty p_{Q,sz}(T_{sz},t)C_0(t-T_{sz})(1-e^{-lT_{sz}})e^{-r_0 T_{sz}}\,dT_{sz}$
	Probability density function of travel times T_{sz} of pesticide in Q_{sz} at time t	$p_{Q,sz}(T_{sz},t)$
Transport zone		
	Parameter	Equation
Storage	Change of pesticide mass	$\frac{dM_{tz}(t)}{dt} = \phi_r(t) - \phi_{et}(t) - \phi_{tz}(t) - D_{tz}(t)$
Fluxes	Via recharge	$\phi_r(t) = R_{tz}(t)C_{sz}(t)$
	Via evapotranspiration	$\phi_{et}(t) = ET_{tz}(t)C_{ET}(t)$
	Via discharge	$\phi_{tz}(t) = Q_{tz}(t)C_{tz}(t)$
	Degradation	$D_{tz}(t) = r_0 e^{-kt}M_{tz}(t)$
Concentration	In discharge (Q_{tz})	$C_{tz}(t) = \int_0^\infty p_{Q,\mathrm{tz}}(T_{tz},t)C_{sz}(t-T_{tz})e^{-\frac{r_0}{k}(1-e^{-kT_{tz}})}\,dT_{tz}$
	In evapotranspiration (ET_{tz})	$C_{ET}(t) = \int_0^\infty p_{ET,\mathrm{tz}}(T_{tz},t)C_{sz}(t-T_{tz})e^{-\frac{r_0}{k}(1-e^{-kT_{tz}})}\,dT_{tz}$
	Probability density function of travel times T_{tz} of pesticide in Q_{tz} at time t	$p_{Q,\mathrm{tz}}(T_{tz},t)$
	Probability density function of travel times T_{tz} of pesticide in ET_{tz} at time t	$p_{ET,\mathrm{tz}}(T_{tz},t)$
Stream		
Concentration	Dissolved phase	$C(t) = \frac{C_{tz}(t)Q_{tz}(t) + C_{sz}(t)OF(t)}{Q_{tz}(t) + OF(t)}$

Carbon isotope ratio	Dissolved phase	$$\delta^{13}C(t) = \frac{C(t)^{13}/C(t)^{12}}{\left(C(t)^{13}/C(t)^{12}\right)_{VPDB}} - 1$$

S5. Model parameters, calibration range and objective functions for optimization

Table S7. Parameters of the hydrological and pesticide model with the lower and upper bounds of the parameter values for model calibration.

Parameter	Symbol	Calibration	
		Lower bound	Upper bound
Source zone			
Storage capacity [mm]	S_{max}	0.1	10
Transport zone			
Mean infiltration capacity [mm d^{-1}]	μ_{OF}	5	50
Standard deviation of infiltration capacity [mm d^{-1}]	σ_{OF}	0.05	25
First fitting parameter of storage-discharge relation [-]	a	0.05	0.1
Second fitting parameter of storage-discharge relation [-]	b	1	1.8
Storage for which discharge from transport zone ceases [mm]	S_0	30	100
Storage for which ET from transport zone starts to reduce [mm]	S_{red}	25	320
Storage for which ET from transport zone ceases [mm]; constrained to below S_{red}	S_{ext}	15	120
Calculation of travel time distributions			
Preference for young (<1) or old (>1) water in discharge from transport zone during dry periods [-]	α_Q	0.2	1.9
Change fraction of α_Q from the driest to the wettest conditions[a] [-]	β_Q	0	0.95
Preference for young water in ET from transport zone [-]	α_{ET}	0.01	0.8
Pesticide model			
Calibration factor for applied pesticide mass [-]	m_{IN}	0.95	1.05
Degradation rate constant [1 d^{-1}]	r_0	0.02	0.14
Coefficient for decrease of degradation rate constant in transport zone with travel time [1 d^{-1}]	k	$5.0 \cdot 10^{-3}$	0.03
Coefficient describing pesticide sorption in the source zone [1 d^{-1}]	L	0.05	0.37
Fraction of pesticide transfer from transport to source zone via ET and plant exudation [-]	f_{ex}	0.01	0.5
Eroded fraction of pesticide mass in the source zone via overland flow [1 mm^{-1}]	f_{er}	$3.4 \cdot 10^{-4}$	0.02
Isotopic enrichment factor [‰]	ε_C	0.5	5
Carbon isotope ratio of the applied pesticide product [‰]	$\delta^{13}C_0$	fixed at -32.5	

a VIM model; van der Velde et al. (2015)

Parameters were optimized with respect to NS_Q, NS_C, and $NS_{\delta 13C}$. NS_Q compares measured with modelled discharge at the catchment outlet, considering the best fit in a window of plus or minus one day to account for potential time lags of measured discharge in response to rainfall events:

$$NS_Q = 1 - \left(\frac{min\left(\sum_{t=1}^{n}(Q_{t,mod}-Q_{t,meas})^2, \sum_{t=1}^{n}(Q_{t-1,mod}-Q_{t,meas})^2, \sum_{t=1}^{n}(Q_{t+1,mod}-Q_{t,meas})^2\right)}{\sum_{t=1}^{n}(Q_{t,meas}-\overline{Q_{meas}})^2} + 0.03 \cdot f \right) \tag{S4}$$

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

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

$$NS_C = 1 - 0.5 \cdot \left(\frac{\sum_{i=1}^{n} tw_i \cdot \left(C_{i,mod} - C_{i,meas}\right)^2}{\sum_{i=1}^{n} tw_i \cdot \left(C_{i,meas} - \overline{C_{meas}}\right)^2} + \frac{\sum_{i=1}^{n} tw_i \cdot \left(ln\left(C_{i,mod}\right) - ln\left(C_{i,meas}\right)\right)^2}{\sum_{i=1}^{n} tw_i \cdot \left(ln\left(C_{i,meas}\right) - \overline{ln\left(C_{meas}\right)}\right)^2} \right) \qquad \text{(S5)}$$

where n is the total number of concentration samples, $C_{i,meas}$ is the concentration of sample i, $C_{i,mod}$ is the flow-weighted average concentration over all days comprised in sample i, $\overline{C_{meas}}$ and $\overline{ln(C_{meas})}$ are the mean of the measured and ln-transformed measured concentrations, respectively, and tw_i is the time-proportional weight of sample i (with flow-proportional samples spanning more than a day considered as a daily sample). Note that the grab sample in November was considered as a daily value. The same tw_i is also used in the calculation of $NS_{\delta 13C}$, which gives the deviations of the flow-proportionally weighted modelled ($\delta^{13}C_{i,mod}$) from the measured carbon isotope ratios ($\delta^{13}C_{i,meas}$):

$$NS_{\delta 13C} = 1 - \frac{\sum_{i=1}^{n} tw_i \cdot \left(\delta^{13}C_{i,mod} - \delta^{13}C_{i,meas}\right)^2}{\sum_{i=1}^{n} tw_i \cdot \left(\delta^{13}C_{i,meas} - \overline{\delta^{13}C_{meas}}\right)^2} \qquad \text{(S6)}$$

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

S6. Simulation results for the model without degradation

The model was run without pesticide degradation and calibrated against measured discharge and concentrations in 1000 simulations. Figure S1 shows that this model setup fails to reproduce the measured concentrations (Fig. S1c), even though erosion increased.

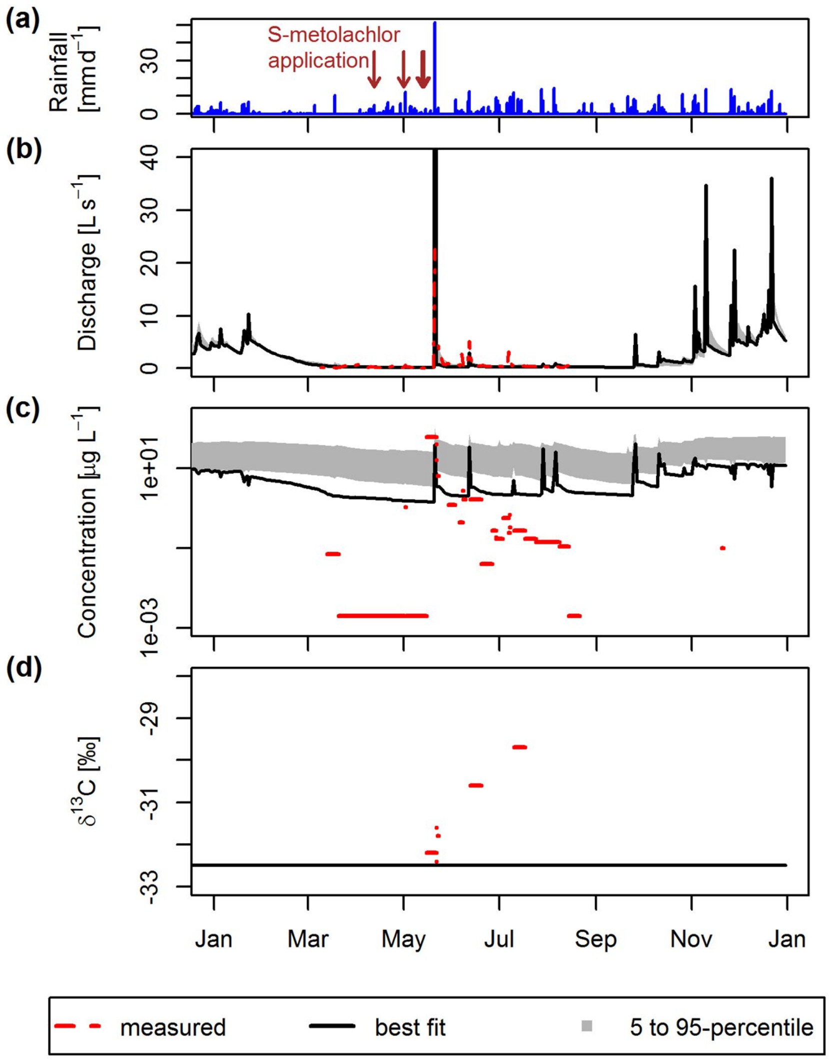


Figure S 1: Measured (red lines) and modelled time series for discharge (b), S-metolachlor concentrations (c; note the log-scaling) and $\delta^{13}C$-values (d) at the catchment outlet in 2012 for the model without degradation (1000 calibration runs). The black line indicates the results of the calibration run with the best fit in terms of the mean of NS_Q, NS_C, and $NS_{\delta 13C}$. Shaded areas show the range between the 5- and 95-percentiles of all simulation results. Blue bars in (a) indicate daily precipitation.

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