Supporting Information

Behavior of the Chiral Herbicide Imazamox in Soils: Enantiomer Composition Differentiates Between Biodegradation and Photodegradation

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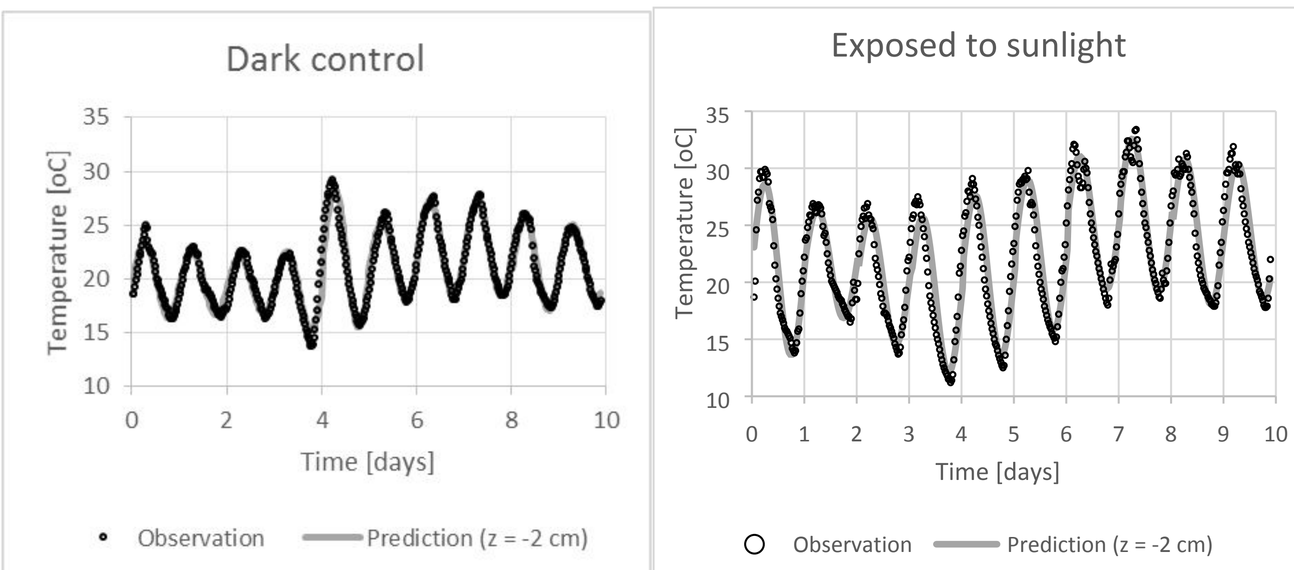
Temperature-Dependent Degradation

For an assessment of the effect of temperature on the dissipation of imazamox, temperature data were available from two experimental setups, one being exposed to sunlight, the other was a shaded (dark control). The setups were equipped with a temperature logger that was burrowed 2 cm below the soil surface. Temperature was logged at a temporal resolution of 30 min for 10 days (Figure S1).

Figure S1

Daily temperature variations for the dark control and sunlight-exposed dissipation experiments. Symbols are measurements and solid lines model fits.



The solution of the heat flow equation, subject to the upper boundary condition of a periodic wave around an average temperature at the soil surface and to the lower boundary of the average temperature far below the soil surface, is given as follows (Carslaw and Jaeger, 1959):

$$T(z,t) = T_A + A \exp\left(\frac{z}{d}\right) \sin\left(\omega t + \frac{z}{d}\right) \qquad -\infty < z < 0, \qquad \text{[Equation S1]}$$

where T [ºC] is the temperature, z [cm] the depth, t the time [d], T_A [ºC] the daily average temperature, A [ºC] is the amplitude of the temperature fluctuations at the surface, d [cm] is the damping depth, and $\omega = 2\pi/\tau$ [d^{-1}] is the angular frequency of the change in temperature at the soil surface, where $\tau = 1$ d is the period of the wave. Although the temperature regime in the clay loam soil was not conform to the solution of the heat flow equation (the soil column was heated up from all sides), Equation S1 was used to describe the effective behavior of the daily temperature variations measured 2 cm below the soil surface. For this, the time series of measured temperatures was split up in waves with a period of 1 day starting at noon.

The measured temperatures at 2 cm depth of each particular wave were averaged (T_A) and treated as constants in the fit. The amplitude A of each wave was fitted, as was the damping depth d, which was assumed to be the same for the whole period. The actual time was corrected for the time lag, $z/(\omega d)$, to account for the phase shift of the wave at 2 cm depth with respect to the surface. Figure S1 shows the adequate fit of Equation S1 to the data and the resulting optimized parameters are summarized in Table S1.

Table S1
Parameters in the solution of the heat flow equation, describing the measured daily temperature variations at 2 cm below the surface for the dark control and the sunlight-exposed dissipation experiments.

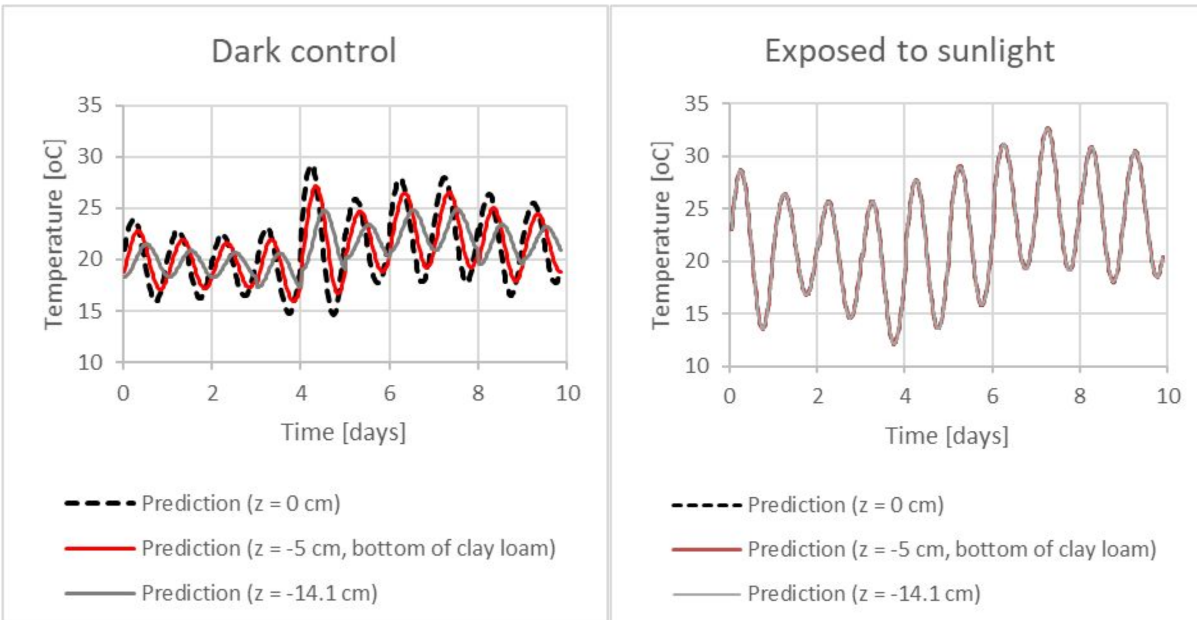
	dark control experiment		**sunlight-exposed experiment**	
damping depth *d*	15.1 cm		3.8×10^5 cm	
day	**T_A [ºC] fixed from measurements**	**A [ºC] fitted**	**T_A [ºC] fixed from measurements**	**A [ºC] fitted**
1	19.9	4.0	21.1	7.6
2	16.6	3.3	21.6	4.8
3	19.5	3.0	20.1	5.6
4	19.0	4.2	18.9	6.8
5	21.9	7.3	20.6	7.1
6	21.8	4.1	22.4	6.6
7	22.8	5.0	25.2	5.9
8	22.9	5.1	25.9	6.8
9	21.5	4.9	24.4	6.4
10	21.6	3.9	24.5	6.0
average (day 1−4)	19.5	3.6	20.4	6.2
average (day 1−10)	21.0	4.5	22.5	6.4

As expected, direct exposure to sunlight increased both, the temperature and the amplitude of the temperature variations, on average by 1.5 and 1.9ºC, respectively, for the 10-day period. The increase of the amplitude was especially large (2.6ºC) during the first four days of the dissipation experiments, when the majority of imazamox dissipated. The physically unrealistic large damping depth for the sunlight-exposed experiment reflects that heat transfer was very fast, because the soil was heated up (and cooled down at night) from all sides in absence of any insulation. The consequence is that temperature is identical at all depths. This effect was not observed in the dark control experiment, because the soil was covered by a bucket wrapped in aluminum foil.

The solution of the heat flow equation was extrapolated to the soil surface ($z = 0$), to the bottom of the soil ($z = -5$ cm), and to the water level ($z = -14.1$ cm), implicitly assuming identical heat properties for soil and florist foam. The extrapolated values to depths of 0 and −14.1 cm represented the upper and lower boundary condition for temperature, respectively, in the numerical simulations. The results of these extrapolations are given in Figure S2 (extrapolation to z = +0.3 cm is not shown as upper boundary for the sand cover).

Figure S2

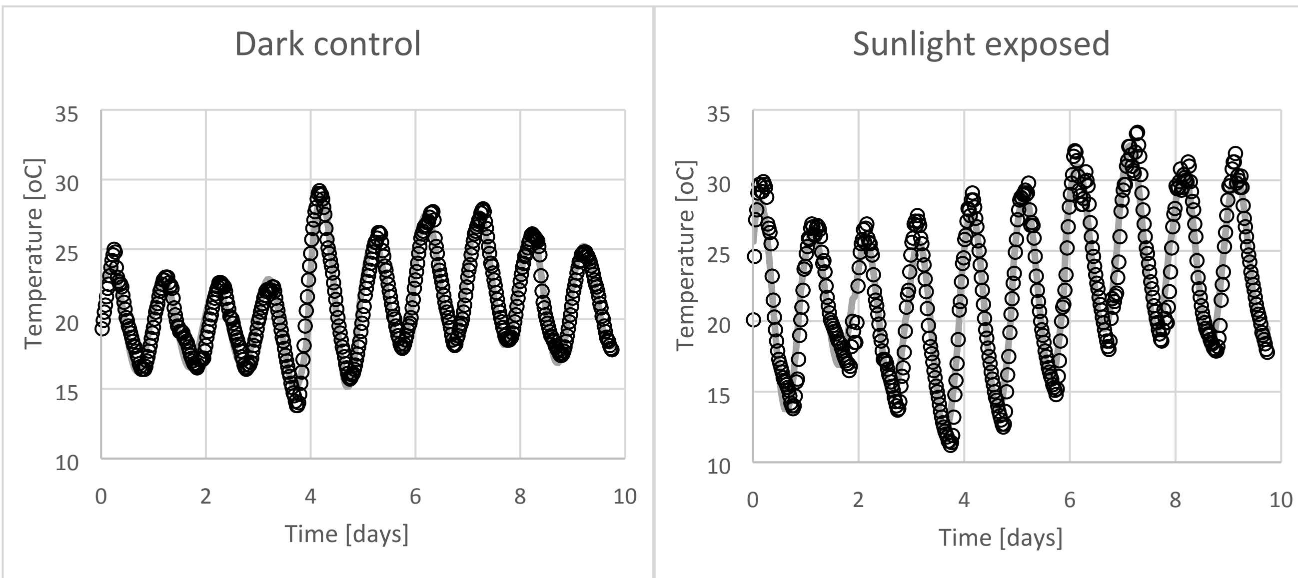
Estimated daily temperature variations for the soil surface (z = 0), the bottom of the soil (z = −5 cm), and for the water level in the florist foam (z = −14.1 cm) for the dark control and sunlight-exposed dissipation experiments.



Numerical simulations of temperature-dependent dissipation of imazamox were performed with the finite element software package Hydrus-1D version 4.16 (Šimůnek et al, 2013). The calculated temperatures at z = 0 (z = +0.3 cm for the sand cover) and z = −14.1 cm for either the dark control or the sunlight-exposed setup were used as variable upper and lower temperature boundary condition. The heat transport parameters in the temperature module of the package were chosen in such a way that the predicted temperature at 2 cm below the soil surface adequately described the measurements. The volume fraction of the solid phase was set to a value complementary to the saturated volumetric water content (0.55 cm^3/cm^3 for the clay loam soil, 0.01 cm^3/cm^3 for the florist foam, and 0.57 cm^3/cm^3 for the sand cover). The longitudinal thermal dispersivity was set either to 5 cm for the dark control or to 1000 cm for the sunlight-exposed setup for all materials (soil, florist foam, and sand cover), which reflects the different thermal regimes observed from the temperature measurements. The thermal conductivity was approximated by the Campbell function which was implemented in the software package. Figure S3 shows the adequate temperature predictions of the numerical model at 2 cm below the soil surface for the dark controls and the sunlight-exposed setup.

Figure S3

Daily temperature variations at 2 cm below the soil surface ($z = -2$ cm) for the dark control and sunlight-exposed (without sand cover) dissipation experiments. Simulation results (grey line) are compared with measurements (symbols).



The software package accounts for temperature-dependent degradation rate constants and this temperature dependency is expressed by the Arrhenius equation as follows:

$$k_{\mathrm{deg,T}} = k_{\mathrm{deg,T_{ref}}} \exp\left(\frac{E_{\mathrm{A}}(T^{\mathrm{A}} - T^{\mathrm{A}}_{\mathrm{ref}})}{R T^{\mathrm{A}} T^{\mathrm{A}}_{\mathrm{ref}}}\right) \qquad \text{[Equation S2]}$$

where $k_{\mathrm{deg,T}}$ and $k_{\mathrm{deg,T_{ref}}}$ [d^{-1}] are rate constants of microbial degradation at the absolute ambient T^A [K] and the absolute reference temperature $T^{\mathrm{A}}_{\mathrm{ref}}$ of 293.15 K (20 ºC), respectively, E_{A} [J mol^{-1}] is the activation energy, and R = 8.314 J K^{-1} mol^{-1} is the universal gas constant. The activation energy for microbial degradation was set to 65400 J mol^{-1} (EFSA 2007).

A $k_{\mathrm{deg,T}}$ of 0.0245 h^{-1} was determined for the dark control experiments without sand cover at an average temperature of 19.5ºC, measured for the first four days when most dissipation occurred. Using Equation S2, the rate constant of microbial degradation was 0.0257 h^{-1} at the reference temperature of 20 ºC. Note that photochemical degradation and microbial degradation are lumped in an effective rate constant of dissipation in the numerical model and that photochemical degradation not necessarily follows the same activation energy as microbial degradation.

References

Carslaw, H.S. and J.C. Jaeger, 1959. Conduction of heat in solids. Oxford University Press, London, p 510.

European Food Safety Authority, EFSA, 2007. Scientific Opinion of the Panel on Plant Protection Products and their Residues on a request from EFSA related to the default Q10 value used to describe the temperature effect on transformation rates of pesticides in soil. The EFSA Journal, 622, 1-32.

Šimůnek J, Šejna, M, Saito H, Sakai M, van Genuchten M.T. The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media, version 4.16; Department of Environmental Sciences, University of California, Riverside: 2013.