Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

A new conceptual model of pesticide transfers from agricultural land to surface waters with a specific focus on metaldehyde

SUPPLEMENTARY INFORMATION

M.J. Whelan[1*], A. Ramos[2], R. Villa[2,3], I. Guymer[4], B. Jefferson[2], M. Rayner[1]

[1] Centre for Landscape & Climate Research, School of Geography, Geology and the Environment, University of Leicester, UK

[2] Cranfield University, UK

[3] Department of Engineering & Sustainability, De Montfort University, Leicester, UK

[4] Department of Civil Engineering, University of Sheffield, UK

*Author for Correspondence: mjw72@le.ac.uk

S1 Arrhenius Equation

The value of k_{deg} is derived from dissipation half lives (DT_{50}) reported in the literature with correction for temperature using the Arrhenius equation:

$$k_{deg} = k_{ref}.e^{\left(\frac{Ea}{R}.\left(\frac{1}{T_{ref}} - \frac{1}{T_{env}}\right)\right)} \quad (14)$$

where k_{ref} is the degradation rate constant derived from a DT_{50} at a reference temperature (T_{ref}, K), Ea is the Activation Energy (J mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T_{env} is the environmental (soil) temperature (K), which varies over time. A value of 65.4 kJ mol^{-1} was used for Ea, as recommended by EFSA (2017).

S2 Soil Properties

Pertinent soil properties for the prevailing soil type in the catchment (the Hanslope soil series) are shown in Table S1 below.

Table S1. Soil Properties for the Hanslope Soil Series, the dominant soil type in the Hanslope Soil Association (Cranfield University, 2019). HOST is the Hydrology of Soil Types (Boorman et al., 1995). BFI is the soil Base Flow Index which is derived from HOST.

Property	**Value**
Soil Group	Calcareous pelosol
Texture	Clay loam over stony, calcareous clay
Clay Content	42%
K_{sat}	1.25 mm h^{-1} (Kellet, 1975)
HOST Class	21
BFI	0.32

S3 Distribution of Metaldehyde Applications

We assumed that the timing of application was distributed as a (discrete) Poisson distribution over (arbitrarily) approximately two weeks around this date (corresponding to λ = 7 days). This is illustrated in Figure S1.

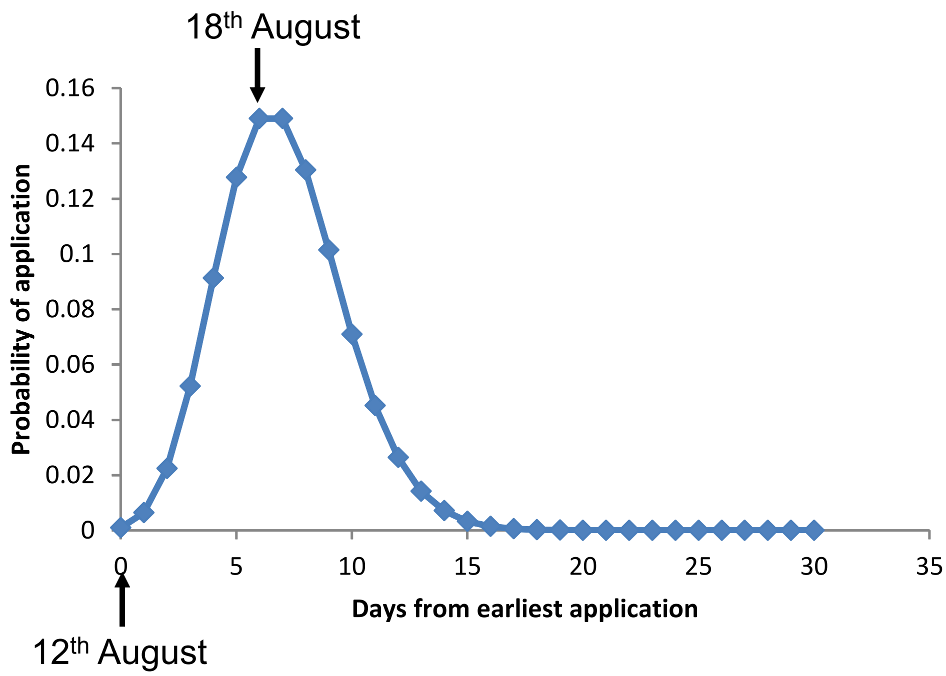

Figure S1. Poisson distribution for the probability of metaldehyde applications in the catchment over 30 days after the initial feasible application date (λ = 7 days). The start of the distribution corresponds to the 12th of August, with peak application occurring on the 18th and 19th of August.

S4 Sensitivity Analysis of the Pesticide Model

A simple one-at-a-time sensitivity analysis of the pesticide model was conducted. The following five parameters were considered: (i) the application rate (E_t); (ii) the dissipation half life (DT_{50}); (iii) the organic carbon to water partition coefficient (K_{OC}); (iv) the initial penetration depth for pesticide (z_{mix}); and (v) the exponent for pesticide displacement (α). Initial default values for each parameter are shown in Table S2. Each parameter was changed one at a time in steps of 25% above and below these default values, leaving all the other parameters at their default values. Sensitivity was assessed in terms of the relative change in three goodness of fit metrics (the correlation coefficient, r; the Root Mean Squared Error, RMSE and the Nash Sutcliffe Efficiency, NSE) comparing predicted metaldehyde concentrations with measured concentrations at the catchment outlet.

Table S2. Initial default values for parameters considered in the pesticide model sensitivity analysis.

Parameter	Default Value	Source
E_t (kg ha^{-1})	0.18	Typical Label Rate
DT_{50} (days)	5.1	PPDB (2018)
K_{OC} (L kg^{-1})	240	PPDB (2018)
zmix (mm)	2	Brown and Hollis, 1998
α (dimensionless)	1.5	This paper

Changes in r, RMSE and NSE with changes in each parameter value are shown in Figure S2. Note that better model fits are suggested by increases in r and NSE and by decreases in RMSE. The model was relatively insensitive to changes in z_{mix} and K_{OC}. All three metrics were most sensitive to changes in DT_{50} across the range of values evaluated, with improved model fit as DT_{50} increased. The model was also quite sensitive to a, but only at values > 1.5. Values of a < 1.5 resulted in numerical instability. The model was moderately sensitive to E_t, with performance decreasing as E_t was increased and decreased away from the default value. This was because the initial peak metaldehyde concentrations were better predicted at moderately high E_t rates but later peaks were still underestimated due to the high default dissipation rate constant assumed.

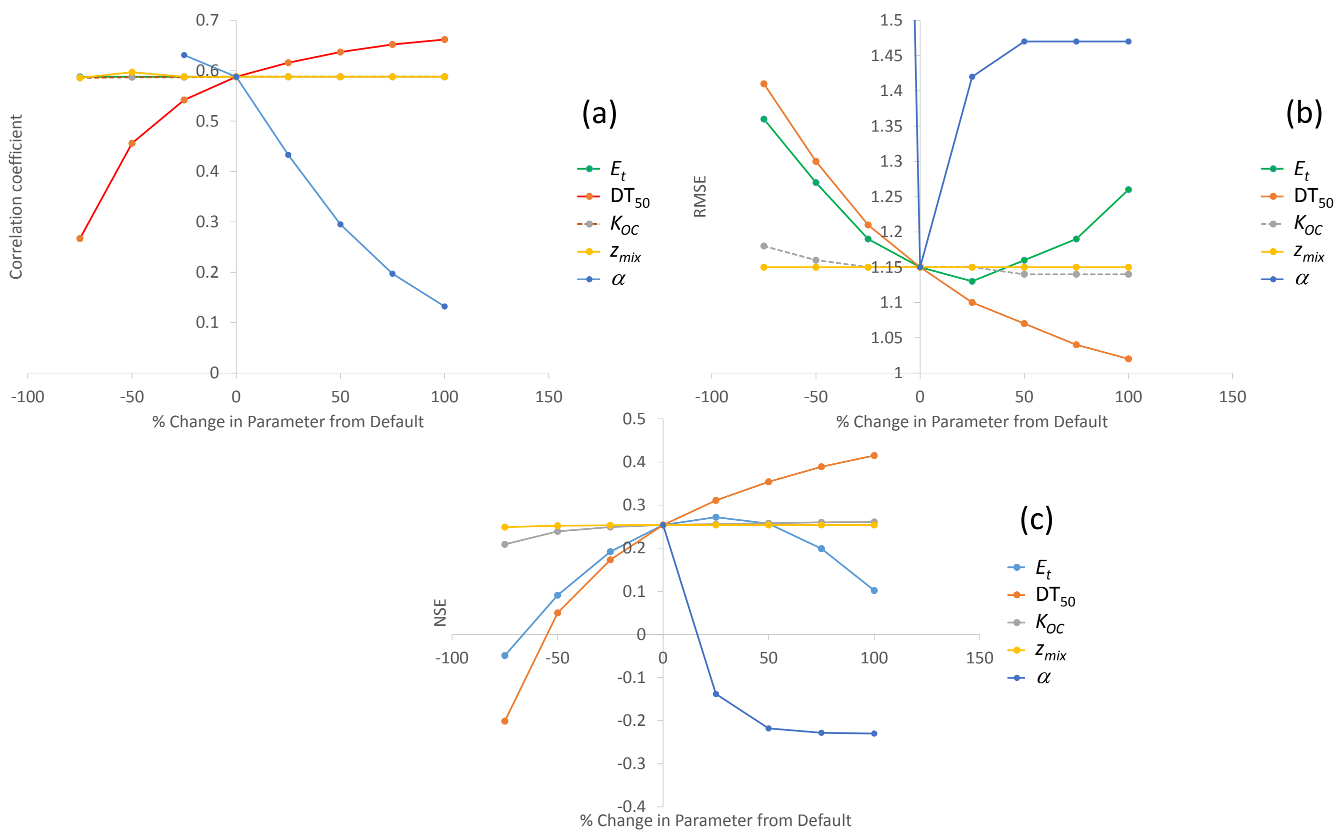

Figure S2. Changes in goodness of fit metrics in response to relative changes in key pesticide parameters in one-at-a-time sensitivity analysis. (a) correlation coefficient; (b) RMSE and (c) NSE.

Additional References

Boorman D.B., Hollis J.M., Lilly, A. (1995) *Hydrology of soil types: a hydrologically based classification of the soils of the United Kingdom*. Institute of Hydrology Report No. 126, Wallingford, UK

Cranfield University (2019) The Soils Guide. Available: www.landis.org.uk. Cranfield University, UK. Last accessed 26/12/2019

EFSA (2017) EFSA Guidance Document for predicting environmental concentrations of active substances of plant protection products and transformation products of these active substances in soil. *EFSA Journal* **15**(10): 4982. European Food Safety Authority.