A DFOP-based PRZM model to predict non-first order degradation and subsurface transport in soil and groundwater

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Background and objectives

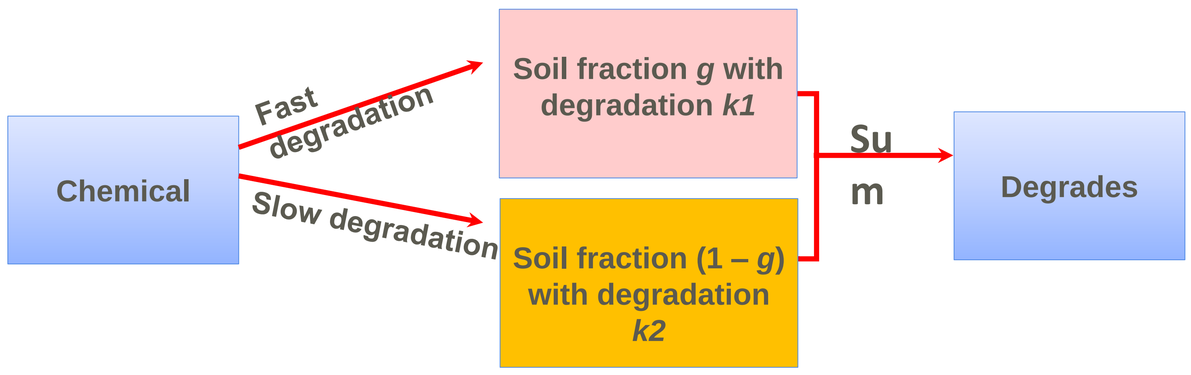
Many soil metabolism and other environmental fate studies have observed non-first order degradation often in a biphasic pattern with fast initial decline followed by a noticeably slower phase. The decline pattern deviates from the classical simple first-order (SFO) kinetics. Although widely recognized, biphasic degradation has never been directly incorporated into regulatory models. Instead, most regulatory models require an SFO curve fit preferentially to the slow portion of the decline data while largely ignoring the fast initial phase. As a result, modelling errors in the predicted exposure levels in surface water and groundwater can be artificially elevated. This poster examines the impact of biphasic degradation on pesticide leaching behavior using an updated EU PRZM model (winPRZM) with code developed by Syngenta and Waterborne.

Conceptual Model

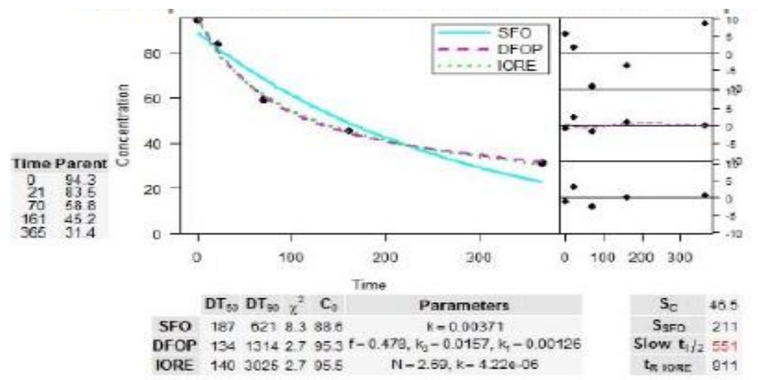
The model directly incorporates the kinetics of Double First-Order in Parallel (DFOP) to account for the complete biphasic decline profile with the option to account for the temperature and soil moisture effects. Sensitivity analysis of winPRZM shows that the model converges to the same results of the original PRZM model when the kinetics fit is SFO. When the kinetics shows DFOP characteristics, winPRZM can represent biphasic degradation in the soil better. Using DFOP, winPRZM is able to predict several field soil residue data sets reasonably well without elaborated model calibration. Predicted soil pore water concentrations from winPRZM were also compared with measured data from field lysimeters (not shown in this poster). The overall model performance suggests winPRZM can be used as a predictive tool to handle biphasic degradation behavior frequently observed in pesticide field studies. The inherent nature of DFOP reflecting the rate-limiting effect of time-dependent sorption on biodegradation has also been examined for the soil-pore water system.

Calculated Biphasic Degradation Rates

- DFOP equation
  $C_t = C_0 g^{-k_1 t} + C_0(1 - g)^{-k_2 t}$
  - g is the fraction of the C_0 as being Fraction 1
  - k1 = rate constant for Fraction 1 in 1/days
  - k2 = rate constant for Fraction 2 in 1/days
- NAFTA kinetics calculation (PestDF) by available laboratory soil metabolism studies
- DFOP fits provided the fraction of the initial chemical that degrades at the fast rate



Example of a kinetics calculation output



Average results from four different soil metabolism studies

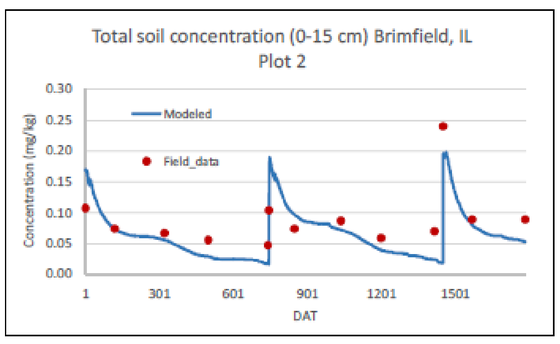
Fraction		K	
g	0.51175	k1	0.051463
1 - g	0.48825	k2	0.009801

WinPRZM DFOP coding enhancements

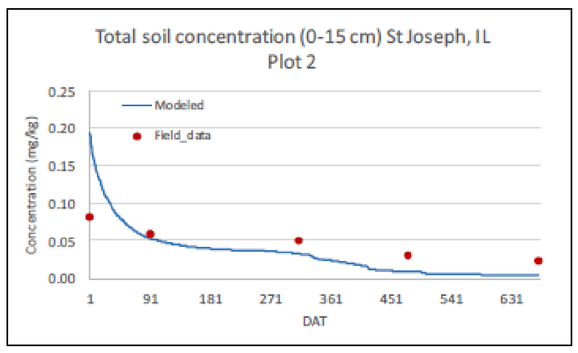
Adding the DFOP code to WINPRZM was straight forward using existing functionality. The new code allows for three DFOP options; DFOP parent only, DFOP parent to non-DFOP metabolite, and non-DFOP parent to DFOP metabolite. First a DFOP flag was added to the WINPRZM execution supervisor file to specify which of the three options is being simulated. DFOP 1 and DFOP 2 distribute the total application rate between chemical 1 and chemical 2. Next, when non-linear sorption (Kf) is on an internal calculation adds the respective soil concentrations at the end of the time step to determine the next day Kf value. DFOP 3 utilizes the degradation yield fractions to transfer parent to the DFOP metabolite. Kf sorption is then handled similarly to parent. Finally, additional output files for the annual summary files were created along with DFOP specific time series variables.

Simulation Results – Field Study Sites in the USA

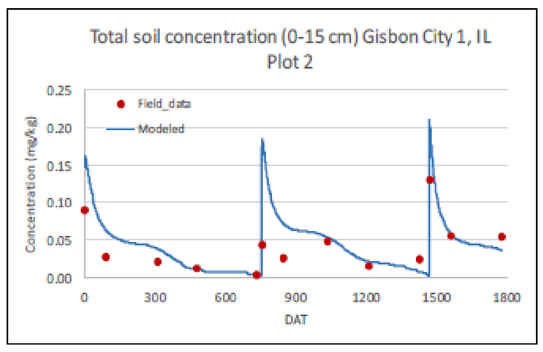
Brimfield, IL



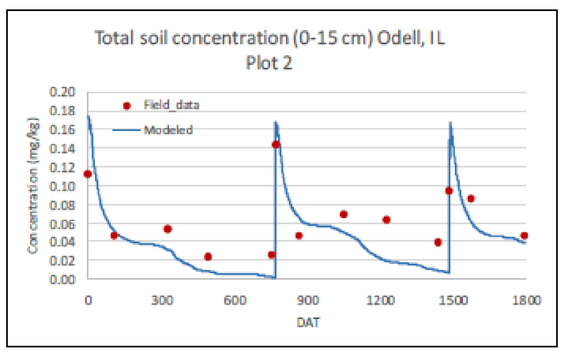
St Joseph, IL



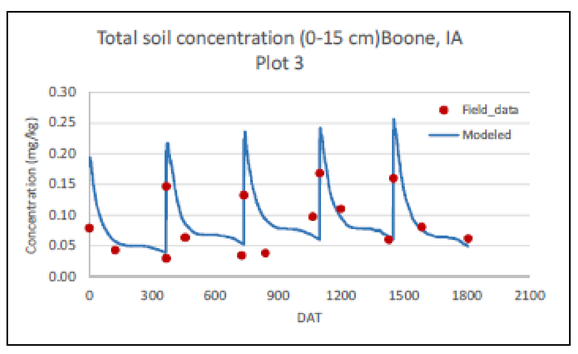
Gibson City, IL



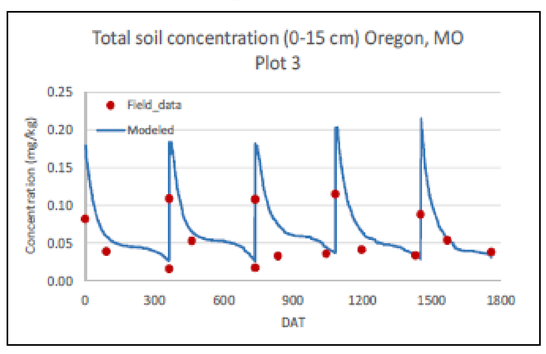
Odell, IL



Boone, IA

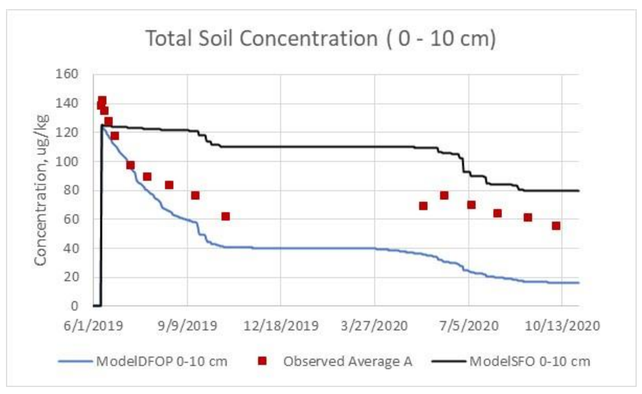


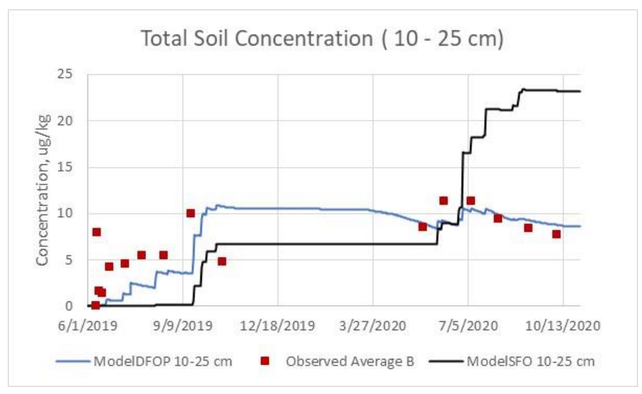
Oregon, MO



Model evaluation was carried out by using independently measured laboratory parameters to predict field dissipation study data from 21 geographical locations in the USA. Biphasic kinetics parameters were obtained from four laboratory soil metabolism studies independent of field dissipation studies. Linear equilibrium soil sorption parameter (Koc) was 113 mL/g (average of 28 soils). Degradation of each fraction was dependent on soil temperature (Q10=2) and moisture (correction factor 0.7). Site-specific soil, weather and irrigation data were used. Modelling results compared to measured data are shown for six of the field studies conducted from 1994 to 1999.

Simulation Results – Field Study Sites in the Canada





Using the DFOP degradation parameters and Koc in the USA modelling, a field site in Canada was modelled to compare to measured soil concentrations. Site-specific soil, weather and irrigation data were used. Modelling results with DFOP and with SFO compared to measured data are shown.

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