

Monod-kinetics rather than first-order degradation explains atrazine fate in soil columns: implementation for pesticide transport modelling



Karlien Cheyns, Jan Mertens, Jan Diels, Erik Smolders and Dirk Springael

Division of Soil and Water Management, Department of Earth and Environmental sciences, Katholieke Universiteit Leuven, Kasteelpark Arenberg 20, B-3000 Leuven

Introduction

- Biodegradation is an important factor that impedes leaching of pesticides in deeper soil layers towards groundwater
- A lag phase is commonly observed in these deeper soil layers in degradation experiments, i.e., a period of proliferation of the inherent small pesticide degrading population (Figure 1) (Alexander, 1999), suggesting that in order to describe pesticide fate in deeper soil layers, the growth kinetics of the degrading population has to be taken in account
- To study this hypothesis, transport of atrazine (AT) was examined through a soil column containing subsoil originating from a field which was annually treated with AT and a model was proposed to describe the observed transport of AT through this column.

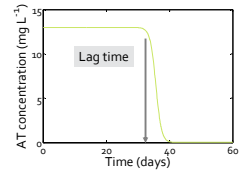


Fig. 1: Lag time in batch degradation experiments with soil samples of deeper soil layers

Materials and Methods

- The used soil was a subsoil sample (30-45 cm) collected in an agricultural field, which has been annually treated with AT since 1973
- Two replicate columns (A and B, 1.65 m, Ø 3 cm) were filled with 80 g of fresh soil (Figure 2).
- AT was solved in a salt solution and applied in 2 successive steps (0.8 pore volume day⁻¹) for 31 and 28 days
- In between the steps the columns were irrigated with a salt solution without AT for 161 days simulating a period in which no AT was applied.
- Glass filter plates were placed below the soil surface and a pressure head of -100 cm was applied using a vacuum pump
- In this way, leachates (Fig. 2) were collected and AT in the leachate was measured using HPLC



Fig. 2: Example of the column set-up to study AT leaching in subsoil

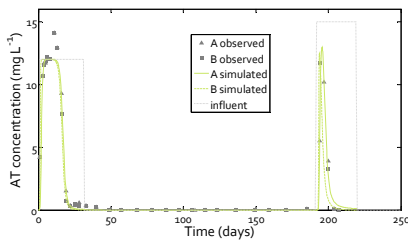


Fig.3: Measured (symbols) and simulated (green lines) AT concentration in the column leachates. The grey dotted line represents the AT concentration in the influent

Results

- Figure 3 shows the AT concentration during both step applications
- The concentration in the effluent increases in time, but decreases after a lag time, when degradation was observed
- During the second step the lag time was much shorter, indicating that the ADB was larger in number at the beginning of this step compared with the initial situation
- These results suggest that the decay of the ADB in absence of AT was slower than the growth rate in presence of AT

- The proposed model was able to describe the transport of AT through the soil column well
- In addition, as shown in figure 4, the proposed model can simulate the ADB in different soil layers (expressed in AT units (mg L⁻¹)).
- The differences in the observed degradation lag times could be ascribed to a different size of ADB at the beginning of each step application.

Model development

- Microbial growth can be described using Monod kinetics (Monod, 1949):

$$\frac{dX}{dt} = \left(\mu_m \frac{C_1}{K_1 + C_1} \right) X - k_{decay} X \quad \frac{dC}{dt} = \frac{1}{Y} \left(\mu_m \frac{C_1}{K_1 + C_1} \right) X$$

X=total AT degrading biomass (ADB) (mg L⁻¹); C₁=AT concentration in liquid phase (mg L⁻¹); C=AT concentration in total soil (mg L⁻¹); μ_m=ADB growth rate (day⁻¹); K₁=half saturation constant (mg L⁻¹); k_{decay}=the ADB decay rate (day⁻¹); Y=yield (-)

- Assuming low C₁ compared with K₁, the model is simplified to:

$$\frac{dX}{dt} = (\mu_{m,mod} C_1) X - k_{decay} X \quad \frac{dC}{dt} = -\frac{1}{Y} (\mu_{m,mod} C_1) X \quad \mu_{m,mod} = \frac{\mu_m}{K_1}$$

μ_{m,mod} = modified ADB growth rate (L_{liq} mg⁻¹ day⁻¹)

- The degradation kinetics is combined with the classical convection-dispersion equation

$$R \frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} - v \frac{\partial C_1}{\partial x} - \frac{\partial C}{\partial t} \quad R = 1 + \frac{\rho_b}{\theta} K_d$$

ρ_b=soil bulk density (kg L⁻¹); θ=volumetric water content (L_{liq}L⁻¹); K_d=adsorption coefficient (L_{liq} kg⁻¹); t=time (days); D=dispersion coefficient (m² day⁻¹); x=distance (m); v=average pore water velocity (m day⁻¹)

- This degradation kinetics is incorporated in the HYDRUS-1D model (Simunek et al., 2005) to describe the observed results
- The model is parameterized by applying an inverse modelling framework combining a sensitivity analysis (Morris Sensitivity Analysis) with an inverse modelling approach (Shuffled Complex Evolution Metropolis)(Vrugt et al. 2003)

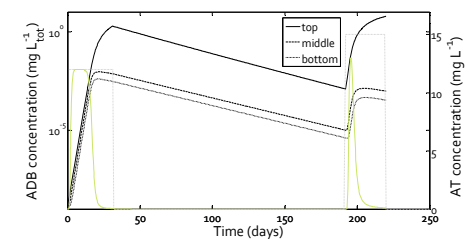


Fig.4: Simulated AT degrading biomass (ADB) at different positions in column A. The grey lines represents the AT concentration in the influent and the green line the simulated AT concentration in the effluent

Conclusions

- The observed transport of pesticides in the column experiment and reduced lag time of biodegradation after pre-exposure show that first-order degradation models, which are often used in pesticide transport models, do not describe the fate of AT in soil
- The observed lag time for AT degradation was successfully described using simplified Monod kinetics
- Incorporating this kinetics in the Hydrus-1D transport model made it possible to simulate the observed results
- Failure of including population dynamics when predicting transport of pesticides through the unsaturated soil will underestimate the risk of break-through of pesticides

