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Enhanced biodegradation of atrazine at high infiltration rates on agricultural soils

Figures:

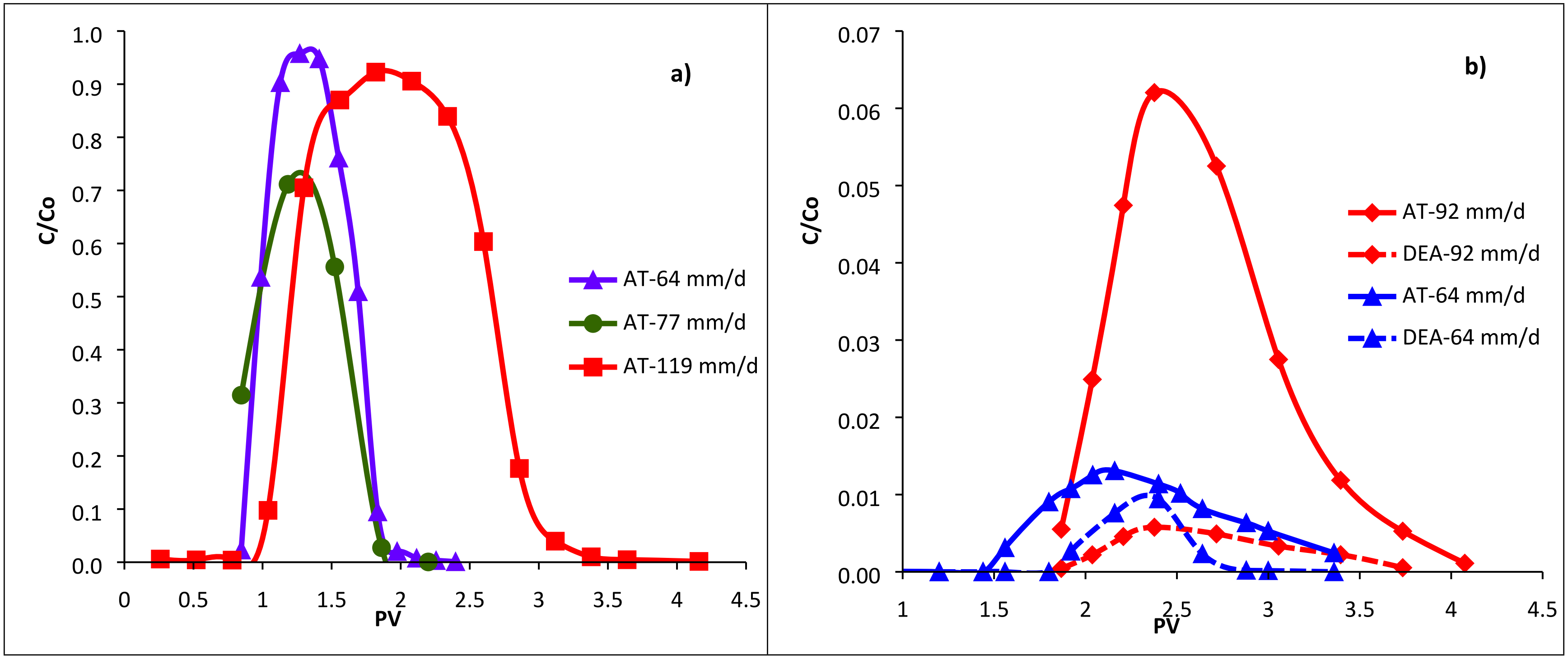

Fig. S1 Atrazine and DEA breakthrough curve for: a) sandy loam and b) loam soil

Tables:

Table S1

Analytical method parameters in water samples

Analyte	Retention time (min)	Detection limits (ng/mL)	Recovery (%)
Terbutylazine	10.01	15.7	120.2
Atrazine	9.44	2.2	116.3
DIA	7.79	11.1	81.7
DEA	8.01	1.5	116.8

Table S2

Analytical method parameters in soil samples

Analyte	Retention time (min)	Detection limits (ng/g)	Recovery (%)
Terbutylazine	28.41	24.6	105.7
Atrazine	25.49	9.1	97.8
DIA	14.58	22.7	93.4
DEA	18.1	14.4	87.5
HA	15.46	16.2	89.4

Relationship between soil moisture content and infiltration rate:

Table S3 shows the average soil moisture content in columns measured at different depths while atrazine was fed continuously. According to the soil moisture data measured in the sandy loam and loam column experiments, average soil moisture content ranged between 11-45% (40% and higher values indicated that the column reached saturation) over the period of this study. Enhanced atrazine degradation was observed in these columns at this moisture range similar to the degradation data obtained from the batch microcosms at 15% and 25% soil moisture. As it was discussed earlier, in the batch experiments, atrazine experienced a rapid degradation at 15% and 25% soil moisture contents. Atrazine was almost completely degraded at 15% and 25% soil moistures in both sandy loam and loam batch microcosms in about 15 days (Figure 3). Column experiments were run for 30 days. Atrazine was not detectable in the column effluent after approximately 15 d and 25 d for sandy loam and loam, respectively (Figure 1). For the loamy columns, the process was longer (25 d) due to a higher sorption. Both column and batch experiments showed an enhanced degradation of atrazine at high soil moistures. This suggests that in agricultural soils, a synergy of factors such as the history of pesticide application and moisture content have developed an enhancement in atrazine microbial degradation over time.

Table S3 Soil moisture content in columns

		Average Soil Moisture Content (%)			
Soil Type	Infiltration Rate (mm/d)	0 cm (Top of the column)	25 cm	50 cm	75 cm
Sandy loam	64	24	26	35	40*
Sandy loam	77	32	11	15	14
Sandy loam	119	36	21	15	39
Loam	64	45*	18	28	20
Loam	92	45*	44*	37	30

*Column reached saturation at this depth.

Detailed description of the model

Water flow model

The mixed form of Richard's equation is as represented below in Equation (1):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial t}\left[K\left(\frac{\partial h}{\partial t}\right) + \frac{\partial K}{\partial t}\right] \tag{S1}$$

θ represents soil moisture content [L^3/L^3]; h is the pressure head *[L]*; $K(h)$ represents the unsaturated hydraulic conductivity [L/T]; t is time [T] and z represents the vertical coordinate [L] positive upwards.

van Genuchten equations are given below:

$$\theta = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\beta|h|)^{\eta}]^m} \tag{S2}$$

$$K(h) = K_s S_e^l [1 - \left(1 - S_e^{\frac{1}{m}}\right)^m]^2 \tag{S3}$$

where m=1-1/η, η>1

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{S4}$$

S_e represents the effective saturation; θ_s represents the saturated water content [L^3/L^3]; θ_r represents the residual water content [L^3/L^3]; K_s represent the saturated hydraulic conductivity (L/T) whereas β, η and l are the fitting parameters.

The one-dimensional water flow was described and solved using a mixed form of Richards equation as in Hydrus 1D[1] using the equations proposed by van Genuchten (Equations S1-S4).[2] This equation was solved by a fully implicit finite difference scheme with modified Picard approximation. The discretization of time and space domain is carried out using a backward Euler technique and a central differencing technique.[3] The error criterion specified was 10^{-2}. The mass balance error was close to 0.1%.

Transport Model

Microbial growth and pesticide degradation can be represented simultaneously by equations S5 and S6.

$$\frac{dX}{dt} = \left(\frac{\mu_m C}{K_C + C}\right)X - k_{decay}X \tag{S5}$$

$$-\frac{dC}{dt} = -\frac{1}{Y}\left(\frac{\mu_m C}{K_C + C}\right)X$$

(S6)

X is the total atrazine degrading soil biomass (ADSB) concentration, expressed on a whole soil volume basis [$\mathrm{mgL^{-1}}_{\mathrm{tot}}$]. C is the dissolved atrazine concentration [$\mathrm{mgL^{-1}}$]. μ_m is the maximum specific growth of ADSB [$\mathrm{day^{-1}}$]. K_C is the half saturation constant [$\mathrm{mgL^{-1}}$]. k_{decay} is the ADSB decay rate [$\mathrm{day^{-1}}$] and Y is the ADSB yield i.e. biomass formed per mass of atrazine degraded.

When $K_s >> C$, equation S5 and S6 can be simplified as equation S7 and S8 respectively.

$$\frac{dX}{dt} = \left(\frac{\mu_m C}{K_C}\right) X - k_{decay} X \tag{S7}$$

$$\frac{dC}{dt} =- \frac{1}{Y}\left(\frac{\mu_m C}{K_C}\right) X \tag{S8}$$

Normalizing with initial microbial concentration, X_0 we get,

$$\frac{dX^{'}}{dt} = \left(\frac{\mu_m C}{K_C}\right) X^{'} - k_{decay} X^{'} \tag{S9}$$

$$-\frac{dC}{dt} =- \frac{X_0}{Y}\left(\frac{\mu_m C}{K_C}\right) X^{'} \tag{S10}$$

where $X^{'} = \frac{X}{X_0}$

Simplifying, $\frac{X_0}{Y}\left(\frac{\mu_m}{K_C}\right) = A$ and $\left(\frac{\mu_m}{K_C}\right) = B$

$$\frac{dX^{'}}{dt} = BCX^{'} - k_{decay} X^{'} \tag{S11}$$

$$-\frac{dC}{dt} =- ACX^{'} \tag{S12}$$

Finally, the final transport equation including the degradation and reactive pesticide transport can be represented by equation S13.

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial^2 t} - v\frac{\partial C}{\partial z} - ACX^{'} \tag{S13}$$

The retardation factor R is $(1 + \frac{\rho_b K_d}{\theta})$, D is the dispersion coefficient [$cm^2 day^{-1}$], θ is the volumetric water content [LL^{-1}], ρ_b is the soil bulk density [$kg\ L^{-1}$], v is the pore water velocity [cm day^{-1}], k_{decay} is the decay constant [day^{-1}], K_d is the linear adsorption coefficient [L kg^{-1}], z is the length of soil profile [cm] and t is the time [day]. A and B are lumped parameters as the Monod kinetic parameters μ_m, K_C and Y in the column were not determined from independent batch study and initial microbial concentration (X_0) was not measured. B can be considered as modified maximum specific growth rate and A can be expressed as is $(B\frac{X_0}{Y})$.

The pesticide transport model including the biodegradation term, provided by equations (10-12) is solved using a finite difference scheme. The advection term, representing the hyperbolic component, is discretized using second-order upwind scheme for all the nodes, except the second node where the first-order upwind scheme is used. The dispersive term, representing the parabolic component is discretized using second-order central difference scheme. The advective term and the dispersive terms of the transport equation are solved using fully implicit and semi-implicit finite difference scheme, respectively. The degradation term including the microbial growth and pesticide degradation was explicitly considered.

References:

1 M. R. Kirkland, R. G. Hills and P. J. Wierenga, Algorithms for solving Richards' equation for variably saturated soils, *Water Resour. Res.*, 1992, **28**, 2049–2058.

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3 M. A. Celia, E. T. Bouloutas and R. L. Zarba, A general mass-conservative numerical solution for the unsaturated flow equation, *Water Resour. Res.*, 1990, **26**, 1483–1496.