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Crop producers have used atrazine as an herbicide for more than forty years and its continuous application may have resulted in a decrease in its half-life in some soils. The fate and transport of atrazine may be further altered with predicted changes in climate. The objective of this study was to assess potential changes in atrazine persistence and transport to groundwater under climate change scenarios predicted for the Midwestern U.S. The transport and transformation of atrazine was monitored in column experiments at high infiltration rates associated with increased precipitation intensity. Atrazine behavior was modeled using an advection-dispersion-sorption-degradation transport model. Batch microcosm studies were conducted to examine the effect of moisture content on atrazine degradation. Results showed that while atrazine was applied continuously to the columns the break-through curves obtained for both soils showed a pattern more characteristic of a pulsed input. The rate of atrazine leaching at higher infiltration rates was not fast enough to counteract the effect of enhanced degradation. Under future climate change scenarios, where more intense precipitation is likely to result in higher infiltration rates and increased soil moisture, the potential for groundwater pollution from atrazine may be reduced, especially in areas with a long history of atrazine application to soil. The influence of climate on production of atrazine metabolites may be dependent on soil type. Degradation of atrazine in the agricultural soils evaluated led primarily to the formation of hydroxyatrazine and deethylatrazine with increased in hydroxyatrazine concentrations observed in sandy soils with low organic carbon

Enhanced biodegradation of atrazine at high infiltration rates in agricultural soils

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Abstract

The objective of this study was to assess the persistence and transport of atrazine at high infiltration rates expected from higher intensity precipitation associated with climate change scenarios in the midwestern U.S. The transport and transformation of atrazine was monitored in column experiments at high infiltration rates (64-119 mm/d) associated with increased precipitation intensity. The optimum linear sorption and the lumped Monod biokinetic parameters were determined by inverting observed break-through curves (BTCs) using the advection-dispersion-sorption-biodegradation model. Batch microcosm studies were also conducted to examine the effect of moisture content (5%, 15% and 25%) on atrazine degradation and support the column results. BTCs from both soil types with continuous atrazine input showed a characteristic pattern of a pulse input i.e. lag phase prior to rapid atrazine degradation. The rate of atrazine leaching at higher infiltration rates was not fast enough to counteract the effect of

enhanced degradation. Higher infiltration rates enriched the distribution of hydroxyatrazine in the soil profile for sandy loam, but their effect was minimal in loam soil. The pattern of degradation obtained in batch microcosms agreed with the column results. In both soils, mean half-life of atrazine was lower (4-8 days) at high soil moisture contents. Under future climate change scenarios, where more intense precipitation is likely to result in higher infiltration rates and increased soil moisture, the potential for groundwater pollution from atrazine may be reduced, especially in areas with a long history of atrazine application to soil.

Keywords

Climate change, enhanced biodegradation, atrazine transport, groundwater, agricultural soils

1. Introduction

Crop producers have used atrazine as an herbicide for more than forty years to control annual grasses and broad-leaved weeds (Solomon et al. 1996). With such widespread use of atrazine, researchers have widely documented its occurrence in groundwater as well as its environmental fate and toxicological effects (Kolpin et al. 2002; Spalding et al. 2003a). Exposure to high concentrations of atrazine (100-250 μg/L in surface water) can cause death during early embryogenesis in frogs (Ji et al. 2016), and induce endocrine disruption in mice and fish (Jin et al. 2014; Du Gas et al. 2017). Desethylatrazine (DEA), deisopropylatrazine (DIA), didealkylatrazine (DDA), and hydroxyatrazine (HA) are the four main metabolites of atrazine. DEA and DIA have reduced toxicity when compared to the parent herbicide, while HA is non-toxic (Kolekar et al. 2014).

Previous studies have reported that atrazine is a moderately persistent herbicide in soil with half-lives (DT_{50}) ranging from 14 to 109 days (Ghadiri et al. 1984; Brejda et al. 1988), however, the continuous application of atrazine has resulted in a decrease in its half-life in some systems (Fang et al. 2015; Yale et al. 2017). The half-life of atrazine in soils with no previous atrazine application was 14.5 days, whereas the atrazine half-life for soils with a history of atrazine application was only 2.3 days (Mueller et al. 2017), suggesting that atrazine degrading bacteria in soils may be enriched over time. In soils with widespread atrazine application, the enriched bacteria developed over years leading to rapid atrazine degradation, thus decreasing their half-lives.

The fate and transport of atrazine may be further altered under future climate scenarios. In corn producing regions, for example in the Midwestern U.S., climate change is predicted to increase the intensity of precipitation events (Bates et al. 2008). As a result, average soil moisture, a key variable for agriculture, is projected to increase (Wuebbles and Hayhoe 2004). Several studies have shown that climate-induced changes in precipitation patterns will result in noticeable variations in the concentration and transport of trace organic contaminants (Bloomfield et al. 2006; Dalla Valle et al. 2007; Lamon et al. 2009; Ficklin et al. 2010; Delcour et al. 2015). Changes in precipitation may influence the runoff of pesticides (Lefrancq et al. 2017) and infiltration rate into the soil (de Paula et al. 2016).

Due to the potential for enhanced biodegradation of atrazine in soils with repeated annual application, and the expected higher infiltration rates under projected intense precipitation events, it is necessary to reevaluate the leaching potential of atrazine in corn production regions in the midwestern U.S. It is necessary to understand whether the enhanced transport of atrazine at higher infiltration rates is enough to counteract the effect of enhanced degradation. There are currently

no experimental studies evaluating the interactions between enhanced biodegradation of atrazine and higher infiltration rates in agricultural soils. In this study, soil column experiments were conducted for atrazine applied to agricultural soils receiving water at high infiltration rates. The transport and transformation of atrazine and its metabolites were measured and evaluated. Column break through curves were modeled using an advection-dispersion-sorption-degradation transport model. In addition, batch microcosm studies were also conducted to examine the effect of moisture content on atrazine degradation.

2. Materials and methods

2.1 Chemicals

Analytical grade atrazine (purity >98.8%), hydroxyatrazine (HA, purity >98.8%), deethylatrazine (DEA, purity >99.9%), deisopropylatrazine (DIA, purity >96.3%), and terbutylazine (purity 98.6%) were purchased from Sigma-Aldrich Chemicals (St. Louis, MO). Isotopically ring-labeled compounds: $^{13}C_3$-atrazine (purity 99% atom of $^{13}C_3$), $^{13}C_3$-deethylatrazine (purity 99.1% atom of $^{13}C_3$), $^{13}C_3$- deisopropylatrazine (purity 99.1% atom of $^{13}C_3$) were purchased from MSD Isotopes (Montreal, Canada) and used as internal standards (Cassada et al. 1994). Methanol and Ethyl acetate (Optima^{TM} grade), potassium bromide (KBr, purity 99%), potassium phosphate dibasic (K_2HPO_4, purity 99.85%) and potassium phosphate monobasic (KH_2PO_4, purity 99.9%) were obtained from Fisher Scientific (Pittsburgh, PA).

2.2 Soil collection and characterization

Two types of soil, loam (from a depth of 0-0.76 m) and sandy loam (from a depth of 0.76-17 m), were collected at the USDA Nebraska Management Systems Evaluations Area (MSEA) site, which was previously intensively monitored to evaluate potential for groundwater contamination in the High Plains Aquifer (Spalding et al. 2003b, a). Atrazine has been used as an herbicide at this location for more than 40 years. The soil properties are represented in Table 1. Soils were collected by hand and preserved at 4°C in a cold room until use. Soils were then dried at 25°C overnight, sieved to obtain soil particles <2 mm in dimension.

2.3 Batch soil microcosm experiments

Ninety (90) grams (g) (dry weight) of soil was added into each 120-mL amber glass jar. An atrazine stock solution (5 μg/μL in methanol) was spiked into the jar to obtain a final concentration of approximately 8mg/kg. After methanol was evaporated, the water content was adjusted by addition of sterile deionized water to obtain soil moisture levels of 5%, 15% and 25% for sandy loam and loamy soils. The soil in the jars was mixed thoroughly using a spatula for approximately one minute to ensure homogeneous distribution of atrazine and soil. Sterile controls were set up for each soil by autoclaving the soil jars three times at 121°C for 30 min. At each moisture level, three jars were conditioned as microcosms under non-sterile conditions and two jars as sterile controls. Two g of soil was periodically (0, 1, 5, 7, 9, 11, 15, 20, 25 and 30 d) transferred from each jar into 20-mL glass scintillation vials for extraction and analysis of atrazine and its metabolites. The jars were covered with foil to prevent evaporation. Water content was determined gravimetrically and adjusted with sterile deionized water in case of any loss. Atrazine degradation rates in soil were calculated using the change in the dimensionless concentration

(C_t/C_0). The best fit model and values of the estimated parameters were found using the non-linear least-squares Levenberg–Marquardt method with OriginPro™ 2017 Student version.

A sigmoidal, or growth category curve, was found to be the best fit model at all three moisture levels for both soil types (equation 1).

$$y = \frac{a}{1 + e^{-k(x - x_c)}} \quad (1)$$

In equation 1, y is % atrazine remaining, x is time (days). a, k and x_c are fitted constants.

2.4 Column experiments

Plexiglass columns (length 100 cm, internal diameter 10 cm) were sealed with a nylon mesh with an effective pore diameter of 60 μm to retain the soil in the column. An approximately 2 cm layer of gravel was placed above and below the soil column for even water distribution. Each soil column was packed by addition of dry soil (approximately 9,300 g for sandy loam and 7,500 g for loam) to the column in small increments to maintain homogeneity in the column to a final bulk density of approximately 1.3-1.6 g/cm^3. The top of the column was covered with parafilm to prevent evaporation. The entire plexiglass column was covered with aluminum foil to prevent photodecomposition of atrazine. Initially, deionized water was added continuously to the top of the column (0.30-0.65 mL/min) using a peristaltic pump until the outlet flow rate was constant. Once steady-state flow was achieved, 1 mg/L atrazine, along with 80 mg/L KBr as a tracer, was fed continuously (0.30-0.65 mL/min) to the column for 30 days. The transport of atrazine was studied at three infiltration rates (i.e., 64, 77 and 119 mm/d) for sandy loam and at two infiltration rates (i.e., 64 and 92 mm/d) for the loamy soil. Higher infiltration rates could not be used for loam

soil due to ponding issues on top of the column. Soil moisture content was measured every 30 minutes at 0, 25, 50 and 75 cm depth in the column using a Watchdog 2400 Station and four WaterScout SM 100 sensors (Spectrum Technologies, Inc), which were previously calibrated for each soil type. Liquid samples were collected from the outlet at the bottom of the column daily and soil samples were collected at 0, 25, 50, 75 and 90 cm depth inside the column at the end of each experiment (i.e., 30 days) to measure the concentrations of atrazine and its metabolites. The sandy loam column at an infiltration rate of 119 mm/d was run in duplicate to confirm atrazine behavior in columns through effluent BTCs. Otherwise, as the column studies were carried out at different infiltration rates, only one column per infiltration rate was run.

2.5 Analytical methods

Extraction and instrumental analysis of the atrazine and its degradation products follow previously published methods (Cassada et al. 1994). Briefly, 10 mL of liquid samples were spiked with surrogate (terbutylazine) and $^{13}C_3$-labelled internal standards. The samples were extracted using preconditioned C-18 solid phase extraction (SPE) cartridges, dried and eluted with 4 mL of ethyl acetate in Supelco VisiPrep Teflon holder. The visible residual water layer from the eluted samples was removed by addition of a spatula of clean and dried anhydrous sodium sulfate. The remainder of the eluent was transferred to a clean tube and evaporated under a dry steam of nitrogen to obtain a final volume of approximately 300 μL. The concentrated extracts were transferred to autosampler vials and analyzed using an Agilent 5972 gas chromatography mass spectrometer (GC/MS) for atrazine, DIA, and DEA concentrations. The separation was carried out on Rtx-1 fused silica capillary column (30 m X 0.25 mm I.D. film thickness) under the following conditions: the sample of volume 1 μL was injected in spitless mode at 80° C, held for 0.75 min then a temperature gradient was programmed at 40°Cmin^{-1} to 140°C, then 4°Cmin^{-1} to 211°C and

finally 39°Cmin^{-1} to 250°C and held for 10 min. Injector and transfer line temperature were both held at 280°C. Retention times, detection limits and recoveries of atrazine and its metabolites in water samples are shown in Table S1.

Soil samples were extracted using microwave assisted solvent extraction and analyzed for nonvolatile degradation products using liquid chromatography with ultraviolet detection (Papadakis and Papadopoulou-Mourkidou 2006). Briefly, 2 g of wet soil was weighed into a Teflon microwave digestion vessel, spiked with surrogate (terbutylazine), and thoroughly mixed with 8 mL of a 100 mM K_2HPO_4 (pH 7): methanol (50:50, v/v) mixture. Samples were subjected to microwave irradiation (440 W) for 20 min at 100°C using a CEM MARS Xpress microwave digestion system. Samples were centrifuged for 10 min at 2500 rpm, supernatant was transferred to a tube and diluted with ~100 mL of distilled deionized reagent water. The aqueous extracts were concentrated using solid phase extractions and the C18 cartridges were eluted with 4 mL methanol followed by 3 mL of ethylacetate. The combined elutes were evaporated to dryness under a dry stream of nitrogen gas.

Residues were redissolved in 200 µL of methanol and transferred into an autosampler vial to be analyzed by high pressure liquid chromatography (HPLC) for measurement of atrazine, HA, DIA and DEA concentrations, on a Waters 2695 HPLC system with a Waters 2996 PDA detector. Separation was carried out on a Thermo Syncronics C18, 250 mm x 4.6 mm column (5 µm particle size). The mobile phase of the HPLC system consisted of a binary gradient mixture of a 10 mM KH_2PO_4 solution (solvent A) and a 90% acetonitrile : 10% water mixture (solvent B). The gradient program was as follows: solvent A, initial 94% (hold for 0.1 min), then linear change to 72%

(solvent A) at 10.0 min followed by a linear change to 46% (solvent A) at 18.0 min, then linear change to 20% (solvent A) at 25.0 min (hold for 5.0 min). A step change to initial conditions (94% solvent A), hold for 5 min to re-equilibrate the column. The mobile phase flow rate was set at 0.8 mL/min and the injection volume was 10 μL. Quantitative measurements were made at 220 nm (atrazine, DIA, DEA, terbutylazine) and 240 nm (HA). Retention times, detection limits and recoveries of atrazine and its metabolites in soil samples are shown in Table S2.

2.6 Atrazine degradation and reactive transport model development

Reactive transport of atrazine in soils can be described using an advection-dispersion equation (ADE) with a sink term representing adsorption and degradation (van Genuchten et al. 2013). Prior studies determined that a nonlinear degradation kinetic model, instead of zero and first order pesticide degradation rate models, was necessary to accurately describe observed atrazine column breakthrough curves (BTCs) (Sniegowski et al. 2009; Cheyns et al. 2010). In this work, a logistic model based on simplified Monod kinetics was applied to simulate atrazine degradation kinetics (Cheyns et al., 2010; De Wilde et al., 2009). The transport model involving sorption coupled biodegradation in unsaturated or variably saturated porous medium was described in earlier studies (Gaonkar et al., 2016a,b). Atrazine transport, including microbial growth, pesticide degradation and linear sorption, is simultaneously represented by equations 2 and 3.

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial^2 t} - v\frac{\partial C}{\partial z} - ACX' \quad (2)$$

$$\frac{dX'}{dt} = BCX' - k_{decay}X' \quad (3)$$

where R is the retardation factor expressed as $(1 + \frac{\rho_b K_d}{\theta})$ where θ is the volumetric water content [cm^3cm^{-3}]; ρ_b is the soil bulk density [kgL^{-1}]; K_d is the linear adsorption coefficient [Lkg^{-1}]; v is

the pore water velocity [cmday^{-1}]; D is the dispersion coefficient [cm^{2}day^{-1}]; z is the length of soil profile [cm]; t is the time [day]; X' is the relative atrazine degrading soil biomass (ADSB) concentration (unitless); k_{decay} is the ADSB decay rate [day^{-1}] and C is the dissolved atrazine concentration [mgL^{-1}]. A and B are lumped parameters represented by Equations (4) and (5):

$$\frac{X_0}{Y}\left(\frac{\mu_m}{K_C}\right) = A \quad (4)$$

$$\left(\frac{\mu_m}{K_C}\right) = B \quad (5)$$

where μ_m is the maximum specific growth of ADSB [day^{-1}]; K_c is the half saturation constant [mgL^{-1}]; and Y is the ADSB yield (i.e. biomass formed per mass of atrazine degraded) [unitless]. Here, microbes were assumed to be immobile, and atrazine concentration was assumed to be significantly lower than K_c (i.e. $K_c >>$ C). The derivation of this simplified equation from the Monod equation can be referred to in the previous studies (Cheyns et al., 2010; De Wilde et al., 2009). Here, A is dependent on the initial values of biomass (ADSB) concentration (X_0), which cannot be directly determined from the BTCs. A corresponds to specific biomass affinity as defined in la Cecilia and Maggi (2016). Although, simulations were carried out considering the relative biomass concentrations with the initial value being equal to one, A can be a valuable quantity to estimate biomass growth when multiple microbes compete for a substrate (Porta et al. 2018). B can be termed as the modified maximum specific growth rate.

The bromide tracer BTCs were fitted using Hydrus 1D to determine the van Genuchten parameters, β, η, K_s and the longitudinal dispersivity, α ($D = \alpha.v$). The initial estimates and selected range of the fitted parameters were based on the studies conducted by Carsel and Parrish, (1988) and Kool et al., (1985). After the physical parameters were characterized, atrazine degradation and transport were analyzed by best-matching experimentally measured atrazine BTCs with modeling results using the Levenberg–Marquardt algorithm in Mat-Lab. Here, the physical transport

parameters obtained using bromide breakthrough data were used as input parameters to the mathematical model and optimized values for sorption parameter, K_d, and biokinetic parameters *A, B* and k_{decay} were estimated. The one-dimensional water flow was described and solved using a mixed form of Richards equation as in Hydrus 1D (Kirkland et al. 1992). Additional information, including other inputs to the flow model is described in the Supplementary Information.

The initial estimates, lower and upper bounds of relevant kinetic parameters used to fit the column effluent data were selected based on the range considered by De Wilde et al. (2009) and are provided in Table 2. The model performance was statistically evaluated using modified coefficient of efficiency (*E*), where a *E* of ≥ 0.5 was determined to represent acceptable model performance (Köhne et al. 2006). A detailed description of the transport equations (**equations S5-S13**) in addition to other details of the model is given in the supplementary information.

3. Results and discussions

3.1 Bromide BTCs

Figure 1 shows the BTCs of tracer bromide against pore volumes (PV). The model curve fit the experimental tracer data well with $R^2 > 0.9$ in all cases. Table 3 presents the fitted physical parameters. The dispersivity length was similar in loam columns at both infiltration rates but was slightly higher in sandy loam column at the higher infiltration rate. The spatial heterogeneity and differences in packing the columns likely explain any differences in the estimated physical transport parameters.

3.2 Atrazine transport in soil columns

3.2.1 Atrazine effluent (BTCs)

Figure 2 shows atrazine BTCs under different infiltration rates for sandy loam and loam soil columns. Atrazine was applied continuously to the columns with the infiltrating water for 30 days, however, the BTCs obtained for both sandy loam and loam soils showed a pattern that is characteristic of a pulse input.

In sandy loam columns, we observed minimal retardation and maximum relative concentrations (C/C_0) close to 1. The atrazine concentration in the effluent was almost negligible by 2.4 (17 d), 2.19 (13d) and 4.16 PV (16 d) for the 64, 77, and 119 mm/d infiltration rates, respectively. These results imply a lag phase prior to atrazine degradation followed by rapid degradation of atrazine. De Wilde et al. (2009) reported similar effluent BTC for metalaxyl in a system where sandy loam soil and different substrates were used for pesticide degradation.

The loamy soil columns exhibited more retardation, more spreading and tailing, and the maximum relative atrazine concentration was much lower than one. The atrazine concentration in the column effluent was negligible by 4.07 PV (24 d) and 3.35 PV (28 d) for the 64 and 92 mm/d infiltration rates, respectively. Atrazine was likely to be more bioavailable in the sandy loam soil with a lower organic matter and clay content when compared with loam soil likely due to decreased sorption in sandy loam soil (Beck and Jones 1996; Jenks et al. 1998). However, the biodegradation potential will depend on ADSB.

Atrazine can be degraded through chemical and biological processes. Chemical processes occurred typically at acidic pH, whereas biological processes at neutral pH (Blumhorst and Weber 1994). Given that the pH of the sandy loam and loam soils was 7.6 and 6.7, respectively (Table 1), and the nonlinear kinetics of degradation, we inferred from Figure 2 that the degradation was

mostly attributable to microbial activities. Atrazine underwent rapid degradation, but we did not detect its degradation products, such as HA, DEA and DIA in the sandy loam soil. Therefore, these intermediate degradation products were likely further degraded. In contrast, we detected DEA in the effluent from the loam soil column at both infiltration rates (Figure S1). It should be noted that approximately 20 to 25 % of the applied atrazine can be accounted for in the form of atrazine and its metabolites from the sandy loam soil column while only about 4.5 % of the applied atrazine can be accounted for in the loam soil. The unaccounted mass of atrazine may be due to atrazine mineralization, or conversion to unmonitored degradation products. It is also possible that some portion of the atrazine or atrazine metabolites formed a bound residue that was not extractable.

Siripattanakul et al. 2008 reported rapid degradation of atrazine at lower infiltration rates (1 and 3 cm/d) in sand columns mixed with free and immobilized *Agrobacterium radiobacter* J14a cells, but when the infiltration rate was increased to 6 cm/d, the atrazine removal efficiency decreased. Another prior study used the same initial atrazine concentration (1 mg/L) and observed complete atrazine degradation only after 24 weeks (Hunter and Shaner 2009). One potential difference is that in the current study, soils used in the column experiments were obtained from a location exposed to atrazine for more than 40 years. It is likely that the history of atrazine application has enriched the atrazine-degrading microorganisms, which resulted in high atrazine removal efficiency (Zablotowicz et al. 2006, 2007; Field et al. 2010; Krutz et al. 2010; Mueller et al. 2017). Atrazine transport at the higher infiltration rates was not fast enough to counteract the effect of this enhanced degradation, reducing the potential for atrazine leaching and pollution to groundwater in regions with a long history of atrazine application even under high infiltration rates.

3.2.2 Atrazine and its metabolites in the soil profile

Figure 3 shows final atrazine and metabolite soil concentration profile in the sandy loam and loam soil columns i.e. at the end of the experiments (30 days). In sandy loam, the atrazine concentration in soil decreased with depth at both infiltration rates. We detected HA throughout the column only at the highest infiltration rate (119 mm/d). Neither DIA nor DEA was found at any depth in the soil. DIA and DEA are more soluble than HA so they tend to be in the aqueous phase and hence more bioavailable (Panshin et al. 2000; Prata et al. 2003). The absence of DIA or DEA inside these columns in either the soil or aqueous phase suggests that the enhanced biodegradation of atrazine in the sandy loam soil led mainly to the formation of HA or alternatively, any DIA and DEA formed was rapidly further degraded. Although HA is generally not found as a biological degradation product, previous studies have reported the formation of HA by atrazine mineralizing bacterial strains (Goux et al. 2000; Smith et al. 2005; Solomon et al. 2013).

In loam soil, we observed atrazine throughout the column at both infiltration rates—with the highest concentration at 25 cm for the 92 mm/d infiltration rate. The HA concentrations in this soil remained stable with depth at both infiltration rates. DIA was identified in the loam soil, but at relatively low concentrations. No DEA was detected at any depth. We observed higher concentration of atrazine and HA in loam soil columns compared with sandy loam columns, because of higher sorption capacity of loam soil.

The difference in HA distribution between low and high infiltration rates was remarkable in the sandy loam soil whereas it was minimal in case of loam soil. HA is less mobile and more persistent than the other metabolites, DEA and DIA. Moreover, it forms the lowest amount of soil bound residue compared to DEA and DIA, resulting in better detection in soil extracts

(Winkelmann and Klaine 1991). Degradation rates may decrease with increasing infiltration rates and the amount of contaminant degraded varies as a function of column residence time and pore water velocity (Langner et al. 1998).. In our study, the increase in infiltration rate within the sandy loam allowed atrazine sufficient residence time to be degraded into HA but restricted its further degradation, hence HA concentration was greater at higher infiltration rate. Although, the atrazine concentration was higher in loam especially in upper layers at higher infiltration rate, probably because of the decrease in degradation, HA concentration was more or less stable (Figure 3). The reduction in degradation can also be confirmed from decrease in A and B values with increasing infiltration rates in loam soil (Table 4). The results clearly indicate variations in degradation, distribution and transport of atrazine and its metabolites in sandy loam and loam soils.

3.2.3 Modelling atrazine transport

The transport model with simplified Monod kinetics described the atrazine BTCs well, as with E between 0.91–0.99 (Figure 2 and Table 4). Table 4 represents the model optimized sorption and degradation parameters.

We estimated low and high K_d values for sandy loam and loam, respectively. Low K_d values for sandy loam is consistent with the observed atrazine BTCs, where retardation is minimal (Figure 2a). Low K_d values (0.001 L/kg and 0.206 L/kg) at high flow rate were also reported in a previous study (Cheyns et al. 2010b) in columns containing similar soil type. The estimated higher K_d values for loam soil agreed with the obvious atrazine retardation observed from the atrazine BTCs (Figure 2b).

The B values were higher for loam soil compared with sandy loam soil. Moreover, A values were also higher for loam soil i.e. about 1000 times greater than sandy loam. A can be expressed

as $\left(\frac{BX_0}{Y}\right)$, indicating X_0 is greater and/or Y is smaller. But, the scientific range possible for Y is 0.1 to 0.9 (Priya and Philip 2013), implying X_0 was much greater for loam soil. During the lag phase, a sufficiently high number of microbes capable of utilizing and degrading a specific chemical as a nutrient or energy source are grown. This period can also be termed acclimation or adaptation time (Alexander 1999). A higher X_0 value indicated presence of greater ADSB and hence a shorter acclimation time. Hence, higher A and B values explains why we did not observe a significant lag phase in the loam soil and implies that ADSB was sufficiently large to observe degradation of atrazine from the beginning. Furthermore, the higher sorption in the loam soil led to a relatively lower concentration of atrazine in the liquid. Biodegradation can be very effective under lower atrazine concentration in the liquid, which might explain the later drop of the concentration.

We estimated a lower microbial decay constant ($>10^{-5}$) in loam soil at both infiltration rates and in sandy loam at higher infiltration rates. A slightly higher value of microbial decay was observed in the sandy loam column only at the lowest infiltration rate of 64 mm/d. The model simulations underpredicted the measured atrazine soil concentrations, especially in the loam soil, despite good fits for the effluent BTCs (Figure 3). This implied that the best estimates of model parameters obtained with BTCs do not yield accurate results for the spatial distribution of atrazine and metabolites along the column. The variations between observed and model predictions are probably because of the uncertain estimates of biokinetic parameters A and B (as quantified by confidence intervals). This uncertainty may have arisen from the model formulation not adequately describing all the kinetic processes taking place in the system and small scale variability (Yoon and McKenna 2012). In addition, the availability of nutrients such as C, N and micronutrients available to the soil microbes might lead to parameter variability in our study (Porta et al. 2018). Lack of consideration of complex reversible or irreversible sorption models may further affect

model predictability as shown by (Wehrhan et al. 2007). It should be noted that performing field scale analyses based on estimates obtained from column studies may lead to propagation of uncertainty, thus impacting understanding of effective transport dynamics.

3.3 Biotransformation microcosms

Figure 4 presents atrazine biotransformation under different soil moisture contents. In both soil types, we observed rapid degradation at higher soil moisture content. Both soils revealed a lag phase. The lag phase was longer at the lowest soil moisture in sandy loam and was not present at the highest soil moisture content in loam soil (Table 6). Atrazine was almost completely degraded in both soils at days 15 and 30 for higher (15% and 25%) and low (5%) soil moisture contents, respectively. The soil moisture range for the column studies was greater than 10% (Table S3), therefore, the pattern of degradation obtained in batch microcosms agreed with the column results.

In both soils, mean half-life of atrazine was lower at high soil moisture contents. (Accinelli et al. 2001) reported that atrazine half-life in surface soils was approximately 40 days. Our study demonstrates a decrease in atrazine half-life, possibly due to the 40-year history of atrazine application at the field site where the soils were obtained. Previous studies have indicated that atrazine half-life decreased in soils with a history of continuous application (Fang et al. 2015; Yale et al. 2017). Both column and microcosm results support the idea that microbial communities in these soils were adapted to atrazine leading to enhanced biodegradation.

Figure 5 shows hydroxyatrazine biodegradation microcosm results under different soil moisture contents for both soil types. In these microcosms, DIA and DEA concentrations were negligible. In both soils, HA was formed in both non-sterile and control (sterile) microcosms. In both the soil types, HA concentration was mostly lower in non-sterile microcosms than control at the lowest moisture content (5%), whereas it was higher in non-sterile microcosms than control

at higher moisture contents (15% and 25%). This difference in HA concentration between control and non-sterile microcosms implies that at low soil moisture content, HA is formed mainly through abiotic processes, but at high soil moisture HA is formed through microbial activity. This finding agreed with our column experiments where HA was formed mainly through biodegradation of atrazine because the soil moisture in our columns ranged from 11-40%. Therefore, soil moisture affected the dominant formation processes.

In the non-sterile reactors, HA concentration was higher at 15% and 25% soil moisture contents (Figure 5). For both soil types, HA concentrations increased rapidly, reached a maximum and then started decreasing for the two higher soil moisture contents. The decrease was more noticeable at 15% soil moisture. One explanation for this tendency could be that adapted bacteria further degraded HA with time. Previous studies have reported that bacteria belonging to the genera *Pseudomonas, Arthrobacter,* and *Sinorhizobium* have the genes *atzA, atzB, atzC, trzN,* and *trzD*. These genes encode enzymes capable of degrading atrazine to hydroxyatrazine which can be further degraded to N-isopropylammelide and cyanuric acid (De Souza et al. 1995, 1998a, b; Bellini et al. 2014; Douglass et al. 2016, 2017), however the specific bacteria present in soils in this study were not determined.

The increasing HA concentration explained most of the decrease in atrazine concentration in the microcosm experiments for both soils (Figures 4 and 5). These results and the column experiments data suggest that the enhanced microbial degradation of atrazine in these agricultural soils leads primarily to the formation of HA and DEA. This finding agreed with a previous study conducted in the same site which showed that the hydrolysis of atrazine and DEA to hydroxyatrazine was likely the major degradation route (Spalding et al. 2003a).

Enhanced degradation of atrazine was observed in the agricultural soils with mean half-life in the range 4-8 days. However, atrazine degradation seems to be impacted by the soil moisture content which is expected to be higher under projected change in intensity of precipitation events in future in the Midwestern U.S. Although HA was found to be the major atrazine metabolite in this study, the preferred degradation pathway will largely depend on biogeochemical conditions and hydrologic conditions in the future.

4. Conclusions

In the Midwestern U.S., climate change will influence hydrology through more intense precipitation events. Increase in precipitation frequency may induce higher infiltration rates in the soils as well as increased soil moisture content. However, it should be noted that climate change will likely result in additional effects not evaluated here including loss of atrazine due to lateral leaching and/or enhanced soil erosion. Batch and column studies confirmed accelerated atrazine degradation in the selected agricultural soils. In such soils with historic atrazine application and enhanced biodegradation, the overall impact of increased infiltration rate on atrazine transport may be limited as the influence of degradation overwhelms the potential for enhanced transport with infiltrating water.

Although DEA and DIA were observed, HA was the major metabolite. The transport and distribution of HA as a function of infiltration rate was influenced by soil texture Taken together, this data demonstrates the potential of climate change to influence contaminant behavior in soils, however, the specific effects will require knowledge of soil properties and the relative rates of contaminant loss mechanisms (i.e. biodegradation) versus transport properties (infiltration rates). The influence of climate on metabolite profiles in soil is an area requiring more study.

This study investigated the influence of infiltration rate and the subsequent influence on moisture content, however, other aspects of climate change including changes in temperature and climate-induced in soil microbial communities will also influence contaminant fate**.** The combined impact of all these climate related factors on pesticide degradation and leaching requires additional investigation.

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10.1614/WS-04-179R3.1

TABLES:

Table 1

Soil properties

Soil Type	Organic Matter (%)	pH	CEC (meq/100 g)	Moisture Content (%)	Sand (%)	Silt (%)	Clay (%)
Loam	1.4	6.7	10.4	15.6	44	42	14
Sandy Loam	0.3	7.6	11.3	6.24	68	26	6

Table 2

Bounds of parameters used for optimization

	Sandy loam		Loam	
Parameters	Lower bounds	Upper bounds	Lower bounds	Upper bounds
A (L/mg.day)	10^{-6}	10^{-3}	10^{-2}	1
B (L/mg.day)	1	4	4	10
K_d (L/kg)	10^{-5}	10^{-3}	10^{-4}	10^{-2}
k_{decay} (1/day)	0	1	0	1

Table 3

Estimated physical transport parameters for bromide tracer using Hydrus 1-D

Infiltration Rate (mm/d)	θ_s (cm^3/cm^3)	θ_r (cm^3/cm^3)	β (1/cm)	η	K_s (cm/day)	l	α* (cm)	R^2
Sandy loam columns								
64	0.41	0.065	0.088	1.62	91.84	0.5	2.167±0.455	0.9568
77	0.41	0.065	0.091	2.12	145.6	0.5	1.35±0.206	0.9927
119	0.41	0.065	0.118	2.25	154.8	0.5	4.69±1.022	0.9651
Loam columns								
64	0.43	0.078	0.07	4	70	0.3	2.217±1.399	0.9937
92	0.43	0.078	0.053	2.9	57.79	0.5	1.37±1.342	0.9974

*Values are with ±95 confidence interval, θ_s represents the effective saturation; θ_r represents the residual water content; K_s represents the saturated hydraulic conductivity (L/T), whereas α, η and l are the fitting parameters.

Table 4

Optimized sorption and degradation parameters for the observed BTCs

Optimized parameters (± 95 % confidence interval)				
Infiltration rates (mm/d)	A (X 10^{-3}) (L/mg.day)	B (L/mg.day)	K_d (L/kg)	k_{decay} (1/day)
Sandy-loam columns				
64	0.1±1.2	1.4523±1.81	0.1±0.05	0.0031±0.0545
77	0.1±2.3	2.3887±12.23	0.2±0.01	$>10^{-5}$
119	0.01±0.1	1.7513±1.746	0.1±0.15	$>10^{-5}$
Loam columns				
64	125.5±2074.9	8.9525±106.2	1.2±0.15	$>10^{-5}$
92	60.5±1255.6	4.5331±45.72	1.3±0.1	$>10^{-5}$

Table 5

Biodegradation microcosm parameters

Soil Type (Moisture Content %)	Lag Phase (d)	Mean Half-life* (d)
Sandy Loam (5)	12	16
Sandy Loam (15)	6	7.4
Sandy Loam (25)	6	8.7
Loam (5)	6	16.5
Loam (15)	4	4.6
Loam (25)	0	8.3

*Calculated from the best fit model

FIGURES:

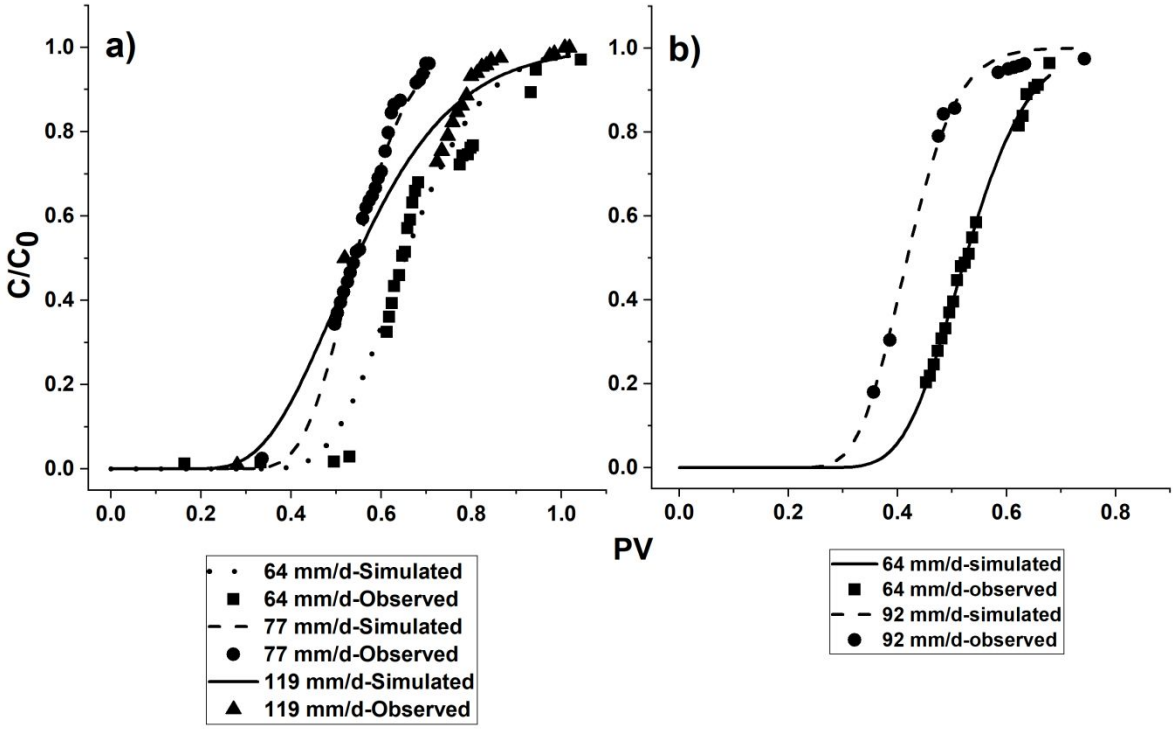

Fig. 1 Observed and model-fitted tracer BTCs for: a) sandy-loam and b) loam soil

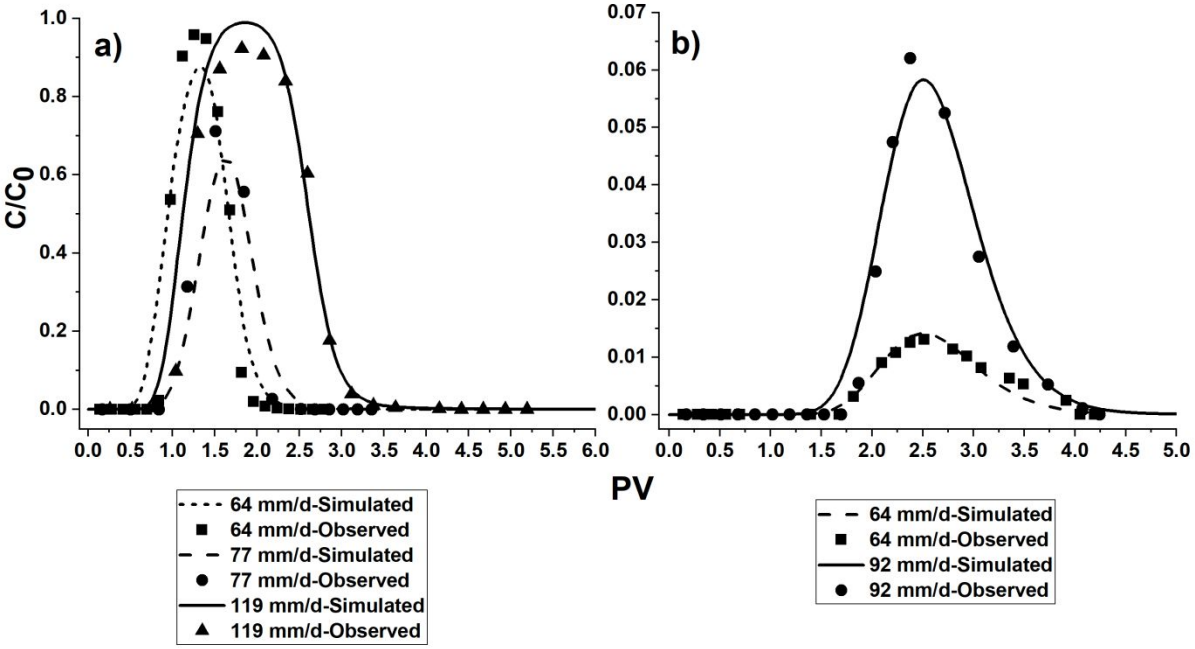

Fig. 2 Observed and model-fitted atrazine BTCs for: a) sandy-loam and b) loam soil

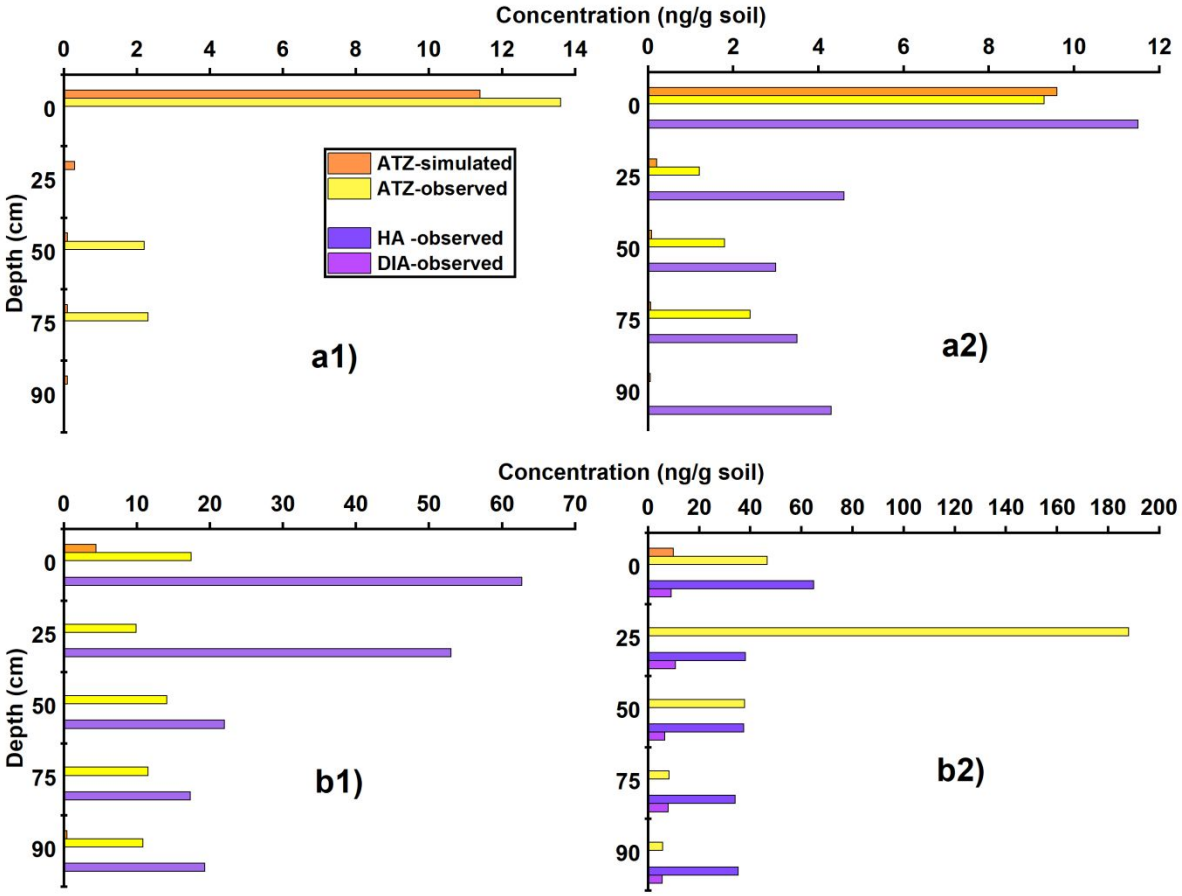

Fig. 3 Final atrazine (observed and simulated) and metabolite concentration profile at different infiltration rates in sandy loam at a1) 64 mm/d and 119 mm/d and loam soil at b1) 64 mm/d and b2) 92 mm/d

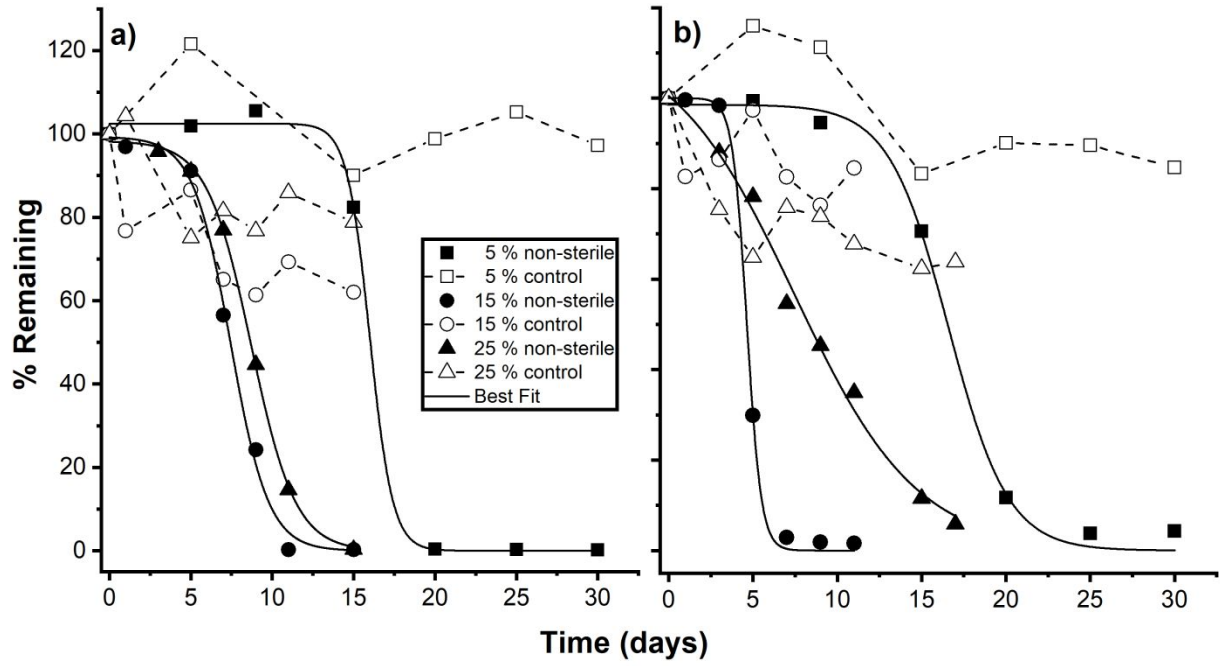

Fig. 4 Atrazine biodegradation in batch soil microcosm in: a) sandy-loam and b) loam

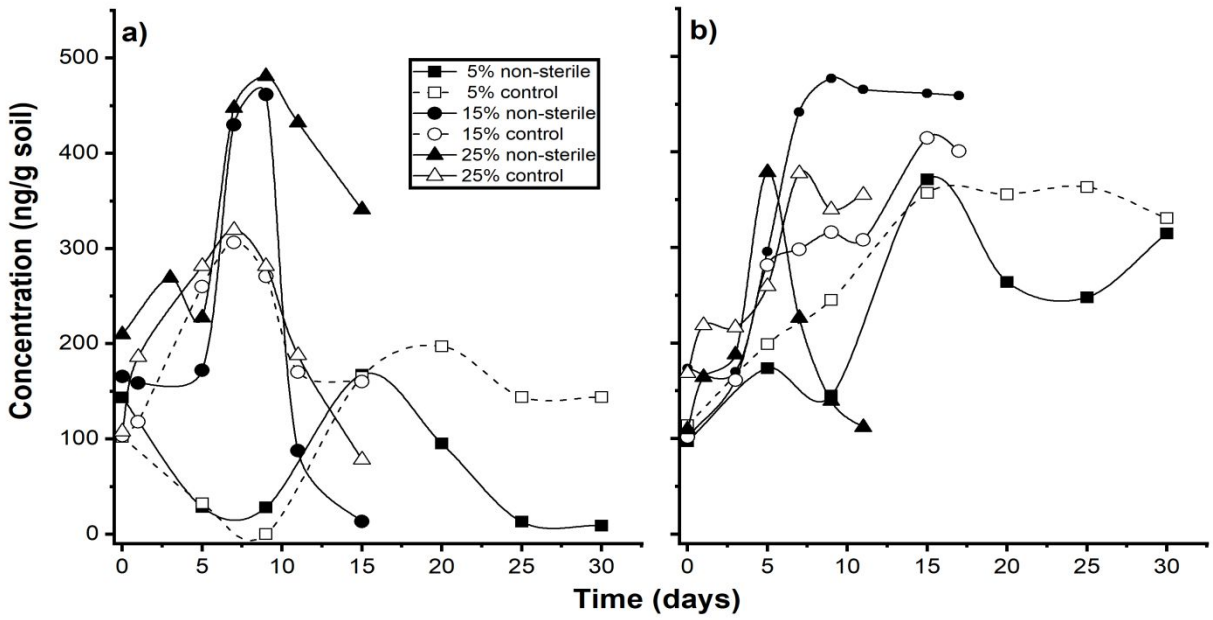

Fig. 5 Hydroxyatrazine formation in batch soil microcosm in: a) sandy-loam and b) loam

Table of Contents Entry

Competing effects of increasing infiltration and enhanced degradation due to historical atrazine application in soils may limit the impact on atrazine transport under scenarios representative of climate change.