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Differential Transport of Atrazine and Glyphosate in Undisturbed Sandy Soil Column

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With increasing awareness and concern for environmental quality, it is important to study the fate of pesticides in the subsurface. Laboratory studies were conducted to determine the behavior of atrazine and glyphosate within the root zone of an undisturbed sandy soil in Jianghan Plain, central China. Chloride as a tracer for water movement was applied to the soil as KCl for 26 hours before pesticide application for another 160 hours. Glyphosate, atrazine, and Cl concentrations (conc.) were determined as a function of time in breakthrough curves (BTCs). Atrazine BTC was fitted better in convection-dispersion equation equilibrium model. For glyphosate, however, a two-site non-equilibrium model was chosen. Leaching rate of atrazine from sandy soil was much higher than that of glyphosate and it took longer for glyphosate to leach through the column due to stronger sorption and degradation to its major metabolite, AMPA (aminomethylphosphonic acid, CH_6NO_3P), which was detected (up to 8890 ng/l) in the final leachate.

Keywords pesticides, BTCs, sorption, degradation

1. Introduction

Glyphosate and atrazine are among the most widely applied pesticides. Glyphosates ([N-phosphonomethyl] glycine) are commonly used as herbicides in agriculture, horticulture, and silviculture, as well as in garden maintenance (including home use). Their vapor pressure is neglectable and their solubility in water is high, 12 g/l at 25°C (Grossbard and Atkinson, 1985). Glyphosate undergoes microbial degradation in soils (Sprankle et al., 1975; Rueppel et al., 1977). Its major metabolite, AMPA (aminomethylphosphonic acid, CH_6NO_3P), has moderate toxicity and probably it is sorbed strongly on the soil due to the phosphate moiety. Atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine) is a selective triazine herbicide used to control broadleaf and grassy weeds in many agricultural crops like corn, sorghum, sugarcane, pineapple, Christmas trees, and other crops, and in conifer reforestation plantings. It is also used as a non-selective herbicide on non-cropped industrial lands and on fallow lands. It is available as liquid, water-dispersible granular, and wettable powder formulations.

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Understanding the environmental fate of pesticides in soils and groundwater is the basis for assessment of their potential hazards. Their fate and transport is generating considerable interest because of concerns for the quality of the subsurface environment. The behavior of solutes over relatively long spatial and temporal scales must generally be assessed with the help of theoretical models since it is usually not feasible to carry out experimental studies over sufficiently long distances and/or time periods. Mathematical models are often used to predict solute concentrations before management strategies are implemented. Advances in software and hardware now permit the simulation of subsurface transport using sophisticated mathematical models. Unfortunately, it is generally difficult to obtain reliable values of transport parameters such as the pore-water velocity, retardation factor, hydrodynamic dispersion coefficient, and/or degradation kinetic parameters. The program CXTFIT 2.1 may be used to estimate such parameters by using several analytical models of solute transport for steady one-dimensional flow and fitting the analytical solutions of models to lab-scale or field-scale data (Simunek et al., 1999).

Data concerning degradation and sorption data for atrazine in soils can be found in Rao and Davidson (1980) and Nash (1988). Field persistence studies have been performed almost exclusively in forest soils, showing high vertical mobility in the treated soils with the glyphosate to reach quickly high concentrations in the subsoil (Dibyendu et al., 1989; Newton et al., 1994; Veiga et al., 2001). Column tracer experiments, also called miscible displacement or breakthrough curve experiments, are another important approach to obtain sorption and degradation properties of contaminants in soil. Tracer tests have been widely conducted in pipelines, lakes, rivers and groundwater to delineate the flowpaths of water. The chemical must be dissolved in water at concentrations that do not change significantly the density of the aqueous phase. The tracer chemicals must be conservative, i.e., no mass is lost through reaction or partitioning into different phases (vapor and solids). Thus, the only solute transport processes affecting the fate of a conservative tracer are advection and dispersion. Advection is the movement of the solute (dissolved tracer) due to groundwater flow and the mean pore-water velocity (calculated from Darcy's Law) is used to predict advection. Due to the variety of pore sizes, the local pore velocities within the groundwater system are not uniform, a fraction of the solute will move at velocities lower than the mean velocity, and another fraction of it will move at velocities higher than the mean velocity. This picture is enhanced by molecular diffusion caused by local solute concentration gradients. The resulting dispersion of the solute causes a broadening of the solute plume. Miscible displacement techniques may be more appropriate since flow conditions, even in the laboratory, are presentative of transient field conditions. This paper reports our work on the transport of atrazine and glyphosate through column experiments with undisturbed sandy soil collected from a field site located in the middle of Jianghan Plain, and using KCl as the conservative tracer. Sorption parameters were estimated through CXTFIT modeling. The leaching behavior of glyphosate was evaluated through undisturbed soil column under controlled laboratory conditions and was compared with that of atrazine. The results provide important information for the assessment of the risk of groundwater contamination by pesticides in agricultural areas like the Jianghan Plain.

2. Materials and Methods

2.1 Soil Column

The soil column used in this study was collected from a natural land free of crops in the Jianghan Plain of Hubei province, central China. The groundwater level depth at the soil sampling site was about 0.5 m. Sampling was performed in early autumn of 2007 when the land was covered with grass. The upper part (5 cm–1 m deep) of the soil sampling site was mostly sand with silt and clay. A stainless-steel hollow column, 33 cm long and 7.5 cm in diameter, was hammered down and the surrounding soil was carefully excavated. Then the undisturbed soil column was removed by digging under it and placing tin foil at the bottom of the column base to retain the soil.

2.2 Soil Characterization

Soil particle size distribution was determined using the laser particle size analyzer (LS 230, Beckman Coulter Co.). The analyzers use the diffraction of laser light by particles as the main source of information about particle size. The particle size distributions are also determined by measuring the pattern of light scattered by the constituent particles in the sample. A 1:5 dilution of soil: water was prepared and shaken for about 2–3 minutes, the soil was left to settle for 2 minutes, and then the pH was measured with a pH-meter, HANNA HI8424A. The total carbon of all samples was determined with combustion at approximately 800°C using a Total Organic Carbon analyzer, liquiTOC from Elementar Company, Germany. Inorganic carbon was released through acid-assisted evolution (50% hydrochloric acid) with heating to 200°C. The detection range is 0 to 100.000 mg/l of TOC and the detection sensitivity is 50 ng/l. The water content is measured by drying the wet sample at 105°C for 2 hours, expressed in terms of the mass of water per unit mass of the moist specimen:

$$u = (m_{wet} - m_{dry})/m_{wet}.$$

2.3 Leaching Column

The leaching column experiment was done at the center of hydrogeology, University of Neuchatel (CHYN) in Switzerland. The column is stainless steel, 15 cm long with an internal diameter of 4 cm and well-fitted sealing at both ends (Fig. 1). Stainless-steel tubing was used in lines to prevent loss of pesticides or other organic compounds. The leaching column was inserted inside the sampling column to get undisturbed soil of the top 15 cm for leaching experiment. The soil column was then placed on a support base. The 2L glass bottle was filled up with stock leaching solution from time to time to keep constant water head and a 50 ml sample bottle was used to sample effluents.

2.4 Chemicals

All chemicals were of analytical reagent grade and used without further purification. Glyphosate and atrazine were bought from Landi (Switzerland) with 90% and 360 g/l certified purity, respectively. Glyphosate in liquid form was produced by Cheminova A/S.P.O. Box 9, DK-7620 Lemvig, Danmark. Atrazine as white powder was produced by Ein Product der Sipcam Management Services SA, Lugano. It was used in this study both as a reference to glyphosate and a representative target pesticide posing a great threat to the environment. Potassium chloride purchased from Fluka-Grantie Company, Switzerland, was used as conservative tracer in the leaching experiments.

2.5 Experimental Set-up

Porous plates and glass fibers were placed on the soil surface at both ends to ensure homogeneous distribution of the water. Two-liter glass bottles were used as reservoirs for

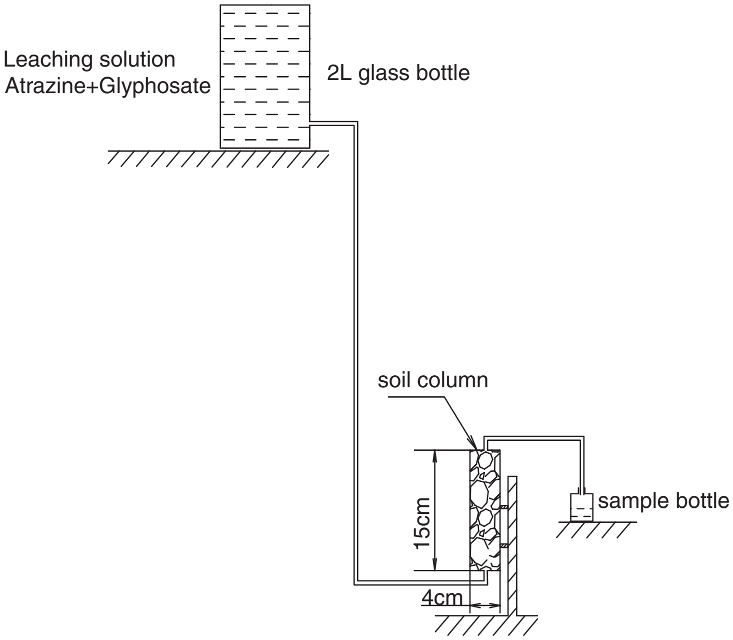

Figure 1. Schematic illustration of the experimental setup.

water supply. The soil column was firstly saturated with at least 10 pore volumes of distilled water to get a constant water head of 136 cm, giving a constant flow rate 0.796 cm/h, which was quite close to the field data 0.781 cm/h (Hubei Hydrogeology and Engineering Geology Station, 1985). Afterwards, the feedwater containing atrazine and glyphosate was supplied. Experiments in the water-saturated columns always involved the following steps: estimating soil column pore volume and physical parameters of the soil column; continuous supply of the feedwater containing atrazine and glyphosate into the soil column and constant water head of 136 cm; and analytical determination of glyphosate concentration in effluent fractions (leachate) to obtain the BTC. Glyphosate, AMPA and atrazine concentrations in the leachate samples were analyzed following the US EPA methods (Winfield et al., 1990; Eichelberger et al., 1988) by RWB Analub Laboratory in Switzerland.

2.6 Tracer Test

In this study, the effluent started to come out after one hour of running. After allowing the column to drain for 48 h, a tracer test using KCl was done to get hydraulic condition of the study column. 50 mg/l KCl (i.e., Cl^- 23.8 mg/l) solution was prepared. Chloride in the form of KCl was used as a non-reactive tracer in the column experiment. A constant flow rate of 10 ml/h (i.e., 0.796 cm/h) was kept during the experiment period. The tracer test was run for 26 h and 45 samples were sampled to analyze Cl content in the effluent with ion chromatography, DX-120, Dionex, Sunnyvale, USA. Effluent samples were collected in plastic bottles periodically, every half an hour. The samples were refrigerated before analysis to obtain breakthrough curves (BTCs). Effluent volumes were measured at regular intervals to determine the flux density of water.

2.7 Transport Parameters from BTCs

It was reported that the CXTFIT code was used to calculate transport parameters based on column experiment Br breakthrough curves BTC data (Parker and Van Genuchten, 1984; Toride et al., 1999). CXTFIT is a nonlinear least square inverse modelling program where the parameter values are varied until the best fitting of the analytical solutions of the convection-dispersion equation (CDE) to the observed BTC is attained. The CXTFIT program may be used either to predict the chemical transport in soil (direct problem) or to solve the inverse problem by fitting an appropriate analytical solution of the transport model to experimental results. The inverse problem is solved by minimizing an objective function that consists of the sum of the squared differences between observed and fitted concentrations. The objective function is minimized using a nonlinear parameter estimation method of Marquardt (1963). In addition, CXTFIT 2.1 may be used for the direct problem to predict solute distributions versus time and/or space for specific values of model parameters (N. Toride et al., 1999). The experimental water flux was calculated as the average flow rate divided by the area of the column. The flow rate Q (L^3/T) was calculated by dividing the collected effluent volumes by the duration of effluent collection. The corresponding solution flux density q (L/T) was obtained from:

$$\mathrm{q} = \mathrm{Q}/\mathrm{A} \tag{2.1}$$

where A is the cross sectional area of the column (L^2).

The average pore water velocity (L/T) was calculated as the ratio of the mean solution flux density to the soil porosity from:

$$V = q/n_e \tag{2.2}$$

where n_e is the soil kinematic porosity.

From Darcy's law, we can get

$$\mathrm{q} = -\mathrm{K}\frac{\Delta H}{\Delta L} \tag{2.3}$$

where ΔL is the length of the column, 15 cm, and ΔH was measured to be 136 cm and q, flux rate of 0.796 cm/h, which leads permeability coefficient, K calculated to be 8.8×10^{-7} m/s. It can also be seen from the original data (Fig. 2) that the pore volume is around 50 ml, because when the Cl content comes to half of the final stable Cl content at the fifth hour, the effluent volume is around 50 ml. The volume of the soil column is calculated as 188 cm^3, n_e could be calculated roughly as 0.266, V as 2.99 cm/h.

The equilibrium adsorption model was used to estimate D (longitudinal dispersion coefficient). The measured potassium chloride concentrations were fitted with the equilibrium transport model that allows the estimation of two parameters, the average pore water velocity V (cm/h), to confirm with the calculated one with above equations, and D (cm^2/h). Sorption and degradation of chloride are neglected, so that the retardation coefficient R and decay coefficient μ were fixed to one and zero, respectively.

2.8 Pesticide Leaching Experiment

The glyphosate and atrazine leaching experiment was run under the same hydraulic condition as the KCl tracer test. The input solution was a mixture of glyphosate and atrazine and the glass bottle containing the leaching solution was wrapped by tin foil completely to

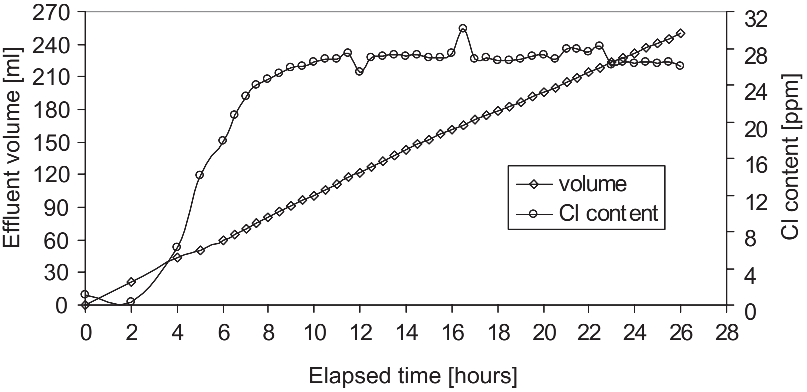

Figure 2. Total effluent volume and Cl content in the effluent versus elapsed time.

keep it from light, minimizing the degradation of glyphosate. A 25 ml effluent sample was collected in a plastic bottle every 5 hours and immediately frozen at $-18°C$ until analysis to avoid possible pesticide adsorption. At the same time, 2 ml of effluent was also collected every 1 hr to measure the Cl^- concentration. The whole experiment was run for 160 hrs and the feed solution was sampled before and after leaching to confirm whether any degradation occurred during the experiment.

3. Results and Discussion

3.1 Soil Characterization

Table 1 summarizes the physico-chemical characteristics of the soil used in this study. This soil exhibited a sandy loam texture according to the international classification scheme and high organic carbon content.

3.2 Tracer Test Calibration

The result of CXTFIT calibration (Fig. 3) shows that the fitting is quite good and the average pore water velocity, v, was 2.799 cm/h and the dispersion coefficient, D, to be 2.541 cm^2/h. So it can be calculated from the above equation (2.2) that n_e is 0.285, quite close to our former calculation. The volume of the soil column is calculated as 188 cm^3, so the pore volume is 53 ml. Although the flux varied a little bit, a constant value of the average pore water velocity was considered, given that CXTFIT is based on steady state conditions. Chloride behaved as an ideal conservative tracer. The assumption of $R = 1$

Table 1
Physical-chemical properties determined for soil

pH	Clay (%)	Silt (%)	Sand (%)	Water Content (%)	Organic Carbon (%)
7.28	19.95	25.64	55.42	21.20%	1.90%

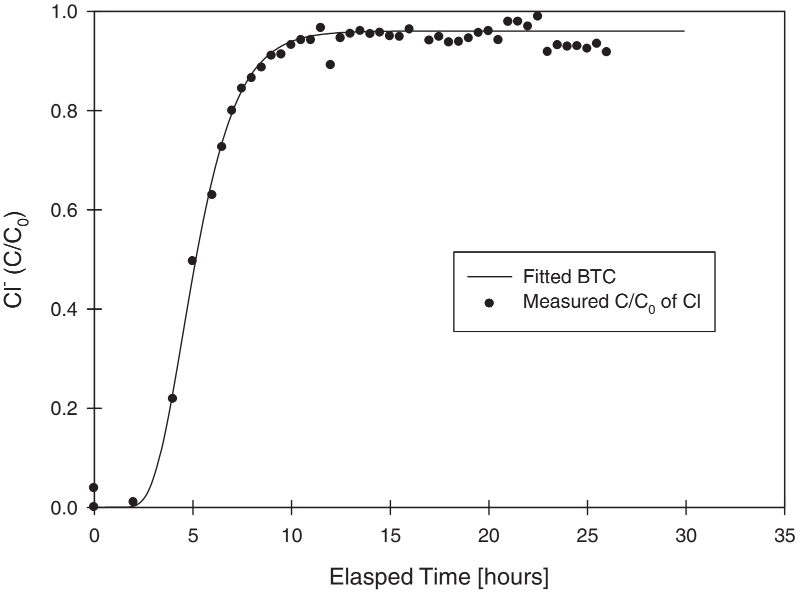

Figure 3. Observed and simulated Cl content in the effluent by CXTFIT.

enabled estimation of v directly from the effluent curve and was in agreement with the direct calculation of v = 2.99 cm/h.

3.3 Inverse KCl Tracer Results

It can be seen from Table 2 that both average pore volume velocity and dispersion coefficient were a little smaller than those of the tracer test, which could also be illustrated from the comparison between Fig. 3 and Fig. 4. In Fig. 3 it takes around 5 hours for the effluent concentration to reach half the initial feed solution ($C/C_0 = 0.5$), while in Fig. 4 5 hours only made it 0.8. Soil hydraulic conductivity was smaller and the residence time was longer than the corresponding ones in the tracer test. Although it is difficult to provide a definitive explanation of the cause of the decrease in hydraulic conductivity, one potential explanation might be the not-fully-saturated soil column due to the air that is dissolved in the feed solution and may create trapped pockets of air within the column during the flow. Under such conditions, instead of the absolute permeability, the water relative permeability is measured.

Table 2

Non-linear least squares analysis results, within 95% confidence limits

Name	Value	S.E. Coeff.	T-Value	Lower	Upper
V	.2371E + 01	.3471E − 01	.6831E + 02	.2294E + 01	.2448E + 01
D	.9425E + 00	.1969E + 00	.4786E + 01	.5037E + 00	.1381E + 01

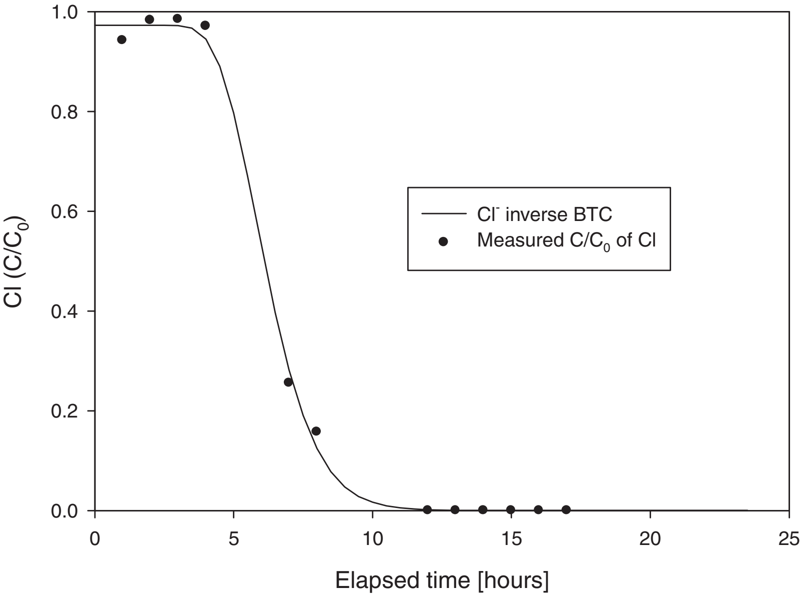

Figure 4. Observed and simulated Cl content in the effluent using parameters from CXTFIT modeling results.

3.4 Fitting of the Atrazine BTCs

The input concentrations of glyphosate and atrazine solution were 1.0765 mg/l and 0.379 mg/l, respectively. All parameters, except R and μ, were kept constant by using the values resulting from either calculations or from the fitted chloride BTCs in the inverse tracer test. The local equilibrium assumption (LEA) that accounts for instantaneous sorption was adopted. The initial concentrations of feedwater before and after the column experiment were analyzed and the results are given in Table 3. It can be seen that C_0 values of Cl, glyphosate and atrazine changed slightly before and after the experiment.

The fixed and estimated parameter values are given in Table 4 and the fitting curve is shown in Fig. 5. The soil had a retardation factor (R) of only 4.636 for atrazine, which means relatively low adsorption.

In order to investigate whether a non-equilibrium model would be more appropriate, the BTC was fitted with the two-region non-equilibrium transport model. In addition to the retardation coefficient R and the dispersion coefficient D, these models incorporate four other parameters (w, u1, u2 and β). First, to minimize the number of parameters to be fitted, no exchanges between the immobile and mobile regions were initially considered (w = 0). Then the situation prevailing in the case of exchanges between the mobile and immobile

Table 3
Concentrations measured in the input solutions before and after leaching

	Cl (mg/l)	Glyphosate(μg/l)	Atrazine(μg/l)
Before experiment	28.463	1076.500	379.000
After experiment	26.10	1063.400	300.000

Table 4

Parameters used to fit atrazine BTCs with the CDE equilibrium model and fitted values of R and μ (R^2-coefficient of determination; R-retardation factor; D -longitudinal dispersion coefficient; V- average pore water velocity)

V (cm/hr)	D (cm^2/hr)	R	μ	R^2
2.371	0.9425	4.636	0	0.99

regions has also been considered. However, in both cases the results didn't significantly improve the fitting curve compared to the previous equilibrium CDE model (data not shown).

3.5 Modeling Glyphosate Transport

Data generated from batch experiments show that glyphosate sorption in soils exhibited isotherm nonlinearity and desorption hysteresis (Melo, 1996). In order to model the transport of this pesticide in soils, additional processes must be taken into account, such as microbial degradation, nonlinear sorption, desorption hysteresis, and nonequilibrium sorption during transport. Under chemical or physical conditions, data from column studies may be interpreted by fitting breakthrough curves to a two-site (or bicontinuum) sorption model with degradation (Van Genuchten and Wagenet, 1989; Brusseau et al., 1989; Magga et al., 2008). The two-site model is a one-dimensional advective–dispersive transport model with a first-order bicontinuumdescription of soil, which allows estimation of the rate parameters for nonequilibrium sorption and irreversible sorption.

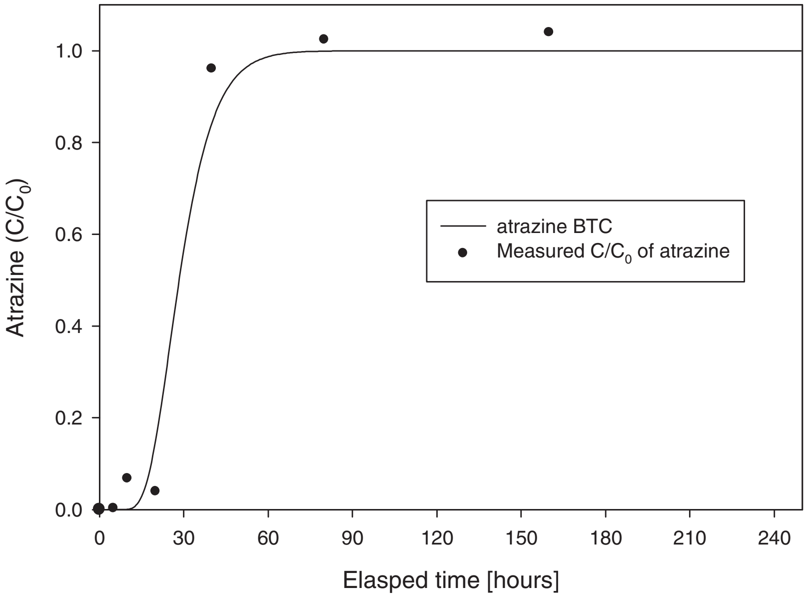

Figure 5. Experimental results of atrazine BTC fitted with the CDE equilibrium model.

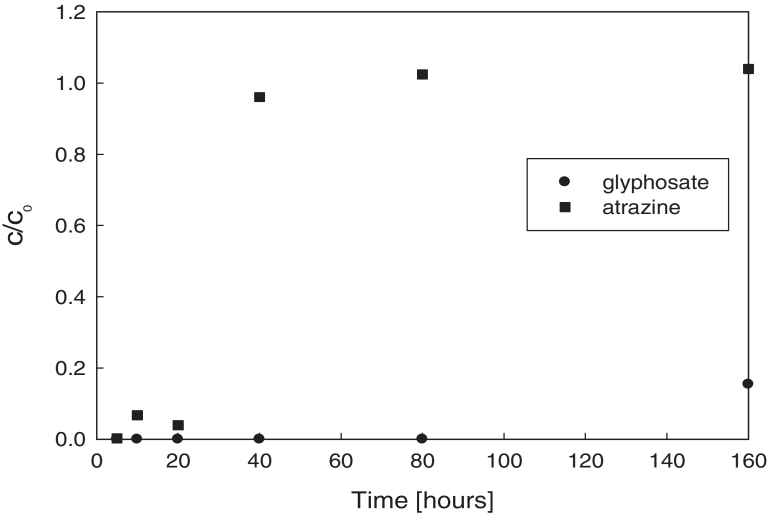

Figure 6. Observed C/C_0 during the 160 hours leaching of atrazine and glyphosate.

The evolution of the concentration in the effluent was described as relative concentration (C/C_0) versus time, where C is the measured concentration and C_0 is the input concentration. The corresponding results of atrazine and glyphosate, expressed as relative concentration (C/C_0) as a function of time, are given in Fig. 6. In addition, glyphosate and its metabolite AMPA were only detected in the 160th hour leachate sample.

It can be seen from Fig. 6 that the concentration of atrazine in the effluent was quite stable after 40 hr but that of glyphose was detected only after 160 hours, whereas the data are insufficient to get an accurate BTC for glyphosate in this column. Less glyphosate (less than 16%) was leached through the column than atrazine (almost 100%). The higher concentration of atrazine in the effluent is due to its weaker adsorption coefficient (Koc), 100, which is about 240 times less than that of glyphosate, 24000, generally speaking (Vogue et al., 1994). Regarding the glyphosate, except for its very strong sorption on the soil, it may have been degraded (the half lifetime ranges from 7.9 to 14.4d, Hornsby et al., 1996), which is consistent with the concentration of 8890 ng/l of AMPA in the leachate. However, no considerable degradation of atrazine (half life time ranges from 19.7 to 91 days) has occurred. In order to simulate the fate of glyphosate in a soil column the two-site sorption model with degradation was adopted.

Generally speaking, the more parameters are included in the estimation procedure, the better the fitting results. However, for a large number of estimated parameters no unique solution results from the optimization algorithm. Different sets of parameter values can satisfactorily fit the experiment data. Using the values of parameters for sandy soil (59% sand, 13% silt and 10% clay) reported by Candela et al. (2007), the initial values $R = 175$, $\beta = 0.17$, $\omega = 0.60$, $\mu 1 = 0$, $\mu 2 = 0$ were used. In order to reduce the uncertainty, commonly embedded in multi-parameter estimation approaches, the later three parameters were estimated by keeping R and β constant. The values of D and v were still kept the same as those in our inverse Cl modeling. The fitting curve is shown in Fig. 7, which can still indicate the leaching of glyphosate during one month to some extent.

It should be noted that the BTC of glyphosate may differ from the curve shown in Fig. 7. The glyphosate recovered in the effluent could be less than the predicted one, for

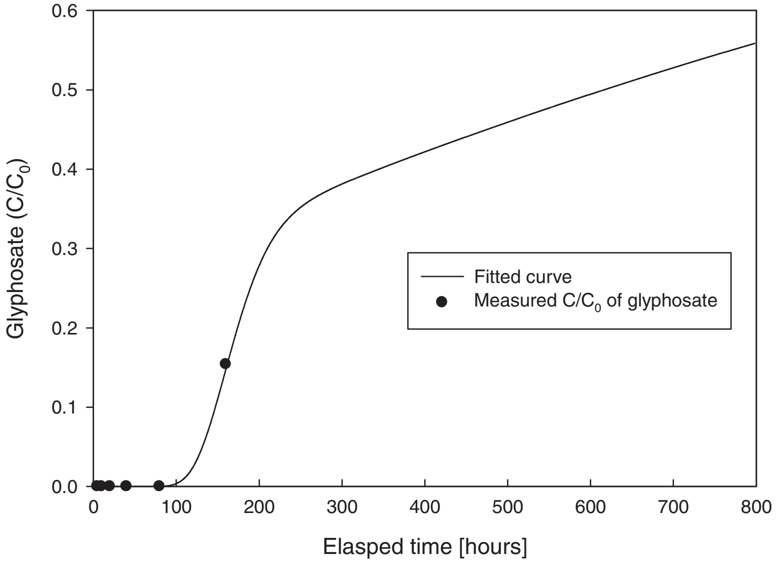

Figure 7. Estimated BTC of glyphosate based on measured and referenced data of Candela et al. (2007).

longer residence times because of microbial degradation or surface complexation, even though the degradation parameters estimated by CXTFIT code ($w = 0.038$ and $\mu_1 = 0.014$) are indicative of mild degradation. The estimated values of the kinetic parameters (high retardation factor $R = 175$ and partitioning coefficient $\beta = 0.016$) suggest that the dominant mechanism of glyphosate loss was its sorption on the soil. Analogous conclusions have also been drawn by a recent experimental and theoretical study of glyphosate fate in soils (Magga et al., 2008). Although glyphosate exhibited a low mobility in the studied soil, the presence of glyphosate and AMPA in the effluent showed the potential leaching in soil with sand texture despite their great adsorption capacity.

4. Conclusions

The leaching experiment conducted with an undisturbed sandy soil column demonstrated the high mobility of atrazine as well as the potential of glyphosate and AMPA leaching. The amount of herbicides leached through the 15-cm-long soil column, in the 160 hours of the experiment, reached almost 100% of the atrazine in the feedwater, whereas less than 16% of the glyphosate in the stock solution was recovered as glyphosate and AMPA. The greater leaching of atrazine through the soil column might be due to its lower adsorption and greater persistence compared with glyphosate.

However, the risk of contamination is different for different soil types and is related to the soil's organic carbon content, structure, and Fe and Al contents of soils. The glyphosate metabolite, AMPA, which was detected in the effluent, may also pose a risk of groundwater contamination. Thus, not only the parent molecules but also the degradation products should be monitored in groundwater.

The results of our experiment using an undisturbed soil column showed that both atrazine and glyphosate can be transported through soils, with atrazine showing a higher contamination potential in the study area. At a watershed scale, surface water could be contaminated by subsurface flow or overland flow. Furthermore, the risk of contaminating groundwater used as drinking water in Jianghan Plain is significant given that groundwater is used as the major source of water supply. Therefore, pesticide management has to be regulated to preserve the quality of the aquatic environment in this region of intense agricultural activities.

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