Effects of Ionic Strength and Temperature on Adsorption of Atrazine, Deethylatrazine and Deisopropyatrazine in an Alkaline Sandy Loam

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Abstract

Atrazine is an agricultural herbicide used in large quantities and consequently companied with its two degradation products, deethylatrazine (DEA), and deisopropylatrazine (DIA), are commonly detected in groundwater and surface water. The retention of these compounds in vadose zone is highly related to their adsorption to soils. Laboratory studies were conducted to determine the sorption behaviour of atrazine, DEA, and DIA on a sandy loamy soil using the batch equilibration technique. The effects ionic strength (adjusted by $CaCl_2$ concentration) and temperature (25±1°C and 40±1°C) of absorption were also investigated. The adsorption isotherms of all three chemicals conformed to the Freundlich equation. Adsorption coefficients decreased in the order atrazine > DIA > DEA, and our calculated organic carbon normalized partition coefficients were 46.76, 46.00, 30.78 L/kg respectively. For atrazine and DEA, there existed a salting-out effect, their adsorption increased as ionic strength increased from 0 to 0.1 mol/L $CaCl_2$, but for DIA, its maximum adsorption occurred in 0.01 mo/ L $CaCl_2$ solution. The adsorption experiment also showed that more effective adsorption of atrazine, DEA and DIA at a lower temperature.

Key Words

Atrazine, deethylatrazine (desethylatrazine), deisopylatrazine (desisoprylatrazine), soil, adsorption

Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), a widely used herbicide in the world, is one among the 52 prior controlling pesticides in China. Because of the wide use of atrazine, byproducts of this compound are of particular interest (Bosch and Truman, 2002). Deethylatrazine (2-amino-4-chloro-6-isopropylamino-s-triazine, DEA) and deisopropylatrazine (2-amino-4-chloro-6-ethylamino-s-triazine, DIA) are the main biotic degradation products of atrazine in the soil environment (Jayachandran, 1994; Bosch and Truman, 2002), and both of them have been detected in surface and ground waters, and in some cases, at higher concentrations than that of atrazine (Seybold and Mersie, 1996; Ren and Jiang, 2002).

Assessment of pesticide adsorption during transport is a prerequisite for minimizing their potential mobility in the vadose zone. To our knowledge, no work dealing directly with temperature and ionic strength effect of atrazine, DEA and DIA adsorption on soils has been published. So, the main objective of the present study was to examine the adsorption characteristics of atrazine and its metabolites in a typical agricultural soil of Beijing. And the influences of ionic strength and temperature on the adsorption of atrazine, DEA and DIA are also demonstrated.

Materials and methods

Adsorption isotherms Adsorption isotherms for atrazine, DEA, and DIA were determined using the batch equilibration technique at 25±1°C. Solution concentrations were prepared of each chemical in 0.01 mol/L $CaCl_2$, and ranged between 0.5 and 30 mg/L for all compounds.

Effect of ionic strength A procedure similar to the one described above was used, with the following modifications: solution concentrations were prepared with ionic strength were made from deionized water (0 mol/L) and 0.1 mol/L $CaCl_2$ solutions.

Effect of temperature The test was carried out the same way as the standard adsorption experiments, but equilibrated at 40±1°C.

Results and discussion

Adsorption isotherms

All the isotherms were of L-type (see Fig. 1), i.e., were nonlinear with the curvature concave to the abscissa (Li *et al.* 2006), indicating a decrease in specific sorption sites when herbicide concentration in solution increases. The parameters of the Freundlich equation were well correlated with the experimental adsorption isotherms obtained (Figure 1). The order of decreasing adsorption coefficients (Kd) was atrazine > DIA > DEA, in agreement with the results reported by Brouwer *et al.* (1990), Seybold and Mersie (1996) and Vryzas *et al.* (2007). Our calculated Koc values of 46.76, 30.78, 46.00 L/kg for atrazine, DEA, and DIA, were less than the Koc values reported by Brouwer *et al.* (1990) and Seybold and Mersie (1996), which may be due to the low content of clay and soil organic carbon, the high pH and CEC of our soil.

The Freundlich adsorption constant represents the degree or strength of adsorption (Seybold and Mersie 1996), our Kf values for adsorption of atrazine, DEA and DIA were1.2574, 0.7992 and 1.3201 respectively, are within the range of previously reported values. And the average slope 1/n is a measure of adsorption nonlinearity (Seybold and Mersie 1996), when the slopes are <1, indicate that the percentage of these chemicals adsorbed to the tested soil decreased as the initial concentration increased (Nemeth-Konda *et al.* 2002).

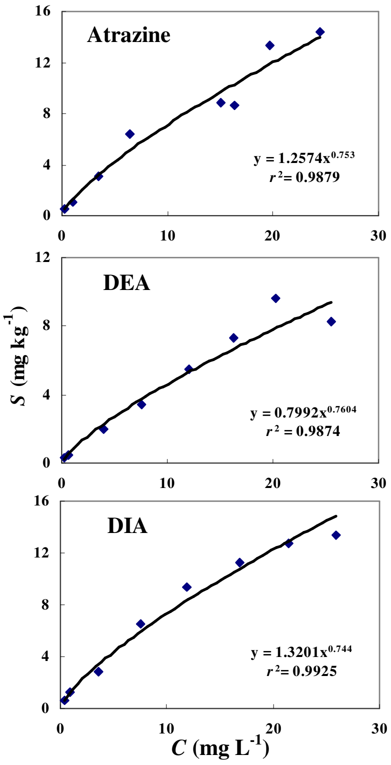
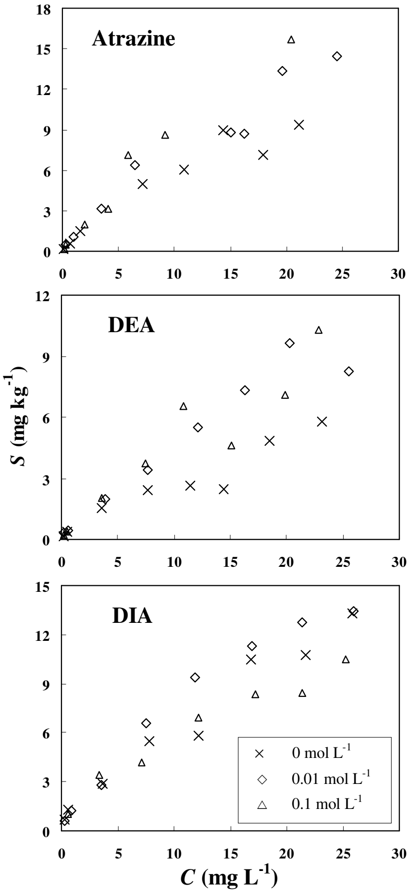


Figure 1. Freundlich isotherms for Atrazine, DEA and DIA adsorption.

Effect of ionic strength on pesticide adsorption

As can be seen, the shape of the isotherms from 0.1 mol/L $CaCl_2$ solution is the same shape as that obtained for pure water solution and for 0.01 mol/L $CaCl_2$ solution (Figure 2). Also, it clearly showed that, for atrazine and DEA, the adsorption increased with increasing ionic strength ($CaCl_2$ concentration in aqueous solution), which suggested that the role of electrostatic interactions in the adsorption process was significant. For a given concentration at equilibrium, the adsorption amount of atrazine on our test soil increased as ionic strength increased, which may be due to the occurrence of "salting out" effect that caused the solubility of atrazine in salt solution decrease. This phenomenon also reported by Spongberg and Lou (2000) and Ureña-Amate *et al.* (2005), the former synchronously pointed out that higher ionic strengths are often encountered in surface horizons when fertilizers and other compounds are applied. For DIA, with the ionic strength increased from 0 to 0.01 mol/L, the adsorption increased, while when the ionic strength increased from 0.01 to 0.1 mol/L, the adsorption onto the soil decreased, the adsorbed amount in 0.1 mol/L $CaCl_2$ background solution even less than that adsorbed when no $CaCl_2$ solution was used. The effect of salt concentration on pesticide sorption was complex, as had been explained by diffuse double-layer theory: Ions that form outer-sphere surface complexes show decreasing adsorption with increasing ionic strength, while ions that form inner-sphere surface complexes show little ionic strength dependence or show increasing adsorption with increasing ionic strength (McBride 1997; Anirudhan and Ramachandran 2007).



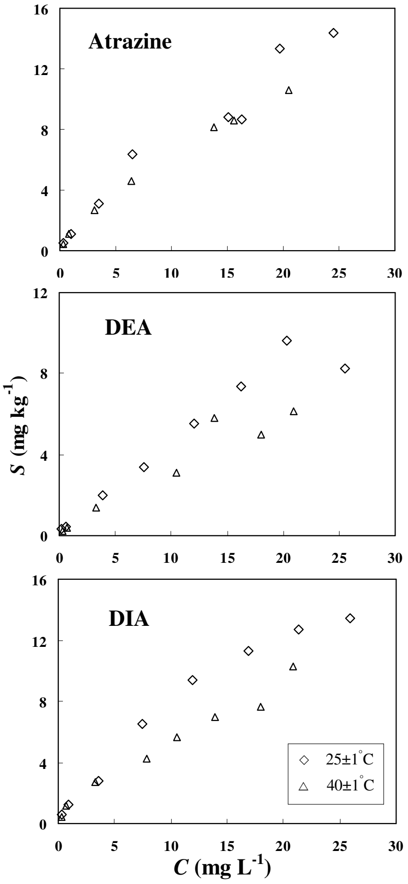


Figure 2. Adsorption isotherms of atrazine, DEA and DIA onto the tested soil for three different values of ionic strength at 25±1°C: (×) 0 mol/LCaCl$_2$; (◇) 0.01 mol/L CaCl$_2$; and (△) 0.1 mol/L CaCl$_2$.
Figure 3. Compared adsorption isotherms for atrazine, DEA and DIA in 0.01 mol/L CaCl$_2$ solution at 25±1°C (◇) and 40±1°C (△) on the tested soil.

Effect of temperature on pesticide adsorption

From Figure 3, again, all the isotherms were L-type, which suggested that the tested soil had an intermediate affinity for atrazine and its metabolites DEA and DIA and that no strong competition from the solvent for adsorption sites occurs (Ureña-Amate *et al.* 2005). Results showed that, with the increases of temperature, the Kf values were decreased for each chemical, while the variation of the exponents n had no clear trend. Kovaios *et al.* (2006) also reported that when temperature increased from 25±1 to 40±1°C, Kf values of atrazine decreased, but the n values increased. The same trend of decreasing Kf with increasing temperature was also reported by Ureña-Amate *et al.* (2005). As temperature increases from 25±1°C to 40±1°C, the adsorbed amount of chemicals at the same equilibrium concentration decreased, suggesting that adsorption is a process of release of activation energy.

Conclusions

In this study, the adsorption of atrazine, DEA, and DIA on a sandy loamy soil was measured using the batch equilibration technique. The Freundlich isotherms described adsorption well in all cases. Most of the isotherms were of L-type, indicating a decrease in specific sorption sites when herbicide concentration in solution increases. Generally, the adsorption coefficients (Kd) decreased in the order atrazine> DIA > DEA, which suggested that the metabolites have greater potential than the parent compound, atrazine, to move

through our test soil and pose a threat to groundwater.
An increase in atrazine and DEA adsorption is accompanied by increasing ionic strength of the solution that represented by $CaCl_2$ concentration. A higher ionic strength would reduce the double layer thickness and result in a stronger interaction between the hydrophobic sorbate and the sorbent. The effect of temperature on the adsorption isotherms, in our case, is that by increasing temperature, adsorption decreases.

Further research will be undertaken to investigate the sorption behaviour of atrazine and its metabolisms in flow equilibrium condition and to estimate their potential migration to the groundwater.

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