

Sorption of dissolved organic matter and its effects on the atrazine sorption on soils

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Abstract: The dissolved organic matter (DOM), water soluble organic matter derived from sewage sludge was separated into hydrophobic fraction (Ho) and hydrophilic fraction (Hi). The sorption of DOM and its fractions on soils and the effects of DOM sorption on a nonionic pesticide (atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine)) distribution between soil and water were investigated using a batch equilibrium technique. The total DOM sorption on soils described by the Langmuir equation reached saturation as the DOM concentration increased. The sorption of Ho fit the Freundlich model. In contrast, a negative retention evidently occurred as adding Hi at higher level in tested soils. The sorption of Ho dominated the total DOM sorption and the release of soil organic matter (SOM). Effects of DOM on the atrazine sorption by soils were DOM-concentration dependent and dominated by the interaction of atrazine, DOM, and soil solids. Generally, the presence of DOM with lower concentration promoted atrazine sorption on soils, namely the apparent partitioning constant (K_d') for atrazine sorption in the presence of DOM was larger than the distribution constant (K_d) without DOM; whereas the presence of DOM with higher concentration inhibited atrazine sorption (i.e., $K_d' < K_d$). The overall effects of DOM on atrazine sorption in soils might be related to the DOM sorption and the release of soil intrinsic organic matter into aqueous solution. The sorption of Ho on soils promoted the atrazine sorption on soil, while the release of SOM by Hi and the competitive sorption between Hi and atrazine on soil surface led to a decrease of atrazine sorption. Information provided in this work may contribute to a better understanding of the DOM sorption and its impacts on the contaminant soil-water distribution.

Keywords: dissolved organic matter (DOM); atrazine; sorption; soil

Introduction

Application of organic amendments, such as sewage sludge to agricultural soils, has been considered as an effective way to improve the soil physico-chemical properties and organic matter compositions. Dissolved organic matter (DOM) released by these organic amendments has been the subject of considerable interest in recent years because of its interaction with organic pollutants such as nonionic pesticides in soil and water (Guo, 1993; Haitzer, 1999; Jarkko, 2001; Leenheer, 2003). Sorption of pesticides on soils is one of the most important processes controlling the movement, persistence, and degradation of these compounds in soil environment. The effects of DOM on pesticide sorption in soils need wide concerns (Guo, 1993; Celis, 1998; Cox, 2000).

The sorption of DOM may elevate the content of soil organic matter (SOM) and the sorbed DOM can change the physico-chemical properties of the soil surface. The DOM coatings may also make the soil hydrophilic surface into hydrophobic surface, which are more capable of sorbing organic contaminants (Gu, 1994). A variety of mechanisms, such as physical adsorption, cation bridging, anion and ligand, have been invoked to account for DOM sorption by soils (Jardine, 1989). Generally, the DOM sorption on soils depends largely on its chemical and structural characteristics. DOM could be separated into hydrophobic fraction (Ho) and hydrophilic fraction (Hi) (Aiken, 1993). The differences of the structural and chemical properties of the DOM hydrophobic and hydrophilic fractions resulted in their different sorption behaviors on soil solids (Kaiser, 1998). It has been speculated that, as Ho has a higher average molecular weight than Hi, Ho is generally preferred to sorb on sorption to mineral surfaces by favorable steric arrangement of functional groups (Jeckel, 1986). Indeed, the fundamental sorption behaviors of Ho and Hi fractions are not well defined.

The sorption of DOM on soils is thought to have a decisive influence on the transport of nonionic pesticides in soil-water systems (Totsche, 1997; Raber, 1998). DOM is found to be distinctly different in the capacity to enhance the solubility of organic contaminant, which might be related to its molecular weight and hydrophobic character. For instance, the affinity of DOM to nonionic organic compounds, as noted by researchers, was controlled largely by the amount of hydrophobic fraction of DOM (Raber, 1998; Chion, 1986). The effects of DOM on the distribution of nonionic pesticides in two-phase systems between water and DOM have been characterized extensively. The DOM sorbed on soils may act as template sorptive site and enhance the sorption of nonionic organic compounds in soils (Torrents, 1997; Entfield, 1989). In contrast, the DOM distribution in solution may compete with the organic compounds sorbed on soils (Johnson, 1995; Gao, 1997). In fact, available data are limited for a three-phase system including soil solid phase, water and DOM. The effects of hydrophobic and hydrophilic fractions of DOM on the sorption of the nonionic pesticides by soils have hardly been investigated.

The objectives of the current study were to investigate the sorption of individual hydrophobic and hydrophilic fractions of DOM on soils. Atrazine, generally viewed as a nonionic pesticide, has been showed to be capable of complexing with DOM in solution (Gamble, 1989). The effects of DOM distribution between soil and water on the sorption of nonionic pesticides were studied and the correlation between structural chemical properties of DOM and atrazine sorption on soil was illustrated.

1 Materials and methods

Three clay loam paddy soils under agricultural use in Zhejiang Province of China, were sampled from the surface layer (0—15 cm), air-dried, and passed through a 60 mesh sieve prior to analysis. Some properties of these soils are given in Table 1.

Table 1 Some physico-chemical properties of three paddy soils tested

| Soil No. | Site | Particle size analysis, % | | | Organic carbon, g/kg | pH |
|----------|-----------|---------------------------|------|------|----------------------|------|
| | | Sand | Silt | Clay | | |
| 1 | Shaoxing | 4.10 | 60.6 | 35.3 | 20.5 | 6.22 |
| 2 | Longyou | 25.5 | 26.2 | 48.3 | 12.7 | 6.03 |
| 3 | Shengzhou | 9.30 | 46.4 | 44.3 | 23.7 | 6.41 |

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5-triazine) is a relatively polar and nonionic herbicide with an aqueous solubility of 30 mg/L, vapor pressure of 1.33×10^{-3} Pa and a degradation half-life from 68 to 74 d (Lesan, 2003). In this work, atrazine with a purity > 98% was provided by the Center of Examination for Pesticides of China.

Solid sewage sludge from a waste treatment plant in Zhejiang Province was used as the source of DOM. The solid sludge was homogenized and stored at -15°C . Aliquots of the sludge were thawed at 4°C overnight prior to the extraction of DOM. The sewage sludge was extracted with deionized water using a solid: water ratio of 1:5 by shaking at 180 r/min for 24 h at 20°C . The suspensions were centrifuged for 30 min at $10000 \times g$ and filtered through a $0.45 \mu\text{m}$ cellulose acetate filters. The filtration, i.e., DOM solution was analyzed for pH(7.5) and conductivity(2.1 ms/cm). A total organic carbon(TOC) analyzer(Shimadzu TOC-5000) was used for analyzing the content of dissolved organic carbon(DOC) in the prepared DOM solution. The measured DOC for the DOM solution was 540 ± 5 mg/L.

The DOM solution was separated into a hydrophobic and hydrophilic fraction by XAD-8 resin following to Aiken (Aiken, 1993). An acidified solution of DOM(at pH 2) was passed through the absorber resin XAD-8 at a flow rate of 1 ml/min until the void volume was completely displaced by DOM solution, i.e. until the concentration in the effluents of resin was constant. The hydrophobic fraction was retained completely on the column filled with XAD-8, and its effluent represented the hydrophilic fraction. The hydrophobic DOM was desorbed from XAD-8 with 0.05 mol/L NaOH. The solutions of hydrophobic and hydrophilic DOM were deprotonated by pumping through a column filled with a strongly acid cation exchanger resin(ZG-D001, Zhengguang, corp., Hangzhou, China). The solutions were freezing-dried and then dissolved with 0.02 mol/L KCl solution for sorption experiments. The percentage of hydrophobic and hydrophilic fraction to total DOM was 58% and 42%, respectively.

1.1 Sorption of DOM and its fractions in soils

Sorption of DOM in soils was achieved by equilibrating 1.00 g of soil sample in 20 ml of DOM solutions with initial concentrations ranging from 0 to 60 mgDOC/L. The DOM solutions were prepared in 0.02 mol/L KCl solution to maintain the same ionic strength, and the pH was adjusted to 7.5. All DOM solutions contained NaN_3 (0.02%) to inhibit microbial activity. The suspensions were shaken at 180 r/min for 24 h at 20°C and then filtered through $0.45 \mu\text{m}$ cellulose acetate filters. DOM sorbed on soils was calculated from the difference between the initial and equilibrium DOC in the DOM solution.

1.2 Sorption of atrazine on soils in the presence of DOM

Sorption of atrazine on soils in the presence or absence of DOM was determined using the standard batch equilibration method. 1.00 g of soil sample was weighed into 25 ml glass centrifuge tube containing 10 ml of 0.02 mol/L

KCl solution with a given DOM concentration. Different amounts of atrazine were added to the centrifuge tubes, and the sample tubes were closed with screw caps. The initial concentration of atrazine in solution varied from 0.0 to 6.3 mg/L. All atrazine solutions contained NaN_3 (0.02%) to inhibit microbial activity. The sample tubes were shaken at 180 r/min for 24 h at 20°C to reach equilibrium. The solution and soil were separated by centrifugation at $1503 \times g$ for 20 min. The amount of atrazine sorbed by soil was calculated from the difference between initial and equilibrium concentrations of atrazine in solution. All sorption studies were run in duplicate. In all batch experiments the sorption of atrazine to the glass wall surface was < 0.2% of the total amount added. The loss due to volatilization or sorption to glass tubes was quantified with control tubes that contained no soil. Biologic degradation was minimized by adding NaN_3 (0.02%) to inhibit microbial activity and can be negligible in 24 h.

The isotherm parameters of atrazine sorption were calculated using Linear distribution-type model, $X/M = K_d \times C$. Here, X/M denotes the amount of atrazine sorbed (X) per kg of soil (M) (mg/kg); C is the concentration of atrazine in equilibrium solution(mg/L); K_d is the partitioning constant of atrazine between soil and water. K_{oc} is the partitioning constant normalized to the soil organic carbon and f_{oc} is the soil organic carbon content(%). Thus $K_{oc} = K_d \times 100/f_{oc}$. K_d^* and K_{oc}^* represented the apparent partitioning constant and apparent carbon-normalized partitioning constant in the presence of DOM, respectively.

1.3 Atrazine analysis

After phase separation, 3 ml aliquots of the centrifuged supernatant was transferred to glass tube and mixed with 7 ml methanol(HPLC grade). After filtration through a $0.22 \mu\text{m}$ filter, the filtrate was analyzed on a high-performance liquid chromatograph (HPLC; Waters, USA). The HPLC was equipped with a reverse phase C_{18} column(4.6×150 mm, $3.5 \mu\text{m}$ particle size, Milford, MA, USA), using methanol-water as mobile phase at a flow rate of 1.0 ml/min. The detection wavelength of atrazine was 220 nm.

2 Results and discussion

2.1 Sorption of DOM on soils

The sorption isotherms of total DOM on tested soils are manifested in Fig. 1, which fits very well Langmuir model ($R^2 > 0.9$). The total DOM sorption on soils showed saturation as DOM concentration was increased. The maximum amount (X_{max}) of DOM sorbed by tested soils followed the order of soil 2 (36 mgDOC/kg) > soil 1 (29 mgDOC/kg) > soil 3(27 mgDOC/kg), which was negatively correlated with the content of soil organic carbon(SOC). This result was in agreement with that reported by Kaiser(Kaiser, 1998). Results indicated that organic matter coating might occupy available binding sites on soil mineral surface, and prevent the soil solid from binding DOM. Soils with lower OC could provide more sorptive sites for DOM on mineral surfaces and sorb more DOM, whereas soils with higher OC have less sorptive sites and less DOM sorption.

Comparing with total DOM, the DOM fractions by XAD chromatography showed evidently different sorption behaviors on soils. As seen from Fig. 2, the sorption of DOM hydrophobic fraction (H_o) fit the Freundlich model ($R^2 > 0.9$), i.e., $X/M = K_f C_{oc}^n$, where X/M is the amount of

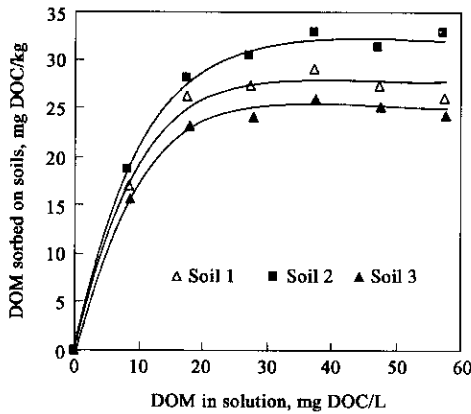


Fig. 1 Langmuir isotherms for DOM sorption on soils

the sorbed Ho per unit mass of soil (mgDOC/kg); C_{eq} is the concentration of Ho in solution (mgDOC/L); K_f and n are empirical coefficients. The K_f value for soil 1, 2 and 3 was 4.23, 7.14 and 5.40, respectively. The respective values of n was 0.8566, 0.8739 and 0.9094 for soil 1, 2 and 3, which indicated that the sorption of Ho was near to linear sorption behavior, and SOM could play a significant role in Ho sorption. On the other hand, soil 2 and soil 3 with higher clay contents showed higher sorptive capability than soil 1 with lower clay content. This suggested that amount of Ho could be bounded to soil mineral surfaces.

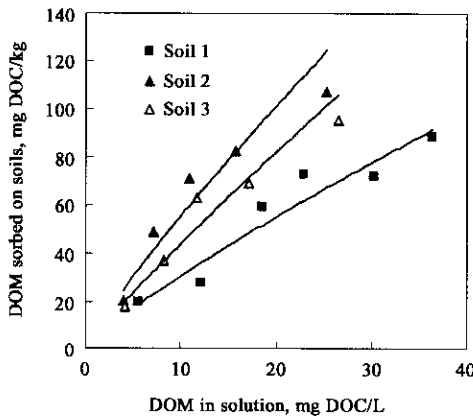


Fig. 2 Freundlich isotherms for hydrophobic DOM sorption on soils

The sorption of DOM hydrophilic fraction (Hi) on soils is displayed in Fig. 3. As the added Hi concentrations in solution were less than 14 mgDOC/L for soil 2 and 8 mg

DOC/L for soil 3, small amounts of Hi were retained on soils, whereas a negative retention clearly occurred with increasing Hi concentration. For soil 1, the addition of Hi resulted in the negative retention over the range of the Hi concentrations tested. The negative retention of Hi indicated that the addition of Hi led to the release of intrinsic SOM. In addition, the release of intrinsic SOC increased with increasing Hi concentration. At the same concentration of Hi added, the release of OC from soil 1 and soil 3 with higher OC was relatively stronger. Generally, the sorption of Ho increased with increasing its concentrations and enhanced SOM. In contrast, the sorption of Hi decreased with increasing its concentrations, and a negative sorption occurred at high level and thus led to the release of SOM.

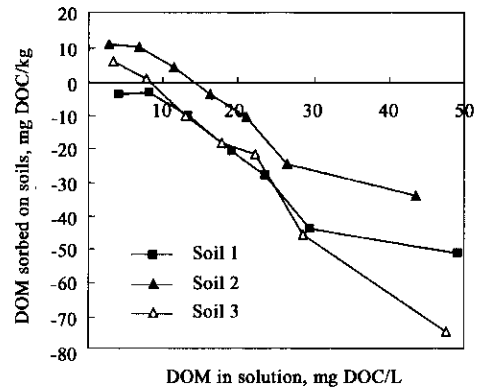


Fig. 3 The sorption of hydrophilic DOM on soils

The expected amount of total DOM sorption was calculated based on the observed results of these two DOM fractions. For total DOM containing 58% Ho and 42% Hi, at a given concentration of DOM added (C_i), the expected amount of total DOM sorption was the sum of Ho sorbed at the concentration of $0.58 \times C_i$ and Hi sorbed at the concentration of $0.42 \times C_i$. The expected and experimented total DOM sorption in soils as a function of DOM concentration in solution are manifested in Fig. 4. The expected sorption isotherms on tested soils also fit the Langmuir equation ($R^2 > 0.9$), suggesting that the saturation behavior of the total DOM sorption on soils can be explained by the sorption of Hi and Ho. Obviously, the sorption of Ho dominated the binding of DOM to soil surface, which led to the increase of the sorption of total DOM in soils. Whereas the addition of Hi at a higher level led to the release of SOM from soils, this would result in the decrease of the total DOM sorption on soil solids. When these two opposite processes reached

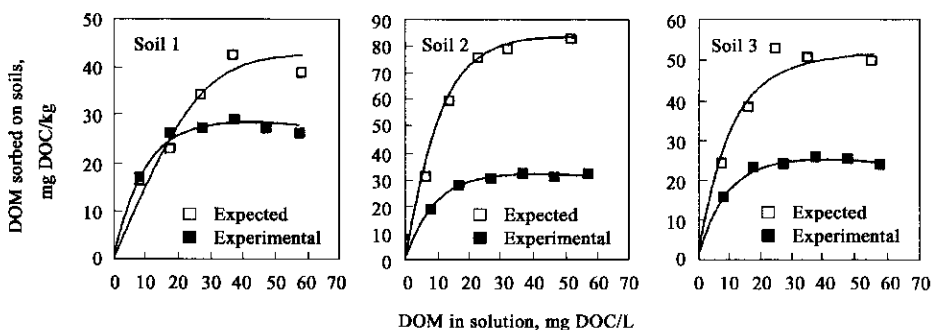


Fig. 4 Expected and experimental Langmuir isotherms for DOM sorption on soils

equilibrium at a certain DOM concentration, the sorption of total DOM showed the saturation.

It was notable that the expected sorption of total DOM was not in agreement with the experimented results. At a given DOM concentration, expected values were generally higher than experimental values. The expected X_m of total DOM sorption, calculated from the Langmuir equation, was 45, 92 and 55 mgDOC/kg for soil 1, 2 and 3, respectively, which were much higher than those calculated from experimental data. This may be related to the much stronger sorption of Ho in the absence of Hi than in the presence of Hi. The release of SOM by the addition of Hi could make the Ho distribute into solution, and change the equilibrium of Ho between soil and water. Thus the sorption of Ho on soils in a solution containing Ho and Hi would be weaker than that in a solution only containing Ho. Additionally, the sorption of Hi on soil mineral surface could make the soil/water interface hydrophilic, thus leading to decrease Ho sorption (Kaiser, 1998).

2.2 Effects of DOM on atrazine sorption on soils

The three-phase system including soil, water and DOM

Table 2 Apparent distribution constants (K_d^*) for atrazine sorption on soils in the presence of the total DOM, DOM hydrophobic fraction, and DOM hydrophilic fraction at various concentrations

| Concentration of DOM in solution, mgDOC/L | Total DOM | | | DOM hydrophobic fraction | | | DOM hydrophilic fraction | | |
|---|-----------|--------|--------|--------------------------|--------|--------|--------------------------|--------|--------|
| | Soil 1 | Soil 2 | Soil 3 | Soil 1 | Soil 2 | Soil 3 | Soil 1 | Soil 2 | Soil 3 |
| 0 | 2.41 | 2.01 | 2.91 | 2.41 | 2.01 | 2.91 | 2.41 | 2.01 | 2.91 |
| 15 | 2.65 | 2.32 | 3.02 | 2.80 | 2.59 | 3.66 | 2.09 | 1.60 | 2.55 |
| 20 | 2.46 | 2.17 | 2.92 | 2.80 | 2.57 | 3.70 | 2.01 | 1.50 | 2.41 |
| 25 | 2.19 | 2.07 | 2.83 | 2.87 | 2.67 | 3.70 | 1.53 | 1.47 | 1.85 |
| 30 | 1.98 | 1.86 | 2.56 | 2.81 | 2.65 | 3.77 | 1.45 | 1.41 | 1.62 |
| 40 | 1.99 | 1.73 | 2.36 | 2.79 | 2.61 | 3.74 | 1.45 | 1.45 | 1.76 |
| 50 | 1.84 | 1.62 | 2.24 | 2.78 | 2.64 | 3.75 | 1.41 | 1.42 | 1.73 |

In the presence of DOM, the apparent distribution coefficients K_d^* are listed in Table 2. The K_d^* values decreased with increasing the total DOM concentrations. When the total DOM concentrations were less than 20 mgDOC/L for soil 1 and 3, and 25 mgDOC/L for soil 2, the presence of DOM promoted the atrazine sorption in soils apparently, which was reflected in being greater than their K_d . However, when concentrations of total DOM were higher, the presence of DOM inhibited the sorption of atrazine, as evident from the fact that K_d^* values were smaller than their K_d . Over the range of Ho concentrations, all K_d^* values for tested soils were higher than individual K_d value, and the K_d^* values averaged about 116%, 128% and 128% of the K_d value for soil 1, 2 and 3, respectively. The increment of K_d^* for soil 2 and soil 3 was higher than that for soil 1. This was related to the higher sorptive capability for Ho in soil 2 and soil 3, as illustrated previously. The concentrations of Ho had minor influence on the increment of K_d^* . However, in the presence of Hi, all K_d^* values were lower than K_d , and tended to decrease with increasing concentrations of Hi added. In the range of Hi from 15 to 20 mgDOC/L, ΔK ($\Delta K = K_d^* - K_d$), indicating the decrement of the distribution constant, was from -0.41 to -0.51 for soil 2, from -0.36 to -0.50 for soil 1, and from -0.32 to -0.40 for soil 3, respectively. In this case, small amount of Hi sorbed on soil 2 and 3 (Fig. 3) seemed to impede the atrazine sorption. In the range of the added Hi concentration

phase was used to investigate the solid-solution distribution of atrazine in the presence of DOM. The isotherms of atrazine sorption in the presence or absence of DOM were all fit to linear equation ($R^2 > 0.9$). As seen from Table 2, the distribution coefficient K_d , for soil 1, 2 and 3 was 2.41, 2.01 and 2.91, respectively. Soil 1 and 3 with higher SOC contents showed higher sorption capability, indicating that SOM could dominate the distribution of atrazine on soils. On the other hand, the distribution coefficients normalized to SOC, K_{oc} , was obtained by $K_{oc} = K_d^* \times 100 / f_{oc}$, where f_{oc} is the percentage of SOC content. K_{oc} value for soil 1, 2 and 3 was 118, 158 and 124, respectively. According to the report by Spark (Spark, 2002), the variation of K_{oc} values suggested that the sorption of pesticides on soils not only depended on the total carbon content of a soil, but also was related to the reactivity of soil organic matter. Furthermore, the reactivity of soil organic matter may be related not only to the nature and origin of the organic matter, but also to the nature of the mineral to which it is sorbed (Spark, 2002).

from 25 to 50 mgDOC/L, the ΔK value was from -0.88 to -1.00 for soil 1, from -1.06 to -1.18 for soil 3, and -0.58 to -0.63 for soil 2, respectively. The decrement of atrazine sorption on soil 1 and 3, from which more SOM was discharged by Hi, seemed stronger than that on soil 2 over this range of Hi concentration.

Several processes may be involved in atrazine sorption on soils in the presence of DOM, including DOM-atrazine interactions in solution, DOM-atrazine interactions at the soil/solution interface, and soil-atrazine interaction (Celis, 1998). The soil-sorbed DOM would act to elevate the solute concentration in the soil phase, and thus increase the K_d^* . The DOM in the aqueous phase would tend to increase the apparent solute concentration in the aqueous phase, and thus reduce the K_d^* . These results revealed that the sorption of DOM affected the atrazine distribution between soil and water system. The sorption of Ho on soils could be responsible for the increase of atrazine sorption. Those of Ho partitioned to SOM in a dispersed molecular state would have little influence on the increase of atrazine sorption. It appears that even a small amount of Ho sorbed on mineral surface, which form an organic-like surface and make the mineral surface more hydrophobic, would significantly enhance the atrazine sorption. The soils with higher clay contents showed higher capability of sorption for Ho, and the enhancement of atrazine sorption on these soils by Ho seemed more significant. Obviously, the additions of Hi into soil/water system led to the decrease of atrazine sorption. The decrease of atrazine

sorption in the presence of Hi could be a result of the release of SOM by Hi. The release of hydrophobic DOM from intrinsic SOM by Hi enlarged the hydrophobic-region in aqueous phase (Kaiser, 1997; 1998) and enhanced the atrazine solubility and thus inhibited the atrazine sorption. For soils with higher OC content, the release of intrinsic DOM could be stronger, and the inhibition of the present hydrophilic DOM on atrazine sorption would be more evident. Additionally, the inhibition of Hi on atrazine sorption implied that there was a competitive sorption between DOM and atrazine on soil surface (Barriuso, 1992).

These results revealed that the effects of DOM on atrazine sorption by soils could be the concurrent effects of its hydrophobic and hydrophilic fraction. At a relatively low DOM level, the increase of atrazine sorption by Ho could overwhelm the decrease of atrazine sorption by Hi, consequently, led to the net increase of atrazine sorption in soil. However, at a higher DOM level, the decrease of atrazine sorption by Hi was dominated, and thus the presence of the total DOM could inhibit the sorption of atrazine on soils.

3 Conclusions

The DOM sorption on soils was described by the Langmuir equation and reached saturation as DOM concentration was increased. The sorption of hydrophobic fraction of DOM (Ho) on soils fit to Freundlich model. Although small amounts of hydrophilic fraction of DOM (Hi) with lower concentration was sorbed on soils, a negative retention was evidently observed at higher Hi concentrations. The sorption of Ho dominated the increase of the total DOM sorption, and the release of soil organic matter (SOM) by the addition of Hi would lead to the saturated sorption of the total DOM on soils.

In the presence of total DOM, the K_d^* for atrazine sorption on soils decreased with increasing DOM concentrations. The sorption of atrazine was promoted in the presence of DOM with lower concentration, but was significantly inhibited at higher concentration. The overall effects of DOM on atrazine sorption on soils were related to the DOM sorption and the release of the soil intrinsic organic matter into aqueous solution. The sorption of Ho on soils promoted the atrazine sorption on soil, while the release of SOM by Hi and the competitive sorption between Hi and atrazine on soil surface led to the decrease of atrazine sorption.

Results of this study may provide improved insights into the sorption of nonionic pesticides in a three-phase system consisting of soil, water and DOM, and a better understanding of the impacts of DOM on the distribution of contaminant between soil and water.

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