

Effect of Surfactants at Low Concentrations on the Sorption of Atrazine by Natural Sediment

Qing H. Tao, Dong S. Wang, Hong X. Tang

ABSTRACT: A series of experiments were carried out to determine the effect of surfactants at low concentrations on the sorption of atrazine by natural sediments. With surfactant concentrations ranging from 0 to 20 mg/L, anionic and cationic surfactants appreciably reduce the adsorption of atrazine, while nonionic surfactant decreases the adsorption of atrazine at concentrations equal to or less than 1 mg/L and increases adsorption at higher concentrations. Desorption of atrazine in the presence of different sodium dodecylbenzene sulfonate (SDBS) concentrations shows that a portion of the bound pesticide resists desorption in the SDBS free system. However, the addition of SDBS accelerates the desorption of atrazine. Furthermore, the nature of sediment and the contacting sequence of SDBS, at 10 mg/L, with the sediment, also influence the adsorption of atrazine. The conclusions in this study could be explained partially by the effect of the type and concentration of surfactants and the characteristics of sediments. *Water Environ. Res.*, **78**, 653 (2006).

KEYWORDS: surfactants, low concentration, atrazine, sorption, natural sediments.

doi:10.2175/106143006X115886

Introduction

The sorption of pesticides in natural sediments is of great interest, both from environmental and ecological points of view. Pesticide sorption affects other processes, such as bioavailability, degradation, and mobility, determining the final fate of the compound in the aquatic environment, and also controls the persistence and irreversible binding of the pesticide. All these processes influence the possible effects of pesticides on nontarget organisms in the environment. Furthermore, sediments are saturated with pore water, which acts as a transport medium and distributing phase for herbicides. The pore water contains dissolved organic matter, colloids, and other macroorganic molecules, which can bind pesticides resulting in a facilitated transport and enhanced bioavailability of these chemicals (Hegeman et al., 1995). Thus, knowledge towards the adsorption-desorption characteristics of pesticides on sediments, especially in presence of other main typical pollutants, such as surfactants, is necessary for predicting their mobility and fate in the aquatic ecosystems.

Atrazine is one of the most widely used herbicides for the control of broadleaf and grassy weeds on both agricultural and non-agricultural land. As a neutral chemical with relatively high water solubility, atrazine is only moderately persistent in the environment, with a half-life of 1 to 12 months, and its appearance in surface waters raises concern because of its possible health hazards (Bouquard et al., 1997). Atrazine is a probable human carcinogen, and its current U.S. Environmental Protection Agency maximum contaminant level in drinking water is 3.0 µg/L (Birardar and

Rayburn, 1995). In addition, atrazine has recently been reported to have long-term reproductive and endocrine-disrupting effects (Tugulea et al., 1998). Therefore, it is considered to be an important environmental pollutant and has been restricted in many countries. In China, it has been one of the most popular herbicides and is still widely used in large quantities. The sorption and mobility of atrazine in soils and sediments depend on the type of herbicide, the content and nature of the colloidal fraction of the soil, sediment, clay, and organic matter (Barriuso et al., 1992; David et al., 1994; Gao et al., 1997, 1998a and b), and environmental factors.

During the last decades, large quantities of surfactants used in industrial and household applications have given rise to concern over the direct and indirect effects of these compounds in the environment. While some surfactants (or their degradation products) could become potential contaminants, their presence might also be expected to influence the behavior of other pollutants. Interactions between surfactants and pollutants are very complex and depend heavily on surfactant concentration compared with critical micelle concentration (CMC). Much attention has been paid to the study of the effects of surfactants on the behavior of hydrophobic organic compounds, when both coexist in soils as a result of human activities, and to the investigation of the possible application of surfactants for chemical remediation of contaminated soils (David et al., 1991; Sandeep et al., 1994; Sun et al., 1995). However, so far, little has been published on surfactants and pesticides in sediments, especially for surfactants at low concentrations. Hence, the experiments were designed to determine the effect of relatively low concentrations of surfactants, which is close to the concentration level in natural water.

The objective of this investigation was to compare the effects of three kinds of surfactants on the sorption behavior of atrazine onto natural sediments. The applied surfactants are sodium dodecylbenzene sulfonate, cetyltrimethylammonium bromide, and emulsifier span-20 (ES-20), representing anionic, cationic, and nonionic type, respectively, which are widely used in industrial and consumer products. Effects of surfactant concentration, surfactant type, and sediment type on atrazine sorption were investigated first, in detail. Effect of sodium dodecylbenzene sulfonate (SDBS) concentration on the desorption of atrazine from the sediment was studied using batch-equilibrium experiments. In addition, tests were carried out of the effect of contacting sequence of SDBS on the adsorption of atrazine by the sediment.

Methods

Sorbate and Chemicals. The pesticide used in this study was atrazine (2-chloro-4-isopropylamino-6-ethylamino-1,3,5-triazine),

Table 1—Physical and chemical properties of sediments.

Sediments	TOC (%)	Texture (%)			pH (1:2.5)	CEC (mmol g ⁻¹)	SSA (m ² /g)
		Clay	Silt	Sand			
SA	2.06	8	67	25	7.76	0.163	6.47
SB	1.28	14	67	19	7.80	0.150	10.60
SC	1.45	17	72	11	8.00	0.168	12.07
SD	1.78	25	62	13	7.94	0.287	27.94

	React. FeOOH (Fe%)	Am. FeOOH (Fe%)	Fe _T (Fe%)	Crypt. MnOOH (Mn%)	Mn _T (Mn%)
SA	0.16	0.26	3.73	0.025	0.084
SB	0.20	0.34	4.03	0.032	0.088
SC	0.29	0.51	5.11	0.019	0.180
SD	0.47	0.74	5.30	0.047	0.120

having a solubility of 30 mg/L and a pK_a value of 1.8 [Weber, 1991]. Standard atrazine, with 100% purity, was purchased from Accustandard, Inc. (New Haven, Connecticut). Technical-grade atrazine used in experiments was supplied by Ruize Pesticide, Ltd. (WuXi, China), with 97.7% purity. Three surfactants are all at reagent grades, including SDBS, cetyltrimethylammonium bromide (CTAB), and ES-20, and were used without further treatment. They represent anionic, cationic, and nonionic type, respectively, the CMC of SDBS and CTAB being 433.5 and 361.0 mg/L.

Sorbents. Four surface-sediment samples were collected from some experimental sites located near Beijing, China, during October 2001. Sediment A (SA) was sampled from Yanhechen River, sediment B (SB) from Guihe River, sediment C (SC) from Yanghekou River, and sediment D (SD) from Guanting Reservoir. All samples were air-dried and homogenized in the laboratory. In this study, the $\leq 63\text{-}\mu\text{m}$ -sediment fraction was chosen to reduce the grain-size effect, as recommended by Horowitz and Elrick (1988). The homogenized sediment samples were sieved through a 63- μm , stainless-steel sieve and were used in the following analyses.

Total organic carbon (TOC) of the sediment was determined by titrimetry, following dichromate oxidation (Gaudette et al., 1974) (Apollo 9000, Tekmar-Dohrmann Co., Niles, Illinois). Specific surface area was measured by blanked-emitter-transistor nitrogen adsorption for the external surface area of the dry sediment (Brunauer et al., 1938) (ASAP-2000, Micromeritics Co., Norcross, Georgia). Cation-exchange capacity (CEC) was determined following the procedures defined by Naoto and Wada (1985) (ICP-AES ULTIMA, Jobin Yvon, Co., Longjumeau Cedex, France). The pH value of the sediments (in 0.01-M calcium chloride [CaCl_2] solution, sediment: solution = 1:2.5) was measured with a glass electrode (Metrohm Co., Herisau, Switzerland). Contents of iron and manganese, including reactive iron oxide (react. FeOOH), amorphous iron oxide (am. FeOOH), cryptocrystalline manganese oxide (crypt. MnOOH), and total iron (Fe_T) and manganese (Mn_T), were analyzed by atomic absorption spectrometry (AAS) (Wang and Chen, 2000) (Z-6100, Hitachi Co., Tokyo, Japan). The main physicochemical characteristics of the sediments are given in Table 1. Mineral components of the sediment were analyzed by X-ray diffraction. The sample was slurried in 95% ethanol and oriented on glass slide by the paste method (Laird et al., 1992). The oriented specimen was air-dried (approximately equal to 45% relative humidity) and analyzed using α -kalium copper (CuK_α) radiation

and an X-ray diffractometer (D/max-2400, Rigaku, Japan). The results of the X-ray diffraction for sediments are shown in Figure 1.

Experimental Procedure. Stock solutions were prepared by weighing an appropriate amount of technical-grade atrazine. The weighed atrazine was dissolved in methanol and diluted to different concentrations with 0.01 mol/L CaCl_2 , containing 0.02% sodium superposition nitrogen (NaN_3). Diluted solutions provided the desired solutions, which contained $<1\%$ methanol for all concentrations ranging from 0 to 50 $\mu\text{mol/L}$, where methanol was assumed to have little effect on solute equilibrium because of its low concentration in the system. In these experiments, somewhat higher atrazine concentrations than typical were used to facilitate the pesticide determination. The 0.01 mol/L CaCl_2 background electrolyte was used to mimic electrolyte concentrations in natural solutions found in many soils and sediments and to enhance separation of solid from aqueous solution after equilibration. The purpose of addition of NaN_3 was to inhibit biotransformation of atrazine during the experiment period. Sodium superposition nitrogen is the salt of a weak acid ($pK_a = 4.7$) and behaves as a very weak pH buffer under the pH range 6.5 to 7.5 of the sediment–water solutions used in this study. Sodium superposition nitrogen was selected, as it adsorbs weakly to the sediments.

One gram of sediment was weighed into 25 mL cone-shaped flasks containing 20 mL solution of atrazine, with and without surfactants. The flasks were sealed with parafilm immediately; samples were then equilibrated on a reciprocating shaker at room temperature for 48 hours. The 48-hour time period was determined previously to be adequate for short-term equilibrium; longer shaking time was avoided to minimize the potential for microbial degradation and volatilization of atrazine. After shaking, the mixtures were centrifuged for 30 minutes at 12 000 g, with a high-speed and refrigerant centrifuge (J2-HS, Beckman Co., Fullerton, California). Preliminary filtration experiments with 0.45- μm cellulose acetate filters (GF/F filter paper, Whatman Co., Maidstone, England) showed that this centrifugation was sufficient to remove atrazine bound to particles and colloids larger than 0.45 μm . Therefore, the concentration measured correctly indicated the concentration in solution. Following centrifugation, 10 mL of supernatant was removed and subsampled to determine the concentration of herbicide remaining in solution by high-performance liquid chromatography (HPLC) analysis. For the desorption of atrazine from SA in the presence of surfactants, supernatant was replaced by an equal amount of 0.01 mol/L CaCl_2 water solution. After shaking for 24 hours at room temperature, the suspensions were centrifuged and the atrazine concentrations were determined as above.

To determine the effect of SDBS concentrations on desorption rates, 2.5 g of sediment was loaded with 50 mL of atrazine solution. After 2 days of contact, the sediment was centrifuged and contacted with 50 mL of sterile solution containing 0, 0.1, 1.0, or 10 mg of SDBS per liter. The flasks were incubated at $25 \pm 1^\circ\text{C}$ on a rotary shaker operating at 150 rpm. At 2 hours and regular intervals thereafter, 3 mL of liquid was removed aseptically and replaced with a sterile solution of the surfactant. The liquid was centrifuged and the atrazine concentration was determined by HPLC.

In the SDBS preloading experiments, the sediment was exposed to the surfactant at the concentration of 10 mg/L for 2 days, and then atrazine was added to the solution. Atrazine samples were taken after an additional 2 days of contact time. In the atrazine preloading experiments, the sediment was loaded with single solute atrazine. After 2 days of contact, SDBS was added to the system for an additional 2 days of contact time.

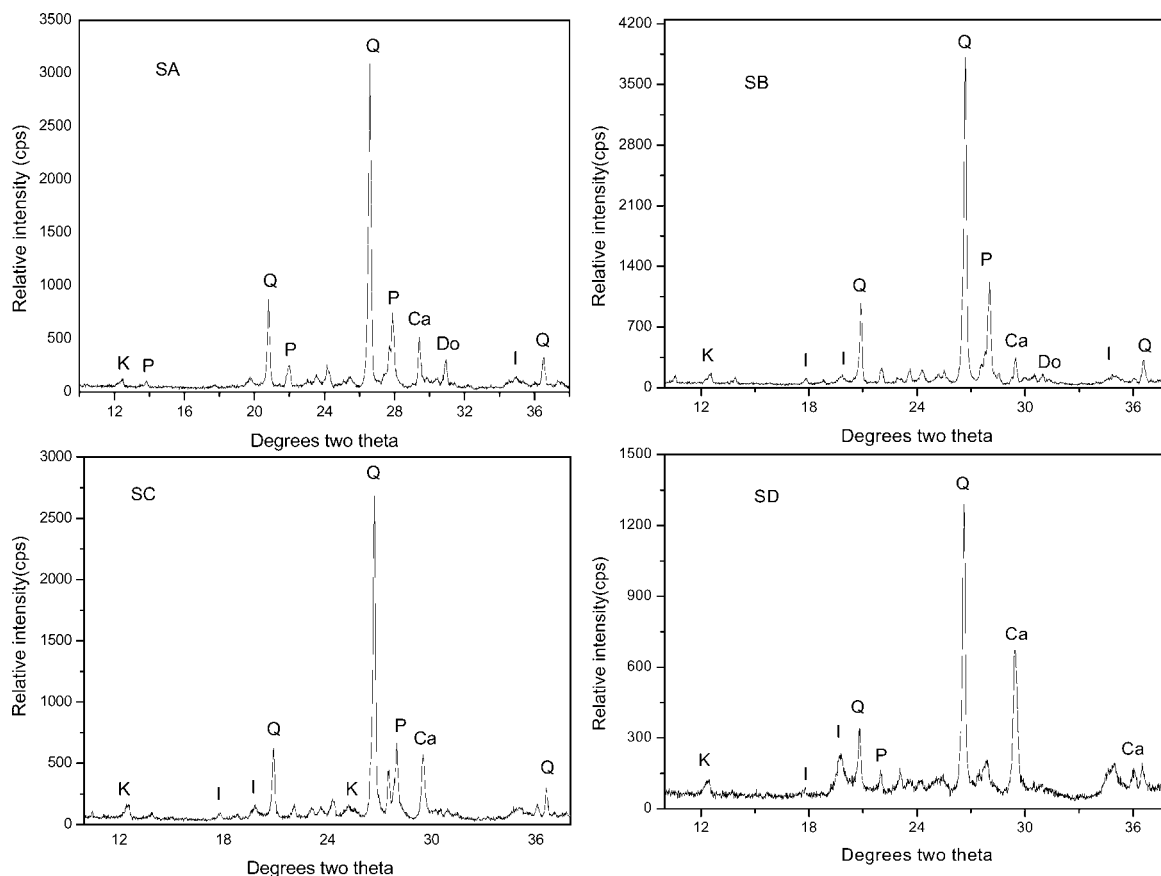


Figure 1—X-ray diffraction patterns of four sediments. Quartz (Q), kaolinite (K), plagioclase (P), calcite (Ca), dolomite (Do), and illite (I) peaks are indicated. The sediments were analyzed by X-ray diffraction using CuK_α radiation.

All experiments were carried out in duplicate, and blanks without sediment were also run for each experimental condition.

High-Performance Liquid Chromatography Analysis. The atrazine concentration in the liquid phase was measured by a HPLC system equipped with an ultraviolet detector (HPLC-10A, Shimadzu Co., Tokyo, Japan) and an Extend- C_{18} reversed-phase column (4.6×250 mm, Agilent Technologies, Palo Alto, California). The mobile phase was methanol/water (85:15, v/v) and the flowrate was 1 mL/min. The detecting wavelength was 223 nm for atrazine. The concentration bound to the sediment was calculated as the difference between the concentrations in solution of the blank and of the sample with sediment.

Results and Discussion

Effect of Surfactant Concentrations on the Adsorption of Atrazine by Sediment A. Figure 2 displays the effect of three surfactants on the adsorption of atrazine by the sediment, at constant atrazine concentration and various surfactant concentrations. At all surfactant concentrations examined of 0, 0.1, 1.0, 5.0, 10, and 20 mg/L, SDBS and CTAB always reduce the adsorption of atrazine, while ES-20 does not. At concentrations ranging from 0 to 1.0 mg/L, three surfactants exhibit a similar influencing tendency for decreasing the adsorption of atrazine. However, when the surfactant concentration is higher than 1.0 mg/L, the type of surfactants plays a significant role in affecting atrazine adsorption. The ES-20 increases atrazine adsorption significantly at higher concentrations

(>1 mg/L), and the adsorption capacity of atrazine is more than two times that of the treatments in the presence of SDBS or CTAB. The effects of surfactant concentrations are insignificant on the adsorption of atrazine when the concentration of SDBS or CTAB ranges from 5.0 to 20 mg/L. However, it should be noticed that the

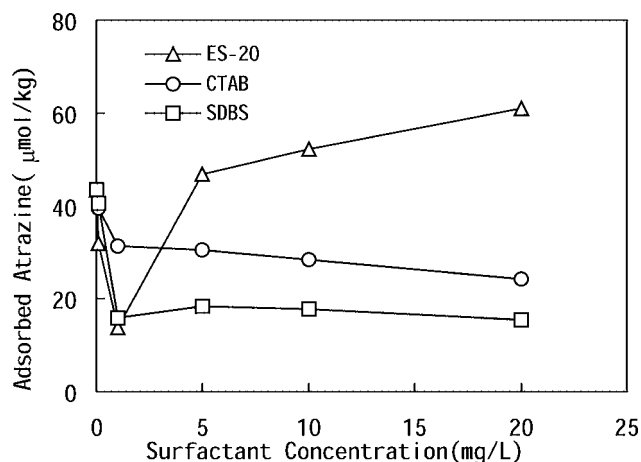


Figure 2—Effect of surfactant concentration on the adsorption of atrazine by sediment A (initial atrazine concentration 20.37 $\mu\text{mol/L}$, surfactant concentration ranged from 0 to 20 mg/L).

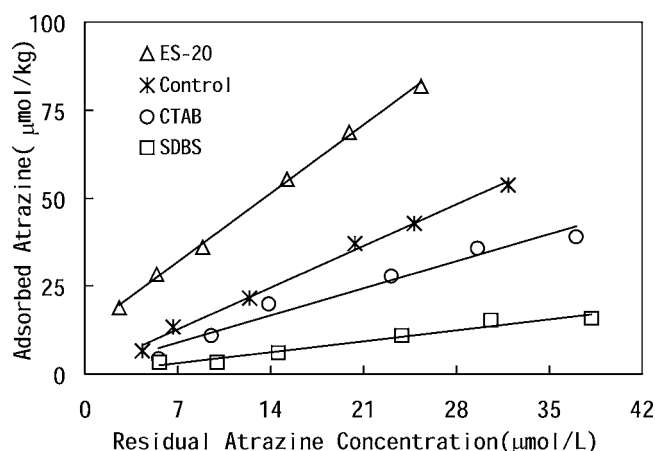


Figure 3—Effect of surfactants on the adsorption isotherm of atrazine for sediment A (all surfactants were set at a constant concentration of 10 mg/L).

presence of SDBS results in a greater decrease in atrazine adsorption than the presence of CTAB.

The mechanism by which surfactants affect sorption of atrazine is complex. The application of surfactants results in a drastic increase in soil dispersion (Abu-Zreig et al., 1994; Mbagwu et al., 1993), thus increasing the soil surface area and the amount of available sites for adsorption (Huggenberger et al., 1973). The mechanical disintegration of particles in batch experiments because of sample shaking may also increase available sites for adsorption, resulting in an increase in the adsorption capacity of sediment. The adsorption capacity of sediment depends on the degree of dispersion. The sorption of surfactants onto the sediment may also influence the adsorption of atrazine. When dissolved in water at a low concentration, surfactant molecules exist as monomers. The hydrocarbon chain, which is incapable of hydrogen bonding, disrupts the normal water structure in its vicinity. The resultant high entropy “structured water”, which surrounds the chain, increases the free energy of the system. The free energy can be minimized if the hydrocarbon chains are partially or totally removed from contact with water, either by adsorption onto or absorption into organic matter. Cationic surfactants tend to adsorb strongly onto clays and colloidal materials and onto organic matter. Anionic materials, on the other hand, tend to be less strongly, but still extensively, sorbed, with a certain amount remaining in the aqueous phase. There is a strong correlation between increase adsorption of anionics and higher sorbent organic matter content. The adsorption of nonionic surfactants, as with other nonpolar compounds, is influenced mainly by the organic carbon content of sediment. Sorption onto sediment not only affects the behavior of surfactants, but, as with other chemicals, it can influence the desorption of other chemicals. Klumpp et al. (1991) found that cationic surfactant (dodecyl trimethyl ammonium bromide, hexadecyl trimethyl ammonium bromide, and didodecyl dimethyl ammonium bromide), far below the CMC, enhanced the soil uptake of organic hydrophobic pollutants, such as nitrophenol and naphthol, because of the formation of hydrophobic adsorbate layers, or hemimicelles. This suggests that the increase in adsorption capacity of sediment is probably because of sediment dispersion and the sorption of surfactants formerly adsorbed by sediment, to some extent.

The relative change in the amount of adsorbed atrazine with surfactant decreased with an increase in the concentration of

Table 2—Effect of surfactants on the distribution coefficient of atrazine for sediment A.

Type of surfactant	K_d	Increased K_d percentage (%)	R^2
Control	1.71	/	0.9960
SDBS	0.45	−73.7	0.9604
CTAB	1.10	−35.7	0.9629
ES-20	2.77	62.0	0.9983

surfactant, indicating a limited sorption phenomena. This behavior emphasizes that mechanisms, other than hydrophobic sorption by organic carbon, are responsible for the marked increase in the adsorption of atrazine. In general, the effects of surfactants on the adsorption of atrazine by the sediment could be attributed to the physical-chemical properties of surfactants, which decide the adsorption extent of surfactants on the sediment, and to the interactions between the sediment and surfactants at various concentrations, which affect atrazine distribution between two phases.

Effect of Surfactants on the Adsorption Isotherm of Atrazine for Sediment A. To compare the effects of surfactants on adsorption isotherm of atrazine, the surfactant concentration was set constant, at 10 mg/L. Isotherms for the adsorption of atrazine in the presence of surfactants are shown in Figure 3. Preliminary analysis indicated a linear relationship between the atrazine adsorbed and the equilibrium concentration. Therefore, linear regression was used to compute the partition coefficient (K_d), and the results are summarized in Table 2. The ES-20 promotes greatly the extent of the adsorption of atrazine, and the adsorption isotherm lies to the left of atrazine adsorption isotherm for the control. On the other hand, SDBS and CTAB reduce significantly the extent of atrazine adsorption, and the adsorption isotherm lies to the right of the control. The data in Table 2 show that the addition of ES-20 resulted in an increase of 62.0% in the K_d value when compared to the control. However, the distribution coefficient of atrazine decreased in the presence of SDBS or CTAB. The corresponding decreases in the K_d values were 73.7 and 35.7%, respectively. Also, SDBS has a greater effect than CTAB on decreasing the adsorption of atrazine. The control treatment had the medial K_d value of 1.71 for sediment A.

It is well known that surfactant molecules are in the form of monomers at the concentrations far below the CMC. As reported in the literature (Edwards et al., 1992; Iglesias-Jimenez et al., 1996; Kile and Chiou, 1989), at these levels, surfactants may increase the apparent solubility of sparingly soluble organic compounds, although is lower than that of surfactants in micellar form. This effect is attributed to a partitionlike interaction with the nonpolar content of the dilute surfactant, similar to the enhancement effect caused by dissolved humic materials (Chiou et al., 1986 and 1987). Atrazine is simultaneously adsorbed by both surfactant monomers in solution and that adsorbed by sediment. The net effect of the surfactant depends on whether the increase in adsorption or the increase in solubility is more important. Following the addition of SDBS and CTAB to the sediment-water system, the adsorption percentage of atrazine decreases, compared to that of the control. The decrease occurs because more pesticide is adsorbed by surfactant monomers in the aqueous solution than by surfactant on the sediment. Another reason for the decrease of atrazine adsorption is probably caused by competition for adsorption sites on the sediment between atrazine and surfactant. The significant

Table 3—Effect of surfactants on atrazine desorption from sediment A (initial atrazine concentration 5.88 to 39.33 $\mu\text{mol/L}$, surfactant concentration 10 mg/L).

Initial atrazine concentration ($\mu\text{mol/L}$)	Atrazine desorbed as % of adsorbed			
	Control	SDBS	CTAB	ES-20
5.88	32.58	44.95	40.89	25.14
10.33	34.43	45.61	41.15	25.97
15.05	35.67	46.41	44.8	26.04
24.61	33.59	50.01	44.37	26.29
31.54	40.00	50.64	45.81	27.87
39.33	41.13	52.72	48.88	28.4

increase of atrazine adsorption in the presence of ES-20 suggests that, at a low concentration of ES-20, more atrazine is adsorbed by the monomers adsorbed by the sediment than that adsorbed by monomers in solution.

Table 3 summarizes the effect of surfactants on atrazine desorption from the sediment. It can be seen that desorption of atrazine from sediment is significantly greater for the treatment containing SDBS or CTAB and becomes less for the treatment in the presence of ES-20, in comparison of surfactant-free system. This indicates that atrazine is more weakly adsorbed on sediment in SDBS or CTAB solutions than in surfactant-free solutions, possibly because of competition for adsorption sites on the sediment. As for ES-20, the inhibited desorption could be attributed to the strong adsorption of atrazine on the sediment under the promotion of the nonionic surfactant. Furthermore, the percentage of atrazine desorption generally increases with increasing of its initial solution concentrations. Barriuso et al. (1992) also found that the desorption of atrazine was dependent on the sorbed herbicide concentration, with the high concentration being retained to a lesser extent and more easily to desorb than the lower concentration. However, Farenhorst and Bowman (1998) gave a result that was contrary to the above.

Adsorption Isotherms of Atrazine on Four Sediments. A set of experiments was run in an attempt to establish the properties of sediments that influence the sorption of atrazine. Isotherms for the adsorption of atrazine on four sediments are shown in Figure 4. The experimental data have been interpreted in terms of linear regression, for which the parameters are given in Table 4. The adsorption isotherms illustrate that atrazine sorption onto four sediments could be well described by linear relationship with values of $r^2 \geq 0.98$ over the solute concentration ranges used in this study. Atrazine was more highly sorbed on SD than on others. From Table 1 and Figure 1, we can observe that SA contains highest organic carbon, followed by SD, SC, and SB. Sediment D has the greatest clay content, specific surface area, CEC, and total iron content of the four sediments. These suggest that not only organic carbon, but also other physical-chemical properties of sediments influence the extent of adsorption of atrazine.

The data (Table 4) shows that there was no clear trend between the organic matter content of sediment and the K_{oc} values. It appears that K_d values may be related to clay content because SD (25% clay) has a K_d value of 1.75 compared to the SB (14% clay), which had 1.05 value for K_d , except for SA. Both clay content and organic matter play important roles in atrazine adsorption in the case of SA. Therefore, for sediments with low organic carbon (<3%), the conclusion could be made that organic carbon does not always play

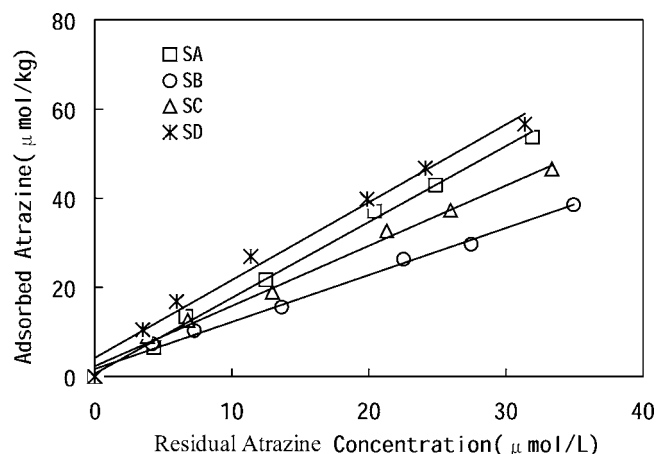


Figure 4—Atrazine adsorption isotherms for various sediments.

a vital role in atrazine adsorption, and many other factors in sediments, such as clay content, specific surface area, CEC, and metal oxides also should be considered, a conclusion which was also approved by other authors (Leticia and Schwab, 1995). Because this observation is for a limited number of sediments, it does not refute the conclusions of others that there is a strong relationship between organic carbon and atrazine adsorption (Brouwer et al., 1990; Karickhoff et al., 1979; McCall et al., 1980). However, our results illustrate the importance of determining adsorption trends on specific sediments of interest rather than relying on published data.

Effect of Sediment Types on the Adsorption of Atrazine in the Presence of Sodium Dodecylbenzene Sulfonate. The adsorption of atrazine by four sediments in the presence of SDBS at different concentrations (0 to 20 mg/L) is shown in Figure 5. An increase in the SDBS concentration resulted in a similar decrease in atrazine sorption by all sediments, indicating that the nature of surfactant is more important than the sediment type. Atrazine sorption decreased significantly in the presence of SDBS at concentrations below 5 mg/L. However, at higher concentrations (>5 mg/L), a further increase in surfactant did not increase desorption of atrazine from sediment, except in the case of SD at 10 mg/L. In this case, 24% of atrazine decreased, compared to treatment in the presence of SDBS at 5 mg/L. The reduction in desorption was attributed to the formation of hemimicelles by the surfactant on the sediment surface, into which the atrazine could partition. Brickell and Keinath (1991) found that soil type, specifically its clay mineralogy, was also a key factor in determining whether a surfactant solution enhanced desorption of hydrophobic organic chemicals (HOCs) from soil. The conclusion could also explain our results obtained in this experiment. Sediment D, with

Table 4—Distribution coefficient of atrazine for various sediments.

Sediment	% Organic carbon	K_d	K_{oc}	R^2
SA	2.06	1.71	83.0	0.9960
SB	1.28	1.05	82.0	0.9937
SC	1.45	1.35	93.1	0.9920
SD	1.78	1.75	98.3	0.9855

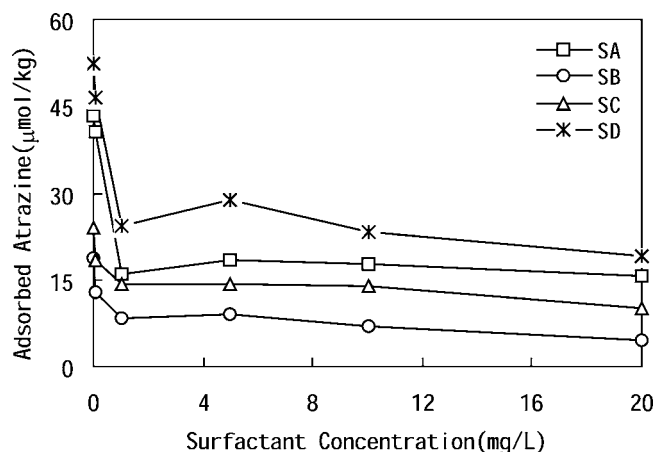


Figure 5—Effect of SDBS on the adsorption of atrazine by various sediments.

the highest clay content of the four sediments, has a relatively lowest desorption percentage, followed by SA, SC, and SB. Although the clay content of SA is lower than that of SB and SC, its organic carbon content is high. Therefore, in the process of atrazine adsorption, both clay content and organic carbon are key influencing factors, resulting in more atrazine being adsorbed by SA than by SB and SC.

Regarding the affinity of anionic surfactants in monomeric form for soils, different authors studying the adsorption of alkylbenzene sulphonates (anionic surfactants similar to SDBS) have observed negative relationships between adsorption and the organic matter content of the soils (Di Toro et al., 1990; Ou et al., 1996) and positive relationships between adsorption and the contents of clay, silt, or iron oxides in soils (Hand and Williams, 1987; Litz et al., 1987; Ou et al., 1996). This effect of the soil composition on the adsorption of anionic surfactants at concentrations below the CMC also explains the variations in the effect of SDBS on atrazine adsorption by four sediments. Overall, the sorption of atrazine was more influenced by the type of surfactant than by the sediment textural class. However, it appears that the relative change in atrazine adsorption capacity with SDBS is also affected by sediment

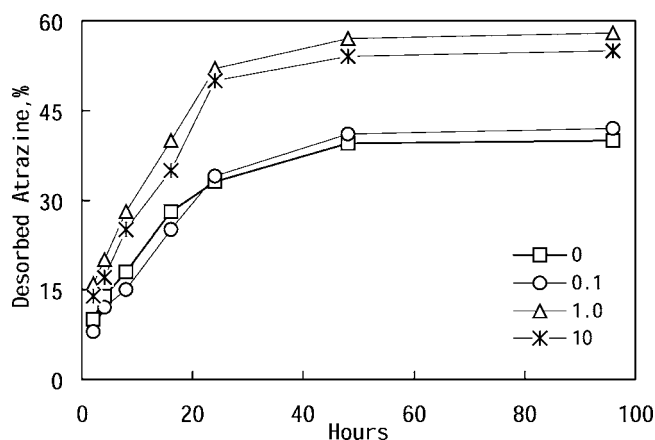


Figure 6—Effect of SDBS concentration on the desorption of atrazine from sediment A. The values in the cutline are milligrams of surfactant per liter.

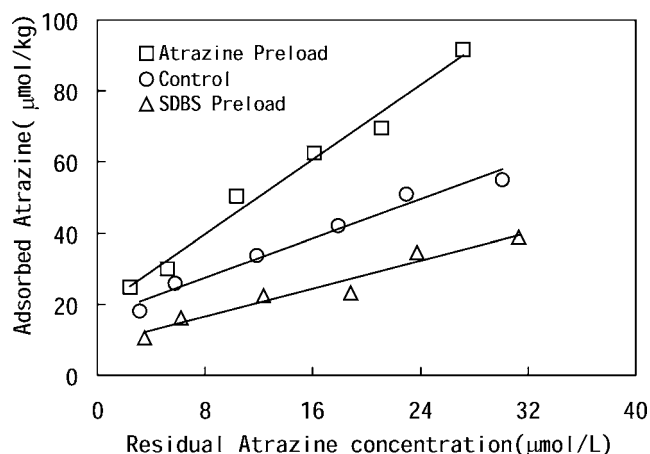


Figure 7—Effects of SDBS preloading and atrazine preloading on atrazine adsorption onto sediment A. SDBS at 10 mg/L preloading with the sediment for 2 days before contact with atrazine and atrazine preloading followed by 2 days of contact with SDBS; the control treatment for atrazine was designed to contact with water alone.

type, which is similar to the treatments in the absence of surfactant (Figure 4).

Effect of Sodium Dodecylbenzene Sulfonate Concentration on the Desorption of Atrazine from Sediment A. Tests were conducted to examine the effect of SDBS concentration on the release of atrazine from SA suspended in water. The extent of desorption of atrazine from SA was enhanced by the anionic surfactant at surfactant concentrations of 0.1, 1.0, and 10 mg/L (Figure 6). The SDBS at concentrations of 1.0 and 10 mg/L greatly increased the extent of desorption of atrazine, as compared to the treatment with no surfactant, and approximately 58 and 55% of the pesticide that had been held by the sediment were desorbed, respectively. The SDBS at 0.1 mg/L also promoted the desorption of atrazine slightly. At all time intervals, the rate of desorption was stimulated by SDBS at 1.0 and 10, but not 0.1 mg/L. The lowest level (0.1 mg/L) of SDBS reduced the extent of desorption up to and including 16 hours, and a promotion was observed beginning at 24 hours. The results show that the higher surfactant concentration, the more atrazine desorbed from the sediment. Anionic surfactant at low concentrations could accelerate the desorption of the pesticide. When contacting time is more than 24 hours, it affects the adsorption of atrazine insignificantly. However, when it is short (<24 hours), desorption time should be taken into account because of its important influence on atrazine desorption. In this period, there exists a linear relationship between the atrazine desorbed and the contacting time.

Effect of the Contacting Sequence of Sodium Dodecylbenzene Sulfonate with Sediment A on Atrazine Adsorption. Effects of SDBS and atrazine preloading on atrazine adsorption onto the sediment are compared in Figure 7. The result shows that SDBS, at a concentration of 10 mg/L, could lead to either an increase or decrease in atrazine adsorption onto sediment. The key factor was the contacting sequence of SDBS with the sediment. When SDBS was added to the sediment before atrazine, the adsorption of atrazine decreased compared with water alone, probably because of the occupation of active hydrophobic adsorption sites by SDBS. When SDBS was added to the sediment after atrazine, the adsorption of atrazine increased, probably because of the additional partitioning

of the material into SDBS hemimicelles on the sediment surface. The conclusion was supported by Ou et al. (1995), who found that linear alkylbenzene sulfonate (LAS), at low concentrations (<50 mg/L), could decrease phenanthrene adsorption onto soil when LAS contacted with the soil before phenanthrene, and vice versa.

Conclusions

The results obtained in this research demonstrate the ability of surfactants, at low concentrations, to change the partitioning behavior of pesticides between sediment surfaces and pore water. The surfactant type, concentration, and sediment nature appear to be the most important parameters in determining whether pesticides are either mobilized or immobilized. At low concentrations, nonionic surfactant increases the adsorption of atrazine, while cationic and anionic surfactants decrease the pesticide adsorption. Contrary to most other evidence (Amonette and O'Connor, 1980; Bayer, 1967), low concentrations of surfactant were found to mobilize atrazine in sediments. This finding suggests that we need to notice that, even at low concentrations, surfactants are able to mobilize potentially toxic substances that have been adsorbed by sediments.

Further work will be needed to quantitatively determine the sorbed surfactants in the mixed system, the effect of atrazine on the adsorption of surfactants, and the effect of high concentration of surfactants (>CMC) on the adsorption of atrazine. Nevertheless, the data presented should lead to a better understanding of the retention process of atrazine by surfactants at low concentrations. They provide evidence for the possible application of surfactants for chemical remediation of sediments contaminated by pesticides and also conducive basis for sediment-quality assessment.

Acknowledgments

Credits. This work was financially supported by the National Science Foundation of China (grant no: 20037010). The technical grade atrazine was kindly supplied by Ruize Pesticide, Ltd., WuXi, China.

Authors. Qing H. Tao is currently a researcher, Dong S. Wang is a professor of Environmental Engineering, and Hong X. Tang is an academician of Chinese Academy of Engineering and professor of Water Quality and Interface Chemistry in the State Key Laboratory of Environmental Aquatic Chemistry at Research Center for Eco-Environmental Science, Chinese Academy of Sciences, China. Correspondence should be addressed to Qing H. Tao, State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, P. O. Box 2871, Beijing 100085, China; e-mail: taoqh2008@yahoo.com.cn.

Submitted for publication September 1, 2003; revised manuscript submitted March 17, 2004; accepted for publication August 2, 2004.

The deadline to submit Discussions of this paper is October 15, 2006.

References

- Abu-Zreig, M.; Rudra, R.; Dickinson, W. T. (1994) Modifications in Soil Hydraulic Properties by Application of Detergents. *American Society for Aerospace Education International Winter Meeting*, Paper No. 942527, Atlanta, Georgia, December 13–16; American Society for Agricultural Engineers: Niles, Illinois.
- Amonette, J.; O'Connor, G. A. (1980) Non-Ionic Surfactant Effects on Adsorption and Degradation of 2,4-D. *Soil Sci. Soc. Am. J.*, **44**, 540.
- Barriuso, E.; Baer, U.; Calvet, R. L. (1992) Organic Chemicals in the Environment: Dissolved Organic Matter and Adsorption-Desorption of Dimefuron, Atrazine and Carbetamide by Soils. *J. Environ. Qual.*, **21**, 359.
- Bayer, D. E. (1967) Effect of Surfactants on Leaching of Substituted Urea Herbicides in Soil. *Weeds*, **15**, 249.
- Birardar, D. P.; Rayburn, A. L. (1995) Chromosomal Damage Induced by Herbicide Contamination at Concentrations Observed in Public Water Supplies. *J. Environ. Qual.*, **24**, 1222.
- Bouquard, C.; Ouazzani, J.; Prom, J. C.; Michel-Briand, Y.; Pliat, P. (1997) Dechlorination of Atrazine by a Rhizobium sp. Isolate. *Appl. and Environ. Microbiol.*, **63**, 862.
- Brickell, J. L.; Keinath, T. M. (1991) The Effect of Surfactants on the Sorption Partition Coefficients of Naphthalene on Aquifer Soils. *Water Sci. Technol.*, **23**, 455.
- Brouwer, W. W. M.; Boesten, J. J. T. I.; Siegers, W. G. (1990) Adsorption of Transformation Products of Atrazine by Soil. *Weed Res.*, **30**, 123.
- Brunauer, S.; Emmett, P. H.; Teller, E. (1938) Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.*, **60**, 309.
- Chiou, C. T.; Malcolm, R. L.; Brinton, T. I.; Kile, D. E. (1986) Water Solubility Enhancement of Some Organic Pollutants and Pesticides by Dissolved Humic and Fulvic Acids. *Environ. Sci. Technol.*, **20**, 502.
- Chiou, C. T.; Kile, D. E.; Brinton, T. I.; Malcolm, R. L.; Leenheer, J. A.; MacCarthy, P. (1987) A Comparison of Water Solubility Enhancements of Organic Solutes Aquatic Humic Materials and Commercial Humic Acids. *Environ. Sci. Technol.*, **21**, 1231.
- David, A. E.; Richard, G. L.; Liu, Z. B. (1991) Solubilization of Polycyclic Aromatic Hydrocarbons in Micellar Nonionic Surfactant Solutions. *Environ. Sci. Technol.*, **25**, 127.
- David, A.; Pau, L.; William, Y. Y.; Koskinen, C.; Tom, R. S.; Robert, H. D. (1994) Sorption of Atrazine on Soil Clay Components. *Environ. Sci. Technol.*, **28**, 1054.
- DiToro, D. M.; Dodge, L. J.; Hand, V. C. (1990) A Model for Anionic Surfactant Sorption. *Environ. Sci. Technol.*, **24**, 1013.
- Edwards, D. A.; Liu, Z.; Luthy, R. G. (1992) Interactions between Nonionic Surfactant Monomers, Hydrophobic Organic Compounds and Soil. *Water Air Soil Pollut.*, **26**, 147.
- Farenhorst, A.; Bowman, B. T. (1998) Competitive Sorption of Atrazine and Metolachlor in Soil. *J. Environ. Sci. Health B*, **33**, 671.
- Gao, J. P.; Maguhn, J.; Spitzauer, P.; Kettrup, A. (1997) Distribution of Pesticides in the Sediment of the Small Teufelsweiher Pond (Southern Germany). *Water Res.*, **31**, 2811.
- Gao, J. P.; Maguhn, J.; Spitzauer, P.; Kettrup, A. (1998a) Sorption of Pesticides in the Sediment of the Teufelsweiher Pond (Southern Germany). I: Equilibrium Assessments, Effect of Organic Carbon Content and pH. *Water Res.*, **32**, 1662.
- Gao, J. P.; Maguhn, J.; Spitzauer, P.; Kettrup, A. (1998b) Sorption of Pesticides in the Sediment of the Teufelsweiher Pond (Southern Germany). II: Competitive Adsorption, Desorption of Aged Residues and Effect of Dissolved Organic Carbon. *Water Res.*, **32**, 2089.
- Gaudette, H. E.; Flight, W. F.; Toner, L.; Folger, D. W. (1974) An Inexpensive Titration Method for the Determination of Organic Carbon in Recent Sediments. *J. Sediment. Petrol.*, **44**, 249.
- Hand, V. C.; Williams, G. K. (1987) Structure-Activity Relationships for Sorption of Linear Alkylbenzene Sulfonates. *Environ. Sci. Technol.*, **21**, 370.
- Hegeman, W. J. M.; Van Der Weijden, C. H.; Loch, G. J. P. (1995) Sorption of Benzopyrene and Phenanthrene on Suspended Harbor Sediment as a Function of Suspended Sediment Concentration and Salinity: A Laboratory Study Using the Cosolvent Partition Coefficient. *Environ. Sci. Technol.*, **29**, 363.
- Horowitz, A. J.; Elrick, K. A. (1988) Interpretation of Bed Sediment Trace Metal Data: Methods for Dealing with the Grain Size Effect. In *Chemical and Biological Characterization of Sludges, Sediments, Dredged Spoils, and Drilling Muds*, James J. Lichtenberg (Ed.); ASTM International: West Conshohocken, Pennsylvania, p. 114.
- Huggenberger, F.; Letey, J.; Farmer, W. J. (1973) Effect of Two Nonionic Surfactants on Adsorption and Mobility of Selected Pesticides in a Soil-system. *Soil Sci. Soc. Am. Proc.*, **37**, 215.

- Iglesias-Jimenez, E.; Sanchez-Martin, M. J.; Sanchez-Camazano, M. (1996) Pesticide Adsorption in a Soil-Water system in the Presence of Surfactants. *Chemosphere*, **32**, 1771.
- Karickhoff, S. W.; Brown, D. S.; Scott, T. A. (1979) Sorption of Hydrophobic Pollutants on Natural Sediments. *Water Res.*, **13**, 241.
- Kile, D. E.; Chiou, C. T. (1989) Water Solubility Enhancements of DDT and Trichlorobenzene by Some Surfactants Below and Above the Critical Micelle Concentration. *Environ. Sci. Technol.*, **23**, 832.
- Klumpp, E.; Heitman, H.; Schwuger, M. J. (1991) Interactions in Surfactant/Pollutant/Soil Mineral Systems. *Tenside Surfactant Detergents*, **28**, 441.
- Laird, D. A.; Barriuso, E.; Dowdy, R. H.; Koskinen, W. C. (1992) Adsorption of Atrazine on Smectites. *Soil Sci. Soc. Am. J.*, **56**, 62.
- Leticia, S. S.; Schwab, A. P. (1995) Adsorption Characteristics of Atrazine and Alachlor in Kansas Soils. *Weed Sci.*, **43**, 461.
- Litz, N.; Doering, H. W.; Thiele, M.; Blume, H. P. (1987) The Behaviour of Linear Alkylbenzene Sulfonate in Different Soils: A Comparison between Field and Laboratory Studies. *Ecotox. Environ. Safety*, **14**, 103.
- Mbagwu, J. S. C.; Piccolo, A.; Mbila, M. O. (1993) Impact of Surfactants on Aggregate and Colloidal Stability of Two Tropical Soils. *Soil Technol.*, **6**, 203.
- McCall, P. J.; Swan, R. L.; Laskowski, D. A.; Unger, S. M.; Vrona, S. A.; Dishburger, H. J. (1980) Estimation of Chemical Mobility in Soil from Liquid Chromatographic Retention Times. *Bull. Environ. Contam. Toxicol.*, **24**, 190.
- Naoto, M.; Wada, K. (1985) A New Equilibration Method for Cation-exchange Capacity Measurement. *Soil Sci. Soc. Am. J.*, **49**, 574.
- Ou, Z.; Yediler, A.; He, Y.; Kettrup, A.; Sun, T. (1995) Effects of Linear Alkylbenzene Sulfonate (LAS) on the Adsorption Behavior of Phenanthrene on Soils. *Chemosphere*, **30**, 313.
- Ou, Z.; Yediler, Y.; He, A.; Kettrup, A.; Sun, T. (1996) Adsorption of Alkylbenzene Sulfonate (LAS) on Soils. *Chemosphere*, **32**, 827.
- Sandeep, P. N.; David, A. S.; Jeffrey, H. H. (1994) Surfactant Adsorption and Modified Adsorption of Nonpolar, Polar, and Ionizable Organic Contaminants. *Environ. Sci. Technol.*, **28**, 1874.
- Sun, S. B.; Willian, P. I.; Stephen, A. B. (1995) Sorption of Nonionic Organic Compounds in Soil-Water System Containing a Micelle-Forming Surfactant. *Environ. Sci. Technol.*, **29**, 903.
- Tugulea, A. M.; Sarna, L. P.; Webster, G. R. B. (1998) Solid Phase Microextraction (SPME) of the Herbicide Atrazine in Aqueous Soil Suspensions. *Inter. J. Environ. Anal. Chem.*, **68**, 137.
- Wang, F. Y.; Chen, J. S. (2000) Relation of Sediment Characteristics to Trace Metal Concentrations: a Statistical Study. *Water Res.*, **34**, 694.
- Weber, J. B. (1991) Fate and Behaviour of Herbicides in Soils. *Appl. Plant Sci.*, **5**, 28.