

Quantifying effects of primary parameters on adsorption–desorption of atrazine in soils

Yufen Huang · Zhongzhen Liu · Yan He · Fang Zeng · Ronghui Wang

Received: 6 April 2012 / Accepted: 16 July 2012 / Published online: 7 August 2012
© Springer-Verlag 2012

Abstract

Purpose Adsorption and desorption are important processes that influence the transport, transformation, and bioavailability of atrazine in soils. Equilibrium batch experiments were carried out to investigate the adsorption–desorption characteristics of atrazine. The objectives of this study were to (1) determine and quantify the main soil parameters governing atrazine adsorption and desorption phenomena; (2) find the correlativity between the identified soil parameters; and (3) investigate the universal desorption hysteresis traits.

Materials and methods Fifteen soils with contrasting physico-chemical characteristics were collected from 11 provinces in eastern China. The equilibrium time was 24 h both for adsorption and desorption experiments. Atrazine was detected by Waters 2695/UV HPLC.

Results and discussion Adsorption isotherms of atrazine could be well described by the Freundlich equation ($r \geq 0.994$, $p < 0.01$). The total organic carbon (TOC) was the first independent variable that described 53.0 % of the total variability of K_f , followed by the pH (9.9 %), and the clay (4.0 %) and silt (1.2 %) contents, separately; while the primary soil properties that affect desorption parameters

included the TOC, pH, free Fe_2O_3 (Fe_d) and the sand content, with the biggest contribution achieved by the TOC (ranged from 48.5–78.1 %). The results showed that when the content ratio of clay to TOC (RCO) was less than 40, the atrazine adsorption was largely influenced by the organic matrix, while when the RCO was greater than 40, they were vital affected by the clay content.

Conclusions Adsorption–desorption isotherms of atrazine in soils were nonlinear. The content of TOC, clay, and iron oxides, as well as the pH value were the key soil parameters affecting the adsorption–desorption of atrazine in soil, among which the RCO especially exhibited relevance. Additionally, the desorption hysteresis existed for atrazine retention in all 15 tested soils, and the hysteretic effect enhanced with the increasing time for desorption. This would be ascribed to the heterogeneity physical–chemical properties of these soils.

Keywords Adsorption and desorption · Atrazine · Hysteretic effect · The content ratio of clay to total organic carbon (RCO) · Soil characteristics

1 Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is one of the most widely used herbicides for broadleaf weed and certain annual grasses controls and is popular because of its effectiveness and low cost (Huang et al. 2003; Gao and Jiang 2010). Since the 1980s, atrazine has been intensively applied in China and the application amount has increased rapidly (about 20 % per year); now, it is one of the 52 kinds of environmental priority control pesticides in China. Due to its relatively high mobility and long half-life (28–440 days) in soil, atrazine is often detected in surface and ground waters worldwide (Sherchan and Bachoon 2011), which has toxicity to aquatic organisms (Hincapie et al. 2005; Botelho et al.

Responsible editor: Bernd Markert

Y. Huang · Z. Liu (✉) · F. Zeng · R. Wang
Key Laboratory of Plant Nutrition and Fertilizer in South Region,
Ministry of Agriculture/Guangdong Key Laboratory of Nutrient
Cycling and Farmland Conservation, Soil and Fertilizer Institute, Soil
and Fertilizer Institute, Guangdong Academy of Agricultural Sciences,
Guangzhou 510640, People's Republic of China
e-mail: lzzgz2001@163.com

Y. He (✉)
College of Environmental and Natural Resource Sciences,
Zhejiang Provincial Key Laboratory of Subtropical Soil and Plant
Nutrition, Zhejiang University,
Hangzhou 310058, People's Republic of China
e-mail: yhe2006@zju.edu.cn

2011), frogs (Hayes et al. 2002), and leads to human cancer, it could even interfere with the production of normal human hormones, which is just inferior to DDT (Rayner and Fenton 2011).

Adsorption–desorption behavior is one of the key processes affecting the fate of agrochemicals in sediment–water environment (Clausen et al. 2001; Mudhoo and Garg 2011). The role of key soil properties, such as organic carbon content, clay content, pH, and cation exchange capacity, as a determinant of pesticide adsorption–desorption behaviors has attracted much interest over the past two decades (Jenks et al. 1998; Spark and Swift 2002; Deng et al. 2007; Flores et al. 2009; Sun et al. 2010). For example, Jenks et al. (1998) constructed the adsorption and desorption isotherms for atrazine retention in a Hastings silty clay loam with six soil depths, and found that atrazine adsorption was highly correlated with organic matter content and soil pH, and desorption hysteresis was also a reflection of the relative organic matter content and pH level in each soil depth. Flores et al. (2009) researched simazine adsorption behavior by using two representative soils (a loam soil with 8.5 % organic matter content and a clay loam soil with 3.5 % organic matter content) from agricultural sites of central Chile. The results and the potentiometric profiles of both soils, suggested that simazine adsorption in loam soil was mainly governed by simazine–organic matter interactions and in clay loam soil by simazine–clay interactions. While the work cited above for the investigation of the correlativity among divers soil properties for controlling adsorption–desorption behaviors of pesticides were collected mainly from relatively small geographical scale regions. The information directly available for various types of natural soils from a large geographical scale region is still limited to date. Furthermore, several studies have pointed out the occurrence of hysteresis in the adsorption–desorption reactions in soils (Lesan and Bhandari 2003; He et al. 2006a, b; Anagu et al. 2011); but whether it was universal for diverse soils is not completely understood, and accurate quantification of the effects of soil properties on adsorption–desorption of atrazine in soils still seems to be lacking.

In this study, 15 representative soils, with contrasting physico-chemical properties that belong to different types of soil classification, were collected from 11 provinces across about 85 % of the total area of entire eastern China, ranging from southern latitude of 19°N to northern latitude of 47°N. Batch adsorption and desorption experiments were carried out using the standard batch equilibration method. The goal of this work was to (1) determine and quantify the main soil parameters governing atrazine adsorption and desorption phenomena; (2) find the correlativity between the identified soil parameters; and (3) investigate the universal desorption hysteresis traits.

2 Materials and methods

2.1 Chemicals and soils

Acetonitrile (HPLC grade) was purchased from Merck Co., Germany. Atrazine (with purity greater than 99.5 %) was obtained from National Standard Material Standard Sample Information Center (China). Stock solution of atrazine was prepared in acetonitrile at 1000 mg L⁻¹, and stored in the dark at 4 °C. Working standard solutions were prepared by appropriate dilutions in 0.02 mol L⁻¹ KCl solution (0.02 % NaN₃). A Waters 2695 series HPLC with UV/Vis spectrophotometry detector was used for the quantification of atrazine.

Fifteen uncultivated soils were sampled in the surface layers (0–20 cm) in 11 provinces from south (19°N) to north (47°N) of eastern China. They were selected on the basis of contrasting taxonomy, sampling sites, and different basic properties (Table 1). Soil types were classified as Mollisols, Alfisols, Inceptisols, Ultisols, and Oxisols from north to south of China according to the USA classification. Soil samples were air-dried, sieved to 2 and 0.25 mm, stored in the dark at room temperature (20±2 °C) and sheltered from humidity. No residual atrazine was detected in these soil samples.

2.2 Adsorption–desorption experiments

Adsorption experiments were carried out using the standard batch equilibration method. A mass of 2.5 g of air-dried (0.25 mm sieved) soils were mixed with 5 mL varied concentrations (C_0) of atrazine (0.1, 0.2, 0.4, 0.8, 1.0, 2.0, 4.0, 8.0, 16.0, 20.0, and 30.0 mg L⁻¹, respectively) in 50-mL glass centrifugal tubes with a background electrolytic solution containing 0.02 mol L⁻¹ KCl (0.02 % NaN₃ was added to minimize bacterial growth and biodegradation of atrazine during batch experiments). One series of vials without soil as control was also monitored. Since the apparent equilibrium could be reached by shaking within 24 h as testified in our preliminary kinetic experiment, the tubes (with two replicates and a blank for each concentration) were shaken for 24 h with a rotary agitator (180 rpm) at 28±2 °C in dark. The soil slurry was thereafter centrifuged at 3,500 rpm for 20 min using a centrifuge (Legend Plus, Thermo). Supernatant solution was sampled from each tube for atrazine analysis by Waters 2695/UV HPLC, under the optimized conditions as follows: acetonitrile/water=60:40 as mobile phase, 1 ml/min of flow rate, 30 °C column temperature, and 221 nm detected wavelength.

Desorption experiments were conducted in sequential decant–refill steps immediately after adsorption procedures. At the end of adsorption experiments, solids were separated from the aqueous solution by centrifugation at 3,500 rpm for

Table 1 Location, classification and properties of soils used in this study

Soil no.	Soil type		Province	Textural class (USDA)	pH (H ₂ O)	TOC g kg ⁻¹	CEC cmol (+)kg ⁻¹	Fe _o g kg ⁻¹	Fe _d g kg ⁻¹	Particles fraction (%)		
	Chinese classification	U.S.taxonomy (Great Groups)								Clay	Silt	Sand
1	Black soils	Argiustoll	Heilongjiang	Silty clay loam	5.77	31.74	37.5	6.3	9.2	38.3	55.3	6.4
2	Brown earth	Paleboralf	Liaoning	Silt loam	6.49	9.40	13.5	4.1	11.5	24.7	62.2	13.2
3	Brown earth	Typustalf	Shandong	Clay loam	6.26	8.96	14.3	3.9	11.7	27.3	37.6	35.0
4	Cinnamon soils	Haplustalf	Henan	Silt loam	8.36	4.17	9.9	1.8	9.8	19.5	60.7	19.8
5	Fluvo-aquic soils	Ustifluent	Henan	Loam	8.32	8.29	7.7	1.4	7.2	15.5	43.2	41.3
6	Yellow-brown earth	Typudalf	Jiangsu	Silt loam	5.12	15.38	18.2	4.7	19.3	25.1	68.4	6.5
7	Red earth	Plinthudult	Zhejiang	Silt clay	4.59	3.57	9.7	2.9	25.0	50.2	41.5	8.3
8	Red earth	Psammaquent	Zhejiang	Sandy loam	4.28	1.46	6.6	0.7	7.2	11.5	14.4	74.4
9	Red earth	Plinthudult	Jiangxi	Silty clay	4.73	6.55	10.1	3.6	24.9	49.3	46.0	4.6
10	Yellow earth	Hapludult	Guizhou	Silty clay loam	4.09	25.68	10.5	6.0	24.6	35.1	61.0	3.9
11	Red earth	Plinthudult	Guangxi	Clay loam	4.23	10.73	9.8	2.1	24.9	37.0	28.7	34.2
12	Latosols	Tropudult	Guangdong	Clay	4.35	27.75	10.4	4.9	25.8	73.1	23.3	3.6
13	Latosols	Tropudult	Hainan	Silty clay loam	4.80	24.59	7.9	2.0	7.0	22.5	13.6	63.9
14	Latosols	Tropudult	Guangdong	Clay	4.82	20.66	145.4	9.6	25.8	60.9	26.3	12.8
15	Cinnamon soils	Haplustalf	Henan	Clay loam	8.32	3.21	117.5	2.8	10.7	26.5	21.5	52.0

TOC total organic carbon, CEC cation exchange capacity, Fe_o amorphous Fe₂O₃, Fe_d free Fe₂O₃

20 min and liquid of supernatant was withdrawn from each tube. The tube was weighed before and after withdrawal to calculate the amount of residue. Then, about 5 mL of background solution was added into each tube to maintain the same ionic strength as that of the background solution. The new atrazine mixtures were then desorbed for a new round shaking for 24 h under the same condition as adsorption, and subsequently determined by HPLC. In total, three rounds of successive desorption procedures were carried out. Desorbed atrazine was calculated at each desorption stage. The amount of atrazine remaining on sorbents at each desorption stage was calculated as the difference between the initial adsorbed amount and the final desorbed amount. Blank samples were also processed at the same time. Atrazine degradation and adsorption loss on the centrifuge tubes was found to be negligible (<1 %).

2.3 Statistical analyses

The mass of atrazine adsorbed onto the soils was detected by measuring the mass of atrazine that disappeared from the solution phase at the end of adsorption experiment. The fraction of atrazine adsorbed on the soils was calculated by the equation:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{M} \quad (1)$$

where Q_e is the quantity of atrazine adsorbed per unit weight of soil (in milligrams per kilograms); C_0 is the initial

concentration of atrazine (in milligrams per liter); C_e is the equilibrium concentration of atrazine at the end of the adsorption experiment (in milligrams per liter); V is the volume of solution (in liters); and M is the mass of the soil (in kilograms).

The fraction of atrazine desorbed from soils every cycle was calculated by the equation:

$$Q_{ej} = \frac{C_j \cdot V_j}{M} - \frac{C_{j-1} \cdot (V_{j-1} - V_{j-2})}{M} \quad (2)$$

where Q_{ej} is the j time's quantity of atrazine desorbed from soils (in milligrams per kilogram); C_j is the j time's solution phase atrazine concentration of the previous equilibrium experiment (in milligrams per liter); V_j is the j time's volume of solution; C_{j-1} is the $j-1$ time's solution phase atrazine concentration of the previous equilibrium experiment (in milligrams per liter); V_{j-1} and V_{j-2} are the $j-1$ and $j-2$ times' volume of the soil slurry with tube.

The adsorption and desorption data are analyzed using the Freundlich equation:

$$Q_e = K_f \cdot C_e^N \quad (3)$$

where Q_e is the solid-phase equilibrium concentration of atrazine (in milligrams per kilogram); C_e is the liquid-phase equilibrium concentration of atrazine (in milligrams per liter); K_f is the Freundlich unit capacity factor; N is the Freundlich exponent.

The content ratio of clay to total organic carbon (TOC; RCO) was calculated by the equation:

$$RCO = \frac{\%clay}{\%TOC} \tag{4}$$

Cox et al. (1997) proposed desorption hysteresis coefficients (*H*) based on the ratio of desorption and adsorption isotherm parameters:

$$H = \frac{N_d}{N_a} \cdot 100 \tag{5}$$

where *N_a* and *N_d* are the Freundlich parameter *N* for adsorption and desorption, respectively.

Ma et al. (1993) reported hysteresis as the maximum difference between adsorption and desorption isotherms:

$$w = \left(\frac{N_a}{N_d} - 1 \right) \cdot 100 \tag{6}$$

where *w* is the hysteresis coefficient.

Although *H* and *w* are easy to use, there is great difference between practical adsorption and desorption isotherms. Zhu and Selim (2000) defined a new hysteresis parameter *λ*, based on the difference in the area between the adsorption and desorption isotherms:

$$\lambda = \left(\frac{N_a + 1}{N_d + 1} - 1 \right) \cdot 100 \tag{7}$$

3 Results

3.1 Adsorption and desorption isotherms

Adsorption isotherms and Freundlich parameters of atrazine in the 15 soils were presented in Fig. 1 and Table 2. The results showed that adsorption amount of atrazine in the 15 soils increased with increasing equilibrium concentrations (Fig. 1). In addition, Freundlich parameters (*K_f* and *N_a*) were significant, and the correlation coefficients were highly significant at 0.01 probability level (Table 2). The *K_f* values ranged from 0.20 to 5.74 (29-fold to 0.2), and a grading in soil *K_f* values has been observed in the following order: soil 1 > soil 10 > soil 13 > soil 9 > soil 8 ≈ soil 6 > soil 11 ≈ soil 14 ≈ soil 12 ≈ soil 7 ≈ soil 2 > soil 3 > soil 5 ≈ soil 4 > soil 15.

Since all desorption isotherms were similar in shape, only the isotherm for soil 1 was shown graphically as example (Fig. 2). Apparently, there are significant differences among adsorption and desorption isotherms, and the desorption amounts of atrazine from the tested soils increased with increasing equilibrium concentrations. Desorption isotherms also conformed well to the Freundlich equation for all the tested soils (*r* > 0.945, *p* < 0.05) (Table 2). The results showed that the average desorption rate of atrazine after three

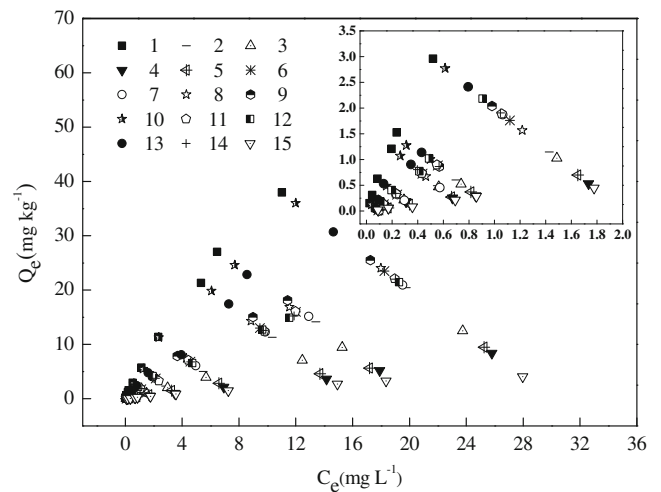


Fig. 1 Sorption isotherms of atrazine on 15 soils. *Q_e* is the amount of atrazine adsorbed per unit weight of soil and *C_e* is the equilibrium atrazine concentration

successive desorption were in the order: soil 5 > soil 15 > soil 4 > soil 2 ≈ soil 3 ≈ soil 13 > soil 14 > soil 6 ≈ soil 1 > soil 7 ≈ soil 12 > soil 11 ≈ soil 10 ≈ soil 8 > soil 9. It obviously revealed that the soils with high *K_f* values (e.g., soils 1, 10, 9, and 8) had lower desorption rate and adsorbed more atrazine than those with low *K_f* values (e.g., soils 15, 4, and 5).

3.2 Relation between atrazine adsorption–desorption and soil properties

Bivariate correlation analysis between soil properties and atrazine adsorption–desorption parameters (*K_f*, *K_{fd1}*–*K_{fd3}*) are showed in Table 3. There was a positive significant relationship between the *K_f* and the TOC content (*r* = 0.728, *p* < 0.01), and a negative relationship between the *K_f* and pH (*r* = −0.577, *p* < 0.05). In addition, there were also significant relationship between desorption parameters and the TOC content (*K_{fd1}*: *r* = 0.355, *p* < 0.05; *K_{fd2}*: *r* = 0.522, *p* < 0.05; *K_{fd3}*: *r* = 0.781, *p* < 0.01). A simple correlation analysis was also analyzed among soil properties (Table 4), which showed that the TOC content was positively correlated with the amorphous Fe₂O₃ (Fe₀) content, and the pH was negative correlated with the Fe_d content, while the Fe_d content was positively correlated with the clay content and negative correlated with the sand content. Therefore, it is difficult to assess the exact relationship among TOC, pH, and *K_f* if only by bivariate correlation analysis.

According to the principle of statistics, a dependent variable which is influenced by many factors cannot be explained by simple correlation analysis. Stepwise

Table 2 Constants and correlation coefficients (r) of atrazine adsorption and desorption on 15 soils based on the Freundlich equation

Soil	Adsorption			First desorption			Second desorption			Third desorption		
	K_f^a	N	r	K_{fd1}	N_{d1}	r	K_{fd2}	N_{d2}	r	K_{fd3}	N_{d3}	r
1	5.74**	0.795**	0.999**	0.86**	0.322**	0.996**	1.25**	0.558**	1.000**	1.31**	0.587**	0.999**
2	0.54**	1.284**	0.997**	0.38**	0.278**	0.999**	0.36**	0.294**	0.987**	0.28**	0.823**	0.986**
3	0.87**	0.849**	0.998**	0.49**	0.194**	0.988**	0.29**	0.389**	0.989**	0.43**	0.547**	0.945**
4	0.20**	1.142**	0.996**	0.13**	0.170**	0.999**	0.15**	0.607**	0.996**	0.11*	1.010**	0.993**
5	0.35**	0.747**	0.998**	0.27**	0.652**	0.996**	0.21**	0.603**	0.998**	0.26**	0.629**	0.998**
6	0.60**	0.781**	0.999**	0.49**	0.101**	0.999**	0.38**	0.285**	0.993**	0.32**	0.651**	0.992**
7	1.71**	0.901**	1.000**	0.55**	0.264**	0.993**	0.61**	0.600**	0.999**	0.52**	0.627**	0.992**
8	1.71**	0.847**	0.999**	0.83**	0.197**	0.999**	0.66**	0.275**	0.990**	0.44*	0.632**	0.991**
9	2.16**	0.840**	0.998**	0.67**	0.150**	0.999**	0.58**	0.454**	0.998**	0.19*	0.429**	0.945*
10	2.78**	0.702**	0.994**	0.39**	0.492**	1.000**	0.74**	0.521**	0.954**	0.19*	0.514**	0.946*
11	1.86**	0.846**	0.998**	0.24**	0.269**	0.996**	0.25**	0.441**	0.976**	0.20**	0.591**	0.993**
12	4.52**	0.835**	0.998**	0.55**	0.153**	1.000**	0.35**	0.231**	0.992**	0.52**	0.473**	0.996**
13	2.15**	0.781**	0.999**	0.41**	0.310**	0.988**	0.52**	0.332**	0.998**	0.44**	0.338**	0.993**
14	3.10**	0.869**	0.994**	0.93**	0.165**	0.999**	0.89**	0.331**	0.998**	1.02**	0.642**	0.999**
15	1.79**	0.844**	0.998**	0.30**	0.295**	0.997**	0.48**	0.402**	0.993**	0.53**	0.455**	0.982**

^a K_f the Freundlich unit capacity factor for adsorption; r the correlation coefficient; K_{fd1} , K_{fd2} , and K_{fd3} , the Freundlich unit capacity factor for the first, second, and third desorption, respectively; N_{d1} , N_{d2} , N_{d3} , the Freundlich exponent for the first, second, and third desorption, respectively
* $p=0.05$; ** $p=0.01$

regression analysis were thus derived in order to further correlate the various soil properties with the adsorption–desorption parameters for atrazine, and leads to a linear predictive model for K_f and K_{fd1} – K_{fd3} , respectively (Table 5). According to Table 5, model (D) is the best regression way to describing the relationship between K_f and soil properties, which had significant coefficient ($p<0.05$) and described nearly 68.1 % of total variability of the K_f . The TOC was the first independent variable that describe 53.0 % of total

variability of the K_f (model A), and followed by the pH (9.9 %), and the content of clay (4.0 %) and silt (1.2 %), respectively. Table 5 also showed that the tendency of relationship between atrazine desorption parameters and soil properties was similar in the three sequential desorption processes. The primary soil properties that affect desorption parameters were the content of TOC, Fe_d , and sand, as well as the pH value, with the biggest contribution achieved by the TOC (ranging from 48.5–78.1 %). The best regression model in the three desorption were model (G), model (K) and model (N), and the contribute rates to capacity of desorption were 75.1, 75.2, and 86.4 %, respectively.

3.3 Correlation of adsorption with the content ratio of clay to TOC (RCO)

Scatter diagram was used to show simple regression between the RCO values and Freundlich constants (K_f) for 15 soil samples used in the present study and 21 soil samples reported by others (Spongberg and Lou 2000; Huang et al. 2003; Amaud et al. 2005; Huo 2006; Gao and Jiang 2010) (Table 6), as shown in Fig. 3. According to Fig. 3, the 15 soils used in the present study had the same trend as the 21 soil samples reported by others. Note that the K_f value was RCO dependent. In most cases, the K_f value sharply decreased with the increase of the RCO values when $RCO<40$, and then approached relative unity in the upper RCO values range until further decrease of the K_f value was

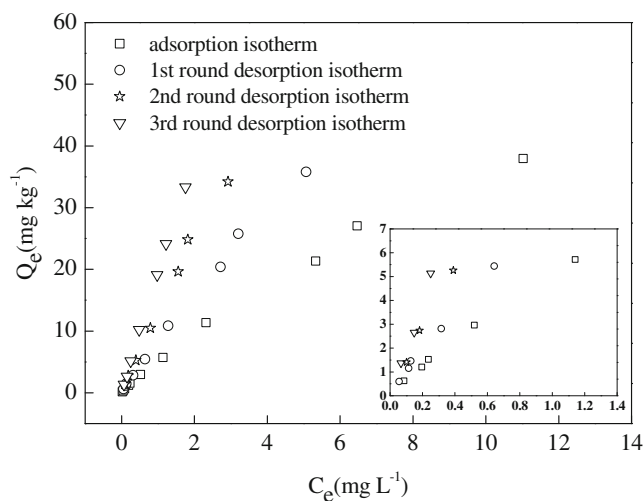


Fig. 2 Desorption isotherms of atrazine in soil 1. Q_e is the amount of atrazine desorbed per unit weight of soil and C_e is the equilibrium atrazine concentration

Table 3 The bivariate correlation between K_f , K_{fd1} – K_{fd3} and soil properties ($N=15$)

	pH	TOC	CEC	Fe _o	Fe _d	Clay	Silt	Sand
K_f	-0.577*	0.728**	-0.123	0.390	0.172	0.258	0.085	-0.258
K_{fd1}	0.385	0.355*	-0.304	0.050	-0.232	0.089	-0.111	-0.154
K_{fd2}	0.393	0.522*	-0.107	0.219	-0.081	0.193	-0.018	-0.128
K_{fd3}	0.218	0.781**	-0.071	0.403	-0.183	0.124	0.010	-0.100

Abbreviations are as in Tables 1 and 2

* $p=0.05$; ** $p=0.01$

not observed when $RCO > 40$. Therefore, the adsorption characteristics of atrazine by the soils could be separated into two groups according to the values of RCO (Fig. 4). The first group of soils with the $RCO < 40$ had the higher K_f values, and their adsorption capability had closer positive correlation with the TOC content ($r=0.315$, $p < 0.05$), but no relationship with the clay content ($r=0.014$, $p=0.942$). The second group of the soils with the $RCO > 40$, nearly 17 % of total tested samples, had lower K_f values, and their adsorption capability had closer positive correlation with the clay content ($r=0.359$, $p=0.058$) than the TOC content ($r=0.009$, $p=0.987$).

3.4 Hysteretic effect of atrazine desorption from soils

From the current results in Table 2, adsorption parameter (N_a) is bigger than desorption parameters (N_{d1} , N_{d2} , and N_{d3}), and discrepancy between adsorption and desorption isotherms had been well documented in Fig. 2. According to Eqs. (5), (6), (7), if $N_d/N_a = 1$, then $H=100$, $\omega=0$, and $\lambda=0$. The desorption rate and the adsorption rate would be similar. There was thus no hysteresis; if $N_d/N_a < 1$, then $H < 100$, $\omega > 0$, and $\lambda > 0$. The desorption rate would be less than the adsorption rate. The positive hysteresis would thus be characterized; if $N_d/N_a > 1$, then $H > 100$, $\omega < 0$, and $\lambda < 0$. It would be in the case of negative hysteresis (O'Connor et al. 1980; Barriuso et al. 1994). The results from Table 7 showed that the hysteretic phenomena existed during all desorption procedures, and all of them were indicative of positive hysteresis ($N_d/N_a < 1$, $H < 100$, $\omega > 0$, and $\lambda > 0$). In addition, Table 7 also revealed that desorption parameters (N_d) and hysteresis

index (H) increased with the increasing times of desorption circles, indicating that desorption hysteresis effect and desorption activation energy enhanced with the increasing times of sequential desorption procedures, and desorption of atrazine became increasingly difficult.

4 Discussion

4.1 Adsorption

The Freundlich equation was developed mainly to allow for an empirical account of the variation in adsorption energy with concentration of an adsorbate on an energetically heterogeneous surface. The adsorption capacity of atrazine on different soils has been estimated by comparing Freundlich parameters K_f in previous studies (Hamaker and Thompson 1972; Si et al. 2006). The results showed that the higher the K_f value, the stronger adsorption of atrazine in soil. According to Table 1, adsorption isotherms of atrazine could also be well described by Freundlich model, and the largest K_f value was observed in the Argiustoll (the silty clay loam with high organic matter content), while the minimal K_f value was found in Haplustalf (the silt loam with low organic matter content). The 15 soils could be divided into three groups: the first group of soil 1 and soil 10 with the strongest adsorption capacity, the second group of soils 13, 9, 8, 6, 11, 14, 12, 7 and 2 with a moderate adsorption capacity, and the third group of soils 3, 5, 4 and 15 with the weakest adsorption capacity (Fig. 1) The values of parameter N_a , which can be used as an index of nonlinearity, were

Table 4 Correlation coefficients among soil properties of the 15 soils

	pH	TOC	CEC	Fe _o	Fe _d	Clay	Silt	Sand
pH	1							
TOC	-0.395	1						
CEC	0.194	0.066	1					
Fe _o	-0.291	0.627*	0.567*	1				
Fe _d	-0.615*	0.197	0.115	0.495	1			
Clay	-0.485	0.437	0.274	0.624*	0.803**	1		
Silt	0.214	0.055	-0.277	0.222	0.074	-0.142	1	
Sand	0.191	-0.367	0.014	-0.636*	-0.653**	-0.630*	-0.679**	1

Abbreviations are as in Tables 1 and 2

* $p=0.05$; ** $p=0.01$

Table 5 Stepwise regression models for predicting parameters of atrazine adsorption (K_f , K_{fd1} – K_{fd3}) based on soil properties

Model	Multiple linear equation	R^2	S.E. ^b
The stepwise regression for K_f			
(A)	$K_f=0.492+0.112[\text{TOC}]^a$	0.530*	1.11
(B)	$K_f=2.690+0.091[\text{TOC}]-0.340[\text{pH}]$	0.629*	1.02
(C)	$K_f=3.783+0.102[\text{TOC}]-0.429[\text{pH}]-0.021[\text{clay}]$	0.669*	1.01
(D)	$K_f=3.550+0.099[\text{TOC}]-0.456[\text{pH}]-0.020[\text{clay}]+0.010[\text{silt}]$	0.681*	1.04
The stepwise regression for K_{fd1}			
(E)	$K_{fd1}=0.828-0.058[\text{TOC}]$	0.485*	0.23
(F)	$K_{fd1}=1.589-0.129[\text{TOC}]+0.022[\text{pH}]$	0.709*	0.18
(G)	$K_{fd1}=1.927-0.147[\text{TOC}]+0.031[\text{pH}]-0.004[\text{sand}]$	0.751*	0.18
The stepwise regression for K_{fd2}			
(H)	$K_{fd2}=0.311-0.015[\text{TOC}]$	0.522*	0.26
(I)	$K_{fd2}=0.576-0.013[\text{TOC}]+0.041[\text{pH}]$	0.560*	0.26
(J)	$K_{fd2}=1.202-0.012[\text{TOC}]+0.099[\text{pH}]-0.018[\text{Fe}_d]$	0.680*	0.24
(K)	$K_{fd2}=2.007-0.006[\text{TOC}]+0.149[\text{pH}]-0.035[\text{Fe}_d]-0.007[\text{sand}]$	0.752*	0.23
The stepwise regression for K_{fd3}			
(L)	$K_{fd3}=0.111-0.025[\text{TOC}]$	0.781**	0.21
(M)	$K_{fd3}=0.313-0.027[\text{TOC}]+0.014[\text{pH}]$	0.853**	0.18
(N)	$K_{fd3}=0.612-0.026[\text{TOC}]+0.018[\text{pH}]-0.037[\text{Fe}_d]$	0.864**	0.18

^aTOC, %; clay, %; silt, %

^bS.E. standard error of the estimate; other abbreviations are as in Table 2

* $p=0.05$; ** $p=0.01$

not equal to 1 (Table 2), suggesting a significant nonlinearity for atrazine adsorption isotherm in the 15 soils. Clay and Koskinen (1990a) also got similar results on atrazine adsorption.

4.2 Desorption

Desorption is an inverse process of adsorption and a key process affecting pesticide sequestration behaviors in soils.

Table 6 Values of the K_f , TOC, clay content, and the content ratio of clay to organic carbon (RCO) for atrazine adsorption in 21 soil samples investigated in the previous studies

Soil No.	Source	K_f	TOC(%)	Clay (%)	RCO	Literature
1'	Jiangsu (China)	10.52	2.17	31.0	14.3	Gao and Jiang (2010)
2'	Shengyang (China)	6.19	1.1	30	27.3	Huang et al.(2003)
3'	Shengyang (China)	10.39	2.01	14	7.0	
4'	Liaoning (China)	2.24	0.58	9	15.5	
5'	Beijing (China)	1.26	1.31	8.96	6.8	Huo (2006)
6'	Ohio (USA)	0.82	0.77	40.4	52.5	Spongberg and Lou (2000)
7'	Ohio (USA)	0.11	0.18	6.96	38.7	
8'	Ohio (USA)	4.47	1.63	22.3	13.7	
9'	Lorraine area (France)	6.3	6.03	17.7	2.9	Amaud et al. (2005)
10'	Lorraine area (France)	4.0	5.81	53.6	9.2	
11'	Lorraine area (France)	3.6	5.59	38.1	6.8	
12'	Lorraine area (France)	3.4	4.8	51.6	10.8	
13'	Lorraine area (France)	3.9	3.66	10.4	2.8	
14'	Lorraine area (France)	2.7	3.63	33.4	9.2	
15'	Lorraine area (France)	2.2	3.64	45.5	12.5	
16'	Lorraine area (France)	3.4	3.32	41.1	12.4	
17'	Lorraine area (France)	2.7	2.77	50.9	18.4	
18'	Lorraine area (France)	2.9	2.62	30.9	11.8	
19'	Lorraine area (France)	1.3	1.5	11.4	7.6	
20'	Lorraine area (France)	2.2	1.43	12.7	8.9	
21'	Brittany (France)	2.7	1.08	20.1	18.6	

Abbreviations are as in Tables 1 and 2

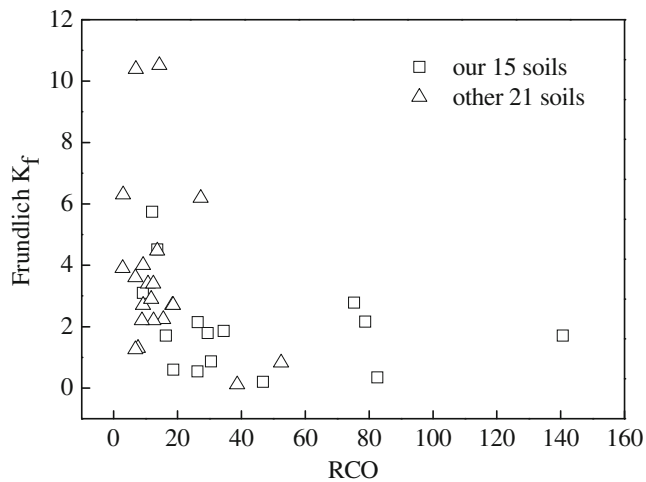


Fig. 3 The content ratio of clay to total organic carbon (RCO) vs. Freundlich K_f value for atrazine adsorption in our 15 soils and other 21 soils reported in the previous studies

Desorption controls the predisposition of a pesticide to be degraded and/or leached at different times (Dur et al. 1998). It is important to assess desorption since it may reflect some of the interactions involved between the chemical and the various soils (Amaud et al. 2005). The current results showed that desorption isotherms could also be well described by Freundlich model for the 15 soils ($r \geq 0.945$, $p < 0.05$) (Table 2). The order of the average desorption rate of atrazine is obviously different from that of adsorption. For example, soils 1, 10, 9, and

8 had higher K_f values but lower desorption rate, while soils 15, 4, and 5 had lower K_f values but higher desorption rate. These results indicate that in soils with low K_f values, less atrazine will be adsorbed, and the adsorbed atrazine would also be less strongly held, resulting in a greater tendency to leach.

Hysteresis is one of several manifestations of non-ideal behavior of hydrophobic organic chemicals in soils (Huang et al. 1998; Deng et al. 2005). The adsorption of atrazine in soil is irreversible when the N_a is greater than N_d (Pusino et al. 2004), and the ratio of Freundlich exponents (N_d/N_a) gives an indication of adsorption–desorption hysteresis (Palvostathis and Mathavan 1992; Carrizosa et al. 2001). The major finding of the current result suggested that some fraction of adsorbed atrazine may be irreversibly bound to all of the 15 soils, and indicated clearly the considerable positive hysteresis (the N_d/N_a values ranged from 0.13–0.88; Table 2, Fig. 2 and Table 7). Sorption–desorption hysteresis has been explained variously as the result of nonattainment of equilibrium (Huang and Weber 1997; Barriuso et al. 2004), degradation (Armstrong and Chesters 1968; Schiavon 1988), irreversible binding to soil constituents such as organic matrices or inorganic structures (Bhandari et al., 1996; Altfelder et al. 2000; Oren and Chefetz 2005; Liao and Xie 2007), or any combination of these. In the present study, degradation was not measured but non-attainment of equilibrium (a relative equilibration time of 24 h was considered the most convenient) may result in hysteresis. Moreover, we observed that the soils with

Fig. 4 Total organic carbon (TOC) content and clay content vs. the Freundlich K_f value for the 30 soils with $RCO < 40$ (a and b), and the 6 soils with $RCO > 40$ (c and d), respectively

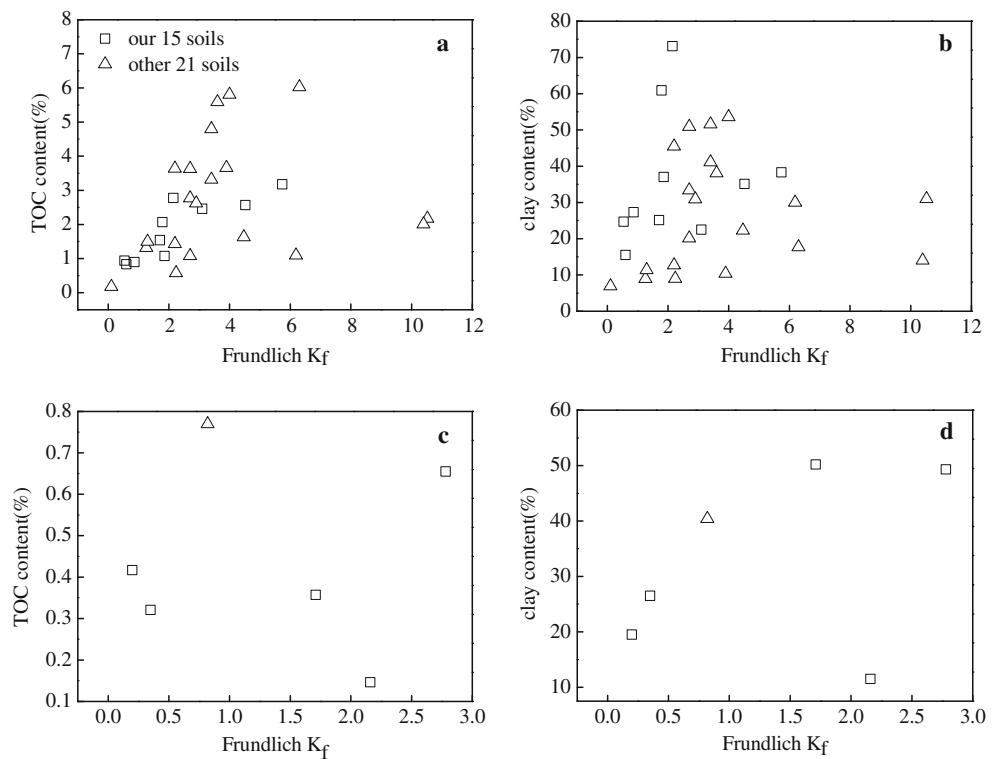


Table 7 Desorption hysteresis index of atrazine for the 15 soils

Soil no.	N_d/N_a			H			ω			λ		
	N_{d1}/N_a	N_{d2}/N_a	N_{d3}/N_a	H_1	H_2	H_3	ω_1	ω_2	ω_3	λ_1	λ_2	λ_3
1	0.40	0.70	0.74	40.44	70.14	73.83	147.26	42.58	35.44	35.83	15.24	13.11
2	0.22	0.23	0.64	21.64	22.90	64.12	362.11	336.71	55.96	78.74	76.50	25.27
3	0.23	0.34	0.64	22.79	34.05	64.39	338.75	193.69	55.32	54.92	43.44	19.55
4	0.15	0.53	0.88	14.85	53.14	88.48	573.33	88.18	13.02	83.14	33.30	6.54
5	0.13	0.36	0.58	12.96	36.48	57.75	671.49	174.10	73.15	61.73	38.61	22.74
6	0.29	0.38	0.47	29.30	37.76	47.44	241.25	164.84	110.79	50.39	41.84	33.18
7	0.23	0.33	0.51	23.27	32.51	51.00	329.74	207.56	96.06	54.29	44.82	28.98
8	0.18	0.54	0.56	17.86	54.06	55.78	459.77	84.97	79.29	59.99	26.54	25.30
9	0.70	0.74	0.76	70.11	74.28	76.01	42.63	34.63	31.56	14.06	11.87	10.98
10	0.18	0.28	0.57	18.30	27.72	56.66	446.55	260.79	76.50	59.18	49.01	24.57
11	0.32	0.52	0.70	31.84	52.10	69.83	214.04	91.93	43.20	45.42	28.12	16.04
12	0.14	0.17	0.18	14.08	16.86	17.61	610.07	493.07	467.94	60.45	57.38	56.57
13	0.19	0.38	0.74	19.01	38.03	73.84	425.94	162.92	35.43	60.40	40.47	13.85
14	0.35	0.48	0.54	34.98	47.68	53.88	185.88	109.72	85.60	42.37	31.48	26.76
15	0.62	0.81	0.84	61.87	80.74	84.16	61.62	23.85	18.82	19.48	8.97	7.27

N_a and N_d the Freundlich exponent for adsorption and desorption; N_{d1} , N_{d2} and N_{d3} the Freundlich exponent for the first, second and third time of desorption, respectively; H , ω , and λ the hysteresis index calculated using Eqs. 5, 6, and 7, respectively; H_1 , ω_1 , λ_1 , H_2 , ω_2 , λ_2 , H_3 , ω_3 , λ_3 , the hysteresis index for the first, second, and third time of sequential desorption processes, respectively

contrasting properties resulted in varying degrees of hysteresis effect (Tables 1 and 7). This may also suggest that the heterogeneity of soil properties have contributed to atrazine hysteresis phenomenon. In a similar study, Weber et al. (1998) found that particle-scale soil organic matter heterogeneity significantly affected the extent of hysteresis of hydrophobic organic contaminants in soils and sediments. Clay and Koskinen (1990b) observed more atrazine desorption from a Plano soil at pH 6.1 than at pH 4.5. Less desorption at the lower soil pH was attributed to greater protonation and ionic bonding of atrazine.

4.3 Primary parameters affecting adsorption–desorption behavior

Several studies have suggested that various soil parameters, including the TOC content, pH, clay silicates, and aluminum and iron oxides, should affect the adsorption and desorption behavior of atrazine and other s-triazine herbicides by soil samples (Stevenson 1972; Huang et al. 1984). It is reported that soil organic matter contains a variety of functional groups such as hydrophobic, hydrophilic, and free radicals that can strongly entrap atrazine (Hamaker and Thompson 1972). Borggaard and Streibig (1988) also showed that atrazine adsorption is highly correlated with total organic matter, especially with pyrophosphate-extractable organic matter. He et al. (2006b) founded that the pH was an important factor affecting adsorption behavior of

pentachlorophenol in soils. When the pH increases, the soil surface tends to be negatively charged, and the organic molecules also tend to be ionized and negatively charged. This is due to the repulsion of same-sex charge, which will be detrimental to the adsorption of organic molecules on the soil surface (Wang et al. 1999). Characteristics of organic matter in different soil particle size composition are very different and may indirectly affect the adsorption–desorption behavior of organic molecules (Chen and Chiu 2003; Chefetz et al. 2004). However, accurate information about the relative importance of the various soil parameters to these behaviors still seems to be lacking. In our study, we found that the TOC was the most important factor for affecting atrazine adsorption behavior (accounted for 53.0 % of the variation in K_f value), then the pH (9.9 %), and the contents of clay (4.0 %), and silt (1.2 %), separately. The TOC was also the first parameters affecting atrazine desorption behavior as it could describe the variation of K_{fd} value ranging from 48.5–78.1 %, and followed by the pH (ranged from 3.8–22.4 %), the Fe_d content (ranged from 1.1–12.0 %), and the sand content (ranged from 4.2–7.2 %).

As indicated by the determination coefficient (R^2), about 31.9 % of the total variability in the K_f and about 13.6–24.9 % of the total variability in the K_{fd} , could not be described by the best stepwise regression models. This indicated that even with the combination of soil properties of the contents of TOC, clay, silt, Fe_d , and sand, as well as the pH value, adsorption and desorption processes of

atrazine in soils could not be assessed exactly. It was reported that the amorphous hydroxyl-Fe and -Al components had high capacity for the retention of the phenolic acids, and provided adsorption sites for atrazine (Huang et al. 1977, 1984). The non-crystalline to poorly crystalline Fe and Al components are often qualified by the term of “active”, because they have high specific surface and proton donor functional groups (Kwong and Huang 1979; Huang and Wang 1997; Huang et al. 2002). In this study, a positive relationship of the content between Fe_o and TOC was observed in the tested soils ($r=0.627$, $N=15$, $p<0.05$) (Table 4). Therefore, the amorphous minerals were likely interacted with the organic matter in soils, and thereby could affect the interfacial behavior of atrazine in soils such as adsorption and desorption.

Our investigation indicated that 53.0 % of the total relevance for K_f values was correlated with the TOC content, and only very small contribution was from the clay content (Table 5). However, the previous study of Wang et al. (1999) verified that K_f had better correlation with the RCO than with the TOC only for the adsorption of acetanilide herbicides. More recently, our previous studies have also testified that the RCO could act as a good parameter to predict the adsorption of butachlor in soils (Liu et al. 2008; He et al. 2011). In this study, by investigation on natural different type soils that showed contrasting characteristics and were collected from large geographical scale region that make up about 85 % of the total area of entire eastern China, the results also indicated that the RCO value would be helpful to understand the atrazine adsorption mechanism in soils. Moreover, Mersie and Seybold (1996) suggested that desorption capability of atrazine in soil could reflect the stability of atrazine; the higher the stability, the better practice restoration effect. Therefore, the RCO may be used to direct the application process of atrazine to achieve adequate weed control and the environmental protection and remediation. That is, in the soils with the $RCO<40$, atrazine might have a higher adsorption capability. The application rates should thus be adjusted upward, and the bioavailability and mobility of atrazine in these soils should be considered; while in the soils with the $RCO>40$, atrazine might have a lower adsorption and desorption capacity and apparently higher bioactivity, leachability, and volatility. The application rates of atrazine should thus be adjusted downward for preventing the environmental risks.

5 Conclusions

Based on investigation of contrasting natural soils from large geographical scale region that make up about 85 % of the total area of entire eastern China, this study indicated that the adsorption and desorption data were of major

importance for understanding the overall fate of atrazine in soils. Adsorption and desorption isotherms of atrazine in soils were nonlinear, and could be well described by the Freundlich equation. The TOC content, pH, and inorganic fraction (such as clay and amorphous sesquioxides) played an important role affecting both adsorption and desorption processes of atrazine in soils, among which the TOC content did a vital contribution. The content RCO was observed as a useful parameter for predicting the atrazine behavior in soils. For soils with high organic matter content ($RCO<40$), the strong binding between atrazine molecules and soil organic compounds can prevent the atrazine from release, thus reducing its bioavailability; for soils with low organic matter content ($RCO>40$), high bioactivity and leachability of atrazine deserved to be taken into account for potential environmental risk control. Positive hysteresis was verified for all of the tested soils. The hysteretic effects enhanced with the increasing times of sequential desorption and atrazine desorption became increasingly difficult.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (40901113), the Natural Science Foundation of Guangdong Province (8451064001001121), the Project Supported by Zhejiang Provincial Natural Science Foundation of China (R5110079) and the Fundamental Research Funds for the Central Universities (2011FZA6020).

References

- Altfelder S, Streck T, Richter J (2000) Nonsingular sorption of organic compounds in soil: the role of slow kinetics. *J Environ Qual* 29:917–925
- Amaud B, Richard C, Michel S (2005) A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere* 61:668–676
- Anagu I, Ingwersen J, Drori Y, Chefetz B, Streck T (2011) Modeling concentration-dependent sorption–desorption hysteresis of atrazine in a sandy loam soil. *J Environ Qual* 40:538–547
- Armstrong DE, Chesters G (1968) Adsorption catalyzed chemical hydrolysis of atrazine. *Environ Sci Technol* 2:683–689
- Barriuso E, Laird DA, Koskinen WC, Dowdy RH (1994) Atrazine desorption from smectites. *Soil Sci Soc Am* 58:1632–1638
- Barriuso E, Koskinen WC, Sadowsky MJ (2004) Solvent extraction characterization of bioavailability of atrazine residues in soils. *J Agric Food Chem* 52:6552–6556
- Bhandari A, Novak J, Berry D (1996) Binding of 4-monochlorophenol to soil. *Environ Sci Technol* 30(7):2305–2311
- Borggaard OK, Streibig JC (1988) Atrazine adsorption by some soil samples in relation to their constituents. *Acta Agric Scandinavica* 38:293–301
- Botelho RG, Santos JBD, Fernandes KM, Neves CA (2011) Effects of atrazine and picloram on grass carp: acute toxicity and histological assessment. *Toxicol Environ Chem* 94:121–127

- Carrizosa MJ, Koskinen WC, Hermosin MC, Cornejo J (2001) Dicamba adsorption–desorption on organoclays. *Appl Clay Sci* 18:223–231
- Chefetz B, Bilkis YI, Polubesove T (2004) Sorption–desorption behavior of triazine and phenylurea herbicides in Kishon river sediments. *Water Research* 38:4383–4394
- Chen JS, Chiu CY (2003) Characterization of soil organic matter in different particle-size fractions in humid subalpine soils by CP/MAS ^{13}C -NMR. *Geoderma* 117:129–141
- Clausen L, Fabricius I, Madsen L (2001) Adsorption of pesticides onto quartz, calcite, kaolinite, and α -Alumina. *J Environ Qual* 30:846–857
- Clay SA, Koskinen WC (1990a) Characterization of alachlor and atrazine desorption from soils. *Weed Science* 38:74–80
- Clay SA, Koskinen WC (1990b) Adsorption and desorption of atrazine, hydroxyatrazine, and *S*-glutathione atrazine on two soils. *Weed Science* 38:262–266
- Cox L, Koskinen WC, Yen PY (1997) Sorption–desorption of imidacloprid and its metabolites in soil. *J Agric Food Chem* 45:1468–1472
- Deng JC, Jiang X, Wang F, Lu X, Yu GF, Yan DY, Bian YR (2005) Hysteretic characteristics of atrazine desorption from fluvo-aquic soil. *Environ Sci* 26(6):137–142
- Deng JC, Jiang X, Lu X, Yu GF, Wang F, Zhang B (2007) Atrazine adsorption behavior on a fluvo-aquic soil as influenced by contact periods. *Pedosphere* 17(6):786–791
- Dur JC, Gouy V, Calvet R, Belamie R, Chaplain V (1998) Influence of adsorption–desorption phenomena on pesticide runoff measured under controlled conditions. *Comptes Rendus de l'Academie des Sciences-Series IIA-Earth Planetary Science* 327(6):405–411
- Flores C, Morgante V, Gonzalez M et al (2009) Adsorption studies of the herbicide simazine in agricultural soils of the Aconcagua Valley, central Chile. *Chemosphere* 74:1544–1549
- Gao HJ, Jiang X (2010) Effect of initial concentration on adsorption–desorption characteristics and desorption hysteresis of hexachlorobenzene in soils. *Pedosphere* 20(1):104–110
- Hamaker JW, Thompson JM (1972) Adsorption of organic chemicals in the soil environment. Dedder, New York. pp 49–143
- Hayes BH, Collins A, Lee M et al (2002) Hermaphroditic, demasculinized frogs after exposure to the herbicide atrazine at low ecologically relevant doses. *PNAS* 99(8):5476–5480
- He Y, Xu JM, Wang HZ, Ma ZH, Chen JQ (2006a) Detailed sorption isotherms of pentachlorophenol on soils and its correlation with soil properties. *Environ Res* 101(3):362–372
- He Y, Xu JM, Wang HZ, Zhang QC, Muhammad M (2006b) Potential contributions of soil minerals and organic matter to pentachlorophenol retention in soils. *Chemosphere* 65(3):497–505
- He Y, Liu ZZ, Zhang J, Wang HZ, Shi JC, Xu JM (2011) Can assessing for potential contribution of soil organic and inorganic components for butachlor sorption be improved? *J Environ Qual* 40:1705–1713
- Hincapie M, Maldonado MI, Oller I et al (2005) Solar photocatalytic degradation and detoxification of EU priority substances. *Catal Today* 101:203–210
- Huang PM, Wang MK (1997) Formation chemistry and selected surface properties of iron oxides. *Adv Geocol* 30:241–270
- Huang WL, Weber WJ (1997) A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis, and the chemical characteristics of organic domains. *Environ Sci Technol* 31(9):2562–2569
- Huang PM, Wang TSC, Wang MK, Wu MH, Hsu NW (1977) Retention of phenolic acids by noncrystalline hydroxyl-aluminum and -iron compounds and clay minerals of soils. *Soil Sci* 123:213–219
- Huang PM, Grover R, Mckercher RB (1984) Components and particle size fractions involved in atrazine adsorption by soils. *Soil Sci* 138:20–24
- Huang W, Hong Y, Weber WJ (1998) Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments. 1. A comparative analysis of experimental protocols. *J Contam Hydrol* 31:129–148
- Huang PM, Wang MK, Kampf N, Schulze DG (2002) Aluminum hydroxides. In: Dixon JB, Schulze DG (eds) *Soil mineralogy with environmental applications*. Soil Science Society of America, Madison, WI, pp 261–289
- Huang G, Li Q, Zhang X (2003) Adsorption and desorption of atrazine by three soils. *Environ Contam Toxicol* 71:655–661
- Huo LJ (2006) Experimental study on adsorption, degradation and leaching of atrazine and its metabolites in sandy loamy soil. Dissertation, China, pp 9–16
- Jenks BM, Roeth FW, Martin AR (1998) Influence of surface and subsurface soil properties on atrazine sorption and degradation. *Weed Science* 46:132–138
- Kwong NKKF, Huang PM (1979) Surface reactivity of aluminum hydroxides precipitated in the presence of low molecular weight organic acids. *Soil Sci Soc Am J* 43:1107–1113
- Lesan HM, Bhandari A (2003) Atrazine sorption on surface soils: time-dependent phase distribution and apparent desorption hysteresis. *Water Res* 37(7):1644–1654
- Liao M, Xie XM (2007) Adsorption of metsulfuron and bensulfuron on a cationic surfactant-modified paddy soil. *Pedosphere* 17(1):101–108
- Liu ZZ, He Y, Xu JM, Huang P, Jilani G (2008) The ratio of clay content to total organic carbon content is a useful parameter to predict adsorption of the herbicide butachlor in soils. *Environ Pollut* 152:163–171
- Ma LW, Southwick LM, Willis GH, Selim HM (1993) Hysteresis characteristic of atrazine adsorption–desorption by a Sharkey soil. *Weed Science* 41:627–633
- Mersie W, Seybold C (1996) Adsorption and desorption of atrazine, deethylatrazine, deisopropylatrazine, and hydroxyatrazine on levy wetland soil. *J Agr Food Chem* 44:1925–1929
- Mudhoo A, Garg VK (2011) Sorption, transport and transformation of atrazine in soils, minerals and composts: a review. *Pedosphere* 21(1):11–25
- O'Connor GA, Wierenga PJ, Cheng HH, Doxtader KG (1980) Movement of 2,4,5-T through large soil columns. *Soil Sci* 130:157–162
- Oren A, Chefetz B (2005) Sorption–desorption behavior of polycyclic aromatic hydrocarbons in upstream and downstream river sediments. *Chemosphere* 61:19–29
- Palvostathis SG, Mathavan GN (1992) Desorption kinetic of selected volatile organic compounds from field contaminated soils. *Environ Sci Technol* 26:532–538
- Pusino A, Pinna MV, Gessa C (2004) Azimsulfuron sorption–desorption on soil [J]. *J Agr Food Chem* 52:3462–3466
- Rayner JL, Fenton SE (2011) Atrazine: an environmental endocrine disruptor that alters mammary gland development and tumor susceptibility. *Environ Breast Cancer* 167–183
- Schiavon M (1988) Studies of the movement and the formation of bound residues of atrazine, of its chlorinated derivatives, and of hydroxyatrazine in soil using ^{14}C ring-labeled compounds under outdoor conditions. *Ecotox Environ Safe* 15:55–61
- Sherchan SP, Bachoon DS (2011) The presence of atrazine and atrazine-degrading bacteria in the residential, cattle farming, forested and golf course regions of Lake Oconee. *J Appl Microbiol* 111(2):293–299
- Si YB, Zhang J, Wang SQ, Zhang LG, Zhou DM (2006) Influence of organic amendment on the adsorption and leaching of ethametsulfuron-methyl in acidic soils in China. *Geoderma* 130:66–76
- Spark KM, Swift RS (2002) Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci Total Environ* 298:147–161

- Spongberg AL, Lou G (2000) Adsorption of atrazine and metolachlor in three soils from Blue Creek wetlands, Waterville. *Ohio Sciences of Soils* 5:1
- Stevenson FJ (1972) Organic matter reactions involving herbicides in soil. *J Environ Qual* 1:333–343
- Sun K, Gao B, Zhang ZY, Zhang GX, Zhao Y, Xing BS (2010) Sorption of atrazine and phenanthrene by organic matter fractions in soil and sediment. *Environ Pollut* 158:3520–3526
- Wang QQ, Yang WC, Liu WP (1999) Adsorption of acetanilide herbicides on soils and its correlation with soil properties. *Pestic Sci* 55:1103–1108
- Weber WJ, Huang WL, Hong Y (1998) Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments: 2. Effects of soil organic matter heterogeneity. *J Contam Hydrol* 31:149–165
- Zhu HX, Selim HM (2000) Hysteresis behavior of metolachlor adsorption–desorption in soils. *Soil Sci* 165(8):632–645