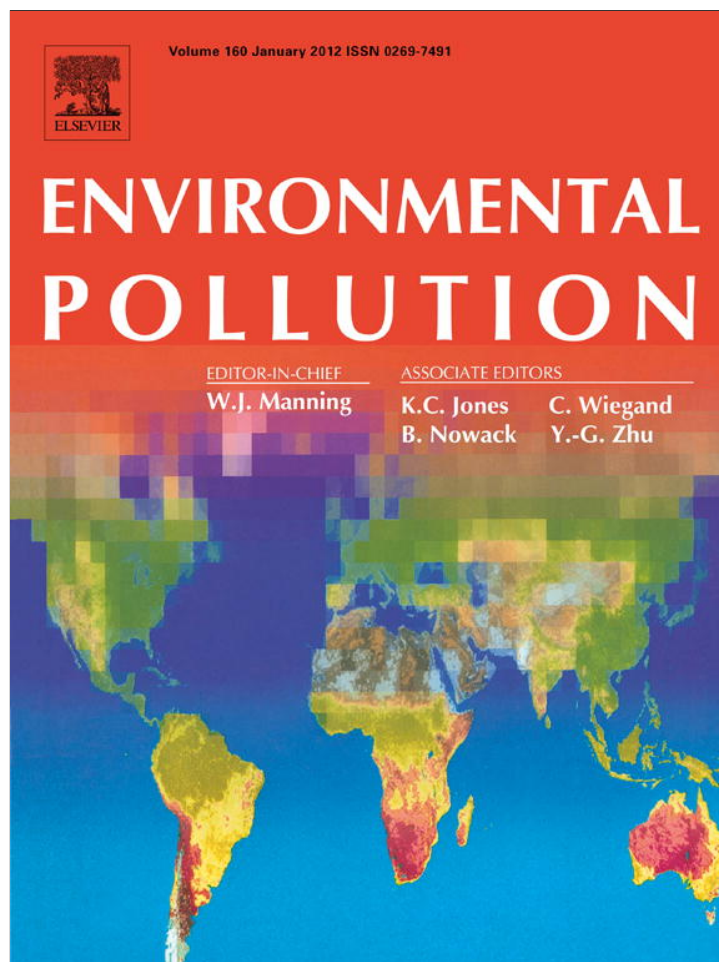


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# Sorption of atrazine and ametryn by carbonatic and non-carbonatic soils of varied origin

G.N. Kasozi<sup>a</sup>, P. Nkedi-Kizza<sup>a,\*</sup>, Y. Li<sup>b</sup>, A.R. Zimmerman<sup>c</sup>

<sup>a</sup> Soil and Water Science Department, University of Florida, Gainesville, FL 32611, USA

<sup>b</sup> Tropical Research and Education Center, Homestead, FL 33031, USA

<sup>c</sup> Department of Geological Sciences, University of Florida, Gainesville, FL 32611, USA

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## ABSTRACT

Sorption of two s-triazines, atrazine and ametryn, by carbonatic soils, Histosols, Spodosols and Oxisols was examined. Linear isotherms were observed and sorption coefficients ( $K_d$ ) of both compounds were significantly lower ( $\alpha = 0.05$ ) onto carbonatic soils compared to non-carbonatic soils. Furthermore, among carbonatic soil types, the marl-carbonatic soils had the lowest sorption affinities.  $K_d$  and organic carbon content were highly correlated, suggesting predominant influence of organic carbon in the sorption of the s-triazine, except in Oxisols and Spodosols where variations suggest other factors. Upon removal of organic matter (OM) using sodium hypochlorite and hydrogen peroxide, the  $K_d$  values were reduced by ~90%, indicating minimal contribution of mineral surfaces. Thus OM compositional differences likely explain the large variation in s-triazine sorption within and between soil orders. This study highlights the need to consider OM composition in addition to quantity when determining pesticide applications rates, particularly for carbonatic soils.

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## 1. Introduction

Atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and its metabolite deethylatrazine constitute the most commonly detected pesticides in surface water and ground-water across the continental United States (Kolpin et al., 1998; Gilliom, 2007). In a study by Harman-Fetcho et al. (2005), atrazine was detected at the highest concentration (108 ng L<sup>-1</sup>) of all target analytes and was detected in 91% of 88 water samples from South Florida, USA.

Between 1991 and 1995, ametryn [*N*-ethyl-*N'*-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine] was among the most detected pesticides in southern Florida sediments (Miles and Pfeuffer, 1997). In addition, atrazine and ametryn constitute the most commonly detected herbicides in Florida irrigation and drainage canals (Pfeuffer and Rand, 2004; Harman-Fetcho et al., 2005).

The current literature provides compelling evidence suggesting sorption as a major process determining the fate of herbicides in

soils (Chefetz et al., 2004; Liyanage et al., 2006; Ahmad and Rahman, 2009). There is a breadth of knowledge on the sorption of herbicides in a variety of terrestrial soils (e.g. Madsen et al., 2000; Inoue et al., 2006; Matallo et al., 2008) but little is known about their fate in the shallow, highly porous, and carbonate-rich (carbonatic) soils of southern Florida. The sub-tropical climate in southern Florida favors all year round agricultural production with more than 85% of Florida's tropical fruits, vegetables and ornamental plants grown on carbonatic soils (Li, 2001). The same favorable climatic conditions of southern Florida also encourage the proliferation of pests and hence the need for application of pesticides for cost effective agricultural production in this region. On average, an estimated 15,000 t of pesticides are used in southern Florida per year, of which, 1400 t is atrazine (Miles and Pfeuffer, 1997).

The combination of the shallow water table and the highly porous Tamiami and Thompson formations underlying carbonatic soils (Parker et al., 1944; Jones, 1948; James et al., 2005), which are themselves thinly layered result in a high potential for leaching of contaminants into the Floridan aquifer and nearby Everglades ecosystem.

Data from literature indicate that organic carbon (OC) controls the sorption of non-ionic organic chemicals to soil (Kile et al., 1995; Kasozi et al., 2010). Thus, the concept of using OC-normalized sorption coefficient ( $K_{oc}$ ) to describe partitioning of non-ionic

Abbreviations: OM, organic matter; OC, organic carbon; USGS, United States Geological Survey; USDA, United States Department of Agriculture; HPLC, high performance liquid chromatography.

\* Corresponding author.

E-mail address: [kizza@ufl.edu](mailto:kizza@ufl.edu) (P. Nkedi-Kizza).

organic chemicals is widely accepted in literature (Karickhoff, 1981; Schwarzenbach and Westall, 1981; Chiou et al., 1983). For such chemicals, sorption has been described to be non-competitive and linear across a narrow solution concentration range (Chiou et al., 1979). Other studies have however described sorption of non-polar organic chemicals to be non-ideal i.e. showing non-linear and competitive behavior (Xing and Chen, 1999; Pignatello et al., 2006). It has become increasingly clear that soil organic carbon (OC) content alone cannot fully account for the adsorption of non-ionic chemicals. Some studies suggest sorption of non-ionic organic chemicals to both organic and mineral surfaces (Koskinen and Harper, 1990; Matallo et al., 2008). However, recent literature suggests that specific components of OM such as pyrogenic OC may account for sorption variability and isotherm nonlinearity (Allen-King et al., 2002; Huang et al., 2003; Cornelissen et al., 2005; Liyanage et al., 2006; Ahmad and Rahman, 2009; Sobek et al., 2009). The influence of pyrogenic OC and other soil components on contaminant sorption may be of greater importance in low OC soils. This study was carried out to investigate the sorption of two common s-triazines onto soils of varied geochemistry and geographic origin.

## 2. Materials and methods

### 2.1. Soils

Surface horizons (0–15 cm) of geographically diverse soils encompassing a wide range of vegetation and OM sources were collected. The soil sample set included 23 carbonatic soils, 15 Histosols, 10 Spodosols, and 38 Oxisols samples. The carbonatic soils collected from Southern Florida and Puerto Rico included marl-carbonatic (which are made up of limnic materials and are formed by secondary calcium carbonate precipitation) and the non-marl carbonatic (marine-derived oolitic limestone soils, produced by rock scarification or plowing using heavy equipment). Both southern Florida and Puerto Rico regions are characterized by a sub-tropical climate. Histosols, which are associated with carbonatic soils were also collected. For regional-scale comparison, common Florida soils (Spodosols) and Oxisols from Uganda (tropical climate) were collected.

### 2.2. Soil characteristics

Calcium carbonate and OC content were measured using thermogravimetric and Walkley-Black methods (Walkley and Black, 1934; Kasozi et al., 2009), respectively. Soil pH was measured using an Accumet 925 pH meter (FisherScientific, U.S.A.) at a soil-solution ratio of 1:2 (USDA, 1996). Detailed methods, soil properties and taxonomic classification are described in Kasozi et al. (2010).

### 2.3. Atrazine and ametryn sorption experiments

A batch-slurry sorption approach was carried out at 25 °C to examine atrazine and ametryn sorption to the soils. Atrazine and ametryn standards were obtained from Accustandard Inc. with purity of ≥98%. Four concentration levels of standard solutions ranging from 2 to 10 mg L<sup>-1</sup> (within recommended field application rates) were prepared by parallel dilution in 0.01 M CaCl<sub>2</sub> solution. Depending on the soil OC content, between 0.2 and 1.5 g of soil were weighed into 50 mL polycarbonate centrifuge tubes, in triplicate, followed by the addition of 10 mL of standard solution of each concentration.

Following kinetic studies, sorption equilibrium was achieved by shaking end-over-end for 24 h. Similar equilibration times have been reported for the s-triazines (Gonzalez-Pradas et al., 1998; Nkedi-Kizza et al., 2006; Chaplain et al., 2008). The mixture was then centrifuged using a Beckman J2-21 model centrifuge and centrifuge rotor JA-18 at 10,000 rpm (14,758 × g) for 15 min and the supernatants filtered using Whatman no. 42 filter paper. The equilibrium concentrations (C<sub>e</sub>) was measured using an HPLC with UV detector set at 230 nm and 250 nm (1 AUFS) wavelengths for atrazine and ametryn, respectively. Methanol, water, and acetonitrile mixture (60:30:10 v/v) was used as a mobile phase at a flow rate of 2.0 mL min<sup>-1</sup> through a 3.9 mm i.d. × 150 mm Nova-Pak C18 column. For quality control purposes and to check for sorption onto container walls, blank controls with only standard solutions but no soil were included.

### 2.4. Organic matter removal

To assess the influence of mineral surfaces, OM was removed using two wet oxidation procedures namely: hydrogen peroxide (peroxide) and sodium hypochlorite (hypochlorite). However, for carbonate rich soils, the hypochlorite (bleach)

procedure is preferable since contrary to peroxide oxidation, hypochlorite does not remove or complex the calcium and magnesium carbonates, sesquioxides and silica (Martin, 1954).

In the peroxide method (USDA, 1996), 200 mL of distilled deionized water (DDI-water) and 25 mL peroxide (30%) were added to 10 g soil samples in a glass beaker. The beaker was allowed to stand overnight, followed by heating at 90 °C and careful addition of small aliquots of peroxide until no further foaming was observed. The residue was centrifuged at 2000 rpm (591 × g) for 15 min and the clear supernatant decanted and discarded. The residue was then washed three times with 200 mL 1 M sodium chloride solution and three times with DDI-water. In each case the mixture was centrifuged and the supernatant discarded. The final residue was dried in a hot air oven at 60 °C and then tested for sorption potential.

In the hypochlorite method, 20 mL of sodium hypochlorite solution (6%, adjusted to pH = 9.5 with sodium hydroxide) was added to 10 g soil samples in a centrifuge tube (USDA, 1996). The tube was placed into a water bath and heated for 30 min and then centrifuged at 2000 rpm (591 × g) for 15 min. The clear supernatant was decanted and discarded and the above step was repeated three times. The residue was washed with three rinses each of 20 mL sodium bicarbonate, 1 M sodium chloride solution and finally with DDI-water and then dried at 60 °C.

### 2.5. Equilibrium sorption modeling and statistics

The sorption isotherms were fitted to the linear sorption model using:

$$S_e = K_d C_e \quad (1)$$

where S<sub>e</sub> is the amount of solute sorbed per unit weight of soil (mg kg<sup>-1</sup>), K<sub>d</sub> is the sorption coefficient (L kg<sup>-1</sup>) and C<sub>e</sub> is the equilibrium solution concentration (mg L<sup>-1</sup>). The OC-normalized sorption coefficients, K<sub>oc</sub> (L kg<sup>-1</sup>), were calculated by dividing K<sub>d</sub> with the fraction of organic carbon in the soil (f<sub>oc</sub>).

Descriptive statistics, linear regression analyses and nonparametric statistics, were performed on the data using SAS (2008).

## 3. Results

Atrazine and ametryn sorption data as well as soil chemical properties including carbonate content, pH, and weight fraction organic carbon (f<sub>oc</sub>) are presented for 23 carbonatic soils, 15 Histosols, 10 Spodosols, and 38 Oxisols (Tables 1–3). The pH of the soils averaged 7.3 ± 0.1 (mean ± standard error), 6.7 ± 0.1, 5.8 ± 0.2, and 3.6 ± 0.1 for carbonatic soils, Histosols, Oxisols, and Spodosols, respectively. The carbonate content within the sample set ranged

**Table 1**

Chemical properties and OC-normalized sorption coefficients for atrazine and ametryn in carbonatic soils.

Soil series	Origin	f <sub>oc</sub>	% CaCO <sub>3</sub>	pH (CaCl <sub>2</sub> )	K <sub>oc</sub> (L kg <sup>-1</sup> )	
					Atrazine	Ametryn
Aguilita	PR	0.05	53	6.9	60	130
Biscayne <sup>a</sup>	FL	0.06	84	7.0	48	116
Biscayne2 <sup>a</sup>	FL	0.03	82	7.2	49	103
Cudjoe <sup>a</sup>	FL	0.10	68	7.2	57	106
Chekika	FL	0.02	89	7.2	61	175
Chekika2	FL	0.04	58	7.0	83	169
Colinas	PR	0.02	80	7.2	84	148
Keyvaca	FL	0.11	65	7.3	61	121
KeyWest1 <sup>a</sup>	FL	0.01	90	8.2	46	113
KeyWest2 <sup>a</sup>	FL	0.01	94	7.7	49	157
Krome1	FL	0.02	64	7.5	80	213
Krome2	FL	0.02	51	7.4	81	181
Lignumvitae1 <sup>a</sup>	FL	0.06	84	7.2	59	131
Lignumvitae2 <sup>a</sup>	FL	0.05	85	7.3	46	103
Pennsuco <sup>a</sup>	FL	0.03	84	7.4	46	108
Perrine1 <sup>a</sup>	FL	0.03	88	7.3	37	87
Perrine2 <sup>a</sup>	FL	0.03	91	7.3	36	95
Perrine-Tamiami assoc.	FL	0.04	90	7.3	105	243
Saddlebunch1 <sup>a</sup>	FL	0.02	ND	7.5	43	95
Saddlebunch2 <sup>a</sup>	FL	0.08	79	7.4	42	60
San Sebastian	PR	0.02	ND	7.2	61	143
Tuque	PR	0.02	86	7.3	50	106
Yauco	PR	0.03	62	7.3	51	97

Abbreviations: FL, Florida; PR, Puerto Rico; f<sub>oc</sub>, organic carbon fraction; K<sub>oc</sub>, sorption coefficient normalized to f<sub>oc</sub>.

<sup>a</sup> Marl-carbonatic soil.

**Table 2**  
Chemical properties and OC-normalized sorption coefficients for atrazine and ametryn in Histosol and Spodosol.

Soil series	$f_{oc}$	pH (CaCl <sub>2</sub> )	$K_{oc}$ (L kg <sup>-1</sup> )	
			Atrazine	Ametryn
<i>Histosols</i>				
Dania 1	0.43	5.9	171	430
Dania 2	0.53	5.7	150	472
Islamorada	0.39	6.7	72	157
Lauderhill1	0.29	7.1	105	226
Lauderhill2	0.21	7.2	82	173
Lauderhill3	0.23	7.2	107	215
Matecumbe1	0.33	7.0	117	244
Matecumbe2	0.20	7.0	80	206
Pahokee1	0.42	7.2	69	135
Pahokee2	0.47	6.3	123	260
Tamiami1	0.40	6.3	97	217
Tamiami2	0.20	6.7	74	157
Tamiami3	0.40	7.2	144	277
<i>Spodosols</i>				
Monteocha1	0.05	3.6	374	2341
Monteocha2	0.01	3.3	913	5084
Pomona1	0.01	3.6	534	2666
Pomona2	0.02	3.2	823	3889
Pomona3	0.01	3.2	1035	5427
Pomona4	0.02	3.3	1060	6969
Pomona Bh1 <sup>a</sup>	0.01	3.9	115	584
Pomona Bh2 <sup>a</sup>	0.02	3.9	229	714

Abbreviations same as Table 1.

<sup>a</sup> Bh horizons depth = 80–100 cm.

from Not Detectable to 94% while the  $f_{oc}$  ranged from 0.01 to 0.11 for all carbonatic soils, from 0.13 to 0.47 for Histosols, from 0.01 to 0.06 for Oxisols, and from 0.01 to 0.05 for Spodosols. X-ray diffraction (XRD) analysis (data not shown) indicated calcite as the dominant mineral in the carbonatic soils and did not reveal presence of clay

**Table 3**  
Oxisol chemical properties and calculated atrazine and ametryn organic carbon-normalized soil sorption coefficients.

Soil series	$f_{oc}$	pH (CaCl <sub>2</sub> )	$K_{oc}$ (L kg <sup>-1</sup> )	
			Atrazine	Ametryn
Bayamon <sup>a</sup>	0.02	6.6	76	139
Bayamon <sup>a</sup>	0.02	4.3	100	228
Buganda Catena (Ferrallitic soils) <sup>b</sup>	0.02	6.0	181	481
Buganda Catena (Ferrallitic soils) <sup>b</sup>	0.01	7.0	139	316
Buganda Catena (Ferrallitic soils) <sup>b</sup>	0.02	7.0	133	245
Buganda Catena (Ferrallitic soils) <sup>b</sup>	0.01	6.8	213	333
Kabira Catena (Ferrisols) <sup>b</sup>	0.02	5.9	194	471
Kabira Catena (Ferrisols) <sup>b</sup>	0.03	5.2	219	771
Kabira Catena (Ferrisols) <sup>b</sup>	0.03	6.2	136	618
Kabira Catena (Ferrisols) <sup>b</sup>	0.03	5.6	174	409
Mabira Catena (Ferrisols) <sup>b</sup>	0.03	4.1	115	491
Mabira Catena (Ferrisols) <sup>b</sup>	0.03	5.3	158	516
Mabira Catena (Ferrisols) <sup>b</sup>	0.03	4.3	157	410
Mabira Catena (Ferrisols) <sup>b</sup>	0.03	4.5	146	568
Buganda Catena (Ferrallitic soils) <sup>b</sup>	0.03	5.2	250	706
Buganda Catena (Ferrallitic soils) <sup>b</sup>	0.02	4.9	165	556
Buganda Catena (Ferrallitic soils) <sup>b</sup>	0.03	5.2	424	1097
Buganda Catena (Ferrallitic soils) <sup>b</sup>	0.02	5.5	281	903
Buganda Catena (Ferrallitic soils) <sup>b</sup>	0.02	5.1	317	945
Mabila Catena (Ferrisols) <sup>b</sup>	0.03	5.1	222	930
Mabila Catena (Ferrisols) <sup>b</sup>	0.02	5.0	190	947
Mabila Catena (Ferrisols) <sup>b</sup>	0.03	4.1	231	726
Mabila Catena (Ferrisols) <sup>b</sup>	0.03	4.7	250	918
Mabila Catena (Ferrisols) <sup>b</sup>	0.03	4.7	254	593
Katera series (Ferrallitic soils) <sup>b</sup>	0.01	4.4	67	468
Katera series (Ferrallitic soils) <sup>b</sup>	0.01	4.0	61	548
Katera series (Ferrallitic soils) <sup>b</sup>	0.02	4.2	85	476
Katera series (Ferrallitic soils) <sup>b</sup>	0.01	4.1	128	289

Abbreviations same as Table 1.

<sup>a</sup> Puerto Rican origin.

<sup>b</sup> Ugandan origin; Ugandan soil classification: (Selvaradjou et al., 2005).

minerals in the soil samples except in the Oxisols from Uganda. The characterized parameters illustrated a wide diversity in soil properties within the sample set.

### 3.1. Atrazine sorption

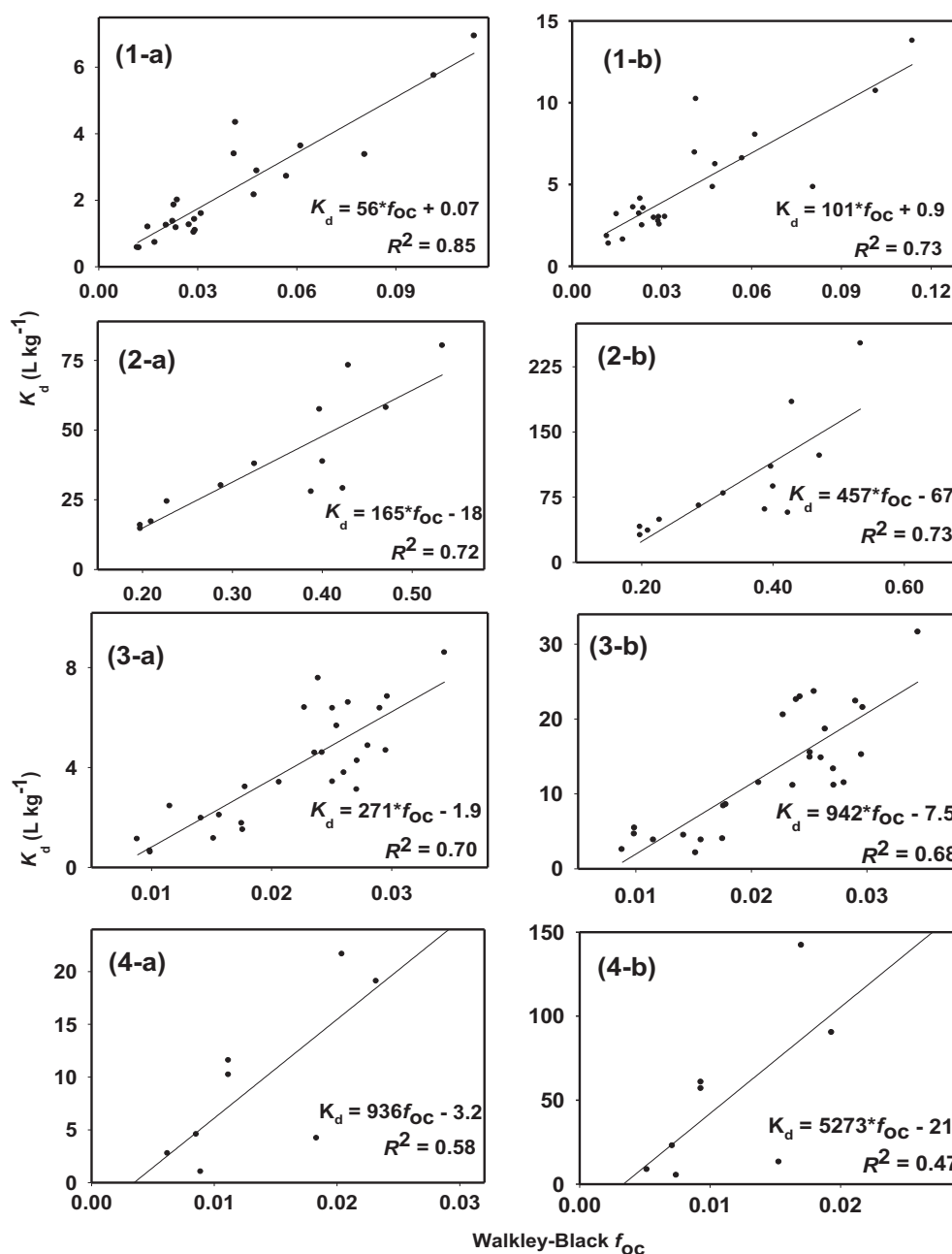
Sorption isotherms were used to describe the partitioning of atrazine between the soil solution and the solid surfaces and to better understand the nature of the interactions between atrazine and the soil matrix. The sorption isotherms were well-described by a linear model within the concentration range studied and no significant sorption of atrazine to the container walls was observed, as the recoveries were greater than 90%. The  $K_d$  values ranged from 0.6–6.9, 14.6–80.2, 0.6–8.6 and 1.0–21.6 L kg<sup>-1</sup> for carbonatic soils, Histosols, Oxisols and Spodosols, respectively and showed a strong relationships with the  $f_{oc}$  (Fig. 1) in carbonatic soils ( $R^2 = 0.85$ ), Histosols ( $R^2 = 0.72$ ), and Oxisols ( $R^2 = 0.70$ ), but a weaker relationship in Spodosols ( $R^2 = 0.58$ ). When normalized to OC, the sorption coefficients ( $K_{oc}$ ) averaged  $58 \pm 4$ ,  $107 \pm 9$ ,  $172 \pm 13$  and  $618 \pm 118$  L kg<sup>-1</sup> (mean  $\pm$  standard error) for carbonatic soils, Histosol, Oxisol, and Spodosols, respectively (Tables 1–3). In carbonatic soils, the  $K_{oc}$  values ranged from 36 to 105 L kg<sup>-1</sup> with Perrine soil series having the lowest  $K_{oc}$  and the Perrine-Tamiami associated series (average OC = 4.1%) having the highest  $K_{oc}$  values (Table 1). The average OC-normalized atrazine sorption coefficients were significantly lower ( $\alpha = 0.05$ ) for marl-carbonatic soils (45 L kg<sup>-1</sup> on average) than for the rock-plowed non-marl carbonatic soils (72 L kg<sup>-1</sup>). The  $K_{oc}$  values for non-marl carbonatic soils, Histosols, Oxisols and Spodosols were 1.4, 2.4, 4 and 18 times higher than for marl-carbonatic soils, respectively.

### 3.2. Ametryn sorption

No sorption of ametryn to container walls was observed as recoveries exceeded 95% in control vials. Similar to atrazine, ametryn sorption isotherms were well-described by the linear model. The  $K_d$  values ranged from 1.4–13.8, 11.7–251.8, 2.1–31.6 and 6.4–12.3 L kg<sup>-1</sup> for carbonatic soils, Histosols, Oxisols and Spodosols, respectively, and showed a strong relationships with the  $f_{oc}$  (Fig. 1) in carbonatic soils ( $R^2 = 0.73$ ), Histosols ( $R^2 = 0.73$ ), and Oxisols ( $R^2 = 0.68$ ), but a weaker relationship in Spodosols ( $R^2 = 0.47$ ). The average  $K_{oc}$  values for ametryn were  $131 \pm 9$ ,  $244 \pm 28$ ,  $556 \pm 45$ , and  $3227 \pm 750$  L kg<sup>-1</sup> for carbonatic soils, Histosols, Oxisols and Spodosols, respectively, and those of marl-carbonatic soils were 2, 2, 6, and 21 times lower than those of non-marl carbonatic soils, Histosols, Oxisols and Spodosols, respectively (Tables 1–3). Generally, the ametryn OC-normalized sorption coefficients were about 4 times higher than for atrazine.

### 3.3. Organic matter removal

Due the high and variable  $K_{oc}$  values in Oxisols and Spodosols, organic matter (OM) was removed from these soil types to investigate the potential contribution of mineral surfaces to the sorption of the s-triazines. The proportions of OM removed in Spodosols and Oxisols by sodium hypochlorite and hydrogen peroxide treatments ranged from 91 to 99% and 78 to 97%, respectively (Table 4). Anova showed that the OM removal methods were statistically different ( $\alpha = 0.05$ ). The atrazine  $K_d$  values were significantly reduced by  $90 \pm 9$  and  $87 \pm 6$  percent using hypochlorite and peroxide oxidation, respectively and by  $95 \pm 5$  and  $92 \pm 8$  percent for ametryn. The concept of OC-normalization was not invoked for the samples after OM removal since their OC content was below the acceptable 1% cutoff (Schwarzenbach and Westall, 1981).



**Fig. 1.** Linear correlations between triazine sorption coefficient ( $K_d$ ) and fraction of organic carbon ( $f_{oc}$ ) for 1) carbonatic soils, 2) Histosols, 3) Oxisols and 4) Spodosols; (a) denotes atrazine and (b) ametryn. The slopes of the lines shown represent average  $K_{oc}$ .

## 4. Discussion

### 4.1. *s*-Triazine sorption mechanism

The sorption coefficient ( $K_d$ ) is the most direct predictor of the potential of chemical movement in a particular soil and the risk they may pose to groundwater contamination (Reddy et al., 1997; Weber et al., 2004; Fava et al., 2006). The order of sorption coefficients, ametryn > atrazine, was the same as has been reported in previous studies conducted on a range of Brazilian rainforest soils (Matallo et al., 2008) and Puerto Rican soils studied by Liu et al. (1970). The hydrophobicity of ametryn and atrazine also decreases in the same order, with  $\log K_{ow}$  values of 2.6 and 2.5 (BCPC, 2000), respectively.

The trends observed in atrazine and ametryn sorption with regard to soil type also shed light on the factors which control the

sorption of these contaminants in soil. The soil OC-normalized sorption coefficients for ametryn and atrazine were generally much lower ( $\alpha = 0.05$ ) in carbonatic soils than other soils, and most so in marl-carbonatic type soils, compared to the non-carbonatic soils. The average ametryn  $K_{oc}$  value of  $131 \text{ L kg}^{-1}$  measured in carbonatic soils of this study was about two and half times lower than of the average  $K_{oc}$  ( $300 \text{ L kg}^{-1}$ ) reported in literature for all soil types pooled (Hornsby et al., 1996). The general trend of  $K_{oc}$  values were the same for ametryn and atrazine across soil orders, suggesting similar controls on sorption for both *s*-triazines.

The positive linear relationships between  $K_d$  and  $f_{oc}$  that was found in this study provides evidence of the dominance of OC in controlling the sorption of atrazine and ametryn in the soils. Previous studies have also reported the dominance of OC in controlling atrazine and ametryn sorption in soils (Payá-Pérez et al.,

**Table 4**  
Adsorption affinities of atrazine and ametryn after oxidization of organic matter using sodium hypochlorite and hydrogen peroxide.

Soil name	% OM removed	Atrazine		Ametryn	
		Oxid $K_d$ (L kg <sup>-1</sup> )	% $K_d$ reduction	Oxid $K_d$ (L kg <sup>-1</sup> )	% $K_d$ reduction
<b>Sodium hypochlorite</b>					
<i>Spodosols</i>					
Manteocha1	95	1.5	92	6.7	95
Manteocha2	94	0.2	98	0.7	99
Pomona1	91	0.5	89	0.5	98
Pomona2	95	0.8	96	1.0	99
Pomona3	95	0.7	94	0.5	99
Pomona4	94	0.1	100	2.5	98
<i>Oxisols</i>					
Buganda Catena (Ferrallitic soils)	96	0.7	94	0.7	98
Buganda Catena (Ferrallitic soils)	99	0.9	89	1.1	95
Mabila Catena (Ferrisols)	95	1.5	67	2.2	90
Mabila Catena (Ferrisols)	95	0.9	86	2.7	82
Mabila Catena (Ferrisols)	96	1.0	84	1.5	93
Mabila Catena (Ferrisols)	99	0.8	86	1.4	88
<b>Hydrogen Peroxide</b>					
<i>Spodosols</i>					
Manteocha1	97	1.2	94	1.5	99
Manteocha2	93	1.0	90	1.4	97
Pomona1	92	0.7	84	1.2	95
Pomona2	87	2.2	88	2.1	98
Pomona3	96	0.9	93	0.9	99
Pomona4	91	1.4	93	3.2	98
<i>Oxisols</i>					
Buganda Catena (Ferrallitic soils)	92	0.8	93	1.4	95
Buganda Catena (Ferrallitic soils)	78	1.2	84	2.4	89
Mabila Catena (Ferrisols)	94	0.9	86	3.1	79
Mabila Catena (Ferrisols)	ND	1.3	79	2.2	90
Mabila Catena (Ferrisols)	85	1.4	74	2.7	76

$K_d$ , sorption coefficient; OM, organic matter; ND, not determined.

1992; Mao et al., 2002; Gunasekara and Xing, 2003). This correlation of sorption coefficient,  $K_d$  with OC content, as well as the linearity of observed sorption isotherms support the well-established view of hydrophobic interaction as the dominant sorption mechanism controlling sorption of these chemicals to the soils (Chiou et al., 1979; Karickhoff et al., 1979; Weber et al., 1992; Schwarzenbach et al., 1993; Liyanage et al., 2006).

#### 4.2. Variations in sorption patterns

While atrazine and ametryn sorption coefficients ( $K_d$ 's) and  $f_{oc}$ 's were significantly linearly correlated within each soil type, in some soil orders, variations were observed particularly for Spodosols, Fig. 1 (4-a) and (4-b), suggesting involvement of other sorption mechanisms for the s-triazines. For example, correlations were found between soil pH (in Spodosols and Histosols) and  $K_d$  values for both atrazine and ametryn. This pH dependency has also been observed in previous studies (Weber, 1970; Novak et al., 1997; Watt et al., 2010). The pKa values of 1.72 and 4.0 for atrazine and ametryn (Yamane and Green, 1972), respectively, suggest neutral form speciation for atrazine and partial ionization for ametryn, particularly in the acidic Spodosols. Although cation exchange sorption mechanism is plausible for ametryn onto Oxisols and Spodosols, in the quartz predominated Florida Spodosols, most of the cation exchange capacity (CEC) has been reported to be associated with OM rather than with clay minerals (Yuan et al., 1967). The mechanism of interaction for the s-triazines then, is presumed with OM.

On the basis of  $K_{oc}$  values, some soil types displayed consistently lower coefficients for ametryn and atrazine than other soil types. For instance, despite its high OC content (39% OC), Islamorada (Histosol) from South Florida, showed a rather low atrazine OC-normalized sorption coefficient ( $K_{oc} = 72 \text{ L kg}^{-1}$ ), comparable with rock-plowed carbonatic soil types Chekika (3% OC) and Krome

(1.5% OC) whose  $K_{oc}$  values were 72 and 81  $\text{L kg}^{-1}$ , respectively. Overall, carbonatic soils showed lower  $K_{oc}$  values than other soil types, irrespective of sampling location. Even within the carbonatic soil grouping, marl-carbonatic soils showed significantly lower  $K_{oc}$  values than that of non-marl carbonatic soils ( $\alpha = 0.05$ ). The OM in marl-carbonatic soils is probably dominated by terrestrial algal mats that develop on the soil surface and drive the marl-soil formation whereas that of non-marl carbonatic soils may be dominated by plant-derived OM. Thus, one would expect marl-carbonatic soil OM to be less aromatic, which may explain its comparatively lowers-triazine sorption. It is interesting to note that even within the marl- and non-marl carbonatic soil classes, there are samples with similar  $f_{oc}$  but different  $K_{oc}$  values, suggesting a significant degree of intra-soil type OM composition heterogeneity or variation in other soil components that play a role in atrazine and ametryn sorption.

Histosols had the next lowest  $K_{oc}$  values despite having the highest average  $f_{oc}$  (0.35) and Spodosols had the highest atrazine and ametryn  $K_{oc}$  values despite having the lowest average  $f_{oc}$  (0.02). The same soil sorption pattern was observed for diuron (Kasozi et al., 2010), an even more hydrophobic compound than atrazine or ametryn. The  $K_{oc}$  values of the present study, varied more than two orders of magnitude across soil orders, and even, to a great extent, within some soil types; For example, atrazine  $K_{oc}$  values varied by almost a factor of ten within the Spodosols. These findings are contrary to studies by Kile et al. (1995) and Chiou et al. (1983) who reported  $K_{oc}$  values for carbon tetrachloride and 1,2-dichlorobenzene to vary by a factor of two among natural soils from a range of geographic origins (United States and China), attributing this relative uniformity in sorption affinity to a similarity of soil OM polarities and compositions.

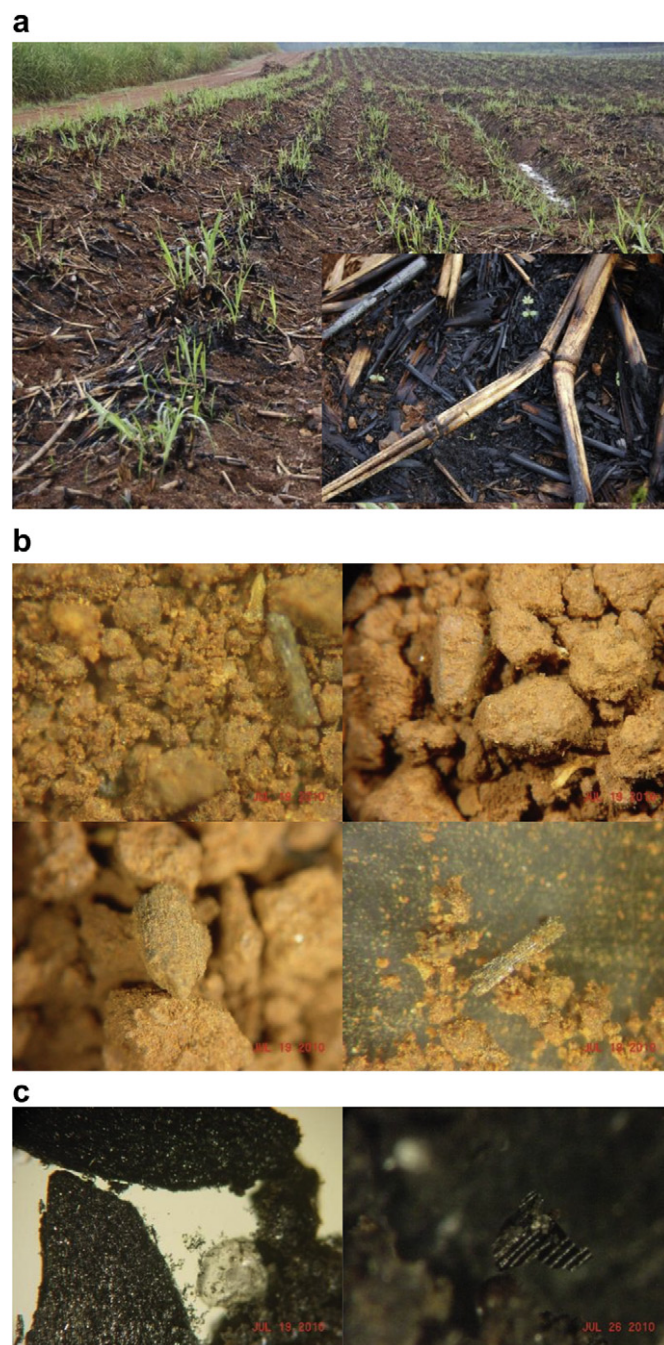
In order to account for the variability in the sorption of the s-triazine compounds, we must therefore look for factors beyond OC quantity. Although it is possible that soil mineralogy and

surface chemistry may control contaminant sorption of ionizable chemicals, the weak bases examined in this study were unlikely to have been sorbed onto mineral surfaces to a significant extent for the following reasons. Calcite (which is the major mineral in carbonatic soils) has not been found to contribute toward the sorption of atrazine (Clausen et al., 2001; Kovaivos et al., 2006). The clay mineralogy of the northern Florida Spodosols is dominated by Quartz (78–100%) and about 5% or less 1:1 kaolinite in the surface horizons (Carlisle et al., 1981). Lastly, though Spodosols and Oxisols exhibited the poorest  $K_d$  versus  $f_{oc}$  correlation and the latter most likely contain significant clay, removal of OM from these two orders using hydrogen peroxide and sodium hypochlorite resulted in reduction of  $K_d$  values by more than 90%, indicating minimal contribution to sorption by mineral matter.

There are a number of reasons to hypothesize that the presence of highly condensed OM probably from pyrogenic carbon (or black carbon, BC), account for the relatively high *s*-triazine soil sorption coefficients in Spodosols and Oxisols. First, the pine flatwoods in which the Spodosols develop are characterized by acidic pine needles and frequent burning (whether natural or by controlled burns in the specific forest where the soils were collected). Many of the Oxisols were collected from sugar plantations where the harvest process involves burning the sugar cane (Fig. 2a). Lastly, microscopic examination of the Spodosols and Oxisols showed presence of charcoal particles within these soils (Fig. 2b and c). However, there is some controversy as to the extent to which BC or non-BC OM is removed by various chemical oxidation methods. Unlike hydrogen peroxide which reportedly removes little BC (Mikutta et al., 2005), sodium hypochlorite has been reported to remove all BC except for soot (Lorenz et al., 2010). Since both employed methods effectively removed OM, we can conclude there was little BC in the soils tested. This conclusion is further supported by the poor *s*-triazine sorption ability after soil OM removal. Based on the above, we propose presence of other highly condensed forms of OM influencing OM quality (functional group composition) and hence responsible for the variation in sorptive affinity, both within and between soil classes. The varying adsorptive abilities may be explained by differences in soil OM compositions (Huang and Weber, 1997; Ahmad et al., 2001; Glaser et al., 2002), which can vary among soils with OM sources or diagenetic states. For example, relative increases in OM aromaticity have been associated with soil diagenetic processes such as weathering (Haumaier and Zech, 1995; Johnson et al., 1999; Xing and Chen, 1999) and age which increases with soil depth (Chen and Pawluk, 1995; Xing and Chen, 1999). This may explain the greater affinity of the OM ( $K_{oc}$ ) for atrazine and ametryn in the highly weathered Oxisols and highly leached Spodosols compared to carbonatic soils which are of recent origin (Entisols).

## 5. Conclusions and research implications

A great deal of variability in sorption affinity within soil orders was observed which we attribute to differences in OM sources and diagenetic state. These findings point to the need to better understand the role of OM composition in controlling contaminant sorption in soils. The low *s*-triazines (atrazine and ametryn) sorption coefficient ( $K_d$ ) and low OC-normalized sorption coefficient,  $K_{oc}$ 's in carbonatic soils, particularly marl-carbonatic soils compared to all other soil types examined, indicate relatively greater potential for *s*-triazines leaching and groundwater contamination. This, combined with the generally shallow water table and the high porosity of the Floridan and Biscayne aquifers, makes the leaching potential of *s*-triazines to be much greater in much of southern Florida and this could explain the frequent



**Fig. 2.** (a) Post-harvest burnt sugar cane debris on Mabila Catena, Ferrisols, Lugazi, Uganda. (b) Microscopic observation of charcoal particles in Oxisols from Lugazi. (c) Microscopic observation of charcoal particles in Spodosols from Alachua County, North Central Florida.

detection of *s*-triazines in the water resources of this region. In consideration of the above, for cost effective agricultural production and environmental protection, we propose lowering field application rates for *s*-triazines in South Florida.

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