

# SORPTION OF S-TRIAZINES IN BRAZILIAN RAINFOREST SOILS

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This research was conducted to evaluate the sorption of Ametryn, Atrazine, Simazine, Prometrine and Metamitron to soils from "Mata Atlântica" at Ubatuba region (Atlantic rainforest soils), employing the batch equilibrium approach. The herbicides were weakly retained in soils with low soil organic matter (SOM) content and thus presenting high potential to water contamination. All herbicides have shown high Koc at Typic Humaquepts soil, the higher in SOM content. The sorption isotherms for the herbicides at Typic Humaquepts soil suggested specific interactions between herbicides and SOM probably with partial protonation of herbicides followed by ion-exchange processes and/or hydrogen bonding formation of hydroxyl groups on the SOM surface.

*KEY-WORDS: HERBICIDES; HPLC; SORPTION; DESORPTION; SOIL; ORGANIC MATTER.*

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## 1 INTRODUCTION

Sorption is a major process controlling the fate of organic pollutants in all compartments of the environment (CHEFEZ BILKIS & POLUBESOVA, 2004). Sorption has a major effect on the accessibility of microorganisms to the pollutant and plays a significant role in the pollutant's mobility (SCHEUNERT, 1993). According CHEFEZ, BILKIS & POLUBESOVA (2004) there are two main factors controlling sorption of organic pollutants: the content and the chemical structure of the soil.

The large use of agrochemicals in agriculture, especially herbicides, has been a serious environmental concern because of the potential run-off and leaching of these compounds through the soil, contaminating surface and groundwaters. Herbicides account for 50% of the total of pesticides employed in agriculture. In Brazil, approximately 160.000 t of these compounds were utilized in 2002, especially in crops of soybean, sugarcane, maize, wheat, citrus, rice and coffee (ABATE & MARSINI, 2005). In 2005, only in São Paulo State, 43.423 t of herbicides were used (FERREIRA et al., 2006). Symmetrical triazines are largely used like herbicides, such as atrazine (2-chloro-4-ethylamino-6-isopropylamine-s-triazine) which has a selective action in the pre and post-emergence in agricultural and forestry applications. Because the large use of atrazine, research has been performed to investigate its environmental impacts, since it has been frequently detected in ground and surface waters (KOPLIN et al., 1997; MILLER et al., 2000). In Brazil, atrazine and simazine residues were detected in wells and in the recharge area of the Guarany Aquifer presenting high and moderate leaching potential (CERDEIRA et al., 2004).

Once applied to soils, s-triazines have the ability to associate with various soil components. Adsorption of s-triazines to clays minerals and soil organic matter has been widely studied. In general, soil organic matter becomes an important factor with s-triazines adsorption in soils with high organic matter content (SHEA, 1989). BARRIUSO et al. (1992) examined atrazine sorption to two Brazilian oxisols and verified that soil organic matter was the most important factor affecting its adsorption. Others studies also indicate that clay minerals can contribute to the physical adsorption of s-triazines, like atrazine, particularly when the soil organic matter content is low (LAIRD et al., 1994). Adsorption isotherms, such as Freundlich, are often used to describe the overall sorption characteristics of a particular soil at a equilibrium with a range of contaminant concentrations and is dependent upon the physical and chemical properties of the sorbate (pesticides) and sorbent (soil) (TRIEGEL & GUO, 1994).

The water resources management system in São Paulo State includes the definition of watersheds as territorial units for the analysis and planning of water management. In order to improve water use management, 21 Watershed Committees were created in all of the State's 22 Water Resource Management Units (UGRHs). Ubatuba county, located in the north coast of São Paulo State (Brazil), is part of the UGRHI 03: "Litoral Norte" and has a drainage system throughout the region of the "Serra do Mar" in direction to the Atlantic Ocean. About 80% of the area is part of state parks of the original Atlantic rainforest "Mata Atlântica" or Environmental Protection Area, are one type of area legally constituted for resource protection in the State, assuring population welfare through the recovery and conservation of natural resources within a well defined area following careful planning and environmental management (IPT, 2001). Although in this county agriculture is not important at the moment it is necessary to establish a program to protect and preserve the area to the present and future generations.

In order to achieve this preservation purpose and based on the fact that the soils vary in relation to sorption of s-triazinas, the objective of this research was evaluate the sorption of "Mata Atlântica" soils' at Ubatuba region of ametryn, atrazine, simazine, prometryne and metamitron and rank the herbicides according to the leaching potential based on the sorption coefficient adapted to the organic matter (Koc).

## 2 MATERIAL AND METHODS

### 2.1 APPARATUS AND REAGENTS

A LC 2010 Shimadzu high performance liquid chromatograph (HPLC) equipped with a UV/VIS photodiode array detector SPD-M20A, and the LC Workstation Class VP 6.0 software was used in all

experiments for quantification atrazine, ametryne, simazine, prometryn and metamitron. A Gemini C-18 Phenomenex column (5.0  $\mu\text{m}$ , 150 x 4.6 mm) connected to a C-18 Phenomenex guard column was employed. The analytical standards of atrazine (ATZ), ametryne (AMT), simazine (SMZ), prometryne (PMT) and metamitron (MTM), all of > 98.7% purity, were supplied by ChemService. Their molecular formula and some physicochemical properties are listed in Table 1. Stock solutions (1000  $\text{mg}\cdot\text{L}^{-1}$ ) were prepared in methanol (HPLC grade). These standards, solids or solutions were stored in freezer at  $-18^\circ\text{C}$ . Acetonitrile and methanol (HPLC grade) were purchased by J. T. Baker. Water used in all experiments was distilled and deionized using the Simplicity Millipore system.

**TABLE 1 - MOLECULAR FORMULA AND SOME PHYSICOCHEMICAL PROPERTIES OF S-TRIAZINES<sup>1</sup>**

S-Triazines	Molecular formula	Molar mass ( $\text{g}\cdot\text{mol}^{-1}$ )	Water solubility ( $\text{mg}\cdot\text{L}^{-1}$ )	pKa
<b>Ametryne</b>	$\text{C}_8\text{H}_{14}\text{ClN}_5$	215.69	33	1.7
<b>Atrazine</b>	$\text{C}_9\text{H}_{17}\text{N}_5\text{S}$	227.33	200	4.1
<b>Simazine</b>	$\text{C}_7\text{H}_{12}\text{ClN}_5$	201.66	3.5	1.6
<b>Prometryne</b>	$\text{C}_{10}\text{H}_{19}\text{N}_5\text{S}$	241.35	33	4.1
<b>Metamitron</b>	$\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}$	202.2	1700	n.d. <sup>2</sup>

<sup>1</sup>WSSA, 2002; <sup>2</sup>Non-dissociated.

## 2.2 STUDY SITE

The UGRHI 03: "Litoral Norte" has an area of 1987  $\text{km}^2$ , formed by the total area of four counties of Ubatuba (682  $\text{km}^2$ ), Caraguatatuba (480  $\text{km}^2$ ), São Sebastião (479  $\text{km}^2$ ) and Ilhabela (336  $\text{km}^2$ ) being defined as 34 watersheds, 26 of them being continental and 8 islander. The geology of the Ubatuba district is composed by igneous and metamorphics rocks (crystalline rocks) inserted in "Precambrian Coast Complex". Gneisses and migmatites are classified *high degree* and granites are domain rocks. These granites have commonly "foliar or banded" structure with a great diversity of the associations, where the more important are: porphyritic granitoid, peraluminous granites, charnockites and isotropic rose granites, intrusives into orthogneisses. The rain index is very high, varying from 1600 to 3000 mm/year, reaching the minimum of 1200 mm/year (PERH, 2004 a, b).

## 2.3 SOILS AND SAMPLING

Five soils were collected based in your agricultural use, classification and organic matter content, all of them without herbicide application in the last 10 years, as informed by homestead owners. All soils were located by global position system (GPS) at  $45^\circ\text{S}$  and  $23^\circ\text{W}$ , covered mainly with vegetable crops and original vegetation of tropical forests. The soils classification at Ubatuba district, includes: *Red Yellow Latosol* (Typic Acrustox - Subgroup in Soil Taxonomy) associated with *Cambisols* (Inceptisols - Order in Soil Taxonomy), both sandy clay granulometry; *Red Yellow Latosol* associated *Red Yellow Podzolic* (Ultic Aploxeralf - Subgroup in Soil Taxonomy) with clayey granulometry; in low occurrence are Litosols (Entisols), Gleysols (Inceptisols), hydromorphics Soils (Alfisols) and Organic Soils (Histosols), according SOIL SURVEY STAFF (1992). Soils characteristics from studied sites are show in Table 2. At each site, samples were collected from the Ap or Hp horizon soil's fractions. A 5 kg sample was prepared in each sampling area by mixing several samples collected from five nearby

spots. Upon reaching the laboratory, samples were air-dried, ground, sieved through a 2-mm sieve and stored dry at room temperature.

**TABLE 2 - BASIC CHARACTERISTICS OF THE STUDIED SOILS**

Site	Horizon (cm)	Texture (g.kg <sup>-1</sup> )			Organic Carbon (%)	pH (H <sub>2</sub> O)	CEC <sup>1</sup> (cmolc/kg)	Sub-group <sup>2</sup>
		Sand	Silt	Clay				
1	Ap (0 -13)	394	185	421	1.9	5.2	14.4	Typic Eutropepts
2	Ap (0 - 9)	950	12	38	2.7	5.6	3.8	Fluvic Quartzipsamment
3	Ap (0 -15)	286	281	433	1.0	5.1	6.9	Typic Plinthaquepts
4	Hd (0 -16)	135	267	598	10.2	4.1	50.0	Typic Humaquepts
5	Ap (0 -13)	905	15	80	0.5	4.9	1.8	Typic Quartzipsamment

<sup>1</sup>Cation Exchange Capacity; <sup>2</sup>According Soil Taxonomy (USDA, 1998)

## 2.4 SORPTION AND DESORPTION EXPERIMENTS

All experiments were performed individually for ATZ, AMT, SMZ, PMT and MTM employing in the first phase the batch equilibrium approach proposed by Environmental Protection Agency (EPA) through OPPTS 835.1220 guideline (EPA 712 - C - 98 - 048, 1998). According this guideline, in the first phase, if adsorption is moderate or high ( $A > 25\%$ ), a single desorption test is performed and if it is readily desorbed ( $D > 75\%$ ) no further sorption tests are required; if  $D < 75\%$ , the screening test is completed with a second phase in which an adsorption isotherm is determined.

In the first phase, a mass of 2.0 g ( $\pm 0.1$  g) of each soil was weighted in polyvinyl chloride (PVC) tubes with capacity of 50 mL. Next, 10.0 mL of the solution containing the selected compound with concentration of 5.0 mg.L<sup>-1</sup> in calcium chloride (CaCl<sub>2</sub>) 0.01 M was added to the PVC tubes and then closed, protected from light and kept under gentle agitation for 16h on a orbital shaker programmed at 32 rpm (or 3.35 rad.s<sup>-1</sup>). At same time, five standards of each s-triazine together with the blank solution were submitted exactly to the same procedure used for the sorption experiments. Previous studies show that the equilibrium was reached after 16h of contact. After this time the pH of the suspensions were measured and solid phases were separated by centrifugation for 20 minutes at 3000 g. Afterwards the supernatant were withdraw and filtered through Wathman number 1, and the volume recorded. Aliquots were filtered through 0.45 mm Durapore membrane Millex<sup>®</sup> from Millipore and the concentrations were determined by HPLC under isocratic conditions and *Diode Array Detection* (DAD). Table 3 summarizes the HPLC conditions. The desorption experiments were performed twice adding 10.0 mL of CaCl<sub>2</sub> 0.01 M to the PVC tubes containing the adsorbing material. The tubes were protected from light and shaken for 16h in an orbital shaker at 32 rpm (or 3.35 rad.s<sup>-1</sup>). After 16h the suspensions were centrifuged and the supernatant phases were treated as in the sorption experiment and analyzed by the HPLC method. All sorption and desorption experiments were performed in room temperature controlled at  $25 \pm 2^\circ\text{C}$ .

To the second phase, where the screening test showed a significant degree of chemical adsorptivity, adsorption isotherms were constructed to evaluate the mobility of herbicides in soil/water systems.

**TABLE 3 - HPLC CONDITIONS FOR DETERMINING S-TRIAZINES CONCENTRATIONS**

Compound	Mobile phase (MeOH:H <sub>2</sub> O)	Wavelength (nm)	Retention times (min)	Limit of detection (mg.L <sup>-1</sup> )
Atrazine	68:32	220	08.396	0.0088
Ametryne	68:32	220	10.927	0.0320
Simazine	50:50	220	15.053	0.0065
Prometryne	68:32	220	15.068	0.0082
Metamitron	68:32	220	04.966	0.0084

Preliminary experiments were conducted to find the time needed for each sorbent-sorbate pair to reach apparent equilibrium with no decomposition of the chemicals. For the adsorption isotherm determination the following concentrations of s-triazines solutions were used: ATZ, 0.03 - 0.18 - 0.95 - 1.94 and 3.91; AMT, 0.16 - 0.98 - 2.02 and 4.16 SMZ, 0.05 - 0.21 - 1.01 - 2.04 and 3.99; PMT, 0.04 - 0.20 - 0.98 - 1.96 and 3.93 and MTM, 0.04 - 0.18 - 0.93 - 1.88 and 3.71 mg.L<sup>-1</sup>. The adsorption test was performed as described in the sorption experiments in the first phase.

## 2.5 DATA TREATMENT

In the screening test the percent of the chemical adsorbed and desorbed were calculated respectively by the equations 1 and 2 according EPA (1998):

$$A = [(G - C_e).V_0] / G.100 \quad (1)$$

$$D = [(C_1 + C_2).V - (V_0 - V). C_e] / x.100 \quad (2)$$

Where, G equals the quantity of material recovered from soilless control (g), C<sub>e</sub> represents the concentration of substance remaining in solution (g.L<sup>-1</sup>), V<sub>0</sub> equals original volume of solution employed (mL), C<sub>1</sub> equals concentration of substance in the first wash (g.L<sup>-1</sup>), C<sub>2</sub> equals concentration of substance in the second wash (g.L<sup>-1</sup>) and V represents volume of solution obtained after adsorption step (mL).

In the following sorption test, data were treated by the linearized Freundlich equation:

$$\log (x/m) = \log K + n \log C_e \quad (3)$$

Where x/m is the amount of s-triazines adsorbed per amount of the soil (µg.g<sup>-1</sup>), C<sub>e</sub> is the solution concentration at equilibrium (µg. L<sup>-1</sup>), and K and n are empirical constants related to sorption. Isotherms were characterized by plotting x/m on the y-axis and C on the x-axis. The sorption distribution coefficient (K) data were calculated for each isotherm point and normalized to the carbon level of each soil to obtain the K<sub>oc</sub> values using the equation 4.

$$K_{oc} = (K/\% OC).100 \quad (4)$$

## 3 RESULTS

The texture of the soils varied from sand to clay. The organic carbon content ranged amply from 0.50% (site 5) to 10.20% (site 4). This is a difference of 9.7%. The pH ranged from 4.1 to 5.6. The cation exchange is associated with the clay minerals (TOWNSEND, 1982), therefore these values were higher in clay soils than in sand soils, varying from 50.0 cmol<sub>c</sub>.kg<sup>-1</sup> at site 4 to 1.8 cmol<sub>c</sub>.kg<sup>-1</sup> to site 5.

The adsorption of s-triazines ranged from 2.0% to 81.8% for ATZ, 8.3% to 92.4% for AMT, 6.2% to 76.0% for SMZ, 6.3% to 72.2% for MTM, and 8.0 to 95.1 for PMT (Table 4).

**TABLE 4 - ADSORPTION PERCENT OF S-TRIAZINES**

s- triazines	Adsorption percent				
	Site 1	Site 2	Site 3	Site 4	Site 5
Atrazine	3.4	7.7	10.3	81.8	2.0
Ametryne	11.2	17.6	22.3	92.4	8.3
Simazine	7.2	8.4	11.8	76.0	6.2
Metamitron	9.5	8.8	10.1	72.2	6.3
Prometryne	9.9	25.1	31.7	95.1	8.0

All sites showed low adsorption ( $A < 25\%$ ) except site 4 (Typic Humaquepts) where adsorption varied from 72.2% for MTM to 92.4% for AMT which is associated with the higher soil organic matter content (SOM). In all sites the percent of desorption were higher than 75% ( $D > 75\%$ ) probably due the SOM, except site 4. The desorption in this site were 17.2% to ATZ, 19.9% to SMZ, 3.3% to AMT, 3.9% to PMT and 31.6% MTM. According VADER (2003) the increase in organic matter decreases the amount desorbed.

The constants of Freundlich equation with their correlation coefficients ( $r$ ) and the regression equation, as well, the sorption isotherms for the five herbicides to the Typic Humaquepts soil (site 4) are presented in Table 5 and Figure 1, respectively.

**TABLE 5 - CONSTANTS  $K_f$  AND  $1/n$  OF FREUNDLICH EQUATION WITH THEIR CORRELATION COEFFICIENTS ( $r$ ) AND THE REGRESSION EQUATION**

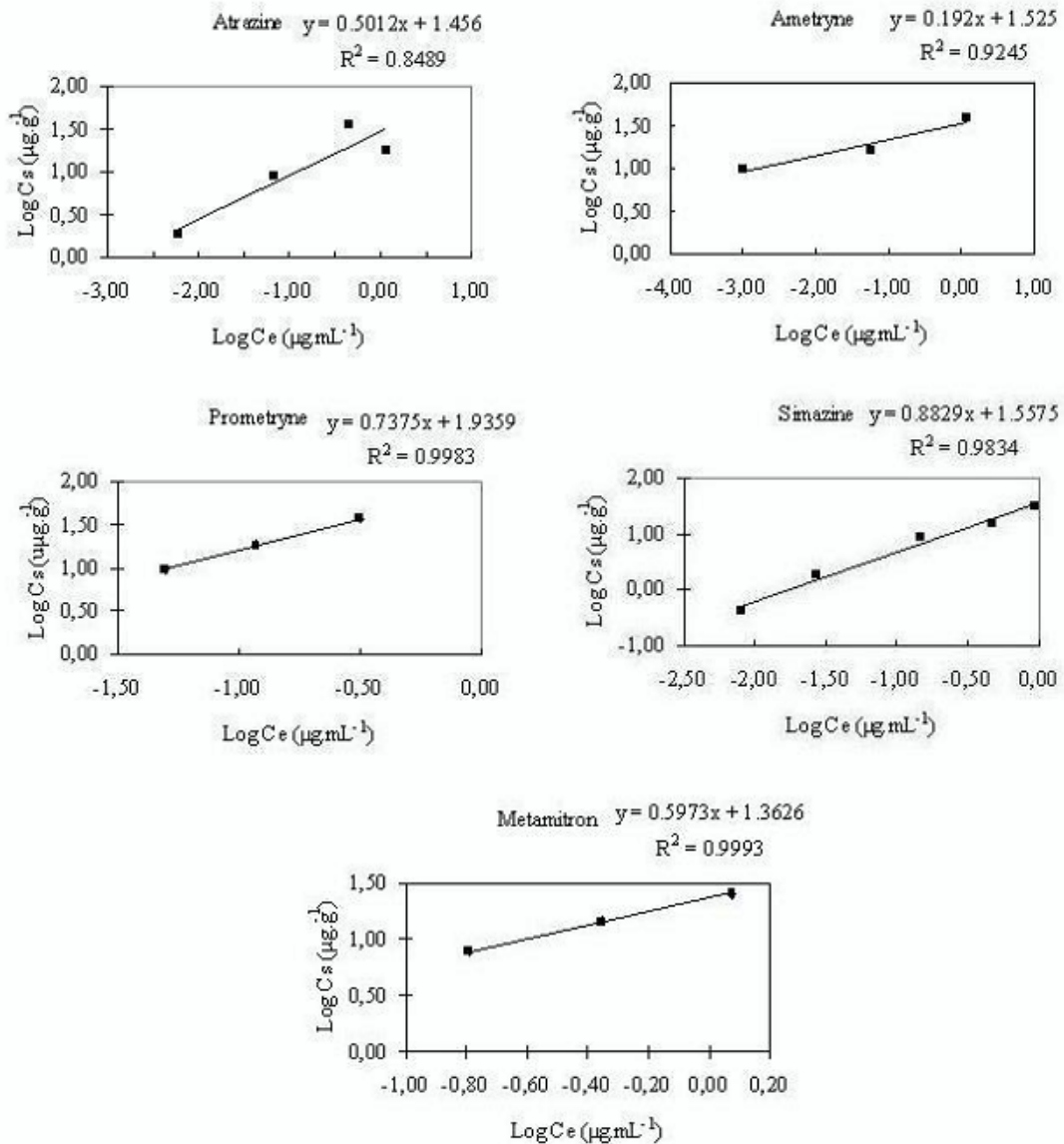
Herbicides	Parameters			regression equation
	$K_f$	$1/n$	$r$	
Atrazine	28.58	0.50	0.9214	$y = 1.4560 + 0.5012 x$
Ametryne	33.50	0.19	0.9615	$y = 1.5250 + 0.1920 x$
Simazine	36.10	0.88	0.9917	$y = 1.5575 + 0.8829 x$
Metamitron	23.05	0.60	0.9995	$y = 1.3626 + 0.5973 x$
Prometryne	86.28	0.74	0.9992	$y = 1.9360 + 0.7375 x$

#### 4 DISCUSSION

The herbicides ATZ, AMT, SMZ and PMT are basic with  $pK_a$ 's ranging from 1.6 to 4.1 while MTM is non-dissociated. The pH of the soils ranged from 4.1 to 4.7 much more higher than the  $pK_a$  of ATZ and SMZ and near to  $pK_a$  of AMT and PMT. In this situation all ATZ and SMZ were in molecular form together with the non-dissociated form of MTM while AMT and PMT were approximately half

dissociated (WEBER, 1994). Table 4 shows that in all soils AMT and PMT were more adsorbed than MTM, ATZ and SMZ indicating that electrostatic forces other than weak forces will be acting especially at Typic Humaquepts (site 4) due to high SOM. The water solubility of ATZ and SMZ allows that hydrophobic partitioning like interactions will be acting (PRATA et al., 2001) while to MTM others weak attractive forces are contributing to the adsorption. It is important to note that the five soils, while containing different amounts of SOM also contain different amount of clay, ranging from 38 (Fluvic Quartzipsamment at site 2) to 598 g.kg<sup>-1</sup> (Typic Humaquepts at site 4). This is important to consider since atrazine-clay associations have been reported to be important to soils that contain less than 6% SOM (SHEA, 1989). Somehow Table 4 shows that, except at Typic Humaquepts soil, all herbicides have potential to leach freely in all soils studied.

**FIGURE 1 - ADSORPTION OF S-TRIAZINES TO TYPIC HUMAQUEPTS SOIL DISPLAYED AS A FREUNDLICH ISOTHERM**



The K values indicate a high adsorption of s-triazines to Typic Humaquepts soil (Table 5). On the basis of Koc values the s-triazines herbicides can be arranged in the following order: PMT>SMZ>AMT>ATZ>MTM. The distinct Koc values calculated for the same sorbent indicate different sorptive properties of the s-triazines with the SOM probably due to the substituents that affect the basicity of the N atoms and the acidity of N-H bonds of the molecule (CHEFETZ, BILKIS & POLUBESOVA, 2004). According to these authors, Cl-triazines are more likely to form relatively stronger H-bonds with carboxylic moieties of SOM as compared to S-triazines, which can result in higher adsorption and lower desorption. This estimation is supported by the lower pKa values of the Cl-triazines as compared to the S-triazines (Table 6).

**TABLE 6 - SORPTION COEFFICIENTS AND FREUNDLICH MODEL PARAMETERS OF TYPIC HUMAQUEPTS SOIL**

<b>s-triazines</b>	<b>K</b>	<b>K<sub>oc</sub></b>	<b>1/n</b>
<b>Atrazine</b>	28.58	271.67	0.50
<b>Ametryne</b>	33.50	318.44	0.19
<b>Simazine</b>	36.10	343.16	0.88
<b>Metamitron</b>	23.05	219.11	0.60
<b>Prometryne</b>	86.28	820.15	0.74

The results show the same order in adsorption according the substitute groups at triazine herbicides as reported by CHEFETZ et al. (2004), however the Cl-triazines were more desorbed than S-triazines. Therefore it was speculated that although H-bonding is important in triazine-SOM interactions, this type of complexation is probably governed by physical adsorption involving weak attractive forces including hydrophobic partitioning like interactions that can be disrupted.

The sorption isotherms for Typic Humaquepts soil exhibited *n* values less than 1 (Table 5) suggesting specific interactions between herbicides and SOM (H-bonding or charge transfer interactions) involving partial protonation of herbicides followed by ion-exchange processes and/or hydrogen bonding formation of hydroxyl groups on the SOM surface (ABATE & MASINI, 2005).

## 5 CONCLUSION

There were differences in herbicides adsorption to the various soils. All herbicides presented low adsorption on soils with low organic matter content presenting high potential to water contamination. Prometryne and ametryne were the most adsorbed s-triazines which is associated with the functional group present. At Typic Humaquepts soil all compounds presented high Koc values with the highest adsorption. Despite the high adsorption the *n* values indicate specific interactions with the SOM mainly with weak attractive forces, allowing that the possibility of disrupt and consequently water contamination by leaching and/or run-off. The elevated reversibility of the sorption process, especially in soils with low SOM indicates a low degree of hysteresis implying that the soils have potential to release the herbicides.

## RESUMO

### SORÇÃO DE S-TRIAZINAS EM SOLOS DE MATA ATLÂNTICA BRASILEIROS

Esta pesquisa foi conduzida para avaliar a sorção de ametryna, atrazina, simazina, prometryna e metamitron em solos de Mata Atlântica na região de Ubatuba, empregando-se o método em batelada. Os herbicidas foram fracamente retidos em solos com baixo teor de matéria orgânica (MO) e, portanto, apresentaram



elevado potencial de contaminação da água. Todos os herbicidas mostraram alto valor de Koc em solos da classe Gleissolo Melânico Distrófico, que contém o teor mais elevado de MO. As isotermas de sorção dos herbicidas no Gleissolo Melânico Distrófico sugerem interações específicas entre os herbicidas e a MO, provavelmente com protonação parcial dos herbicidas seguida por processos de troca-iônica e/ou formação de pontes de hidrogênio dos grupos hidroxila sobre a superfície da MO.

**PALAVRAS-CHAVE:** HERBICIDAS; CLAE; SORÇÃO; DESSORÇÃO; MATÉRIA ORGÂNICA; SOLO.

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