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SOIL AND PLANT NUTRITION - Article

Aminocyclopyrachlor and mesotrione sorption–desorption in municipal sewage sludge-amended soil

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ABSTRACT: The application of sewage sludge (SS) in agriculture is a practice used worldwide, and it is commonly applied in sugarcane to supply nutrients, with beneficial effects on crop productivity and soil; but SS can increase sorption and decrease desorption of herbicides. However, in tropical soils such as in Brazil, there are no studies regarding the behavior of pre-emergent herbicides, mainly aminocyclopyrachlor and mesotrione, in SS-amended soil. The aim of the present study was to determine the effect of municipal SS applied in agriculture on the sorption–desorption of aminocyclopyrachlor and mesotrione in clay soil. Aminocyclopyrachlor (pyrimidine-2-^{14}C-aminocyclopyrachlor) and mesotrione (cyclohexane-2-^{14}C-mesotrione) sorption–desorption was evaluated using a batch equilibrium method. Soil was amended at 0% (control – unamended), 0.1%, 1%, and 10% (w·w^{-1}) of air-dried SS corresponding to 1.2, 12, and 120 t·ha^{-1}. The Freundlich K_f sorption values of aminocyclopyrachlor and mesotrione were similar for all treatments, ranging from 1.07 to 1.45 and 3.48 to 4.25 μmol$^{(1-1/n)}$ L$^{1/n}$·kg^{-1}, respectively. Overall, the lowest K_d sorption value of these herbicides was reported for SS-amended soil (1%), while in the SS-amended soil (10%) it was higher than unamended soil. The H value for aminocyclopyrachlor was ~1 (no hysteresis) and for mesotrione was on average 0.4 (hysteresis occurring). In conclusion, the present study indicates that SS applied in any crop to supply nutrients can slightly affect the sorption–desorption of aminocyclopyrachlor and mesotrione, but this small difference does not affect the bioavailability of these herbicides for weed control.

Key words: organic amendments, tropical soil, leaching potential, weak acid.

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INTRODUCTION

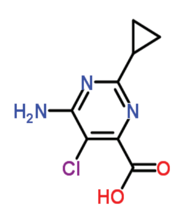
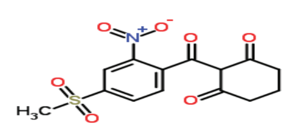
The application of municipal sewage sludge (SS) in agriculture is a practice used worldwide, with beneficial effects on crop productivity, such as in sugarcane in Brazil (Franco et al. 2010). The SS addition in the soil increases organic carbon (OC), nitrogen and phosphorus (Pires et al. 2015), besides increasing cation exchange capacity (CEC) and water retention. However, SS may carry high amounts of heavy metals and other pollutants, which can cause serious problems of plant injury, accumulation in the food chain, and surface and groundwater contamination with high environmental impacts (Saito 2007). In order to ensure that the SS does not pose any danger to the environment, the Conselho Nacional do Meio Ambiente – CONAMA (2006) legislation regulated by resolution N.375/06 was created in Brazil, together with Companhia de Tecnologia de Saneamento Ambiental – CETESB (1999) regulated by rule P4.230 in São Paulo State, to regulate the agricultural use of SS on soil.

The application of SS to soil can increase sorption and decrease desorption of herbicides, depending on both the organic amendments and herbicide properties (Pinna et al. 2009). Sorption and desorption are important processes as they regulate the leaching of an herbicide in soil. Among various physical, chemical and biological processes, sorption to organic matters is one of the dominant processes determining the fate of herbicides in the environment (Cheng 1990).

Aminocyclopyrachlor (6-amino-5-chloro-2-cyclopropylpyrimidine-4-carboxylic acid) and mesotrione (2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione) are weak acid herbicides applied on sugarcane and maize in pre- and post-emergent for the control of woody weeds, some grasses and broad-leaved weeds, respectively. The properties influencing the concentration of aminocyclopyrachlor and mesotrione in the aqueous phase of a soil include the soil pH value, soil texture, mineral composition (including the proportion of clay, iron, and manganese oxides), its CEC, the amount and type of organic compounds present in the soil and its aqueous phase, temperature, moisture content, and the amount and types of microorganisms inhabiting the soil (Brady and Weil 2016). The physicochemical properties of these herbicides are shown in Table 1.

Several authors have studied the impact of SS addition on the sorption–desorption of veterinary pharmaceuticals (Kim et al. 2010), microconstituents (Banihashemi and Droste 2014), metal (Majewska et al. 2007), estrogen (Stumpe and Marschner 2010), and 2,4-D, ametryn, atrazine, cyhalofop-butyl, diuron, linuron, simazine, terbuthylazine and triasulfuron herbicides (O'Connor et al. 1981; Celis et al. 1998; Sluszny

Table 1. Structural formula and physicochemical properties of the herbicides.

Attribute	Aminocyclopyrachlor	Mesotrione
Structural formula		
Molecular formula	$C_8H_8ClN_3O_2$	$C_{14}H_{13}NO_7S$
IUPAC name	6-amino-5-chloro-2-cyclopropylpyrimidine-4-carboxylic acid	2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione
Chemical group	pyridine carboxylic acid	triketones – F2
Molecular weight ($g \cdot mol^{-1}$)	213.62	339.32
Water solubility at 20 °C ($mg \cdot L^{-1}$)	3130	1500
Log Kow	–2.48	0.11
pKa at 25 °C	4.6 (weak acid)	3.12 (weak acid)
Vapor pressure at 25 °C (Pa)	6.92×10^{-6}	5.70×10^{-6}
DT50 (days)	31	19.6

Adapted from AERU (2018).

et al. 1999; Cox et al. 2000; Pinna et al. 2009; Rodríguez-Cruz et al. 2012; Imache et al. 2012) in the soil. However, there are no studies regarding the behavior of pre-emergent herbicides, mainly aminocyclopyrachlor and mesotrione, in SS-amended tropical soils, such as in Brazil. Thus, the aim of the present study was to determine the effect of municipal SS applied in agriculture on the sorption–desorption of aminocyclopyrachlor and mesotrione in clay soil.

MATERIAL AND METHODS

Soil sample

Sample (5 Kg) was collected from soil that had not been treated with the herbicides aminocyclopyrachlor and mesotrione in the past 2 years. Soil was collected from only one surface layer (0 – 10 cm depth) in an area cultivated with sugarcane in Tangará da Serra, Mato Grosso State, Brazil (14°39’01” S; 57°25’54” W; and altitude = 321.5 m), after pre-cleaning the vegetable layer. After drying, sample was sieved through a 2.0-mm mesh and stored at room temperature. The soil was classified as Oxisol-Typic Hapludox (clay texture) and with the following physicochemical properties: CEC = 107 $mmol_c \cdot kg^{-1}$, pH (H_2O) = 6.0, OC = 2.21%, clay = 60.5%, silt = 11.3%, and sand = 28.2%.

Sewage sludge

The SS was a compost supplied by the municipal sewage treatment plant in Piracicaba, São Paulo State, Brazil. The soil was amended at 0% (control – unamended), 0.1%, 1%, and 10% ($w \cdot w^{-1}$) of air-dried SS, corresponding to 1.2, 12, and 120 $t \cdot ha^{-1}$, respectively, assuming a soil bulk density of 1.2 $g \cdot cm^{-3}$ and a tillage incorporation depth of 10 cm. The SS was milled and homogenized in a mechanical mill. Selected physicochemical properties of the SS are listed in Table 2. Chemical analysis of the metals was performed with the solid waste method – SW 3015A (USEPA 2008). N was determined by using the Kjeldahl method and consisted of three main steps: sample digestion, distillation, and ammonia determination, as described by Sáez-Plaza et al. (2013). P, K, Na, Ca, and Mg were measured by atomic absorption after nitric-perchloric digestion. The soil-amended and SS pH was determined on slurries with a soil/water ratio of 1:1. OC content was determined by digestion with potassium dichromate. The contents of heavy metals were within the Brazilian regulatory limits for SS agricultural use as regulated by rule P4.230 (CETESB 1999).

Table 2. Selected properties of sewage sludge and values permitted for application in agricultural areas.

Property	Value	Permitted value[a]
Zn ($mg \cdot kg^{-1}$)	667	7500
Hg ($mg \cdot kg^{-1}$)	< 0.05	57
Pb ($mg \cdot kg^{-1}$)	45.4	840
Cu ($mg \cdot kg^{-1}$)	308	4300
Ni ($mg \cdot kg^{-1}$)	30.6	420
As ($mg \cdot kg^{-1}$)	3.26	75
Se ($mg \cdot kg^{-1}$)	< 1	100
Mo ($mg \cdot kg^{-1}$)	8.03	75
Cd ($mg \cdot kg^{-1}$)	2.4	85
Ba ($mg \cdot kg^{-1}$)	629	
Cr ($mg \cdot kg^{-1}$)	60.9	
Na ($mg \cdot kg^{-1}$)	1800	
S ($g \cdot kg^{-1}$)	23.8	
Mg ($g \cdot kg^{-1}$)	5	
K (total, %)	19.6	
P (total, %)	2.95	
N (total, %)	3.65	
OC (%)	16.64	
pH (H_2O)	6.8	
humidity (% at 105 °C)	65.57	
volatile solids (%)	49.37	
ashes (% at 650 °C)	50.63	

[a]CETESB (1999).

Chemical products

^{14}C-aminocyclopyrachlor (pyrimidine-2-^{14}C-aminocyclopyrachlor) was kindly provided by DuPont (Wilmington, DE, USA). Five solutions (0.08, 0.16, 0.32, 0.48, and 0.64 $Bq \cdot L^{-1}$) were prepared and ^{14}C-aminocyclopyrachlor showed 99.5% radiochemical purity and 1.57 $MBq \cdot mg^{-1}$ of specific activity. ^{14}C-mesotrione (cyclohexane-2-^{14}C-mesotrione) acquired from Izotop (Budapest, Hungary) showed 98.4% radiochemical purity and 3.45 $MBq \cdot mg^{-1}$ of specific activity and analytical standards non-radiolabeled with purities of 99.9% (Sigma Aldrich, Saint Louis, MO, USA), and five solutions (0.28, 0.57, 1.13, 1.70, and 2.27 $Bq \cdot L^{-1}$) were prepared. Radiolabeled and non-radiolabeled standards were carefully mixed in 0.01 $mol \cdot L^{-1}$ $CaCl_2$.

Sorption–desorption experiments

The methodology of sorption–desorption experiments with ^{14}C-aminocyclopyrachlor and ^{14}C-mesotrione was established according to the guidelines of the OECD-106 (OECD 2000), with two repetitions. Each experimental unit consisted of a 50 mL Teflon tube with a screw cap. Aliquots with 10 g of soil were weighed in duplicate in the tubes and 10 mL of solution $CaCl_2$ 0.01 mol·L^{-1} was used, resulting in a soil–solution ratio of 1:1 (m·v^{-1}). In the sorption experiments, 1 mL aliquots of radiolabeled solutions were transferred in duplicate to separate vials containing 10 mL of the scintillation solution, and the initial concentration of ^{14}C-aminocyclopyrachlor and ^{14}C-mesotrione after 15 min was determined by liquid scintillation counting (LSC) with a Tri-Carb 2910 TR LSA counter (PerkinElmer, Waltham, MA, USA).

In duplicate, 10 mL of the radiolabeled concentrations of all solutions were added to the Teflon tubes containing the soil samples. The tubes were agitated in a horizontal shaker tabletop in a dark room (20 ± 2 °C) for 24 h to achieve the equilibrium concentration, according to Oliveira Jr. et al. (2011) and Mendes et al. (2016) for aminocyclopyrachlor and mesotrione, respectively. At the equilibration concentration, the tubes were centrifuged at 755 g for 15 min, and 1 mL aliquots of the supernatant from each tube were transferred in duplicate to scintillation vials containing 10 mL of the scintillation solution, and analyzed by LSC to determine the concentration of the ^{14}C-aminocyclopyrachlor and ^{14}C-mesotrione solution by counting the radioactivity. Then, 9 mL of the initial supernatant was removed. The amount of sorbed herbicide was calculated using the difference between the initial concentration and the concentration in the supernatant after equilibration of the same soil.

Desorption experiments were performed immediately after sorption under the same conditions. For that, $CaCl_2$ solution (10 mL, 0.01 mol·L^{-1}) was added to the Teflon tubes containing the soil and the radiolabeled herbicide sorbed from the sorption experiment. The tubes were agitated in a horizontal shaker tabletop in a dark room (20 ± 2 °C) for 24 h to reach the equilibrium concentration. After re-equilibration, the tubes were centrifuged and 1 mL aliquots of the supernatant were pipetted in duplicate to scintillation vials containing 10 mL of the scintillation solution and analyzed by LSC. The desorbed amount was calculated as the difference between the radioactivity sorbed in the soil and in the remaining supernatant.

Sorption–desorption model

Sorption coefficients were calculated using the equation: $K_d = C_s/C_e$, where C_s is the concentration of herbicide sorbed to the soil (μmol·kg^{-1}) and C_e is the concentration of herbicide in the liquid phase at equilibrium (μmol·L^{-1}). To normalize the sorption data to soil OC, the K_{oc} was calculated by dividing the sorption coefficient by the following: $K_{oc} = K_d/[\%OC/100\%]$, where %OC is the percentage of organic carbon in the soil. The units of K_d and K_{oc} were L·kg^{-1}.

In order to estimate the parameters for sorption–desorption, the logarithms of C_s (x-axis) and C_e (y-axis) were plotted using Sigma Plot® (version 10.0 for Windows, Systat Software Inc., Point Richmond, CA, USA), which mathematically fit the log-transformed Freundlich equation: $log\ [C_s] = log\ [K_f] + 1/n\ log\ [C_e]$, where $log\ [K_f]$ was the y-intercept of the line and 1/n was the slope. The resulting units of K_f were μmol $^{(1-1/n)}$ L$^{1/n}$·kg^{-1}. The hysteresis coefficient, *H*, was calculated by dividing the Freundlich desorption slope ($1/n_{desorption}$) by the Freundlich sorption slope ($1/n_{sorption}$), or mathematically: $H = [1/n_{desorption}]/[1/n_{sorption}]$ (Barriuso et al. 1994). However, this was only calculated for soils which exhibited hysteresis, which is defined where $1/n_{desorption}$ is less than $1/n_{sorption}$.

GUS index

Groundwater Ubiquity Scores (GUS) for surface soils were calculated using the equation: GUS = log (DT50) × (4 – log (K_{oc})), where DT50 is the dissipation time herbicide half-life (days) in soil (Gustafson 1989). The DT50 values calculated in existing studies available in the database and shown in Table 1 were used (AERU 2018).

Statistical data analysis

Aminocyclopyrachlor and mesotrione sorption–desorption coefficients (K_d and K_{oc}) data were subjected to ANOVA, data were normally distributed by the Shapiro–Wilk normality test ($p < 0.05$) and averages were compared by Dunnett's honest significant difference (HSD) test ($p < 0.05$).

RESULTS AND DISCUSSION

Aminocyclopyrachlor and mesotrione sorption–desorption

The Freundlich equation fitted well the sorption of aminocyclopyrachlor ($R^2 = 0.99$) and mesotrione ($R^2 \geq 0.98$) applied to unamended soil and SS-amended soils (Table 3). In all cases the isotherms are linear with a slope value (1/n) of ~1 for aminocyclopyrachlor, according to Francisco et al. (2017) and Oliveira Jr. et al. (2011), and ranging from 0.92 to 0.94 for mesotrione, according to Mendes et al. (2016), resembling the C-type curve described by Giles et al. (1960). This shape suggests the partition of solute between solution and sorbent (Pinna et al. 2009).

The K_f sorption values of aminocyclopyrachlor were similar for all treatments, ranging from 1.07 to 1.45 $\mu mol^{(1-1/n)}\ L^{1/n} \cdot kg^{-1}$ (Table 3). Francisco et al. (2017) also found that the calculated K_f values for the aminocyclopyrachlor sorption were low in the three soils, at 0.37, 0.85, and 1.34 $\mu mol^{(1-1/n)}\ L^{1/n} \cdot kg^{-1}$ for loamy sand, sandy clay, and clay, respectively. The same behavior was observed for mesotrione, whose K_f values were higher (3.48 to 4.25 $\mu mol^{(1-1/n)}\ L^{1/n} \cdot kg^{-1}$). Mendes et al. (2016) also reported that the K_f values of mesotrione sorption were low, ranging from 0.10 to 4.01 $\mu mol^{(1-1/n)}\ L^{1/n} \cdot kg^{-1}$) in soil samples from seven Brazilian sites cultivated with maize. For the K_{foc} sorption values in relation to the soil OC, the means ranged from 48.63 to 65.91 and from 158.18 to 193.18 $\mu mol^{(1-1/n)}\ L^{1/n} \cdot kg^{-1}$ for the aminocyclopyrachlor and mesotrione applied in all treatments, respectively (Table 3).

Overall, the higher sorption measured on SS-amended soil (10%) is due to the higher OC content of the soil, even though the pH of the soil solution was higher (Table 3). Although aminocyclopyrachlor and mesotrione are weak acids (Table 1) and increased pH SS-amended soil decreases the sorption of these herbicides in the soil, in this study the OC content was responsible for the higher sorption of aminocyclopyrachlor and mesotrione. This low decrease of K_f values was only observed in the lower amounts of SS (0.1% and 1%) in the soil (Table 3). Juan et al. (2015) found that the higher OC content of SS-amended soil could explain both the higher sorption of mesotrione by the soil and the higher DT50 value. Studies in the literature also reported a positive correlation between the sorption of mesotrione (Dyson et al. 2002; Chaabane et al. 2008) and aminocyclopyrachlor (Oliveira Jr. et al. 2011) and the soil OC content.

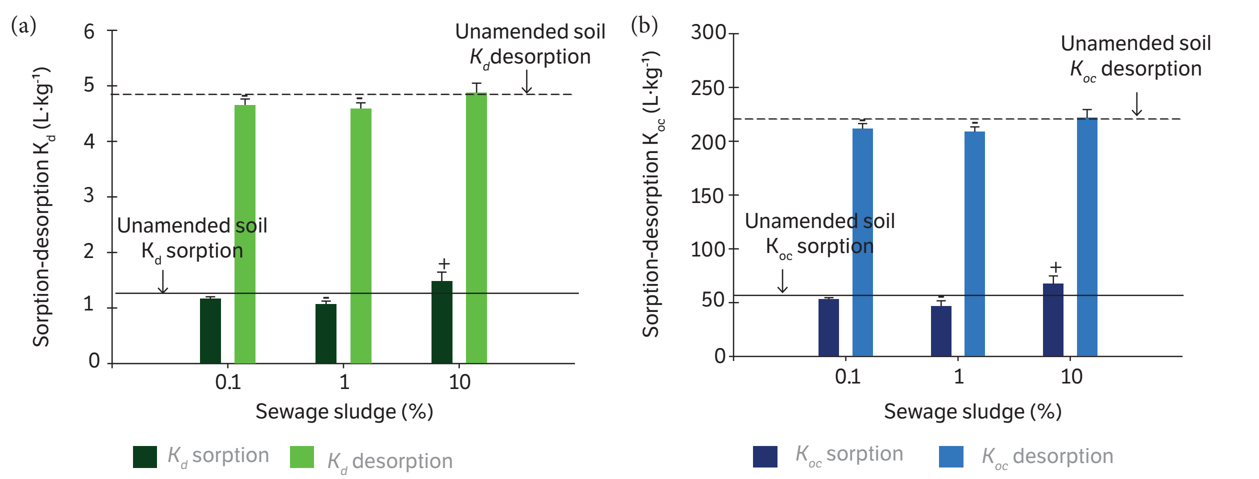
Even though we found little difference between the sorption-desorption in the SS-amended soils and unamended soil for both herbicides in this study, other authors such as Celis et al. (1998) reported that the incorporation of insoluble and soluble organic matter into soil by liquid SS addition increases the atrazine sorption behavior in soil, and Pinna et al. (2009) also reported that SS-amended soil influences triasulfuron retention by reducing the groundwater contamination risk. Cox et al. (2000) found that SS-amended soils sorbed simazine and 2,4-D to a greater extent than the unamended soils. This can be explained by the difference in physicochemical properties of these herbicides and the characteristics of the organic amendments (SS).

Table 3. Freundlich sorption parameters and leachability for aminocyclopyrachlor and mesotrione applied in unamended soil and sewage sludge (SS)-amended soil.

Treatment	pH (H_2O)	OC (%)	$K_{f\,(sorption)}$	$K_{foc\,(sorption)}$	$1/n_{\,(sorption)}$	R^2	Sorption (%)	GUS index[b]	Leaching potential
			($\mu mol^{(1-1/n)}\ L^{1/n} \cdot kg^{-1}$)						
Aminocyclopyrachlor									
Unamended soil	6.0	2.21	1.13 ± 0.05[a]	51.36	0.99 ± 0.02	0.99	37.22 ± 1.32	3.38	high
Soil + SS (0.1%)	6.3	2.23	1.18 ± 0.06	53.64	1.00 ± 0.04	0.99	36.76 ± 0.71	3.39	high
Soil + SS (1%)	6.4	2.38	1.07 ± 0.03	48.63	1.00 ± 0.03	0.99	34.61 ± 2.51	3.45	high
Soil + SS (10%)	6.6	3.87	1.45 ± 0.05	65.91	0.99 ± 0.04	0.99	42.40 ± 2.47	3.24	high
Mesotrione									
Unamended soil	6.0	2.21	4.12 ± 0.02	187.27	0.93 ± 0.08	0.98	67.28 ± 2.11	2.23	moderate
Soil + SS (0.1%)	6.3	2.23	3.95 ± 0.02	179.54	0.92 ± 0.05	0.99	66.33 ± 1.52	2.25	moderate
Soil + SS (1%)	6.4	2.38	3.48 ± 0.04	158.18	0.92 ± 0.04	0.98	63.50 ± 1.66	2.32	moderate
Soil + SS (10%)	6.6	3.87	4.25 ± 0.03	193.18	0.94 ± 0.05	0.99	68.00 ± 1.49	2.21	moderate

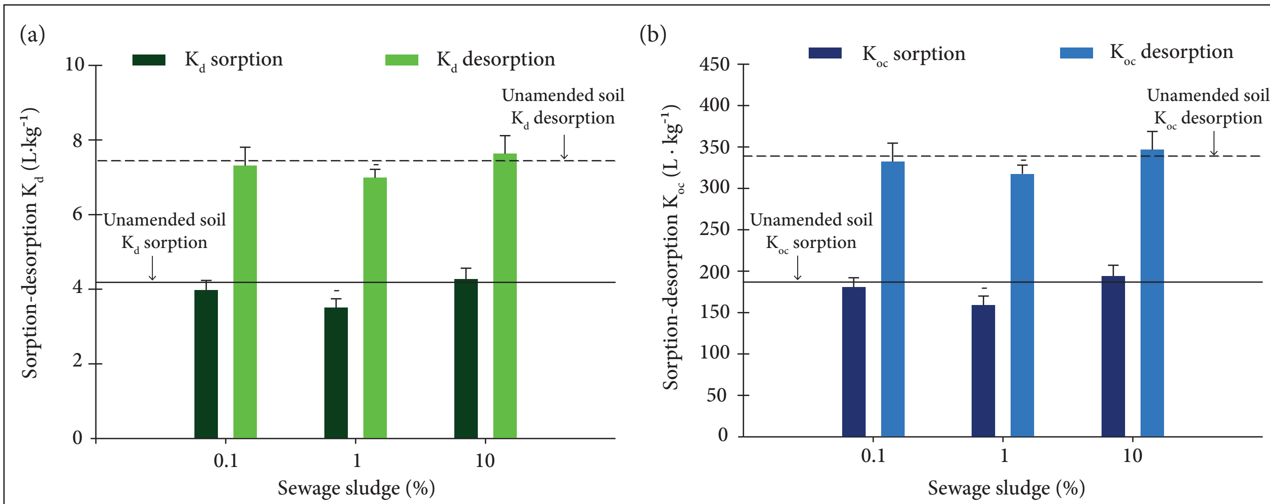
[a]Mean value ± standard deviation of the mean (n = 2); [b]GUS = log (DT50) × (4 – log (K_{oc})).

This data corroborates the aminocyclopyrachlor sorption coefficient – K_d of 1.19 ± 0.07 L·kg^{-1} to unamended soil, for which the lowest K_d sorption value was reported for SS-amended soil (1%), while for the SS-amended soil (10%) the K_d sorption value was 1.24-fold higher than unamended soil (Fig. 1a), similar to the K_{oc} sorption values described in Fig. 1b. Similar sorption behavior to aminocyclopyrachlor was found for mesotrione with the K_d sorption value of 4.17 ± 0.36 L·kg^{-1} for unamended soil, where the lowest K_d sorption value was reported for SS-amended soil (1%) (Fig. 2a), similar to the K_{oc} sorption values described in Fig. 2b. However, K_d of mesotrione was ~3.5-fold higher than aminocyclopyrachlor. This can be explained by the higher water solubility of aminocyclopyrachlor (3130 mg·L^{-1}) compared with mesotrione (1500 mg·L^{-1}), as shown in Table 1, enabling water solubility to provide more bioavailability



A "–" sign above the color bars indicates lower sorption–desorption K_d and K_{oc}, and a "+" sign indicates great sorption–desorption K_d and K_{oc} than unamended soil (Dunnett's test at $p < 0.05$). The vertical bars associated with each column represent the ±SD of each mean value (n = 2).

Figure 1. Sorption–desorption (A) K_d and (B) K_{oc} values of aminocyclopyrachlor applied in Oxisol-Typic Hapludox amended with SS (0.1%, 1%, and 10% w·w^{-1}). K_d sorption–desorption value of aminocyclopyrachlor to unamended soil averaged about 1.19 ± 0.07 and 4.84 ± 0.17 L·kg^{-1}, respectively. K_{oc} sorption–desorption value of aminocyclopyrachlor to unamended soil averaged about 54.13 ± 3.28 and 220.06 ± 7.82 L·kg^{-1}, respectively.



A "–" sign above the color bars indicates lower sorption–desorption K_d and K_{oc}, and a "+" sign indicates great sorption–desorption K_d and K_{oc} than unamended soil (Dunnett's test at $p < 0.05$). The vertical bars associated with each column represent the ±SD of each mean value (n = 2).

Figure 2. Sorption-desorption (A) K_d and (B) K_{oc} values of mesotrione applied in Oxisol-Typic Hapludox amended with SS (0.1%, 1%, and 10% w·w^{-1}). K_d sorption–desorption value of mesotrione to unamended soil averaged about 4.17 ± 0.36 and 7.45 ± 0.65 L·kg^{-1}, respectively. K_{oc} sorption–desorption value of mesotrione to unamended soil averaged about 189.60 ± 6.41 and 338.58 ± 20.49 L·kg^{-1}, respectively.

of aminocyclopyrachlor in soil solution for absorption by weeds and crops.

The Freundlich equations fitted well the desorption of aminocyclopyrachlor (R^2 = 0.99) and mesotrione ($R^2 \geq 0.97$) applied to unamended soil and SS-amended soils (Table 4). The 1/n desorption values obtained from the aminocyclopyrachlor desorption isotherms were similar to the sorption values (~1), and the 1/n desorption values from the mesotrione were lower (0.38 – 0.44) than the sorption values, suggesting that mesotrione desorption is more influenced by the concentration of the herbicide in the soil, according to Mendes et al. (2016).

For aminocyclopyrachlor, the K_f desorption values ranged from 4.74 to 5.51 μmol $^{(1-1/n)}$ $L^{1/n}$ $\cdot kg^{-1}$ for all SS doses added to the soil (Table 4). On the other hand, the K_f desorption values of mesotrione were higher than the K_f desorption values of aminocyclopyrachlor and ranged from 6.98 to 7.60 μmol $^{(1-1/n)}$ $L^{1/n} \cdot kg^{-1}$. These data corroborate with the K_{foc} desorption values, which ranged from 215.45 to 246.36 and from 317.27 to 345.45 μmol $^{(1-1/n)}$ $L^{1/n} \cdot kg^{-1}$ for the aminocyclopyrachlor and mesotrione applied in all treatments, respectively (Table 4).

The K_d desorption – K_d sorption ratio of aminocyclopyrachlor was 2.1-fold higher than the ratio of mesotrione (Table 4). Lastly, the *H* values for aminocyclopyrachlor were ~1 and for mesotrione were on average 0.4 (Table 4), where *H* values below 1 indicate that the mesotrione desorption percentage is less than that of the sorption and that hysteresis occurs (Pinna et al. 2014), and *H* values ~1 indicate that the desorption of herbicide showed no hysteresis, indicating that the sorption of aminocyclopyrachlor is reversible, and offers appreciable leaching, as addressed by Francisco et al. (2017). Similarly to our study, mesotrione and aminocyclopyrachlor *H* values ranged from 0.32 to 0.77 (Mendes et al. 2016) and from 1.04 to 1.07 (Francisco et al. 2017), respectively.

The incorporation of SS to the soil had little effect on the sorption–desorption of the aminocyclopyrachlor and mesotrione, and therefore this practice may not have an effect on weed management in agricultural fields. Concomitantly, given the low sorption of aminocyclopyrachlor under even the best case scenario, the ability of three biochars (wood pellet, wood chip, and corn stover) to increase the sorption of aminocyclopyrachlor was tested by Hall et al. (2015), but none of these biochars succeeded in increasing the sorption of aminocyclopyrachlor when added to the different Hawaiian soils. Based on this study, neither SS nor such biochar appears to be an effective means of reducing aminocyclopyrachlor leaching in soil, which will be explained below with the potential risk of leaching.

Leachability of aminocyclopyrachlor and mesotrione

GUS index was used to determine whether aminocyclopyrachlor and mesotrione were mobile in the soil, according to Rittenhouse et al. (2014). For aminocyclopyrachlor and mesotrione applied in SS-amended soils and unamended soil, the GUS indices ranged from 2.21 to 2.32 and from 3.24 to 3.45, respectively (Table 3). Several authors have found GUS indexes values for mesotrione similar to this study, such

Table 4. Freundlich desorption parameters and hysteresis coefficient (*H*) for aminocyclopyrachlor and mesotrione applied in unamended soil and sewage sludge (SS)-amended soil.

Treatment	pH (H_2O)	OC (%)	$K_{f\,(desorption)}$ (μmol $^{(1-1/n)}$ $L^{1/n}$ kg^{-1})	$K_{foc\,(desorption)}$ (μmol $^{(1-1/n)}$ $L^{1/n}$ kg^{-1})	1/n $_{(desorption)}$	R^2	*H*	$K_{d\,(desorption)}$ / $K_{d\,(sorption)}$	Desorption (%)
Aminocyclopyrachlor									
Unamended soil	6.0	2.21	5.42 ± 0.05[a]	246.36	1.01 ± 0.03	0.99	1.02	4.06	29.28 ± 0.69
Soil + SS (0.1%)	6.3	2.23	5.51 ± 0.02	250.45	1.03 ± 0.03	0.99	1.03	3.99	30.08 ± 0.65
Soil + SS (1%)	6.4	2.38	5.02 ± 0.02	228.18	1.02 ± 0.01	0.99	1.02	4.29	30.40 ± 0.45
Soil + SS (10%)	6.6	3.87	4.74 ± 0.03	215.45	0.99 ± 0.01	0.99	1.00	3.29	29.12 ± 0.66
Mesotrione									
Unamended soil	6.0	2.21	7.32. ± 0.02	332.72	0.41 ± 0.02	0.97	0.44	1.78	21.28 ± 1.47
Soil + SS (0.1%)	6.3	2.23	7.28 ± 0.07	330.91	0.38 ± 0.01	0.99	0.41	1.83	21.55 ± 1.09
Soil + SS (1%)	6.4	2.38	6.98 ± 0.06	317.27	0.37 ± 0.02	0.98	0.40	1.99	22.35 ± 1.28
Soil + SS (10%)	6.6	3.87	7.60 ± 0.03	345.45	0.44 ± 0.01	0.99	0.47	1.78	20.84 ± 1.02

[a]Mean value ± standard deviation of the mean (n = 2).

as 2.34 – 2.85 (Mendes et al. 2017), 2.2 (Dyson et al. 2002), and 1.9 – 3.2 (Chaabane et al. 2008), corroborating studies of column mesotrione leaching (Pinna et al. 2014). The same is true for the leaching potential of aminocyclopyrachlor described in the literature, with GUS indices ranging from high (3 – 4) to very high (> 4) (Rittenhouse et al. 2014). Overall, the high leaching of aminocyclopyrachlor is of concern to researchers because this herbicide is proven to contaminate groundwater by studies in columns (Adams and Lym 2015; Francisco et al. 2017) and mathematical modeling (Hall et al. 2015).

Aminocyclopyrachlor and mesotrione display a low ecotoxicity to the environment (Dumas et al. 2017; AERU 2018), but low concentrations of both herbicides are able to damage crops, and can consequently cause a reduction in crop yields (O'Sullivan et al. 2002; Riddle et al. 2013; Patton et al. 2013; Guerra et al. 2014). That is why the high leaching of these herbicides in the soil is very worrying for producers in agricultural fields.

According to Gustafson (1989), an herbicide with a GUS score less than 1.8 is regarded as a nonleacher, a value greater than 2.8 qualifies as an easy leacher, and those between 1.8 and 2.8 are considered to be transitional, where the herbicide can be leached in favorable conditions with high intensity rain. Based on the aminocyclopyrachlor and mesotrione GUS indices from this study, these herbicides can be considered highly (GUS = 3.24 – 3.45) and moderately (GUS = 2.21 – 2.32) leachable when applied to all soils, respectively. Therefore, aminocyclopyrachlor and mesotrione can contaminate underground water resources and surface water. One potential explanation could be due to the different sorption capacity of aminocyclopyrachlor and mesotrione as previously shown.

As expected, the addition of SS to the soil also did not affect the leaching potential of both herbicides, remaining the same as unamended soil. More research is needed with different aging or incubation times of the SS-amended soil to confirm that the addition of SS has no or very little effect on the sorption–desorption and leaching of aminocyclopyrachlor and mesotrione in agricultural fields.

In conclusion, the present study indicates that SS applied to any crop to supply nutrients can slightly affect the sorption–desorption of aminocyclopyrachlor and mesotrione, but this small difference can not affect the bioavailability of these herbicides for weed control. The addition of SS does not appear to be an effective means of reducing aminocyclopyrachlor and mesotrione leaching in soil, which means that these herbicides can contaminate water resources, based on their GUS index.

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