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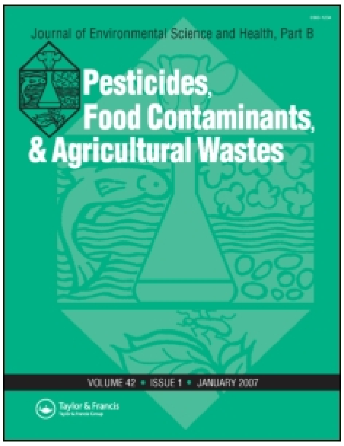

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Adsorption and desorption variability of four herbicides used in paddy rice production

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This investigation was performed to determine the effect of physicochemical soil properties on penoxsulam, molinate, bentazon, and MCPA adsorption–desorption processes. Four soils from Melozal (35° 43′ S; 71° 41′ W), Parral (36° 08′ S; 71° 52′ W), San Carlos (36° 24′ S; 71° 57′ W), and Panimavida (35° 44′ S; 71° 24′ W) were utilized. Herbicide adsorption reached equilibrium after 4 h in all soils. The Freundlich L-type isotherm described the adsorption process, which showed a high affinity between herbicides and sorption sites mainly because of hydrophobic and H-bonds interaction. Penoxsulam showed the highest adsorption coefficients (4.23 ± 0.72 to 10.69 ± 1.58 mL g^{-1}) and were related to soil pH. Molinate showed K_d values between 1.72 ± 0.01 and 2.3 ± 0.01 mL $g^{-1}$and were related to soil pH and organic matter, specifically to the amount of humic substances. Bentazon had a high relationship with pH and humic substances and its K_d values were the lowest, ranging from 0.11 ± 0.01 to 0.42 ± 0.01 mL g^{-1}. MCPA K_d ranged from 0.14 ± 0.02 to 2.72 ± 0.01 mL g^{-1}, however its adsorption was related to humic acids and clay content. According to these results, the soil factors that could explain the sorption process of the studied herbicides under paddy rice soil conditions, were principally humic substances and soil pH. Considering the sorption variability observed in this study and the potential risk for groundwater contamination, it is necessary to develop weed rice management strategies that limit use of herbicides that exhibit low soil adsorption in areas with predisposing conditions to soil leaching.

Keywords: Adsorption; desorption; isotherms; Freundlich.

Introduction

The principal herbicides used in paddy rice production, such as penoxsulam (3-(2,2-difluoroethoxy)-*N*-(5, 8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-α, α, α-trifluorotoluene-2-sulfonamide) and molinate (*S*-ethyl azepane-1-carbothioate), are applied either directly into the water, or after draining the paddies and exposing weed foliage as in the case of bentazon (3-isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide) and MCPA (2-methyl-4-chlorophenoxyacetic acid). The use of these herbicides, in this particular condition, has generated great concern with respect to the risk of superficial and groundwater contamination in several countries generating monitoring programs to evaluate their effect on water quality.[1−6]

One useful tool for monitoring and regulating the environmental contamination, especially water contamination, is the use of predictive models.[7−9] However, prior to using any model to predict pesticide behavior in a particular condition, it is necessary to generate local information that allows calibration and evaluation of their accuracy. Moreover, model calibration using field data represents the main factor for pesticides assessment.[10]

Although pesticide soil dynamic is a complex phenomenon and can be affected by several variables, there is enough scientific knowledge that indicates a strong relationship between soil properties and pesticide sorption, especially the effect of texture, clay type, organic matter and pH.[11−13] This relationship between soil and pesticide can be more important in explaining soil dissipation because of other processes such as degradation, lixiviation, and volatilization.[11,14,15]

The objectives of this study were: (i) to determine the sorption variability of four herbicides used in paddy rice production and its relationship with the main soil properties, and (ii) to generate a data set that can be used to validate predictive models to regulate and modify pesticide management to avoid groundwater contamination.

Materials and methods

Selected soils and physicochemical properties

The soils were collected from the 0–15 cm soil layer from the principal paddy rice production areas: Melozal (35° 43′

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Table 1. Physicochemical properties of the soils.

					Inorganic soil phase			*Organic soil phase*				
Soil	*pH*	*EC mS cm^{-1}*	*CEC meq 100 g^{-1}*	*Bulk density g cm^{-3}*	*Sand*	*Clay*	*Loam*	*Organic matter %*	*Organic carbon*	*Humic substances*[1]	*Humic acids*[1]	*E4/E6*[2]
Melozal	5.40	0.08	15.00	1.21	39.63	21.07	39.33	1.92	1.03	0.34	0.32	3.08
Parral	5.81	0.09	21.16	1.30	34.20	34.40	31.40	2.09	1.14	0.33	0.11	5.32
San Carlos	5.15	0.09	17.73	1.26	39.05	26.85	34.10	3.93	2.39	0.89	0.54	6.14
Panimavida	6.11	0.14	22.92	1.33	38.00	34.00	28.00	2.43	1.41	0.35	0.24	4.38

[1] Humic substances and humic acids expressed as percentage of organic carbon content.
[2] E4/E6 absorbance ratio 465 nm and 665 nm relation of humic/fulvic acids organic matter content.
[3] CEC: cationic exchange capacity.

S; 71° 41′ W), Parral (36° 08′ S; 71° 52′ W), San Carlos (36° 24′ S; 71° 57′ W), and Panimavida (35° 44′ S; 71° 24′ W). Main soils properties (Table 1) were characterized as follows: electric conductivity (EC), pH, cationic exchange capacity (CEC), organic matter (OM), organic carbon (OC), and texture according to Kalra and Maynard,[16] and also humic substances (HS) and humic acids (HA) were determined.

Extraction of humic substances

The procedure to determine HS and HA in the soil organic phase was according to the general procedure proposed by Rocha et al.[17] Dried soil was grounded and passed through a 2 mm sieve. Five grams of the resulting material were transferred to a round-bottom flask and 20 mL of KOH (0.5 M) were added per gram of soil. The suspension was stirred for 3 h. Then, the humic extract was centrifugated at 2012 g for 10 min. The non-dissolved fraction was separated and discarded. One aliquot of this supernatant (25 mL) was carried out to reach dryness at 60°C in an oven with air circulation and the HS were quantified by oxidation with $KCrO_2$ according to Metson et al.,[18] expressed as % OC. The remnant supernatant was acidified at pH 1 with H_2SO_4 1:1 to precipitate the HA at 4°C. The HA concentration was determined following the same procedure done with HS.

Isotherms studies

Six milliliters of aqueous 0.01 M $CaCl_2$ solution in concentrations of 0.01, 0.025, 0.05, 0.1, and 0.2 μg mL^{-1} for penoxsulam, and 1, 5, 10, 15, and 25 μg mL^{-1} for molinate, bentazone, and MCPA, were added to 3 g air-dried of each study soil in polypropylene centrifuge tubes, in triplicate for each herbicide and soil. These soil suspensions were shaken end-over-end for 6 h at 180 rpm at 20 ± 1°C in darkness. Preliminary kinetic studies showed that the potential adsorption was reached at 2 h and equilibrium after 4 h. At the end of equilibrium, each tube was centrifuged for 15 min at 5000 rpm, and 1 mL of each supernatant was passed through a 0.45 μm fiberglass filter and directly quantified using high performance liquid chromatography (HPLC) (Hitachi model Elite LaChrom L-2300). The amount of herbicide adsorbed was calculated as the difference between the amount in the initial solution and the amount remaining in solution after centrifugation.

After measuring adsorption, 4.5 mL of the supernatant solution remaining in each of the centrifuge tubes with the maximum herbicide concentration was replaced with the same volume of fresh background solution containing no herbicide. The new soil suspensions were shaken for 6 h and centrifuged as described earlier. This desorption procedure was repeated twice, and the amount of herbicide desorbed was calculated by determining its concentration in each of the three new supernatant solutions. Control samples were included at the different herbicide concentrations in the adsorption and desorption batch experiments to determine herbicide stability and possible losses. No herbicide losses were determined during the sorption experiments.

Herbicide quantification

For penoxsulam quantification, the HPLC unit was equipped with a Lichrospher 100 RP-18 5 μm column (125 mm length). The liquid phase used was acetonitrile (25 %) and 10 mM ammonium acetate (75 %). Column temperature was 30°C, flow rate was 1 mL min^{-1}, and the injection volume was 40 μL. Molinate HPLC conditions were: Performance RP-18e 5 μm column (100 mm length), methanol (45 %) and water HPLC (65 %) were used as liquid phase, the column temperature was 25°C, flow rate was 1.2 mL min^{-1}, and the injection volume was 40 μL. For Bentazon and MCPA the HPLC was equipped with a Lichrospher 100 RP-18 5 μm column (125 mm length). The liquid phase used was acetonitrile and buffer phosphate was 13 mM pH 3.4. Acetonitrile gradient was: 0 at 6 min 15 %; 6–15 min 30 %; 15–16 min 60 %, and 16–17 min 90 %. Column temperature was 30°C and flow rate 1 mL min^{-1}. Injection volume was 40 μL.

The diode-array detector (DAD) (Hitachi model Elite LaChrom L-2450) was set at 230 for penoxsulam

Table 2. Freundlich adsorption and desorption isotherms parameters of penoxsulam, molinate, bentazon and MCPA in the study soils.

	Penoxsulam			*Molinate*			*Bentazon*			MCPA		
Soil	Kf^1_{ads}	$1/n_{ads}$	r^2	Kf_{ads}	$1/n_{ads}$	r^2	Kf_{ads}	$1/n_{ads}$	r^2	Kf_{ads}	$1/n_{ads}$	r^2
Melozal	5.84 ± 0.55	0.88 ± 0.03	0.99	2.72 ± 0.11	0.85 ± 0.02	0.99	0.51 ± 0.04	0.81 ± 0.03	0.99	3.62 ± 0.09	0.78 ± 0.01	0.99
Parral	4.21 ± 0.55	0.79 ± 0.04	0.99	3.47 ± 0.22	0.79 ± 0.03	0.99	0.41 ± 0.11	0.74 ± 0.10	0.95	0.63 ± 0.17	0.55 ± 0.09	0.89
San Carlos	6.34 ± 0.5	0.85 ± 0.02	0.99	2.99 ± 0.08	0.88 ± 0.01	0.99	0.90 ± 0.10	0.75 ± 0.04	0.99	4.65 ± 0.11	0.77 ± 0.01	0.99
Panimavida	2.54 ± 0.23	0.82 ± 0.03	0.99	2.99 ± 0.17	0.77 ± 0.03	0.99	0.36 ± 0.07	0.64 ± 0.07	0.96	1.37 ± 0.09	0.79 ± 0.03	0.99
	Kf_{des}	$1/n_{des}$	r^2	Kf_{des}	$1/n_{des}$	r^2	Kf_{des}	$1/n_{des}$	r^2	Kf_{des}	$1/n_{des}$	r^2
Melozal	1.88 ± 0.44	0.54 ± 0.07	0.91	4.64 ± 0.19	0.63 ± 0.02	0.99	2.76 ± 0.09	0.26 ± 0.01	0.99	3.44 ± 0.13	0.81 ± 0.02	0.99
Parral	2.44 ± 0.66	0.64 ± 0.08	0.91	10.85 ± 0.27	0.32 ± 0.01	0.99	1.45 ± 0.17	0.33 ± 0.05	0.88	1.24 ± 0.20	0.34 ± 0.08	0.82
San Carlos	2.89 ± 0.51	0.63 ± 0.05	0.96	3.43 ± 0.18	0.82 ± 0.03	0.99	3.64 ± 0.16	0.29 ± 0.02	0.98	5.21 ± 0.17	0.73 ± 0.02	0.99
Panimavida	1.75 ± 0.19	0.68 ± 0.04	0.99	6.77 ± 0.22	0.42 ± 0.02	0.99	1.03 ± 0.14	0.31 ± 0.06	0.83	2.59 ± 0.16	0.58 ± 0.02	0.99

[1] Kf_{ads} and Kf_{des} = mg $^{1-\mathrm{n}}$ $\mathrm{L^n kg^{-1}}$.

(retention time: 3.16), 205 for molinate (retention time: 8.13), 244 for bentazon (retention time: 8.78) and 234 for MCPA (retention time: 12.4).

Recovery was determined in triplicate from spiked water samples with concentration of 0.025; 0.05 and 0.125 mg $\mathrm{L^{-1}}$ for penoxsulam (average recovery: 91 ± 15 %). Molinate concentrations were 0.32; 0.95 and 1.57 mg $\mathrm{L^{-1}}$ with an average recovery of 92 ± 8 %. Bentazon and MCPA concentrations were 0.1; 0.5 and 1 mg $\mathrm{L^{-1}}$ with an average recovery of 90 ± 9 % and 106 ± 5 %, respectively.

Statistical data analysis

Adsorption and desorption isotherms were expressed by the Freundlich equation:

$$Cs = Kf * Ce^{1/n} \tag{1}$$

where C_s (mg $\mathrm{kg^{-1}}$) is the sorbed herbicide and Ce (mg $\mathrm{L^{-1}}$) is the herbicide in solution after the equilibrium period. Kf_{ads} and Kf_{des} are the Freundlich adsorption and desorption constants (mg $^{1-\mathrm{n}}$ $\mathrm{L^n}$ $\mathrm{kg^{-1}}$) that reflect the amount of adsorption sites and $1/n$ is a parameter that indicates the degree of favorability of adsorption or intensity of adsorption.[19]

The hysteresis (*H*) was calculated as the ratio between $1/n_{des}$ and $1/n_{ad}$, corresponding to desorption and adsorption Freundlich constants, respectively.[20] When this ratio increases, it is an indication of herbicide desorption from the sorption sites or a sorption reaction with a high degree of reversibility.

All statistical analyses were performed using SAS® program. The isotherm fitting was made using nonlinear regression analysis PROC NLIN. Correlations and regressions between soil properties and adsorption–desorption parameters were estimated using PROC CORR and PROC REG with stepwise selection model at $p \leq 0.05$.

Results and discussion

Sorption process

The Freundlich model was capable of describing the sorption process for all herbicides in the different soils (Table 2; Fig. 1). All herbicides showed L-Type isotherms that indicates high affinity for sorption sites. According to the estimated $1/n_{ads}$ values and free energy (ΔG) (Table 3), the herbicides sediment adsorption could be explained by physical reactions (London-van der Waals forces/hydrophobic retention) and H-bonds interactions (Table 3).[21–23] Kf_{ads} values ranged from 0.36 ± 0.07 to 6.34 ± 0.5 mg $^{1-\mathrm{n}}$ $\mathrm{L^n}$ $\mathrm{kg^{-1}}$ according to soil type and herbicide, whereas *Kd* values ranged from 0.14 ± 0.01 to 10.69 ± 1.6 mg $^{1-\mathrm{n}}$ $\mathrm{L^n}$ $\mathrm{kg^{-1}}$ (Tables 2 and 3).

Penoxsulam adsorption showed greater *Kd* values than those reported by Jabusch and Tjeerdema,[24] except in the Panimavida soil (Table 3), where soil pH was the highest (Table 1). According to these authors, penoxsulam soil adsorption relates not only with soil pH, but also to clay content. However, in this study, correlations showed that *Kd* was affected principally by pH followed by loam and HS present in the soil, but not by clay content (Table 4). Concordant with this, in the multiple regression model pH was the only parameter selected (Table 5). The *H* values showed a low hysteresis, indicating that penoxsulam was bound with low energy at high concentration in the solution and it was desorbed easily,[25] which is concordant to the low free energy estimated for this soil (Table 3).

Molinate adsorption was relatively homogeneous in all studied soils (Tables 2 and 3; Fig. 1), but it showed much lower adsorption coefficients than those reported in the literature.[26]On the other hand, the hysteresis between adsorption and desorption depended on soil type. In Parral and Panimavida soils, molinate was adsorbed with more energy than in the other soils (Table 3; Fig. 1) and the regression model selected principally pH, HS and relation E4/E6 (Table 4). The adsorption free energy was low, as

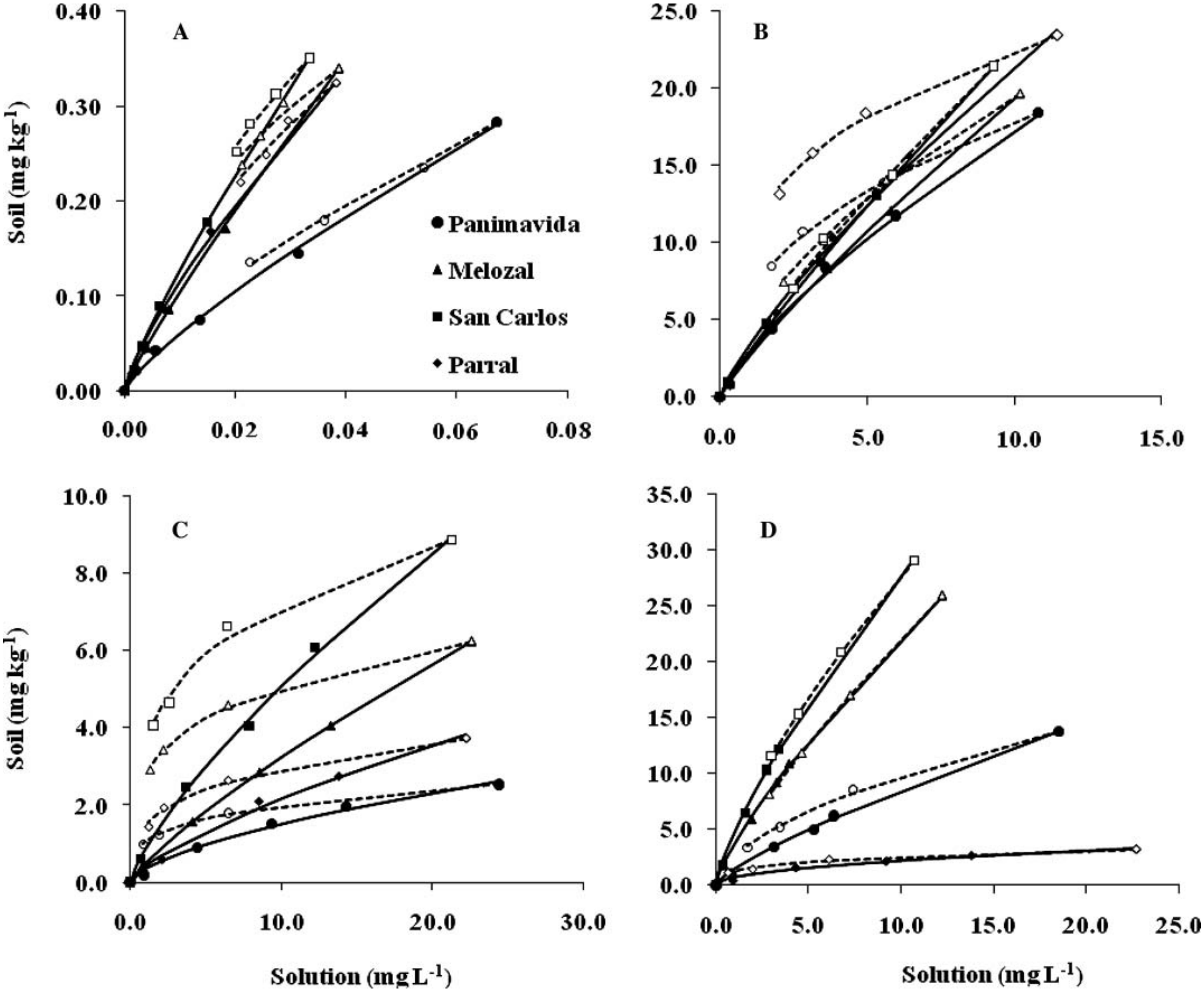

Fig. 1. Adsorption (black line) and desorption (dashed line) isotherms for penoxsulam (A), molinate (B), bentazon (C) and MCPA (D) in four soils. Values are an average of tree replications ± Standard Error.

occurred with the other studied herbicides, which could be explained because of physical adsorption.[22]

Contrary to penoxsulam, molinate was a compound with high affinity to the soil organic phase.[26,27] Thus, correlations showed a relationship between *Kd* and pH (r = −0.805; p = 0.0016) and organic carbon (OC) (r = 0.683; p = 0.014). Nevertheless, the correlation obtained for HS (r = 0.791; p = 0.002), was more significant than the correlation for HA (r = 0.576; p = 0.049). HS is composed of HA plus fluvic acid and humins. Therefore, the low correlation between *Kd* and HA could indicate that molinate organic phase adsorption is also related to fulvic acids or to other constituents of the HS fraction. According to Tan (2003), E4/E6 ratios (absorbance of HS extract at 465 and 665 nm) from 6 to 8 corresponds to a predominance of fulvic acids in the HS fraction, and ratios from 3 to 5 are indicative of HA. Thus, the regression model found that the relation E4/E6 could explain molinate soil adsorption beside pH and HS (Table 5). The pH effect on molinate adsorption, a non ionic pesticide, could be explained by variations in the chemical shift position on carboxyl and phenolic functional groups of HS[28] and the ionization in these functional groups.[29]

Bentazon showed the lowest adsorption coefficients (Tables 2 and 3), presenting hysteresis in all soils, as the *H* values were below 0.7 which is indicative of this phenomenon according to Mamy et al.[30] Although MCPA is an acidic herbicide as bentazon, hysteresis was not important, and its *Kd* values were in general greater than for bentazon (Table 3).

Bentazon adsorption was affected mainly by pH and followed by HS and HA with the same correlation values

Table 3. Adsorption coefficient (*Kd*), hysteresis (*H*) and sorption energies (ΔG) for penoxsulam, molinate, bentazon and MCPA in soils.

Soil	*Penoxsulam* *Kd*[1] *(mL g^{-1})*	*H*	ΔG^2 *(kJ mol^{-1})*	*Molinate* *Kd (mL g^{-1})*	*H*	ΔG *(kJ mol^{-1})*
Melozal	8.85 ± 1.58	0.61 ± 0.06	−13.95 ± 0.23	1.93 ± 0.01	0.74 ± 0.01	−12.11 ± 0.09
Parral	8.84 ± 2.14	0.80 ± 0.07	−12.93 ± 0.33	2.08 ± 0.02	0.40 ± 0.01	−12.49 ± 0.02
San Carlos	10.69 ± 1.58	0.73 ± 0.04	−12.59 ± 0.19	2.30 ± 0.01	0.93 ± 0.01	−10.59 ± 0.01
Panimavida	4.23 ± 0.73	0.84 ± 0.02	−11.34 ± 0.22	1.72 ± 0.01	0.55 ± 0.01	−11.76 ± 0.01
	Bentazon			*MCPA*		
	Kd (mL g^{-1})	*H*	ΔG *(kJ mol^{-1})*	*Kd (mLg^{-1})*	*H*	ΔG *(kJ mol^{-1})*
Melozal	0.28 ± 0.01	0.33 ± 0.01	−7.97 ± 0.20	2.08 ± 0.03	1.03 ± 0.02	−12.80 ± 0.07
Parral	0.17 ± 0.01	0.43 ± 0.01	−7.11 ± 0.71	0.14 ± 0.02	0.61 ± 0.03	−8.14 ± 0.73
San Carlos	0.42 ± 0.01	0.39 ± 0.01	−7.63 ± 0.28	2.72 ± 0.01	0.94 ± 0.01	−11.67 ± 0.06
Panimavida	0.11 ± 0.01	0.47 ± 0.05	−6.49 ± 0.48	0.74 ± 0.01	0.73 ± 0.01	−9.85 ± 0.17

[1] $Kd = Kf_{ads}$*Ce$^{(1/nads-1)}$. Ce = Herbicides in solution at maximum concentration.
[2] ΔG = -R*T*Ln (Kf$_{ads}$). R = Gas Constant (8.314 J K^{-1} mol^{-1}); T = absolute temperature (°K).[36]

and significance (Table 4). In addition, MCPA adsorption was correlated to pH, followed by clay content and in a third level HA (Table 4). Multiple linear regressions gave a high determination coefficient ($r^2 = 0.98$ and 0.99 respectively) for both herbicides (Table 5). However, in the case of MCPA the model did not include soil pH as a significant parameter. Thus bentazon sorption is more sensitive to soil pH variations than other acidic herbicides.[15] The same authors found that 2,4-D and bentazon soil adsorption were explained in a 91 % by pH and organic matter content, which agrees in part with our results. The adsorption values were correlated to HS, a principal component of organic matter. Correlations were improved to r = 0.884 and r = 0.727 for bentazon and MCPA, respectively, in comparison to the correlation observed for organic carbon content (r = 0.767 and r = 0.614, respectively). Contrary to other results,[31,32] in this study, HA showed a high relationship with bentazon and MCPA adsorption, being more important in the case of the last one (Table 4).

The variations observed in the correlations values between herbicide *Kd* and HS or HA for this type of soils (paddy rice sediment) are indicative of specific relationship. In the case of penoxsulam and molinate, the highest correlation to organic phase was related to HS rather than HA, indicating that other components of the humic fraction, like fulvic acids and humins, would not be significant for these herbicides adsorption. On the other hand, bentazone adsorption did not show any variation for the correlation values respect to HS or HA (Table 4), indicating no affinity for any HS components (humic or fulvic acids). Finally, MCPA adsorption was more related to HA content; the other components of the HS. These results suggest that considering only organic matter content to describe herbicide soil adsorption is not enough. Humic substances should be included in the analysis to determine pesticide availability in soil solution and their leaching potentials.[32]

Environmental considerations

The sorption results obtained in each soil were incorporated in the *Rf* leaching index proposed by Hamaker.[33] The Rf index characterizes potential for herbicide leaching better than other more complex indexes.[34]

The Hamaker *Rf* (Eq. 2) is calculated by considering soil organic adsorption coefficient (K_{oc}), organic carbon

Table 4. Pearson correlation values between soil properties and *Kd*. Numbers between parentheses are *p* values.

Soil properties	*Penoxsulam*	*Molinate*	*Bentazone*	*MCPA*
pH	−0.902 (*0.0001*)	−0.805 (*0.0016*)	−0.947 (*0.0001*)	−0.884 (*0.0001*)
CEC	−0.693 (*0.012*)	−0.420 (*0.174*)	−0.659 (*0.019*)	−0.785 (*0.002*)
Sand	0.107 (*0.739*)	−0.003 (*0.991*)	0.494 (*0.102*)	0.836 (*0.0007*)
Clay	−0.533 (*0.073*)	−0.258 (*0.416*)	−0.596 (*0.041*)	−0.819 (*0.001*)
Loam	0.655 (*0.021*)	0.345 (*0.271*)	0.541 (*0.068*)	0.664 (*0.018*)
OC	0.445 (*0.146*)	0.683 (*0.014*)	0.767 (*0.003*)	0.614 (*0.033*)
HS	0.614 (*0.033*)	0.791 (*0.002*)	0.884 (*0.0001*)	0.727 (*0.007*)
HA	0.525 (*0.079*)	0.576 (*0.049*)	0.885 (*0.0001*)	0.941 (*0.0001*)
E4/E6	0.376 (*0.227*)	0.686 (*0.013*)	0.427 (*0.165*)	0.039 (*0.903*)

Table 5. Herbicide multiple regression models for soil adsorption. Parameters included in the model are significant at $p < 0.05$.

Herbicide	*Adsorption regression model*	*Multiple r²*
Penoxsulam	$Kd = -5.338\ \mathrm{pH} + 38.104$	0.81*
Molinate	$Kd = -0.604\ \mathrm{pH} - 0.508\ \mathrm{HS} + 0.165\ \mathrm{E4/E6} + 4.857$	0.97*
Bentazon	$Kd = -0.238\ \mathrm{pH} + 0.239\ \mathrm{HS} + 1.508$	0.98*
MCPA	$Kd = 3.918\ \mathrm{HA} - 0.082\ \mathrm{Clay} + 0.378\ \mathrm{HS} + 2.472$	0.99*

(*) Indicates that multiple correlation coefficient between the observed and predicted *Kd* are highly significant ($p \leq 0.001$)

content (OC), soil bulk density (ρ), and volumetric soil water content (θ).

$$Rf = \frac{1}{1 + \left(Koc * 0.01 * OC * \rho * \left(\left(\frac{1}{\theta^{0.67}}\right)^{-1}\right)\right)} \tag{2}$$

The Koc was determined according to Equation 3, OC and ρ comes from Table 1, and θ at saturation soil condition was obtained from Rosseta 1.2 program surrogate soil texture data and bulk density (Table 1).[35]

$$Koc = \frac{Kd}{OC} * 100 \tag{3}$$

The results showed that the herbicides soil leaching risk was variable depending on soil properties and their effect on herbicides adsorption. Using the calculated Rf values and according to Helling mobility class,[36] penoxsulam should be considered as an immobile herbicide in San Carlos soil ($Rf < 0.1$), and low mobility in Melozal, Parral, and Panimavida soils ($0.1 < Rf < 0.34$) (Table 6). On the other hand, molinate could be classified as a low mobility herbicide in Melozal, Parral, and San Carlos soils. However, in Panimavida, molinate could be classified as having an intermediate mobility ($0.35 < Rf < 0.64$). Bentazon, can be definitively classified as a mobile herbicide in Melozal, Parral, and San Carlos soils ($0.65 < Rf < 0.89$), and very mobile in Panimavida soil ($0.9 < Rf < 1.0$). MCPA, compared to the others, was the only herbicide that showed a very variable leaching risk that depended on the soil type. Thus, MCPA in Parral soil would be the most mobile herbicide, more than bentazon (Table 6), whereas in Panimavida soil it could be classified with a leaching risk between molinate and bentazon. However, in Melozal and San Carlos, MCPA could be considered as low mobility herbicide.

Table 6. Herbicides leaching risk analysis using the Rf leaching index.

	Herbicide Rf value			
Soil	*Penoxsulam*	*Molinate*	*Bentazon*	*MCPA*
Melozal	0.104	0.343	0.785	0.322
Parral	0.107	0.331	0.856	0.876
San Carlos	0.087	0.303	0.705	0.269
Panimavida	0.211	0.393	0.912	0.604

Conclusions

Based on the experimental results, we can conclude that the adsorption processes for these four herbicides in paddy rice soil would be related principally to the soil pH and the humic substances present in the organic phase. The interrelation of these two soil-parameters would have generated conditions that modified the adsorption process of nonionic herbicides, like molinate, or ionic compounds, like MCPA. According to soil–herbicide sorption relationship, and considering its variability in each soil and the potential for groundwater contamination, it would be adequate to develop weed control management strategies in rice production, limiting the use of some herbicides in areas that predispose conditions for soil leaching.

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