

Sorption of Aceto Lactase Synthase Inhibiting Rice Herbicides in Texturally Different Soils

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The aceto lactase synthase inhibiting herbicides are used frequently to control weeds in wetland rice ecosystems due to low dose and flexibility in time of application. Their occurrence in surface and groundwater is a cause for concern as they have medium to high mobility in environment. Thus, the present study was undertaken to assess the sorption behaviour of pyrazosulfuron ethyl and bispyribac sodium in different agricultural soils. Adsorption of both pyrazosulfuron ethyl and bispyribac sodium was best correlated with clay and organic carbon content, soil reaction and base saturation percent of soils. Pyrazosulfuron ethyl sorption was high in low organic carbon soils and bispyribac sodium sorption was high in high organic carbon soils. Bispyribac sodium sorption was masked by high organic carbon content in sandy clay and silty clay soils. The soil organic carbon coefficient (K_{oc}) ranged from 11.6 to 81.8 for pyrazosulfuron ethyl and 4.6 to 198.1 for bispyribac sodium. The sorption of these herbicides fitted well with Freundlich equation. Freundlich constant (K_f) ranged from 0.38 to 0.76 and 0.30 to 1.05 mL g⁻¹ for pyrazosulfuron ethyl and bispyribac sodium, respectively. The desorption rate of both the herbicides was high in high organic carbon soils. The hysteresis index was ranged from 1.7 to 4.1 for pyrazosulfuron ethyl and from 0.22 to 0.64 for bispyribac sodium in different soils and found that desorption of both herbicides from clay and silty clay loam soils was more difficult. The results indicate that the mobility of pyrazosulfuron ethyl is medium to high and bispyribac sodium is low to medium and varied according to soils.

Keywords: Adsorption, Bispyribac sodium, Organic carbon, Desorption, Hysteresis, Pyrazosulfuron ethyl, Soil texture.

INTRODUCTION

Use of herbicides for weed control has made a significant contribution in increasing the crop productivity and reducing the labor in agriculture through efficient control of unwanted plants and weeds. The efficacy of herbicides on weed control depends on several factors like method and time of application, chemical property of herbicide, its mode of action and fate in soil environment. The fate of herbicides applied in agricultural ecosystems is governed by the transfer and degradation processes and their interaction with soil microorganisms. The ability of the herbicides to adsorb and desorb from soil is a key process that affects its mobility, rate of degradation and ecotoxicological impact [1] on environment. The adsorption is a reversible process involving the nonspecific attraction and retention of a chemical to the soil particle surface. The affinity of the chemical to the surface is affected mainly by the nature and properties of the soil components, the physico-chemical properties of the pesticide and the soil environment [2]. The adsorption is also related to the water solubility of the herbicide that lesser the solubility, stronger will be the sorption to soil particles [3]. The soil properties which influence the pesticide

sorption are organic matter content, clay content, surface area, pH, temperature and moisture content [2-4]. It is generally established that the sorption checks the pesticide degradation rate by reducing their partition into the soil liquid phase [5].

The sorption of pesticides is usually studied using the linear and non-linear sorption isotherms built using the residual concentration of pesticides in soil solution at equilibrium and the quantity that is sorbed to or from the soil sorption sites. The degree of sorption from solution to solid phase of the soil is described by a soil-water partition coefficient (K_d) and Freundlich model, a most popular sorption isotherm for a single-solute system at equilibrium. The K_d for most nonionic chemicals is determined primarily by the soil organic carbon fraction [6] and K_{oc} values provide a correlation between K_d and soil organic carbon fraction. Hence the sorption and desorption study of an herbicide, can generate useful information regarding its fate in soil and also provide a basis for its effective use in agricultural field to reduce undesirable effects by carry over, contamination and phytotoxicity. The literature survey [7,8] showed that less attention has been paid to desorption compared to adsorption, especially for the new generation sulfonyl area and pyrimidine benzoate group herbicides.

Among the herbicides with various modes of action of current use, the aceto lactase synthase inhibitors are in widespread use worldwide. These herbicides are more popular due to its high activity at low application rates and low mammalian toxicity. Bispyribac sodium and pyrazosulfuron ethyl are the two important aceto lactase synthase inhibiting herbicides occupying the central position for weed control in paddy cultivation. They are systemic and moves throughout the plant tissue and works by interfering with production of a plant enzyme aceto lactase synthase which is necessary for the growth of plants.

Bispyribac-sodium [sodium 2,6-bis(4,6-dimethoxy-pyrimidin-2-yl-oxy)benzoate] is a selective, moderately persistence pyrimidine benzoates group herbicide and is mobile in most soils [9]. It is considered highly toxic and belongs to the toxicological class II with a soil half-life of less than 10 days [10,11]. The bispyribac sodium has potential for leaching and runoff due to medium K_{oc} value of 114 which showed significant correlation with the organic carbon, clay content and cation exchange capacity of the soils. Further the cationic nature of bispyribac sodium in soil solution influences its sorption to soil with the desorption coefficient (K_d) values ranged from 0.604 to 2.01 mL/g [12]. EFSA [9] found that it is moderately mobile in environment and reported the K_{foc} value of 143-604 mL/g for bispyribac sodium in different soils.

Pyrazosulfuron ethyl {ethyl 5-[(4,6-dimethoxy-pyrimidin-2-ylcarbamoyl)-sulfamoyl]-1-methylpyrazole-4-carboxylate}, a new rice herbicide belonging to the sulfonylurea group is registered in India to use in paddy fields. It is moderately mobile and has a soil half-life of 5.8 to 7.1 days with the K_{oc} of 83-141 [13]. The persistence and fate of sulfonylurea compounds in soil are determined by many factors *viz.*, soil acidity, temperature and moisture content, soil microbial diversity and biochemical activity [14]. Abiotic degradation of sulfonyl ureas was rapid at low pH than at neutral or basic pH and its removal by plant, bio-efficacy and transport mainly depend on sorption equilibrium [15]. Naveen *et al.* [16] reported that the sorption of pyrazosulfuron ethyl was significantly increased by the organic matter content of soil and not by clay content.

Assessing various factors that may impact sorption of rice herbicides is fundamental for predicting and understanding the mobility in soil, degradation in the field and possibility of its movement to water bodies. Hence, a systematic study on the sorption and movement of these rice herbicides in different agricultural soils would help in the assessment of surface and ground water contamination. Consequently, a comprehensive study was conducted to find out the sorption and mobility of aceto lactase synthase inhibiting herbicides namely bispyribac sodium and pyrazosulfuron ethyl in different agricultural soils to assess their risk potential to the environment.

EXPERIMENTAL

Chemical and physical characterization of agricultural

soil: The four representative soils used in the present study were collected from different agricultural sites namely clay from wet land farm, Tamilnadu Agricultural University, Coimbatore (30.48°N, 76.6°E); silty clay loam from Agricultural Research Station, Tamilnadu Agricultural University, Bhavanisagar

(30.48°N, 76.6°E) and silty clay from RRS, IARI, Ooty (30.48°N, 76.6°E), sandy clay from the farmer's field, Ooty (30.48°N, 76.6°E) in Tamil Nadu, India. The surface soils from a depth of 0-30 cm were collected, air-dried and sieved to pass through 2 mm mesh. The chemical and physical characterization of these soils was done following the methods described by Jackson [17]. The soil textural fractions were assessed by the International pipette method and organic carbon was analyzed by the wet digestion method.

Sorption study: The adsorption and desorption isotherm studies were performed using varying concentrations of each herbicides at 0, 0.5, 1, 2.5, 5, 10, 20, 40 and 50 mg L⁻¹. To minimize the changes in ionic strength and to avoid dispersion, 0.01 mM CaCl₂ solution was used as a background. First, the herbicides were dissolved in methanol and diluted by 0.01 mM CaCl₂ solution to obtain the working solutions of different concentrations. For adsorption studies, 2 g of processed soil samples were placed in a centrifuge tubes to which different concentrations of each herbicides prepared in 0.01 mM CaCl₂ were added and the experiment was duplicated. The soil: solution ratio of 1:5 was used for this study. The soil solution suspension in centrifuge tubes was shaken for 12 h in an end over end shaker at ambient temperature to attain equilibrium [18]. After equilibration, the soil suspension was centrifuged at 1200 rpm for 15 min and the supernatant was filtered through Paul nylon membrane filters of < 2 μm. The herbicides equilibrium concentration was determined in HPLC-DAD after extracting them from the filtrate. The amount of pesticide adsorbed was calculated as the average of the three replicates. A blank sample was also kept to assess the effects of herbicide adsorption onto the centrifuge tubes and to assess the possible degradation during the process.

The desorption experiment for each herbicide molecule was performed instantly after the adsorption experiment. The supernatant was decanted and the herbicides residue present in the soil was analyzed. Then equal volume of the fresh 0.01 mM CaCl₂ solution was added to the tubes which contain the soil sediments after the completion of sorption experiment. The mixture was shaken on a horizontal shaker at 200 rpm for 8 h at ambient temperature, centrifuged at 5000 rpm for 5 min and then filtered. These steps were repeated three times consecutively and the combined filtrate from each treatment was subjected to herbicides residue analysis.

Chemicals, reagents and soil: A certified reference standard of bispyribac sodium (purity 96.55 %) and pyrazosulfuron ethyl (purity 98 %) was purchased from Sigma-Aldrich and the test chemicals of the herbicides namely Nominee gold (bispyribac sodium 10 % EC) and sathi (pyrazosulfuron ethyl 10 % WP) was purchased from the market. All the solvents were of analytical grade and purchased locally. Anhydrous sodium sulfate (AR grade) was used as a drying agent for different samples. The HPLC-grade hexane and 0.2 μm filtered Milli-Q water were used for HPLC analysis.

Instrument and operating conditions: The Agilent HPLC (1200 series) equipped with diode array detector (DAD) detector, binary pump and auto sampler with rheodyne injection assembly was used for the quantitative analysis of herbicides residue and the computer enabled software EZChrom was used for the

acquisition of chromatograms. The separation of compounds achieved by the Agilent Eclipse XDB-C 18, 5 μm , 4.6 \times 150 mm column kept in thermo stated oven maintained at 30 $^{\circ}\text{C}$. The acetonitrile: water with 0.1 % H_3PO_4 (70:30 v/v) was used as mobile phase for both the herbicides. The injection volume of sample was 10 μL and the flow rate of mobile phase was 0.5 mL min^{-1} . The detection was performed at 250 and 236 nm for bispyribac sodium and pyrazosulfuron ethyl respectively since the interferences were minimal at these wavelengths. The retention time of bispyribac sodium and pyrazosulfuron ethyl under the above instrumental conditions was 4.52 and 3.44 \pm 0.2 min respectively. A calibration curve of each herbicide was prepared by plotting concentrations on X-axis against the average peak area on Y-axis.

Extraction and clean-up of herbicides: Bispyribac sodium was extracted from the soil solution with 100 mL mixture of methanol and acetonitrile. This mixture was subjected to 1 h shaking and filtered through Whatman no. 42 filter paper. The filtered solution was passed through a bed of sodium sulphate using dichloromethane and elute was acidified using formic acid and concentrated in a rotary vacuum evaporator at 40 $^{\circ}\text{C}$. The concentrated elute was cleaned using Bond elut PLEXA PAX SPE cartridge of Varian using 2 % methanol as eluent. The final dried residue was re-dissolved in acetonitrile for HPLC analysis.

Pyrazosulfuron ethyl was extracted from the soil solution with 100 mL of methanol and the solvent was removed in rotary vacuum evaporator at 40 $^{\circ}\text{C}$. The residue was re-dissolved in 50 mL of dichloromethane and eluted through the bed of anhydrous sodium sulfate. The eluted layer was concentrated in a rotary vacuum evaporator at 40 $^{\circ}\text{C}$ to moistened level and finally re-dissolved in HPLC grade methanol for HPLC analysis.

Method validation and detection limits: Method validation was accomplished through recovery studies before analyzing the herbicide treated soil samples as described by Janaki *et al.* [19]. The extraction and cleanup of each herbicide was completed as described in the methodology. The quantification of herbicides residue was done by comparing the peak response for samples with peak area of the standards. The standards were injected seven times to confirm the precision of the method and to fix the instrument detection limit (IDL).

Data analysis: The herbicide sorption is described using simple linearized relationship.

$$K_d = C_s/C_e \quad (1)$$

where C_s is the amount of herbicide sorbed by the soil [mg kg^{-1}] and C_e is the herbicide concentration in the soil solution at equilibrium [mg L^{-1}]. The value of K_d (partition coefficient) was determined from the slope of the linear plots of sorbed *vs.* aqueous herbicide concentrations. The normalized non-linear Freundlich equation was also used to describe the adsorption isotherm for both the herbicides since the soils are heterogeneous in nature.

$$x/m = K_f C_s^{1/n} \quad (2)$$

where x/m is the micro moles of herbicide adsorbed per kilogram of soil, C_s is micro moles of herbicide per liter of solution after equilibration, K_f is the Freundlich coefficient (mL/g) and $1/n$ is a dimensionless parameter. Sorption coeffi-

cients K_f and n were determined by plotting the logarithmic form of the Freundlich equation.

The adsorption coefficient (K_f) was calculated as a function of the organic carbon content of the soil using the equation $K_{OC} = K_f/\%OC \times 100$. The affinity of the herbicides towards the clay content of the soils was also evaluated by calculating K_c using the formula $K_c = (K/C) \times 100$, where K is the Freundlich constant and C is the percent of clay content in soil.

Hysteresis index (HI) was calculated for the adsorption-desorption isotherms according to the equation hysteresis index (HI) = (n desorption)/(n adsorption), where n desorption and n adsorption are the Freundlich constants obtained for desorption and adsorption isotherms, respectively.

Pearson correlation analysis was carried out between the sorption coefficients (K_d) of each herbicides and different soil physico-chemical properties at a significance level of $P = 0.05$.

RESULTS AND DISCUSSION

Chemical and physical characterization of soils: Table-1 shows chemical and physical features of the agricultural soil samples used in the present study. Sandy clay and silty clay soils has higher organic carbon content (4.52-6.58 %) than silty clay loam (0.59 %) and clay (0.53 %) soils. Hence the former two soils were referred as high organic carbon soils while later are known as low organic carbon soils. The clay content of the soils varied from 23.5 to 44.5 % across different soils with high clay in clayey soil and low in silty clay loam soil. The herbicides studied were not detected in the soil samples used for the sorption experiment suggesting the absence of pre-contamination of both the herbicides in the soils used for the study.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS
OF THE SOILS USED FOR THE STUDY

Properties/details	Clay	Silty clay loam	Sandy clay	Silty clay
Clay (%)	44.50	23.52	34.06	36.12
Sand (%)	18.64	52.00	51.20	11.04
Silt (%)	36.79	24.50	11.00	52.79
Soil reaction (pH)	8.21	7.01	5.81	4.29
EC (dS/m)	0.52	0.18	0.19	0.16
Organic carbon (%)	0.53	0.59	4.52	6.58
Available N (kg/ha)	172	232	297	298
Available P (kg/ha)	17.5	16.7	13	12.1
Available K (kg/ha)	512	274	266	212
CEC (c.mol (p ⁺)/kg soil)	36.15	23.52	41.52	46.15
Bispyribac sodium (%)	97.2	81.2	16.15	11.52

Sorption behaviour in soils: The equilibrium distribution of both pyrazosulfuron ethyl and bispyribac sodium in the sorbed and solution phases is presented in Figs. 1 to 2. The adsorbed content C_s (mg/kg) showed increasing trend with increase in the equilibrium concentration of the herbicide C_e (mg/L) in solution (Fig. 1) for both the herbicides. While the sorption of pyrazosulfuron ethyl was found to be high in low organic carbon (clay and silty clay loam) soils, bispyribac sodium sorption was high in high organic carbon soils (sandy clay and silty clay). The adsorption of pyrazosulfuron ethyl was in the order of clay \geq silty clay loam $>$ sandy clay $>$ silty

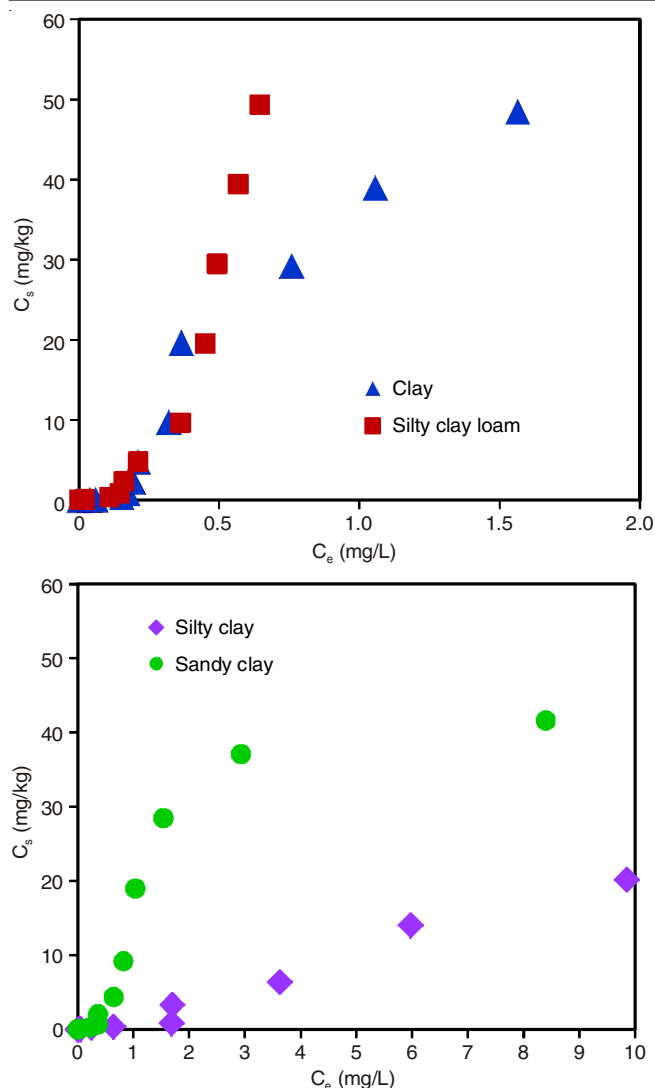


Fig. 1. Sorption of pyrazosulfuron ethyl to different soils

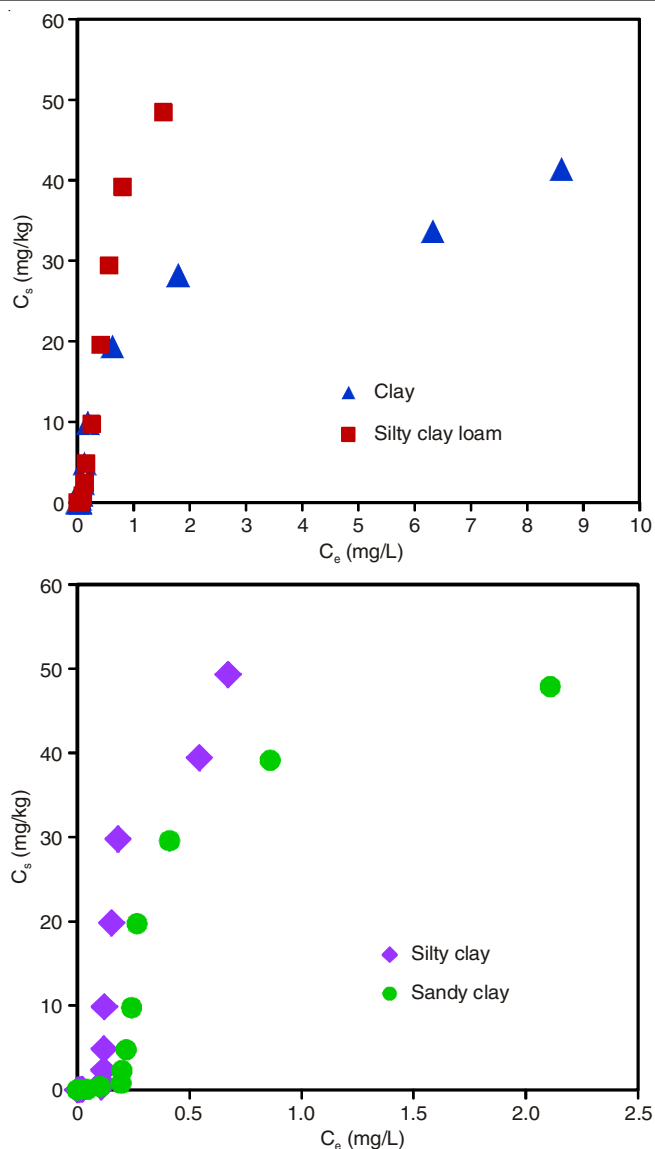


Fig. 2. Sorption of bispyribac sodium to different soils

clay while bispyribac sodium followed the order of silty clay > sandy clay ≥ silty clay loam > clay soils. Hence it was found that, not only the organic carbon content but also interaction of other properties of soils and herbicide molecules were also influenced the herbicides sorption in different soils [2]. In the present study, the pyrazosulfuron ethyl and bispyribac sodium sorption was influenced highly by the clay and organic carbon contents respectively, besides the solubility of the herbicides have also played a role in influencing the sorption of these herbicides [20]. The results were confirmed by the distribution coefficient (K_d) values (Table-2) which was high in clay and silty clay soils for pyrazosulfuron ethyl and sandy clay and silty clay loam soils for bispyribac sodium. The K_d values were calculated based on the solution concentration and assumes

that the rest of the herbicides were sorbed by the adsorbent and ignores the degradation, volatilization and other processes that may cause dissipation or non-recovery of herbicides from the soil system [4]. Though the force of attraction couldn't be suggested by K_d values, the saturation capacity of the soil for a particular herbicide could be predicted. The K_d showed significant saturation of the pyrazosulfuron ethyl and bispyribac sodium (Figs. 1 and 2) to the adsorption sites over the broad concentration range studied and found that the K_d values decreased beyond pyrazosulfuron ethyl and bispyribac sodium concentration of 20 mg kg⁻¹ in all soils excluding silty clay loam soil for pyrazosulfuron ethyl and silty clay loam and silty

Soil types	Pyrazosulfuron ethyl			Bispyribac sodium		
	Equation	r ²	K _d	Equation	r ²	K _d
Clay	y = 0.027x + 0.076	0.939**	21.2	y = 0.183x - 0.886	0.790*	21.5
Silty clay loam	y = 0.011x + 0.166	0.928**	7.9	y = 0.025x + 0.017	0.900**	32.9
Sandy clay	y = 0.129x - 0.232	0.652	1.51	y = 0.030x - 0.004	0.752	66.4
Silty clay	y = 0.558x + 0.116	0.965*	29.7	y = 0.011x + 0.051	0.810*	31.5

clay soils for bispyribac sodium. The soil characteristics such as organic carbon ($r^2 = 0.719-0.956^*$), soil reaction ($r^2 = 0.822-0.829^*$) and base saturation percent ($r^2 = 0.859-0.898^*$) showed a significant and good correlation with partitioning coefficient (K_d) of both the herbicides. While CEC showed good correlation with bispyribac sodium sorption ($r^2 = 0.959^{**}$), the EC showed significant correlation with pyrazosulfuron ethyl sorption ($r^2 = 0.953^{**}$). Accordingly it was observed that both pyrazosulfuron ethyl and bispyribac sodium sorption in soil was influenced by the clay, organic carbon, base saturation percent and soil reaction. In addition, it was found that while pyrazosulfuron ethyl sorption was significantly influenced by the EC, bispyribac sodium sorption was influenced by CEC of the soils.

The results of the linearized and non-linearized Freundlich sorption isotherms of pyrazosulfuron ethyl and bispyribac sodium herbicides in different soils are presented in Table-2. The linearized sorption of pyrazosulfuron ethyl showed good fit in clay (0.939**), silty clay loam (0.928**) and silty clay (0.964**) soils and the fit for bispyribac sodium was good only in silty clay loam soil (0.900*). The linear sorption fit of both pyrazosulfuron ethyl and bispyribac sodium was very poor in sandy clay soil and could be due to the high sand content which might have reduced the sorption of these herbicides by the low interaction of the binding sites with sorbate and also by masking the effect of clay and organic carbon content.

The most accepted and established non-linear sorption isotherm in describing the herbicides in heterogeneous medium is the Freundlich equation and the K_f (Freundlich constant), $1/n$ (slope) and K_{oc} (organic carbon constant) values of both the herbicides are given in Tables 3 and 4. The sorption of both pyrazosulfuron ethyl and bispyribac sodium were found linear in all the soils as 'n' is nearer to unity and adsorption coefficient (K_f) of bispyribac sodium was high in low organic carbon soils (clay and silty clay loam) and *vice versa* for pyrazosulfuron ethyl. This confirmed that the sorption of bispyribac sodium depends on clay content and when the organic carbon was high, the effect of clay was masked on influencing its sorption in soils. However the pyrazosulfuron ethyl sorption was highly influenced by both the clay and organic carbon

content and has high K_f value (0.760) in silty clay soil followed by sandy clay (0.552), clay (0.435) and silty clay loam (0.377) soils. The value of the exponent $1/n$ was nearer to 1 for both the herbicides in all the soils except silty clay and sandy clay for pyrazosulfuron ethyl signified a linear relationship between the herbicide concentration and adsorption. This indicates that these aceto lactase synthase inhibiting herbicides could adsorb to the clay and organic carbon fractions in the soil.

The organic carbon normalized sorption coefficients (K_{oc}), a major mechanism responsible for the pesticide sorption in soils, was found to be ranged from 11.6 to 81.8 for pyrazosulfuron ethyl and 4.6 to 198.1 for bispyribac sodium across different soils with highest K_{oc} in low organic carbon soil. Hence it is established that the sorption is not only influenced by the organic carbon content but also by the type of clay and organic matter [21] fractions, soil texture [22], soil pH, CEC, sand, silt fraction and also the chemical properties of the herbicides itself [23]. It was found that the soil low in organic carbon content sorbed higher quantity of both the herbicides per unit of soil organic carbon and *vice versa*; consequently, higher K_{oc} was found in clay and silty clay loam soils for both the herbicides. As K_{oc} decreases, mobility of the herbicides increases hence the potential of these herbicides to leach is high in sandy clay and silty clay soils when compared to clay and silty clay loam soils. Affinity of the herbicides to the clay content (K_c) was found to be low in clay and high in silty clay for pyrazosulfuron ethyl and *vice versa* for bispyribac sodium in the different soils studied. K_{oc} value of pyrazosulfuron ethyl was high in low organic carbon soils and K_c was high in high organic carbon soils and confirms that the pyrazosulfuron ethyl sorption was influenced by both clay and organic carbon content whereas the effect of clay on sorption was masked when organic carbon was high. Hence the ratio of clay and organic carbon is a significant parameter in predicting the sorption of herbicides in soil [23].

Influence of soil and herbicide properties on sorption:

The variable soil and herbicide properties may also have resulted in significant variations of the K_d and K_f value. It was found that the lower K_{oc} of pyrazosulfuron ethyl in silty clay and sandy clay soils is not only due to high organic carbon content

TABLE-3
NON-LINEAR FREUNDLICH CONSTANTS, K_{oc} , K_c AND HYSTERESIS INDEX
VALUES FOR PYRAZOSULFURON ETHYL SORPTION IN DIFFERENT SOILS

Soil types	Sorption					Desorption			Hysteresis index
	K_f (mL/g)	$1/n$	r^2	K_{oc}	K_c	K_f (mL/g)	$1/n$	r^2	
Clay	0.434	0.785	0.805*	81.8	0.97	1.982	0.483	0.935**	2.528
Silty clay loam	0.377	0.853	0.972**	63.8	1.60	2.008	0.995	0.788*	2.355
Sandy clay	0.553	0.457	0.792	12.2	1.62	0.551	0.635	0.896*	1.717
Silty clay	0.760	0.026	0.939**	11.6	2.10	1.071	0.851	0.890*	4.075

TABLE-4
NON-LINEAR FREUNDLICH CONSTANTS, K_{oc} AND HYSTERESIS INDEX
VALUES FOR BISPYRIBAC SODIUM SORPTION IN DIFFERENT SOILS

Soil types	Sorption					Desorption			Hysteresis index
	K_f (mL/g)	$1/n$	r^2	K_{oc}	K_c	K_f (mL/g)	$1/n$	r^2	
Clay	1.050	1.244	0.801*	198.1	2.36	0.596	0.311	0.953**	0.250
Silty clay loam	0.568	1.036	0.901**	96.3	2.42	0.237	0.226	0.871*	0.218
Sandy clay	0.430	0.850	0.552	9.5	1.13	0.503	0.541	0.860*	0.637
Silty clay	0.304	1.004	0.929**	4.6	0.84	0.959	0.582	0.884*	0.580

and type of organic matter but also the low soil pH (4.29 to 5.81) which might have enhanced the hydrolysis and abiotic degradation of pyrazosulfuron ethyl in soils. Similarly, the bispyribac sodium sorption in soil was influenced by the cationic nature in addition to its high solubility (73,000 mg/L). The high sorption in clay and silty clay loam soils could be attributed to the higher clay content and restricted mobility and availability in solution. Hence it is observed that the soil adsorption of herbicide is inversely related to the herbicide mobility [24]. From K_{oc} values, it is inferred that the mobility of pyrazosulfuron ethyl is low to high while bispyribac sodium is low to medium [25] and has been influenced by the content of clay, organic carbon and soil pH and the chemical properties of herbicides and its water solubility. Unlike pyrazosulfuron ethyl, the adsorption coefficient (K_f) of bispyribac sodium in soils was significantly influenced by both the clay and organic carbon content and was confirmed by the high K_{oc} and K_c values of bispyribac sodium in low organic carbon soils which inferred that the sorption in soils was influenced also by the clay content and its type. Singh and Singh [26] also reported a positive correlation of soil pH and clay content with the bispyribac sodium sorption in soils. The presence of expanding type of clays like montmorillonite and vermiculite in low organic carbon soils (clay and silty clay) increased the herbicide sorption per unit of organic carbon and clay content through the greater availability of surface area and the high energy sites for binding. Calvet [7] also reported that the inorganic and organic surfaces make up the soil adsorption complex.

The influence of other soil properties on K_d and K_f was studied and found that they exhibited interactive effect on the sorption of both the herbicides in different textured soils (Tables 3 and 4). It was found that the K_f value of pyrazosulfuron ethyl and bispyribac sodium was significantly influenced by the soil pH, EC, available nitrogen, phosphorus, CEC and base saturation percent. This result confirms that the sorption of herbicides in soil is not only influenced by the organic carbon and clay but also by other soil properties and by their own property. Singh *et al.* [4] also found that the soil reaction and CEC significantly influenced the sorption of s-triazine and thiocarbamate in different soils.

Shape of sorption isotherm in soils: The information on the sorption mechanisms is provided by the shape of adsorption isotherms. According to the classification of Giles *et al.* [27], the shape of pyrazosulfuron ethyl and bispyribac sodium sorption isotherms in the present study based on the initial slope of sorption curves was found to be 'S' type in all soils (Figs. 2 and 3). This showed that the sorption of both the herbicides to the binding sites becomes easier as their concentration in soil solution increased due to the reduced competition of the solvent or another species. Though the 'S' curve is a charac-

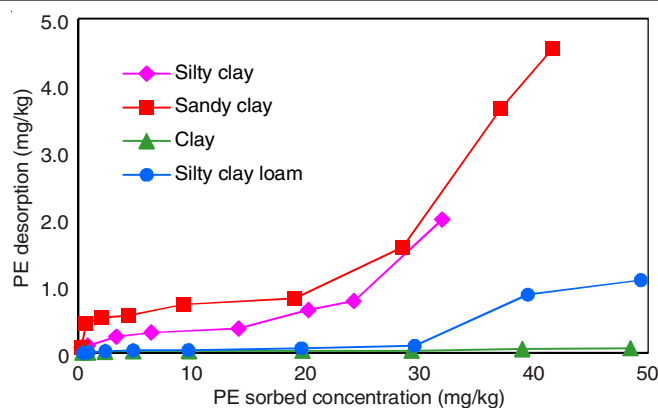


Fig. 3. Desorption of pyrazosulfuron ethyl from different soils

teristics of the organic molecules sorption on clay surfaces [28], the type of clay and organic matter content also have influence on the sorption. Weber *et al.* [29] have noted that adsorption of fluridone was S-isotherm in soils having a high montmorillonite content and a low organic matter content. Angemar *et al.* [30] found that the adsorption isotherm of bromacilis transformed from an 'L' to an 'S' type when the organic matter of a montmorillonitic soil is oxidized. In the present study, organic matter rich soils *viz.*, silty clay and sandy clay expressed 'S' curve and established that if the soils are high in clay %, the effect of organic matter is additive in enhancing the sorption of pyrazosulfuron ethyl and bispyribac sodium. However it is difficult to find out the exact effect of clay and organic carbon individually on herbicides sorption in soils. It confirms that the shape of pyrazosulfuron ethyl and bispyribac sodium isotherm reveals only the type of sorption and not the force of attraction and nature of sorbent involved in the sorption process.

Desorption from soils and hysteresis in sorption: The desorption behaviour of herbicides is crucial as it determines the release rate and potential mobility of herbicides in the soil and is essential to develop management measures for the highly persistence herbicides contaminated soils. Thus, desorption isotherm for both pyrazosulfuron ethyl and bispyribac sodium was studied to assess the desorption potential of adsorbed quantity and the results are revealed in Figs. 3 and 4. The amount of adsorbed pyrazosulfuron ethyl desorbed from soil was ranged from 0.01, 0.09, 0.36 and 0.09 % respectively for clay, silty clay loam, sandy clay and silty clay soils (Table-5). Similarly the bispyribac sodium desorption was ranged from 0.09, 0.16, 0.33 and 0.06 % respectively for clay, silty clay loam, sandy clay and silty clay soils. Irrespective of herbicides and soil type, maximum 2.0 % of the sorbed quantity alone desorbed from the soils and showed extensive hysteresis. The hysteric behaviour is extensive for silty clay loam soil followed

TABLE-5
LINEARIZED DESORPTION AND K_d VALUES FOR PYRAZOSULFURON ETHYL AND BISPYRIBAC SODIUM IN DIFFERENT SOILS

Soil types	Pyrazosulfuron ethyl			Bispyribac sodium		
	Equation	r^2	K_d	Equation	r^2	K_d
Clay	$y = 0.001x + 0.014$	0.903**	0.08	$y = 0.016x + 0.271$	0.959**	1.98
Silty clay loam	$y = 0.022x - 0.011$	0.789	1.03	$y = 0.016x + 0.683$	0.797	2.89
Sandy clay	$y = 0.099x - 0.021$	0.859*	0.11	$y = 0.072x - 0.143$	0.933**	2.14
Silty clay	$y = 0.045x + 0.088$	0.859*	0.51	$y = 0.033x + 0.081$	0.808*	3.88

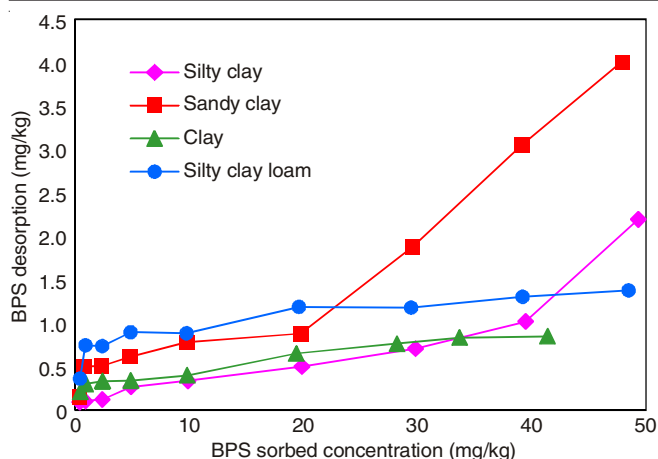


Fig. 4. Desorption of bispyribac sodium from different soils

by clay, silty loam and sandy clay soils for pyrazosulfuron ethyl and clay followed by silty clay loam, sandy clay and silty clay soils for bispyribac sodium. The results showed that the organic matter content plays a major role influencing desorption of herbicides from soils [22,29].

The degree of reversibility of the adsorption-desorption reaction of pesticides in the soils was studied by many researchers using hysteresis and suggests that it depends on both the physico-chemical properties of the molecules and the soil properties [31,32]. Generally, lower the value of hysteresis index, higher the degree of hysteresis which indicates that it is very difficult to desorb the herbicides from soils. In the present study, the hysteresis index was low for both pyrazosulfuron ethyl and bispyribac sodium in clay and silty clay loam soils and confirms that desorption from these soils are highly depends on the clay and silt fractions of the soil. While in other two soils, hysteresis index is close to 1 and showed that the rate of desorption is comparatively higher in organic carbon rich soils namely sandy clay and silty clay soils and this could be attributed to the type of organic matter and clay fraction present in the soil. The desorption rate in these soils is high since they are rich in kaolinite and illite clay fractions and the hysteresis occurs as a result of binding of herbicide molecules by physical entrapment to specific sites. Hence the amount desorbed may represents the weakly sorbed or retained fractions of the pyrazosulfuron ethyl and bispyribac sodium in the present study. The differences in hysteresis were decreased with increase in the initial concentration of herbicides in all soil types [33]. In general, there were only limited sites of high energy in the clay and soil organic matter fraction in which the herbicide molecules were tightly sorbed when they were added at lower concentrations. While at higher concentrations, high energy sites were completely saturated and the proportion of resistant fractions were lower, the overall desorption was easier and high [34]. Xia and Pignatello [35] found that desorption causes the removal of herbicide molecules thus creating the new holes which might trapped more molecules and thus becomes resistant to desorption in swelling type sorbents. Hence the hysteresis index values observed in the present study showed the diverse behaviour of aceto lactase synthase inhibiting rice herbicides in different soils especially in soils with high clay and organic carbon content. While applying

these herbicides to the soil with high organic matter and high sand content, attention should be given to the risk of ground-water and surface water contamination from these herbicides. It is concluded that the most likely cause of hysteresis of pyrazosulfuron ethyl and bispyribac sodium is due to irreversible or slowly reversible sorption and is consistent with Zhu and Selim [36] and Ding *et al.* [34]. When desorption commenced, the herbicides sorbed at the lowest energy sites comes to solution easily, then it becomes increasingly difficult as a result of the high resistance of herbicides sorbed in high energetic sites with an increase in the desorption steps.

The adsorption of both pyrazosulfuron ethyl and bispyribac sodium was found to be significantly correlated with the clay and organic carbon content, soil reaction, CEC and base saturation percent. A relatively higher affinity of the bispyribac sodium to the high energy sorption sites than pyrazosulfuron ethyl was observed in low organic carbon soils. The effect of clay on sorption of bispyribac sodium was masked by the high organic carbon content in sandy clay and silty clay soils. At equilibrium, these herbicides are easily sorbed and the order of sorption capacity (K_{oc}) for pyrazosulfuron ethyl was clay > silty clay loam > sandy clay > silty clay and vice versa for bispyribac sodium. The hysteresis index of both the molecules was high in sandy clay and silty clay soils have high organic carbon content when compared to clay and silty clay loam soils. The desorption of both the herbicides from clay and silty clay loam soils were more difficult than the sandy clay and silty clay soils and indicated by the lower hysteresis index. The low soil organic carbon partitioning coefficient (K_{oc}) in sandy clay and silty clay soils showed their weak sorption and increased mobility to the water sources. The results indicate that the mobility of pyrazosulfuron ethyl is medium to high and bispyribac sodium is low to medium and varied according to the soil types and their properties. Hence being rice herbicides, they could be used prudently based on soil physico-chemical properties to check the biomagnifications of these herbicides residue in water sources and subsequent contamination of the environment by their medium mobility in different soils.

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