List of Abbreviations
LIST OF ABBREVIATIONS

HPLC : High Performance Liquid Chromatography
DAD : Diod Array Detector
nm : Nanometer
LC-MS/MS : Liquid Chromatography - Mass Spectrometry/Mass Spectrometry
ESI : Electro Spray Ionization
m/Z : Mass/Charge
°C : Degree Centigrade
mg : Milli Gram
mL : Milli Litre
L : Litre
µg/mL : Micro gram per milli litre
µg/L : Micro gram per litre
mg/L : Milli gram per litre
ppm : Parts per million
µV : Micro Volt
µL : Micro Liter
% : Percentage
LOD : Limit of Detection
LOQ : Limit of Quantification
DT₅₀ : Time for 50% degradation (Half life)
DT $90_0$ : Time for 90% degradation

pH : negative logarithm of hydrogen ion concentration

AR : Analytical grade Reagent

GR : Guaranteed Reagent grade

RPM : Rotation per Minute

min. : Minutes

CAS RN : Chemical Abstract Service Registration Number

PTFE : Polytetrafluroethylene

NaOH : Sodium hydroxide

M : Molarity

SD : Standard deviation

RSD : Relative standard deviation

OECD : Organization for Economic Co-operation and Development

E : Energy

$\lambda$ : Wavelength

LC : Liquid Chromatography

MS : Mass spectra

CV : Coefficient of Variation

cm : Centimeter

$\mu$ : Micron

cmc : Critical misile concentration
# GLOSSARY OF TERMS

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
<td>A negatively charged ion.</td>
</tr>
<tr>
<td>Cation</td>
<td>A positively charged ion.</td>
</tr>
<tr>
<td>Chemical Name</td>
<td>The name applied to a pesticide active ingredient that describes its chemical structure according to rules prescribed by the American chemical society and published in the chemical abstract indexes.</td>
</tr>
<tr>
<td>Common Name</td>
<td>A name applied to a pesticide active ingredient usually agreed upon by the American national standards institute and the international organization for standardization.</td>
</tr>
<tr>
<td>Herbicides</td>
<td>A chemical used to control, suppress or kill plants or to severely interrupt the normal growth process.</td>
</tr>
<tr>
<td>LOD</td>
<td>Lowest concentration of an analyte that can be detected</td>
</tr>
<tr>
<td>LOQ</td>
<td>The lowest concentration of an analyte that can be detected and quantified with an acceptable accuracy and precision.</td>
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List of Publications
LIST OF PUBLICATIONS:


Adsorption and Degradation of Herbicide Halosulfuron-methyl in Indian Soils.

Chirukuri Rajasekharam and Atmakuru Ramesh*

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ABSTRACT

Halosulfuron-methyl is a new, low rate, sulfonylurea herbicide that is being promoted for annual broadleaf and gramineal weed control; however, there is a lack of published information on its behavior in soils. The adsorption and degradation of Halosulfuron-methyl by four soils were measured using a batch equilibrium technique. The soil sorption coefficient $K_s$, the soil organic carbon sorption coefficient $Koc$ and Herbicide degradation DT$_{50}$ are the basic parameters used for describing the environmental fate of the herbicide. The results showed that the Freundlich equation fitted its adsorption well, and the Freundlich constant value ($K_f$) ranged from 1.1-6.1. Soil organic carbon coefficient $Koc$ ranged from 105-173. Soil pH, organic matter (OM), and clay content were the main factors influencing its adsorption. Adsorption was negatively correlated with pH 6.0-8.0 while positively correlated with OM and clay content. Persistence of Halosulfuron-methyl conducted in all the 4 kinds of soil shows the DT$_{50}$ at 8.1 to 10.9 days. The sorption coefficient (Koc) and half-life (DT$_{50}$) were determined by combining the values of Koc and DT$_{50}$, and the mobility of residues of Halosulfuron-methyl in soil was calculated using GUS (Ground water Ubiquity Score) equation. The GUS values were found to be less than 1.9 in all the types of soils studied.

INTRODUCTION

Sorption is an important process in determining the fate and distribution of herbicides in environmental soil and water, thereby determining the amount of herbicide that can reach the target and the amounts that degraded and leached through the soil. The persistence and sorption properties of the compound will vary based on physical, chemical properties, texture and organic carbon content of the soils. The degradation of residues of isoproturon is significantly influenced by organic carbon, pH of the soil, the degradation rate varied based on the soil properties when incubated at 15°C [14]. The degradation of acidic and basic herbicides was significantly affected due to presence of organic carbon content, the pH influenced based on the degradation mode [9]. Prosulfuron was highly influenced by the pH of the soil, and was found highly stable in soils having basic pH [11]. The adsorption of acidic and basic herbicide was negatively influenced due to soil pH, and positively by organic carbon content [8]. The adsorption of aminocyclopyrachlor was found to be directly proportional to the organic carbon content in the soil [12]. Sorption of endosulfan, Methiozylsufuron and sulcotrine and its hydrolysis products were greatly influenced due to clay content and pH of the soil was reported in various literatures [10, 3, 7]. The adsorption of diuron [15] and monosulfuron [17] was found to be high at a lower soil pH. Batch sorption study with eleven pesticides in thirteen types of soil showed that the adsorption coefficient was influenced by organic matter, salinity, pH, cation exchange capacity, soil complex saturation and clay content of the soil, and the above parameters varied based on the compound nature also soil pH, organic matter (OM), and clay content were the main factors influencing its adsorption and Desorption [13]. The adsorption and Desorption of Monosulfuron-ester were negatively co-related with pH 4.0-8.0 while positively correlated with soil organic matter and clay content [4]. In the adsorption-desorption of phenylurea herbicides, the organic carbon was the main factor affecting urea sorption [5]. The carbofuran adsorption capacity was significantly higher in the soil with high organic matter [1]. The adsorption/Desorption of...
butachlor, mcylobutanil and chloropyrifos were mainly controlled by soil organic matter (OM) and octanol/water-partitioning coefficient content \cite{16}. Atrazine, isoproturon and trifluralin adsorption were correlated to soil organic matter content bentazon adsorption was governed by soil pH while insignificant effect has been shewn in the case of 2,4-D \cite{2}.

From the literature survey, it was observed that no information has been published concerning the fate of Halosulfuron-methyl in soil. Halosulfuron-methyl is a selective, systemic post emergence herbicide used to control annual broad laved weeds and nusedge in maize, sugar cane and paddy field. The herbicide, used in the paddy field under flooded condition, can contaminate the ground water through leaching or runoff. The study was conducted to evaluate the risk of contamination of Halosulfuron-methyl to water by determining its sorption characteristics and dissipation behavior in different Indian soils having different textural, physical and chemical properties and to correlate the factors influencing the leaching, degradation and sorption of Halosulfuron-methyl.

**MATERIALS AND METHODS**

Halosulfuron-methyl (purity 99.9%), reference analytical standard was pursed from Sigma-aldrich (USA). HPLC grade Acetonitrile, Ortho-phosphoric acid, Magnesium chloride, Potassium chloride, Ammonium chloride, Potassium dihydrogen phosphate and Calcium chloride were all GR grade obtained from Merck India limited. Distilled water was purified by using the Milli-Q Plus apparatus (Millipore, Bedford, MA, USA).

**Experimental procedures**

Soil (0 to ≤ 20 cm depth) was collected from agricultural fields of different states in India; there was no previous history of Halosulfuron-methyl herbicide application. The different types of collected soils were sieved using a 2 mm diameter sieve and analyzed according to standard protocol to characterize physical and chemical properties. Soil texture was determined by using the international pipette method, Organic carbon was estimated according to the Walkley, and black and soil pH was measured in a 1:2 (w/w) soil /deionized water mixture.

**Soil Degradation**

A laboratory study was conducted to determine the fate of Halosulfuron-methyl in the four different kinds of soil collected from the locations: Kerala, Karnataka, Punjab and Andhra Pradesh. The physical and chemical properties viz., pH, conductivity, organic carbon content, cation exchange capacity and texture were determined. Soil samples collected from the different states in India are sieved through a 2 mm sieve and quantitatively transferred in to the vials. The soil samples were exposed to sunlight with one third content of its moisture holding capacity, acclimatized for a period of three days before fortification. Following the acclimatization, the soil samples were fortified at 0.1 mg/kg of Halosulfuron-methyl and exposed to direct sunlight. On pre-determined intervals, duplicate soil samples were removed and extracted for the determination of residues.

**Extraction procedure**

The soils were extracted using the mixture of 20 mL of Acetonitrile: water (90/10 v/v) and tumbled for a period of four hours using end over end mechanical shaker. After tumbling the solvent layer was separated by using centrifuge, the extraction procedure was repeated with another 20 mL of extraction solvent. The extracts were pooled together and concentrated under the stream of nitrogen at 30°C. The residues were reconstituted using 5 mL of acetonitrile for the HPLC analysis.

**Soil adsorption**

The batch equilibrium technique was used to determine the soil adsorption constants of Halosulfuron-methyl in four different types of soil. A preliminary study was conducted to determine the soil/solution ratio, the equilibrium time for adsorption, the adsorption of the test substance on the surface of the test vessels and the stability of the test substance during the equilibration process. Before initiation of the experiment, the soil samples were sterilized by drying in the oven at 105°C for a period of 6 hours. Sterilization process was performed to restrain (to prevent the biodegradation of Halosulfuron-methyl) microbial degradation, the 100 mL polypropylene centrifuge tubes were filled with 5 g of sterile soil. An aliquot each of 5, 10, 25 and 50 mL of 10 mM CaCl₂ solution was added to each vial and equilibrated for four hours at room temperature. To the test vessels, a 5, 10, 25 and 50 mL of 5 µg/mL dosing solution was added to get the soil solution ratio 1:2, 1:4, 1:10 and 1:20, and kept in a horizontal shaker at 50-60 rpm. On pre-determined sampling occasions (2, 4, 8, 16 and 24 hours), triplicate samples were removed for the quantification of residues. After the adsorption process described above, a 5 ml of the supernatant solution was withdrawn and the amount of adsorbed was calculated. The remaining slurry was again brought to 10 ml by the addition of 5 mL of 0.01 M CaCl₂, equilibrated for 24 hr. these steps were repeated three times consecutively. Based on the preliminary results, sorption study was conducted with soil solution ratio 1:2 (5 g soil + 5mL of 0.01M CaCl₂ + 5 mL of respective concentration of Halosulfuron-methyl in 0.01M CaCl₂) and
compound concentrations are 0.1, 0.5, 1.0, 2.0 and 5.0 µg/mL, having equilibration time 16 hours and triplicate samples of each soil and each concentration were used to determine the sorption study. To check the interferences in solution and stability of the test item, one rotating soil free control, one static soil free control and standard free soil control were analyzed simultaneously. All vials except the static soil free control were tumbled on a rotator for 16 hours at 50-60 RPM at room temperature. The vials were removed from the rotator and centrifuged for 5 minutes at approximately 2000 RPM in a cooling centrifuge at 5 – 10 °C. After centrifugation, the supernatant was filtered using 0.45 µ PTFE membrane filter and transferred to HPLC vials for analysis.

**Instrumentation**

An Agilent® 1200 series High Performance Liquid Chromatograph equipped with Diode array detector was used for the quantification of residue. The detector wavelength was set at 240 nm. The separation of herbicide residues was carried out using the Zorbax® column SB-C18 (3.5 µm particle size, 4.6 mm i.d. and 75 mm length). The mobile phase used was (ACN: 0.1% H3PO4). The flow was programmed and a 1.0 ml per minute flow rate was set. The injection volume 50 µl was set for standard and sample. Halosulfuron-methyl was eluted at 8.0 minutes.

**Method validation**

Specificity, linearity, assay accuracy and precision were done to validate the method. The specificity of the method was confirmed by injecting the control soil extracts, mobile phase, acetonitrile, extraction solvent and diluting solvents, buffer solutions. Different known concentrations 5.0, 2.5, 1.25, 0.1, 0.05 and 0.01 mg L\(^{-1}\) of Halosulfuron-methyl was injected for linearity. Mobile phase was used for the preparation of calibration solutions by diluting the stock solution. The peak area was measured after injecting each calibration solution. Correlation coefficient was calculated from the plot against concentration of the standards versus area observed. Based on the signal to noise ratio of 3:1, the limit of detection of the instrument was established. Recoveries of residues in four different textured soils were studied by fortifying known concentration 0.02 (LOQ) and 0.2 mg kg\(^{-1}\) (10x LOQ level) of standard in each soil. Five replicate determinations were used to check the precision of the method. The samples were homogenized using homogenizer after fortification of standard, extracted and analysed for the residues of Halosulfuron-methyl by HPLC-DAD method. Based on the recovery study, the limit of quantification was established as 0.02 mg kg\(^{-1}\). Repeatability of the method showed acceptable RSD% according to the ‘Hurwitz equation’ (1).

\[
\text{RSD}\% < 2^{(1.0.5 \log C)} \times 0.67
\]

Where C is the concentration of the analyte expressed in percentage. The maximum acceptable RSD% calculated based on the above equation for the analyte concentrations 0.2 mg Kg\(^{-1}\) was 12.89% and for 0.02 mg Kg\(^{-1}\) 18.10%.

**Adsorption analysis**

The amount of Halosulfuron-methyl adsorbed after equilibrium was calculated according to the difference between the initial and final equilibrium solution concentrations by the following equation (2)

\[
Cs = (Co-Ce)\times V/m
\]

Where, Cs (mg/kg) is the amount of Halosulfuron-methyl adsorbed by soil and Co (mg/L) is the initial and equilibrium aqueous concentration, respectively. V (mL) is the volume of the solution and m is the mass of the soil.

Adsorption and Desorption were described by the linearized form of the Freundlich equation (3)

\[
\log Cs = \log Kf + \frac{1}{nf} \log Ce
\]

Where, \(K_f\) is the adsorption coefficient characterizing the adsorption-desorption capacity, and \(n_f\) is the Freundlich equation exponent related to adsorption intensity that is used as an indicator of the adsorption isotherm nonlinearity. \(K_{f,ads}\) is the adsorption coefficient and \(K_{f,des}\) is the desorption coefficient of the Freundlich equation.

The OM normalized adsorption constant (\(K_{om}\)) was calculated by normalizing \(K_{f,ads}\) to the fraction of OM according to equation (4)

\[
K_{om}=K_{f,ads}/OM*100\%
\]

The free energy of adsorption of the herbicide in soil is calculated using the thermodynamic equation (5)
\[ \Delta G = -RT \ln K_{OM} \]

Where, \( \Delta G \) (kJ/mol) is the free energy of adsorption, \( R \) (8.314*10^{-3} \text{ kJ/(K.mol)}) is the mol gas constant, mol gas constant, and \( T \) (K) is the absolute temperature.

RESULT AND DISCUSSION

Adsorption data

Figure 1 shows the adsorption kinetics after shaking four soils with 5 \( \mu \text{g/mL} \) of Halosulfuron-methyl in 0.01M aqueous solution. The rapid adsorption phase took place within 5 hours after shaking. After 5 hours, the herbicide concentration in solution varied with small changes, the adsorption phase slowed. This study found that adsorption equilibrium was reached 8 hours in all soils tested. Moreover, the amount adsorbed by soil remained steady. Further decreases in the Halosulfuron-methyl concentration in the supernatant after 24 hr were not significant. For laboratory convenience, 16 hr was taken as the equilibrium time.

![Figure 1: Adsorption Kinetics of Halosulfuron-methyl](image)

The Freundlich adsorption isotherms are shown in Figure 2. The values for the adsorption coefficient \( (K_f) \), were calculated for all the test soils. The Freundlich constant values \( K_f \) ranged from 1.1 to 6.1 mL/g and sorption isotherms were non linear with 1/n values < 1 among the soils tested in 0.01M CaCl\(_2\) as a background electrolyte. The adsorption coefficients were normalized to the organic carbon contents for each soil to calculate the soil sorption coefficients \( (K_{oc}) \). The \( (K_{oc}) \) values ranged from 105-173 among the soils tested. The adsorption isotherm of Halosulfuron-methyl dependant on soil types, and the order of \( K_f \)-ads was Punjab > Kerala > Karnataka > Andhrapradesh. The \( K_f \) and \( K_{oc} \) values were low for the soils having low organic carbon and clay content, adsorption of Halosulfuron-methyl was high for the soils having higher organic carbon and clay content, as confirmed from the \( K_f \) and \( K_{oc} \) values. The comparison between pH of the soil, distribution coefficient, organic carbon content and half life was presented in Figure 3, observed that these parameters found directly related each other. The sorption coefficient found directly proportional to the soils having higher organic carbon and lower half life. Results are presented in Table 1.

![Table 1: A summary of soil physical-chemical properties and Halosulfuron methyl results](image)

<table>
<thead>
<tr>
<th>Soil name</th>
<th>Soil texture</th>
<th>pH in water</th>
<th>Organic matter %</th>
<th>Organic Carbon%</th>
<th>CEC (meq/100 g)</th>
<th>DT 50 (Days)</th>
<th>Kd (mg/L)</th>
<th>Koc</th>
<th>Gus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerala</td>
<td>66</td>
<td>18</td>
<td>16</td>
<td>5.0</td>
<td>5.9</td>
<td>3.4</td>
<td>12.0</td>
<td>8.1</td>
<td>5.1</td>
</tr>
<tr>
<td>Karnataka</td>
<td>26</td>
<td>36</td>
<td>38</td>
<td>6.0</td>
<td>2.3</td>
<td>1.3</td>
<td>24.1</td>
<td>8.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Punjab</td>
<td>54</td>
<td>34</td>
<td>12</td>
<td>7.8</td>
<td>7.8</td>
<td>4.5</td>
<td>19.0</td>
<td>10.9</td>
<td>6.1</td>
</tr>
<tr>
<td>Andhra Pradesh</td>
<td>82</td>
<td>8</td>
<td>10</td>
<td>5.3</td>
<td>1.1</td>
<td>0.6</td>
<td>9.6</td>
<td>10.6</td>
<td>1.1</td>
</tr>
</tbody>
</table>

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Figure 2: Freundlich adsorption isotherm of Halosulfuron-methyl

![Figure 2: Freundlich adsorption isotherm of Halosulfuron-methyl](image)

Figure 3: Comparisons between soil pH and organic carbon, Adsorption coefficient, and half life of Halosulfuron-methyl

![Figure 3: Comparisons between soil pH and organic carbon, Adsorption coefficient, and half life of Halosulfuron-methyl](image)

Free energy ($\Delta G$)

The $\Delta G$ value of 40kJ/mol was considered as a threshold for identifying the physical and chemical mechanisms of adsorption, and physical adsorption mainly was involved below threshold. The $\Delta G$ values of four soils at 25°C ranged from -4.96 to -4.42 kJ/mol, the $\Delta G$ of halosulfuron-methyl in four soils was less than 40 kJ/mol, indicating that the adsorption of halosulfuron-methyl by four soils was mainly physical process. The adsorption of halosulfuron-methyl by soils also was a spontaneous process for negative value of $\Delta G$.

Degradation data

The soils collected from the different locations around India had the following compositions of Clay (10-38%), Silt (8-36%), Sand (26-66%) and organic carbon (0.6-3.4%) and the pH was found in the range 5.0 – 7.8. Dissipation of Halosulfuron-methyl followed first order kinetics in all the tested soil. From the dissipation study it
was observed that the degradation of residues was not much significantly influenced by the soil organic carbon and pH. Dissipation data in soils is presented in Figure 4.

![Figure 4: Soil dissipation of Halosulfuron-methyl](image)

**Ground water ubiquity score (GUS)**

Environmental effect of Halosulfuron-methyl was studies using the Gustafson equation [6]. The leaching potential of the residues can be determined from the formula, higher the GUS value indicates higher risk of contamination of ground water through leaching of residues from surface. Sorption coefficient ($K_{oc}$) and Half life ($DT_{50}$) were used to obtain GUS values. These values are numerical and obtain GUS values following formula

$$GUS = \log_{10}(DT_{50}) \times [4 - \log_{10}(K_{oc})]$$

Where,

- $DT_{50}$ - Time taken for the test item to degrade half of its concentration
- $K_{oc}$ - soil sorption coefficient

From half life and $K_{oc}$, the GUS values calculated for each soil are in the range 1.3 to 1.9. The value indicates the leaching potential of the herbicide residue was found to low leachable through the soil. A comparative results stating the physical, chemical properties of soil, half life of Halosulfuron-methyl in soil, $K_{oc}$ value for each soil and GUS value calculated are presented in Table 1.

**CONCLUSIONS**

Dissipation of Halosulfuron-methyl followed first order kinetics in all the tested soil. From the dissipation study it was observed that the degradation of residues was not much significantly influenced by the soil organic carbon and pH. By using the batch equilibrium experiments, the sorption characteristics of Halosulfuron-methyl were determined in four soil types. The Freundlich constant ($K_{ads}$) values ranged from 1.1 to 6.1 mL/g, and soil clay content, OM were the main factors affecting Halosulfuron-methyl adsorption. Adsorption was positively influenced by organic carbon content and clay content. From the analytical results, it was concluded that the Halosulfuron-methyl might be low leachable with the soils studied. The $\Delta G$ values of four soils ranged from -4.96 to -4.42 kJ/mol, the $\Delta G$ of Halosulfuron-methyl in the four soils was less than 40 kJ/mol. The negative value of $\Delta G$ indicates that the adsorption of Halosulfuron-methyl was mainly physical process and also a spontaneous process.

**ACKNOWLEDGEMENT**

The authors thank the management of IIBAT for providing necessary facilities to conduct the research.
REFERENCES

Adsorption and Degradation of herbicide Pyrazosulfuron-ethyl in Indian soils
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Department of Analytical Chemistry, International Institute of Biotechnology and Toxicology (IIBAT), Padappai, Kanchipuram District, Tamil Nadu, India
*Email : raamesh_a@yahoo.co.in

Abstract
Pyrazosulfuron-ethyl is a new, low rate, sulfonylurea herbicide that is being promoted for control of annual and perennial broad-leaved weeds; however, there is a lack of published information on its behavior in soils. The adsorption and degradation of Pyrazosulfuron-ethyl by four soils were measured using a batch equilibrium technique. The soil sorption coefficient $K_{oc}$, the soil organic carbon sorption coefficient $K_{oc}$ and Herbicide degradation $DT_{50}$ are the basic parameters used for describing the environmental fate of the herbicide. The results showed that the Freundlich equation fitted its adsorption well, and the Freundlich constant value ($K_f$) ranged from 0.7-5.8. Soil organic carbon coefficient $K_{oc}$ ranged from 83-141. Soil Organic matter (OM), and clay content were the main factors influencing its adsorption. Adsorption was positively correlated with OM and clay content. Persistence of Pyrazosulfuron-ethyl conducted in all the 4 kinds of soil shows the $DT_{50}$ at 5.8 to 7.1 days. The sorption coefficient ($K_{oc}$) and half-life ($DT_{50}$) were determined by combining the values of $K_{oc}$ and $DT_{50}$. The mobility of residues of Pyrazosulfuron-ethyl in soil was calculated using GUS (Ground water Ubiquity Score) equation. The GUS values were found to be less than 1.7 in all the types of soils studied.

Keywords
Adsorption, Degradation, GUS, Pyrazosulfuron-ethyl

INTRODUCTION
Sorption is an important process in determining the fate and distribution of herbicides in environmental soil and water, thereby determining the amount of herbicide that can reach the target and the amounts that degraded and leached through the soil. The persistence and sorption properties of the compound will vary based on physical, chemical properties, texture and organic carbon content of the soils. The degradation of residues of isoproturon is significantly influenced by organic carbon, pH of the soil, the degradation rate varied based on the soil properties when incubated at 15°C [14]. The degradation of acidic and basic herbicides was significantly affected due to presence of organic carbon content, the pH influenced based on the degradation mode [9]. Prosulfuron was highly influenced by the pH of the soil, and was found highly stable in soils having basic pH [13]. The adsorption of acidic and basic herbicide was negatively influenced due to soil pH, and positively by organic carbon content [3]. The adsorption of aminocyclopyrachlor was found to be directly proportional to the organic carbon content in the soil [2]. Sorption of endosulfan, Methioprylsulfuron and sulcotrine and its hydrolysis products were greatly influenced due to clay content and pH of the soil was reported in various literatures [10, 3, and 7]. The adsorption of diuron [15] and monosulfuron [17] was found to be high at a lower soil pH. Batch sorption study with eleven pesticides in thirteen types of soil showed that the adsorption coefficient was influenced by organic matter, salinity, pH, cation exchange capacity, soil complex saturation and clay content of the soil, and the above parameters varied based on the compound nature also soil pH, organic matter (OM), and clay content were the main factors influencing its adsorption and Desorption [13]. The adsorption and Desorption of Monosulfuron-ester were negatively co-related with pH 4.0-8.0 while positively correlated with soil organic matter and clay content [4]. In the adsorption-desorption of phenylurea herbicides, the organic carbon was the main factor affecting urea sorption [5]. The carbofuran adsorption capacity was significantly higher in the soil with high organic matter [11]. The adsorption/Desorption of butachlor, myclobutanil and chloropyrifos were mainly controlled by soil organic matter (OM) and octanol/water-partitioning coefficient content [16]. Atrazine, isoproturon and trifluralin adsorption were correlated to soil organic matter content bentazone adsorption was governed by soil pH while insignificant effect has been shewn in the case of 2,4-D [21]. From the literature survey, it was observed that no information has been published concerning the fate of Pyrazosulfuron-ethyl in soil. Pyrazosulfuron-ethyl is a selective, systemic post emergence herbicide used to control annual broad leafed weeds in wet-sown and transplanted rice crops. The herbicide, used in the paddy field under flooded condition, can contaminate the ground water through leaching or runoff. The study was conducted to evaluate the risk of contamination of Pyrazosulfuron-ethyl to water by determining its sorption characteristics and dissipation behavior in different Indian soils having different textural, physical and chemical properties and to correlate the factors influencing the leaching, degradation and sorption of Pyrazosulfuron-ethyl.
MATERIALS AND METHODS

Pyrazosulfuron-ethyl (purity 99.9%), reference analytical standard was pursed from Sigma-aldrich (USA). HPLC grade Acetonitrile, Ortho–phosphoric acid, Magnesium chloride, Potassium chloride, Ammonium chloride, Potassium dihydrogen phosphate and Calcium chloride were all GR grade obtained from Merck India limited. Distilled water was purified by using the Milli-Q Plus apparatus (Millipore, Bedford, MA, USA).

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A laboratory study was conducted to determine the fate of Pyrazosulfuron-ethyl in the four different kinds of soil collected from the locations: Kerala, Karnataka, Punjab and Andhra Pradesh. The physical and chemical properties viz., pH, conductivity, organic carbon content, cation exchange capacity and texture were determined. Soil samples collected from the different states in India are sieved through a 2 mm sieve and quantitatively transferred in to the vials. The soil samples were exposed to sunlight with one third content of its moisture holding capacity, acclimatized for a period of three days before fortification. Following the acclimatization, the soil samples were fortified at 0.1 mg/g of soil. After an equilibration period of three days before fortification. Following the acclimatization, the soil samples were fortified at 0.1 mg/g of soil. After an equilibration period of three days before fortification. 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Soil adsorption

The batch equilibrium technique was used to determine the soil adsorption constants of Pyrazosulfuron-ethyl in four different types of soil. A preliminary study was conducted to determine the soil/solution ratio, the equilibrium time for adsorption, the adsorption of the test substance on the surface of the test vessels and the stability of the test substance during the equilibration process. Before initiation of the experiment, the soil samples were sterilized by drying in the oven at 105°C for a period of 6 hours. Sterilization process was performed to restrain (to prevent the biodegradation of Pyrazosulfuron-ethyl) microbial degradation, the 100 mL polypropylene centrifuge tubes were filled with 5 g of sterile soil. An aliquot each of 5, 10, 25 and 50 mL of 10 mM CaCl2 solution was added to each vial and equilibrated for four hours at room temperature. To the test vessels, a 5, 10, 25 and 50 mL of 5 µg/mL dosing solution was added to get the soil solution ratio 1:2, 1:4, 1:10 and 1:20, and kept in a horizontal shaker at 50-60 rpm. On pre-determined sampling occasions (2, 4, 8, 16 and 24 hours), triplicate samples were removed for the quantification of residues. After the adsorption process described above, a 5 ml of the supernatant solution was withdrawn and the amount of adsorbed was calculated. The remaining slurry was again brought to 10 mL by the addition of 5 mL of 0.01 M CaCl2, equilibrated for 24 hr. these steps were repeated three times consecutively. Based on the preliminary results, sorption study was conducted with soil solution ratio 1:2 (5 g soil + 5mL of 0.01M CaCl2 + 5 mL of respective concentration of Pyrazosulfuron-ethyl in 0.01M CaCl2) and compound concentrations are 0.1, 0.5, 1.0, 2.0 and 5.0 µg/mL, having equilibration time 16 hours and triplicate samples of each soil and each concentration were used to determine the sorption study. To check the interferences in solution and stability of the test item, one rotating soil free control, one static soil free control and standard free soil control were analyzed simultaneously. All vials except the static soil free control were tumbled on a rotator for 16 hours at 50-60 RPM at room temperature. The vials were removed from the rotator and centrifuged for 5 minutes at approximately 2000 RPM in a cooling centrifuge at 5 – 10°C. After centrifugation, the supernatant was filtered using 0.45 µ PTFE membrane filter and transferred to HPLC vials for analysis.

Instrumentation

An Agilent® 1200 series High Performance Liquid Chromatograph equipped with Diode array detector was used for the quantification of residue. The detector wavelength was set at 240 nm. The separation of herbicide residues was carried out using the Zorbax® column SB-C18 (3.5 µm particle size, 4.6 mm i.d. and 75 mm length). The mobile phase used was (ACN: 0.1% H3PO4). The flow was programmed and a 1.0 ml per minute flow rate was set. The injection volume 50 µl was set for standard and sample. Pyrazosulfuron-ethyl was eluted at 7.7 minutes.

Method validation

Specificity, linearity, assay accuracy and precision were done to validate the method. The specificity of the method was confirmed by injecting the control soil extracts, mobile phase, acetonitrile, extraction solvent and diluting solvents, buffer solutions. Different known concentrations 5.0, 2.5, 1.25, 0.1, 0.05 and 0.01 mg L⁻¹ of Pyrazosulfuron-ethyl was injected for linearity. Mobile phase was used for the preparation of calibration solutions by diluting the stock solution. The peak area was measured after injecting each calibration solution. Correlation coefficient was calculated from the plot against concentration of the standards versus area observed. Based on the signal to noise ratio of 3:1, the limit of detection of the instrument was established. Recoveries of residues in four different textured soils were studied by fortifying known concentration 0.02
(LOQ) and 0.2 mg kg⁻¹ (10 x LOQ level) of standard in each soil. Five replicate determinations were used to check the precision of the method. The samples were homogenized using homogenizer after fortification of standard, extracted and analysed for the residues of Pyrazosulfuron-ethyl by HPLC-DAD method. Based on the recovery study, the limit of quantification was established as 0.02 mg kg⁻¹. Repeatability of the method showed acceptable RSD% according to the ‘Hurwitz equation’ (1).

\[ \text{RSD\%} < 2 \left(1 - 0.5 \log C \right) x 0.67 \]

Where C is the concentration of the analyte expressed in percentage. The maximum acceptable RSD% calculated based on the above equation for the analyte concentrations 0.2 mg Kg⁻¹ was 12.69% and for 0.02 mg Kg⁻¹ 18.19%.

**Adsorption analysis**

The amount of Pyrazosulfuron-ethyl adsorbed after equilibrium was calculated according to the difference between the initial and final equilibrium solution concentrations by the following equation (2)

\[ C_s = \left( \frac{C_o - C_e}{V} \right) \times m \]

Where, \( C_s \) (mg/kg) is the amount of Pyrazosulfuron-ethyl adsorbed by soil and \( C_o \) (mg/L) is the initial and equilibrium aqueous concentration, respectively. \( V \) (mL) is the volume of the solution and \( m \) is the mass of the soil.

Adsorption and Desorption were described by the linearized form of the Freundlich equation (3)

\[ \log C_s = \log K_f + \frac{1}{n_f} \log C_e \]

Where, \( K_f \) is the adsorption coefficient characterizing the adsorption-desorption capacity, and \( n_f \) is the Freundlich equation exponent related to adsorption intensity that is used as an indicator of the adsorption isotherm linearity. \( K_{f, ads} \) is the adsorption coefficient and \( K_{f, des} \) is the desorption coefficient of the Freundlich equation.

The OM normalized adsorption constant (\( K_{om} \)) was calculated by normalizing \( K_{f, ads} \) to the fraction of OM according to equation (4)

\[ K_{om} = \frac{K_{f, ads}}{OM} \times 100\% \]

The free energy of adsorption of the herbicide in soil is calculated using the thermodynamic equation (5)

\[ \Delta G = -RT \ln K_{om} \]

Where, \( \Delta G \) (kJ/mol) is the free energy of adsorption, \( R \) (8.314*10⁻³ kJ/(K·mol)) is the mol gas constant, mol gas constant, and \( T \) (K) is the absolute temperature.

**RESULT AND DISCUSSION**

**Adsorption data**

Figure 1 shows the adsorption kinetics after shaking four soils with 5 µg/mL of Pyrazosulfuron-ethyl in 0.01M aqueous solution. The rapid adsorption phase took place within 5 hours after shaking. After 5 hours, the herbicide concentration in solution varied with small changes, the adsorption phase slowed. This study found that adsorption equilibrium was reached 8 hours in all soils tested. Moreover, the amount adsorbed by soil remained steady. Further decreases in the Pyrazosulfuron-ethyl concentration in the supernatant after 24 hr were not significant. For laboratory convenience, 16 hr was taken as the equilibrium time.

**Figure 1: Adsorption Kinetics of Pyrazosulfuron-ethyl**

![Adsorption Kinetics](image)

**Figure 2: Freundlich adsorption isotherm of Pyrazosulfuron-ethyl**

The Freundlich adsorption isotherms are shown in Figure 2. The values for the adsorption coefficient (\( K_f \)), were calculated for all the test soils. The Freundlich constant values \( K_f \) ranged from 0.7 to 5.8 mL/g and sorption isotherms were non linear with 1/n values < 1 among the soils tested in 0.01M CaCl₂ as a background electrolyte. The adsorption coefficients were normalized to the organic carbon contents for each soil to calculate the soil sorption coefficients (\( K_{oc} \)). The \( K_{oc} \) values ranged from 83-141 among the soils tested. The adsorption isotherm of Pyrazosulfuron-ethyl dependant on soil types, and the order of \( K_{ads} \) was Punjab > Kerala > Karnataka > Andhra Pradesh. The \( K_f \) and \( K_{oc} \) values were low for the soils having low organic carbon and clay content, adsorption of Pyrazosulfuron-ethyl was high for the soils having higher organic carbon and clay content, as confirmed from the \( K_f \) and \( K_{oc} \) values. The comparison between pH of the soil, distribution coefficient, organic carbon content and half life was presented in Figure 3, observed that these parameters found directly related each other. The sorption coefficient found directly proportional to the soils having higher organic carbon and lower half life. Results are presented in Table 1.
Figure 3: Comparisons between soil pH and organic carbon, Adsorption coefficient, and half life of Pyrazosulfuron-ethyl

Table 1: A summary of soil physical-chemical properties and Pyrazosulfuron-ethyl results

<table>
<thead>
<tr>
<th>Soil name</th>
<th>Soil texture</th>
<th>pH in water</th>
<th>Organic matter%</th>
<th>Organic Carbon%</th>
<th>CEC (meq/100 g)</th>
<th>DT 50 (Days)</th>
<th>Kd (mg/L)</th>
<th>Koc</th>
<th>Gus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerala</td>
<td>66 18 16</td>
<td>5.0</td>
<td>5.9</td>
<td>3.4</td>
<td>12.0</td>
<td>6.2</td>
<td>4.8</td>
<td>141</td>
<td>1.5</td>
</tr>
<tr>
<td>Karnataka</td>
<td>26 36 38</td>
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<td>2.3</td>
<td>1.3</td>
<td>24.1</td>
<td>5.8</td>
<td>1.1</td>
<td>83</td>
<td>1.6</td>
</tr>
<tr>
<td>Punjab</td>
<td>54 34 12</td>
<td>7.8</td>
<td>7.8</td>
<td>4.5</td>
<td>19.0</td>
<td>6.8</td>
<td>5.8</td>
<td>129</td>
<td>1.6</td>
</tr>
<tr>
<td>Andhra Pradesh</td>
<td>82 8 10</td>
<td>5.3</td>
<td>1.1</td>
<td>0.6</td>
<td>9.6</td>
<td>7.1</td>
<td>0.7</td>
<td>110</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Free energy (ΔG)
The ΔG value of 40kJ/mol was considered as a threshold for identifying the physical and chemical mechanisms of adsorption, and physical adsorption mainly was involved below threshold (Carter et al., 1995). The ΔG values of four soils at 25°C ranged from -4.74 to -4.16 kJ/mol, the ΔG of Pyrazosulfuron-ethyl in four soils was less than 40 kJ/mol, indicating that the adsorption of Pyrazosulfuron-ethyl by four soils was mainly physical process. The adsorption of Pyrazosulfuron-ethyl by soils also was a spontaneous process for negative value of ΔG.

Degradation data
The soils collected from the different locations around India had the following compositions of Clay (10-38%), Silt (8-36%), Sand (26-66%) and organic carbon (0.6-3.4%) and the pH was found in the range 5.0 – 7.8. Dissipation of Pyrazosulfuron-ethyl followed first order kinetics in all the tested soil. From the dissipation study it was observed that the degradation of residues was not much significantly influenced by the soil organic carbon and pH. Dissipation data in soils is presented in Figure 4.

Ground water ubiquity score (GUS)
Environmental effect of Pyrazosulfuron-ethyl was studies using the Gustafson equation [6]. The leaching potential of the residues can be determined from the formula, higher the GUS value indicates higher risk of contamination of ground water through leaching of residues from surface. Sorption coefficient (Koc) and Half life (DT50) were used to obtain GUS values. These
values are numerical and obtain GUS values following formula
\[ GUS = \log_{10}(DT_{50})[4-\log_{10}(K_{oc})] \]
Where,
\[ DT_{50} \] - Time taken for the test item to degrade half of its concentration
\[ K_{oc} \] - soil sorption coefficient
From half life and \( K_{oc} \), the GUS values calculated for each soil are in the range 1.5 to 1.7. The value indicates the leaching potential of the herbicide residue was found to low leachable through the soil. A comparative results stating the physical, chemical properties of soil, half life of Pyrazosulfuron-ethyl in soil, \( K_{oc} \) value for each soil and GUS value calculated are presented in Table1.

CONCLUSIONS

Dissipation of Pyrazosulfuron-ethyl followed first order kinetics in all the tested soil. From the dissipation study it was observed that the degradation of residues was not much significantly influenced by the soil organic carbon and pH. By using the batch equilibrium experiments, the sorption characteristics of Pyrazosulfuron-ethyl were determined in four soil types. The Frendlich constant (\( K_{ads} \)) values ranged from 0.7 to 5.8 mL/g, and soil clay content, OM were the main factors affecting Pyrazosulfuron-ethyl adsorption. Adsorption was positively influenced by organic carbon content and clay content. From the analytical results, it was concluded that the Pyrazosulfuron-ethyl might be low leachable with the soils studied. The \( \Delta G \) values of four soils ranged from -4.74 to -4.16 kJ/mol, the \( \Delta G \) of Pyrazosulfuron-ethyl in the four soils was less than 40 kJ/mol. The negative value of \( \Delta G \) indicates that the adsorption of Pyrazosulfuron-ethyl was mainly physical process and also a spontaneous process.

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Sorption characteristics and persistence of herbicide bispyribac sodium in different global soils

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HIGHLIGHTS
- Sorption characteristics of bispyribac sodium was evaluated in 21 global soils.
- The amount of electrolytes significantly influenced the adsorption characteristics.
- Cationic surfactants increased the adsorption phenomena.
- Effect of temperature increased the desorption of bispyribac sodium from soil.
- Ground water ubiquity score for bispyribac sodium plausible leaching.

ABSTRACT
The dissipation kinetics and the adsorption characteristics of bispyribac sodium, a pyrimidinylxybenzoic herbicide, in 21 types of soil collected from different locations in the U.S., Italy, Spain, Greece, France, U.K., the Netherlands, Germany, and India were evaluated under laboratory conditions. The soil sorption study was conducted using the batch equilibrium process. The paper also investigated the adsorption efficiency of bispyribac sodium in the presence of different kinds of background electrolytes, surfactants, and different temperatures in two different soils. The results showed that the Freundlich equation fits its adsorption well, and the Freundlich adsorption constant values ($K_f$) ranged from 0.3 to 5.6 mL g$^{-1}$. Adsorption isotherms were nonlinear, with $1/n_f$ values <1. Bispyribac sodium adsorption by two soils increased with increasing electrolytes concentration using CaCl$_2$, KCl, NH$_4$Cl, KH$_2$PO$_4$ and MgCl$_2$ as a background electrolytes. The adsorption coefficient value decreased when anionic and nonionic surfactants were used at the three surfactant concentrations in two types of soil but increased with cationic surfactant, and temperature. Sorption was positively correlated with OM and negatively correlated with a soil pH of 5.0 to 8.1. The free energy ($D_G$) values of bispyribac sodium in the soils were less than 40 kJ mol$^{-1}$ and negative values were obtained. This indicates that the adsorption of bispyribac sodium is mainly a physical and spontaneous process. The GUS values were less than 2.9 in all the soil types studied, and the residues of bispyribac sodium were low to moderate to leacher (mobile) in the soil.

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1. Introduction

Sorption of pesticides by soils is one of the most significant processes influencing the fate of pesticides in soil environments. Interaction at interfaces between soil components and pesticide affects not only the movement, volatilization, and degradation of the latter, but also their bioavailability, transformation by biotic agents, and the possibility of contamination of underground water or surface water (Patakioutas and Albanis, 2002). The extent of adsorption and desorption of a chemical compound is related to various soil properties, including organic matter, soil type, amount of clay, ion exchange capacity, and pH. Moreover, various physico-chemical parameters of the compound, such as water solubility, octanol–water partition coefficient, and $p_K_a$ value also play important roles in determining the extent of adsorption (Fernandes et al., 2003; Farahani et al., 2007; Shi et al., 2010). Degradation of residues of isoproturon is significantly influenced by organic carbon and the pH of the soil. Walker et al. (2001) reported that when incubated at 15°C, the degradation rate varied according to the properties of the soil. Kah et al. (2007) found that the organic carbon content and the pH influenced the degradation of acidic and basic herbicides (Kah et al., 2007). The degradation of residues of metribuzin and its metabolites was reported to be greater in top
soil than in subsoil and influenced by the organic matter (OM) content in the soil (Henriksen et al., 2004). The pH of the soil was found to have a profound influence on the degradation of prosulfuron; this compound was also found to be very stable in soils with a basic pH (Hultgren et al., 2002). The soil pH had a negative influence on the adsorption of acidic and basic herbicides, whereas the organic carbon content had a positive influence (Kah and Brown, 2007). The adsorption of aminocyclopyrachlor was found to be directly proportional to the organic carbon content in the soil (Oliveira et al., 2011). The sorption of endosulfan (Kumar and Philip, 2006), methiophosphosulfuron (Wu et al., 2011a), and sulcotriazine and their hydrolysis products (Chaabane et al., 2005) were greatly influenced by the clay content and the pH of soils. The adsorption of diuron (Liu et al., 2010) and monosulfuron (Tang et al., 2008) was high at a lower soil pH. A batch sorption study with 11 pesticides in 13 types of soil showed that the OM, salinity, pH, cation exchange capacity, soil complex saturation, and clay content of the soil influenced the adsorption coefficient and that these parameters varied depending on the nature of the compound (Kodesova et al., 2010). The adsorption and desorption of monosulfuron-ester were negatively correlated with a pH of 4.0–8.0 and positively correlated with soil OM and clay content (Wu et al., 2011b). In a study of the adsorption–desorption of phenylurea herbicides, organic carbon was the main factor affecting urea sorption (Fouque-Brouard et al., 1996). The carbofuran adsorption capacity was significantly higher in soil with high OM (Bermudez-Couso et al., 2012). Soil OM and the octanol/water-partitioning coefficient content mainly controlled the adsorption/desorption of butachlor, myclobutanil, and chlorpyrifos (Yu et al., 2006). Atrazine, isoproturon, and trifluralin adsorption were correlated with the soil OM content, and bentazon adsorption was governed by the soil pH (Boivin et al., 2005). The same study found that these factors had an insignificant effect on 2,4-D. The adsorption and desorption behavior of n-Alkylpyridinium Bromide surfactants in the absence and presence of different electrolytes (NaCl, CaCl₂ and Na₂SO₄) were compared in batch and continuous column experiments (Paria and Yuet, 2006). To investigate the effect of different types of surfactants on the adsorption behavior of the pesticide picloram (Shariff, 2011), surfactant-enhanced desorption of aldicarb from soil was investigated (Xu et al., 2006). Monosulfuron-ester adsorption was found to increase the CaCl₂ concentration (Wu et al., 2011b). Another study found that the rate of adsorption in soil pores was governed by temperature (Bansal, 2004). Alonso et al. (2011) used the leachability index model and the groundwater ubiquity score (GUS) to determine potential offsite mobility of indaziflam. The GUS score is a simple method for assessing pesticide leachability (Gustafson, 1989). Wu et al. (2011b) concluded that the adsorption of monosulfuron-ester was mainly a physical process because its free energy (ΔG) in seven types of soil was less than 40 kJ mol⁻¹. In another study, negative values for ΔG, ΔH, and ΔS constants confirmed that diazinon adsorption is greater at lower temperatures (Shariff, 2012).

From the literature survey, it was observed that no information has been published on the fate of bispyribac sodium in soil. Bispyribac sodium is a selective, systemic postemergence herbicide used to control grasses and broad leaf weeds in paddy fields. The herbicide, which is applied in paddy fields under flooded conditions, can contaminate groundwater through leaching or runoff. To evaluate the risk of water contamination by bispyribac sodium, this study evaluated its sorption characteristics and dissipation behavior in different global soils having different textural and physical and chemical properties. The aim was to identify the factors influencing the leaching, degradation, and sorption of bispyribac sodium. The effect of the electrolytes concentration, surfactant concentration, and temperature on the adsorption of bispyribac sodium in the selected soils was also investigated.

2. Materials and methods

2.1. Materials

Bispyribac sodium (purity 99.9%) reference analytical standard was purchased from Sigma–Aldrich (USA). HPLC-grade acetonitrile, ortho-phosphoric acid, magnesium chloride, potassium chloride, ammonium chloride, potassium dihydrogen phosphate, and calcium chloride (all GR grade) were obtained from Merck India Limited. SDS, CTAM and Tween – 80 were analytical grade and used without further purification. Distilled water was purified using the Milli-Q Plus apparatus (Millipore, Bedford, MA, USA).

2.2. Experimental procedures

2.2.1. Soil characterization

Twenty-one soil samples (0 to 120 cm depth) were collected from agricultural fields in different countries where there was no previous history of bispyribac sodium herbicide application. The different types of collected soils were sieved using a 2 mm diameter sieve and analyzed according to a standard protocol to characterize their physical and chemical properties. Soil texture was determined using the international pipette method. Organic carbon was estimated according to the Walkley–Black method, and soil pH was measured in a 1:2 (w/v) soil/deionized water mixture.

2.2.2. Dissipation in soil

A laboratory study was conducted to determine the fate of bispyribac sodium in the 21 different kinds of soil collected from the following locations: U.S., Italy, Spain, Greece, France, U.K., the Netherlands, Germany, and India. The following physical and chemical properties were determined: pH, conductivity, organic carbon content, cation exchange capacity, and texture. The soil samples collected from the different countries were sieved through a 2 mm sieve, and transferred 5 g soil to each vial. The soil samples (vials) were exposed to sunlight with one-third content of its moisture holding capacity and acclimatized for a period of three days before fortification with 0.1 mg kg⁻¹ of bispyribac sodium. They were then exposed to direct sunlight again. At predetermined intervals, duplicate soil samples were removed to determine bispyribac sodium residues.

2.2.3. Extraction

The soils were extracted using a mixture of 20 mL of acetonitrile: water (90/10 v/v) and tumbled for 4 h using an end over end mechanical shaker. After tumbling, the solvent layer was separated using a centrifuge, and the extraction procedure was repeated with another 20 mL of extraction solvent. The extracts were pooled together and concentrated under a stream of nitrogen at 30 °C. The residues were reconstituted using 5 mL of acetonitrile for the HPLC analysis.

2.2.4. Adsorption in soil

The batch equilibrium technique was used to determine the soil adsorption constants of bispyribac sodium in the 21 different soil types. A preliminary study was conducted to determine the soil/solution ratio, the equilibrium time for adsorption, the adsorption of the test substance on the surface of the test vessels, and the stability of the test substance during the equilibration process. Before initiation of the experiment, the soil samples were sterilized by drying in an oven at 105 °C for 6 h. Sterilization was performed to restrain (prevent the biodegradation of bispyribac sodium) microbial degradation, and 50 mL polypropylene centrifuge tubes were filled with 5 g of sterile soil. An aliquot each of 5, 10, 25, and 50 mL of 0.01 M of CaCl₂ solution was added to each vial and
equilibrated for 4 h at room temperature. To the test vessels, 5, 10, 25, and 50 mL of 5 μg mL⁻¹ dosing solution were added to produce soil solution ratios of 1:2, 1:4, 1:10, and 1:20, and they were placed in a horizontal shaker at 50–60 rpm. At predetermined sampling points (1, 2, 4, 8, and 24 h), triplicate samples were removed to quantify the amount of bispyribac sodium residue. The preliminary study was conducted only with four types of soils having significant variation in their physical and chemical properties. The soils used to determine the equilibration process were USA1, USA6, GER, and USA4. After the adsorption process described above, 5 mL of the supernatant solution were withdrawn, and the amount of adsorbed was calculated. The remaining slurry was again brought to 10 mL by the addition of 5 mL of 0.01 M CaCl₂, equilibrated for 24 h. These steps were repeated three times consecutively. Based on the preliminary results, a sorption study was conducted with a soil solution ratio of 1:2 (5 g soil + 5 mL of 0.01 M CaCl₂ + 5 mL of a respective concentration of bispyribac sodium in 0.01 M CaCl₂). In the sorption study, bispyribac sodium concentrations of 0.1, 0.5, 1.0, 2.0, and 5.0 μg mL⁻¹ were used with an equilibration time of 16 h. In all soil adsorption analysis were conducted in triplicate samples. To check the interferences in samples and the stability of the test item, one rotating soil-free control, one static soil-free control, and one standard-free soil control were analyzed simultaneously. All vials, except the static soil-free control, were tumbled on a rotator for 16 h at 50–60 RPM at room temperature. The vials were removed from the rotator and centrifuged for 5 min at approximately 3000 RPM in a cooling centrifuge at 5–10 °C. After centrifugation, the supernatant was filtered using a 0.45 μm PTFE membrane filter and transferred to HPLC vials for analysis. In addition, the effects of different surfactants and surfactant concentrations, different background electrolytes and electrolys, and different test temperatures were examined in two different types of soils with different physical and chemical properties.

2.2.5. Instrumental

An Agilent® 1200 series high-performance liquid chromatograph equipped with a diode array detector was used for the quantification of the residue. The detector wavelength was set at 240 nm. The separation of herbicide residues was carried out using a Zorbax® column SB-C18 (3.5 μm particle size, 4.6 mm i.d., and 75 mm length). The mobile phase used was: ACN:0.1% H₃PO₄. The flow rate was programmed at 1.0 mL per minute. An injection volume of 50 μL was set for the standard and the sample. Bispyribac sodium was eluted at 6.1 min.

2.3. Data analysis

2.3.1. Method validation

The specificity, linearity, accuracy, and precision of the assay were determined to validate the method. The specificity of the method was confirmed by injecting the control soil extracts, mobile phase, acetonitrile, extraction solvent, diluting solvents, and buffer solutions. Different known concentrations of 5.0, 2.5, 1.25, 0.1, 0.05, and 0.01 mg L⁻¹ of bispyribac sodium were injected to determine the linearity. The mobile phase was used for the preparation of calibration solutions by diluting the stock solution. The peak area was measured after injecting each calibration solution. The correlation coefficient was calculated from the plot against the concentration of the standards versus the area observed. Based on a signal to noise ratio of 3:1, the limit of detection of the instrument was established.

2.3.2. Recovery, limit of quantification, and repeatability

The recovery of residues from the four different textured soils was examined by fortifying a known concentration (0.03 mg kg⁻¹) limit of quantification [LOQ] and 0.3 mg kg⁻¹ (10 × LOQ level) of standard in each soil. Five replicate determinations were used to check the precision of the method. The samples were homogenized using a homogenizer after fortification of the standard. They were then extracted, and residues of bispyribac sodium in the samples were analyzed with the HPLC-DAD method. Based on the results, the LOQ was established as 0.03 mg kg⁻¹. The repeatability of the method showed an acceptable RSD% according to the Hurwitz Eq. (1) below:

$$\text{RSD}^2 < 2^{(1-0.5 \log C)} \times 0.67,$$

where C is the concentration of the analyte expressed in the percentage. The maximum acceptable RSD% calculated based on Eq. (1) for an analyte concentration of 0.3 mg kg⁻¹ was 12.85%, and for 0.03 mg kg⁻¹ it was 18.17%.

2.3.3. Adsorption analysis

The amount of bispyribac sodium adsorbed after equilibrium was calculated according to the difference between the initial and the final equilibrium solution concentrations by Eq. (2) as follows:

$$C_s = (C_o - C_r) \times V/m,$$

where Cₛ (mg kg⁻¹) is the amount of bispyribac sodium adsorbed by the soil, and C₀ (mg L⁻¹) is the initial and equilibrium aqueous concentration. V (mL) is the volume of the soil, and m is the mass of the soil.

Adsorption was described by the linearized form of the Freundlich equation, as shown in Eq. (3) below:

$$\log C_s = \log K_f + 1/n \log C_o,$$

where Kᵢ is the adsorption coefficient characterizing the adsorption capacity and nᵢ is the Freundlich equation exponent related to the adsorption intensity, which is used as an indicator of the adsorption isotherm nonlinearity. Kᵢ-ads is the adsorption coefficient of the Freundlich equation.

The OM normalized adsorption constant (K₉₅ₐ₅) was calculated by normalizing Kᵢ-ads to the fraction of OM according to Eq. (4):

$$K_{om} = K_{i-ads}/OM \times 100\%.$$

(4)

The free energy of adsorption of the herbicide in the soil was calculated using the thermodynamic Eq. (5):

$$\Delta G = -RT \ln K_{OM},$$

(5)

where ΔG (kJ mol⁻¹) is the free energy of adsorption, R (8.314 x 10⁻³ kJ (K mol⁻¹)) is the mol gas constant, and T (K) is the absolute temperature.

2.3.4. Effect of different electrolytes and their concentrations on the adsorption analysis

The effect of the electrolytes and their concentration on the adsorption of bispyribac sodium in two different types of soils (USA4 and USA5) was studied using CaCl₂, KCl, NH₄Cl, KH₂PO₄, and MgCl₂. The concentrations of the electrolytes were 0.01 M, 0.1 M, and 0.5 M. The adsorption coefficient (Kᵢ) of bispyribac sodium was described by the Freundlich adsorption Eq. (3).

2.3.5. Effect of cationic, anionic, and nonionic surfactants and their concentrations on the adsorption analysis

The effect of cationic, anionic, and nonionic surfactants and different surfactant concentrations on the adsorption of bispyribac sodium in two different types of soils (USA4 and USA5) was studied using 0.01 M CaCl₂, 0.01 M KCl, and 0.01 M MgCl₂ as background electrolytes. The following surfactants were used in the study: sodium dodecyl sulphate (anionic), Tween-80 (nonionic) and cetyl trimethyl ammonium bromide (CTAB, cationic). Based
on the critical micelles concentration (cmc) of the surfactant was used to determine the adsorption. The surfactant concentrations were cmc, cmc/10, and cmc x 2. The adsorption coefficient (Kf) of bispyribac sodium was described by the Freundlich adsorption Eq. (3).

2.3.6. Influence of test temperature on the adsorption analysis

The influence of the temperature on the adsorption of bispyribac sodium in two different types of soils (USA4 and USA5) was studied using 0.01 M CaCl2 as a background electrolyte. The test temperatures were 20, 25, and 30 °C. The adsorption coefficient (Kf) of bispyribac sodium was described by the Freundlich adsorption Eq. (3).

3. Results and discussion

3.1. Dissipation

The soils collected from the different locations around the world had the following compositions: clay (0–43%), silt (1–53%), sand (18–96%), and organic carbon (0.41–4.4%). The pH of the soils was in the range of 5–8.3. Apart from the microbes, the above soil properties have a significant influence on the fate of pesticides. The USA4, USA6, NET1, and NET2 soil samples with organic carbon content greater than 3 and a pH less than 6.5 had a DT50 value between 5.1 and 5.9 d. The dissipation was faster in the soils with higher organic carbon and an acidic pH. The USA3, UK1, UK2, UK3, IND1, and IND2 soils with an organic carbon content of 1.1–1.8 and an acidic pH had a DT50 value of 6.1–10 d, and the dissipation of the residues was significantly higher when compared with the soils with a higher organic carbon content. The SPA1, ITA1, ITA2, GRE1, GER2, USA5, and FRA soils with a neutral and basic pH with less organic carbon content had a DT50 value greater than 14 d. The results of the dissipation study demonstrated that the availability of organic carbon and the acidity of the soil had a significant influence on the degradation of the residues. Residue of bispyribac sodium was more stable in the soils with a basic and neutral pH than in the soils with an acidic pH. The dissipation data for the soils are presented in Fig. 1 and the data shoes first order kinetics.

3.2. Adsorption kinetics

Fig. 2a. shows the adsorption kinetics after shaking four soils with 5 µg mL⁻¹ of bispyribac sodium in 0.01 M of aqueous solution. A rapid adsorption phase took place within 4 h after shaking. After 4 h, the herbicide concentration in the solution varied, with small changes, and the adsorption phase slowed. The adsorption equilibrium was reached within 8 h in all the soils tested. Moreover, the amount adsorbed by the soils remained steady. Further decreases in the bispyribac sodium concentration in the supernatant after 24 h were not significant. For laboratory convenience, the equilibrium time was taken as 16 h.

3.3. Adsorption characteristics

The Freundlich adsorption isotherms are shown in Fig. 2b. The values for the adsorption coefficient (Kf), were calculated for all the test soils. The Freundlich constant values Kf ranged from 0.31 to 5.71 mL g⁻¹, and the sorption isotherms were nonlinear, with 1/n values < 1 among the soils tested with 0.01 M CaCl2 as a background electrolyte. The adsorption coefficients were normalized to the organic carbon contents for each soil to calculate the soil sorption coefficients (Koc). The (Koc) values ranged from 34.0 to 169 among the soils tested. The adsorption isotherm of bispyribac sodium was dependent on the soil type, and the order of Kf_ads was clay loam (USA4) > loam (Ger) > sandy loam (UK3) > sand (IND1) > sand (NET1) > sand (UK2) > sand (NET2) > sandy loam (ind2) > clay (spa2) > silty clay loam (usa6) > loamy sand (ITA2) > loamy sand (UK1) > loamy sand (USA2) > sandy loam (USA3) > loamy sand (SPA1) > sandy loam (FRA) > sandy loam (GRE1) > sand clay loam (USA5) > sand (USA1) > sand (ITA1). The Kf and Koc values were low for the soils with a low organic carbon and clay content, and the adsorption of bispyribac sodium was high for the soils with a higher organic carbon and clay content, as confirmed from the Kf and Koc values. The comparison graph between the pH, distribution coefficient, organic carbon content, and half-life of the 21 soils are presented in Fig. 3. It shows that these parameters are directly related to each other. The pH of the soil and the organic carbon content of the soil had a significant effect on the dissipation of the residues of bispyribac sodium. The adsorption coefficient was directly proportional to the organic carbon content and half-life of bispyribac sodium in the soils as shown in Table 1.

The ΔG value of 40 kJ mol⁻¹ was employed as a threshold for identifying the physical and chemical mechanisms of adsorption, and physical adsorption was mainly involved below the threshold (Carter, 1995). The ΔG values of the 21 soils at 25 °C ranged from −4.78 to −3.23 kJ mol⁻¹, and the ΔG of bispyribac sodium in the soils was less than 40 kJ mol⁻¹, indicating that the adsorption of bispyribac sodium in these soils mainly occurs via physical processes. The adsorption of bispyribac sodium by the soils was a spontaneous process; it was confirmed based on the negative values of ΔG.

3.4. Effect of background electrolytes and the concentration of the electrolytes on bispyribac sodium adsorption

The results are shown in Fig. 4a. Bispyribac sodium adsorption in the two types of soil showed an increase with an increase in the concentrations of the aforementioned electrolytes.

Previous studies showed that the adsorption of different kinds of pesticides was different when CaCl2 was added as a background electrolyte (Gimsing and Borggaard, 2001; Spark and Swift, 2002). One study found that monosulfuron-ester adsorption in three kinds of soils increased with increasing CaCl2 concentrations (Wu et al., 2011b). Cheng and Huang (2009) found that the sorption of m-dinitrobenzene and nitrobenzene was significantly promoted with an increase in the electrolyte concentration (KCl or NH₄Cl). Pari and Yuet (2006) demonstrated that NaCl-, CaCl2-, and Na₂SO₄-specific adsorption increased with increasing ionic strength. The sorption enhancement was attributed to the interaction between the exchanged cations (K⁺ or NH₄⁺). Ali and Dzombak (1996) demonstrated that Ca⁺ is capable of forming complexes.

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Fig. 2. Sorption kinetics of bispyribac sodium in global soils and Freundlich adsorption isotherms of bispyribac sodium.

Fig. 3. The comparison graphs between the pH and organic carbon of the 21 soils with distribution coefficient and half-life of the bispyribac sodium.

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with simple organic acids and that adding CaCl₂ to the experiment leads to a possible complex between the anionic pesticides and Ca²⁺, which results in nonsorbing Ca²⁺ pesticide solution complexes. Haderlein and Schwarzenbach (1993) demonstrated that Ca²⁺ can adsorb onto silanol surface sites, resulting in positive Ca²⁺ sites, to which negatively charged compounds are attached due to electrostatic interactions. The adsorption coefficient values also varied according to the electrolyte and the electrolyte concentration in the present study. The Freundlich constant values of K_f also varied according to the electrolyte and the electrolyte concentration in the present study. The Freundlich constant values of K_f also varied according to the electrolyte and the electrolyte concentration in the present study.

The adsorption coefficient values of picloram between 1.194 and 2.45 mL g⁻¹ at all three surfactant concentrations (cmc, cmc/10, and cmc × 2) and with all three electrolytes (CaCl₂, KCl, and MgCl₂). In contrast, with the cationic surfactant, the adsorption coefficient (K_s) for the USA4 soil ranged from 2.0 to 19.52 mL g⁻¹ and from 0.9 to 24.5 mL g⁻¹ at all three surfactant concentrations (cmc, cmc/10, and cmc × 2) and for all the three electrolytes (CaCl₂, KCl, and MgCl₂).

3.6. Effect of temperature on bispyribac sodium adsorption

The results are presented in Fig. 4e. An adsorption coefficient (K_s) ranging from 3.1 to 6.2 mL g⁻¹ was observed in the USA4 soil, whereas it was 0.2–0.7 mL g⁻¹ in the USA5 soil. In both the soils, the adsorption coefficient was directly proportional to the temperature. Shariff (2012) reported Freundlich adsorption coefficient values of picloram between 1.194 and −1.506 mL g⁻¹ at 10, 25, and 40 °C.

3.7. Groundwater ubiquity score

The Gustafson (groundwater) ubiquity score (GUS) was used to determine the potential of groundwater contamination by bispyribac sodium. The leaching potential of the residues was determined from the GUS formula, with a higher GUS value indicating a greater risk of contamination of groundwater through leaching of residues from the surface. The following values illustrate the risk of groundwater contamination based on the GUS values.

<table>
<thead>
<tr>
<th>GUS value</th>
<th>Leaching potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.1</td>
<td>Negligible</td>
</tr>
<tr>
<td>0.1–1.0</td>
<td>Very low</td>
</tr>
<tr>
<td>1.0–2.0</td>
<td>Low</td>
</tr>
<tr>
<td>2.0–3.0</td>
<td>Moderate</td>
</tr>
<tr>
<td>3.0–4.0</td>
<td>High</td>
</tr>
<tr>
<td>&gt;4.0</td>
<td>Very high</td>
</tr>
</tbody>
</table>

The sorption coefficient (K_oc) and the half-life (DT₅₀) of bispyribac sodium were used to obtain the GUS values. These values are numerical, and the GUS values were obtained with the following formula:

Table 1
Comparison of soil physical–chemical properties, sorption, half life and GUS value.

<table>
<thead>
<tr>
<th>Country</th>
<th>Soil name</th>
<th>Soil texture</th>
<th>Soil type</th>
<th>pH</th>
<th>Organic carbon%</th>
<th>CEC (meq/100 g)</th>
<th>DT₅₀ (Days)</th>
<th>K_oc</th>
<th>K_m</th>
<th>GUS value</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>USA1</td>
<td>96</td>
<td>4</td>
<td>0</td>
<td>6.8</td>
<td>0.41</td>
<td>3.0</td>
<td>15.3</td>
<td>0.3</td>
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<td></td>
<td>USA2</td>
<td>81</td>
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<td>7</td>
<td>6.0</td>
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<td>2.0</td>
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<td>0.5</td>
<td>57</td>
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<tr>
<td></td>
<td>USA3</td>
<td>53</td>
<td>36</td>
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<td>7.5</td>
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<td>0.8</td>
<td>55</td>
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<td></td>
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<td>30.5</td>
<td>5.1</td>
<td>5.6</td>
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</tr>
<tr>
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<td>57</td>
<td>20</td>
<td>23</td>
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<td>30.4</td>
<td>16.1</td>
<td>0.3</td>
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<tr>
<td></td>
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<td>18</td>
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<td>29</td>
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<td>3.94</td>
<td>20.7</td>
<td>7</td>
<td>3.4</td>
<td>86</td>
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<tr>
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<td>9</td>
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<td>0.41</td>
<td>14.2</td>
<td>15</td>
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<td>40</td>
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<tr>
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<td>SPA2</td>
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<td>11</td>
<td>1.2</td>
<td>94</td>
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<tr>
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<td>ITA1</td>
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<td>0.5</td>
<td>20</td>
<td>16.2</td>
<td>0.3</td>
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<tr>
<td></td>
<td>ITA2</td>
<td>85</td>
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<td>0.6</td>
<td>25.6</td>
<td>15</td>
<td>0.5</td>
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<td>47</td>
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<td>1.2</td>
<td>14.1</td>
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<td>1.7</td>
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<td>62</td>
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<td>11</td>
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<td>1.2</td>
<td>18.3</td>
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<td>31</td>
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<td>1.5</td>
<td>21.7</td>
<td>16.2</td>
<td>0.5</td>
<td>34</td>
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<tr>
<td>Netherlands</td>
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<td>3</td>
<td>1</td>
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<td>114</td>
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<tr>
<td></td>
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<td>90</td>
<td>9</td>
<td>1</td>
<td>5.2</td>
<td>4.4</td>
<td>8.6</td>
<td>5.3</td>
<td>4.8</td>
<td>109</td>
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<tr>
<td>UK</td>
<td>UK1</td>
<td>86</td>
<td>7</td>
<td>7</td>
<td>6.3</td>
<td>1.8</td>
<td>12.2</td>
<td>8</td>
<td>2</td>
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<tr>
<td></td>
<td>UK2</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>6.3</td>
<td>1.8</td>
<td>12.2</td>
<td>8</td>
<td>2</td>
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<tr>
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<td>UK3</td>
<td>76</td>
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<td>11</td>
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<td>1.3</td>
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<td>5.8</td>
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<td>1.3</td>
<td>6.5</td>
<td>6.3</td>
<td>1.4</td>
<td>105</td>
</tr>
</tbody>
</table>
GUS = log_{10}(DT_{50}) + \frac{4}{C_0} \log_{10}(K_{oc}) / C_3^{\frac{4}{C_0}} \log_{10}(K_{oc}) / C_3^{\frac{4}{C_0}};

where DT_{50} is the time taken for the test item to degrade half of its concentration and K_{oc} is the soil sorption coefficient.

Based on the half-life and K_{oc}, the GUS values calculated for each soil were in the range of 1.3–2.9. The value indicates that the leaching potential of the herbicide residue through the soil was low to moderately leachable. The risk of leaching was low in the soils with a higher organic carbon and clay content. Sandy soils with low OM and low clay content with a GUS value >2.9 potentially have a high risk of contamination. Alonso et al. (2011) stated that solely on the basis of sorption, indaziflam has low to moderate mobility. Comparative results showing the physical and chemical properties of the soils, the half-life of bispyribac sodium in the soils, the K_{oc} value for each soil, and the GUS values calculated are presented in Table 1.

4. Conclusion

There were marked differences between the soils in their ability to degrade bispyribac sodium. The soil OC content had a positive influence on degradation rates of bispyribac sodium, and the soil
pH had a negative influence. Bispyribac sodium residue was persistent in neutral and basic conditions. The dissipation of bispyribac sodium followed first-order kinetics in tested soils. The soil pH and OM were the main factors affecting bispyribac sodium adsorption. The organic carbon content had a positive influence on adsorption, and the soil pH had a negative influence on adsorption. From the analytical results, it was concluded that there is a low to moderate risk of bispyribac sodium leaching in the soils studied. The ΔG values of the 21 soils ranged from −4.78 to −3.23 kJ mol⁻¹, and the ΔG of bispyribac sodium in these soils was less than 40 kJ mol⁻¹. The negative value of ΔG indicates that the adsorption of bispyribac sodium was mainly due to physical processes and also a spontaneous process. The adsorption of bispyribac sodium by two soils increased when the electrolyte concentration was increased. This was possible due to electrostatic interactions between bispyribac sodium and the background electrolyte concentration. The sorption coefficient values varied with the electrolyte and the electrolyte concentration in the order of CaCl₂ > MgCl₂ > KCl > NH₄Cl > KH₂PO₄. The variation may explained by the valency of the cations in the solution. Surfactants were influenced by the sorption coefficient of bispyribac sodium in two types of soils. The sorption coefficient value decreased when anionic and nonionic surfactants were used at the three surfactant concentrations in two types of soil but increased with cationic surfactants. The difference is possibly due to electrostatic interactions between cationic surfactant CTAB and anionic pesticide bispyribac sodium.

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References