DYNAMIC OF HERBICIDES IN SOIL AND SOIL MODIFIED WITH CLAY AND /OR HUMUS

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ABSTRACT

Herbicides are one of the most widely used agrochemical classes around the world. They help farmers to protect their crops against weeds. However, they can move through the soil profile polluting water resources and adversely affect human health. Groundwater is an important source for the production of drinking water in many places of the world and the presence of pesticide residues in groundwater is a serious threat to the health of consumers of drinking water. In this work, the behavior of two herbicides Atrazine and Trifluralin were study in an agricultural soil: Alhue soil and this soil modified whit clay (Kaolinite) and organic matter (Humus). The original soil and modified soil samples were characterized by their physicochemical properties: pH, EC, OC and texture. The analytical method was optimized for the quantification of Atrazine and Trifluralin by High Performance Liquid Chromatography (HPLC). The contact time, adsorption/desorption isotherms, persistence of both compounds in the soil samples and modified soil samples with clay and/or organic matter was studied. In general, all sorption curves for Trizine and Trifuralin in the modified soil samples were similar with relatively low adsorption for Trifuralin indicating that the soil modifications were not significant. The kinetic of sorption process was described by Elovich model. Both herbicides present a low Koc value, however, they present different types of adsorption, being for Atrazine a moderate adsorption and for Trifluralin a weak adsorption, which implies that both herbicides could be distributed in bodies of water as they are not fixed by organic matter. However, it should be noted that Atrazine presents higher Koc values than Trifluralin in all soil samples, which could mean that Atrazine would be less bioavailable than Trifluralin. Values obtained in the Pearson correlation of CO (%) and % of clay are expected since, when observing the results obtained in the Kd parameters for soils modified by both herbicides, they show that the higher the % of the physicochemical parameter, the higher the adsorption of the compound by the soil. The persistence of the pesticides showed that with both the addition of Kaolinite and Humus to the soil increases the half-life time for both herbicides. The results of the GUS index showed that both Atrazine and Trifluralin would be classified as leachable compounds in all soil samples.

Keywords: Soils; Humus; Kaolinite; Atrazine; Trifuralin; Elovich model; sorption constant Kd; Freundlich model, persitance, leaching.

1. INTRODUCTION

Herbicides are one of the most widely used agrochemical classes around the world. They help farmers to protect their crops against weeds. However, they can move through the soil profile polluting water resources and adversely affect human health. Groundwater is an important source for the production of drinking water in many places of the world and the presence of herbicides residues in groundwater is a serious threat to the health of consumers of drinking water. In spite of the regulations, activities and policies in place with respect to agrochemical compounds usage and the reduction of leaching, pesticides are still found in drinking water wells in practically every country around the world[1]. The contamination of aquifers by herbicides is a global environmental problem[2]. In various parts of the world such as Mexico, Brazil, Colombia, Argentina and Chile[3], Asia[4], Europe[5], and the USA[6], have found amounts from nanograms per liter (ngL^{-1}) to micrograms per liter (μgL^{-1}) of pesticides in groundwater.

Adsorption, degradation and transport are the main processes influencing the fate (persistence and mobility) of herbicides in the soil[7, 8]. Adsorption limits the movement influenced by factors such as clay and organic matter (OM) content and soil pH. Herbicides with greater water solubility usually have lower sorption capacity, which makes them more mobile in the soil and hence more prone to leaching. On the other hand, the persistence of herbicides in the soil differs greatly and is dependent on chemical (photolysis, hydrolysis, oxidation and reduction) and biological (non-enzymatic and enzymatic transformation) processes, soil temperature and water content[8]. Finally, the leaching behavior currently represents an important topic of research regarding environmental pollution. From the physical-chemical data of adsorption, degradation and mobility, obtained at lab-scale, it is possible to predict to model the behavior of herbicides in the soil.

The organic matter (OM) content in the soil is considered as the main factor responsible on herbicide adsorption due to the affinity of hydrophobic compounds by some fractions of OM [9-12]. Consequently, the retention of herbicides in the soil generally increases and their mobility decreases with addition of OM. On the other hand, the addition of organic wastes (OW) to soil results in an increase in the microbiological activity. Therefore, pesticide biodegradation is expected to be enhanced. In this context, different urban, farming and agro-industrial wastes have been explored as possible barriers to avoid or at least decrease pesticide leaching[13-18]. For this reason, the soil organic adsorption coefficient (*K*oc), is commonly used to appraise the mobility of herbicides through the soil[19, 20]. Low sorption coefficient indicates that an herbicide will be likely to leach. In addition, the determination of the disappearance half-life time (t½) in the soil is a valuable tool for calculating a mobility index. Long half-lives mean high persistence. Consequently, most of the indices used to evaluate the hazard of pesticide leaching such as Groundwater Ubiquity Score (GUS), Relative Leaching Potential Index (RLPI) and/or Leachability Index (LIX) consist of degradation and sorption as key factors[20, 21]. These indices based on both the characteristics of soils and physical-chemical properties of herbicides are easy to apply because agrochemical mobility can be estimated with limited data. However, soil-herbicide interactions may be altered by soil organic and inorganic colloids as well as by soil pH (pH < p*K*a neutral state and pH > p*K*a negative charge).

In soils with low organic matter contents, the adsorption of pesticide often depends on active compounds of the inorganic fraction, which is dominantly the clay fraction. An increase in clay content result increasing adsorption of pesticide [22-25].

1.1 Clay properties

Kaolinite (Kao) is predominantly a layered white clay mineral denoted by the chemical composition $Al_2Si_2O_5(OH)_4$. Formation of kaolinite occurs through hydrothermal modification or weathering of acidic igneous rocks containing aluminum-rich silicates like feldspars and muscovite. The mineral may also be present in granite and gneisses. The 1:1 aluminosilicate structure includes a silicon-centered tetrahedral sheet and an aluminum-centered octahedral sheet. Two-thirds of oxygen atoms are shared between the silicon and aluminum centers from the two layers while the remaining occur as hydroxyl groups in the octahedral layer. Further, aluminum centers are present only in two thirds sites of the octahedral sheet resulting in vacant sites. The two types of octahedral sites surrounded by hydroxyl groups impart a distorted hexagonal distribution to the sheet. Kaolinite surface may bear a small negative charge arising from isomorphic substitution of tetrahedral silicon ions. It is a non-swelling clay mineral and lacks the presence of exchangeable cations in the intermammillary region. Therefore, kaolinite offers far smaller surface areas and cation exchange capacities in comparison to swelling clay groups like montmorillonite. Kaolinite sheets occur in stacks from hydrogen bonding[26, 27].

1.2 Herbicides properties

1.2.1 Atrazine

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) (figure 1, table 1) is a s-triazine herbicide, used extensively to control annual grass and broadleaf weeds for over 50 years[28]. Atrazine is mobile in soil and does not get

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adsorbed by the soil particle and therefore has been frequently detected in surface and groundwater[29]. Major degradation pathways of atrazine include either biotic degradation governed by microorganisms[30], or abiotic degradation such as chemical and photochemical reactions[31]. Environmental conditions such as temperature[32], soil moisture content[33], pH[34], the oxygen content of the surrounding matrix[35], and soil type[36], have been reported to affect the persistence of atrazine in soil and natural environmental conditions.

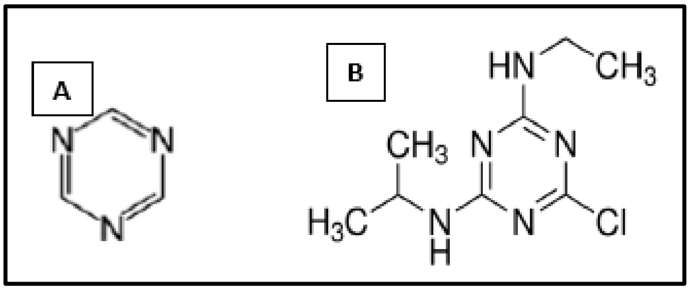


Figure 1. Basic structure of Triazines (A) and structure of Triazine (B)

Table 1. Physicochemical properties of Atrazine.

Physicochemical properties	Values
Melting point (° C)	173 – 177
Vapor pressure (mmHg at 25 ° C)	$2,89x10^{-7}$
Density (20 ° C)	1,23 g L^{-1}
Solubility	34,7 mg/L (water 27 °C)
Kow	2,6
Acidity (pKa)	1,60
Koc	100

Trifluralin (2,6-dinitro-N,N-dipropyl-4-trifluoromethylaniline) (figure 2, table 2) is a pre-emergent, soil applied herbicide used to control annual grass and broadleaf weeds. Trifluralin can adsorb onto the organic matter in soil; preventing absorption by the plants [37]. Leaching and soil lateral movement is restricted and therefore trifluraline tends to remain in the soil incorporation zone[38]. Trifluralin degradation in soil occurs through photo degradation, chemical processes, and microbial activities. However, the persistence of trifluralin has been reported to be affected by soil and environmental conditions [38].

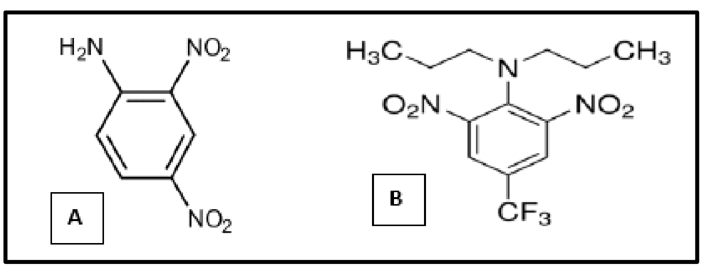


Figure 2. Basic structure of Dinitroanilines (A) and strucutre of Trifuralin (B)

Table 2. Physicochemical properties of Trifuralin.

Physicochemical properties	Values
Melting point (° C)	47,2
Vapor pressure (mmHg at 25 ° C)	$4,8x10^{-5}$
Densidad (20 °C)	1,06 – 1,09 g L^{-1}
Solubility	0,221 mg/L (water 20 °C)
Kow	5,3
Acidity (pKa)	Not applicable
Koc	15800

The objective of this work was to study the bhaviour of two herbicides: Atrazine and Trifluralin in the soil, through controlled applications of clay (Kaolinite) and the content of organic matter (Humus). Therefore, it is expected that the retention of herbicides in the soil will increase, reducing their diffusion into groundwater.

2. MATERIALS AND METHODS

2.1 Soil samples

Samples of Alhue soil from VI region, General Libertador Bernardo O`Higgins, Chile, was used in this study. Samples of soil (0-10 cm) were air dried and sieved (2 mm) before using. The physical and chemical properties of soil were determined by described methods[39].

2.2 Reagents and material

The agrochemicals chosen for this study were Atrazine; Trifluralin, both herbicides were purchased from Aldrich Chemical Company Inc. whit reported purity > 98%. Stock solutions 100 mgL^{-1} of each compounds standard was prepared by dissolving the weighed in acetonitrile (Merck HPLC grade).

Working standard mixed solutions were prepared weakly by diluting each individual stock solution with acetonitrile and storing at 4°C. Purifies water was prepared using a Milli-Q purification system (Simplicity) for HPLC analysis.

2.3 Soil samples preparation

The soil will be modified both with clay (Kaolinite, Sigma Aldrich $Al_2O_7Si_2 \cdot 2H_2O$ MM: 258.16 g / mol) and with humus (Earthworm Humus, Best Garden 100% natural).

The modifications made are as follows:

- Soil + 1% Clay (Kaolinite): The mixture was prepared based on 1 kg of soil, where 10 equal portions of 99 g of soil + 1 g of clay were mashed.
- Soil + 10% Clay (Kaolinite): The mixture was prepared based on 1 kg of soil, where 10 equal portions of 90 g of soil + 10 g of clay were mashed.
- Soil + 1% Organic matter (Humus): The mixture was prepared based on 1 kg of soil, where 10 equal portions of 99 g of soil + 1.0 g of humus were mashed.
- Soil + 10% organic matter (Humus): The mixture was prepared based on 1 kg of soil, where 10 equal portions of 90 g of soil + 10 g of humus were mashed.
- Soil + clay 1% (Kaolinite) + Organic matter (Humus 1%): The mixture was prepared based on 1 kg of soil, where 10 equal portions of 98 g of soil + 1.0 g of humus and 1.0 g of clay were mashed.

2.4 Chemical analysis.

The determination of Atrazine and Trifluralin was carried out with the help of a high performance liquid chromatography device with diode array detector (HPLC - PDA) WATERS 1525 BINARY HPLC Pump. Column: Atlantis C_{18}, 5.0 µm (Waters); Detector: Photodiode Arrangement, PDA (Waters 2996); Injection volume: 20 µL; flow 1.0 mL / min.

Compositions of mobile phases for the different compounds:

- Atrazine: Acetonitrile / water pH = 3.0 (H_3PO_4) 70/30 v / v; Injection volume: 20 µL, λ = 221.7 nm.
- Trifluralin: Acetonitrile / water pH = 3.0 (H_3PO_4) 80/20 v / v; Injection volume: 20 µL, λ = 273.7 nm

Standard solutions of atrazine and trifluraline of 100 mgL^{-1} were prepared in Acetonitrile. On the other hand, an equilibrating solution of $CaCl_2$ (Merck, PA) 0.01 M was prepared in a 1000 mL volumetric flask making volume with deionized water, degree Milli-Q, which fulfills the function of maintaining a fixed volume without any modification that may affect the results.

2.5 Determination of contact time.

The time in which the pesticide is applied to the soil reaches equilibrium between the different phases, that is, the time at which the concentrations of pesticide adsorbed to soil or dissolved in the solution remains constant. This step is necessary to validate the subsequent adsorption isotherm studies in which is required a periods of continuous stirring of set soil-pesticide, which must be greater than time needed to reach equilibrium. For this purpose 1 gram of each soil type was weighed separately in 20 mL conical centrifuge bottles containing 10 mL of each pesticide solution 100 mg/L. The mixtures were shaken on a horizontal orbital shaker at 100 rpm time intervals were 3, 6, 12, 24, 48,and 72 hours. Next, the suspensions were centrifuged at 3500 rpm for 15 min and the supernatant sieved 0.22 µm filter (PVDF) in a syringe filter (1.5 mL) before injected into HPLC for its quantification.

2.6 Sorption of herbicides in Alhue soil and its modifications.

Then, experiments were carried out in "Batch" that consisted of a battery of 22 flasks to carry out the tests of the samples and their duplication. These contained approximately 1.0 g of Alhue soil or soil modified samples, with decreasing amounts of the two herbicide (Atrazine or Trifluraline), and a balancing solution of 0.01 M $CaCl_2$ in increasing form, until completing a 10 mL total volume.

These tests were kept under constant agitation between 100-150 rpm for 48 hours (Heating Magnetic F20520162), to reach the minimum equilibrium time necessary between the soil and the herbicide. Once the time had elapsed, the soil solution in each flask was centrifuged for 15 minutes at 3500 rpm, and after that, the supernatant of each sample was filtered and stored refrigerated in plastic tubes. Finally, for the determination of the adsorption of each herbicide in the samples, it was determined by using the High Resolution Liquid Chromatography with Diode Arrangement Detector (HPLC-PDA) equipment.

2.7 Desorption of herbicides in Soil and modified soil samples

The respective bottle 6 of each compound was taken, which had 5 mL herbicide / 5 mL $CaCl_2$ 0.01 M where, only the soil content was saved, these were allowed to air dry for approximately a week until they were completely dry. Once dry, a washing was carried out with 5 mL of 0.01 M $CaCl_2$ with stirring for 1 hour at 100 rpm for each one, at the end of this stage, it was centrifuged for 15 minutes at 3500 rpm and the supernatant was filtered, keeping the resulting solution in a plastic tubes under refrigeration. The washing, centrifuging and filtering process for each bottle was repeated 3 times in total.

2.8 Persistence studies

The persistence studies of a pesticide consist in determining its concentration as a function of the elapsed time. For this, the incubation of the soils and modified with pesticides is carried out; where separate plastic cups were prepared into two groups (Atrazine and trifluralin) according to the persistence time to be studied: 0-3-6-9-24 hours, 2-3-4 days and 1-2-3-4-5-6 weeks (duplicate trials). All were added 5 g of soil and soil modified with clay and 2.5 mL of the pesticide solution whose concentration was 100 mgL^{-1}. A control cup was also prepared for each time, to which 2.5 mL of water was added. Humidity was maintained at field capacity in all samples.

The samples were left for the respective times, under conditions of constant temperature and humidity. Once the time of each test was finished, the soil was quantitatively extracted from the vessels into square flasks, using 10 mL of water / AN (50/50). The flasks are capped and shaken at 100 rpm for half an hour. The entire content is transferred to 15 mL centrifuge tubes, centrifuged at 3500 rpm for 15 min. Subsequently, the supernatant is extracted with a 5 mL syringe and filtered through a 0.22 µm PDVF membrane. Finally the tube is saved for later analysis.

2.9 Statistical analysis: Pearson's correlation

The adsorption constants (Kd) for each herbicide were related to the physicochemical characteristics of the soil alone and modified soil samples using Pearson's correlations. Parameters showing a value of $r > 0.7$ were considered strongly correlated, while values of $0.7 \geq r \geq 0.5$ were considered to exhibit a moderate correlation[40] .

3. RESULTS AND DISCUSSION

3.1 Physicochemical characterization of the studied soil and its modifications

Tables 3 and 4 show the results corresponding to the physicochemical characterization of the Alhue soil and the modified soil samples.

Table 3. Texture of soil and modified soils samples

Samples	**Sand (%)**	**Silt (%)**	**Clay (%)**	**Texture USDA**
Alhue Soil	91.20	6.20	2.60	Sandy
Soil + Kaolinite 1%	84.11	12.40	3.49	Sandy loam
Soil + Kaolinte 10%	72.66	20.06	7.28	Sandy loam
Soil + Humus 1%	86.84	10.68	2.48	Sandy
Soil + Humus 10%	87.66	9.85	2.49	Sandy
Soil + Kaolinite/Humus 1%	85.39	11.16	3.45	Sandy loam

In Table 3 it is observed that both the Alhue soil and modified soil present a similarity in the percentages of sand, clay and silt. As can be seen, the percentage of sand is the one that predominates in all the soil samples; therefore, they are soils that have high permeability. On the other hand, the clay content is the one that influences the adsorption of the various compounds and ions present in the soil. The sample of soil + Kaolinite 10% is the one with the highest clay content as expected, the soil with the mixture of Kaolinite and Humus also shows an increase in the percentage of clay.

Table 4. pH, CE and OC for soil and modified soils samples

.Muestra	**pH**	**EC [dS/m]**	**OC (%)**
Alhue Soil	7.07 ± 0.03	0.87 ± 0.04	1.61 ± 0.00
Soil + Kaolinite 1%	7.97 ± 0.01	0.71 ± 0.00	1.59 ± 0.01
Soil + Kaolinite 10%	7.98 ± 0.00	0.68 ± 0.00	1.61 ± 0.01
Soil + Humus 1%	8.27 ± 0.02	1.32 ± 0.00	1.67 ± 0.00
Soil + Humus 10%	8.42 ± 0.04	1.42 ± 0.00	3.02 ± 0.00
Soil + Kaolinite/Humus 1%	8.09 ± 0.01	1.02 ± 0.00	1.64 ± 0.01

According to the values obtained in Table 4, the Alhue Soil presented a “Neutral” pH, while all the modified Soil samples presented a “Moderately alkaline”. According to the electrical conductivity values, they allow the Alhue Soil and the Kaolinite-modified Soil samples to be classified as "Non-saline", which indicates that they are suitable for any crop, while the others show fall into the classification of “Low saline”, which indicates that very sensitive crops could be restricted [41].

The OC percentage for the Alhue Soil, which is a volcanic soil, is considered "Very low"; as for all modified soil samples, which are also considered “Very low. Considering the percentages of organic matter obtained for all the samples, the sample of "Soil + Humus 10%" would present a higher adsorption of pesticides, since it is known that the capacity of the soil to adsorb chemical compounds increases with the content of organic matter [42].

3.2 Equilibrium time: Elovich model.

There are several models to determine the kinetic adsorption process; one of them is the Elovich kinetic model that is applied to heterogeneous solid-liquid adsorption systems. This model is suitable for general applications that have chemistry kinetics.

To determine if the adjustment made by the kinetic model is good, analyze two experimental parameters: $R^2 > 0.8$ and relative error (RE) <10%, which difference between experimental values and those obtained from the model, that is, difference of the measured value and the theoretical value divided by the exact value (Han et al., 2009). The correlation values obtained by applying equation 1 and the relative error values (RE) are shown below (eq. 1).

To apply the model, the adsorbed concentration (Cs exp.) is plotted as a function of Ln of the stirring time (Ln (t)), from which a logarithmic equation (equation 3) is applied from which the value of Cs.

$$Cs = 1 / b \, Ln (ab) + 1 / b \, Ln (t) \qquad \text{(eq. 1)}$$

Tabla 5. R^2 and RE (%) values calculated from the adjustment of the Elovich Model for the herbicides Atrazine and Trifluralin in Alhué Soil and Modified Soil.

Suelo	Parámeter	Atrazine	Trifluralin
Alhué Soil	R^2	0.99	0.95
	RE	9.86%	10.07%
Soil + Kao 1%	R^2	0.95	0.93
	RE	10,09%	10.02%
Soil + Kao 10%	R^2	0.96	0.91
	RE	9.62%	10.00%
Soil + Humus 1%	R^2	0.95	0.92
	RE	9.87%	9.28%
Soil + Humus 10%	R^2	0.96	0.93
	RE	8.99%	8.82%
Soil + Kao/Humus 1%	R^2	0.93	0.91
	RE	9.93%	9.83%

According to the values obtained experimentally and shown in Table 5, it is possible to infer that the determination of the equilibrium time of Atrazine in the Alhue Soil and the modified Soil samples (except Alhué Soil + Kao 1%), as in Trifluralin (except Soil Alhue and Soil Alhue + Kao 1%) are adjusted to the Elovich Kinetic Model, since for all these cases the correlation coefficient (R^2) is greater than 0.80 and the relative error (RE) is less than 10%, so the adsorption rate can be described by means of this model for these samples with these two herbicides.

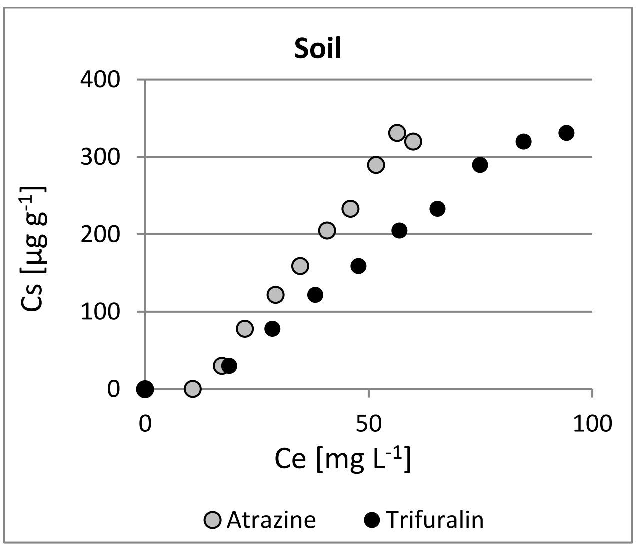
3.3 Adsorption isotherms

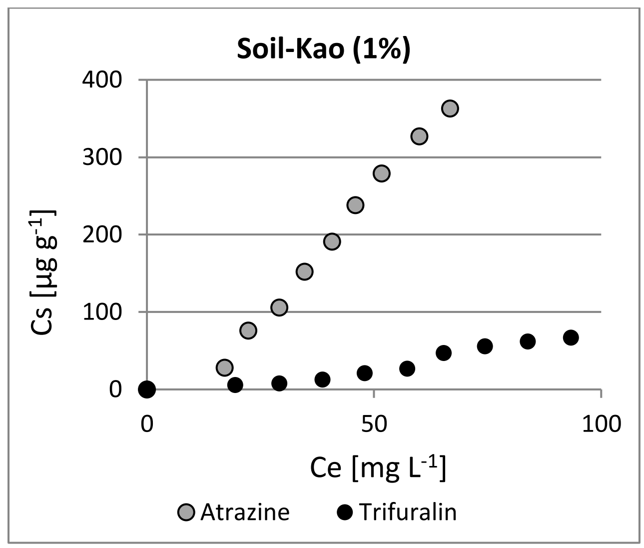
The adsorption process is defined as the concentration of substances on colloidal surfaces, where it occurs because the adsorbent has active sites that depend on the physicochemical characteristics and the affinity of the compounds, in which sorption sites and surfaces can become saturated and forms an adsorbed film. In the event that the existing concentration is sufficient, an equilibrium state will be created at the same moment in which no more molecules are adsorbed, leaving a residual concentration in the solution.

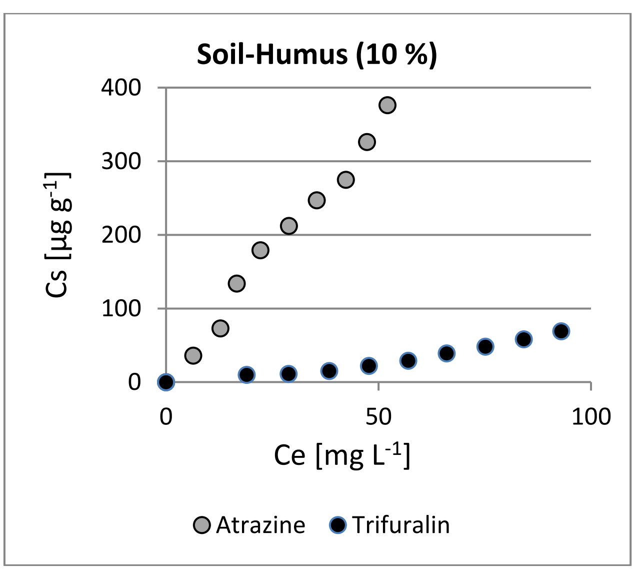
In general, the sorption process is described by curves called sorption isotherms, which are representations that contrast a relationship between the adsorbed concentration (Cs) vs the equilibrium concentration (Ce) at a constant temperature. For this reason, known amounts of pesticides that have different initial and solid concentrations are made to interact, where once equilibrium is reached, the amount of the pesticide that is in solution (Ce) is determined, as well as the amount of pesticide sorbed (Cs) for the different initial concentrations [43]. This is why the adsorbate sorption process can be described as linear, favorable or unfavorable, which allows predicting the mobility of the compounds in the soil.

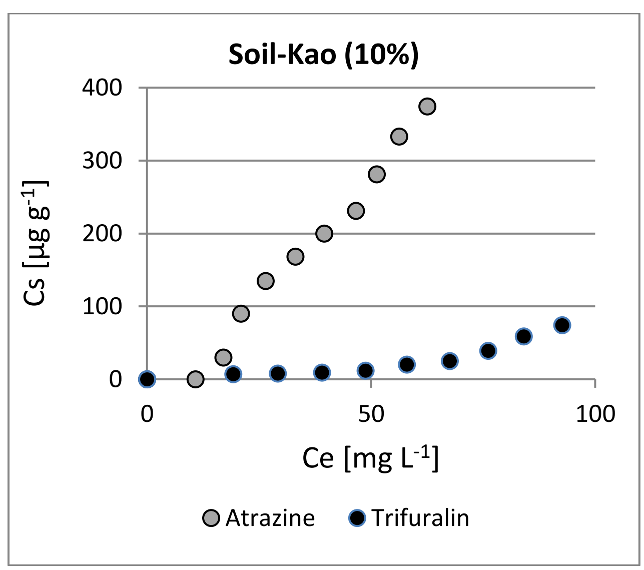
When it comes to linear adsorption, it refers to the fact that the adsorbate is weakly retained on the surface. On the other hand, when speaking of a favorable adsorption, it refers to the fact that the adsorbate has an affinity with the surface of the adsorbent, while, for an unfavorable sorption, it refers to the fact that it is not possible to observe a clear affinity between adsorbate - adsorbent.

The soption isotherms are shown in the next figures.









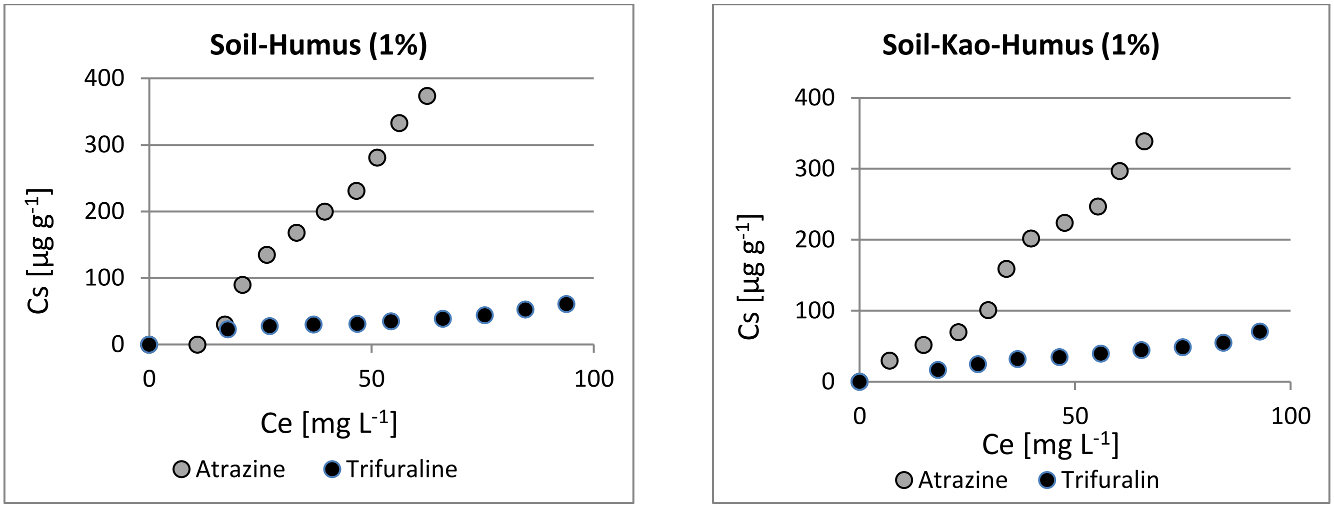


Figure 3. Adsorption curves of Triazine and Trifuralin in samples of soil and soil modified with clay and / or humus.

The sorption curves of both herbicicdes in soil shown a similar behavior with significant adsorption.

In general, all sorption curves for Trizine and Trifuralin in the modified soil samples were similar with relatively low adsorption for Trifuralin indicating that the soil modifications were not significant

When comparing the Atrazine adsorption isotherms for the Alhué Soil and the modified Soil samples, with the general types of adsorption curves it can be determined that for the Alhué Soil and modified Soil samples a linear adsorption was presented.

When comparing the adsorption isotherms of Trifluraline with the general types of adsorption curves it can be determined that for most of the samples it had a favorable trend.

3.3 Kd and Koc parameters

These coefficients provide information on the interaction between adsorbate and adsorbent; however, in this case as the study will be carried out in the Alhue Soil and modifications for both compounds, the Kd parameter will be the most important for this work [44,45].

The adsorption coefficient (kd) was defines by Equation 2.

$$kd = Cs/Ce \qquad \text{(eq. 2)}$$

The linear or distribution coefficient (Kd) is related to soil organic carbon (OC) and soil organic matter (OM) by the following equations [46, 47].

$$Koc=100\ Kd / (\%OC) \qquad \text{(eq. 3)}$$

The values obtained for atrazine and trifluraline, calculated with an average of all the points of the graph with equations 1 and 2, in the Alhue soil and the modified soil samples are shown in Table 6.

Table 6. Kd and Koc values for both herbicides.

ATRAZINE		
SOIL SAMPLES	**Kd**	**Koc**
Alhue soil	4.15	207.5
Soil-Kaolinite 1%	4.38	219.0
Soil-Kaolinite 10%	4.69	234.5
Soil-Humus 1%	5.07	253.5
Soil-Humus 10%	7.30	365.0
Soil-Kaolinite/Humus 1%	4.68	233.8
TRIFLURALIN		
	Kd	**Koc**
Alhue soil	0.25	12.5
Soil-Kaolinite 1%	0.43	21.5
Soil-Kaolinite 10%	0.48	24.0
Soil-Humus 1%	0.47	23.5
Soil-Humus 10%	0.67	33.5
Soil-Kaolinite/Humus 1%	0.76	38.0

When analyzing the values obtained in Table 3, it is observed that atrazine has a higher Kd value in the Soil-Humus 10% sample, which could be explained due to the greater amount of organic matter that this soil has, compared to the other soil samples. However, it is observed that Trifluraline presents a higher Kd value in the Soil –Kao-Humus 1% sample, which could be explained due to the higher content of clay and humus present in the soil. This would indicate that Atrazine and Trifluraline have different behaviors regarding the aggregates that were added to the soil; therefore, they would be adsorbed with greater intensity by different soil samples.

Both herbicides present a low Koc value, however, they present different types of adsorption, being for Atrazine a moderate adsorption and for Trifluralin a weak adsorption, which implies that both herbicides could be distributed in bodies of water as they are not fixed by organic matter. However, it should be noted that Atrazine presents higher Koc values than Trifluralin in all soil samples, which could mean that Atrazine would be less bioavailable than Trifluralin.

As can be seen, when adding clay and humus it is seen that the amount of adsorbed herbicide increases slowly, the adsorption order being as follows: "Herbicide - Soil <Herbicide - Soil / Kaolinite 1% <Herbicide - Soil / Humus 1% <Herbicide - Soil / Kaolinite 10% <Herbicide - Soil / Humus 10%.

Thus with a floor it can be fulfilled that:

S***or***ption = organic components $\boldsymbol{f}$ (***org***) + inorganic components $\boldsymbol{f}$ (***ino***r)

Where, $\boldsymbol{f}$ (org) is the contribution factor of organic matter that participates in adsorption and $\boldsymbol{f}$ (inor) is the contribution factor of inorganic matter that participates in adsorption. Furthermore, both factors range from 0 to 1 [48].

Therefore, in this work there are three situations:

- Adsorption = organic components · $\boldsymbol{f}$ (org) + inorganic components · $\boldsymbol{f}$ (inor), in which $\boldsymbol{f}$ (inor) has been increased.
- Adsorption = organic components · (org) + inorganic components · $\boldsymbol{f}$ (inor), in which (org) has been increased.
- Adsorption = organic components · f$\boldsymbol{f}$ (org) + inorganic components · (inor), in which $\boldsymbol{f}$ (inor) and (org) have been increased.

The union that exists between organic matter and clays on a molecular scale occurs through different ways, such as ligand change, polyvalent cationic bridges, hydrophobic interactions, hydrogen bonds, dipole, induced dipole and complexation [49, 50], which are those that affect the adsorption of the pesticide in the soil. In addition, it should be noted that Kaolinite and Humus, when added to the soil, can be inferred that these types of interactions increase, giving an increase in the adsorption processes for Atrazine and Trifluralin. In addition, it should be noted that the adsorption of these two pesticides on Kaolinite occurs clearly on its surface, which has been studied in various works [51, 52], due to the difference in polarity between the molecule and the faces of the Kaolinite, not being possible an internal adsorption in the structure of this one.

3.4 Freundlich model

The Freundlich model, considers that the surface on which the adsorption occurs is heterogeneous and, in addition, reveals the capacity to adsorb added pesticides for each soil. To determine this, the Freundlich equation (equation 4) is applied, which relates the Log of the adsorbed concentration (Cs) as a function of the Log of the concentration at equilibrium (Ce) and is described as follows:

$$\boldsymbol{Log}\ (\mathrm{Cs}) = \boldsymbol{n_f}\ \boldsymbol{Log}\ (\boldsymbol{Ce}) + \boldsymbol{Log}\ (\boldsymbol{K_f}) \qquad \text{(eq 4)}$$

Where Cs is the adsorbed concentration of the herbicide; Ce is the equilibrium concentration of the herbicide; nf is the adsorption intensity constant and Kf is the adsorption capacity constant.

One way to analyze the results obtained by the Freundlich model is through the adsorption intensity constant (n_f), which corresponds to the slope and the adsorption capacity constant (K_f) that corresponds to the intercept of the equation. It is worth mentioning that it should be taken into account that:

• nf> 1 adsorption is considered favorable [53].

• nf ~ 0 greater heterogeneity presents the system. [54].

• Kf determines adsorbate-adsorbent affinity, where the higher the Kf, the higher the affinity.

R^2> 0.95 tells whether the model fits or not.

Table 7. Values obtained from the Freundlich model.

ATRAZINE			
Samples	$\mathbf{K_f}$	$\mathbf{n_f}$	$\mathbf{R^2}$
Alhue Soil	0.388	0.60	0.97
Suelo + Kaolinite 1%	0.589	0.64	0.99
Suelo + Kaolinite 10%	0.687	0.65	0.98
Suelo + Humus 1%	2.127	0.80	0.99
Suelo + Humus 10%	5.293	0.93	0.98
Suelo + Kaolinite/Humus 1%	3.119	0.92	0.96
TRIFLURALIN			
Samples	$\mathbf{K_f}$	$\mathbf{n_f}$	$\mathbf{R^2}$
Alhue Soil	0.260	0.81	0.96
Suelo + Kaolinite 1%	0.014	0.51	0.97
Suelo + Kaolinite 10%	0.227	0.92	0.95
Suelo + Humus 1%	0.057	0,64	0.95
Suelo + Humus 10%	3.672	1.71	0.99
Suelo + Kaolinite/Humus 1%	2.181	1.36	0.98

According to the values observed in Table 4, both Atrazine and Trifluraline can be explained by the Freundlich model, since they have an R^2 greater than 0.95. The adsorption intensity nf, turned out to be favorable (> 1) for Trifluraline in S-Humus 10% and Soil –Kao-Humus 1%, while the other samples for both herbicides present values close to 1. It should be noted that, when adding Kaolinite and Humus to the soil, slightly increases its adsorption.

Regarding the adsorption capacity constant K_f, the results obtained for atrazine are the highest, which, in turn, would indicate that it would be retained with greater force in Soil and Modified Soil, while Trifluraline would have a weaker affinity with the solid phase of the soil, since its K_f values are the lowest, so it could be mobilized through the soil profiles. With regard to aggregates, a slight increase can be observed when 10% Kaolinite is added to the soil, while when the soil is added

Add 10% Humus increases considerably for both herbicides. Other studies have found that Atrazine adsorption is time dependent and that the Freundlich adsorption model fits well with experimental adsorption isotherms [22].

3.7 Desorption of herbicides

To achieve the extraction of herbicides from the soil, 0.01 M $CaCl_2$ was used as an extracting, which allows maintaining the ionic strength of the solution and achieving the same level of aggregates in the porous medium [43]. Next, Table 5 shows the values obtained in the study of desorption for Atrazine and Trifluraline in the Alhue Soil and the modified Soil samples.

Table 8. Desorption of Atrazine and Trifluraline for Alhue Soil and Modified Soil.

ATRAZINE			
Samples	Added concentration (mgL-1)	Desorption concentration (mgL^{-1})	**Desorption (%)**
Alhue Soil	50	5.9	11.9
Soil + Kaolinite 1%	50	5.7	11.5
Soil + Kaolinite 10%	50	5.6	11.2
Soil + Humus 1%	50	5.2	10.4
Soil + Humus 10%	50	5.0	10.0
Soil + Kaolnite/Humus 1%	50	5.4	10.9
TRIFLURALIN			
Samples	Added concentration (mgL-1)	Desorption concentration (mgL^{-1})	**Desorption (%)**
Alhue Soil	50	8.2	16.5
Soil + Kaolinite 1%	50	7.6	15.3
Soil + Kaolinite 10%	50	7.4	14.9
Soil + Humus 1%	50	7.2	14.4
Soil + Humus 10%	50	6.9	13.8
Soil + Kaolinite/Humus 1%	50	6.6	13.2

Regarding Table 8, it can be observed that Trifluraline presents higher percentages of desorption in Soil and Modified Soil, being approximately 14.0%, which coincides with the values of the Kd and Koc constants previously determined, which are much lower than those obtained for Atrazine (table 6). Therefore, according to these values of these constants, it can be determined that Atrazine has a higher adsorption than Trifluraline for Soil alone and modified Soil, indicating that it would have higher retention, which is reflected in its lower desorption percentages.

When analyzing the percentages obtained for each soil sample, it can be determined that they are higher in Alhue Soil for both herbicides, which could be related to their lower percentage of organic matter and clay present (Kd Alhue Soil - Atrazine: 4.15; Kd Soil Alhue - Trifluraline: 0.25). On the other hand, the sample of S-Humus 10% presents lower percentages of desorption, since it has a higher percentage of organic matter, which favors the retention of both herbicides (Kd S-Humus 10% - Atrazine: 7.30; Kd S-Humus 10% - Trifluraline: 0.67).

3.8 Persistence of Atrazine and Trifluraline

When an herbicide is applied to the soil, several processes occur: a very brief initial stage in which a high concentration of the pesticide is maintained called the lag phase, a dissipation phase in which the initial concentration of the pesticide begins to decline rapidly, and, finally, a stage in which the decrease of these is slow.

To understand the dynamics of a pesticide in the soil, it is important to determine the persistence that it will have in it, since this parameter could indicate the period in which the compound will be bioavailable. The next tables showed the persistence stages for Atrazine and Trifluraline in Soil and modified soil.

Table 9. Atrazine % values at time zero and at the end of the study for the different soil samples.

Samples	**Atrazine concentration at Initial time (0 h)**	**Atrazine concentration at Final time (42 days)**	**Decaiment (%)**
Alhue Soil	21.62	14.55	32.7 0
Soil-Kao 1%	20.89	15.24	27.0 5
Soil-Kao 10%	25.22	15.91	36.9 2
Soil-Humus 1%	22.15	14.79	33.22
Soil-Humus 10%	23.60	16.56	29.83
Soil-Kao-Humus 1%	21.27	16.23	23.22

Table 10. Trifulaline % values at time zero and at the end of the study for the different soil samples.

Samples	Trifuraline concentration at Initial time (0 h)	Trifuraline concentration at Final time (42 days)	Decaiment (%)
Alhué Soil	50.31	0	100
Soil-Kao 1%	59.52	0	100
Soil-Kao 10%	65.60	15.12	76.95
Soil-Humus 1%	59.92	9.12	84.78
Soil-Humus 10%	62.64	11.15	82.20
Soil-Kao-Humus 1%	56.19	9.10	83.80

In table 9, it is observed that the concentration of Atrazine decreases slowly for all the soil samples as the days pass. At time zero, the percentage of Atrazine for the different soil samples can be seen to be quite low, indicating the absence of the latency period and a strong initial adsorption, relatively similar for all the soil samples. In addition, it is possible to observe that at 42 days (end time of the study) a certain percentage of Atrazine is still found in all the soil samples.

Table 11. Gus index values and half time (days) for both herbuicides.

Soil samples	ATRAZINE		TRIFLURALIN	
	ÍGUS index	Half-life time (days)	ÍGUS index	Half-life time (days)
Alhué Soil	3.34	96.27	4.37	32.09
Soil + Kao 1%	3.58	144.41	4.31	41.26
Soil + Kao 10%	3.52	144.41	4.41	41.26
Soil + Humus 1%	3.17	96.27	3.96	32.09
Soil + Humus 10%	3.54	288.81	3.85	48.14
Soil + Kao/Humus 1%	3.52	144.41	3.65	32.09

The half-life time (Table11), which is the data that indicates the persistence of pesticides, it was found that the dissipation of 50% of the initial concentration is at 96 days for Alhué Soil and from 144 to 288 days for the modified soils, which would explain why at the end of the persistence study, it is still possible to find between 15 - 20% of Atrazine in all the modified soil samples. According to the values obtained for the half-life time, Atrazine for "Alhué Soil" and "Soil + Humus 1%" could be classified as a "moderately persistent" pesticide, while all other samples can be classified as "persistent". These results are similar to those obtained in other works since, a study carried out by[50], reported that the half-life of Atrazine for a soil sample in Mexico was 120 days. In addition, it has been reported through other studies that the presence of allophanic clays and organic carbon content determine a greater persistence or adsorption of Atrazine in soils [51].

However, there are many more studies on the determination of the half-life of Atrazine in the soil worldwide, where values between 54 - 56 days have been found in soils of Brazil [52], while in soils from Minnesota was found that after 16 months, Atrazine and its degradation products were still present in the soil, with a potential for mobility that can contaminate groundwater [53].

In addition, it is possible to observe through Table 10 that at 42 days (end time of the study) a certain percentage of Trifluralin is still found in almost all the soil samples, except for the samples of "Alhué Soil" and "Soil + Kaolinite 1 % ". On the other hand, when determining the half-life time (Table 11), which is the data that indicates the persistence of pesticides, it was found that the dissipation of 50% of the initial concentration is between 32 and 48 days for all the soil samples, which would explain why at the end of the persistence study, it is possible to find between 10 - 20% of Trifluralin in some soil samples and not in others, as is the case of "Alhué Soil" and "Soil + 1% kaolinite ". According to the values obtained for the half-life time, Trifluralin could be classified as a "moderately persistent" pesticide for all soil samples (Table 8). A study by M.J. Calderón et al. (1999), reported that the half-life of Trifluraline for field soils in Seville, in which conservation tillage is carried out, was 90 days during the years 1995 and 1997[55]. On the other hand, another study carried out by Corbin Jr. et al. , (1994), which lasted 30 months and when extrapolating the half-life time for this pesticide was 110 days [56].

3.9 Pearson correlation

In this study, a Pearson correlation was carried out, which considers the Kd parameters of both herbicides together with the physicochemical factors of pH, MO (%) and% of clay for the soil samples modified with Kaolinite and Humus. Next, Tables 9 and 10 are shown, which show the values obtained corresponding to modification with Kaolinite and modification with Humus, respectively.

Table 12. Pearson's correlation matrix for Kaolinite-modified samples

	pH	OC %	Clay %	Kd – Atrazine	Kd – Trifluralin
pH	1				
OC (%)	-0,492	1			
Clay %	0,654	0,337	1		
Kd – Atrazine	**0,826**	0,085	**0,967**	1	
Kd – Trifluralin	**0,980**	-0,310	**0,791**	**0,921**	1

Table 13. Pearson's correlation matrix for samples modified with Humus.

	pH	OC %	Clay %	Kd – Atrazine	Kd – Trifluralin
pH	1				
MO (%)	0,615	1			
Clay %	-0,980	-0,467	1		
Kd – Atrazine	**0,791**	**0,969**	-0,672	1	
Kd – Trifluralin	**0,923**	**0,871**	-0,841	**0,966**	1

The correlation factors calculated and highlighted in black indicate that there is a strong correlation between the pH and Kd of both herbicides (Tables 12 and 13), that is, there may be a dependency relationship of pH-herbicide, indicating that Atrazine has lower values (R = 0.826; R = 0.791) compared to Trifluralin (R = 0.980; R = 0.923), since its adsorption is affected by pH due to the simple fact that at low pH values it protone and can form ionic bonds, while Trifluralin will depend on the characteristics of the soil under study.

Another factor that shows a strong correlation is the % of clay with the Kd of both herbicides shown in Table 6, which may indicate that this parameter influences the increase in adsorption of pesticides in the soil, indicating that there is a high correlation higher for Atrazine (R = 0.967) than for Trifluralin (R = 0.791). Likewise, another factor that shows a strong correlation is with the OC (%) with the Kd of both herbicides shown in Table 10, which may indicate that it can also influence the increase in adsorption of pesticides in the soil, being again a higher correlation for Atrazine (R = 0.969) than for Trifluralin (R = 0.871).

Both the values obtained in the Pearson correlation of CO (%) and % of clay are expected since, when observing the results obtained in the Kd parameters for soils modified by both herbicides, they show that the higher the % of the physicochemical parameter, the higher the adsorption of the compound by the soil.

Finally, when observing the values obtained between Kd-Atrazine versus Kd-Trifluralin in Tables 12 and 13 (R = 0.921; R = 0.966 respectively), it can be assumed that if both herbicides are placed together they could experience a competition for the adsorption in the soil, being Atrazine the one that adsorbs with greater intensity.

CONCLUSIONS

- The characterization of the affinity, adsorption - desorption and retention processes suggest that the physicochemical characteristics of the different soil samples have similar effects on the dynamics of Atrazine and Trifluralin, however, in magnitudes they are different.
- A slight increase in the adsorption of pesticides was observed when the soil was modified with Kaolinite and Humus, being more noticeable in the samples modified with 10% Humus.
- The Freundlich parameters, the Kf values for Atrazine were higher in all the soil samples, which indicates that this compound would be retained with greater force compared to Trifluralin, while the nf parameter values were slightly higher for Trifluralin. Therefore, it could be inferred that Atrazine would present a higher affinity in the soil samples.
- From the persistence results, it was appreciated that, with the Kaolinite and Humus aggregates, there was an increase in the half-life time compared to the Alhué Soil for both herbicides.

- The GUS index values showed that both pesticides are leachable, being able to appreciate that Trifluralin presents higher values compared to Atrazine.
- Finally, the difference in the dynamics of these two compounds could arise from their structural differences. Atrazine is a molecule with more basic characteristics than Trifluralin, it also shows a greater possibility of hydrogen bonding from the NH bonds of the side chains, in addition to having a higher solubility in water (34.7 mg / L at 27 ° C). Furthermore, the Kow value of Atrazine (Kow = 2.6) suggests that this compound would have little affinity for lipophilic matrices such as soil organic matter in comparison with Trifluralin (Kow = 5.3). Therefore, the acid-base interactions by hydrogen and lipophilic bonds with the different soil samples would be defining the dynamics of these two herbicides.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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