



Correlation between surface and underground aquatic environment pH and pKa in pesticide ionization and contribution to water contamination

Luzia Suerlange Araújo dos Santos Mendes

Doutoranda em Geologia, UFC, Brasil.
luzia.suerlange@bol.com.br

Eveline Cunha Lima

Mestre em Engenharia Química, UFC, Brasil.
evelineclima@yahoo.com.br

Joyce Shantala Fernandes de Oliveira Sousa

Doutoranda em Geologia, UFC, Brasil.
joyceshantala@gmail.com

Tomaz Alexandre da Silva Neto

Mestre em Geologia, UFC, Brasil.
tomaz.neto@alu.ufc.br

Itabaraci Nazareno Cavalcante

Professor Doutor, UFC, Brasil.
itabaracicavalcante@gmail.com

ABSTRACT

The behavior of a pesticide in the environment depends on the physical and chemical properties of the environment. The migration of these substances between the environmental matrices depends on the physicochemical properties of these compounds, including pH and the acid or base ionization equilibrium constant (pKa), which define the time these substances remain in the environment, considering that pH more acid is more conducive to a longer permeation time in the environment. The research aimed to correlate the pH values, measured in the water samples collected in the superficial aquatic environment, irrigation channel of the Perimeter Irrigated Board of Russas (PITR), and underground in the municipality of Russas - Ceará. The properties were analyzed in four collection cycles for pesticides: Acephate, Aldicarb, Ametrine, Dimethoate, Imidacloprid, Permethrin and Tebuconazole. The pKa values of the pesticides were obtained from the International Union of Pure and Applied Chemistry (IUPAC), the pH measurements were carried out in situ. The study showed that the results show an acid tendency in the samples collected in the rainy season, which favors the leaching of substances and a longer period of permanence in the environment. It is also observed that the waters of the PITR showed a basic trend, and this is possibly due to the presence of organic matter along the channel. In this study, it was observed that the substances Acephate, Tebuconazole, are weak acids of moderate intensity, which can remain longer in the environment, and Aldicarb and Ametrine, are very weak acids with moderate intensity.

KEYWORDS: Ionization constant. Hydrogen potential. Pesticides.

1 INTRODUCTION

The presence of pesticides in the environment can be influenced by certain factors and physicochemical properties of substances, such as volatility, application method, type of formulation, and solubility of the compound in water; soil and plant characteristics; adsorption of molecules to soil particles; persistence and mobility of compounds; and environmental, climatic conditions.

The behavior of a substance in the environment, from its application to its final destination, is identified through the study of the physical and chemical properties of the environment. Each pesticide has its molecular structure, individualizing how it interacts with the environment.

When applied in the field, pesticides can contaminate not only soil, water, and air but also sediment (DELLAMATRICE; MONTEIRO, 2014). The migration of these substances between environmental matrices depends on the physicochemical properties of the compounds, such as water solubility (S), coefficient of adsorption normalized by organic carbon (KOC), octanol-water partition coefficient (KOW), Henry's Law constant (KH), vapor pressure (PV), acid or base ionization equilibrium constant (pKa), sorption coefficient (Kd), soil half-life ($t_{1/2}$ soil), water half-life ($t_{1/2}$ sed/water) (CASSAMASSINO, 2005, p. 16-17), and also environmental conditions such as temperature, humidity, wind speed, and direction (GAMA, 2018).

Hydrolysis, one of the processes of pesticide transformation in water, is probably the most important chemical degradation reaction of herbicides. Hydrolysis refers to the breaking of chemical bonds and the incorporation of water components,

hydrogen ions (H⁺), or hydroxide ions (OH⁻) into the molecular structure of the herbicide (BARROSO; MURATA, 2021). Another important chemical process for the transformation of herbicides is oxidation-reduction reactions. These reactions mainly involve the transfer of electrons to ionizable compounds (SPADOTTO, 2010).

The water pH is important for both the degradation by hydrolysis (whose speed depends on pH) and the dissociation of ionizable herbicides (CARVALHO, 2013). By the pH value of a solution, it is possible to calculate the concentration of free hydrogen ions (H⁺) and classify the ionic character of pesticides. Ionizable pesticides have pH-dependent charges and can be acidic when dissociating into an anion (HA⁻) releasing (H⁺) and basic when dissociating into a cation (HB⁺) releasing (OH⁻). Non-ionizable pesticides do not have pH-dependent charges and can be non-ionic as they do not have free charges (nonpolar) (CARVALHO, 2013).

Herbicides are classified as strong or weak acids. The terms weak or strong acids relate to the ease with which the product loses hydrogen ions (H⁺), also called protons, when dissolved in water. Some herbicide molecules easily lose hydrogen ions; others do not. Herbicides that provide hydrogen (or protons) are called weak acids. The solubility of weak acids depends on the solution's pH (ROMAN; VARGAS, 2005, p. 12).

The electrolytic dissociation constant (pK) is defined as the potential dissociation of an acid (pKa) or a base (pKb) in a liquid medium (CARVALHO, 2013). This constant represents the pH value at which there is a balance between the ionic (polar and more hydrophilic) and non-ionic (neutral or nonpolar and more lipophilic) forms of ionizable herbicides (which dissociate in a liquid medium). For herbicides, pKa is used for both acidic and basic herbicides. Depending on the pH, acidic herbicides dissociate into anions (HA⁻) and release hydrogen ions (H⁺), acidifying the medium; however, basic herbicides dissociate into cations (HB⁺) and release hydroxides (OH⁻) (CARVALHO, 2013).

The degree of ionization of acids is given by pKa, i.e., the pH at which 50% of the molecules are ionized, or at which there are equal amounts of herbicide with and without a bound protein; herbicides that behave as weak acids have a pKa less than 7.0 (ROMAN; VARGAS, 2005, p. 12). The acid ionization constant (Ka) is equal to the concentration of ionizable hydrogen ([H⁺]). By the pH of a solution, it is possible to calculate the concentration of free hydrogen ions because $\text{pH} = (-\log[\text{H}^+])$ at 25°C. KW values also vary with temperature; the concentrations of H₃O⁺ and OH⁻ ions in water increase with temperature. Consequently, the value of KW also increases (CARVALHO, 2013).

The ionization constant (pKa) is related to the possibility of ionization of herbicide molecules in the solution with different pH values. It is the pH value of the solution at which 50% of the herbicide will be in its molecular form and 50% in its ionized form. The higher the pKa of the herbicide, the lower the probability of being in the ionic

form. The ionic form is more soluble. According to Reis (2018), the behavior of a pesticide in an acidic medium depends on pH and pKa:

- a. If $\text{pH} < \text{pKa}$ of the pesticide \rightarrow molecular form
- b. If pH of the medium $>$ pKa of the pesticide \rightarrow dissociated form

Acid herbicides when introduced into a more acidic environment ($\text{pH} < \text{pKa}$) do not dissociate, so there is a higher percentage of herbicide in the non-ionic form (HA) and a lower percentage of herbicide in the ionic form (dissociated -HA-); however, when introduced into a more basic environment ($\text{pH} > \text{pKa}$), these herbicides dissociate, so there is a lower percentage of herbicide in the non-ionic form (HA) and a higher percentage of herbicide in the ionic form (dissociated -HA-). Basic herbicides, on the other hand, dissociate when introduced into a more acidic medium ($\text{pH} < \text{pKa}$), so there is a lower percentage of herbicide in the non-ionic form (HB) and a higher percentage of herbicide in the ionic form (dissociated -HB+); however, when introduced into a more basic medium ($\text{pH} > \text{pKa}$), these herbicides do not dissociate, so there is a higher percentage of herbicide in the non-ionic form (HB) and a lower percentage of herbicide in the ionic form (dissociated -HB+). In the case of fungicides and insecticides, most are neutral compounds that do not ionise (CARVALHO, 2013).

The ionization constant of the acid (K_a) is equal to the ionizable hydrogen (H^+), and the higher the (K_a), the stronger the acid ($K_a < 1$). Similarly, a base's dissociation constant (K_b) is equal to the hydroxyl (OH^-) released, and the higher the (K_b), the stronger the base ($K_b < 1$). The electrolytic dissociation constant (pKa) is the dissociation potential of an acidic or basic herbicide in a liquid medium about the pH of the medium. It indicates the ability of the herbicide to form ions in solution (CARVALHO, 2013).

Equations 1, 2, 3, and 4.

$$\text{pH} = -\log[\text{H}^+] \text{ e } [\text{H}^+] = 10^{-\text{pH}} \quad (1)$$

$$\text{pOH} = -\log [\text{OH}^-] \quad (2)$$

$$\text{pKa} = \text{pH} - \log ([\text{A}^-] / [\text{AH}]) \quad (3)$$

$$\text{pKa} = \text{pH} - \log([\text{B}^+] / [\text{BOH}]) \quad (4)$$

Where:

pH = hydrogen potential of the environment

A^- = acid herbicide in dissociated form

AH = acid herbicide in molecular form

B^+ = basic herbicide in dissociated form

BOH = basic herbicide in molecular form

As $\text{pKa} = (-\log K_a) \rightarrow K_a = ([\text{H}^+]) \rightarrow$, therefore, lower (pKa) \rightarrow higher (K_a) and more ionizable is the pesticide molecule.

The ionization constant (pKa) value is a crucial reference used to classify an acid or base in terms of its strength, i.e., its ability to ionize or dissociate when dissolved in water.

1.1 Acids

Acids are classified as strong ("highly ionized"), moderate or weak ("weakly ionized"). In order to classify them, the value of an acid's ionization constant is sufficient. In general, the higher value of the ionization constant, the stronger the acid, as shown in Table 1.

Table 1 - Relation between pKa and acid strength

Dissociation constant (pKa)	Acid	Intensity
Lower (< 3,0)	Strong acid	High
Medium ($\geq 3,0$ e $\leq 9,0$)	Weak acid	Moderate
Higher (> 9,0)	Very weak acid	Low

Source: University of Hertfordshire, 2013.

1.2 Bases

Regarding strength, bases are classified as strong (they dissociate a lot) or weak (they dissociate little). To make this classification, all you need is the value of a base's ionization constant, as shown in Table 2.

Table 2 - Relation between pKa and base strength.

Dissociation constant (pKa)	Base	Intensity
Lower (< 3,0)	Very weak base	Low
Medium ($\geq 3,0$ e $\leq 9,0$)	Weak base	Moderate
Higher (> 9,0)	Strong base	High

Source: University of Hertfordshire, 2013.

According to the Ministry of Agriculture, Livestock and Supply (MAPA), pesticides are chemical, physical, or biological products used in the agricultural and pasture production sector, among others, to alter the chemical composition of flora and fauna and preserve them. Their use is associated with environmental and health problems, according to research by bodies such as the World Health Organization (WHO) and the National Health Surveillance Agency (ANVISA). They are also known as pesticides, agrochemicals, and pesticides.

Pesticides can enter the aquatic environment in various ways, the main sources of which are their use in agriculture and the control of aquatic weeds and insects. Once in the aquatic environment, the pesticide can undergo a series of interactions, and the nature of these interactions will depend on the physical-chemical characteristics of the aquatic environment (DORES E FREIRE, 1999).

The physicochemical characteristics of the aquatic environment determine the likelihood of degradation of a given compound and/or its fate in this ecosystem. The hydrogen potential (pH) of water can influence the decomposition of pesticides. For example, the hydrolysis of organophosphates and carbamate-class insecticides is strongly influenced by pH. Although stable at a slightly acidic pH (5 - 7), these insecticides are rapidly hydrolyzed at a more basic pH (> 7 - 10). On the other hand, triazine-based herbicides are more stable at a pH greater than (7) (DORES E FREIRE, 1999).

In the municipality of Russas, water contamination by pesticides is mainly due to the release of water with residues from cultivation areas. As the most used pesticides in the region do not ionize and/or dissociate when dissolved in water, to reduce the risk of environmental contamination, it is important to know the capacity of the pesticide to ionize or dissociate through the pH values of the surface and underground aquatic environment and the pKa of the pesticide, to reduce the concentration of the pesticide in the water.

1.3 Objectives

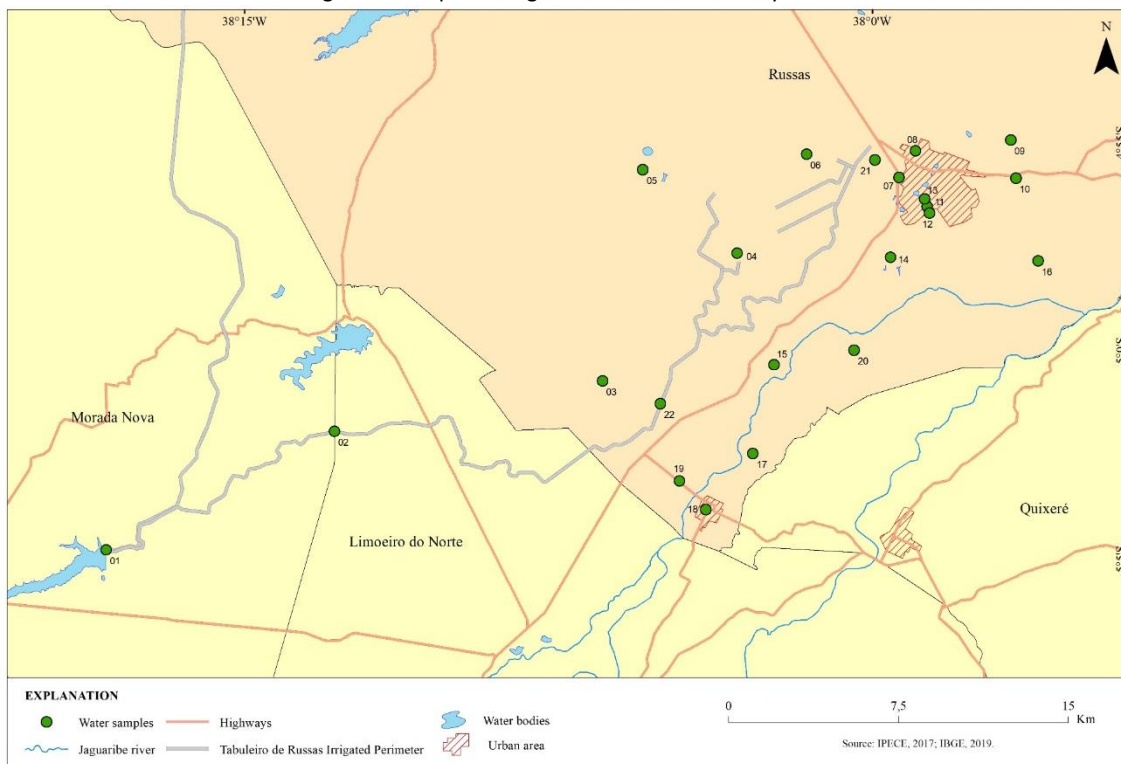
The research aimed to correlate the hydrogen potential (pH) values measured in water samples collected from surface and underground aquatic environments in the municipality of Russas, state of Ceará, in which pesticide residues were analyzed, with the values of the ionization constants (pKa) of the pesticides that were detected, since this correlation is significant because it affects the ionization and/or dissociation of the molecule.

2 METHODOLOGY

2.1 Localization of the Study Area

The Tabuleiros de Russas Irrigated Perimeter is located in the municipalities of Russas, Limoeiro do Norte and Morada Nova, more precisely in the Lower Jaguaribe Valley and 160 kilometres from the Ceará capital, Fortaleza. The area is made up of a continuous strip of arable land along the left bank of the Jaguaribe River, from the city of Russas to the confluence of the Banabuiú River, in the north-eastern region of Ceará (figure 1).

Figure 1 – Map showing the location of the study area



Source: Authors, 2023.

2.2 Water sampling methodology

Samples were collected at 24 points in four sampling cycles. Surface water samples were collected along the Tabuleiro and Russas Irrigated Perimeter, in the municipalities of Morada Nova, Curral Velho reservoir, Limoeiro do Norte and Russas. Groundwater samples were only collected in the municipality of Russas - CE.

2.3 Data collection and analysis methodology

The pH measurements of the water samples collected were carried out in the field using a Digimed pH meter. During all collection periods, the portable equipment was duly calibrated at the Environmental Chemistry Laboratory (LQA) of the Ceará Industrial Quality and Technology Centre (NUTEC) before being used for field measurements. The equipment was washed with distilled water to calibrate the pH meter, followed by a pH 7 buffer solution.

Those available on the International Union of Pure and Applied Chemistry (IUPAC) website were used to determine the properties of the pesticides (LEWIS, 2016).

3 RESULTS AND DISCUSSION

Table 1 and Figure 1 show the results of the average pH values measured at 25°C in the water samples collected in the municipality of Russas/CE for pesticide analyses. The water samples were collected during May, August, November 2021, and May 2022, corresponding to the 1st, 2nd, 3rd, and 4th cycles. May corresponds to the rainy season and the months of August and November to the dry season.

Of the total of 24 water samples collected, one sample, sample 1, was collected from the Curral Velho reservoir in the municipality of Morada Nova - CE; seven samples, 2, 3, 4, 5, 6, 21 and 24 from the canal of the Tabuleiro de Russas Irrigated Perimeter; fourteen samples, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 are groundwater; and samples 22 and 23 from the Jaguaribe River in the municipality of Russas-CE.

Table 1 - Average pH values measured at 25°C for the water samples collected.

Samples	Average pH results obtained in the 4 collection cycles				Average
	1st Cycle May/21	2nd Cycle Aug/21	3rd Cycle Nov/21	4th Cycle May/22	
1	7,65	7,64	8,30	7,60	7,80
2	8,60	8,53	8,41	9,24	8,70
3	-	8,67	8,55	9,55	8,92
4	7,43	7,65	7,70	7,70	7,62
5	7,80	7,80	7,89	7,50	7,75
6	8,06	7,73	7,85	7,65	7,82
7	6,91	7,20	7,20	7,17	7,12
8	5,57	5,95	-	-	5,76
9	7,31	7,11	7,15	6,89	7,12
10	7,0	7,36	7,32	7,33	7,25
11	7,4	7,12	5,85	7,65	7,01
12	6,92	6,99	6,98	7,21	7,03
13	7,56	7,62	7,57	7,55	7,58
14	5,42	5,55	5,4	5,48	5,46
15	6,9	6,32	4,54	6,05	5,95
16	6,5	6,62	6,38	6,97	6,62
17	7,34	7,63	7,34	7,21	7,38
18	7,35	7,50	7,27	7,15	7,32
19	7,23	7,44	7,23	6,91	7,20
20	-	6,57	6,75	6,74	6,69
21	-	8,12	8,54	7,95	8,20
22	-	-	-	7,0	7,00
23	-	-	-	6,70	6,70
24	-	-	-	8,75	8,75

Source: Authors, 2023.

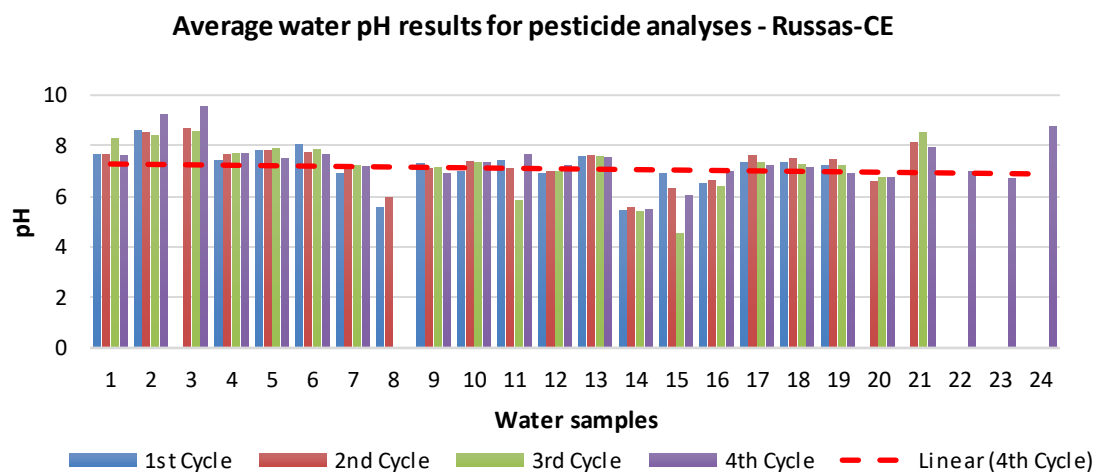
With regard to pH values: as shown in Table 1, the results ranged from (5.42 to 8.60) with an average of (6.79) for the 1st cycle, from (5.55 to 8.67) with an average of 7.29 for the 2nd cycle, from (4.54 to 8.55) with an average of 6.87 for the 3rd cycle and from (5.48 to 9.55)

with an average of 7.39 for the 4th cycle. In May/2021 (rainy), August/2021 (dry), November/2021 (dry) and May/2022 (rainy) 66.6%, 71.43%, 70.0% and 69.56% respectively of the water had a more basic pH ($pH < 7.0$). In May/2021 (rainy), August/2021 (dry), November/2021 (dry) and May/2022 (rainy) 33.3%, 28.57%, 30.0% and 30.43% respectively of the waters had a more acidic pH ($pH > 7.0$).

Variations in temperature and the composition of the water (concentrations of salts, acids, metals) influence the pH; small variations in the pH value represent multiple changes of 10 in the concentration of hydrogen ions (H^+). Armas et al. (2007, p. 1125) observed in their work that the persistence and partitioning of pesticide molecules in the aquatic environment are largely dependent on temperature, pH, redox potential and the amount of colloids and ions (electrical conductivity) in the aqueous environment.

Except for samples 2 ($pH = 9.24$) and 3 ($pH = 9.55$) collected in May 2022 during the rainy season (4th cycle), the average pH values obtained in each cycle were in line with the quality standard of Resolution 357 of 17 March 2005 of the National Environment Council (CONAMA), which establishes the pH standard for surface waters, fresh waters classes 1, 2, 3 and 4 at pH 6.0 to 9.0. For class 1, 2, and 3 saline waters, the pH value is 6.5 to 8.5, and there should be no change in the natural pH greater than 0.2 units. For brackish waters class 1 and 2 the pH value is 6.5 to 8.5 and class 3 the pH value is 5.0 to 9.0. Figure 2 compares the average pH results obtained in the four collection cycles for the surface and groundwater samples.

Figure 2 - Average pH results of water collected in the municipality of Russas-CE.



Source: Authors, 2023.

Figure 2 shows that there was an acidic trend in the samples collected during the rainy season, which favors the leaching of substances and a longer residence time in the environment. It can also be seen that the water from the irrigation canal showed a basic trend, which is possibly due to the presence of organic matter along the canal.

The ionization constant can refer to an acid (pK_a) or a base (pK_b) and is closely related to the substance's acid equilibrium constant (K_a). Equation 5 can be simplified as follows:

$$pK_a = \log[A^-]/[HA] = \log K_a - \log(Y_{H^+} [H^+]) = pH - pK_a \quad (5)$$

Where:

[A-] = concentration of the acid anion to be dissociated in the solution

[HA] = concentration of the acid to be dissociated in the solution

[H⁺] = concentration of the hydrogen ions to be dissociated from the acid in the solution

YH⁺ = ionic strength coefficient of the acid in the solution or activity coefficient of the solute

As such, it directly interferes with the proportionality and speed of the substance's degradation in liquid media and must be taken into account when calculating the chemical transformation and degradation of the substance and the reactions resulting from these processes. Therefore, it should always be borne in mind that, environmentally, the behavior of a pesticide that undergoes dissociation differs significantly from a non-dissociated one (GEBLER; SPADOTTO, 2004).

Table 2 - Effect of pH and pKa on the solubility of weakly basic substances in water.

pH – pKa	Solubility in water
< -2,0	Soluble
-1,0	Soluble
0,0	Soluble except in high concentrations
+ 1,0	Soluble in low concentrations
> +2,0	Insoluble

Source: ANFARMAG, 2023.

The table shows the effect of pH and pKa on the solubility of weakly acidic substances in water.

Table 3 - Effect of pH and pKa on the solubility of weakly acidic substances in water.

pH – pKa	Solubility in water
< -2,0	Insoluble
-1,0	Insoluble
0,0	Soluble in low concentrations
+ 1,0	Soluble except in high concentrations
> +2,0	Soluble

Fonte: ANFAMARG, 2023

Table 4 shows the ionization constant (pKa) values for the pesticides detected in the water samples collected in Russas/CE.

Table 4 - Ionisation constant (pKa) of the pesticides analyzed

Agrochemicals	pKa at 25°C	Acid/base strength
Acephate (insecticide)	8,35 (IUPAC)	Weak acid
Aldicarbe (insecticide)	NA (IUPAC)	Does not dissociate
Amethrin (herbicide)	10,07 (IUPAC)	Very weak base
Dimethoate (insecticide)	NA (IUPAC)	Does not dissociate
Imidacloprid (insecticide)	NA (IUPAC)	Does not dissociate
Permethrin (insecticide)	*	*
Tebuconazole (fungicide)	5,0 (IUPAC)	*

Explanation: NA = not applicable, (*) data not reported in IUPAC.

Source: Authors, 2023.

Table 4 shows that the pesticides acephate has a value of (pKa = 8.35), ametrine has a value of (pKa = 10.07) and tebuconazole has a value of (pKa = 5.0), which means that at these pKa values, (50%) of the pesticide molecule is in molecular form and (50%) is in ionic form. Note that the higher the (pKa) value, the weaker the acid and/or base.

For the purposes of classifying the strength of an organic acid, if the pKa is between 0 and 3.0, it can be considered a strong acid. If it varies between 4.0 and 10.0, it is in the range found in natural waters, mainly in its dissociated forms; between 10.0 and 12.0, it can be considered a weak acid, and above 12.0, it is a very weak organic acid. Weak acids/bases in solution show partial dissociation, establishing a chemical equilibrium between the ionized (dissociated) and molecular (non-dissociated) forms (CHRISTOFFOLETI et al., 2008).

The herbicide Ametrin, a chemical group of triazines, behaves like a weak base in solution. When introduced into a more acidic medium, it dissociates (generating the conjugate acid (pKa = 4.1), which is the protonated species). Basic herbicides are compounds whose neutral (molecular) forms can receive protons and form positively charged ions. Since it is expected to find indistinguishable pKa values for acidic and basic herbicides, it should be considered that the protonated chemical species is a conjugate acid of the basic herbicide. This is why the same pKa notation can be used for basic herbicides, for which the higher the pKb value of the basic herbicide (or the lower the pKa value of the basic herbicide), the weaker its basic strength, i.e., the less chance there is of the herbicide becoming cationic (OLIVEIRA; BRIGHENTI, 2011, p. 273).

About the degree of ionization/dissociation of the herbicide ametrine, when the pH value of the water is lower than the pKa of the basic herbicide (pH < pKa), there is a higher percentage of the dissociated form (cationic or protonated) and a lower percentage of the non-dissociated form (neutral molecular). This occurs mainly at one or more pH units below the pKa

value of the basic herbicide. Under these conditions, the herbicide will likely remain adsorbed to the sediment components and not be transported to other parts of the aquatic environment.

According to the results in Table 1, the most basic pH values, two units below the pKa value, were obtained for samples 2 (pH = 8.60) and 6 (pH = 8.06) collected in May/21 (rainy season)

for samples 2 (pH = 8.53), 3 (pH = 8.67) and 21 (pH = 8.12) collected in August/21 (dry period), for samples 1 (pH = 8.30), 2 (pH = 8.41), 3 (pH = 8.55) and 21 (pH = 8.54) collected in November/21 (dry period) and for samples 2 (pH = 9.24), 3 (pH = 9.55), 24 (pH = 8.75) collected in May/22 (rainy period). All the pH values obtained were lower than the pKa value = 10.07 of the herbicide Ametrine, and therefore, theoretically, the percentage of the molecule in dissociated form (cationic or protonated) was higher.

A weak base has a high dissolution rate at a more acidic pH (ionized form), but as the pH increases, the dissolution rate decreases (non-ionized form). The higher the ionized (dissociated) mole fraction, the greater the solubility in water. In other words, the lower the pKa of a herbicide, the greater and faster its dissociation in water will be, in the pH range found in natural waters in Brazil, its point of maximum dissociation being when pKa = pH.

The pesticide permethrin is stable in neutral and weak acid media, but hydrolysis can occur under alkaline or strongly acidic conditions (ZWEIG; SHERMA, 1984), and the pesticide aldicarb is stable in acidic conditions, degradable in concentrated alkaline media, (XAVIER et al., 2007, p. 1207). Generally, we can say that herbicides, insecticides, and fungicides work best in slightly acidic waters between (pH 4 to 6).

4 CONCLUSIONS

Measuring pH "in situ" is important for checking the degree of ionization/dissociation of the pesticide molecule in the aquatic environment as a function of pKa.

This is important because, depending on this correlation, the molecules may be in molecular form (neutral) or dissociated (protonated), influencing the degradation of the pesticide, which contributes to the presence of this substance in water, becoming a threat to public health.

When applying pesticides in the agroecosystem, it is necessary to consider important factors such as the depth of the water table, soil conservation practices, terrain relief (degree of slope and soil type), the substance applied and its properties, since when they are carried or leached, they can reach the surface and underground aquatic environments.

In this study, it was observed that the substances Acephate and Tebuconazole are weak acids of moderate intensity, which is why they can remain in the environment for longer; Aldicarb and Ametrine, on the other hand, are very weak acids of moderate intensity; which is why they have a shorter residence time in the environment.

5 REFERENCES

ANFARMAG. *Influência do pH e do pKa na solubilidade de fármacos* - ANFARMAG. 2023. Available in:

<<https://anfarmag.org.br/ler-comunicado/influencia-do-ph-e-do-pka-na-solubilidade-de-farmacos/>>.

ARMAS, E. D. DE *et al.* Diagnóstico espaço-temporal da ocorrência de herbicidas nas águas superficiais e sedimentos do Rio Corumbataí e principais afluentes. **Química Nova**, v. 30, n. 5, Oct. 2007, p. 1119 –1127.

BRASIL. Ministério do Meio Ambiente (MMA) **Conselho Nacional do Meio Ambiente (CONAMA)**. Resolução CONAMA Nº 357, de 17 de março de 2005. Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências.

BARROSO, Arthur Arrobas Martins; MURATA, Afonso Takao. **Matologia: estudos sobre plantas daninhas**. Jaboticabal: Fábrica da Palavra, 2021, p.282.

CARVALHO, Leonardo Bianco de. **Herbicidas** / Editado pelo autor, Lages, SC, 2013 vi, 62 p.

CASSAMASSINO, Ricardo Eugênio. **Dissipação e mobilidade dos herbicidas glifosato e oxifluorfen em um solo manejado no sistema de cultivo mínimo e florestado com eucaliptus grandis**. Piracicaba-SP, 2005. Dissertação (Mestrado em Recursos Florestais). Escola Superior de Agricultura "Luiz de Queiroz" – USP.

CHRISTOFFOLETI, Pedro Jacob; OVEJERO, Ramiro Fernando López; DAMIN, Virginia; CARVALHO, Saul Jorge Pinto de. NICOLA, Marcelo. **Comportamento dos herbicidas aplicados ao solo na cultura da cana-de-açúcar**. 1ª Edição. PIRACICABA – SP. 2008.

CORREIA, Núbia Maria. **Comportamento dos herbicidas no ambiente**. Brasília, DF: Embrapa Hortaliças, 2018. p.30

DELLAMATRICE, P. M.; MONTEIRO, R. T. R. Principais aspectos da poluição de rios brasileiros por pesticidas. **Rev. bras. eng. agríc. ambient.** v.18 n. 12 Campina Grande, 2014

DORES, Eliana Freire Gaspar de Carvalho. FREIRE, Ermelinda Nara de Lamônica. *Contaminação do ambiente aquático por pesticidas: vias de contaminação*. **Pesticidas: Revista de Ecotoxicologia e Meio Ambiente**, v. 9, 31 dez. 1999.

GAMA, Allyne Ferreira. **Avaliação espaço/temporal e influência da composição sedimentar na distribuição dos agrotóxicos mais utilizados na mesorregião do Rio Jaguaribe**. 174f. Tese (Doutorado em Ciências Marinhas Tropicais). Instituto de Ciências do Mar, da Universidade Federal do Ceará – Ceará, Em Fortaleza – CE, 2018.

GEBLER, Luciano; SPADOTTO, Cláudio Aparecido. Comportamento ambiental dos herbicidas. In: **Manual de manejo e controle de plantas daninhas**. Bento Gonçalves: Embrapa Uva e Vinho, 2004. Available in: <https://www.alice.cnptia.embrapa.br/handle/doc/543494>. Accessed: 10 Apr. 2023.

LEWIS, Kathleen A.; TZILIVAKIS, John; WARNER, Douglas J.; et al. An international database for pesticide risk assessments and management. **Human and Ecological Risk Assessment: An International Journal**, v. 22, n. 4, p. 1050–1064, 2016.

OLIVEIRA, Maurílio Fernandes de. BRIGHENTI, Alexandre Mágnio. In. **Biologia e manejo de plantas daninhas**. Embrapa, 2011. Cap 11. P. 263-304. Available in: <https://www.embrapa.br/busca-de-publicacoes/-/publicacao/904895/comportamento-dos-herbicidas-no-ambiente>. Accessed: 4 May. 2023.

REIS, Fabricia Cristina dos. **Comportamento de herbicidas no ambiente**. UNIVERSIDADE DE SÃO PAULO ESCOLA SUPERIOR DE AGRICULTURA “LUIZ DE QUEIROZ”. Disciplina LPV0672 - Biologia e Manejo de Plantas Daninhas, 2014. Available in: <http://www.ipv.esalq.usp.br>. Accessed: 4 May. 2023.



ROMAN, Erivelton Scherer; VARGAS, Leandro. **Como funcionam os herbicidas: da biologia à aplicação** / Editado por. Passo Fundo: Gráfica Editora Berthier, 2005, p. 12

SPADOTTO, Claudio Aparecido; SCORZA JUNIOR, Rômulo Penna; DORES, Eliana Freire Gaspar de Carvalho; GEBLER, Luciano; MORAES, Diego Augusto de Campos. **Fundamentos e aplicações da modelagem ambiental de agrotóxicos** – Campinas: Embrapa Monitoramento por Satélite, 2010, p. 18.

UNIVERSITY OF HERTFORDSHIRE. **Pesticide Properties Database**. PPDB: Pesticide Properties DataBase. 2013. Available in: <<http://sitem.herts.ac.uk/aeru/ppdb/en/>>. Accessed: 5 Feb. 2023.

ZWEIG, Gunter.; SHERMA, Joseph. Synthetic pyrethroids and other pesticides. In: **Analytical methods for pesticides, plant growth regulators**. Orlando: Academic Press, 1984. v. 13.

XAVIER, Fabiana Galtarossa; RIGHI, Dario Abbud; SPINOSA, Helenice de Souza. Toxicologia do praguicida aldicarb (“chumbinho”): aspectos gerais, clínicos e terapêuticos em cães e gatos. **Ciência Rural**, v.37, n.4, jul-aug, 2007.