

# Mineralization of S-metolachlor in soil as affected by moisture content, application history, and association with glyphosate

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**Abstract:** Herbicide mineralization in the soil is affected by several factors, including the herbicide application history of the soil, soil moisture, and whether the herbicide is co-applied with another herbicide. The objective of this work was to evaluate S-metolachlor mineralization in the soil as affected by soil moisture content, history of herbicide application, and association with glyphosate. <sup>14</sup>C-S-metolachlor mineralization increased with increasing soil moisture content. The average cumulative mineralization of S-metolachlor at 63 days of incubation was 0.03, 0.80, and 1.80% in air-dried, field capacity, and saturated soil, respectively. The mineralization rate of S-metolachlor was greater under saturated conditions and affected by

the association with glyphosate. Greater mineralization of S-metolachlor occurred in cornfield soil with a history of S-metolachlor application. The average cumulative mineralization was 0.24% in cornfield and 0.89% in non-cultivated area. We can conclude that the higher the soil moisture content the higher S-metolachlor mineralization and that the mixture of this herbicide with glyphosate increased its degradation compared to the application of the herbicide alone. While there is evidence suggesting enhanced degradation of S-metolachlor in soil previously subjected to corn cultivation and S-metolachlor application, drawing a definitive conclusion is challenging due to the influence of sorption observed in our dataset.

**Keywords:** Degradation; Herbicide; Environmental Fate; Enhanced Mineralization

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## 1. Introduction

S-metolachlor is a soil-applied herbicide used worldwide for preemergence control of annual grass and small-seeded broadleaf weeds in many crops, including corn, soybean, and cotton (Adegas et al., 2022; Bedmar et al., 2011; Goldreich et al., 2011). S-metolachlor is slightly soluble in water (488 mg L<sup>-1</sup>) and moderately sorbed in most soils with an average  $K_{oc}$  of 200 mL g<sup>-1</sup>. It exhibits low volatility, moderate leaching potential, and is susceptible to photodegradation in the soil surface (Munoz et al., 2011; Shaner, 2014; Zemolin et al., 2014a).

Compared to other chloroacetamide herbicides such as alachlor, S-metolachlor is more persistent in soil with a half-life ranging from 2.5 to 289 days (Sanyal, Kulshrestha, 1999; Shaner, 2014). The wide variability reported for chloroacetamide herbicides' persistence has been attributed to differences in soil management, edaphic factors, and environmental conditions that affect microbial degradation, a major pathway for its dissipation in the environment (Wu et al., 2011; Alletto et al., 2013; Sun et al., 2019).

Moisture content plays a vital role in the microbial degradation of herbicides in soil; several results demonstrated that the influence of soil moisture on the degradation of: saflufenacil (Camargo et al., 2013), sulfentrazone (Martinez et al., 2010), metsulfuron-methyl (Wang et al., 2010), metolachlor (Rice et al., 2002), imazapic (Sun et al., 2019), dicamba, imazethapyr, and clodinafop-propargyl (Rao et al., 2019). For S-metolachlor, it has been demonstrated that degradation occurs more rapidly when soil moisture content is higher, with a half-life of 39.4 days at the low moisture content (20% water holding capacity - WHC) and 23.4 days at high moisture content (80% WHC) (Long et al., 2014). Other research involving S-metolachlor has predominately focused on the sorption and mineralization of primary metabolites to determine their propensity to leach and contaminate groundwater (Bedmar et al., 2011; Goldreich et al., 2011; Baran, Gourcy, 2013).

Enhanced degradation is another process that may affect the mineralization of soil-applied herbicides. Accelerated or enhanced herbicide degradation consists of faster herbicide degradation in areas where it has been previously applied due to the adaptation of the microbial population to that compound (Bundt et al., 2015). After

consecutive herbicide applications, enhanced atrazine degradation has been shown under laboratory and field conditions (Krutz et al., 2009; Zablutowicz et al., 2006). The persistence of atrazine in s-triazine-adapted, independent of soil depth, was at least fourfold shorter than that of the non-adapted soil (Krutz et al., 2010). For metolachlor, conflicting results regarding the previous application of the herbicide have been found. (Sanyal, Kulshrestha, 1999) found enhanced degradation for metolachlor, with dissipation half-life in soil decreasing from 18 days after the first application to 2.5 days after the fourth consecutive metolachlor application.

In contrast, Shaner and Henry (2007) did not find a clear relationship between metolachlor degradation and history application after an extensive study conducted in Colorado's agricultural fields in the USA. Previous applications of alachlor or metolachlor did not affect the rate of degradation when the same herbicide was reapplied up to eight times before the experiment (Dowler et al., 1987). Therefore, additional research is required to determine whether previous application influences S-metolachlor degradation in soil.

Since S-metolachlor is degraded via cometabolism (Munoz et al., 2011), mixing this herbicide with a readily degradable herbicide such as glyphosate may accelerate its degradation. The mixture of S-metolachlor and glyphosate is a relatively common and efficient tool for weed management (Clewis et al., 2006; Zemolin et al., 2014b). For example, glyphosate's addition increased the cumulative degradation rate of fluometuron relative to fluometuron alone (Lancaster et al., 2008). For S-metolachlor, a study has demonstrated that association with burndown herbicides such as glyphosate decreased soil persistence under Brazilian conditions (Nunes, Vidal, 2016). It is important to study the combination of S-metolachlor and glyphosate and to study the effect of moisture content as this herbicide is being used in areas prone to excess of water. Thus, this study evaluated the effect of moisture content, history of S-metolachlor application, and association with glyphosate on S-metolachlor mineralization in soil.

## 2. Material and Methods

### 2.1 Experimental design

Mineralization and sorption studies were conducted using a completely randomized design in a factorial arrangement with four replications and repeated in time. The mineralization study included two experiments. In experiment I, using the corn-field soil, treatments were combinations between moisture contents (-100 kPa, -33 kPa, 0 kPa) and herbicides ( $^{14}\text{C}$ -S-metolachlor, and  $^{14}\text{C}$ -S-metolachlor plus glyphosate). In experiment II, treatments consisted of combinations between herbicides ( $^{14}\text{C}$ -S-metolachlor, and  $^{14}\text{C}$ -S-metolachlor plus glyphosate) and soil (cornfield with history of S-metolachlor application,

and non-cultivated soil without a history of S-metolachlor application). Controls without herbicide treatment were included for the  $^{14}\text{C}$ -herbicide mineralization and sorption studies.

### 2.2 Soil sampling

Two soil samples were collected in 2013 from a corn-soybean farm located in western Bolivar County, Mississippi, near the Mississippi River. Topsoil (0-5 cm) was collected from a cornfield managed using conventional tillage and treated annually with atrazine and S-metolachlor since 2010. This sample was referred to as S-metolachlor "cornfield". Another soil was collected from a non-cropped grass area immediately across the turnrow that had not been cultivated and had not been treated with S-metolachlor treatment for at least the past five years; We refer this soil as a "non-cultivated area" soil. Sample points were georeferenced with a global position system, and coordinates were 33°44'23.48" N and 90°43'59.17" W and, 33°40'28.46" N and 90°44'03.98" W for the "cornfield" and "non-cultivated" soils, respectively.

The samples were taken to the laboratory, air-dried, and passed through a 2mm-mesh sieve to remove roots and non-decomposed plant residues and stored at room temperature (23 ± 2 °C) until the beginning of the experiment. Soils were stored for 30 days until the experiment was performed. A representative subsample was submitted to the Mississippi State University Extension Center Soil Testing laboratory in Starkville, Mississippi, to analyze the particle size distribution, organic matter content, pH, and cation exchange capacity. Based on soil survey data (United States Department of Agriculture, 1951), both samples were classified as *Brittain silt loam*, and their characteristics are presented in Table 1.

### 2.3 Herbicides

The experiments were conducted with a mixture of  $^{14}\text{C}$ -S-metolachlor (phenyl- $^{14}\text{C}$ ) supplied by Syngenta Crop Protection (Greensboro, NC, USA) and technical grades of S-metolachlor and glyphosate (Sigma-Aldrich, Saint Louis, MO, USA). The specific radioactivity and radiochemical purity of  $^{14}\text{C}$ -S-metolachlor were 1,857.4 kBq mg<sup>-1</sup> and 99.4%. The chemical purity of S-metolachlor and glyphosate technical grades was 99.1% and 97.6%, respectively. The field rate of both herbicides was applied.

### 2.4 Mineralization

Twenty-five grams of air-dried weight equivalent soil were placed in a 500-mL glass biometer flask and fortified with a 1.00-mL solution containing either (A)  $^{14}\text{C}$ -S-metolachlor +  $^{12}\text{C}$ -S-metolachlor or (B)  $^{14}\text{C}$ -S-metolachlor +  $^{12}\text{C}$ -S-metolachlor plus  $^{12}\text{C}$ -glyphosate in methanol solvent. The amount of radioactivity added

Table 1 - Soil characterization

| Sample         | Clay (%) | Silt (%) | Sand (%) | Organic matter (%) | CEC (meq/100g) | pH  |
|----------------|----------|----------|----------|--------------------|----------------|-----|
| Cornfield      | 5.00     | 61.50    | 33.50    | 1.35               | 24.56          | 4.9 |
| Non-cultivated | 2.50     | 78.00    | 19.50    | 4.73               | 24.80          | 5.0 |

per biometer flask was 14.06 kBq, equating to 0.30  $\mu\text{g}$   $^{14}\text{C}$ -S-metolachlor per gram of topsoil. Technical-grade S-metolachlor was added to solutions (A) and (B) to result in a final S-metolachlor concentration of 8.4  $\mu\text{g}$  per g of soil which summed corresponded to the herbicide field-rate. Technical-grade glyphosate was added to the solution (B) to produce a final glyphosate concentration of 15.4  $\mu\text{g}$  per g of soil, corresponding to the field-rate of the herbicide. The final herbicide concentrations assumed a labeled rate fully incorporated to a 1.3 cm depth in a silt loam soil.

After spiking, the biometers were kept open in a fume hood for 24 hours at room temperature to allow the methanol solvent to evaporate. The moisture contents were further adjusted with distilled water to air-dried (-100 kPa), field capacity (-33 kPa), and saturated (0 kPa) for experiment I (moisture content) and field capacity (-33 kPa) for experiment II (soil history). Soil water-holding capacity was estimated for each soil using the methods of Saxton et al. (1986).

The biometers flasks were equipped with glass vials filled with 10 mL of 0.5 M NaOH (sodium hydroxide) to capture evolved  $\text{CO}_2$ . Above each  $\text{CO}_2$  trap, polyurethane foam plugs were installed to remove non- $\text{CO}_2$  volatiles from entering the alkaline traps. The flasks were sealed using aluminum-foil lined stoppers and incubated in the dark at  $22 \pm 2^\circ\text{C}$  for 63 days. The  $^{14}\text{CO}_2$  evolution was measured every seven days by completely removing the NaOH solution via pipet and placing 2 mL of the solution into glass scintillation vials containing 10 mL of Ultima Gold™ liquid scintillation cocktail (Perkin Elmer, Shelton, CT, USA). The radioactivity in each vial was measured by liquid scintillation spectroscopy (Tri-Carb 2900TR, PerkinElmer, Shelton, CT, USA). Radioactivity in each sample was measured until 10,000 counts accumulated or for 20 minutes, whichever came first.

Before use, the polyurethane foam plugs were extracted with MeOH and allowed to air-dry. At each sampling period, the plugs were removed, placed in glass test tubes equipped with Teflon-lined caps, and extracted with 30-mL MeOH for 60 minutes on a rotisserie-style shaker. Radioactivity in the MeOH traps was determined by placing one mL of the MeOH extract into glass scintillation vials containing 10-mL of Ultima Gold™ liquid scintillation cocktail (Perkin Elmer, Shelton, CT, USA) and measuring by liquid scintillation spectroscopy as described. Because the foam plugs contained insignificant amounts (i.e., less than 0.01%) of the applied radioactivity, these results are not shown here.

## 2.5 Mass balance determination

After the final sampling of NaOH, the soil in each flask was dried to a constant weight in a freeze dryer and pulverized using mortar and pestle. A 0.25 g sub-sample from each replication was combusted using a Packard 307 sample oxidizer (Packard Instruments, Chicago, IL, USA). The evolved  $^{14}\text{CO}_2$  was trapped in scintillation vials containing 10 mL of Carbo-Sorb and Permafluor (Packard Instruments, Chicago, IL, USA). Radioactivity was determined by liquid scintillation counting (Tri-Carb 2900TR, PerkinElmer, Shelton, CT, USA). The amount of  $^{14}\text{CO}_2$  recovered from the combusted samples was added to the cumulative  $^{14}\text{CO}_2$  evolved from the terminal time course sampling to determine the  $^{14}\text{C}$  mass balance.

## 2.6 Sorption

S-metolachlor sorption coefficients in the cornfield and the non-cultivated soil were determined using a batch-equilibrium method. The herbicide solutions were prepared in 0.01M  $\text{CaCl}_2$  with S-metolachlor concentrations of 1.46, 2.92, 5.84, 11.68, and 23.36  $\mu\text{M}$ .  $^{14}\text{C}$ -S-metolachlor was added to produce solutions that contained approximately 0.125 kBq  $\text{mL}^{-1}$ . Technical grade S-metolachlor was added to achieve the respective solution concentrations. A 5-mL aliquot of each solution was added to 1 g of air-dried soil in a glass 15-mL centrifuge tube sealed with a Teflon-lined cap. A 24-h sorption time was used with the slurry mechanically shaken at 30 rotations per minute. After 24 hours, tubes were centrifuged for 10-min at 1,800  $\times g$ , and 1-mL aliquots of supernatant removed and added to 10-mL scintillation cocktail (Ultima Gold™ Perkin Elmer, Shelton, CT, USA). Radioactivity in solution was determined by liquid scintillation spectroscopy (Tri-Carb 2900TR, Perkin Elmer, Shelton, CT, USA). The amount of herbicide adsorbed by the soil was determined calculating the difference between the initial  $^{14}\text{C}$ -S-metolachlor concentrations in the fortification solutions and the corresponding final concentrations after equilibrium with the soil. The sorption distribution coefficient ( $K_d$ ) was calculated using the equation  $K_d = C_s / C_e$ , where  $C_s$  is the amount of herbicide sorbed by the soil [ $\mu\text{g g}^{-1}$ ], and  $C_e$  is the herbicide concentration in the soil solution at equilibrium [ $\mu\text{g mL}^{-1}$ ].

The distribution coefficient was determined at each concentration and averaged across all equilibrium concentrations to obtain a single estimate of  $K_d$  for each replication.

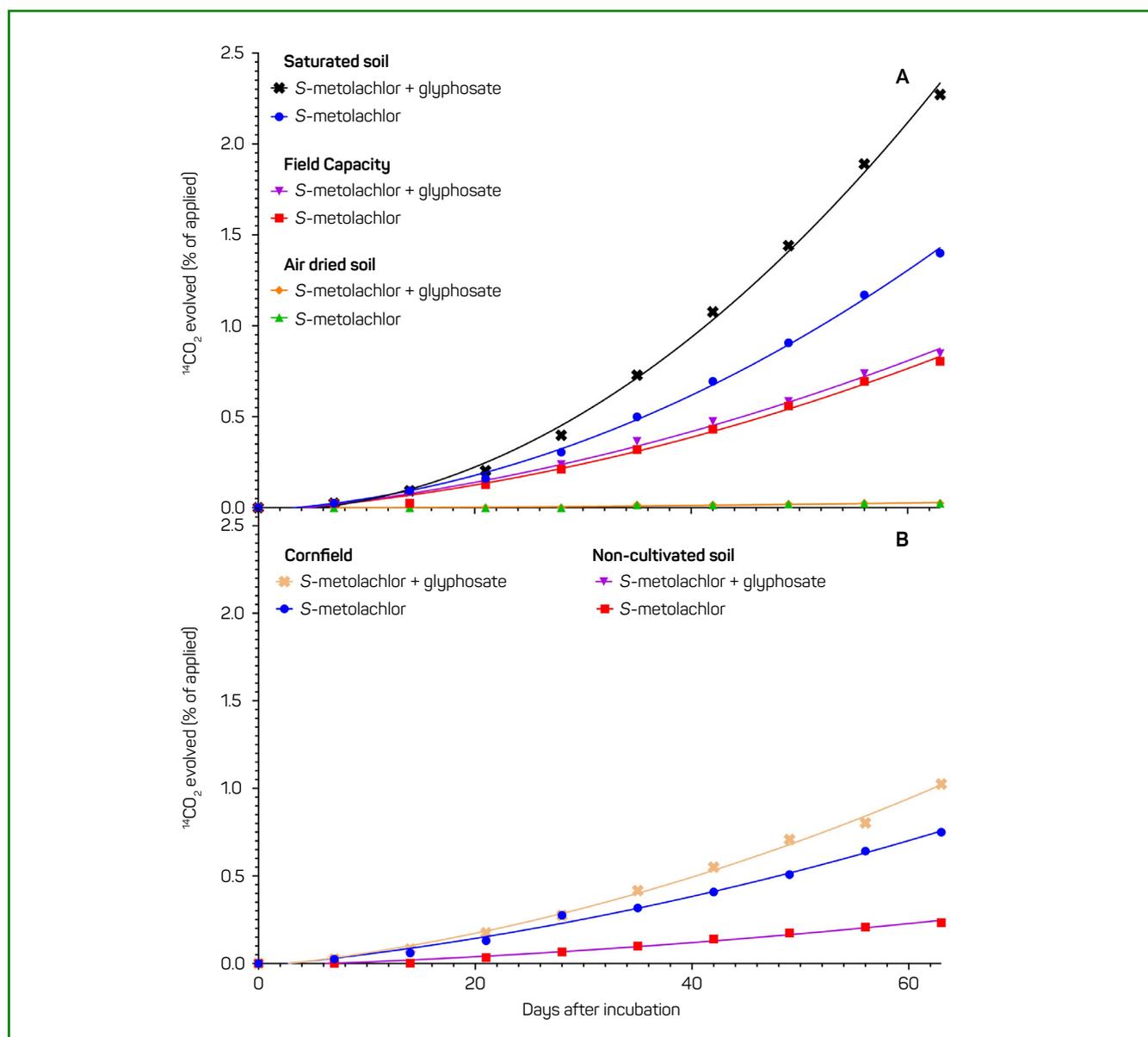
### 2.7 Statistical analysis

Cumulative mineralization after 63 days of incubation, and  $K_d$  were tested for the assumptions of the ANOVA (normality by Shapiro Wilk test, homogeneity of variances using Hartley's test, and independence of the errors checked graphically) and followed by the analysis of variance (ANOVA). All the data were normally distributed, and the errors were independent. Linear regression analysis of the percent  $^{14}\text{C}$ -S-metolachlor remaining in soil versus time was performed to obtain mineralization rate constant ( $k$ ). Means were separated by overlapping 95% confidence intervals. The analysis was performed using SAS and the figures produced using GraphPad Prism Version 10.0.1.

### 3. Results and Discussion

#### 3.1 Effect of moisture content and association with glyphosate on S-metolachlor mineralization

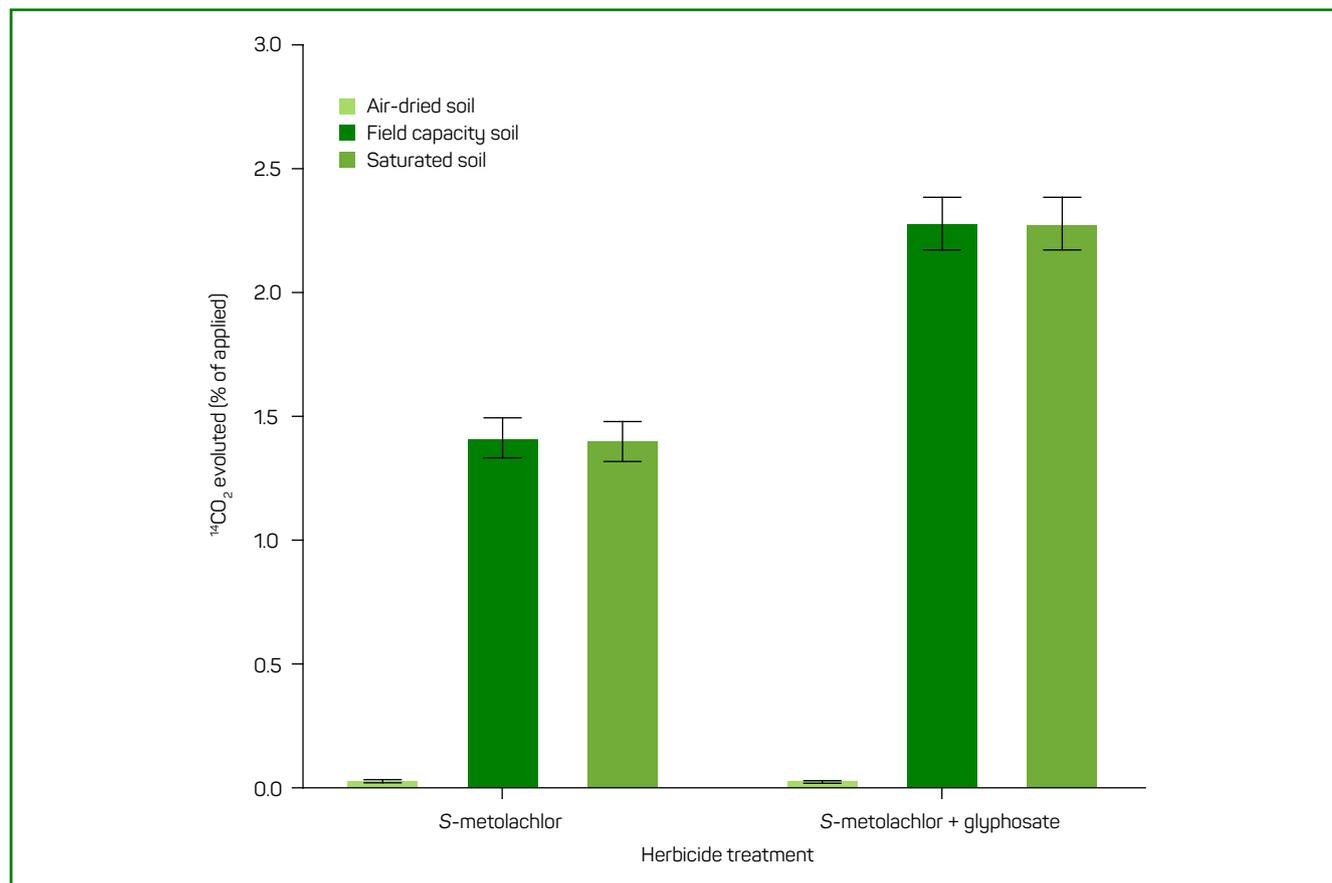
The average  $^{14}\text{C}$  recovery for mineralization experiments I and II was 75.5%. Similar results regarding lower  $^{14}\text{C}$  recovery of metolachlor have been reported by (Krutz et al., 2006). The mineralization kinetics of S-metolachlor and S-metolachlor plus glyphosate under three soil moisture contents are presented in Figure 1A. During the first 14 days of incubation, the percentage of  $^{14}\text{CO}_2$  evolved varied little among the treatments evaluated. However, after 14 days, analysis of variance indicated an interaction between soil moisture content and herbicide treatment for



**Figure 1** - Kinetics of S-metolachlor alone and in mixture with glyphosate as affected by soil moisture content (A) and soil history (B). Cornfield area received S-metolachlor application for three consecutive years; Non-cultivated soil have been a pasture field for five years and did not receive herbicide application. Data point correspond to eight replications

cumulative mineralization of <sup>14</sup>C-S-metolachlor ( $p \leq 0.001$ ). Under saturated conditions, cumulative mineralization of <sup>14</sup>C-S-metolachlor plus glyphosate was greater ( $p < 0.05$ ) relative to <sup>14</sup>C-S-metolachlor alone. The amount of <sup>14</sup>CO<sub>2</sub>

evolved after 63 days was 2.27% for <sup>14</sup>C-S-metolachlor plus glyphosate, whereas 1.42% was observed for <sup>14</sup>C-S-metolachlor alone (Figure 2). A similar trend was observed for the mineralization rate constant (Table 2).



**Figure 2** - Cumulative mineralization of S-metolachlor alone and associated with glyphosate under air-dried, field capacity, and saturated conditions at 63 days after incubation. Error bars represent 95% confidence intervals (n = 8)

**Table 2** - First-order rate constant (*k*) and adjusted coefficient determination (*R*<sup>2</sup>) for S-metolachlor and S-metolachlor plus glyphosate under three moisture levels in soil with different histories of S-metolachlor application

| Moisture content          | Herbicide                | Rate constant ( <i>k</i> ) | 95% confidence intervals (d <sup>-1</sup> ) | <i>R</i> <sup>2</sup> |
|---------------------------|--------------------------|----------------------------|---|-----------------------|
| Air-dried                 | S-metolachlor            | 0.0005                     | 0.00045 – 0.00054                           | 0.97                  |
|                           | S-metolachlor+glyphosate | 0.0005                     | 0.00046 – 0.00053                           | 0.98                  |
| Field capacity            | S-metolachlor            | 0.0134                     | 0.0116 – 0.0152                             | 0.96                  |
|                           | S-metolachlor+glyphosate | 0.0139                     | 0.0123 – 0.0155                             | 0.97                  |
| Saturated                 | S-metolachlor            | 0.0231                     | 0.0192 – 0.0270                             | 0.94                  |
|                           | S-metolachlor+glyphosate | 0.0373                     | 0.0301 – 0.0445                             | 0.91                  |
| Soil history <sup>1</sup> |                          |                            |   |                       |
| Cornfield                 | S-metolachlor            | 0.0040                     | 0.0037 – 0.0045                             | 0.98                  |
|                           | S-metolachlor+glyphosate | 0.0041                     | 0.0036 – 0.0043                             | 0.97                  |
| Non-cultivated            | S-metolachlor            | 0.0124                     | 0.0108 – 0.0139                             | 0.97                  |
|                           | S-metolachlor+glyphosate | 0.0170                     | 0.0148 – 0.0191                             | 0.96                  |

<sup>1</sup> Cornfield area received S-metolachlor application for three consecutive years; Non-cultivated soil have been a pasture field for five years and did not receive herbicide application

*S*-metolachlor half-life is directly affected by moisture content (Figure 3A), with greater half-life under saturated and field capacity conditions. There was difference between saturated and field capacity, with half-lives of 30 and 52 days, respectively for the *S*-metolachlor alone. In mixture with glyphosate half-lives were 19 and 50, for saturated and field capacity conditions, respectively.

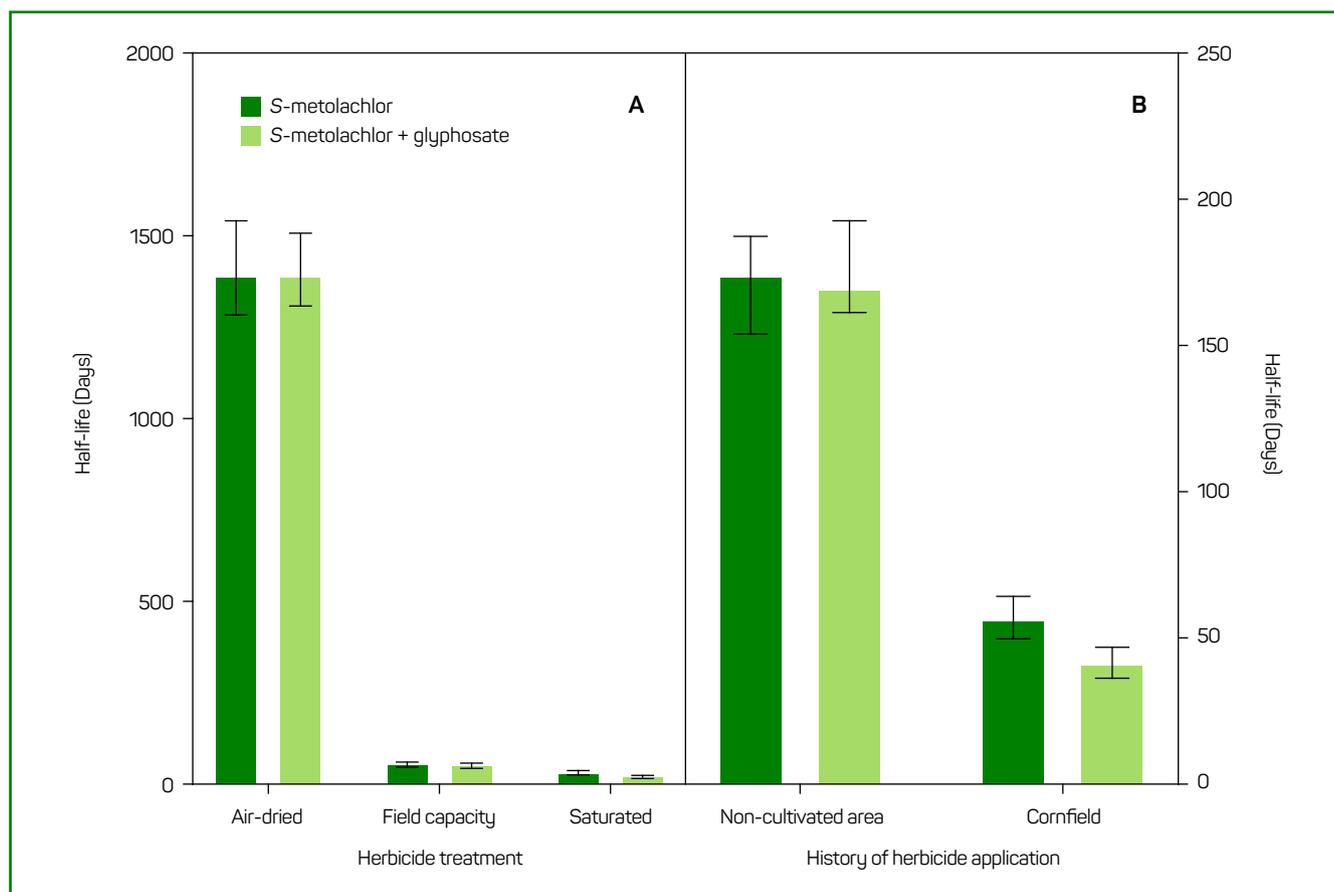
These results demonstrated that the association of *S*-metolachlor with glyphosate increased the mineralization of *S*-metolachlor under saturated and field-capacity conditions. Similarly, studies have shown that combinations between glyphosate and fluometuron or glyphosate and atrazine enhanced mineralization and provided faster dissipation of the soil-applied herbicides than their application alone (Haney et al., 2000; Lancaster et al., 2008). Other researchers have reported increased soil microbial biomass, respiration, and carbon and nitrogen mineralization after consecutive glyphosate applications (Haney et al., 2002; Bonfleur et al., 2015; Partoazar et al., 2011). Therefore, it is plausible that greater cumulative mineralization observed for *S*-metolachlor plus glyphosate is related to a glyphosate-induced increase in *S*-metolachlor's cometabolism. Important to notice that

this experiment is in a controlled environment and may not directly transfer to the field at such a level to affect herbicide efficacy.

The cumulative mineralization and mineralization rate constant of *S*-metolachlor in soil were also affected by moisture content. After 63 days of incubation, cumulative mineralization of *S*-metolachlor was less than 0.04% under air-dried soil regardless of association with glyphosate. Increased *S*-metolachlor mineralization was observed with the increase of moisture content. The average amount of  $^{14}\text{CO}_2$  evolved at field capacity was 0.8%, whereas 1.8% of the applied  $^{14}\text{C}$ -*S*-metolachlor was mineralized in saturated soil.

These results demonstrate that soil moisture content is essential in *S*-metolachlor mineralization. Greater cumulative mineralization of *S*-metolachlor occurred under saturated conditions. As *S*-metolachlor exhibits moderate water solubility, the high moisture content in saturated soil may have enhanced herbicide solubilization, reduced adsorption to the soil particles, and increased its availability to micro-organisms.

Many other studies have reported the effect of soil moisture content on herbicide degradation. For



**Figure 3** -  $^{14}\text{C}$ -*S*-metolachlor half-life alone and in mixture with glyphosate as affected by the soil moisture content (A) and the history of use (B). Cornfield area received *S*-metolachlor application for three consecutive years; non-cultivated soil has been a pasture field for five years and did not receive herbicide application. Error bars represent 95% confidence intervals (n = 8)

metsulfuron-methyl, enhanced mineralization was observed with increased moisture content in paddy soil. Total  $^{14}\text{C}$ -metsulfuron-methyl recovered as  $^{14}\text{CO}_2$  ranged from 2.2 to 3.6% in soil with 20% water-holding capacity (WHC) and from 3.5 to 6.0% with 50% WHC (Wang et al., 2010). In a study with sulfentrazone, the degradation rate was higher at 80% WHC than at 30% WHC (Brum et al., 2013). This behavior was also verified in a recent study with dicamba, imazethapyr, clodinafop-propargyl, and metsulfuron-methyl, which was degraded faster with the addition of moisture content in loamy sand soil (Rao et al., 2019).

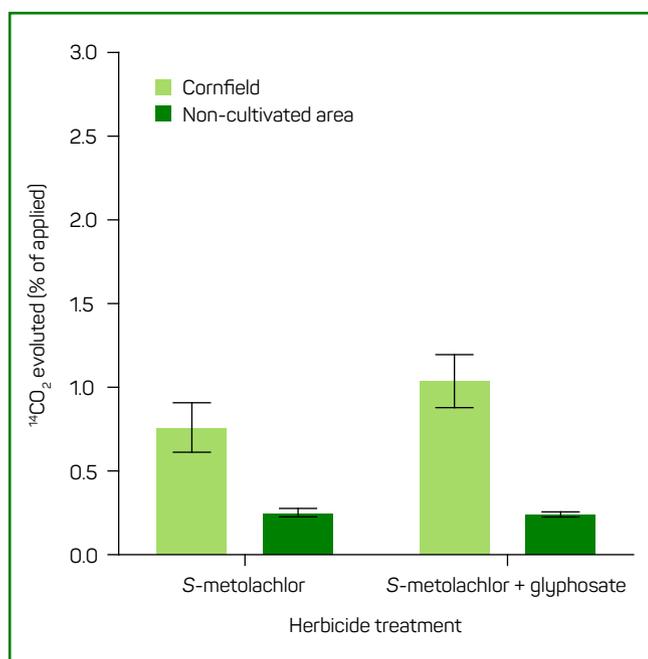
Although there is a lack of consistent information elucidating the processes involved in *S*-metolachlor mineralization under anaerobiosis, it appears to include a combination of sulfate-reducing bacteria and reductive dechlorination reactions (Stamper, Tuovinen 1998). This is supported by evidence that certain bacteria species effectively remove halogen atoms from halogenated compounds via reductive dehalogenation under anaerobic conditions (Futagami et al., 2008). This reaction plays a crucial role in the initial degradation of herbicides under anaerobiosis (Mohn, Tiedje, 1992; Middeldorp et al., 1999; Smidt et al., 2000). Thus, greater mineralization of *S*-metolachlor under saturated conditions might have resulted from a combination of the aforementioned factors. However, because the redox potentials of soil samples in

the present study were not measured, we can only speculate about the nature of reactions that led to these differences.

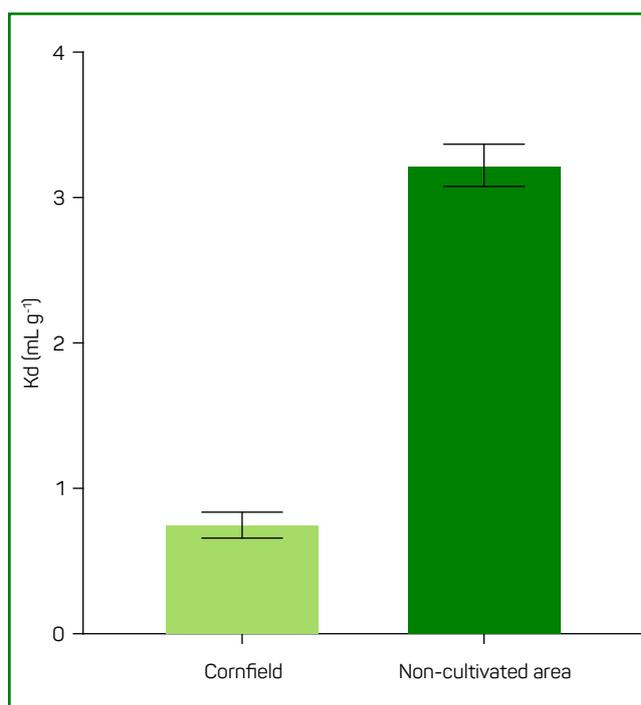
### 3.2 Effect of soil history and association with glyphosate on *S*-metolachlor mineralization

The mineralization kinetics of *S*-metolachlor alone and in mixture with glyphosate in soils having a history or no history of *S*-metolachlor application is presented in Figure 1B. According to the analysis of variance, the association with glyphosate did not affect the cumulative mineralization of *S*-metolachlor regardless of soil history ( $P > 0.050$ ). However, cumulative mineralization of *S*-metolachlor differed among the tested soils ( $P \leq 0.001$ ). Non-cultivated soil averaged 0.24% mineralization, the cornfield averaged 0.89% (Figure 4).

The first order rate constant for herbicide dissipation showed an effect of history of soil use (Table 2), and the calculated of *S*-metolachlor had an average of 171 days in non-cultivated soil and 49 days for the cornfield with history of herbicide application (Figure 3B). High mineralization of *S*-metolachlor in cornfield with a history of *S*-metolachlor application might have resulted from a microbial population that developed an ability to degrade the herbicide or another compound with a similar chemical structure or due to enhanced sorption as will be discussed later. The enhanced degradation process has



**Figure 4** - Cumulative mineralization of *S*-metolachlor alone and in mixture with glyphosate in soils with and without a history of herbicide application at 63 days after incubation. Cornfield area received *S*-metolachlor application for three consecutive years; non-cultivated soil has been a pasture field for five years and did not receive herbicide application. Error bars represent 95% confidence intervals ( $n = 8$ )



**Figure 5** - Sorption coefficients of *S*-metolachlor ( $K_d$ ) for soil with and without herbicide application history. Soil with history of herbicide application had received *S*-metolachlor for three years; Soil with no history of herbicide application have been a pasture field for five years. Error bars represent 95% confidence intervals ( $n = 8$ )

been extensively demonstrated to atrazine in the United States' agricultural soils (Krutz et al., 2009; Shaner, Henry, 2007). According to (Zablotowicz et al., 2006), atrazine's cumulative mineralization was 7-fold higher in *S*-triazine-adapted soil than in non-adapted soils. In Brazil, enhanced degradation was observed for atrazine with 8.6-fold faster degradation in a previously applied soil (Leal et al., 2019). For metolachlor, the half-life declined from 18 to 2.5 days in soils with one and four consecutive herbicide applications, respectively (Sanyal, Kulshrestha 1999). A glyphosate study showed that the dissipation rate enhanced around 58 and 66% for soil with 10 and 5 years of consecutive application, respectively, compared to the untreated soil (Guijarro et al., 2018). This behavior was also demonstrated to sulfosulfuron, which shown a degradation rate enhanced by a factor of 1.35 following consecutive applications in the field (Paporisch et al., 2020).

The results obtained for the sorption distribution coefficients ( $K_d$ ) was higher for the non-cultivated soil than in the cornfield. The average  $K_d$  value of *S*-metolachlor in cornfield soil was 0.74 mL g<sup>-1</sup>, whereas 3.22 mL g<sup>-1</sup> was observed for the non-cultivated soil (Figure 5). Since *S*-metolachlor mineralization in soil has been demonstrated to be negatively correlated with sorption (Alletto et al., 2013, Cabrera et al., 2012), likely, mineralization of the herbicide from cornfield soil was confounded by differences in herbicide sorption owing to differences in soil organic matter content. Thus, further research is required to determine the extent of *S*-metolachlor mineralization that could be solely attributable to enhanced adaptation.

#### 4. Conclusion

Soil moisture content and co-application with glyphosate affect *S*-metolachlor mineralization in the soil. The latter result is relevant as *S*-metolachlor is often tank-mixed with glyphosate as part of burndown treatments. There was also evidence of enhanced degradation, but these results were likely confounded by differences in sorption related to soil organic matter contents. The cumulative mineralization of *S*-metolachlor was greater

in saturated soil than in soils at field capacity or air-dried moisture levels. Also, the association with glyphosate enhanced *S*-metolachlor mineralization in field capacity and saturated soil. *S*-metolachlor sorption was higher under non-cultivated soil.

For future research it is important to test if *S*-metolachlor cometabolism with glyphosate application can affect preemergent herbicide efficacy. Another important study to confirm the enhanced degradation is to start an experiment designed to apply the herbicide for multiple growing seasons in the same location and soil type and evaluate at the end of the experiment if there is enhanced degradation of this herbicide.

#### Authors contribution

All authors read and agreed to the published version of the manuscript. JHM, CRZ, and LAA: conceptualization of the manuscript and development of the methodology. CRZ, GVC, and JHM: data collection and curation. CRZ, GVC, and JHM: data analysis. CRZ, JHM, GVC, ERC, and LAA: data interpretation. JHM, and LAA: funding acquisition and resources. LAA and JHM: project administration. LAA and JHM: supervision. CRZ and GVC: writing the original draft of the manuscript. JHM, CRZ, ERC, MCF, GVC, and LAA: writing, review and editing.

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