agrochemicals

Article

Oxyfluorfen and Linuron: Residual Effect of Pre-Emergence Herbicides in Three Tropical Soils

Dilma F. de Paula [1], Guilherme A. de P. Ferreira [1], Tiago Guimarães [2], Maura G. da S. Brochado [1], Leandro Hahn [3] and Kassio F. Mendes [1,*]

[1] Department of Agronomy, Universidade Federal de Viçosa, Viçosa 36570-900, MG, Brazil
[2] Department of Chemistry, Universidade Federal de Viçosa, Viçosa 36570-900, MG, Brazil
[3] Agricultural Research and Rural Extension Company of Santa Catarina, Caçador 89500-000, SC, Brazil
* Correspondence: kfmendes@ufv.br

Abstract: Knowledge about the residual effect of herbicides is important in order to increase agronomic efficacy and reduce environmental problems. Therefore, the objective of this study was to evaluate the residual effect of oxyfluorfen and linuron in three soils. Pots of 0.35 dm^3 were filled with three Brazilian soils: Ultisol, Oxisol, and Inceptisol. Then, the herbicides were applied at different times at 0, 15, 30, 45, 60, 90, 120, 150, 180, and 200 days and the bioindicator species of linuron and oxyfluorfen were sown. Then, the injury was evaluated at 7, 14, and 21 days after emergence (DAE) to find the half-life of the herbicide residue level (RL_{50}) and the dose of herbicide that provides a 50% reduction in dry matter (GR_{50}). In the soil with oxyfluorfen application, the RL_{50} at 21 DAE was 59, 57, and 51 days and GR_{50} was 49, 47, and 31 days for Ultisol, Oxisol, and Inceptisol, respectively. Soils with linuron application had RL_{50} of 75, 92, and 149 days and GR_{50} of 52, 48, and 120 days for Ultisol, Oxisol, and Inceptisol, respectively. The higher organic matter and clay content of Ultisol compared to Oxisol and Inceptisol resulted in a lower residual effect of linuron. There was little difference between soil type and the residual effect of oxyfluorfen, which may be related to the physicochemical characteristics of the molecule.

Keywords: bioavailability; bioindicator species; efficient management; soil texture; weeds

Citation: Paula, D.F.d.; Ferreira, G.A.d.P.; Guimarães, T.; Brochado, M.G.d.S.; Hahn, L.; Mendes, K.F. Oxyfluorfen and Linuron: Residual Effect of Pre-Emergence Herbicides in Three Tropical Soils. *Agrochemicals* **2023**, *2*, 18–33. https://doi.org/10.3390/agrochemicals2010003

Academic Editors: Christos G. Athanassiou and Maria K. Sakka

Received: 14 November 2022
Revised: 8 December 2022
Accepted: 3 January 2023
Published: 9 January 2023

1. Introduction

The use of herbicides applied in the pre-emergence (PRE) is indispensable in controlling germination flushes of weed seeds/propagules in crops. However, it is necessary to know the behavior of herbicides in the soil and the bioavailability of the residual effect to avoid injury to sensitive crops planted in succession/rotation (carryover). The application of herbicides without this knowledge can lead to the loss of crop yield, economic losses, and environmental problems [1,2].

Among the herbicides with residual effects on the soil are oxyfluorfen (2-chloro-α,α,α-trifluoro-p-tolyl 3-ethoxy-4-nitrophenyl ether) and the linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea). Oxyfluorfen is a contact herbicide with a broad spectrum of diphenyl-ether group, protoporphyrinogen oxidase (PPO) inhibitor [3]. This herbicide is registered for use in coffee, soybean, cotton, pine and eucalyptus, citrus, irrigated rice, and sugarcane crops. According to physicochemical characteristics, oxyfluorfen has a low water solubility (Sw = 0.116 mg L^{-1} at 20 °C) and is considered moderately persistent in the soil (dissipation time half-life, DT_{50} = 73 days) [4].

The linuron belongs to the chemical group of urea; it is an herbicide of systemic and selective action, positioned in PRE- and POST-emergence control of annual grass and broad-leaved weeds [5]. It acts by inhibition of photosynthesis at PSll-Serine 264 Binders. In Brazil, linuron is registered for use in garlic, chamomile, coriander, ginger, cassava, potatoes, carrots, and onions [6]. According to its physicochemical properties, linuron can be classified as moderately water-soluble (Sw = 63.8 mg L^{-1} at 20 °C) and moderately persistent in the soil (DT_{50} = 57.6 days) [5].

While oxyfluorfen and linuron, applied in the PRE should have a residual effect, i.e., the period when the herbicide has control over weeds, being active in the soil solution, it is not desirable that the residual effect causes injury to subsequent sensitive crops, an effect known as carryover [7]. Therefore, the need to understand the behavior of these herbicides in different tropical soils.

The residual effect of herbicides is influenced by biotic and abiotic factors. Microbial degradation of the herbicide is essential in the residual effect; however, it is dependent on temperature and water content in the soil [8]. In tropical climate environments, high temperatures and high precipitation contribute to increased soil microbial activity due to higher water availability and soil temperature, resulting in increased herbicide degradation. In addition, the organic matter content in tropical soils also tends to be lower, influencing the occurrence of lower sorption and, consequently, lower residual effect. The less sorbed herbicides are more available for microbial degradation and leaching to the lower soil layers to occur [2].

Data on the behavior of linuron and oxyfluorfen in Brazilian soils are poorly known. Studies by Novo et al. [9] indicate that linuron (788 g a.i. ha^{-1}) remains bioactive in soil at a depth of 0 to 10 cm, three weeks after its application [9]. In studies with oxyfluorfen, residues of the product were observed up to 140 days after application; moreover, the toxic effect decreased when organic compounds were added to the substrate [10]. Due to the influence of soil characteristics on the agronomic efficiency of herbicides, biological tests are important.

In order to understand the residual effect of herbicides, it is common to use bioassays with bioindicator species to understand the bioavailability of the herbicide in the soil solution [2]. The cucumber (*Cucumis sativus* L.) has been used as a bioindicator species for determining the bioavailability of linuron in soils [11]. As for oxyfluorfen, sorghum (*Sorghum bicolor* (L.) Moench) and oats (*Avena sativa* L.) have been used as bioindicator species for the presence of herbicides in soils [12].

The use of bioassays with bioindicator plants in determining the dissipation of herbicides brings satisfactory results, capable of simulating conditions observed in the field because these plants present morphological alterations by the high sensitivity to the herbicide in the soil [13]. The bioindicator species present injuries according to the levels of herbicide present in the soil solution [2].

Thus, the objectives of this study were to evaluate the residual effect of oxyfluorfen and linuron applied in PRE in three soils with different physical-chemical attributes using bioassays. The results obtained in this research may help producers and researchers to evaluate the importance of soil characteristics to define safe intervals in the use of sensitive crops in succession, increase the effectiveness of herbicides, and serve as a tool for planning the chemical control of weeds with sequential applications.

2. Materials and Methods

2.1. Location of Soil Collections

The soil samples were collected in Brazilian agricultural areas at a depth of 0–10 cm in the region of Oratórios-MG (492 m altitude, latitude: 20°25′5″ S, longitude: 42°47′28″ W) being classified as Inceptisol (loamy sand), Rio Paranaíba-MG (1.073 m de altitude, latitude: 19°11′39″ S, longitude: 46°14′37″ W) being classified as Oxisol (clay), and Curitibanos-SC (987 m de altitude, latitude: 27°16′58″ S, longitude: 50°35′04″ W) being classified as Ultisol (clay). The soils of the Rio Paranaíba and Curitibanos regions are cultivated with garlic annually.

After being sieved in a 4 mm mesh, 500 g of each type of soil was taken to the soil laboratory of the Federal University of Viçosa-MG, Brazil, and submitted for physical-chemical analysis. The results are presented in Table 1.

Table 1. Physicochemical attributes of the soils of Curitibanos: Ultisol (clay), Rio Paranaíba: Oxisol (clay), and Oratórios: Inceptisol (loamy sand) from the regions of Santa Catarina and Minas Gerais, Brazil, respectively.

Soil Classification [1] (Textural Class)	OM	pH	P	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	CEC	Sand	Silt	Clay
	%	H_2O	mg dm^{-3}		----------------$cmol_c$ dm^{-3}----------------						%	
Ultisol (clay)	4.6	6.2	9.3	203.0	6.7	2.9	0.0	3.9	14.1	3.4	17.3	79.3
Oxisol (clay)	3.7	6.7	217.6	68.0	5.1	2.4	0.0	0.7	8.4	9.0	38.5	52.5
Inceptisol (loamy sand)	0.5	5.6	59.0	57.0	1.2	0.4	0.0	2.6	4.4	78.6	6.5	14.9

OM = organic matter, P = phosphorous, K^+ = potassium, Ca^{2+} = calcium, Mg^{2+} = magnesium, Al^{3+} = aluminum, H+Al = potential acidity, CEC = cationic exchange capacity. [1] Soils classified by the Brazilian Soil Classification System [14] and Soil Taxonomy. Source: Laboratory of Soil Analysis of the Federal University of Viçosa, Viçosa, MG, Brazil.

The studies were carried out in a greenhouse during the period from November 2021 to July 2022.

2.2. Sample Preparation and Herbicide

The study of the residual effect of herbicides on soils was carried out in two stages: The first stage with the application of the herbicides and the second stage with the evaluation of the level of injury using indicator plant, cucumber and sorghum to evaluate the presence of linuron and oxyfluorfen, respectively, in the soils.

The design used was entirely randomized, in a 3x10+3 factorial scheme, with 4 repetitions. The first factor corresponds to the three different soils and the second factor corresponds to the 10 evaluation periods, and three control treatments (one for each soil), for each herbicide.

The experimental unit consisted of plastic pots of 0.35 dm^3, filled with the soils and weighed on scales to ensure that they have 370 g of soil in each pot. Next, linuron (Afalon 450C®, 450 g L^{-1}, Adama, Israel) at 810 g a.i. ha^{-1} and oxyfluorfen (Goal BR®, 240 g L^{-1}, Shangyu Nutrichem®, China) at 180 g a.i. ha^{-1}) were applied.

The herbicides were applied on the soil surface (simulating a field application) at different times. In this procedure, a CO_2 pressurized sprayer equipped with two TT110.02 spray tips was used, spaced 0.5 m apart, and maintained at a pressure of 200 kPa.

The herbicides were applied to the three soils at different times, at 0, 15, 30, 45, 60, 90, 120, 150, 180, and 200 days before the seeding of the indicator species. The pots were exposed in the greenhouse and irrigated according to the average amount of rainfall of the years 2018, 2019, and 2020, in the Viçosa region (taken from the national meteorological institute), during the 200 days of evaluation, with an average of 7 mm daily. The climatic data of temperature were collected throughout the experiment in the greenhouse, with an average maximum temperature of 32 °C and a minimum of 26 °C.

After the last application of herbicides, the seeds of the bioindicator species of each herbicide were sown in the soil samples, five sorghum and cucumber seeds per pot, as well as soil samples without herbicide, constituting the control treatment. After four days of plant emergence, the plants were thinned, leaving three plants per pot. Then, a complete Hoagland and Arnon nutrient solution [15] was applied to the experimental units, to allow the plants to develop well. This solution has been the most used in research on mineral nutrition and is the basis for the formation of numerous commercial solutions, composed of both macro and micronutrients [16]. The pots were irrigated daily.

2.3. Evaluation of the Residual Effect

The evaluation of the residual effect of the herbicides was carried out using the level of injury on the plants with the function of detecting the presence of bioavailable herbicide in the soil solution. The study was conducted in an entirely randomized design with four repetitions for each of the three tropical soils of the regions Curitibanos-MG: Ultisol (clay), Rio Paranaíba-MG: Oxisol (clay), and Oratórios-MG, Brazil: Inceptisol (loamy sand), with the application of linuron and oxyfluorfen, as well as the control treatment (without herbicide application).

The analyses were performed at 7, 14, and 21 days after emergence (DAE), assigning grades from 0 (zero) to 100% (one hundred), where 0 refers to the absence of symptoms and 100 refers to the death of the plant. This scale aims to quantify the degree of bioindicator damage, always considering the plants in soil without residue (control), as the maximum standard for the growth/development of the species [9]. The scale was adapted according to the evolution of the injury symptoms in the bioindicator species caused by oxyfluorfen [17–19] and linuron [19–22] (Table 2).

Table 2. Rating scale used to score the level of injury (%) in the bioindicator species sorghum and cucumber after application of oxyfluorfen and linuron, respectively.

Injury Level (%)	Symptoms Observed in Sorghum in the Presence of Oxyfluorfen Residues	Symptoms Observed in Cucumber in the Presence of Linuron Residues
1–9	Slight reduction in growth	Very similar to the control, with slight reductions in growth
10–19	Slight whitish spots	Reductions in aerial growth
20–29	White spots on most of the leaves	Few chloroses on cotyledonary leaves
30–39	Small reductions in aerial growth and whitish spots	High chlorosis symptoms on cotyledonary leaves
40–49	Leaf shriveling	Few symptoms of necrosis on cotyledonary leaves
50–59	Growth reduction to 50% of the control	Growth reduction to 50% of the control
60–69	Hoarsening of young leaves	Evolution of necrosis symptoms in the cotyledonary leaves with reduction in the growth of the aerial part
70–79	Intense growth reduction and leaf shriveling	Few symptoms of necrosis on the apex leaves
80–89	Hoarsening of the youngest leaves and necrosis	Limited growth, with symptoms of necrosis in most leaves
90–99	Dying plants, all leaves with advanced symptoms of necrosis	Plant dying, all leaves with advanced necrosis symptoms
100	Dead plant	Dead plant

At 21 DAE, the effects of the grown reduction in aerial dry matter (ADM) were also evaluated. For this, the aerial part was cut close to the ground and placed in paper bags. The cut plant material was placed in a forced air circulation oven (FANEM, 320, São Paulo, Brazil) at a temperature of 70 °C for 72 h to reach the constant mass. Finally, using an analytical precision balance (0.0001 g) (SHIMADZU, AY220, São Paulo, Brazil), the dry matter of the plants was weighed. The dry matter values of the cucumber and sorghum plants were transformed into the percentage of reduction of the dry matter of the control treatment plants.

2.4. Statistical Analysis

In studying the residual effect of herbicides through indicator species, the Residual Lifetime, RL_{50}, was used. In these cases, RL_{50} values were determined using first-order kinetics, using Equations (1) and (2) plotted in the SigmaPlot® program (version 14.0 for Windows, Systat Software Inc., Point Richmond, CA, USA) [23–25].

$$Ct = C_0 e^{-kt} \tag{1}$$

$$RL_{50} = \frac{ln2}{k} \tag{2}$$

where Ct represents the concentration of the herbicide at time t measured indirectly by the injury level of the bioindicator species, C_0 represents the initial concentration based on the injury level, and k is the herbicide dissipation rate constant in days. RL_{50} is then determined from the k value [25].

In the analysis of the dry matter variable, the model proposed by Seefeldt et al. [26] was used, according to Equation (3):

$$y = a + \frac{b}{\left[1 + \left(\frac{x}{c}\right)^d\right]} \quad (3)$$

where y is herbicide residual percentage based on the dry matter; x is herbicide dose; and a, b, c, and d are the parameters of the curve, so that a is the lower limit of the curve, b is the difference between the maximum and minimum points of the curve, c is the number of days the herbicide is causing 50% reduction in aerial dry matter (ADM) (GR_{50}), and d is the slope of the curve.

The normality of the residuals was checked by the Shapiro–Wilk test at $p < 0.05$.

3. Results

3.1. Oxyfluorfen

The symptoms caused by the residual effect of oxyfluorfen at 7 DAE on sorghum were few in all soils; however, the symptoms evolved over the days. At 14 DAE, leaf shriveling and necrosis symptoms were observed, especially with the decrease between the herbicide application period and sorghum sowing. However, at 21 DAE, the damage caused by the residual effect of oxyfluorfen was more evident in the bioindicator species, coinciding with those observed by Araújo et al. [27]: whitish spots evolving to necrosis, leaf shriveling, and reduction in plant size. The symptoms decreased with increasing time of herbicide application (Figure 1).

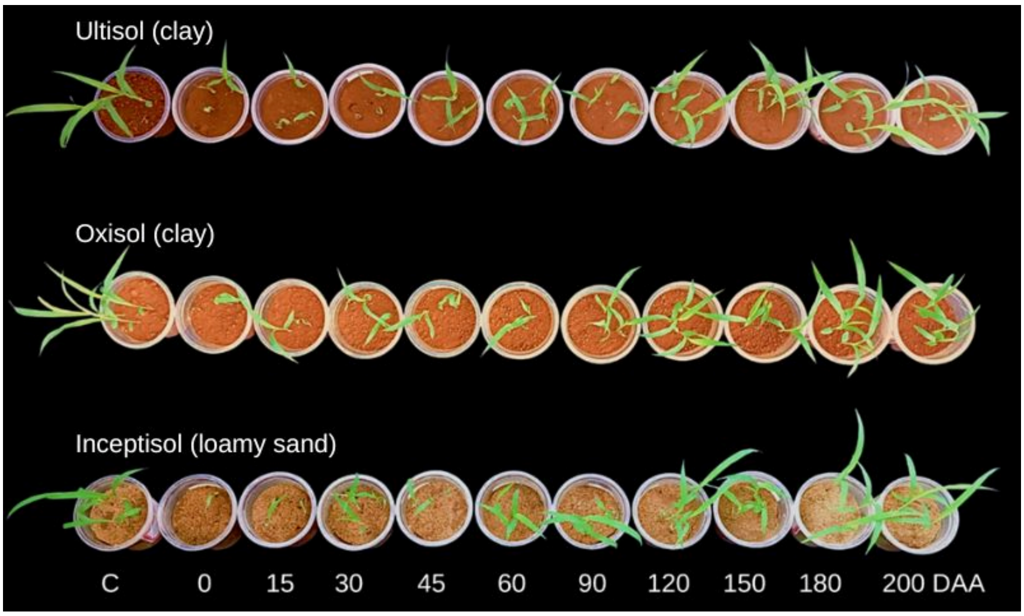

Figure 1. Injury symptoms caused by the residual effect of oxyfluorfen on sorghum. Injury symptoms caused by the residual effect of oxyfluorfen on sorghum at 0, 15, 30, 45, 60, 90, 120, 150, 180, and 200 days after application (DAA) of the herbicide in comparison with the control treatment (C), in soils in the region of Curitibanos-SC: Ultisol (clay), Rio Paranaíba-MG: Oxisol (clay), and Oratórios-MG, Brazil: Inceptisol (loamy sand).

The behavior of the injury level curve of oxyfluorfen was similar at 7, 14, and 21 DAE in the three soils. In Ultisol (clay), the greatest injury was observed in the bioindicator species at 0, 15, and 30 DAA. At 45 days, there was a reduction in injury as the residual effect of oxyfluorfen on the bioindicator species decreased. At 120 DAA, a little residual effect of the herbicide was observed (<20%), and at 200 DAA, there was no injury effect (Figure 2). In Oxisol (clay), the behavior of the curve was very similar to Ultisol (clay), with high injury to the bioindicator species at 0, 15, and 30 DAA, and a significant reduction in injury between 45 and 60 DAA, with symptoms less than 20% at 150 DAA and no residual effect was observed at 200 DAA (Figure 2). In Inceptisol (loamy sand), high injury scores were observed up to 30 DAA, and a high injury decline (45 to 20%) from 60 to 90 DAA; with a complete reduction of herbicide symptoms 200 DAA. It was noted that the level of injury did not reach close to 100% at 7 DAE, which occurred at evaluations 14 and 21 DAE in all soils evaluated (Figure 2).

The difference in days to reach the RL_{50} value of this herbicide at the different evaluation times was minimal, following the increasing order of days in soils 7 DAE: Inceptisol (loamy sand) (35 days), Oxisol (clay) (36 days), and Ultisol (clay) (40 days). Additionally, at 14 DAE: Oxisol (clay) (49 days), Inceptisol (loamy sand) (50 days), and Ultisol (clay) (51 days). The last evaluation at 21 DAE: Inceptisol (loamy sand) (51 days), Oxisol (clay) (57 days), and Ultisol (clay) (59 days). At 7 DAE, it was not possible to reach 100% in the level of plant injury in any of the soils evaluated (Figure 2).

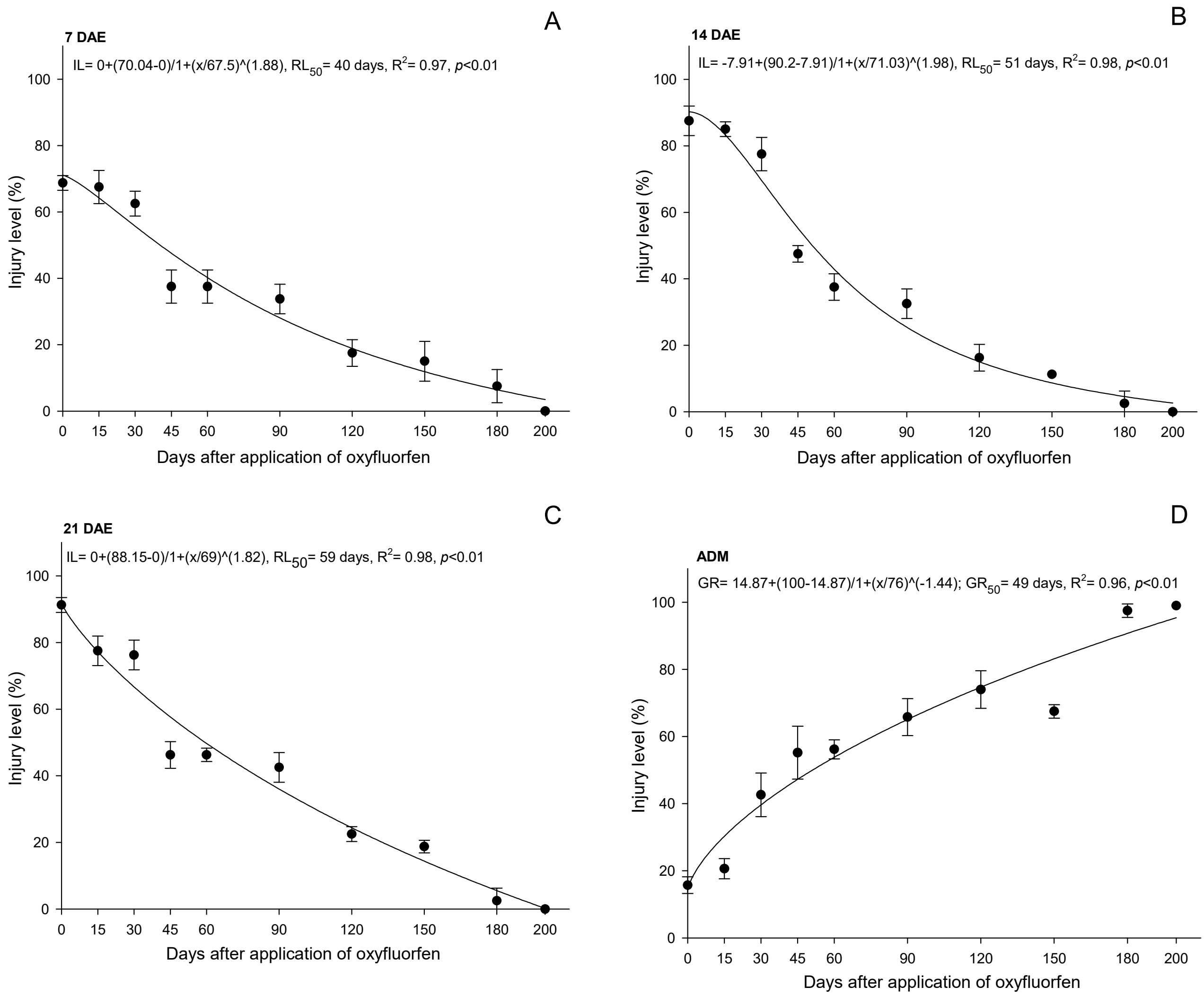

Figure 2. *Cont.*

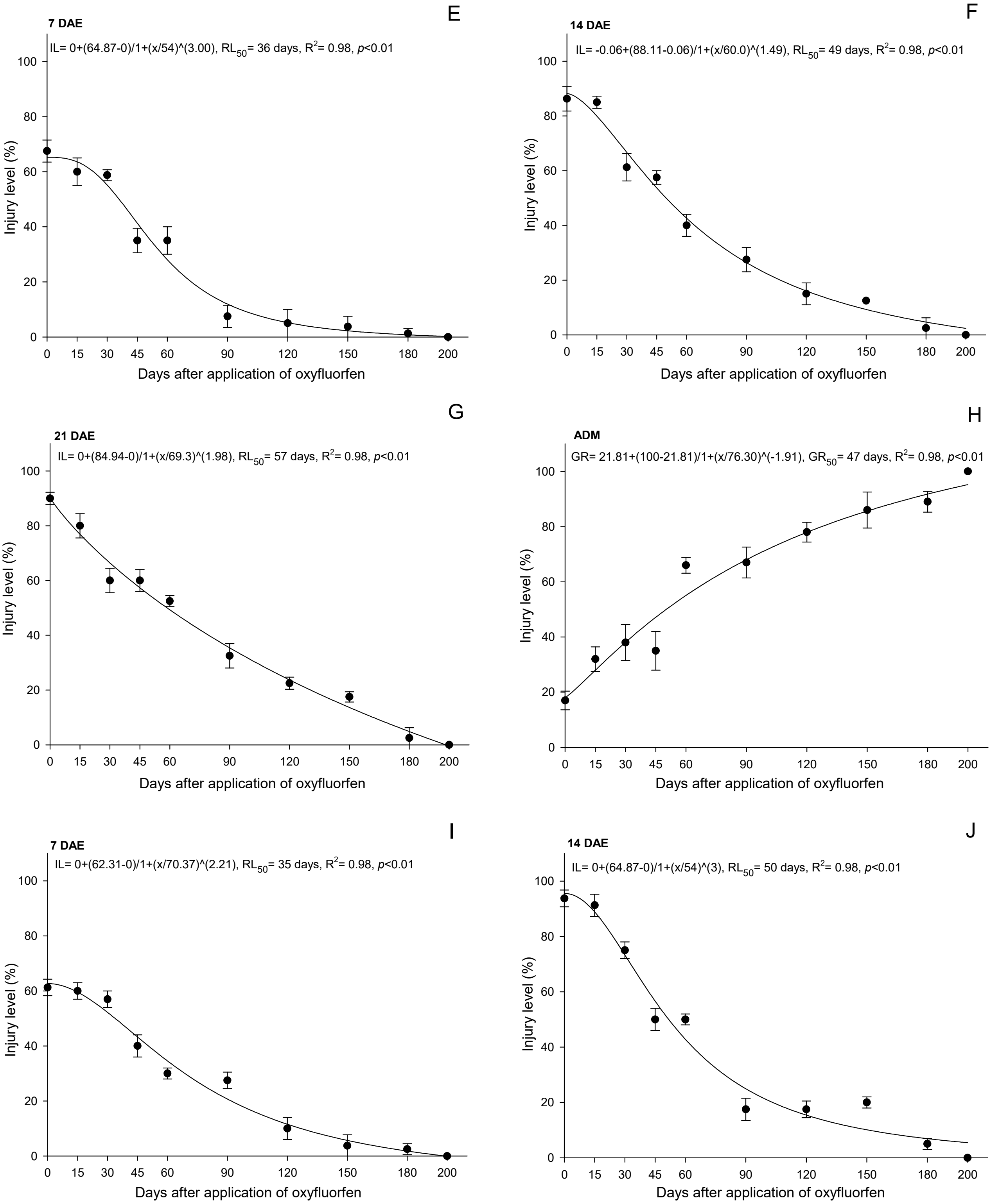

Figure 2. *Cont*.

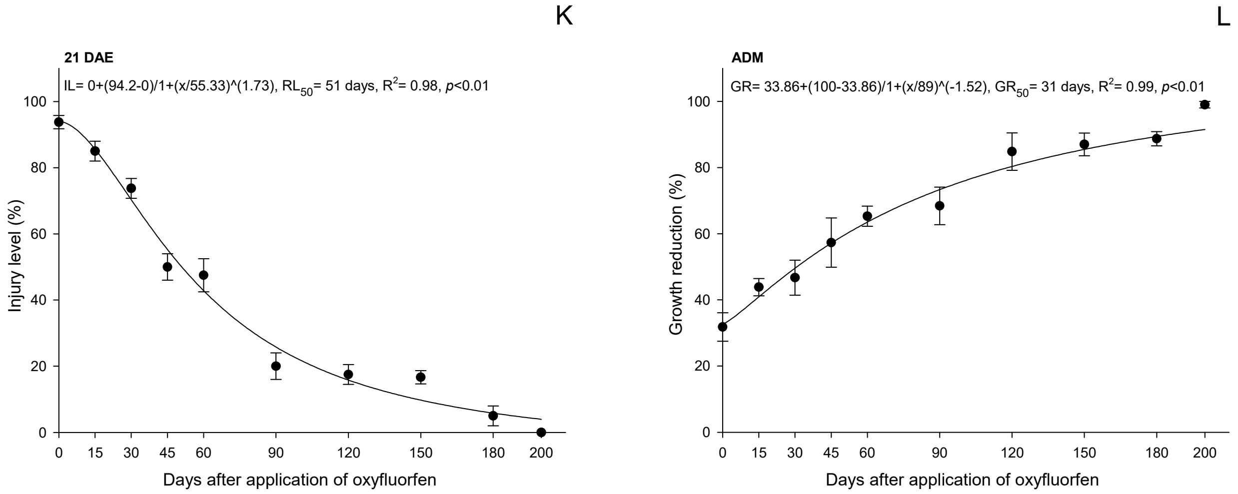

Figure 2. The residual effect of oxyfluorfen (180 g a.i. ha^{-1}), and the values of the residual half-life time with 50% of injury (RL_{50}) in sorghum at 7, 14, and 21 days after emergence (DAE) and reduction of the dry matter of the aerial part (ADM) in 50% (GR_{50}) about the control treatment, in the soils of Curitibanos-SC: Ultisol (clay) (**A**–**D**), Rio Paranaíba-MG: Oxisol (clay) (**E**–**H**), and Oratório-MG, Brazil: Inceptisol (loamy sand) (**I**–**L**) at 0, 15, 30, 45, 60, 90, 120, 150, 180, and 200 days after application (DAA). When necessary, the parameters were normalized by fitting the regression equation. The vertical bars in each symbol are equivalent to the standard error of the mean (n = 4).

The number of days required to reach 50% in the level of injury in the bioindicator species was higher at 21 DAE compared to 14 DAE in all soils evaluated and very small differences were found in the behavior of the residual effect of oxyfluorfen, regardless of soil, being at 14 DAE < 52 days and at 21 DAE < 60 days.

According to the test of normality of residuals (Shapiro–Wilk) p = 0.12, the residuals can be considered normal. there is significant interaction between the factors soil and herbicide. According to the Tukey's test, the residual effect of oxyfluorfen was higher on Inceptisol (loamy sand) compared to Oxisol (clay) and Ultisol (clay), which did not differ statistically. The GR_{50} was achieved in fewer days with Inceptisol (loamy sand) (31 days) compared to Oxisol (clay) and Ultisol (clay) (49 and 47 days, respectively) (Figure 2).

The RL_{50} followed the same trend as the 7 and 21 DAE evaluation, with more days on Ultisol (clay) than the other herbicides, following the order: Inceptisol (loamy sand) (31 days), Oxisol (clay) (47 days), and Ultisol (clay) (49 days) (Figure 2). As well as the levels of injury, this result can be explained by the increased availability of oxyfluorfen in the solution of Inceptisol (loamy sand) compared to the others, being a symptom of the herbicide the reduction of growth, decreasing the ADM, this symptom was intensified in sorghum in a shorter time.

3.2. Linuron

The symptoms of the residual effect of linuron caused in the bioindicator species cucumber at 21 DAE were: chlorosis first observed on the veins and evolving between the veins of the leaves, followed by necrosis and death of the plants. The symptoms decreased with increasing time of herbicide application (Figure 3).

The behavior of the injury level curve on cucumber caused by linuron at 7, 14, and 21 DAE was similar in Ultisol (clay) and Oxisol (clay), showing at 14 and 21 DAE, plant death until 30 DAA. Injury reduced to approximately 50–60% in Ultisol (clay) and Oxisol (clay) at 45 DAA, respectively. At 200 DAA of linuron, no further residual effect was observed in these soils. In Inceptisol (loamy sand), the behavior of the herbicide was different, plant death was observed until 60 DAA, and at 200 DAA, there were still residues of linuron in the soil (Figure 4). At 7 DAE, high values of injury level could not be observed in any of the soils but were observed at 14 and 21 DAE in all soils (Figure 4).

According to the results, it was not possible to find the RL_{50} of linuron at 7 DAE in any of the evaluated soils (>200 days). This can be explained by the reduction in temperature and luminosity in the days after the emergence of the bioindicator species. As temperature and light increased, symptoms caused by linuron intensified in the indicator species at 14 DAE, with 100% lesion symptoms at 0 and 15 DAA of the herbicide in all soils (Figures 3 and 4). However, to reach RL_{50}, a much longer period (130 days) was required with Inceptisol (clayey sand) compared to Oxisol (clay) (84 days) and Ultisol (clay) (73 days). Linuron remains less sorbed in Inceptisol (loamy sand), this greater availability of the herbicide in the soil solution results in the death of the bioindicator species by 60 DAA of the herbicide.

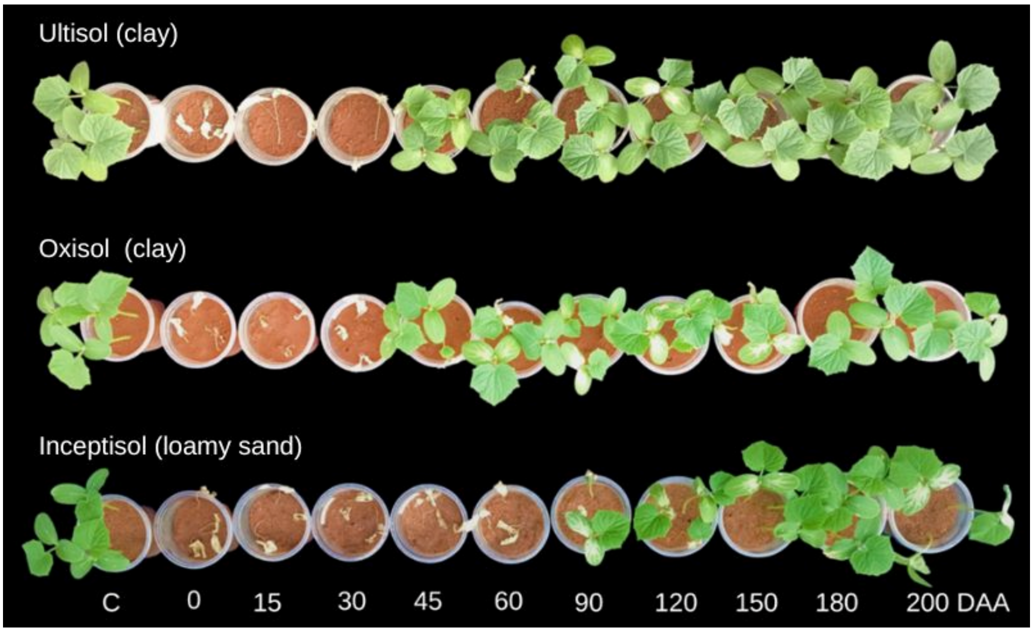

Figure 3. Injury symptoms caused by the residual effect of linuron on cucumber at 0, 15, 30, 45, 60, 90, 120, 150, 180, and 200 days after application (DAA) of the herbicide in comparison with the control treatment (C), in soils in the region of Curitibanos-SC: Ultisol (clay), Rio Paranaíba-MG: Oxisol (clay), and Oratórios-MG, Brazil: Inceptisol (loamy sand).

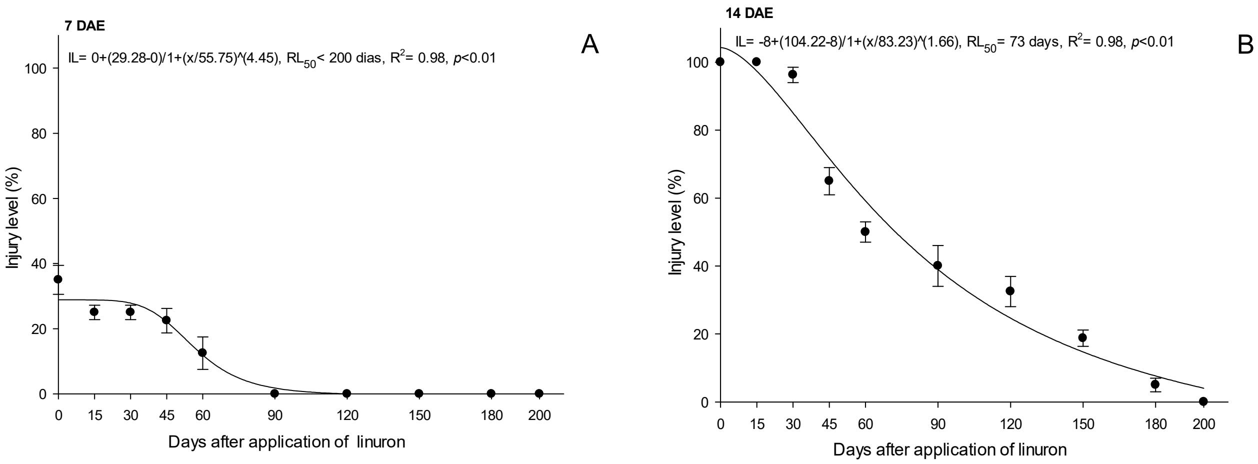

Figure 4. *Cont.*

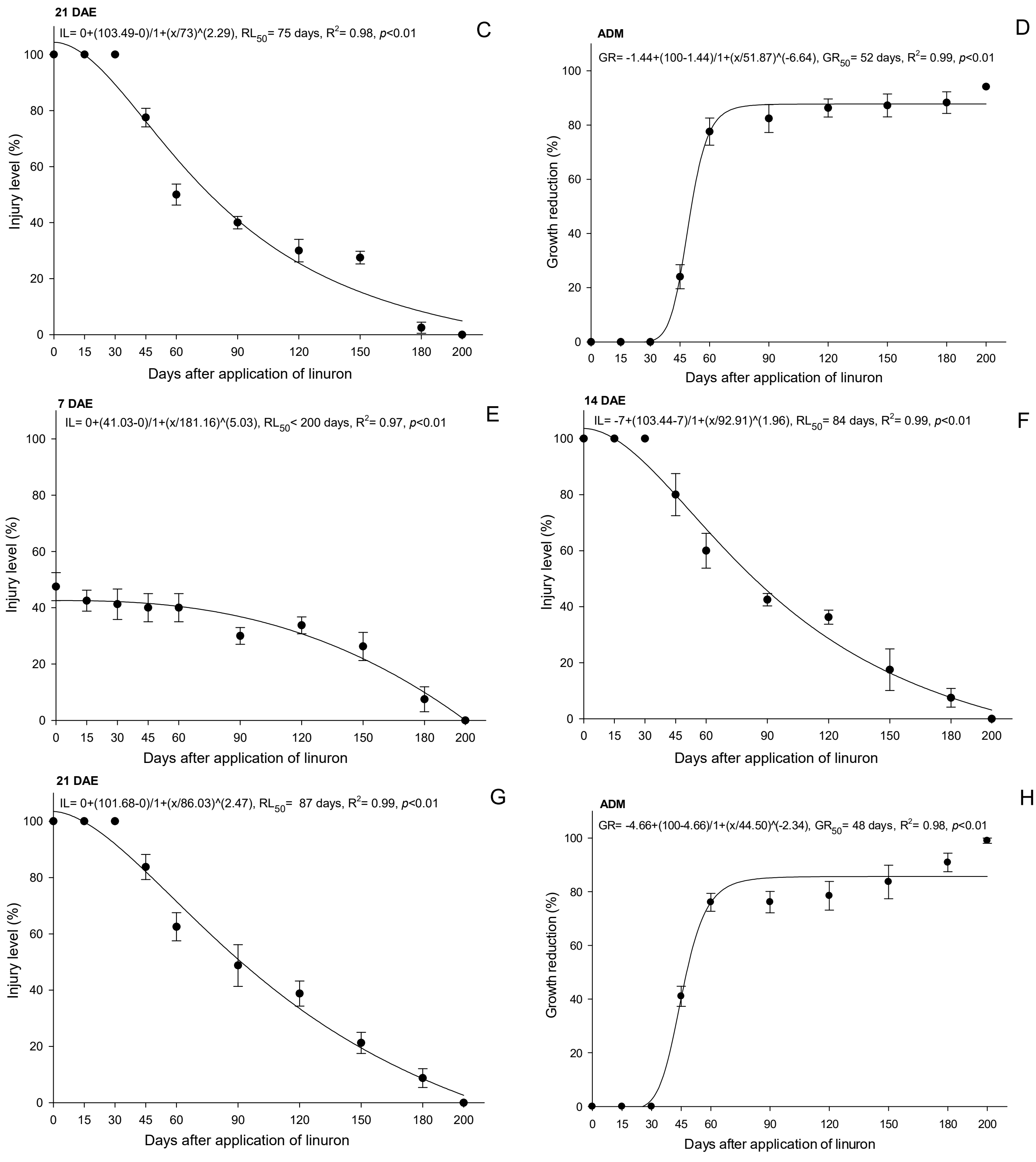

Figure 4. *Cont.*

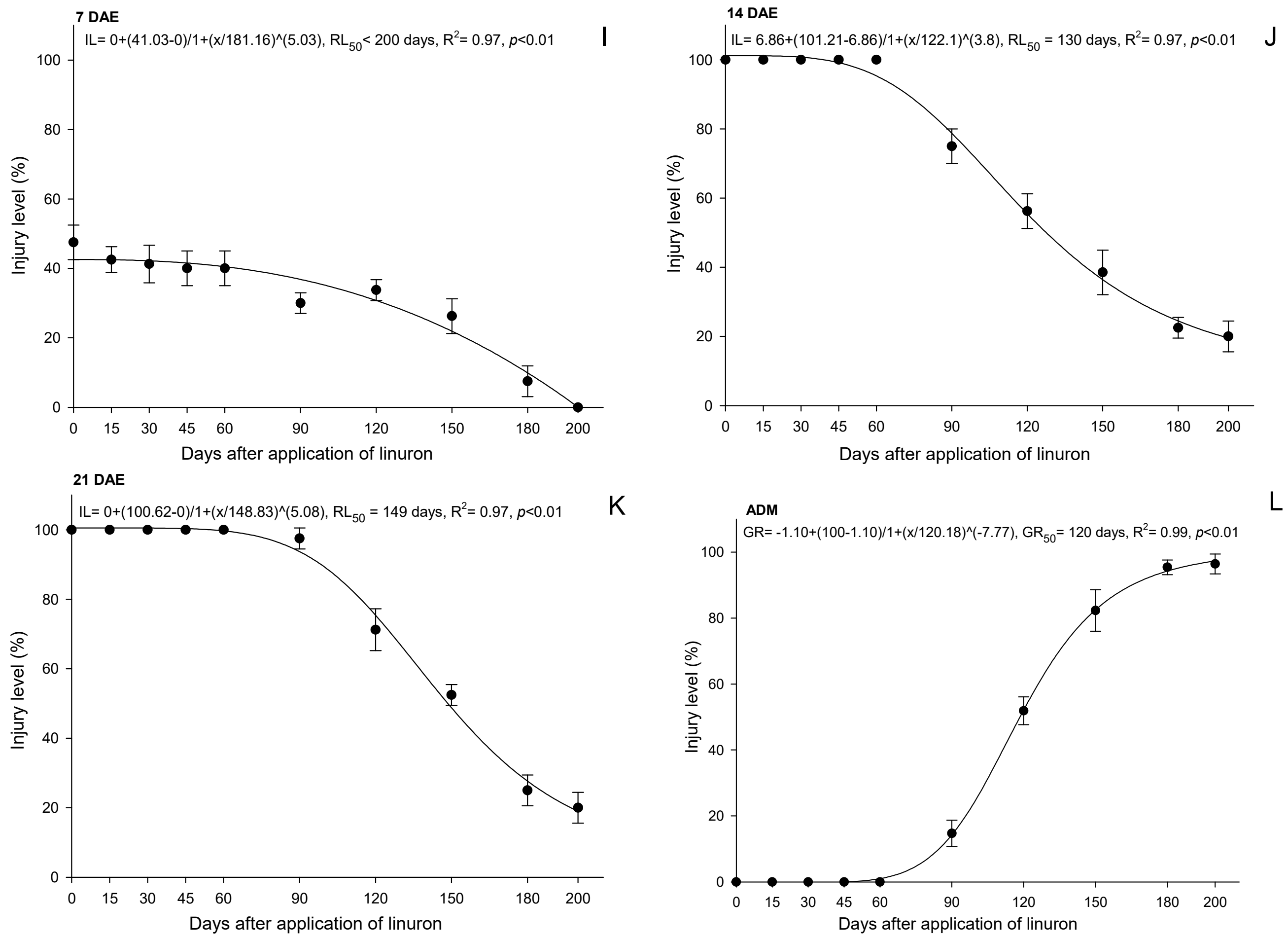

Figure 4. The residual effect of oxyfluorfen (180 g a.i. ha^{-1}), and the values of the residual half-life time with 50% of injury (RL_{50}) in cucumber at 7, 14, and 21 days after emergence (DAE) and reduction of the dry matter of the aerial part (ADM) in 50% (GR_{50}) about to the control treatment, in the soils of Curitibanos-SC: Ultisol (clay) (**A**–**D**), Rio Paranaíba-MG: Oxisol (clay) (**E**–**H**), and Oratório-MG, Brazil: Inceptisol (loamy sand) (**I**–**L**) at 0, 15, 30, 45, 60, 90, 120, 150, 180, and 200 days after application (DAA). When necessary, the parameters were normalized by fitting the regression equation. The vertical bars in each symbol are equivalent to the standard error of the mean (n = 4).

According to the Tukey's test, the residual effect of linuron (GR_{50} = 120 days) on Inceptisol was statistically higher than on Ultisol and Oxisol for both herbicides. The effect of linuron on Ultisol (GR_{50} = 52 days) and Oxisol (GR_{50} = 48 days) did not differ statistically. This was due to the residual effect of linuron on Inceptisol (loamy sand) killing the plant up to 60 days after herbicide application, increasing the days to reach GR_{50}. As the herbicide was more retained in Ultisol (clay) and Oxisol (clay), causing complete plant death only by 30 DAA of the herbicide, GR_{50} was reached in shorter times (Figures 3 and 4).

Evaluations at 21 DAE showed results close to 14 DAE, with small increases in RL_{50} at 75, 92, and 149 days for Ultisol (clay), Oxisol (clay), and Inceptisol (loamy sand), respectively. This increase in days to reach the RL_{50} is due to the evolution of symptoms in the bioindicator species, especially in the first days after herbicide application.

4. Discussion

4.1. Oxyfluorfen

At 7 DAE, it was not possible to reach 100% in the level of plant injury in any of the soils evaluated (Figures 1 and 2). This result is due to the mechanism of action of the herbicide and the climatic conditions in which the experiment was conducted. Oxyfluorfen is an herbicide that inhibits PPO, which requires the presence of light for the production of singlet oxygen (O^-), which destroys the cell membrane, leading the plant to death [28]. At low temperatures and luminosity, the symptoms in sorghum take longer to be reached. With the increase in temperature and luminosity at 14 and 21 DAE, the symptoms intensified, reaching close to 100% of plant injury in all soils evaluated (Figure 1).

The Ultisol (clay) showed 64% and 26.8% higher clay contents compared to Inceptisol (loamy sand) and Oxisol (clay), respectively (Table 1). In addition, it presented OM contents about 9 and 1.22 times higher than these soils, respectively. These different physicochemical attributes of the soils may justify the higher number of days to reach the RL_{50} in Ultisol (clay) in most evaluations, this behavior is repeated in GR50 with the increasing order of days: Inceptisol (loamy sand) (31 days), Ultisol (clay) (47 days) and Oxisol (clay) (49 days). Oxyfluorfen being more retained in the colloids of the Ultisol (clay) soils, results in more time to cause the injury to the bioindicator species. Inceptisol (loamy sand), because it has lower clay and OM contents, the bioavailability of the herbicide may have been greater in the soil solution, resulting in fewer days to cause injury and reduce the ADM of sorghum.

In evaluating the residual effect of oxyfluorfen (720 g a.i. ha^{-1}) in contrasting soils, 50% injury to sorghum was observed at 60 DAA in clayey soils (9% OM and 56% clay) and 90% injury in sandy loamy soils (0.4% OM and 14% clay) [12]. Different results were found in the following study, which may be related to the dose, climatic conditions, soil water content, and microbiological activity of these soils. Thus, it is of great importance all these factors in evaluating the behavior of residual herbicides [2].

When analyzing the residual effect of oxyfluorfen in constricting soils, Inoue et al. [29] observed that the dose of 480 g a.i. ha^{-1} of the herbicide resulted in injury above 80% at 56 DAA in clayey soil and 36 DAA in sandy soil, using the species *Urochloa decumbens* (bioindicator species). These studies contribute to highlighting the lower number of days to reach the RL_{50} in Inceptisol (loamy sand) compared to the other soils because of the increased bioavailability of the herbicide results in the control of the bioindicator species in a shorter period.

Soil microorganisms are of great importance in the degradation of oxyfluorfen. According to a study with *Azotobacter chroococcum* in a sterilized mineral salt medium, the bacteria degraded more than 60% of this herbicide in 7 days [30]. The evaluation of the microbiological degradation potential of oxyfluorfen at different temperatures was observed by [31], and the results indicated that the biodegradation of oxyfluorfen in soil incubated at 40 °C after 45 days of incubation was better (55.2–78.3%) than in soil incubated at 28 °C (17.5–36.6%). Important species with the ability to degrade oxyfluorfen in 21 days were: *Bacillus* spp. With the ability to degrade between 80 and 95.6%, followed by *Pseudomonas* spp. (82.2%) and *Arthrobacter* spp. These authors mentioned that these microorganisms were considered the potential for the use of decontamination of sites polluted with oxyfluorfen, due to their ability to degrade the herbicide. Soils with higher clay content have a higher abundance of bacterial genes supposedly involved in the degradation of numerous organic substances [32].

With the evaluation of the residual effect of the herbicide, it was possible to evaluate the time of availability of the herbicide in the soil that is causing an effect on the bioindicator species; however, it is important to point out that the persistence time of the molecule is longer than the residual effect, and it may be present in the soil in the form of bound residues or transformed into other metabolites and that the soil management practices have a direct relationship with the availability of herbicides. The addition of organic compounds to the soil and the relationship with the residual effect of oxyfluorfen was observed by Souza et al. [10], and as a result, there was an increase in sorption of the herbicide and an increase in microbial activity in the degradation, causing a less toxic effect on the bioindicator species in time, reducing the damage from 140 to 110 days.

Studies on the behavior of oxyfluorfen are still scarce in the scientific literature; however, as it is an herbicide positioned in PRE, a PPO inhibitor, it is important to continue the study with this herbicide, since this mode of action is essential to preventing the development of resistant weed biotypes. According to Hao et al. [28], PPO inhibitor herbicides tend to select weeds with resistance at a much slower level than other herbicides.

4.2. Linuron

According to the results, it was not possible to find the RL_{50} of linuron at 7 DAE in any of the evaluated soils (>200 days). This can be explained by the reduction in temperature and luminosity in the days after the emergence of the bioindicator species. Linuron is a PSII inhibitor herbicide, which depends on light incidence for symptom intensification, and it is necessary for the accumulation of energy in the chlorophyll molecules from solar energy. This accumulation of energy together with oxygen form Reactive Oxygen Species (ROS) that damage the cell membrane and cause the death of the plant [33]. Therefore, the climatic conditions explain why the symptoms appeared more slowly in the evaluation at 7 DAE.

Linuron is an herbicide that is poorly soluble in water, and hydrophobic interactions with soil OM decrease the residual effect of this herbicide in soils. Among the soil OM fractions, humic substances are the main sorbents of herbicides [34]. The higher the K_{ow} value of the herbicide, the higher its retention potential on hydrophobic surfaces, such as soil OM (higher degree of humification) [35]. In the scientific literature, there are reports of a positive correlation between the aromatic C of humic acids and K_{oc} values of herbicides [36,37]. For linuron, Dorado et al. [38] found higher retention affinity in soils with humic acids.

This increase in days to reach the RL_{50} is due to the evolution of symptoms in the bioindicator species, especially in the first days after herbicide application. The highest sorption and microbial activity occur in soils with higher OM content, in Ultisol (clay), decreasing the residual effect of linuron in this soil compared to Oxisol (clay) and Inceptisol (loamy sand).

Like oxyfluorfen, the degradation of linuron is influenced by soil microbiological activity [39]. Some soil microorganisms can utilize urea-derived herbicides as a source of nitrogen to supply energy needs. However, studies by Breugelmans [40] showed that the degradation of linuron was carried out by a group of metabolically interacting bacteria rather than by individual strains.

Another important factor is that Ultisol (clay) and Oxisol (clay) are soils where garlic is grown, and the use of linuron in weed management is frequent in these soils. Inceptisol (loamy sand), on the other hand, there is no use of this herbicide. Thus, there is selection pressure of linuron on the microbiota in Ultisol (clay) and Oxisol (clay), which may be selecting microorganisms better adapted to degrade this herbicide, resulting in a lower residual effect of linuron in these soils compared to Inceptisol (loamy sand). Similar results were found by Medo et al. [41], in which the use of linuron altered the microbial composition of the soil, with an abundance of Proteobacteria, particularly the genera *Pseudomonas* and *Achromobacter*. In addition, increased expression of microbial genes related to xenobiotic degradation pathways was observed.

One study demonstrated that linuron has low solubility and mobility and as a consequence remains in the topsoil layers (0–10 cm), with 70% being found after 245 days. The main metabolites detected were DCPMU [3-(3,4-dichlorophenyl)-1-methylurea] and DCA (3,4-dichloroaniline). Furthermore, volatilization losses of linuron are minimal [42]. This study contributes to demonstrating that the main form of herbicide degradation in the soil is by microbiological activities.

The microbiological activity, when evaluated in the field, tends to be more intense than in a protected environment. Thus, the degradation of linuron tends to be faster. Studies developed by Novo et al. [9], in soils with 4% OM contents, showed that the dose 2000 g a.i. ha^{-1} that the level of injury caused by the herbicide tends to be high at 28 days, causing the death of the bioindicator species; however, it did not cause injury in the bioindicator species at 42 DAA. In the following study, up to 120 days in soils with near

OM content in Ultisol (clay), there was still a mild injury level in the bioindicator species (Figure 4).

This study evidences that the different physicochemical characteristics of the soils interfere with the residual effect of linuron, weed control, and the degradation of the molecules in the soil.

5. Conclusions

The physicochemical characteristics of the soils and of oxyfluorfen and linuron are indispensable in the knowledge of the residual effect. In soils with higher OM and clay contents, such as Ultisol (clay) and Oxisol (clay), the residual effect was lower than in Inceptisol (loamy sand) due to the bioavailability in the soil solution observed by injury level in the bioindicator species.

Information regarding the residual effect of herbicides in different soils can be used as a weed control strategy and sequential placement of herbicides, according to management needs. Furthermore, carryover problems can be avoided when the behavior of herbicides applied in PRE in soils is known.

Author Contributions: Conceptualization, D.F.d.P. and K.F.M.; methodology, D.F.d.P. and K.F.M.; software, D.F.d.P.; validation, D.F.d.P., T.G., and K.F.M.; formal analysis, D.F.d.P. and G.A.d.P.F.; investigation, M.G.d.S.B.; resources, L.H. and K.F.M.; data curation, D.F.d.P., G.A.d.P.F. and K.F.M.; writing—original draft preparation, D.F.d.P. and G.A.d.P.F.; writing—review and editing, T.G.; visualization, M.G.d.S.B.; supervision, K.F.M.; project administration, D.F.d.P.; funding acquisition, D.F.d.P. and K.F.M. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) (number 001) for the first-author scholarship and financial support.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Priya, R.S.; Chinnusamy, C.; Janaki, P.; Arthanari, P.M. Persistence and carryover effect of oxyfluorfen residues in red sandy clay loam soil. *J. Pharmacogn. Phytochem.* **2017**, *6*, 527–532.
2. Mendes, M.F.; Sousa, R.N.; Dias, R.C.; Reis, M.R. Efeito residual de herbicidas em solos agricultáveis. In *Contaminantes Orgânicos da Análise a Biorremediação*; Tornisielo, V.L., Vilca, F.Z., Guimarães, C.D., Mendes, K., Eds.; FFEALQ: Piracicaba, Brazil, 2019; pp. 157–178.
3. Ohadi, S.; Godar, A.; Madsen, J.; Al-khatib, K. Response of rice algal assemblage to fertilizer and chemical application: Implications for early algal bloom management. *Agronomy* **2021**, *11*, 542. [CrossRef]
4. Pesticide Properties Data Base—PPDB. Oxyfluorfen. 2022. Available online: http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/502.htm (accessed on 8 August 2022).
5. Pesticide Properties Data Base—PPDB. Linuron. 2022. Available online: http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/419.htm (accessed on 8 August 2022).
6. Ministério da Agricultura, Pecuária e Abastecimento—MAPA. Available online: https://www.gov.br/agricultura/pt-br (accessed on 8 August 2022).
7. Curran, W.S. Persistence of herbicides in soil. *Crop. Soils* **2016**, *49*, 16–21. [CrossRef]
8. Guimarães, A.C.D.; Inoue, M.H.; Mendes, K.F.; Santos, A.W.; Oliveira, A.M. Processos de degradação biológica (biodegradação) dos herbicidas no solo. In *Herbicidas No Ambiente: Impacto e Detecção*, 1st ed.; Mendes, K.F., Inoue, M.H., Tornisielo, V.L., Eds.; Editora UFV: Viçosa, Brazil, 2022; pp. 9–35.
9. Novo, M.D.; Cruz, L.S.P.; Lopes, E.S.; Nagai, V.; Ambrósio, L.A.; Pereira, J.C.V.N.A.; Lombardi, M.L.C.d.O. Persistência de linuron e orizalina em latossolo roxo sob cultivo de soja. *Bragantia* **2020**, *51*, 177–184. [CrossRef]
10. Souza, A.P.; Lourdes, E.G.; Da Silva, J.F.; Ruiz, H.A. Efeito do oxyfluorfen, 2,4-D e glyphosate na atividade microbiana de solos com diferentes texturas e conteúdo de matéria orgânica. *Planta Daninha* **1996**, *14*, 55–64. [CrossRef]
11. Deuber, R.; Pastre, W.; Giusto, A.B. Lixiviação de linuron em dois diferentes latossolos. *Rev. Bras. Herbic.* **2009**, *8*, 27–36.
12. Melo, C.A.D.; Medeiros, W.N.; Tuffi, L.D.; Ferreira, F.A.; Tiburcio, R.A.S.; Ferreira, L.R. Lixiviação de sulfentrazone, isoxaflutole e oxyfluorfen no perfil de três solos. *Planta Daninha* **2010**, *28*, 385–392. [CrossRef]

13. Inoue, M.H.; Fernandes, T.; Mendes, K.F.; Oliveira, R.S., Jr.; Guimaraes, A.C.D.; Maciel, C.D.G. Métodos de Detecção de Herbicidas no Solo Utilizando Bioensaios. In *Herbicidas No Ambiente: Impacto e Detecção*, 1st ed.; Mendes, K.F., Inoue, M.H., Tornisielo, V.L., Eds.; Editora UFV: Viçosa, Brazil, 2022; pp. 331–374.
14. Empresa Brasileira de Pesquisa Agropecuária-EMBRAPA. *Sistema Brasileiro de Classificação de Solos*, 5th ed.; Editora Embrapa Solos: Brasília, Brazil, 2018; pp. 317–325.
15. Hoagland, D.R.; Arnon, D.I. *The Water Culture Method for Growing Plants without Soils Berkeley*; California Agricultural Experimental Station: Berkeley, CA, USA, 1950; p. 347.
16. Cometti, N.N.; Furlani, P.R.; Ruiz, H.A.; Fernandes, E.I. Soluções nutritivas: Formulação e aplicações. In *Nutrição Mineral de Plantas*, 2nd ed.; Editora SBCS: Viçosa, Brazil, 2006; pp. 90–112.
17. Concenço, G.; Andres, A.; Schreiber, F.; Palharini, W.G.; Martins, M.B.; Moisinho, I.S.; Melo, T.S.; da Silva, L.B.X. Sweet Sorghum Establishment after Application of Residual Herbicides. *Int. J. Adv. Eng. Res. Sci.* **2018**, *5*, 296–304. [CrossRef]
18. Dan, H.A.; Dan, L.G.M.; Barroso, A.L.L.; Procópio, S.O.; Oliveira, R.S., Jr.; Silva, A.G. Residual activity of herbicides used in soybean agriculture on grain sorghum crop succession. *Planta Daninha* **2010**, *28*, 1087–1095. [CrossRef]
19. Alves, C.; Galon, L.; Kaizer, R.R.; Holz, C.M.; Winter, F.L.; Basso, F.J.M.; Forte, C.T. Selection of Species with Soil Phytoremediation Potential After the Application of Protox-Inhibiting Herbicides. *Planta Daninha* **2018**, *36*, e018174765. [CrossRef]
20. Kuratle, H., III. *The Mode of Action and Basis for Selectivity of Linuron Herbicide*; University of Delaware: Newark, DE, USA, 1968.
21. Geetha, A. Phytotoxicity due to fungicides and herbicides and its impact in crop physiological factors. In *Advances in Agriculture Sciences*; AkiNik Publications: New Delhi, India, 2019; Volume 16, pp. 29–66.
22. El-Nahhal, Y.; Abadsa, M.; Affifi, S. Leaching potential of diuron and linuron in Gaza soils. *Am. J. Plant Sci.* **2014**, *5*, 4040. [CrossRef]
23. Hoskins, W.M. Mathematical treatment of the rate of loss of pesticide residues. *FAO Plant Prot. Bull.* **1961**, *9*, 214–215.
24. Fantke, P.; Juraske, R. Variability of pesticide dissipation half-lives in plants. *Environ. Sci. Technol.* **2013**, *47*, 3548–3562. [CrossRef]
25. Lewis, K.; Tzilivakis, J. Development of a data set of pesticide dissipation rates in/on various plant matrices for the pesticide properties database (PPDB). *Data* **2017**, *23*, 28. [CrossRef]
26. Seefeldt, S.S.; Jensen, J.E.; Fuerst, P. Loglogistic analysis of herbicide dose response relationships. *Weed Technol.* **1995**, *9*, 218–227. [CrossRef]
27. Araújo, A.C.; José, A.R.S.; Soares, M.R.S.; Moreira, E.D.S. Eficiência e toxicidade do oxyfluorfen em água de irrigação na implantação a campo do gênero Eucalyptus. *Ciênc. Florest.* **2021**, *31*, 634–657. [CrossRef]
28. Hao, G.F.; Zuo, Y.; Yang, S.G.; Yang, G.F. Protoporphyrinogen oxidase inhibitor: An ideal target for herbicide discovery. *Chimia* **2011**, *65*, 961–969. [CrossRef]
29. Inoue, M.H.; Mendes, K.F.; Santana, C.T.C.; Possamai, A.C.S. Atividade residual de herbicidas pré-emergentes aplicados em solos contrastantes. *Rev. Brasil. Herbic.* **2011**, *10*, 232–242. [CrossRef]
30. Chakraborty, S.K.; Bhattacharyya, A.; Chowdhury, A. Degradation of oxyfluorfen by Azotobacter chroococcum. *Bull. Environ. Contam. Toxicol.* **2002**, *69*, 203–209. [CrossRef]
31. Mohamed, A.T.; El-hussein, A.A.; El-siddig, M.A.; Osman, A.G. Degradation of oxyfluorfen herbicide by soil microorganisms biodegradation of herbicides. *Biotechnology* **2011**, *10*, 274–279. [CrossRef]
32. Xia, Q.; Rufty, T.; Shi, W. Soil microbial diversity and composition: Links to soil texture and associated properties. *Soil Biol. Biochem.* **2020**, *149*, 107953. [CrossRef]
33. Mendes, K.F.; Silva, A.A. *Plantas Daninhas: Herbicidas*, 1st ed.; Oficina de Textos: São Paulo, Brasil, 2022; p. 200.
34. Dorado, J.; Almendros, G. Organo-mineral interactions involved in herbicide sorption on soil amended with peats of different maturity degree. *Agronomy* **2021**, *11*, 869. [CrossRef]
35. Prado, A.B.C.A.; Obara, F.E.B.; Brunharo, C.A.G.; Melo, M.S.C.; Christoffoleti, P.J.; Alves, M.C. Dinâmica de herbicidas aplicados em pré-emergência sobre palha de cana-de-açúcar em diferentes regimes hídricos. *Rev. Brasil. Herbic.* **2013**, *12*, 179–187. [CrossRef]
36. Ebeling, A.G.; Anjos, L.H.C.D.; Pereira, M.G.; Pinheiro, É.F.M.; Valladares, G.S. Substâncias húmicas e relação com atributos edáficos. *Bragantia* **2011**, *70*, 157–165. [CrossRef]
37. Mitchell, P.J.; Simpson, M.J. High Affinity sorption domains in soil are blocked by polar soil organic matter components. *Environ. Sci. Technol.* **2013**, *47*, 412–419. [CrossRef] [PubMed]
38. Dorado, J.; López-fando, C.; Zancada, M.C.; Almendros, G. Sorption−desorption of alachlor and linuron in a semiarid soil as influenced by organic matter properties after 16 years of periodic inputs. *J. Agric. Food Chem.* **2005**, *53*, 5359–5365. [CrossRef]
39. Cycoń, M.; Piotrowska-seget, Z.; Kozdrój, J. Linuron effects on microbiological characteristics of sandy soils as determined in a pot study. *Ann. Microbiol.* **2010**, *60*, 439–449. [CrossRef]
40. Breugelmans, P. Characterization of novel linuron-mineralizing bacterial consortia enriched from long-term linuron-treated agricultural soils. *FEMS Microbiol. Ecol.* **2007**, *62*, 374–385. [CrossRef]

41. Medo, J.; Maková, J.; Medová, J.; Lipková, N.; Cinkocki, R.; Omelka, R.; Javoreková, S. Changes in soil microbial community and activity caused by application of dimethachlor and linuron. *Sci. Rep.* **2021**, *11*, e12786. [CrossRef]
42. Guzzella, L.; Capri, E.; Corcia, A.; Giuliano, G. Fate of diuron and linuron in a field lysimeter experiment. *J. Environ. Qual.* **2006**, *35*, 312–323. [CrossRef]