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Cover Crop Straw Interferes in the Retention and Availability of Diclosulam and Diuron in the Environment

Gustavo Vinícios Munhoz-Garcia *, Vanessa Takeshita , Rodrigo Floriano Pimpinato, Nicoli Gomes de Moraes , Daniel Nalin and Valdemar Luiz Tornisielo

Center of Nuclear Energy in Agriculture, University of São Paulo, Av. Centenário, 303, Piracicaba 13400-970, Brazil; vanessatakeshita@usp.br (V.T.); ropimpinato@cena.usp.br (R.F.P.); nicoligm@usp.br (N.G.d.M.); danielnalin@usp.br (D.N.); vltornis@cena.usp.br (V.L.T.)
* Correspondence: gvmgarcia@usp.br

Abstract: Pre-emergent herbicides are applied directly in the soil or over the straw in no-till systems and can be retained, reducing the product's availability. The current study characterizes the retention of diclosulam and diuron in forage turnip (FT), buckwheat (BW), and black oat (BO) straws. Radiometric techniques evaluated the sorption–desorption and leaching processes. Spectroscopic and microscopic methods characterized chemical and morphological alterations in the straw. Sorption rates (Kf) of diclosulam and diuron followed the order BO > BW > FT. Irreversible sorption (hysteresis < 0.7) occurs to diclosulam applied to BO straw. The BO straw showed porous structures, indicating physical entrapment of the herbicides. Straw fragments (<1 mm) increased the sorption of herbicides. The increase in straw amount (2.5 to 5 t ha^{-1}) reduced herbicide leaching to 18.8%. Interactions between chemical groups (C-Cl, C-F, and C-N) from herbicides with straw characterize a chemical barrier. The present research suggests that entrapment and chemical interaction are involved in the sorption–desorption process of herbicides, such as diclosulam and diuron, in the straw matrix, directly interfering with their availability in the environment. This process can reduce the herbicide environmental risk but can decrease weed control efficiency.

Keywords: sorption–desorption; no-till system; leaching; herbicide behavior; chemical interaction; environmental risk

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1. Introduction

Herbicides are essential for the maintenance of agroecosystem productivity because weeds can cause losses of between 30–94% if not controlled [1–4]. No-tillage systems (NTS) allow the application of integrated control methods, such as crop rotation, and the use of cover crops along with herbicide application, increasing efficiency in weed control [5,6]. The countries with the largest area cultivated in NTS are the USA and Brazil, with approximately 42 and 33 million hectares (ha), respectively, followed by Canada, with 19 million, and Australia, with 14 million ha [7]. In this system, the straw is maintained on the soil surface, which contributes to the control of the seed bank, but does not completely dispense with the use of herbicides [8,9]. Pre-emergent herbicides, such as diclosulam and diuron, are applied to the soil and have been used in weed management in crops, such as soybean, cotton, and sugarcane grown in NTS.

Diclosulam is a weak acid herbicide (pKa = 4.0 at 25 °C) that acts in the inhibition of the acetolactate synthase enzyme (ALS), belonging to the chemical group of triazolopyrimidine sulfonanilides, recorded for soybean and sugarcane crops [10]. It has low water solubility (Sw = 6.32 mg L^{-1} at 20 °C) and low affinity for lipophilic compounds (log Kow = 0.85 at pH 7) [11,12]. Diuron is a non-ionic herbicide and an inhibitor of photosystem II, of the chemical group of urea, registered for crops, such as sugarcane, cotton, and coffee [10]. It has low water solubility (Sw 35.6 mg L^{-1} at 25 °C) and a higher affinity for lipophilic compounds (log Kow 2.87) [11,12].

After application, herbicides, such as diclosulam and diuron, are subject to degradation, transport, and retention processes [13]. Sorption–desorption and leaching are processes that regulate the concentration of herbicides in the soil solution. Organic materials, such as straw and crop remains, present in NTS can act as a barrier between the herbicide and soil [14], reducing the amount of herbicide available for plant absorption, degradation, and leaching through the soil profile. From the agronomic point of view, when intercepted by different types and amounts of straw, lower herbicide concentrations are available in the soil solution, impairing weed control [15–17]. On the other hand, the reduction in the concentration of the active ingredient (a.i.) in the soil profile reduces the potential for environmental contamination [18,19].

Sorption–desorption and leaching processes are influenced by physical and chemical factors involved in the interaction between pesticides and organic materials [20–22]. Plants, such as forage turnip, buckwheat, and black oat, are used as cover crops in tropical systems, producing a straw layer on to soil, which can retain pre-emergent herbicides. At the first contact, straw acts as a physical barrier, and rainwater or irrigation is required to carry the herbicide into the soil [23]. Factors, such as the physical–chemical characteristics of the herbicide, herbicide–straw contact time, amount of rain, type and amount of straw, degree of decomposition of organic matter, and composition, hydrophobicity, and aromaticity of the material are also involved in the mechanisms of retention of herbicides and pollutants in organic materials [16,21,22,24–30]. As herbicide retention in organic materials occurs through complex mechanisms [31] and the retention in straw is still undefined, it is necessary to characterize them to elucidate the availability of these products in the environment after application [32].

The aim of this research was to investigate the retention mechanisms of pre-emergent herbicides in different types of straw under controlled conditions. In addition, the chemical interactions of the herbicides with the straw were studied, as well as the effect of this material as a physical barrier. Our hypotheses are based on differences in herbicide sorption–desorption as a function of the type of straw, and that there is an effect of the type and amount of straw on the leaching process. These hypotheses were tested by sorption–desorption and leaching studies of diclosulam and diuron in forage turnip (*Raphanus sativus*—FT), buckwheat (*Fagopyrum esculentum*—BW), and black oat (*Avena strigosa*—BO) straw, using radiometric, microscopic, and spectroscopic techniques.

2. Materials and Methods

2.1. Cultivation of Cover Crops and Straw Preparation

The cover crops (FT, BW, and BO) were grown in pots in a plant growing chamber until they reached flowering (Figure S1). The soil used was classified as Ultisoil (PVAd—Argissolo Vermelho-Amarelo Distrófico) and the results of the chemical and physical analyses are shown in Table S1 (Supplementary Materials). The plants were cut close to the soil, harvested, dried in an air circulation greenhouse for 72 h to 45 ± 2 °C, and stored in craft paper bags until the herbicide and sorption–desorption tests were carried out. Straw composition analyses were performed.

The straws were crushed and pressed in sieves with a mesh of 1 and 2 mm to homogenize the material. The size of the straw fractions was between 1 and 2 mm [33–36].

2.2. Test Substances

The work solutions were composed of ^{14}C-diclosulam herbicides with the specific activity of 2.55 MBq mg^{-1} and ^{14}C-diuron with the specific activity of 5.74×10^3 MBq mg^{-1}, both with radiochemical purity above 95%, as recommended by [37] OECD (2000). Technical herbicides (diclosulam and diuron) were also used to adjust the dose to the equivalent to the recommended field-level dose (purity > 95%). The radioactivity used in the sorption–desorption experiments was about 0.83–1.6 kBq per experimental unit, while in the leaching studies it was about 0.66–2.0 kBq per experimental unit.

2.3. Sorption–Desorption Studies

The study was adapted from the guidelines established for soil sorption–desorption studies by OECD 106, "Adsorption and desorption using the batch equilibrium" [37]. In the current study, the adsorbent/solution ratio used was 1:50 (*m*/*v*), determined according to the OECD guidelines [37]. The equilibrium time was also determined in preliminary tests, and both herbicides reached equilibrium in 24 h (Table S2).

For the determination of sorption–desorption isotherms, the experimental design was entirely randomized, with two replications for each treatment, in a 3 × 5 factorial scheme, containing 3 types of straw (FT, BW, and BO) in the amount equivalent to 2.5 t ha^{-1}, and 5 doses of herbicides (D, ¼ D, ½ D, 2D, 4D). Independent experiments were carried out for each herbicide (diclosulam and diuron). The doses used for diclosulam (35 g a.i. ha^{-1}) and diuron (2250 g a.i. ha^{-1}) were equivalent to those recommended at field level for crops, such as soybean and sugarcane, calculated based on the straw mass used. Each experimental unit consisted of a Teflon tube (50 mL) plus 0.19 g of straw (equivalent to 2.5 t ha^{-1}). The tubes were weighed, and then, in sequence, 10 mL of $CaCl_2$ solution (0.01 mol L^{-1}) were added in the proportion 1:50 (straw/solution, *m*/*v*). The study also included control treatments without the addition of straw, only with ^{14}C-herbicide and $CaCl_2$ solution, to determine the stability of the active ingredient during the experiment. The tubes were shaken for 24 h using a horizontal shaker (TE 140, Technal, Piracicaba, SP, Brazil) at 180 rpm under controlled environmental conditions (25 ± 2 °C). Subsequently, the tubes were centrifuged (Hitachi CF16RXII, Hitachi Koki Co., Ltd., Indaiatuba, SP, Brazil) at 4500 rpm for 15 min at 10 °C. Two aliquots of 500 μL of the supernatant (of each experimental unit) were added in vials with scintillator solution (Insta-gel Plus PerkinElmer, Waltham, MA, USA) for quantification of radioactivity in a liquid scintillation spectrometer (LSS) (Tri-Carb 2910 TR LSA counter, PerkinElmer) for 5 min. The pH of the solution was measured after the sorption process and was close to 6.5 for all treatments. The percentage of ^{14}C-herbicide sorbed was calculated by the difference between the amount of initial product and the quantity of the product present in the supernatant.

The desorption study was carried out after the sorption study, under the same conditions, using the same experimental unit. After the collection of sorption aliquots, the supernatant was discarded, and the tubes were weighed again. A new solution of $CaCl_2$ 0.01 mol L^{-1} was added to the vials. The procedure occurred in the same way as in sorption. The percentage of the desorbed product was calculated considering the amount of product sorbed in the straw and the quantity of the product present in the supernatant.

Another sorption assay was carried out to evaluate the influence of the size of the straw fragment on the process of diclosulam and diuron sorption. A completely randomized design was used, in a 3 × 3 factorial scheme with two replications, for each herbicide separately, at doses equivalent to those recommended at field level (diclosulam 35 g a.i. ha^{-1} and diuron 2250 g a.i. ha^{-1}). Three sizes of straw fragments (<1 mm, between 1 and 2 mm, and >2 mm) separated by sieves, and three types of straw (FT, BW, and BO), were tested. The experiments were conducted in the same way as in the study for the determination of sorption isotherms.

For the calculation and expression of the results, the sorption and desorption models described below were used. The sorption distribution coefficient (Kd, mL g^{-1}) was calculated according to the following Equation (1) [38]:

$$\mathrm{Kd} = \mathrm{Cs}/\mathrm{Ce} \tag{1}$$

where Cs is the herbicide concentration (μg g^{-1}) sorbed in straw after equilibrium and Ce is the herbicide concentration (μg mL^{-1}) in the solution after equilibrium.

The sorption distribution coefficient normalized to organic carbon (Koc, mL g^{-1}) was calculated using the following Equation (2) [39]:

$$\mathrm{Koc} = (\mathrm{Kd}/\mathrm{OC}) \times 100 \tag{2}$$

where Kd is the sorption distribution coefficient (mL g^{-1}) and OC is the organic carbon content in straw (%).

The sorption and desorption coefficients, Kf and 1/n, were calculated according to Equation (3) using the Freundlich model [40], as follows:

$$\mathrm{Cs} = \mathrm{Kf} \times \mathrm{Ce}^{1/\mathrm{n}} \tag{3}$$

were Cs is the herbicide concentration (μg g^{-1}) in straw after equilibrium, Kf is the Freundlich equilibrium constant ($\mu g^{(1-1/n)}$ $mL^{1/n}$ g^{-1}, which corresponds to mL g^{-1}), Ce is the herbicide concentration (μg mL^{-1}) in solution after equilibrium, and 1/n is the degree of linearity of the isotherm.

The hysteresis coefficient (H) for the desorption isotherms was calculated by considering the following Equation (4) [41,42]:

$$\mathrm{H} = 1/\mathrm{n}\ \mathrm{desorption}/1/\mathrm{n}\ \mathrm{sorption} \tag{4}$$

2.4. Chemical and Structural Characterization of Straw

For characterization of the straw before and after sorption of the herbicides, sorption–desorption studies were performed in the same way as described above; however, only non-radiolabeled molecules were used. Characterization of the functional groups of the straw was performed by Fourier transform infrared spectroscopy (FTIR) (Bruker, Vertex 70, Billerica, MA, USA) using attenuated total reflectance (ATR), in 4 cm^{-1} of resolution, with 64 scans in the wavelength range 4000–400 cm^{-1}.

The structural aspects of the straw were characterized by scanning electron microscopy (SEM). The straw samples were mounted on aluminum plates on double-sided carbon strips and coated with a gold layer (Balzers-SCD050, Wetzlar, Germany), before being analyzed using a scanning electron microscope (Jeol JSM IT300-LV, Tokyo, Japan) operated at 20 kV with printed scales.

2.5. Leaching Study

The study was inspired by the methodology proposed by OECD 312—"Leaching in Soil Columns" [43]. An entirely randomized design was used in a 3 × 2 factorial scheme with two repetitions. Three types of straw (FT, BW, and BO) were used in two quantities (equivalent to 2.5 and 5.0 t ha^{-1}) under six consecutive rainfall simulations of $CaCl_2$ (0.01 mol L^{-1}) solution equivalent to 10 mm were applied with manual spray-type applicators. Independent experiments were conducted for each herbicide. The herbicides were used at the recommended field doses (diclosulam 35 g a.i. ha^{-1}; diuron 2250 g a.i. ha^{-1}).

Each experimental unit consisted of a plastic sieve (5 cm diameter) used as a support for the straw (Figure S2). The straws were contaminated with the working solution (technical herbicide + ^{14}C-herbicide) 24 h before rainfall simulation. After contamination, the straws were air-dried at room temperature. Five 0.1 g samples of each straw were weighed, burned in a biological oxidizer (OX500, R.J. Harvey Instrument Corporation, Tappan, NY, USA) and analyzed by LSS for 5 min to quantify the radioactivity applied in each treatment.

The straws were packed in the sieves in quantities equivalent to 2.5 and 5 t ha^{-1} calculated based on the sieve area (1.9×10^{-3} m^2). Six consecutive showers of $CaCl_2$ (0.01 mol L^{-1}) solution equivalent to 10 mm were applied with manual spray-type applicators. The leached liquid was collected separately after each rainfall. For quantification of leached herbicide, 3 aliquots of 5 mL of the leached solution were pipetted into vials containing 10 mL of scintillator solution and analyzed by LSS for 5 min. After rainfall application, the straws were air-dried (room temperature) for 72 h. Five 0.1 g samples were weighed and burned in a biological oxidizer (OX500, R.J. Harvey Instrument Corporation, Tappan, NY, USA), and were read by LSS for 5 min to quantify the remaining radioactivity in the straw. The percentage of herbicide leached was calculated from the initial radioactivity applied.

For the calculation and expression of the herbicide leached in function of rainfall amount, the Mitscherlich nonlinear regression model described in the following Equation (5) was used [44]:

$$Y = A(1 - 10)^{-c(x+b)} \quad (5)$$

where Y is the amount of herbicide leached (%); A is the maximum asymptote of the curve ($0 \leq A \leq 100$), corresponding to the maximum amount of herbicide leached (%); b is the lateral displacement of the curve; c is the concavity of the curve; x is the rainfall amount (mm).

The water holding capacity of the straw was measured by the difference between the mass of $CaCl_2$ solution applied and the mass recovered in each repetition. The results are expressed as the mean retention (mL g^{-1}) as a function of the straw type and amount ($n = 4$). The mass balance (Table S3) included the initially applied radioactivity, measured by burning the samples before the experiment, the leached radioactivity, and the radioactivity remaining in the straw.

2.6. Statistical Analysis

The percentage of sorption, desorption, and leaching data were submitted to analysis of variance (ANOVA). When necessary, the data were transformed to meet the variance analysis assumptions (normality and homoscedasticity). When significant, the means were compared using Tukey's test with Sidak adjustment ($p < 0.05$). The software Origin® 2020 (Version 9.7.0.185 to Windows, OriginLab Corporation, Northampton, MA, USA) was used for data representation, construction of sorption–desorption isotherms, and regression analysis in the leaching models.

3. Results

3.1. Sorption Process of Herbicides in Straw

The sorption of diclosulam and diuron (Figure 1) was influenced by the type of straw ($p < 0.05$). BW and BO straws showed the highest sorption of diclosulam herbicide (27.61 ± 0.73–27.86 ± 0.42%), while FT sorbed only 22.41 ± 1.69% of the herbicide. The sorption of diuron in BO straw was 45.45 ± 0.7%, in BW it was 39.36 ± 1.36%, and in FT it was 32.90 ± 0.55%. The sorption coefficient normalized to organic carbon (OC) content (Koc sorption) of diclosulam in FT straw was 37.83 ± 3.69 mL g^{-1}, increasing in BW and BO straws to 46.16 ± 0.23 mL g^{-1} and 49.94 ± 0.17 mL g^{-1}, respectively (Table 1). For diuron, Koc sorption was highest in BO straw (111.63 ± 0.5 mL g^{-1}), followed by BW (90.48 ± 3.13 mL g^{-1}) and FT (81.63 ± 1.64 mL g^{-1}) (Table 1).

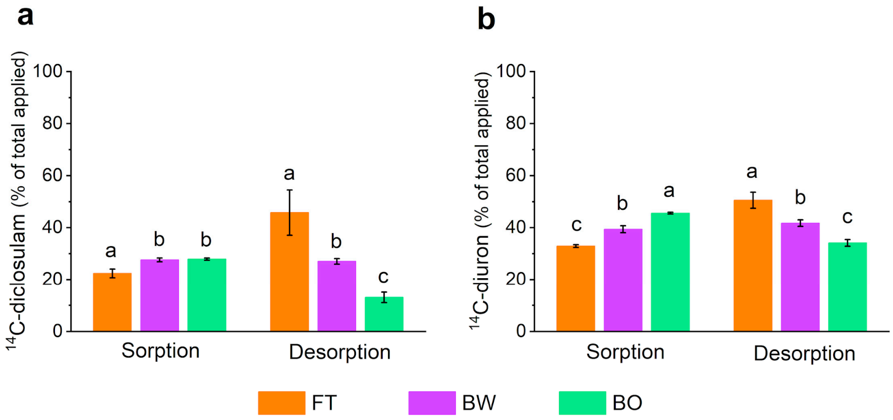

Figure 1. Percentage of sorption and desorption of diclosulam (**a**) and diuron (**b**) in different straw types. The bars represent the standard error of the mean ($n = 2$). Equal lowercase letters in sorption and desorption processes do not differ between the straw type (on the same herbicide) by Tukey's test ($p < 0.05$). FT—forage turnip, BW—buckwheat, and BO—black oat.

Table 1. Parameters of sorption–desorption isotherms of ^{14}C-diclosulam and ^{14}C-diuron based on the Freundlich model. Data indicates parameter value ± standard error of the mean (n = 2). * Lowercase letters indicate differences between the straws within each herbicide, using Tukey's test ($p < 0.05$). Kd—sorption distribution coefficient. Koc—sorption distribution coefficient normalized to organic carbon. Kf—Freundlich equilibrium constant. 1/n—degree of linearity of the isotherm. R^2 adj—adjusted determination coefficient. H—hysteresis. FT—forage turnip, BW—buckwheat, and BO—black oat.

Parameters		**^{14}C-Diclosulam**			**^{14}C-Diuron**		
		FT	**BW**	**BO**	**FT**	**BW**	**BO**
Sorption	Sorption (%) [a]	22.41 ± 1.69 b *	27.61 ± 0.73 a	27.86 ± 0.42 a	32.90 ± 0.55 c	39.36 ± 1.36 b	45.45 ± 0.70 a
	K_d (mL g^{-1}) [c]	15.24 ± 1.45	20.08 ± 0.74	20.33 ± 0.43	25.81 ± 0.64	34.21 ± 1.76	43.86 ± 1.25
	K_{OC} (mL g^{-1})	37.83 ± 3.69	46.16 ± 0.23	49.94 ± 0.17	81.63 ± 1.64	90.48 ± 3.13	111.63 ± 0.50
	K_f (mL g^{-1})	16.06 ± 1.23	21.79 ± 0.98	22.44 ± 2.41	26.27 ± 3.02	44.20 ± 2.44	44.27 ± 3.47
	1/n	1.047 ± 0.04	1.039 ± 0.02	1.073 ± 0.06	0.98 ± 0.04	0.93 ± 0.02	0.97 ± 0.04
	R^2 (adj)	0.987	0.995	0.981	0.989	0.993	0.992
Desorption	Desorption (%) [b]	45.79 ± 8.69 a *	27.05 ± 1.08 b	13.06 ± 2.03 c	50.56 ± 3.09 a	41.75 ± 1.26 b	34.16 ± 1.27 c
	K_d (mL g^{-1}) [c]	54.75 ± 14.41	93.76 ± 5.94	262.41 ± 15.39	37.9 ± 3.86	48.5 ± 1.39	76.4 ± 5.59
	K_{OC} (mL g^{-1})	135.87 ± 43.09	215.54 ± 6.82	654.59 ± 37.83	94.24 ± 11.65	111.57 ± 0.35	187.68 ± 14.25
	K_f (mL g^{-1})	51.24 ± 11.92	93.55 ± 16.17	63.57 ± 19.78	43.3 ± 5.68	53.2 ± 1.31	75.9 ± 6.32
	1/n	0.97 ± 0.08	1.02 ± 0.06	0.74 ± 0.10	0.98 ± 0.05	0.97 ± 0.01	0.97 ± 0.06
	R^2 (adj)	0.929	0.968	0.855	0.982	0.998	0.968
	H	0.926	0.982	0.689	0.986	1.04	0.999

[a] Percentage in relation to the total applied. [b] Percentage in relation to the total sorbed in straw. [c] Field-recommended dose.

The Kf sorption values obtained from the sorption isotherms indicate the strength of herbicides' sorption on the straw (Table 1, Figure S3). The Kf sorption values for diclosulam were higher for BW and BO (21.79 ± 0.98 and 22.44 ± 2.4 mL g^{-1}, respectively) than FT (16.06 ± 1.23 mL g^{-1}). For diuron, Kf values were 26.27 ± 3.02, 44.20 ± 2.44, and 44.27 ± 3.47 mL g^{-1} for FT, BW, and BO, respectively. The 1/n values were close to 1 (0.93–1.073) for both herbicides in straws, indicating curve type C [45] (Table 1).

3.2. Herbicide Desorption from Straw

The desorption process of diuron and diclosulam herbicides was influenced by the type of straw ($p < 0.05$). Lower amounts of diclosulam returned to the solution when they were sorbed into BO (13.06 ± 2.03%) straw, followed by BW (27.5 ± 1.08%) and FT (45.8 ± 8.69%) (Table 1). For diuron, black oat straw was also responsible for the lowest desorption (34.16 ± 1.27%), followed by buckwheat (41.75 ± 1.26%) and forage turnip (50.56 ± 3.09%) (Table 1). The Kd desorption for both herbicides had the following increasing order: BO > BW > FT (Table 1). For diclosulam, Kd desorption was 3.5-fold higher in BO straw (262.41 mL g^{-1}) compared to diuron (76.4 ± 5.59) (Table 1). The highest Koc value for diclosulam was BO straw (654.59 ± 37.83), followed by BW and FT (215.54 ± 6.82 and 135.87 ± 43.09 mL g^{-1}, respectively). This same tendency was found in Kd desorption for diuron (Table 1).

The Kf desorption value for diclosulam was higher for BW (93.55 ± 16.17 mL g^{-1}) followed by BO and FT (63.57 ± 19.78 and 51.24 ± 11.92 mL g^{-1}, respectively). On the other hand, for diuron, the highest Kf value was BO (75.9 ± 6.32 mL g^{-1}), followed by BW (53.2 ±1.31 mL g^{-1}) and FT (43.3 ± 5.68 mL g^{-1}). The behavior of diclosulam in BO straw is represented by an L-type (1/n < 1) curve [45], whereas the desorption isotherms for diclosulam in FT and BW straws as well as diuron in FT, BW, and BO straws are classified as type C curves (1/n between 0.97 and 1.02, close to 1) (Table 1 and Figure S3). The calculation of hysteresis (H) enables inferences about the reversibility of the sorption process. For diclosulam in BO, FT, and BW straws, H values were 0.68, 0.92, and 0.98, respectively; for diuron, H values ranged from 0.98 to 1.04 among the straws (Table 1).

3.3. Characterization and Structural Changes of Straw in the Sorption Process

Scanning electron microscope images shows alterations in the structure of straw due to the sorption (Figure 2). The structures of the FT and BW straws (Figure 2d,e) were degraded by reduced or deformed roughness after the sorption process, compared to the structures before sorption (Figure 2a,c). The roughness presented by BW was uncharacterized from the sample that was not submitted to the sorption experiment (Figure 2e). No structural differences were observed in the straws between the herbicides used. The structures of the BO straw were not altered with the sorption process (Figure 2f). The BO straw can be characterized as a structure that is rich in spaces available for water trapping through the cracks and pores observed in this straw (Figure 3), enhancing herbicide sorption by physical entrapment [46].

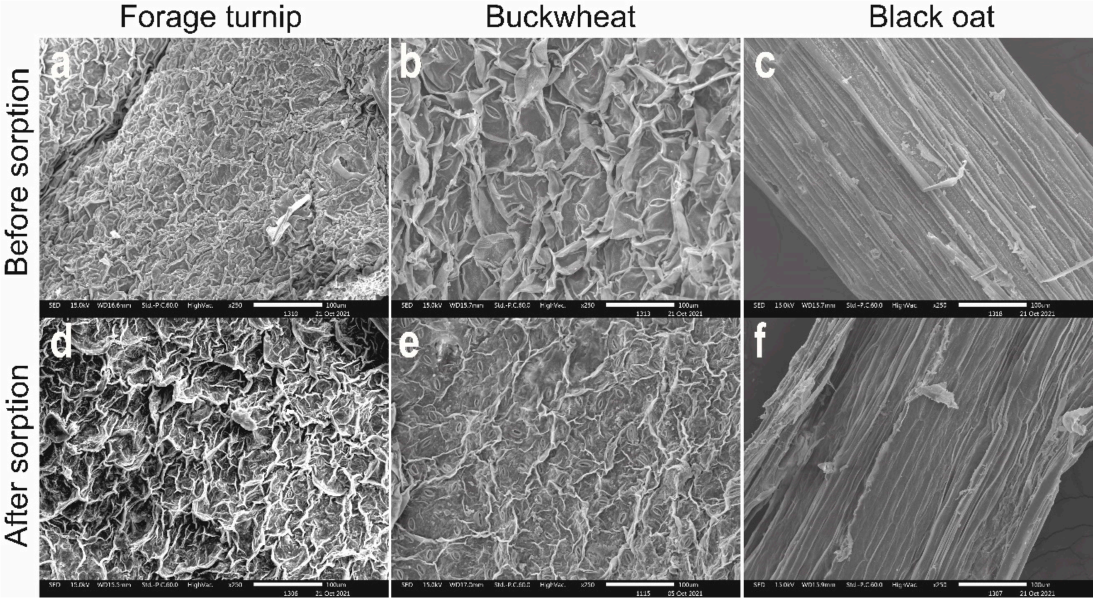

Figure 2. Scanning electron microscopy of the straws before ((**a**)—forage turnip, (**b**)—buckwheat, and (**c**)—black oat)) and after the sorption process ((**d**)—forage turnip, (**e**)—buckwheat and (**f**)—black oat)).

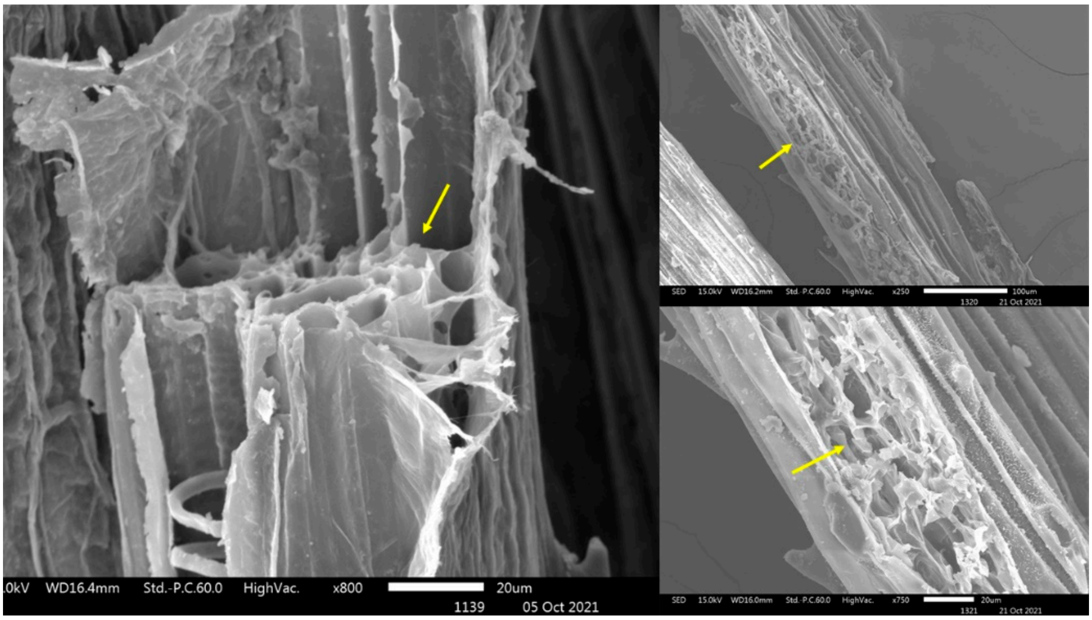

Figure 3. Porosity of the black oat straw by scanning electron microscopy. The arrows indicate the porous structures in the straw that can act on herbicide retention.

3.4. Chemical Interactions between Straw and Herbicide

Chemical interactions of diclosulam with straw were observed in the BW spectra by the appearance of a region with lower transmittance around 1564 to 1515 cm^{-1} and the increase in the peak around 1320 cm^{-1} (Figure 4), resulting from the binding between hydrocarbons and aromatic amines of diclosulam with the straw surface [47]. In BO, the appearance of new absorption bands (1159 cm^{-1} and 800 cm^{-1}) concerning the binding of aliphatic amines (C-N stretching) and haloalkane bonds, such as C-Cl or C-F, respectively, occurred [48]. After sorption with diuron, the spectrum of FT straw pointed only to structural changes by alkene bending (peak at 962 cm^{-1}) and surface changes by the shift in the peak around 1629 to 1608 cm^{-1}. The BW spectrum after sorption with diuron showed the appearance of a peak around 719 cm^{-1}, resulting from the stretching of C bonds of the straw with the Cl present in the herbicide [48]. In BO straw, the low-intensity band around 1053 cm^{-1} indicated the characteristic stretching of C-N groups of diuron with the straw.

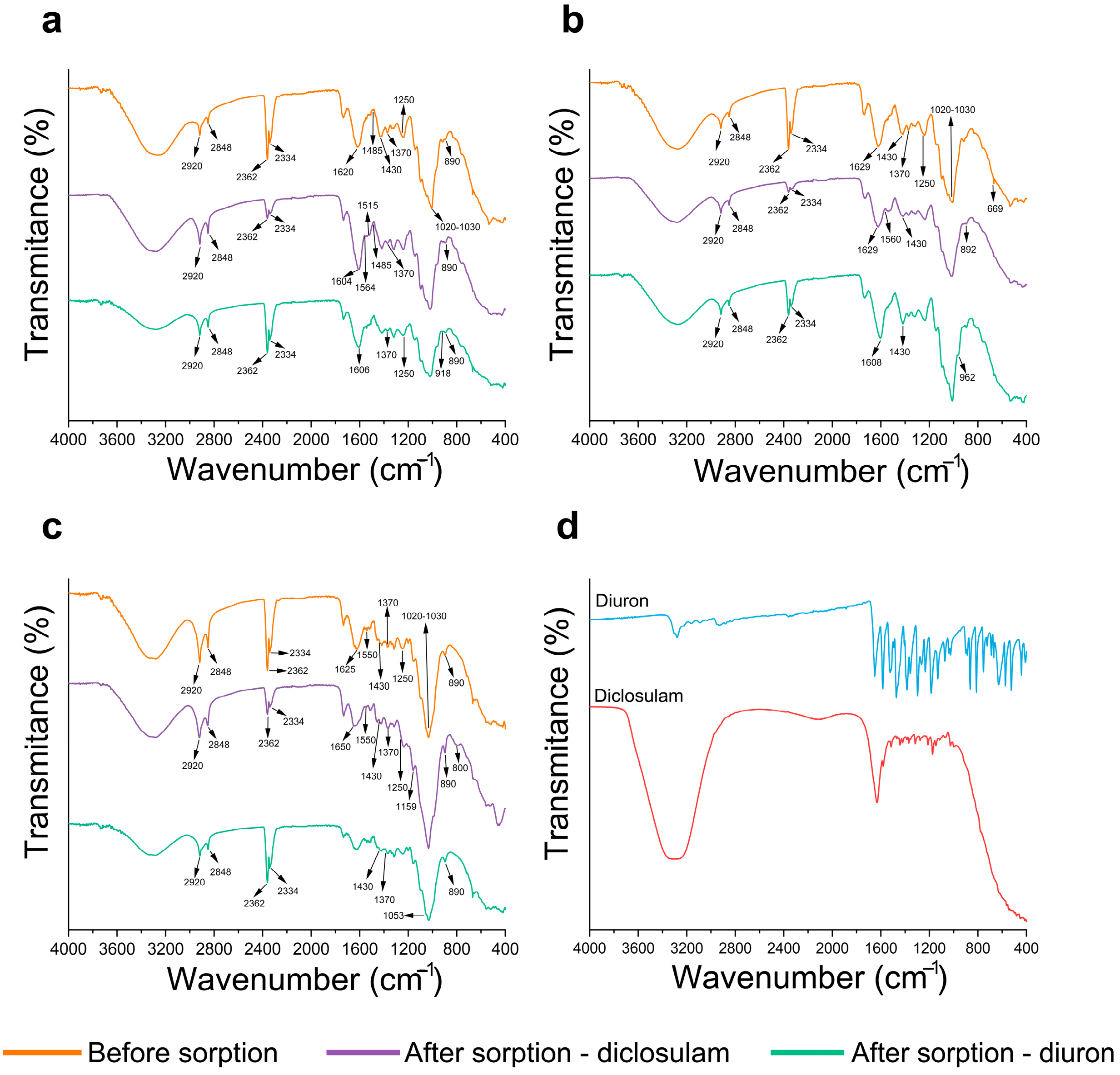

Figure 4. FTIR spectra of forage turnip (**a**), buckwheat (**b**), and black oat (**c**) straws before and after sorption with diuron and diclosulam. The graph in (**d**) represents the FTIR spectra of the technical products of diclosulam and diuron. The numbers represent the wavelength, and the arrows indicate the peak transmittance.

3.5. Straw Composition and Effect of Fragment Size on Diuron and Diclosulam Retention

The BW and BO straws have ethereal extract contents 1.3- and 2.3-fold higher than FT, respectively (Table S4). This fact points to an increasing relationship between the sorption of the herbicides studied with the ether extract of the straws (Table S4). In desorption, an opposite response was observed, where increasing straw ether extract (23.3–53.1 g kg^{-1} dry matter) reduced the desorption of diuron (50.56–34.16%) and diclosulam (45.8–16.06%) (Table S4).

Straw fragments smaller than 1 mm were responsible for the sorption of higher amounts of the herbicides ($p < 0.05$) (Table 2). For diclosulam, there was a trend of reduced sorption (38.82–21.28%) with increasing fragment size from <1 mm to >2 mm. This trend was not observed for diuron (Table 2).

Table 2. Sorption of diclosulam and diuron on FT, BW, and BO straws fragmented into portions < 1 mm, between 1 and 2 mm, and <2 mm. Data represent the mean ± standard error ($n = 2$). Different lowercase letters between columns represent a significant difference between fragment sizes within the same straw by Tukey's test ($p < 0.05$). FT–forage turnip, BW—buckwheat, and BO—black oat.

Herbicide	**Straw**	**Sorption (%)** [a]		
		<1 mm	**Between 1 and 2 mm**	**>2 mm**
^{14}C-diclosulam	FT	27.39 ± 1.35 a	22.41 ± 1.69 b	22.00 ± 0.19 b
	BW	38.82 ± 0.79 a	27.60 ± 0.73 b	21.28 ± 2.47 c
	BO	34.99 ± 0.59 a	27.86 ± 0.42 b	22.12 ± 0.05 c
^{14}C-diuron	FT	40.81 ± 0.11 a	32.89 ± 0.78 b	40.31 ± 0.63 a
	BW	47.65 ± 1.57 a	39.36 ± 1.75 b	42.09 ± 1.03 b
	BO	50.13 ± 1.04 a	45.44 ± 0.98 b	47.33 ± 0.75 ab

[a] Percentage in relation to the total applied.

3.6. Leaching of Diclosulam and Diuron in Different Straws

The nonlinear regression parameters (Mitscherlich model) that demonstrate the trend of herbicide leaching as a function of simulated rainfall [44] are presented in the Supplementary Materials (Table S5, Figure S4). The Mitscherlich model showed a significant ($p < 0.05$) fit to the data with adjusted R^2 in the range 0.92–0.99. Diclosulam applied on 2.5 t ha^{-1} of FT and BW straw tended to be 100% leached (Table S5). When applied on BO straw, only 81.10% of the herbicide was able to transpose the straw (Table S5). Diuron showed the greatest tendency to be leached in BO straw (93.09%), followed by FT (91.76%) and BW (76.89%) (Table S5). The interception of herbicide by the straw increased from around 8.7 to 23.5% with increasing amounts of straw from 2.5 t ha^{-1} to 5 t ha^{-1} (Table S5). These results are similar to those found by Clark et al. [16], who reported a 14% increase in the interception of the herbicides imazapic, indaziflam, and rimsulfuron (69.9 to 79.6%) with increasing amounts of *Bromus tectorum* straw (1.3 t ha^{-1} to 2.6 t ha^{-1}).

The leaching trend calculated by the Mitscherlich model allows for inferences about the leaching of the product as a function of the simulated rainfall but does not calculate the actual amount of product leached in each treatment after a given volume of rainfall. To circumvent this gap, in the current work we also analyzed the total amount of each herbicide leached after 60 mm of rainfall. The leaching of both herbicides was significantly influenced, without interaction between the factors straw type and amount ($p > 0.05$) (Figure 5). Approximately 69% of the herbicides diuron and diclosulam were leached when applied over 2.5 t ha^{-1} of straw and only 56% were transported from the 5 t ha^{-1} straw layer, a reduction of 18.8% in the amount of product that can be leached into the soil (Figure 5). Diclosulam leached less from the BW straw (59.52 ± 4.63%) while diuron was leached to a lesser extent when applied to the BO straw (55.46 ± 3.19%) (Figure 5).

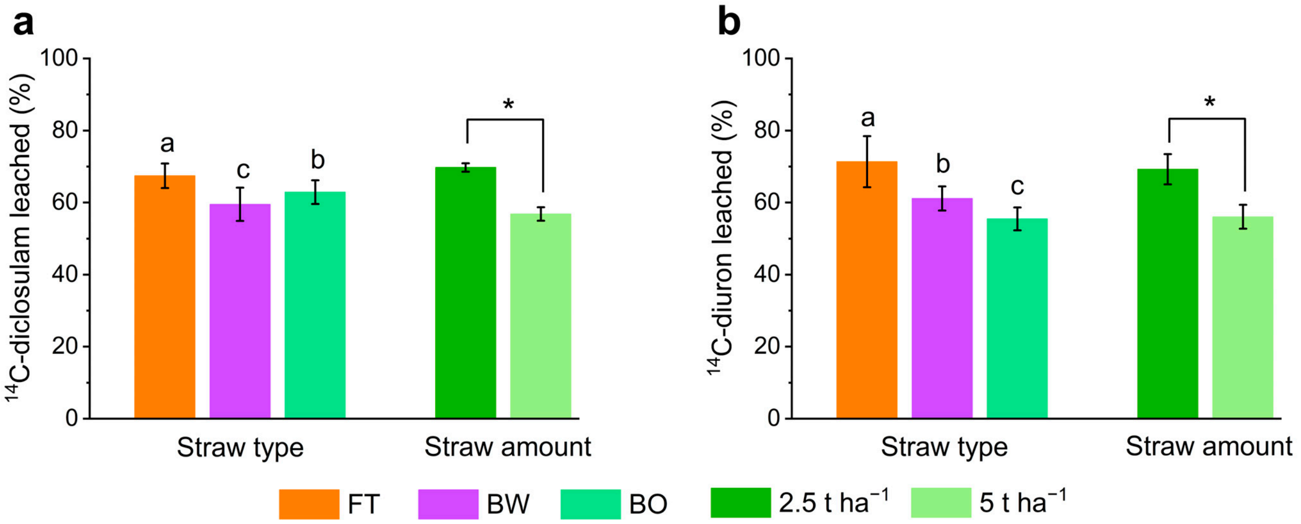

Figure 5. Amount of diclosulam (**a**) and diuron (**b**) leached as a function of straw types and amount after 60 mm rainfall. Bars represent the standard error of the mean (n = 4). Since the interaction between straw type and amount is not significant, lowercase letters differ between straws (regardless of amount) and asterisks (*) indicate differences between amounts (regardless of type) by Tukey's test ($p < 0.05$). FT—forage turnip, BW—buckwheat, and BO—black oat.

4. Discussion

Weak acidic herbicides, such as diclosulam (pKa 4.0), are molecules that are dissociated (pH soil > pKa herbicide) in agricultural soils (pH 6.0–7.0); thus, their retention capacity in soil colloids is low [49]. In our study, the pH of the solutions was close to 6.5, so this factor may have contributed to lower retention of the herbicide. Although diclosulam has a low affinity for organic matter (log Kow 0.85), the Kd sorption values obtained in this study (15.24 ± 1.45–20.33 ± 0.43 mL g^{-1}, Table 1) are higher than those reported by Yoder et al. [50] in different soil types (0.04–9.75 mL g^{-1}). In biochar-enriched soils, the Koc sorption values of diclosulam ranged from 37.93 to 86.20 mL g^{-1} for soils with 0% and 1% biochar, respectively, according to the organic matter increment in the system [51]. The explanation to elucidate the affinity of diclosulam for straw (even with low log Kow 0.89) is based on the theories presented by Smernik and Kookana [52] and Li et al. [29]. Li et al. [29] proposes that in materials with low mineral content, the sorption capacity of ionic compounds (such as diclosulam) is reduced because the sorption sites are more reactive with hydrophobic compounds. It should be noted that in our study the system adopted for the sorption–desorption experiments relies on the straw without the presence of the soil and its mineral fraction, assuming that diclosulam is more sorbed in materials with a greater affinity for mineral compounds.

Diuron is a non-ionic herbicide that shows high retention in soil and high affinity for organic matter via hydrophobic interactions [53], justifying the higher affinity for straw compared to diclosulam (Figure 1). In general, the sorption of diuron is greater in soils with higher organic matter content [54]. The partitioning of diuron at the soil/solution interface (Kd sorption) varies depending on the soil types in which the diuron is applied. In studies with 43 soil types, Liyanage et al. [55] observed an increase in Kd sorption (0.5–75.0 mL g^{-1}) as a function of increasing OC (0.2–8.3%). Almeida et al. [56] also found an increase in Kd sorption from 0.5 to 28.34 mL g^{-1} in soils with 0.33 and 4.71% OC, respectively. The Koc sorption values (Table 1) of diuron in the FT (81.63 ± 1.64 mL g^{-1}), BW (90.4 ± 3.13 mL g^{-1}), and BO (111.63 0.50 mL g^{-1}) straws indicate the retention of diuron in organic matter. This retention may be associated with the nature of the OM in the system and not just the quantity [22,57].

In general, for both diclosulam and diuron, the Kf sorption values increased with increasing sorption percentage and Koc sorption. The Kf sorption values obtained in this research (Table 1) are not considered as the maximum capacity of the sorption of the herbicide in the straw, but as the sorption strength existing in the straw–herbicide interaction due to the principles adopted in the Freundlich equation for heterogeneous systems, which do not consider the saturation of the adsorbent material [58]. The values of 1/n indicate the linearity of the curve and explain the sorption behavior of the herbicide on the straw [45]. Values of 1/n close to 1.0 represent type C curves, such as those obtained in the sorption of diclosulam and diuron in all the straws (0.93–1.073) (Table 1). These values represent a linear behavior and indicate that as the concentration of the herbicide increases, sorption also increases; that is, there are constantly available sorption sites until their saturation is reached [45]. In the same way, the desorption isotherms of diuron in FT, BW, and BO straws (1/n between 0.97 and 0.98) are classified as type C curves, as well as for diclosulam in FT and BW straws (1/n between 0.97 and 1.02) (Table 1 and Figure S3). C-type curves represent the increase in desorption as a function of the increasing concentration of sorbed herbicide and linear behavior [45,51].

Sorption kinetics and hysteresis are factors that influence the return of the herbicide into solution. A fast interaction of the herbicides with the straw was observed, where approximately 30–50% of the herbicides were sorbed within the first 4 h (Figure S5, Table S2). After 4 h of straw/herbicide contact, small variations in sorption occurred until the herbicides reached equilibrium, in this case in 24 h (Figure S5). With this rapid adsorbent/adsorbate interaction, the specific sites with high binding energy are filled quickly in the sorption process, resulting in herbicide fractions that are not desorbed [59]. Physical trapping of the herbicide in porous structures (such as BO straw) is also a factor that can reduce desorption; however, it is difficult to measure the isolated contribution of each factor to herbicide desorption [60–62]. In our research, the desorption kinetics were not measured, as desorption was evaluated after 24 h.

Hysteresis indices (H) close to 1 indicate that the sorption process is reversible and that desorption occurs in degrees very close to those of sorption [63] (Liu et al., 2010), whereas values less than 1 indicate an irreversible sorption process because desorption occurs with greater difficulty in releasing the sorbed herbicide [41,63]. Thus, the sorption process of diclosulam in BO straw has a higher degree of irreversibility, while the sorption of both herbicides is reversible in the other straws (Table 1, Figure S3). Hysteresis ($H = 0.22–0.62$) was found for herbicides, such as azimsulfuron, in soils with added biochar [21]. Irreversible sorption processes with $H < 0.7$ [41] imply reduced availability of the product in the environment through binding of the herbicide at sites with high affinity, and physical trapping of the molecule in sorbate structures [59].

The differences observed between the spectra before and after the sorption process indicated that the herbicide retention process in the straw relies on a chemical interaction between the straw components and the chemical groups present in the herbicide molecule. This interaction was more pronounced in BO straw and can be justified by the higher sorption and lower desorption of both herbicides in this straw. These interactions are evident in the results of the FTIR analyses, and the structural aspects of the herbicide retention are evidenced by SEM. The binding of diclosulam and diuron to the straw can occur through hydrogen bonds in the side chains of cellulose that constitute a hydrophilic portion of the material [64]. Other straw components, such as lignin, also have the potential for forming these bonds [12]. Overall, it can be pointed out that the behavior of herbicides in the black oat straw (characterized by high sorption and low desorption) is the result of the action of the interaction of more than one sorption mechanism, such as the presence of sites with high binding energy leading to chemical binding, the physical trapping of the herbicide in pores, and the partitioning of the herbicide into aromatic structures in the straw [65].

The results of this research showed that the straw and herbicide interaction is not determined only by its affinity for organic matter (log Kow). The ethereal extract content of the straw (Table S4), cellulose, hemicellulose, and lignin contents can increase the sorption of herbicides [24,28,29]. However, no relationship was observed between herbicide retention with the cellulose, hemicellulose, and lignin contents of the straw (Table S4). The specific surface area (SSA) of organic materials can also influence herbicide sorption [65]. Increased sorption as a function of SSA is observed for herbicides, such as atrazine, cyalofop, isoproturon, and volatile organic compounds in biochar [65–69]. Based on the results of this study, the sorption sites of diclosulam may be shallow and influenced by the specific surface area of the straw.

Herbicide leaching to soil is reduced in the presence of straw. Low amounts of straw (0.5–5.7 t ha^{-1}) are sufficient to intercept the herbicide applied on the soil, as they form a physical barrier where amounts close to 3 t ha^{-1} cover 90% of the soil surface [16,70–73]. As the amount of straw increases, an increase in the physical barrier occurs, making it more difficult for the herbicide to reach the soil seed bank (Macedo et al., 2020) [74]. Water solubility (Sw) and affinity for organic matter (log Kow) are the two main physicochemical properties of herbicides involved in the process of straw transposition. Herbicides, such as diuron (Sw = 35.6 mg L^{-1} and log Kow 2.87 [11]), have greater difficulty in transposing straw and require larger rainfall volumes for transposition to occur, compared to other herbicides, such as metribuzin (Sw = 10,700 mg L^{-1} and log Kow 1.75) [11,27].

Factors, such as the interval between application and the occurrence of the first rainfall, also influence the transposition process. As the contact time of the herbicide with the straw increases, a reduction in transposition occurs [16,23]. The water holding capacity of the straw can also influence the retention of the herbicide, which, through the capillarity existing in the process of hydration of the pores with water and herbicide, causes the physical trapping of the product in the straw pores to occur (Table S6) [75]. The results of our research corroborate the results obtained by other researchers, where insufficient amounts of rainfall and the presence of straw reduces the transposition process and can compromise the effectiveness of the product [18,76–78]. On the other hand, the reduction in the availability of these compounds in cropping systems containing straw, especially of black oats, can contribute to the reduction in environmental risks and dissipation of herbicides.

In this sense, it is possible to cite the factors that affect the retention of herbicides in organic materials (e.g., in straw) as (I) amount and type of straw, (II) composition of the straw, (III) degree of decomposition, (IV) hydrophilic and hydrophobic character of the constituents of the material, (V) the decomposition process, and (VI) interactions of the physicochemical characteristics of the product with the material [16,22,26,28,29].

5. Conclusions

Straw type has a significant impact on both the sorption and leaching of diclosulam and diuron herbicides. Therefore, it is crucial to consider this factor when evaluating herbicide retention. The sorption of diclosulam was influenced by straw size, with smaller fragments (less than 1 mm) providing greater sorption. With increasing ethereal extract content, there is increased sorption and reduced desorption of the herbicides, confirming the straw composition as another factor affecting the retention of diclosulam and diuron. Sorption occurs on chemical bonds between herbicides and straw, through C, N, and H radical bonds of the straw and C, H, N, Cl, and F radicals of the herbicide molecule, highlighting the role of the straw as a chemical barrier for the herbicide.

The leaching of diclosulam was lower in BO, while that of diuron was lower in BW. There was a reduction in the amount of herbicide leached as the amount of straw increased, characterizing a physical barrier. Understanding how diclosulam and diuron retention occurs in the straw is essential for efficient placement in the agroecosystem since tropical production or no-till systems have different organic materials on the surface. The herbicide retention and active ingredient concentration reduction that reaches the soil can reduce the product efficacy, causing a decrease in weed control and losses in crop productivity by weed competition. However, the environmental risks can be mitigated by the reduction in availability in tropical or non-tillage systems.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy13071725/s1, Figure S1: Cover crop plants cultivated in growing chamber in Ecotoxicology Laboratory in 2020–2021 season; Figure S2: Scheme representing the materials and method used for leaching experiments of diclosulam and diuron in different straw types. The mass balance was considerate of the initial amount applied the total amount of herbicide leached and the radioactivity that remained in straw after the rainfall's simulations; Figure S3: Sorption (**a**,**c**) and desorption (**b**,**d**) isotherms for diclosulam and diuron, respectively. Symbols are the punctual values of Kd (Cs/Ce). Lines are the curve according to Freundlich model for each straw type. Bars represent the standard error of the mean (n = 2); Figure S4: Diclosulam and diuron leaching curves adjusted to the Mitscherlich model. (**a**) is diclosulam leaching through 2.5 t ha^{-1} and (**b**) is through 5 t ha^{-1} of straw; (**c**) is diuron leaching over 2.5 t ha^{-1} and (**d**) 5 t ha^{-1} of straw. The data indicate parameter value ± standard error of the mean (n = 6); Figure S5: Sorption kinetics of diclosulam (**a**) and diuron (**b**) in cover crop straws. The symbols represent the data ± standard error of the mean (n = 2); Table S1: Physical-chemical soil properties; Table S2: Percentage of sorption of diclosulam and diuron as a function of time. The data indicate sorption mean ± standard error of the mean (n = 2); Table S3: Mass balance obtained in leaching experiment. The data indicate the percentage of radioactivity recovered for each herbicide; Table S4: Physical–chemical properties of forage turnip (FT), buckwheat (BW), and black oat (BO) straw (n = 2); Table S5: Leaching tendence of diclosulam and diuron as a function of types and amounts of straw, under sequential rainfalls (10 mm each). The data indicate the estimated value for the parameter of non-linear regression (Mistscherlich model, n = 6), where a = maximum asymptote, which is the maximum amount of herbicide that can pass through straw, b = lateral displacement of the curve and c = concavity; Table S6: Water retention in straw in leaching experiment. The data are the mean of water retention (n = 4).

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