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

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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

Tables—Supplementary Material

Table S1. Physical-chemical soil properties.

Properties*	Unit	Soil
Sand	%	70.4
Silt	%	2.1
Clay	%	27.5
Texture Class	-	md-arg
pH ($CaCl_2$)	-	5.9
Organic matter (OM)	%	2.9
Organic carbon (OC)	%	1.69
Available Phosphorus (P)	%	0.56
Available Potassium (K)	%	0.0179
Available Calcium (Ca)	%	0.086
Available Magnesium (Mg)	%	0.00534
H+Al	mmolc.dm^{-3}	10
Sum of bases (SB)	mmolc dm^{-3}	69.6
Cation Exchange Capacity (CEC)	mmolc dm^{-3}	79.6
Base saturation	%	87

* Soil analyzed at the Mineral Fertilizer Laboratory of the "Luiz de Queiroz" College of Agriculture, University of São Paulo, São Paulo, Brazil.
**Value calculated using the analyzed Organic Matter data multiplied by the correction factor of 1.72.

Table S2 Percentage of sorption of diclosulam and diuron in function of time. The data indicate sorption mean ± standard error of the mean (*n*=2).

Herbicide	Time (h)	Sorption (%)[a]		
		FT	*BW*	*BO*
^{14}C-diclosulam	4	26.49±1.28	29.18±2.04	29.01±1.73
	8	25.35±3.25	28.68±0.11	23.14±2.34
	12	20.32±0.98	26.14±0.65	22.98±0.95
	24	20.30±0.84	28.16±0.78	25.38±0.96
	48	19.03±2.12	29.60±1.07	26.40±1.51
^{14}C-diuron	4	30.68±0.84	30.96±3.38	26.04±0.81
	8	25.61±1.56	35.90±0.53	25.63±2.18
	12	28.43±0.35	35.17±1.84	33.34±2.32
	24	29.84±1.96	37.80±3.69	27.44±0.53
	48	34.77±0.62	45.07±7.02	42.78±1.57

[a]Calculated in relation of total applied.

Table S3. Mass balance obtained in leaching experiment. The data indicate the percentage of radioactivity recovered for each herbicide.

Herbicide	Radioactivity recovered (%) [a]
^{14}C-diclosulam	89.67
^{14}C-diuron	102.98

[a]Calculated in relation of total applied.

Table S4 . Physical-chemical properties of forage turnip (FT), buckwheat (BW) and black oat (BO) straw (*n*=2).

Componente analisado	FT	BW	BO
Dry matter (105ºC)[a]	905.54	924.45	925.27
Ether extract[b]	23.30	30.82	53.11
Hemicellulose[b]	101.07	75.83	206.06
Cellulose[b]	213.10	204.22	312.68
Lignin[b]	85.11	218.16	94.79
pH[c]	5.70	5.10	6.10
C/N ratio	12	10	24
Density (g cm^{-3})	0.29	0.30	0.20
Organic matter (%)	72.54	78.30	73.28
Organic carbon (%)	40.30	43.50	40.71
Total Nitrogen (%)	3.24	4.27	1.68
Total phosporus (%)	1.28	1.02	0.42
Total potassium (%)	3.72	5.65	2.34
Total calcium (%)	3.08	2.32	1.03
Total magnesium (%)	0.67	1.42	0.22
Total sulfur (%)	0.53	0.15	0.11

[a]Values expressed in g kg^{-1} of fresh matter. [b]Values expressed in g kg^{-1} of dry matter

Table S5. Leaching tendence of diclosulam e diurom in function of types and amounts of straw, under sequential rainfalls (10 mm each). The data indicates the estimated value for the parameter of non-linear regression (Mistscherlich model, *n*=6). Where a = maximum asymptote, wich is the maximum amount of herbicide that can pass through straw. b = lateral displacement of the curve. c = concavity.

Herbicide	Straw	Estimated parameters*			
		a	*b*	*c*	(adj) R^2
^{14}C-diclosulam	$FT_{2.5\ t\ ha^{-1}}$	100.00	-4.77	0.00994	0.9972
	$FT_{5.0\ t\ ha^{-1}}$	76.43	-5.17	0.01315	0.9986
	$BW_{2.5\ t\ ha^{-1}}$	100.00	-2.07	0.00735	0.9231
	$BW_{5.0\ t\ ha^{-1}}$	81.09	3.62	0.00689	0.9997
	$BO_{2.5\ t\ ha^{-1}}$	81.10	-2.46	0.01338	0.9892
	$BO_{5.0\ t\ ha^{-1}}$	70.23	-5.32	0.01316	0.9936
^{14}C-diuron	$FT_{2.5\ t\ ha^{-1}}$	91.76	-2.86	0.01690	0.9999
	$FT_{5.0\ t\ ha^{-1}}$	70.59	-4.23	0.01538	0.9997
	$BW_{2.5\ t\ ha^{-1}}$	76.89	-0.948	0.01405	0.9999
	$BW_{5.0\ t\ ha^{-1}}$	70.17	-6.801	0.01407	0.9973
	$BO_{2.5\ t\ ha^{-1}}$	93.09	-6.22	0.00633	0.9999
	$BO_{5.0\ t\ ha^{-1}}$	77.05	-3.51	0.01176	0.9985

* Significant at 5% level of significance ($p < 0.05$).

Table S6. Water retention in straw in leaching experiment. The data is the mean of water retention (*n* = 4).

Straw	Water retention (mL g^{-1})
$FT_{2.5\ t\ ha^{-1}}$	7.8
$FT_{5.0\ t\ ha^{-1}}$	10.5
$BW_{2.5\ t\ ha^{-1}}$	6.6
$BW_{5.0\ t\ ha^{-1}}$	10.7
$BO_{2.5\ t\ ha^{-1}}$	8.7
$BO_{5.0\ t\ ha^{-1}}$	13.2

Figures—Supplementary Material

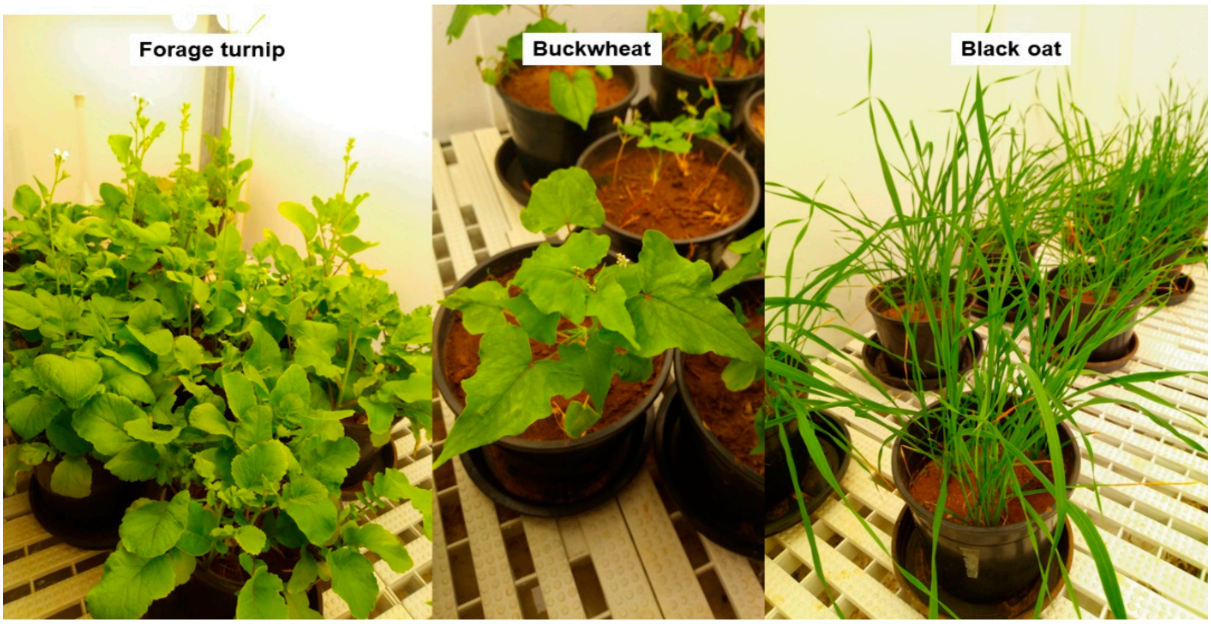

Figure S1. Cover crops plants cultivated in growing chamber in Ecotoxicology Laboratory in 2020-2021 season.

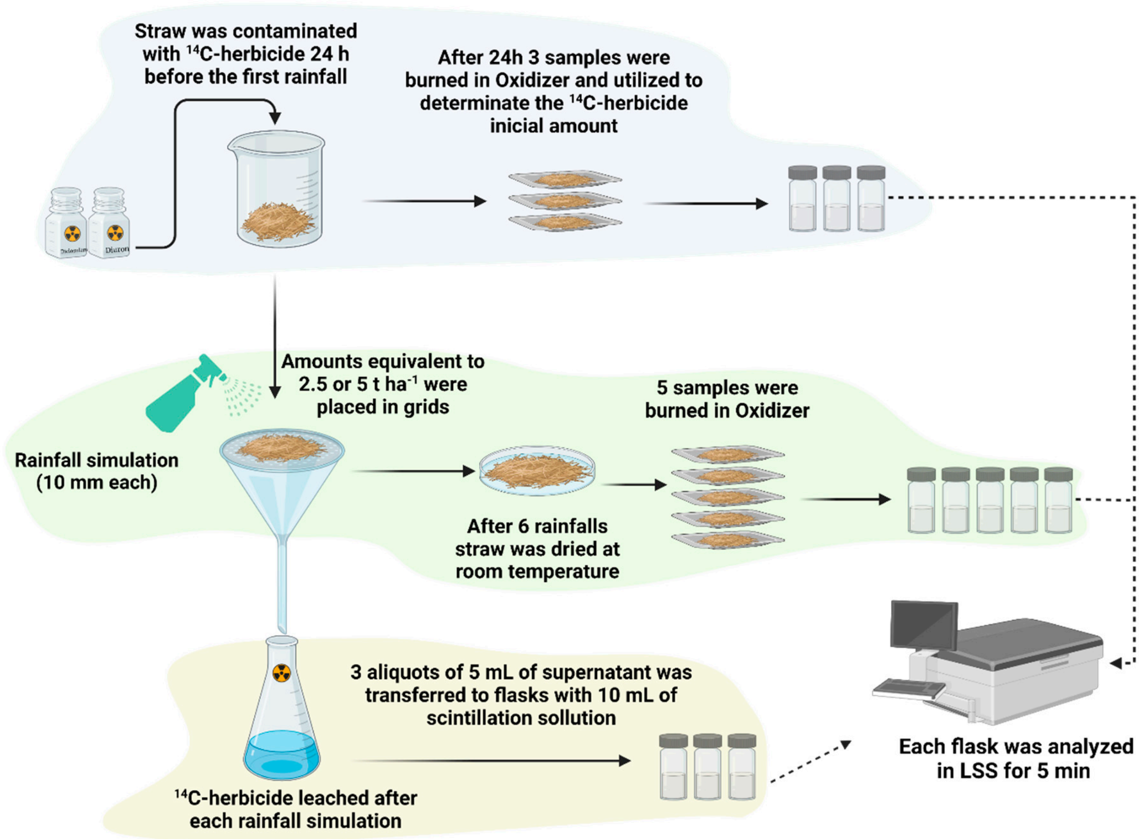

Figure S2. Scheme representing the materials and method used to leaching experiments of diclosulam and diuron in different straw types. To the mass balance was considerate the initial amount applied the total amount of herbicide leached, and the radioactivity that remained in straw after the rainfall's simulations.

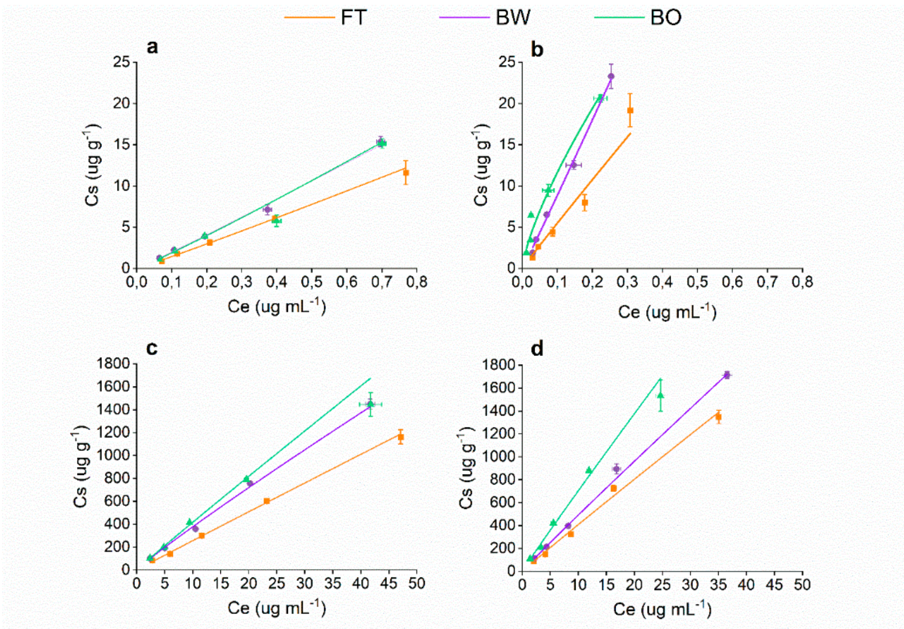

Figure S3. Soprtion (a and c) and desorption (b and d) isotherms for diclosulam and diuron, respectively. Symbols are the punctual values of *Kd* (*Cs*/*Ce*). Lines are the curve according to Freundlich model for each straw type. Bars represent the standard error of the mean (n = 2).

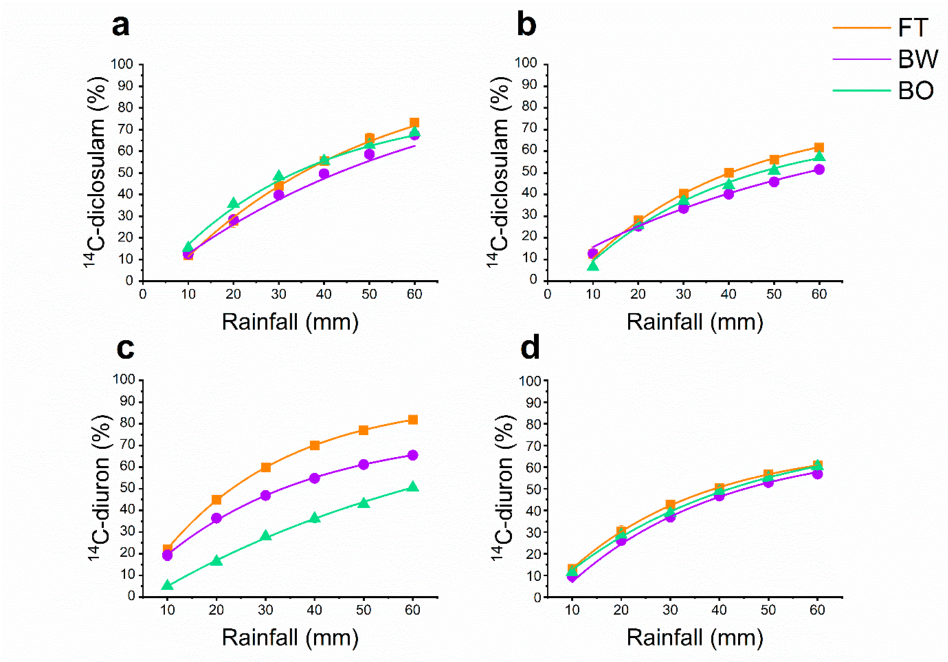

Figure S4. Diclosulam and diuron leaching curves adjusted to Mitscherlich model. (a) is diclosulam leaching through 2.5 t ha-1 and (b) through 5 t ha-1 of straw; (c) is diuron leaching over 2.5 t ha-1 and (d) 5 t ha-1 of straw. The data indicate parameter value ± standard error of the mean (*n* = 6).

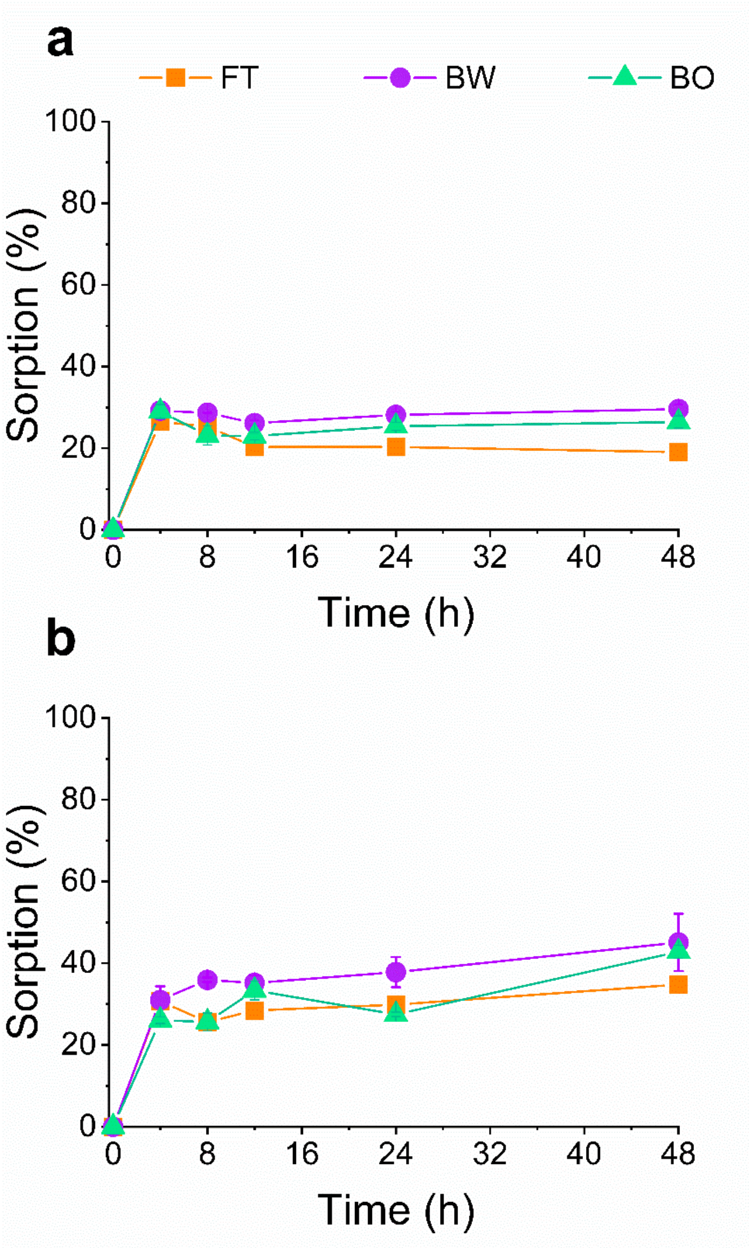

Figure S5. Sorption kinetics of diclosulam (a) and diuron (b) in cover crop straws. The symbols represent the data ± standard error of the mean (n = 2).