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Research on Controllable Degradation of Novel Sulfonylurea Herbicides in Acidic and Alkaline Soils

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Abstract: The degradation issue of sulforylurea (SU) has become one of the biggest 1 2 challenges that hamper the development and application of this class of herbicides, especially in alkaline soils of Northern China. On the basis of previous discovery that 3 some substituents on the 5th position of the benzene ring in Chlorsulfuron could 4 hasten its degradation rate apparently in acidic soil, this work on Metsulfuron-methyl 5 showed more convincing results. Two novel compounds (I-1 and I-2) were designed 6 7 and synthesized, at the same time, they still retained potent herbicidal activity against 8 both tested dicotyledon and monocotyledon. The half-lives of degradation (DT_{50}) assay revealed that I-1 showed accelerated degradation rate in acidic soil (pH 5.59). 9 Moreover, we delighted to find that the degradation rate of I-1 was 9~10 folds faster 10 than that of Metsulfuron-methyl and Chlorsulfuron when in alkaline soil (pH 8.46), 11 12 which have more practical value. This research suggests that a modified structure which has potent herbicidal activity as well as accelerated degradation rate could be 13 realized and this approach may provide a way to improve the residue problem of SUs 14 in farmlands with alkaline soil. 15

Keywords: Sulfonylurea herbicide, Metsulfuron-methyl, herbicidal activity, soil
degradation, DT₅₀.

18 Introduction

Sulfonylurea (SU) herbicides have been widely applied due to their ultra-low dosage, broad spectra and good selectivity.¹⁻² Their sole target is Acetolactate Synthase (ALS) which exists only in plants and microbes, not in mammals. The inhibition of ALS results in the disruption of three essential amino acids synthesis in meristem and eventually death of weeds.³⁻⁶

24 Many sulfonylurea herbicides have been introduced into China and are widely available in Chinese plant protection market.⁷ The common cultivation practice in 25 China is to rear $2\sim3$ different crops successively within a year on the same plot of 26 land. The short crops cycle demands herbicides with high activity, low toxicity and 27 28 fast degradation rate. Due to the relatively long persistence of Chlorsulfuron, 29 Metsulfuron-methyl and Ethametsulfuron that can injure next season crops including wheat, corn, paddy rice, cotton and bean,⁸⁻¹⁰ the Ministry of Agriculture of China 30 suspended their field application in 2014.¹¹ From an environmental and ecological 31 standpoint, we took a green approach to study this issue according to the Anastas 10th 32 Principle of Green Chemistry—Design for Degradation.¹² 33

pH is one of the most important factors that influences the degradation rate of sulfonylurea herbicides in soil. Walker *et al* reported that the DT_{50} of Metsulfuron-methyl was 23 days in pH 5.8 soil and 73 days in pH 7.3 soil.¹³ Yadav *et al* found that there was 83% dissipation of Metsulfuron-methyl in low pH 5.6 soil and

38	53% in high pH 8.1 soil after 120 days. ¹⁴ After research of the hydrolysis of
39	sulfonylurea herbicides in water at different pH, we concluded that the 5 th position on
40	the benzene ring in SU structures is the key factor influencing their degradation
41	behaviors. ¹⁵⁻¹⁸ Our previous study reported that the introduction of some substituents
42	onto the 5 th position of the benzene ring in Chlorsulfuron could speed up its
43	degradation rate in acidic soil relatively. ¹⁹⁻²⁰ Based on these previous findings,
44	dimethylamino and diethylamino groups were introduced into the Metsulfuron-methyl
45	structure (Figure 1) to investigate their influence on biological activities as well as
46	soil degradation behaviors. Considering the difference of soil pH in China and the soil
47	degradation of sulfonylurea herbicides has strong negative correlation with soil
48	pH, ^{13-14, 21} two representative standard soil samples (pH 5.59 Jiangxi Province and pH
49	8.46 Hebei Province) were selected to carry out our research.

50 Materials and Methods

Instruments and Materials. All reaction reagents were analytical grade, all 51 analytical reagents for high performance liquid chromatograph (HPLC) were HPLC 52 53 grade including methanol and acetonitrile. The melting points were determined on an X-4 binocular microscope melting point apparatus (Beijing Tech Instrument Co., 54 Beijing, China), and the temperatures were uncorrected. ¹H and ¹³C nuclear magnetic 55 resonance (NMR) spectra were obtained on a Bruker AV-400 spectrometer (Bruker 56 57 Co., Switzerland) in Acetone- d_6 or DMSO- d_6 solution with tetramethylsilane (TMS) as the internal standard, and chemical-shift values (δ) were given in parts per million 58 59 (ppm). High-resolution mass spectrometry (HRMS) data were obtained on a Varian QFT-ESI instrument. Ultraviolet (UV) spectra were performed on a TU-1810 60 61 ultraviolet-visible spectrophotometer (Persee general analysis Co., Beijing, China). 62 HPLC data were obtained on a SHIMADZU LC-20AT (SHIMADZU Co., Japan). Column chromatography purification was carried out using silica gel (200~300 63 64 mesh).

65	General Procedure for the Synthesis of Target Compounds I-1.
66	1-(2-Methoxycarbonyl-5-dimethylaminophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,
67	5-triazin-2-yl)urea I-1 was synthesized by the following method. ²² To a toluene
68	solution of 10a (1.0 mmol), 2-amino-4-methoxy-6-methyl-1,3,5-triazine (1.2 mmol)
69	was added under stirring. The mixture was heated to reflux with continuous removal
70	of the azeotrope formed by ethanol and toluene. After completion of the reaction, the
71	solvent was evaporated in vacuum and the residue was purified on silica gel column
72	eluting with petroleum/ethyl acetate $(v/v, 1:1)$ to obtain I-1.
73	1-(2-Methoxycarbonyl-5-dimethylaminophenylsulfonyl)-3-(4-methoxy-6-methyl-1,
74	3,5-triazin-2-yl)urea (I-1). White solid, yield 87%, m.p. 195-197 °C. 1 H NMR (400
75	MHz, Acetone) δ 12.60 (s, 1, NH), 9.59 (s, 1, NH), 7.77 (d, 1, J = 8.7 Hz, Ph-H), 7.60
76	(d, 1, J = 2.7 Hz, Ph-H), 6.95 (dd, 1, J = 8.8, 2.8 Hz, Ph-H), 4.06 (s, 3, CO ₂ CH ₃), 3.84
77	(s, 3, OCH ₃), 3.13 (s, 6, N(CH ₃) ₂), 2.56 (s, 3, CH ₃). ¹³ C NMR (101 MHz, DMSO) δ
78	178.6, 170.2, 166.0, 163.9, 151.4, 148.5, 138.7, 132.7, 115.1, 114.4, 114.2, 55.3, 52.3,
79	39.7, 25.1. HRMS (ESI) Calcd for $C_{16}H_{21}N_6O_6S [M+H]^+$ 425.1243, found 425.1239.
80	I-2 was prepared with the same procedure.

81 1-(2-Methoxycarbonyl-5-diethylaminophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3, 82 5-triazin-2-yl)urea (**I-2**). White solid, yield 85%, m.p. 189-191 °C. ¹H NMR (400 83 MHz, Acetone) δ 12.58 (s, 1, NH), 9.54 (s, 1, NH), 7.74 (d, 1, J = 8.8 Hz, Ph-H), 7.61 84 (d, 1, J = 2.8 Hz, Ph-H), 6.93 (dd, 1, J = 8.8, 2.8 Hz, Ph-H), 4.06 (s, 3, CO₂CH₃), 3.83

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- 85 (s, 3, OCH₃), 3.54 (q, 4, J = 7.1 Hz, N(CH₂CH₃)₂), 2.56 (s, 3, CH₃), 1.23 (t, 6, J = 7.1
- 86 Hz, N(CH₂C<u>H</u>₃)₂). ¹³C NMR (101 MHz, DMSO) δ 178.6, 170.2, 166.0, 164.0, 149.0,
- 87 148.6, 138.8, 133.0, 114.3, 113.8, 99.6, 55.3, 52.3, 44.3, 25.1, 12.1. HRMS (ESI)
- 88 Calcd for $C_{18}H_{25}N_6O_6S[M+H]^+$ 453.1556, found: 453.1548.

89	X-ray Diffraction Analysis. A colorless crystal of I-1 was obtained by
90	self-evaporation in the mixture solvent of dichloromethane and n-hexane. The crystal
91	with dimensions of 0.20 $\times 0.20$ $\times 0.20$ mm was mounted on a glass fiber for X-ray
92	diffraction analysis. The data was collected at 113 K on a Rigaku Saturn 724 CCD
93	diffractometer (Rigaku Co. Japan) with graphite monochromated Mo K α radiation (λ
94	= 0.71075 Å), θ_{max} = 25.01°. The molecular formula is C ₁₆ H ₂₀ N ₆ O ₆ S, and the formula
95	weight is 424.44 g·mol ⁻¹ . The crystal was a monoclinic system, space group P $2_1/c$,
96	with cell parameters existed as $a = 13.5479(19)$ Å, $b = 9.9822(12)$ Å, $c = 15.552(2)$ Å;
97	cell ratio as $a/b = 1.3572$, $b/c = 0.6419$, $c/a = 1.1479$; calculated density was 1.46883
98	g/cm ³ ; $V = 1919.22(43)$ Å ³ ; $Z = 4$, μ (Mo K α) = 0.217 mm ⁻¹ . In total, 14901 integrated
99	reflections were collected, reducing to a data set of 3263 unique with $R_{int} = 0.0405$
100	and the completeness of data was 96.8%. Data were collected and processed using
101	CrystalClear (Rigaku). An empirical absorption correction was applied using
102	CrystalClear (Rigaku). The structure was solved by direct methods with the
103	SHELXS-97 program. ²³ Full-matrix least-squares refinement based on F^2 gave final
104	values of $R = 0.1195$, $wR = 0.3482$. Hydrogen atoms were observed and refined with
105	a fixed value of their isotropic displacement parameter.

106	Biological Assay. The root growth inhibition of oil seed rape (<i>Brassica campestris</i>)
107	was tested using the reported method. ²⁴ Pot trials for herbicidal activities against oil
108	seed rape (Brassica campestris), amaranth (Amaranthus retroflexus), barnyard grass
109	(Echinochloa crusgalli) and crab grass (Digitaria sanguinalis) were tested in
110	greenhouse (25 ± 2 °C) according to the procedures in the literature. ^{24, 25}

Molecular Docking. The surflex-dock method²⁶ was applied to study the binding mode of SU structures with the AHAS using the SYBYL 6.9 software package. I-1 was manually docked into the active site of *yeast* AHAS on the basis of the crystal complex of Chlorimuron-ethyl and *yeast* AHAS²⁷ which was retrieved from the RCSB Protein Data Bank (PDB code: 1N0H). The receptor and the ligand molecule were prepared by standard procedures.

117 Soil Degradation Experimental Strategies. Soil Selection. To investigate the 118 degradation behaviors of Metsulfuron-methyl and its derivatives, a red acidic soil (pH 5.59) from Ji'an, Jiangxi Province and an alkaline soil (pH 8.46) from Cangzhou, 119 Hebei Province in China were selected. The soil from the fresh farmland was sampled 120 from the upper layer (0-25 cm), air-dried in the shade and passed through a 2 mm 121 sieve according to the Chinese National Standard GB/T 31270.1-2014.²⁸ The soil 122 123 texture, pH value, organic matter, cation exchange capacity (CEC) and mechanical composition of the test soils were listed in Table 1, which were determined by Tianjin 124 125 Institute of Agriculture Resource and Environment.

126 HPLC Processing and Establishment of Standard Curves. The samples were analyzed by HPLC following the Chinese National Standard GB/T 16631-2008.²⁹ The 127 128 method employed a Shimadzu HPLC (series LC-20AT), equipped with a binary pump (Shimadzu, LC-20AT), an UV/VIS detector (Shimadzu, SPD-20A), an auto sampler 129 (Shimadzu, SIL-20A), a column oven (Shimadzu, CTO-20AC) and a Shimadzu 130 131 shim-pack VP-ODS column (5 mm, 250 mm \times 4.6 mm) connected to a Shimadzu 132 shim-pack GVP-ODS (10 mm \times 4.6 mm) pre-column, and a computer (model Dell) 133 for carrying out the data analysis. Chromatographic pure methanol, acetonitrile and 134 ultra-pure water (pH 3.0) were used as mobile phase. After that, standard curves used for quantitative conversion were established with the injection volume of 10 μ L and 135 the temperature was set at 20 °C. 136

137 *Measurement of the Recovery Rate.* Appropriate extraction solvents were adopted 138 and mixed to guarantee the eligible average recovery rate, standard deviation and 139 coefficients of variation (Table 2) according to the Chinese Agricultural Industry Standard NY/T 788-2004.³⁰ The concentrations of target compound in soil were 5, 2, 140 $0.5 \text{ mg} \cdot \text{kg}^{-1}$, and the soil humidity was kept at 60% of the water holding capacity. 141 Different extraction solvents were decanted into the homogeneous soils, followed by 142 shaking for 3 h at 200 rpm·min⁻¹ with a SHZ-88 thermostatic oscillator (Jintan 143 Medical Instrument Factory, Jiangsu, China). The samples were then centrifuged for 2 144 145 min at 6500 rpm min⁻¹ with a Thermo Scientific Legend Mach 1.6 R centrifuge to 146 obtain supernatant which was then concentrated in vacuum at room temperature. After the residue was extracted by dichloromethane (30 mL \times 2) and distilled water (30 mL), the combined organic solution was dried by anhydrous sodium sulfate, filtered and concentrated. The product was dissolved in acetonitrile (10 mL), and filtered through a millipore filter (organic, nylon 66, 0.22 µm) for HPLC analysis. The addition recovery rate were measured and calculated according to the corresponding average values of 5 replicates.

153 *Cultivation of Samples and Management.* Testing soil (20.00 g) was weighed 154 into 6 groups in 100 mL conical flasks, triplications in each group, and the standard sample solutions were added to a concentration of 5 a.i. $mg \cdot kg^{-1}$. Then an appropriate 155 156 volume of distilled water was added to adjust the soil moisture content to 157 approximately 60% of water holding capacity and thoroughly mixed. The bottles were 158 then sealed with Para film and put into a SPX-150B-Z biochemical incubator (Boxun 159 Industrial Co., Shanghai, China) at 25 ± 1 °C and 80% humidity in the dark. In the 160 process of cultivation, the moisture content in conical flasks was adjusted regularly to 161 maintain the original water-holding state. The samples were taken periodically for 162 HPLC analysis at 6 different intervals and each sample was repeated 3 times. 163 According to previous studies, the initial degradation of sulfonylurea herbicides follows the first-order kinetic equation.^{19,31-34} The degradation curves of first-order 164 165 kinetic equation of tested compounds were established according to the data from six samplings. After that, half-lives of degradation (DT_{50}) were calculated using the 166 formula: $DT_{50} = LN(2)/K$. 167

168 Results and Discussion

Chemistry. The synthetic procedures of all compounds were showed in Figure 2. 169 The reactions of diazotization of 1, ammoniation of 2 and successive reduction of 5 170 were prepared according to reported methods,¹⁹ and **10** was synthesized through the 171 reaction of **9** and ethyl chlorocarbonate using the procedure in literature.²⁴ Compound 172 4 was obtained in the aqueous solution of chromium trioxide by adding concentrated 173 174 sulfuric acid and 2-methyl-5-nitrobenzenesulfonamide successively, for 24h at room temperature.³⁵ The ring-opening reaction of **4** was prepared by leading in hydrogen 175 chloride gas continuously in methanol.¹⁷ The protection and deprotection of 176 177 sulphonamide were carried out for the alkylation of aniline, and DMF-DMA was taken as the protective agent.³⁶⁻³⁸ The intermediate 8a was obtained as previous 178 reported.¹⁹ Compound **8b** can be prepared as **8a**, and can also be synthesized by the 179 180 following procedure that 7 was dissolved in glacial acetic acid, and then NaBH₄ was 181 added in batches, the mixture was stirred overnight to adjust pH until there was no longer white solid produced,³⁹ this method was more effective and with more higher 182 183 yield than 8a.

In assay of alkaline soil degradation, the soil extraction of **I-2** failed due to an unexpected peak overlapped with the sample which resulted in a >130 % recovery. By numerous replacement of the mobile phases and change of their ratios, we successfully separated the mixed peaks by HPLC condition as CH₃OH/CH₃CN/H₂O (pH 3.0) = 35/35/30. As a result, the alkaline soil degradation of **I-2** was determined

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in another batch, taking Chlorsulfuron as a control.

190	Crystal Structure Analysis. The crystal structure of I-1 was showed in Figure 3
191	(CCDC number. 1540975). The sum angles of O(5)-C(11)-N(2) 123.878(535)°,
192	O(5)-C(11)-N(3) 120.792(502)° and N(2)-C(11)-N(3) 115.314(471)° was 359.984°,
193	indicating the plane sp^2 hybridization state of C(11) atom. The bonds angles of
194	O(3)-S(1)-C(1), O(4)-S(1)-C(1), N(2)-S(1)-C(1) were 109.858(271)°, 108.886(256)°
195	and $105.792(250)^{\circ}$ respectively which indicated the sp ³ hybridization state of the S(1)
196	atom. The torsion angle of O(5)-C(11)-N(2)-H(2) was $-175.66(53)^{\circ}$ while the
197	O(5)-C(11)-N(3)-H(3) showed as 8.376(799)°. The benzene ring and the triazine ring
198	were non-plane for their dihedral angle was 74.041(146)°. From Figure 3, one kind of
199	<i>H</i> -bond could be found: $N(2)$ -H(2)···N(5), it could be explained as the reason of the
200	torsion angles of O(5)-C(11)-N(2)-H(2) and O(5)-C(11)-N(3)-H(3).

Biological Assay. The inhibition rate of the root growth oil seed rape (*Brassica campestris*) was measured to evaluate the herbicidal activities of the target compounds and the corresponding results were listed in Table 3. From the results, it was observed that the new compound I-1 matched commercial Metsulfuron-methyl in herbicidal potency at the rate of $0.1 \text{ ug} \cdot \text{mL}^{-1}$, whereas I-2 was slightly weaker.

On this basis, the herbicidal activities of target compounds against dicotyledon *Brassica campestris, Amaranthus retroflexus* and monocotyledon *Echinochloa crusgalli, Digitaria sanguinalis* were further screened through pot experiments at 15

and 150 a.i. g·ha⁻¹ with Metsulfuron-methyl as a positive control. The results were 209 210 showed in Table 4. From the data, it was found that the target compounds retained 211 their efficient herbicidal activities, where I-1 exhibited excellent inhibition effect against Digitaria sanguinalis at 150 a.i. g ha⁻¹. The 100% inhibition rate against 212 Brassica campestris was showed at 15 a.i. g·ha⁻¹ by soil treatment as well as foliage 213 spray. The effect on *Echinochloa crusgalli* of **I-1** was also 100% at 15 a.i. g·ha⁻¹ in 214 215 post-emergence treatment. Overall the introduction of dimethylamino and diethylamino groups onto the 5th position of the benzene ring in Metsulfuron-methyl 216 retained or improved their herbicidal activities. 217

218 Molecular Docking Results. I-1 was taken in the molecular docking study for its hyper herbicidal activity, and the result was illustrated in Figure 4. As it showed the 219 220 conformations of the aromatic ring and triazine ring connected to the sulfonyl urea 221 bridge were situated in approximately mutual vertical position which was similar to 222 the binding structure of Chlorimuron-ethyl and AHAS that the heterocyclic part 223 blocks the substrate access channel. The section of methoxy carbonyl was also located 224 in the channel to block the substrate. There was a $\pi - \pi$ stacking interaction between 225 the indole side chain of B/Trp 586 and the triazine moiety of I-1. There was also several *H*-bonds interaction between the urea-triazine moiety of **I-1** and the guanidine 226 group of B/Arg 380. The docking results ascertained that I-1 is also a typical AHAS 227 228 interaction.⁵ From the conformation of the docking results, the dimethylamino group 229 was located along the extended plane of the benzene ring outside the channel, it could explain its high biological activity. The conformation of sulfonylurea bridge was rotated for the better docking with AHAS through the torsion of C(11)-N(3) bond, and it was consistent with the active conformation of Chlorimuron-ethyl and Monosulfuron.⁴⁰⁻⁴¹

Soil Degradation. The degradation curves of first-order kinetic equation of tested
compounds were established according to the data from six samplings (Figure 5 and
Figure 6). After that, half-lives of degradation (DT₅₀) were calculated (Table 5).

237 The soil degradation behaviors of target compounds in acidic soil (pH 5.59) with 238 Metsulfuron-methyl as a positive control were investigated preliminarily to explore 239 the corresponding relationship between structural modification and soil degradation. 240 From the half-lives of degradation, the degradation rate of dimethylamino substituted 241 compounds I-1 was increased significantly that its DT_{50} was 2.85 days, 2 folds faster 242 than Metsulfuron-methyl. Furthermore, the degradation rate of I-2 with its DT_{50} as 243 5.11 days, which had approximately the same degradation rate as metsulfuron-methyl 244 (5.50 days).

Then, the alkaline soil (pH 8.46) degradation behaviors of target compounds were examined to survey their difference in degradation rate in two types of soils, taking Metsulfuron-methyl and Chlorsulfuron as positive controls.

From Table 5, the DT_{50} of compound I-1 was 8.40 days which showed a significant 10 folds faster degradation rate than Chlorsulfuron (84.53 days) and 9 folds faster than Metsulfuron-methyl (75.34 days). The DT_{50} of compound **I-2** was 26.56 days while the DT_{50} of Chlorsulfuron was longer than 100 days. The experimental data demonstrated that the introduction of dimethylamino and diethylamino groups onto the 5th position of the benzene ring in Metsulfuron-methyl could efficiently accelerate its soil degradation rate. The research provide critical information for the solution to soil degradation problems in our green chemistry approach especially in alkaline soil.

256 After structural modification, the optimized new structure I-1 upgraded its 257 degradation rate not only in standardized acidic soil, but also in standardized alkaline 258 soil. From the degradation results in acidic soil (pH 5.59), DT_{50} of I-1 accelerated to 259 2.85 days while I-2 was 5.11 days comparing with the 5.50 days of 260 Metsulfuron-methyl. Particularly in alkaline soil (pH 8.46), the DT_{50} of I-1 hastened 261 nearly 9 folds from 75.34 to 8.40 days in comparison with Metsulfuron-methyl that 262 there was considerable faster degradation in alkaline soil than acidic soil, the same as 263 compound I-2. Interestingly I-1 and I-2 also retained their active herbicidal activity in 264 comparison with the parent structure. The perfect surflex-docking results also 265 confirmed that I-1 was a typical AHAS interaction. Our study further ascertained that in Metsulfuron-methyl, the 5th position substituted approach also has apparent 266 influence on its degradation rate, though the influence mensuration is somewhat 267 different. This might be due to the difference in their molecular structures. 268 269 Considering the particular planting practice in China which requires individual 270 cultivation cycle for each crop, it convinces us that by modifying SU structures

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delicately, a control of their degradation rate which is in accordance with our cultivation pattern is possible.⁴² After further understanding of their structure/activity/degradation relationship, it will be possible to optimize the novel herbicidal application in the particular planting system.

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276 ABBREVIATIONS USED

277 AHAS: acetohydroxy acid synthase; DMF-DMA: *N*,*N*-Dimethylformamide dimethyl

acetal; THF: tetrahydrofuran; RT: room temperature; Trp: tryptophan; Arg: aginine.

279

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286 Supporting Information Description

¹H NMR, ¹³C NMR spectra for the target compounds; Crystal data of the compound
I-1; Determination results of tested soils. This material is available free of charge via
the Internet at http: //pubs.acs.org.

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FIGURE CAPTIONS

- Figure 1 Design Strategy of Target Compounds.
- Figure 2 Synthesis Strategy for Target Compounds.
- Figure 3 The Crystal Structure of I-1.
- Figure 4 Binding Mode of I-1 to Yeast AHAS.
- Figure 5 Degradation Curves in Acidic Soil (pH 5.59).
- Figure 6 Degradation Curves in Alkaline Soil (pH 8.46).

Tables

Table 1 Analysis data of Soils

			Mechanical composition						
		Organi pH matter (%)	<u> </u>	Cation exchange capacity (cmol·kg ⁻¹)	Sand	Silt		Clay	
Soils	Soil texture		matter (%)		(1-0. 05 mm) (%)	Coarse (0.05-0. 01 mm) (%)	Fine (0.01-0. 005 mm) (%)	Coarse (0.005-0 .001 mm) (%)	Fine (<0.00 1 mm) (%)
Acidic soil	loam	5.59	0.763	13.55	36	10	10	12	32
Alkali ne soil	clay	8.46	0.757	10.39	30	26	8	8	28

	Compou	HPLC analysis	Extraction solvents	Adding	Average	Coefficient
	nds	conditions	(v/v)	concentration	recovery	of
		(wavelength, flow rate,		$(mg \cdot kg^{-1})$	5	variation/%
		235 nm, 0.8 mL·min ⁻¹ ,	CH ₃ COCH ₃ :CH ₂ Cl ₂	5	84.82	1.23
	I-1	CH ₃ OH/H ₂ O (pH 3.0) =	:CH ₃ OH:H ₃ PO ₄	2	78.78	2.12
		65/35	aqueous solution	0.5	74.06	3.49
			(pH 2.0) = 40:5:5:5	5	80.52	1 27
Acidic		$230 \text{ nm}, 0.8 \text{ mL} \cdot \text{min}^{-1},$		5	80.33	1.27
soil	I-2	$CH_{3}OH/H_{2}O(pH 3.0) =$: CH ₃ OH: H ₃ PO ₄	2	76.74	1.42
(nU		70/30	aqueous solution (pH 2.0) = 40:5:5:5	0.5	77.58	2.50
(p11 5 59)			<i>a i</i>	5	88.60	1.61
5.57)	Metsulf 230 nm, 1.0 mL·min ⁻¹ ,	CH ₃ COCH ₃ :CH ₂ Cl ₂	2	85.12	3.14	
	uron-me	CH ₃ OH/H ₂ O (pH 3.0) =	$: H_3PO_4$ aqueous	0.5	76.90	3.33
	thyl	55/45	solution (pH 2.0) =	2	84 74	1 76
			+0.3.5	0.5	77.20	2 92
				0.5	11.29	5.62
		235 nm, 0.8 mL·min ⁻¹ ,	CH ₃ COCH ₃ :CH ₂ Cl ₂	5	83.73	1.19
	I-1	I-1 $CH_3OH/H_2O(pH 3.0) =$: H ₃ PO ₄ aqueous	2	77.16	2.87
Allcoli	65/35	65/35	solution (pH 2.0) = 40:5:10	0.5	74.05	1.23
ne soil		230 nm, 0.8 mL·min ⁻¹ ,	CH ₃ COCH ₃ :CH ₂ Cl ₂	5	74.13	0.62
ne son	I-2	CH ₃ OH/CH3CN/H ₂ O	: H ₃ PO ₄ aqueous	2	70.80	1.04
(pH		(pH 3.0) = 35/35/30	solution (pH 2.0) =	0.5	73.19	3.27
8.46)			40:5:5	-	00.65	1.00
	Metsulf	230 nm, 1.0 mL·min ⁻¹ ,	CH ₃ COCH ₃ :CH ₂ Cl ₂	5	90.65	1.98
	uron-me	CH ₃ OH/H ₂ O (pH 3.0) =	: H_3PO_4 aqueous	2	85.83	1.51
	thyl	55/45	solution (pH 2.0) = 40:5:10	0.5	72.75	2.90

Table 2	Analytical Conditions for Soil Degra	dation.

		Inhibition rate (%)	
compounds	0.1 μg·mL ⁻¹	1 μg·mL ⁻¹	10 μg⋅mL ⁻¹
I-1	61.8	67.9	68.4
I-2	45.8	61.4	67.5
Metsulfuron-methyl	61.2	66.6	67.3

Table 5 Initional of the Root Orowth of Rape (<i>Drassica cumpestris</i>)	Table 3	Inhibition	of the Root	Growth of Rape	(Brassica campes	stris).
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Table 4 Herbicidal Activity of Target Compounds by Soil Treatment and Foliage

Spray.

	Inhibition rate (%)								
compounds	Concentration (a.i g·ha ⁻¹)	Brassica campestris		Amaranthus retroflexus		Echinochloa crusgalli		Digitaria sanguinalis	
	-	Pre	Post	Pre	Post	Pre	Post	Pre	Post
	15	100	100	91.4	92.5	77.4	100	27.7	12.2
1-1	150	100	100	100	100	100	100	98.1	65.6
	15	100	100	91.8	97.8	53.4	85.2	49.9	0
1-2	150	100	100	100	100	100	100	90	0
Metsulfuron-me	15	100	100	100	100	64.7	84.1	61.5	31.7
thyl	150	100	100	100	100	96.7	98.9	100	45.4

	Compound	Kinetic equations of soil degradation	Correlation coefficient/R ²	$\mathrm{DT}_{50}/\mathrm{days}$
Acidic	I-1	$C_t = 4.1498e^{-0.243t}$	0.9925	2.85
soil	I-2	$C_t = 5.5989 e^{-0.136t}$	0.9945	5.11
(pH 5.59)	Metsulfuron-meth	$C_t = 4.8674e^{-0.126t}$	0.9965	5.50
	yl I-1	$C_t = 4.9253 e^{-0.082t}$	0.9734	8.40
Alkaline	Metsulfuron-meth	$C_t = 4.7002 \mathrm{e}^{-0.009 \mathrm{t}}$	0.9998	75.34
soil	Chlorsulfuron	$C_t = 4.1900 \mathrm{e}^{-0.008 \mathrm{t}}$	0.9992	84.53
(pH 8.46)	I-2 [*]	$C_t = 4.8264 e^{-0.026t}$	0.9978	26.56
	Chlorsulfuron*	-	-	>100

Table 5Kinetic Parameters for Soil Degradation.

 $\frac{1}{a *}$ the degradation research of these two compounds were conducted in another batch.

Figure Graphics



Figure 1



^{*a*}Reagents and conditions: (i) HCl, AcOH, NaNO₂ \rightarrow HCl, CuCl₂, NaHSO₃, < 0 °C ; (ii) 28% NH₃·H₂O, THF, RT, 4h; (iii) CrO₃, H₂O, H₂SO₄, 0 °C \rightarrow RT, 24 h; (iv) HCl (g), CH₃OH, reflux for 7h; (v) Fe, HCl, C₂H₅OH, H₂O, reflux for 2h; (vi) DMF-DMA, CH₂Cl₂, RT, 2h; (vii) NaBH₃CN, 37% formalin, CH₃COOH, CH₃CN, reflux for 4 h; (viii) NaBH₄, CH₃COOH, RT, 4 h; (ix) H₂NNH₂·H₂O, C₂H₅OH, RT, 2 h; (x) K₂CO₃, ClCO₂C₂H₅, Acetone, reflux, 3 h; (xi) 2-amino-4-methoxy-6-methyl-1,3,5-triazine, toluene, reflux for 8 h.

Figure 2



Figure 3



^{*a*}The yellow dashed line represents the *H*-bond.

Figure 4



Figure 5



Figure 6

Table of Contents Graphic

