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### Article

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# Chromatography and High Resolution Mass Spectrometry for the Characterization of the Degradation Products of the Photodegradation of Amidosulfuron: an Analytical Approach

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| 1  | Chromatography and High Resolution Mass Spectrometry for the  |  |  |  |
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| 2  | Characterization of the Degradation Products of the   |  |  |  |
| 3  | Photodegradation of Amidosulfuron: an Analytical Approach   |  |  |  |
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| 24                   | ABSTRACT: Simulated sunlight irradiation causing degradation of amidosulfuron, a   |
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| 25                   | pyrimidinylsulfonylurea herbicide, has been investigated in aqueous solution. The main   |
| 26                   | degradation products were followed up by ultra-high pressure liquid chromatography with  |
| 27                   | UV detector (UHPLC-UV) and identified by combining ultra-high pressure liquid  |
| 28                   | chromatography mass spectrometry (UHPLC-MS) and Fourier transform ion cyclotron  |
| 29                   | resonance mass spectrometry (FT-ICR-MS). Based on the retrosynthetic analysis, the most  |
| 30                   | identified degradation products were mainly due to the losses of methylsulfamic acid   |
| 31                   | (CH <sub>5</sub> NO <sub>3</sub> S), sulfocarbamic acid (CH <sub>3</sub> NO <sub>5</sub> S), carbamic acid (CH <sub>3</sub> NO <sub>2</sub> ), |
| 32                   | methyl(methylsulfonyl)sulfamic acid $(C_2H_7NO_5S_2)$ , N-methylmethanesulfonamide   |
| 33                   | $(C_2H_7NO_2S)$ and sulfonic acid $(H_2SO_4)$ molecules. Accordingly, O and S-demethylation as   |
| 34                   | well as hydroxylation processes were also observed. Sum formulas of the main degradation   |
| 35                   | products were assigned and a mechanistical pathway is proposed.  |
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| 37                   | <b>KEYWORDS:</b> Amidosulfuron, degradation products, UHPLC-UV, UHPLC-MS, FT-ICR-MS  |
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#### 50 **INTRODUCTION**

The use of herbicides in agriculture is the most effective way to control weed growth and increase agricultural crop yields<sup>1,2</sup>. However, the presence of herbicides even in trace levels in the nature is hazardous for human and mammals health. Furthermore, due to their slow biodegradation, the herbicides could easily reach the surface and ground water. Thus, information on bio- and chemical degradation of these substances is of great interest and laboratory setups are necessary to follow up and understand their fate in the environment.

57 Amidosulfuron (IUPAC: 1-(4,6-dimethoxypyrimidin-2-yl)-3-mesyl(methyl)sulfamoylurea) 58 is a herbicide which belongs to sulfonylurea family of pesticides and is used worldwide in 59 agronomic crops, rangeland/pasture, and forestry as well as plants organization<sup>3-5</sup>. Upon 60 application, sulfonylurea inhibits the activity of acetolactase synthase (ALS) which is well 61 known as a first enzyme liable to the biosynthesis of amino acid e.g. valine and isoleucine.

The degradation of sulfonylurea herbicides has been widely conducted in several matrices 62 e.g., waters<sup>6-10</sup>, humic acids and organic amendments in soils<sup>11-12</sup>, clay minerals<sup>13</sup> and strains 63 bacteria from contaminated soils.<sup>14</sup> Among the sulfonylurea herbicides, the photolysis of 64 65 chlorsulfuron, tribenuron-methyl, thifensulfuronmethyl, metsulfuron-methyl, and ethametsulfuron-methyl is already reported in different water matrices.<sup>15-20</sup> Several mass 66 spectrometric tools like LC-MS, LC-MS-MS, as well as different ionization sources such as 67 68 electrospray (ESI) and atmospheric pressure chemical ionization (APCI) were employed to identify the degradation products of sulfonylurea herbicides<sup>15, 21</sup>, but analyses based on fourier 69 70 transform Ion cyclotron resonance (FT-ICR) mass spectrometer have not been performed for 71 this type of compounds yet. In a previous work, we showed that high resolution mass 72 spectrometry (FT-ICR-MS) could also be used as an efficient technique for the identification of the photolysis, photocatalytic and hydrolysis products.<sup>22-25</sup> 73

To date there is no published work which discusses the degradation of amidosulfuron under simulated sunlight irradiation. In the present study, we used both UHPLC-MS and FT-ICR-MS to identify the main degradation products of amidosulfuron. Accordingly, a schema showing the main pathways of the degradation products of amidosulfuron is provided.

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## MATERIALS AND METHODS

Chemicals. Amidusulfuron (Figure 1), Purity>97%, was purchased from Sigma Aldrich
(Augsburg, Germany). Solvents for UHPLC analysis were of UPLC-MS grade (Biosolve,
Walkenswaard, Netherlands) and all other chemicals were of analytical grade. All chemicals
were used without further purification. Ultra pure water was produced with a MilliQ system
(Millipore, Billerica, MA, USA).

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Figure 1. Emission spectral distribution of the sun and Xenon arc lamp simulator (only
wavelengths range from 280 to 400nm is shown). Insert figure shows the absorption spectrum
of amidosulfuron and its chemical structure.

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Photoreactor. A cylindrical Pyrex glass vessel of 250 ml is used horizontally as a batch reactor. Solar irradiation was simulated by using a Suntest apparatus from Heraeus (Hanau, Germany) equipped with a Xenon lamp; UV-B (280 to 320 nm), 2.71 W/m<sup>2</sup> and UV-A (320 to 400 nm), 58.0 W/m<sup>2</sup>). The total radiation in wavelength range between 300 and 830 nm is 820W/m<sup>2</sup>. About 500 cm<sup>2</sup> exposure area. The UV radiation is limited at 280 nm using a filters restricting transmission of light below this value. The illuminance is approximately 150 k Lux. The temperature was approximately maintained at 30°C by an unbroken cooling and an

96 internal water re-circulating systems. The emission spectral distribution of the sun and Xenon

arc lamp simulator in the wavelength range from 280 to 400 nm is shown in Fig 1.

98 UHPLC-MS. The LC/MS analysis was performed using a Maxis instrument (Bruker 99 Daltonics, Bremen, Germany) in combination with an UPLC System (Acquity, Waters, 100 Eschborn, Germany) equipped with a PDA detector (photo diode-array) and an ACQUITY 101 BEH C18 column (1. 7 μm, 2.1 x 100 mm, Germany). A gradient of methanol/water (A: 10% 102 methanol, 0.1% formic acid in water, B: methanol) was used for the chromatographic 103 separation. The gradient used was increased from 50% (B) to 70% (B) in 2 min, and then was 104 kept stable to 70% of B for 1 min and decreased to 50% until 3.5 min. A total time of 3.5 min 105 was reached for each measurement. The column oven temperature, the injection volume at 106 partial loop with needle overfills and the flow rates were 313K, 5  $\mu$ L and 0.4 mL min<sup>-1</sup>, 107 respectively. Mass spectra were acquired using Maxis TOF-MS in both negative and positive 108 ion modes. Samples were introduced into the electrospray source at a nitrogen flow rate of 12 109 L/min (350°C) with a nebulizer gas pressure of 50 psi, capillary voltage of 4000V and 110 acquisition rate of 10 Hz. Data processing was done by the use of Compass DataAnalysis 4.0 111 (Bruker, Bremen, Germany).

112 FT-ICR-MS. High-resolution mass spectra for sum formula assignment were acquired on a 113 Bruker (Bremen, Germany) APEX Qe Fourier transform ion cyclotron resonance mass 114 spectrometer (FTICR-MS) equipped with a 12 Tesla superconducting magnet and an 115 APOLLO II electrospray ionization source. The samples were diluted in methanol to final a concentration of 2.7 x  $10^{-6}$  M. For negative and positive electrospray ionization modes, 116 117 methanol was used. Samples were introduced into the electrospray source at a flow rate of 118 120 µl/h with a nebulizer gas pressure of 20 psi and a drying gas pressure of 15 psi. The 119 spectra were acquired with a time domain of one-megaword over a mass range of 100-500

m/z and the spectra were internaly calibrated using appropriate reference lists. The plausible
elemental formulas were calculated for each peak in batch mode using home-made software.

#### 122 **RESULTS AND DISCUSSIONS**

**Degradation products.** Off-line ultrahigh performance liquid chromatography with UV detector (UHPLC-UV) is used to follow the disappearance of amidosulfuran as well as the formation of its degradation products. Five main degradation products were detected by UHPLC-UV. Figure 2A shows the UHPLC-UV chromatogram after the end of the degradation (20 hours) whereas Figure 2B shows the changes of the peak areas of the amidosulfuran and its degradation products during time of irradiation. In addition, the half-life  $(t_{1/2})$  of amidosulfuron was 6.3 hours.

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131 Figure 2. (A) UPHLC Chromatogram. (B) Peak area changes of amidosulfuron and its

132 degradation products. Conditions:  $[AMD] = 2.71 \times 10^{-5} \text{ M}$  in ultrapure water at  $\approx 30^{\circ}\text{C}$ .

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134 Online UHPLC-UV coupled to an electrospray ionization quadrupole time-of-flight (ESI Q-135 TOF) is used to extract ions mass spectra of the main degradation products of the degradation 136 of amidosulfuran. The extracted negative ions mass spectra (Figure 3) showed the presence of 137 seven degradation products with their characterized retention times and sum formulas of the 138 [M-H] ions: AMD1 (1.35min; m/z 386.0081; C<sub>8</sub>H<sub>12</sub>N<sub>5</sub>O<sub>9</sub>S<sub>2</sub>), AMD2 (1.37min; m/z 139 293.0197; C<sub>7</sub>H<sub>9</sub>N<sub>4</sub>O<sub>7</sub>S), AMD3 (1.9min; m/z 354.0183; C<sub>8</sub>H<sub>12</sub>N<sub>5</sub>O<sub>7</sub>S<sub>2</sub>), AMD4 (2.4min; m/z 140 277.0248; C7H9N4O6S), AMD5 (2.8min; m/z 199.054; C7H11N4O3), AMD6 (3.0min; m/z 141 166.0150; C<sub>7</sub>H<sub>8</sub>N<sub>3</sub>O<sub>2</sub>) and AMD8 (2.78min; m/z 385.0362; C<sub>9</sub>H<sub>15</sub>N<sub>5</sub>O<sub>8</sub>S<sub>2</sub>).

Figure 3. Top left shows the extracted ions chromatogram of amidosulfuron (AMD; 3.2 min) and its degradation products (AMD1-6 and AMD8) in negative ion mode (the chromatogram's insert reveals the presence of three degradation products with very low UVabsorbance (AMD5, AMD6 and AMD8). The Extracted ion mass spectra of the [M-H]<sup>-</sup> of Amidosulforon and its degradation products AMD1, AMD2, AMD3, AMD4, AMD5, AMD6, AMD8 are also shown.

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In positive ionization mode, the extracted ion chromatogram shows presence of only three degradation products, namely: (AMD4, AMD6 and AMD7) with their retention times (2.4, 2.9 and 1.8 min), respectively (Figure 4). The extracted positive ions mass spectra showed abundant peaks at masses m/z 156.0769, 279.0408 and 168.0768 which were attributed to the following sum formulas:  $C_6H_{10}N_3O_2$  (AMD7),  $C_7H_{11}N_4O_6S$  (AMD4) and  $C_7H_{10}N_3O_2$ (AMD6).

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Figure 4. Top left shows the extracted ion chromatogram of amidosulfuron (AMD; 3.2 min) and its degradation products (AMD7; 1.8 min, AMD6; 2.9 min and AMD4; 2.4 min) in positive mode. Extracted ion mass spectra of AMD7, AMD6, AMD4 and AMD are also shown.

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In order to validate these results, high resolution mass spectrometry (FT-ICR-MS) is used. Fourier transform mass spectra of the UV degradation of amidosulfuron in positive and negative ionization modes are shown in Figures 5A and 5B. Enlarged views for each of these mass spectra in the mass range (m/z 140-220) amu are also provided (5A1 and 5B1). To

| 167 | summarize, Table 1 shows accurate masses of the neutrals which present Amidosulforon and   |
|-----|--|
| 168 | its degradation products together with their detected retention times (in minutes) and sum |
| 169 | formulas, as well as chemical structures.  |
| 170 |  |
| 171 | Table 1. Positive and negative FT-ICR/MS and UPLC/MS analyses data of Amidosulfuron        |
| 172 | and its degradation products.  |
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| 175 | Figure 5. (A) FT-ICR mass spectrum of amidosulfuron degradation in positive mode. (A1)     |
| 176 | An enlarged mass view which shows the degradation products AMD3, AMD5, AMD6 at             |

molecular masses of m/z 156.0767, 168.0767 and 199.0825, respectively. (B) FT-ICR mass

spectrum of amidosulfuron degradation in negative mode. (B1) An enlarged mass view which

shows the degradation products AMD1, AMD2, AMD7 and AMD at molecular masses of

m/z 386.0082, 293.1792, 354.01844 and 368.0339, respectively.

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182 The sum formulas of the neutrals which are provided in Table1 could be revealed by 183 performing calculations on the measured masses. These calculations took into consideration 184 the presence of carbon, hydrogen, nitrogen, oxygen and sulphur. A home made program was 185 used to generate possible sum formulas according to the following criteria: O/C ratio≤1; H/C 186 ratio $\leq 2n+2$ ; element counts: C $\leq 20$ , H $\leq 30$ , O $\leq 6$ , N $\leq 6$  and S $\leq 2$ ). The nitrogen rule was also 187 checked and only those sum formulas which adhere to this rule were considered. This was 188 important because all measured masses correspond to ions with closed electronic shell (even 189 electron species), so that nitrogen rule should apply. No radical ions can be detected for this type of compounds under the used electrospray conditions.<sup>22-26</sup> 190

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191 Figure 6 shows a further step forward which has been performed in case of the degradation 192 product AMD4 in order to show the importance of the fine isotopic structure (FIS) for 193 revealing further validation of the detected sum formula. We performed the mentioned FIS 194 analysis specifically for the degradation product AMD4 (as an example) due to its high 195 abundance. FIS analysis requires very high resolution so that an enlarged mass spectrum of 196 the [M-H]<sup>-</sup> of AMD4 at m/z 277.02477 and sum formula C<sub>7</sub>H<sub>9</sub>N<sub>4</sub>O<sub>6</sub>S which shows each 197 heavy isotope should be feasible. This is illustrated in Figure 6 which shows the presence of species with the following sum formulas e.g. (ISO 1;  $C_7H_9N_3O_6S^{15}N$ ), (ISO 2;  $C_7H_9N_4O_6^{33}S$ ), 198 (ISO 3;  $C_6H_9N_4O_6S^{13}C_1$ ), (ISO 4;  $C_7H_9N_4O_6^{34}S$ ), (ISO 5;  $C_6H_9N_3O_6S^{13}C^{15}N$ ), (ISO 6; 199  $C_7H_9N_4O_5S^{I8}O$  and (ISO 7;  $C_5H_9N_4O_6S^{I3}C_2$ ) that correspond to the natural abundance 200 201 isotopes of the [M-H]<sup>-</sup> of AMD4. These sum formulas which contain heavy isotopes (Table 202 2) were also calculated and a very good match in regard to the isotopic patterns of both 203 experimental and simulated isotope patterns could be achieved. This validates that the ion M-204 H]<sup>-</sup> with m/z 277.02477 does indeed belong to the sum formula C<sub>7</sub>H<sub>9</sub>N<sub>4</sub>O<sub>6</sub>S. The same 205 principle can be applied for all other degradation products.

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Figure 6. (A) Enlargement of the mass 277.02477 with sum formula  $[C_7H_9N_4O_6S]^$ corresponding to the degradation product AMD4 (see Figure 5B) with its observable isotopologues present in high intensity (see also Table 2 where the assigned formula of each ISO-abbreviation is given). (B) Show simulated mass spectrum of the same mass.

211

212 Table 2. High accuracy measurements (FIS analysis) which show the assigned formulas of

the degradation product AMD4 (mass 277.02477) as well as its corresponding heavy

214 isotopes in negative mode FT-ICR/MS (see also Figure 6).

216 **Degradation pathways.** The main proposed pathways of the degradation of amidosulfuron 217 are shown in Figure 7. Most of these pathways involve the following competing process: (i) 218 carbon – nitrogen (C - N) and sulfur – nitrogen (S - N) bond cleaveages (ii) O or S-219 demethylation and (iii) hydroxylation process. Thus, the degradation product AMD8 with 220 385 1-(5-hydroxy-4,6-dimethoxy-pyrimidin-2-yl)-3mass  $(C_9H_{15}N_5O_8S_2,$ IUPAC: 221 [methyl(methylsulfonyl)sulfamoyl]urea) (Figure 7) is obtained as a result of a hydroxylation 222 process in the para-position of pyrimidine ring of amidosulfuron. Furthermore, S-223 demethylation (S-C cleavage bond) of AMD8 can also take place to form AMD1 with a 224 (C<sub>8</sub>H<sub>13</sub>N<sub>5</sub>O<sub>9</sub>S<sub>2</sub>, IUPAC: (5-hydroxy-4,6-dimethoxy-pyrimidin-2nominal mass 387 225 yl)carbamoylsulfamoyl-methyl-sulfamic acid).

The degradation product AMD2 with a nominal mass 294 ( $C_7H_{10}N_4O_7S$ ; IUPAC: (5hydroxy-4,6-dimethoxy-pyrimidin-2-yl)carbamoylsulfamic acid) can be formed from AMD1 by substitution of one molecule of methylsulfamic acid ( $CH_5O_3NS$ ) by a hydroxyl group.

O-demethylation of amidosulfuran by loss of one of the two methyl's group in meta position of pyrimidinyl group leads to the formation of the degradation product AMD7 with a nominal mass 355 ( $C_8H_{13}N_5O_7S_2$ ; IUPAC: 1-(4-hydroxy-6-methoxy-pyrimidin-2-yl)-3-[methyl(methylsulfonyl)sulfamoyl]urea). This step of the degradation is considered as a first step of the degradation not only for the degradation of amidosulfuron, but also for the degradation of bensulfuronmethyl and triasulfuron.<sup>27,28</sup>

The degradation product AMD4 with a nominal mass 278 ( $C_7H_{10}N_4O_6S$ ; IUPAC: (4,6dimethoxypyrimidin-2-yl)carbamoylsulfamic acid) can be obtained either by loss of Nmethylmethanesulfonamide molecule directly from amidosulfuron (S–N bond cleavage) or by dehydroxylation of AMD2. A similar degradation product was identified in the degradation of imazosulfuron in aqueous medium.<sup>29</sup>

240Accordingly,N–Sbondcleavagefromamidosulfuronbylossof241methyl(methylsulfonyl)sulfamic acid and / orN–SbondcleavagefromAMD4bylossof

| 242 | sulfuric acid (H <sub>2</sub> SO <sub>4</sub> ) molecule can lead to the degradation product AMD5 with a nominal                   |
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| 243 | mass 198 (C <sub>7</sub> H <sub>10</sub> N <sub>4</sub> O <sub>3</sub> ; IUPAC: (4,6-dimethoxypyrimidin-2-yl)urea). The final AMD3 |
| 244 | degradation product can be the result of either -NH-C(O)- cleavage from amidosulforon ,  |
| 245 | AMD4 or from AMD5 (Figure7).   |
| 246 | Accordingly, the degradation of the herbicides e.g. iodosulfuron methyl ester, chlorsulfuron,                                      |
| 247 | and tribenuron methyl in aqueous solution has also been explained as a result of -NH-C=O   |
| 248 | bond cleavages. <sup>15,21,25</sup> It has been reported that the degradation products AMD3 and AMD5                               |
| 249 | were identified as degradation products of imazosulfuran, azimsulfuran, [ <sup>14</sup> C]Amidosulfuron,                           |
| 250 | pyrazosulfuran ethyl and halosulfuran methyl under abiotic and biotic conditions. 9,19,29-31                                       |
| 251 |  |
| 252 | Figure 7. Proposed pathways for the degradation of amidosulfuron in neutral form   |
| 253 | To sum up, the degradation of amidosulfuran under simulated sunlight irradiation is studied  |
|     |  |

To sum up, the degradation of amidosulfuran under simulated sunlight irradiation is studied and the related degradation products were identified by combining UHPLC-UV, UHPLC-MS and FT-ICR-MS. This combination allowed us to draw up the most plausible pathways concerning the degradation products of amidosulfuron. It should be noted that the pyrimidine ring existing in the amidosulfuron structure is retained during amidosulfuron degradation. This analytical approach can be used to unequivocally identify the key degradation products of related organic contaminants in the environment without specific separation.

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# **365** Figures and Tables Captions

- 366 Figure 1. Emission spectral distribution of the sun and Xenon arc lamp simulator (only
- 367 wavelengths range from 280 to 400nm is shown). Insert figure shows the absorption spectrum
- 368 of amidosulfuron and its chemical structure.
- 369 Figure 2. (A) UPHLC Chromatogram. (B) Peak area changes of amidosulfuron and its
- degradation products. Conditions:  $[AMD] = 2.71 \times 10^{-5} M$  in ultrapure water at  $\approx 30^{\circ}C$ .
- Figure 3. Top left shows the extracted ions chromatogram of amidosulfuron (AMD; 3.2 min)
- 372 and its degradation products (AMD1-6 and AMD8) in negative ion mode (the
- 373 chromatogram's insert reveals the presence of three degradation products with very low UV-
- absorbance (AMD5, AMD6 and AMD8). The Extracted ion mass spectra of the [M-H] of
- 375 Amidosulforon and its degradation products AMD1, AMD2, AMD3, AMD4, AMD5, AMD6,
- AMD8 are also shown.
- Figure 4. Top left shows the extracted ion chromatogram of amidosulfuron (AMD; 3.2 min)
  and its degradation products (AMD7; 1.8 min, AMD6; 2.9 min and AMD4; 2.4 min) in
  positive mode. Extracted ion mass spectra of AMD7, AMD6, AMD4 and AMD are also
  shown.
- **Figure 5.** (A) FT-ICR mass spectrum of amidosulfuron degradation in positive mode. (A1) An enlarged mass view which shows the degradation products AMD3, AMD5, AMD6 at molecular masses of m/z 156.0767, 168.0767 and 199.0825, respectively. (B) FT-ICR mass spectrum of amidosulfuron degradation in negative mode. (B1) An enlarged mass view which shows the degradation products AMD1, AMD2, AMD7 and AMD at molecular masses of m/z 386.0082, 293.1792, 354.01844 and 368.0339, respectively.

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| 388 | Figure 6. (A) Enlargement of the mass 277.02477 with sum formula $[C_7H_9N_4O_6S]^-$         |
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| 389 | corresponding to the degradation product AMD4 (see Figure 5B) with its observable            |
| 390 | isotopologues present in high intensity (see also Table 2 where the assigned formula of each |
| 391 | ISO-abbreviation is given). (B) Show simulated mass spectrum of the same mass.               |
| 392 | Figure 7. Proposed pathways for the degradation of amidosulfuron in neutral form.            |
| 393 | Table 1. FT-ICR/MS and UPLC/MS analyses data of Amidosulfuron and its degradation            |
| 394 | products.  |
| 395 | Table 2. High accuracy measurements (FIS analysis) which show the assigned formulas of       |
| 396 | the degradation product AMD4 (mass 277.02477) as well as its corresponding heavy             |
| 397 | isotopes in negative mode FT-ICR/MS (see also Figure 6).                                     |
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412 Figure 1. Emission spectral distribution of the sun and Xenon arc lamp simulator (only
413 wavelengths range from 280 to 400nm is shown). Insert figure shows the absorption spectrum
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Figure 3. Top left shows the extracted ions chromatogram of amidosulfuron (AMD; 3.2 min) and its degradation products (AMD1-6 and AMD8) in negative ion mode (the chromatogram's insert reveals the presence of three degradation products with very low UVabsorbance (AMD5, AMD6 and AMD8). The Extracted ion mass spectra of the [M-H]<sup>-</sup> of Amidosulforon and its degradation products AMD1, AMD2, AMD3, AMD4, AMD5, AMD6, AMD8 are also shown.





451 **Figure 5.** (A) FT-ICR mass spectrum of amidosulfuron degradation in positive mode. (A1) An enlarged mass view which shows the 452 degradation products AMD3, AMD5, AMD6 at molecular masses of m/z 156.0767, 168.0767 and 199.0825, respectively. (B) FT-ICR mass

- 453 spectrum of amidosulfuron degradation in negative mode. (B1) An enlarged mass view which shows the degradation products AMD1, AMD2,
- 454 AMD7 and AMD at molecular masses of m/z 386.0082, 293.1792, 354.01844 and 368.0339, respectively.
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**Figure 6.** (A) Enlargement of the mass 277.02477 with sum formula  $[C_7H_9N_4O_6S]^-$ 459 corresponding to the degradation product AMD4 (see Figure 5B) with its observable 460 isotopologues present in high intensity (see also Table 2 where the assigned formula of each 461 ISO-abbreviation is given). (B) Show simulated mass spectrum of the same mass.



- 472 Figure 7. Proposed pathways for the degradation of amidosulfuron in neutral form.
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# 476 **Table 1.** FT-ICR/MS and UPLC/MS analyses data of Amidosulfuron and its degradation products.

| Degradation<br>products | Chemical structure   | Calculated mass | Retention time<br>(min) | Neutral<br>Sum formulas |
|-------------------------|--|-----------------|-------------------------|-------------------------|
| AMD1                    | $H_{3}C-O$ $HO$ $HO$ $HO$ $HO$ $HO$ $HO$ $HO$ $H$  | 387.0155        | 1.34                    | $C_8H_{13}N_5O_9S_2$    |
| AMD2                    | $\begin{array}{c} H_{3}C-O \\ HO \\ HO \\ H_{3}C-O \end{array} \xrightarrow{N} \begin{array}{c} O \\ H \\ H \\ H \\ H \\ H \\ H \\ O \end{array} \xrightarrow{N} \begin{array}{c} O \\ H \\ H \\ H \\ O \\ H \\ O \end{array} \xrightarrow{N} \begin{array}{c} O \\ H \\ H \\ H \\ O \\ O \\ H \\ O \\ O \\ H \\ O \\ O$ | 294.0270        | 1.36                    | $C_7H_{10}N_4O_7S$      |
| AMD3                    | $H_3C-O$<br>$H_3C-O$<br>N<br>$NH_2$<br>$H_3C-O$  | 155.0695        | 1.84                    | $C_6H_9N_3O2$           |
| AMD4                    | $\begin{array}{c} H_{3}C-O \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$   | 278.0321        | 2.46                    | $C_7 H_{10} N_4 O_6 S$  |
| AMD5                    | $H_3C-O$<br>$H_3C-O$<br>$H_3C-O$<br>$H_3C-O$   | 198.0753        | 2.8                     | $C_7H_{11}N_4O_3$       |

| AMD6 | Not proposed   | 167.0695 | 3.0  | $C_7H_9N_3O_2$ 478   |
|------|--|----------|------|--|
|      | HO O O O CH3   |          |      | 479  |
|      | $ \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & $ |          |      | 480  |
| AMD7 | $H_3C = O O O O CH_3$  | 355.0256 | 1.8  | C <sub>8</sub> H <sub>13</sub> N <sub>5</sub> O <sub>7</sub> S <sub>2</sub><br>481 |
|      | $ \begin{array}{c} \begin{pmatrix} & & \\ & \end{pmatrix} - N & N - S - N & O \\ \end{pmatrix} = N & H & H & H & H \\ H & O & CH_3 \\ H O & \end{array} $  |          |      | 482  |
|      | H <sub>3</sub> C-O O CH <sub>3</sub>   |          |      | 483  |
| AMD8 | $HO \longrightarrow N \qquad HO \qquad S \qquad O \qquad S \qquad O \qquad HO \qquad HO \qquad HO \qquad H$  | 385.0362 | 2.78 | $C_9H_{15}N_5O_8S_{484}$   |
|      | H <sub>3</sub> C−Ó   |          |      | 485  |
| AMD  | $ \begin{array}{c} H_{3} O = O \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$   | 369.0413 | 3.2  | $C_9H_{16}N_5O_7S_2^{486}$   |
|      | )=N 11 11 Ö С́H₃<br>H₃C−O  |          |      | 487  |

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- 494 **Table 2.** High accuracy measurements (FIS analysis) which show the assigned formulas of
- the degradation product AMD4 (mass 277.02477) as well as its corresponding heavy
- 496 isotopes in negative mode FT-ICR/MS (see also Figure 6)

|            |                | Assigned formula            | Meas. m/z | Calc. m/z | Error<br>(ppm) |
|------------|----------------|-----------------------------|-----------|-----------|----------------|
|            | Parent ion     |                             |           |           |                |
|            | AMD4           | $C_7H_9N_4O_6S$             | 277.02477 | 277.02483 | 0.2            |
|            | Isotope labels |                             |           |           |                |
|            | ISO 1          | $C_7H_9N_3O_6S^{15}N$       | 278.02185 | 278.02186 | 0.0            |
|            | ISO 2          | $C_7H_9N_4O_6^{33}S$        | 278.02421 | 278.02422 | 0.0            |
|            | ISO 3          | $C_6H_9N_4O_6S^{13}C$       | 278.02814 | 278.02818 | 0.2            |
|            | ISO 4          | $C_7H_9N_4O_6^{34}S$        | 279.02059 | 279.02062 |                |
|            |                |                             |           |           | 0.1            |
|            | ISO 5          | $C_6H_9N_3O_6S^{13}C^{15}N$ | 279.02529 | 279.02522 | 0.3            |
|            | ISO 6          | $C_7H_9N_4O5S^{18}O$        | 279.02905 | 279.02907 | 0.1            |
|            | ISO 7          | $C5H_9N_4O_6S^{13}C_2$      | 279.03147 | 279.03154 | 0.2            |
|            |                |                             |           |           |                |
| 497        |                |                             |           |           |                |
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# **"TOC Graphic"**

