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## DEGRADATION OF NICOSULFURON IN SOIL

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### ABSTRACT

Nicosulfuron (2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino] carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamide) is a sulfonylurea herbicide (SU) used for selective postemergence control of annual and perennial grasses in corn. In contrast to traditional herbicides used in corn that are applied at rates  $>1 \text{ kg ha}^{-1}$ , nicosulfuron is typically applied at rates  $<100 \text{ g ha}^{-1}$ . Because of the low application rates, it has been thought to have a lower potential for contamination of surface and ground waters than other traditional corn herbicides [1]. Degradation of the herbicide nicosulfuron in three samples of soil was investigated under laboratory conditions. Degradation of nicosulfuron in soils was pH-dependent; calculated half-life ( $t_{1/2}$ ) values ranged from 0.37 to 9.11 days. Nicosulfuron was more persistent in neutral or weakly basic soil than in acidic soil. The degradation pathways included the cleavage of the sulfonylurea bridge to form the pyridine sulfonamide and pyrimidine amine, and hydrosylation on the pyrimidine ring were the main metabolic pathways.

### INTRODUCTION

Sulfonylurea herbicides are a class of herbicides that are spread over 20 compounds, and widely used as control chemicals for most broad-leaved weeds and common grasses in agricultural crops and vegetables. Agriculturally applied pesticides and herbicides are one class of chemicals that pose a threat to the environment. Therefore, there is an increasing concern about the persistence of pesticide and herbicide residues in soils and subsequent contamination of groundwater. The fate and mobility of pesticides in the environment involve complex mechanisms that are influenced by many processes, including volatilization, leaching, adsorption, as well as chemical and biological degradation. Sulfonylurea herbicides typically degrade via a combination of bridge hydrolysis by a chemical route and microbial degradation [2]. Chemical hydrolysis cleaves the sulfonylurea bridge, resulting in sulfonamide and s-triazine derivatives [3]. Sulfonylurea degradation is influenced not only by the chemical structure of the parent herbicide but also by soil organic matter, soil pH, and environmental conditions resulting from varying moisture and temperature combinations [4]. In the environment, sulfonylurea herbicides are mainly decomposed by chemical hydrolysis [5] and microbial degradation [6]. Some recent reports suggest that photolysis may be an alternative pathway to hydrolysis [7]. Several studies have investigated the degradation paths in soil [8]. The degradation products have been analyzed by liquid chromatography–ultraviolet detection (LC–UV) [9] capillary electrophoresis (CE)–UV [10] and LC–mass spectrometry (MS) [11]. The structural identification of the degradation compounds was performed by nuclear magnetic resonance [12].



In recent years, sulfonylurea herbicides have become very popular worldwide because of their low application rates (10–40 g ha<sup>-1</sup>), low toxicity to mammals, and unprecedented herbicidal activity.

## MATERIALS AND METHODS

### Chemicals

Nicosulfuron (purity 95.0 ± 0.05%) was supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany) and used in all experiments. All solvents were of high performance liquid chromatography (HPLC) grade and were used without further purification. All other reagents were of analytical grade. Deionized water used for sample preparation and LC mobile phase. Stock nicosulfuron standard solutions were prepared in acetonitrile. Standard dilutions were made in acetonitrile.

### Soil

Samples of soil were collected from three different locality were air-dried and sieved to pass through a 2-mm sieve, and thoroughly mixed before use.

Soil samples were autoclaved at 1.5 atm and 121°C for 1h. Physical and chemical characteristics of each soil are summarized in Table 1.

Table 1. Physical and chemical properties of soil used in experiment

	Total sand (%)	Clay (%)	pH		Humus (%)
			KCl	H <sub>2</sub> O	
Sample 1	73.76	27.24	5.36	6.48	4.80
Sample 2	88.80	11.20	6.50	7.33	1.36
Sample 3	90.36	9.64	7.67	8.51	2.53

### Laboratory experiment

#### *Degradation studies in Sterile Soil*

The soil degradation experiments were conducted according to SETAC procedures [13]. An appropriate amount of nicosulfuron solution was added on to each of soil sample. Hereby, initial nicosulfuron concentration of 5 mg kg<sup>-1</sup> which was equivalent to an application dose of 50g active ingredient ha<sup>-1</sup> was obtained. Soil moisture of the samples was adjusted to approximately 75% of field water holding capacity (FC) by adding deionized water. The treated soil samples were kept at temperature 30 ± 1 °C in the dark (excluding every photochemical reaction). The moisture level of the soil samples was checked daily by weighing and adjusting as above.

#### *Soil extraction method*

A portion (10 g) of the fortified soil was extracted twice with 10 ml of extraction solvent (methanol– phosphate buffer pH 7, 2:1, v/v) for 30 min followed by centrifugation at 3200 rpm for 10 min. The methanol was removed by rotary evaporation and the aqueous extract acidified with of glacial acetic acid. [14]

Nicosulfuron was then extracted from the clear supernatant by solid-phase extraction SPE. For each extraction procedure, two SPE cartridges were used. The first cartridge was, Chromabond-NH<sub>2</sub>. This cartridge removed much of the coextracted organic matter (OM) from the sample. The second cartridge was a Oasis HLB cartridge. Calibration curves were obtained by plotting peak areas against concentration of nicosulfuron in spiked soil samples. Extract samples were analyzed by high-performance liquid chromatography (HPLC).



### Analytical methods

The concentrations of the nicosulfuron residues on soil were determined by high performance liquid chromatography (HPLC) using an Agilent 1100 HPLC instrument (Agilent Technologies Co. Ltd., USA), equipped with an UV variable wavelength diode array detector (DAD), set at 230 nm. The column used was a 1.8  $\mu\text{m}$  Zorbax Eclipse XDB C18 reversed phase column; mobile phase was acetonitrile and water; volume injected was 20  $\mu\text{l}$ . The flow rate of mobile phase was constant at 1.0  $\text{ml min}^{-1}$ . Nicosulfuron standard solutions was prepared in acetonitrile from a 100  $\mu\text{g mL}^{-1}$  stock solution and stored at 4  $^{\circ}\text{C}$  in the dark until use. The limit of quantification, estimated to be 10 times the background noise, was 10  $\mu\text{g mL}^{-1}$ .

### RESULTS

Typical chromatograms obtained for the extracts of soil samples 1, 2 and 3 are shown in Fig. 1. The degradation of nicosulfuron occurred more rapidly in sample 1 than in other samples, as it represented in Fig.1. The significant difference in the degradation rate of nicosulfuron in samples of soil may be due to the difference in the soil properties. The present study suggested that nicosulfuron degraded relatively fast in acidic soil, and the degradation potential will be enhanced with soil organic matter increasing.

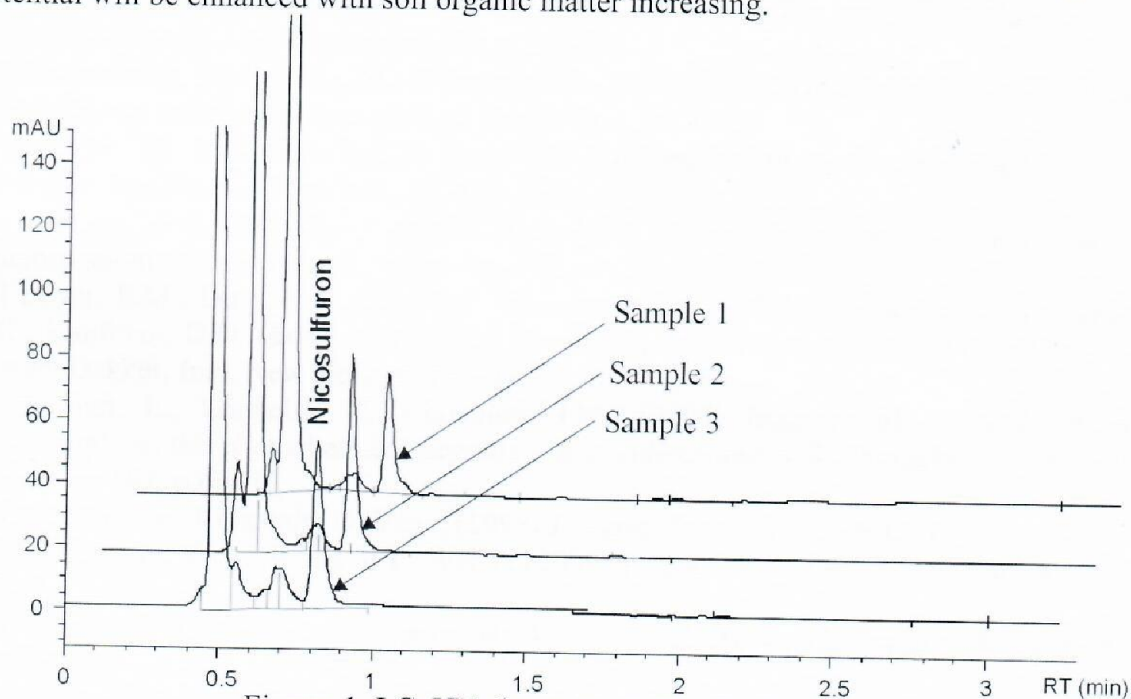


Figure 1. LC-UV chromatograms of soil samples

The first-order model [15] is the most common and was used in the present study. The corresponding first-order degradation rate constant ( $k$ ) can be calculated from the following equation

$$k = \frac{-\ln C / C_0}{t},$$

where  $C_0$  is the initial concentration of nicosulfuron ( $\text{mg/kg}$ );  $C$  is the concentration of nicosulfuron ( $\text{mg/kg}$ );  $k$  is the first-order degradation rate constant ( $\text{days}^{-1}$ );  $t$  is time (days). The half-life coefficient  $t_{1/2}$  (days) can be calculated from the following term

$$t_{1/2} = \frac{\ln 2}{k}.$$



Degradation of nicosulfuron in soils was pH-dependent; calculated half-life ( $t_{1/2}$ ) values ranged from 0.37 to 9.11 days. Nicosulfuron was more persistent in neutral or weakly basic soil than in acidic soil.

## CONCLUSIONS

- From the results of this laboratory study it could be concluded that half-life of degradation nicosulfuron in soils ranged from 0.37 to 9.11 days
- The degradation of nicosulfuron was relatively rapid in acidic soil and slow in neutral or weakly basic soil.
- The LODs were too high to allow for the method to be used for monitoring nicosulfuron in field samples.

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