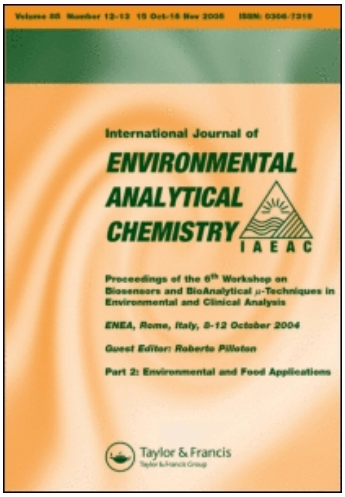

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GAS-CHROMATOGRAPHIC METHOD FOR DETERMINATION OF DIFLUFENICAN IN SOIL

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Decomposition in soil of the herbicide diflufenican, N-(2,4-difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]-3-pyridinecarboxamide, was studied after application for weed control on Swedish railway embankments. A new sensitive method has been developed for determination of aged residues of diflufenican in soil by GC-ECD. A sample extraction using 100% methanol with "extended shake" was performed. The extract was concentrated and purified on a C_{18}-SPE column. Further clean-up was made by using a Silica SPE column. Minimum level of detection for diflufenican was 0.001 μg g^{-1} soil. Recovery of diflufenican over the range 0.02 μg g^{-1} to 0.2 μg g^{-1} soil by this method was generally between 94.3% and 121.2% (15 out of 15 determinations). The amounts of diflufenican found in the soil samples at various times after their application were mainly between 0.2 μg g^{-1} and level of detection.

Keywords: Diflufenican; herbicide; GC-ECD-method; soil; degradation

INTRODUCTION

Diflufenican, N-(2,4-difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]-3-pyridinecarboxamide (DFF), is a relatively new herbicide[1,2]. It is selective and principally absorbed by shoots of germinating seedlings. DFF inhibits carotenoid biosynthesis, and interferes indirectly with plant photosynthesis. Methods to determine DFF in plant and soil have earlier been described[3,4]. The aim of this study was to develop a simple and efficient method for determination of decomposition and transport of DFF in railway embankments after application of the herbicide for weed control.

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EXPERIMENTAL

Materials

DFF, pure certified (Dr Ehrenstorfer, Augsburg, Germany) and formulated product, 500g/l (Rhône-Poulenc, France) were used for calibration. HPLC-grade methanol, hexane, acetonitrile and toluene (Labkemi, Stockholm, Sweden) and analytical grade diethyl ether (KeboLab, Spånga, Sweden) were used. The filter used for the extract filtration was Munktell OOH, 11 cm (KeboLab, Spånga, Sweden). Solid Phase Extraction (SPE) columns Bond Elut C18, 3 ml 500 mg, and Isolut Silica, 3 ml, 500 mg, (Sorbent AB, Gothenburg, Sweden) were used for the clean-up of extracts. The soil (A) used for recovery and sensitivity tests was collected from an area not earlier treated with DFF on a railway embankment in Falköping, Sweden. Soils analysed after application of DFF to railway embankments were collected from Marmaverken (B) and Bollnäs (C and D), Sweden. Some characteristics of the soils used can be seen in Table I.

TABLE I Loss on ignition and pH for soils A-D

Depth (cm)	*A*		*B*		*C*		*D*	
	L. on ignit. (%)	*pH*	*L. on ignit. (%)*	*pH*	*L. on ignit. (%)*	*pH*	*L. on ignit. (%)*	*pH*
0-10	0.71	7.6	2.33	7.9	0.42	6.0	0.72	5.9
10-20	0.36	8.3	0.54	8.1	0.26	6.2	0.57	6.0
20-30	1.04	8.3	0.52	8.1	0.41	6.2	0.62	6.1
30-40	3.01	8.0	0.31	7.8	1.26	6.3	0.63	6.3
40-50	1.76	8.0	0.62	8.1	0.68	6.4	0.48	6.4

Instrumentation

A gas chromatograph GC 9000 with a split injector for capillary columns, an Electron Capture Detector 902 A and an auto-injector CP 911 were used. All instruments were from Chrompack Sverige AB, Nacka, Sweden.

Gas Chromatography and Conditions

A fused silica column, 50 m X 0.25mm inner diameter, CP-SIL 8 DB for pesticides (Chrompack Sverige AB) was used with helium (N47 grade, 99.997%) as the carrier gas (Air Liquide, Malmö, Sweden).

Temperature program: 1.0 min at 210°C, 5°C/min to 260°C, held for 7 min. A 0.8 µl volume of sample was injected, applying the split technique. The injector temperature was 275°C and the split flow was 25 ml/min. The ECD operated at 350°C.

Calibration

For long-term storage, a stock solution of diflufenican diluted in acetonitrile was prepared at a concentration of 100 µg ml^{-1}. Stock solutions containing DFF (1µg ml^{-1}) were diluted to prepare working standards in the required concentration ranges (0.02-2.0 µg), which were evaporated and stored at -20°C. The working standards were diluted in toluene daily or as required for use in calibration. Peak heights were obtained from the chromatograms generated by the data handling program PCI (Chrompack Sverige AB). For DFF, second order exponential calibration curves were used for calculating analyte concentrations.

Sampling

The field samplings were made from April to November when the soil was unfrozen. The samples were taken from a randomly chosen area of 25 × 40 cm within the experimental plots of 3 × 25 m. They were collected using two different spades, a small one (9 × 14 cm) and a bigger one (23 × 33 cm).

The uppermost layer (0-10 cm) was sampled by cutting a cubic sample of an area of 9 X 9 cm and 10 cm depth with the small spade. After that the whole 10 cm layer within the sample area (25 × 40 cm) was removed. Then the procedure was repeated for each of the remaining layers to be sampled. The field samples were stored in plastic bags at -20°C until analysis (within three months), when they were thawed.

Preparation of Field Samples

The samples were carefully mixed by shaking the plastic bags. One sample from each layer was taken for analysis. Ca 25 g of soil was placed in a small aluminum vessel and dried at room temperature in the laboratory. 10 g of dried soil was placed in a 100 ml centrifuge tube and 25 ml of methanol was added. The sample was shaken vigorously (220 rpm) for 30 min on a shaker. The sample was left overnight and the shaking was repeated. This procedure is called "extended shake"[5]. The sample was centrifuged for 5 min (4000 rpm) and the

extract was filtered into a 250 ml flask. The extraction was repeated once (not overnight), and 75 ml of deionised water was added to the combined extracts.

Sample Clean-up

The sample was passed through a Bond Elut C_{18} cartridge and the elute was discarded. The column was dried for 10 min under full vacuum and diflufenican was eluted with 6 ml toluene/hexane (50:50, v/v). The sample was evaporated at 30°C under air stream. For further clean-up an Isolut Si cartridge was used as follows. The column was prewashed with 3 ml of hexane. The residue obtained above was dissolved in 1 ml of toluene/hexane (50:50, v/v), passed through the column, and sample tube was washed twice with toluene/hexane (2 × 1 ml), also applied to the column. The column was washed with 5 ml of 10 % v/v diethyl ether in hexane. The elutes were discarded. DFF was eluted with 25 ml of 10 % v/v diethyl ether in hexane. The collected elute was evaporated to dryness and the residue was dissolved in 1 ml of toluene for GC analysis.

Sample Analysis

Samples were analysed by GC-ECD with a split injector. At high concentrations samples were diluted 1:10 with toluene prior to analysis. Peak heights were measured by the software automatically. Concentrations were calculated from second order exponential calibration curves. The analytical method detection limit (DL) was calculated as 3 × background noise for the matrix.

Recovery Studies

Known concentrations of DFF in 1 ml of acetonitrile (0.02-2 $\mu g^{-1}g$) were spiked into untreated soil samples. The samples were kept at room temperature for one hour prior to analysis. Extraction and analysis of spiked samples was performed as described for the field samples (above).

RESULTS

The percentage recoveries of DFF in soil (A) are summarised in Table II. The percentage recovery of DFF varied from 95.1 ± 0.7 to 113.9 ± 3.8.

These results confirm that the recoveries of DFF are consistent and reliable. Fig.1 shows two chromatograms from samples with and without DFF.

TABLE II Recoveries of Diflufenican From Spiked Soil (A)

Fortified level (µg/g dry weight)	*Recovery (%)*	*C.V. (%)*
0.02	113.9	3.7
0.1	98.4	1.6
0.2	95.1	0.7

Results are the mean percentage recovery from five replicates

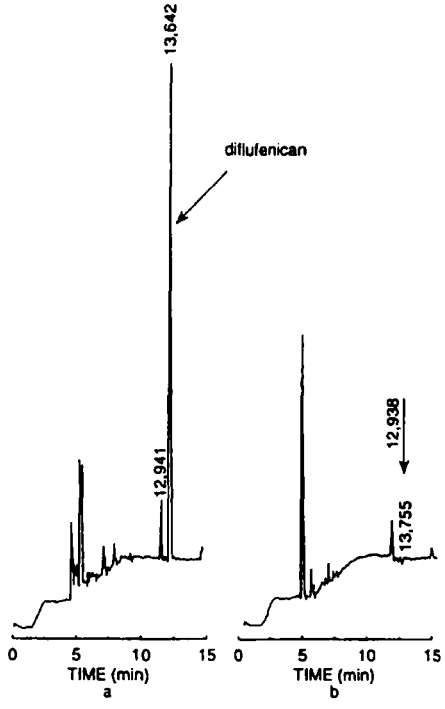

FIGURE 1 GC-ECD chromatograms from soil extracts (a) with 0.88 µg diflufenican/ml, (b) without any detectable amounts of diflufenican (< 0.001 µg/ml). 0.8µl extract injected

To control the general background level, ten soil samples from different areas in the middle part of Sweden were analysed. All of them were found to have no detectable amounts of DFF.

Fig.2 shows concentrations of DFF at two experimental sites on railway embankments in Marmaverken (B) and Bollnäs (C and D), situated about 300 km north of Stockholm. The sites were treated with 0.3, 0.2 and 0.3 kg a.i. ha^{-1}, respectively, on 20 June 1994 (B) and on 2 June 1993 (C and D).

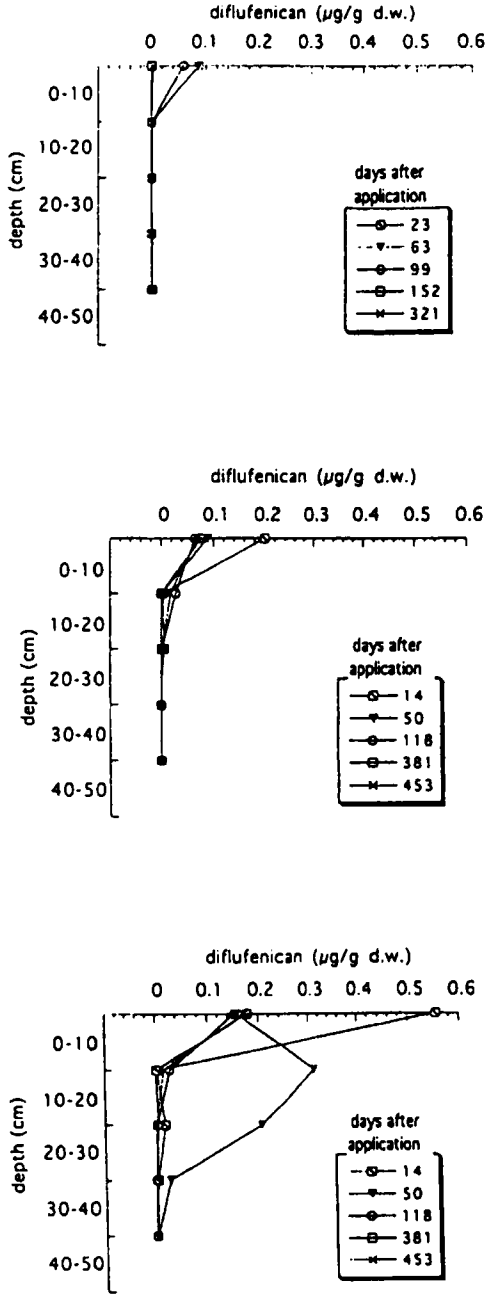

FIGURE 2 Degradation pattern of diflufenican at certain times after application at sites B-D

DISCUSSION

In this paper, a new GC-ECD method is reported which is comparatively simple and gives a satisfactory clean-up and an excellent recovery.

During this study, weathered soils treated with pesticide are used in order to examine the effectiveness of the extraction. The samples were dried in room temperature and extracted with 100% methanol. The extraction procedure, "extended shake", involves shaking for 30 minutes, standing for 12 hours and shaking for 30 minutes. This was found to be the most efficient way to increase the herbicide recovery.

The simple clean-up procedure now developed consumes much less organic solvents than those previously described. The two-step column clean-up procedure was found to be very efficient and reliable.

The experience from extraction and analysis of soil samples from DFF-treated railway embankments clearly shows that the new method will be very useful in field studies of occurrence and persistence of DFF under these conditions.

The concentrations in different railway embankments mirrors the application situation. In site B there was a dense layer of vegetation catching part of the herbicide, resulting in a low amount found in the soil. In sites C and D there was a more sparse vegetation, resulting in higher concentrations of DFF found in the soil. A certain mobility of DFF in the studied embankments are illustrated in the data shown in Figure 2. However, in neither of the sampling sites more than minor amounts were transported deeper down than 20 cm. This can be compared to findings of the herbicide diuron down to at least 150 cm depth in a comparable railway embankment[6]. DFF is degraded relatively fast, half lives < 6 months have been found, compared to diuron, which has half lives ≈ 2 years[6]. It should therefore be a small risk of DFF contamination of deeper soil layers or ground water.

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