Determination of 2,4-D Amine in Soils Using Anion Exchange Membranes

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A new method for the quantitative determination of 2,4-D in soils by use of anion exchange membranes with GC detection was developed. Preliminary investigation of ion exchange properties of pure 2,4-D acid on the membranes revealed that when a suitable solvent system is used, a quantitative recovery of 2,4-D acid can be achieved. Linear relationships between 2,4-D acid removed by the membrane and 2,4-D concentration in solutions and soils were obtained within the range tested. The developed method was successfully applied for the determination of 2,4-D amine from a commercial formulation applied on soil surfaces. The method was tested in two concentration ranges representing a typical farm-spraying application rate and a spill. The relationship between the amount of 2,4-D amine detected by membranes and the spike level on the soil surface was linear for both concentration ranges. The applicability of the method was examined for a degradation study of 2,4-D amine after a spill. The low detection limit and the simplicity of the procedure make this method very suitable for 2,4-D determination in soils.

Keywords: *2,4-D; anion exchange membranes; soil surfaces*

INTRODUCTION

The determination of pesticides in soils usually consists of several steps: pesticide extraction, sample cleanup, and determination by gas chromatography (GC) or high-pressure liquid chromatography (HPLC) (Smith et al., 1989; Gutenman et al., 1964; Greer and Shelton, 1992). Contaminating organic compounds are often coextracted and may interfere with chromatographic analysis. Therefore, frequently sample cleanup can be complicated and tedious.

Ion exchange resins have been used for extraction of ionic species from a variety of materials. The advantage of using ion exchange extraction over a solvent extraction is that it is more specific for compounds under investigation, and thus the sample requires less or no purification before chromatographic determination. Use of ion exchange and nonpolar resins for extraction of pesticides has been reported in the literature. It was observed that many pesticides can be easily adsorbed and desorbed from nonpolar resins (Basta and Olness, 1992; Junk et al., 1976; Rees and Au, 1979; Sundaram et al., 1979). Ion exchange resins were found to adsorb pesticides well but showed poor desorption characteristics (Basta and Olness, 1992; Storherr and Burke, 1963; Grover and Smith, 1974).

The goal of this work was to first explore the ability of anion exchange membranes to exchange with 2,4-D acid and then develop a rapid method for 2,4-D amine determination on soil surfaces using the ion exchange membranes. 2,4-D acid is ionized in alkaline solutions, while 2,4-D amine is ionized in water solutions. Therefore, both may be isolated from soil and other materials by an ion exchange process. The advantage of ion exchange membranes over ion exchange resins in bead form is that they are very easy to use and many samples can be prepared at the same time (Schoenau and Huang, 1991; Qian et al., 1992), while resin beads require columns and larger volumes of solvents.

Because 2,4-D amine is applied by spraying the surface of plants and the soil, our goal was to develop a method for determination of 2,4-D amine on the soil surface rather than in the bulk of the soil. By placing the membranes on the soil surface and allowing the ion exchange process to take place between the soil surface and the membrane surface, a proportion of 2,4-D amine is extracted by the membrane. Thus, knowing this proportion, the extent of soil surface contamination can be determined. The ability to extract a consistent proportion also enables evaluation of relative contamination among a group of soils.

Our work was divided into two parts. In part 1 the exchange of 2,4-D acid on the anion exchange membranes was studied. Different solvents systems were examined for adsorption and desorption of 2,4-D acid in solution and in bulk soil. In part 2 removal of 2,4-D amine by membranes from soil surfaces was investigated within two different concentration ranges, simulating a typical farm spraying of 2,4-D amine to control weeds and a 2,4-D amine spill on the soil. The developed method for 2,4-D amine determination on soil surface by membranes was applied to a degradation study of 2,4-D amine after a spill.

EXPERIMENTAL PROCEDURES

Instrumentation. GC analysis of methylated 2,4-D was performed on a Hewlett-Packard Model HP5790(A) gas chromatograph equipped with a flame ionization detector. A glass column (2.1 m × 4 mm i.d.) was packed with 5% DC200 on Chromosorb W AW DMCS 100/120 mesh. The following temperature conditions were found to be optimal for the determination of methylated 2,4-D: oven = 220 °C, detector = 250 °C, injector = 245 °C. Nitrogen at a flow rate of 40 mL/min was used as a carrier gas. Air and hydrogen flow rates were set at 300 and 30 mL/min, respectively. The injected volume was 5 μL at a sensitivity setting of 8×10^{-10} afs. The retention time of methylated 2,4-D was only 2.8 min, making the GC monitoring of membrane elution process very fast and efficient.

Materials and Methods. *Sample Preparation for GC.* Boron trifluoride methanol (BF_3–MeOH) from Supelco was used for methylation of 2,4-D. All solvents for extraction and derivatization of 2,4-D were of reagent grade.

For part 1 of our investigation, 2,4-D acid was obtained from Sigma. Standard solutions for GC analysis were prepared in

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0.5 M $NaHCO_3$ (pH adjusted to 9 with 1.5 g of NaOH/L) in the range 25–150 ppm. One milliliter of each solution was transferred to a small vial and acidified with 50% H_2SO_4 until pH 3 was achieved (or until no CO_2 bubbles appeared). Three milliliters of diethyl ether was added, the sample shaken, and after layer separation, the ether layer withdrawn and transferred to another vial. The ether extraction was repeated with a 2 mL portion of ether. Ether fractions were combined and evaporated under a gentle stream of nitrogen; 1 mL of methanol was added and the sample subjected to derivatization.

One milliliter of the solution of 2,4-D eluted from the membranes was transferred to a vial, methanol was evaporated under a gentle stream of nitrogen, and sample was treated the same way as standard (acidified, extracted with ether, evaporated, methanol added, and sample derivatized).

Methylation was carried out by adding 0.5 mL of BF_3–MeOH reagent to 1 mL of a methanolic solution of 2,4-D and heating in a water bath for 15 min. The vials were allowed to cool; 1 mL of 5% Na_2SO_4 and 1 mL of hexane were then added. After the vials were vigorously shaken, layers were allowed to separate and 5 μL of the hexane layer containing esterified 2,4-D was injected onto the GC.

2,4-D Extraction with Ion Exchange Membranes. Anion exchange membranes from BDH were used. New membranes were washed five times with 0.5 M HCl and regenerated to bicarbonate form by washing five times in 0.5 M $NaHCO_3$ (pH adjusted to 8.5 with 0.5 g of NaOH/L). Regenerated membranes were stored in deionized water.

In part 1 of our study, the membranes (18 cm^2) were placed in centrifuge tubes containing 25 mL of 2,4-D acid solution in 0.5 M $NaHCO_3$ (pH 9) and shaken overnight on a mechanical shaker. Next, the membranes were removed and the following solvents were tested for efficiency of 2,4-D elution from the membranes: 0.5 M NaOH, 0.5 M Na_2CO_3, 0.25 M Na_2CO_3 + 0.125 M $NaHCO_3$, 0.25 M Na_2CO_3 + 20% MeOH, 0.25 M Na_2CO_3 + 0.25 M Na_2SO_4, and 0.25 M Na_2CO_3 + 0.125 M $NaHCO_3$ + 20% MeOH. Membranes were shaken overnight with 25 mL of each solvent on a mechanical shaker. 2,4-D content was determined in the solution left after membrane removal and in membrane eluate to monitor the rate of adsorption and desorption of 2,4-D to and from the membrane. To test if 2,4-D acid can be extracted from the soil by the membranes, the membranes were buried in soil contaminated with 2,4-D acid. Contaminated soils were prepared by adding 2,4-D acid directly or in a methanol solution, evaporating the methanol, and then further mixing the soil. Each membrane (9 cm^2) was buried in 70 g of contaminated soil; the soil was saturated to field capacity with 0.5 M $NaHCO_3$ (pH 9) and left overnight. Membranes were removed, washed with deionized water, shaken with 25 mL of 0.25 M Na_2CO_3 + 0.125 M $NaHCO_3$ + 20% MeOH overnight on a mechanical shaker, and analyzed by GC.

In part 2 of our study, the 2,4-D amine used was a commercial formulation from IPCO containing 470 g of 2,4-D amine in 1 L. Standard solutions for GC analysis were prepared by diluting the original formulation to yield solutions of 2,4-D amine in the range 29.5–118 ppm. One milliliter of each solution was extracted and methylated the same way as described in part 1.

Two different soils, a Brown Chernozem (Haverhill) and a Dark Brown Chernozem (Sutherland), were used for investigation of method performance within a typical concentration range used to control weeds on a farm in Saskatchewan. The Brown Chernozem (Haverhill) was used for a spill concentration range. Characteristics of the soils are listed in Table 1. To simulate either a farm application of 2,4-D amine or a 2,4-D amine spill on the soil surface, 2,4-D amine solutions were sprayed onto the soil contained in 10 × 10 cm plastic trays. Determination of 2,4-D amine was achieved by placing membranes onto the soil surface. To ensure a complete contact of the membrane surface with soil, a beaker filled with water was placed on top of each membrane and the membrane was gently pushed down. The surrounding soil area was wetted with water. For a typical farm application of 2,4-D amine (commercial formulation diluted 100 times and applied at a rate of 100 L/ha), 5 mL solutions containing 2,4-D amine in the range 0.06–1.41 mg were sprayed evenly onto a 10 × 10 cm soil surface. For a 2,4-D amine spill (commercial formulation diluted 50 times), 10 mL solutions containing 2,4-D amine in the range 23.5–94.0 mg were sprayed onto a 10 × 10 cm soil surface.

Table 1. Selected Characteristics of Soils Used To Test the Method

soil	texture	pH (1:1)	organic matter (%)	cation exchange capacity (cmol/kg)
Brown Chernozem (Haverhill)	loam	8.5	2.0	19
Dark Brown Chernozem (Sutherland)	heavy clay	7.3	4.0	30

To work out the most efficient conditions for 2,4-D amine determination on the soil surface within both concentration ranges, the size of membranes, the contact time, and the volume of membrane eluate taken for GC analysis were varied. The following were tested for a farm-spraying concentration range: 7 and 16 cm^2 membranes at contact times of 1, 3, and 8 h and overnight with 15 and 25 mL of membrane eluate used for GC determination. Variables tested for a simulated spill included 2 and 7 cm^2 membranes, contact times of 5, 10, and 15 min and 1 h, and 1, 5, and 10 mL of membrane eluate taken for analysis. After membranes were removed from soil surface and soil particles were rinsed off with deionized water, all membranes were shaken with 25 mL of 0.25 M Na_2CO_3 + 0.125 M $NaHCO_3$ + 20% MeOH overnight on a mechanical shaker. Sample treatment was the same as in part 1 except for the volume of diethyl ether used for extraction. Larger volumes of membrane eluates taken for GC analysis required larger amounts of ether, which were adjusted accordingly.

Using the selected optimal conditions for 2,4-D amine determination on soil surface, degradation of 2,4-D amine within a spill concentration range was studied from 0 to 10 days. Fresh membranes were placed on the soil surface each day of testing. Areas where membranes had been previously applied were marked so that the measurements would reflect the actual 2,4-D amine residue on the soil surface. Trays containing contaminated soil were kept covered through the entire period of testing to avoid drying of the soil.

RESULTS AND DISCUSSION

Part 1: Optimization of Ion Exchange Parameters Using 2,4-D Acid. 2,4-D acid forms salts in alkaline solutions and becomes soluble at pH 9–10. Therefore, for an ion exchange process to take place, 2,4-D had to be in alkaline solution when exposed to the membrane and eluted from the membrane; 0.5 M $NaHCO_3$ (pH 9) was found suitable for 2,4-D acid solubilization.

Percentage adsorption from solutions onto the membrane was between 76 and 80% using 18 cm^2 membranes as determined by measuring 2,4-D concentration left in solutions after membrane removal. Six different solvent systems were tested for efficiency of 2,4-D elution from the membranes. The highest efficiency was obtained using 0.25 M Na_2CO_3 + 0.125 M $NaHCO_3$ mixed with 20% MeOH. A series of solutions in the range 25–150 ppm in 0.5 M $NaHCO_3$ (pH 9) was prepared and extracted by membranes, and membranes were eluted with 0.25 M Na_2CO_3 + 0.125 M $NaHCO_3$ + 20% MeOH. As seen in Figure 1, a linear relationship between 2,4-D concentration as determined by the membrane and 2,4-D concentration in solution was obtained, showing that ion exchange membranes can be used as an indicator of 2,4-D contamination in solutions. The slope of 0.24 indicated that the propor-

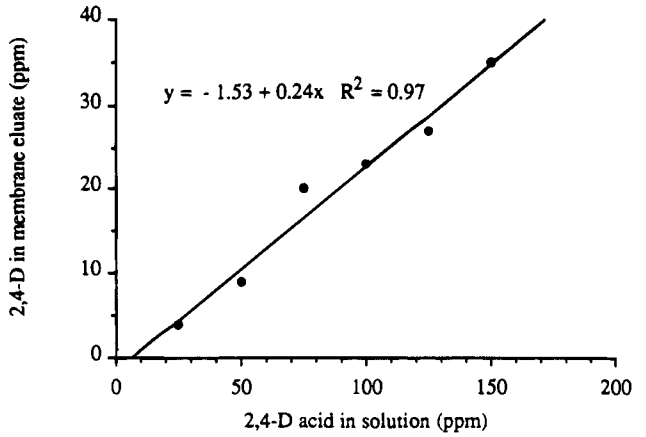

Figure 1. Relationship between 2,4-D acid detected by anion exchange membranes (18 cm^2) and 2,4-D concentration in solution.

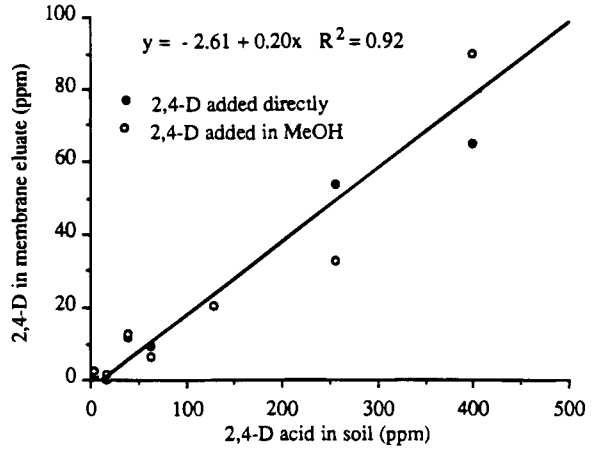

Figure 2. Relationship between 2,4-D acid detected by anion exchange membranes (9 cm^2) and 2,4-D spike level in the bulk soil.

tion of 2,4-D acid extracted from solutions by the membranes was near 25% and that it was constant in the range tested. It has been reported that 2,4-D adsorbs onto ion exchange materials but cannot be desorbed (Basta and Olness, 1992; Storherr and Burke, 1963; Grover and Smith, 1974). We found that by adjusting solvent composition a consistent rate of desorption can be achieved. Used membranes were washed with consecutive 25 mL portions of 0.25 M Na_2CO_3 + 0.125 M $NaHCO_3$ + 20% MeOH, and after five washes 75–85% of 2,4-D was recovered. Shaking times longer than overnight did not increase the amount of 2,4-D eluted. Further washes would probably clean the membranes; however, the use of new membranes for reliable results is recommended for each test.

To test if 2,4-D can be extracted from soils by the membranes, a wide range of 2,4-D acid contamination in the soil, from 4 to 400 ppm, was examined. Membranes (9 cm^2) were buried directly in the soil. The relationship between 2,4-D acid removed from the soil by the membranes and 2,4-D spike level in soil was linear over the entire range tested (see Figure 2), demonstrating the diffusion of 2,4-D ions from the soil toward the membrane and accumulation on the membrane in proportion to contamination rate.

Part 2: Determination of 2,4-D Amine on Soil Surfaces. Farm application of 2,4-D to control broadleaf weeds is accomplished by spraying 2,4-D onto the plant and soil surface. Therefore, placing the membranes on the soil surface rather than burying the membranes in the soil was examined. 2,4-D amine salt is soluble in water; therefore, after the membrane was placed on the soil surface, it was wetted with deionized water. However, for it to be extracted from the membrane and solubilized, the same solvent system as for 2,4-D acid (0.25 M Na_2CO_3 + 0.125 M $NaHCO_3$ + 20% MeOH) was required. By varying membrane size, contact time, and volume of membrane eluate used for GC analysis, we found the most suitable conditions for 2,4-D amine determination. As seen in the example for a farm-spraying concentration range, the amount of 2,4-D amine removed by the membrane from the soil surface was linear with the soil surface spike level and it increased with increased contact time (Figure 3). For this experiment, 7 cm^2 membranes were used and 15 mL of membrane eluate was taken for GC analysis. It was also found that the amount of 2,4-D amine removed by the membrane from the soil surface increased when a larger membrane was used and that the sensitivity of the GC analysis improved with increased volume of membrane eluate. Similar relationships were obtained for all combinations of membrane size, contact time, and volume of membrane eluate. With the preference for shorter contact times, the following conditions were selected for fast, reliable, and sensitive 2,4-D amine determination on soil surfaces: in a farm-spraying concentration range a 3 h test using 16 cm^2 membranes and 25 mL membrane eluate taken for GC analysis; because of a higher 2,4-D concentration in a spill concentration range, a contact time as short as 10 min using small 2 cm^2 membranes and 10 mL of membrane eluate taken for GC analysis were found to be optimal.

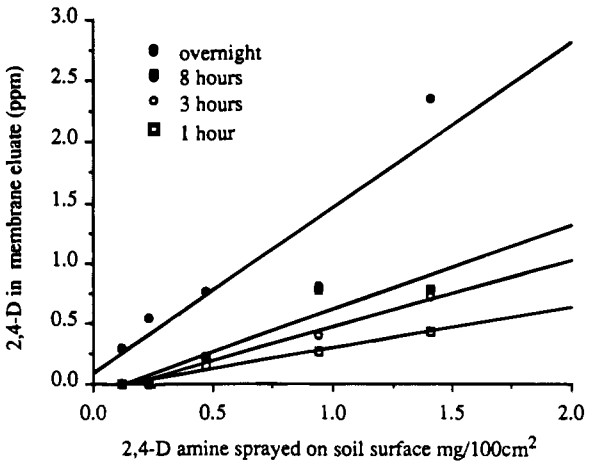

Figure 3. Relationship between 2,4-D amine detected by membranes and the soil surface spike level at different contact times for a typical farm spraying concentration range (7 cm^2 membranes used and 15 mL of membrane eluate taken for GC analysis).

Using the developed parameters, standard curves were constructed for both concentration ranges. Standard curves obtained for two different soils within a farm-spraying concentration range are presented in Figure 4. The relationship between 2,4-D amine in membrane eluate and the soil surface application rate was linear. The regression lines for both soils were not different at a 95% confidence level, indicating that a single standard curve could be used for 2,4-D amine determination on the surfaces of these two substantially different soils. Further testing of more diverse types would be required to determine if this is truly independent of soil type. A standard curve for a spill concentration range was established using one soil; it was linear

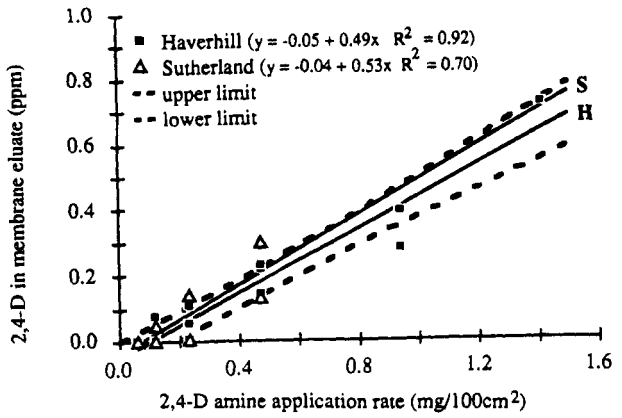

Figure 4. Standard curves for 2,4-D amine determination on soil surfaces (H, Brown Chernozem (Haverhill); S, Dark Brown Chernozem (Sutherland)) within a farm spraying concentration range (3 h contact time, 16 cm^2 membranes, 25 mL of membrane eluate taken for GC analysis).

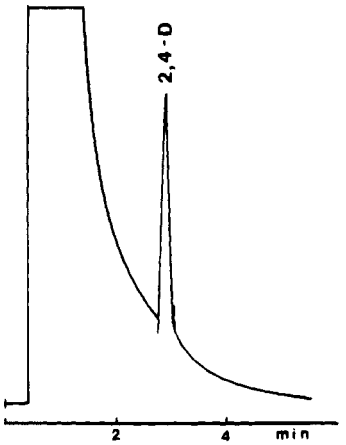

Figure 5. Gas chromatogram of methylated 2,4-D amine standard; 5 μL of 59 ppm solution injected at 8×10^{-10} afs. Column (2.1 m × 4 mm i.d.) was packed with 5% DC200 on Chromosorb W AW DMCS 100/120 mesh; column temperature was 220 °C, and nitrogen flow rate was 40 mL/min.

within the range tested ($y = -1.525 + 0.095x$, $R^2 = 0.978$). Thus, by relating the surface contamination with the concentration of 2,4-D in membrane eluate, we achieved quantification of this contamination. A coefficient of variation of 7.2% or below ($n = 5$) in the Haverhill soil indicated good reproducibility of the method and represented variability within this soil type. Coefficients of variation were evaluated by repeating the 2,4-D amine determination using the developed parameters at selected soil surface contamination levels. For contamination levels of 1.41, 0.94, and 94.0 mg/100 cm^2, the concentrations of 2,4-D amine in membrane eluate were 0.72 ± 0.05, 0.33 ± 0.02, and 7.86 ± 0.57 ppm, respectively. All values in Figures 1–4 and 9 are the average of two replications.

One batch of membranes from BDH was used. Membranes from Bio-Rad were also tested, and the results of 2,4-D amine extraction from the soil surface were similar. The BDH membranes were selected for this study because they were more rigid and therefore easier to handle. However, every batch of membranes should be examined and standard curves determined because of the possible differences between membranes from different manufacturers.

The GC retention time of methylated 2,4-D was only 2.8 min (Figure 5), making the GC monitoring of 2,4-D concentration in membrane eluate fast and efficient.

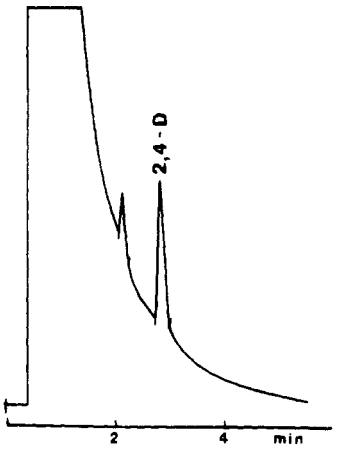

Figure 6. Gas chromatogram of methylated membrane eluate obtained from the soil surface spiked with 47 mg of 2,4-D amine/100 cm^2 (10 min contact time, 2 cm^2 membrane, 10 mL of membrane eluate taken for GC analysis). GC conditions were as in Figure 5.

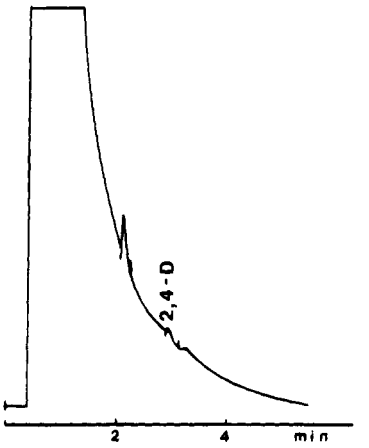

Figure 7. Gas chromatogram of methylated membrane eluate obtained from the soil surface spiked with 0.12 mg of 2,4-D amine/100 cm^2 (3 h contact time, 16 cm^2 membrane, 25 mL of membrane eluate taken for GC analysis). GC conditions were as in Figure 5.

Because of the purity of the methylated membrane eluate injected onto GC, the column performance was excellent through the entire investigation and the column packing did not have to be replaced (Figures 6 and 7).

Detection Limit and Recovery. The detection limit of ca. 0.09 kg/ha found for this method is close to the values reported in the literature for the solvent extraction procedures: 0.02 kg/ha or 0.02 mg/kg (Smith et al., 1989) and 0.07 kg/ha or 0.05 mg/kg (Smith et al., 1991). Assuming a bulk density of 1.3 g/cm^3 and a standard sampling depth of 10 cm, the detection limit of 0.09 kg/ha would be equivalent to 0.069 mg/kg. The detection limit was estimated from the standard curve constructed from combined results from both soils tested for the farm-spraying concentration range. The value was calculated as a mean of the lowest concentration tested for which a detectable amount of 2,4-D amine was found by this method (Figure 7) and the next lower concentration tested for which no 2,4-D amine was detected (Figure 8). However, if needed, the detection limit can be improved by increasing any of the variables discussed above such as membrane size, contact time, or volume of membrane eluate taken for GC analysis. Further improvement of the detection limit can be achieved with the use of electron capture detection,

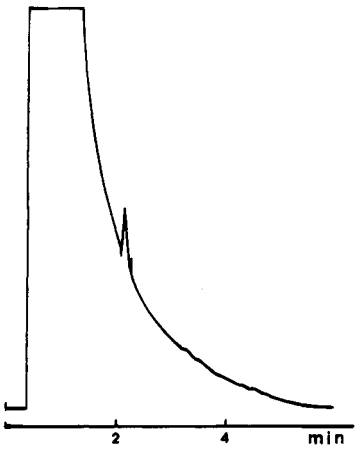

Figure 8. Gas chromatogram of methylated membrane eluate obtained from the soil surface spiked with 0.06 mg of 2,4-D amine/100 cm^2. Test and GC conditions were as in Figures 7 and 5, respectively.

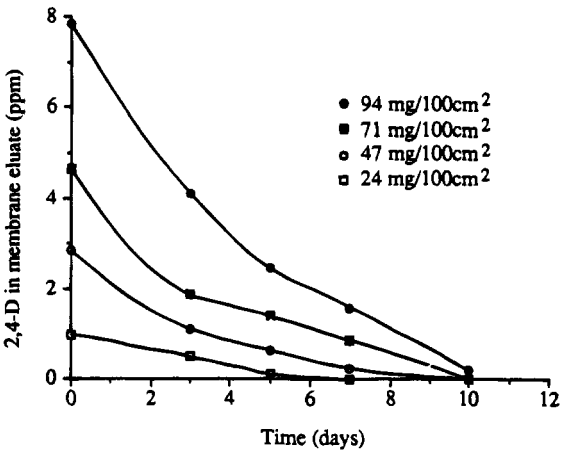

Figure 9. Degradation curves of 2,4-D amine as determined using anion exchange membranes.

especially after derivatization that increases an electron capture response such as pentafluorobenzylation or HPLC of UV or fluorescence sensitive derivatives (Roseboom et al., 1982).

Recoveries of 2,4-D amine from the soil surface were 5.3 and 3.1% for farm-spraying and spill concentration ranges, respectively. These values were estimated by relating the amount of 2,4-D amine found in the membrane eluate to the amount of 2,4-D amine on the soil surface beneath the membrane used (16 and 2 cm^2 for farm-spraying and spill concentration ranges, respectively). Compared to the solvent extraction methods (Smith et al., 1989), these recovery values are lower; however, in this method, we are interested in extracting a consistent proportion of 2,4-D amine, to act as an index of surface contamination, rather than in extracting a total amount of 2,4-D. As with the detection limit, recovery could be improved by increasing any of the three parameters, i.e. membrane size, contact time, or volume of membrane eluate taken for GC analysis. Also, subsequent elutions of the membranes would increase the amount of 2,4-D desorbed from the membranes as discussed in part 1. However, to keep the method as simple and fast as possible, one membrane elution was used and the above-mentioned parameters were adjusted so that chromatograms within a quantifiable range were obtained.

2,4-D Amine Degradation on Soil Surfaces. The present study demonstrated that the anion exchange membranes are a useful tool for 2,4-D determination in soils. To further examine the applicability of the method, degradation of 2,4-D amine within a spill concentration range was investigated. As seen in Figure 9, at the lowest concentration tested (23.5 mg/100 cm^2) no 2,4-D amine was detected on the soil surface by membranes after 5 days, while 10 days was required for 2,4-D amine at the highest concentration tested (94.0 mg/100 cm^2) to be degraded to a near zero level. It is known that 2,4-D is rapidly degraded in the soil by soil microorganisms (Smith, 1989). When a different chemical form of herbicide other than acid is applied, it undergoes a fast hydrolysis or dissociation to the phenoxyalkanoic ion prior to biological breakdown. The rate of 2,4-D breakdown depends on a variety of factors such as soil type, temperature, moisture, pH, 2,4-D formulation, concentration, and repeat treatments (Smith, 1989); however, these factors were not investigated. Our goal was to demonstrate that the developed method can be applied for monitoring 2,4-D amine degradation. Our results are in good agreement with results of persistence studies carried out in a variety of Saskatchewan soils under laboratory conditions at 20 °C and 85% of field capacity with values reported for the half-life ranging from <7 to 20 days (Smith et al., 1991). There is a possibility that, with time, the nondegraded residues become bound to the soil particles and therefore might not be extracted by the membranes. We consider that the amount of 2,4-D amine detected by the membranes represented the labile portion of 2,4-D amine present on the soil surface. Comparable rates of degradation for both soluble and sorbed 2,4-D in soil have been reported within 20 h after bacterial inoculation, presumably as a result of 2,4-D desorption and solubilization (Greer and Shelton, 1992).

Conclusions. The developed method for 2,4-D amine determination on soil surfaces using anion exchange membranes is very fast and simple and does not require any special skills. Soil samples are not collected, and no solvent extraction of soil is required. Membranes are simply placed in contact with moist soil surface after 2,4-D application. After membrane removal from the soil, the remaining steps, i.e. 2,4-D elution from the membranes and GC analysis, are performed in an analytical laboratory. However, it should be noted that because in this method only a proportion of 2,4-D amine from the soil surface is extracted, the method is intended as a semiquantitative technique for rapid screening of the 2,4-D surface contamination. Despite its shortcomings, such as somewhat higher detection limit and lower recovery, compared to traditional solvent extraction procedures, the developed method offers the advantage of being simple and rapid. Also, because of this method's limitation to the 2,4-D soil surface contamination, for the determination of 2,4-D residues in the bulk soil the traditional solvent extraction would be required.

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