Quantitative Determination of the Acidic Metabolites of Dacthal in Ground Water by Strong Anion Exchange Solid-Phase Extraction

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Solid-phase extraction using strong anion exchange disks was evaluated as an alternative extraction method to conventional liquid–liquid extraction (LLE) for the quantitative analysis of the herbicide Dacthal (DCPA) and its mono- and dicarboxylic acid metabolites in ground water. The average recoveries of DCPA and its acid metabolites from deionized water were 93.7 ± 2.6% and 85.6 ± 2.5%, respectively. The detection limit of the SAX disk method is 0.05 μg/L for a 100 mL water sample. While no DCPA was detected in ground water from the Malheur River Basin in eastern Oregon, the total concentrations of the acid metabolites of DCPA in 100 mL samples of ground water ranged from less than the detection limit (0.05 μg/L) to 158.2 μg/L and were in good agreement with those determined by means of conventional LLE.

Keywords: *Solid-phase extraction; metabolites; ground water*

INTRODUCTION

In the Malheur River Basin of eastern Oregon, the use of the herbicide Dacthal (dimethyl 2,3,5,6-tetrachloroterephthalate), or DCPA, for the production of onions has resulted in the contamination of a ground water aquifer. In a recent national survey of ground waters, the diacid metabolite of DCPA was the most frequently detected pesticide residue (U.S. EPA, 1990), presumably due to its high water solubility and relative stability in soil environments (Ross et al., 1990; Wettasinghe and Tinsley, 1993).

In the soil environment, DCPA is hydrolyzed (Figure 1) to give the corresponding mono- (1-methyl-4-carboxyl-2,3,5,6-tetrachloroterephthalate) and diacid (2,3,5,6-tetrachloroterephthalate) metabolites (Gershon and McClure, 1966). The degradation of DCPA to the monoacid is considered a biologically mediated reaction, while the conversion of the monoacid to the diacid metabolite potentially occurs by both biotic and abiotic processes (Hurto and Turgeon, 1979; Tweedy et al., 1968; Ross et al., 1990; Wettasinghe and Tinsley, 1993). While estimates of the half-life of DCPA in soil range from 11 to 295 days depending upon soil conditions, DCPA has been detected in soils up to 12 months after application (Ross et al., 1990; Miller et al., 1978). Ross et al. (1990) found the monoacid metabolite to be less stable than the diacid metabolite, with the diacid metabolite accounting for up to 12% of the mass of DCPA applied to soils. Furthermore, Wettasinghe and Tinsley (1993) found virtually no degradation of the diacid metabolite over a period of 300 days in batch soil experiments.

At present, concentrations of DCPA and its metabolites in water are determined by means of conventional liquid–liquid extraction (LLE) prior to separation by gas chromatography (GC) and electron capture detection (ECD) (EPA Method 515.1, 1988). Unfortunately, conventional LLE is a labor-intensive, time-consuming, and costly procedure that requires relatively large volumes of solvents.

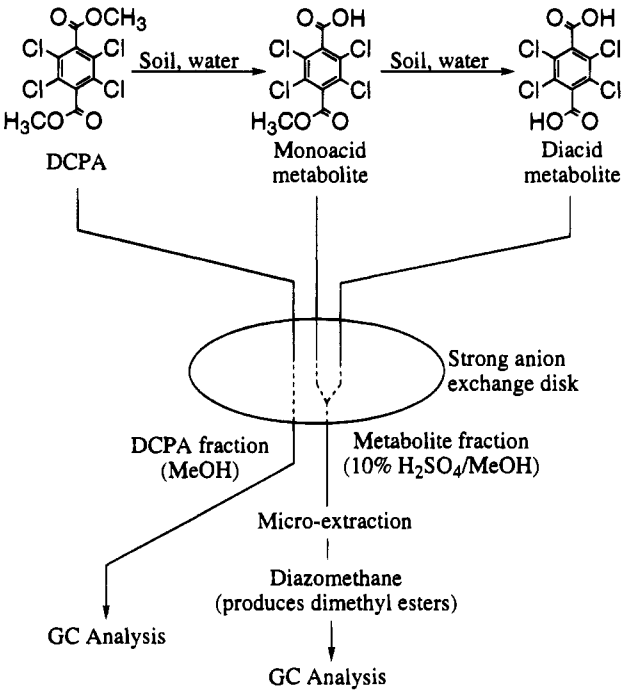

Figure 1. Generalized pathway for the degradation of DCPA to mono- and diacid metabolites in the environment and the analytical solid-phase (anion exchange) extraction and derivatization procedure for the fractionation of DCPA from its carboxylic acid metabolites in ground water.

Solid-phase extraction technology has a number of advantages over conventional extraction methods, especially liquid–liquid extraction. Because solid-phase extraction concentrates analytes from water samples onto a relatively small mass of sorbent, relatively small volumes (5–20 mL) of organic solvents are required to elute analytes compared to that needed for liquid–liquid extraction (100–1000 mL). In addition, solid-phase extraction is a faster technique than liquid–liquid extraction. Together, reduced solvent use and shorter analysis times make solid-phase extraction more cost-effective than conventional liquid–liquid extractions.

Solid-phase extraction medium was released in a membrane or disk format in 1989 and has advantages

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over the cartridge format including higher sample flow rates and less back pressure due to the high cross-sectional area of the disk. Compared to cartridge formats, disks have improved mass transfer characteristics due to their smaller (8 mm) sorbent particles. In addition, bed channeling is eliminated for disks because the sorbent particles are immobilized in a Teflon mesh (Hagen et al., 1990).

Using C_8 and C_{18} bonded-phase silica disks, Crepeau et al. (1991) found recoveries of 70–100% for pesticides spiked into soil leachate. Less variability in organochlorine, triazine, and other neutral pesticides recovery was found by Davi et al. (1992) using C_8 disks for extraction than by liquid–liquid extraction. Triazine, organophosphorus, phenylurea, and carbamate pesticides were recovered (80–125%) from river and sea water by C_{18} disks (Barcelo et al., 1993). Chiron et al. (1994) reported recoveries for 2,4-dichlorophenoxyacetic acid (2,4-D) of 74% and 82% from river water with C_{18} and SDB disks, respectively, in an on-line HPLC system with diode array detection.

The versatility of SPE disks is further illustrated with their use for preserving and shipping samples from the field to the laboratory. The use of SPE media, including disks, has been successfully demonstrated for preserving hydrocarbons and pesticides (Evans et al., 1991; Green and Le Pape, 1987; Senseman et al., 1993).

In this paper, we present an alternative method to the conventional LLE method for the isolation of DCPA and its acidic metabolites in ground water. Solid-phase extraction using strong anion exchange (SAX) disks was combined with gas chromatography with electron capture detection to provide a simple, specific procedure for the fractionation and quantitative determination of trace levels of both DCPA and its acid metabolites in ground water. Because the diacid metabolite is the dominant form of DCPA found in ground water (Wettasinghe and Tinsley, 1993), the determination of the diacid metabolite in this study was emphasized while DCPA and the monoacid metabolite were of secondary interest. For this study, the concentrations of DCPA and its metabolites are determined using solid-phase extraction disks and compared to those determined by conventional liquid–liquid extraction.

EXPERIMENTAL PROCEDURES

Reagents. A standard of the diacid metabolite of DCPA (100% purity) was obtained from Chem Service (West Chester, PA). A standard of the monoacid metabolite of DCPA (99.7% purity) was obtained from the EPA (Research Triangle Park, NC). A standard of DCPA (95% purity) was also obtained from ChemService.

The precursor reagent (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, or Diazald) for making diazomethane was obtained from Aldrich (Milwaukee, WI). The method of McKay et al. (1950) was used to prepare diazopropane from 1-N-propyl-1-nitroso-3-nitroguanidine that was also obtained from Aldrich. Derivatization of the diacid and monoacid metabolites was performed using diazomethane. The dipropyl ester of DCPA (dipropyl 2,3,5,6-tetrachloroterephthalate), used as the internal standard in this study, was prepared from the diacid standard using diazopropane as the derivatization reagent. **CAUTION:** Precursors to diazomethane and diazopropane are carcinogenic. The conditions for preparing diazomethane and diazopropane are potentially explosive. All procedures and work using these reagents should be performed in a laboratory hood, and proper laboratory clothing should be worn.

Samples. The ground water samples used for the survey were collected from domestic wells from private homes in the Malheur River Basin in eastern Oregon by the Soil Conservation Service, Ontario, OR. All samples were collected from taps nearest the well pump after running the tap for only 10 min to flush the lines since the wells are in constant use. No reliable information is available on the depth and construction of each well sampled for this study. All samples were collected in baked glass bottles with aluminum-lined lids and neither filtered nor preserved. The samples were stored in the dark, refrigerated at 4 °C, and analyzed within 2 weeks of the sampling date. A surface water, found not to contain DCPA or its metabolites, was obtained as a grab sample from Oak Creek near Corvallis, OR, and used as a blank sample for recovery and detection limit experiments.

Solid-Phase Extraction. Three different types of solid-phase extraction disks including C_{18} bonded phase silica (C_{18}), polystyrene divinylbenzene copolymer (SDB), and strong anion exchange (SAX) disks were purchased from Varian (Sugarland, TX) and evaluated to determine the most suitable phase for the efficient recovery of the diacid metabolite of Dacthal. The 47 mm disks were placed in a glass, Teflon, and stainless steel extraction apparatus kindly donated by 3M (Minneapolis, MN).

Initial spike and recovery experiments were performed using the C_{18} and SDB phases. The 47 mm disks were first preconditioned with successive rinses of 7 mL each of acetone, dichloromethane, and ethyl acetate. Deionized water samples (100 mL) were spiked with the diacid metabolite to give a concentration of 2 μg/L, acidified to pH 2 using concentrated HCl, amended with 10 g of sodium sulfate, and applied to the 47 mm C_{18} and SDB disks. Elution of the C_{18} and SDB disks was performed by pulling 3 × 5 mL of dichloromethane through each disk, followed by a 7 mL aliquot of ethyl acetate. The dichloromethane/ethyl acetate extracts were derivatized with diazomethane at room temperature until the yellow color persisted and spiked with the dipropyl ester internal standard for quantitation.

The SAX disks were first preconditioned with a 10 mL aliquot of acetone and then dried under vacuum suction. The second preconditioning step is the addition of a 10 mL aliquot of 1 N HCl/MeOH, which is added to ensure that the disk is uniformly wetted and that chloride is the counterion of the SAX phase. At this point it is important that the disk be kept wet and not allowed to dry until the sample has been fully extracted. The last preconditioning step is the addition of 2 × 10 mL of deionized water. After completion of the preconditioning steps, the sample is added to the reservoir and pulled through the disk at full vacuum (approximately 100 mL/min), and the water that passes through the disk is then discarded. The disks are then air-dried for 1 min using vacuum suction.

Elution of the SAX disk takes place in two steps to fractionate the parent compound, DCPA, from the monoacid and diacid metabolites. In the first elution step, a total of 12 mL of methanol is used to elute DCPA. The first 7 mL is used to rinse the sample bottle before it is applied to the disk, while the last 5 mL is applied directly to the disk. Each aliquot of methanol is allowed to soak into the disk for 1 min before it is pulled through by vacuum. To prepare the methanol fraction for analysis, 3 g of granular anhydrous sodium sulfate is added to the methanol extracts and placed on a heat plate at 60 °C, where the extract is evaporated to near dryness under a stream of dry nitrogen. The sample is then brought to approximately 1 mL in ethyl acetate and spiked with 1.2 mg of the dipropyl ester internal standard.

In the second elution step, the monoacid and diacid metabolites are eluted together from the SAX disk using 4 × 4 mL aliquots of 10% (v/v) H_2SO_4 in MeOH. Each aliquot of solvent is allowed to soak into the disk for 1 min before it is pulled through by vacuum. The H_2SO_4/MeOH extracts are then combined and placed on a heated plate at 60 °C and evaporated to approximately 3 mL under a stream of dry nitrogen gas. Because H_2SO_4/MeOH is not compatible with diazomethane, a liquid–liquid microextraction is used to transfer the analyte into diethyl ether. To perform the microextraction, a 10 mL aliquot of deionized water is added to the vial containing the H_2SO_4/MeOH extract so that two distinct layers form. Next, the extraction is performed using a 6 mL aliquot of diethyl ether, followed by two additional extractions, each using 4 mL of diethyl ether. The ether

fractions are transferred to a clean vial and combined before derivatizing with 1 mL of diazomethane. Once derivatized, the sample is evaporated to near dryness under a stream of dry nitrogen gas, diluted to 1 mL in ethyl acetate, and spiked with 1.2 μg of the dipropyl ester internal standard.

Breakthrough Experiments. To assess the potential for analyte breakthrough during sample extraction, two types of experiments were employed using 2 μg/L of the diacid metabolite. In the first type of breakthrough experiment, a liquid–liquid extraction was performed on the water that had passed through the disk. The collected water was transferred to a 250 mL separatory funnel. In the case of the SAX disk, it was necessary to adjust the pH to 2. A 3 × 40 mL diethyl ether extraction was then performed, and the water fraction was discarded. The diethyl ether fractions were combined and concentrated to 5 mL using a steam bath, derivatized with 1 mL of diazomethane, and spiked with 1.2 μg of the dipropyl ester internal standard.

In the second type of breakthrough experiment, two disks were stacked together and eluted separately to quantify the analyte that had passed through the first disk and been retained by the second disk. For this type of experiment, single samples of 100, 200, and 500 mL and 1 L, which were spiked to give 38 μg/L of the diacid metabolite standard, were passed through the stacked disks in the extraction apparatus. After sample extraction, the two disks were separated and each disk was placed on a clean extraction base and eluted in a manner appropriate for disk type, as described above.

Spike and Recovery. A series of spike and recovery experiments was performed on deionized water and a blank surface water to determine the accuracy and precision of the SAX isolation procedure. Spike recoveries of the diacid metabolite were evaluated at two concentrations. Five replicate sample extractions were performed for 100 mL of both deionized water and a blank surface water that were each spiked to give a diacid metabolite concentration of 38 μg/L. In addition, five 500 mL replicate sample extractions were performed on the blank surface water that had been spiked to give a lower diacid metabolite concentration of 0.1 μg/L. To compare the precision of the SAX extraction method to that of LLE, four replicate aliquots of a composite ground water sample taken from the Malheur River Basin of eastern Oregon were analyzed by both the SAX disk method and LLE.

To determine the detection and quantitation limits of the method, single samples at five concentrations (0.02, 0.05, 0.07, 0.14, and 0.21 μg/L) of the diacid metabolite in distilled water were extracted using a single SAX disk.

Although the diacid metabolite is the dominant species in ground water (Wettasinghe and Tinsley, 1993), the monoacid metabolite and DCPA may be present in environmental samples. To test the ability of the SAX phase to quantitatively retain DCPA from water, a set of four replicate samples of deionized water were spiked to yield a DCPA concentration of 25.2 μg/L and extracted by the SAX disk method. Both the methanol and H_2SO_4/MeOH fractions from the disk were collected and analyzed for DCPA. In addition, the ability of a single SAX disk to fractionate DCPA from its acid metabolites was tested by extracting five replicate 100 mL samples of deionized water, spiked to give 38 μg/L of the diacid metabolite, 29.3 μg/L of the monoacid metabolite, and 25.2 μg/L of DCPA. The methanol fraction was retained and analyzed for DCPA, while the H_2SO_4/MeOH fraction was analyzed for the acid metabolites of DCPA.

Conventional Liquid–Liquid Extraction. Conventional LLE (EPA Method 515.1, 1988) was performed on the nine ground water samples collected from the Malheur River Basin of eastern Oregon to validate the SAX disk method. The procedure used for LLE is briefly described. A 400 mL sample is acidified to pH 2 using 50% sulfuric acid and amended with 40 g of NaCl. In a 1 L separatory funnel the sample is extracted with 3 × 150 mL aliquots of diethyl ether. The diethyl ether extracts are combined and dried over acidic sodium sulfate. Using 1 mL of hexane as a keeper solvent, the diethyl ether extract is evaporated to approximately 5 mL under a stream of dry nitrogen. After derivatization with diazomethane, the sample is evaporated to 0.5 mL and then diluted with hexane to give a final total extract volume of 4 mL.

Table 1. Recovery and Breakthrough of the Diacid Metabolite at 2 μg/L on 47 mm C_{18}, SDB, and SAX Disks

	disk phase		
	C_{18}	SDB	SAX
recovered from disk (%)	nd[a]	63	85
breakthrough[b] (%)	95	43	nd[c]

[a] nd, none detected. [b] Breakthrough measured by liquid–liquid extraction. [c] Breakthrough measured by liquid–liquid extraction and a stacked disk experiment.

Chromatographic Analysis. Chromatographic separations were performed with a Hewlett-Packard Model 5890 Series II gas chromatograph equipped with an SE-54 column (30 m × 0.25 mm × 0.25 μm film thickness; Hewlett-Packard). The oven temperature program consisted of an initial temperature of 130 °C, which was held for 3 min. The oven was then ramped at 10 °C/min to 200 °C, followed by a 4 °C/min ramp to 240 °C, followed lastly by a 25 °C/min ramp to a final temperature of 270 °C, which was then held for 3 min. Injection conditions included an injector temperature of 260 °C, splitless injection, and an injection volume of 1 mL. The ^{63}Ni electron capture detector was operated at a temperature of 300 °C. A Hewlett-Packard mass selective detector Model 5972 was used to confirm the identity of DCPA and the dimethyl ester of the acid metabolites in samples of ground water. The mass spectrometer was operated in electron impact ionization (70 eV) mode under full scan conditions (50–400 amu).

Quantitation. The quantitation of DCPA and the mono- and diacid metabolites isolated by the SAX disk method was performed using conventional internal standard gas chromatography calibration techniques. A known amount of the dipropyl ester of the diacid metabolite standard, which was used as an internal standard, was spiked into each sample extract at the end of the isolation and concentration procedure for quantitation purposes. The dipropyl ester of the diacid metabolite was chosen as the internal standard because it does not occur in commercial products of DCPA and its chromatographic behavior is similar to that of the dimethyl ester.

Samples for the five-point calibration curve were constructed for quantitation of field samples by spiking 0.1–20 μg of the diacid metabolite standard into 16 mL of 10% (v/v) H_2SO_4/MeOH and extracted using the microextraction method described above. After derivatization with diazomethane to form the dimethyl ester, each extract was spiked with the dipropyl ester internal standard. Concentrations of DCPA, the monoacid metabolite, and the diacid metabolite were determined from the calibration curve constructed from the methylated diacid metabolite standard.

A second five-point quantitation curve was constructed for quantitating the low amount of acid metabolites in distilled water samples prepared for the purpose of determining the method's detection and quantitation limits. The amount of diacid metabolite standard spiked into 16 mL of 10% (v/v) H_2SO_4/MeOH ranged from 0.002 to 2.1 μg. This level was not used for quantitating metabolite concentrations in field samples, since field sample concentrations were typically higher than the levels represented in this curve.

RESULTS AND DISCUSSION

Solid-Phase Extraction. Initial mass balance experiments with the three disk phases used in this study indicated that C_{18} and SDB phases did not quantitatively isolate the diacid metabolite from 100 mL samples of water (Table 1). None of the diacid metabolite was recovered by C_{18} disks from duplicate 100 mL sample extractions. Poor recovery was due to breakthrough of the diacid metabolite, with 95% recovered by LLE from water that had passed through the disk. For SDB disks,

Table 2. Recovery of the Diacid Metabolite of DCPA at 0.1 and 38 μg/L from Deionized Water and a Blank Surface Water Using a 47 mm SAX Disk

spike level (mg/L)	sample size (mL)	% recovery[a]	
		deionized water	surface water
0.1	500	na[b]	84.5 ± 1.3
38.0	100	81.1 ± 0.9	80.1 ± 2.3

[a] Recoveries based on five replicate sample extractions. [b] na, not analyzed.

the average recovery of the diacid metabolites was 63%, with 43% breakthrough determined by LLE. Even though the water samples had been amended with salt and acidified to pH, it is apparent that the capacity of the C_{18} and SDB resins had been exceeded even for relatively small sample sizes (100 mL).

By contrast, a single SAX disk gave 85% recovery of the diacid metabolite in the 10% H_2SO_4/MeOH fraction for single samples of 100 mL to 1 L. Unlike the C_{18} and SDB phases, no breakthrough of the diacid metabolite was detected either by LLE or from the bottom disk in a stacked disk experiment. In addition, none of the diacid metabolite was detected in the methanol fraction from the SAX disk. Apparently, the remaining 15% of the mass of diacid metabolite is strongly retained by the SAX disk. Increasing the total volume of the 10% H_2SO_4/MeOH to 32 mL increased recovery to 95%. However, the increased elution volume (32 mL) required to achieve a 95% recovery of the diacid metabolite was considered to be impractical because of the increased handling difficulty and time required for analysis.

Quantitation and Detection. Extractions of deionized water and the blank surface water were performed without the addition of DCPA, its acid metabolites, or the dipropyl ester internal standard. Both deionized water and the blank surface water were found not to contain any of the analytes or any coeluting interferences. Therefore, the surface water was used as a blank sample to determine the detection and quantitation limits of the method. The detection limit of the method, based on a signal-to-noise ratio of 3, was 5 pg/μL injected, which corresponds to a concentration of 0.05 μg/L for a 100 mL sample. The quantitation limit, based on a signal-to-noise ratio of 10, corresponds to a concentration of 0.14 μg/L for 100 mL samples. The detection and quantitation limits of the LLE method for 400 mL samples were 0.1 and 0.3 μg/L, respectively.

Recovery and Precision. Spike and recovery experiments for the diacid metabolite were performed at two different diacid metabolite concentrations using distilled water and an uncontaminated surface water (Table 2). Average recovery of the diacid metabolite from five replicate samples spiked at a concentration of 38 μg/L in 100 mL of deionized water was 81.1 ± 0.9%. The average recovery of the diacid metabolite in surface water at 0.1 μg/L was 84.5 ± 1.3%, while the average recovery of the diacid metabolite at 38 μg/L in surface water was 80.1 ± 2.3%. When the average recoveries were pooled together, the 10 surface water samples yielded an average diacid metabolite recovery of 82.6 ± 2.8%. By comparison, the average recovery of 10 μg/L of the diacid metabolite from duplicate 400 mL samples of deionized water determined by the conventional LLE method was 88%.

Because environmental samples may potentially contain DCPA as well as its metabolites, a series of samples was analyzed to determine the ability of the SAX disk method to recover DCPA from water. In a set of four

Table 3. Fractionation and Recovery of DCPA and the Monoacid Diacid Metabolites of DCPA[a]

	spike level (μg/L)	sample size (mL)	% recovery
DCPA[b]	25.2	100	93.7 ± 2.6
mono- and diacid metabolites[c]	67.3	100	85.6 ± 2.5

[a] DCPA, monoacid, and diacid were spiked together into deionized water and fractionated as described under Experimental Procedures; recovery was determined from five replicate sample extractions. [b] Eluted in the methanol (first) fraction from the SAX disk. [c] Eluted in the 10% H_2SO_4/MeOH (second) fraction from the SAX disk.

replicate samples using deionized water, 91.5 ± 2.3% of the DCPA spiked was recovered in the MeOH fraction from the SAX disk (Figure 1). While the diacid metabolite is retained by the SAX disk through ionic interactions, DCPA is presumably retained by the SAX disk through interactions with the stryrene divinylbenzene copolymer matrix.

To test the ability of the method to fractionate DCPA from its metabolites, a set of five samples of deionized water containing a mixture of DCPA and the mono- and diacid metabolites were each extracted using a single SAX disk. The MeOH fraction contained an average recovery of 93.7 ± 2.6% of the DCPA, while 85.6 ± 2.5% of the combined mono- and diacid metabolites were recovered in the H_2SO_4/MeOH fraction (Table 3). Since DCPA can be separated from its metabolites, the SAX disk method can be used to distinguish between the parent compound and metabolites in surface and ground water samples.

Application to Environmental Samples. The SAX disk method described in this paper was used to quantitatively determine the concentrations of DCPA and its metabolites in ground water obtained from the Malheur River Basin in eastern Oregon. Shown in Figure 2 is an example of a typical chromatogram of a ground water sample, containing 46.5 μg/L of the acid metabolites of DCPA. The mass spectrum inset in Figure 2 indicates the molecular ion at m/z 332 and gave a 98% library match quality.

Eight individual ground water samples and one composite sample (prepared by combining five individual samples) from the Malheur River Basin were analyzed both by the SAX disk method and by conventional LLE and analyzed by GC/ECD (Table 4). Concentrations of the acid metabolites of DCPA ranged from below detection (0.05 μg/L) to 158.2 μg/L as determined by the SAX disk method and from below detection (0.1 μg/L) to 163.9 μg/L by LLE. Linear regression of the mean concentrations determined by the SAX disk method and the conventional LLE method gave an r^2 value of 0.9969, indicating good agreement. The precisions of the two extraction methods are equivalent, since they are not statistically significant at the 95% confidence level. Although DCPA is fractionated from its acid metabolites using this method, no DCPA was detected in any of the ground water samples.

Conclusions. Strong anion exchange proved to be the most efficient phase for quantitatively isolating the water-soluble acid metabolites of DCPA. The concentrations of the acid metabolites of DCPA in samples of eastern Oregon ground water determined by the SAX disk method ranged from below detection to 158.2 μg/L and were in good agreement with those determined by conventional LLE. Although the method is capable of distinguishing between the parent compound and the

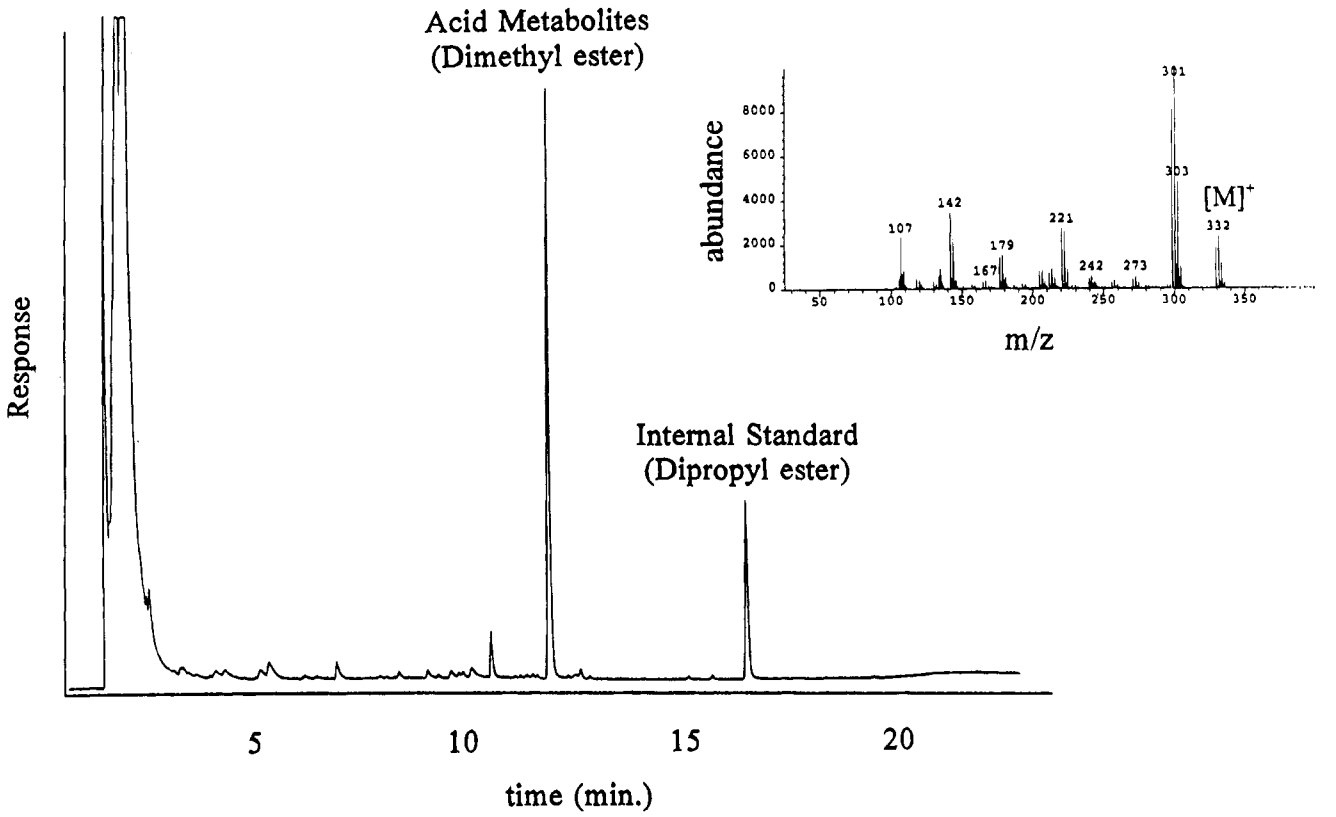

Figure 2. Gas chromatogram of a ground water sample extracted by solid-phase (strong anion exchange) extraction containing 46.5 μg/L of the carboxylic acid metabolites of DCPA, including the electron impact mass spectrum (see inset) indicating the molecular ion of m/z 332.

Table 4. Concentrations of the Acid Metabolites of DCPA Detected in the Malheur River Basin of Eastern Oregon by Strong Anion Exchange (SAX) Solid-Phase Extraction and Liquid–Liquid Extraction (LLE)

	acid metabolites of DCPA (μg/L)	
ground water sample	SAX	LLE
1.00	98.4 ± 3.1[a]	117.0 ± 7[a]
2.00	62.0 ± 1.9[b]	71.0 ± 2.1[c]
3.00	*d*	*d*
4.00	158.2 ± 5.0[b]	163.9 ± 4.7[c]
5.00	74.0 ± 2.3[b]	71.3 ± 2.1[c]
6.00	2.5 ± 0.1[b]	3.8 ± 0.1[c]
7.00	46.5 ± 1.4[b]	49.5 ± 1.4[c]
8.00	4.6 ± 0.1[b]	6.9 ± 0.2[c]
9.00	50.2 ± 1.6[b]	62.1 ± 1.8[c]

[a] Average of four replicate analyses of a composite ground water sample. [b] Duplicate samples analyzed; standard deviation from replicate analyses of composite (sample 1) applied to measured average concentration. [c] Single sample analyzed; standard deviation from replicate analyses of composite (sample 1) applied to measured average concentration. [d] Less than detection limit of the methods (0.05 μg/L for SAX and 0.1 μg/L for LLE).

acid metabolites, DCPA was not detected in any of the ground water samples.

The average recovery of the diacid metabolite by the SAX solid-phase extraction method was 82.6%, compared to an average of 88% by conventional LLE. The SAX disk method was used to quantitate the concentration of the acid metabolites of DCPA in ground water over 3 orders of magnitude. The reproducibilities of the SAX and LLE methods, expressed in terms of the relative standard deviation, were comparable at 3.1% and 2.9%, respectively. The detection limit of the SAX disk method was 0.05 μg/L from a 100 mL sample compared to 0.1 μg/L from a 400 mL sample for LLE. However, the total solvent volume needed for analysis decreased from 450 mL of diethyl ether for the LLE method to less than 65 mL for the SAX disk method, of which only 14 mL was diethyl ether. Ongoing research is aimed at further reducing the volume of solvent required, handling difficulty, and time required for analysis by coupling disk elution and metabolite derivatization into a single step.

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