Diuron and Its Metabolites in Surface Water and Ground Water by Solid Phase Extraction and In-Vial Elution

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A simple and rapid method was developed to determine concentrations of diuron [*N*′-(3,4-dichlorophenyl)-*N*,*N*-dimethylurea] and three of its major metabolites, *N*′-(3,4-dichlorophenyl)-*N*-methylurea (DCPMU), 3,4-dichlorophenylurea (DCPU), and 3,4-dichloroaniline (DCA), in ground water and surface water. The analytical method utilizes a 25 mm C_{18} Empore disk to quantitatively determine diuron and its metabolites in 100 mL water samples. All analytes are eluted by placing the disk directly into a 2 mL autosampler vial in 1.5 mL of methanol/acetonitrile (50/50) for analysis by HPLC with UV detection. Recoveries from spiked field sample matrices were 98.8 ± 1.6, 98.1 ± 4.5, 98.2 ± 3.6, and 77.8 ± 4.5% for diuron, DCPMU, DCPU, and DCA, respectively. The method precision, indicated by the relative standard deviation, was typically ±5%. The method detection and quantitation limits are 0.5 and 1 μg/L for all analytes except dichloroaniline (1.0 and 2.0 μg/L, respectively). The concentrations of diuron and its metabolites determined in surface water and ground water samples collected from a field study site are presented.

Keywords: *Diuron; metabolites; solid phase extraction; Empore disks; surface water; ground water*

INTRODUCTION

Diuron [*N*′-(3,4-dichlorophenyl)-*N*,*N*-dimethylurea] is a herbicide commonly used to control broadleaf weeds in a wide variety of crops (Montgomery, 1993). Although diuron was not ranked in the top 10 pesticides in terms of potential impact to human health or risks to aquatic organisms, diuron was recently ranked as the third most hazardous pesticide to groundwater resources (Newman, 1995). The lifetime health advisory for diuron in drinking water in the United States is 10 μg/L (U.S. EPA, 1995). Diuron degrades by N-demethylation under aerobic conditions to metabolites (Figure 1) including *N*′-(3,4-dichlorophenyl)-*N*-methylurea (DCPMU), 3,4-dichlorophenylurea (DCPU), and 3,4-dichloroaniline (DCA) (Dalton et al., 1966; Tillmanns et al., 1978). Under anaerobic soil conditions, formation of a dechlorinated product *N*′-(3-chlorophenyl)-*N*-methylurea (mCPMU) also was reported (Attaway et al., 1982; Stepp et al., 1985). The mutagenic, potentially carcinogenic, and toxic condensation product of DCA, 3,3′,4,4′-tetrachloroazobenzene, also is a potential metabolite of diuron (Bartha, 1971; Bartha and Pramer, 1967; Hill et al., 1981).

The conventional extraction method for determining diuron in water is liquid−liquid extraction using dichloromethane as the organic solvent (Bowmer and Adeney, 1978; Farrington et al., 1977; Goewie and Hogendoorn, 1987; Zahnow and Riggleman, 1980). Solid phase extraction cartridges containing C_8 or C_{18} bonded-phase silica were used to isolate diuron from aqueous samples in an off-line mode (Balinova, 1993; Nielen et al., 1987; Nouri et al., 1995; Moore et al., 1995; Parrilla et al., 1993; Scott, 1993). Reversed-phase C_{18} columns have been used in on-line configurations for the preconcentration of diuron from water and separation and detection by either HPLC/UV (Hatrík et al., 1994; Sancho et al., 1997) or HPLC/MS (Marcé et al., 1995; Maris et al., 1985; Sennert et al., 1995).

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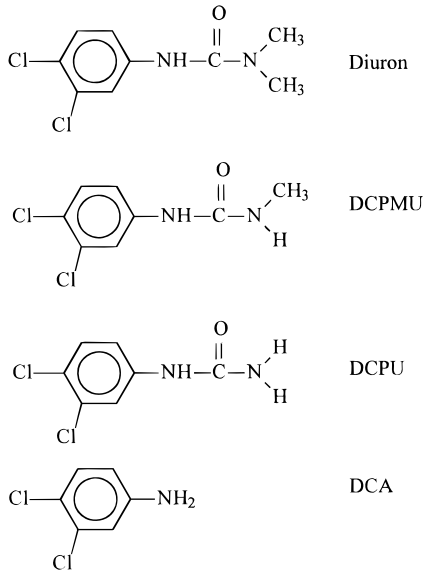

Figure 1. Structures of diuron and its major metabolites.

Solid phase extraction Empore disks are an alternative to liquid−liquid extraction and to solid phase extraction cartridges. Empore disks eliminate steps and reduce organic solvent use compared to solid phase extraction cartridges, especially when disks are eluted by placing them directly into autosampler vials filled with a small volume (<2 mL) of solvent. Variations of this "in-vial" approach to disk elution were used for the quantitative determination of acid herbicides and their metabolites in surface water (Field and Monohan, 1995, 1996) and of surfactants and their metabolites in municipal sewage effluents, paper mill effluents, and river water (Krueger and Field, 1995; Field and Reed, 1996). Few papers document the use of Empore disks to concentrate diuron from water (Barnabas et al., 1994). To the best of our knowledge, no papers document the use of solid phase extraction Empore disks for the quantitative determination of diuron and its major metabolites (DCPMU, DCPU, and DCA) in aqueous environmental samples.

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Although gas chromatography and HPLC have been applied to the determination of diuron, HPLC typically is the method of choice. Because diuron is nonvolatile, gas chromatographic analysis requires that diuron be derivatized either by acylation or methylation (Brinkman et al., 1984; Scott, 1993), hydrolysis to its corresponding aniline, (Lawrence, 1976), or pyrolysis to phenyl isocyanate (Cotterill, 1980). The low-temperature conditions associated with HPLC minimize thermal decomposition of diuron and its metabolites and therefore preserve the "speciation" of diuron in environmental samples (Goewie and Hogendoorn, 1987). For these reasons, in addition to the availability of UV detectors, HPLC/UV typically is the separation and detection method of choice for diuron (Balinova, 1993; Crathorne et al., 1984; Goewie et al., 1984; Goewie and Hogendoorn, 1987; Nouri et al., 1985; Parrilla et al., 1993). Mass spectrometry has been coupled with HPLC for the determination of diuron and its metabolites in blood and urine (Verheij et al., 1989) and water (Moore et al., 1995; Crathorne et al., 1984). Unfortunately, mass spectrometric detection for HPLC requires expensive instrumentation.

The objective of this work was to couple in-vial disk elution with HPLC analysis for the determination of diuron and its major metabolites in ground water and surface water samples. The in-vial elution method reduces the amount of organic solvents used and eliminates tedious sample preparation steps compared to conventional methods of analysis. The developed method was then validated and applied to the detection of diuron and its metabolites in field samples as part of an ongoing study aimed at understanding the fate and transport of diuron and its metabolites in water originating from fields used for the production of perennial ryegrass seed.

MATERIALS AND METHODS

Standards and Reagents. Standards of diuron (98%) and DCA (99%) were obtained from Chem Service (West Chester, PA). Standards of DCPU (99%) and DCPMU (99.9%) were donated by DuPont. All standards were prepared in acetonitrile/methanol (50:50). Acetone and methanol (HPLC grade) were purchased from EM Science (Gibbstown, NJ), and HPLC grade acetonitrile was purchased from J. T. Baker (Phillipsburg, NJ).

Samples. Ground water samples (250 mL) were obtained from shallow (15−35 cm below land surface) PVC ground water wells. Surface water samples (250 mL) were collected in 500 mL polyethylene bottles using ISCO Model 2900 autosamplers. Ground water ranged from less than 1 mg/L (detection limit) dissolved organic carbon to 17 mg/L and from pH 6.8 to 7.3. The surface water sampled for this study ranged from 1 to 8 mg/L dissolved organic carbon and from pH 7.4 to 7.8. All samples were stored in 250 mL brown glass bottles with Teflon-lined caps and were stored at 4 °C for no more than 2 weeks, as stability studies in our laboratory indicated no degradation of diuron or it metabolites during that time period.

Filtration and Solid Phase Extraction. The samples first were filtered through 25 mm 0.2 μm Nyflo filters (Gelman Sciences, Ann Arbor, MI) in polypropylene filter holders (MFS Systems, Dublin, CA). To facilitate faster filtration, 1−2 mL of deionized water was added to a dry filter and holder assembly to evenly wet the filter and displace air. After wetting, a 75 mL polypropylene reservoir (J. T. Baker, Union City, CA) was fitted to the filter holder to which 5 mL of water was added. Water samples (100 mL) were then poured into the reservoir and filtered under 25 mmHg vacuum. The reservoir was rinsed with 2 × 2 mL deionized water, and the filtrate was collected together with the samples in a 125 mL baked glass bottle.

Diuron and its metabolites were extracted from the filtered sample with a 25 mm C_{18} bonded-phase silica Empore disk (Varian, Sugar Land, TX). The disk was first placed in a polypropylene filter holder fitted with a 75 mL polypropylene reservoir and rinsed with 8 mL of acetone followed by 8 mL of methanol and 10 mL of deionized water. After the acetone rinse, the disk was allowed to dry. However, once methanol was added and allowed to soak for 30 s before it was drawn through the disk, the disk was not allowed to go dry. The filtered sample was then added to the reservoir and the sample bottle rinsed with 2 × 2 mL deionized water; all water was drawn through the C_{18} disk under vacuum (10−15 mmHg). Once the sample was extracted and the reservoir removed, about 60 mL of air was pushed through the disk using a syringe to facilitate removal of excess water from the disk. The C_{18} disk was then dried for 10−15 min by drawing air through the disk. The disk was then removed from the filter holder and placed in a 2 mL glass autosampler vial together with 1.5 mL of methanol/acetonitrile (50:50). The vial contents were allowed to equilibrate for a minimum of 2.4 h before analysis, although samples typically were analyzed 24 h after the disks were placed in autosampler vials for elution. The autosampler vials were then placed directly in autosampler trays without removing the disk.

In-Vial Elution. To determine the minimum time that disks should be allowed to equilibrate in the vial with the elution solution (acetonitrile/methanol), diuron and its metabolites were extracted from deionized water onto a single 25 mm C_{18} disk. The disk was then placed in an autosampler vial with 1.5 mL of 50:50 acetonitrile/methanol. The autosampler then injected a 20 μL aliquot of the vial contents at 6 min after the disk was placed in the vial and at 20 min intervals thereafter; the 20 min interval corresponded to the total HPLC run time.

Recovery and Precision. To determine the recovery of diuron and its metabolites from deionized water, six 100 mL samples were spiked to give a final concentration of 10 μg/L of each analyte and then filtered and extracted as described above. Pooled surface water and pooled ground water samples that were found to have undetectable levels of each analyte were used to determine the recovery of diuron and its metabolites from spiked field samples.

The precision of the method was determined by spiking six replicate samples of blank unfiltered ground water and surface water samples (100 mL) to give a final concentration of 10 μg/L of diuron and each of its metabolites. The spiked field samples then were filtered and extracted after a 6 h equilibration time.

High-Performance Liquid Chromatography. All sample extracts were separated and analyzed by HPLC (Beckman System Gold) with UV detection (Beckman 167 scanning detection module) at 252 nm. The analytes were separated by means of a 0.46 cm × 15 cm, reversed-phase Supelcosil LC-18-DB column (Supelco, Bellefonte, PA) that was fitted with a guard column cartridge of the same composition. Separations were carried out in 20 min with acetonitrile and water using gradient elution at a flow rate of 0.8 mL/min. Gradient elution was performed by increasing the percentage of acetonitrile in water from 5 to 70% exponentially over the first 5 min. The acetonitrile/water (70:30) mix was then maintained for 10 min, after which time the initial solvent conditions were restored using a linear ramp over a 3 min period. The column was equilibrated for an additional 3 min before the next sample injection.

Quantitation. The concentrations of diuron and its metabolites were calculated from a six-point standard calibration curve constructed from the peak areas corresponding to each analyte. The concentrations of analytes in the calibration samples ranged from 0.025 to 2.0 μg/mL, which corresponded to concentrations of analytes in environmental water samples ranging from 0.375 to 30 μg/L. Calibration curves were linear with typical R^2 values of 0.990 or greater.

RESULTS AND DISCUSSION

Solid Phase Extraction. Initial experiments were conducted to determine the effect of pH on the recovery

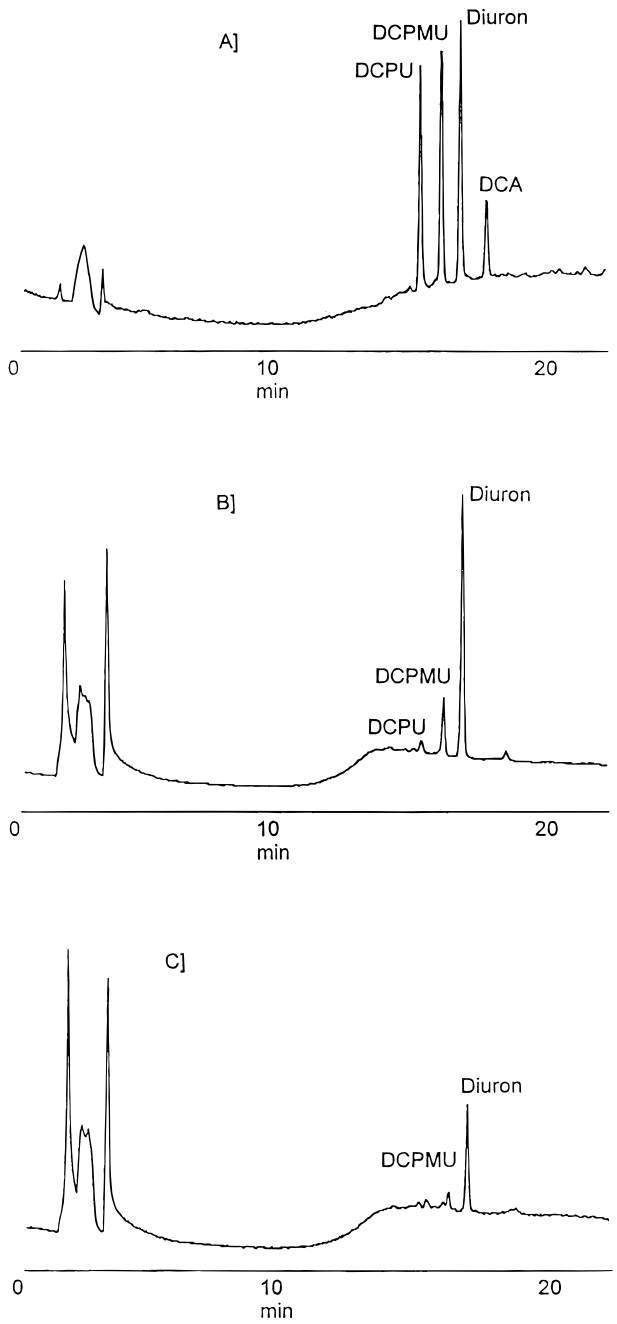

Figure 2. Typical HPLC chromatograms (UV detection at 252 nm) indicating diuron and its metabolites in (A) deionized water, (B) surface water, and (C) ground water.

of diuron and DCA from deionized water buffered using 0.002 M phosphate buffer. Recoveries of diuron and DCA were unaffected by solution pH over the range from pH 3 to 8. Because our field samples fell within that range (pH 6.8−7.8), no adjustments in sample pH were made prior to extraction of the field samples. A typical chromatogram of standard diuron and its metabolites recovered from deionized water indicates that the analytes elute in the order DCPU, DCPMU, diuron, and DCA (Figure 2A).

The in-vial elution technique is an equilibrium-based approach to elution. Therefore, it is important first to determine the extent and rate of analyte elution from the disk to optimize analyte recovery and method precision. Diuron, DCPMU, and DCPU eluted quantitatively from the C_{18} disk, achieving 92−100% recovery in 24 min, while 84.8% recovery of DCA was achieved in 144 min or 2.4 h (Figure 3). The maximum recoveries

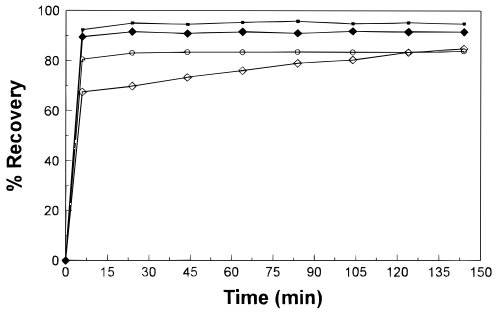

Figure 3. Elution of diuron and its metabolites from 25 mm C_{18} disk with time.

Table 1. Recovery of Diuron and Its Metabolites from Deionized Water and Blank Surface and Ground Water Samples

	% recovery ± SD[a] (%)		
analyte	deionized water	surface water	ground water
diuron	92.2 ± 1.1	98.8 ± 1.6	92.5 ± 2.8
DCPMU	90.6 ± 3.4	98.1 ± 4.5	85.5 ± 3.0
DCPU	92.7 ± 2.5	98.2 ± 3.6	88.5 ± 2.7
DCA	88.0 ± 7.7	77.8 ± 4.5	73.5 ± 5.1

[a] Average ± standard deviation for six replicate samples spiked to give a final concentration of 10 μg/L for each analyte.

obtained for diuron and its metabolites that were achieved in the 144 min equilibration period were in good agreement with those obtained for spiked samples of deionized water where disks were allowed to equilibrate for 15−20 h (Table 1). For reasons of convenience, samples typically were analyzed after a 15−20 h (overnight) equilibration. Good agreement between the amount of DCA eluted in 2.4 h and in 15−20 h suggests that the lower recovery of DCA from water samples is not likely due to incomplete elution but rather due to incomplete extraction from water onto the 25 mm C_{18} disk.

From the C_{18} disk elution profiles (Figure 3), it is evident that the elution of the more basic analyte (DCA) from the C_{18} disk differs from that of diuron and its other more weakly basic metabolites. Diuron, DCPMU, and DCPU eluted rapidly within the first 6 min, while the elution profile of DCA indicates an initially rapid rate of elution followed by a slower rate of elution. Because DCA is readily soluble in acetonitrile/methanol (50:50), it is not likely that the rate of DCA elution is controlled by solubility. Rather, the two different rates that characterize DCA elution potentially indicate that DCA interacts with the C_{18} bonded-phase silica through two different mechanisms. We hypothesize that a fraction of DCA partitioned into the C_{18} alkyl chains elutes rapidly while the fraction associated through hydrogen bonding with the un-end-capped silanol groups elutes more slowly. This hypothesis is supported by the order of chromatographic elution on the reversed-phase C_{18} HPLC column, where DCA is the last to elute even though it is the most water-soluble analyte and would elute first if hydrophobic partitioning was the only mechanism of interaction.

Accuracy and Precision. The percent recoveries and standard deviations for diuron, DCPMU, DCPU, and DCA from deionized water were 92.2 ± 1.1, 90.6 ± 3.4, 92.7 ± 2.5, and 88.0 ± 7.7%, respectively (Table 1). Replicate analyses of the blank surface water spiked to give 10 μg/L concentration of each analyte gave recoveries ranging from 98.8 ± 1.6% for diuron to 77.8 ± 4.5% for DCA (Table 1). Recoveries from the blank ground water were lower and ranged from 92.5 ± 2.8% for

diuron to 73.5 ± 5.1% for DCA (Table 1). The higher recoveries found for the surface water used in the spike and recovery studies may be partially due to the presence of diuron, DCPMU, and DCPU just below their detection limits. The relative standard deviations for six replicate analyses were <7% for the surface and ground water samples. Lower recoveries and higher relative standard deviations for DCA are consistent with other reports of low DCA recovery by liquid−liquid extraction (Goewie and Hogendoorn, 1987) and may be due to binding to particulate organic matter (You and Bartha, 1982).

Detection and Quantification Limits. Detection and quantification limits were determined by spiking blank surface water samples to give final concentrations of 0.25, 0.5, 0.75, 1.0, and 2.0 μg/L for each analyte. The detection limit, defined as a signal to noise ratio of 3, was 0.5 μg/L for all analytes, except DCA (1 μg/L). The quantitation limit, defined as a signal to noise ratio of 10, for all analytes was 1 μg/L, except DCA (2 μg/L). Therefore, the quantitation limit of the method is 10-fold below that of the health advisory limit for diuron in drinking water.

Suitability of Polyethylene Materials for Sampling. Because ISCO autosamplers (Model 2900, Lincoln, NE) were used to collect surface water samples in the field, the recovery of diuron and its metabolites from the polyethylene bottles that fit inside the autosampler was evaluated. Deionized water (100 mL) was added to three 500 mL polyethylene ISCO sample bottles and spiked to give a total concentration of 10 μg/L of diuron and each of its metabolites. The samples were kept at room temperature for 3 days, which is the maximum time that field samples were allowed to remain in contact with the ISCO sample bottles in the field. No significant loss of diuron, DCPMU, or DCPU was observed, with recoveries of 95.9 ± 1.0, 87.9 ± 2.0, and 93.9 ± 1.5%. The recovery of DCA, a semivolatile analyte with a vapor pressure of 9.75×10^{-3} mmHg at 20 °C (National Library of Medicine, 1997), was 59.3 ± 1.0%, which indicates some loss upon storage. By comparison, diuron has a vapor pressure of 1.5×10^{-6} mmHg at 20 °C (Suntio et al., 1988).

Surface and Ground Water Samples. Replicate samples (100 mL) of ground water and surface water, obtained from a field that received a diuron application, were analyzed to determine the method's precision for environmental samples containing native diuron and its metabolites. To obtain a sufficient volume for replicate analyses, two composite ground water samples were assembled by combining a number of ground water samples containing native analytes. Only diuron, DCPMU, and DCPU were detected in the replicate samples of surface and ground water. The precision of the method for two samples each of surface water and ground water, indicated by the relative standard deviation (RSD), varied from 1.3 to 13.6% for analytes occurring at concentrations >1.0 μg/L quantitation limit (Table 2). The RSD for analytes at concentrations less than the quantitation limit were typically higher (10−20%).

To demonstrate the method for analyzing environmental samples, a number of surface water and ground water samples were obtained from a field site that was sprayed on October 24, 1996, with Karmex, an 80% active formulation of diuron. The types of surface waters sampled for this study included field runoff that directly drained the study field, Lake Creek stream that flowed through the study site, and Calapooia River that receives the discharge from Lake Creek.

Table 2. Precision of Diuron and Metabolite Analyses for Surface Water and Ground Water

		concentration (μg/L ± SD)			
sample	no. of samples	diuron	DCPMU	DCPU	DCA
surface water 1[a]	6	23.1 ± 0.3 (1.3%)	2.2 ± 0.1 (4.5%)	2.2 ± 0.3 (13.6%)	<dl[b]
surface water 2[a]	3	12.5 ± 0.3 (2.4%)	2.4 ± 0.1 (4.2%)	0.9 ± 0.1 (11.1%)	<dl
ground water 1[c]	6	5.4 ± 0.2 (3.7%)	1.0 ± 0.1 (10%)	<dl	<dl
ground water 2[c]	3	3.0 ± 0.1 (3.3%)	0.5 ± 0.1 (20%)	0.5 ± 0.0 (−)	<dl

[a] Lake Creek stream water. [b] <dl, below the detection limit of 0.5 μg/L for all analytes except DCA (1.0 μg/L). Values between 0.5 and 1.0 μg/L are above detection but below the quantitation limit. [c] Composite sample.

Table 3. Survey of Diuron and Metabolite Concentrations in Surface Water and Ground Water

		concentration[a] (μg/L)			
sample type	date of sample	diuron	DCPMU	DCPU	DCA
field runoff	Nov 18, 1996	20.7	7.9	3.0	<dl[b]
	Nov 22, 1996	10.9	3.8	1.3	<dl
	Nov 27, 1996	9.5	4.3	1.7	<dl
stream water	Oct 29, 1996	18.2	1.7	1.3	<dl
	Nov 2, 1996	8.7	1.4	0.9	<dl
	Nov 7, 1996	5.7	1.3	<dl	<dl
	Nov 12, 1996	5.2	1.3	0.9	<dl
	Nov 17, 1996	13.7	1.9	1.3	<dl
	Nov 27, 1996	10.1	1.4	<dl	<dl
river water	Oct 29, 1996	1.4	<dl	<dl	<dl
	Nov 2, 1996	<dl	<dl	<dl	<dl
	Nov 7, 1996	1.5	<dl	<dl	<dl
	Nov 12, 1996	0.5	<dl	<dl	<dl
	Nov 27, 1996	1.6	<dl	<dl	<dl
ground water	Nov 18, 1996				
	well 1	10.9	1.3	0.6	<dl
	well 2	7.2	1.1	<dl	<dl
	well 3	6.1	0.8	<dl	<dl
	well 4	3.1	0.8	<dl	<dl
	well 5	2.7	1.1	<dl	<dl

[a] Single samples analyzed. [b] <dl, below the detection limit of 0.5 μg/L for all analytes except DCA (1.0 μg/L). Values between 0.5 and 1.0 μg/L are above detection but below the quantitation limit.

Field runoff and stream water samples typically contained higher concentrations of diuron and its metabolites than river water or ground water. Diuron concentrations in the field runoff and stream water ranged from 5.2 to 20.7 μg/L, while DCPMU concentrations ranged from 1.3 to 7.9 μg/L and DCPU concentrations ranged from below detection to 3.0 μg/L (Table 3). No DCA was detected in any of the surface waters analyzed for this study. A chromatogram typical of a surface water sample containing diuron, DCPMU, and DCPU is shown in Figure 2B. Calapooia River water only contained detectable concentrations of diuron (up to 1.6 μg/L), presumably due to dilution of stream water and runoff once it enters the Calapooia River.

Five ground water samples obtained on a single sampling day contained diuron, DCPMU, and DCPU. Diuron concentrations ranged from 2.7 to 10.9 μg/L, while only low concentrations of DCPMU (0.8−1.3 μg/L) were measured. A trace of DCPU was detected in a single well, while no DCA was detected in any of the wells. A chromatogram typical of a ground water containing diuron and DCPMU is shown in Figure 2C. For the samples of surface and ground water analyzed

for this survey, the concentrations of DCPMU and DCPU were 9−40 and 5−18% of the diuron concentrations, respectively.

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