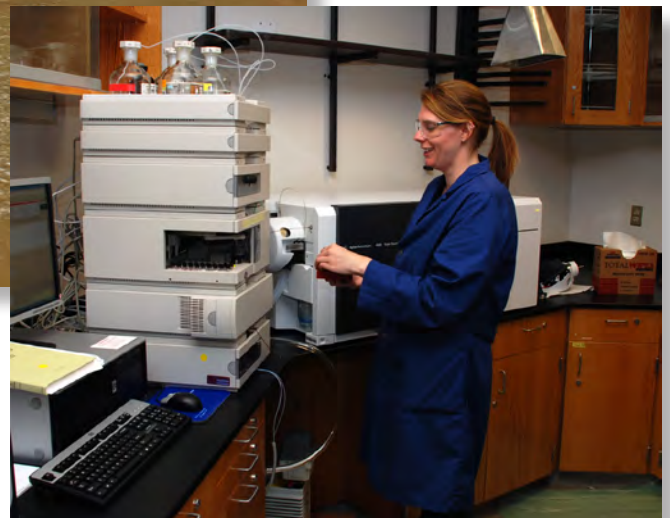


Prepared in cooperation with the National Water Quality Assessment Program and the Georgia Department of Agriculture

# Analysis of the Herbicide Diuron, Three Diuron Degradates, and Six Neonicotinoid Insecticides in Water— Method Details and Application to Two Georgia Streams



Scientific Investigations Report 2012–5206

**Cover:** Photograph of field work by Alan Cressler, U.S. Geological Survey, Georgia Water Science Center.  
Photograph of laboratory by Cathy Munday, U.S. Geological Survey, California Water Science Center.

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By Michelle L. Hladik and Daniel L. Calhoun

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**U.S. Department of the Interior**  
**U.S. Geological Survey**

**U.S. Department of the Interior**  
KEN SALAZAR, Secretary

**U.S. Geological Survey**  
Marcia K. McNutt, Director

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## Conversion Factors and Abbreviations

SI to Inch/Pound

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
<b>Area</b>		
square kilometers (km <sup>2</sup> )	0.3861	square miles (mi <sup>2</sup> )
<b>Length</b>		
centimeter (cm)	0.3937	inch (in.)
micrometer (μm)	$3.937 \times 10^{-5}$	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	39.37	inch (in.)
<b>Mass</b>		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)
microgram (μg)	$3.527 \times 10^{-8}$	ounce, avoirdupois (oz)
milligram (mg)	$3.527 \times 10^{-5}$	ounce, avoirdupois (oz)
nanogram (ng)	$3.527 \times 10^{-11}$	ounce, avoirdupois (oz)
<b>Pressure</b>		
kilopascal (kPa)	0.1450	pound-force per inch (lbf/in)
<b>Volume</b>		
liter (L)	0.2642	gallon (gal)
microliter (μL)	$2.642 \times 10^{-7}$	gallon (gal)
milliliter (mL)	0.000264	gallon (gal)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$$

## Conversion Factors and Abbreviations

Abbreviations used in this report:

(additional information or clarification given in parentheses)

ACS	American Chemical Society
ACN	acetonitrile
amu	atomic mass unit
CAS	Chemical Abstracts Service (American Chemical Society)
DCM	dichloromethane
DF	dilution factor
ESI	electrospray ionization
GC/MS	gas chromatography with mass spectrometry
GF/F	glass-fiber filter (grade GF/F)
HLB	hydrophilic-lipophilic balance
HPLC	high-performance liquid chromatograph or high-performance liquid chromatography
i.d.	inner diameter
ISTD	internal standard
L/min	liter per minute
LC/MS/MS	liquid chromatography with tandem mass spectrometry
LOD	limit of detection
$\log K_{ow}$	base-10 logarithm of the octanol-water partition coefficient
MDL	method detection limit
mg/mL	milligram per milliliter
mg/L	milligram per liter
min	minute
mL/min	milliliter per minute
mm	millimeter
MRL	minimum reporting level
MRM	multiple reaction monitoring
MS	mass spectrometer or mass spectrometry
MS/MS	tandem mass spectrometry
<i>m/z</i>	mass-to-charge ratio
psi	pound per square inch
NA	not available
ND	not detected
ng	nanogram
ng/L	nanogram per liter
ng/ $\mu$ L	nanogram per microliter
NWIS	National Water Information System (USGS)
QA/QC	quality assurance and quality control
RPD	relative percentage difference
RSD	relative standard deviation
RT	retention time
s	second
SD	standard deviation
SPE	solid-phase extraction
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
V	volts
$\mu$ g/mL	microgram per milliliter
$\mu$ A	microampere





# Analysis of the Herbicide Diuron, Three Diuron Degradates, and Six Neonicotinoid Insecticides in Water— Method Details and Application to Two Georgia Streams

By Michelle L. Hladik and Daniel L. Calhoun

## Abstract

A method for the determination of the widely used herbicide diuron, three degradates of diuron, and six neonicotinoid insecticides in environmental water samples is described. Filtered water samples were extracted by using solid-phase extraction (SPE) with no additional cleanup steps. Quantification of the pesticides from the extracted water samples was done by using liquid chromatography with tandem mass spectrometry (LC/MS/MS).

Recoveries in test water samples fortified at 20 nanograms per liter (ng/L) for each compound ranged from 75 to 97 percent; relative standard deviations ranged from 5 to 10 percent. Method detection limits (MDLs) in water ranged from 3.0 to 6.2 ng/L using LC/MS/MS. The method was applied to water samples from two streams in Georgia, Sope Creek and the Chattahoochee River. Diuron and 3,4-dichloroaniline (3,4-DCA) were detected in 100 and 80 percent, respectively, of the samples from the Chattahoochee River, whereas Sope creek had detection frequencies of 15 percent for diuron and 31 percent for 3,4-DCA. Detection frequencies for the neonicotinoid insecticide, imidacloprid, were 60 percent for the Chattahoochee River and 85 percent for Sope Creek. Field matrix-spike recoveries for each compound, when averaged over four water samples, ranged from 79 to 100 percent. The average percentage difference between replicate pairs for all compounds detected in the field samples was 10.1 ( $\pm 4.5$ ) percent.

## Introduction

The U.S. Geological Survey (USGS) Organic Chemistry Laboratory in Sacramento, California (Sacramento Laboratory), has developed robust analytical methods for

a broad array of current-use and legacy pesticides in water, sediment, and tissue by using gas chromatography/mass spectrometry (GC/MS) and gas chromatography tandem mass spectrometry (GC/MS/MS) (Hladik and others, 2008, 2009; Smalling and Kuivila, 2008; Smalling and others, 2010). The use of only GC-based methods, however, has limitations because a certain subset of pesticides cannot be analyzed by GC. These pesticides are not volatile enough for GC or degrade in a hot GC injection port, which makes them potential candidates for liquid chromatography-based analysis.

The Sacramento Laboratory has targeted a set of pesticides of local and national interest as the highest priority for liquid chromatography with tandem mass spectrometry (LC/MS/MS) methods development. The herbicide, diuron, is one of the most frequently used herbicides in California with 264,000 kg applied in 2010 (ranking number 33 for kilograms applied). Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is applied in agricultural areas (alfalfa, citrus), as well as for use on “rights of way,” such as highways, which makes its use ubiquitous throughout the State (California Department of Pesticide Regulation, 2010). Diuron is one of the most frequently detected pesticides in water in the San Francisco Bay-Delta and nearby areas (Guo and others, 2010). Concentrations of diuron can reach several thousand ng/L, as has been documented in samples collected in spring when runoff from the Bay-Delta is high, from the State Water Project distribution system (California Department of Water Resources, 2010). Diuron is also widely used on agricultural crops across the United States, ranking 22<sup>nd</sup> in 2007 in terms of mass of active ingredient applied (0.9-1.8 million kg; U.S. Environmental Protection Agency, 2011).

Elevated levels of diuron in water could lead to aquatic toxicity and can have human health implications (U.S. Environmental Protection Agency, 2003a). Diuron is moderately toxic to fish and highly toxic to aquatic invertebrates (Turner, 2003). In addition to diuron, the three primary diuron degradates are included in the analysis method

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described in this report [DCPMU (3-(3,4-dichlorophenyl)-1-methylurea), DCPU (3,4-dichlorophenylurea), and 3,4-DCA (3,4-dichloroaniline)] (figure 1; table 1). The occurrence of diuron degradates in the aquatic environment is of concern because, in some cases, the degradates are more toxic than the parent compounds (Tixier and others, 2000). Additionally because some degradates are more stable than diuron, they can persist longer in the environment (table 1). Diuron can also be a disinfection by-product precursor; under certain water-treatment conditions, diuron can form *N*-nitrosodimethyl amine (NDMA) (Chen and Young, 2008), which is a class B2 carcinogen (reasonably considered to be a human carcinogen; U.S. Environmental Protection Agency 2010).

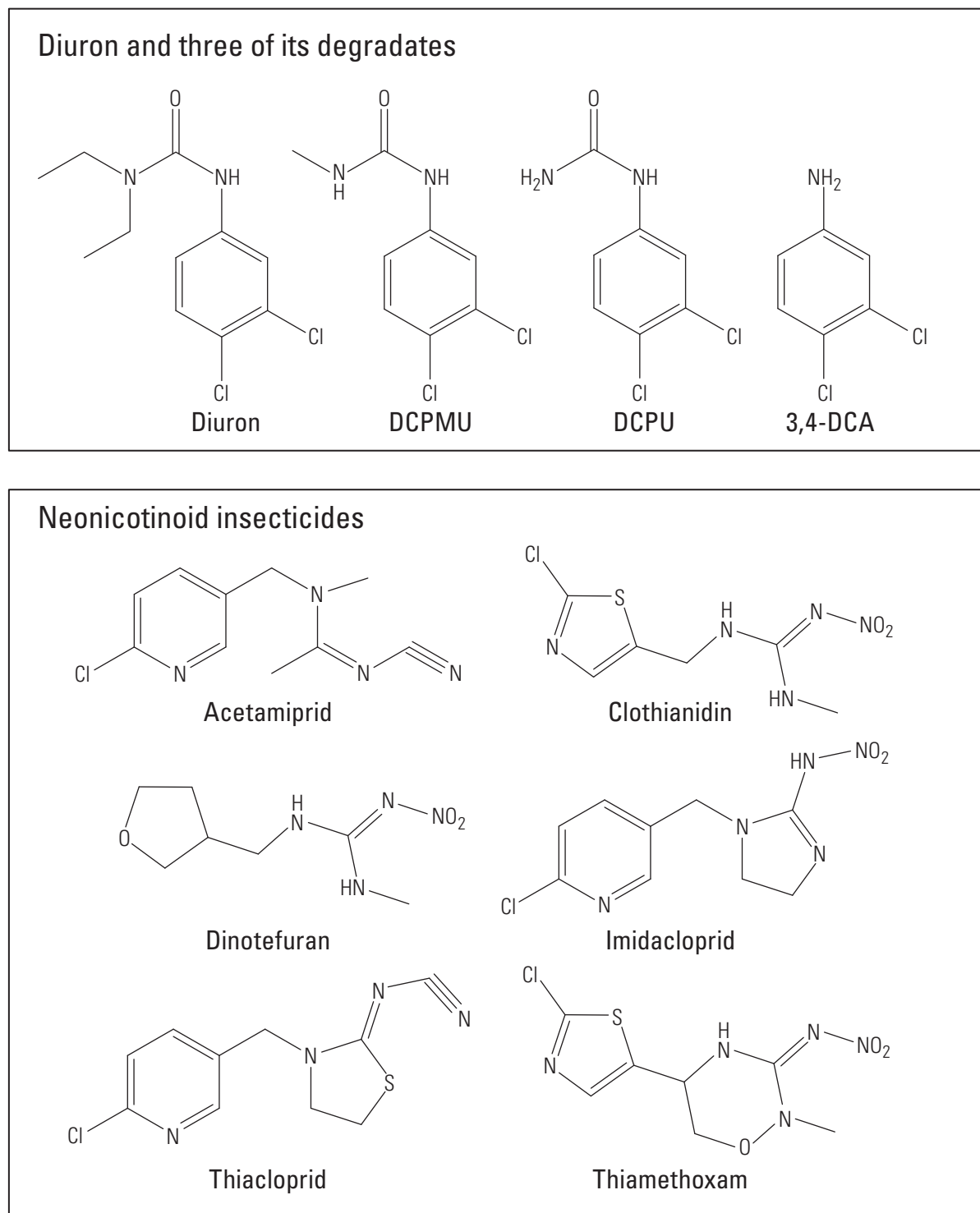
Neonicotinoid insecticides are the second class of compounds that are of interest. This class of compounds have a common mode of action that affects the central nervous system of insects, are increasing in use throughout the United States, and have been linked to colony collapse disorder in bees (CRS, 2007). This group includes acetamiprid, clothianidin, dinotefuran, imidacloprid, thiacloprid and thiamethoxam (figure 1; table 1). Imidacloprid is the most widely used neonicotinoid in the United States and has a broad

range of uses; other neonicotinoids, such as clothianidin, are used for more-specialized applications such as seed coatings on corn (U.S. Environmental Protection Agency, 2003b). Imidacloprid, and other neonicotinoids, have increasingly been used over much of the Eastern United States during the previous decade to treat Eastern and Carolina Hemlocks for infestation by the hemlock woolly adelgid (Cowles, 2009) and ash trees for the emerald ash borer (Kreutzweiser and others, 2007). Possible leaching of these insecticides to surface waters and transport by way of leaf litter has been of concern. Recently, thiamethoxam has been linked to decreased survival in honeybees (Henry and others, 2012) and imidacloprid has been linked to reduced growth in bumble bees (Whitehorn and others, 2012). Bees are essential pollinators of agricultural crops, and their recent decline in population has triggered an increase in research to understand and combat the decline (vanEngelsdorp and others, 2009). Monitoring data for imidacloprid and other neonicotinoids in environmental waters are scarce; analysis of the neonicotinoid insecticides would help in determining their fate in the environment and possible implications to biota, which include pollinators and aquatic invertebrates.

**Table 1.** CAS Registry number, molecular weight, solubility, octanol-water partition coefficient ( $K_{ow}$ ) and hydrolysis half-life and laboratory parameter code for each pesticide and degrade.

[This report contains Chemical Abstracts Service Registry Numbers (CASRN), which is a Registered Trademark of the American Chemical Society. Chemical Abstracts Service (CAS) recommends the verification of the CASRNs through CAS Client Services. Solubility,  $\log K_{ow}$ , and hydrolysis data were obtained from the Pesticide Properties Database (University of Hertfordshire, 2011). The five-digit parameter codes are used by the U.S. Geological Survey to uniquely identify a specific constituent or property in the National Water Information System (NWIS) database. **Abbreviations:** amu, atomic mass units, mg/L, milligrams per liter;  $\log K_{ow}$ , octanol-water partition coefficient; NA, not available]

Compound	CAS number	Molecular weight (amu)	Water solubility (mg/L)	Log $K_{ow}$	Aqueous dissipation half life (days)	Parameter code
Diuron and degradates						
Diuron	330-54-1	233.1	35.6	2.87	8.8	66598
DCPMU	3567-62-2	219.1	490	NA	NA	68231
DCPU	2327-02-8	205	940	2.35	NA	68226
3,4-DCA	95-76-1	162	580	2.69	NA	66584
Neonicotinoid insecticides						
Acetamiprid	135410-20-7	222.7	2,950	0.8	4.7	68302
Clothianidin	210880-92-5	249.7	340	0.91	40.3	68221
Dinotefuran	165252-70-0	202.1	39,800	-0.55	NA	68379
Imidacloprid	138261-41-3	255.7	610	0.57	30	68426
Thiacloprid	111988-49-9	252.7	184	1.26	8.5	68485
Thiamethoxam	153719-23-4	291.7	4,100	-0.13	30.6	68245



**Figure 1.** Chemical structures of the pesticides and degradates analyzed for in the method.

### Purpose and Scope

The purpose of this report is to describe a method for the extraction and quantification of selected pesticides and degradates from water samples and to present data from the application of this method to water samples collected from two streams in Georgia. The methods described in this report were developed by the USGS Sacramento Laboratory to analyze the herbicide diuron and three of its degradates, along with six neonicotinoid insecticides, in filtered water samples. The compounds included in this method are listed in [table 1](#), including their Chemical Abstracts Service (CAS) Registry numbers, molecular weights, and USGS laboratory parameter codes. The extraction of the target compounds from 1-L filtered water samples is achieved with solid-phase extraction (SPE), and all target compounds are separated, detected, identified and quantified LC/MS/MS. The performance of this method was evaluated by using MDLs, surrogate recoveries, field and laboratory spiked recoveries, and field and laboratory blanks. This method was applied to stream samples from two locations in Georgia. The Georgia sampling is ongoing. Further interpretation of the Georgia data will occur upon completion of the project.

### Field and Laboratory Methods

#### Sample Collection

For the described analysis method, water samples are collected in the field into 1-L amber glass bottles by using the methods outlined by U.S. Geological Survey (2006) and Ward and Harr (1990). Samples are chilled immediately, shipped to the Sacramento Laboratory, and refrigerated at 4°C until extraction (within 48 hours of collection). Samples are filtered either in the field (preferred) or in the laboratory using a baked 0.7-mm nominal pore size GF/F-grade glass-fiber filters (Whatman, Piscataway, New Jersey).

#### Sample Extraction

Each filtered water sample is spiked with recovery surrogate standards, monuron (Chem Service, West Chester, Pennsylvania) and (or) imidacloprid-*d*<sub>4</sub> (Cambridge Isotope Laboratories, Andover, Massachusetts). The surrogates that were chosen as compounds are similar in structure to

the target analytes; deuterated imidacloprid is not found in the environment, and monuron was canceled for use in the United States in 1977 (U.S. Environmental Protection Agency, 1998). The sample is loaded onto a precleaned Oasis HLB SPE (6 mL, 500 mg; Waters, Milford, Massachusetts) cartridge that has been cleaned with one column volume of dichloromethane followed by one column-volume of acetone and two column-volumes of deionized water. The water sample is pumped through the SPE cartridge at a flow rate of 10 mL/min; the SPE cartridge is then dried under carbon dioxide for approximately 1 hr or until the SPE sorbent is dry. The analytes are eluted into a clean glass concentrator tube by using 10 mL of 50:50 DCM:acetone. The eluent is evaporated to less than 0.5 mL in a fume hood by using a gentle stream of dry nitrogen, solvent-exchanged into acetonitrile (ACN), and further evaporated to less than 0.2 mL. The internal standard (<sup>13</sup>C<sub>3</sub>-caffeine, Cambridge Isotope Laboratories) is then added (10 µL of a 1-ng/µL solution). The sample extracts are stored in a freezer at -20°C until analysis (up to 30 days).

#### Quantitation

Neat target pesticides—diuron, acetamiprid, clothianidin, dinotefuran, imidacloprid, thiacloprid and thiamethoxam—were obtained from the U.S. Environmental Protection Agency Pesticide Repository (Ft. Meade, Maryland); 3,4-DCA was purchased from Chem Service (West Chester, Pennsylvania); and, DCPMU and DCPU were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Compounds were dissolved into acetone to make concentrated stock solutions (1 mg/mL) which were further diluted to make appropriate standards in ACN.

Aliquots of the sample extracts (10 µL) are injected, and the compounds, separated on an Agilent (Palo Alto, California) 1100 HPLC coupled to a 6430 tandem MS system with a Zorbax Eclipse XDB-C18 column (2.1 mm × 150 mm × 3.5 mm; Agilent). The column flow rate is 0.6 mL/min, and the column temperature is 30°C. The mobile phases are ACN (A channel) and 5 millimolar (mM) formic acid in water (B channel). The column gradient is 2 percent: 98 percent (A:B) from 0 to 2 min; 2 to 4 min increase to 50 percent : 50 percent (A:B), hold for 3 min (7 min); 7 to 7.5 min decrease to 2 percent : 98 percent (A:B), hold for 4.5 min (12 min). MS/MS conditions are electrospray (ESI) ionization, positive mode, drying gas temperature 350°C, drying gas flow 10 L/min, capillary voltage 4,000 V, and nebulizer 40 psi. Data are collected in the multiple-reaction-monitoring (MRM) mode; details of the MRM parameters are given in [table 2](#).

**Table 2.** Multiple-reaction-monitoring mode parameters for pesticides analyzed by LC/MS/MS.

[Abbreviations: LC/MS/MS, liquid chromatography with tandem mass spectrometry; m/z, mass-to-charge ratio; V, Volts; min, minute]

Compound	Precursor ion (m/z)	Quantitation ion (m/z)	Qualitative ion (m/z)	Fragmentor voltage (V)	Quantitation ion collision energy (V)	Qualitative ion collision energy (V)	Retention time (min)
Diuron and degradates							
Diuron	233	72	160	106	20	24	7.4
DCPU	205	127	162	116	28	12	6.5
DCPMU	219	127	162	106	32	12	6.9
3,4-DCA	162	127	109	123	20	32	7.7
Monuron (recovery surrogate)	199	72	126	96	12	24	6.5
Neonicotinoid insecticides							
Acetamiprid	223	126	56	45	20	12	6.0
Clothianidin	250	169	132	79	8	12	5.8
Dinotefuran	203	113	129	45	4	4	5.1
Imidacloprid	256	209	89	89	12	12	5.9
Imidacloprid- <i>d4</i> (recovery surrogate)	260	213	179	91	12	16	5.9
Thiacloprid	253	126	90	45	16	40	6.3
Thiamethoxam	292	211	181	84	8	20	5.6
Internal standard							
<sup>13</sup> C <sub>3</sub> -Caffeine	198	140	112	121	16	24	5.3

## Results

### Method Performance

Method performance was evaluated for recovery by using water collected from the Lower American River (California) that was spiked at 100 ng/L with the target compounds. The American River water was used in place of laboratory reagent water because this water better represents real-world conditions. The American River carries snowmelt and drainage from the Sierra Nevada Mountains, and the water is detained by a series of dams upstream of the collection point, which makes this matrix water consistent in composition; the river has low suspended sediment and low dissolved organic carbon (less 1 percent) and has not had any pesticide detections in blank samples of the target compounds during the development of this method. Because all initial recoveries of the target analytes (listed in [table 2](#)) were greater than 70 percent (data not shown), all the compounds were included in the final method for analysis of environmental water samples.

Final method recoveries and MDLs were determined by using seven samples of American River water spiked at 20 ng/L ([table 3](#)). The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the compound concentration is greater than zero; MDLs were determined according to the procedure outlined by the U.S. Environmental Protection Agency in 40 CFR 136, Appendix B, assuming a 1-L (water) sample (U.S. Environmental Protection Agency, 1997).

$$\text{MDL} = S \times t(n-1, 1-\alpha = 0.99) \quad (1)$$

where

$S$  is the standard deviation of replicate analyses, in nanogram per liter or microgram per gram, at the lowest spike concentration;  $t(n-1, 1-\alpha = 0.99)$  is the Student's  $t$ -value for the 99 percent confidence level with  $n-1$  degrees of freedom.

## 6 Analysis of the Herbicide Diuron and Six Neonicotinoid Insecticides in Water—Method Details and Application

The MDLs in [table 3](#), which were determined by using the previous equation, ranged from 3.0 ng/L (DCPMU) to 6.2 ng/L (clothianidin). Average method recoveries shown in [table 3](#) ranged from 75 to 99 percent, with relative standard deviations (RSDs) of 5 to 10 percent.

This analytical method was then applied to environmental samples. Water samples were collected from two sites in Georgia; 10 samples from the Chattahoochee River near Whitesburg, Georgia, and 13 samples from Sope Creek near Marietta, Georgia. Additional samples were collected for quality assurance and quality control (QA/QC).

Dissolved-pesticide concentrations were validated against a comprehensive set of quality-control parameters that included laboratory and field blanks, matrix spikes, matrix spike replicates, replicate field samples, and surrogate recovery. Laboratory and field blanks were analyzed: there was one field blank at each site and two laboratory blanks. No target compounds were detected in any of the blanks. The recovery surrogate, imidacloprid-*d*<sub>4</sub>, was used to assess the efficiency of sample extraction; mean percent recovery ( $\pm$  standard deviation) for all samples analyzed (including QC samples) was  $87.6 \pm 9.6$  percent, and no single sample had lower than 75-percent recovery. Thirteen sets of replicate field samples had relative percentage differences of less than 16 percent for all pesticides detected; average percentage difference for the replicate pairs was 10.1 percent ( $\pm 4.5$ ). Four field matrix spikes were analyzed, and average recoveries ranged from 79 to 100 percent. Historically, the dissolved organic carbon content of these streams (in 2010 and 2011) was usually around 1 percent, and matrix effects, therefore, were not expected to be large. Although the samples analyzed to date have not shown large matrix effects, this could change with different sample matrices—such as higher organic carbon content water—and strict QA/QC, such as surrogate and matrix spike recoveries, must be adhered to. If the proper QA/QC cannot be met with this method, then other quantification methods, such as standard addition, can be used instead.

### Environmental Pesticide Concentrations

Concentrations of detected pesticides for the sites sampled are shown in [table 4](#). Sope Creek near Marietta, Georgia, which is an urban site with a catchment size of 79.5 square kilometers, had detections of imidacloprid (86 percent detection frequency) throughout the sampling period (October through April); concentrations ranged from 4.5 to 35.3 ng/L, with the highest concentrations detected in winter. Diuron and its degradates DCPMU and 3,4-DCA were

**Table 3.** Analytical method mean percentage recovery at 20 nanograms per liter (ng/L) of spike concentration in American River water, relative standard deviation, and method detection limits.

[Abbreviations: RSD, relative standard deviation; MDL, method detection limit; ng/L, nanogram per liter]

Compound	Recovery (percent)	RSD (percent)	MDL (ng/L)
Diuron and degradates			
Diuron	94	5	3.2
DCPU	83	7	4.3
DCPMU	99	5	3.0
3,4-DCA	97	8	5.2
Neonicotinoids			
Acetamiprid	91	7	3.6
Clothianidin	93	10	6.2
Dinotefuran	75	9	5.5
Imidacloprid	97	8	4.9
Thiacloprid	89	7	3.8
Thiamethoxam	87	6	3.9

detected less frequently (14, 7, and 36 percent, respectively) than imidacloprid. The highest concentrations of diuron and its degradates occurred in spring (March/April); highest concentration for 87 ng/L for diuron and 36 ng/L for 3,4-DCA.

The Chattahoochee River near Whitesburg, Georgia (catchment size 6,290 square kilometers), is downstream of Sope Creek and of Metropolitan Atlanta, and integrates forest, urban and agricultural land uses within its basin. Imidacloprid was detected less frequently (60 percent) in the Chattahoochee River than in Sope Creek (85 percent), and, in general, its concentrations were lower in the Chattahoochee River. Diuron and 3,4-DCA were detected much more frequently (100 and 90 percent, respectively) in the Chattahoochee River; maximum concentrations were 39 ng/L for diuron and 68 ng/L for 3,4-DCA. Diuron is primarily used on agricultural crops, and this is reflected by the typically higher concentrations of diuron in the Chattahoochee River than in Sope Creek.

For this data set, 3,4-DCA is the only diuron degradate detected frequently. Because many studies do not measure DCPMU or DCPU in environmental waters, little data are available for comparison. These degradates could be less stable and quickly degrade further, and 3,4-DCA could be more stable. 3,4-DCA was sometimes found at concentrations higher than those of the parent diuron; because 3,4-DCA is also a degradate of two other herbicides, propanil and linuron, there could be other sources.

**Table 4.** Dissolved pesticide concentrations measured in samples collected at sites located in Georgia, October 2011 through April 2012.

[Numbers in brackets are U.S. Geological Survey National Water Information System (NWIS) parameter codes. Values are reported in nanograms per liter. Results in parentheses ( ) are below method detection limits and are estimates and have a higher degree of uncertainty. The following compounds were analyzed but were not detected in any samples: acetamiprid, chlothianidin, DCPU, thiacloprid and thiamethoxam. **Abbreviations:** hh:mm, hours:minutes; ND, not detected]

Site name (USGS Site ID)	Sample date (mm-dd-yy)	Time [hh:mm]	Diuron [66598]	DCPMU [68231]	3,4-DCA [66584]	Dinotefuran [68379]	Imidacloprid [68426]
Sope Creek near Marietta, GA (02335870)	10-04-11	13:00	ND	ND	3.4	ND	17.5
	10-18-11	13:00	ND	ND	3.6	ND	ND
	11-02-11	14:00	ND	ND	ND	ND	ND
	11-17-11	13:00	ND	ND	ND	ND	8.5
	12-05-11	13:00	ND	ND	ND	ND	6.8
	12-22-11	8:30	ND	ND	ND	ND	10.4
	01-05-12	14:00	ND	ND	ND	ND	8.8
	01-19-12	13:30	ND	ND	ND	ND	35.3
	02-02-12	14:00	ND	ND	ND	ND	11.0
	02-14-12	9:00	ND	ND	ND	ND	4.5
	03-06-12	13:30	ND	ND	ND	ND	8.6
	03-22-12	10:30	20.9	ND	35.8	ND	7.0
	04-09-12	14:00	86.7	7.5	(1.8)	ND	6.4
Chattahoochee River near Whitesburg, GA (02338000)	10-18-11	10:30	33.7	ND	68.2	ND	ND
	11-02-11	11:00	38.9	ND	52.4	ND	ND
	11-17-11	10:00	27.8	ND	12.4	ND	ND
	12-05-11	10:00	33.5	ND	30.3	ND	ND
	01-05-12	11:00	25.9	ND	20.4	ND	7.9
	01-19-12	10:00	32.8	ND	19.7	ND	6.1
	02-02-12	11:00	13.1	ND	26.3	ND	4.3
	03-06-12	10:00	28.5	ND	7.2	ND	3.4
	03-22-12	8:30	10.4	ND	ND	ND	7.5
04-09-12	11:00	24.8	ND	27.5	(1.6)	10.1	

## Summary

This method is appropriate for determining diuron, three diuron degradates, and six neonicotinoid insecticides at low nanogram-per-liter concentrations in natural water by using SPE and LC/MS/MS. This method has been validated with a set of environmental samples and corresponding quality-control samples, which include field replicates, field matrix spikes, and field blanks. Matrix spikes had recoveries of greater than 70 percent for all compounds, and replicate samples had differences less than 20 percent. Diuron and its degradate 3,4-DCA were detected in more than one-half of the stream samples from Georgia, with the majority of detects in the Chattahoochee River (urban and agricultural inputs). Imidacloprid was detected in 74 percent of all the stream samples; 85 percent of the urban samples (Sope Creek) had imidacloprid detects. This method can be used for tracking the environmental fate and transport of these pesticides in water, including those in urban and agricultural areas.

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## 10 Analysis of the Herbicide Diuron and Six Neonicotinoid Insecticides in Water—Method Details and Application

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