

National Water-Quality Assessment Program

Pesticides in Air and Rainwater in the Midcontinental United States, 1995—Methods and Data

Open-File Report 2007-1369

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

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By Michael S. Majewski, William T. Foreman, Richard H. Coupe, Donald A. Goolsby, and Frank W. Wiebe

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Suggested reference:

Majewski, M.S., Foreman, W.T., Coupe, R.H., Goolsby, D.A., and Wiebe, F.W., 2008, Pesticides in air and rainwater in the midcontinental United States, 1995—Methods and data: U.S. Geological Survey Open-File Report 2007-1369, 24 p. Available at <http://pubs.water.usgs.gov/ofr/2007/1369>

FOREWORD

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). The NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991 to 2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>).

Multiple national and regional assessments are ongoing in the second decade (2001–2012) of the NAWQA Program as 42 of the 51 Study Units are reassessed. These assessments extend the findings in the Study Units by determining status and trends at sites that have been consistently monitored for more than a decade, and filling critical gaps in characterizing the quality of surface water and ground water. For example, increased emphasis has been placed on assessing the quality of source water and finished water associated with many of the Nation's largest community water systems. During the second decade, NAWQA is addressing five national priority topics that build an understanding of how natural features and human activities affect water quality, and establish links between sources of contaminants, the transport of those contaminants through the hydrologic system, and the potential effects of contaminants on humans and aquatic ecosystems. Included are topics on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on aquatic ecosystems, and transport of contaminants to public-supply wells. These topical studies are conducted in those Study Units most affected by these issues; they comprise a set of multi-Study-Unit designs for systematic national assessment. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology are continuing.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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Abbreviations and Acronyms

(Clarification or additional information given in parentheses)

degrees/10	wind direction in degrees divided by 10
GC	gas chromatography
GC/ECD	gas chromatography/electron capture detection
GC/EIMS	gas chromatography/electron-impact mass spectrometry
GC/MS	gas chromatography/mass spectrometry
GC/MS-SIM	gas chromatography/mass spectrometry–selective ion mode
GFF	glass-fiber filter
IADN	Integrated Atmospheric Deposition Network (U.S. and Canadian collaborative project)
ID	identification
IDL	instrument detection level
MDL	method detection limit
MSEA	Management Systems Evaluation Area (U.S. Dept. of Agriculture)
NAWQA	National Water-Quality Assessment (USGS)
NADP	National Atmospheric Deposition Program (Illinois Department of Natural Resources)
n.d	no date
NTN	National Trends Network
PUF	polyurethane foam
QC	quality control
RSD	relative standard deviation
SPE	solid-phase extraction
TSP	total suspended particles
U.S.	United States

Organizations

NOAA	National Oceanic and Atmospheric Administration (NWS)
NWQL	National Water Quality Laboratory (USGS)
NWS	National Weather Service
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Units of Measurement

cm	centimeter (0.3937 in.)
d	day
g	gram (0.0353 ounce)
h	hour
in.	inch (2.54 cm)
kg	kilogram (2.205 pounds)
km	kilometer (0.6214 miles)
L	liter (0.264 gallons)
mL	milliliter (10^{-3} liter)
m	meter (3.28 feet)
m ²	square meter
m ³	cubic meter
mg	milligram (10^{-3} gram)
min	minute
mL	milliliter (10^{-3} liter)
ng	nanogram (10^{-9} gram)
yr	year
μg	microgram (10^{-6} gram)
μL	microliter (10^{-6} liter)
μm	micrometer (10^{-6} meter)

Notes

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

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

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

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$$

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Elevation data were not recorded.

Concentrations of chemical constituents in rainwater are given in micrograms per liter (μg/L); in air, are given in nanograms per cubic meter (ng/m³); and in TSP, are given in micrograms per cubic meter (μg/m³).

NOTE TO USGS USERS: Use of liter (L) as a special name for cubic decimeter (dm³) is restricted to the measurement of liquids and gases.

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Abstract

Weekly composite high-volume air and wet-only deposition samples were collected from April through September 1995 at paired urban and agricultural areas in Mississippi, Iowa, and Minnesota, and at a background site in Michigan's Upper Peninsula. This report describes the methods used to collect, analyze, and quality assure the samples, and presents the results of all chemical analyses and quality control procedures. Each sample was analyzed for 49 compounds, including several pesticides not examined in previous atmospheric studies. Eighty-five percent of the herbicides, 70 percent of the insecticides, and 100 percent of the transformation products that were targeted for analysis were detected in one or more samples at each paired site.

Introduction

The atmosphere is an important, but often neglected, part of the hydrologic cycle with regard to investigating pesticide movement in the environment. The U.S. Geological Survey's (USGS) Toxic Substances Hydrology program (Kolpin, 2000) and the National Water-Quality Assessment (NAWQA) program (Gilliom and others, 1995; Larson and others, 1999; Barbash and others, 1999) are providing a wealth of information on pesticide occurrence and trends in our nation's surface and ground waters. For a more complete understanding of the environmental fate of pesticides, however, the atmospheric component must also be investigated.

Background

A wide variety of pesticides has been detected in the atmosphere throughout the world (Bidleman and others, 1990; Tatsukawa and others, 1990; Majewski and Capel, 1995; van Dijk and Guicherit, 1999, Waite and others, 2005). Pesticides become airborne through volatilization and wind erosion of particles both during and after the application process. Many are applied to agricultural fields by aircraft and some are sprayed directly into the atmosphere, in the attempts to control insects in orchards and mosquitoes and other pests in urban areas. Volatilization from treated areas is a continuous process and can be a major dissipative route for many pesticides (Seiber and Woodrow, 1995; Majewski, 1991; Glotfelty, 1978).

Once airborne, a pesticide will be distributed between the gas and particle phases by adsorptive or absorptive processes, or both (Pankow, 1994a, 1994b; Harner and Bidleman, 1998). This distribution can be estimated from the vapor pressure and octanol-air partition coefficient of the pesticide, and is influenced by the ambient air temperature, humidity, and the type and concentration of airborne particulate matter. The airborne pesticide can be carried by wind and deposited in unintended areas by dry deposition (gases, particles, and fog) and wet deposition (rain and snow). These deposited residues can revolatilize, reenter the atmosphere, and be transported and redeposited downwind repeatedly until they are transformed or they accumulate, usually in areas with cooler climates (Risebrough, 1990; Wania and Mackay, 1996). This same process also can occur for the products from abiotic or biotic transformations of pesticides. For persistent compounds, this deposition and revolatilization process can continue for decades.

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In 1995, more than 550 million kg of pesticides were used in the United States (U.S.) to control many different types of weeds, insects, and other pests in a wide variety of agricultural, commercial, and urban settings (Aspelin, 1997; Aspelin and Grube, 1999). Seventy-seven percent of this amount was used in agriculture. The highest density of agricultural activity and harvested cropland in the U.S. is in the upper Midwest and along the lower Mississippi River. A wide variety of herbicides and insecticides are used on many of the diverse crops grown in this region. Pesticides are not only used in agriculture, however. The U.S. Environmental Protection Agency (USEPA) estimates that about one quarter of all conventional pesticides used in the U.S. are for nonagricultural purposes, primarily for home and garden uses (Whitmore and others, 1992). Pest control applications are also used in and around industrial, commercial, and governmental properties, parks, golf courses, and other public areas. Many of the same pesticides used in agriculture also are used in urban areas, but others are not and should not be detected in urban areas. Increased pesticide use has resulted in increased crop production, more visually appealing produce, insect-population-controlled living and work environments, and weed-free lawns. Concurrently, concerns about the potential adverse effects of pesticides and pesticide transformation products on the environment and human health have grown.

To address the lack of information on pesticides and pesticide transformation products in the atmosphere, the USGS has conducted several studies to determine the occurrence, concentrations, and geographic distribution of pesticides in the atmosphere of the Midwestern U.S. During 1991–92, a study was conducted in 26 Midwestern and Northeastern states to determine the occurrence, spatial distribution, and deposition of several corn and soybean herbicides in precipitation (Goolsby and others, 1995; Goolsby and others, 1997). This study found detectable concentrations of herbicides in precipitation in all 26 states. Estimated deposition rates for atrazine and alachlor ranged from more than 240 mg/m²/yr in some Corn Belt states to 12–63 mg/m²/yr on the Great Lakes to less than 10 mg/m²/yr in New England. In 1994, a brief study of pesticides in air along the Mississippi River from New Orleans, Louisiana, to Saint Paul, Minnesota, analyzed samples for 42 pesticides and 3 pesticide transformation products. Twenty-five compounds—15 herbicides, 7 insecticides, and 3 transformation products—were detected in concentrations ranging from 0.05 to 80 ng/m³ (Majewski and others, 1998). In 1995, the USGS conducted

a detailed study of the atmospheric occurrence of pesticide compounds in atmospheric gases, particles, and rainwater at three locations in the Mississippi River Valley plus a reference site. Partial interpretations of the results from this study have been published by Majewski and others (2000), Foreman and others (2000), and Coupe and others (2000).

Purpose and Objectives of Study and Report

This study was designed to characterize the atmospheric occurrence, temporal, transport, and wet depositional patterns for a variety of pesticides used in the agricultural and urban environments of three geographically different regions of the Mississippi River Valley—Mississippi, Iowa, and Minnesota. Atmospheric monitoring in each geographic region consisted of paired monitoring sites, with one station located in an urban area and the other in an agricultural area. A background site in Michigan's Upper Peninsula far from major metropolitan and agricultural areas was also included in the study. Samples from this site allowed for the investigation of long-range atmospheric transport and deposition into a more remote and pristine area. Scientists conducting the study collected air (both operationally defined gas and particle phases) and precipitation (rain) for 6 months, from April to September 1995. Each sample was a weekly composite and was analyzed for a wide variety of currently used pesticides and several transformation products.

The principal objectives of the study were to:

1. Document the occurrence and detection frequency of a wide variety of herbicides, insecticides, and selected transformation products in three atmospheric matrices (operationally defined gas and particle phases, and precipitation) over one growing season.
2. Compare the types of pesticides detected at urban and agricultural environments in three geographically different areas of the Mississippi River Valley.
3. Investigate the long-range transport potential for the targeted pesticides.

The objective of this report is to describe the methodology used to collect, analyze, and quality assure the samples, and presents the results of all chemical analyses and quality control results.

Acknowledgments

We thank Larry Shelton, USGS Hydrological Technician, for his valuable assistance in the initial instrument design modifications and set-up of the rain samplers, and with the air sampler calibration at each site. We also thank the USGS NAWQA personnel and others involved in the maintenance and service of the collectors, the sample processing and shipping, as well as in the installation and removal of the sampling equipment: Mississippi—Mike Manning; Iowa—Brenda Nations, Debra Sneck-Fahrer, Ron Kuzniar; Minnesota—Greg Stratton; Michigan—Dr. Martin Auer, Department of Civil and Environmental Engineering, Michigan Technical University, Houten, Michigan, and his graduate students James Pauer and Aron Cromwell. We also thank J.R. Drivas, Buddy Hyde, Scott McBride, and John C. McKenzie for their help in preparing the glass-fiber filters, Bill Battaglin and Mike Thurman for their thoughts, suggestions, and efforts in the initial planning and design of the study, and Mike McGinley, Galen Frahm, Jeff Coup, Steve Glodt, Mark Sandstrom, and Mike Schroeder for their analytical or technical support.

Site Selection, Description, Criteria, and Identification

Paired monitoring sites were established in agricultural and urban–suburban settings in each of three geographic areas within the Mississippi River Valley ([fig. 1](#)). These areas were (1) the delta region in west-central Mississippi, (2) east-central Iowa, and (3) the Minneapolis vicinity in east-central Minnesota. The urban–agricultural paired sites were chosen to be within 100 km of each other to allow comparison of pesticide occurrence in these different land-use environments. Each of the monitoring sites was also chosen to be within or near an existing USGS NAWQA study unit (Gilliom and others, 1995). Each sampling site was uniquely identified by latitude and longitude. In addition, a background monitoring site was established in northern Michigan near Lake Superior, far from major metropolitan and agricultural areas. The logistical requirements for each site were that they be easily accessible to USGS personnel, reasonably secure from public access, and have a 120-volt power source available to operate the samplers.

To the extent possible, the sampling sites and the sample-collector placement followed the protocols recommended by the NADP/NTN (National Atmospheric Deposition Program/ National Trends Network) (Bigelow, 1984; Bigelow and Dossett, 1988). Briefly, these requirements state that the collector should be located in an area that:

- typifies the region;
- minimizes the impact of local point or area sources;

- is at least 10 km from major industrial operations (including power plants, chemical plants, and large manufacturing facilities); and
- is far enough removed from objects and structures surrounding the collector that would interfere with the sample collection (the 45° angle rule).

Because the NADP/NTN sampling system was developed to study atmospheric deposition at sites that are regionally representative of surrounding ecoregions, the guidelines pertaining to urban influences could not be strictly adhered to at the urban sites, and the 45° angle rule was not always attainable with respect to utility poles. Care was taken, however, to locate these sites to minimize impacts from local point or area sources.

Mississippi Study Area

The USGS NAWQA study unit responsible for maintaining these sites and sample collection was the Mississippi Embayment Study Unit (Mallory, 1994), based in Pearl, Mississippi.

Urban Location—Jackson (site ID number 321604090124050).

This urban site is located near a residential neighborhood at the intersection of Interstate 55 and McDowell Road, in the southeast Jackson metropolitan area (population 202,062 in 1996, U.S. Census Bureau, 1998) of Hinds County in central Mississippi ([fig. 1](#)). The samplers were located within the confines of a Highway Department construction facility, but no pesticide operations were staged from this facility. The air and precipitation samplers were installed on a wooden platform elevated about 1 m above the ground ([photo 1](#)). This site was representative of a suburban airshed and was several kilometers from the nearest agricultural field.



Photo 1. Urban sampling site at Jackson, Mississippi.



Figure 1. Study area showing sampling locations. Urban sites (Jackson, Mississippi; Iowa City, Iowa; and Minneapolis, Minnesota); agricultural sites (Rolling Fork, Mississippi; Cedar Rapids, Iowa; and Princeton, Minnesota); and background site (Eagle Harbor, Michigan).

Agricultural Location—Rolling Fork (site ID number 325626090553650).

This agricultural site is located in the center of a catfish-aquaculture complex ([photo 2](#)) near the town of Rolling Fork in Sharkey County (population 6,833 in 1995, U.S. Census Bureau, 1995) in the Mississippi River Delta region of upper Mississippi ([fig. 1](#)). No pesticides were used within the aquaculture complex, but the complex is surrounded by intense agricultural activity including cotton, soybeans, pecan, corn, and some rice production. The nearest field was located about 0.5 km away. This site was representative of an agricultural airshed in this region of Mississippi even though the micrometeorology would be different from that in an actual crop field. This site was about 80 km northwest of the Jackson urban site.



Photo 2. Agricultural sampling site at Rolling Fork, Mississippi.

Iowa Study Area

The NAWQA study unit responsible for maintaining these sites and sample collection was the Eastern Iowa Basins Study Unit (Kalkhoff, 1996), based in Iowa City, Iowa.

Urban Location—Iowa City (site ID number 413937091314501).

This urban site is located in downtown Iowa City (population 59,735 in 1996, U.S. Census Bureau, 1998) in Johnson County, Iowa ([fig. 1](#)) in east-central Iowa. The sampler was located on the roof of the Iowa City police station ([photo 3](#)) at 410 East Washington Street. The area immediately surrounding the site consists of a mixture of residential housing, small businesses, and light industry. Iowa City is situated in the heart of the Corn Belt, and is surrounded by intense corn production. The nearest agricultural fields were about 5 km to the west and about 4 km to the east.



Photo 3. Urban sampling site at Iowa City, Iowa.

Agricultural Location—Cedar Rapids (site ID number 415236091423401).

This agricultural site is located at the Cedar Rapids airport in Linn County ([fig. 1](#)) and situated about 16 km south of the city of Cedar Rapids (population 108,772 in 1996, U.S. Census Bureau, 1998). The samplers were placed in a grassy area, but were within about 15 m from a cornfield ([photos 4A](#) and [4B](#)). The area surrounding the sampling site, with the exception of the airport, was agricultural fields, mostly used for corn production. It is not known how much or what type of herbicides were used at the airport. This sampling site was about 34 km north of the Iowa City urban site.



Photo 4A. Agricultural sampling site at Cedar Rapids, Iowa.



Photo 4B. Agricultural sampling site at Cedar Rapids, Iowa, alternate view.

Minnesota Study Area

The NAWQA study unit responsible for maintaining these sites and sample collection was the Upper Mississippi River Basin Study Unit (Stark and others, 1996) based in Mounds View, Minnesota.

Urban Location—Minneapolis (site ID number 445557093173001).

This urban site is located in a suburban area of the city of Minneapolis, (population 368,383 in 1990, U.S. Census Bureau, 1998) near Lake Harriet in Hennepin County ([fig. 1](#)). The population of the Minneapolis metropolitan area is approximately two million. The samplers were located within the confines of the Minneapolis Park and Recreation Board field office and storage area ([photo 5](#)), but no pesticide use or preparation activities were staged from this facility. The land use in the immediate area surrounding the site was mainly residential (94 percent) with some light commercial (4 percent). The Minneapolis metropolitan area is surrounded by agricultural areas that are intensively farmed with row crops. The nearest substantial agricultural fields were about 30 km or more in all directions from this site. Other, related USGS atmospheric studies have been conducted at this site, including co-located samples collected in 1995 (Capel and others, 1998; Young, 1998; Ma, 2000) along with those described in this report.



Photo 5. Urban sampling site at Minneapolis, Minnesota.

Agricultural Location—Princeton (site ID number 453136093365101).

This agricultural site is located about 5 km southwest of Princeton, Minnesota, (population 52,809 in 1995, U.S. Census Bureau, 1998) in Sherburne County ([fig. 1](#)). The samplers were located about 300 m west of a U.S. Department of Agriculture MSEA (Management Systems Evaluation Area) research field ([photo 6](#)) near observation well MC19 (see [fig. 4](#) in Delin and others, 1994). Information on crop type and pesticide application activities on the MSEA fields was known. Agricultural activities to non-MSEA fields located across 136th Street to the east and across 305th Street south of the sampler, however, were unknown. Related atmospheric studies by the USGS have been conducted at this MSEA location (Capel and others, 1998). This site was about 80 km northwest of Minneapolis.



Photo 6. Agricultural sampling site at Princeton, Minnesota.

Michigan Background Site

There were no NAWQA study units in Michigan's Upper Peninsula that could maintain this site or collect the samples. This site was managed by graduate students from Michigan Technical Institute in Houghton, Michigan.

Background Location—Eagle Harbor (site ID number 47274708808590)

Eagle Harbor is a summer resort town on the north shore of upper Michigan's Keweenaw Peninsula ([fig. 1](#)). This site was located near Eagle Harbor in Keweenaw County (population 1,953 in 1995, U.S. Census Bureau, 1995). The sampling site was located at the Integrated Atmospheric Deposition Network (IADN) sampling site ([photos 7A](#) and [7B](#)), 100 m from Lake Superior. IADN was established by the U.S. and Canadian governments for conducting air and precipitation monitoring in the Great Lakes Basin (Egar and Adamkus, 1990; Mills and Ullrich, 1998).



Photo 7A. Background sampling site at Eagle Harbor, Michigan.



Photo 7B. Background sampling site at Eagle Harbor, Michigan, alternate view.

Sample Collection Methods

The techniques used for collecting both the air and the rain samples were based on established methodologies (Thrane and Mikalsen, 1981; U.S. Environmental Protection Agency, 1997; Bigelow and Dossett, 1988). Each sampling site consisted of a conventional high-volume air sampler to collect atmospheric particles and gas-phase pesticides, an automatic wet-dry precipitation collector to collect wet-only deposition, and a precipitation gage to record the total rainfall amount during the sampling period.

Field Sampling

Air

Air samples were collected using a modified high-volume air sampler (Anderson, Inc., Cleves, Ohio). The sampling train consisted of a stainless-steel filter holder connected to an 18-cm-long aluminum cylindrical cartridge (the modification) that was connected to an electric blower motor ([photo 8](#)). The whole assembly was housed in an aluminum shelter. The top of the filter holder was covered with a fine-mesh, stainless-steel screen that held a 20.3 × 27.9 cm GFF (glass-fiber filter, Whatman, Inc., number EPM2000). The GFF was used to collect airborne particles and was rated to have a 99.999 percent retention efficiency for sodium chloride particles having a mass median diameter of 0.6 μm at a 5 cm/s face velocity (Whatman, n.d.). The aluminum cartridge held two 7.6-cm long by 8.6-cm diameter PUF (polyurethane foam) plugs positioned in series. The PUF was used to collect pesticides present in the gas phase. The blower motor pulled ambient air through the GFF and the PUF at a constant flow rate (ranging from 0.90 to 1.26 cubic meters of air per minute [m^3/min]) that was monitored and controlled by a mass flow controller. Most air samples were 7-d composites taken concurrently with the rain sample collection. Initially, the air samples were collected for a continuous 4-h period each day from 10 a.m. to 2 p.m. By mid-May, sampling times at all sites except Eagle Harbor were modified to sample for 5 min every hour, 24 h a day, for the 7-d period. The sample timing at Eagle Harbor was changed by mid-June. This change in the sampling procedure was made to include the diurnal variations in ambient concentrations and to provide a more representative air sample (Wallace and Hites, 1996). Typical week long air volumes for the 4 h/d sampling regime were about 2,000 m^3 per sample. The 5-min/h sampling regime averaged about 850 m^3 per sample.



Photo 8. Air sampler showing the glass-fiber filter holder and the polyurethane foam cartridge.

Prior to use, the GFFs were precleaned by the USGS's Quality of Water Service Unit in Ocala, Florida, by baking at 500 °C (degrees Celsius) for several hours. Each GFF was then desiccated overnight, preweighed to 0.1 mg, packaged in heat-treated aluminum foil, and sealed inside a plastic bag for storage and shipment. The cleaned GFFs were then shipped to each of the NAWQA study unit offices responsible for sample collection. All subsequent handling of the GFFs (and the PUF plugs) was performed using solvent-rinsed stainless-steel forceps.

The PUF plugs were precleaned, prior to use, by initial extractions with water, rinsed with acetone to remove excess water, followed by sequential overnight extractions in a Soxhlet apparatus with pesticide-grade acetone followed by hexane. Residual solvent was drained from the extracted PUFs, and the plugs were dried in a vacuum oven. Individual plugs were stored and shipped in heat-treated, wide-mouth glass jars with Teflon-lined lids.

At the field office prior to sampling, two clean PUF plugs were carefully placed into the aluminum cartridge using clean forceps. The plugs were designated as “front” (or “top”) and “back” (or “bottom”) depending on their position in the cartridge relative to the airflow direction through the cartridge. The ends of the cartridge were sealed using screw caps with solvent-rinsed silicone gaskets. The cartridge was then sealed in a large plastic bag for transport to the sampling site.

At the field site, the air sampler was assembled by attaching the PUF cartridge to the sampler blower motor, attaching the stainless-steel filter holder to the top of the PUF cartridge, followed by placing a clean GFF on the screen of the filter holder using forceps. The GFF was held in place with a solvent-rinsed gasket and a rigid aluminum frame that was secured to the filter holder assembly. At the end of each sampling period, the exposed GFF was carefully removed from the screen of the filter holder and placed back into the original aluminum foil. Any GFF fragments adhering to the filter holder screen and gasket were carefully removed with the forceps and placed onto the center of the GFF sample. Recovery of the entire filter matrix was required, because the weight of the collected particulate material was used to determine a total suspended particle concentration (TSP; see below). The loss of any filter fragments would result in a lower than actual TSP calculation. The GFF was gently folded in half and again into a quarter of its original size, with the air particles inside the filter. The GFF was then wrapped in the original aluminum foil and sealed in the original plastic bag. The used PUF cartridge was removed from the sampler and the ends sealed with the caps from the new PUF cartridge. The used PUF cartridge was then sealed in a plastic bag and stored, along with the GFF, in a cooler containing ice for transport to the field office. The new PUF cartridge and GFF were placed into the air sampler to begin the next sample. Basic sample collection information recorded for each air sample included the sampling period start and stop dates and times, elapsed run time from the blower motor counter, and the airflow rate.

Before each air sampler was used to collect an environmental sample, the airflow rate was calibrated according to the manufacturer specifications and set to about 1.1 m³/min. The calibration on each sampler was rechecked in late June. The electric blower motors that pulled the air through the GFF and PUF plugs use graphite brushes to operate. These brushes wear down with use and needed to be replaced periodically. The air sampling unit was recalibrated and the airflow rate set to about 1 m³/min after the graphite brushes were replaced and seated properly, or if a new motor was installed.

Rain

Weekly wet-only precipitation samples were collected using a modified automatic wet-dry precipitation collector (Aerochem Metrics, Model 301, Bushnell, Florida). Modifications to the collector included replacing the plastic collection bucket with a 31-cm diameter, Teflon coated,

metal funnel connected by corrugated Teflon tubing to a 9-L glass carboy inside a small refrigeration unit located beneath the deposition collector ([photo 9](#)). The tubing was held in place and the top of the carboy was covered with aluminum foil. Teflon sheeting also lined the rain sampler lid that automatically covered the funnel during dry periods.

Before the first use, the funnel, connecting tubing, and carboy were thoroughly cleaned by washing with a 1 percent Liquinox detergent solution, followed by thorough sequential rinsing with tap water, distilled or deionized water, and organic-free water. Finally, each component was rinsed with pesticide-grade methanol and allowed to air dry. The carboy was then capped with a stopper covered with solvent-rinsed or heat-treated aluminum foil until used.



Photo 9. Modified automatic wet-deposition collector showing the refrigerated water-collection container.

During a rainfall event, a rain sensor on the sampling unit activated a motor that moved the lid, exposing the collection funnel to precipitation. The collected rainwater was funneled into the carboy and refrigerated at 4 °C. Refrigeration was used to help minimize evaporative losses of the water and to reduce volatilization losses and biotic and abiotic degradation of the pesticides during the sample collection period.

The total amount (in cm) of rainwater accumulated during the sample collection period was obtained from a rain gauge (Belfort recording precipitation gage) at each site. The amount of rain that fell in a 1-week period ranged from zero to several centimeters. Most samples were a composite of precipitation events that occurred during a 1-week (7-d) period. If more than 1-L of rainwater was collected during a sampling period, the total volume was recorded and a 1-L subsample was taken for analysis as describe below. Large rain events in mid-April, 1995, resulted in shorter collection periods for several samples collected at Jackson and Rolling Fork, Mississippi. In two cases (April 12 and July 18 samples), the sample collection bottles filled to overflowing and the total sample volume was estimated. To ensure reasonable analytical results, at least 75 mL of rainfall were required as a minimum sample size. This volume of rainwater would be produced by a rainfall of about 0.1 cm (about 0.04 in.) being collected by the precipitation sampler. Sufficient rainwater was collected to provide 75 mL or greater volumes of water used for the analysis of all samples in this study with the exception of two weekly samples from Cedar Rapids (69 mL, July 11 and 62 mL, August 1) and one weekly sample from Minneapolis (64 mL, August 24). Typically, if less than 75 mL of rainwater was collected at the end of the 1-week sampling period, it was left in the container, and the sampling period was extended for another week. If at the end of the 2-week period, there still was not sufficient rainwater for an appropriate sample extraction, the liquid was discarded, and a clean carboy was placed into the refrigerator, and a new collection period began. Each glass container was marked to show the 75-mL, 350-mL, and 1-L fill volumes to help quickly make decisions about whether enough rainwater was collected to warrant processing the sample.

At the end of a sample collection period, the corrugated Teflon tubing attached to the funnel was shaken to dislodge and transfer any trapped rainwater into the collection carboy. The carboy was then removed from the refrigerator and capped with an aluminum-foil covered stopper. The carboy was placed into a cooler with ice and transported to the local field office for subsequent sample processing (see below).

In preparation for the next sample, the Teflon-coated funnel and tubing were washed with the detergent solution, using a soft brush if necessary, followed by thorough sequential rinsing with tap water and distilled or deionized water, followed by a rinse with pesticide-grade methanol and allowed to air dry. This cleaning was done on-site in the field laboratory vehicle. A precleaned 9-L collection carboy was placed in the refrigerator, the tubing inserted into the carboy,

and clean aluminum foil wrapped around the mouth of the carboy to secure the tubing in place.

Meteorological Data

Meteorological measurements (air temperature, relative humidity, wind speed, and wind direction) were not taken at the sampling sites with the exception of the Princeton, Minnesota, and the Eagle Harbor, Michigan, sites. Each of these two sites had fully instrumented weather stations near the sampling location that were operated as part of existing research operations in the immediate area. Meteorological information for the other sites was obtained from the nearest National Weather Service (NWS) site, usually located at the nearest airport. Often the closest meteorological site was several kilometers from the sampling site and consisted of hourly maximum and minimum air temperature and wind speed and direction. The rainfall amounts accumulated during the sampling period were recorded continuously at each site by the co-located recording rain gage. The units that the meteorological parameters were recorded in were often different from one site to the next.

Meteorological data for the Jackson and Rolling Fork sites were obtained from the National Climatic Data Center, Asheville, North Carolina. Daily maximum, minimum, and mean air temperature (°F) values, plus daily means of wind speed (mi/h), and wind direction (degrees) for Jackson were recorded at the Allen C. Thompson Air Field (site ID number 321909005). Weekly mean, maximum, and minimum values of these data are listed in [Appendix 1](#). Meteorological data for Rolling Fork was obtained from two sites: Rolling Fork and Greenville, Mississippi. The Rolling Fork site (site ID number 325409053) recorded daily maximum, minimum, and mean air temperature (°F), and the Greenville Municipal Airport site (site ID number 3329090 04) recorded hourly wind speed (knots) and direction (degrees/10) from about noon to midnight each day. Weekly mean, maximum, and minimum values of these data are listed in [Appendix 2](#). The same meteorological data were used for both the Iowa sites because the only available data for the area was from the Cedar Rapids International Airport (site ID number 415209142). Data for the Iowa and Minneapolis sites were obtained from the NWS's National Oceanic and Atmospheric Administration (NOAA), Midwest Regional Climatic Center, Champaign, Illinois. These data consisted of hourly measurements of air temperature (°F), relative humidity (percent), wind speed (mi/h), and wind direction (degree/10) and were measured at the Cedar Rapids International Airport and at the Minneapolis–St. Paul International Airport (site ID number 445209313). Weekly mean, maximum, and minimum values of these data for the Iowa sites are listed in [Appendix 3](#), and in [Appendix 4](#) for the Minneapolis site.

Both the Princeton and the Eagle Harbor sites had on-site meteorological stations operated and maintained by other organizations conducting research in the area. The University of Minnesota at Minneapolis operated the MSEA site at which the USGS–Princeton site was located and provided the meteorological data for the site. Weekly means of air temperature (°C) wind speed (m/s), and wind direction (degrees) are listed in [Appendix 5](#). The University of Indiana at Bloomington operated the IADN site at which the USGS–Eagle Harbor site was located and provided the meteorological data for the site. Weekly mean, maximum, and minimum values of air temperature (°C), relative humidity (percent), wind speed (m/s), and wind direction (degrees) are listed in [Appendix 6](#).

Analytical Methods

The rain samples were analyzed using a USGS method designed for the determination of 44 primarily high-use pesticides and 5 pesticide degradates ([table 1](#)) in 1-L filtered water samples (Zaugg and others, 1995). The method was developed initially to support analysis of water samples collected by the USGS's NAWQA program (Gilliom and others, 1995). Dissolved-phase analytes were extracted from water using an octadecyl (C-18) solid-phase extraction (SPE) column and determined by gas chromatography/mass spectrometry (GC/MS). This study represents one of the first applications of this water method to rain samples. The degradates that were targeted for analysis included 2,6-dichloroaniline, formed from alachlor; 2-chloro-4-isopropylamino-6-amino-*s*-triazine (CIAT), a potential degradation product of either atrazine or propazine; and 4,4'-DDE (*p,p'*-DDE), the primary aerobic microbial and photooxidative degradation product of the insecticide 4,4'-DDT (Crosby and Moilanen, 1977). Neither DDT nor the anaerobic degradation product 4,4'-DDD were included as compounds in the rain or air method. The air method targeted the same 47 analytes determined in the rain method, plus dimethoate and 2-chloro-4-ethylamino-6-amino-*s*-triazine (CEAT), a potential degradation product of atrazine, cyanazine, simazine, and terbuthylazine ([table 1](#)). The custom air method was based, in part, on aspects of other high-volume air methods (Foreman and Bidleman, 1990; U.S. Environmental Protection Agency, 1997), and incorporated some extract preparation and the GC/MS analytical procedures of the water method to facilitate data interpretation. Portions of this air method previously were used for the determination of gas-phase pesticides in air samples collected along the Mississippi River (Majewski and others, 1998).

Sample Preparation—Air

The GFF and PUF plugs from the field samples were prepared and analyzed individually to facilitate interpretation of apparent gas–particle distributions of the detected pesticides. In addition, each of the two in-series PUF plugs was individually extracted and analyzed to monitor the field collection efficiency of the PUF for pesticides in the gas phase.

Upon receipt at the NWQL (National Water Quality Laboratory), each sample component (one GFF wrapped in aluminum foil and sealed within a plastic storage bag, and two PUF plugs in separate glass jars) were stored at –10 °C until prepared for analysis. Storage times ranged from several days to up to 5 months. No storage stability experiments were conducted as a part of this study. Each air sample was prepared for analysis in batches that are identified by a “set number” in this document. Samples or components of samples from weeks 1 through 5 overlapped two or more sets. For weeks 6 through 24, all samples for a given week were contained within a discrete set. The set numbers are provided in many of the data tables to provide a cross reference link between the field-sample and the quality-control data.

Prior to extraction the foil wrapped GFF was removed from the storage bag, the foil partially opened, was then placed in a desiccator containing moisture-indicating drying agent for 24 h at room temperature. Following desiccation, the GFF was immediately weighed to 0.1 mg. The difference in this weight and the original GFF tare weight provided the mass of particles collected on the GFF, assuming the entire GFF matrix was recovered when removed from the sample holder. The TSP concentration (in micrograms per meter cube of air, $\mu\text{g}/\text{m}^3$) was obtained by dividing the mass of particles collected by the volume of air sampled.

Next, each GFF was cut into approximately 6-cm- by 2-cm-wide strips and placed into a 500-mL boiling flask containing extraction solvent (see below) for reflux extraction as used by Foreman and Bidleman (1990). Each PUF plug was inserted sideways into a Soxhlet extractor using solvent-cleaned, stainless-steel forceps. Each PUF plug was handled carefully to avoid tearing the foam, because most plugs were reused at least once (see below). To each sample component, 100 μL of a methanol surrogate solution containing 1 ng/ μL each of $^2\text{H}_{10}$ -diazinon (diazinon-d10), $^2\text{H}_6$ - α -hexachlorocyclohexane (α -HCH-d6), and terbuthylazine was added. This addition was made to the top of the PUF plug or directly into the round bottom flask containing the GFF strips. Each component was then extracted with 300 mL of either a 1:1 by volume acetone:hexane solution (samples collected prior to May 16, 1995; sets 95.168 and lower) or a 36 percent ethyl acetate in hexane solution (May 16, 1995 and later samples; sets 95.177 and higher) for at least 16 h. Following extraction, clean, granular sodium sulfate was added to the extracts to remove any residual water. The extracts were then stored at either –10 °C or 4 °C between subsequent preparation steps, as necessary.

Table 1. Analyte list, grouped by chemical class, and associated reporting levels for rainwater and air methods.

[m³, cubic meter; na, compound not included in water sample analysis; ng/m³, nanogram per cubic meter; PUF, polyurethane foam; µg/L, microgram per liter; —, reporting level not estimated because of poor PUF collection efficiency; >, greater than; ≥, greater or equal to]

Herbicides	Reporting level		Insecticides	Reporting level	
	Air samples ¹ (ng/m ³)	Rain samples ² (µg/L)		Air samples ¹ (ng/m ³)	Rain samples ² (µg/L)
Chloroacetanilides			Organophosphates		
Acetochlor	0.012	0.002	Azinphos-methyl ⁹	0.076	0.001
Alachlor	0.012	0.002	Chlorpyrifos	0.024	0.004
2,6-Diethylaniline ^{3,4}	—	0.003	Diazinon	0.012	0.002
Metolachlor	0.012	0.002	Dimethoate	0.047	na
Propachlor	0.041	0.007	Disulfoton ⁹	0.100	0.017
Triazines			Ethoprop ⁵		0.003
Atrazine	0.006	0.001	Fonofos	0.018	0.003
CEAT ⁶	0.018	na	Malathion	0.058	0.005
CIAT ⁷	0.012	0.002	Methyl parathion	0.035	0.006
Cyanazine	0.024	0.004	Parathion	0.024	0.004
Metribuzin	0.024	0.004	Phorate ⁴	—	0.002
Prometon ⁸	0.106	0.018	Terbufos ⁴	—	0.013
Simazine	0.029	0.005	Carbamates		
Dinitroanilines			Carbaryl ⁹	0.036	0.003
Benfluralin ⁵	0.100	0.002	Carbofuran ⁹	0.036	0.003
Ethalfuralin ⁵	0.100	0.004	Organochlorines		
Trifluralin ⁵	0.100	0.002	α-HCH	0.012	0.002
Pendimethalin	0.024	0.004	γ-HCH (Lindane)	0.024	0.004
Thiocarbamates			4,4'-DDE ¹⁰	0.035	0.006
Butylate ⁴	—	0.002	Dieldrin	0.006	0.001
EPTC ⁴	—	0.002	cis-Permethrin	0.029	0.005
Pebulate ⁴	—	0.004	Fungicide		
Triallate	0.012	0.001	Propargite I and II ¹¹	0.076	0.013
Thiobencarb	0.012	0.002			
Miscellaneous					
Dacthal	0.012	0.002			
Linuron	0.012	0.002			
Molinate ⁴	—	0.004			
Napropamide	0.018	0.003			
Pronamide	0.018	0.003			
Propanil	0.024	0.004			
Tebuthiuron ⁸	0.175	0.010			
Terbacil ⁹	0.082	0.007			

¹ Estimated for an air volume of 850 m³.

² Reporting levels for rain method are set at the method detection limit (MDL) values listed in table 9 of Zaugg and others (1995).

³ An alachlor degradation product.

⁴ Gas-phase compound poorly collected by two PUF plugs at air volumes used in this study. No reporting levels for air samples were calculated for these compounds.

⁵ Typical PUF plug breakthrough >50 percent at ≥ 850 m³ air volume.

⁶ CEAT, 2-chloro-4-ethylamino-6-amino-*s*-triazine, a transformation product of atrazine, cyanazine, simazine, and terbuthylazine.

⁷ CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine, a transformation product of atrazine and propazine. CIAT concentrations in the rain method are all estimated because of low recovery of this compound during the solid-phase extraction step (Zaugg and others, 1995).

⁸ Variably low recovery during extract preparation in the air method.

⁹ Estimated quantitation in both rain and air methods because of thermal instability during gas chromatography (Zaugg and others, 1995).

¹⁰ A DDT transformation product. DDT was not determined in the analytical methods used.

¹¹ Propargite consists of two isomeric forms that were incompletely resolved with the analytical conditions used.

The extracts were then reduced to 6 to 10 mL by distillation at 90 °C in a Kuderna-Danish apparatus fitted with a 10-mL receiver tube. This extract was further reduced to 8 mL or less under a gentle stream of nitrogen gas, if needed. A 0.25-mL equivalent amount of granular sodium sulfate was added to the extracts to scavenge any residual water. The extracts were then mixed on a vortex mixer, and more sodium sulfate was added in similar aliquots as required to ensure that all residual water was scavenged from the extracts. The extracts were then reduced to 0.5 mL under a gentle stream of nitrogen gas.

Sample Cleanup

The samples from extraction set 95.118 (including selected sample components from week 1, April 5 and week 2, April 12) initially were passed through a Pasteur pipette column containing about 0.75 g of powdered sodium sulfate and eluted with ethyl acetate to a final volume of 2 mL. This cleanup procedure, however, was inadequate in eliminating unwanted interferences, even after repeating. These extracts were again reduced to about 0.5 mL and introduced into an octadecylsilane (C18) solid-phase extraction (SPE) column (the same column type used to isolate the pesticides from the rainwater samples, see below). The pesticides were eluted from the C18 column with ethyl acetate to a final volume of 4 mL. This C18 column cleanup step was also inadequate in removing sufficient amounts of co-extracted interferences from the PUF extracts, so a Florisil column cleanup procedure was employed for all subsequent samples in this study.

Extracts from sets 95.122 (selected samples from weeks 1 through 3) and above were passed through a Pasteur pipette column containing 0.75 g of Florisil (EMD Chemicals, Inc. number FX0284-1, fully activated at 150 °C for at least 2 h) overlain with 1 cm of powdered sodium sulfate. The Florisil columns were prerinse with at least 6 mL of ethyl acetate prior to introducing the 0.5-mL sample extracts to the columns. The pesticides were eluted from the column with ethyl acetate and collected into a test tube containing 0.1 mL of a perdeuterated polycyclic aromatic hydrocarbon internal standard solution in toluene. The initial column elution volumes were 2 mL for extraction set 95.122. This was increased to 3 mL for sets 95.130 and 95.138 (selected samples from week 3 and all samples from weeks 4 and 5), to 3.5 mL for sets 95.168 through 95.237 (weeks 6 to 13), and finally to 4 mL for all remainder sets (weeks 14 to 24). The ethyl acetate volumes were increased to ensure an adequate elution of all the pesticides from the Florisil column (see Quality Control—Air Samples section below). Any glass fibers in GFF extracts that were not removed during previous sample transfer steps were removed during sample cleanup.

Polyurethane Foam Plug Reuse

Limitations in the total number of PUF plugs available for this study required that the PUF plugs not torn or damaged during handling be reused. After the PUF sample was solvent extracted, the residual solvent was squeezed from it. Each PUF was then vacuum dried at 90 °C, then individually sealed in heat-treated glass jars. The recycled PUF plugs were used in at least one subsequent field sample collection, either as a field air sample or field air blank component.

Sample Preparation—Rain

The rainwater samples were prepared and analyzed according to the procedures detailed in Zaugg and others (1995) and Lindley and others (1996). For all sites except Eagle Harbor, Michigan, the rainwater samples were filtered, and the pesticides were isolated on a C18 SPE column at the field offices using an “on-site” processing procedure (Zaugg and others, 1995). Briefly, this processing procedure included swirling the rainwater sample in the 9-L carboy, then removing approximately 1 L (or less, if 1 L was unavailable) from the carboy and filtering it through a 0.7- μ m pore size GFF into a 1-L heat-treated, amber glass bottle (Sandstrom, 1995). The filtrate was fortified with methanol (volume equivalent to 1 percent of the sample volume) and 100 μ L of a surrogate solution containing 1 ng/ μ g each of diazinon-d10, α -HCH-d6, and terbuthylazine. The water was then passed through a 0.5-g C18 SPE column at about 25 mL/min. The excess water was removed from the cartridge by passing a small volume of air through it. The cartridge was then sealed in a plastic bag, packaged with ice, and shipped to NWQL. The Eagle Harbor water samples were sent to NWQL unfiltered. Both the GFF filtration and SPE isolation steps for these samples were performed at NWQL.

At NWQL, the rainwater extraction cartridges were prepared for analysis along with other water extraction cartridge samples that were submitted from other USGS studies. The samples were processed similar to the air samples, in batches identified by “set number.” Any residual water remaining in the cartridge was removed by briefly passing a gentle stream of dry nitrogen gas through it. The pesticides were eluted from each cartridge with 2 mL of ethyl acetate (substituted for the hexane–isopropanol elution solvent described in Zaugg and others, 1995 and Lindley and others, 1996) into a test tube containing 0.1 mL of a toluene solution containing 1 ng/ μ L each of three perdeuterated polycyclic aromatic hydrocarbon internal standards.

Sample Analysis

Each air and rainwater extract was reduced in volume by evaporating it to about 150 μL using nitrogen gas and a Zymark TurboVap evaporator. They were then transferred into a 400- μL autosampler vial insert along with a 100- μL toluene rinse. Analysis was accomplished using gas chromatography/electron-impact mass spectrometry (GC/EIMS) operated in the selected-ion-monitoring mode. Chromatographic conditions and a listing of quantitative and secondary ions monitored are detailed in Zaugg and others (1995) and Lindley and others (1996). Qualitative identification of an analyte in a sample required meeting both chromatographic and mass spectrometric criteria. The observed retention time of the gas chromatography (GC) peak for the quantitation ion for the analyte needed to be within ± 6 seconds of the expected retention time. These times were computed relative to the internal standard, with expected retention times derived from injections of the calibrations. Mass-spectral verification for each analyte was accomplished by comparing the relative integrated abundance values of the three or four ions monitored with the relative integrated abundance values obtained from the calibration standards. The relative ratios of the monitored ions needed to be within 20 percent of the relative ratios of those obtained on injection of a 1-ng calibration standard in the absence of any obvious interference (Zaugg and others, 1995). Qualitative analysis using dual-column GC with electron capture detection (GC/ECD) (Foreman and others, 1995) was used to verify the presence of 4,4'-DDE in the Rolling Fork 12th week air sample, and dacthal in the Eagle Harbor 12th week air sample.

Method Analyte Reporting Levels

The reporting levels for the water method used for the rainwater samples were set equivalent to the method detection limit (MDL) calculated by Zaugg and others (1995) and Lindley and others (1996) using the approach of the U.S. Environmental Protection Agency (1997). The reporting levels for all the analytes included in the air and rain methods are shown in [table 1](#). An MDL determination was not performed for the air method. Reporting levels for the air method were estimated on the basis of reporting levels for the water method. These estimates were based on a typical 850- m^3 sample volume and were set with consideration for the recoveries from the air method laboratory-spike samples, the field PUF collection efficiency experiments, and interfering compounds observed in the samples and blanks. For seven compounds, the PUF collection efficiencies were so poor at the typical air volumes used in this study (see below) that reporting levels were not estimated. Reported concentrations for these seven analytes in field samples are, most likely, substantial underestimates of the true air concentration.

The concentrations of four analytes—azinphos-methyl, carbaryl, carbofuran, and terbacil—if detected, were reported as an estimated value and qualified with an “E” code. These compounds were susceptible to thermal instability during GC/MS–SIM (selective ion mode) analysis that could result in a high or low bias during analyte quantitation (Zaugg and others, 1995). CIAT exhibited a reduced collection efficiency on the SPE column (42 percent mean recovery in laboratory water spike recovery results, see below), and its concentration was also qualified with an E code for the rainwater samples only. CIAT was well recovered in the air method and the E code qualification was not needed. Reported concentrations for those analytes detected in either the air or water samples that were at or below the reporting level for the method were also qualified with an E code. Tebuthiuron and prometon exhibited variably poor recoveries in the laboratory preparation of the air sample extracts and are coded with an “R.”

Field Data Results

The pesticide concentration data for each site are presented in tables starting with the most southern site at Jackson, Mississippi, and ending with the most northern site at Eagle Harbor, Michigan. The air concentration units are in ng/m^3 , and the rainwater concentration units are in $\mu\text{g}/\text{L}$. The analytes in each table are sorted by type (herbicide or insecticide) and ordered by chemical class, as shown in [table 1](#).

Air

Tables 2 through 8 (for access to tables 2 through 8, see list of [Tables](#)) show the GFF and PUF air concentration data for each sampling site. Each data table includes the start sampling date, the week number, the type of sample component (GFF, front PUF, back PUF), set number, total air sample volume (m^3), total particle weight (g), TSP concentration ($\mu\text{g}/\text{m}^3$), and analytical results (ng/m^3) for each sample. At the bottom of each analyte column is the number of times and percent that the analyte was detected on a GFF and PUF during the study at that site. At the bottom of each of the surrogate compounds at the end of each table are the mean percent recovery and standard deviation for the number of samples analyzed. Table 9 (see at [table 9.xls](#)) lists the field and laboratory comments associated with each air sample component.

Rain

Tables 10 through 16 (for access to tables 10 through 16, see list of [Tables](#)) show the rainwater concentration data for each sampling site. Each data table includes the start sampling date, set number, sample volume (mL), rainfall amount (cm), and analytical results ($\mu\text{g/L}$) for each sample. At the bottom of each analyte column is the number of times and percent that the analyte was detected during the study at that site. At the bottom of each of the surrogate compounds at the end of each table are the mean percent recovery and standard deviation for the number of samples analyzed. Table 17 (see at [table 17.xls](#)) lists the field comments associated with each rainwater sample.

Quality Assurance Program

A number of quality control (QC) activities were performed during this study to ensure the quality of the sampling and analytical methods. They were designed to monitor various aspects of the field sampling and analytical method performance for both the air and the rain samples, and included field blanks, laboratory blanks, equipment blanks, PUF collection efficiency spike experiments, field checks of the PUF trapping efficiency, and analyte storage stability in rainwater. The surrogate compounds diazinon-d10, α -HCH-d6, and terbuthylazine were added to all the samples (including the QC samples), as detailed above, to monitor sample-specific preparation and analytical efficiencies. Both the air and rain methods had QC procedures designed for the specific method and are discussed in detail below.

Quality Control for Air Samples

The sampling method used in this study to trap airborne pesticides is dependent on the capability of the GFF to trap the wide range of particulate matter that pesticides will sorb to, and the capability of the PUF to effectively sorb and retain the pesticides in the gas phase. The particle size range trapped by the GFF is based on the physical properties of the filter and is determined by the manufacturer. The capability of the PUF to trap and retain gas-phase pesticides is dependent on the physical and chemical properties of each pesticide and the PUF matrix that allow sorption to occur. Once sorbed to the PUF, each pesticide can also migrate through the PUF during the course of the sampling period. This migration is influenced

by the physical and chemical properties of the pesticide as well as by environmental conditions such as the airflow rate through the PUF, the air temperature, and the atmospheric moisture content (Pankow, 1989; Bidleman, 1985). The PUF collection efficiencies for each pesticide and their migration potential were assessed in two ways. The first was with a spike experiment, and the second was by separate analyses of each PUF plug in almost all field samples as described below.

Sample-specific estimates of collection efficiencies for pesticides in the gas phase by the two PUF plugs were assessed by separate analysis of the front and back PUF plugs on nearly all field air samples. The presence of minimal amounts of an analyte on the back plug relative to the front plug suggested minimal penetration of the pesticide beyond the front plug and a complete collection of the gas phase by both plugs. The presence of an analyte in the back PUF at a concentration greater than in the front PUF, or its presence only in the back PUF, suggested that the collection efficiency for that compound was low, that the compound migrated through the PUF during the sampling period. In this situation, the total measured analyte concentration in the sample may represent a lower than actual air concentration.

Air Method Set Blanks

One (or more) air method set-blank sample (air set blank) was processed with each set of field air samples. Most air set blanks were prepared using the field equipment air blanks submitted on a rotating basis from each of the seven sampling locations. These field air blanks were taken by briefly installing one GFF and two PUF plugs into the air sampler, then removing and placing them back into their original storage containers. The sampler was not turned on, and no air was pulled through the GFF and PUF plugs. The field air blanks used as air set blanks typically consisted of a GFF plus two PUF plugs, and were used to assess contamination derived from both the field handling and the laboratory analytical procedures. The GFF from the field air blank also was weighed to measure any blank contribution to the total suspended particle concentration determination. For five sets of samples, field blanks were not provided for use as the set-blank sample. Therefore, a lab blank sample (consisting of only one PUF plug) was substituted for the field blank sample as the set blank. The PUF plugs used for the field blanks or laboratory blanks included reused, cleaned PUF from previous field samples in this study.

Analyte concentrations in the air method set-blank samples were calculated assuming a typical air volume of 850 m³ and are shown in table 18 (see at [table 18.xls](#)). Only 6 of the 49 analytes were detected in any of the 21 field blanks. Dieldrin, EPTC, and tebuthiuron were each detected only once, whereas trifluralin and chlorpyrifos were detected three times, and diazinon was detected four times. CEAT was only detected once in a laboratory blank sample with a concentration near the instrument detection level (IDL). The GFF blanks were substantially cleaner than the PUF plug blanks in terms of the chromatographic baseline noise. For most analytes detected in field and laboratory blank samples, secondary ion responses were near the IDL, and one or more of the relative ion abundance ratios was not within 20 percent of the expected value. The procedure for classifying an analyte as “detected” in field samples was more conservative than that used for the blanks. An analyte was “detected” in an air sample component only if all the characteristic ions were present at sufficient intensity above the IDL and if the relative ion abundance ratios were correct so the analyte could be adequately distinguished from typical GFF or PUF plug blank noise.

Air Method Set Spikes

An air method laboratory spike sample (air-method spike) was processed with each set of field samples to monitor compound recoveries from the preparation of a sample through the analytical process. An air-method spike sample consisted of one clean (often reused) PUF plug that, after placing it into a Soxhlet extractor, was fortified with 100 µL of a methanol solution containing 1 ng/µL each of the 49 air method analytes listed in [table 1](#).

For set numbers 95.177 and greater, either 3.5 or 4 mL (fraction F1) of the ethyl acetate elution solvent was collected from the florisil cleanup column. This F1 aliquot was used to quantitate the pesticide concentrations in the field and QC samples. For these sets, an additional 1-mL aliquot (fraction F2) of ethyl acetate was collected from the florisil column for the air-method spike samples. This F2 aliquot was analyzed separately from the F1 aliquot to assess the pesticide elution recovery from the Florisil column.

Recoveries for laboratory air-method spike samples are shown in table 19 (see at [table 19.xls](#)). The recoveries for the F1 aliquot are reflective of compound recoveries from sample extraction through analysis for each set of field samples. Sample-specific preparation errors resulted in low analyte recoveries in set 95.243 air-method spike, and recoveries for this spike sample were omitted from the statistical summaries. Set 95.118 recoveries were obtained after three cleanup column steps (which included two sodium

sulfate columns and one C18 SPE column). Although recoveries were acceptable for most analytes in set 95.118, these columns still were inadequate for eliminating unwanted interferences. Implementation of the Florisil column cleanup step removed additional, but not all, unwanted interference, especially in PUF extracts. Recoveries for most pesticides in F1 were acceptable (greater than 70 percent) using a 3.0-mL elution volume. Prometon and tebuthiuron, however, exhibited variably low recoveries. Increasing the F1 volume to 3.5 mL further improved the recoveries of all the analytes, although analysis of the F2 aliquots of the air-method spike sample still revealed low amounts (usually less than 10 percent of F1) of some pesticides. Increasing F1 to 4.0 mL seemed to provide acceptable recoveries for most compounds, with few analytes detected at low levels in F2. Prometon and tebuthiuron, however, continued to exhibit highly variable recoveries even at the 4.0-mL F1 volume. Partial loss of these two compounds appeared to be the result of irreversible sorption to highly active sites on the Florisil sorbent. Prometon occasionally exhibited a similar sorptive loss on the C18 SPE column used for isolating pesticides in the water method applied to the rain samples (see below).

Mean laboratory method-spike recoveries exceed 65 percent for all compounds except prometon and tebuthiuron. Thirty-one of the 49 air method analytes had mean recoveries of 90 percent or greater. Relative standard deviation of the mean recoveries ranged from 7 to 67 percent, with 29 compounds at 20 percent or less.

Polyurethane Foam Plug Collection Efficiency Spike Experiments

Three spike collection-efficiency experiments were performed to monitor the migration of pesticides through the two PUF plugs (front and back) and to estimate the total air sampling and analysis method recoveries. These tests were carried out by spiking a GFF with 80 µg of each of the air method pesticides and drawing ambient air through the GFF-PUF assembly at about 1 m³/min under the following total sample volume/mean temperature conditions: 310 m³/19.2 °C, 850 m³/23.3 °C, and 1,730 m³/24.0 °C. Pesticide concentrations were determined on the GFF and both PUF plugs from each test. The PUF collection efficiency for each test was calculated as the total amount of each analyte on both PUFs divided by the original spiked amount minus the concentration remaining on the GFF, times 100 (table 20 [see at [table 20.xls](#)]). The migration of each analyte from the front PUF into the back PUF was defined as “breakthrough” and calculated as the amount of each analyte recovered on the back PUF divided by the amount recovered on the front PUF, times 100.

High amounts (80 µg) of each method analyte were used in the PUF collection efficiency spike tests. This was done to ensure easy detection of the analytes and because the test was an elution and not a frontal (continuous gas-phase pesticide introduction) chromatography experiment (Bidleman, 1985). During the extraction set, each sample component was fortified with 100 µL of a surrogate solution containing 1 ng/µg each of diazinon-d10, α -HCH-d6, and terbuthylazine. The high analyte-to-surrogate amounts resulted in an inability to adequately quantitate some surrogate recoveries because of interferences. These PUF plug collection efficiency tests were conducted using continuous air sampling over the sample period and not the 4 h/d or 5 min/h sampling schemes used to collect the week-long field air samples. It is not known how, or if, the 4 h/d or 5-min/h field-sampling scheme would change these PUF efficiency results.

The sampling and meteorological conditions and the pesticides recoveries from the spiked GFF and front and back PUF plugs for the three spike collection-efficiency experiments are shown in table 20 (see at [table 20.xls](#)). The total recoveries from all three components are also shown. Thirty of the 49 compounds tested had total recoveries of 70 percent or greater at the 1,730-m³ air volume. Fifteen of these analytes exhibited greater than 90 percent total recovery, indicating a quantitative collection by the sampler at the highest air-volume test. Cyanazine, tebuthiuron, azinphos-methyl, and *cis*- and *trans*-permethrin exhibited less than 10-percent migration from the GFF to the front PUF plug, even at the highest (1,730 m³) air volume. This finding was not unexpected because most of these compounds have low liquid phase (or subcooled-liquid phase) vapor pressures (Majewski and Capel, 1995). Tebuthiuron, however, has a vapor pressure comparable to other analytes that exhibited greater migration to the PUF. This analyte was only observed in the 13 June (week 11) Iowa City air sample (see table 4 [see at [table 4.xls](#)]) and was detected only on the PUF with a 123-percent breakthrough into the back plug (table 21 [(see at [table 21.xls](#))]). Retention of tebuthiuron on the GFF in the spike experiment might be a result of strong adsorption of this pesticide to the GFF matrix (comparable to the apparent strong adsorption to active sites on the Florisil cleanup column). In fact, evidence of this partial strong adsorption to the GFF matrix in the spike experiment was indicated for most analytes, because small amounts of many, even volatile analytes (for example, 2,6-diethylaniline, butylate, pebulate, and EPTC) remained on the filter at all three test volumes. These four analytes also were observed on the GFF in low amounts in some field samples. Sometimes they were detected on the GFF only and not the PUF (see tables 2 through 8 [for access to tables 2 through 8, see list of [Tables](#)] and table 21 [see at [table 21.xls](#)]). This further implicated binding of a small portion of the analyte to active sites on the GFF or to the particles collected on the GFF for a number of the analytes, even when most of the gas-phase component was poorly retained by the two PUF plugs.

Thirty-one analytes exhibited little or no breakthrough into the back PUF plug for all three test volumes. Although well recovered overall, several analytes (for example, propachlor and triallate) exhibited substantial breakthrough at the 1,730-m³ air volume sample. Benfluralin, ethalfluralin, trifluralin, and α -HCH exhibited substantial migration into the back PUF at the 850-m³ air volume, but total recoveries of each were in excess of 85 percent. Phorate was only well recovered at the 310-m³ air volume. Breakthrough was nearly 90 percent for molinate at the 310-m³ air volume, and PUF appeared ineffective at collecting the more volatile pesticides 2,6-diethylaniline, butylate, EPTC, and pebulate, because these compounds were poorly recovered at the 310-m³ air volume. Degradation losses during sampling were implicated for napropamide, terbacil, disulfoton, malathion, and propargite, because these compounds exhibited poor overall recoveries at one or more air volume, and there was little or no evidence of pesticide migration into the back PUF plug. These losses likely were a result of reaction of the pesticide with hydroxyl radical or other photochemical oxidants. Degradative losses might have occurred for some of the other poorly recovered analytes, as well. The reported concentrations in the field samples may substantially underestimate the true atmospheric concentration for those analytes that were poorly collected by the two PUF plugs at the 850 m³ and greater air volumes typically used for collection of the air samples.

Polyurethane Foam Plug Collection Efficiency Estimation from Field Samples

Sample-specific estimates of collection efficiencies for pesticides in the gas phase were assessed by separate analysis of the front and back PUF plugs on nearly all field air samples. Thirty-eight of the 49 analytes were detected in one or more of 148 air samples where front and back PUF plugs were individually analyzed (table 21 [see at [table 21.xls](#)]). Fourteen of these 38 analytes were not detected in the back plug, and the maximum observed breakthrough did not exceed 17 percent for acetochlor, metolachlor, atrazine, CIAT, thiobencarb, chlorpyrifos, and methyl parathion (table 21 [see at [table 21.xls](#)]). These results indicate a complete gas-phase collection by the dual PUF-plug sorbent trap for these 21 analytes. Minimal amounts, if any, of these 21 compounds were also detected on the back plug in the PUF collection efficiency spike tests (table 20 [(see at [table 20.xls](#))]). Most of the compounds that exhibited a moderate-to-high (100 percent) breakthrough in the spike tests also exhibited a high breakthrough percentage in the field air samples. Propanil, fonofos and malathion exhibited breakthrough in few samples (<15 percent), but when breakthrough did occur, it sometimes exceeded 100 percent. Five compounds were detected only on the back PUF in at least one sample. This observation can occur for compounds that show considerable breakthrough at air volumes less than the sample volume, especially when the ambient air concentration decreased substantially during

the week-long sampling period. Three of the most volatile pesticides—2,6-diethylaniline, pebulate, and EPTC—were detected on the filter, but not on the PUF plugs in one sample. This suggests apparent complete collection but, in fact, complete breakthrough likely occurred on the basis of PUF collection efficiency spike tests (table 20 [(see at [table 20.xls](#))]). These results highlight the importance of conducting spike experiments to verify field observations.

Surrogate Recoveries in Air Sample Components and Associated Quality Control Samples

Individual recoveries of surrogate compounds are provided in table 18 (see at [table 18.xls](#)) for air method set blanks, in table 19 (see at [table 19.xls](#)) for air method set-spike samples, and in tables 2–8 (for access to tables 2–8, see list of [Tables](#)) for the GFF and PUF plug components of field air samples. Surrogate recoveries indicated overall acceptable performance for the sample preparation and analysis steps for many samples. Some surrogate recoveries were uniformly low and reflective of sample preparation problems.

Mean and standard deviation of surrogate recoveries for the air method set blank, set spikes, and the field sample GFFs and PUF plugs are shown in table 22 (see at [table 22.xls](#)). The mean recoveries of diazinon-d10 were comparable in each of the four categories and ranged from 72 to 138 percent. The diazinon-d10 purity problem that resulted in high biased recoveries of this surrogate for some field-prepared rain samples (see below) was not a problem for the air method samples because the same diazinon-d10 source material was used to prepare both air method calibration and surrogate solutions. Recoveries of α -HCH-d6 and terbuthylazine in the field sample PUF plugs were higher and much more variable than observed in the air method laboratory set spikes, laboratory and field set blanks, and the GFF field sample components. This was due, in part, to one or more unidentified co-eluting compounds in the field PUF sample extracts that interfered with accurate quantification of the surrogates. As an indication of these interferences, high-biased recoveries or an interferent code are reported for the surrogate compounds in the data tables for field air samples. A conservative approach was used for reporting concentrations of target pesticides in field samples compared with the reporting of surrogate recoveries in these samples, as well as in the method set-blank and set-spike samples, because of the interfering ions (noise) in PUF plug analyses. Concentrations for method analytes were reported only if the compound met detection (correct relative retention time and ion ratios) and quantitation (including no coeluting interferents with the quantified ion)

criteria. If interferences occurred, target analytes were not reported as detected, and the reporting level was increased to a value above the concentration shown in [table 1](#), if necessary. In addition, although not registered for use as an agrochemical in the U.S., terbuthylazine is used as an algicide, microbicide, and microbistats in industrial water-cooling systems as well as in residential and commercial ornamental ponds, fountains, and aquaria (U.S. Environmental Protection Agency, 1995). This added environmental concentration produced an undesirable positive bias in terbuthylazine surrogate recoveries for some field samples and diminished its effectiveness as a reliable surrogate. As noted above, a more conservative approach was used for classifying target pesticides as “detected” in the field samples than was used in establishing surrogate recoveries in the air method set-blank and set-spike samples because of the noise in PUF plug analyses.

Quality Control for Rain Samples

The rain sampling method used in this study composited the collected rainfall during 7-d periods in a refrigerated glass container. Laboratory QC procedures (water-blank and water-spike samples) were routinely done. In addition, several field QC studies were done and included taking field equipment blanks and a pesticide stability in a rainwater test.

Field Equipment Water Blanks

During the 6-month study, one field equipment water-blank sample was collected at each sampling site to assess the extent of combined field and laboratory-derived contamination. The field equipment water-blank sample consisted of pouring 3 L of pesticide-residue grade water (Mallinckrodt-Baker) into a clean, 9-L glass carboy, then pouring it into the cleaned sampler collection funnel and Teflon tubing and collecting the water in another clean glass carboy. A 1-L aliquot of this water was then processed in the same manner as the rainwater samples. No target analytes were detected in any of the seven field blanks with the exception of atrazine (0.002 $\mu\text{g/L}$) in the Jackson, Mississippi, blank (collected 28 April 95; set 1942), and metolachlor (0.003 $\mu\text{g/L}$) and propanil (0.011 $\mu\text{g/L}$) in the Rolling Fork, Mississippi, (16 May 95; set 2042) field-blank sample.

Laboratory Water Blank and Spike Samples

Laboratory reagent-water blank (laboratory water blank) and spike (laboratory water spike) samples were processed with each set of rain samples that were analyzed. The laboratory water blanks were used to monitor for laboratory-derived contamination, whereas laboratory water spikes were used to monitor matrix extraction efficiency of the target pesticides. These QC water samples were processed identically as the regular rainwater samples described above, but they were not filtered (comparable to the whole-water samples submitted from Eagle Harbor). The laboratory water blank and water spike samples were included in the laboratory sample preparation procedure beginning with the surrogate fortification step just prior to the SPE isolation step. The laboratory water blanks and water spikes were prepared using approximately 1 L of pesticide-free reagent water. Each laboratory water spike was fortified with 100 µL of a methanol solution containing 1 ng/µL each of the method analytes.

Table 23 (see at [table 23.xls](#)) shows the analytes detected in eight laboratory water blanks (coded by set number). No analytes were detected at less than the reporting level listed in [table 1](#) in any of the other 52 laboratory water blanks processed with the rain samples. Only 9 of 47 water-method analytes were detected in the blanks. All detections were near or below the reporting level. Six analytes were detected only once, with five of them occurring in set 2058 laboratory water blank. The most commonly detected analyte was 4,4'-DDE in three blanks. The compound 4, 4'-DDE, however, was not detected in any rain sample.

Laboratory Water Spike Recoveries

Recoveries of analytes in laboratory water spikes from 59 sets of samples are shown in table 24 (see at [table 24.xls](#)). Mean recoveries were greater than 85 percent for most analytes and were generally excellent. Mean recoveries were comparable to, or somewhat greater than, those observed by Zaugg and others (1995) and Lindley and others (1996), but variability (as indicated by percent relative standard deviation [RSD] of the mean) in the recoveries were somewhat greater than previously reported by these authors for a number of analytes. Prometon had substantially lower mean recovery and greater variability than previously reported. Prometon appears to exhibit partial irreversible sorption to the SPE column when sample conductivity is low (as occurs in reagent water used to prepare laboratory water spikes). Disulfoton and, especially, linuron had higher than expected variability in their recoveries. Disulfoton is reportedly unstable in solution (Munch and Frebis, 1992), and linuron may be susceptible to variable thermal instability during GC/MS analysis. Both *cis*-permethrin and 4,4'-DDE had mean recoveries near 60 percent, and recoveries in this range or lower were expected because these two analytes have the lowest water solubilities and highest octanol-water partition coefficients of any method analytes (Mackay and others, 1997). Loss of these analytes by

sorption to surfaces such as the glass-fiber filter matrix during filtration, glass bottle walls and tubing during SPE steps, and to particles or dissolved organic matter in the rain samples, are likely to have contributed to their reduced recoveries.

Surrogate Recoveries in Rainwater and Associated Quality Control Samples

Recovery data and statistical summaries of surrogate compounds in laboratory water blanks and spike samples are shown in table 25 (see at [table 25.xls](#)). Most surrogate recoveries exceeded 80 percent and no sample preparation problems were evident for any field rain samples that were based on the surrogate recoveries. Table 26 (see at [table 26.xls](#)) shows the statistical summaries of the surrogate recoveries for (1) all laboratory water blanks and spike samples combined, (2) rain samples from six sites where surrogate compounds were fortified into the water and the water was processed through the SPE column by field staff, and (3) rain samples from Eagle Harbor where surrogate fortification and SPE steps were performed at NWQL. Mean recoveries of the three surrogates exceeded 90 percent in each of these categories. Mean recovery for diazinon-d10 in the field-prepared rain samples (136 percent) were higher than mean recoveries observed for laboratory water blank and spike samples and for the Eagle Harbor rain samples. The high bias in the field-prepared rain samples was attributed to a purity problem encountered with a diazinon-d10 standard used to prepare surrogate and calibration standards by NWQL during part of 1995. Issues regarding the use of terbuthylazine as a surrogate were addressed in the air method surrogate recoveries section above.

Pesticide Stability in Rainwater Test

The stability of each pesticide targeted for analysis in rainwater during the week-long collection periods was tested by spiking 3 L of excess, unfiltered rainwater from the 20–27 June (week 14) Iowa City sample to a concentration of 0.17 µg/L for each analyte (acetochlor was not added). After a thorough mixing, 1 L of the spiked rainwater was immediately filtered through a 0.7-µm GFF. The surrogate compounds were added next, and the sample was processed through a C18 SPE column. The excess water was removed from the SPE column and it was stored at 4 °C until extracted. This sample provided the initial, day-zero (30 June 1995) recovery. The remaining spiked rainwater sample was then stoppered and allowed to sit on a laboratory bench, at ambient temperature (about 23 °C), but protected from direct sunlight, for 5 d. After 5 d, another 1 L of the spiked water sample was processed in the same manner as the day zero rainwater sample, and both SPE columns were sent to NWQL for extraction and analysis. This matrix spike experiment was done at only one location to minimize the possibility of contamination of samples and equipment with the spike material. The matrix spike recoveries

for each compound were corrected for ambient concentrations of the pesticide in the rainwater, if present. The results for this test are listed in table 27 (see at [table 27.xls](#)).

This stability study did not mimic the exact storage conditions of the field samples. Instead, ambient indoor temperatures (about 23 °C) were used in an attempt to simulate a more extreme, worst case, storage condition than an actual sample might encounter when stored 7 d at 4 °C in the field. No statistical comparison of recoveries for this holding time experiment was possible because the experiment was not replicated. The results of this test, however, do provide an indication of the storage stability for the target analytes and revealed that degradation during the 5-d holding period at ambient temperature was not a problem for most analytes (table 27 (see at [table 27.xls](#))). Thirty-five compounds had overall test recoveries (defined as [day 5 recovery/day 0 recovery] × 100) above 70 percent, and no obvious losses of these compounds was observed over the 5-d experiment. Five analytes—benfluralin, butylate, ethalfluralin, terbufos, and trifluralin—exhibited recoveries at day 5 that were below the range of expected recoveries on the basis of method performance data collected using laboratory reagent spike samples (table 24 [see at [table 24.xls](#)]). These results indicated a possible loss for these analytes during the 5-d experiment.

Five other compounds—diazinon, disulfoton, phorate, 4,4'-DDE, and terbufos—exhibited recoveries below the level of expected method performance at both day 0 and day 5. Although the recoveries for these compounds were unusually low at day 0, they showed a definite loss in concentration during the 5-d experiment. The low recovery for 4,4'-DDE is indicative of sorption to the glass carboy and other surfaces (such as suspended particles), as well as to the GFF during the filtration step, and likely not a result of degradation. Other analytes, like *cis*-permethrin and trifluralin, which have low water solubilities (Mackay and others, 1997), might also be susceptible to sorptive losses. A complete mass balance assessment for the pesticides was not possible because no attempt was made to recover pesticides sorbed to these sample-processing components. For several of the organophosphorus pesticides, losses during sample filtration might have accounted for some of the reduced recoveries. Reactive degradation processes, however, probably accounted for most of the losses for these pesticides. Indeed, Zaugg and others (1995) observed that of all 47 water method analytes, diazinon, phorate, and terbufos exhibited the most rapid degradation times in storage stability tests on SPE columns.

The average recoveries for all the analytes in the laboratory reagent-water (set) spike samples (table 24 [see at [table 24.xls](#)]) exceed 75 percent except for 4,4'-DDE (63 percent) and *cis*-permethrin (60 percent). Losses attributable to the GFF filtration step, however, were not accounted for in the laboratory set-spike recoveries because these QC samples were not filtered through a GFF. The surrogate compounds were added to day 0 and day 5 aliquots of the spiked rainwater sample immediately after the GFF filtration

step, and recoveries for the unfiltered α -HCH-d6 surrogate were comparable to day 0 and 5 recoveries for filtered α -HCH analyte in the spiked rainwater test. This indicates that no sorptive losses to the GFF occurred for α -HCH. Diazinon-d10 surrogate recoveries were much greater than observed for the unlabelled diazinon. A direct comparison of recoveries for these diazinon analogs is complicated by the apparent high-bias recoveries observed for diazinon-d10 because of standard purity issues, as mentioned above.

Acetochlor was not included in the spike solution, but it was present at a substantial concentration in the rainwater used in the experiment. The overall test recovery for acetochlor (82 percent) was estimated from the difference in the actual concentrations in rainwater at day 0 (0.028 $\mu\text{g/L}$) and day 5 (0.023 $\mu\text{g/L}$). Although acetochlor was not tested, Goolsby and others (1995) found no sorption, degradation, or other losses for alachlor, atrazine, cyanazine, or metolachlor in spiked rain samples stored outdoors or indoors at ambient temperatures for up to 3 weeks.

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