



Quality of Wet Deposition in the Grand Calumet River Watershed, Northwestern Indiana, April 29, 1997–April 28, 1998

Water-Resources Investigations Report 99-4205

*Prepared in cooperation with the
Indiana Department of Environmental Management*

Quality of Wet Deposition in the Grand Calumet River Watershed, Northwestern Indiana, April 29, 1997–April 28, 1998

By Timothy C. Willoughby

Water-Resources Investigations Report 99-4205

*Prepared in cooperation with the
Indiana Department of Environmental Management*

Indianapolis, Indiana
2000

U.S. Department of the Interior
BRUCE BABBITT, SECRETARY

U.S. Geological Survey
Charles G. Groat, Director

The use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

For additional information, write to:
District Chief
U.S. Geological Survey
5957 Lakeside Boulevard
Indianapolis, IN 46278-1996

Copies of this report can be purchased from:
U.S. Geological Survey
Branch of Information Services
Box 25286
Federal Center
Denver, CO 80225-0286

Contents

Abstract	1
Introduction	2
Purpose and Scope	3
Site Description	3
Study Methods	3
Sampling-Site Selection	5
Constituent Selection and Analytical Techniques	5
Collector Modifications	5
Sample Collection and Processing	7
Equipment Cleaning	9
Statistical Analysis	10
Quality of Wet Deposition	10
Constituent Concentrations	11
Comparison of Concentrations to Previous Sampling Phases	20
Constituent Loadings	20
Comparison of Estimated Annual Loadings to Previous Sampling Phases	24
Quality Assurance	24
Laboratory Quality Assurance	25
Field Quality Assurance	37
Summary	38
References Cited	41
Supplemental Data	43

Figures

1. Map showing location of wet-deposition sampling site at the Gary (Indiana) Regional Airport	4
2. Diagram showing modified AeroChem Metric 301 wet/dry collector	7
3-6. Graphs showing:	
3. Weekly wet-deposition amounts collected at the Gary airport	12
4. Distributions of pH and specific conductance measured in wet-deposition samples collected at the Gary airport during the third sampling phase, April 29, 1997, to April 28, 1998	14
5. Distributions of major-ion concentrations measured in wet-deposition samples collected at the Gary airport during the third sampling phase, April 29, 1997, to April 28, 1998	15
6. Distributions of trace-metal concentrations measured in wet-deposition samples collected at the Gary airport during the third sampling phase, April 29, 1997, to April 28, 1998	16
7. Map showing location of wet-deposition sampling site at the Gary airport and two National Atmospheric Deposition Program/National Trends Network sampling sites at the Indiana Dunes National Lakeshore and Huntington Reservoir	17

Contents—Continued

Figures—Continued

8-12. Graphs showing:

8. Distributions of pH and specific conductance measured in wet-deposition samples collected at the Gary airport and National Atmospheric Deposition Program/National Trends Network sites located at the Indiana Dunes National Lakeshore and Huntington Reservoir. 18
9. Distributions of major-ion concentrations measured in wet-deposition samples collected at the Gary airport and National Atmospheric Deposition Program/National Trends Network sites located at the Indiana Dunes National Lakeshore and Huntington Reservoir. 19
10. Distributions of pH and specific conductance measured in wet-deposition samples collected at the Gary airport 21
11. Distributions of major-ion concentrations measured in wet-deposition samples collected at the Gary airport 22
12. Distributions of trace-metal concentrations measured in wet-deposition samples collected at the Gary airport 23

13-16. Graphs showing:

13. Estimated weekly major-ion loadings determined from wet-deposition samples collected at the Gary airport 26
14. Estimated weekly trace-metal loadings determined from wet-deposition samples collected at the Gary airport 28
15. Estimated annual loadings of major ions from samples collected at the Gary airport during the three sampling phases 32
16. Estimated annual loadings of trace metals from samples collected at the Gary airport during the three sampling phases 34
17. Median constituent concentrations computed for the acidified deionized-water funnel rinses, the acidified deionized-water system blanks, and the wet-deposition samples and the method reporting limit for constituents with median acidified deionized-water funnel rinses greater than the method reporting limit 39

Tables

1. Method of analysis and the method reporting limits for the 27 constituents analyzed for in samples collected at the Gary (Indiana) Regional Airport 6
2. Water-quality characteristics measured in wet-deposition samples collected at the Gary airport 13
3. Estimated annual loadings determined from wet-deposition samples collected at the Gary airport for April 29, 1997, to April 28, 1998 25
4. Median concentrations measured for the standard reference water samples T117 and P17 and the most probable value. 31
5. Concentrations for wet-deposition samples collected at the Gary airport. 44
6. Concentrations for laboratory quality-control samples 50
7. Concentrations for field quality-control samples processed at the Gary airport 53

Conversion Factors, Vertical Datum, and Abbreviated Water-Quality Units

Multiply	By	To obtain
centimeter (cm)	0.394	inch
gram (g)	0.0353	ounce
hectare (ha)	2.471	acre
kilogram (kg)	2.205	pound
kilometer (km)	0.6214	mile
square kilometer (km)	0.4	square mile
liter (L)	1.057	quart
meter (m)	3.281	foot
microgram (μg)	3.530×10^{-8}	ounce
milligram (mg)	3.530×10^{-5}	ounce
milliliter (mL)	0.03381	ounce, fluid
millimeter (mm)	0.0394	inch

Temperature is given in degrees Celsius ($^{\circ}\text{C}$) which can be converted to degrees Fahrenheit ($^{\circ}\text{F}$) as follows:

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

Vertical datum: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviated water-quality units used in this report: Chemical concentrations and temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) and micrograms per liter ($\mu\text{g/L}$). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. Loadings are reported in kilograms per hectare (kg/ha) and grams per hectare (g/ha).

Specific conductance of water is expressed in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S/cm}$). This unit is equivalent to micromhos per centimeter at 25 degrees Celsius ($\mu\text{mho/cm}$), formerly used by the U.S. Geological Survey.

Sample volumes are given in liters (L).

Quality of Wet Deposition in the Grand Calumet River Watershed, Northwestern Indiana, April 29, 1997–April 28, 1998

By Timothy C. Willoughby

Abstract

The Grand Calumet River, in northwestern Indiana, drains a heavily industrialized area along the southern shore of Lake Michigan. Steel production and petroleum refining are two of the area's predominant industries. High-temperature processes, such as fossil-fuel combustion and steel production, release contaminants to the atmosphere that may result in wet deposition being a major contributor to major-ion and trace-metal loadings in northwestern Indiana and Lake Michigan.

A wet-deposition collection site was established at the Gary (Indiana) Regional Airport to monitor the quantity and chemical quality of wet deposition. During a first phase of sampling, 48 wet-deposition samples were collected weekly between June 30, 1992, and August 31, 1993. During a second phase of sampling, 40 wet-deposition samples were collected between October 17, 1995, and November 12, 1996. Forty-two wet-deposition samples were collected during a third phase of sampling, which began April 29, 1997, and was completed April 28, 1998. Wet-deposition samples were analyzed for pH, specific conductance, and selected major ions and trace metals. This report describes the quantity and quality of wet-deposition samples collected during the third sampling phase and compares these findings to the results of the first and second sampling phases.

All of the samples collected during the third phase of sampling were of sufficient

volumes for at least some of the analyses to be performed. Constituent concentrations from the third sampling phase were not significantly different (at the 5-percent significance level) from those for the second sampling phase. Significant increases, however, were observed in the concentrations of potassium, iron, lead, and zinc when compared to the concentrations observed in the first sampling phase.

Weekly loadings were estimated for each constituent measured during the third sampling phase. If constituent concentrations were reported less than the method reporting limit, a range for the weekly loading was computed. The estimated annual loadings of chloride, silica, bromide, copper, and zinc during the third sampling phase were greater than those estimated for the first two sampling phases. The only estimated annual loading in the third sampling phase that was less than the estimated annual loadings observed during the first two sampling phases was sulfate. The estimated annual loadings of calcium, magnesium, nitrate, potassium, barium, lead, iron, and manganese observed during the third sampling phase were greater than the loadings observed during the first sampling phase but less than those observed during the second sampling phase. No significant differences were observed between the quantity of wet deposition collected during the three sampling phases.

Introduction

The atmosphere is an important component of the hydrologic cycle to be considered when assessing the effects of contaminants in the environment. The atmosphere is recognized as a major pathway by which contaminants are deposited to the Earth's surface, possibly far removed from their source (Majewski and Capel, 1995). The deposition of contaminants by wet and dry deposition may have a significant adverse effect on water quality in surface and near-surface waters and is becoming more widely acknowledged as an important contributor to the declining health of aquatic ecosystems.

Natural and anthropogenic processes emit contaminants to the atmosphere that are later deposited to the Earth's surface. The atmospheric-depositional process can be classified into two categories: those involving precipitation, called wet deposition, and those not involving precipitation, called dry deposition (Bidleman, 1988). Removal of contaminants from the atmosphere involving fog, mist, and dew lies somewhere between the wet and dry processes but is more closely related to dry deposition. The chemical composition of wet deposition is affected by the chemistry of atmospheric aerosols and airborne particles (Schroder and others, 1989).

Rainout and washout are the two major processes that introduce contaminants to wet deposition. Rainout is the process that occurs in clouds, such as nucleation, condensation, or gas dissolution. Washout is the process that scavenges the airborne particulates between the cloud base and the Earth's surface. Rainout and washout probably both occur continuously during a wet-deposition event because most storms produce convective air-current components that add large masses of near-surface air to overlying clouds (Schroder and Hedley, 1986).

The Great Lakes compose the largest area (244,000 km²) of fresh water on Earth (Herdendorf, 1982). This important natural resource for the United States and Canada is managed under the Great Lakes Water Quality Agreement, Annex 15 (Airborne Toxic Substances). This agreement mandates that "the parties, in cooperation with State and Provincial Governments, shall conduct research, surveillance, and monitoring and implement pollution control measures for the purpose of reducing atmospheric deposition of toxic substances, particularly persistent toxic substances, to the Great Lakes Basin Ecosystem."

Northwestern Indiana, including the watershed of the Grand Calumet River, is the State's highest priority area for nonpoint-source pollution control (Indiana Nonpoint Source Task Force, 1989). Recommendations made by the Indiana Nonpoint Source Task Force are (1) to evaluate and quantify water-quality impacts of airborne pollutants in inland waters and Lake Michigan, (2) cooperate in Great Lakes air-monitoring programs, (3) initiate a statewide monitoring program for airborne toxic and acid pollutants, (4) improve integration of State air- and water-pollution-control programs, and (5) develop and implement enhanced air-pollution-control strategies. In 1992, U.S. Geological Survey (USGS), in cooperation with the Indiana Department of Environmental Management (IDEM), began a study to evaluate some of these recommendations. As part of this study, the USGS established a wet-deposition sampling site at the Gary (Indiana) Regional Airport (hereafter referred to as the Gary airport) in June 1992 to monitor the quantity and quality of wet deposition.

Three phases of wet-deposition sampling have been completed at the Gary airport. Wet-deposition samples were collected during the first phase of sampling beginning in June 1992; that phase was completed in August 1993. The second sampling phase began in October 1995 and was completed in November 1996. The third sampling phase began in April 1997 and was completed in April 1998.

Purpose and Scope

This report describes the chemistry of wet-deposition samples collected at the Gary airport and analyzed for pH, specific conductance, and selected major ions (calcium, magnesium, sodium, potassium, sulfate, chloride, fluoride, bromide, silica, nitrate, and phosphate) and trace metals (aluminum, antimony, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, silver, uranium, and zinc) during the third sampling phase. In addition, this report:

- (1) examines the distribution of constituent concentrations found in samples collected at the Gary airport;
- (2) statistically compares the results of major-ion concentrations found in wet deposition collected at the Gary airport with results from two National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites (Indiana Dunes National Lakeshore and Huntington Reservoir) located in northern Indiana. This comparison is intended to determine if the chemistry of wet-deposition samples collected at the Gary airport is localized or if the chemistry of these samples is consistent with sites outside the industrialized Gary area;
- (3) statistically compares the concentration of major ions and trace metals measured in wet-deposition samples collected during the first phase of sampling (June 30, 1992, to August 31, 1993), the second phase of sampling (October 17, 1995, to November 12, 1996) and concentrations measured in samples collected during the third phase of sampling (April 29, 1997, to April 28, 1998). This comparison is intended to determine if concentrations of major

ions and trace metals are changing over time;

- (4) presents estimated weekly and annual constituent loadings determined during the third sampling phase and compares the annual estimated loadings to the loadings determined for the first two sampling phases; and
- (5) describes the constituent concentrations measured in 29 quality-assurance samples and compares these concentrations to the constituent concentrations measured in wet-deposition samples collected during the third sampling phase.

Site Description

The wet-deposition sampling site was located at the Gary airport in northwestern Indiana (fig. 1). The sampling equipment, a modified AeroChem Metric 301 wet/dry collector and a Belfort weighing rain gage, was located 30.5 m and 40 m, respectively, north of the airport's traffic-control tower. The sampling equipment was installed at an altitude of 178 m above sea level, approximately 400 m north of Interstate 90, 3.5 km south of Lake Michigan, and 18 km west of the Lake and Porter County boundary. Access to the sampling site was by a paved single-lane road. The airport grounds were enclosed with a fence to limit access. Air traffic at the airport did not pass over the sampling equipment.

Study Methods

This section describes the selection of the sampling site, constituents selected and the analytical methods used to measure their concentrations, and the modifications made to the AeroChem Metric 301 wet/dry collector for the collection of trace metals in wet deposition. This section also describes procedures used for cleaning the equipment and for processing the samples.

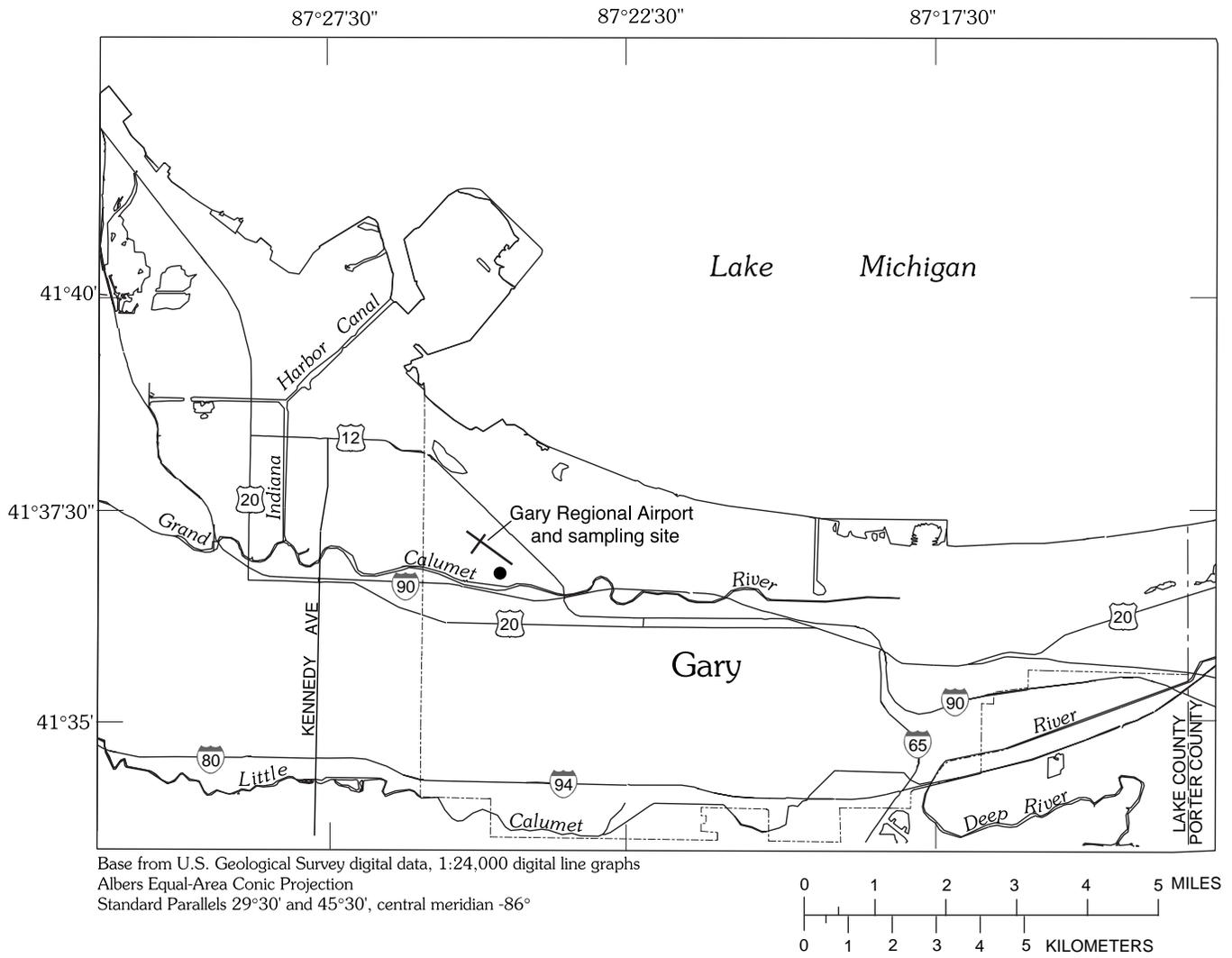


Figure 1. Location of wet-deposition sampling site at the Gary (Indiana) Regional Airport.

Sampling-Site Selection

The sampling site at the Gary airport was chosen in cooperation with IDEM prior to the start of the first phase of sampling. Factors that were considered when evaluating possible sampling locations included the need to minimize the possibility of local point sources directly affecting the sample chemistry; the need for a secure location for the sampling equipment; the need for an electrical power source; and the need for an open, flat field with no obstruction projecting onto the collector or rain gage with an angle greater than 45 degrees from horizontal, as recommended by the NADP/NTN. The sampling equipment was installed at ground level and in accordance with NADP/NTN protocols (Bigelow, 1984).

Constituent Selection and Analytical Techniques

Calcium, magnesium, sodium, potassium, sulfate, chloride, and nitrate are constituents measured in samples collected by the NADP/NTN. These constituents were analyzed in wet-deposition samples collected at the Gary airport to evaluate their differences with concentrations measured at the NADP/NTN sites located at the Indiana Dunes National Lakeshore and Huntington Reservoir. Ammonia was the only major constituent determined by the NADP/NTN that was not determined as part of this study. The Indiana Dunes National Lakeshore site is approximately 26 km east of the Gary airport, and the Huntington Reservoir site is approximately 180 km southeast of the Gary airport.

The trace metals measured for this study were selected because they are by-products of industrial processes located in the Gary, Ind., area and because of their toxic potentials. Trace metals selected include cadmium, chromium, copper, lead, manganese, and zinc. Although copper, manganese, and zinc are necessary for proper cellular

development, these metals may bioaccumulate, especially in aquatic organisms, and therefore may present a health risk (Amdur and others, 1993). Cadmium, chromium, and lead are not essential metals and may present a health risk at very low concentrations.

All laboratory analytical techniques used for this study were standard USGS methods for the determination of inorganic substances in water. Unless otherwise noted, all of the techniques are described in Fishman and Friedman (1989). Calcium, magnesium, sodium, silica, and iron were analyzed by inductively coupled argon plasma atomic emission spectrometry (ICAP, method I-1472-85, p. 24–32). Potassium was measured by flame atomic absorption spectrometry (FAAS, method I-1630-85, p. 393–394). Sulfate, bromide, chloride, fluoride, nitrate, and phosphate were analyzed by ion chromatography (IC, method I-2058-85, p. 527–530). Aluminum, antimony, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, silver, uranium (natural), and zinc were measured by inductively coupled argon plasma-mass spectrometry (ICAP/MS, Faires, 1993).

All samples were submitted to the National Water Quality Laboratory (NWQL) in Arvada, Colo., for analysis. The analytical procedure and the method reporting limits are listed in table 1. The analytical methods used during the third sampling phase were the same as those used during the second sampling phase.

Collector Modifications

The AeroChem Metric 301 wet/dry collector was modified to decrease possible sources of trace-metal contamination to the sample (fig. 2). The bottom of the collector was enclosed with aluminum sheeting to house the collection bottle, a thermostat, and a maximum-minimum thermometer. Access to the inside of the bottom enclosure was through an aluminum door on the front of the collector. A latch and lock were used to secure the door and limit access to the collection bottle.

Table 1. Method of analysis and the method reporting limits for the 27 constituents analyzed for in samples collected at the Gary (Indiana) Regional Airport

[ICAP, inductively coupled argon plasma atomic emission spectrometry; mg/L, milligrams per liter; FAAS, flame atomic absorption spectrometry; IC, ion chromatography; ICAP/MS, inductively coupled argon plasma-mass spectrometry; µg/L, micrograms per liter]

Constituent	Method of analysis	Method reporting limit
Calcium	ICAP	0.02 mg/L
Magnesium	ICAP	.01 mg/L
Sodium	ICAP	.2 mg/L
Potassium	FAAS	.01 mg/L
Sulfate	IC	.01 mg/L
Bromide	IC	.01 mg/L
Chloride	IC	.01 mg/L
Fluoride	IC	.01 mg/L
Silica	ICAP	.01 mg/L
Nitrate	IC	.04 mg/L
Phosphate	IC	.03 mg/L
Aluminum	ICAP/MS	1 µg/L
Antimony	ICAP/MS	1 µg/L
Barium	ICAP/MS	1 µg/L
Beryllium	ICAP/MS	1 µg/L
Cadmium	ICAP/MS	1 µg/L
Chromium	ICAP/MS	1 µg/L
Cobalt	ICAP/MS	1 µg/L
Copper	ICAP/MS	1 µg/L
Iron	ICAP	3 µg/L
Lead	ICAP/MS	1 µg/L
Manganese	ICAP/MS	1 µg/L
Molybdenum	ICAP/MS	1 µg/L
Nickel	ICAP/MS	1 µg/L
Silver	ICAP/MS	1 µg/L
Uranium	ICAP/MS	1 µg/L
Zinc	ICAP/MS	1 µg/L

The bottom was removed from a 13-L polyethylene bucket, and a hole was cut through the collector frame to allow a collection funnel to pass through the collector frame into the bottom enclosure. The lid and lid arms of the collector were coated with Teflon to minimize contamination from wet deposition splashing off the lid or lid arms into the collection funnel. A 31-cm-diameter high-density polyethylene funnel was installed so that the funnel rested on the top of the 13-L polyethylene bucket. The bucket housing was adjusted so a polyethylene-covered foam pad, attached to the bottom of the collector lid, fit tightly against the top of the funnel. A tight fit between the polyethylene-covered foam pad and the top of the funnel assisted in preventing contaminants from blowing into the funnel when the sampler lid was closed. A polyethylene fitting was attached to a silicon stopper in the bottom of the funnel so that a 1.3-cm Teflon tube could be attached to the funnel. The Teflon tube then passed through a 1.3-cm hole drilled in the top of a cap for the 5-L Teflon collection bottle. Three 100-watt light bulbs were installed as close as possible to the hole cut in the collector frame and were used to heat the area around the collection funnel to minimize snow and ice buildup in the funnel. The light bulbs were turned on by a thermostat that was set to activate at approximately 5°C.

The collector was activated by a sensor unit that consists of a plate and a sensor grid. The sensor unit has two functions: (1) to initiate the movement of the collector lid by activating the motor-box unit when the start and stop of precipitation is detected; and (2) to regulate two heating modes: the ambient mode to melt snow and the wet-collect mode to evaporate water from the sensor. The sensor grid is separated from the sensor plate by approximately 1 mm. When water bridges the gap between the sensor grid and the plate, the motor box is activated; this causes the collector lid to move over the dry-side bucket, leaving the wet side open to capture wet deposition. The sensor's ambient heating mode controls the temperature of

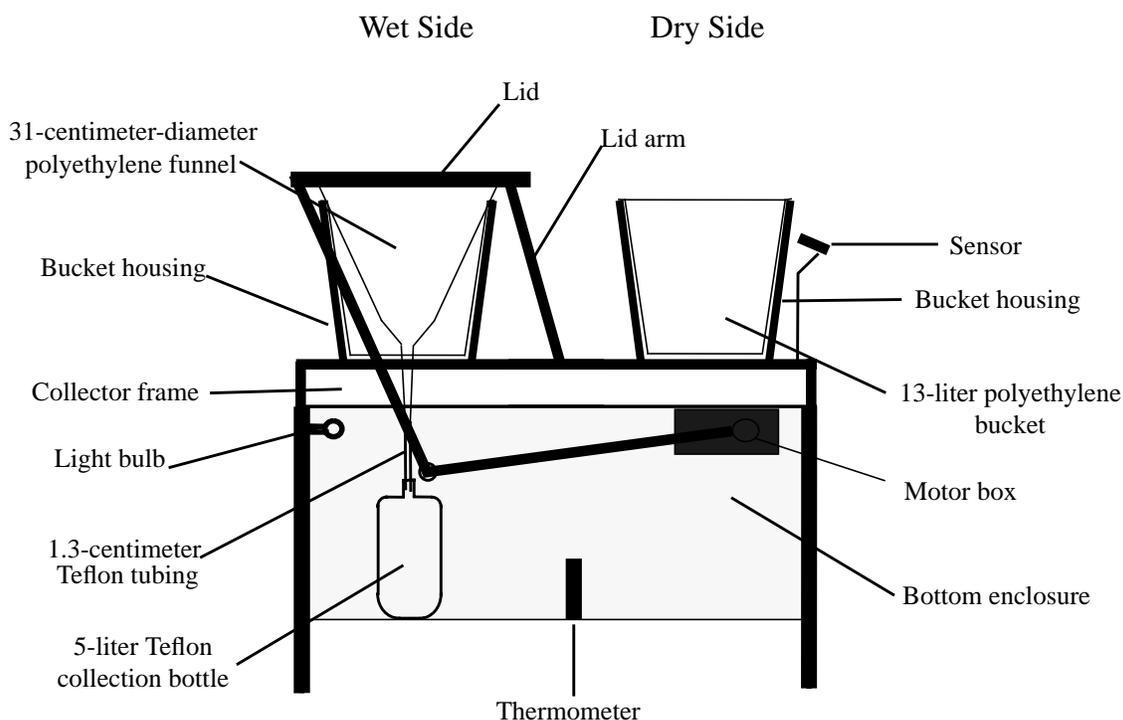


Figure 2. Modified AeroChem Metric 301 wet/dry collector.

the sensor plate. If the ambient temperature drops below 4°C, a heater is activated to heat the sensor plate to a temperature greater than 4°C; this melts snow or ice, so the resulting water can bridge the gap between the sensor grid and plate. The wet-collect mode of the sensor unit is then activated, heating the plate to a maximum of 50°C; the water that is bridging the gap between the plate and the sensor grid is evaporated, closing the collector (S.R. Dossett, Aerochem Metrics precipitation collector maintenance manual, written commun., 1984).

Sample Collection and Processing

Wet-deposition samples were removed from the collector on Tuesdays. The Tuesday to Tuesday sampling period was the same as the

sampling period used during the first two sampling phases. The procedures used to remove the samples and install clean equipment were the same as those used during the first two sampling phases (Willoughby, 1995, and Willoughby, 2000). The site operators did change between each sampling phase.

Each week, a clean 5-L Teflon collection bottle, a cap for the 5-L Teflon bottle, an additional cap with a 1.3-cm hole, a funnel, a Teflon tube, approximately 1 L of deionized water (DIW) used to clean the collector, and any other supplies needed by the site operator were packed in a cooler and sealed with packing tape. The cooler was shipped to the site operator by an overnight shipping service. The cooler generally was shipped on Thursday and would arrive at the residence of the site operator on Friday. Approximately every

third week, an additional clean collection bottle, funnel, Teflon tube, and a quality-control sample also were shipped to the site operator. Processing of the quality-control samples is discussed in the Field Quality Assurance section of this report.

Contamination was of concern because the concentrations of many of the constituents of interest for this study were low. The site operator took every possible precaution to minimize contamination during the removal of the samples and the installation of clean equipment. These precautions included always standing downwind from the collector to prevent contaminants blowing off the site operator's clothing or body into the collection funnel or collection bottle, always wearing polyethylene or vinyl gloves when working around the collector, and ensuring that the collector was not activated until the collection bottle was removed.

The following procedures were used in servicing the sampling equipment:

- (1) the site operator inspected the sampling site and equipment and noted on a field form if anything looked out of the ordinary, the ambient conditions, and whether the collector lid was open or closed;
- (2) the collector was opened and the 5-L collection bottle containing the sample was removed;
- (3) the cap (with the hole) on the collection bottle was replaced with the original cap to seal the collection bottle;
- (4) the collector lid was opened, the funnel and tubing were removed, and the collector was wiped clean;
- (5) a clean funnel and tubing were installed, and the collector lid was closed;
- (6) the cap on the collection bottle was replaced with the cap that had the 1.3-cm hole, and the original cap was sealed in a polyethylene zip-lock plastic bag and placed in the enclosed bottom of the collector;
- (7) the rain-gage chart was removed from the Belfort rain gage, and the precipitation collected in the rain gage was discarded. The site operator indicated on the rain-gage chart the date and time the chart was removed;
- (8) the date and time were recorded on a new rain-gage chart, and the chart was installed in the rain gage; and
- (9) the rain gage was zeroed.

The site operator completed the field form, indicating the date and time the sample was removed and the clean equipment installed, the empty weight of the 5-L collection bottle, current weather conditions, and the maximum and minimum temperatures measured inside the enclosed area of the collector for the previous sampling week. The maximum and minimum temperatures were recorded to ensure the sample did not freeze. The bottle removed from the collector, all other equipment used to collect the sample and clean the collector, and the field form were placed in a cooler and sealed with strapping tape. The cooler was shipped to the USGS office in Indianapolis, Ind., by an overnight shipping service. After the cooler was received by personnel at the USGS office in Indianapolis, the following steps were used to process the sample before it was shipped to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo., for analyses:

- (1) sample volume was determined by subtracting the empty weight of the bottle from the weight of the bottle plus the sample;
- (2) 15 mL of the sample were removed and the pH was determined (this pH value will be referred to as the "field pH");
- (3) approximately 250 mL of the raw sample were transferred to a polyethylene bottle for the laboratory determination of specific conductance;

- (4) approximately 250 mL of the sample were filtered through a 47-mm, 0.45-micrometer polycarbonate filter into a 250-mL high-density polyethylene bottle for laboratory determination of major anions;
- (5) the 5-L collection bottle then was re-weighed, and the volume of the sample remaining was computed. The remaining sample was acidified with nitric acid to 0.2 percent by volume;
- (6) 15 mL of the acidified sample were removed after shaking, and the pH was measured. If the pH were greater than 2.0, additional acid was added and this step was repeated.
- (7) the sample was allowed to stand for 24 hours at 4°C to allow the sample to undergo a mild digestion of any particulate material; and
- (8) 250 mL of the acidified sample were filtered through a 47-mm, 0.45-micrometer polycarbonate filter into a 250-mL Teflon bottle for laboratory analysis of trace metals and major cations.

All sample handling performed at the USGS office in Indianapolis was done on a laboratory bench top covered with an adhesive-backed Teflon sheet to help minimize contamination during the preservation and filtering processes. The samples then were packed in ice and sent to the NWQL by an overnight shipping service.

The NWQL required a minimum of 750 mL of sample for the analysis of specific conductance, major ions, and trace metals. Small-volume samples less than 750 mL were not diluted to prevent decreasing concentrations of some of the constituents of interest below the method reporting limit. Therefore, a priority was established for the analysis of small-volume samples. Weekly samples with measured volumes less than 250 mL were analyzed only for field pH. Samples with volumes between

250 and 500 mL were analyzed for field pH, major cations, and trace metals. Samples with volumes between 500 and 525 mL were analyzed for major cations, major anions, and trace metals. Samples with volumes between 525 and 775 mL were analyzed for field pH, major cations, trace metals, and major anions. Samples with volumes greater than 775 mL were analyzed for field pH, specific conductance, major cations, trace metals, and major anions. These priorities for analyses were adjusted occasionally to best utilize the sample volume collected.

Equipment Cleaning

All DIW used in this study met the American Society for Testing and Materials type 1 standard (greater than 16.7 megOhm). The equipment was cleaned at the USGS office laboratory in Indianapolis. The 5-L Teflon bottles and caps were cleaned by rinsing three times with deionized water. The bottles then were filled with a 1-percent nitric-acid solution and allowed to leach for 24 hours. The bottles then were rinsed three more times with DIW, filled with DIW, and leached for an additional 24 hours. The bottles then were rinsed three more times with DIW, and the excess water was shaken from the bottle. The 5-L Teflon bottles were stored in sealed polyethylene bags pre-rinsed with DIW.

The funnels were rinsed three times with large amounts of DIW. Any debris attached to the sides of the funnel was removed with a polyethylene brush. A stopper was used to close off the polyethylene funnel, and the funnel was filled with a 1-percent nitric-acid solution. The funnel was allowed to leach for 24 hours. The funnel then was rinsed three more times with DIW, filled with DIW, and leached for an additional 24 hours. The funnel then was rinsed a final time with large amounts of DIW. The excess water was shaken from the funnel, and the funnel was stored in a sealed polyethylene bag pre-rinsed with DIW.

The Teflon tubing and the cap used for sampling (the cap with the hole for the Teflon tube to pass through) were rinsed three times with large amounts of DIW, followed by three 100-mL rinses with a 1-percent nitric-acid solution. The Teflon tubing and the cap then were rinsed a final time with DIW and stored in sealed polyethylene bags pre-rinsed with DIW.

The 250-mL Teflon bottles used to ship the samples to the laboratory for analyses of trace metals and major cations were cleaned in the same manner as the 5-L Teflon bottles. New 250-mL high-density polyethylene bottles used to ship the samples to the laboratory for analyses of anions were cleaned by rinsing the bottles three times with DIW, filling with DIW, and leaching for 24 hours. The polyethylene bottles then were rinsed an additional three times with DIW. The 250-mL Teflon and polyethylene bottles were stored in sealed polyethylene bags pre-rinsed with DIW at the USGS office laboratory in Indianapolis.

The filters used during sample processing were cleaned immediately before use; the filters were rinsed with 50 mL of a 1-percent nitric-acid solution, followed by three 50-mL rinses with DIW. The filters then were rinsed with 20 mL of the sample (if sufficient volumes were collected) before the sample was filtered into the 250-mL bottles.

The collector was cleaned weekly after the previous sample was removed and before a clean funnel was installed for the next week of sampling. The lid, lid arms, polyethylene lid pad, and the top of the collector frame were wiped clean with a laboratory-quality paper towel and DIW to remove dust, bird droppings, and debris that collected during the previous sampling week.

Statistical Analysis

A Kruskal-Wallis test (Conover, 1980, p. 229) was done to determine if there were statistically

significant differences among the distributions of pH, specific conductance, and constituent concentrations measured at the Gary airport and two NADP/NTN sites and among the three sampling phases done at the airport. In applying this test, concentrations measured less than the largest reporting limit reported for the three sites or the three sampling phases were set equal to that reporting limit. The Kruskal-Wallis test only gives an indication that there are statistically significant differences among the distributions for each parameter measured at each site or sampling phase; it does not, however, indicate which site or sampling phase is significantly different from one or both of the other sites or sampling phases. To determine which pairs of sites or sampling phases were statistically different, a Tukey's test was performed on the ranks of the data (Helsel and Hirsch, 1992, p. 200). The Tukey's test is a multiple-comparison test based on a "least significant range," which is the difference between any two means that must be exceeded for them to be significantly different. For this report, a 5-percent level of significance ($\alpha=0.05$) was selected for the Kruskal-Wallis test and the Tukey's test. The significance level is the probability of rejecting the hypothesis that the three sites or sampling phases have the same distribution, for the Kruskal-Wallis test, or that any two means are equal for the Tukey's test. At a significance level of 5 percent, the null hypothesis of 1 out of 20 tests will be rejected incorrectly. Because of the large number of hypothesis tests done in this study, the reader should be aware that some null hypotheses may be rejected solely because of the significance level used.

Quality of Wet Deposition

Forty-two wet-deposition samples were collected during the 52-week sampling period. Three samples were lost because of sampler malfunctions and one sample was lost because of improper installation of the sampling equipment. No wet deposition was collected during five of the weeks. One sample was removed on Wednesday instead

of Tuesday, resulting in an 8-day sample that was followed by a 6-day sample. During a major winter storm, the site operator was unable to service the site for a week, resulting in one sample consisting of wet deposition collected over a 2-week period. The 8-day, 6-day, and 2-week samples were included in the statistical analysis of the data and the computation of loads.

Weekly wet-deposition amounts were measured from the continuous-monitoring rain-gage charts and compared to the wet-deposition amounts computed from the volume of sample collected. Catch efficiencies were computed by dividing the wet-deposition amounts determined from the sample volume collected in the 5-L collection bottle by the wet-deposition amounts measured with the rain gage. During this phase of sampling, a variety of problems occurred with the rain gage. These problems included inadvertent adjustment to the calibration mechanism, the clock stopping during the sampling week, and the pen not writing on the rain-gage chart. Because of these problems, catch efficiencies could only be computed for 30 of the 42 possible weeks that wet deposition was collected. A median catch efficiency of 101 percent was computed for this phase of sampling. Because of the problems experienced with the rain gage during this phase of sampling, and to be consistent with the first two phases of sampling, the volume collected in the 5-L collection bottle was used to calculate precipitation amounts and loadings. Wet-deposition amounts computed from the sample volumes collected during the three sampling phases are shown in figure 3.

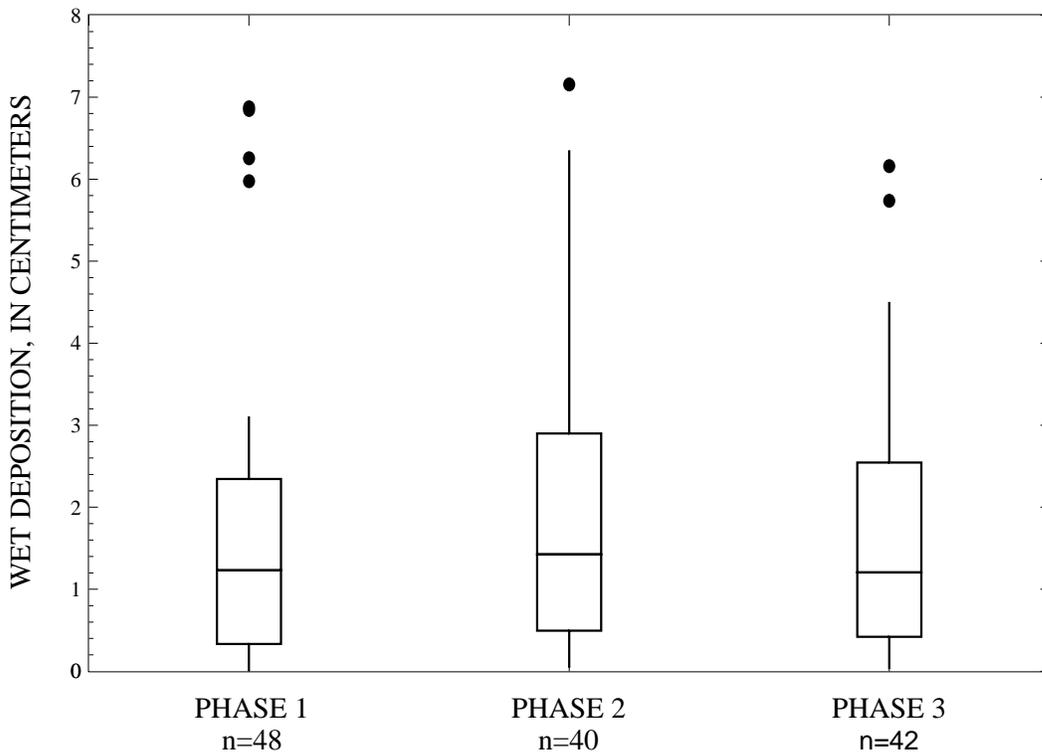
Constituent Concentrations

The number of samples analyzed for each constituent during the third sampling phase; the number of times the constituent was measured at a concentration greater than the method reporting limit; and the 25th, 50th, and 75th percentiles are shown in table 2. Table 5, at the back of this report,

lists the measured constituent concentrations of samples collected during the third sampling phase. None of the samples collected during the third sampling phase had measured concentrations greater than the method reporting limit for antimony, beryllium, cadmium, cobalt, molybdenum, silver, and uranium. The distributions of pH, specific conductance, major-ion and trace-metal concentrations measured in wet-deposition samples collected during the third phase of sampling at the Gary airport for all constituents that had more than 50 percent of the concentrations measured greater than the method reporting limit are shown in figures 4, 5, and 6. The pH was converted to hydrogen-ion concentrations prior to computing the whiskers for the boxplots and any statistical analyses. The hydrogen-ion concentrations then were converted back to pH for displaying in the figures.

Selected major-ion concentrations measured in wet-deposition samples collected at the Gary airport during the third sampling phase were compared to the concentrations from the NADP/NTN sites located at the Indiana Dunes National Lakeshore and Huntington Reservoir (fig. 7) during the same sampling period. Distributions of pH, specific conductance, and major-ion concentrations measured at these sites are shown in figures 8 and 9.

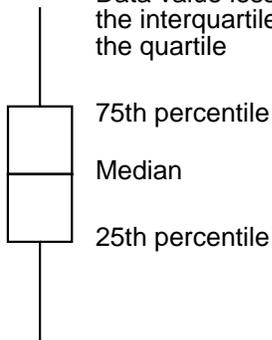
Statistically significant differences were determined for pH (as hydrogen ion, $p < 0.001$), specific conductance ($p = 0.004$), calcium ($p < 0.001$), magnesium ($p < 0.001$), potassium ($p < 0.001$), and sulfate ($p < 0.001$), where p is the significance level attained by the data. All three sites were significantly different from each other for pH (as hydrogen ion) and calcium. The median pH and the median calcium concentrations decreased as the distance from the Gary airport increased. The specific conductance measured at the Gary airport was not significantly different than the specific conductance measured at Huntington Reservoir; however, the Indiana Dunes National



EXPLANATION

● Outlier data value greater than 1.5 times the interquartile range outside the quartile

— Data value less than or equal to 1.5 times the interquartile range outside the quartile



n Number of samples

Figure 3. Weekly wet-deposition amounts collected at the Gary (Indiana) Regional Airport. (Phase 1 samples were collected from June 30, 1992, to August 31, 1993. Phase 2 samples were collected from October 17, 1995, to November 12, 1996. Phase 3 samples were collected from April 29, 1997, to April 28, 1998.)

Table 2. Water-quality characteristics measured in wet-deposition samples collected at the Gary (Indiana) Regional Airport

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; NA, not applicable; mg/L , milligrams per liter; <, less than the method reporting limit; $\mu\text{g}/\text{L}$, micrograms per liter]

Water-quality characteristic	Number of samples analyzed	Number of samples measured at concentrations greater than the method reporting limit	Percentile ranking			Method reporting units
			25th	50th	75th	
Specific conductance	29	29	17.8	20.7	24.4	$\mu\text{S}/\text{cm}$
Field pH	41	NA	4.60	4.75	6.17	units
Calcium	38	38	.71	.97	2.16	mg/L
Magnesium	38	38	.11	.16	.34	mg/L
Sodium	38	12	<.2	<.2	.3	mg/L
Potassium	39	39	.04	.06	.13	mg/L
Sulfate	29	29	2.5	3.3	4.1	mg/L
Bromide	29	1	<.01	<.01	<.01	mg/L
Chloride	29	25	.10	.22	.42	mg/L
Fluoride	29	18	<.01	.04	.06	mg/L
Silica	38	38	.15	.24	.77	mg/L
Nitrate	25	24	1.53	1.99	2.45	mg/L
Phosphate	26	3	<.03	<.03	<.03	mg/L
Aluminum	39	39	48	75	204	$\mu\text{g}/\text{L}$
Antimony	39	0	<1	<1	<1	$\mu\text{g}/\text{L}$
Barium	39	38	2.2	2.6	5.2	$\mu\text{g}/\text{L}$
Beryllium	39	0	<1	<1	<1	$\mu\text{g}/\text{L}$
Cadmium	39	0	<1	<1	<1	$\mu\text{g}/\text{L}$
Chromium	39	4	<1	<1	<1	$\mu\text{g}/\text{L}$
Cobalt	39	0	<1	<1	<1	$\mu\text{g}/\text{L}$
Copper	39	32	1.2	1.8	2.9	$\mu\text{g}/\text{L}$
Iron	38	37	20	33	89	$\mu\text{g}/\text{L}$
Lead	39	34	1.5	2.3	3.1	$\mu\text{g}/\text{L}$
Manganese	39	39	6.6	10	31	$\mu\text{g}/\text{L}$
Molybdenum	39	0	<1	<1	<1	$\mu\text{g}/\text{L}$
Nickel	39	3	<1	<1	<1	$\mu\text{g}/\text{L}$
Silver	39	0	<1	<1	<1	$\mu\text{g}/\text{L}$
Uranium	39	0	<1	<1	<1	$\mu\text{g}/\text{L}$
Zinc	39	39	9.3	17	26	$\mu\text{g}/\text{L}$

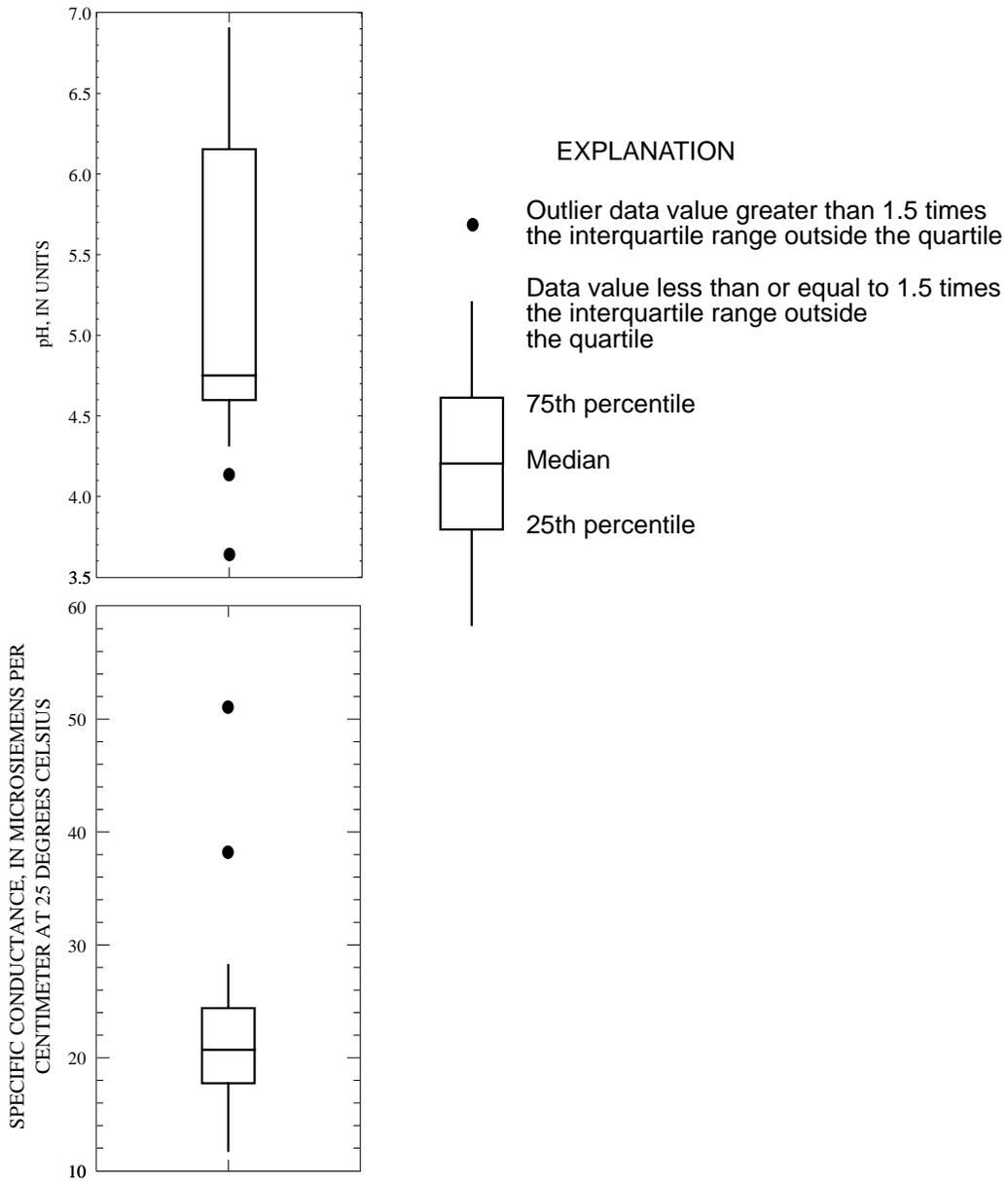


Figure 4. Distributions of pH and specific conductance measured in wet-deposition samples collected at the Gary (Indiana) Regional Airport during the third sampling phase, April 29, 1997, to April 28, 1998.

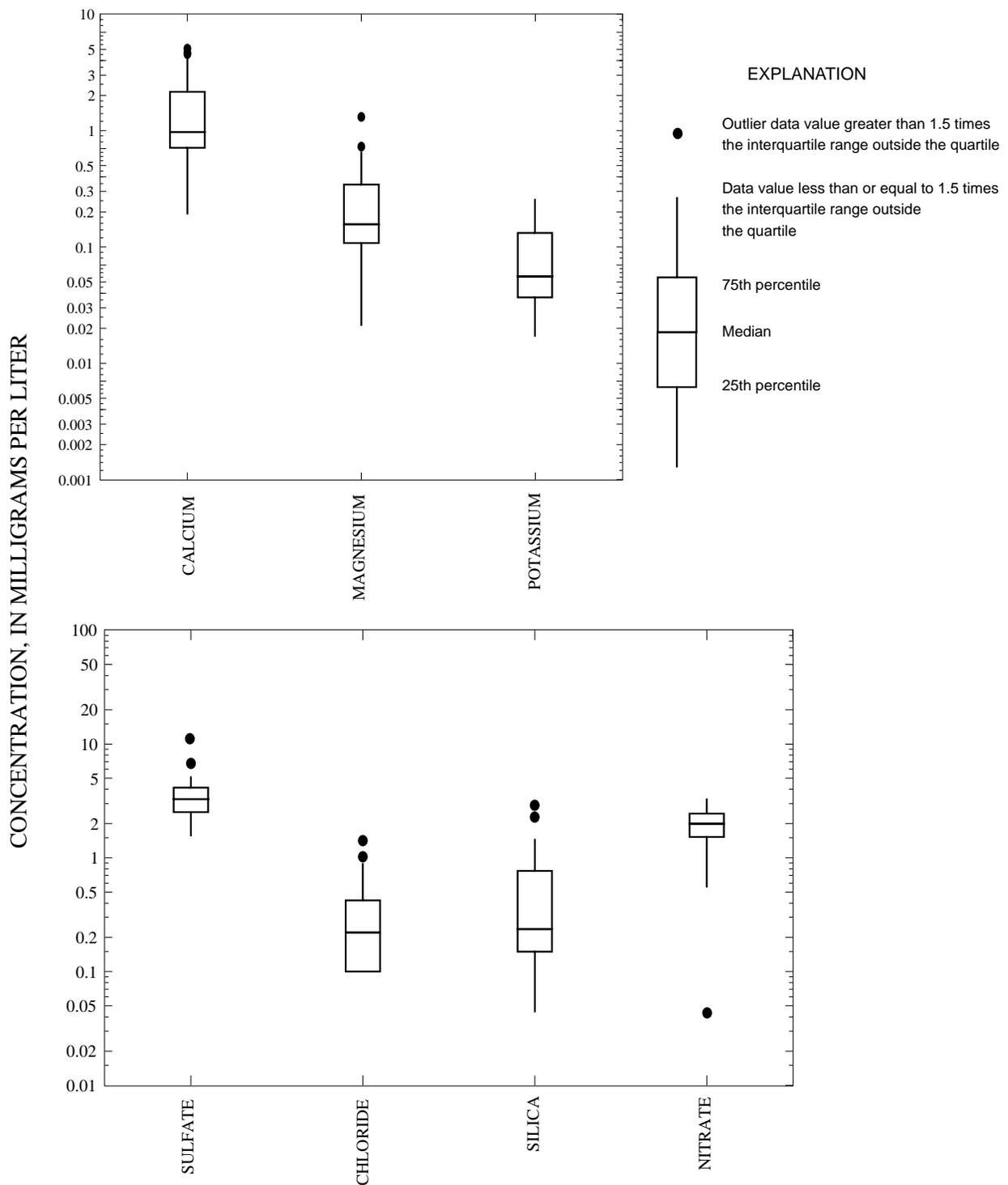


Figure 5. Distributions of major-ion concentrations measured in wet-deposition samples collected at the Gary (Indiana) Regional Airport during the third sampling phase, April 29, 1997, to April 28, 1998.

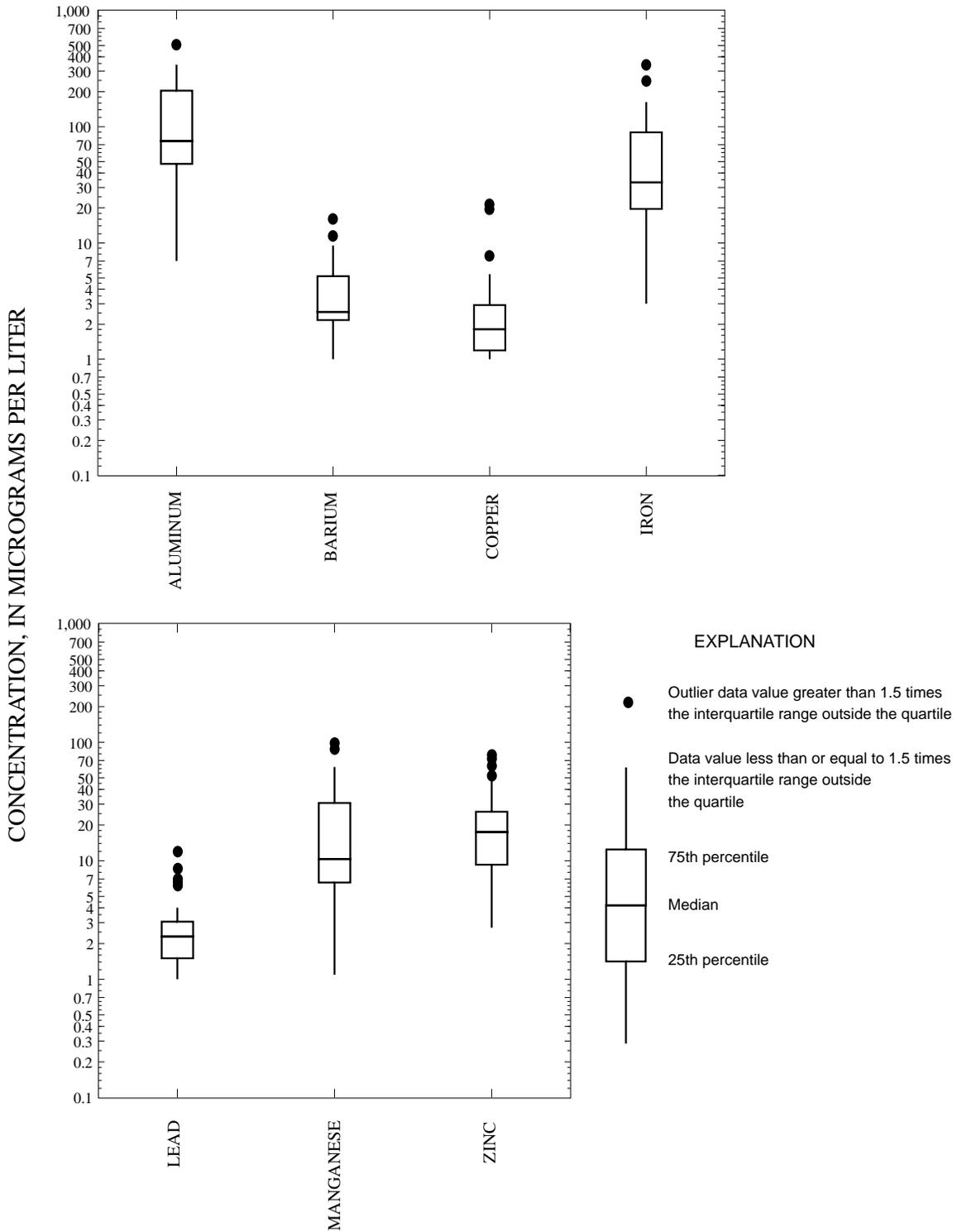


Figure 6. Distributions of trace-metal concentrations measured in wet-deposition samples collected at the Gary (Indiana) Regional Airport during the third sampling phase, April 29, 1997, to April 28, 1998.



Base from U.S. Geological Survey, 1:100,000, 1983
 Albers Equal-Area Conic projection
 Standard parallels 29°30' and 45°30', central meridian -86°

Figure 7. Location of wet-deposition sampling site at the Gary (Indiana) Regional Airport and two National Atmospheric Deposition Program/National Trends Network sampling sites at the Indiana Dunes National Lakeshore and Huntington Reservoir.

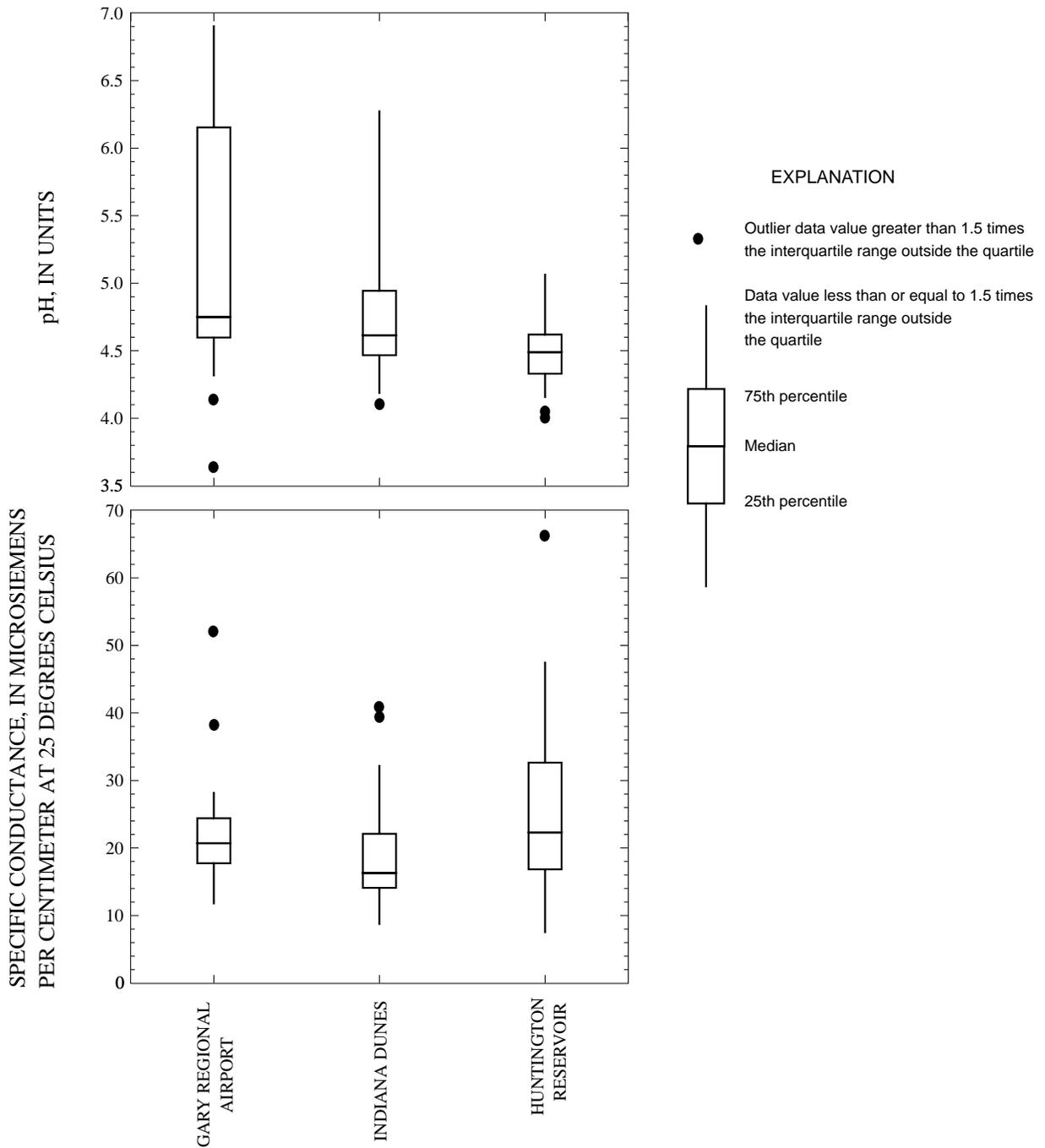


Figure 8. Distributions of pH and specific conductance measured in wet-deposition samples collected at the Gary (Indiana) Regional Airport and National Atmospheric Deposition Program/National Trends Network sites located at the Indiana Dunes National Lakeshore and Huntington Reservoir.

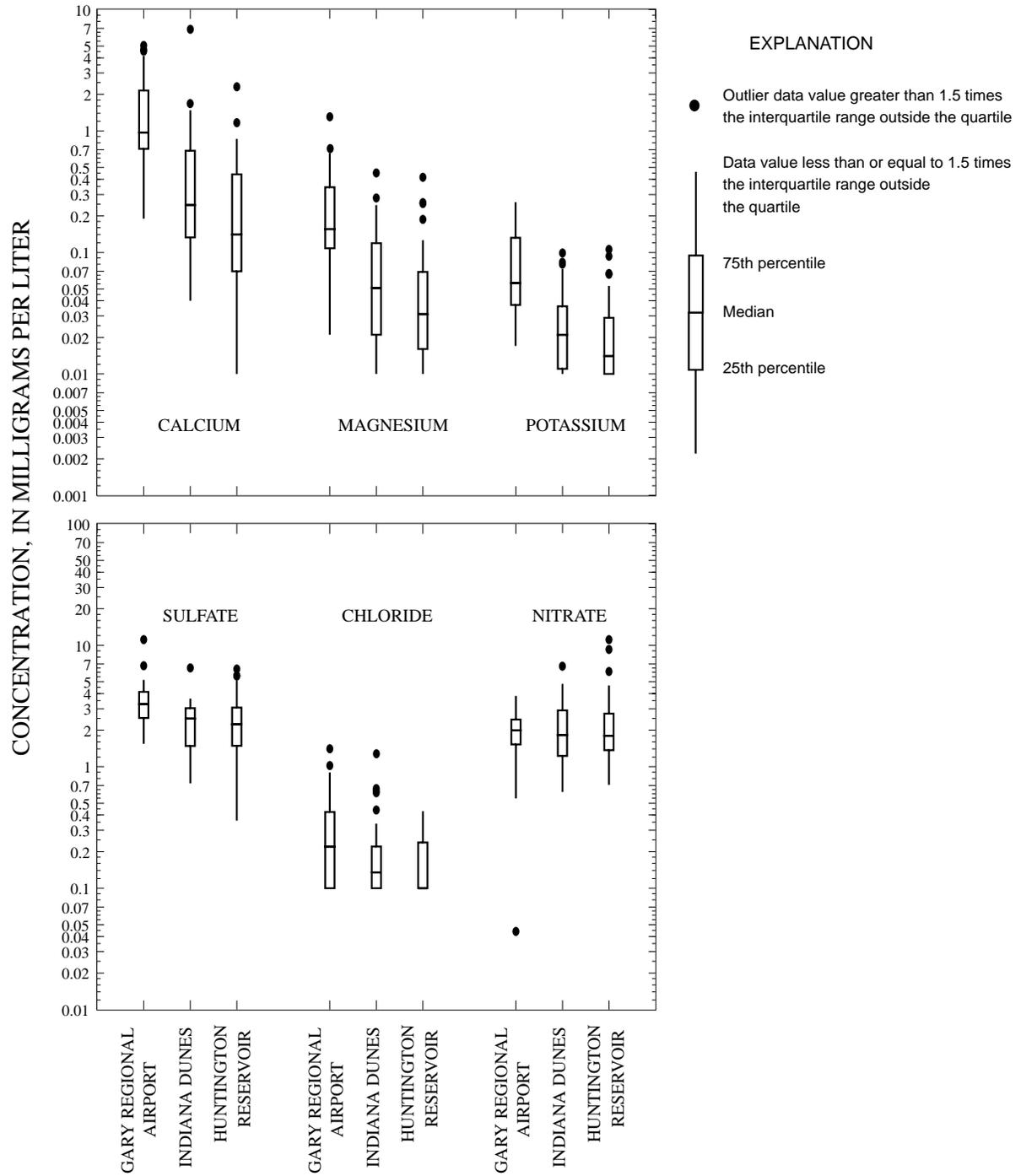


Figure 9. Distributions of major-ion concentrations measured in wet-deposition samples collected at the Gary (Indiana) Regional Airport and National Atmospheric Deposition Program/National Trends Network sites located at the Indiana Dunes National Lakeshore and Huntington Reservoir.

Lakeshore had a significantly lower specific conductance than the other two sites. The Gary airport had significantly greater concentrations of magnesium, potassium, and sulfate, compared to the other two sites. The Indiana Dunes National Lakeshore and Huntington Reservoir did not have significantly different concentrations of magnesium, potassium, and sulfate. No statistically significant differences were determined for chloride and nitrate.

Comparison of Concentrations to Previous Sampling Phases

Concentrations measured in samples collected at the Gary airport during the third sampling phase then were compared to the concentrations measured in samples collected during the first and second sampling phases. Figures 10, 11, and 12 show the distributions of pH, specific conductance, and constituent concentration measured during the three sampling phases.

Statistically significant differences in the distributions were determined for pH (as hydrogen ion, $p=0.001$), sodium ($p=0.014$), potassium ($p=0.012$), silica ($p=0.016$), iron ($p=0.006$), lead ($p=0.003$), and zinc ($p<0.001$). Hydrogen-ion concentrations for the first sampling phase were higher than hydrogen-ion concentrations determined for the second and third phases, resulting in lower pH values. Concentrations for the first and second phases of sampling were significantly different for pH (as hydrogen ion), potassium, iron, lead, and zinc. The first sampling phase was significantly lower from the third sampling phase for potassium, silica, lead, and zinc. There were no statistically significant differences between constituent concentrations measured during the second and third sampling phases. Concentrations for the first sampling phase that were determined to be significantly different were smaller than the con-

centrations determined for the second and third sampling phases. Because Gary, Ind., is an urbanized industrialized area, determining the reason for these increases is difficult. The trace metals iron, lead, and zinc, however, are components of steel production. The observed increases in these trace-metal concentrations may be attributed to increases in steel production. The increases in concentrations observed for the major constituents sodium, potassium, and silica may be attributed to increased contamination entering the collection funnel. The same sampling equipment was used for all three sampling phases. By the end of the third sampling phase, the seal between the collector lid and the collection funnel may not have been as tight as it was for the first sampling phase; this may have allowed more dust to enter the sampling funnel (see the Quality Assurance section of this report).

Constituent Loadings

Weekly surface loadings were computed for the third phase of sampling by multiplying the wet-deposition amounts determined from the volume collected in the collection bottle and the constituent concentration. For this report, the loadings are reported for an area of 1 hectare. Prior to computing the constituent surface load for the third phase of sampling, it was necessary to address missing concentrations that resulted from insufficient sample volumes for measurement of all parameters listed in table 1. Therefore, the following method was used to substitute a "reasonable" value for these missing concentrations. Median constituent concentrations were determined for samples collected during warm weather (April 1 through October 31) and cold weather (November 1 through March 31). These median constituent concentrations then were substituted for missing concentrations from samples collected during the same periods that had insufficient volumes for analysis of all the constituents listed in table 1.

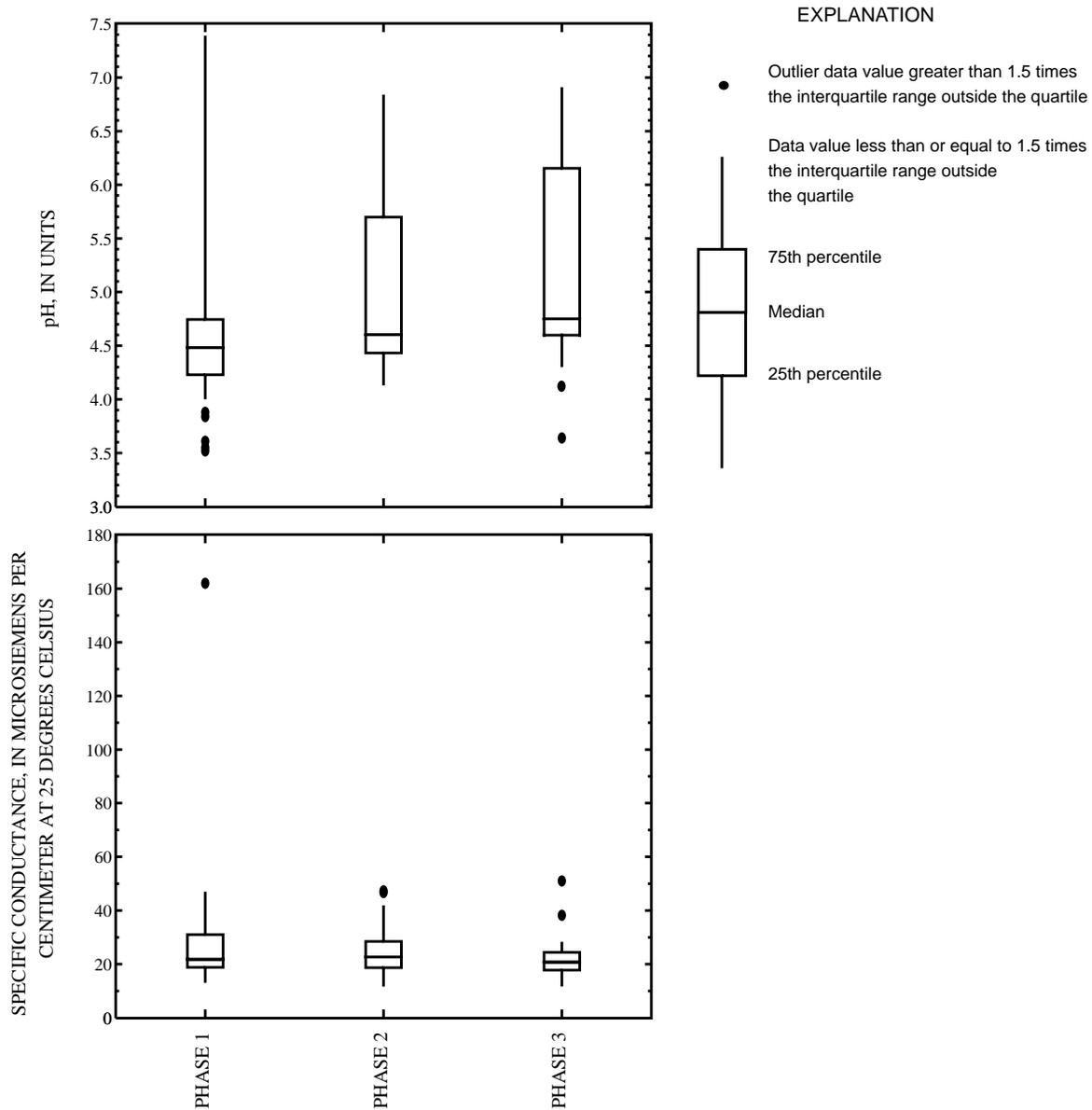


Figure 10. Distributions of pH and specific conductance measured in wet-deposition samples collected at the Gary (Indiana) Regional Airport. (Phase 1 samples were collected from June 30, 1992, to August 31, 1993. Phase 2 samples were collected from October 17, 1995, to November 12, 1996. Phase 3 samples were collected from April 29, 1997, to April 28, 1998.)

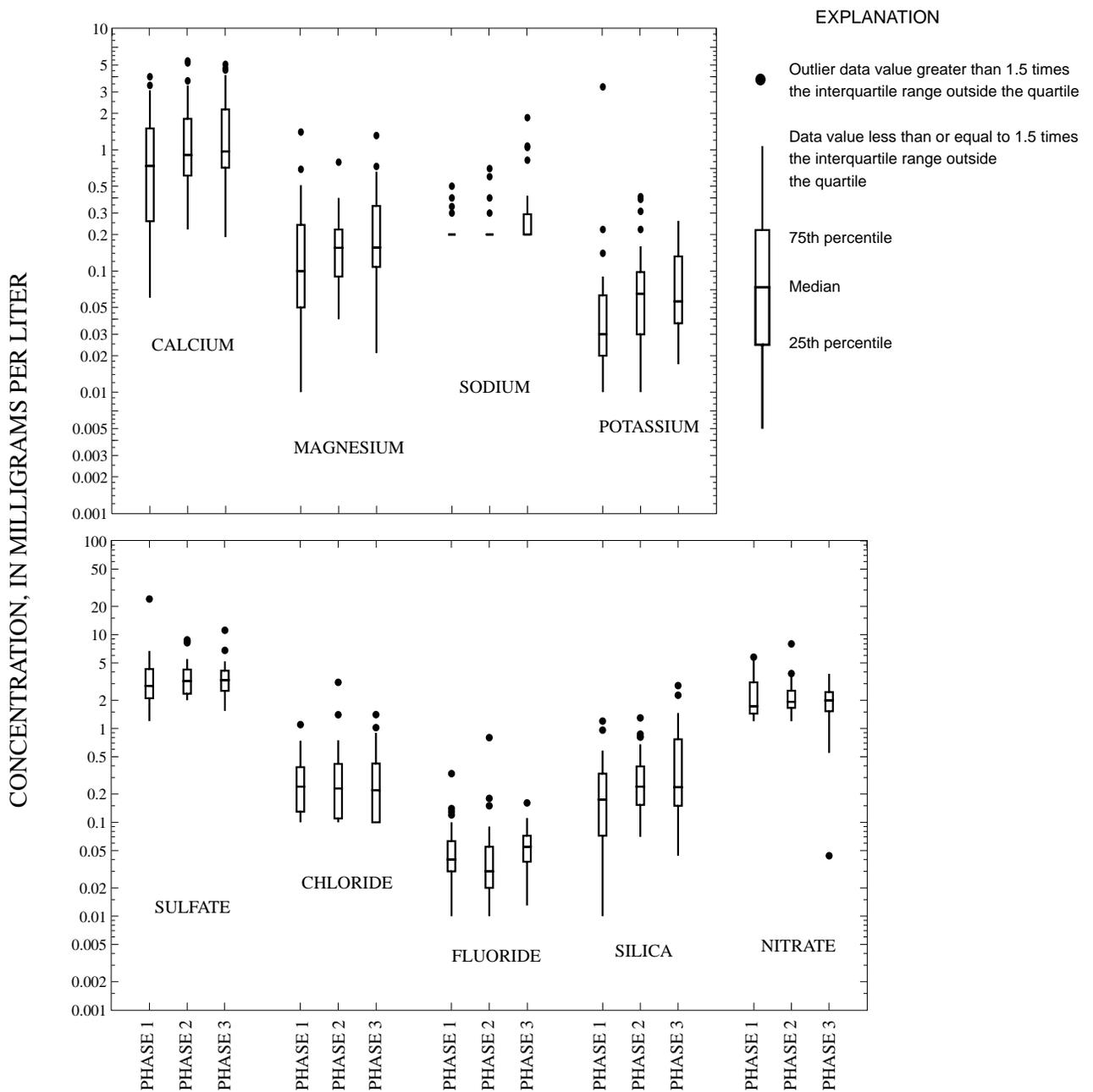


Figure 11. Distributions of major-ion concentrations measured in wet-deposition samples collected at the Gary (Indiana) Regional Airport. (Phase 1 samples were collected from June 30, 1992, to August 31, 1993. Phase 2 samples were collected from October 17, 1995, to November 12, 1996. Phase 3 samples were collected from April 29, 1997, to April 28, 1998.)

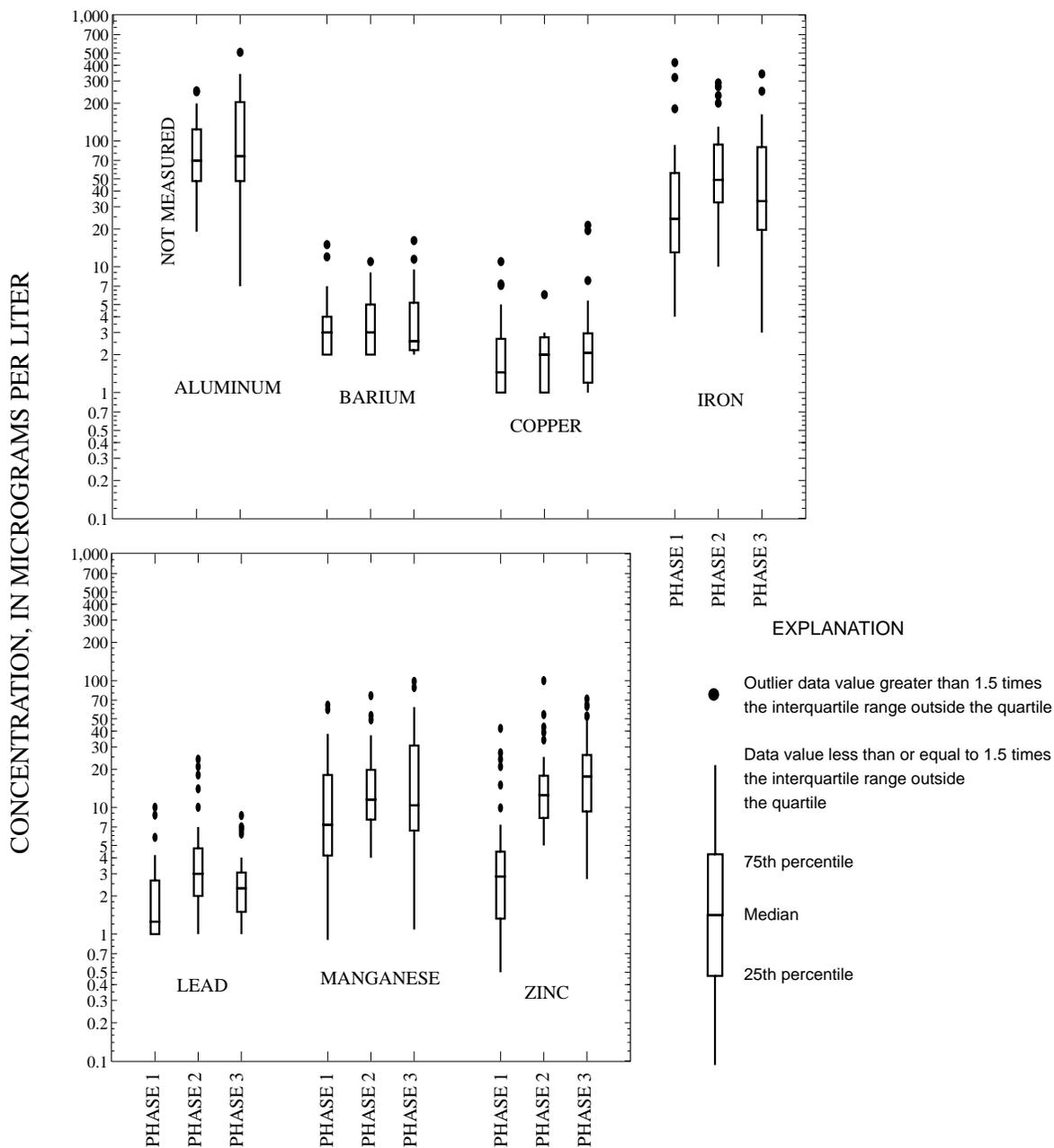


Figure 12. Distributions of trace-metal concentrations measured in wet-deposition samples collected at the Gary (Indiana) Regional Airport. (Phase 1 samples were collected from June 30, 1992, to August 31, 1993. Phase 2 samples were collected from October 17, 1995, to November 12, 1996. Phase 3 samples were collected from April 29, 1997, to April 28, 1998.)

The calculated weekly and annual loadings are therefore referred to as “estimated loadings.” If a measured constituent concentration were measured less than the method reporting limit, a range for that constituent’s weekly loading was computed. The minimum value for this range was computed by substituting zero for the constituent concentration. The maximum value for this range was computed by substituting the method reporting limit for the constituent concentration. A single value for the weekly loadings was calculated when the measured constituent concentration was measured greater than the method reporting limit. Estimated weekly major-ion and trace-metal loadings are presented in figures 13 and 14. The short horizontal bars indicate that the concentration for that week’s sample was less than the method reporting limit and, therefore, a range for the weekly loading is presented.

The range for the estimated annual constituent loadings (table 3) was calculated from the sum of the weekly loadings. Weekly loadings for 42 samples collected during the 1-year sampling period were used to calculate a range for the estimated annual loadings. The 6- and 8-day and the 2-week samples were included in the annual load calculation. The three samples lost because of sampler malfunctions and the one sample lost because of improper installation of the sampling equipment were not included in the annual load calculation. Because of the lost samples, the annual loadings may be underestimated. The minimum annual loading was calculated by summing the minimum weekly loadings, and the maximum annual loading was calculated by summing the maximum weekly loadings. If a single value were calculated for a weekly loading, that value was included in the calculation as the minimum and maximum annual loading. If a constituent concentration for all of the 42-weekly samples were measured greater than the method reporting limit, a single value for the range of the loading was computed.

Comparison of Estimated Annual Loadings to Previous Sampling Phases

Estimated annual loadings for the three sampling phases are shown in figures 15 and 16. Of the three sampling phases, chloride, silica, bromide, copper, and zinc had the largest estimated annual loading in the third sampling phase. The largest estimated annual loading of aluminum was also in the third sampling phase; however, aluminum was measured only during the second and third sampling phases. The only estimated annual loading in the third sampling phase that was smaller than the previous two phases was sulfate. The estimated annual loadings of calcium, magnesium, nitrate, potassium, barium, lead, iron, and manganese observed during the third sampling phase were greater than the estimated annual loadings observed during the first sampling phase but were less than those observed during the second sampling phase.

Quality Assurance

Two types of quality-control samples were submitted to the NWQL to evaluate the precision and accuracy of results reported for wet-deposition samples collected at the Gary airport. Laboratory quality-control samples (table 6, at the back of the report) were used to evaluate the quality of the DIW and nitric acid used in preparing quality-control samples, cleaning equipment, and acidifying samples. Field quality-control samples (table 7, at the back of the report) were used to evaluate possible contamination resulting from cleaning, transporting, and installing the clean equipment in the collector and evaluating the possible contamination resulting from the funnel, tubing, and collection bottle remaining in the collector for the 1-week sampling period. All sample-processing procedures remained the same for field quality-control samples and all parameters and analytical techniques remained the same for the laboratory and field quality-control samples as those used for the wet-deposition samples.

Table 3. Estimated annual loadings determined from wet-deposition samples collected at the Gary (Indiana) Regional Airport for April 29, 1997, to April 28, 1998

[kg/ha, kilograms per hectare; g/ha, grams per hectare]

Constituent	Estimated annual loading
Calcium	7.6 kg/ha
Magnesium	1.1 kg/ha
Sodium	1.0 to 2.1 kg/ha
Potassium	.39 kg/ha
Sulfate	25 kg/ha
Bromide	1.1 to 1.2 kg/ha
Chloride	2.3 to 2.4 kg/ha
Fluoride	.22 to .55 kg/ha
Silica	2.5 kg/ha
Nitrate	14.1 kg/ha
Phosphate	.17 to .40 kg/ha
Aluminium	840 g/ha
Antimony	less than 7.7 g/ha
Barium	24 g/ha
Beryllium	less than 7.7 g/ha
Cadmium	less than 7.7 g/ha
Chromium	.42 to 7.8 g/ha
Cobalt	less than 7.7 g/ha
Copper	16 to 18 g/ha
Iron	370 g/ha
Lead	21 to 22 g/ha
Manganese	95 g/ha
Molybdenum	less than 7.7 g/ha
Nickel	.53 to 7.9 g/ha
Silver	less than 7.7 g/ha
Uranium	less than 7.7 g/ha
Zinc	143 g/ha

Laboratory Quality Assurance

DIW blanks were submitted four times during the study to determine if there were any sources of contamination resulting from the DIW or nitric acid used to prepare quality-control solutions and clean equipment. None of the constituents measured had median concentrations greater than the method reporting limit; however, of the four blanks submitted for analysis, one sample had measured concentrations of iron (3 µg/L) and aluminum (1 µg/L). A second sample had measured concentrations of fluoride (0.03 mg/L) and aluminum (3 µg/L). The results of the DIW laboratory blanks indicate that neither the DIW nor nitric acid used for preserving the major cations and trace metals, preparing acidified DIW funnel rinses and acidified DIW system blanks, and cleaning the equipment contributed significant levels of contamination to the wet-deposition samples collected at the Gary airport.

Two USGS standard reference water samples (SRWS), P17 and T117, with known most probable values (J.W. Farrar, U.S. Geological Survey, written commun., 1995) also were submitted to the laboratory for analysis. SRWS's are prepared by the SRWS Project and are used as quality-control samples for the NWQL and for evaluation of laboratories used by the USGS. For this study, two SRWS solutions were selected to include as many of the constituents as possible. To evaluate the accuracy of results reported by the NWQL for wet-deposition samples collected at the Gary airport, four samples were prepared from each of the two SRWS solutions and submitted for analysis. Four SRWS P17 samples were submitted to evaluate the accuracy of major anions, and four SRWS T117 samples were submitted to evaluate the accuracy of major cations and trace elements. The SRWS's were rebottled at the USGS laboratory in Indianapolis and submitted to the laboratory in the same manner as the wet-deposition samples. Table 4 lists the most probable value (MPV), F-pseudosigma (eq. 1), and the median concentration measured by the NWQL. F-pseudosigma is a measure of variability in data as is standard deviation (Hoaglin and others, 1983).

ESTIMATED WEEKLY LOADINGS, IN KILOGRAMS PER HECTARE

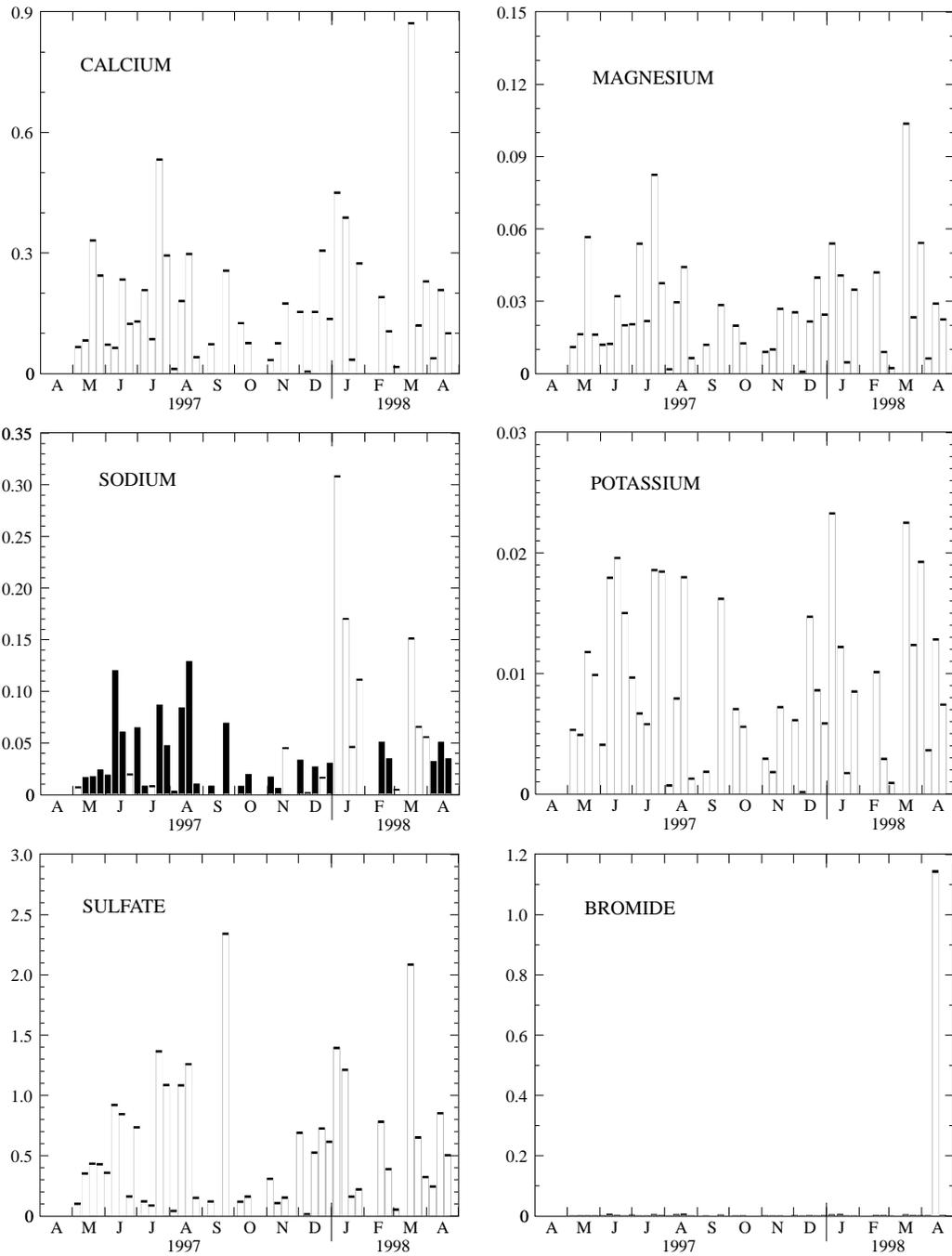


Figure 13. Estimated weekly major-ion loadings determined from wet-deposition samples collected at the Gary (Indiana) Regional Airport. Short horizontal bars indicate a possible range for the weekly loadings and were computed when a measured constituent concentration was measured less than the method reporting limit. The minimum value for a range is zero; the maximum value was computed by substituting the method reporting limit for the constituent concentration.

ESTIMATED WEEKLY LOADINGS, IN KILOGRAMS PER HECTARE

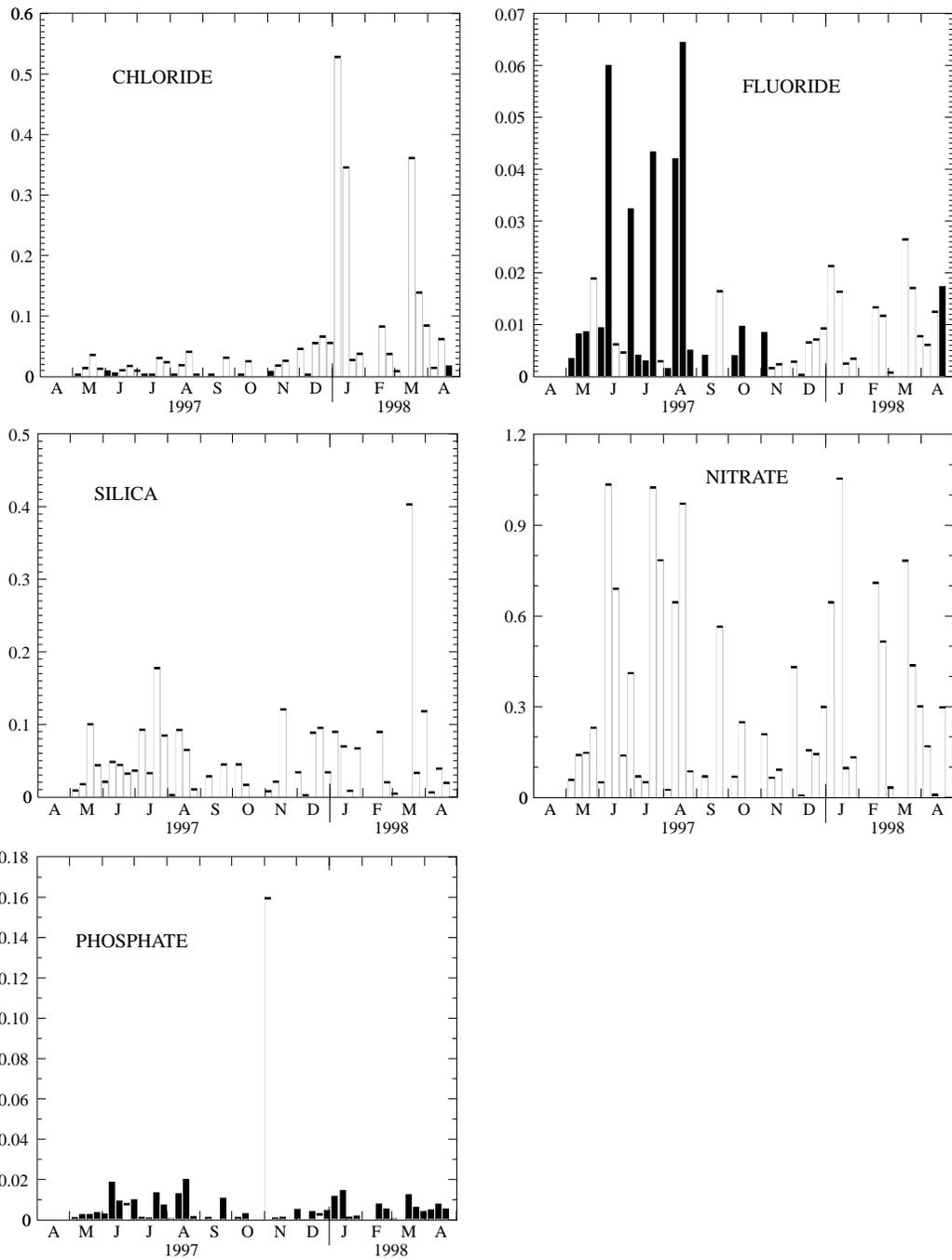


Figure 13. Estimated weekly major-ion loadings determined from wet-deposition samples collected at the Gary (Indiana) Regional Airport—Continued.

ESTIMATED WEEKLY LOADINGS, IN GRAMS PER HECTARE

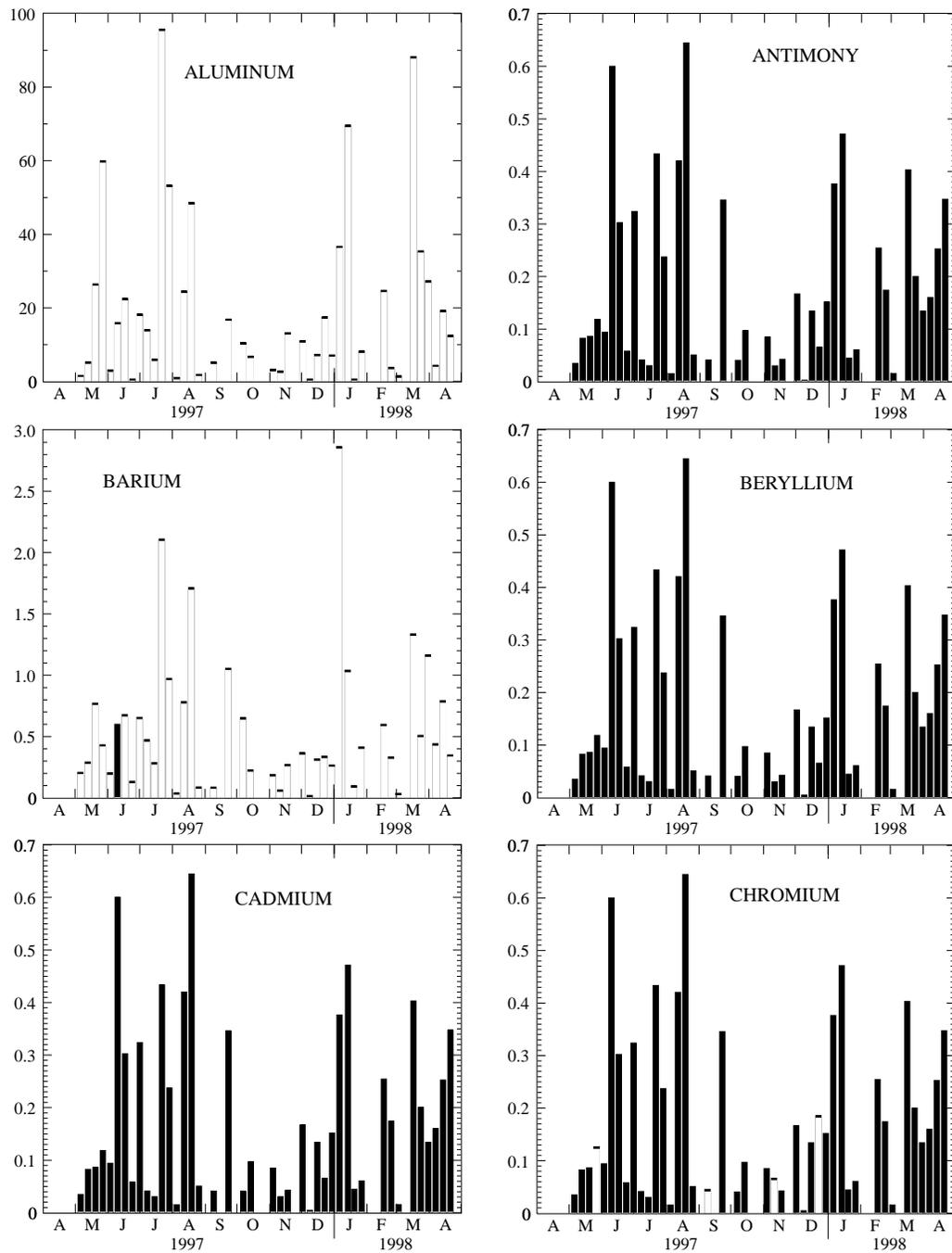


Figure 14. Estimated weekly trace-metal loadings determined from wet-deposition samples collected at the Gary (Indiana) Regional Airport. Short horizontal bars indicate a possible range for the weekly loadings and were computed when a measured constituent concentration was measured less than the method reporting limit. The minimum value for a range is zero; the maximum value was computed by substituting the method reporting limit for the constituent concentration.

ESTIMATED WEEKLY LOADINGS, IN GRAMS PER HECTARE

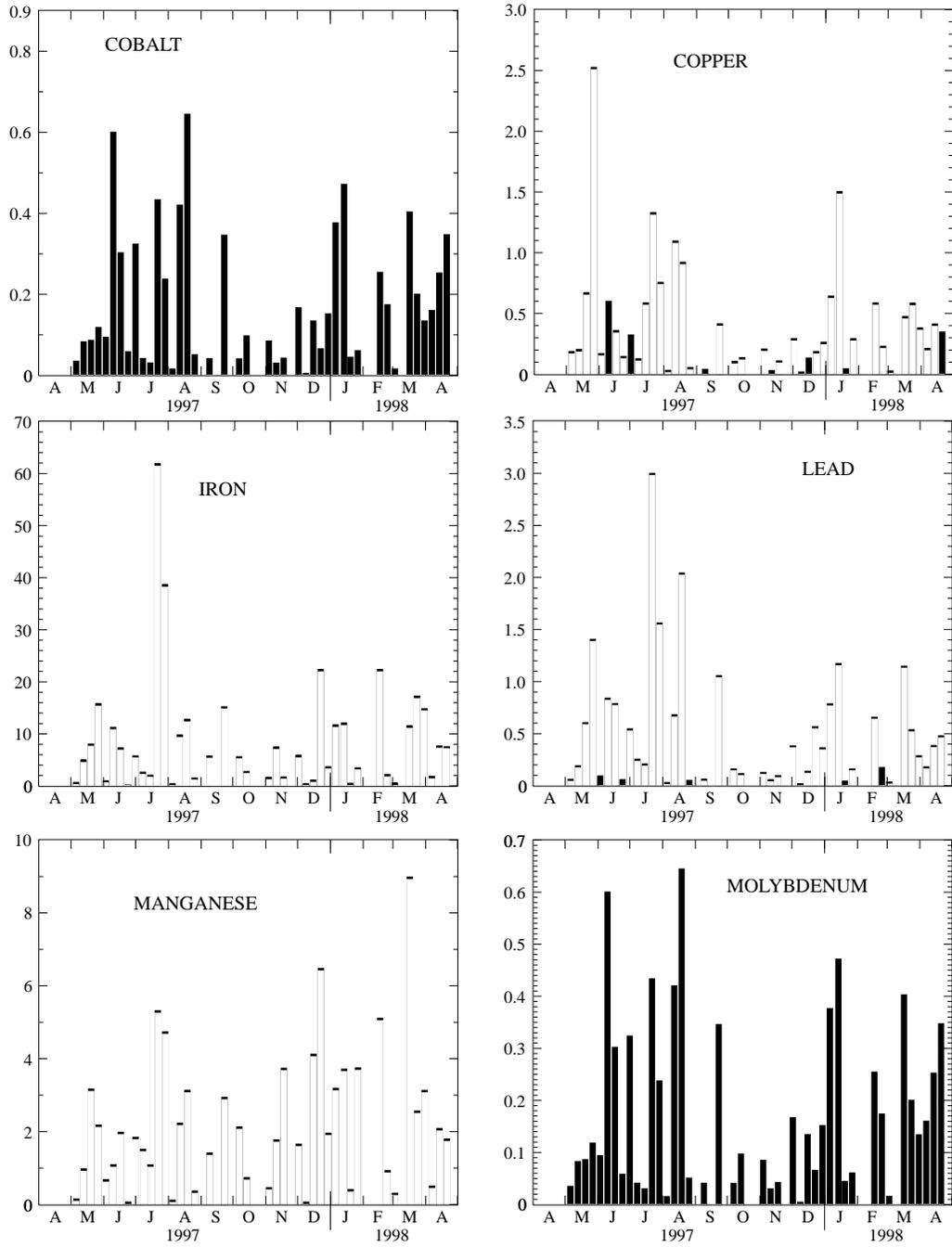


Figure 14. Estimated weekly trace-metal loadings determined from wet-deposition samples collected at the Gary (Indiana) Regional Airport—Continued.

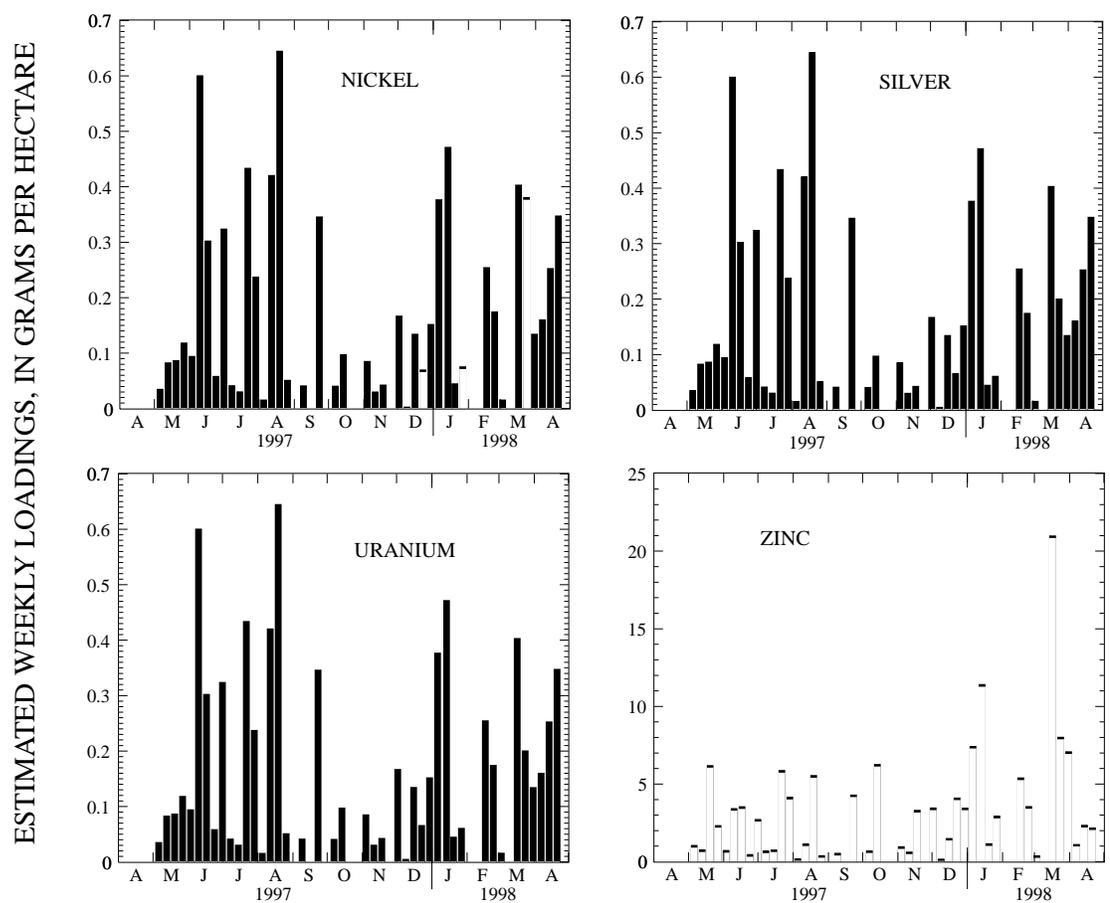


Figure 14. Estimated weekly trace-metal loadings determined from wet-deposition samples collected at the Gary (Indiana) Regional Airport—Continued.

Table 4. Median concentrations measured for the standard reference water samples (SRWS) T117 and P17 and the most probable value

[mg/L, milligrams per liter; NR, not reported; NA; not applicable; µg/L, micrograms per liter]

Constituent	Most probable value	F-pseudosigma	SRWS	Measured median concentration	F-pseudosigma	Reporting unit
Calcium	20.9	1.2	T117	21.2	0.3	mg/L
Magnesium	10.1	.4	T117	9.7	.2	mg/L
Sodium	20.0	1.3	T117	20.3	.2	mg/L
Potassium	2.11	.19	T117	2.15	.06	mg/L
Sulfate	.50	.11	P17	.50	.07	mg/L
Bromide	NR	NR	NA	<.01	0	mg/L
Chloride	.42	.29	P17	.37	.02	mg/L
Fluoride	NR	NR	NA	<.01	0	mg/L
Silica	11.9	.6	T117	11.6	.4	mg/L
Nitrate	NR	NR	NA	1.17	.01	mg/L
Phosphate	.012	.009	P17	<.03	0	mg/L
Aluminum	79	19	T117	72	5	µg/L
Antimony	6	1	T117	6	0	µg/L
Barium	99	6	T117	98	3	µg/L
Beryllium	5	1	T117	5	0	µg/L
Cadmium	2	1	T117	2	0	µg/L
Cobalt	4	1	T117	4	0	µg/L
Copper	6	2	T117	6	0	µg/L
Iron	474	18	T117	467	7	µg/L
Lead	5	1	T117	5	0	µg/L
Manganese	220	3	T117	212	4	µg/L
Molybdenum	12	2	T117	11	0	µg/L
Nickel	10	2	T117	9	0	µg/L
Silver	1	1	T117	<1	0	µg/L
Uranium	NR	NR	NA	2	0	µg/L
Zinc	176	9	T117	174	2	µg/L

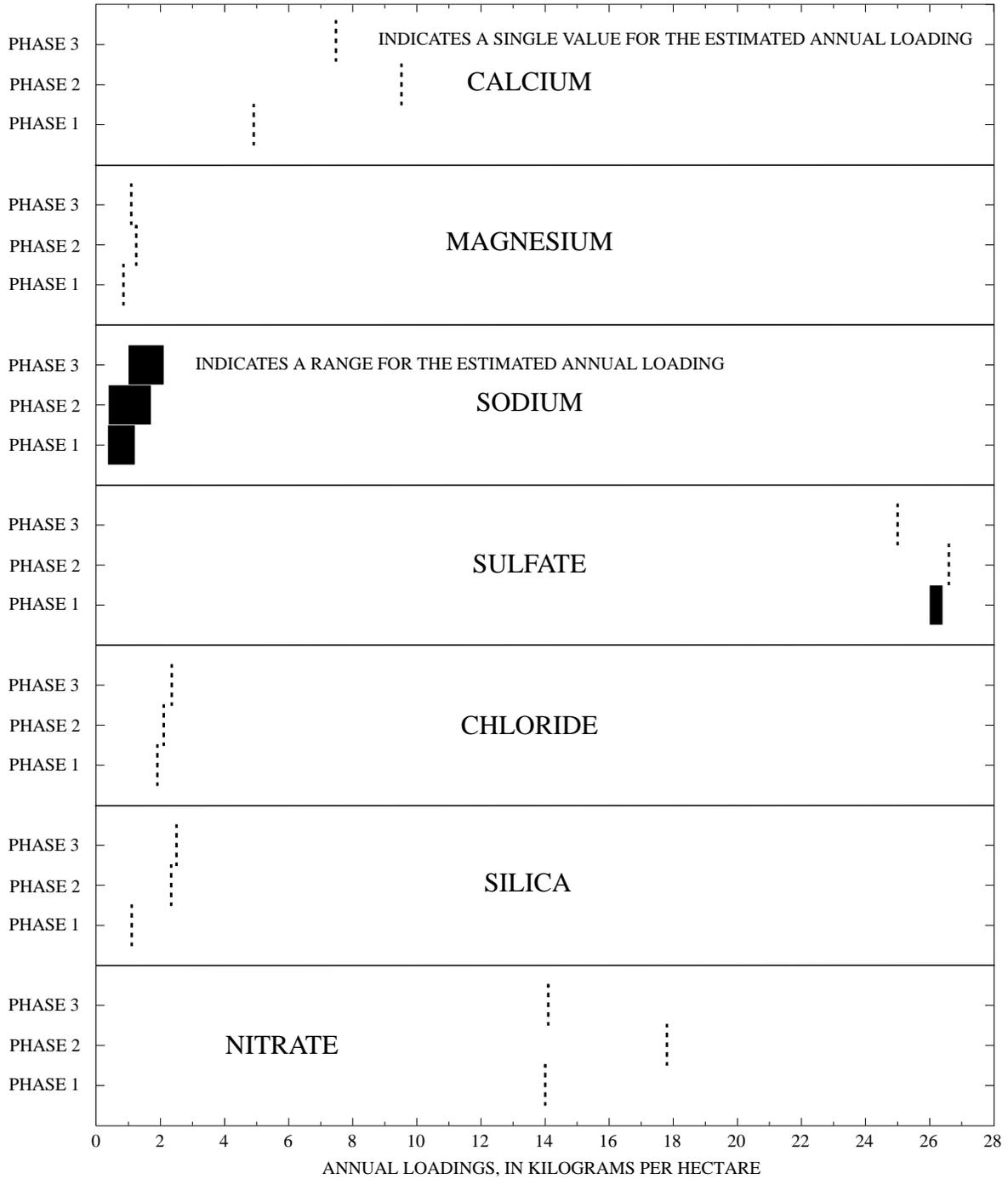


Figure 15. Estimated annual loadings of major ions from samples collected at the Gary (Indiana) Regional Airport during phase 1 (June 30, 1992, to August 31, 1993), phase 2 (October 17, 1995, to November 12, 1996), and phase 3 (April 29, 1997, to April 28, 1998).

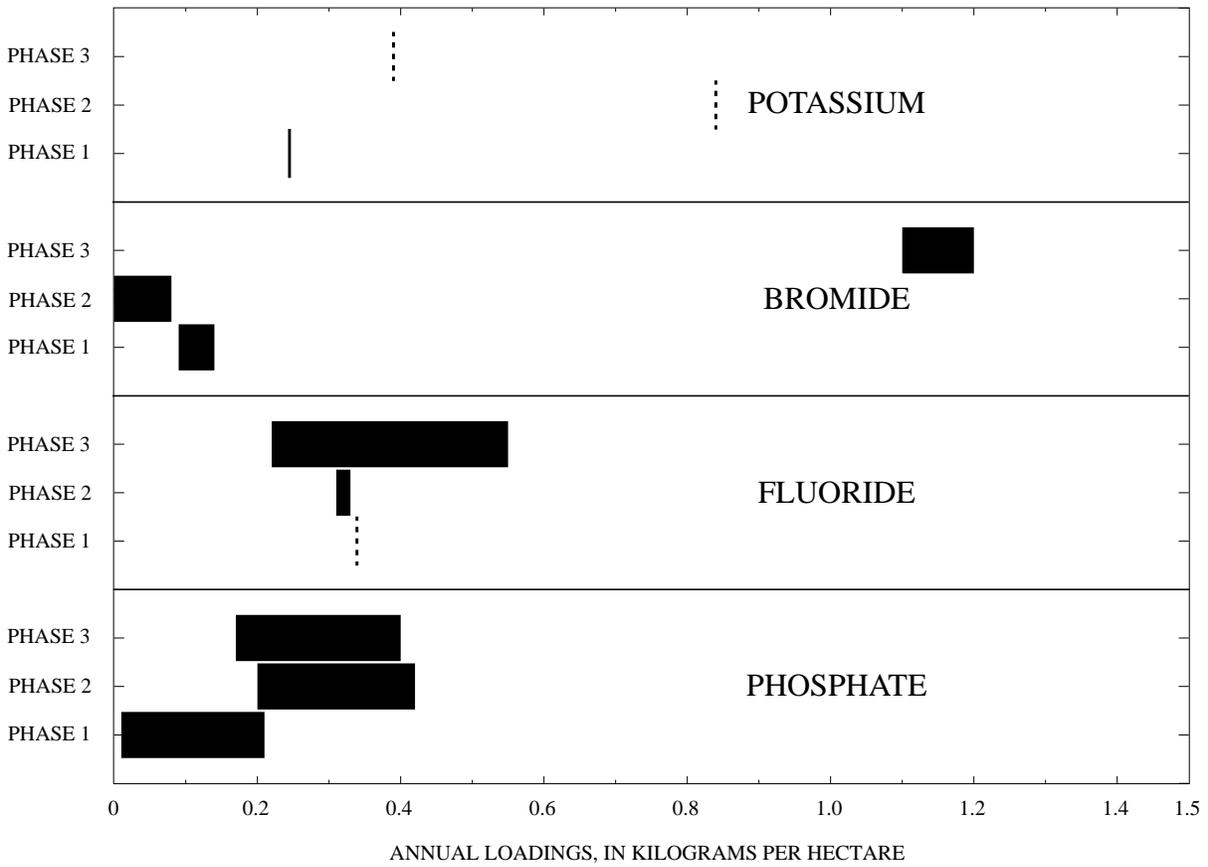


Figure 15. Estimated annual loadings of major ions from samples collected at the Gary (Indiana) Regional Airport during phase 1 (June 30, 1992, to August 31, 1993), phase 2 (October 17, 1995, to November 12, 1996), and phase 3 (April 29, 1997, to April 28, 1998)—Continued.

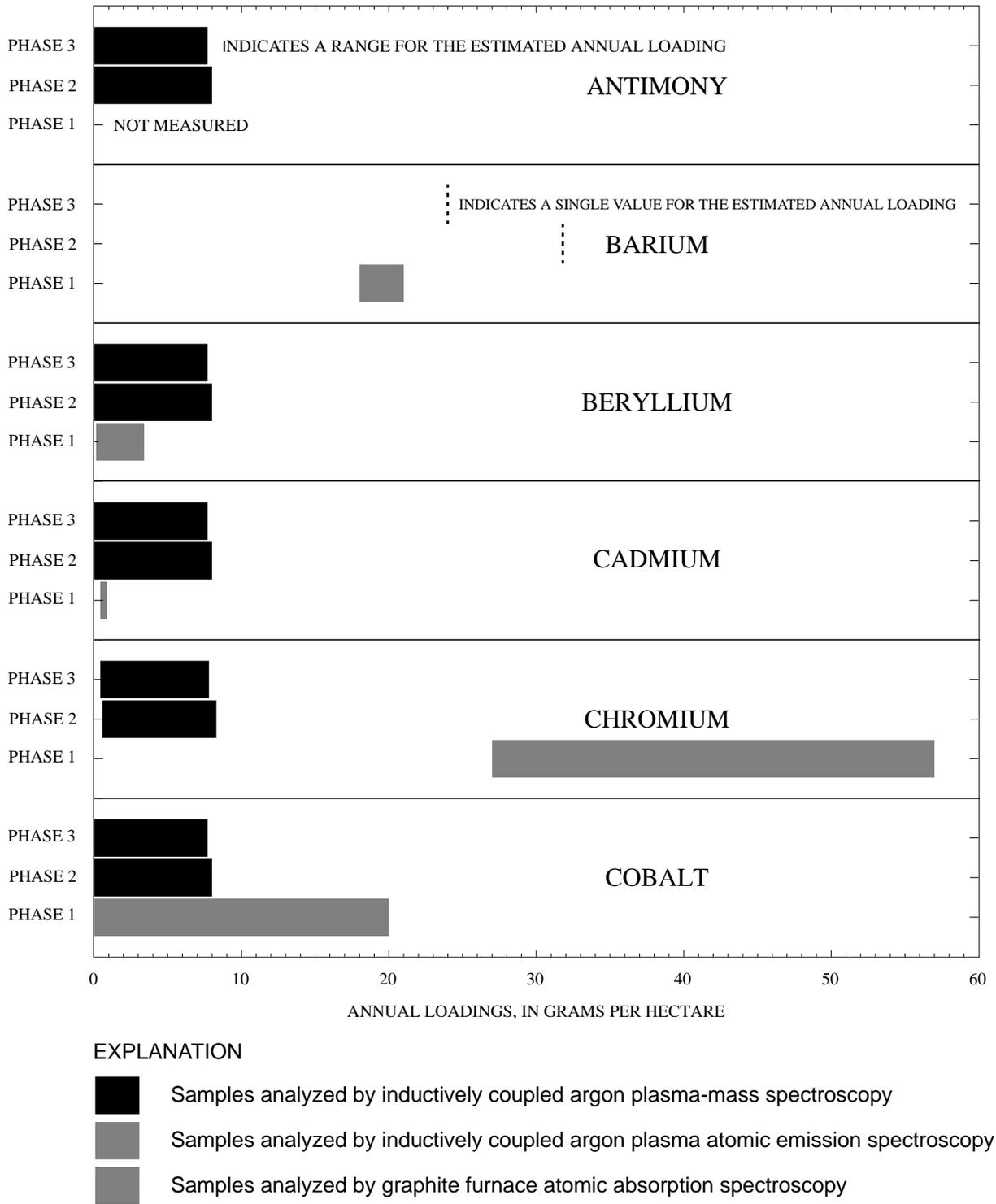


Figure 16. Estimated annual loadings of trace metals from samples collected at the Gary (Indiana) Regional Airport during phase 1 (June 30, 1992, to August 31, 1993), phase 2 (October 17, 1995, to November 12, 1996), and phase 3 (April 29, 1997, to April 28, 1998).

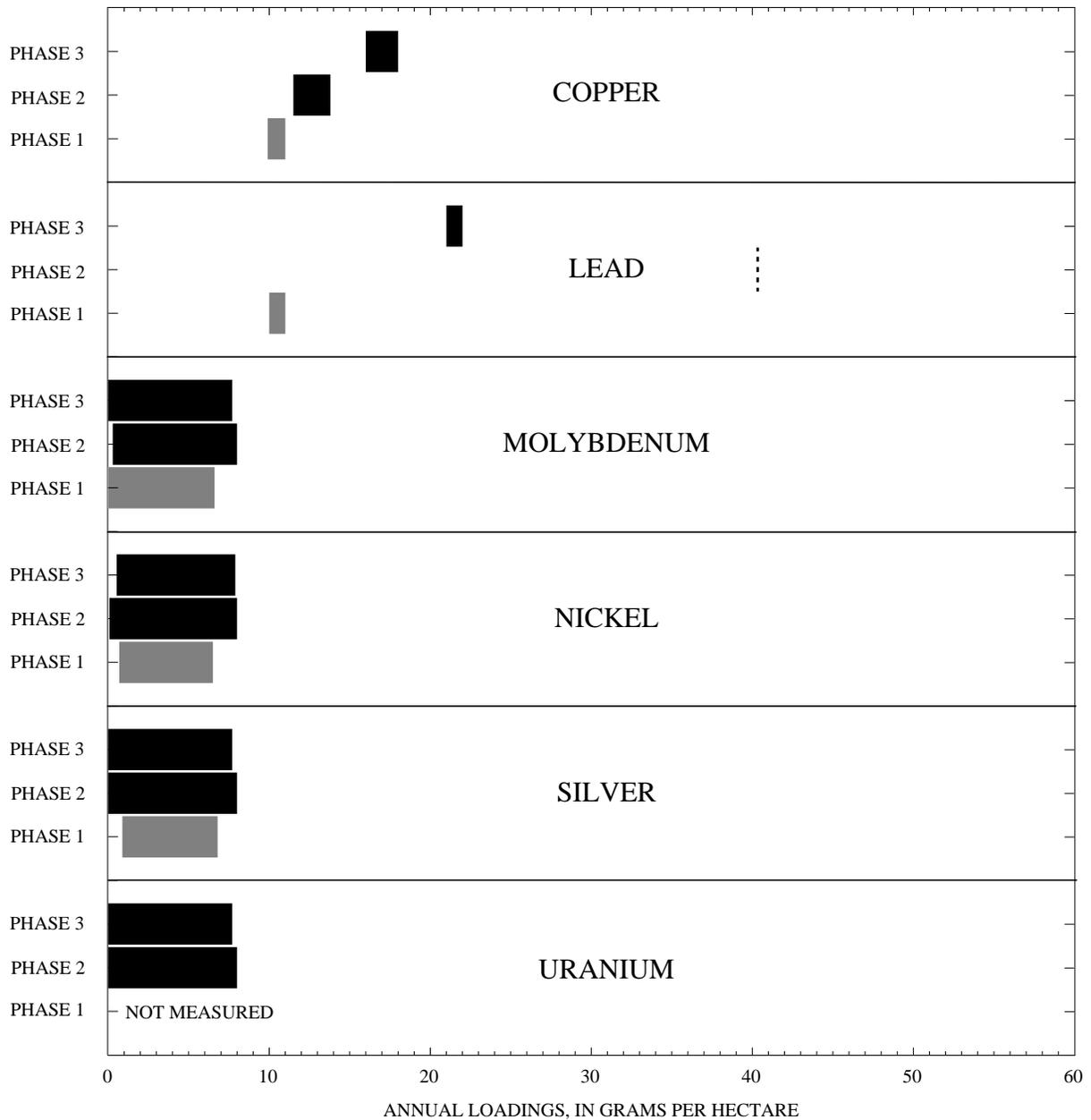
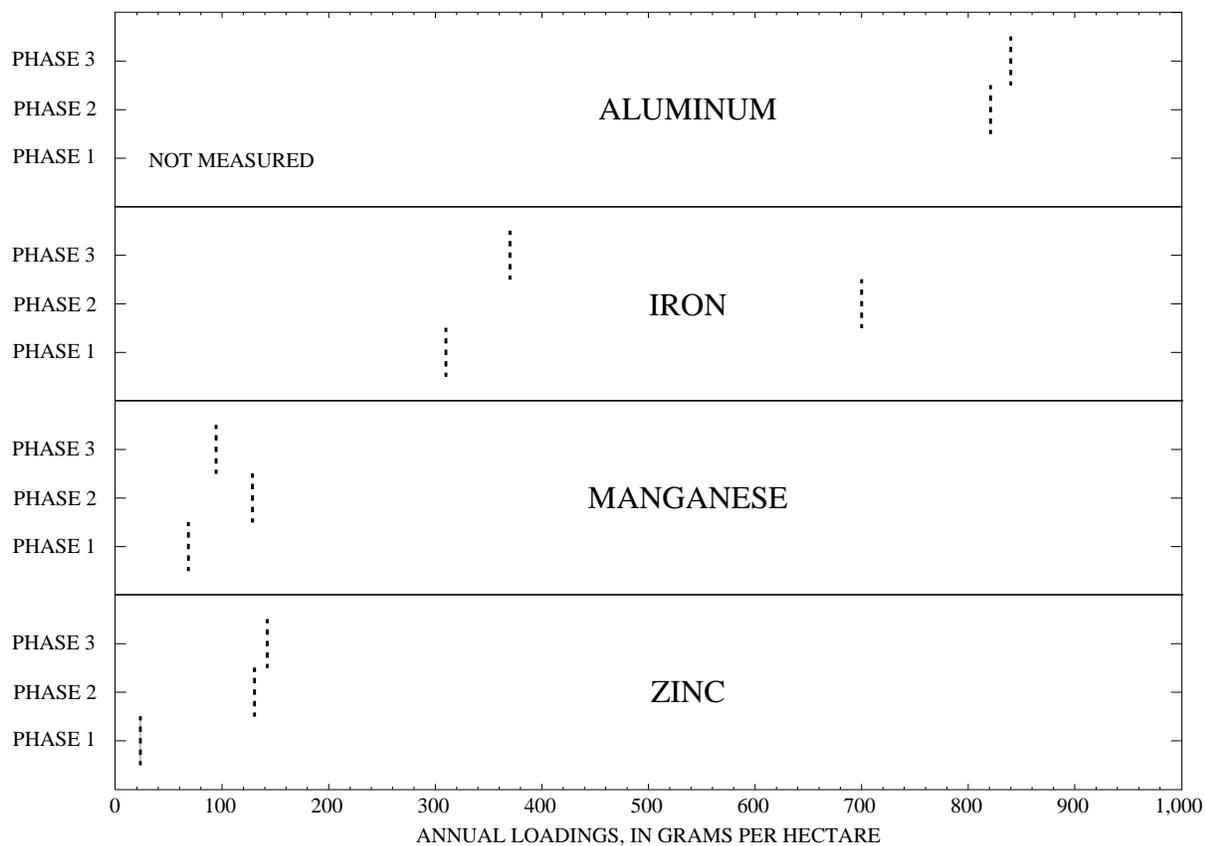


Figure 16. Estimated annual loadings of trace metals from samples collected at the Gary (Indiana) Regional Airport during phase 1 (June 30, 1992, to August 31, 1993), phase 2 (October 17, 1995, to November 12, 1996), and phase 3 (April 29, 1997, to April 28, 1998)—Continued.



Note: During phase 1, iron was measured by inductively coupled argon plasma atomic emission spectroscopy. Manganese and zinc were analyzed by graphite furnace atomic absorption spectroscopy

Figure 16. Estimated annual loadings of trace metals from samples collected at the Gary (Indiana) Regional Airport during phase 1 (June 30, 1992, to August 31, 1993), phase 2 (October 17, 1995, to November 12, 1996), and phase 3 (April 29, 1997, to April 28, 1998)—Continued.

$$F - pseudosigma = \frac{P75 - P25}{1.349}, \quad (1)$$

where

P75 is the 75th percentile; and

P25 is the 25th percentile.

Median concentrations were computed for each constituent and compared to the reported MPV. All of the constituents measured for the SRWS solutions were within the reported MPV plus or minus the F-pseudosigma, with the exception of manganese. The median concentration determined for manganese was 212 µg/L, which is 8 µg/L (3.6 percent) lower than the reported MPV.

Field Quality Assurance

Three types of field quality-control samples were processed periodically during the length of the study: (1) split wet-deposition samples, (2) funnel rinses, and (3) system blanks (table 7, at the back of the report). Four wet-deposition samples with sufficient volumes (greater than 1,500 mL) were split. Each split from the sample was processed independently and submitted to the laboratory to evaluate analytical precision. The concentrations measured for the split samples were subtracted from the wet-deposition samples collected at the Gary airport, and a median difference was computed for each constituent. For all of the constituents listed in table 1, the median difference between the split sample and the wet-deposition sample was less than the method reporting limit, with the following exceptions: sulfate (-0.02 mg/L), fluoride (0.05 mg/L), aluminum (3 µg/L), and iron (2 µg/L). These differences between the split samples for sulfate, aluminum, and iron were within 10 percent of the median concentrations determined from the wet-deposition samples. The median difference between the split

samples and the median concentration determined for the wet-deposition samples during the third sampling phase for fluoride, however, was 125 percent of the concentration measured in samples collected during the third sampling phase.

The funnel rinses and system blanks were prepared prior to use by diluting Ultrex nitric acid to a target pH of 4.5 with DIW. The target pH of 4.5 was the median pH determined from wet-deposition samples collected during the first phase of sampling. Six acidified DIW funnel rinses were processed during the length of the study to evaluate possible contamination resulting from cleaning the equipment, shipping the clean equipment to the Gary airport, installing the equipment in the collector, and processing the sample prior to shipping it to the NWQL. The funnel rinses were processed immediately after installation of clean equipment in the collector. The rinses were completed by passing 750 mL of the pH 4.5 solution through the funnel, with as much of the inside of the funnel surface as possible exposed to the solution; the solution was collected in the collection bottle. The collection bottle was removed and processed in the same manner as the wet-deposition sample collected at the Gary airport. Median concentrations for the six acidified DIW funnel rinses were computed. Median concentrations greater than the method reporting limit were observed for silica (0.07 mg/L), aluminum (11 µg/L), and iron (7 µg/L). Nitrate had a median concentration in the funnel rinses of 2.2 mg/L, which was contributed by the nitric acid when preparing the funnel rinses.

Five system blanks were processed during the length of the study on weeks when no precipitation was collected in the collection bottle. System blanks were processed in the same manner as funnel rinses, except they were done at the end of the sampling week before installation of clean equipment in the collector. Median concentrations were computed for the system blanks. Of the constituents measured, calcium (0.37 mg/L), magnesium (0.06 mg/L), potassium (0.02 mg/L), sulfate (0.27 mg/L), chloride (0.02 mg/L),

fluoride (0.09 mg/L), silica (0.19 mg/L), aluminum (53 µg/L), iron (28 µg/L), manganese (5 µg/L), and zinc (6 µg/L) had median concentrations greater than the method reporting limit. All of the median concentrations determined for the system blanks were greater than the median concentration determined for the funnel rinses, indicating that contamination of the wet-deposition samples increased during the period the funnel, Teflon tubing, and Teflon collection bottle remained in the collector. System-blank concentrations measured greater than the concentrations measured in the funnel rinses, suggesting that dry deposition may be contributing to the concentrations measured in the wet-deposition samples. This may result in a positive bias in the concentrations measured in the wet deposition and an overestimate of the wet-deposition loads. This increased contamination observed for the system blanks also was observed for many of the same constituents during the second phase of sampling; however, the median concentrations measured in the system blanks during the third sampling phase were larger than those measured in the system blanks during the second phase of sampling.

A comparison was made between the method reporting limit, acidified DIW funnel rinses, system blanks, and the wet-deposition samples collected at the Gary airport (fig. 17). Median concentrations were compared to evaluate the significance of contamination observed in field quality-control samples when compared to the wet-deposition samples. Contamination in the field quality-control samples was greater than 50 percent of the median concentration computed in the wet-deposition samples for fluoride (225 percent), silica (79 percent), aluminum (70 percent), iron (85 percent), and manganese (50 percent). Contamination in field quality-control samples was less than 50 percent of the median concentration computed in the wet-deposition samples for calcium (38 percent), magnesium (38 percent), potassium (33 percent), sulfate (8 percent), chloride (9 percent), and zinc (35 percent).

Summary

The USGS has completed the third phase of sampling wet deposition at the Gary (Indiana) Regional Airport to evaluate the quantity and quality of wet deposition in the Grand Calumet River Watershed. Wet-deposition samples were collected from June 30, 1992, to August 31, 1993 (phase 1); October 17, 1995, to November 12, 1996 (phase 2); and April 29, 1997, to April 28, 1998 (phase 3). Forty-eight samples were collected weekly during the first phase of sampling, 40 samples were collected during the second phase of sampling, and 42 samples were collected during the third phase of sampling that had sufficient volumes for at least some of the analyses.

The sampling site at the Gary airport was selected in cooperation with Indiana Department of Environmental Management before the start of the first sampling phase. The constituents selected for this study were chosen because they are by-products of industrial processes located in the Gary, Ind., area and because of their toxic potentials. Samples were submitted to the U.S. Geological Survey National Water Quality Laboratory for analysis. The standard AeroChem Metric 301 wet/dry collector installed at the sampling site was modified for the collection of wet-deposition samples for the analysis of trace metals. These modifications included using a polyethylene funnel connected to a 5-L Teflon collection bottle. Stringent cleaning and sample-processing methods were used to minimize contamination of the samples.

Selected major-ion concentrations measured in wet-deposition samples collected at the Gary airport were compared to two NADP/NTN sampling sites—at the Indiana Dunes National Lakeshore site, 26 km east of the airport, and at the Huntington Reservoir site, 180 km southeast of the airport. Wet-deposition samples collected at the Gary airport were significantly higher for pH than the pH measured in samples collected at either of the NADP/NTN sites. Significantly higher concentrations of calcium, magnesium, potassium, and sulfate also were measured at the Gary airport when compared to the NADP/NTN sites.

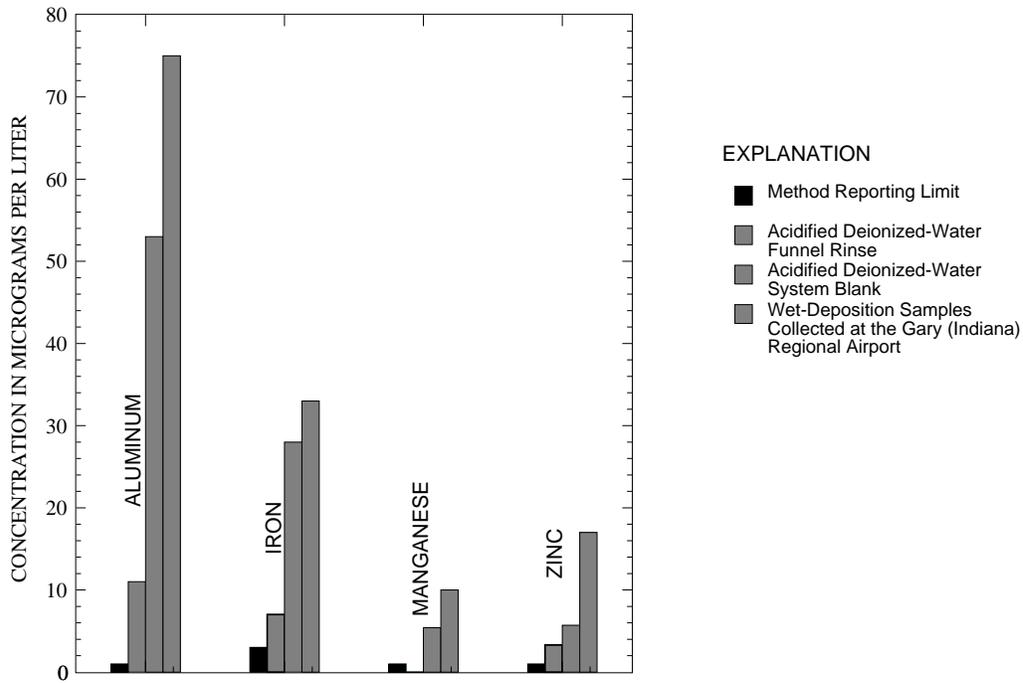
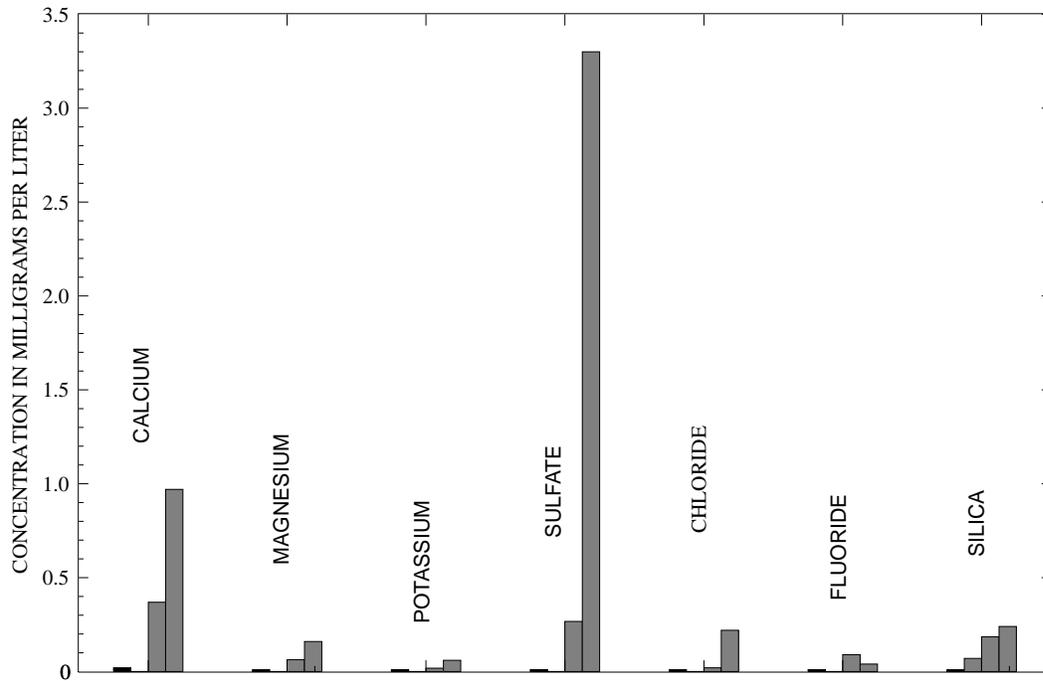


Figure 17. Median constituent concentrations computed for the acidified deionized-water funnel rinses, the acidified deionized-water system blanks, and the wet-deposition samples and the method reporting limit for constituents with median acidified deionized-water funnel rinses greater than the method reporting limit.

The constituent concentrations found in samples collected during the third phase of sampling were compared to constituent concentrations found in samples collected during the first and second sampling phases. Statistically significant increases (at the 5-percent level of significance) in pH were observed in samples collected during the third phase of sampling compared to the pH observed in the first phase of sampling. Statistically significant increases in sample concentrations were observed for potassium, silica, lead, and zinc when compared to sample concentrations collected during the first phase of sampling. None of the constituent concentrations evaluated, however, was significantly different from those collected during the second phase of sampling.

Estimated annual loadings were computed for the third phase of sampling and compared to loadings computed for the first and second sampling phases. The greatest estimated annual loadings were observed during the third sampling phase for chloride, silica, bromide, copper, and zinc when compared to the first two sampling phases. The only estimated annual loading for the third sampling phase that was smaller than the estimated annual loadings observed during the first two sampling phases was for sulfate. The estimated

annual loadings of calcium, magnesium, nitrate, potassium, barium, lead, iron, and manganese observed during the third sampling phase were greater than the estimated annual loadings observed during the first sampling phase but were less than the estimated annual loading observed during the second sampling phase.

Eleven acidified DIW samples—six acidified DIW funnel rinses and five acidified DIW system blanks—were submitted to the laboratory to evaluate possible contamination resulting from the equipment remaining in the collector for the 1-week sampling period. All of the median constituent concentrations determined for the system blanks were greater than the median constituent concentrations determined for the funnel rinses, indicating that contamination of wet-deposition samples collected at the Gary airport increased during the time that the equipment remained in the collector; this possibly resulted in an overestimate of the loads. This increased contamination observed for the system blanks also was observed for many of the same constituents during the second sampling phase; however, the median constituent concentrations determined in the system blanks for the third sampling phase were greater than those determined in the system blanks during the second phase of sampling.

References Cited

- Amdur, M.O.; Dull, John; and Klaassen, C.D., eds., 1993, Casarett and Doull's toxicology, the basic science of poisons (4th ed.): New York, McGraw-Hill, p. 623–680.
- Bigelow, D.S., 1984, Instruction manual—NADP/NTN site selection and installation: National Atmospheric Deposition Program, National Resources Ecology Laboratory, Colorado State University, Fort Collins, Colo., 23 p.
- Bidleman, T.F., 1988, Atmospheric processes: Environmental Science and Technology, v. 22, no. 4, p. 361–367.
- Conover, W.J., 1980, Practical nonparametric statistics, (2d ed.): New York, John Wiley and Sons, 493 p.
- Faires, L.M., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of metals in water by inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 92-634, 28 p.
- Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments (3d ed.): U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.
- Herdendorf, C.C., 1982, Large lakes of the world: Journal of Great Lakes Research, v. 8, no. 3, p. 379–412.
- Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources, studies in environmental science 49, Elsevier Science Publishing Co., Inc., New York, p. 118–124.
- Hoaglin, D.C.; Mosteller, F.; and Tukey, J.W., 1983, Understanding robust and exploratory data analysis, John Wiley & Sons, Inc., New York, p. 40.
- Indiana Nonpoint Source Task Force, 1989, Indiana Nonpoint Source Water Pollution Management Program, p. 68, 98.
- Majewski, M.S., and Capel, P.D., 1995, Pesticides in the atmosphere, distribution, trends, and governing factors: vol. 1, Pesticides in the hydrologic system, Ann Arbor Press, Inc., Chelsea, Mich., p. 3–4, 124–126.
- Schroder, L.J., and Hedley, A.G., 1986, Variation in precipitation quality during a 40-hour snowstorm in an urban environment—Denver, Colo., International Journal of Environmental Studies, 28 p.
- Schroder, L.J.; Willoughby, T.C.; See, R.B.; and Malo, B.A., 1989, The chemical composition of precipitation, dew and frost, and fog in Denver, Colo., in Atmospheric Deposition, Proceedings of the Baltimore Symposium: Baltimore, Md., May 1989, p. 83.
- Willoughby, T.C., 1995, Quality of wet deposition in the Grand Calumet River Watershed, northwestern Indiana, June 30, 1992–August 31, 1993, U.S. Geological Survey Water-Resources Investigations Report 95-4172, 55 p.
- 2000, Quality of wet deposition in the Grand Calumet River Watershed, northwestern Indiana, October 17, 1995–November 12, 1996: U.S. Geological Survey Water-Resources Investigations Report 99-4253, 47 p.

Supplemental Data

Table 5. Concentrations for wet-deposition samples collected at the Gary (Indiana) Regional Airport, April 1997–April 1998

[ICAP, sample analyzed by inductively coupled argon plasma atomic emission spectroscopy; FAAS, sample analyzed by flame atomic absorption spectroscopy; IC, sample analyzed by ion chromatography; ICAP/MS, sample analyzed by inductively coupled argon plasma-mass spectroscopy; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L , milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter; --, not analyzed; <, concentration reported less than the method reporting limit]

Date on	Time on (24-hour time)	Date off	Time off	Wet deposition (centimeters)	Specific conductance ($\mu\text{S}/\text{cm}$)	Field pH (standard units)	Calcium (ICAP) (mg/L)	Magnesium (ICAP) (mg/L)	Sodium (ICAP) (mg/L)	Potassium (FAAS) (mg/L)	Sulfate (IC) (mg/L)	Chloride (IC) (mg/L)	Fluoride (IC) (mg/L)	Bromide (IC) (mg/L)	Silica (ICAP) (mg/L)
04/29/97	1235	05/06/97	1205	0.344	--	6.42	1.94	0.32	0.2	0.15	--	--	--	--	0.28
05/06/97	1210	05/13/97	1200	.815	28.3	4.57	1.01	.20	<.2	.06	4.3	.18	<.10	<.01	.22
05/13/97	1215	05/20/97	1100	.852	38.2	6.74	3.85	.66	<.2	.14	5.1	.43	<.10	<.01	1.17
05/20/97	1115	05/27/97	1045	1.167	17.8	5.33	2.08	.14	<.2	.08	3.7	.12	.16	<.01	.38
05/27/97	1105	06/03/97	1100	.929	17.7	4.39	.78	.13	<.2	.04	3.9	<.1	<.10	<.01	.23
06/03/97	1105	06/10/97	1115	5.922	20.7	4.31	.11	.02	<.2	.03	1.5	<.01	<.10	<.01	.08
06/10/97	1115	06/17/97	1430	2.982	22.2	4.35	.78	.11	<.2	.07	2.8	.04	.02	<.01	.15
06/17/97	1430	06/24/97	1100	.574	26.5	6.80	2.15	.35	.3	.26	2.9	.32	.08	<.01	.57
06/24/97	1100	07/01/97	1030	3.196	15.0	4.53	.41	.06	<.2	.03	2.3	.03	<.10	<.01	.12
07/01/97	1030	07/08/97	1130	.408	--	6.91	5.06	1.31	<.2	.16	--	--	--	--	2.26
07/08/97	1130	07/15/97	1200	.299	--	6.53	2.87	.73	.3	.19	--	--	--	--	1.11
07/15/97	1200	07/22/97	1000	4.277	16.6	5.18	1.23	.19	<.2	.04	3.2	.07	<.10	<.01	.41
07/22/97	1000	07/29/97	1015	2.341	24.3	4.68	1.25	.16	<.2	.08	4.6	.10	.01	<.01	.36
07/29/97	1030	08/05/97	1015	.152	--	5.60	--	--	--	--	--	--	--	--	--
08/05/97	1015	08/12/97	0900	4.147	17.1	4.61	.43	.07	<.2	.02	2.6	.05	<.10	<.01	.22

Table 5. Concentrations for wet-deposition samples collected at the Gary (Indiana) Regional Airport—Continued

Date on	Time on (24-hour time)	Date off	Time off	Wet deposition (centimeters)	Specific conductance (μS/cm)	Field pH (standard units)	Calcium (ICAP) (mg/L)	Magnesium (ICAP) (mg/L)	Sodium (ICAP) (mg/L)	Potassium (FAAS) (mg/L)	Sulfate (IC) (mg/L)	Chloride (IC) (mg/L)	Fluoride (IC) (mg/L)	Bromide (IC) (mg/L)	Silica (ICAP) (mg/L)
08/12/97	0915	08/19/97	0800	6.360	14.4	4.67	0.46	0.07	<0.2	0.03	2.0	0.07	<0.10	<0.01	0.10
08/19/97	0800	08/26/97	0830	.502	--	5.70	--	--	--	.03	--	--	--	--	--
09/02/97	1030	09/09/97	1000	.405	--	6.30	1.81	.30	<.2	.05	--	--	--	--	.71
09/16/97	1000	09/23/97	0830	3.412	16.6	4.75	.75	.08	<.2	.05	6.8	.09	.05	<.01	.13
09/30/97	1030	10/07/97	1530	.400	--	6.60	3.12	.50	<.2	.18	--	--	--	--	1.13
10/07/97	1530	10/14/97	0815	.958	20.5	4.66	.80	.13	<.2	.06	1.7	.27	<.10	<.01	.18
10/28/97	0945	11/04/97	0930	.839	19.0	4.59	.41	.11	<.2	.04	3.7	<.10	<.10	<.01	.10
11/04/97	0945	11/11/97	1645	.297	--	--	2.56	.34	<.2	.06	--	--	--	--	.73
11/11/97	0940	11/18/97	0930	.419	--	6.05	4.14	.64	1.1	.17	--	--	--	--	2.87
11/25/97	1030	12/02/97	1000	1.647	25.4	4.63	.93	.15	<.2	.04	4.2	.28	.02	<.01	.21
12/02/97	1030	12/09/97	1100	.028	--	3.64	--	--	--	--	--	--	--	--	--
12/09/97	0830	12/16/97	1000	1.325	18.7	4.87	1.15	.16	<.2	.11	4.0	.42	.05	<.01	.67
12/16/97	1000	12/23/97	1230	.648	51.0	6.29	4.68	.61	.3	.13	11.1	1.02	.11	<.01	1.46
12/23/97	1230	12/30/97	1130	1.496	22.1	4.70	.91	.16	<.2	.04	4.1	.37	.06	<.01	.23
12/30/97	1130	01/06/98	1645	3.715	24.3	4.87	1.20	.14	.8	.06	3.7	1.41	.06	<.01	.24

Table 5. Concentrations for wet-deposition samples collected at the Gary (Indiana) Regional Airport—Continued

Date on	Time on (24-hour time)	Date off	Time off	Wet deposition (centimeters)	Specific conductance ($\mu\text{S}/\text{cm}$)	Field pH (standard units)	Calcium (ICAP) (mg/L)	Magnesium (ICAP) (mg/L)	Sodium (ICAP) (mg/L)	Potassium (FAAS) (mg/L)	Sulfate (IC) (mg/L)	Chloride (IC) (mg/L)	Fluoride (IC) (mg/L)	Bromide (IC) (mg/L)	Silica (ICAP) (mg/L)
01/06/98	1645	01/14/98	1200	4.650	20.4	4.65	0.83	0.09	0.4	0.03	2.6	0.74	0.04	<0.01	0.15
01/14/98	1200	01/20/98	1600	.440	--	4.84	.81	.11	1.0	.04	--	--	--	--	.21
01/20/98	1600	01/27/98	1000	.599	--	4.73	4.54	.58	1.8	.14	--	--	--	--	1.12
02/10/98	0925	02/17/98	1045	2.509	25.0	4.59	.75	.17	<.2	.04	3.1	.33	.05	<.01	.36
02/17/98	1045	02/24/98	1230	1.718	24.2	4.14	.61	.05	<.2	.02	2.3	.22	.07	<.01	.12
02/24/98	1245	03/03/98	0915	.154	--	6.53	--	--	--	--	--	--	--	--	--
03/03/98	0930	03/17/98	0915	3.977	22.5	5.81	2.17	.26	.4	.06	5.2	.90	.07	<.01	1.00
03/17/98	0915	03/24/98	1425	1.975	22.1	4.75	.60	.12	.3	.06	3.3	.70	.09	<.01	.17
03/24/98	1430	03/31/98	1030	1.324	20.1	6.36	1.72	.41	.4	.14	2.4	.64	.06	<.01	.89
03/31/98	1030	04/07/98	1330	1.579	11.7	4.85	.25	.04	<.2	.02	1.6	.10	.04	<.01	.04
04/07/98	1400	04/14/98	0930	2.492	24.5	4.54	.83	.12	<.2	.05	3.4	.25	.05	4.54	.16
04/14/98	0830	04/21/98	0930	1.713	19.1	4.69	.58	.13	<.2	.04	2.9	<.10	<.10	<.01	.12

Table 5. Concentrations for wet-deposition samples collected at the Gary (Indiana) Regional Airport—Continued

Date on	Date off	Nitrate (IC) (mg/L)	Phosphate (IC) (mg/L)	Aluminum (ICAP/MS) (µg/L)	Anti-mony (ICAP/MS) (µg/L)	Barium (ICAP/MS) (µg/L)	Beryllium (ICAP/MS) (µg/L)	Cadmium (ICAP/MS) (µg/L)	Chromium (ICAP/MS) (µg/L)	Cobalt (ICAP/MS) (µg/L)	Copper (ICAP/MS) (µg/L)	Iron (ICAP) (µg/L)	Lead (ICAP/MS) (µg/L)	Manganese (ICAP/MS) (mg/L)	Molybdenum (ICAP/MS) (µg/L)	Nickel (ICAP/MS) (µg/L)	Silver (ICAP/MS) (µg/L)	Uranium (natural) (ICAP/MS) (µg/L)	Zinc (ICAP/MS) (µg/L)
04/29/97	05/06/97	--	--	48	<1	6	<1	<1	<1	<1	5	20	2	4	<1	<1	<1	<1	30
05/06/97	05/13/97	--	--	65	<1	4	<1	<1	<1	<1	2	60	2	12	<1	<1	<1	<1	9
05/13/97	05/20/97	--	--	307	<1	9	<1	<1	<1	<1	8	93	7	37	<1	<1	<1	<1	72
05/20/97	05/27/97	1.97	<.03	508	<1	4	<1	<1	1	<1	21	134	12	18	<1	<1	<1	<1	20
05/27/97	06/03/97	.55	<.03	33	<1	2	<1	<1	<1	<1	2	11	<1	7	<1	<1	<1	<1	8
06/03/97	06/10/97	1.73	<.03	27	<1	<1	<1	<1	<1	<1	<1	19	1	2	<1	<1	<1	<1	6
06/10/97	06/17/97	2.29	<.03	75	<1	2	<1	<1	<1	<1	1	24	3	7	<1	<1	<1	<1	12
06/17/97	06/24/97	2.41	.14	7	<1	2	<1	<1	<1	<1	3	<3	<1	1	<1	<1	<1	<1	8
06/24/97	07/01/97	1.28	<.03	56	<1	2	<1	<1	<1	<1	<1	18	2	6	<1	<1	<1	<1	8
07/01/97	07/08/97	--	--	342	<1	11	<1	<1	<1	<1	3	64	6	37	<1	<1	<1	<1	17
07/08/97	07/15/97	--	--	201	<1	10	<1	<1	<1	<1	19	69	7	36	<1	<1	<1	<1	25
07/15/97	07/22/97	2.37	<.03	221	<1	5	<1	<1	<1	<1	3	143	7	12	<1	<1	<1	<1	14
07/22/97	07/29/97	3.31	<.03	225	<1	4	<1	<1	<1	<1	3	163	7	20	<1	<1	<1	<1	17
07/29/97	08/05/97	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
08/05/97	08/12/97	1.54	<.03	58	<1	2	<1	<1	<1	<1	3	23	2	5	<1	<1	<1	<1	3

Concentrations 47

Table 5. Concentrations for wet-deposition samples collected at the Gary (Indiana) Regional Airport—Continued

Date on	Date off	Nitrate (IC) (mg/L)	Phosphate (IC) (mg/L)	Aluminum (ICAP/MS) (µg/L)	Antimony (ICAP/MS) (µg/L)	Barium (ICAP/MS) (µg/L)	Beryllium (ICAP/MS) (µg/L)	Cadmium (ICAP/MS) (µg/L)	Chromium (ICAP/MS) (µg/L)	Cobalt (ICAP/MS) (µg/L)	Copper (ICAP/MS) (µg/L)	Iron (ICAP) (µg/L)	Lead (ICAP/MS) (µg/L)	Manganese (ICAP/MS) (mg/L)	Molybdenum (ICAP/MS) (µg/L)	Nickel (ICAP/MS) (µg/L)	Silver (ICAP/MS) (µg/L)	Uranium (natural) (ICAP/MS) (µg/L)	Zinc (ICAP/MS) (µg/L)
08/12/97	08/19/97	1.51	<0.03	75	<1	3	<1	<1	<1	<1	1	20	3	5	<1	<1	<1	<1	9
08/19/97	08/26/97	--	--	38	<1	2	<1	<1	<1	<1	1	--	<1	7	<1	<1	<1	<1	8
09/02/97	09/09/97	--	--	128	<1	2	<1	<1	1	<1	<1	140	2	34	<1	<1	<1	<1	13
09/16/97	09/23/97	1.64	<.03	49	<1	3	<1	<1	<1	<1	1	44	3	9	<1	<1	<1	<1	12
09/30/97	10/07/97	--	--	260	<1	16	<1	<1	<1	<1	3	139	4	53	<1	<1	<1	<1	17
10/07/97	10/14/97	2.58	<.03	71	<1	2	<1	<1	<1	<1	1	29	1	8	<1	<1	<1	<1	64
10/28/97	11/04/97	2.48	1.88	38	<1	2	<1	<1	<1	<1	2	20	2	6	<1	<1	<1	<1	11
11/04/97	11/11/97	--	--	95	<1	2	<1	<1	2	<1	<1	249	2	59	<1	<1	<1	<1	21
11/11/97	11/18/97	--	--	312	<1	6	<1	<1	<1	<1	3	41	2	88	<1	<1	<1	<1	78
11/25/97	12/02/97	2.60	<.03	66	<1	2	<1	<1	<1	<1	2	35	2	10	<1	<1	<1	<1	21
12/02/97	12/09/97	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
12/09/97	12/16/97	1.18	<.03	55	<1	2	<1	<1	<1	<1	<1	9	1	31	<1	<1	<1	<1	11
12/16/97	12/23/97	--	.05	267	<1	5	<1	<1	3	<1	3	341	9	99	<1	1	<1	<1	62
12/23/97	12/30/97	1.99	<.03	48	<1	2	<1	<1	<1	<1	2	24	2	13	<1	<1	<1	<1	23
12/30/97	01/06/98	1.72	<.03	98	<1	8	<1	<1	<1	<1	2	31	2	8	<1	<1	<1	<1	20

Table 5. Concentrations for wet-deposition samples collected at the Gary (Indiana) Regional Airport—Continued

Date on	Date off	Nitrate (IC) (mg/L)	Phosphate (IC) (mg/L)	Aluminum (ICAP/MS) (µg/L)	Antimony (ICAP/MS) (µg/L)	Barium (ICAP/MS) (µg/L)	Beryllium (ICAP/MS) (µg/L)	Cadmium (ICAP/MS) (µg/L)	Chromium (ICAP/MS) (µg/L)	Cobalt (ICAP/MS) (µg/L)	Copper (ICAP/MS) (µg/L)	Iron (ICAP) (µg/L)	Lead (ICAP/MS) (µg/L)	Manganese (ICAP/MS) (mg/L)	Molybdenum (ICAP/MS) (µg/L)	Nickel (ICAP/MS) (µg/L)	Silver (ICAP/MS) (µg/L)	Uranium (natural) (ICAP/MS) (µg/L)	Zinc (ICAP/MS) (µg/L)
01/06/98	01/14/98	2.24	<0.03	148	<1	2	<1	<1	<1	<1	3	26	2	8	<1	<1	<1	<1	24
01/14/98	01/20/98	--	--	10	<1	2	<1	<1	<1	<1	<1	12	<1	9	<1	<1	<1	<1	26
01/20/98	01/27/98	--	--	136	<1	7	<1	<1	<1	<1	5	58	3	62	<1	1	<1	<1	48
02/10/98	02/17/98	2.80	<.03	97	<1	2	<1	<1	<1	<1	2	88	3	20	<1	<1	<1	<1	21
02/17/98	02/24/98	2.97	<.03	22	<1	2	<1	<1	<1	<1	1	13	<1	5	<1	<1	<1	<1	20
02/24/98	03/03/98	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
03/03/98	03/17/98	1.95	<.03	219	<1	3	<1	<1	<1	<1	1	29	3	22	<1	<1	<1	<1	52
03/17/98	03/24/98	2.19	<.03	177	<1	3	<1	<1	<1	<1	3	86	3	13	<1	2	<1	<1	40
03/24/98	03/31/98	2.26	<.03	204	<1	9	<1	<1	<1	<1	3	111	2	23	<1	<1	<1	<1	53
03/31/98	04/07/98	1.07	<.03	28	<1	3	<1	<1	<1	<1	1	12	1	3	<1	<1	<1	<1	7
04/07/98	04/14/98	<.04	<.03	76	<1	3	<1	<1	<1	<1	2	31	2	8	<1	<1	<1	<1	9
04/14/98	04/21/98	--	--	72	<2	2	<2	<2	<2	<2	<2	44	3	10	<2	<2	<2	<2	13

Table 6. Concentrations for laboratory quality-control samples

[ICAP, sample analyzed by inductively coupled argon plasma atomic emission spectroscopy; FAAS, sample analyzed by flame atomic absorption spectroscopy; IC, sample analyzed by ion chromatography; ICAP/MS, sample analyzed by inductively coupled argon plasma-mass spectroscopy; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L , milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter; SRWS, standard reference water samples; --, not analyzed; <, concentration reported less than the method reporting limit]

Date	Sample type	Specific conduc- tance ($\mu\text{S}/\text{cm}$)	pH (stan- dard units)	Calcium (ICAP) (mg/L)	Magnes- ium (ICAP) (mg/L)	Sodium (ICAP) (mg/L)	Potassium (FAAS) (mg/L)	Sulfate (IC) (mg/L)	Chloride (IC) (mg/L)	Fluoride (IC) (mg/L)	Bromide (IC) (mg/L)	Silica (ICAP) (mg/L)	Nitrate (IC) (mg/L)	Phosphate (IC) (mg/L)
10/01/97	Blank	1.4	5.53	<0.02	<0.01	<0.2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.04	<0.03
10/01/97	Blank	1.5	5.53	<.02	<.01	<.2	<.01	<.01	<.01	<.01	<.01	<.02	<.04	<.03
10/01/97	SRWS (T117)	--	--	21.51	9.63	20.5	2.22	--	--	--	--	11.85	--	--
10/01/97	SRWS (P17)	7.7	5.24	--	--	--	--	.52	.38	<.01	<.01	--	1.16	<.03
10/01/97	SRWS (T117)	--	--	21.27	9.59	20.2	2.13	--	--	--	--	11.77	--	--
10/01/97	SRWS (P17)	7.5	5.24	--	--	--	--	.53	.38	<.01	<.01	--	1.17	--
05/06/97	Blank	.9	5.66	<.02	<.01	<.2	<.01	<.10	<.10	<.10	<.01	<.02	--	--
05/06/97	Blank	.9	5.66	<.02	<.01	<.2	<.01	<.01	<.01	<.03	<.01	<.02	<.04	<.03
05/06/97	SRWS (T117)	--	--	21.03	9.67	20.4	2.19	--	--	--	--	11.28	--	--
05/06/97	SRWS (P17)	6.9	5.35	--	--	--	--	.42	.34	<.01	--	--	--	--
05/06/97	SRWS (T117)	--	--	21.15	9.93	20.2	2.13	--	--	--	--	11.46	--	--
05/06/97	SRWS (P17)	7.2	5.35	--	--	--	--	.49	.37	.04	<.01	--	1.19	<.03

Table 6. Concentrations for laboratory quality-control samples—Continued

Date	Sample type	Aluminum (ICAP/ MS) (µg/L)	Antimony (ICAP/ MS) (µg/L)	Barium (ICAP/ MS) (µg/L)	Beryllium (ICAP/ MS) (µg/L)	Cadmium (ICAP/ MS) (µg/L)	Chromium (ICAP/ MS) (µg/L)	Cobalt (ICAP/ MS) (µg/L)	Copper (ICAP/ MS) (µg/L)	Iron (ICAP) (µg/L)	Lead (ICAP/ MS) (µg/L)	Manga- nese (ICAP/ MS) (µg/L)	Molyb- denum (ICAP/ MS) (µg/L)
10/01/97	Blank	<1	<1	<1	<1	<1	<1	<1	<1	<3	<1	<1	<1
10/01/97	Blank	1	<1	<1	<1	<1	<1	<1	<1	3	<1	<1	<1
10/01/97	SRWS (T117)	77	6	100	5	2	10	4	6	469	5	209	11
10/01/97	SRWS (P17)	--	--	--	--	--	--	--	--	--	--	--	--
10/01/97	SRWS (T117)	74	6	100	5	2	10	4	6	468	5	209	11
10/01/97	SRWS (P17)	--	--	--	--	--	--	--	--	--	--	--	--
05/06/97	Blank	<1	<1	<1	<1	<1	<1	<1	<1	<3	<1	<1	<1
05/06/97	Blank	3	<1	<1	<1	<1	<1	<1	<1	<3	<1	<1	<1
05/06/97	SRWS (T117)	71	6	96	5	2	10	4	6	456	5	214	11
05/06/97	SRWS (P17)	--	--	--	--	--	--	--	--	--	--	--	--
05/06/97	SRWS (T117)	70	6	96	5	2	10	4	6	466	5	214	11
05/06/97	SRWS (P17)	--	--	--	--	--	--	--	--	--	--	--	--

Table 6. Concentrations for laboratory quality-control samples—Continued

Date	Sample type	Nickel (ICAP/ MS) (µg/L)	Silver (ICAP/ MS) (µg/L)	Uranium (natural) (ICAP/ MS) (µg/L)	Zinc (ICAP/ MS) (µg/L)
10/01/97	Blank	<1	<1	<1	<1
10/01/97	Blank	<1	<1	<1	<1
10/01/97	SRWS (T117)	9	<1	2	173
10/01/97	SRWS (P17)	--	--	--	--
10/01/97	SRWS (T117)	9	<1	2	174
10/01/97	SRWS (P17)	--	--	--	--
05/06/97	Blank	<1	<1	<1	<1
05/06/97	Blank	<1	<1	<1	<1
05/06/97	SRWS (T117)	9	<1	2	176
05/06/97	SRWS (P17)	--	--	--	--
05/06/97	SRWS (T117)	9	<1	2	175
05/06/97	SRWS (P17)	--	--	--	--

Table 7. Concentrations for field quality-control samples processed at the Gary (Indiana) Regional Airport

[ICAP, sample analyzed by inductively coupled argon plasma atomic emission spectroscopy; FAAS, sample analyzed by flame atomic absorption spectroscopy; IC, sample analyzed by ion chromatography; ICAP/MS, sample analyzed by inductively coupled argon plasma-mass spectroscopy; $\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; $\mu\text{g/L}$, micrograms per liter; DIW, deionized water; < , concentration reported less than the method reporting limit]

Date on	Time on (24-hour time)	Date off	Time off	Sample type	Sample matrix	Specific conductance ($\mu\text{S/cm}$)	pH (standard units)	Calcium (ICAP) (mg/L)	Magnesium (ICAP) (mg/L)	Sodium (ICAP) (mg/L)	Potassium (FAAS) (mg/L)	Sulfate (IC) (mg/L)	Chloride (IC) (mg/L)
05/27/97	1101	05/27/97	1101	Funnel Rinse	Acidified DIW	13.2	4.46	0.03	<0.01	<0.2	0.02	<0.01	0.02
06/03/97	1116	06/10/97	1116	Split	Natural	20.8	4.31	.11	.02	<.2	.03	1.55	<.01
07/01/97	1032	07/01/97	1032	Funnel Rinse	Acidified DIW	8.1	4.48	<.02	<.01	<.2	.02	<.01	<.01
07/29/97	1016	07/29/97	1016	Funnel Rinse	Acidified DIW	16.4	4.344	<.02	<.01	<.2	<.01	<.01	<.01
08/05/97	0901	08/12/97	0901	Split	Natural	17.1	4.61	.46	.08	<.2	.04	2.65	.05
08/26/97	1030	09/02/97	1030	System Blank	Acidified DIW	17.6	4.43	.22	.04	<.2	.03	.75	.05
09/09/97	1000	09/16/97	1000	System Blank	Acidified DIW	13.6	4.41	.52	.06	<.2	.02	.55	<.01
09/16/97	0831	09/23/97	0831	Split	Natural	16.8	4.75	.75	.08	<.2	.05	2.77	.09
09/30/97	1101	09/30/97	1101	Funnel Rinse	Acidified DIW	44.0	4.02	.13	<.01	<.2	<.01	<.01	<.01
09/23/97	1030	09/30/97	1030	System Blank	Acidified DIW	7.3	5.63	1.11	.35	<.2	.04	.27	.02
10/14/97	0745	10/21/97	0745	System Blank	Acidified DIW	11.4	4.61	.15	.04	<.2	<.01	.14	.02
11/18/97	1030	11/25/97	1030	System Blank	Acidified DIW	9.1	4.85	.37	.10	<.2	<.01	.12	.16
02/03/98	0931	02/03/98	0931	Funnel Rinse	Acidified DIW	22.1	4.35	.14	.01	<.2	<.01	<.01	<.01
04/07/98	0931	04/14/98	0931	Split	Natural	24.7	4.54	.83	.12	<.2	.05	3.43	.26
04/21/98	0940	04/21/98	0940	Funnel Rinse	Acidified DIW	13.6	4.42	<.02	.01	<.2	<.01	<.01	<.01

Table 7. Concentrations for field quality-control samples processed at the Gary (Indiana) Regional Airport—Continued

Date	Sample type	Sample matrix	Fluoride (IC) (mg/L)	Bromide (IC) (mg/L)	Silica (ICAP) (mg/L)	Nitrate (IC) (mg/L)	Phosphate (IC) (mg/L)	Aluminum (ICAP/MS) (μg/L)	Antimony (ICAP/MS) (μg/L)	Barium (ICAP/MS) (μg/L)	Beryllium (ICAP/MS) (μg/L)	Cadmium (ICAP/MS) (μg/L)	Chromium (ICAP/MS) (μg/L)
05/27/97	Funnel Rinse	Acidified DIW	<0.01	<0.01	0.09	2.14	<0.03	5	<1	<1	<1	<1	<1
06/03/97	Split	Natural	<.01	<.01	.07	1.72	<.03	25	<1	1	<1	<1	<1
07/01/97	Funnel Rinse	Acidified DIW	<.01	<.01	.09	2.25	<.03	13	<1	<1	<1	<1	<1
07/29/97	Funnel Rinse	Acidified DIW	<.01	<.01	.07	2.04	<.03	20	<1	<1	<1	<1	<1
08/05/97	Split	Natural	<.01	<.01	.23	1.29	<.03	54	<1	2	<1	<1	<1
08/26/97	System Blank	Acidified DIW	.11	<.01	.12	2.76	<.03	28	<1	<1	<1	<1	<1
09/09/97	System Blank	Acidified DIW	.12	<.01	.37	2.55	<.03	53	<1	<1	<1	<1	<1
09/16/97	Split	Natural	.05	<.01	.11	1.68	<.03	49	<1	3	<1	<1	<1
09/30/97	Funnel Rinse	Acidified DIW	.10	<.01	.04	7.44	<.03	10	<1	<1	<1	<1	<1
09/23/97	System Blank	Acidified DIW	.09	<.01	.55	2.43	<.03	127	<1	2	<1	<1	<1
10/14/97	System Blank	Acidified DIW	<.01	<.01	.08	2.10	<.03	21	<1	<1	<1	<1	<1
11/18/97	System Blank	Acidified DIW	<.01	<.01	.19	2.16	<.03	65	<1	2	<1	<1	<1
02/03/98	Funnel Rinse	Acidified DIW	<.01	<.01	.04	3.67	<.03	7	<1	<1	<1	<1	<1
04/07/98	Split	Natural	.05	<.01	.17	3.15	<.03	73	<1	3	<1	<1	<1
04/21/98	Funnel Rinse	Acidified DIW	.03	<.01	.07	<.04	<.03	28	<1	<1	<1	<1	1

Table 7. Concentrations for field quality-control samples processed at the Gary (Indiana) Regional Airport—Continued

Date	Sample type	Sample matrix	Cobalt (ICAP/ MS) (µg/L)	Copper (ICAP/ MS) (µg/L)	Iron (ICAP) (µg/L)	Lead (ICAP/ MS) (µg/L)	Manga- nese (ICAP/ MS) (µg/L)	Molyb- denum (ICAP/ MS) (µg/L)	Nickel (ICAP/ MS) (µg/L)	Silver (ICAP/ MS) (µg/L)	Uranium (natural) (ICAP/ MS) (µg/L)	Zinc (ICAP/ MS) (µg/L)
05/27/97	Funnel Rinse	Acidified DIW	<1	<1	6	<1	<1	<1	<1	<1	<1	3
06/03/97	Split	Natural	<1	<1	19	2	2	<1	<1	<1	<1	6
07/01/97	Funnel Rinse	Acidified DIW	<1	<1	<3	<1	<1	<1	<1	<1	<1	3
07/29/97	Funnel Rinse	Acidified DIW	<1	<1	13	<1	<1	<1	<1	<1	<1	1
08/05/97	Split	Natural	<1	2	21	2	5	<1	<1	<1	<1	3
08/26/97	System Blank	Acidified DIW	<1	<1	18	<1	3	<1	<1	<1	<1	6
09/09/97	System Blank	Acidified DIW	<1	<1	28	<1	7	<1	<1	<1	<1	2
09/16/97	Split	Natural	<1	1	42	3	9	<1	<1	<1	<1	11
09/30/97	Funnel Rinse	Acidified DIW	<1	<1	7	<1	<1	<1	<1	<1	<1	16
09/23/97	System Blank	Acidified DIW	<1	1	39	5	13	<1	<1	<1	<1	6
10/14/97	System Blank	Acidified DIW	<1	<1	9	<1	2	<1	<1	<1	<1	<1
11/18/97	System Blank	Acidified DIW	<1	<1	30	1	5	<1	<1	<1	<1	6
02/03/98	Funnel Rinse	Acidified DIW	<1	<1	6	<1	1	<1	<1	<1	<1	18
04/07/98	Split	Natural	<1	2	28	2	8	<1	<1	<1	<1	8
04/21/98	Funnel Rinse	Acidified DIW	<1	<1	19	<1	<1	<1	<1	<1	<1	3