

# **PRECIPITATION-QUALITY MONITORING IN SOUTHERN MISSISSIPPI, 1982-87**

**By Gene A. Bednar and Paul E. Grantham**

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# **PRECIPITATION-QUALITY MONITORING IN SOUTHERN MISSISSIPPI, 1982-87**

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## **ABSTRACT**

In 1982, the U.S. Geological Survey, in cooperation with the Bureau of Pollution Control of the Mississippi Department of Natural Resources, began a program to monitor selected inorganic chemical constituents and physical properties of atmospheric precipitation in southern Mississippi. The monitoring program was implemented primarily because of concerns about the potential for acidification of the environment by atmospheric contaminants from sources of emissions within the State and surrounding areas. The three monitoring stations, combined with four monitoring stations operated as part of other programs, provide the framework for a long-term statewide monitoring network that will provide the data necessary for environmental assessments within the State.

The report describes monitoring stations and procedures used to monitor the chemistry of precipitation at the three stations in the southern part of the State. Analytical methods and quality assurance of on-site and laboratory measurements are discussed. A summary of analytical data for the period of record, 1982-87, is presented.

## INTRODUCTION

In 1982, the U.S. Geological Survey (USGS), in cooperation with the Mississippi Bureau of Pollution Control (MBPC), began a program to monitor the quality of precipitation in southern Mississippi. Utilities companies, private citizens, and State and Federal government officials have expressed considerable interest in the program, particularly as it relates to potential chemical degradation by acidification of the environment from emissions within the State and emissions that are transported into the State from nearby areas.

Methods for the collection and analysis of samples from the three cooperative-program monitoring stations are comparable to those at four other stations operated in the central and northern parts of the State by the National Atmospheric Deposition Program and National Trends Network (NADP/NTN), and the U.S. Environmental Protection Agency (EPA). The network of seven stations (fig. 1) provides the framework for long-term, statewide monitoring and provides the data necessary for statewide or regional assessments of chemical-quality trends and possible effects on the environment.

### Purpose and Scope

The primary objective of the cooperative monitoring program for southern Mississippi is to systematically collect long-term data required to assess the effect that selected inorganic chemical constituents and physical properties of atmospheric precipitation may have on the environment. The purposes of the program are: (1) To monitor and analyze atmospheric precipitation at two stations (three stations after 1985), (2) to document these data, and (3) to evaluate water-quality trends in streams and lakes in the State after several years of monitoring. Data from stations in the NADP/NTN (stations 4, 5, and 6, fig. 1) and EPA network (station 7, fig. 1) may be used to broaden the scope of the program to include statewide assessments of long-term trends and effects

of atmospheric deposition on the ecology. Data obtained from the statewide monitoring network also will be valuable for site-specific and regional investigations to evaluate the need and effectiveness of proposed Federal regulations that may be promulgated to minimize acid deposition.

The purpose of this report is to document the methods used to monitor the precipitation at the three monitoring stations located in southern Mississippi and to present a summary of analytical data obtained during the period of monitoring from 1982 through 1987. A description and history of the stations are discussed. Instructions that describe routine station operating procedures to the station operators are included in an appendix.

The summary of chemical analyses in the analytical data section of the report are from USGS files. These data and other information that pertain to atmospheric precipitation-quality monitoring in Mississippi are available at the USGS District Office in Jackson, Mississippi.

### Location

The location of the three cooperative-program monitoring stations in the southern part of the State are shown in figure 1. The monitoring station in Perry County is located at the U.S. Forest Service Erambert Seed Orchard on Highway 29, 3.4 miles east of Janice. The monitoring station in Hancock County is located at the USGS Hydrologic Instrumentation Facility, John C. Stennis Space Center [formerly the National Space Technology Laboratories (NSTL)] near Bay St. Louis. The monitoring station in Wilkinson County is located near Rosetta, on an oil-field service road, 0.1 mile southeast of U.S. Forest Service Road 193 in the Homochitto National Forest.

### History

The acidification detected during the 1960's of ecosystems in Europe, Canada, and the northeastern United States has been linked to increased nitrogen and sulfur oxide concentrations in the atmosphere. Legislative actions since the 1970's have been proposed to significantly decrease

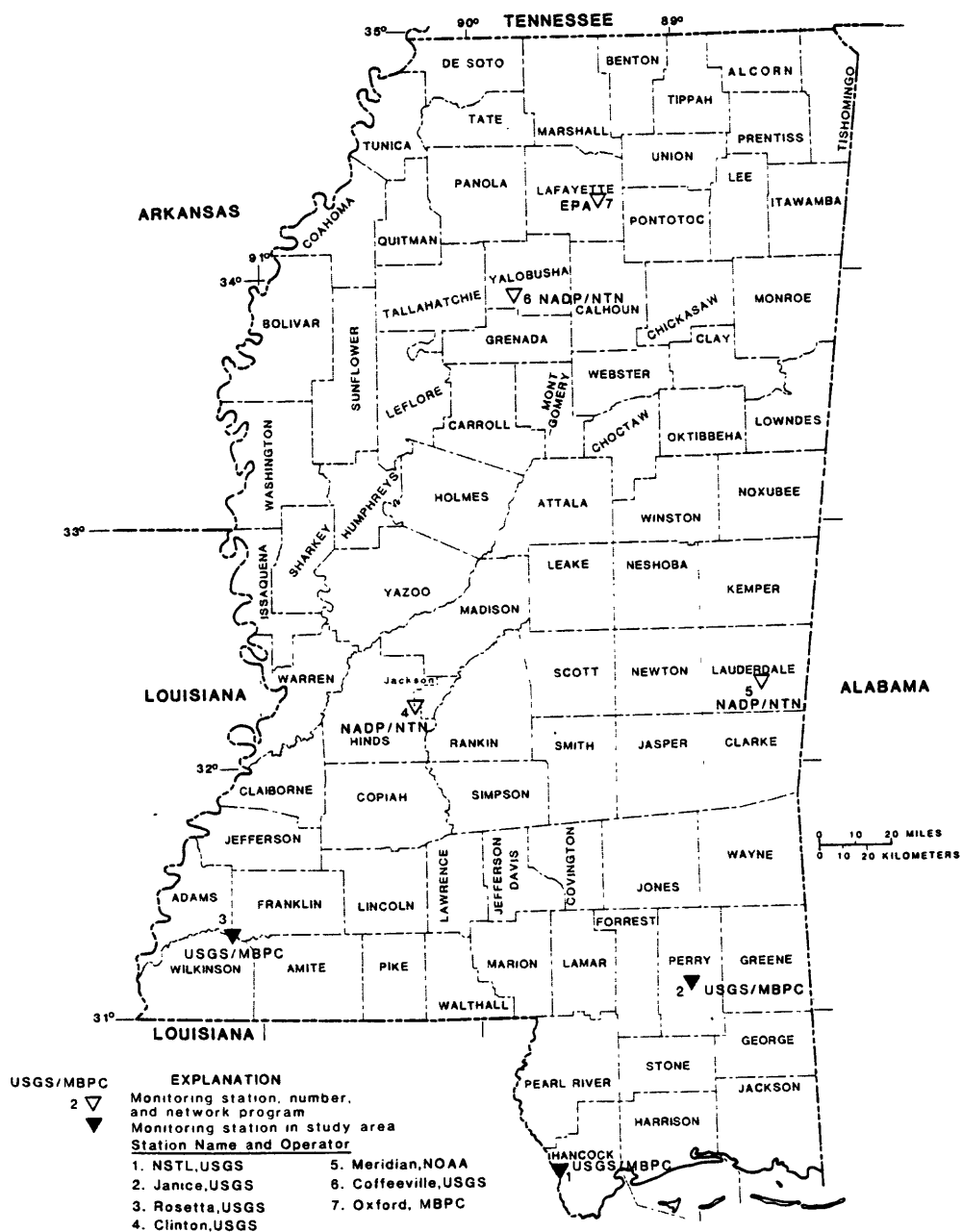


Figure 1.--General location of precipitation-quality stations in Mississippi.

emissions from sources such as automobiles and fossil-fuel burning plants. Current data suggest that the problem is not confined to large industrial or metropolitan areas, but is more widespread because of the mobility of the airborne contaminants in the atmosphere. The chemistry of precipitation has gained more interest in Mississippi with the realization that more information is needed to determine the effects that contaminants in precipitation may have on terrestrial and aquatic ecosystems in the State.

Monitoring stations were established at Janice in February 1982, at NSTL in October 1982, and at Rosetta in February 1986, and are operated by on-site observers. Precipitation samples obtained at the three monitoring stations were analyzed by three USGS laboratories beginning in February 1982 at the USGS National Water-Quality Laboratory (NWQL) in Doraville, Georgia. When the Doraville, Georgia, NWQL was closed in 1985, samples were analyzed by the Denver, Colorado, NWQL from October 1985 to May 1987. Samples presently (1988) are shipped to the USGS atmospheric-precipitation laboratory in Doraville, Georgia, for chemical analysis.

#### STATION DESCRIPTION

The cooperative-program monitoring stations are located in remote areas and the rainfall data obtained are believed to represent typical meteorological and atmospheric processes that influence the chemistry of precipitation in this region of the State. Airborne emissions may be transported considerable distances from their source before particulate matter, dissolved gases, or droplets of rain are deposited on land surfaces. Although the number of sources of emissions within a given radius of a monitoring station may not accurately reflect the type and amount of deposition, this information may be used to determine if monitoring stations are installed too near possible sources of local contamination. According to Eaton and Moore (1988), there are no sources of significant emissions of nitrogen and sulfur oxides within a 6-mile radius of any of the

three monitoring stations. Within a 30-mile radius, the NSTL station has the largest number of emission sources (11) and the Rosetta station the fewest (4); however, the total annual emission loads at the Janice station are slightly larger than that at the NSTL station. The annual emission loads at the Rosetta station are significantly less (about 90 percent less) than the emission loads at either the Janice or NSTL stations.

The guidelines used to establish, equip, and operate the monitoring stations are described by Bigelow (1984), and Bigelow and Dossett(1988). The same guidelines are used at the four NADP/NTN and EPA atmospheric precipitation monitoring stations located in the central and northern parts of the State.

#### Equipment

An automatic wet-dry precipitation collector and a standard 8-inch recording rain gage to measure the quantity of precipitation are operated continuously during each sampling period. To avoid collection of dry deposition in the wet sample reservoir, the collector is designed to remain closed during dry periods and automatically opens during periods of heavy dew, rain, or snow. The recording rain gage is equipped with an event recorder to document the opening and closing of the collector lid and to verify that the lid functioned properly during all events. The length of sampling time and number of events that occurred during the sampling period also are recorded on the rain-gage chart.

The meters used to measure the physical properties (pH and specific conductance) of precipitation are temperature compensated and equipped with digital displays; thus, manual adjustments are not required for on-site measurements and results of measurements are easily read. The pH electrode and specific conductance cells for the meters are designed specifically for measurements of low-ionic-strength waters.

## Data Collection

Emission products that are deposited in southern Mississippi usually are in the form of rain (wet fall) and particulate matter (dry fall); however, only wet fall (rain, snow or heavy dew) samples are collected. Particulate matter in the dry form is not collected or quantified because reliable methods have not been developed. Samples obtained at the monitoring stations are 7-day accumulations of atmospheric precipitation collected on Tuesday morning by the observer. To ensure that the quantity of water in composite samples is in correct proportion to the measured amount in the rain gage, a "percent collection efficiency" is calculated for each 1-week sampling period by comparing inches of precipitation in the rain gage with that collected by the automatic sampler.

## QUALITY ASSURANCE

Goals to obtain reliable data are approximately those stated by the NADP Quality Assurance Steering Committee (1984). These are: (1) 100-percent sample collection, (2) between 90 and 110-percent collection efficiency of automatic collector, (3) rain-gage accuracy of 0.05 inch or less, and (4) sample-weight accuracy of 1 gram. The goals for field measurement proficiency of pH and specific conductance meters are less stringent than manufacturers' specifications for ideal operating conditions and the values reported for on-site measurements conform to practical operator precision. These are: (1) pH measurements to nearest 0.05 pH unit, and (2) specific conductance measurements to the nearest 1.0  $\mu\text{S}/\text{cm}$  (microsiemens per centimeter at 25 °C).

Operators of the monitors use "Instructions to Station Observers" (Appendix A) for all data-collection activities. These instructions are virtually the same as those given by Bigelow and Dossett (1988). Equipment, supplies, standard reference samples and on-site assistance and training are provided by USGS personnel as needed. Standard reference samples (SRS) are used routinely

to check the calibration and operating condition of pH and specific conductance meters including the performance of pH electrodes and specific conductance cells. The USGS project chief conducts regular inspections of each station to evaluate observer operating procedures and to check calibration and performance of instruments. Field-notes forms and rain-gage charts are mailed weekly by observers to the USGS office for review. The original record is corrected and updated before results of laboratory analyses are given final approval for entry into the USGS permanent data storage system.

Various aspects of on-site, office, and USGS atmospheric-precipitation laboratory quality assurance are discussed in detail by Eaton and Moore (1988). Tables 1 and 2 list analytical-precision data and methods used by the USGS atmospheric-precipitation laboratory and USGS NWQL. Quality-assurance practices and statistical techniques used in the USGS NWQL are discussed by Freidman and Erdmann (1982).

Ion chromatography, 4-channel autoanalyzer, and atomic absorption methods include operating procedures for calibrating, timing, and SRS protocol. The methods also include procedures for online calibration, operating precautions, and conditions that require instrument recalibration. SRS data are used to prepare computer-generated quality-control (QC) charts. In the NWQL, new QC charts are constructed each month to determine if a bias in the data has developed. On a daily basis, SRS values must fit within 1.5 standard deviations of the mean or samples are reanalyzed. The atmospheric-precipitation laboratory performs comparatively few analyses and requires less sophisticated QC charts than the NWQL; however, more comprehensive quality-assurance checks of completed analyses are applied before analytical data are released from the atmospheric-precipitation laboratory.

Methods for ion chromatography requires that a blank and SRS be placed at the beginning and the end of each line of samples and after at least 6 samples in the line. The atmospheric-precipitation

laboratory requires two SRS after every 10 samples and a complete set of calibration standards at the end of each run to check instrument performance. The 4-channel autoanalyzer method of analysis requires that an SRS followed by a blank be analyzed after every eight samples. The atomic absorption method of analysis requires that one or more SRS's be analyzed after every 10 samples.

## ANALYTICAL DATA

USGS analytical methods for the analysis of precipitation of low-ionic concentration are the same or are equivalent to NADP/NTN analytical methods for on-site and laboratory analyses. When precipitation amounts exceed about 0.05 inch, on-site specific conductance and pH measurements are performed by observers during the time that samples are removed from the collector and processed for shipment to the laboratory. Information pertinent to the collection of each sample is recorded on "Field-Notes Forms" and retained by the USGS in permanent record files with rain-gage charts.

There are a few rainfall periods in which samples either were not analyzed by the laboratory or the analyses were rejected because on-site contamination was suspected. Some constituents are deleted from laboratory analyses when sample volumes are insufficient for a regular scheme of analyses. When sample volumes are small, priority is given to sulfate, nitrate, and the other anions determined by ion chromatography. Methods and types of analyses performed by the USGS atmospheric-precipitation laboratory and NWQL are given in tables 1 and 2.

A summary of selected analytical data for the years of monitoring station operation are given in tables 3, 4, and 5. The exact beginning and ending dates may overlap years. The rainfall amounts are the summation of measured 7-day accumulations in the rain gage for each year of operation and for the period of record. There are occasions when composite periods are less than 7-days in duration. Usually, this results during a 7-day period when it is

anticipated that rainfall amounts may exceed the capacity of the collector's sample container and the container is replaced. The observations for field measurements and constituent concentrations are the number of measurements or chemical analyses during the indicated period.

The total deposition load of a constituent is the product of the precipitation-weighted average concentration and total measured rainfall converted to pounds per acre for the indicated period. It is assumed that the average concentration represents that for rainfall periods when chemical analyses are missing. The product of the total rainfall and the precipitation-weighted average constituent concentration may not equal the sum of the products of annual rainfall and annual precipitation-weighted average concentration; therefore, the total load for the period of record may not equal the sum of the annual loads for each constituent.

Results of analyses are published annually by the USGS in reports entitled "Water Resources Data, Mississippi" for respective water year (October 1 to September 30). Results of analyses also are available from the USGS WATSTORE and EPA STORET data-management systems.

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## **TABLES**

Table 1.--U.S. Geological Survey atmospheric-precipitation laboratory  
analytical precision for ion chromatography methods

[Data are the result of sequential analysis of 20 standard reference samples, each in the range of mean concentration shown; all units are in milligrams per liter. Compiled from USGS, Doraville, Georgia, laboratory, written commun., 1988]

Constituent	Mean	Standard	Detection	Calibration range	
	concentration	deviation	range	Low	High
Calcium	0.06	0.01	0.05 - 0.07	0.10	3.00
	.09	.01	.09 - .13		
	2.99	.05	2.83 - 3.06		
Magnesium	.07	.01	.06 - .07	.10	2.00
	.10	.00	.10		
	1.99	.02	1.94 - 2.01		
Sodium	.04	.00	.04 - .06	.10	3.00
	.11	.00	.10 - .12		
	3.01	.03	2.91 - 3.05		
Potassium	.05	.00	.05 - .07	.10	3.00
	.11	.00	.10 - .12		
	2.99	.03	2.92 - 3.04		
Sulfate	.10	.00	.10 - .11	.10	6.00
	6.01	.01	5.99 - 6.03		
Chloride	.10	.01	.10 - .11	.10	2.20
	2.51	.01	2.50 - 2.52		
Bromide	.02	.00	.02	.02	.20
	.20	.00	.20 - .21		
Fluoride	.02	.00	.02	.02	.20
	.20	.01	.19 - .22		
Ammonia as NH <sub>4</sub>	.04	.00	.04 - .06	.10	2.00
	.10	.00	.10		
	1.97	.02	1.91 - 2.01		
Nitrate as NO <sub>3</sub>	.02	.00	.02	.02	1.00
	1.01	.00	1.00 - 1.01		
Orthophosphate as PO <sub>4</sub>	.02	.00	.02	.02	.20
	.21	.01	.19 - .24		

Table 2.--U.S. Geological Survey National Water-Quality Laboratory  
analytical method precision

[Computed as the relative standard deviation of analysis of natural  
waters by multiple analysts; data from Feltz and others (1985)]

Constituent	Applicable range (milligrams per liter)	Precision (percent)			Method <sup>a</sup>
		Low	Medium	High	
Calcium	0.01 - 5.0	40	10	1	AA
Magnesium	.01 - 5.0	21	3	4	AA
Sodium	.01 - 1.0	26	3	1	AA
Potassium	.01 - 1.0	39	2	4	AA
Sulfate	.01 - 10.0	3	2	3	IC
Chloride	.01 - 3.0	4	--	3	IC
Bromide	.01 - .60	--	--	--	IC <sup>b</sup>
Fluoride	.01 - .50	8	--	--	IC <sup>b</sup>
Ammonia as NH <sub>4</sub>	.01 - 1.8	13	3	2	CA
Nitrate as NO <sub>3</sub>	.04 - 2.6	6	4	--	IC <sup>b</sup>
Orthophosphate as PO <sub>4</sub>	.01 - .60	9	--	--	IC <sup>b</sup>
Phosphorus as P	.001- .20	--	--	--	CA

<sup>a</sup> AA, atomic absorption spectroscopy; IC, ion chromatography; CA, colorimetry,  
autoanalyzer.

<sup>b</sup> Evaluation of method precision not completed.

Table 3.--Summary of selected analytical data for the precipitation-quality station at NSTL, Mississippi, September 28, 1982, to December 31, 1987

Calendar year	Obser- vations	Minimum <sup>1</sup>	Maximum	Percentile			Aver- age <sup>2</sup>	Total deposition <sup>3</sup>
				25th	50th	75th		
RAINFALL, IN INCHES								
1982	11	0.15	5.60	0.47	1.70	2.10	1.70	18.68
1983	48	.10	6.30	.44	1.10	2.07	1.45	69.42
1984	45	.01	4.70	.40	.81	1.55	1.07	48.25
1985	42	.02	5.12	.43	1.50	2.42	1.64	68.74
1986	41	.04	3.37	.46	.82	1.69	1.14	46.66
1987	42	.01	7.99	.23	1.04	1.92	1.54	64.57
1982-87	229	.01	7.99	.44	1.00	1.90	1.38	316.32
SPECIFIC CONDUCTANCE, IN MICROSIEMENS PER CENTIMETER AT 25 °C								
1982	11	4	35	7	12	18	10	--
1983	48	4	43	11	16	20	14	--
1984	43	6	71	14	18	30	20	--
1985	39	6	129	10	16	29	14	--
1986	39	6	80	11	22	28	17	--
1987	39	7	74	11	17	23	15	--
1982-87	219	4	129	11	17	26	15	--
pH, IN STANDARD UNITS								
1982	11	4.35	5.30	4.55	4.70	4.90	4.79	--
1983	48	3.95	6.10	4.30	4.52	4.75	4.54	--
1984	43	3.70	6.10	4.10	4.55	4.70	4.29	--
1985	38	4.10	6.20	4.38	4.57	4.86	4.63	--
1986	39	3.95	5.90	4.30	4.55	4.70	4.56	--
1987	39	3.85	5.65	4.50	4.65	4.90	4.70	--
1982-87	218	3.70	6.20	4.35	4.57	4.80	4.55	--
CALCIUM CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	11	.13	.77	.15	.23	.36	.22	.9
1983	46	.06	1.10	.11	.16	.27	.18	2.8
1984	39	.07	2.30	.12	.17	.26	.21	2.3
1985	37	.04	.75	.14	.22	.30	.19	2.9
1986	36	.01	.77	.12	.18	.31	.17	1.8
1987	32	.05	.60	.07	.17	.24	.18	2.6
1982-87	201	.01	2.30	.12	.19	.29	.19	13.3
SODIUM CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	11	.10	3.10	.23	.52	1.50	.62	2.6
1983	46	.04	3.40	.19	.39	.65	.54	8.4
1984	38	.05	1.40	.12	.28	.67	.37	4.1
1985	37	.06	2.40	.16	.31	.62	.42	6.5
1986	36	.03	1.50	.17	.34	.61	.38	4.1
1987	32	.02	2.10	.14	.24	.46	.32	4.8
1982-87	200	.02	3.40	.16	.31	.61	.43	30.7

Table 3.--Summary of selected analytical data for the precipitation-quality station at NSTL, Mississippi, September 28, 1982, to December 31, 1987--Continued

Calendar year	Obser- vations	Minimum <sup>1</sup>	Maximum	Percentile			Aver- age <sup>2</sup>	Total deposition <sup>3</sup>
				25th	50th	75th		
CHLORIDE CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	11	0.30	6.30	0.33	0.92	2.00	1.20	5.1
1983	46	<.02	6.00	.39	.58	1.10	.98	15.4
1984	37	<.02	2.30	.38	.60	1.55	.73	8.0
1985	37	.04	3.80	.34	.64	.97	.80	12.4
1986	36	.15	2.60	.35	.64	1.10	.67	7.1
1987	32	.13	2.10	.26	.49	.74	.60	8.7
1982-87	199	<.02	6.30	.35	.59	1.10	.79	56.9
SULFATE CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	11	<.20	2.30	.43	1.10	2.00	.91	3.8
1983	46	<.20	4.20	.81	1.25	1.55	1.16	18.3
1984	36	.46	6.10	.95	1.30	2.50	1.57	17.2
1985	37	.38	9.70	.77	1.30	1.85	1.13	17.5
1986	36	.39	4.40	.93	1.45	2.00	1.32	14.0
1987	32	.40	5.90	.91	1.20	1.75	1.20	17.6
1982-87	198	<.20	9.70	.87	1.30	1.90	1.24	88.6
NITRATE AS NO <sub>3</sub> CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	11	<.04	1.72	.39	.62	.88	.58	2.4
1983	46	<.04	3.18	.57	.86	1.15	.81	12.7
1984	36	<.04	4.82	.63	1.06	1.71	1.16	12.7
1985	35	.22	4.29	.35	.93	1.28	.67	10.5
1986	36	.26	3.32	.58	1.17	1.70	.91	9.7
1987	32	<.04	2.12	.44	.68	1.21	.74	10.8
1982-87	196	<.04	4.82	.48	.88	1.36	.82	58.9
AMMONIA AS NH <sub>4</sub> CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	11	<.01	.43	<.01	.04	.07	.04	.2
1983	45	.01	.77	.07	.19	.29	.18	2.8
1984	39	.01	2.96	.13	.27	.47	.24	2.7
1985	35	.04	3.73	.08	.13	.21	.15	2.4
1986	36	<.01	.97	.08	.18	.28	.23	2.4
1987	32	<.01	.93	.09	.18	.30	.18	2.7
1982-87	198	<.01	3.73	.08	.18	.30	.18	13.2

<sup>1</sup> Minimum detection levels for some constituents may vary with analytical operating conditions.

<sup>2</sup> Precipitation-weighted average; average pH is calculated from the precipitation-weighted hydrogen-ion concentration.

<sup>3</sup> Rainfall in inches and constituent loads in pounds per acre for indicated period. Total for period of record may not equal the sum of annual loads.

Table 4.--Summary of selected analytical data for the precipitation-quality station at Janice, Mississippi, February 23, 1982, to December 31, 1987

Calendar year	Obser- vations	Minimum <sup>1</sup>	Maximum	Percentile			Aver- age <sup>2</sup>	Total deposition <sup>3</sup>
				25th	50th	75th		
RAINFALL, IN INCHES								
1982	39	0.03	5.40	0.23	0.80	1.70	1.21	47.36
1983	48	.05	11.00	.45	1.20	1.87	1.58	75.67
1984	47	.02	7.00	.36	.85	1.60	1.23	57.97
1985	50	.01	6.42	.32	1.00	2.25	1.43	71.45
1986	44	.01	3.30	.32	.85	1.87	1.15	50.51
1987	45	.01	5.85	.22	.63	1.89	1.24	55.91
1982-87	273	.01	11.00	.30	.93	1.85	1.31	358.87
SPECIFIC CONDUCTANCE, IN MICROSIEMENS PER CENTIMETER AT 25 °C								
1982	36	6	51	13	21	26	15	--
1983	47	7	39	10	13	22	14	--
1984	46	6	49	12	17	24	15	--
1985	43	4	32	11	16	22	13	--
1986	38	7	64	14	21	31	17	--
1987	36	6	55	11	17	26	17	--
1982-87	246	4	64	12	17	24	15	--
pH, IN STANDARD UNITS								
1982	36	3.60	5.30	4.12	4.40	4.68	4.45	--
1983	47	3.05	6.35	4.55	4.80	5.15	4.32	--
1984	46	3.80	6.25	4.35	4.65	4.85	4.51	--
1985	43	4.05	5.60	4.30	4.50	4.85	4.56	--
1986	39	3.90	4.95	4.15	4.35	4.50	4.42	--
1987	36	3.90	5.70	4.35	4.65	4.85	4.57	--
1982-87	247	3.05	6.35	4.30	4.55	4.80	4.46	--
CALCIUM CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	25	.02	.29	.08	.14	.21	.13	1.4
1983	45	.04	1.90	.09	.13	.24	.25	4.2
1984	42	.03	1.10	.12	.18	.35	.21	2.8
1985	40	.04	.73	.11	.17	.22	.14	2.2
1986	39	.01	1.30	.13	.22	.31	.22	2.5
1987	34	<.01	.55	.06	.11	.26	.14	1.8
1982-87	225	<.01	1.90	.10	.17	.26	.19	15.1
SODIUM CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	25	.13	3.40	.17	.23	.49	.39	4.2
1983	45	.06	1.80	.21	.44	.60	.52	8.8
1984	41	.06	3.90	.10	.19	.53	.37	4.7
1985	41	.05	1.40	.14	.23	.47	.36	6.0
1986	39	.10	1.70	.17	.34	.51	.32	3.7
1987	35	<.01	1.00	.08	.22	.46	.32	4.0
1982-87	226	<.01	3.90	.15	.27	.53	.39	31.5

Table 4.--Summary of selected analytical data for the precipitation-quality station at Janice, Mississippi, February 23, 1982, to December 31, 1987--Continued

Calendar year	Obser- vations	Minimum <sup>1</sup>	Maximum	Percentile			Aver- age <sup>2</sup>	Total deposition <sup>3</sup>
				25th	50th	75th		
CHLORIDE CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	25	<0.01	7.00	0.27	0.48	0.72	0.73	7.8
1983	45	<.01	3.40	.24	.48	.81	.75	13.1
1984	42	.01	6.90	.24	.51	1.12	.82	10.6
1985	42	.09	2.70	.24	.43	.99	.63	10.4
1986	39	.20	2.60	.32	.48	.74	.47	5.4
1987	34	<.01	1.50	.19	.32	.70	.49	6.2
1982-87	227	<.01	7.00	.25	.44	.82	.66	53.3
SULFATE CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	25	.36	3.40	.87	1.40	2.15	1.21	13.0
1983	45	.52	8.70	.89	1.20	1.90	1.57	27.0
1984	42	.44	5.30	1.00	1.30	2.17	1.29	17.0
1985	42	.40	6.30	.93	1.45	2.00	1.21	19.5
1986	39	.51	6.40	1.20	1.80	3.40	1.69	19.4
1987	34	.50	5.20	.77	1.30	2.40	1.45	18.3
1982-87	227	.36	8.70	.97	1.40	2.20	1.41	114.6
NITRATE AS NO <sub>3</sub> CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	25	<.04	2.34	.46	.75	1.21	.73	7.8
1983	45	<.04	3.40	.53	.70	1.28	.87	14.8
1984	40	.22	4.82	.62	.90	1.47	.71	9.3
1985	41	<.04	5.75	.35	.84	1.21	.73	11.9
1986	39	.26	5.31	.66	.97	1.54	.91	10.5
1987	34	<.04	2.25	.47	.81	1.32	.74	9.4
1982-87	224	<.04	5.75	.48	.88	1.32	.79	63.9
AMMONIA AS NH <sub>4</sub> CONCENTRATION, IN MILLIGRAMS PER LITER								
1982	25	<.01	.35	.01	.03	.16	.07	.7
1983	44	<.01	1.04	.07	.15	.24	.28	4.8
1984	44	<.01	1.80	.12	.24	.39	.27	3.6
1985	41	<.01	3.09	.09	.17	.28	.18	3.0
1986	38	<.01	1.80	.11	.18	.27	.22	2.5
1987	34	<.01	1.41	.05	.20	.32	.21	2.7
1982-87	226	<.01	3.09	.08	.17	.28	.21	17.4

<sup>1</sup> Minimum detection levels for some constituents may vary with analytical operating conditions.

<sup>2</sup> Precipitation-weighted average; average pH is calculated from the precipitation-weighted hydrogen-ion concentration.

<sup>3</sup> Rainfall in inches and constituent loads in pounds per acre for indicated period. Total for period of record may not equal the sum of annual loads.

Table 5.--Summary of selected analytical data for the precipitation-quality station at Rosetta, Mississippi, February 18, 1986, to December 31, 1987

Calendar year	Obser- vations	Minimum <sup>1</sup>	Maximum	Percentile			Aver- age <sup>2</sup>	Total deposition <sup>3</sup>
				25th	50th	75th		
RAINFALL, IN INCHES								
1986	36	0.10	8.47	0.34	1.17	1.71	1.36	48.85
1987	43	.05	5.32	.32	1.05	2.00	1.43	61.61
1986-87	79	.05	8.47	.32	1.10	1.90	1.40	110.46
SPECIFIC CONDUCTANCE, IN MICROSIEMENS PER CENTIMETER AT 25 °C								
1986	33	5	46	8	13	20	12	--
1987	39	4	48	9	14	18	13	--
1986-87	72	4	48	9	13	18	12	--
pH, IN STANDARD UNITS								
1986	29	3.75	6.35	4.35	4.70	4.85	4.53	--
1987	39	4.00	6.05	4.40	4.60	4.75	4.56	--
1986-87	68	3.75	6.35	4.40	4.65	4.80	4.55	--
CALCIUM CONCENTRATION, IN MILLIGRAMS PER LITER								
1986	27	.02	.46	.14	.21	.31	.20	2.3
1987	34	.03	.82	.07	.13	.32	.17	2.4
1986-87	61	.02	.82	.10	.20	.31	.18	4.6
SODIUM CONCENTRATION, IN MILLIGRAMS PER LITER								
1986	27	.10	.78	.18	.28	.47	.28	3.1
1987	36	<.01	1.80	.08	.17	.36	.22	3.1
1986-87	63	<.01	1.80	.14	.22	.40	.25	6.2
CHLORIDE CONCENTRATION, IN MILLIGRAMS PER LITER								
1986	27	.22	1.40	.28	.35	.59	.41	4.5
1987	36	<.01	2.60	.19	.25	.56	.33	4.6
1986-87	63	<.01	2.60	.22	.29	.58	.36	9.1
SULFATE CONCENTRATION, IN MILLIGRAMS PER LITER								
1986	27	.50	4.50	.90	1.10	2.10	1.26	14.0
1987	36	.35	5.00	.76	1.20	1.70	1.23	17.1
1986-87	63	.35	5.00	.80	1.20	1.80	1.24	31.1
NITRATE AS NO <sub>3</sub> CONCENTRATION, IN MILLIGRAMS PER LITER								
1986	27	.26	3.18	.57	.79	1.06	.74	8.2
1987	35	<.04	2.70	.44	.88	1.06	.73	10.2
1986-87	62	<.04	3.18	.48	.81	1.06	.74	18.4
AMMONIA AS NH <sub>4</sub> CONCENTRATION, IN MILLIGRAMS PER LITER								
1986	27	<.01	1.01	.12	.19	.33	.26	2.9
1987	36	<.01	1.80	.10	.18	.34	.23	3.2
1986-87	63	<.01	1.80	.10	.19	.33	.25	6.2

<sup>1</sup> Minimum detection levels for some constituents may vary with analytical operating conditions.

<sup>2</sup> Precipitation-weighted average; average pH is calculated from the precipitation-weighted hydrogen-ion concentration.

<sup>3</sup> Rainfall in inches and constituent loads in pounds per acre for indicated period. Total for period of record may not equal the sum of annual loads.

## APPENDIX A

**PRECIPITATION-QUALITY DATA COLLECTION IN  
MISSISSIPPI: INSTRUCTIONS TO STATION OBSERVERS**

Revised June 1989

## INTRODUCTION

In 1982, the U.S. Geological Survey, in cooperation with the Mississippi Bureau of Pollution Control, established a program designed to define and monitor trends in the chemical quality of precipitation in southern Mississippi. Instructions to the observers for the operation of the monitoring stations are given in this report. It is essential that these specific instructions are followed to ensure that the data obtained are reliable and compatible with data from other networks operated in the State and in other parts of the United States.

Early detection and reporting of problems encountered by the observer are important. It is anticipated that parts of these instructions will be modified as more experience is gained. Comments and suggestions by the field observer are needed to develop more effective field procedures and to collect reliable precipitation-quality data.

Requests for information concerning the collection of precipitation-quality data in Mississippi and related technical information should be addressed to:

District Chief  
U.S. Geological Survey  
100 W. Capitol Street, Suite 710  
Jackson, MS 39269

Telephone calls for technical assistance concerning the routine operation of precipitation-quality monitoring stations should be directed to:

Project Chief  
U.S. Geological Survey  
Precipitation-Quality Project  
(601) 965-4600

## SAMPLE COLLECTION AND SITE INSPECTION SCHEDULE

Samples should be allowed to accumulate for 1 week (168 hours). These samples will be removed from the collector at 9:00 a.m. each Tuesday unless it is raining. The sample should be removed as soon as possible after the cessation of precipitation, but in no case later than 5:00 p.m. on Tuesday.

Site inspections will be conducted on Tuesday at the time of rainfall-sample collection and on Friday at any time during the day. The Friday inspection may be postponed 1 day if weather conditions do not allow proper servicing. Each site inspection will be recorded as prescribed in the "Field-Notes Form" procedures.

## SERVICE AND MAINTENANCE

### Sample Collector

The precipitation collector has a sensor that is activated by precipitation (wet fall). When activated by either rain or snow, the sensor sends an electronic signal to the mechanism which moves the collector cover from the "wet" side to the "dry" side, exposing the "wet" collection bucket. When precipitation ends, the sensor grid plate is dried by the built-in heater and the cover automatically closes over the "wet" collection bucket. The "wet" precipitation collection bucket remains covered to prevent "dry fallout" collection in the "wet" bucket. The sample collector will be connected either to a 110-volt AC or DC (battery) power source.

### **Routine Service**

- Test the precipitation sensor by placing one or two drops of water on the sensor grid plate. The collector cover should move to cover up the "dry fall" bucket and expose the "wet fall" bucket. Do not manually force the cover from one bucket to the other.
- Verify heater operation by placing a finger on the base of the sensor plate, the plate should feel warm after a minute or so. With one or two drops of water on the sensor, the collector should complete the

cycle by moving the cover back to the "wet" bucket within a period of about 5 minutes.

- Once a month, clean the collector plastic seal (attached to underside of collector cover) and the lip around the "dry" bucket by wiping with clean lab tissues wetted with demineralized water. The seal should be cleaned after removal of the "wet" bucket and prior to placement of the next "wet" bucket. While cleaning, allow the collector cover to cycle back to the "dry" position so the "wet" bucket is not exposed to possible contamination. The collector cover also has a spring pressure device in the connecting arms that allows the collector cover to be lifted (approximately ½ inch) for cleaning and inspection. Check the collector cover plastic seal for cracks and make sure the seal fits snugly against the rim of the bucket. A tight seal reduces sample loss through evaporation. To install the clean bucket after inspection and cleaning, again place a drop of water on the sensor grid plate to cycle the collector to the "wet" position.
- Once each month, wash the sensor grid plate with demineralized water and a toothbrush to remove any material that has accumulated. Be very careful not to contaminate the sample bucket during the cleaning procedure.

### **Recording Rain Gage**

The 8-inch recording rain gage is a "weighing-type" gage used to measure the total amount of precipitation deposited over the 7-day sampling period. It provides rainfall data necessary to determine sample-collection efficiency and to check the amount of precipitation in the sample collector.

#### **Routine Service**

- Change and install a new recorder chart and rewind and reset the clock each Tuesday during routine station visit.
- Clean the metal rain gage bucket when necessary to avoid accumulation of foreign matter that can prevent zero (baseline) adjustment on the recorder chart.

- Clean the recorder pen when necessary; old ink can be washed out using the wash bottle and paper towels supplied.
- The rain gage will be calibrated periodically and serviced by U.S. Geological Survey personnel.

### Weighing Balance

Precipitation samples from the "wet" bucket will be weighed to determine the volume of rainfall deposited during the sampling period. The balance used is a double-beam type with a 20 kilogram weight capacity. The balance features magnetic damping, undivided extra large capacity tare with locking poise, and precision-ground knives protected by positive platform stops. The balance is sensitive and must be handled with care to maintain proper calibration.

#### Routine Service

- Keep the balance clean and covered when not in use, being particularly careful not to allow dust and dirt to accumulate on the weighing pan and near the bearings.
- The accumulated matter usually can be easily removed by merely blowing it away.
- The calibration of the balance will be checked routinely by U.S. Geological Survey personnel.

### Sample-Collection Bucket

Extreme care must be taken when cleaning sample-collection buckets to ensure that precipitation samples are not contaminated when samples are collected. Avoid touching the inside of the bucket and do not allow perspiration or airborne material to enter the bucket during the cleaning, storage, and sample-preparation process. Clean sample-collection buckets using the following procedure:

- Rinse bucket and lid with demineralized water. Never use detergents or scouring powder to clean the bucket and lid. If the bucket and lid cannot be cleaned as follows, they should be replaced.
- Fill bucket with sufficient demineralized water to allow scrubbing with a clean brush. (Keep brush stored in a clean container when not in use.)
- Scrub the inside of bucket to remove material that may adhere to the sides and bottom.
- After scrubbing, rinse bucket several times with demineralized water until the specific conductance of the rinse water is the same as the conductance of the demineralized water used for rinsing. The specific conductance of the demineralized rinse water should not exceed 2.0 microsiemens per centimeter at 25 °C. Record specific conductance of final rinse water in remarks (part H) of the "Field-Notes Form" (see attached example).
- Shake excess water from bucket and lid.
- Immediately place bucket (unsealed) and lid inside a plastic bag to avoid airborne contamination. Store plastic bag with bucket and lid tilted on their side to allow draining and drying.
- Remove bucket and lid from bag on-site at the time of installation.

### FIELD-NOTES FORM

The precipitation-quality "Field-Notes Form" is used to record essential information for each sample and to provide information needed to process samples in the laboratory. Entries on the form must be legible and care must be taken to ensure that this record is accurate.

### Preparation

The lettered parts and numbered items that follow refer to a corresponding letter or number in the attached example.

- A. The begin and end date for year, month, day (Items 3 and 5), and local time (Items 4 and 6), should be entered when a collector bucket is installed and removed. The time used on the form is 24-hour time; that is, 12:00 noon = 1200 hours and 12:00 midnight = 2400 hours. A sample collected at 9:15 a.m. will be recorded 0915 in the space designated on the form. A "Field-Notes Form" will be started when a clean bucket is installed in the sampling equipment. The form will be completed at the time a "wet" bucket is removed from sampler.
- B. More than one measurement of specific conductance and pH will be taken. Record the final measurement after meters are calibrated (Part G) and are performing properly. Record precipitation amount (inches) from rainchart and sample weight from calculation in Part E. Efficiency will be determined at the USGS office.
- C. Space is provided to indicate that routine inspection checks and calibrations have been made.
- Date should be entered as month and day.
  - Clock time and recorder time should be entered as correct local time, either "standard" or "daylight savings." Mark and record time on recorder chart each time a chart is installed or removed. If clock and recorder time do not agree, do not adjust recorder time until a new recorder chart is installed.
  - Rain gage (inches) is the amount of rainfall indicated on rain gage chart at the time of each inspection.
  - Collector cover will be activated by placing one or two drops of water on the sensor grid. Check the operation of event marker during the cycle of collector cover operation. If it is raining, proper operation may be verified at a later time.
  - Clock on the recording rain gage should be wound each Tuesday.
  - Space is provided for any additional inspection during the week.

- D. Events are indicated by the upward mark of event-marking pen at the top of the rain-gage chart. An event is a record of times the cover is opened. The downward pen stroke for a cover closing is not counted as an event.
- E. Sample weight: A "Field-Notes Form" is started by entering the initial (first) weight of the empty bucket and lid (item 2). After the 7-day sampling period, the bucket lid and sample (if any) is weighed. This weight is entered as the final weight (item 1). Record sample weight (item 3) by subtracting the initial weight from the final weight. Also record final weight in the appropriate space in Part B.
- F. Sample condition is determined from a visual observation of the precipitation in the sample-collector bucket. Circle the number(s) for the item(s) best describing visual observation. Any comment as to obvious causes of the condition should be noted. Comments such as "dust particles," "bird droppings," "leaves," or "insects," are important, descriptive comments.
- G. Meter calibration: Space is provided to record the known value and the measured value of standard reference samples (SRS) used to verify specific conductance and pH meter calibration. Space is also provided to measure the specific conductance of demineralized water. The temperature of both the pH 4 buffer and the precipitation sample are recorded to verify that the temperature of each is within 2 °C of the other.
- H. Remarks: Record unusual conditions such as weather or other occurrences either at the field site or during sample processing. Unusual conditions may include nearby plowing, application of agricultural chemicals, harvesting, burning, or increased atmospheric pollution or dust. The importance of the information cannot be overemphasized. Careful observation is very useful in evaluating the validity of the sample and the interpretation of the data. All problems and malfunctions of equipment also should be recorded and immediately reported to the U.S. Geological Survey for

assistance. The observer will confirm if a water sample was sent to the lab by marking yes or no.

- I. Observer: The Observer's name, address, and telephone number is recorded in this space. The observer should sign the form when it is completed. All observers will receive on-site training under U.S. Geological Survey supervision.

### Distribution

The "Field-Notes Form" may be completed with either ball point pen or a medium-hardness sharp pencil. Observers should be certain that recorded notations are legible and that the form is completed as described. A completed "Field-Notes Form" and rain-gage chart will be mailed each week to the following address:

U.S. Geological Survey  
100 W. Capitol St., Suite 710  
Jackson, MS 39269

A duplicate "Field-Notes Form" or carbon copy will be included with each shipment of samples to the laboratory. A supply of preaddressed envelopes will be provided.

### **SAMPLE HANDLING AND PREPARATION**

Careful handling of equipment and samples to prevent sample contamination is extremely important. To avoid windblown contaminants, approach the sampler and work from the down-wind side, if possible. At the end of the 7-day collection period, remove the sample bucket from the sample collector and prepare samples as follows:

- Do not touch those surfaces that will come in contact with the precipitation sample. Fasten the lid on each bucket securely enough to minimize contamination during sample handling. Remove the bucket from the collector and replace with a clean bucket. The sample bucket for the new collection period is placed in the "wet" sample position. The bucket in the "dry" position will not be removed. If there has been no precipitation (no water in sample bucket), record a

sample weight of zero on "Field-Notes Form" Part B under "sample weight" and replace exposed bucket with a clean bucket.

- Allow sample to reach near room temperature. Weigh the sample bucket including the lid as accurately as possible. Record the final weight on the preceding week "Field-Notes Form." The difference between the initial and final weights is the sample weight. If the sample weight is less than 50 grams, no field analysis will be required.
- With a clean 50-cubic-centimeter disposable syringe, transfer about 30 cubic centimeters of sample to a clean, dry sample cup. Seal the cup with a plastic lid, place lid on sample bucket, and proceed to "Field-Measurement Procedure."

## FIELD-MEASUREMENT PROCEDURE

Space on the "Field-Notes Form" is provided to record one measurement of specific conductance and the temperature of both the sample and the pH 4 buffer solution. Only one measurement is necessary, but if the validity of the measurement is doubted, it should be repeated with only the final value recorded on the form. Problems that are experienced during the field-measurement procedure should be described in the "Remarks" section.

Always measure the specific conductance before measuring the pH of a sample. Do not measure specific conductance and pH until the temperature of the sample and the pH buffer solution compare within about 2 °C.

### Specific Conductance Measurement

- Record (on the "Field-Notes Form") the known specific-conductance value of the standard reference sample (SRS). Measure the specific conductance of the SRS. Repeat this step if the measured value does not agree with the known value given on the SRS bottle. Record the final reading on the Field-Notes Form." IMPORTANT: The specific conductance probe must be positioned in the center of sample cup and at least inch from the bottom. The dip-cell probe should be

moved up and down several times to remove all air bubbles inside the cell. The cell side-hole opening of the probe must be below the water surface when reading specific conductance. Replace the lid on the cup and save the SRS sample for pH meter calibration check.

- Rinse the probe repeatedly with demineralized water. Measure and record the specific conductance of the demineralized water. This value should be 2.0 microsiemens or less.
- Gently shake excess demineralized water from the tip of the probe. Without re-rinsing the probe, measure the temperature and specific conductance of the precipitation sample. Read specific conductance to the nearest 0.1 microsiemens below 10 microsiemens and to whole numbers above 10 microsiemens. Record the specific conductance and temperature values on the "Field-Notes Form."
- Replace lid on sample cup and save for pH measurement.

#### pH Measurement

- Calibrate pH meter using certified pH 4 and 7 buffer solutions. Record the temperature of the solutions on the "Field-Notes Form." Rinse electrode thoroughly with demineralized water after each measurement (be sure to rinse the tip). Gently blot (do not rub) the electrodes dry with a clean absorbent lab tissue. Discard used pH buffer solutions after calibration.
- Record the known pH value of SRS used to calibrate the specific conductance meter. Measure pH of SRS. Repeat calibration when measurement is not the same as pH of SRS.
- Record the length of time required to reach the pH of the SRS value.
- Rinse electrodes thoroughly with demineralized water and blot dry. Measure and record the temperature of the precipitation sample used to determine specific conductance.

- Measure pH of sample. Allow the electrodes to equilibrate in the sample without stirring. Equilibration will take about the same length of time as that for the measurement of the pH of the SRS. Read pH to the nearest 0.05 unit and record the pH value of the sample on the "Field-Notes Form."
- Discard the precipitation sample used for the specific conductance and pH measurements.
- When not in use, always keep the tip of the pH electrode emersed in a solution specified by USGS. Do not store pH electrodes dry.

### SAMPLE SHIPMENT

Samples for laboratory analysis will be prepared each Tuesday when sufficient rain has occurred. One 250-cubic-centimeter plastic bottle will be shipped to the laboratory. The sample from the sample bucket will be transferred to the 250-cubic-centimeter bottle using the same 50-cubic-centimeter disposable syringe that was used for sample preparation and field measurements. Samples are prepared for shipment as follows:

- Add ice to sample cooler to about one-fourth full. Place sample bottle in a plastic bag. Fill and place remainder of the space with ice. Leave space for the plastic bag containing duplicate "Field-Notes Form."
- Fold "Field-Notes Form" and place inside small plastic bag. Tie ends of bag making a water-tight seal. Lay sealed bag on top of ice.
- Screw on cooler lid. Tape laboratory mailing address card on top of cooler lid.
- Ship cooler to laboratory as soon as possible, but no later than Wednesday. Preaddressed labels will be provided.

MISSISSIPPI DISTRICT  
PRECIPITATION QUALITY FIELD NOTES

Station Name \_\_\_\_\_

A. Sample Information

(1) Agency Code: USGS (2) Station Number: 310152088590950  
 (3) Begin Date: 19\_\_\_\_ (4) Begin Time: \_\_\_\_  
 (5) End Date: 19\_\_\_\_ (6) End Time: \_\_\_\_ (7) Medium Code: 7  
 (8) Hydrologic Conditions: A (9) Sample Type: H (10) Hydrologic Event: 9  
 (11) Project Number: 452800500 (12) Analysis Types: CHNU  
 (13) (14) Data Category: QW  
 (15) Collecting Agency (00027): 99001 (16) Analyzing Agency (00028): 1028  
 (17)  
 (18) Analysis Status: H(19) Analysis Source: 1 (20) Lab Number:

B. Field Values

Code	Name	Value	R	Q	M	P	Code	Name	Value	R	Q	M	P
00095	Conductance	—	—	G	—	2	00400	pH	—	—	G	—	3
00193	Precipitation	—	—	G	—	3	32002	Sample Weight	—	—	G	—	4
72005	Sample Source	1001	—	G	—	4	82284	Efficiency	—	—	G	—	3
82398	Sampling Method	8010	—	G	—	4							

C. Inspections

	Tuesday	Friday	
Date	_____	_____	_____
Clock Time	_____	_____	_____
Recorder Time	_____	_____	_____
Rain Gage-Inches	_____	_____	_____
Collector Cover	_____	_____	_____
Clock	_____	_____	_____

D. Events

Number of times sampler cover is opened: \_\_\_\_\_

E. Sample Weight (total accumulation)

1. Final Weight (sample + bucket + lid) \_\_\_\_\_ grams  
 2. Initial Weight (dry bucket + lid) \_\_\_\_\_ grams  
 3. Sample Weight (1-2=3) \_\_\_\_\_ grams

F. Sample Condition

1. Clear 2. Turbid (Cloudy) 3. Floating material 4. Settled material  
 Describe items 3 & 4: \_\_\_\_\_

G. Meter Calibration

Specific Conductance (uS/cm)	pH (units)	Temperature (deg C)
SRS (known) _____	SRS (known) _____	pH 4 buffer _____
SRS (measured) _____	SRS (measured) _____	Sample _____
Demineralized water _____		

SRS=Standard Reference Sample of known Specific Conductance and pH value

H. Remarks

Sample sent to lab: YES NO  
 \_\_\_\_\_  
 \_\_\_\_\_

I. Observer:

(H) (O) \_\_\_\_\_

EXAMPLE OF FIELD-NOTES FORM FOR STATION OBSERVERS AT  
 U.S. GEOLOGICAL SURVEY PRECIPITATION-QUALITY STATIONS.