UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

ATMOSPHERIC DEPOSITION: SAMPLE HANDLING, STORAGE, AND ANALYTICAL PROCEDURES FOR CHEMICAL CHARACTERIZATION OF EVENT-BASED SAMPLES IN NORTH DAKOTA

By Robert L. Houghton, Mary E. Berger, Nancy Zander, and Sandra K. Dutchek

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For those readers who may prefer to use the International System of Units (SI) rather than inch-pound units, the conversion factors for the terms used in this report are given below.

Multiply inch-pound units	By	To obtain SI units
Foot (ft)	0.3048	meter
Gallon, U.S., liquid (gal)	3.7854	liter
Quart, U.S., liquid (qt)	0.9463	liter
Inch (in.)	2.54	centimeter
	25,400	micrometer
Micromho per centimeter at 25°Celsius (μmho/cm at 25°C)	1	microsiemen per centimeter at 25°Celsius
Mile (mi)	1.609	kilometer
Mile per hour (mi/h)	0.4470	meter per second
Ohm-inch (ohm-in.)	2.539	ohm-centimeter
Ounce, U.S. fluid (oz)	29.57	milliliter
Pound, avoirdupois (lb)	453.6	gram
Pound per cubic foot (lb/ft^3)	0.0160	gram per milliliter

To convert degrees Celsius (°C) to degrees Fahrenheit (°F), use the following formula: °F = 9/5(°C) + 32.

GLOSSARY

Atmospheric deposition is the total of all solids removed from the atmosphere to the ground surface, whether deposited as dry particulate matter or dissolved or suspended in water. Atmospheric deposition includes dry deposition and wet deposition as discussed below.

Dry deposition is the air-borne particulate matter that is deposited on the ground surface by processes not involving water or its phases.

Micrograms per liter (µg/L) is a unit expressing the relative concentration of a chemical constituent in solution as weight (micrograms) of solute per unit volume (liter) of water; 1,000,000 µg/L equals 1 gram per liter (g/L).

Microgram equivalents per liter (µeq/L) is a unit expressing the relative concentration of a chemical constituent in solution. It is calculated by dividing concentration values, expressed in micrograms per liter, by the combining weight (atomic or molecular weight of ion divided by the ionic charge) of the ion in question. In equivalents, unit concentrations of all ions are chemically equivalent.

Micromolal (m) is a unit of concentration that describes the amount of solute, in micromoles, dissolved in 1 kilogram of solvent.

Milligrams per liter (mg/L) is a unit expressing the concentration of a chemical constituent in solution as weight (milligrams) of solute per unit volume (liter) of water; 1 mg/L equals 1,000 micrograms per liter (µg/L).

Mole is the amount of a pure substance containing the same number of chemical units as there are atoms in exactly 12 grams of carbon-12 (that is, 6.023×10^{23}). One mole is equal to the gram formula weight of the substance.

Precipitation is the deposition of water from the atmosphere as rain, snow, or condensation. Fog is not included as a form of precipitation but may result in atmospheric deposition of water by condensation on ground-surface materials.

Wet deposition is the deposition of solids from the atmosphere as dissolved or suspended material in water or its phases.

ATMOSPHERIC DEPOSITION: SAMPLE HANDLING, STORAGE, AND ANALYTICAL PROCEDURES FOR CHEMICAL CHARACTERIZATION OF EVENT-BASED SAMPLES IN NORTH DAKOTA

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ABSTRACT

The North Dakota atmospheric-deposition network uses HASL-type collectors to sample wet and dry deposition on an event basis for analysis of 8 principal mineral, 3 nutrient, and 15 trace constituents. Comparison of the compositions of wet deposition collected in adjacent collectors sampled on weekly and event bases indicates that weekly sampling leads to significant contamination of wet deposition samples with dry deposition. Elevation of the collectors 10 feet above ground surface may decrease wind-blown soil contamination significantly.

This manual presents a summary of the research procedures adopted by the North Dakota District of the U.S. Geological Survey to investigate the consequences of increased fossil-fuel combustion on the quality of atmospheric deposition. The manual has been tested by field operatives for 3 years and shown to be an effective field guide and management tool.

INTRODUCTION

Most chemical constituents of the atmosphere eventually are removed by wet and dry deposition. The processes of removal involve both chemical and physical reactions which may include transformation of atmospheric constituents into other chemical forms. Resultant atmospheric deposition contains chemical forms that are beneficial to the environment, such as nutrients, and forms that may be harmful, such as acids and trace metals. Most investigations into the chemistry of atmospheric deposition center around acid components. Wet deposition (precipitation usually as rain or snow) is defined as acidic if its pH is less than 5.6, the theoretical pH of precipitated water in equilibrium with atmospheric carbon dioxide in the absence of other chemical constituents.

The President's Council on Environmental Quality has cited acid precipitation as one of the two most important environmental problems affecting the United States today. Numerous investigators have demonstrated that pollutant loading (such as acidification) from atmospheric deposition is a major cause of deterioration in the quality of the Nation's natural waters

(Matheson and Elder, 1976; Wright and Gjessing, 1976; Gjessing and others, 1976; de Ruiter, 1977; Schofield, 1977; Seip and Tollan, 1978; Martin, 1979; Scheider and others, 1979) and soils (Haines, 1976; Malmer, 1976; Norton, 1976; Tamm, 1976; Anderson and Keith, 1976; Reuss, 1978; Glass and others, 1979). The President's Council recommended that monitoring networks be established nationwide to document the quality of atmospheric deposition and to determine its effects on the environment.

Because precipitation samples consist of dilute solutions containing micromolar quantities of constituents, small changes in concentrations due to contamination accompanying sample collection and handling and to chemical and biological degradation subsequent to sampling can result in appreciable error. Therefore, collection of representative chemical data on atmospheric deposition that are suitable for evaluation of a specific problem requires the development and conscientious application of stringent procedures and protocol from the initial stages of planning to data verification and evaluation.

This manual represents a summary of the research procedures adopted by the North Dakota District of the U.S. Geological Survey for operation of an event-based monitoring network to investigate the consequences of increased fossil-fuel combustion in North Dakota on the quality of atmospheric deposition. These procedures are designed to maximize data accuracy and quality assurance while minimizing operational costs of the North Dakota atmospheric-deposition network.

Because other monitoring networks will differ in sampling objectives and equipment available, this manual will have to be modified by most prospective users to fit individual requirements. However, the manual should serve as an outline of items to be considered in the operation of atmospheric-deposition networks. Field use of this manual in North Dakota for 3 years provides an assurance of the operational practicality of the procedures.

ACKNOWLEDGMENTS

This manual owes its existence to the support and cooperation of Robert T. Angelo, Kurt W. Anderson, and Martin Schock of the North Dakota State Health Department. Their suggestions constitute the major revisions which have occurred in the manual since its preliminary formulation in 1980.

The comments and reviews of site observers who have used an administrative version of this manual for 3 years have increased the utility of the manual immensely. Their conscientious adherence to the systematic procedures outlined in this manual has provided the field testing required to assure the practicality of these procedures.

Additionally, the numerous requests for this manual from other investigators have provided the impetus for its publication in this form. Their encouragement is greatly appreciated.

SAMPLING PERIOD

The interval over which samples are collected is partly determined by the objectives of the network. Many of the emissions of coal-fired powerplants, such as mercury, selenium, silver, and sulfur- and nitrogen-oxides, are volatile and may be lost from precipitation samples which are left standing for extended periods following collection. Additionally, correlation of constituents in precipitation with powerplant emissions requires information about the meteorological conditions that resulted in the precipitation. Therefore, network objectives can only be achieved by collecting samples on a subevent or event basis. Because most air in North Dakota meets Class 1 or 2 air-quality standards under the Clean Air Act, subevent samples contain concentrations of many constituents of interest to the program that are below detection limits. Event sampling of wet deposition is undertaken at all network sites in North Dakota. For the purposes of consistency with most other event-based precipitation networks in North America, an event is defined as a period of wet deposition that is separated from other periods of wet deposition by a dry interval of at least 6 hours in the winter and at least 3 hours in the summer.

Collection of wet-deposition samples on an event basis limits the potential for contamination with dry deposition. When wet deposition is allowed to sit in buckets for extended periods, dry deposition may enter the bucket during periods when wind lifts the wet-deposition bucket cover. In a dry, windy climate, like that of North Dakota, such contamination can be a significant source of sample alteration.

Because dusty conditions do prevail in North Dakota, dry-deposition accumulations are appreciable. In the current network, dry-deposition samples are retrieved monthly as opposed to the bimonthly schedule adopted by the National Atmospheric Deposition Program. This increased sampling frequency is possible because of the large amount of atmospheric dust carried by prairie winds. The amount of dry-deposition collected in currently available collectors is known to vary widely even between closely spaced samplers. Thus, collected dry deposition may be interpreted as only a qualitative indication of the magnitude of dry ambient fluxes of analyzed constituents. However, frequent sampling also enhances the sensitivity of the samples to input from fly ash and other dry deposition originating from the combustion of coal, and minimizes dilution with soil-derived dust. Thus, the dry-deposition input of coal-fired powerplants may be monitored.

SITE SELECTION

The location of collector sites is critical to the interpretation of atmospheric-deposition data. The selected sites must be located to yield samples representative of the processes under investigation and must be free of local obstructions that might affect the results.

For the purpose of evaluating the effects of coal-fired powerplants on atmospheric deposition in North Dakota, computer simulations of atmospheric transport were used to select regionally appropriate collection sites. With the assistance of meteorologists from the North Dakota State Health Department and agronomists from the U.S. Agricultural Research Service, a computer program developed at the Oak Ridge National Laboratory (Mills and Reeves, 1973; Culkowski and Patterson, 1976) has been modified to help select the most appropriate sample sites. Based on multiple-point sources at specified coordinates that correspond to the locations of coal-fired powerplants in the State; average meteorologic conditions, including mean wind speed and direction, temperature, and rainfall data; and source characteristics, including element emission rates, the computer program has been modified to yield a predicted surface-deposition map. The program also yields maps of associated air concentrations of particulates and major strong acid constituents. This computer simulation also is the basis for North Dakota regulations for the prevention of significant deterioration (PSD) of air quality in the State as authorized by Title 1, Part C of the U.S. Clean Air Act of 1974 and its amendments of 1977. A critique of the simulation and its regulatory usage has been made by Uman (1982).

Once regional siting was determined using the computer simulation, local site selection was made based on data gathered from maps, aerial photographs, and ground reconnaisance. Principal local siting criteria closely corresponded to those established by the National Atmospheric Deposition Program and the National Trends Network. These criteria include:

(1) The site should be situated on flat or gently sloping terrain (slope should be less than approximately 20 degrees) that is free from topographic obstructions that might alter meteorologic patterns within a 1-mile radius of the site.

(2) No continuous atmospheric-emission sources, except those to be investigated in the study, should be located within 30 miles in the mean wind direction from the site or within 20 miles in all other directions. For baseline sites, all continuous emission sources must be outside this ovate zone.

(3) The collection site should be on undisturbed land with no tilled land within a 1-mile radius in order to limit local dust uptake by wind.

(4) The land immediately around the site should have a single land use.

(5) No moving sources of pollution, such as routine air, ground, or water traffic, should occur within 100 yards of the site, but year-round access is essential.

Other site criteria apply to construction aspects of site installations and are discussed in subsequent sections.

All sites should be documented with as complete a description as possible. Supplement 1 is a form which was developed to provide this documentation. All sites should be photographed from the four principal compass directions. Photographs should show both installation arrangement and adjacent land use.

The locations of collection sites in the North Dakota atmospheric-deposition network are shown in figure 1. Site descriptions will be presented in another report.

FIELD INSTRUMENTATION

Instrumentation for each site must be selected to collect data of a type and precision appropriate to the needs of the network as a whole. To maintain comparability of data collected at North Dakota atmospheric-deposition network sites, common instrumentation is used throughout. Use of standard instrumentation also facilitates stocking of spare parts for field maintenance and development of training procedures for field observers and technicians.

Although the North Dakota network is not part of one of the national networks, such as the National Trends Network or the National Atmospheric Deposition Program, network data must be suitable for comparison with data collected by these national networks or by other networks in adjacent states if regional interpretation is to be possible. Standardization of all instrumentation in the regional networks would limit the scope of investigations and the innovative development of new methodology. However, to maintain compatibility of data among the regional networks, instrumentation should respond similarly to the physical aspects of deposition. If network design requires the use of instrumentation with different response characteristics, side-by-side response evaluation is recommended to establish the limits of data comparability.

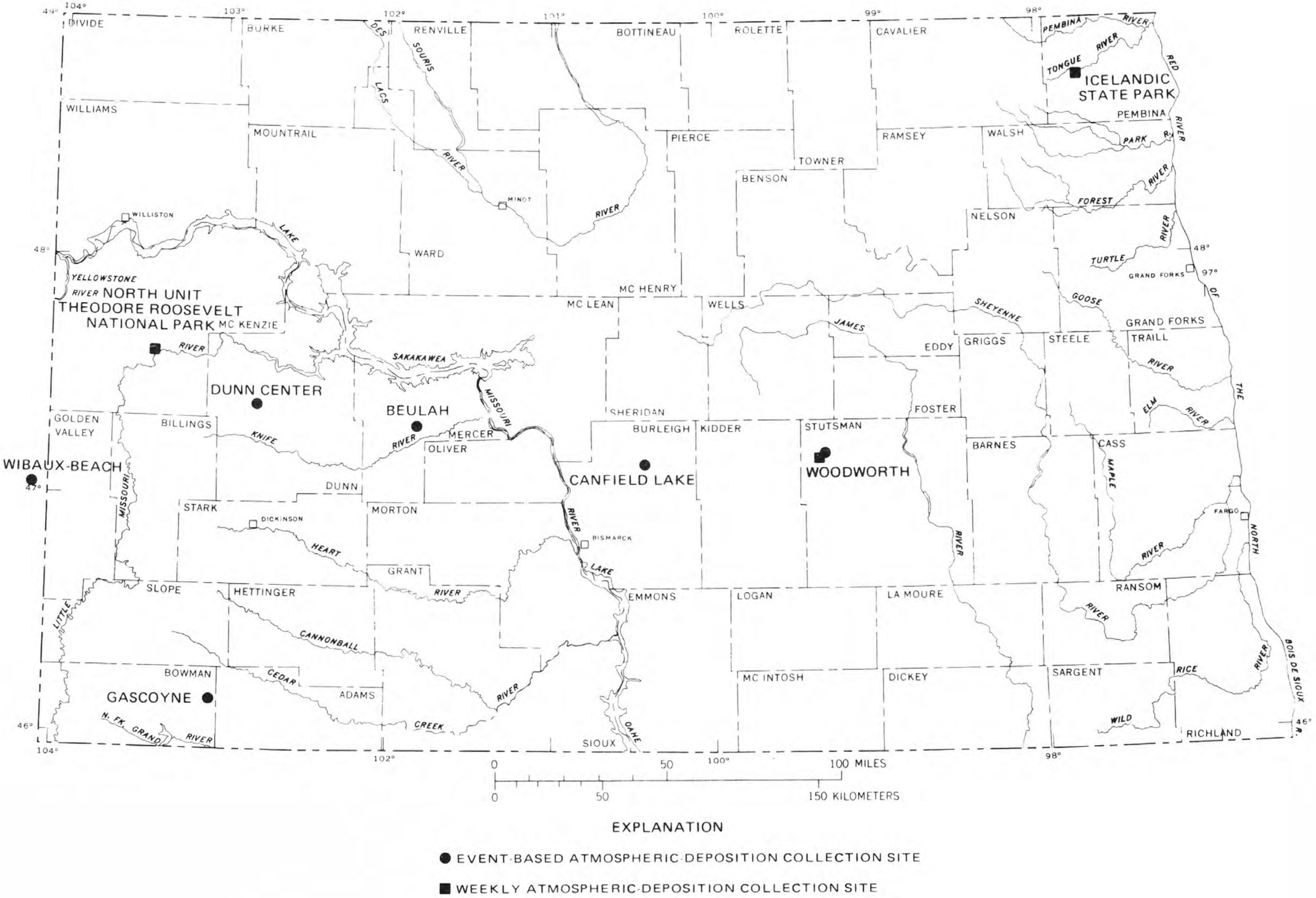

FIGURE 1.—Locations of collection sites in the North Dakota atmospheric-deposition network.

A National Trends Network site is scheduled to be located adjacent to one of the North Dakota sites (Canfield Lake) to determine data comparability between the two networks. Adjacent operation of a network event collector and a National Atmospheric Deposition Program weekly collector in the North Unit of Theodore Roosevelt National Park was undertaken for 6 weeks. Data comparability between the National Atmospheric Deposition Program and the North Dakota network is summarized in table 1. Weekly precipitation samples are characterized by higher calcium, magnesium, sodium, sulfate, and chloride concentrations than composited event samples collected over the same period. The additional concentrations may be accounted for by contamination with dry deposition. This contamination also increases sample pH. Weekly samples also are lower in nitrate and higher in ammonia concentrations than composited event samples collected over the same period. Conversion of nitrate to ammonia and subsequent volatile loss of some of this ammonia is believed to to explain these observations. This conversion may be mediated by biological activity within the sample containers.

All field instrumentation currently in use in the North Dakota network is listed in table 2. Complete descriptions of each principal piece of instrumentation follow.

Collector

The importance of simultaneously collecting both wet and dry deposition has long been established (Garland, 1976; Wiersma and Crockett, 1978). The National Atmospheric Deposition Program and the National Trends Network have both adopted collectors based on the design of the U.S. Department of Energy's Health and Safety Laboratory (HASL) that are capable of sampling both wet and dry deposition (Galloway and Likens, 1976). The Aerochem Metrics Model 301 Automatic Sensing Wet/Dry Precipitation Collector, the Geotech Environmental Equipment Model 0600 Automatic Wet-Dry Precipitation Collector, or their equivalents are usually employed for this purpose. A schematic diagram of the HASL-type collector used in the North Dakota network is shown in figure 2.

The HASL-type collection system consists of two containers and a common lid. The collectors are designed to hold dual 3.5 gallon buckets. Bucket composition varies depending upon the constituents to be measured in the collected sample. Plastic or teflon buckets are recommended for inorganic constituents and glass buckets for organic constituents. The seal between the bucket and lid consists of a plastic foam gasket attached under the lid. The lid is held in place by a spring. Unless the tension on the spring is very tight, strong winds may lift the lid allowing contamination of the wet-deposition bucket to occur. The lid seals the wet-deposition bucket when precipitation is not occurring, minimizing alteration of the sample by evaporation and contamination by dry deposition and other

TABLE 1.--Statistical comparison of samples collected by the North Dakota atmospheric-deposition network event collector and an adjacent National Atmospheric Deposition Program (NADP) weekly collector in the North Unit, Theodore Roosevelt National Park, June 1-July 15, 1980

[All concentrations are volume-weighted means of all wet deposition collected over the test period in microequivalents per liter (μeq/L)]

Constituent	Mean composition of weekly wet deposition (NADP) (2 samples)	Mean composition of event wet deposition (5 events)	Mean composition of composited wet deposition (composited 5 events)	Percent difference weekly:event
Ammonium as NH_4	38	27	25	+41
Calcium as Ca	42	18	17	+133
Chloride as Cl	36	16	16	+125
Hydrogen ion as H	8	17	16	-53
Magnesium as Mg	19	8	8	+138
Nitrate as NO_3	27	44	42	-39
Potassium as K	4	4	4	0
Sodium as Na	16	5	5	+220
Sulfate as SO_4	48	16	15	+200

TABLE 2.--Field instrumentation

Precipitation collection apparatus

1 - Aerochem Metrics 301 Automatic sensing Wet/Dry Precipitation Collector or equivalent HASL-type collector1/.

Weather station

2 - Belfort No. 5-780 dual traverse weighing rain gage.

1 - Omni Data Datapod data logger.

1 - Campbell Scientific Model CR5 digital data logger and cassette recorder.

1 - Weathertronics Model F110 recording analog barometer.

Air-quality instrumentation

1 - Research Appliance Total Particulate Membrane Sampler with Research Appliance Stacked Filter Unit.

Optional air-quality instrumentation

Bendix 8101C Oxides of Nitrogen Analyzer.

Meloy Sulfur Dioxide Analyzer.

Meloy Ozone Analyzer.

Thermal Electron Sulfur Dioxide Analyzer.

Thermal Electron Hydrogen Sulfide Analyzer.

Field laboratory

1 - 8x8 ft metal building.

1/ The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

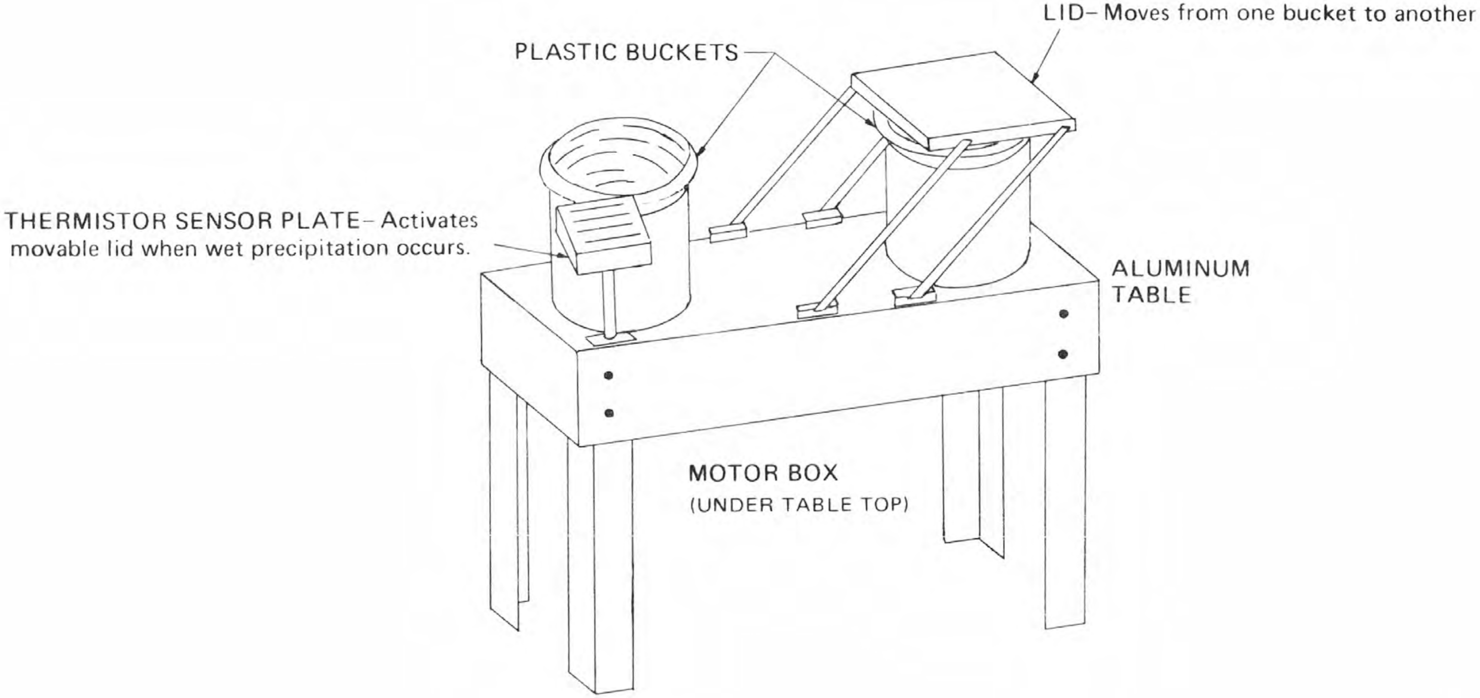

FIGURE 2.—HASL-type automatic wet-dry atmospheric-deposition collector.

external sources. When precipitation occurs, the lid moves off the wet-deposition bucket and covers the dry-deposition bucket. The common lid is driven by a motor activated by a moisture sensor. The sensor consists of a heated plate and a grid superimposed closely above it. To modify sensor response, spacing between the plate and the grid may be varied by adjusting a screw or by adding or removing teflon spacers. The sensor is activated when moisture causes a short between the plate and the grid. Two heating circuits are connected to the plate. The principal heating circuit is activated whenever the lid lifts off the wet-deposition sample bucket. The circuit heats the sensor plate to about 55°C, increasing the rate of evaporation of water from the sensor. The more rapidly the lid covers the wet-deposition bucket after a precipitation event has occurred, the less potential exists for contaminating the sample. The second heating circuit is activated when the temperature falls below approximately 2°C and assists in keeping the sensor free of ice or snow buildup. Temperatures generated by the heating circuits are only slightly variable but also may be used to adjust sensor response.

Side-by-side evaluations of the Aerochem Metrics Model 301 and the Geotech Environmental Equipment Model 0600 were conducted by the North Dakota District in 1981. It was determined that both collector models could be calibrated over comparable sensitivity ranges in terms of their response to precipitation events. The Aerochem Metrics Model 301 has a flat grid plate on the sensor, whereas the Geotech Environmental Equipment Model 0600 has a rounded grid plate. Because of its shape, the rounded grid plate was slightly less consistent in its response to moisture and was more difficult to adjust. The Freund Can Company linear polyethylene buckets supplied with the Geotech Environmental Equipment Model 0600 were less dense and contained more impurities than the Vulcalon linear polyethylene buckets supplied with the Aerochem Metrics Model 301. Acid leaches of Freund Can Company buckets were significantly more enriched in several trace elements than leaches of Vulcalon buckets (table 3). Representatives of Geotech Environmental Equipment and Freund Can Company have subsequently indicated that this problem has been corrected. Aerochem Metrics Model 301 collectors are used as standard equipment in the North Dakota network; Geotech Environmental Equipment Model 0600 collectors are substituted when equipment failure requires collector substitution. All buckets used in the project are supplied from Vulcalon in order to minimize questions of inconsistent background bucket contamination.

Several modifications to the standard design of the Aerochem Metrics Model 301 collector have been made for the purposes of the North Dakota network; however, none of these modifications affect the basic operation of the collector. Because the purpose of the network requires analysis for trace metals that might be

TABLE 3.--Statistical comparison of acid leaches of Freund Can Company and Vulcalon Corporation sample buckets

[For purposes of statistical treatment, values of <x are treated as 1/2 x; all concentrations are in micrograms per liter (μg/L); < indicates less than. Leach volumes of 1 liter were used in all cases]

Constituent	Freund Can Co. Mean of 10 acid leaches (μg/L)	Vulcalon Mean of 10 acid leaches (μg/L)	Percent difference
Aluminum	<3	<3	--
Arsenic	<1.0	<1.0	--
Cadmium	.2	<.2	100
Chromium	<1	<.5	100
Copper	4	1.0	300
Iron	2	<2	100
Lead	2	1	100
Manganese	2	.2	900
Mercury	.11	.03	270
Molybdenum	3	2	50
Nickel	<1.0	<1.0	--
Selenium	.2	.1	100
Silver	.4	.2	100
Vanadium	<5	<5	--
Zinc	5	<3	230

major pollutants resulting from combustion of coal, all exposed metal surfaces of the collector are coated with tetrafluoroethylene (Fluoro-Glide CPG Spray Film, Chemplast, Inc., Wayne, New Jersey) to minimize contamination from weathering. Similarly, a teflon-coated polypropylene antisplash screen has been installed to reduce splash over. Because North Dakota usually is very windy, collectors also must be protected from ground-level aeolian saltation. Accordingly, collectors are equipped with alter-type wind screens and elevated 10 feet above ground surface on steel scaffoldings. Elevation of the collectors also limits contamination of dry-deposition samples with locally derived soil particles. Scaffoldings are painted with marine epoxy paint and surfaced with tetrafluoroethylene. Plastic foam gasket seals under the collector lid and butyl rubber gasket seals in the sample container lids are covered with teflon tape.

Additionally, a 1-quart (2.4-inch outside diameter), high density, linear polyethylene container is strapped to the wet-deposition bucket with teflon-coated hose clamps. This container is positioned under one of the outside corners of the collector lid so that it acts identically to the main wet-deposition bucket. Preliminary wet-deposition temperature, specific conductance, and pH are determined on samples removed from this smaller container to preserve the integrity of the sample.

Collectors may be powered either by 12-volt DC storage batteries or 110-volt AC power. Both power sources have their advantages and disadvantages. With storage batteries, operation is not lost if AC power failure occurs. However, batteries must be recharged; and discharge time varies with regional and seasonal changes in climate. It is particularly difficult to maintain battery charge levels during North Dakota winters. North Dakota collectors are powered by standard 12-volt DC marine lead-acid batteries continuously recharged by a trickle charger connected to the 110-volt AC powerline at each site. Similar procedures were adopted by the U.S. Geological Survey in Montana to recharge 12-volt DC batteries from solar panels (J. R. Knapton, oral commun., 1983).

Two Aerochem Metrics collectors are installed at each site in the North Dakota network. Dual collectors produce a larger volume of sample at these semiarid sites where precipitation volumes often are very small. Usually, the sample from one collector is analyzed for "major" constituents (minerals and nutrients); and the sample from the other collector is analyzed for trace constituents and special parameters. The bucket used for collection of the sample for trace-element analyses is cleaned by acid leaching; but the bucket used for collection of the sample for nutrient analysis is cleaned without use of acids, which might leave nutrient-rich residues behind. Recovery of different constituent concentrations from buckets of different collectors requires the collector efficiencies to be comparable.

The site chosen for installation of the collector must be free of all obstructions within a cone above 30° from the horizon. As a general rule of thumb, this requirement means that no object should be closer to the collector than twice its height. Adjacent collectors and rain gages should be separated by at least a distance equal to the height of the collector. This spacing minimizes interference and splash effects. To ensure that the dry-deposition bucket does not act as an obstruction for the wet-deposition bucket, the collector should be oriented with the dry-deposition bucket downwind of the wet-deposition bucket. Orientation perpendicular to the prevailing wind direction as advocated by Topol and others (1981) in high-wind prone areas like North Dakota usually results in damage to the motor drive for the collector lid. However, if stronger motor drives become available, it would be preferable to follow the suggestions of Topol and others (1981).

Weather Station

As the composition of atmospheric deposition is controlled by meteorological conditions as well as atmospheric emissions, all atmospheric-deposition collectors should be coupled with a weather station. Where suitable, atmospheric-deposition collectors are sited adjacent to or near weather stations of the surface-water coal-hydrology program, the North Dakota State Health Department, or the National Weather Service. Where the locations of existing weather stations do not correspond to collector siting requirements discussed previously, similar weather stations (fig. 3) are installed at collector sites. Recording rain gages at the weather stations provide information on rain volume necessary to determine collector efficiency. Other meteorologic instrumentation at the weather stations provide data required to trace storm tracks across North Dakota.

Surface-water coal-hydrology weather installations have been described by Reid and Ghering (written commun., 1980). Wind speed, run, and direction; solar radiation; air temperature; relative humidity; and precipitation volume (table 4) are continuously recorded by a Campbell Scientific Model CR5 digital data logger and cassette recorder. At atmospheric-deposition collection sites, this system is supplemented by a Weathertronics Model F110 recording analog barometer.

North Dakota State Health Department weather installations have been described by Schock and Crawford (1977) and National Weather Service stations by Jensen (1974). Weather stations operated by both agencies include the above instrumentation or its equivalents.

The recording rain gage is required by all stations in the National Atmospheric Deposition Program and in the National Trends Network. The recording rain gage at each site measures

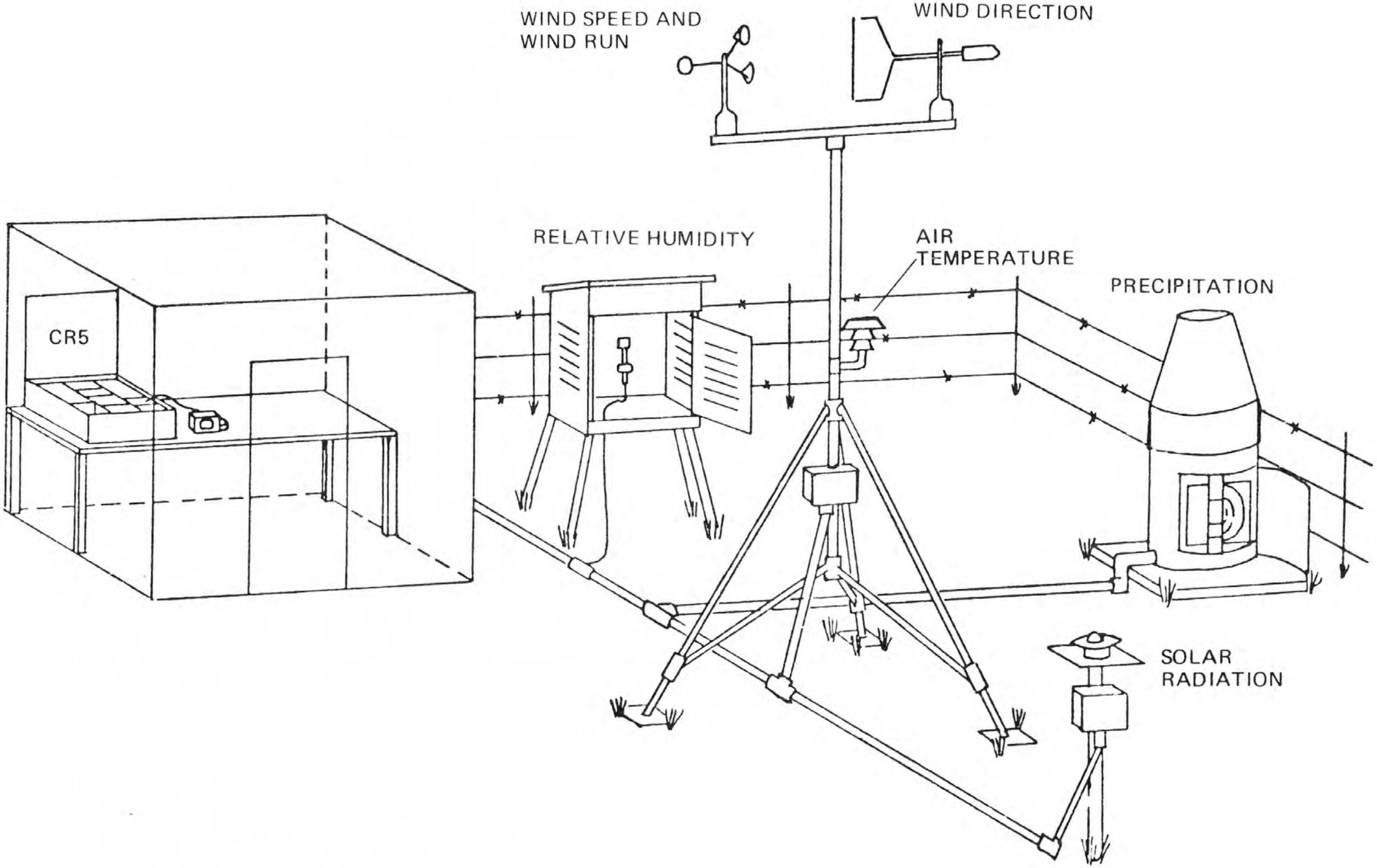

FIGURE 3.—Meteorological data-acquisition system for the North Dakota atmospheric-deposition network. (Modified from Reid, Joe, and Ghering, Garth, Jr., written commun., 1980.)

TABLE 4.--North Dakota weather station sensors and specifications

[Modified after Reid and Ghering, written commun., 1980; mi/h = mile per hour]

Measurement	Sensor	Supplier and manufacturer	Accuracy	Range
Precipitation.	Weighing-bucket precipitation gauge, model 5-780 with dual traverse, rain trace, and event marker.	Belfort Equipment Corporation.	±0.01 inch.	0 to 20 inches.
Wind run, wind speed.	Anemometer model 2030.	Weathertronics, Inc.	±0.15 mi/h.	0.5 to 100 mi/h.
Wind direction.	Wind vane model 2020.	Weathertronics, Inc.	±2 degrees.	0 to 360 degrees.
Solar radiation.	Spectral pyranometer model PSP.	Eppley Laboratory, Inc.	±1 percent from -50 degrees C to +50 degrees C.	0.3 to 3.0 microns.
Air temperature.	Linear thermistor model 4480.	Weathertronics, Inc.	±0.1 degree C.	-50 to +50 degrees C.
Relative humidity.	Solid state model 5120.	Weathertronics, Inc.	±1 percent nominal.	0 to 100 percent.

the total amount of precipitation that occurs during an event. To serve as a reference for determining the collection efficiency of the collectors, the rain gages must be able to measure precipitation to approximately 0.01 inch and be accurate within 2 percent. Two basic types of rain gages are available: the weighing-bucket-type and the tipping-bucket-type gage. Because the accuracy of the weighing-bucket-type rain gage is independent of precipitation rate, the North Dakota network uses Belfort No. 5-780 dual traverse weighing gages, which have been modified to use battery-operated clocks and chart recorders. Rain gages also are modified with an event marker which indicates when the atmospheric-deposition collector wet-deposition bucket is open or covered. The correlation of the event marker with actually plotted rain accumulations serves as a check on the performance of the collector and indicates when adjustments should be made or when malfunctions have occurred. If rain gages are to serve as references for the collectors, they must be installed adjacent to and at the same height as the collector (10 feet above land surface). Adjacent collectors and rain gages should be no closer than the height of the taller of the two (approximately 4 feet). Accumulated precipitation is recorded every 5 minutes on an Omni Data Datapod data logger attached to the rain gage. The data logger is powered by batteries adequate for up to 6 months of operation; however, during operation in the coldest months of winter, battery replacement may be necessary as often as every 2 months. The data logger records precipitation volumes on an electronic memory chip which is read and interpreted by the U.S. Geological Survey computer. At North Dakota sites, a second rain gage is installed at ground level to provide an indication of ground-truth magnitudes and for comparison with ground-mounted National Atmospheric Deposition Program and National Trends Network installations.

In addition to meteorological instrumentation, North Dakota State Health Department stations usually are instrumented with air-quality monitoring equipment as part of the PSD program. This additional instrumentation usually includes a Bendix 8101C Oxides of Nitrogen Analyzer, Meloy Sulfur Dioxide Analyzer, Meloy Ozone Analyzer, Thermal Electron Sulfur Dioxide Analyzer, and Thermal Electron Hydrogen Sulfide Analyzer.

A modified Research Appliance Total Particulate Membrane Sampler (0.4 μm) attached to a Research Appliance Stacked Filter Unit also is installed at each collection site to sample ambient air aerosol composition. Filters are analyzed to determine suspended particulate and aerosol nitrate and sulfate concentrations as described by the North Dakota State Health Department (1979) according to guidelines set forth by the U.S. Environmental Protection Agency (1971).

FIELD LABORATORY

All atmospheric-deposition collection sites should have clean, dry laboratory space available to facilitate field processing of the samples and provide shelter for some of the instrumentation. At sites in the North Dakota network, 8-foot square metal sheds are installed. Sheds are insulated with untreated fiberglass bats, and interiors are finished with easily cleaned vinyl panels. A temperature controller is installed to maintain the facility above 4°C in the winter and below 30°C in the summer. Infrared heat lamps are utilized to provide additional heating to some instrumentation during winter months. Laboratory benches attached to shelter walls support the meteorological data logger and provide space for the field processing of atmospheric-deposition samples.

Each shelter is equipped with the laboratory instrumentation required to weigh atmospheric-deposition samples; to determine sample volume; and to measure sample pH, conductivity, and temperature. Facilities also are provided to filter and preserve samples. At sites where temporary storage of an event sample collected by a field observer may become necessary, a refrigerator is installed in the shelter to maintain the sample at approximately 4°C. A list of the typical laboratory instrumentation maintained at a field laboratory is presented in table 5. A detailed discussion of field laboratory instrumentation is presented in subsequent sections.

The shelters also serve as on-site storage areas for extra clean sample buckets, spare parts for the instrumentation, and tools necessary for repair and maintenance of site instrumentation. A list of stored equipment is presented in table 6. Manufacturers' manuals for operation and repair of all site instrumentation are shelved at each site for easy reference.

Resistance Thermistor

A Cole-Parmer Model 8520 Digi-Sense Digital Thermistor Thermometer is used to determine field precipitation temperature. Periodic calibration with respect to a Curtin Matheson 63C ASTM Precision Thermometer assures instrument accuracy of ±0.2 percent and repeatability of ±0.3°C. A precision of at least ±0.5°C is necessary for accurate correction of pH and specific-conductance data. The wide temperature range (-30° to +100°C) of the Model 8520 Thermometer permits measurement of snow as well as rain temperatures using the Model 8410-22 Tubular Thermistor. Substitution of the Model 8415-25 Air Temperature Thermistor permits accurate determination of ambient air temperature and calibration of the weather-station thermistor.

TABLE 5.--Field laboratory instrumentation

Field analysis equipment

Cole-Parmer Model 8520 Digi-Sense Digital Thermistor Thermometer.

Cole-Parmer Model 8410-22 Tubular Thermistor.

Cole-Parmer Model 8415-25 Air Temperature Thermistor.

Beckman Model RC-19 Conductivity Bridge.

Beckman CEL-6J Fill-type Conductivity Cells 0.1 and 1.0 cell constants.

Orion Research Model 801A Digital Ionanalyzer.

Orion Research Model 91-62 Combination pH Electrode.

Field processing equipment

Mettler PC4400 Top-loading Balance.

U.S. Geological Survey Cone Splitter.

Manostat Junior Cassette Peristaltic Pump.

Fisher 9-788 Filtration Apparatus.

Millipore XX1104710 Filter Holder.

Koolatron P34A Thermistatically Controlled Portable Refrigerator.

National Appliance Company 630 Oven.

Gelman Water-I Water Purifier.

TABLE 6.--Support equipment stored in the field laboratory

[Supplies maintained at indicated levels by field technician; kg, kilogram; mL, milliliter]

Miscellaneous laboratory supplies

1 - Set ASTM standard weights (0.5, 1.0, and 2.0 kg weights).
3 - Wash bottles.
1 - Case of sterile, singly wrapped pipets (5 mL).
1 - Case of sterile, singly wrapped pipets (10 mL).
1 - Box of lint-free tissues, such as Kimwipes.

Miscellaneous collector supplies

8 - Buckets for collector, clean and doubly wrapped.
12 - Fuses for sampler.
2 - Sampler sensors.
2 - Sampler motor boxes.
16 - Polyethylene bags with plastic ties, clean.
1 - Polypropylene antisplash screen.
1 - Alter-type wind screen.
2 - Plastic foam gasket seals.
2 - Butyl rubber gasket seals.
2 - One-quart polyethylene wide-mouth bottles.

Miscellaneous weather station supplies

1 - Rain-gage clock.
3 - Rain-gage chart clips.
3 - Rain-gage chart paper (package of 100).
1 - Rain-gage pen and ink, set.
16 - AA batteries for Omni Data data logger.
1 - Electronic memory chip for Omni Data data logger.
3 - Relative humidity/temperature chart paper (package of 100).
3 - Relative humidity/temperature chart clips.
1 - Relative humidity/temperature pen and ink, set.
3 - Barometer chart paper (package of 100).
3 - Barometer chart clips.
1 - Barometer pen and ink, set.
3 - CR5 paper tape rolls.
3 - CR5 magnetic tape cassettes.
3 - CR5 printer ribbons.
1 - Relative humidity sensor.
2 - Particulate membrane filter holders.
1 - Particulate membrane filter, box.

Miscellaneous repair supplies

1 - Marine epoxy paint, pint.
2 - Spray cans of tetrafluoroethylene.
1 - Tool chest.
2 - Infrared heat lamps.

Conductivity Bridge

Most precipitation samples have a specific conductance between 5 and 100 µmhos/cm. Thus, the conductivity meter and cell selected must have a range of 0 to 1,000 µmhos/cm. A precision of at least ±0.5 percent of the selected range and an accuracy of at least ±1.0 percent of the range are desirable in the conductivity meter selected for measurement.

For precision determination of field conductivity at North Dakota atmospheric-deposition collection sites, a Beckman Model RC-19 Conductivity Bridge is used in conjunction with a fill-type cell (Beckman CEL-6J). The cell is of the form designed by Jones and Bollinger (1931). The Model RC-19 is manual or automatic temperature compensating; in practice, automatic temperature compensation has been found to yield 0.5 percent to 1.0 percent greater precision in the compositional range of samples measured. In the field, routine determinations are made simultaneously both with and without the use of the automatic temperature compensator.

Fill-type cells require slightly more sample but have been determined to be more accurate on low concentration samples than dip cells. Cells of constants 0.1 per cm^{-1} and 1.0 per cm^{-1} are employed depending upon expected specific conductance (table 7). Precise cell constants are determined for each new cell using ASTM Test Method D1125. Thereafter, cell constants are reconfirmed during each calibration relative to Beckman Model CEL-BB1-Y8F laboratory standard cells.

TABLE 7--Selection of appropriate conductivity cell

Specific conductance (micromho per centimeter at 25 degrees Celsius)	Specific resistance (ohm-centimeter)	Use cell constant (per centimeter)
<2	>500,000	0.1 or less
2-200	500,000-5,000	0.1
20-2,000	50,000-500	1
200-20,000	5,000-50	10
2,000-200,000	500-5	100
>200,000	<5	100 or higher

pH Meter

Because pH is such a critical parameter for environmental interpretation of precipitation composition, it must be measured as precisely as possible. The pH meter and electrode should be able to measure to ±0.03-pH unit precision with an accuracy of 0.05 unit. To accomplish this precision, meters must have an impedance of least 1,011 ohms.

An Orion Research Model 801A Digital Ionanalyzer is used in conjunction with an Orion Research Model 91-62 Combination pH Electrode for precision measurement of field pH at North Dakota network sites. The Orion 801A Ionanalyzer displays either pH in 0.001 unit increments with a repeatability of ±0.001 pH unit or electrode potentials in 0.1 mv increments with ±0.1 mv repeatability. A combination electrode is used because it requires less sample and washing than two separate electrodes. The Orion 91-62 electrode has an unshielded conical glass bulb, which is much easier to clean than a shielded electrode. The electrode is filled with Orion low-conductivity filling solution to shorten response time and limit contamination of the low-conductivity precipitation samples.

Analytical Balance

The volume of precipitation samples collected can be measured with a balance or with graduated cylinders. However, the use of graduated cylinders to measure precipitation volume can introduce contamination and is time consuming. Because the density of precipitation rarely deviates from 1.0 g/mL at 20°C, the weight of the sample may be used as an accurate measurement of sample volume. For event sampling in semiarid climates, the balance should have a capacity of 3,000 g and a sensitivity of at least ±1 g.

Mettler PC4400 Top-loading Balances are used at North Dakota network sites to determine field volumes of precipitation samples. The PC4400 balance has a capacity of 4,200 g, a readability of 0.1 g, and a sensitivity of ±0.1 g. The balance is automatically taring, which reduces the opportunity for measurement errors resulting from nonlevel benches in the field laboratories.

Precipitation volume is compared to the rain-gage values to determine the collection efficiency of the collector. Collection efficiencies of less than 85 percent indicate that collector malfunction may have occurred. Collection differences greater than 5 percent between adjacent collectors at a site indicate the collectors should be recalibrated to comparable sensitivities; resultant data should be used with care if samples from each collector are to be analyzed for different constituents.

Miscellaneous Field Laboratory Instrumentation

Field laboratories also are required to have a variety of supplemental equipment to support the principal instrumentation already discussed. Wet-depositiion samples are split using a lucite cone splitter, as described by U.S. Geological Survey, Water Resources Division, Quality of Water Branch Technical Memorandum 80.17. Sample transfer is performed using a Manostat Junior Cassette Peristaltic Pump. Appropriate splits are filtered using a Fisher 9-788 Filtration Apparatus and a Millipore XX1104710 Filter Holder. All materials in contact with precipitation samples are cleaned as described in a subsequent section on bucket cleaning. Prepared samples are maintained at 4°C in a Koolatron P34A Thermostatically Controlled Portable Refrigerator until analysis. Filters are dried in a National Appliance Company 630 Oven.

Type I water is prepared on site. Distilled water from the central support laboratory in Bismarck is transported to the site regularly by field technicians. The quality of the distilled water is assured by passing it through a Gelman Water-I unit in the field laboratory prior to use.

PROGRAM PERSONNEL

Because the potential for collection of nonrepresentative samples, contamination of collected samples, and analytical error is so great in sampling and processing atmospheric deposition, all personnel involved in an atmospheric-deposition program must be chosen and trained with care. For the purposes of the North Dakota network, it was decided that all personnel involved in the network should have scientific training, preferably in chemistry. Personnel should include a network manager, field observers, field technicians, laboratory technicians, and laboratory analysts.

Field Observers

The principal responsibility of the field observer is to notify the network manager immediately upon termination of a precipitation event or of malfunction of any of the field instrumentation. Because precipitation events in North Dakota may be very localized, it is desirable that the field observer live within a few miles of the collection site. Thus, the requirement of field-observer proximity to the collection site is a limitation on either siting or observer qualifications.

In the North Dakota Atmospheric-Deposition Network, the availability of qualified field observers was included in criteria for collection-site selection. As observers serve on a voluntary basis, it is imperative that they have an interest in the program as well as technical ability. Accordingly, all individuals approached to serve as field observers in the North

Dakota program were selected from the membership roles of the North Dakota Academy of Science or the North Dakota Chapter of the American Chemical Society or from other State or Federal agencies.

Field observers also keep records of meteorological conditions within each event period. The form used by observers in the North Dakota program to record meteorological information is shown in Supplement 2.

The most chemically knowledgeable observers eventually may perform the field processing of precipitation samples. Then, the field technician need only retrieve the sample from the field laboratory cooler and transport it to the analytical laboratory. Under these circumstances, the field technician may visit more sites during the prescribed 12-hour period following the termination of an event in which he has to deliver the samples to the analytical laboratory. Thus, fewer field technicians may be required to collect samples from all sites receiving precipitation during the passage of a storm cell.

Field observers are instructed in their responsibilities by the network manager and reviewed at least quarterly by the field technician. Observers also are provided with copies of this manual and all manufacturers' manuals for instrumentation located at their site. Additional training is provided as required.

Field Technicians

Field technicians provide all the support necessary for routine operation and maintenance of the sites. At a minimum, the field technician is responsible for the retrieval of samples processed by the field observer within 12 hours of the termination of the event. At sites where the resident observer has minimal chemical training and background, the field technician also is responsible for field processing of the atmospheric-deposition samples collected. Because of the diversity of responsibilities with which the field technician is entrusted, it frequently is desirable to spread the responsibilities for a site among several technicians with differing abilities.

In North Dakota, field technicians commonly are responsible for either the water-quality or mechanical aspects of the operation of two to three sites. Technicians, trained in water-quality sample processing and retrained in the complexities of handling atmospheric deposition, normally perform field processing or retrieval of event samples. These technicians are on call 24 hours a day, 7 days a week. Other technicians trained in mechanical and electrical aspects of site instrumentation perform repairs when notified of a malfunction by the field observer and perform routine maintenance on a regular schedule, usually once a month.

Laboratory Technicians

Laboratory technicians are responsible for the cleaning of all surfaces which may come in contact with sampled atmospheric deposition. These surfaces include sampling buckets, filter apparatus, cone splitters, and sample bottles.

Because laboratory technicians must handle hazardous chemicals and be very careful of contamination, a chemical background is required. In North Dakota, a single laboratory technician with at least a 2-year college degree in chemistry is assigned responsibility for cleaning all sample collection and handling equipment. Use of a single person for this purpose maintains cleaning consistencies which minimize quality-assurance procedures.

Laboratory technicians are trained by the network manager who is responsible for supervision and quality assurance of the technician's work. Training includes preparation of triple-distilled acids and their use for cleaning plastics and glass after the methods of Zief and Mitchell (1976). This manual serves as the guide for laboratory practices.

Laboratory Analysts

Laboratory analysts must possess a degree in chemistry and be experienced in an aspect of analysis of precipitation for one or more of the desired parameters. Techniques required include ion chromatography; flame, graphite furnace, and metal hydride atomic-absorption spectrometry; X-ray diffractometry; and acid dissolution.

Supervision and quality control of laboratory analysts is the direct responsiblity of the network manager. Analysts are encouraged to suggest and experiment with alternative analytical procedures, but approval of analytical methods is the responsibility of the network manager.

Analysts receive a copy of this manual and are provided with additional training in analysis of atmospheric deposition as appropriate. When possible, analysts are encouraged to spend a period of time working at one of the U.S. Geological Survey National Water-Quality Laboratories to observe their practices in the analysis of precipitation and low-ionic strength natural waters.

MAINTENANCE OF FIELD INSTRUMENTATION

Maintenance of field instrumentation includes acceptance tests upon installation and at regularly scheduled intervals thereafter, periodic instrument calibration, and servicing as required. Acceptance testing and calibration should be performed by field technicians with the support and assistance of qualified electrical technicians as required. It is the responsibility of the field observer to regularly inspect the operation of all instrumentation and report malfunctions to the project manager. Simple repairs may be performed by the field observer, but all other repairs should be referred to a qualified technician. All maintenance steps performed should be recorded in the field maintenance log (Supplement 3).

Collector Maintenance

Collector acceptance tests include proper operation of the following components:

1) Sensor heating element should be activated when the sensor is shorted. Sensor-plate temperature should attain 50-60°C. Temperatures attained may be determined by placing a thermistor probe on the sensor plate near the screw head in the plate. If the sensor temperature is incorrect, it can be adjusted by turning the potentiometer screw marked "TH" inside the sensor box. Sensor should cool when shorting material is removed.

2) Sensor heating element should be activated when sensor temperature falls below 2°C. Sensor performance may be checked by placing ice on the sensor or by using a heater/ammeter test plug which is available from Aerochem Metrics. The test plug connects between sensor and table cannon plugs and records the current being received by the sensor plate. A current flow of 0.6-0.7 amperes is considered acceptable. Lesser currents can be boosted only by changing the resistor in the circuit. Thus, in the event acceptable current levels are not attained, the sensor should be replaced with a new sensor.

3) Bucket lid should move off the wet-deposition bucket when sensor is shorted and return to cover the wet-deposition bucket when shorting material is removed from the sensor. If the lid fails to move, first check all fuses. If the fuses are all right, the problem may be either in the sensor or the motor box. Check that the sensor is connected to the motor box and the power is on. If the lid still fails to operate, replace the sensor and motor box separately until operation is restored.

4) Bucket lid should seal tightly over the buckets in each position. If the lid fails to seal, check that the teflon-wrapped foam gasket is in the proper position. If the lid still cannot be made to seal, the collector should be replaced.

Acceptance tests should be conducted on every visit to the site by either the field observer or the field technician. At a minimum, the acceptance tests should be performed during the weekly visit made by the field observer to service the total particulate filter sampler.

The only part of the collector requiring calibration is the sensor. Sensor efficiency of adjacent collectors must be identical, and the sensor efficiencies of all collectors in the network should be comparable. As previously discussed, sensor efficiency may be adjusted by modifying the spacing between the sensor plate and grid. This spacing may be adjusted by varying the number of thin teflon washers used as spacers between the grid and the heating plate. Sensor efficiency also may be adjusted by changing the temperature of the sensor within the prescribed ranges.

The only additional service the collector should require is winterizing. The normal operation of the collector is impaired in many winter conditions. Snow may fall off the sensor before melting and thus not short the sensor, or the sensor may freeze over completely leaving the wet-deposition bucket uncovered during periods of nonprecipitation. Even more seriously, moving parts of the collector may freeze which can result in burning out the motor.

For winter operation, the heating cycle on both sensor circuits should be adjusted near their maxima, while still maintaining network calibration. This adjustment will assist in keeping the sensor free of ice build-up and will melt snow more rapidly so that flakes will be more likely to melt and short the sensor before blowing away.

Freezing of the collector lid to the bucket may be a significant problem, especially if snow is allowed to build up on the collector lid or ice fogs are prevalent in the area of the collector site. To prevent snow accumulation on the lid, a peaked roof should be attached to the lid. The roof sold by Aerochem Metrics also fits the Geotech Environmental Equipment collector. To maximize roof efficiency and prevent ice accumulations from fog, a heat lamp is installed under the roof as described by Topol and Ozdemir (1981). The roof also is lined with styrofoam to prevent formation of a hot spot on the roof. To compensate for the additional weight of the lid, two 3-inch U-bolts are added to the counterweight.

The National Atmospheric Deposition Program also recommends that the lid arms be wrapped in plastic to decrease the potential for freezing of the lid arms to the table (C. W. Martin, Hubbard Brook Experimental Forest, written commun., 1980). The experience of the North Dakota network is that the teflon coating used on all North Dakota collectors is sufficient to prevent such freezing under all but the most extreme circumstances.

For preventive maintenance, the collector lid seal should be replaced at least annually. Additionally, the sensor plate should be cleaned monthly with a mild detergent.

Weather Station Maintenance

All weather station instrumentation requires regular maintenance. The field observer is responsible for routine maintenance and record keeping. All other services should be provided by qualified field or electrical technicians.

Rain-gage acceptance tests should be performed prior to installation and once a month thereafter. Acceptance tests include a check of:

1) Sensitivity and accuracy. Weights are provided by the manufacturer equivalent to 1-inch multiples of water equivalents. The rain gage should be adjusted according to manufacturer's instructions to provide a correct reading for weights covering the expected range of rainfall equivalents.

2) Clock function. The clock should be wound and set for the correct time. After 24 hours, clock time and pen traces on the chart recorder should be correct to within 30 minutes. If the clock fails to meet these specifications, it should be replaced.

3) Pen and recorder function. Offset the event and weight trace pens by about 4 hours so that they do not interfere with each other. Make sure that both pens contact the paper and are writing. If pens touch the chart paper but do not write, check ink and use a toothpick to draw some ink down the pen to the chart paper. Check to see that the Omni Data Datapod data recorder registers the same times and weights as the chart.

4) Event-recorder pen function. To check the event-recorder pen, connect the collector and the rain gage according to manufacturer's instructions and short the collector sensor. The event-recorder pen should move upwards about 1/8 inch and return to baseline once the short is removed. If the event-recorder pen fails to function, replace the entire event recorder and return it to the manufacturer for repair.

Routine weekly servicing of the rain gage to be undertaken by the field observer includes:

1) Checking the zero setting on the rain-gage pen. With no precipitation in the rain-gage bucket, the zero setting may be adjusted by turning the red fine adjust screw.

2) Checking the batteries in the rain-gage clock and resetting the time if neçessary.

3) Inspecting the pens to see if they have sufficient ink and are writing.

4) Replacing the rain-gage chart. Be sure access door is closed when you are finished.

5) Inspecting the rain-gage bucket for water and removing any excess water.

Additional monthly servicing requirements include:

1) Checking the rain gage with a level to insure that it is still horizontal.

2) Replacing the batteries in the Omni Datapod recorder.

3) Replacing the electronic memory chip in the Datapod and returning the old memory chip to the District office for data processing.

4) Replacing the microbarograph chart.

5) Replacing the relative humidity chart.

Winter maintenance for the rain gage is designed to minimize problems that may develop due to snow filling or drifting out of the gage or to precipitation freezing in the bucket. For winter use, the funnel should be removed from the inlet mouth to prevent sealing of the weighing gage by snow or ice. Also, about 2 inches of an ethylene glycol-methyl alcohol (40-60) antifreeze mixture should be added to the bucket to prevent freezing of precipitation in the gage. Also, addition of about 6 ounces of 10W motor oil to the antifreeze retards evaporation. The bucket should be emptied before the total volume reaches 5-inches depth, as the weighing gage is less accurate above that volume. Antifreeze and motor oil should be replaced prepatory to the next precipitation event.

Performance of the remaining meteorological sensors should be checked on each visit of the field technician, or at least every 2 weeks. Meteorological parameter values printed on the paper-tape output of the data logger are hourly averages so they will not correspond exactly to instantaneous readings. However, the scan button on the CR5 data logger may be used to print instantaneous data for the parameters it records. Instantaneous measurement of wind velocity and direction may be made using a AirGuide WinDial hand-held anemometer. Extreme care must be used in interpreting instantaneous readings of wind velocity and direction before deciding that recorded values are within acceptable ranges because both values may range widely over very short intervals of time. Instantaneous air temperature may be measured with the field laboratory resistance thermometer equipped with the Model 8415-25 Air Temperature Thermistor. Instantaneous relative humidity may be measured using a sling psychrometer. Instantaneous barometric pressure may be measured using a Wallace and Tiernan Model WP Barometer corrected for air temperature and relative humidity. As a general rule, discrepancies of more than 10 percent between instantaneous and hourly values should be reported immediately to the network manager unless these discrepancies may be accounted for by trends suggested by previous hourly averages recorded by the data logger. If the relative humidity values are suspect, the gold bead sensor should be carefully inspected for corrosion. Any malfunction should be referred to a qualified electronics technician for repair.

On a weekly basis, the field observer should replace the chart on the back-up Belfort relative-humidity and temperature recorder and on the microbarograph. The paper tape output of the data logger should be rolled up and the amount of remaining magnetic tape confirmed to be adequate.

High volume filters are replaced at 6-day intervals by the field observer. Operation of the filter pump is tested for suction level prior to installation of the new filter. The activator clock is reset prior to restoring power to the filter unit in preparation for the next sample. Malfunction of any aspect of the filtration apparatus should be reported immediately to the program manager. To preserve calibration, the filtration unit should be adjusted and repaired only by trained electronics technicians. Calibration of the filter apparatus must be made annually in accordance with U.S. Environmental Agency (1971) instructions.

Field Laboratory Maintenance

To maintain operation efficiency and to prevent contamination of collected atmospheric-deposition samples, supplies in the field laboratory must be kept at full stock and the area must be kept as free from dirt as possible. It is the responsibility of the field technician to inventory all supplies during each routine visit to the site. Additionally, the operation of the heating system and the charge of all batteries should be checked and serviced as required. Finally, the walls, counter tops, and floors of the laboratory space should be sponged clean using a mild, phosphate-free[1] detergent. All stray refuse and used solutions should be removed from the site. Chemical solutions used as standards should be replaced at least monthly with freshly made solutions.

FIELD METHODS

Field methods include methodology for sampling atmospheric deposition and for maintaining field instrumentation. All these methods are somewhat variable dependent upon local instrumentation and conditions. The following text prescribes recommended procedure under normal network conditions as previously described. All field data from an event are recorded on a single field sheet (Supplement 4) stored in the field laboratory. When the field technician completes his fieldwork and retrieves the sample to the laboratory, field sheets also are returned to the laboratory for entry into the computer data bases. All sample containers are handled wearing nonpowdered, sterile polyethylene gloves.

Sampling Methodology for Wet Deposition

Within 1 hour of the termination of a storm meeting the prescribed definition of an event, the field observer notifies the network manager of the occurrence of an event at his site and of its approximate magnitude. If the event is too small to permit chemical analysis of major minerals and nutrients (<0.1 inch for a single collector or 0.05 inch for composited dual collectors), the network manager will advise the field observer to measure sample temperature, pH, and specific conductance. Wet-deposition buckets should then be sealed, double wrapped in polyethylene bags, and placed in the refrigerator for subsequent retrieval by the field technician. Clean buckets stored in the field laboratory should be placed in the wet-deposition collectors. After retrieval by the field technician, the sample will be measured again to determine pH and specific conductance and then discarded.

If precipitation amounts exceeded the requisite minimum but resumption of precipitation is anticipated, the field observer is requested to remove the wet-deposition buckets, seal them, double

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[1] Most commercial detergents that are labeled phosphate-free actually contain measurable concentrations of this nutrient. The manufacturer of all detergents to be used in this study should be contacted to assure the detergents are truly phosphate-free prior to purchase and use. Labtone, distributed by VWR Scientific Company, is one phosphate-free detergent found suitable for use.

wrap them in polyethylene bags, and place them in the field-laboratory refrigerator for subsequent retrieval by the field technician. Temperature, pH, and specific-conductance measurements should be made on the sample in the special container attached to the wet-deposition bucket. Clean buckets stored in the field laboratory should be used to replace wet-deposition buckets before precipitation resumes. Only field observers with a background in chemistry and also trained as field technicians are permitted to perform the subsequent field processing of collected samples.

If precipitation amounts exceed the requisite minimum and new precipitation is not anticipated, the field observer will be instructed to perform the temperature, pH, and specific-conductance measurements on the sample in the separate container. Unless the field observer is qualified to perform field processing, all remaining sample handling will be undertaken by the field technician upon his arrival at the site.

During performance of the above duties, the field observer also will inspect all field instrumentation for malfunction. In the event he suspects a problem may exist, the field observer immediately should make a return call to the network manager informing him of the problem. Attempted repairs by untrained personnel are discouraged.

The field technician will visit each site assigned to him; complete field processing of the precipitation sample, if necessary; and return to the laboratory within 12 hours of notification of an event. Details of field processing follow.

Sample Volume

Sample volume is determined by a field technician or a qualified field observer. The wet-deposition bucket first is sealed with the cover numbered to correspond with the bucket. Covers are kept in the field laboratory wrapped in the double polyethylene bags used to transport the clean bucket from the laboratory to the field. The bucket then is weighed using the PC4400 balance. Preliminary sample volume is estimated as:

$$\begin{array}{r}\text{(weight of field wet-deposition bucket and cover in grams)}\\ -\ \text{(weight of clean wet-deposition bucket and cover in grams)}\\ \hline \text{(preliminary approximation of sample volume in cubic centimeters)}\end{array}$$

The above approximation assumes that sample density is 1.00 gram per cubic centimeter and that dirt accumulated on the exterior of the bucket during its period in the field is negligible. Once all sample processing is complete and the sealed, double-wrapped bucket returned to the laboratory, the bucket may be dried in an oven and reweighed to correct for changes in bucket weight which may result from exterior dirt.

Because the PC4400 is self-taring, measurement of these weights is very simple. A warm-up time of at least 20 minutes should be alotted the balance. Once the balance is ready, its calibration should be checked using the 2-kilogram National Bureau of Standards standard weight provided with the balance. The balance may be tared by pressing the control bar with no weight on the pan. If after placing a standard weight on the pan, the balance displays a result to the last decimal place in variance with the weight, the balance must be calibrated. Calibration is accomplished by adjusting the marked calibration screw on the rear of the balance until the display reads the desired value. Once calibration is assured, the balance may be retared by pressing the control bar with the pan empty. The sample bucket and cover may be weighed by placing it on the pan and reading the display.

Sample Temperature

The temperature of the sample is important to evaluate thermodynamic effects on measurements of chemical composition such as specific conductance and pH. It is determined by the field observer on the sample collected in the container strapped to the wet-deposition bucket and, if sample volume is less than required for chemical analysis, on the sample in the wet-deposition bucket. It also is measured by the field technician or qualified field observer on all wet-deposition samples.

Measurement of temperature also is necessary to correct measurements of conductivity and pH, so it is one of the first field parameters that must be determined. However, insertion of the thermistor into the sample may be a source of sample contamination. Accordingly, temperature should be measured on a separate aliquot of sample that has been transferred to a clean, disposable test tube using a disposable, sterile, singly-wrapped pipet. Use of a test tube as the container for measurement permits maximum coverage of the thermistor with the minimum volume of sample, thus increasing accuracy and response time. Before insertion of the thermistor in the test tube, the probe should be thoroughly rinsed with distilled water and shaken dry.

Using the above procedures, the Cole-Parmer Model 8520 will respond within 30 seconds to sample temperature over the range 0°C to 100°C with an accuracy of ±0.5°C. Temperature should be recorded to the nearest 0.1°C on the standard field sheet.

Sample Specific Conductance

Conductivity is a measure of the ability of a solution to transmit an electrical current. In practice, most meters measure the resistance of the solution to a current of known voltage and translate this resistance into its reciprocal, conductivity. The conductivity of a solution is a function of the total concentration and species of free ions present in the solution. The conductivity is also a function of the temperature of the solution, so for comparative purposes it usually is corrected to its equivalent conductivity at a fixed temperature (25°C). Electrode area and the spacing between sensors of the electrode in the measuring apparatus also affect the apparent conductivity of the solution. To standardize measurements, a fixed scale of apparatus response has been established. The value of this scale is termed the cell constant. As the cell constant of a conductivity electrode is known to change with time, it should be reconfirmed during each calibration using Beckman Model CEL-BB1-Y8F laboratory standard cells.

Specific conductance is measured by the field observer on an aliquot of the sample collected in the container strapped to the wet-deposition bucket within 1 hour of the termination of every event and on an aliquot from the wet-deposition bucket when precipitation volumes are less than required for chemical analysis. Specific conductance also is measured by the field technician or a qualified field observer on a 20 mL aliquot removed from the wet-deposition bucket on all samples exceeding this volume. A final measurement of specific conductance is made by the analytical laboratory within 12 hours of termination of the event.

As precipitation conductivities usually are low (<100 μmho/cm), it is important to measure sample conductivity first on a sample aliquot that has been exposed to no extraneous source of contamination. To minimize potential contamination, cells that compensate automatically for temperature variations are preferred; and the following procedures are strictly used.

Select a conductivity cell with a cell constant appropriate to the anticipated conductivity of the sample (table 7). A cell constant of 0.1 most frequently will be appropriate. Confirm the cell constant. Rinse the selected cell with Type I distilled water and shake dry. Transfer an appropriate potassium-chloride standard (table 8) to the cell and measure its specific conductance as:

Specific conductance (μmhos/cm at 25°C) =
(meter reading)x(conductivity multiplier)x(cell constant).

If the measured value of this standard does not conform to its theoretical value, additional standards should be made to construct a calibration curve to correct sample measurements. Once meter-cell calibration has been established, the cell should be rinsed copiously before measuring the conductance of the precipitation sample. Then transfer about 5 mL of sample to the cell using a disposable, sterile, singly-wrapped pipet. Measure the specific conductance of the sample as above and record on the field sheet.

TABLE 8.--Specific conductance standards

[Made with distilled water and potassium chloride (KCl), gram formula weight 74.555]

KCl solution	Specific conductance (micromho per centimeter at 25 degrees Celsius)	Concentration of KCl (gram per liter)	Concentration of KCl (milligram per liter)
0.0001N	14.94	0.00746	7.46
0.0002N	29.86	.01491	14.91
0.0005N	73.90	.03728	37.28
0.0006819N	100.00	.05084	50.84
0.001N	147.8	.07456	74.56

Sample pH

The pH of a solution is a measure of its relative acidity. Solution pH is defined as:

$$pH = -\log [H^+] \qquad (1)$$

where $[H^+]$ is the acitivity (or effective concentration) of the free hydrogen ion.

In practice, the activity of the free hydrogen ion is measured as a function of the difference between the electrical potential of a reference electrode and a glass electrode whose potential varies as the activity of the free hydrogen ion in the subject solution varies. A meter is used to measure this potential difference in millivolts. Usually, meters are calibrated with standard buffer solutions to translate measured potential differences to pH units.

In the field, the pH of precipitation samples is measured by the field observer on sample collected in the container strapped to the wet-deposition bucket within 1 hour of the termination of each event. When precipitation volumes are less than required for chemical analysis, the field observer also will measure the pH of a 20 mL aliquot removed from the wet-deposition bucket. When the wet-deposition buckets are retrieved by the field technician or a qualified field observer for field processing, the pH of a 20 mL aliquot of sample from the bucket also will be measured. A third determination of pH will be made upon arrival of the sample at the laboratory for initiation of analysis within 12 hours of the termination of the event. Comparison of these measured pH values provides an indication of any changes in sample chemistry that may have occurred between collection and analysis and provides a check against erroneous measurements.

In dilute solutions such as precipitation, interferences to ideal electrode response to free hydrogen-ion activity in the sample may arise from stray electromagnetic fields associated with the electrode-sample interface. These fields include electrode streaming potentials caused by the motion of the sample solution past the electrode, junction potentials inherent in the construction of the electrode and arising from charge accumulation along material interfaces, and plasma potentials caused by differential response of the electrode and solution to temperature variations. Unless controlled, extraneous potential fields will result in electrode drift, nonlinearity between ion activity and electrode potential, and slow response to reach "stable" readings. Proper electrode preparation and calibration can elminate streaming potentials and minimize junction and plasma potentials. Calibration must include determination of reference potential (E°) and slope (S).

Choice of standards also is critical for accurate determination of pH in low-conductivity solutions, as discussed by Galloway and others (1979). To minimize electrode response time, to maximize accuracy and reproducibility, and to reduce matrix interferences, it is necessary to choose standards compositionally similar to the samples to be measured. Therefore, high-conductivity National Bureau of Standards reference buffers or their equivalents should be used only in checking the behavior of new electrodes. In field and laboratory measurements of precipitation pH, "artificial acid rain" standards always should be used. For use at North Dakota atmospheric-deposition sites, "artificial acid rain" pH standards are manufactured as dilute solutions of sulfuric acid buffered with potassium chloride (table 9). These solutions have been demonstrated to remain stable for at least 4 months under field laboratory conditions. Low-conductivity pH buffers also may be manufactured by saturating distilled water with carbon-dioxide gas (Hydrolab Corporation, 1982). Although carbon-dioxide buffers appear to remain stable for even longer periods of time, they can be manufactured to ranges of only a few tenths of a pH unit under normal temperatures and pressures. Because of the limited range of carbon-dioxide standards and the desirability of having multiple standards available to calibrate a meter-electrode system, sulfuric-acid standards are preferred over the carbon-dioxide standard. The true pH of these standard solutions can be calculated from a thermodynamic model of the aqueous solution to within ±0.03 pH unit (Whewell and Hughes, 1976), which yields resultant pH measurements within ±0.05 pH unit when the following procedures are followed (modified after U.S. Geological Survey Quality of Water Branch, written commun., 1980; Technical Memorandum No. 80.19). Technicians and observers are referred to the manual for the Orion 801A Digital Ionanalyzer for detailed operating instructions; a copy is available with each instrument. Only procedural steps relevant to the meter-electrode pair are presented here.

TABLE 9.--Sulfuric acid pH standards buffered with potassium chloride

$m_{H_2SO_4}$	m_{KCl}	Theoretical pH
5.024×10^{-6}	0.010	5.04
5.093×10^{-5}	.010	4.03
5.424×10^{-4}	.010	3.02
6.969×10^{-3}	.010	2.00

After the meter has been allowed to warm up for at least 30 minutes, meter response may be checked using the shorting cord; and the ideal isopotential point (7.00 on the pH scale) and potential slope may be set. Standard buffers should be selected to bracket the anticipated pH of the sample. The buffer with a pH value closest to the isopotential point is selected first. Rinse a disposable beaker with Type I distilled water and shake out the excess water. Electrodes are stored in field laboratories in soaker bottles filled with distilled water. Upon removing the electrode from its storage, the electrode must be rinsed copiously with fresh distilled water. Such rinses are necessary between all measurements. After rinsing the electode, excess water should been shaken from the electrode, but under no circumstance is the probe tip to be wiped with a tissue or otherwise touched. At low working conductivities excess water on electrodes and beakers may introduce significant error. The selected standard should be poured into the cleaned beaker and the electrode inserted into the solution. Although the electrode may be swirled gently in the solution to assure good contact between the solution and probe membrane, all measurements must be performed on unstirred, quiescent solutions to minimize distortions of the potential field (streaming potential). Only experience with a particular electrode pair will indicate how long it will be necessary to wait for a steady reading. In general, 5 to 15 minutes may be required to reach steady readings to ±2 mv. As soon as this stability is achieved, the pH of the standard should be read. If the electronic circuit of the meter was properly balanced above, the meter should indicate a value close to the true value of the buffer, corrected to standard temperature. The meter should be calibrated to this correct value. Following rinsing of the electrode and a fresh disposible beaker, the second standard should be measured. If the true value of the second standard is not displayed, the slope-correction dial should be utilized to calibrate the meter-electrode pair to that value. The slope correction should be recorded on the field measurement sheet. If the slope correction falls outside the range 98.5 percent to 99.5 percent, the electrode should be returned to the laboratory for cleaning and a new electrode should be used. Once calibration has been achieved, the pH of a low-ionic strength solution of known pH should be measured. An artifical precipitation sample prepared by the U.S. Geological Survey National Water-Quality Laboratory may be used for this purpose. If the displayed pH value for this reference sample is within ±0.03 pH unit of the accepted value, the calibration is assumed to be true and the collected sample may be measured. If the displayed pH value exceeds this range, recalibration should be undertaken.

Once the meter is calibrated, approximately 10-20 mL of sampled precipitation should be transferred to a clean disposable beaker using a sterile, individually wrapped pipet. The pH of the sample should be measured to the above criteria. In the analytical laboratory, the accuracy of this measurement may be improved by recalculating the pH as follows:

$$pH = (E_t - E_t^\circ)/S_t \qquad (2)$$

where E_t° and S_t are the time averaged values of E and S as determined during the two calibrations and E_t is the sample potential at the averaged time of measurement.

Sample Processing

Once the physical properties of the the wet-deposition sample have been determined, the sample must be prepared for chemical analysis by the analytical laboratory. Sample processing consists of separating the sample into fractions by constituent groupings that may be analyzed by the same technique and that require the same handling and preservation prior to analysis. The constituent groupings that have been selected for the purposes of the North Dakota network are listed in table 10. If the field observer is qualified, he may proceed with the processing. Otherwise, the field observer simply should seal the buckets, place them in the refrigerator to maintain sample temperature at 4°C, and immediately notify the network manager that a field technician is required for further sample handling.

TABLE 10.--Precipitation sample fractions and associated preservation methods

[Information in parentheses indicates methods appropriate for samples intended for analysis by the U.S. Geological Survey National Water-Quality Laboratories. All other information refers to samples intended for analysis by the North Dakota State Health Department Laboratory. LPE indicates linear ployethylene; FEP fluorinated ethylene-propylene resins; and TFE tetrafluoroethylene polymers; mL, milliliter]

Sample fraction	Container type	Sample volume	Preservation method
Physical properties			
Specific conductance	LPE bottle and screw cap.	20 mL	Raw; refrigeration at 4 degrees C.
pH			
Minerals			
Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}	LPE bottle and screw cap.	50 mL (250 mL)	Filtration; at 4 degrees C.
Nutrients			
SO_4^{-2}, NO_3^{-2}, PO_4^{-3}, Cl^{-}, F^{-}, (Br^{-})	FEP teflon bottle and TFE teflon screw cap	50 mL (100 mL)	Filtration; refrigeration at 4 degrees C.
Ammonia			
NH_4^{+}	FEP teflon bottle and TFE teflon screw cap.	50 mL (250 mL)	Filtration; acidification with sulfuric acid (mercuric chloride instead of acid); refrigeration at 4 degrees C.
Trace elements			
Al, As, Cd, Cr, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, V, Zn	FEP teflon bottle and TFE teflon screw cap, acid rinsed.	125 mL (250 mL)	Filtration; acidification with nitric acid to pH <2; refrigeration at 4 degrees C.
Mercury			
Hg	Soft glass bottle TFE teflon-lined plastic screw cap.	250 mL	Filtration; acidification with sulfuric acid to pH <2 and treatment with 5 percent potassium dichromate (nitric acid); refrigeration at 4 degrees C.
Filter			
Al, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Ag, Na, V, Zn	Polystyrene petri dish sealed with TFE teflon tape.		Dried at 60 degrees C for 60 minutes; refrigeration at 4 degrees C.

Prior to further handling of the sample, the sealed bucket should be wiped clean with a clean, dry cloth to minimize the possibility of contaminating processing equipment. Clean, acid-rinsed processing equipment is unwrapped from its double polyethyelene bagging and assembled on the laboratory bench. This equipment includes silicone tubing to be inserted into the peristaltic pump which will be used to transfer the sample, the cone splitter, and the filtration apparatus. Provided sample volume is sufficient, all the constituent fractions listed in table 10 are prepared. If sample volume is limited, priority is given to processing these fractions in the following order: physical properties sample fraction, nutrient sample fraction, mineral sample fraction, ammonia sample fraction, trace elements sample fraction, mercury sample fraction, and special applications sample fraction.

Once the silicone tubing has been installed in the peristaltic pump, the sample is transferred to the cone splitter and separated into volumes appropriate for each of the designated fractions. Two 20 mL raw samples are designated for laboratory physical properties determinations. The remainder of the sample is filtered through a 0.45-µm membrane filter for analysis of "dissolved" parameters. Prior to filtration of the sample, the filter is placed in the filter apparatus and rinsed with at least 2 liters of Type I distilled water to remove detergent and manufacturer's processing chemicals from the filter. Then, a volume of distilled water equivalent to the sample volume is filtered and split into fractions identical to those planned for the sample. This distilled water blank is preserved and processed identically to the sample and serves to index contamination unique to a single processing event. The filter is dried as completely as practical with a pure dichlorodifluoromethane gas jet and rinsed with 20-50 mL of sample. Subsequently, the remaining sample is split and preserved according to table 10.

The filter is transferred to a polystyrene petri dish with teflon-tipped forceps and placed in the oven at 60°C for 60 minutes. Thereafter, the petri dish is covered, sealed with tetrafluoroethylene (TFE) Teflon tape, and refrigerated for transport.

While the filter is drying, one of the unfiltered, raw, 20-mL sample fractions is used to determine field alkalinity or acidity. Depending on the pH of the sample determined earlier, incremental titration is employed to determine alkalinity (Franson, 1976) or acidity (Galloway and others, 1979).

To limit cross contamination, preservation of the nutrient sample with mercuric chloride (U.S. Geological Survey Quality of Water Branch, written commun., 1980; Technical Memorandum No. 80.26) is delayed until the filter is dried and all other fractions are sealed and stored in the refrigerator. The preserved nutrient sample is stored and transported in a separate cooler used only for nutrient preservation.

In the event the wet-deposition sample is frozen or in the form of snow, sample temperature is measured as usual. Then the sample is melted by placing the sealed collection containers in the oven at 60°C. Thereafter, the procedure is comparable to liquid wet-deposition sample processing.

All wet-deposition samples are transported back to the analytical laboratory in Koolatron P34A Thermostatically-Controlled Portable Refrigerators mainatined at 4°C. There, either further analyses are conducted or the sample is packaged in coolers for shipment to another laboratory.

Supplementary Sampling Methodology for Snowfall

Because the efficiency of the HASL-type collector for snowfall is highly variable depending on snow conditions, the representativeness of precipitation-quality data for snow sampled by the collector is suspect. As a supplementary means of evaluating snow quality, duplicate snow cores are taken at two locations at each station shortly before anticipated snowmelt (usually late February). Cores are taken in a drift and in a wind-swept prairie site in each location.

Cores are obtained using a 2-inch diameter Wildco Model 2420 Stratification Corer. Polyethylene core liners, egg-shell core catchers, and cutter nose pieces are removed from their double-wrapped polyethylene bags just prior to use. Each 2-foot core segment is taken in a separate polyethylene liner. Using a diamond scribe pen, liners are labelled with station identification number (15-digit latitude-longitude sequence number), core interval from snow surface in feet, and a letter designation for drift (D) or prairie (P). Cores are double-wrapped in polyethylene bags and maintained frozen until analysis. Cores are transported to the laboratory from field stations in Koolatron Portable Refrigerators maintained at -2°C.

Sampling Methodology for Dry Deposition

Dry-deposition samples are collected at 1-month intervals. At every visit to the collection site, field observers and field technicians are to inspect the dry-deposition containers for evidence of contamination. Contamination of dry-deposition samples most often consists of wet-deposition if the collector is malfunctioning or bird guano and insect debris if it is operating properly. If a dry-deposition bucket is found to be visibly contaminated, the bucket is immediately replaced with a clean bucket. The date a new dry-deposition bucket was installed should be indicated on the log sheet (Supplement 5) that is maintained in the field laboratory.

If no contamination of the bucket occurs in the interim, the field observer is reponsible for removing the dry-deposition bucket 30 days after installation. The bucket is immediately covered and sealed with its mate cover, which has been numbered to correspond with the bucket. Then the exterior of the bucket is wiped clean with a clean, dry cloth and the bucket weighed. Weighing provides the only possible quantification of dry-deposition volume. Once weighed, the buckets are placed in the refrigerator at 4°C until the next visit by a field technician to return samples to the analytical laboratory.

At selected sites, an attempt is being made to determine dry-deposition mineralogy as well as composition. At these sites, one of the dry-deposition buckets contains a glass slide coated with an epoxy adhesive. Slides are retrieved from these buckets on a quarterly (120-day) basis. The longer sampling time is required to accumulate sufficient sample for mineralogical determination by X-ray diffraction. Slides must be carefully removed from the buckets to prevent contamination and then heated in the oven at 60°C for 1 hour to cure the epoxy. Once the epoxy has cured, the slides may be stored vertically in slide trays for transport to the analytical laboratory. Slide trays should be maintained in refrigerators at 4°C and under low humidity until analysis. Like dry-deposition buckets, the stored slides may be retrieved by the field technician on a visit to retrieve event wet-deposition samples.

LABORATORY METHODS

Precipitation samples typically are characterized by a low dissolved-solids concentration (≤20 mg/L) which results in a highly unbuffered system. Therefore, prompt analysis in a competent laboratory with superior quality control procedures is critical. Prompt analysis obviously favors a local laboratory. Quality control and comparability of nationwide networks favors use of a centralized major laboratory. Whether analysis of precipitation samples occurs at a local or distant laboratory, a local laboratory is still needed to handle the support function of cleaning the collection buckets and any other materials that will contact the sample prior to analysis.

For the purposes of the North Dakota atmospheric-deposition network, laboratory analyses of all wet-deposition and dry-deposition samples are performed by the North Dakota State Health Department Laboratory in Bismarck. At least 10 percent of the wet-deposition samples are split, and duplicate samples are sent to a national laboratory for analysis. At present, approximately half of these duplicate samples are analyzed by the U.S. Geological Survey National Water-Quality Laboratory in Denver and half by the U.S. Geological Survey National Water-Quality Laboratory in Atlanta. About 10 percent of the duplicates are analyzed by the Illinois State Water Survey (National Atmospheric

Deposition Program's Central Analytical Laboratory). Laboratory processing and analysis of samples at each laboratory are outlined in the following sections.

North Dakota State Health Department Laboratory

Whenever possible, all instrumentation and facilities used to analyze precipitation for the North Dakota Atmospheric-Deposition Network are devoted solely to this network as a means of reducing the potential for contamination. Instrumentation that must be employed for other purposes is utilized for batch runs of precipitation samples. Instrument surfaces to contact precipitation samples are extensively rinsed prior to analysis. Analyses are performed as rapidly as possible once the samples are retrieved from the field. Prior to analysis, the sample bottles are sorted and stored separately, by fraction to minimize potential cross contamination from preservatives. All samples are stored in separate refrigeration units devoted to a single fraction. Laboratory analytical methods are summarized in table 11. Detection limits and resolutions for these laboratory procedures are presented in table 12.

Analysis of Wet-Deposition Samples

Wet-deposition sample pH, specific conductance, and alkalinity are determined on the physical properties sample fraction using procedures comparable to those outlined for field determinations within 1 hour of receipt of the sample. The Orion 901 pH meter and the Yellow Springs Instruments Model 32 conductivity meter used in these determinations are devoted solely to the atmospheric-deposition network.

Calcium, magnesium, sodium, and potassium concentrations are determined by flame atomic absorption spectroscopy on the mineral sample fraction. The Perkin-Elmer Model 5000 flame atomic absorption spectrophotometer used for these determinations also is used for routine analysis of North Dakota surface waters. A single nebulizer is devoted to the atmospheric-deposition network to limit contamination from more concentrated surface-water samples. Analytical methods are consistent with those presented by Skougstad and others (1979). Analysis of the mineral fraction is complete within 3 days of sample retrieval.

Fluoride, chloride, nitrate, phosphate, and sulfate concentrations are determined by ion chromatography on the nutrient sample fraction after the methods of Fishman and Pyen (1979). The Dionex 303 Ion Chromatograph used for these determinations is solely devoted to analysis of atmospheric deposition. Analysis of the nutrient sample fraction is complete within 2 days of sample retrieval.

Ammonium-ion concentrations are determined on the ammonia sample fraction by automated colorimetry after the methods of

TABLE 11.--Laboratory analytical methods

Chemical constituent or physical property	Analytical method(s)
Aluminum	Non-flame atomic absorption spectroscopy.
Ammonium as NH_4	Automated colorimetric phenate.
Arsenic	Hydride generation atomic absorption spectroscopy.
Cadmium	Non-flame atomic absorption spectroscopy.
Calcium	Flame atomic absorption spectroscopy.
Chloride	Ion chromatography.
Chromium	Non-flame atomic absorption spectroscopy.
Copper	Non-flame atomic absorption spectroscopy.
Fluoride	Ion chromatography.
Hydrogen ion	Specific ion electrode.
Iron	Non-flame atomic absorption spectroscopy.
Lead	Non-flame atomic absorption.
Magnesium	Flame atomic absorption spectroscopy.
Manganese	Non-flame atomic absorption spectroscopy.
Mercury	Cold vapor atomic absorption spectroscopy.
Molybdenum	Non-flame atomic absorption spectroscopy.
Nickel	Non-flame atomic absorption spectroscopy.
Nitrate as NO_3	Ion chromatography.
Phosphate as PO_4, ortho	Ion chromatography.
Potassium	Flame atomic absorption spectroscopy.
Selenium	Hydride generation atomic absorption spectroscopy.
Silver	Non-flame atomic absorption spectroscopy.
Sodium	Flame atomic absorption spectroscopy.
Specific conductance	Resistance.
Sulfate as S_4	Ion chromatography.
Vanadium	Non-flame atomic absorption spectroscopy.
Zinc	Flame atomic absorption spectroscopy.

TABLE 12.--Laboratory detection limits and resolutions

[Values expressed in micrograms per liter (µg/L). NDSHD indicates North Dakota State Health Department Laboratory; USGS indicates U.S. Geological Survey National Water-Quality Laboratory, Denver]

Constituent or physical property	Minimum detection limit		Resolution of detection	
	NDSHD	USGS	NDSHD	USGS
Aluminum	3	10	1	10
Ammonium as NH_4	60	12	10	12
Arsenic	1.0	1	.1	1
Cadmium	.2	1	.1	1
Calcium	20	10	10	10
Chloride	200	100	10	100
Chromium	.5	1	.1	1
Copper	1.0	1	.1	1
Fluoride	10	10	10	10
Iron	2	10	1	10
Lead	1	1	1	1
Magnesium	20	10	10	10
Manganese	.2	1	.1	1
Mercury	.03	.1	.01	.1
Molybdenum	2	1	1	1
Nickel	1.0	1	.1	1
Nitrate as NO_3	50	65	10	44
Phosphate, ortho, as PO_4	60	30	10	30
Potassium	40	10	10	10
Selenium	.1	1	0.1	1
Silver	.2	1	.1	1
Sodium	40	10	10	10
Sulfate as SO_4	200	100	10	100
Vanadium	5	.1	1	1
Zinc	3	10	1	1

Skougstad and others (1979). The Technicon Auto Analyzer II system used in these determinations is used only for atmospheric-deposition samples and low ionic-strength surface waters. Ammonium analyses are complete within 2 days of sample retrieval.

Trace-element concentrations (aluminum, arsenic, cadmium, copper, chromium, iron, lead, manganese, molybdenum, nickel, selenium, silver, and vanadium) are determined by nonflame atomic absorption spectroscopy on the trace-element sample fraction after the methods of Skougstad and others (1979). The Perkin-Elmer HGA-500 and 2100 Atomic Absorption Spectrophotometers used for these determinations are general use instruments, but a single furnace system is devoted to analysis of atmospheric deposition. Trace element analysis generally is complete within 1 week of sample collection but occasionally may take longer.

Mercury concentrations are determined on the mercury sample fraction by cold vapor generation atomic absorption spectrometry after the methods of Sorba and others (1980). The Perkin-Elmer 403 Vapor Generation Spectrophotometer used in these determinations is in general use in the laboratory, so blanks are used extensively to bracket atmospheric-deposition samples and confirm minimum background levels. Mercury determinations are complete within 2 days of sample retrieval.

Acid dissolution of filters bearing the nonfilterable portion of wet-deposition samples is accomplished according to the methods of Peden and others (1979), except that only triple-distilled reagents are used and all work is performed in a laminar flow, clean air environment. Once dissolved, filters are analyzed for calcium, magnesium, potassium, sodium, aluminum, cadmium, chromium, copper, iron, lead, manganese, molybdenum, nickel, silver, vanadium, and zinc by flame atomic absorption spectrometry as described above. Analyses are complete within 2 days of dissolution.

Analysis of Snow Cores

In the laboratory, one set of snow cores from each location is subsampled for analysis as wet deposition. Subsamples constitute all snow between visible wind-blown dirt layers (snirt). Dirt layers are discarded.

The second set of snow cores from each location is composited into a single column with core-liner interfaces sealed with teflon tape following the example of Colbeck (1981). The snow column is allowed to melt at room temperature with the resultant effluent being captured in 1,060 mL aliquots. Sample aliquots are split according to the fractions listed in table 10 and analyzed accordingly. These samples provide an approximation of changes in snowmelt quality with time that may be expected to be reflected in adjacent surface-water systems during spring runoff.

Analysis of Dry-Deposition Samples

Once delivered to the laboratory, dry-deposition collection buckets are wiped free of exterior dirt using clean, dry cloths and weighed on a Sartorius 3802-BCD analytical balance. Then, buckets are placed in clean air/dead air sample handling boxes and their covers removed.

If mineralogic determination is required to supplement epoxy slide collections, all particulate matter inside a dry-deposition bucket is carefully transferred to a variable-volume slide. The slide is prepared according to the procedures of Allman and Lawrence (1972) and subjected to X-ray diffraction analysis. Subsequent X-ray diffraction analysis of the epoxy slide provides a measure of the relative collection efficiencies and biases of the two systems being employed.

After mineralogic determination, the dry deposition in the variable slide and any still residual to the dry-deposition bucket and brush are prepared as described by Peden and others (1979), with the exception that 250 mL of Type I distilled water intially is added to the sample rather than 50 mL. Additional rinse water is used because dry-deposition rates are greater in North Dakota than in those parts of the country for which National Atmospheric Deposition Program methods were developed. Measurement of solution pH and specific conductance are made prior to filtration. Filtration and analysis of dry-deposition filter and filtrate are consistent with procedures previously outlined for wet-deposition samples.

Analysis of Total Particulate Membrane Filter Samples

High-volume filters exposed for 24 hours at 6-day intervals are mailed by the field observer to the North Dakota State Health Department Laboratory for analysis. Concentrations of total suspended particulates are determined by gravimetric analysis. Nitrate and sulfate determinations are performed by automated colorimetric analysis after ultrasonic extraction (North Dakota State Health Department, 1978).

Cleaning and Preparation of Sampling Materials

Prior to use, all sample collection buckets and containers and any instrument part expected to contact the atmospheric-deposition sample are cleaned following a procedure modified from Zief and Mitchell (1976), as detailed in table 13. All reagents used in the cleaning process are of the highest quality available, usually triple-distilled. All cleaning operations are conducted in clean-air environments as appropriate to the

TABLE 13.--Laboratory preparation and cleaning of materials contacting precipitation samples

[LPE indicates linear polyethylene; mL, milliliter]

Equipment type	Initial preparation	Final preparation
LPE sample collection buckets.	Interior/exterior wash with no-phosphate detergent followed by a distilled water wash and rinse; 24-hour soak in a solution of 5 percent nitric acid, 15 percent hydrochloric acid, and 80 percent distilled water; 2-hour soak in 5 percent hydrochloric acid.	20 interior rinses with Type I water; laminar flow, clean air dried; sealed; stored in doubly wrapped polyethylene plastic bags until ready for use.
LPE mineral and physical properties fraction storage containers.	15-minute soak in concentrated nitric acid.	10 interior rinses with Type I distilled water; clean air dried; sealed; stored in doubly wrapped polyethylene plastic bags until ready for use.
Teflon storage containers for trace element and nutrient fractions, soft glass storage containers for Hg fractions.	24-hour soak in solution of 16 percent nitric acid, 48 percent hydrochloric acid, and 36 percent distilled water.	20 interior rinses with Type I water; clean air dried; sealed; stored in doubly wrapped polyethylene plastic bags until ready for use.
Acid storage ampules (Wheaton "200" glass) used in sample preservation.	24-hour soak in concentrated nitric acid.	5 interior rinses with Type I water; clean air dried; filled with 1 mL triple-distilled sulfuric or nitric acid; sealed using oxygen/acetylene flame.
Polycarbonate filter apparatus, Teflon filter tweezers, polystyrene petri dishes, peristaltic silicone tubing.	Interior/exterior distilled water wash and rinse; 10-minute soak in solution of 2 percent concentration of nitric acid, 2 percent hydrochloric acid, 96 percent distilled water.	20 rinses with Type I water; clean air dried; stored in similarly prepared polyethylene plastic bags until ready for use.
Filters (cellulose acetate/nitrate composition).		Leached with 2,000 mL of distilled water immediately prior to use.

operations. Once cleaned, all sample containers are inspected to ensure that the substrata have not been damaged by cleaning methods or contain visible impurities. Clean vessels are double wrapped in polyethylene bags for storage until use. These bags have been cleaned using the same procedures as used for sample collection buckets and sterilized by ultraviolet light.

U.S. Geological Survey National Water-Quality Laboratories

Wet-deposition filters and filtrates prepared in the field for analysis by one of the U.S. Geological Survey National Water-Quality Laboratories represent duplicate splits of the samples prepared for the North Dakota State Health Department. Processing and preservation are identical to that used for State Health Department samples, except as noted in table 10. The mercury sample fraction is preserved with nitric acid instead of sulfuric acid and a strong oxidant. Filtrate is shipped to the selected National Water-Quality Laboratory in coolers by air mail, arriving at the laboratory within 24 hours of collection. Wet-deposition filters are dissolved at the North Dakota State Health Department Laboratory, and a sample acidified to pH less than 2 and chilled to 4°C is mailed to the National Water-Quality Laboratory. Dry-deposition samples are similarly processed at the North Dakota State Health Department Laboratory and mailed as appropriately preserved solutions to the National Water-Quality Laboratory. All samples are accompanied by a distilled-water blank processed identically to the sample.

National Water-Quality Laboratory analytical procedures generally are comparable to those already described for the North Dakota State Health Department Laboratory. However, ion-chromatography determinations include bromine concentrations; and the methods of Skougstad and others (1979) are used to determine mercury concentrations. Additionally, trace-element concentrations are determined both by atomic absorption spectroscopy and by ion-coupled plasma-emission spectroscopy as outlined by Fishman and Bradford (1982). Nutrient- and mineral-fraction constituents usually are analyzed within 10 days of receipt. Analyses of remaining constituents usually are complete within 30 days.

QUALITY ASSURANCE

Precipitation samples are very susceptible to contamination because of their low dissolved-solids concentrations. Furthermore, because precipitation usually is poorly buffered, precipitation quality is very susceptible to change unless promptly and properly preserved. Finally, most laboratories are not used to analyzing such low-concentration waters and are not equipped or trained in precipitation analysis. Accordingly, quality-assurance procedures may be as important, or more important, to the success of a precipitation chemistry program than the investigation plan.

All procedures detailed herein are in addition to the quality-assurance procedures undertaken by each analytical laboratory. The quality-assurance program routinely employed by the North Dakota State Health Department Laboratory has been previously reported (North Dakota State Health Department, 1978). Similarly, quality-assurance procedures undertaken by the U.S. Geological Survey National Water-Quality Laboratories and quality-assurance results are published annually (for example, Friedman and Erdmann, 1981, and Peart and Thomas, 1983).

Definition and documentation of appropriate data-collection methods is the foundation of any good quality-assurance plan. These aspects of the North Dakota atmospheric-deposition network have already been discussed. To determine the levels of contamination introduced by field-processing procedures, blank samples handled identically to the samples are analyzed with each atmospheric-deposition sample. Sample splits analyzed by two or more laboratories serve to define laboratory biases. At least 5 percent of the collected atmospheric-deposition samples are split for this purpose. Sample precision is determined by submitting duplicate samples to the same laboratory for analysis approximately an additional 5 percent of the time. Additionally, analytical accuracy is measured by submission of reference samples of "known" concentration. Reference samples were submitted to laboratories as normal precipitation samples, using dummy station identification numbers to distinquish them from collected precipitation. Reference samples included dilutions of U.S. Environmental Protection Agency standard water ampules and U.S. Geological Survey Standard Reference Water samples and total at least 10 percent of the collected samples. Half of the blind reference samples analyzed also are spiked with concentrations of certain elements to test the accuracy of certain analyses in specific concentration ranges. The North Dakota State Health Department Laboratory also participates in the U.S. Geological Survey Standard Reference Precipitation Sample Program.

Approximately 2 percent of the containers in each batch cleaned for sample handling are tested to determine levels of leachable impurities and contaminants. Concentrations of such contaminants above the minimum detection limits of the analytical methods used require recleaning of the entire batch of prepared containers. Membrane-filter extracts also are assayed to monitor for detectable levels of soluble impurities.

Analytical and test results are stored in the North Dakota State Health Department Laboratory's Mitts 80-80b microcomputer system, which checks for ionic balance and calculated versus measured specific conductance and pH. Computer programs also perform statisical comparison of constituent data from sample sets to determine if there is any relationship between the concentration levels in contaminent test samples and atmospheric-deposition samples. Duplicates and splits are averaged for each sample and stored with data standard deviations. Constituent concentrations differing by more than 5 percent in duplicate- or split-sample analyses are immediately reanalyzed. Reference samples are compared with previous analyses of the standard and a new most probable value (MPV) for the concentration of each constituent is defined. Constituent concentrations in reference samples exceeding 2 standard deviations are not used to redefine the MPV.

Approved data are entered secondarily into the North Dakota State Health Department IBM 370/158 Data Processing System and the U.S. Geological Survey WATSTORE system. Every 3 months, data are evaluated using the Statistical Analysis System (SAS) to determine seasonal-data variance and trend from previous years' data.

Combined, these quality-assurance procedures lend credibility to the data collected and provide a preliminary basis for evaluation of the observed quality changes. Further data evaluation assumes data quality and is undertaken only for interpretative purposes.

Similar quality-assurance procedures were instituted governing the collection of meteorologic and ambient air-quality data, consistent with Federal regulations governing such activity (Code of Federal Regulations, Title 40, Part 58, as amended). Quality-control inspection of ambient air-quality instrumentation is conducted at 2-week intervals by North Dakota State Health Department personnel. The North Dakota State Health Department participates in the Environmental Protection Agency Quality Assurance Auditing Program, with technician and analyst performance evaluated through the National Performance Audit Program (U.S. Environmental Protection Agency, 1980). Ambient air-quality and meteorological data are stored in one or both of the computer data-management files and evaluated by statistical analysis using SAS. Meteorological data are compared in SAS to meteorological data collected at nearby National Weather Service Stations.

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SUPPLEMENTARY INFORMATION

SUPPLEMENT 1. -- Site documentation form

I. SITE IDENTIFICATION

A. Station identification number ______________________

B. Local identification number ______________________

C. Station name ______________________

____

II. SITE LOCATION

A. County ______________ State ______________

B. Latitude ______________ Longitude ______________

C. Elevation __________(ft) Map quadrangle______________

III. SITE OBJECTIVE

A. Description______________________

____

____

____

B. Monitoring objectives and frequency

1. Rain ______________ 2. Snow ______________

3. Dryfall ______________ 4. Lake ______________

5. Stream ______________ 6. Soil water ______________

7. Ground water ______________ 8. Soil ______________

9. Vegetation ______________ 10. Air quality ______________

C. Cooperating agency ______________________

D. Supporting agency ______________________

E. Additional projects at site ______________________

IV. SITE PERSONNEL

A. Network manager

1. Name ______________________________

2. Address ______________________________

3. Phone __/________ (commercial) __/________ (FTS) ______ (ext.)

B. Field observer

1. Name ______________________________

2. Address ______________________________

3. Phone __/________ (commercial) __/________ (FTS) ______ (ext.)

4. Qualifications ______________________________

5. Responsibilities ______________________________

____

C. Field technician

1. Name ______________________________

2. Address ______________________________

3. Phone __/________ (commercial) __/________ (FTS) ______ (ext.)

4. Qualifications ______________________________

5. Responsibilities ______________________________

____

D. Additional support personnel

____

____

____

____

____

- -

V. INSTRUMENTATION

A. Precipitation collector

1. Type ______________ 2. Manufacturer ________________

3. Model _____________ 4. Serial No. __________________

5. W-No. _____________ 6. Bucket type _________________

7. Modifications ____

____

8. Installed ____________________________ ________________
(date) (by)

B. Weather station

1. Rain gauge

a. Type ____________ b. Manufacturer _____________

c. Model ___________ d. Serial No. _______________

e. W-No. ___________ f. Recorder __________________

g. Recorder serial and W-Nos. ______________________

h. Installed _______________________ ________________
(date) (by)

2. Wind speed sensor

a. Type ____________ b. Manufacturer _____________

c. Model ___________ d. Serial No. _______________

e. W-No. ___________ f. Installed _________________

3. Wind direction sensor

a. Type ____________ b. Manufacturer _____________

c. Model ___________ d. Serial No. _______________

e. W-No. ___________ f. Installed _________________

4. Temperature sensor

a. Type __________ b. Manufacturer __________

c. Model __________ d. Serial No. __________

e. W-No. __________ f. Installed __________

5. Relative humidity sensor

a. Type __________ b. Manufacturer __________

c. Model __________ d. Serial No. __________

e. W-No. __________ f. Installed __________

6. Solar radiation sensor

a. Type __________ b. Manufacturer __________

c. Model __________ d. Serial No. __________

e. W-No. __________ f. Installed __________

7. Barometer

a. Type __________ b. Manufacturer __________

c. Model __________ d. Serial No. __________

e. W-No. __________ f. Installed __________

8. Other meteorological sensor

a. Type __________ b. Manufacturer __________

c. Model __________ d. Serial No. __________

e. W-No. __________ f. Installed __________

9. Data logger

a. Type __________ b. Manufacturer __________

c. Model __________ d. Serial No. __________

e. W-No. __________ f. Installed __________

C. Air-quality Instrumentation

1. Total particulate membrane filtration apparatus (hi-vol)

a. Type ____________ b. Manufacturer ____________

c. Model __________ d. Serial No. ______________

e. W-No. __________ f. Installed ________________

2. NO_x monitor

a. Type ____________ b. Manufacturer ____________

c. Model __________ d. Serial No. ______________

e. W-No. __________ f. Installed ________________

3. SO_2 monitor

a. Type ____________ b. Manufacturer ____________

c. Model __________ d. Serial No. ______________

e. W-No. __________ f. Installed ________________

4. H_2S monitor

a. Type ____________ b. Manufacturer ____________

c. Model __________ d. Serial No. ______________

e. W-No. __________ f. Installed ________________

5. Hydrocarbon monitor

a. Type ____________ b. Manufacturer ____________

c. Model __________ d. Serial No. ______________

e. W-No. __________ f. Installed ________________

6. Other air-quality monitor

a. Type ____________ b. Manufacturer ____________

c. Model __________ d. Serial No. ______________

e. W-No. __________ f. Installed ________________

D. Laboratory instrumentation

1. pH meter

a. Type __________ b. Manufacturer ___________

c. Model _________ d. Serial No. _____________

e. W-No. _________ f. Probe __________________

2. Conductivity meter

a. Type __________ b. Manufacturer ___________

c. Model _________ d. Serial No. _____________

e. W-No. _________ f. Cell ___________________

3. Thermistor

a. Type __________ b. Manufacturer ___________

c. Model _________ d. Serial No. _____________

e. W-No. _________ f. Probe __________________

4. ASTM Thermometer

a. Type __________ b. Manufacturer ___________

c. Model _________ d. Serial No. _____________

5. Analytical balance

a. Type __________ b. Manufacturer ___________

c. Model _________ d. Serial No. _____________

e. W-No. _________

6. Peristaltic pump

a. Type __________ b. Manufacturer ___________

c. Model _________ d. Serial No. _____________

e. W-No. _________

7. Cone splitter

a. Type __________ b. Manufacturer ___________

c. Model _________ d. Serial No. _____________

e. W-No. _________

8. Other instrumentation

a. Type ___________ b. Manufacturer ___________

c. Model ___________ d. Serial No. ___________

e. W-No. ___________

VI. ENVIRONMENT

A. Topography:

Sector		Terrain	Ground Slope	Soil Type
(Direction)	(Distance, miles)	(valley, hill, etc.)	(%)	
N	______	__________	____	1. Cultivated___2. Orchard___ 3. Lawn ___4. Pasture___ 5. Forest ___6. Other ___
NE	______	__________	____	1. Cultivated___2. Orchard___ 3. Lawn ___4. Pasture___ 5. Forest ___6. Other ___
E	______	__________	____	1. Cultivated___2. Orchard___ 3. Lawn ___4. Pasture___ 5. Forest ___6. Other ___
SE	______	__________	____	1. Cultivated___2. Orchard___ 3. Lawn ___4. Pasture___ 5. Forest ___6. Other ___
S	______	__________	____	1. Cultivated___2. Orchard___ 3. Lawn ___4. Pasture___ 5. Forest ___6. Other ___
SW	______	__________	____	1. Cultivated___2. Orchard___ 3. Lawn ___4. Pasture___ 5. Forest ___6. Other ___
W	______	__________	____	1. Cultivated___2. Orchard___ 3. Lawn ___4. Pasture___ 5. Forest ___6. Other ___
NW	______	__________	____	1. Cultivated___2. Orchard___ 3. Lawn ___4. Pasture___ 5. Forest ___6. Other ___

B. Obstructions

1. Trees ______________ (species) Max. height ______________ (feet)

   Distance from site __________ (feet) Direction __________

2. Buildings __________ (type) Height ______ (feet) Width ______ (feet)

   Use ____________ Distance ______ (feet) Direction ____

3. Others:

   a. Object _________ Height ______ (feet) Width ______ (feet)

      Direction ____________ Distance ____________ (feet)

   b. Object _________ Height ______ (feet) Width ______ (feet)

      Direction ____________ Distance ____________ (feet)

   c. Object _________ Height ______ (feet) Width ______ (feet)

      Direction ____________ Distance ____________ (feet)

C. Pollutant Sources -- Emission inventory of sources within 16 miles

Source type	Source location		Distance	Pollutants
(line/point)	(latitude)	(longitude)	(miles)	(SO_2, NO_x)

D. Site maps

1. Map of emissions sources within 16 miles

2. Map of environment within 1/2 mile radius of the site

   Include:
   Site diagram and equipment configuration in center
   Roadways with names (paved and unpaved)
   Buildings
   Land use
   Water bodies
   Power lines (high and low voltage)
   Tree lines or clusters

3. Site photographs, labelled to indicate the 4 compass directions.

SUPPLEMENT 2. -- Field observer recording form for meteorological data

Station name ______________________ Observer ______________________
(signature)

Station No. ______________________ ______________________
(printed name)

Date (mo/day)	Rain gage (in.)	Precipitation			Sky Conditions	Comments
		Time				
		Begin	End	Type		
/01						
/02						
/03						
/04						
/05						
/06						
/07						
/08						
/09						
/10						
/11						
/12						
/13						
/14						
/15						
/16						
/17						
/18						
/19						
/20						
/21						
/22						
/23						
/24						
/25						
/26						
/27						
/28						
/29						
/30						
/31						

Remarks ____

____

SUPPLEMENT 3. -- Field maintenance log

Station name ______________ Station No. ____________________

Date	Tech. initials	Instrument	Chart/tape on off	Batteries replaced	Repairs

SUPPLEMENT 4. -- Field data sheet

1. STATION NAME (a) ______________________

STATION I.D. (b) ______________________

2. OBSERVER (a) ______________________ Signature

(b) ______________________ Printed Name

3. SAMPLE TYPE (a) Wet________ Dry________

SAMPLE NUMBER (b) ____________

4. SAMPLE INTERVAL Date Time

(a) ON ________ mo/day/yr ________ 0000-2400

(b) OFF ________ mo/day/yr ________ 0000-2400

(c) TIME ZONE (circle one)

CST MST

CDT MDT

5. SAMPLE CONDITION

Visible Material

CLEAR ____________ FLOATING ____________

CLOUDY ____________ SETTLED ____________

6. WET SAMPLE ____________g initial wt. ____________g final wt.

____________________g net wt. of precipitation

RAIN VOLUME __________l RAIN DEPTH __________cm

COLLECTION EFFICIENCY ____________%

7. FIELD ANALYSIS Aliquot removed ____________ml

Date (mo/day/yr) Time (0000-2400)

__/__/__ ________

a) Conductivity: Diluted standard ________ Distilled water ________ Sample ________ Cell constant ________ Temperature(^{o}C) ________

b) pH: Buffer certified ________ Buffer observed ________ Sample ________ Temperature(^{o}C) ________

8. WEATHER

Day		Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday
Date (mo/day)		/	/	/	/	/	/	/	/
PRECIPITATION	Rain gauge reading (in.)								
	Began/Ended	/	/	/	/	/	/	/	/
	Type								
SKY CONDITION									

RAIN GAUGE DEPTH: __________cm

9. REMARKS ____

____

(Laboratory use only)

A. LAB LOG BOOK I.D. ____________

B. DATE SAMPLE RECEIVED ____________

C. LAB CONDITION ______________________

____

____

D. NOTES ______________________

____

____

SUPPLEMENT 5. -- Dry-deposition-bucket log sheet

Station name ____________________ Station No. ____________________

Bucket No.	Initial bucket weight (g)	Date on	Date off	Final bucket weight (g)	Comments (including contaminants)