

3. FIELD PROTOCOLS

This chapter presents methods for Global Atmosphere Watch (GAW) field measurements of precipitation chemistry and wet deposition. It describes how samples should be collected and handled and the documentation that should accompany each sample. The focus is on rain, snow, and mixed precipitation; fog and cloud water are not addressed. Since wet deposition is the mass of a chemical deposited by precipitation per unit area, it is calculated as the product of the concentration of a chemical in a precipitation sample and the amount of precipitation. Ideally, this involves two different field instruments. Samples for measuring chemical concentrations are collected using a wet-only precipitation sampler designed to be open only during precipitation, while precipitation amounts are measured using a standard precipitation gauge designed to optimize the collection of precipitation with no consideration for chemistry.

3.1 Essential Components of Field Measurements

The following points summarize the ideal components for performing field measurements of precipitation chemistry and wet deposition:

- Assign responsibility for field operations to a single person who ensures that facilities are equipped properly, supplies are available, equipment operates according to specifications, and standard operating procedures are followed. (Section 3.2)
- Provide every station with a clean shelter or laboratory where precipitation chemistry samples can be weighed, other observations made, and sample handling activities performed. Weigh samples to measure sample size; never transfer samples to a graduated cylinder or similar container to measure volume. (Section 3.2.1)
- Equip every station with an automated wet-only precipitation chemistry sampler. The primary goal is to exclude dry deposition and prevent contamination by using a sampler that is open only during precipitation. While this is the primary goal, there may be local conditions under which this may not be possible. (Section 3.2.1.1)
- Equip every station with a standard precipitation gauge for measuring the precipitation amount. The NMHS or designated responsible agency should select the most accurate and representative gauge for the range of meteorological conditions encountered at each location. (Section 3.2.1.2)
- Collect samples daily at 0900 local time. Where the cost of field operations and analytical services makes daily sampling impractical, a multi-day sampling period, up to a maximum of 7 days (i.e., weekly sampling), is recommended. Weekly sampling that commences at 0900 local time on Tuesday is the 7-day sampling period of choice. Sampling periods longer than 7 days are strongly discouraged. (Section 3.2.2)
- Minimize sample handling, keep storage times short, ship samples rapidly to the analytical laboratory, and analyze samples promptly. Consider sample preservation practices where NMHS objectives require accurate measurements of labile species, such as organic acids. (Section 3.2.3)
- Clean all surfaces that precipitation samples may contact (e.g., funnels, bottles, tubing, buckets, etc.), preferably at a single central facility. Use reagent-grade deionized water (conductivity $<0.5 \mu\text{S cm}^{-1}$). Assess the cleanliness of precipitation sample containers by ensuring that the conductivity of the final rinse does not exceed $1.5 \mu\text{S cm}^{-1}$. (Section 3.3.1)
- Conduct tests of the cleanliness of sample collection and handling procedures (i.e., field blanks) at least once per month. Summarize and report the results of these and other QA/QC tests so that scientists have the data needed to evaluate the lower quantifiable limit of ion concentration measurements. (Section 3.3.2.3)
- For every sample, measure the sample volume gravimetrically. Also, measure the standard precipitation gauge amount following standard NMHS protocols. Field chemistry measurements are not recommended unless supported by a comprehensive QA/QC program. (Section 3.4)
- Record information about every sample on a sample history form that documents quantitative information and observations by the site operator. (Section 3.5)

3.2 Sample Collection

Precipitation samples are characterized by low ionic concentrations and are very susceptible to contamination. The goal of field sampling is to collect samples for chemical analysis that represent

the precipitation that occurred at the station and to preserve the integrity of these low ionic-strength samples from the time of collection to chemical analysis. Ideally, the station meets all the siting criteria described in [Chapter 2](#) and the chemical signature at the station is representative of the larger geographical region.

Samples must be protected from exposure to atmospheric deposition that occurs during dry weather, i.e., dry deposition. This requires a wet-only precipitation sampler, which exposes a precipitation sample container only during the occurrence of rain or snow and closes and isolates the container at all other times. A wet-only sampler prevents the loss of water due to evaporation or sublimation and eliminates exposure to windblown dust, debris, and other airborne pollutants during dry weather.

Protection of the samples remains of utmost importance while samples are removed from the sampler and during transport to the field laboratory. In practice, this is best accomplished by assigning a single trained person the responsibility for sample collection. Care in sample handling is of equal importance in the analytical laboratory (See section 4.4, Sample Handling, in [Chapter 4](#)).

Accompanying the wet-only precipitation sampler, each station also must operate a rain/snow gauge that is the NMHS standard or its equivalent. Both the sampler and gauge are required because of their distinct functions. The sampler is for measuring precipitation chemistry. The gauge is for measuring precipitation amount. The product of these independent measurements is used to calculate wet deposition fluxes.

It is desirable for the sampler and gauge to be located at a standard meteorological station where temperature, wind direction, and wind speed at a standard height are also measured. It is important to ensure that siting criteria are met for all instruments. These meteorological instruments require strict adherence to manufacturers' specifications and regular calibration checks, topics not covered here. Electricity to power these field instruments may be supplied by alternating current (ac) from an electrical utility company or direct current (dc) from a battery or solar array.

Field Components

Automated wet-only precipitation chemistry sampler
Standard precipitation gauge
<u>Shelter or field laboratory equipped with</u>
electric power
temperature control
table or laboratory bench
electronic scale or triple-beam balance
refrigerator (if necessary for temporary sample storage)
<u>Required if sample containers are cleaned at field site</u>
sink
conductivity meter
deionized water supply ($<1.0 \mu\text{S cm}^{-1}$), possibly requiring a water purification system
<u>Optional</u>
data logger
personal computer

3.2.1 Facilities

Each station should have a clean shelter or laboratory where field measurements can be performed. To avoid any effect of this facility on sample collection, it should be 50 m or more from any sampler. Where the shelter is remote from the field station, the sample must be sealed and protected from spillage and contamination during transport to this shelter. At a minimum, the shelter should provide a clean

environment where sample mass can be measured. It should have electric power and be temperature-controlled. A table or laboratory bench provides a clean surface where the site operator can use an electronic scale or triple-beam balance (15 kg capacity, 1 g sensitivity) to measure sample mass, which can be converted to volume using the density of water ($\sim 1.0 \text{ g L}^{-1}$). To minimize the potential for contamination, a graduated cylinder or other volumetric container should never be used to measure sample volume. Where a sample cannot be transported promptly to the analytical laboratory, the shelter should be equipped with a refrigerator where it can be stored temporarily. Where the sample collection containers must be cleaned for re-use at the shelter, a sink and supply of deionized water (conductivity $< 1.0 \mu\text{S cm}^{-1}$) is required. Deionized water (DI) either can be provided by the analytical laboratory and transported to the shelter in clean, tightly sealed polyethylene containers or can be produced by a water purification system in the shelter. The shelter also might be equipped with a data logger or personal computer for recording field measurements and observations.

3.2.1.1 Precipitation Chemistry Samplers

The GAW does not endorse the make or model of a specific manufacturer of precipitation chemistry samplers, but defers to each NMHS, or sponsoring agency, to select a sampler that meets these design and operational features:

- 1) The sampler is automated to collect wet-only deposition samples.
- 2) The sensitivity of the sampler to open during precipitation and close during dry periods is set by the manufacturer or is adjusted for local conditions to ensure wet-only deposition sampling.
- 3) The sampler must seal and protect the sample from contamination during dry periods.
- 4) The precipitation sample container (e.g., bucket or funnel-and-bottle) and all surfaces that the precipitation sample contacts must be chemically inert for the constituents measured.
- 5) The height of the opening through which precipitation enters the sampler (i.e., the collection orifice) must be 1 to 1.5 m above ground, except for areas that receive high snowfall accumulations, where the sampler may be raised onto a platform above the snow (see Section 2.4.2 for guidance).

Table 3.1 offers detailed specifications that can serve as a guide for evaluating sampler performance.

A typical, automated, wet-only deposition sampler has a precipitation sample container (funnel-and-bottle, bucket, etc.), a lid that opens and closes over the orifice of the sample container, a precipitation sensor, a motorized drive mechanism with associated electronic controls, and a support structure to house these components. A system that can be activated manually for testing, cleaning, and routine maintenance is recommended. A modular design that allows removal of individual components, such as the sensor, facilitates rapid repair with a minimum of tools and expertise.

Precipitation sample containers should have a volume sufficient for all precipitation that occurs during the sampling period. The precipitation sample should come in contact only with the sample container and depending on the sampler design, the funnel, tubing, etc., that direct the sample into this container. It is essential that all surfaces contacting the sample be chemically inert so that major inorganic constituents neither adsorb to nor desorb from these surfaces. Tests have shown that polyethylene, polypropylene, and Teflon™ (or a Teflon™-coating) are satisfactory materials. Glass and metal containers are not good materials for measuring major ions and must be avoided, as they are prone to both positive and negative artefacts for cations.

A sensor detects precipitation and sends an electronic signal, activating a motorized drive that uncovers the sample container orifice. When precipitation ends, the lid seals the sample container orifice. Typical sensors are heated to melt snow or ice and to prevent false openings from dew or ice. This requires optimal temperature control. A sensor that is too hot evaporates precipitation too rapidly and disrupts airflow, interfering with the fall of snowflakes and tiny droplets approaching sensor surfaces. For a comprehensive evaluation of sensor performance, see Winkler (1993) and Vet (1991). Droplet size, precipitation type and intensity, temperature, wind speed, and sensor shape and orientation all affect sensor response. Avoid sensors lacking adequate sensitivity (consult Winkler for examples). To preclude repeated cycling of the lid during periods of light precipitation, some samplers delay closure for one or two minutes after the last precipitation is detected. The duration of the delay must be balanced against the requirement to minimize sample exposure to dry deposition. In a network of sites, it is important to standardize sensor performance according to NMHS policies.

Table 3.1: Automated Wet-Only Precipitation Chemistry Sampler Performance Characteristics.

Range	Unattended (no user intervention) collection of precipitation samples of 0.05 to 25 cm liquid equivalent depth
Sensitivity and false positive operation	Opens within 5 seconds of the onset of precipitation of any type or rate. Closes within 120 seconds of the cessation of precipitation. Does not open in the absence of precipitation
Accuracy: sample volume in relation to standard precipitation gauge amount	+0% to -20% for liquid equivalent depths of 0.05 to 0.25 cm of precipitation and +0% to -10% for liquid equivalent depths ≥ 0.25 cm of precipitation, except for snow*
Real time recording	Records opening and closing within 5 minutes of a polled request and reports on the status of important functional components (e.g., sensor)
Operating temperature range	-45°C to +50°C
Operating wind limit	Sample container opens and closes properly, 15 m s ⁻¹ steady, 25 m s ⁻¹ gust
Reliability, maintainability, availability	Periodic maintenance interval ≥ 90 days, mean time between failures >500 days, and mean time to repair or maintain ≤ 60 minutes
Electrical Power	AC line power (with optional 12-volt DC battery operation during line power interruptions) or powered by 12-volt DC battery with solar panel recharge
Height	Precipitation sampler orifice and sensor are 1.0 to 1.5 m above surface and can be adjusted readily to maintain 1.0 m height above accumulated snow
Precipitation sample container	All container surfaces (funnel, bottle, tubing etc.) contacted by precipitation are chemically inert for the constituents measured; capacity should be adequate to hold all precipitation occurring during the sampling period
Precipitation sample container orifice	A lid must seal the orifice against evaporation or gas and particle intrusion during dry weather
Contamination from splash	Splash from instrument surfaces must not enter the collection orifice

* Goodison et al., 1998

During dry weather, it is essential that the sample container orifice remain covered and tightly sealed. This limits evaporation, ensures that no gas exchange occurs between the sample and the atmosphere, and prevents aerosols and other airborne contaminants from entering the container. A chemically inert compressible pad or gasket should be mounted on the underside of the lid to ensure that the lid tightly seals the sample container orifice.

Nothing should interfere with the free fall of precipitation into the sampler, and the sampler design should prevent splash, rebounding snowflakes, and ice pellets from entering or exiting the container. Special adaptations may be required in regions where snow may accumulate on sampler surfaces. One way to prevent snow from blowing from the cover into the sampler is to mount a stainless steel or TeflonTM-coated, peaked roof atop the cover. These adaptations should only be implemented if consistent with standard operating procedures. The instrument manufacturer's guidelines or experiences of other networks may help if adaptations are needed.

Some circumstances make it impossible or impractical to use an automated wet-only deposition sampler. Under these circumstances, there are two alternatives that may be considered. Both alternatives entail compromises in one or more of the sampler performance characteristics listed in Table 3.1.

Alternative 1 - Collect samples using a manual wet-only sampler. Uncontaminated, manual wet-only sampling requires round-the-clock availability of field observers alert to weather conditions, so that they can uncover clean sample containers just before the onset of precipitation and cover samples when precipitation ceases. Data from a manual wet-only deposition sampler are acceptable, if the observer verifies that the samples were exposed only during precipitation. The beginning and end times of precipitation and start and stop times of sample collection should be carefully documented (see Section 3.5) so that an independent observer can verify that the sample meets the wet-only standard.

Alternative 2 – Collect samples using a bulk (i.e., continuously open) sampler. Although this is strongly discouraged, data from a bulk sampler are acceptable where the NMHS verifies that bulk samples are collected in locations sufficiently remote from pollution and local dust (coarse particle) sources so that contamination from dry deposition is negligible. Even in these settings, bulk sample containers must be changed daily. Bulk sample data are specially annotated warning that "These data may be biased by an

unknown amount due to sample exposure during dry weather.” If a NMHS has data that quantify these biases and will make these data available on request, the following statement will accompany the warning: “Data are available that estimate the size of these biases. Contact the data provider for information.”

3.2.1.2 Precipitation Depth Measurements

The GAW requires every station to measure precipitation depths using the NMHS-designated standard precipitation gauge or its equivalent. Manual gauges are preferred. Precipitation depths are used to calculate the mass of a chemical deposited by precipitation on an area of earth surface (i.e., the wet deposition flux or loading). Standard precipitation gauges are designed to be the most accurate and representative means of measuring precipitation depths. Thus, each site must operate a precipitation gauge in parallel with its precipitation chemistry sampler. Precipitation chemistry sampler volumes are used to calculate wet deposition fluxes only when the standard gauge fails or is temporarily out of service. The data record should document such cases.

Environmental factors may cause precipitation gauge measurements to be too high or too low. Among the factors are wind speed, precipitation type, temperature, ground cover and blowing snow. Since the disruption in air flow around a gauge grows as the wind increases, measurement inaccuracies increase as the wind speed rises. For rain, the WMO recommends the use of pit gauges to reduce wind effects on gauge catch (Sevruk and Hamon, 1984), but pit gauges are impractical at many stations. Under-catch of snow in high winds and low temperatures is a particularly well-documented problem. In a WMO publication on measurements of solid forms of precipitation, Goodison et al. (1998) report on snow under-catch from gauges in current use. The following recommendations result from this seven-year multinational study:

- Avoid heated, automated (e.g., tipping bucket) gauges.
- Sheltered sites are preferred over open exposures. Locate gauges on level ground where vegetation offers a natural buffer from the direct force of the wind. Be careful to have sufficient separation from trees and other tall vegetation so that precipitation will not blow from the vegetation into the gauge nor will the vegetation interfere with the free fall of precipitation into the gauge. The precipitation chemistry sampler may require additional separation to avoid sample contamination (Section 2.4.2).
- Where snow comprises at least 20% of annual precipitation, gauges must be equipped with a suitable wind shield (Section 2.4.2). Measurements of wind speed and temperature at gauge height can be used to estimate the under-catch of snow. Presently, correcting gauge measurements for snow under-catch is not recommended. Wind shields around precipitation chemistry samplers are discouraged because of the potential for contamination.
- NMHS personnel are encouraged to read the Goodison et al. (1998) report to avoid poorly performing gauges when selecting a model for wind-exposed locations. The Hellmann, Belfort (shielded and unshielded), Tretyakov (unshielded and dual fence), and Nipher gauges were evaluated; some of these gauges exhibited extremely poor performance at high wind speeds.

3.2.1.3 Collection of Snow for Precipitation Chemistry Measurements

Collecting a representative snow sample for precipitation chemistry measurements poses special problems. Most electronic sensors on precipitation chemistry samplers do not detect snow, particularly light, dry snow, as efficiently as rain. Light, dry snow also may fall into and then blow out of an open container or funnel. Snow may stick to sampler parts and later blow into the sample container. Ice may coat sampler parts and prevent proper operation. Heavy snow may even fill the container to overflowing and block sampler operation. Because winter conditions and ice and snow characteristics vary widely by location, elevation, and exposure, there is no standard snow chemistry sampler, and there is no universal way to address these problems.

Some samplers are especially adapted to improve snow collection. Heating the collector lid and other moving parts to about 4° to 5°C may help prevent snow and ice buildup from interfering with sample collection or sampler operation. For samplers with funnels, applying enough heat to melt snow and ice may be necessary, if the funnel depth is too shallow to accommodate the entire accumulation. Care should be taken when applying heat to avoid increased sample loss due to evaporation or sublimation. One way to preclude heating the sample is to use an open container instead of a funnel. In extremely cold regions, an open cylindrical polyethylene sample container (diameter of 20 to 30 cm) is recommended for use on wet-

only samplers. The container height should be at least twice its diameter to reduce the potential for snow to blow out of the container.

3.2.1.4 Routine Instrument Checks and Maintenance

Standard operating procedures should include routine checks and maintenance of the precipitation chemistry samplers and standard precipitation gauges. Routine checks include:

- Check for proper precipitation chemistry sampler operation, especially sensor response and heating (i.e., check that the sensor activates the sampler to collect precipitation; otherwise, the sampler is closed and seals the precipitation sample container).
- Check the precipitation gauge for leaks, damage, and proper operation.

Routine maintenance includes cleaning sampler and gauge parts essential to proper instrument operation. Cleaning all sampler surfaces that contact the sample (e.g., funnels, buckets, bottles, tubes) is essential. Additional periodic or seasonal maintenance may be necessary to prepare the equipment for winter operations, e.g., installing/removing a precipitation gauge funnel, installing a wind shield, or charging the standard precipitation gauge with antifreeze or oil.

Every station should have an operating manual for each instrument, including trouble-shooting guides.

3.2.2 Sampling Period

The sampling period is the time from installation to removal of the sample container in the precipitation chemistry sampler. Choosing a sampling period depends on network objectives, sample quality considerations, and operational costs. As sampling periods lengthen and the time between collection and analysis increases, the potential for sample degradation increases.

The GAW recommends a 24-hour sampling period with sample removal set at a fixed time each day, preferably 0900 local time. This requires a laboratory having adequate resources to analyze daily samples and support daily field operations, and it requires adequate personnel for daily site visits. Where the cost of site visits and large numbers of samples makes daily sampling impractical, a multi-day sampling period, up to a maximum of 7 days (i.e., weekly sampling), is recommended. Weekly sampling that commences at 0900 local time on Tuesday is the 7-day sampling period of choice. Whether samples are collected daily or weekly, it is important to avoid removing samples during precipitation. This reduces the high likelihood of contamination from handling a sample during rain or snow and is best accomplished by waiting for a pause in the event. If the precipitation has not paused after a few hours, the sample should be collected and a note made on its sample history form (see Section 3.5).

Two alternative weekly sampling protocols may be considered: 1) removing and analyzing samples that have accumulated in an automated wet-only sampler after one full week or 2) removing samples from an automated wet-only sampler after each day of precipitation, pouring the sample into a storage vessel kept in a dark and cool (refrigerated) location, and analyzing the accumulated sample after one full week. The first alternative minimizes the cost of site visits and field operations; however, samples left in the collector at ambient conditions are subject to contamination, evaporation, and chemical degradation. Since the potential for chemical changes increases as the sampling period lengthens, the GAW strongly discourages sampling periods that exceed one week. An additional concern of long-term sampling periods is that loss of just a few samples over the course of a year makes it difficult to calculate representative seasonal or annual deposition values.

Some GAW sites are equipped with automated wet-only samplers that offer daily sampling without requiring daily site visits. These samplers have the capacity to change sample containers every 24 hours at a fixed time (for consistency, preferably 0900 local time) and store the containers in a refrigeration unit. These collectors have higher power requirements than other automated collectors and require careful cleaning of the connecting tubes and other apparatus.

An alternative sampling protocol followed at some sites is sample collection on a storm-by-storm or precipitation event basis. This requires the site operator to collect samples at all times of day or night. It also requires an unambiguous definition of an event and a method for operators to identify when an event

has ended and a sample is to be removed. Weather radar, information on the storm track and intensity, and good communications are essential elements in accurately following an event sampling schedule. The scheduling demands and information needs make event sampling especially costly and unless a rigorous sampling schedule can be met, event sampling is discouraged.

3.2.3 Sample Preservation Practices

Regardless of the length of the sampling period, there is always the possibility of chemical degradation of the sample in the field during sample collection, during shipment from the field to the laboratory, and prior to analysis at the laboratory. Sample preservation practices often slow but do not completely stop chemical degradation. A recommended practice is refrigerating samples below 4°C in the laboratory before analysis. Refrigeration alone does not prevent loss of some labile species, such as formic and acetic acids, nitrite, and sulfite. Fluoride and nutrients, such as orthophosphate and ammonium, may be compromised as well. Organic acid losses may result in an increase of a few tenths of a pH unit for samples between about pH 4.5 and 5.0. Ammonium losses can average up to 15 percent on an annual basis, depending on conditions of sample storage and shipment. The best practice is to minimize sample handling, keep storage times short, ship samples rapidly, and analyze samples promptly at the laboratory.

Sampling Period Specifications

Sampler Type	Duration	Start Time	Appropriateness for GAW	Note
Wet-only	24-hour	0900 local time	Highly recommended	1
Wet-only	Multi-day Not to exceed 7 days	0900 local time	Recommended	2
Wet-only	>7 days 2 week or monthly	0900 local time	Strongly Discouraged	3
Wet-only	Event or Storm	Collection time variable	Discouraged	4
Bulk	24-hour	0900 local time	Discouraged	5
Bulk	Multi-day	0900 local time	Strongly discouraged	6

1. Requires daily visits to site, which may not be possible for some remote locations.
2. Provides a less costly option than daily sampling, with fewer samples and site visits.
3. Greater chance that samples may be altered if they remain in the field for such lengthy periods. Infiltration of dust or other materials is more likely than with daily or weekly sampling. A missing or invalid sample due to sampler malfunction or sample contamination may compromise or invalidate seasonal or annual averages.
4. Requires a full-time site operator and constant monitoring of precipitation. Labor-intensive and costly. Provides valuable research data but may not be practical for long-term monitoring.
5. While discouraged due to the possibility of sample contamination, 24-hour bulk data may be accepted for certain remote, harsh environments where dry deposition is minor and where wet-only sampler designs have been proven ineffective.
6. Bulk samples with a sampling period longer than 24 hours are assumed to be contaminated by dry deposition and/or other materials.

3.2.3.1 Refrigeration

Refrigeration below 4°C is the most common preservation practice, and it slows most chemical and biological sample degradation. Ideally, collectors would be equipped to refrigerate samples during collection, although this is costly and places extra demands on power requirements in remote locations. Because most collectors are not equipped to refrigerate samples, it is desirable to refrigerate samples upon removal from the field. For daily sample collection protocols, refrigeration immediately after sample collection and throughout sample storage and shipment reduces ammonium losses. For weekly sample collection protocols, refrigeration is effective if samples are removed from the precipitation chemistry sampler daily, poured into a refrigerated storage vessel that accumulates samples for one full week, and refrigerated throughout shipment and storage until analysis. Following these procedures does not preclude losses of organic acids and other labile species (e.g., sulfite and nitrite).

3.2.3.2 Biocides

Another preservation practice is to prevent microbes from consuming the organic acids and nutrients in precipitation by adding chemical biocides to the samples. This requires strict quality control procedures that ensure these additives contain nothing that will contaminate the samples. Biocides have been used primarily for research purposes and only on a limited basis in operational measurement programs.

Chloroform is a common biocide used for preserving samples (Keene, et al., 1983, 2002, Keene and Galloway, 1984, 1986, 1988). Chloroform is toxic, volatile, and easily contaminated, but it is highly effective in stopping microbiological activity, degradation of organic acids, and loss of ammonium. Adding 0.5 mL of ultrapure chloroform to samples is typically adequate. Since chloroform is denser than water and immiscible, samples may be drawn for analysis from above the chloroform layer. This prevents chloroform from being a concern during sample analysis. This is an important consideration, because chloroform degrades ion chromatography columns, rendering them ineffective.

Another biocide that is added to precipitation is 2-isopropyl-5-methyl phenol, also known as thymol (Gillet and Ayers, 1991, Ayers et al., 1998). Unlike chloroform, which is a volatile liquid, thymol is a solid at ambient temperatures. Although it sublimates (vapor pressure = 1 mm Hg at 64°C) under ambient conditions, the sublimation rate is sufficiently slow that it can be added directly to the sample container in the collector. Precipitation entering the container is “fixed” on contact with the thymol, effectively arresting biodegradation of the sample at the point of contact. Although it is an effective biocide, thymol is not immiscible and may interfere with some analytical procedures. Thymol may cause respiratory irritation and should be handled in a fume hood, and prolonged exposure may have other harmful health effects. Prior to using thymol, laboratory personnel must test its purity to ensure that it does not contain any of the chemicals being measured in precipitation and to ensure it does not interfere with the chromatographic, spectrophotometric, colorimetric, or other analyses.

Consider using a biocide where the NMHS objective is to report accurate measurements of organic acids and orthophosphate or where refrigeration is not practical, such as in tropical areas. Rigorously follow special handling precautions that ensure the safety of field and laboratory personnel. If the central laboratory is near the site, the biocide should be added to the precipitation sample container by laboratory personnel. Before using biocides, carefully check for purity and interferences with all analytical procedures. Since biocide use requires extra sample handling, perform quality control checks of the potential for sample and biocide handling contamination. In some cases biocides may be used so that chemical analysis can be delayed, however, biocides do not stop dissolution of particles and other inorganic chemical reactions that can alter cation and anion concentrations and free acidity.

See Keene and Galloway (1984, 1986, 1988), Keene et al. (1983), Herlihy et al., (1987), and Galloway et al. (1989, 1996) for studies on the use of chloroform in precipitation samples. See Ayers et al. (1998) and Gillet and Ayers (1991) for information on the use of thymol. Section 4.4.3 describes the laboratory precautions and sample handling precautions that must be taken when biocides are added to samples.

3.3 Sample Handling and Shipping

3.3.1 Cleaning and Preparation of Precipitation Sample Containers

Precipitation samples are characterized by low ionic concentrations and are very susceptible to contamination. Reducing contamination from sample collection and handling requires that all surfaces that the sample may contact be cleaned with deionized water (DI) until the conductivity of the final rinse water is $1.5 \mu\text{S cm}^{-1}$ or less. This applies to surfaces in the precipitation chemistry sampler and to all other surfaces that contact the sample (funnels, tubing, syringes, pipettes). For ease of description in this section, the terms “precipitation sample containers” will refer to all these surfaces.

Precipitation sample containers must be cleaned with DI of known and assured quality. Since the quality of DI limits container cleanliness, the best practice is to clean precipitation sample containers at a single central facility, such as the analytical laboratory, where the DI quality can be controlled most rigorously. Analytical laboratories should be equipped to supply Type I DI, which has a resistivity $>18.0 \text{ M}\Omega$. Where it is impractical to clean precipitation sample containers at the analytical laboratory, cleaning at the field laboratory is an option, provided there is a supply of DI and provided this laboratory is equipped to measure conductivity. Whether containers are cleaned at a central facility or a field laboratory, it is necessary to exercise routine quality control checks of the DI. Fresh DI before any significant CO_2 uptake should measure approximately $0.5 \mu\text{S cm}^{-1}$ (termed reagent-grade DI). A conductivity $<1.0 \mu\text{S cm}^{-1}$ is essential for DI that has been in storage for any length of time.

Use of a detergent or acid solution to clean precipitation sample containers is typically unnecessary and is discouraged. If detergents or acids are used, particular care must be taken to rinse away residues, which requires more time and more water. An alternative to using detergents or acids is to allow the containers to soak in DI for 24 to 48 hours, leaching away soluble and exchangeable residues that may contaminate precipitation. Removing visible residues from precipitation sample container surfaces often requires wiping these surfaces with a sponge that is cleaned and soaked in DI. Wear rubber gloves when cleaning and handling precipitation sample containers and rinse surfaces repeatedly.

If precipitation sample containers are not used immediately after cleaning, shake off excess water and seal or cover the containers in clean plastic and store them in a clean area. Avoid open-air drying since airborne contaminants may stick to and contaminate surfaces.

Independent of where or how precipitation sample containers are cleaned, the conductivity of the final rinse water must be no higher than $1.5 \mu\text{S cm}^{-1}$. Routinely checking the rinsate conductivity is a necessary quality control procedure. It is strongly recommended that container blanks for precipitation sample containers, transfer bottles, funnels, and other containers be prepared and analyzed routinely to check for cleanliness. This can be done by adding 25 mL of DI (conductivity of $0.5 \mu\text{S cm}^{-1}$ if fresh or $<1.0 \mu\text{S cm}^{-1}$ if stored) to the containers and submitting these samples to the laboratory for analysis.

Section 4.3.7 describes DI water systems and cleaning procedures and testing that is needed to ensure sample quality.

3.3.2 Handling and Transporting Samples and Sample Containers

Every effort should be made to minimize sample handling and transfer between containers. Each surface that contacts the sample is a potential source or sink of the dissolved constituents in precipitation. Soluble or exchangeable contaminants on container surfaces may introduce positive concentration biases. Similarly, container surfaces may adsorb dissolved ions, introducing negative biases.

3.3.2.1 Handling and Transferring Samples

Because of the potential for chemical changes, the GAW recommends that samples be transported to the laboratory in the precipitation sample container. However, this is not always practical, because of the container size, shape, or some other characteristic. If the sample must be transferred to another container, always do this in a laboratory or clean shelter, never in the open environment of the field site. If possible, transfer the sample by pouring it directly from one container to another to avoid another

contact surface. High density polyethylene (HDPE) containers are recommended. The use of pipettes, syringes, funnels, etc., is unacceptable.

An acceptable practice is to send samples from the field site to the analytical laboratory in clean bottles provided by the laboratory. These bottles are often too small to accommodate the entire sample, particularly for exceptionally large volumes, and so only a portion of the sample can be sent for analysis. For frozen samples, exceptional care is needed to ensure that the samples are thawed completely and well-mixed before being poured into shipping bottles. When pouring, decant the liquid in an effort to leave insects, leaves, and other debris behind.

Always handle the sample with care and with a minimum of atmospheric exposure. These same considerations apply to precipitation sample containers before they are used. Once exposed, samples should be covered quickly and sealed tightly to minimize the potential for contaminants to fall into the sample. Never move hands, arms, or face over an exposed sample. Wear disposable plastic gloves when transferring the sample between containers, even if your hands do not move over the sample. Never allow anything, even a gloved hand, to contact a surface the sample may contact. As an added precaution, it is advisable to place sealed sample containers in clean plastic bags, which protect the samples from exposure to soil, water, and other contaminants.

3.3.2.2 Sample Storage and Shipping

Containers used to store and ship samples should be unbreakable and sealable against leakage of liquids or gases. During storing and shipping, steps should be taken to slow chemical change, especially biodegradation. The recommended procedure is to refrigerate samples below 4°C (refer to Section 3.2.3 for preservation practices). The best practice is to keep storage and shipment times short. Samples should be sent for analysis as soon after collection as practical. Rapid shipping services can speed delivery to the laboratory. Samples should be sent in insulated containers with “chill packs” that maintain the inside temperature below 4°C.

Although rapid delivery of samples to the laboratory is recommended, cost and logistics may result in longer shipment times. An alternative is to send samples to the analytical laboratory weekly, using regular mail services. Before shipping samples to the laboratory, inspect each container to ensure it is properly sealed, labelled, and packed.

For refrigerated shipments, “chill packs” should be placed above and below the sample containers. There should be some way to check that sample temperatures do not exceed 4°C. One way to do this is to include with the shipment a thermometer that records maximum temperatures. Another frequent practice is to include a container of water (not a sample) that is measured when the shipment arrives at the laboratory. Laboratory personnel should record the temperature when the sample is received and take corrective actions when temperature limits are exceeded, e.g., adding insulation or more “chill packs” to future shipments. If a sample history form (Section 3.5) accompanies the shipment, it should be protected from damage or destruction from sample leakage.

3.3.2.3 Field Blanks

A recommended practice for checking the cleanliness of sample collection and handling procedures is to collect field blanks. Field blanks test the total field measurement system, not just container cleanliness (as described in Section 3.3.1). It is recommended that for daily sampling, two to four field blanks be collected randomly every month, and for weekly sampling, one to two field blanks per month.

To collect a field blank, wait for a sampling period when no precipitation has occurred. Add DI to the precipitation sample container that was in the precipitation chemistry sampler during this dry sampling period. With ambient temperatures above freezing, add the DI to the sample container while it is installed in the precipitation chemistry sampler. With ambient temperatures below freezing, remove the sample container from the sampler to a clean, warm room and add DI to the sample container there. Treat this container, now containing DI, as if it were a precipitation sample. Follow the same stepwise procedures used for a precipitation sample. For the test to be complete, it is important that the DI contact all the

same surfaces as precipitation. For example, for funnel and bottle collectors DI should contact the funnel, connecting tubes, and bottle. It is important that the procedures for conducting the field blank test be followed and documented.

Field blank samples should be sent to the analytical laboratory where the entire suite of anions and cations are measured, just as for precipitation samples. Field blank analyses should be reported along with other quality assurance information, so that scientists have the data needed to evaluate the lower quantifiable limit of ion concentration measurements.

There is no universally correct volume of water to add to the precipitation sample container when preparing a field blank. Choose a volume that approximates the smallest volume required for a complete suite of laboratory measurements. This also represents the smallest amount of precipitation that the precipitation chemistry sampler can reliably collect for laboratory measurements. For example, if the laboratory requires 60 mL, choose a blank volume of 100 mL. If available, consider using simulated precipitation solutions, instead of DI, for field blank tests. The results of using both DI and simulated precipitation is an effective means of quantifying the overall positive **and** negative biases in the precipitation chemistry measurement system.

3.4 On-Site Measurements

At least two measurements should be reported for every sampling period, the sample volume from the precipitation chemistry sampler and the precipitation amount from the standard precipitation gauge. These measurements should be compared with one another as a routine check of the performance of the precipitation chemistry sampler and gauge. Significant differences may mean there is a measurement error or malfunction in one or both instruments. Because of aerodynamic differences in the sampler and gauge and because the sampler must first sense precipitation before opening, the sample depth typically is less than the gauge depth. For a properly functioning precipitation chemistry sampler, differences between and sampler and gauge depths should be smaller than about 10 percent, except in high wind, blowing snow, or ice conditions.

Sample volumes must be measured gravimetrically, since this method is efficient, accurate, and less prone to contamination and spillage than volumetric measurements. Periodically (at least annually) the accuracy of the balance should be checked using a known reference weight. Volumetric measurements using graduated cylinders are strongly discouraged because of the potential for sample contamination and spillage.

Precipitation gauge measurements should be taken at the same time as the precipitation chemistry sample is collected. Gauge measurements should be reported for every sampling period, whether or not the precipitation chemistry sampler collected a sample. Beyond serving as a crosscheck of the efficiency and accuracy of precipitation sampler operation, gauge measurements are used to calculate annual wet deposition and wet deposition fluxes.

In addition to sample volume and precipitation gauge measurements, some programs record field pH and conductivity measurements. These values are compared with laboratory measurements to evaluate chemical changes that can occur between the field and laboratory. The GAW does not recommend field chemistry measurements unless supported by a comprehensive QA/QC program that can verify the measurements.

If field chemistry measurements are made, they must never be done on the sample sent to the laboratory for analysis but rather on a portion that is removed from the sample sent for analysis. Measurements should be consistent with manufacturer's instructions and follow standard operational procedures. Any sample remaining after completion of field chemistry measurements must be discarded. Never return the portion removed for field chemistry to the portion sent to the laboratory for analysis.

3.5 Documentation

Information about every sample must be recorded on a sample history form. This form documents quantitative and qualitative information and observations by the site operator. It provides information used in data screening and verification. Data from this form are entered directly into the database management

system. There is no universally accepted form or format for GAW measurements. As a minimum, the sample history form must document the following:

- 1) Station name
- 2) Station identification number
- 3) Operator/observer name
- 4) Sample start date and time
- 5) Sample end date and time
- 6) Sample weight (including collection vessel weight)
- 7) Precipitation amount from gauge measurement
- 8) Precipitation type (snow, rain, freezing rain, hail, or mixed types)
- 9) Visible sample contamination (suspended particles, bird feces, insects, plant debris, etc.)
- 10) Instrument conditions (operating correctly/incorrectly)
- 11) Operator remarks (unusual circumstances, non-standard operating procedures, agricultural, industrial, or vehicular activity at the site, other observations or problems)
- 12) Supply requirements (sample containers, DI, field chemistry supplies, chill packs)
- 13) An entry on the form to report dry or nearly dry conditions during the sampling period (“no precipitation” or “trace amount”).

Examples of two sample history forms used by GAW networks are shown in Figures 3.1 and 3.2. The sample history form should be a multi-copy form. At least one copy should accompany the sample shipment to the laboratory and another should be retained at the field station. Having copies at both locations helps to ensure that this valuable record is not lost, and it facilitates communication between field and laboratory personnel, should questions arise about on-site conditions, the sample, or the equipment. To complement the sample history form, it is a good practice to maintain a field logbook that records arrivals and departures from the field station, general weather conditions during the visit, and explanations of any unusual conditions, problems, or deviations from the normal routine. Any information that may bear on the sample quality or integrity should also be recorded on the sample history form.

3.6 Documentation

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