

3. FIELD PROTOCOLS

This chapter presents methods for measuring wet deposition in the GAW-PC Programme. It discusses sample collection, handling, documentation and shipping procedures. Methods for measuring fog or cloud water and not addressed within the current programme. Since wet deposition is calculated as the product of the concentration of a chemical and the amount of precipitation, two different field instruments are used. Precipitation chemistry measurements are made using a wet-only precipitation sampler designed to be open only during precipitation. Precipitation amount is measured using a standard precipitation gauge designed to maximize collection efficiency for rain and snow with no consideration of the chemistry.

3.1 Essential Components of Field Measurements

The following points summarize the essential components of all GAW precipitation chemistry field measurements:

- Assign the responsibility for field operations to a single person. This person will ensure that facilities are equipped properly, supplies are available, equipment operates according to specifications, and standard operating procedures are followed. (Section 3.2)
- Every site must have a clean shelter or laboratory where samples can be weighed and where other observations and sample handling activities can be performed. Samples are weighed to measure sample size, not transferred to a graduated cylinder or similar container to measure volume. (Section 3.2.1)
- Equip every site with a precipitation chemistry sampler for collecting samples for chemical analysis. The primary goal is to collect wet-only deposition using an automated wet-only precipitation chemistry sampler; however, the GAW Precipitation Chemistry Programme recognizes there are local conditions under which this may not be possible. (Section 3.2.1.1)
- Equip every site 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 site. (Section 3.2.1.2)
- Collect samples daily at 0900 local time. Where the cost of site visits 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. The GAW Precipitation Chemistry Programme strongly discourages sampling periods longer than 7 days. (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 deionised water (conductivity $<0.5 \mu\text{S cm}^{-1}$). Test 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. Report the results of these and other QA/QC tests to the WDCPC on an annual basis. (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 among the standard set of measurements archived at the WDCPC and are not recommended. (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 representative samples for chemical analysis and handle samples in a way that preserves their chemical integrity. In principle, this is best accomplished by assigning a single person the responsibility for sample collection.

Field Components

Automated wet-only precipitation chemistry sampler

Standard meteorological rain/snow gauge

A shelter or field laboratory equipped with

Electric power

Temperature control

Refrigerator

Sink

Deionised water supply ($<1.0 \mu\text{S cm}^{-1}$)

Electronic scale or triple-beam balance

Tables or laboratory benches and chairs

Optional

pH meter

Data logger

Personal computer

Telephone

Required if sample containers are cleaned at field site

Conductivity meter

Deionised water purification system

3.2.1 Site Facilities

The GAW Precipitation Chemistry Programme recommends that each site have a shelter or laboratory where field measurements can be performed. This facility should be more than 50 m from the field instruments. The shelter should be equipped with electric power, temperature control, a refrigerator, a sink, a deionised water supply (conductivity $<1.0 \mu\text{S cm}^{-1}$), an electronic scale or balance (capacity of 15 kg and sensitivity of 1 g), tables or laboratory benches, and chairs. If deionised water cannot be produced at the operations shelter, it may be supplied by the analytical laboratory and delivered in clean, tightly sealed, polyethylene containers. Use of a graduated cylinder or other volumetric container for measuring sample volumes is strongly discouraged, because of the contamination potential from the container itself. Instead, volumes should be measured by weighing the samples and converting weights to volumes (density $\sim 1.0 \text{ g L}^{-1}$). Optional equipment for the operations shelter includes a data logger for recording field measurements, a personal computer, and a telephone.

The primary goal is to measure wet-only deposition, although the GAW Precipitation Chemistry Programme recognizes there are local conditions under which that may not be possible (see Section 3.2.1.1). Collecting wet-only deposition means opening a sampling container only when precipitation occurs. To do this, every site should be equipped with a wet-only precipitation sampler. Accompanying this sampler, each site must operate a rain/snow gauge that is the NMHS standard for precipitation chemistry network operations. As previously mentioned, both the collector and gauge are required because of their different functions. Electricity to power the field instruments may be supplied by alternating current (ac) from an electrical utility company or direct current (dc) from a battery or solar array.

It is desirable for the field site to be located at a standard meteorological station (Section 2.4.2) or to have measurements of temperature, wind direction, and wind speed at a standard height, as long as no GAW-PC siting criteria are violated. Use of commercial meteorological instrumentation requires strict adherence to manufacturers' specifications, as well as periodic calibration checks. Their installation and field operation is not covered in this document.

3.2.1.1 *Precipitation Chemistry Samplers*

As mentioned previously, the primary goal is to measure the chemistry of wet-only deposition. A precipitation chemistry sampler with the following design and operational features can meet this goal:

- 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 either set by the manufacturer or adjusted for local conditions in accordance with standard operating procedures.
- 3) The precipitation sample container (e.g., a bucket or funnel-and-bottle) and all surfaces that the precipitation sample contacts must be chemically inert for the constituents measured.
- 4) The sampler must seal and protect the sample from contamination during dry periods.
- 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).

The GAW Precipitation Chemistry Programme does not endorse the use of specific precipitation chemistry samplers, but defers to each NMHS to select a sampler that meets the above conditions and is best suited to the environment in which it will be used. NMHS personnel who require information on acceptable precipitation samplers should contact the WMO Secretariat or the QA/SAC for recommendations. (See Chapter 1 for contact information.) Table 3.1 offers detailed specifications that can serve as a guide for evaluating sampler performance.

A typical, automated, wet-only deposition sampler has the following components: a precipitation sample container (funnel-and-bottle, bucket, etc.), a lid that opens and closes over the sample container orifice, a precipitation sensor, a motorized drive mechanism with associated electronic controls, and a support structure to house the components. Precipitation sample containers should have sufficient volume to hold all precipitation collected during the sampling period. 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.

The precipitation sample should come in contact only with the precipitation 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. Typically, sensors are heated to prevent false openings due to dew or rime ice and to melt snow 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 provides a report 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	Powered by ac line power (with optional 12-volt dc battery operation during line current 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 sample container surfaces (funnel, bottle, tubing etc.) contacted by precipitation are chemically inert for the constituents measured; capacity should be adequate to hold all precipitation from 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.

Under limited situations, it may be possible to adopt a sampling strategy that does not use an automated wet-only precipitation sampler.

- One alternative is to 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. This should be done on the sample history form (see section 3.5). NOTE: When submitting manual wet-only data to the WDCPC, select 'Manual_Wet_Only' for the Sampling_Type field of the #SAMPLE_PROTOCOL metadata structure. This will allow the WDCPC to properly flag the data. See Chapter 5 for details about data submission and format.

- Another alternative is to collect samples using a bulk (i.e., continuously open) sampler, although the GAW Precipitation Chemistry Programme strongly discourages this option. 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, the bulk sample containers must be changed daily. The WDCPC will identify these data as bulk data and will attach a warning that states, "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 WDCPC will append the following statements to the warning: "Data are available that estimate the size of these biases. Contact the WDCPC for more information."

3.2.1.2 Precipitation Depth Measurements

The GAW Precipitation Chemistry Programme requires every site 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 most important 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 GAW sites. Snow undercatch 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 undercatch from gauges in current use. Based on this seven-year multinational study, the GAW Precipitation Chemistry Programme makes the following recommendations:

- Avoid using 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 (see Section 2.4.2).
- Where snow comprises at least 20% of annual precipitation, gauges must be equipped with a suitable wind shield (see Section 2.4.2) and wind speed and temperature should be measured at gauge height. These data can be used to correct for snow undercatch, although presently the GAW Precipitation Chemistry Programme does not recommend such corrections. 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 tested; some of these gauges exhibit very poor performance at high wind speeds.

3.2.1.3 Precipitation Chemistry Collection of Snow

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 according to site 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 (and other meteorological instruments, when present). Routine checks include:

- Checking for proper precipitation chemistry sampler operation, especially sensor response and heating (i.e., that sensor activates sampler to collect precipitation and otherwise closes and seals precipitation sample container).
- Checking 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, filters) 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.

Operating manuals, including trouble-shooting guides, should be available for each instrument at each site.

3.2.2 Sampling Period

The sampling period is the time from installation to removal of the sample container in the precipitation chemistry sampler. Choice of the 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 deterioration increases.

The GAW Precipitation Chemistry Programme recommends 24-hour sampling periods 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 is done to reduce 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).

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	Not recommended	3
Wet only	Event or Storm Duration variable	Collection time variable	Not recommended	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 long 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. Labour-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. Approval by the GAW Precipitation Chemistry Programme Science Advisory Group is required prior to the establishment of new bulk sampling sites.
6. Bulk samples with a sampling period longer than 24 hours are assumed to be contaminated by dry deposition and/or other materials. Data from existing sites will be made available by the WDCPC only upon request. Acceptance of new bulk sampling sites is unlikely.

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 and 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 (possibly refrigerated) location, and analyzing the accumulated sample after one full week. Method 1 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 Precipitation Chemistry Programme 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 generally 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 removal on a storm-by-storm or precipitation event basis. This means that site operator must 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 important 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, the GAW Precipitation Chemistry Programme discourages event sampling.

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 the course of sample collection, during shipment from the field to the laboratory, and prior to analysis at the laboratory. Sample preservation practices followed by most networks often 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 partial or complete loss of 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.

Various practices are used to reduce or eliminate chemical degradation. These practices are described briefly in the following sections. Whether or not biocides are used, the best practice is to minimize sample handling, keep storage times short, ship samples rapidly to the analytical laboratory, and analyze samples promptly.

3.2.3.1 Refrigeration

Refrigeration below 4°C is perhaps 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 collector power requirements in remote settings. Because most collectors are not equipped to refrigerate samples, it is desirable to refrigerate samples immediately upon removal from the field. For daily sample collection protocols, refrigeration immediately after 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. However, following these procedures does not preclude losses of organic acids and other labile species (e.g., sulfite and nitrite).

3.2.3.2 Use of Biocides

Another preservation practice is to prevent microbes from consuming the organic acids and nutrients in precipitation by adding chemical biocides to the collected samples. This requires strict quality control procedures that ensure these additives contain nothing that will contaminate samples. To date, biocides have been used primarily for research purposes and only on a limited basis in operational measurement programmes. Chloroform is a common biocide used for this purpose (Keene, et al., 1983, 2002, Keene and Galloway, 1984, 1986, 1988). Chloroform is toxic, volatile, and easily contaminated, but it is very effective in stopping microbiological activity, degradation of organic acids, and loss of ammonium. Adding approximately 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 or 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 (vapour 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.

In general, consider using a biocide where the NMHS objective is to measure accurately the organic acids and orthophosphate in precipitation 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, exercise regular quality control procedures that check the potential for sample and biocide handling contamination. While biocides may be used as a means to delay chemical analysis, particle dissolution and inorganic chemical reactions can continue to alter cation and anion concentrations and the free acidity of precipitation. 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 4.4.6 describes the laboratory analytical procedures and sample handling precautions that must be taken when samples that contain chloroform are analyzed for organic acids.

3.3 Sample Handling and Shipping

3.3.1 Cleaning and Preparation of Precipitation Sample Containers

Clean all surfaces that the sample may contact to a pre-specified level of cleanliness (conductivity below $1.5 \mu\text{S cm}^{-1}$) before use. This applies to surfaces in the precipitation chemistry sampler and to other surfaces that contact the sample, such as funnels, tubing, syringes, or pipettes. For ease of description in this section, the term “precipitation sample containers” will refer to all of the surfaces that the sample may contact.

Precipitation sample containers must be cleaned with deionised water of known and assured quality. Since the quality of deionised water often limits container cleanliness, **the best and most consistent practice is to clean precipitation sample containers at a single central facility, such as the analytical laboratory, where the deionised water quality can be controlled most efficiently.** Where this is impractical or too costly, cleaning precipitation sample containers at field sites is an option. Field sites must have a supply of deionised water and, as a minimum, be equipped to measure conductivity, if precipitation sample containers are cleaned there. Whether containers are cleaned at a central facility or at the field sites, it is necessary to exercise routine quality control checks of the water. Conductivity of fresh deionised water (measured before any significant CO₂ uptake can occur) should be approximately 0.5 $\mu\text{S cm}^{-1}$ (i.e., reagent-grade deionised water). A conductivity <1.0 $\mu\text{S cm}^{-1}$ is essential for deionised water that has been in storage for any period 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, special care must be taken to rinse away residues, which requires more time and water. An alternative to using detergents or acids is to allow the containers to soak in deionised water 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 deionised water. Wear rubber gloves when cleaning and handling precipitation sample containers and rinse surfaces repeatedly, until the conductivity of the rinse water falls below 1.5 $\mu\text{S cm}^{-1}$.

The GAW Precipitation Chemistry Programme recommends that precipitation sample containers be cleaned until the conductivity of the final rinse water (i.e., the rinsate) does not exceed 1.5 $\mu\text{S cm}^{-1}$ whether cleaned in the field or the laboratory. Routinely checking that the rinsate conductivity does not exceed 1.5 $\mu\text{S cm}^{-1}$ is a necessary quality control procedure. See Section 4.3.1.1 for discussions on cleaning of precipitation sample containers at the central analytical laboratory and for additional testing that is needed there to ensure sample quality.

After being cleaned, precipitation sample containers that are not used immediately must be dried by shaking off the excess water, and while still damp, sealed or covered in plastic and stored in a clean area. Air drying should be avoided as many contaminants are soluble in water and stick to dry surfaces.

It is strongly recommended that container blanks for precipitation sample containers, transfer bottles, funnels, and other containers be prepared and analyzed on a routine basis to ensure cleanliness. This can be done by adding 25 mL of deionised water (conductivity of 0.5 $\mu\text{S cm}^{-1}$ if fresh or <1.0 $\mu\text{S cm}^{-1}$ if stored) to the container and submitting to the laboratory for analysis.

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 comes in contact with a sample is a potential source or sink for the dissolved constituents in precipitation. Soluble or exchangeable contaminants on container surfaces may introduce positive concentration biases. Similarly, container surfaces may adsorb dissolved ions, thereby introducing negative biases.

3.3.2.1 Handling and Transferring Samples

Because of the potential for chemical changes, the GAW-PC programme recommends that samples be transported to the laboratory in the precipitation sample container. This is not always practical, however, because of 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. Only transfer the sample by pouring it directly from one container to another, if at all possible, 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 shipping bottles provided by the laboratory. These bottles are often too small to accommodate the entire sample, particularly for very large volumes, and so only a portion of the sample is sent for analysis. Care must be exercised to ensure that frozen samples are completely thawed 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 precipitation sample with care and with a minimum of exposure to the atmosphere. These same considerations apply to precipitation sample containers before they are put to use. Once exposed, samples should be covered quickly, and then sealed tightly to minimize the potential for contaminating materials to fall into the sample, for evaporation, and for spillage. Never move any body part (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 come in contact with a surface the sample may contact. As an added precaution, it is advisable to place sealed sample containers in clean plastic bags prior to use and after sample transfer. This additional layer of plastic protects the sample 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 also sealable against leakage of liquids or gases. During storing and shipping, steps should be taken to slow chemical change or biodegradation of samples. The recommended storage procedure is to refrigerate samples below 4°C (see 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 sample 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 common 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 action when temperature limits are exceeded, e.g., add insulation or more “chill packs” to future shipments. If a sample history form (Section 3.5) accompanies the shipment, it should be protected against damage or destruction from possible 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. A field blank tests the total field measurement system, not just container cleanliness. (The container blank, described in Sections 3.3.1 and 4.3.1.3, uses a container selected randomly from the supply ready for use and it is limited to testing the cleanliness of container cleaning procedures.) It is recommended that for daily sampling, two to four blanks be collected randomly per month, and for weekly sampling, one to two blanks per month.

To collect a field blank, wait for a sampling period when there was no precipitation, add deionised water to the precipitation sample container and treat the container as a precipitation sample.

Use a container that was installed in the precipitation chemistry sampler for a sampling period when no precipitation occurred. Handle the field blank by following the same stepwise procedures used to

handle a precipitation sample. For the test to be complete, it is important that the water come in contact with all of the same surfaces as precipitation. For funnel and bottle collectors, the field blank test should ensure that the water comes in contact with the funnel, connecting tubes, and bottle. With ambient temperatures above freezing, the water (or test solution) can be added to the sample container (funnel/ bottle etc.) 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, where the test should be performed. Wait for a sampling period when there was no precipitation. It is important that the exact procedures for conducting the field blank test be followed and documented.

Field blank samples should be sent to the analytical laboratory, which measures the entire suite of anions and cations, 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. This information should be provided to the WDCPC on an annual basis.

There is no universally correct volume of water to add to the precipitation sample container when preparing a field blank. The volume chosen should approximate 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 deionised water, for field blank tests. The results of a programme that uses both deionised water and simulated precipitation can be a very 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. Large 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 is typically less than the gauge depth. For a properly functioning precipitation chemistry sampler, differences between and sampler and the 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 programmes 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 Precipitation Chemistry Programme does not recommend field chemistry measurements unless supported by a comprehensive QA/QC programme that can verify the measurements. The WDCPC does not archive field pH and conductivity measurements, since they are not among the standard 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 Sample 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 that affects laboratory decisions about the sequence and nature of the chemical analyses. It also provides information used in data screening and verification. Data from the sample history form are entered directly into the database management system. Required fields on the sample history form include:

- 1) Site name
- 2) Site identification number
- 3) Site operator 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, deionised water, 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").

GAW Precipitation Chemistry Programme does not recommend a specific sample history form, since many sites already use forms as part of regional or international networks. 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 site. 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 the conditions of the site, the sample, or the equipment.

In addition to the sample history form, it is a good practice to maintain a field log book that records arrivals and departures from the field site, 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.

CAPMoN SAMPLE HISTORY FORM



Canadian Air and Precipitation Monitoring Network (CAPMoN)
Réseau canadien d'échantillonnage des précipitations et de l'air (RCEPA)

PERIOD COVERED: DAY MO YR DAY MO YR

DATE RECD: DAY MO YR

STATION NAME SUBMITTER'S NAME

SAMPLE CONDITION: 1 = WARM, 2 = COOL, 3 = COLD, 4 = FROZEN

DATE SHIPPED: DAY MO YR COLLECTOR NO.

FOR LABORATORY USE ONLY			SAMPLE		SAMPLING PERIOD				PRECIPITATION				WEIGHT		STANDARD GAUGE			FIELD COMMENTS								
LAB NUMBER	LAB WEIGHT (g)	COMMENT 1-7	NUMBER (01-40)	TYPE (METEOR)	START DATE				END DATE				NO. OF DATE	TYPE	REFERENCE (g)	SAMPLE BAG (g)	CATCH (mm)	TYPE 10-12	NO. OF DATE	SNOW ON GROUND (mm)	SAMPLE QUALITY (20-29)	UNUSUAL OCCURR (40-49)	SITE HISTORY (50-59)	OPERATOR'S (60-69)		
DAY	MO	YR	HR	DAY	MO	YR	HR	NO. OF DATE	TYPE	REF	WGT	WGT	TYPE	NO. OF DATE	NO. OF DATE	NO. OF DATE	NO. OF DATE	NO. OF DATE	NO. OF DATE	NO. OF DATE	NO. OF DATE	NO. OF DATE	NO. OF DATE	NO. OF DATE		
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- LAB COMMENTS**
 - 1 = LEAKED IN TRANSIT
 - 2 = LESS THAN SML
 - 5 = NOT RECEIVED
 - A = TOO CONTAM. TO ANALYSE
 - J = LEAKING BUT PARTITION OK
 - M = 1/2 DRY BAG ACCEPTED
 - N = < 1/2 DRY BAG REJECTED
 - O = MOISTURE IN DRY BAG
- SAMPLE SUBMISSION**
 - 0 = NO SUBMISSION
 - 1 = PRECIPITATION SAMPLE SUBMITTED
 - 2 = DRY BAG SUBMITTED
- DISTRIBUTION**
 - 1 WHITE - LABORATORY
 - 2 YELLOW - LABORATORY
 - 3 PINK - SITE
- PRECIPITATION**
 - 0 = NO
 - 1 = YES
 - 2 = UNCERTAIN
- PRECIPITATION TYPE**
 - 1 = RAIN
 - 2 = SNOW
 - 3 = FREEZING RAIN
 - 4 = MIXED
 - 5 = DEW OR FROST
- STANDARD GAUGE TYPE**
 - 10 = RAIN GAUGE
 - 11 = SNOW GAUGE
 - 12 = RECORDING GAUGE
- SAMPLE QUALITY**
 - 20 = SAMPLE CLEAN AND CLEAR
 - 21 = PARTICLES IN SAMPLE (E.G. LEAF, GRASS) - SPECIFY
 - 22 = ORGANIC MATERIAL IN SAMPLE
 - 24 = BULK SAMPLE - COLLECTOR OPEN WHEN PRECIPITATION NOT OCCURRING
 - 25 = PARTIAL SAMPLE - PART OF EVENT MISSED
 - 26 = SAMPLE SPILLED OR LEAKED BEFORE BEING WEIGHED
 - 27 = SAMPLE LEAKED AFTER BEING WEIGHED
 - 28 = OTHER - SPECIFY
- INSTR - INSTRUMENTS**
 - 30 = COLLECTOR OPERATED PROPERLY
 - 31 = COLLECTOR DID NOT OPEN DURING PRECIPITATION (NO SAMPLE)
 - 32 = COLLECTOR OPENED ONLY FOR PART OF EVENT (PARTIAL SAMPLE)
 - 33 = COLLECTOR OPENED BEFORE AND/OR AFTER PRECIPITATION (BULK SAMPLE)
 - 34 = COLLECTOR OPERATED MANUALLY
 - 35 = POOR HOOD-BUCKET SEAL
 - 36 = CRANK STAND NOT OPERATING PROPERLY
 - 37 = RAIN OR SNOW GAUGE NOT OPERATING PROPERLY - SPECIFY DETAILS
 - 38 = BALANCE OR HEAT SEALER NOT OPERATING PROPERLY
 - 39 = OTHER - SPECIFY
- UNUSUAL OCCURRENCES**
 - 40 = DUST IN AIR
 - 41 = CULTIVATION/SPRAYING/FERTILIZING NEAR SITE
 - 42 = CONSTRUCTION AT OR NEAR SITE
 - 43 = SNOW PLOUGH/BLOWER ON SITE
 - 44 = WIND BLOWN SNOW COLLECTED AT SITE
 - 45 = SMOKE/ODDOR/ASH DETECTED AT SITE
 - 46 = STANDARD GAUGE SPILLED OR OVERFLOWED - MEASUREMENTS LOW
 - 47 = OPERATOR NOT ABLE TO COLLECT SAMPLE - SPECIFY REASONS
 - 48 = BUCKET TOP LESS THAN 1 M ABOVE SNOW SURFACE
 - 49 = OTHER - SPECIFY
- SITE HISTORY**
 - 50 = REGION CONTACTED REGARDING PROBLEM - NOTE NAME AND PROBLEM DESCRIPTION
 - 51 = REGION RETURNED CONTACT - NOTE NAME
 - 52 = INSTRUMENT(S) REPAIRED - SPECIFY DETAILS
 - 53 = NEW COLLECTOR - SPECIFY I.D. NUMBER
 - 54 = NEW HOOD GASKET
 - 55 = QUARTERLY SITE INSPECTION
 - 56 = NEW OPERATOR - NOTE NAME
 - 57 = NEW PROCEDURE - SPECIFY
 - 58 = SITE CHANGE - SPECIFY DETAILS
 - 59 = OTHER - SPECIFY

LABORATORY REMARKS:

FIELD REMARKS:

Figure 3.2: Example sample history form used in the Canadian Air and Precipitation Monitoring Network (CAPMoN).

3.6 References

- Ayers, G. P., Fukuzaki, N., Gillet, R. W., Selleck, P. W., Powell, J. C. and Hara, H. (1998) Thymol as a biocide in Japanese rainwater. *J. Atmos. Chem.* **30**, 301-310. For more information on use of thymol as a biocide, contact: greg.ayers@dar.csiro.au.
- Galloway, J. N., Keene, W. C. and Likens, G. E. (1996) Processes controlling the composition of precipitation at a remote southern hemispheric location: Torres del Paine National Park, Chile. *J. Geophys. Res.* **101**, 6883-6897.
- Galloway, J. N., Keene, W. C., Artz, R. S., Church, T. M. and Knap, A. H. (1989) Processes controlling the concentrations of SO_4^{2-} , NO_3^- , NH_4^+ , H^+ , HCOO^- and CH_3COO^- in precipitation on Bermuda. *Tellus* **41B**, 427-443.
- Gillett, R. W. and Ayers, G. P. (1991) The use of thymol as a biocide in rainwater samples. *Atmos. Environ.* **25A**(12), 2677-2681.
- Goodison, B. E., Louie, P. Y. T. and Yang, D. (1998) WMO Solid Precipitation Measurement Intercomparison. In *Final Report, Instruments and Observing Methods*, WMO Report No. 67. WMO, Case postale No. 2300, CH-1211 Geneve 2.
- Herlihy, L. J., Galloway, J. N. and Mills, A. L. (1987) Bacterial utilization of formic and acetic acid in rainwater. *Atmos. Environ.* **21**, 2397-2402.
- Keene, W. C. and Galloway, J. N. (1984) Organic acidity in precipitation of North America. *Atmos. Environ.* **18**, 2491-2497.
- Keene, W. C. and Galloway, J. N. (1986) Considerations regarding sources for formic and acetic acids in the troposphere. *J. Geophys. Res.* **91**(D13), 14,466-14,474.
- Keene, W. C. and Galloway, J. N. (1988) The biogeochemical cycling of formic and acetic acids through the troposphere: an overview of current understanding. *Tellus* **40B**, 322-334.
- Keene, W. C., Galloway, J. N. and Holden, J. D., Jr. (1983) Measurement of weak organic acidity in precipitation from remote areas of the world. *J. Geophys. Res.* **88**(C9), 5122-5130.
- Keene, W. C., Montag, J. A., Maben, J. R., Southwell, M., Leonard, J., Church, T. M., Moody, J. L. and Galloway, J. N. (2002) Organic nitrogen in precipitation over Eastern North America. *Atmos. Environ.* **36**, 4529-4540.
- Sevruk, B. and Hamon, W. R. (1984) International comparison of national precipitation gauges with a reference pit gauge. In *WMO Instrument and Observing Methods*, WMO Report No. 17. WMO, Case postale No. 2300, CH-1211 Geneve 2.
- Vet, R. J. (1991) Wet Deposition: Measurement Techniques. In *The Handbook of Environmental Chemistry, Volume 2 Part F, Reactions and Processes* (edited by Hutzinger, O.). Springer-Verlag, Berlin.
- Winkler, P. (1993) Response of precipitation sensor to rain. *Meteorol. Zeitschrift* **2**, 35-44.