

NOAA Technical Memorandum ERL ARL-222

## THE NADP ATMOSPHERIC INTEGRATED RESEARCH MONITORING NETWORK-WET (NADP/AIRMON-WET) - SITE OPERATOR'S MANUAL

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Air Resources Laboratory Silver Spring, Maryland April 1997

**NOCA** NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

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UNITED STATES DEPARTMENT OF COMMERCE

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#### SITE OPERATOR'S MANUAL

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#### 1. INTRODUCTION

#### 1.A. <u>OBJECTIVE</u>

The objective of the National Atmospheric Deposition Program/Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN) for wet deposition is to detect, as rapidly as possible, air quality and deposition changes that result from emissions changes. This activity is being promoted by the National Oceanic and Atmospheric Administration (NOAA) as part of its "Health of the Atmosphere" initiative, under guidance contained in the Clean Air Act Amendments of 1990 (CAAA)<sup>1</sup>, and as a contribution to the National Acid Precipitation Assessment Program (NAPAP)<sup>2</sup>. The NADP/AIRMoN program is designed to provide deposition information required to evaluate the progress of the emissions reductions mandated by the CAAA. NADP/AIRMoN started in October, 1992 to establish deposition levels prior to Phase I emission rollbacks in 1995. It will be necessary to continue sampling at least until early in the next century to determine the full impact of the CAAAs on deposition, which will not occur until after 2000.

#### 1.B. BACKGROUND

The NADP/AIRMoN program is designed to augment the EPA Clean Air Status and Trends Network (CASTNET)<sup>3</sup>. While CASTNET is designed to assess changes in regional deposition as these might affect ecosystems, NADP/AIRMoN is focused on early detection of change in atmospheric quantities - air quality and deposition. To accomplish this, NADP/AIRMoN will use an array of sites where shorter-term measurements are made and more variables are measured than in many current routine monitoring programs. This will permit examination of the data in more detail and allow correction for meteorological and other factors that may otherwise obscure trends in air quality and atmospheric deposition. NADP/AIRMoN is built upon the daily monitoring program, "MAP3S"<sup>4-12</sup>, previously operated by the Department of Energy, and operates as a research subnetwork of the NADP<sup>13</sup>. NADP/AIRMoN sites are located in places where changes should be most easily detected, at sites where experienced and interested supervisors are

already on hand, and where research opportunities (such as may result from collocation with other activities) can be maximized.

## I.C. GOALS

The NADP/AIRMoN is operated as an NADP subnetwork. The NADP/National Trends Network (NADP/NTN) uses a weekly collection protocol to provide information on the chemical climate of North America with particular interest in geographical patterns and temporal trends in wet deposition of chemical species that may affect sensitive aquatic and terrestrial ecosystems, the productivity of agricultural and forest lands, and materials. The NADP/AIRMoN component will add an understanding of the processes that define the chemical climate of North America and establish the relationships between emissions sources or source regions and deposition to specific receptors. By providing high-quality, daily data to fuel process models on a routine basis, the subnetwork will contribute to the improved predictive capability of the models and provide a better understanding of the effects of emissions controls and new sources of emissions on the chemistry of deposition to sensitive receptors. This is critical to assessments of the effectiveness of CAAA emissions controls and to evaluating the effects of emissions trading practices on deposition chemistry to regions of concern.

#### 2. TERMS

- 2.A. "temperature only" bottle The "temperature only" bottle is a 60 mL square polyethylene bottle filled with deionized water and placed in a sealed bag. It is stored in the refrigerator (not freezer) along with precipitation samples and is placed in the shipping box at the time samples are sent to the Central Analytical Laboratory (CAL). It is a surrogate precipitation "sample" which is used at the CAL to estimate the sample temperature during transit from the site laboratory to the CAL.
- 2.B. **ice packs** Ice packs ("Ice Brix"<sup>i</sup> or "Blue Ice<sup>•"ii</sup>) are used to keep the precipitation samples cold during transit from the site to the CAL. Each ice pack is doubly sealed to preclude any contamination of the sample by the coolant. An ice pack MUST NEVER BE USED if there is any evidence of leakage outside the bags. Operators should store ice packs in the freezer so that they will be ready for shipment when needed.
- 2.C. **insulation blocks** There are 2 to 4 blocks of Styrofoam on the sides of the shipping boxes and a block in the lid. These must be in place when shipping samples back to the CAL, Without them the black shipping boxes will **not** keep the sample(s) cool.

i Ice Brix' is a registered tradename of Polar Tech Industries, Inc., Elgin IL 60123

<sup>&</sup>lt;sup>ii</sup> Blue Ice is a registered tradename of Gott Corp., Winfield, KS 67156

# 3. OBSERVERS INSTRUCTIONS FOR OPERATING AN NADP/AIRMoN MONITORING SITE

## 3.A. INTRODUCTION

The primary responsibility of site operators is to collect daily, representative, wet-only deposition samples and submit them to the CAL. This manual is intended as a guide for NADP/AIRMoN site operations. The procedures herein have been adopted from 16 years of the MAP3S network and 14 years of NADP/NTN operations. These procedures describe the level of effort required of site operators and were developed in keeping with NADP/AIRMoN objectives. Changes may be necessary as improved procedures are adopted or as network objectives are amended.

We have done our best to incorporate necessary information. Ambiguities, inconsistencies, errors or incompleteness should be reported to the appropriate person below. Site operators are urged to consult us whenever questions arise and communicate any suggestions bearing on improvements to this manual or the smooth operation of the network.

For site supply needs, data logging, procedural, or equipment questions contact:

Scott Dossett	800/952-7353 sdossett@uiuc.edu
Jane Rothert	217/333-7942 rothert@uiuc.edu
Van Bowersox	217/333-7873 sox@sun.sws.uiuc.edu

## 3.B. <u>REQUIREMENTS FOR COLLECTION OF WET DEPOSITION</u>

Each site must commit to the adherence of the following general guidelines:

- \* Sites will use the precipitation collection equipment listed in the *Instruction Manual NADP/NTN Site Operation*<sup>14</sup> to collect wet deposition samples.
- \* Sites will maintain this equipment in good working order at the original location specified in the SITE DESCRIPTION QUESTIONNAIRE submitted to the NADP/NTN Program Coordination Office and NOAA. Sites will also maintain the area surrounding the collector as specified in the *Instruction Manual for NADP/NTN Site Selection And Installation*<sup>15</sup>.
- \* Changes or modifications at the site or to its equipment will be submitted to the Program Coordination Office prior to implementation and documented in the REMARKS block on the Field Observer Form. This includes moving the site, siting other equipment in close proximity to the existing NADP/AIRMoN sampler or precipitation gages (within 30

meters), installation of snow roofs or event recorders, etc. See also the *Instruction Manual for NADP/NTN Site Selection And Installation*<sup>15</sup>.

\* Sites will adhere to the daily sample collection schedule specified in this manual, and submit samples with a completed FIELD OBSERVER FORM (FOF) and 24-HOUR RAIN GAGE CHART to the CAL at the Illinois State Water Survey, Champaign, Illinois for analysis.

#### 4. ROUTINE SAMPLE COLLECTION

#### 4.A. PREPARATION FOR SAMPLE BUCKET CHANGE

- 4.A. 1. A bucket mailer from the CAL should be checked on arrival to verify that it contains the following:
  - \* 2 clean buckets each encased in its own plastic bag
  - \* 2 clean snap-on lids each encased in its own plastic bag
  - \* 2 clean 250 mL wide-mouthed polyethylene bottles bagged individually
  - \* 8 ice packs, each triple-bagged and sealed and then all stored in a large plastic bag
  - \* insulation blocks
  - \* "temperature-only" bottle.
  - Note: Some bucket mailers will arrive from the CAL without all of the items listed above. When bucket mailers are sent to the CAL without all of the items then the bucket mailers are returned with only the items needed to resupply the site. This is to avoid accumulating large supply inventories at the sites.

In addition the black-box mailer may contain preliminary field or laboratory data sent for verification, and/or items previously requested in Supplies, Block 10, of the FIELD OBSERVER FORM (Report Forms, pH buffers, quality control check solutions, pH electrode, etc.)

4.A.2. Take to the site a CAL-cleaned bucket and snap-on lid, each separately bagged. Always keep these items sealed in bags until the moment of installation. Buckets and lids are cleaned at the CAL and require no further cleaning or rinsing. Careful handling of buckets and lids is necessary to prevent contamination. This is extremely important because the dissolved substances naturally occurring in precipitation have very low concentrations and even the slightest contamination will cause erroneous results. For example, one drop of human perspiration can completely invalidate a sample for sodium, chloride, ammonium, and possible other ions. Even a fingerprint on the inside of a bucket or lid may contain more sodium than the entire sample. Keep the bags as you will need them to return the used buckets and lids to the CAL.

- 4.A.3. Additional items that must be taken to the site include the following:
  - \* fresh deionized or distilled water in a wash bottle reserved for NADP/AIRMoN use only (not necessary during freezing weather)
  - \* indelible ink marker
  - \* Field Observer Form and a precipitation gage chart
  - \* dry-side bucket if this is the first sample change of the month
  - \* Kimwipes<sup>•iii</sup> or other lint-free, clean wipes

## 4.B. DAILY SAMPLE COLLECTION

- 4.B.1. Visit the site daily! Weekends and holidays are to be covered routinely as are weekdays.
- 4.B.2. Always collect samples at 9 AM  $\pm$  1 hour (8 AM-10 AM) *LOCAL TIME*. The minimum time a bucket is in the collector in the field will be approximately 24 hours. This applies to weekends and holidays as well.
- 4.B.3. The sample bucket should be removed at 9 AM and the sample processed if one of the following conditions exist:
  - 1. precipitation is measured by either rain gage, the Belfort recording rain gage or the NWS "stick" gage or
  - 2. the lid of the collector was open for more than one hour or 6 (six) or more shorter lid openings occurred regardless of whether any precipitation was measured by the rain gage.
- 4.B.4. If intermittent precipitation is occurring at collection time or the precipitation is expected to end, wait until there is a break in the precipitation but not longer than about 10 minutes. If the precipitation is steady and continuous and not expected to quit within 10-15 minutes, change the bucket during the 8 AM to 10 AM collection period. If the bucket is changed during precipitation take special care to ensure a minimal chance of splash contamination from the operator, the lid, the collector, or any other surfaces.

<sup>&</sup>lt;sup>iii</sup> Kimwipe' is a registered trademark of the Kimberly-Clark Corporation, Roswell, GA 30076

4.B.5. On the first Tuesday of each month a field blank sample should be obtained, provided the criteria in Sec. 10 are met. Otherwise the maximum time a bucket will remain in the field is seven (7) days. If neither of the two conditions in 4.B.3. have been met nor has the sample bucket been changed for seven consecutive days, the bucket needs to be changed, regardless of what day it is. Otherwise, do NOT change the bucket every Tuesday.

#### 4.C. <u>BUCKET CHANGES</u>

- 4.C. 1. Approach the collector and work from the downwind side to minimize wind blown contaminants from entering the buckets.
- 4.C.2. Checks and inspections to be performed.
  - a. Inspect the site and equipment for any damage.
  - b. Check the temperature of the sensor on the Aerochem Metrics collector by pressing a finger against the *sensor plate*. It should not be hot to the touch unless the collector has been open within the last several minutes.
  - c. Inspect the contents of the DRY-SIDE bucket and note any water that may be present. Large amounts of water in this bucket indicate the collector has malfunctioned.
- 4.C.3. "Short out" the *sensor grid* with water. DO NOT USE METAL TO SHORT THE GRID! Apply enough water to assure that the collector stays open for 5-10 minutes.
- 4.C.4. Allow the lid mechanism to move over and cover the DRY-SIDE bucket. Observe the movement of the lid. It should operate freely with little motor noise and rest snugly over the bucket.
- 4.C.5. Examine the contents of the WET-SIDE bucket, but BE CAREFUL NOT TO PLACE YOUR HEAD, HANDS, OR ANYTHING BUT A CLEAN LID OVER this bucket. Note any contamination (e.g. bird droppings).

#### 4.D. <u>BUCKET REMOVAL AND INSTALLATION</u>

4.D.1. Unbag the lid and using the bag as a glove snap the lid tightly onto the "old" bucket. Be careful when handling the lid that nothing but the inside of the plastic bag touches the lid. Make sure the lid is sealed the whole

way around. If the lid does not seat easily on the bucket, use the white polyethylene tape to tape it securely to the bucket. This will help to avoid any accidental spillage of the sample. Remove the "old" bucket with the "new" lid from the collector and place them in the lid bag. Secure the bag with a twist-tie. Note the DATE and the bucket TIME OFF on the bag as well as the presence of any soil, bugs, bird droppings, etc. as noted in step 4.C.5. Bagging the sample bucket decreases the chance of contamination during transport to the laboratory and catches any leakage that might occur.

- 4.D.2. Clean the *lid seal pad* on the underside of the collector lid with a clean Kimwipe' or other lint free wipe, wetted with deionized or distilled water. Note any material which is not easily removed on your FIELD OBSERVER FORM. Use a second clean, wet wipe on the rim of the DRY-SIDE bucket. At the same time check the arm and the top of the collector lid for debris. Clean off any dirt using a clean wipe. In freezing weather perform these cleaning procedures without using water.
- 4.D.3. Install a "new" bucket in position on the WET-SIDE of the collector. Remove the plastic bag in which it was shipped. *Buckets (and lids) are not to be removed from plastic bags until they have been placed on the collector.* Secure the bucket to its holder. Be careful not to touch the bucket rim or inside of the bucket with your hands or the securing device!
- 4.D.4. Note the TIME of the bucket change. This TIME will be used to complete two different FIELD OBSERVER FORMS (FOF) (see Sec. 8.B.). On the "old" (i.e. previous sample) FOF, it is entered as the BUCKET OFF TIME. On the "new" (i.e. current) FOF it is used for the BUCKET ON TIME. BUCKET OFF TIME of the "old" bucket must be the same as the BUCKET ON TIME of the "new" bucket!

#### 4.E. FINAL AEROCHEM METRICS COLLECTOR CHECKS

- 4.E. 1. While the collector is open (WET-SIDE bucket exposed) walk over to the recording rain gage to make sure the *event recorder pen* is up. The "up" position indicates the wet-side bucket is open or exposed and the sensor heater is on high heat.
- 4.E.2. Confirm that the sensor heater is warm to the touch, blow any remaining water off the sensor, and observe the lid movement as it covers the WET-SIDE bucket. The lid should move smoothly and complete its cycle in approximately 15 seconds. Check to make sure the lid fits snugly over the bucket.

- 4.E.3. IF THE COLLECTOR HAS FAILED TO PERFORM PROPERLY IN ANY OF THESE CHECKS LISTED IN 4.C. USE THE TROUBLESHOOTING GUIDE IN THE *INSTRUCTION MANUAL NADP/NTN SITE OPERATION*<sup>14</sup> TO DIAGNOSE AND RESOLVE THE PROBLEM. Contact the Central Analytical Laboratory for additional help and to determine which, if any, components may require replacement and which, if any, additional samples may have been affected.
- 4.E.4. If the collector has failed any one of the previous sensor or motor box checks, you may need to unplug the collector until repairs can be made. NADP/AIRMoN does not collect or analyze Bulk Samples, therefore do not place the collector into a bulk sampling mode. A Bulk Sample is a WET-SIDE sample that has been exposed continuously to both wet and dry deposition for the entire sampling period (see Sec. 4.G.).

#### 4.F. TRANSPORTING OF SAMPLE BUCKET

- 4.F. 1. Care is necessary when transporting the sample bucket from the site to the laboratory. Although the lid is secured tightly to the bucket and the sample bucket and lid are placed in a plastic bag, spillage can still occur. To minimize contamination or loss of sample, avoid sloshing as much as possible. Ideally, the sample would never come in contact with the lid and all particulate matter that had settled to the bottom of the bucket would not be resuspended.
- 4.F.2. The sample bucket should be transported without delay to the laboratory. The chemistry of the sample will change with time, especially during the summer, so avoid prolonged delays in getting the sample to the laboratory where it can be refrigerated. In the winter, unless the sample is frozen, it may warm above refrigerated temperatures (about 5°C) if left inside a warm vehicle for any length of time. The best rule is: collection followed by rapid transport to the laboratory where the sample can be processed and refrigerated quickly. A routine should be worked out to facilitate the quick and efficient transport of the samples to the laboratory.
- 4.F.3. If any of the sample is spilled or if the bucket is accidentally dropped or if a long delay occurs between collection and arrival at the laboratory, note this on the FIELD OBSERVER FORM along with your opinion as to whether the sample could have been contaminated or in any way compromised.

## 4.G. <u>BULK SAMPLE COLLECTION</u>

- 4.G.1. In the AIRMoN program, bulk sampling is defined when the sampler remains open for more than one (1) hour after an event ends. There are many reasons why this might occur, e.g. there is a power failure during the event or the sampler freezes while it is in the 'open' mode. If there is a power failure and you are aware of the problem, unplug the collector to avoid a power surge to the collector when the power comes back on. The same thing should be done if the arm is frozen open in order to prevent the motor from overheating.
- 4.G.2. Even though the collector itself is not functional, the rain gage data is necessary for record completeness. If at all possible, keep the rain gage working at all times.
- 4.G.3. If for any reason a bulk sample is collected by the sampler, the bucket should be changed following protocols given in Sections 4.A. through 4.F. However, no sample should be sent to the CAL for analysis and no field chemistry need be done on the sample.
- 4.G.4. A FOF needs to be prepared for ALL bulk sampling periods with as much information filled in as possible and with an explanation of the situation given in Block 11, Remarks.

#### 5. PRECIPITATION MEASUREMENTS

## 5.A. <u>BELFORT RECORDING RAIN GAGE</u>

- 5.A.1. For troubleshooting guidelines refer to the *Instruction Manual NADP/NTN* Site Operation<sup>14</sup>.
- 5.A.2. Open the sliding access door of the gage and move both pens up and down about half a centimeter to mark their positions on the chart. Lift the pens from the chart by moving the pen shifter outward.
- 5.A.3. Remove the chart and *chart drum*. Note the TIME and DATE on the chart. Check the event pen trace to be sure that the collector opened and closed with each precipitation event.
- 5.A.4. Rewind the *clock* if necessary.
- 5.A.5. Remove the catch bucket and empty it except during winter operation when it is charged with antifreeze solution (See Section 5.A.10). Replace the bucket.
- 5.A.6. Record the time of the chart change on the new chart and install it on the drum and clock mechanism. Rotate the drum until the lower pen, the one that records precipitation amounts, lines up with the current local time. Return the pen shifter to its normal position so both pens touch the chart. Make any final adjustments in the drum to ensure that the lower pen is right on the local time. Mark the beginning of the precipitation and event pen traces by moving the pens up and down about a half centimeter.
- 5.A.7. The ink level of each pen should be checked and refilled if necessary. Ink frequently absorbs water vapor in humid weather and can double its original volume. If the lines on the chart are very light or smeared, the pen ink has possibly become diluted with water. Replace the diluted ink with fresh ink. Tissue paper can be used to absorb the ink out of the pen nibs.
- 5.A.8. As a final check, make sure both the event pen and the rain amount pen are inking properly.
- 5.A.9 During winter operation, antifreeze is added to the catch bucket to prevent the precipitation collected in the catch bucket from freezing. The precipitation and antifreeze should NOT be poured out after every event, nor should the pen be rezeroed. The rain amount is additive and will rise up the chart and start down upon reaching the top of the chart. When the

amount in the catch bucket has caused the rain gage pen to start down on the rain gage chart, the catch bucket should be emptied and more antifreeze added. For more information on the amount of antifreeze to add, see *Instruction Manual NADP/NTN Site Operation*<sup>14</sup>.

5.A.10. On rare occasions, you may need to rezero the rain amount pen. Adjustments to the baseline are usually not required and *should only be done when the rain gage catch bucket is dry^{jv}*. Avoid adjustments to the pen before emptying the catch bucket, since this may cause the pen to fall below the zero line on the chart when the catch bucket is dry.

#### 5.B. <u>NWS "STICK" GAGE</u>

- 5.B.1. The National Weather Service (NWS) "stick" Gage is the rain gage measurement of choice for the AIRMoN-wet. However, it cannot show when precipitation occurs, so the Belfort Recording Rain Gage is used for that. The "stick" gage is the standard for precipitation amount measurements in the United States.
- 5.B.2. Make sure the gage is mounted in its stand and is level.
- 5B.3. Use the "stick" included with the gage to measure the amount of precipitation in inches. This "stick" is calibrated especially for the gage. A ruler or other uncalibrated measuring device will not give accurate measurements.
- 5.B.4. To measure liquid-only precipitation (to the nearest 0.01 inches), insert the "stick" through the hole in the funnel until it rests on the bottom of the 2-inch diameter inner catch tube. After a few seconds remove the "stick" and read the depth of the wetted surface of the "stick". This is the amount of precipitation received by the gage. Next detach the funnel and remove and empty the inner catch tube. Finally replace the catch tube and funnel.

<sup>&</sup>lt;sup>iv</sup> The rain amount pen should never be rezeroed to remove the elevated baseline that results when the rain gage bucket is filled with antifreeze during the winter months. It is further recommended that the baseline of the rain amount pen be set at approximately 0.15 to 0.25 inches during non-winter months. See *Instruction Manual NADP/NTN Site Operation*<sup>14</sup> for further details.

- 5.B.5. During the winter, when precipitation is likely to freeze or be frozen, remove the funnel and the inner catch tube, permitting the precipitation to fall directly into the 8 inch diameter can. When there is frozen precipitation, carefully pour a known, measured amount of hot water into the can to melt the contents. When all of the frozen precipitation is melted, measure and pour out the exact amount of water added. Pour the remainder (the melted precipitation) into the 2-inch diameter inner tube for measurement. Use the "stick" to measure the amount of precipitation.
- 5.B.6. Record the amount of precipitation in inches in Block 8 in the space marked "NWS gage" on the FOF. Record a precipitation amount for every bucket change even if that amount is "0".

### 5.C. <u>CAPMoN RAIN GAGE</u>

- 5.C.1. The CAPMoN Rain Gage is similar to the above NWS "stick" gage in that it has no moving parts. It is smaller than the "stick" gage and the amount is measured in millimeters rather than inches.
- 5.C.2. It is important to mount the Canadian gage properly as per the Canadian instructions. Amounts from this gage are being compared to the NWS stick gage amounts.
- 5.C.3. Since it is made of plastic, the CAPMoN Rain Gage, should be removed during the winter months or whenever the precipitation might freeze in the inner plastic graduate. Do NOT use this gage during the winter months.
- 5.C.4. To measure the amount of precipitation, remove the funnel and inner plastic graduate from the outer cylinder. Hold the inner plastic graduate vertical and read the level of water at the lowest part of the curved water surface (meniscus). Discard the water after the measurement has been made.
- 5.C.5 Take a CAPMoN Rain Gage reading EVERY time you take a Belfort Recording Rain Gage reading and a NWS "stick" gage reading. This includes times when one or more of these gages record zero precipitation. Record the CAPMoN amount for every bucket change during warm weather in the "Remarks" section of the FOF.

#### 6. LABORATORY TREATMENT OF SAMPLES

## 6.A. <u>SAMPLE VOLUME</u>

- 6.A.1. Remove the sample bucket from the plastic bag and note leakage, if any. Fill in the FIELD OBSERVER FORM with the Date and Time Off as written on the bag. Save the bags for sending used buckets and lids to the CAL.
- 6.A.2. Leave the lid on and weigh and record the (bucket + lid + sample) weight in grams on the FIELD OBSERVER FORM. Note the tare weight written on the bucket and lid and record the (bucket + lid) weight on the FIELD OBSERVER FORM, too. Calculate the sample weight. See the FIELD OBSERVER FORM Block 4.
- 6.A.3. Remove the lid carefully. In cold weather, verify that the sample is <u>completely</u> thawed. If the sample is frozen, replace the lid. The sample must be completely thawed before proceeding. Thaw in a refrigerator if possible to avoid the sample accidentally coming to room temperature. If this is not possible or more than 4 hours is required for the sample to thaw in the refrigerator, thaw the sample to <u>refrigerator</u> temperature (4°C) by sitting the sample bucket on the laboratory bench. <u>CAUTION</u>: The sample integrity is compromised if the sample temperature goes above 5°C! DO NOT ALLOW THE BUCKET AND THE SAMPLE TO COME TO ROOM TEMPERATURE! Do not leave the sample unattended. The thawing process must be monitored closely. If the sample warms up above 4 to 5°C, note this on the FIELD OBSERVER FORM in Block 11, Remarks.
- 6.A.4. The large exposed area of the sample bucket is especially prone to contamination. The dissolved substances in precipitation have very low concentrations. One dust particle from the laboratory or even the ammonium in a small room generated by human perspiration can invalidate a sample. Therefore, perform the following steps in section 6.B. with great care.

#### 6.B. <u>DIVISION AND HANDLING</u>

6.B.1. Sample handling and division procedures depend on sample volume. Samples are shipped to the CAL in shipping bottles, never in the sample buckets. 6.B.2. All volumes refer to the amount of sample that can be decanted from the bucket, not the sample volume determined by the weight of the (bucket + lid + sample) - (bucket + lid) calculation.

6.B.3.	Sample Volume (mL)	Volume Shipped (mL)	Handling
	$0  <  V  \leq  10$	none	Return the bucket and lid to the CAL for cleaning
	10 < V < 50	all	Ship the entire sample to the CAL along with the used bucket and lid for cleaning
	V = 50	35	Using no more than 15 mL of sample, measure field pH and conductivity. Ship 35 mL sample to the CAL along with the used bucket and lid for cleaning
	V > 50	35 +	Send between 35 and 250 mL to the CAL. Use the rest for field pH and conductivity. Send the used bucket and lid to the CAL for cleaning

- 6.B.4 Maximum shipped to the CAL is 250 mL and the minimum shipped is 10 mL.
- 6.B.5. If volume is 0 (zero) go to Section 9. A.2.
- 6.B.6. Remove the shipping bottle from the plastic bag in which it was sent and mark it with the following information: SITE ID, DATE/TIME ON, DATE/TIME OFF. Bucket TIME ON and TIME OFF are in *LOCAL TIMES* ONLY!

6.B.7. Site ID's for the 9 NADP/AIRMoN sites are:

NY67	Ithaca, NY
DE02	Lewes, DE
OH09	Oxford, OH
TNOO	Oak Ridge, TN
VT99	Burlington, VT
IL11	Bondville, IL
PA15	State College, PA
MD15	Ewell, MD
FL18	Tampa, FL

- 6.B.8. Remove the cap from the bottle and set it aside in a clean area with the lip up.
- 6.B.9 Tip and turn the bucket gently to wash down as much of the sides as possible. Be careful not to disturb and resuspend any material which has settled or precipitated to the bottom of the bucket. Let this material resettle if it is disturbed and resuspended.
- 6.B.10. When pouring sample from the large bucket to the sample bottle, be careful to avoid touching the rim of the bucket to the lip of the bottle. If this should occur, the potential for contamination of the sample is great.
- 6.B.11. Rinse the shipping bottle with a small amount of sample prior to pouring in the entire sample. Pour approximately 10 mL of sample into the bottle from the bucket for rinsing. Replace the cap on the bottle and shake the bottle vigorously.

NOTE: Rinse the shipping bottle only if there is at least 100 mL of sample!

- 6.B. 12. Remove the cap from the bottle and once again place it in a clean area with the lip up.
- 6.B.13. Discard the rinse.
- 6.B. 14. Carefully pour the sample from the bucket into the shipping bottle, trying to keep the stream from touching the lip of the shipping bottle mouth. Fill the shipping bottle to no more than about <sup>1</sup>/<sub>2</sub> inch below the neck of the bottle.
- 6.B. 15. Replace the cap.

- 6.B.16. Dry the exterior of the bottle with Kimwipes<sup>•</sup> if necessary. Note the integrity of the markings on the bottle and refresh if necessary.
- 6.B. 17. Return the sample/shipping bottle to the plastic bag in which it was sent and refrigerate the sample at 4°C. Be careful not to freeze the sample.

## 7. pH AND CONDUCTANCE MEASUREMENTS

- 7.A. pH and conductance measurement procedures depend on sample volume.
- 7.B. All sample volumes refer to the volume decanted from the bucket into the sample/shipping bottle, not the amount determined from the (bucket + lid + sample) (bucket + lid) sample calculation.
- 7.C. If there are between 10 and 50 mL of sample, all of the sample must be shipped to the CAL with NO FIELD CHEMISTRY performed!
- 7.D. If there is 50 mL or more of sample, 15 mL of the sample can be used for measuring the field pH and specific conductance of the sample with appropriate rinses.

## 7.E. <u>SPECIFIC CONDUCTANCE MEASUREMENTS</u>

- 7.E.1. Bring all solutions to room temperature. The conductance standard supplied by the CAL, your deionized or distilled water and the aliquot of the sample to be measured plus the rinses must all be at the same temperature as conductivity is very temperature sensitive. CAUTION: DO NOT BRING YOUR ENTIRE SAMPLE TO ROOM TEMPERATURE. Just the amount to be used to measure the specific conductance should be allowed to warm up over 4°C.
- 7.E.2. Rinse your conductance cell at least three times with distilled or deionized water. Rinse once with the  $75\mu\mu$ S/cm standard supplied by the CAL. Using a second portion of the standard, measure the specific conductance of the 75  $\mu$ S/cm standard.
- 7.E.3. If your conductance meter has a calibration control, standardize your instrument according to the instruction manual using the 75  $\mu$ S/cm standard solution. Record the value to the nearest 0.1 $\mu\mu$ S/cm in the space marked STANDARD MEASURED on the FIELD OBSERVER FORM. Alternatively, if your meter does not have a calibration control, record the value obtained in Section 7.E.2. to the nearest 0.1  $\mu$ S/cm in the space marked STANDARD MEASURED on the FIELD OBSERVER FORM. Block 9.
- 7.E.4. Calculate the CORRECTION FACTOR to the nearest .001 by dividing the STANDARD CERTIFIED value ( $75\mu\mu$ S/cm) by the STANDARD MEASURED. Record this value in the three spaces marked CORRECTION FACTOR on the FIELD OBSERVER FORM, Block 9.

- 7.E.5. Rinse the cell three times with deionized or distilled water, discarding each rinse. Use a fourth portion to determine the specific conductance of your distilled or deionized water. Record the value as DISTILLED WATER on the FIELD OBSERVER FORM, Block 9. to the nearest 0.  $l\mu\mu$ S/cm. This value should be the lowest reading you are able to obtain after repeated rinsings. The value should not exceed 2  $\mu$ S/cm. If a value of more than 10  $\mu$ S/cm is measured do not continue with the measurements. Instead obtain a new supply of distilled or deionized water and repeat Sections 7.E.2. 7.E.5.
- 7.E.6. Without rinsing the cell, but with shaking off the excess water, rinse the cell with the quality control check sample furnished by the CAL. Use a second portion to determine its specific conductance. Record this value to the nearest 0.1  $\mu$ S/cm as the CHECK SAMPLE MEASURED on the FIELD OBSERVER FORM, Block 9. Multiply this value by the CORRECTION FACTOR and record the result as the CHECK SAMPLE CORRECTED on the FIELD OBSERVER FORM. This value should be 21.8  $\mu$ S/cm  $\pm$  3.0  $\mu$ S/cm. If the corrected value falls outside of these limits there is a potential measurement problem and the CAL should be contacted.
- 7.E.7. Rinse the cell three time with deionized or distilled water, discarding each rinse. If the conductance cell is of the recommended small volume type (see Instruction Manual NADP/NTN Site Operation<sup>14</sup>), next rinse the cell with approximately 3 mL of the precipitation sample aliquot. Use a second 3-4 mL aliquot to determine the PRECIPITATION SAMPLE MEASURED. Record this value to the nearest 0.01  $\mu$ S/cm on the FIELD OBSERVER FORM, Block 9. Multiply this value by the CORRECTION FACTOR to obtain the PRECIPITATION SAMPLE CORRECTED. Record this value on the FIELD OBSERVER FORM. If the conductance cell is not of the recommended type, shake off the excess deionized or distilled water from the third rinse and measure the necessary size portion of the precipitation sample to the nearest 0.01  $\mu$ S/cm. Record this value as the PRECIPITATION SAMPLE MEASURED on the FIELD **OBSERVER FORM.** Multiply this value by the CORRECTION FACTOR to obtain the PRECIPITATION SAMPLE CORRECTED and record this number on the FIELD OBSERVER FORM, Block 9.
- 7.E.8. Rinse the cell three more times with deionized or distilled water, and then fill the cell with water. Cover the cell with Parafilm<sup>•v15</sup> or an inverted sampling vial to prevent evaporation during storage. SPECIFIC CONDUCTANCE CELLS MUST NOT BE STORED DRY!

<sup>&</sup>lt;sup>v</sup> Parafilm<sup>•</sup> is a registered tradename of American National Can, Greenwich, CT 06830

## 7.F. <u>pH MEASUREMENTS</u>

- 7.F.1. The Central Analytical Laboratory supplies a standard combination pH electrode, Broadley-James, to all sites. This is the only electrode to be used in making NADP/AIRMoN field pH measurements. It should not be used for any other samples. Notify the CAL prior to making measurements if the use of another electrode becomes necessary. Replacement electrodes are available through the CAL. The CAL also provides small volume polystyrene sampling vials to be used for each pH measurement. Each vial should be rinsed with the solution it is to contain just prior to use. To keep the vials free of dust and contamination, store them in the bag in which they arrived.
- 7.F.2. Adjust the temperature control on the meter to room temperature. If no thermometer is available set the temperature control to 25°C.
- 7.F.3. Carefully remove the soaker bottle from the tip of the electrode. Use extreme care in removing the soaker bottle. Remove the cap, the O-ring, and the bottle all at once by simply slowly pulling the electrode out of the bottle with a gentle back and forth twisting motion. Handle the electrode gently and carefully so that the fragile electrode barrel doesn't crack during the process. Rinse the electrode several seconds in a flowing stream of deionized water. Make sure any accumulated salts are dissolved from the tip of the electrode.
- 7.F.4. BLOT the tip of the electrode with a clean absorbent wipe (e.g. Kimwipe') to remove excess water. NEVER wipe down the electrode! Uncover the filling port of the electrode by removing the plug or Parafilm' or sliding off the sleeve at the top of the electrode and replenish the filling solution, *using only the filling solution provided by the CAL or part #AS3120-C20-0250.* The fill hole must be open during measurements and should be closed for storage. Add filling solution if needed and <u>carefully</u> shake the electrode as you would a fever thermometer to remove any air bubbles that may have formed. Hold the electrode near the filling port when shaking. Rinse the electrode bulb and junction area with deionized water after filling.
- 7.F.5. Bring all solutions to room temperature. Buffers for standardization, QC check solution samples, and precipitation samples must all be at the same temperature for pH measurements. This temperature should be as close as possible to the temperature control adjustment made on the pH meter.
- 7.F.6. Standardize the pH meter each time the pH of a sample is measured. A QC check sample must be measured each time as well. If several samples are measured at one time, recalibrate the pH meter once every 10 samples plus QC check solution samples.

- 7.F.7. Fill one of the small sampling vials with pH 7.00 buffer. Insert the electrode into the vial and allow it to remain there for 30 seconds. Dump the buffer out of the sample vial and without any other rinses refill the vial with fresh 7.00 pH buffer. Insert the electrode tip directly into this *conditioned* vial of pH 7.00 buffer. Allow sufficient time for the reading to become stable. Stable means the pH value does not change more than 0.01 pH units in 30 seconds. This step may take at most 3 minutes. Use the Auto Read Function on your pH meter if available. Make sure you stand away from the electrode or very still when performing pH measurements to allow the electrode a chance to stabilize. The Broadley-James electrode is **very sensitive to movement** and may continually flash numbers rapidly if there is continual movement around it. Adjust the calibration or standardize control to read pH 7.00.
- 7.F.8. Rinse the electrode thoroughly with deionized water. Fill a clean vial with pH 4.00 buffer. Repeat the conditioning rinse as described in Section 7.E.7 by inserting the electrode into the vial and allowing it to remain there for 30 seconds. Remove the electrode, dump the buffer, refill the vial with fresh pH 4.00 buffer and insert the electrode tip again. Allow sufficient time for the reading to become stable. Stable means that the pH value does not change more than 0.01 pH units in 30 seconds. Adjust the slope control of the pH meter to read pH 4.00.
- 7.F.9. Rinse the electrode with deionized water. Repeat step 7.F.7 but do not readjust the calibration/standardization control. If the pH reads 7.00 +/-0.03 pH units then repeat step 7.F.8 with the pH 4.00 buffer. If this buffer, too is within +/- 0.02 pH units with no slope control readjustments, then proceed with the measurements. If either the pH 7 or pH 4 buffer solution does not measure within +/- 0.03 pH units or +/- 0.02 pH units respectively, repeat the calibration procedure entirely, steps 7.F.7 and 7.F.8 with the appropriate readjustments to the calibration and slope controls. If you still can not calibrate the electrode/meter *stop* the analysis and call the CAL for assistance.
- 7.F.10. Thoroughly rinse the electrode with deionized water. Measure the QUALITY CONTROL (QC) CHECK SAMPLE using the same conditioning rinse technique outlined in steps 7.F.7 and 7.F.8 above. Allow the system to stabilize until the readings differ by no more than +/-0.01 pH unit within a 30 second period, but wait no more than 3 minutes. Record the reading in the space marked "pH Check Sample" on the Field Operator Form (FOF). The check sample should read 4.30 +/- 0.10 pH units. If your measurement is outside of this range contact the CAL for assistance. If your measurement is within this range, *continue* with the measurement of the PRECIPITATION SAMPLE pH.

- 7.F.11. Rinse the electrode thoroughly with deionized water. Fill a clean vial with room temperature precipitation sample. If there is sufficient sample, condition the vial and electrode by inserting the tip of the electrode into the sample in the vial for 30 seconds. Decant the sample from the vial and without any other rinses, refill the vial with fresh precipitation sample. Reinsert the electrode into the vial and allow the system to stabilize until the readings differ by no more than +/- 0.01 pH units within a 30 second period, but wait no more than 3 minutes. Record the measured pH value in the space marked "Precipitation Sample" on the FOF, Block 9.
- 7.F.12. Samples may be agitated slightly (i.e., carefully shaken) to more rapidly reach the expected pH range, but must be quiescent or stationary when the pH measurement is being taken. Never wipe down the electrode. Simply BLOT the tip with a clean absorbent wipe to remove excess water.
- 7.F.13. Discard any remaining sample or standard aliquots and any used sample vials. Rinse the electrode thoroughly with deionized water one last time. Cover the filling port of the electrode either with Parafilm<sup>•v</sup> or the sleeve to prevent evaporation and crystallization of the KC1 solution inside. Carefully replace the soaker bottle. Be sure the O-ring is still in the lid. Make sure the electrode bulb is immersed in the solution.

## 8. NADP/AIRMoN FIELD OBSERVER FORM

- 8.A. The FIELD OBSERVER FORM (FOF), provided to each site by the CAL, is used to record essential information for the interpretation of chemical analysis and precipitation data. Be certain recorded notations are legible and that the form is filled out completely. Incomplete or illegible forms require additional time to process and phone inquiries by the CAL to the site observer or site supervisor.
- 8.B. For each bucket change, fill out one of the Field Observer Forms. It is suggested that at the time of the bucket change TWO FOFs be filled out, the one for the bucket just removed from the collector and the one for the bucket that was just put on the collector. This will allow substitute observers to complete the forms without errors caused by mixups in time reporting or record keeping. This will also ensure that the TIME OFF for one sample will always equal the TIME ON for the next sample and will avoid data and sample gaps. The data should be collected at the time of the bucket change or as soon as possible there after and, when possible, recorded directly on the FOF. Please <u>LEAVE NO</u> <u>BLANK SPACES</u> explain any and all gaps in Block 11, REMARKS.

## 8.C. FIELD OBSERVER FORM (FOF)

CAL Use Only - this area is the only area on the form that you do not write in. It is for the CAL to record the ID, temperature of the samples upon arrival at the lab, sample type and other information. Leave this area blank.

- Block 1 STATION ID Record the 4 digit Site ID supplied by the CAL, (also known as the CAL code). See Sec. 6.B.7. for your code. The code identifies your site location by state. Print the station name.
- Block 2 OBSERVER Carefully print the *actual observer's* initials in the boxes provided even if he or she is only substituting for the regular observer. Also legibly print the observer's name. The observer must sign his or her name for chain-of-custody purposes. This section must be filled in by the person collecting the sample, doing the field chemistry and filling in the rest of the FOF. If more than one person has done the work, the person in charge or the one responsible for the work or the person to whom communications concerning this sample should be directed must fill in this section.
- Block 3 SHIPMENT DATE fill in the actual date that the samples leave your site for the CAL. This data may be used to improve shipping time or in conjunction with sample temperature upon arrival at the CAL.

- Block 4 BUCKET carefully record the actual date and time on and off of each bucket. THERE SHOULD BE NO TIME GAPS! The date/time off of one bucket <u>must</u> be the date/time on of the next bucket regardless of whether any precipitation was collected or not. This is very important! Each FOF must follow with no time or date gaps from the last FOF. If for some reason there is a gap, it should be explained in Block 11, Remarks.
- Block 5 SITE OPERATIONS this block keeps the CAL informed of how the equipment is operating. Please check "Yes" or "No" for each question. If "No" for 1 or 2, please explain what happened in Block 11, Remarks, and call the CAL for servicing information.
- Block 6 SAMPLE CONDITION there are 7 possibilities for sample contamination or other conditions. Check "Yes" for all that apply. If something is not relevant to the sample, check "No". Each of the 7 possibilities must have either "Yes" or "No" checked or the operator will receive a call from the CAL. All "Yes" responses should have an explanation in Block 11, Remarks, with an attempt at quantifying the condition made when possible or applicable. Since the personnel at the CAL do not see the entire sample, it is necessary to be as accurate as possible when describing the original sample condition.
- Block 7 SAMPLE WEIGHT Record the (bucket + lid) weights as written on the bucket and lid. Each bucket and lid have been previously weighed at the CAL and that weight is listed on each bucket and lid. Weigh the bucket and lid with the sample. Record the amount. Subtract the weight of the (bucket + lid) from the (bucket + lid + sample) to obtain the amount of sample in grams. This is approximately equal to the amount of sample in mL. This number should agree within 10% of the predicted volume of precipitation as calculated from the National Weather Service "stick" gage. See Block 8.
- Block 8 PRECIPITATION RECORD there are several parts to this data block. The bucket-on-to-off total is from the National Weather Service "stick" gage reading which is the method of choice for determining the predicted volume. Multiply this measured amount by 1724 mL/inch to determine the expected collected volume. This should be compared to the actual volume collected (Data Block 7). If there is more than a 10% variance between the predicted and actual sample volume, recheck the weights on the bucket, lid, and sample and the "stick" gage reading just to verify that there were no transcription or math errors.

The Recording gage volume will normally be the Belfort rain gage volume. Record this volume as read from the chart recorder. The two measured volumes of precipitation may or may not be the same. Record both regardless of the amounts logged.

The precipitation type is based on the National Weather Service weather codes. Please circle all that apply. Place a " + " or a "-" beside the appropriate precipitation type if more than one type of precipitation has occurred.

For example, for a fall thunderstorm that changes to freezing rain then to freezing drizzle then to snow showers and finally to steady snow as a cold front goes through the codes would be marked like the following:

TR+ R W ZR ZL SW- S

The definitions of the National Weather Service weather codes are as follows:

T P	Thunder Bain	IC IP	Ice Crystals Ice Pellets
R	Rain		
RW	Rain Showers	BS	Blowing Snow
S	Snow	E	Sleet
SW	Snow Showers	F	Fog
L	Drizzle	Κ	Smoke
ZL	Freezing Drizzle	Н	Haze
ZR	Freezing Rain	D	Dust
А	Hail	BD	Blowing Dust
SP	Snow Pellets	BN	Blowing Sand
SG	Snow Grains	(+)	Heavy Amounts
		(-)	Light Amounts

Block 9 SAMPLE CHEMISTRY - There are three (3) sections in this block. The first is the date and time the sample chemistry is done in the field laboratory. It should be the same day as sample collection if at all possible. The second section is the calculation of the field specific conductance. Refer to Section 7.E for details, measure the conductance standard provided by the CAL and record it in the appropriate boxes. Divide 75.0 by the measured value of the conductance standard. This gives you a correction factor. Measure the conductance/pH check solution and the precipitation sample. Record these values in the appropriate boxes. Multiply the measured values by the calculated correction factor obtained above and record the corrected conductance values for the check solution and the sample in the appropriate boxes. Calibrate the pH meter as described in Sec. 7.F. Record the pH of the pH check solution and of the precipitation sample. There should be values in this section for every sample above 50 mL. If there are no field chemistry measurements, please explain in Block 11, REMARKS. Report that the sample was too small for shipment to the CAL or for doing field measurements. Otherwise, report that the entire sample was shipped to the CAL or that the sample is a routine bucket change with no precipitation occurring, etc. Remember, every block must be filled in completely or an explanation is needed in Block 11, REMARKS.

- Block 10 SUPPLIES circle all supplies that are needed at your site. Continue to circle the supplies until you receive them. If you need supplies that are not listed, write what you need in Block 11, REMARKS.
- Block 11 REMARKS - his is the most important block on the FOF! Please make all comments and information as legible as possible as all information will be typed into the computer. If there is any reason that any of the other blocks are not completely filled in, an explanation must appear in the REMARKS block. Any details about the sample type, the sample condition or the precipitation type or amounts must be in the REMARKS block. This is also where the CAPMoN rain gage amount should be recorded. Make certain it is identified as such and that it is easy to read and see. Fill in the FOF as completely as possible, but when NOT possible, explain any gaps in the this REMARKS block. For TYPE I samples, those samples with no precipitation (see Sec. 8.A.2.), please be sure to note in this block that there was no precipitation collected or shipped.

	NADP/AIRMoN						
<b>58</b> v	VET DEPOSITION FIELD OBSERVER FORM	CAL Use Only					
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM	Send Completed Form with Each Sample						
A Cooperative Research Program of the State Adjustuce Experiment Stations (NRSP 3)	Central Analytical Leb Hilinois State Water Survey						
Federal Acid Precipitation Task Farce State Agencies and Private Research Organizations	2204 Griffith Dr. Champeign, Illinois 51820						
	1-800-952-7353						
1. STATION ID	2. OBSERVER	<b>3. SHIPMENT DATE</b>					
	Print Name	MO DAY YR					
Station Name ID	Signature						
4. BUCKET	5. SITE OPERATIONS YES NO						
4. DOORET	2 1. The sensor heater and motor	tox operated properly and the <u>event recorder</u> indicates the promptly at the end of each precipitation event.					
MO DAY YR 0001-2400	If No, to 1 or 2, explain in Block 11, 2 1 2. <u>Rain gage</u> operated properly. Remarks, and call CAL, 2 1 3. Collector opened and closed at	t least once during sampling parind					
		NO 4 langets colored method					
	Check <u>YES</u> or <u>NO</u> . <u>YES</u> NO If Yes, explain and quantify <u>2</u> 1 1. Bird droppings <sup>2</sup>	4. Insects, animal matter     5. Leaves, twigs, polien, other plant matter					
7. SAMPLE WEIGHT	in Block 11, Remarks. 2 1 2. Cloudy or discolored 2	6. Handling contaminants					
For <u>all</u> sample buckets	3. Soot, ash, dirt particles						
Bucket + Lid + Sample (grams)	8. PRECIPITATION RECORD NWS gage (Bucket on to off the	inches					
= Bucket + Lid (grams)	Circle as types and apply - for deviation are operators wanted						
	TRRWSBWLZZRASPOCKPBSEFKHDBOBN+-	X 1 7 2 4 • mL inch					
= Sample Weight (grams)	Recording gage I I I Inches Predicted Volum						
	Recheck weights if predicted volume is not within 10% of actual volume						
	ductance in µS/cm	PH 10. SUPPLIES					
Only for Wet-Side buckets with a Sample Weight of more than 30 grains 7 5 0 0		Circle until received     pH 4 Buffer ice Packs					
MO DAY YR Standard Certified		PH 7 Buffer Bottles					
	X Check Sample Measured Check Sample Corrected	Field Forms Bags pH Electrode (d Seal Rain Gage Charts Vials					
		Rain Gage Charts Vials Rain Gage Ink Cond Std Desh Pot Fluid					
Correcton Factor							
11. REMARKS							
	····	ferin Date 2/1794					

#### 9. SHIPMENT AND DATA LOGGING

#### 9.A. SHIPMENT

- 9.A.1. Prepare to make a shipment by getting a black shipping box with insulation blocks, two used buckets, two lids, and plastic bags. Two types of shipments can be made.
  - **TYPE I.** Two used buckets and lids and NO precipitation samples (no ice packs needed).

or

**TYPE II.** Two used buckets and lids with one or two precipitation samples (8 ice packs, frozen solid, are needed).

#### 9.A.2. Shipment **TYPE I**

- a. When NO precipitation samples are sent (shipment **TYPE I**), place each bucket in a bag and stack the buckets together in the shipping box.
- b. Put each lid in a bag and place beside the buckets in the box.
- c. FOF's for **TYPE I** samples should only be sent to the CAL with a shipment that contains samples. Shipments without samples (i.e. TYPE I) are not sent "Next Day" as are shipments with samples (i.e. TYPE IT). Send ALL FOF's, regardless of sample type, with sample shipments arriving at the CAL the NEXT DAY! This will help ensure consistency and continuity in sample numbering and sample on/off Dates and Times.
- d. Skip to Section 9.A.5.

#### 9.A.3. Shipment **TYPE** II

- a. When one or two precipitation samples are sent (shipment **TYPE II**), place each used bucket in a bag and stack the buckets together in the shipping box.
- b. Place 4 frozen ice packs in the bottom of the top bucket. Arrange the ice packs in the bottom and along the inside of the bucket.

- c. Remove the sample(s) and a 60 mL "temperature only" bottle from the refrigerator. Make sure the lid(s) are tight and check the integrity of the markings (see Section 6.B.6.).
- d. Seal the sample bottle cap with the white polyethylene tape. Pull tape tightly so that it stretches slightly around the cap lip and the bottle. Pull the tape clockwise so that the cap is tightened further with the addition of the tape.
- e. Put each sample bottle in a zip-lock bag and make sure the bags are sealed tightly and are free of nearly all the trapped air.
- f. Place the 250 mL sample/shipping bottle(s) on top of the first layer of 4 frozen ice packs.
- g. Place the 60 mL "temperature only" bottle next to the sample bottle(s). It, too, should be sealed in a zip-lock bag and be at refrigerator temperature.
- h. Place the second bag of 4 frozen ice packs on top of the bottle(s) and arrange the packs so that you can snap one of the used lids securely to the top of the top bucket.
- i. Pull the plastic bag up around the top bucket and lid and twist-tie the bag. Put the other used lid in a bag and tuck it beside the buckets.
- j. Put the FIELD OBSERVER FORM that goes with the buckets on top of the sealed bag. The FIELD OBSERVER FORM should record data for the sampling periods covered by both of the buckets regardless of whether one or two samples are being shipped.
- k. Add FOF's that may have accumulated from TYPE I shipments. (See 9.A.2.b.)
- 9.A.4. Make sure there are 2 to 4 insulation boards surrounding the buckets, one on each side if possible. A fifth board should be in the shipping box lid.
- 9.A.5. Secure the box tightly with the 4 straps and turn the address label on the side to show:

NADP/AIRMoN Illinois State Water Survey 2204 Griffith Dr. Champaign, IL 61820

- 9.A.6. Make sure the box and or the Bill of Lading has "Government Rate" clearly written on it.
- 9. A.7. If *no* samples are being sent to the CAL, just used buckets and lids, the box should not be sent at Next Day rates. Regular ground shipment should be used, but Government Rate should still be requested.
- 9. A.8. If there is a sample or samples in the shipping box going to the CAL, then the shipment <u>must</u> be NEXT DAY with Government Rate clearly identified.

#### 9.B. <u>SITE RECORDS</u>

- 9.B.1. A copy of the FIELD OBSERVER FORM for each bucket change must be maintained at the site. Any additional information should be stapled to the FIELD OBSERVER FORM for future use if needed. The third sheet, the green sheet, of the triplicate carbon-less copies should be retained at the site.
- 9.B.2. Copies of the rain gage and event recorder charts should be filed at the site laboratory with the FIELD OBSERVER FORMS. These charts should be clearly dated and initialed for quality accountability purposes.

## 10. SPECIAL AND SYSTEM BLANKS HANDLING PROCEDURES

## 10.A. FIELD BLANK SAMPLES

Field Blank samples should be obtained on the first Tuesday of the month when there has been no precipitation and no lid openings since the last bucket change or the lid of the collector was open for less than one hour and fewer then 6 (six) times with no precipitation occurring since the last bucket change. See Sec. 4.B.3. If these conditions are not met on the first Tues. of the month, then the next Tues. should be used for a Field Blank or the first Tues. of the month when the conditions do exist. Only one Field Blank per month should be prepared.

Only if both conditions are met, can a field blank be prepared. If <u>both</u> of those conditions do not exist on the first Tuesday of the month, then the field blank should be obtained on the first Tuesday that both conditions are met. Only one field blank per month should be prepared.

- 10. A.1. When visiting the site on the first Tuesday of each month, in addition to the items listed in 4.A.3. take along a Field Blank bottle (supplied by the CAL.)
  - a. Field Blank bottles are 250 mL bottles of solution shipped from the CAL.
  - b. Field Blank bottles are marked FB### with indelible ink and the same color ink is used to clearly mark the cap. The identification, FB###, represents Field Blank followed by a three digit sequential number. This number is also assigned at the CAL.
- 10.A.2. Check the event recorder for any lid openings.
- 10.A.3. Check the rain gage for any evidence of precipitation, however small.
- 10.A.4. The following conditions MUST be met before a field blank can be prepared:
- CONDITION 1. No precipitation whatsoever has occurred since the last bucket change.

If precipitation (however light) has occurred, do NOT treat as a Field Blank! If there is moisture in the hucket not from precipitation, a Field Blank can still be obtained, hut a note about the moisture should he included on the Field Observer Form.

- CONDITION 2. There are fewer than 6 (six) lid openings and the total time the lid was open is less than 1 hour. Record the number of lid openings in Block 11, Remarks on the FOF as well as the total length of time the lid was open.
  - 10.A.5. Following routine sample collection procedures as discussed in Section 4, prepare the used bucket for removal from the collector.
  - 10.A.6. Before placing the lid on the used bucket, uncap the lid from the Field Blank bottle furnished by the CAL and carefully pour about half of the liquid into the used bucket still on the collector. Be careful to avoid any contamination of the bottle or the sample.
  - 10.A.7. Recap the bottle tightly for return to the laboratory.
  - 10.A.8. Secure the clean lid onto the used bucket and continue with the sample collection protocols as described in Section 4.
  - 10.A.9. Return the bucket to the laboratory (covered as per procedure). Transport the Field Blank bottle with its approximately 125 mL of sample back to the laboratory, seal the lid on with the tape furnished by the CAL and refrigerate immediately. This bottle will be returned to the CAL for analysis without further analysis or handling by the site operator.
  - 10.A.10. At the laboratory, without removing the lid, slosh the water gently in the bucket and then let it stand over night or at least two hours. Please note in Block 11, REMARKS on the Field Observer Form how long the sample stayed in the bucket.
  - 10.A.11. After the solution has remained in the bucket, follow the procedures for Laboratory Treatment of Samples, Section 7, pH and Conductance Measurements, Section 7, and Shipment and Data Logging, Section 9. From this point the field blank sample in the bucket is to be treated exactly like any other precipitation sample brought into the laboratory from the field.
  - 10.A.12. The (bucket + lid + sample) are weighed, pH and specific conductance are measured, and the sample is shipped in a clean 250 mL sample bottle. The sample bottle is marked with the Date and Time On and Off of the used bucket. The field blank ID from the original Field Blank bottle should also be written on the shipping bottle.
  - 10.A.13. Refrigerate the field blank sample in the shipping bottle.
  - 10.A.14. Include both field blanks, the original Field Blank bottle with the approximately 125 mL of sample left in it and the lid reseated and the field

blank sample that was prepared from the solution poured into the used bucket, in the next shipment of samples. Ice packs should be use and the samples packed exactly as in Section 9. These two samples should always be handled as if they were real precipitation samples.

- 10.A. 15. Fill out a Field Observer Form as completely as possible for the field blank sample. If there is a section on the Field Observer Form that can not be completed explain why in Block 11, Remarks. State in Block 11, Remarks, that this is a Field Blank.
- 10. A. 16. No Field Observer Form is needed for the original Field Blank bottle being returned to the CAL.
- 10.B. Buckets need not be changed on Tuesday providing there has been no precipitation in the last 24 hours, it is not the first Tuesday of the month (this Tuesday is reserved for Field Blanks, see Sec. 10.A.), the lid of the collector has been open for less than one hour or fewer then 6 times since the last bucket change, and there has been at least one bucket change within the last 7 days. If the bucket has been in the field for 7 (seven) days it should be replaced with a clean bucket regardless of any other conditions or criteria. No bucket should ever be out in the field more than one week.

## 11. PRECIPITATION LOG FORM

#### 11.A. USE DAILY CLOCK (HOURLY RECORDING)

Follow the rain gage manufacturer's instructions for operating in a daily recording mode. When mounting or removing charts or at any other time an operator visits the site and checks the gage, place time marks on the chart. The clocks sometimes do not keep good time, so time marks are helpful to reconcile time discrepancies. Be sure the rain gage is level and free of debris.

#### 11.B. RECORDING HOURLY RAINFALL AMOUNTS ON PRECIPITATION LOG FORM

- 11.B.1. Fill in all of the information at the top of the form. Print the Station Name. The Station ID is the CAL Code as found in Sec. 6.B.7. Print the Operator's Name legibly and fill in the Month/Year and the Time Zone.
- 11.B.2. There is one row for each day of the month and 24 columns for the hours of the day. The last column in the row is for recording the time the bucket was removed from the collector. The spaces on the form should be filled with the amount of rainfall in <u>HUNDREDTHS OF INCHES</u> for the hour <u>ENDING AT THE TIME AT THE TOP OF COLUMN</u>. Write the number as an integer (no decimal point).
- 11.B.3. The times are *LOCAL TIMES* only!
- 11.B.4. Hour spaces with no precipitation and the rain gage functional <u>SHOULD</u> BE LEFT BLANK. Otherwise, fill in the amount or the symbol below:
  - ML = Data record missing, precipitation likely

MU = Data record missing, precipitation unlikely

T = Trace (if there is a personal observation of precipitation too small to generate a record on the rain gage chart)

0 = Space of record where time resolution is greater than one hour. Enter the amount for that period within the parentheses. Not to be used on a routine basis for recording rain amounts and should only be used when absolutely necessary.

- 11.B.5. Explanations for missing data or special circumstances should be either written at the bottom of the page or on the log form in spaces where data will not be covered. Since this is a triplicate, carbonless form, it is not possible to write on the back of the form.
- 11.B.6. Log precipitation amount on the FIELD OBSERVER FORM.

11.B.7. The bottom or green copy should be kept on file at the field laboratory. The other two copies should be sent to the CAL with the first shipment that contains samples.

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\*NOTE: All times are LOCALI 00-01 means 0001 through 0100 hours and 23-24 means 2301 through 2400 hours. Precipitation is reported in inches.

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