Standard Operating Procedure for Sampling Trace Metals in Precipitation Using Modified Aerochem Collectors

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1.0 Overview

This SOP is intended to provide a step by step procedure for the proper collection of a precipitation sample using a modified wet-only Aerochem Metric sampler. Procedures include replacement of the Teflon sampling train and inspection and maintenance of the sampling equipment.

Data collected from analysis of precipitation samples from the modified Aerochem samplers will be primarily used for the Lake Michigan and Lake Superior Load Monitoring Program and for the Integrated Atmospheric Deposition Network (IADN). Samples at the Sleeping Bear Dunes site, which is part of the Integrated Atmospheric Deposition Network, were sampled and analyzed by Indiana University. The sampling method is identical apart from a few minor differences in QC samples. This site represents 10 % of the samples for this method. The data will be used to assess the atmospheric loadings of trace metals to the Great Lakes.

The modified wet-only Aerochem sampler is used to collect weekly precipitation samples for trace metals analysis. Wet-only deposition samplers are designed to open only during a precipitation event in order to minimize contamination from dry deposition and blowing dust, etc. Due to the very high susceptibility of precipitation samples to trace metal contamination, the procedures seek to minimize operator contact with the sample and allow the sample to contact only Teflon surfaces. The Teflon sampling train, which consists of a Teflon-coated funnel, Teflon tubing and Teflon bottle, is shipped to the site each week by Buffalo State University (BUF). After a one week collection period, the entire sampling train is returned to BUF for cleaning and analysis of the precipitation sample. The trace metals listed in Table 1 will be analyzed by ICP/MS as detailed in the laboratory SOP.

Any questions concerning sampling methods or operation of equipment should be directed to the following individuals. The ISWS Contact will be the prime contact for all methodologies and general operation questions. The EPA Project Lead is the second contact if the ISWS Contact cannot be reached. Specific questions should be directed as indicated below.

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Table 1. Analytes from Modified Aerochem Metric Sampler

Parameters:	
Aluminum	Arsenic
Cadmium	Chromium
Copper	Lead
Manganese	Nickel
Sodium	Selenium
Titanium	Vanadium
Zinc	

2.0 Sampling Equipment Description

The Aerochem Metric (ACM) sampler is modified so that the sample will contact only Teflon surfaces to minimize trace metals contamination. The precipitation will be caught in a Teflon-coated aluminum funnel and stored in a 2 L Teflon bottle. The 2 L bottle can collect a volume equivalent to 3 cm of precipitation. The funnel is fitted with a Teflon o-ring and Teflon fitting and is connected to the bottle by Teflon tubing. The metal lid and pad are replaced with a polyethylene lid and Teflon wrapped foam pad. A new polyethylene bag is inserted in the dry bucket each week so that the lid will contact a clean surface. The arms of the ACM are Teflon coated and, at the pivot points, are covered with plastic sleeves to prevent freezing in the winter. The base of the ACM is enclosed with aluminum and insulated to control the temperature and minimize contamination. A heater and fan inside the enclosure operate to regulate the winter temperature to between 5 and 25°C. In the winter, heat from the enclosure warms the funnel to melt any snow caught by the collector. Summer temperature will be maintained at ambient temperature using the fan.

3.0 Summary of Method

The sampling period, the time between bottle/funnel installation and removal, is one week. The sampling train will be replaced each Tuesday at or about 10:00 am local time. If it is raining or snowing at collection time, the train should be changed after the precipitation stops, but no later than midnight Tuesday. Bottles/funnels are sent to the laboratory even if no precipitation was

collected. If the sample can not be collected on the prescribed sampling day, the ISWS Contact must be notified. The following sampling activities will take place in the order listed.

1) Initial inspection
2) Removal of collection bottle
3) Replacement of polyethylene bag over the dry-side bucket
4) Removal of funnel
5) Replacement of sampling train (funnel/tubing/bottle in that order)
6) Sample shipment
7) Field log reporting and sample reporting form completion and submission

All steps will be conducted weekly and are detailed in Sections 9.1 through 9.8. Heavy precipitation may cause the collection bottle to overflow. Changing the bottle during the week to prevent overflow is discussed in Section 9.3.

4.0 Sample Handling and Preservation

Every sample is important and represents a significant portion of that site's yearly estimate. Any contamination through mishandling could cause a bias in the program results. Plastic gloves should be worn while removing, handling, and replacing the Teflon sampling train. (Do not use latex gloves with powder.) All procedures for sample handling, packaging and shipping should be followed.

5.0 Interferences

Ideally, the sampler should collect 100% of the precipitation. However, due to losses of precipitation and/or mechanical malfunctions, not all of the precipitation is collected. The validity of the sample is not based on the amount of precipitation collected but on the integrity of the precipitation collected. The sampler should not remain open for periods greater that 30 minutes after precipitation stops. Any sample exposed to dry deposition for greater than six hours during a standard sampling period will be considered invalid and flagged as such.

Examples of other events which will result in invalid data are malfunctioning of the lid so that continuous cycling occurs during a precipitation event, use of non-standard or modified equipment, or inadequate documentation by operator. Data corresponding to these events will be flagged appropriately.

Samples may also be contaminated by the site operator from water and/or other contaminants entering the sampling train from hands or clothing. Plastic gloves must be worn during all contact with the sampling train. If the sample must be collected during a precipitation event, a Tyvek jacket should be worn and returned to the plastic pouch after completion of sampling.

Extreme temperatures may result in improper operation of the equipment. Freezing temperatures may inhibit flow of precipitation through the funnel opening, while high temperatures may enhance evaporation. A heater and fan are provided to regulate the temperature and should be maintained and inspected weekly. A max-min thermometer is also provided inside the sampler and should be recorded and reset weekly.

6.0 Safety

In any field operation, emphasis must be placed on safety. Site operators must be aware of the potential safety hazards to which they are subjected. Follow all safety protocols and equipment guidelines, and be prepared for emergency situations. The sites operator is responsible for his/her safety from potential hazards including but not limited to:

Travel: When traveling to the site be sure to check on road conditions and weather advisories. Carry emergency supplies (warm clothes, food, water) when traveling in winter. Always let someone know where you are going and when you expect to return. Always carry a first aid kit.

Electrical: For obvious problems (fire, scorching, continuously blowing fuses), turn off the power of the circuit involved and notify ISWS. Never attempt electrical repairs other than replacing fuses and circuit boards. Be sure to unplug the sampler before changing fuses. Be especially cautious if conditions are wet.

Insects/pests: If you are allergic to insect stings, you should carry a kit prescribed by a physician. Be especially cautious if nests or large numbers of stinging insects are present. Notify ISWS of all problems.

7.0 Equipment and Supplies

Proper use, maintenance and cleaning will extend the life of serviceable equipment. The equipment and supplies specified in these lists (supplied by ISWS) should be used at the site. Any modifications or changes must be approved by the ISWS Contact.

7.1 Serviceable Equipment

These items will be maintained at the site at all times:

- Modified Aerochem Metric wet/dry precipitation collector (Model 301)
- Space heater
- Maximum/minimum thermometer
- One extra sampling train (Teflon bottle, tubing, and funnel) in packaging as sent by laboratory
- One extra Teflon bottle in laboratory packaging
- Jack to hold bottle in place
- Overflow tray
- Enclosure filter
- Plastic gloves
- Log book
- Report forms
- Tyvek jacket (in plastic bag)
- Kimwipes
- Squirt bottle to wet precipitation sensor

A diagram of the Aerochem Metric collector and Teflon sampling train is shown in Figure 1.

General maintenance and trouble shooting are covered in Section 11.0.

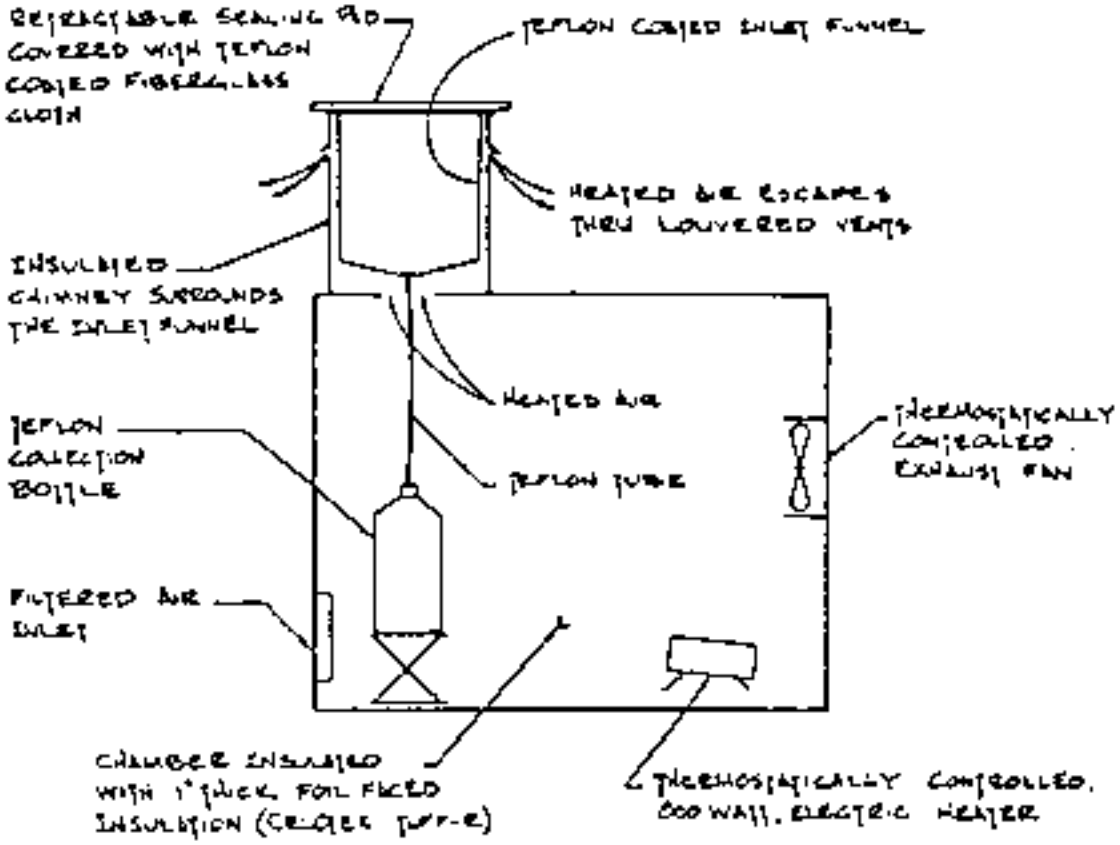

Figure 1. Modified Aerochem Precipitation Sampler (Dry-side bucket not shown)

7.2 Consumable Equipment

These items will be shipped to the operator every week.

- Sampling train (Teflon bottle and cap, tubing, and funnel in polyethylene bags)
- Shipping box and packaging materials

8.0 Calibration and Standardization

8.1 Rain Sensor

The Aerochem Metric (ACM) sampler consists of a collection container which is covered by a motor-activated lid. In a precipitation event a sensor activates a motor to move the lid off the collector. Each week the sensor should be checked to ensure proper operation. The procedure for this is covered under Section 1.4.4.

8.2 Heater and Fan

The heater must operate properly in freezing temperatures to maintain proper operation of sampling equipment. The heater must maintain a 15° ± 10°C temperature in the sample enclosure. The heater will be calibrated at ISWS. When cold weather is expected, check that the heater is operational by turning up the heater thermostat until the heater comes on; set this thermostat at the calibration mark. During the warm weather, make sure that the fan is operational by turning down the fan thermostat; set this thermostat at the calibration mark. Reset the maximum/minimum thermometer and record the temperatures each week.

9.0 Procedures

The site operator is responsible for maintenance of the site and for weekly sample collection, submission and documentation. The site operator will conduct routine maintenance, request needed supplies or parts in a timely manner, complete the weekly data sheet and maintain the field log book.

In order to ensure a representative wet deposition sample the following detailed procedures on the removal and installation of the sampling train, documentation, and maintenance should be implemented.

The following procedures should be adhered to each week:

1) Initial inspection
2) Removal of collection bottle
3) Replacement of polyethylene bag over dry-side bucket
4) Removal of funnel
5) Replacement of sampling train (funnel/tubing/bottle in that order)
6) Waste disposal and clean up
7) Sample shipment
8) Field log reporting and sample reporting form completion

9.1 Reporting and Labeling

All observations should be recorded on the sample reporting form and in the site log book. All entries should be made with a permanent ink marker. All times will be recorded in local time on 2400 hour clock. Labels are placed only on the sample bottles and only after the sample has been collected.

9.2 Initial Inspection

Carrying a box containing the new sampling train (bottle, tube, and funnel) approach the collector from downwind if possible.

9.2.1 Inspect the immediate site and surrounding area for any conditions which may affect the integrity of the sample, i.e. fire in the area, wind storm, vandalism, etc. Note these in the site log book and on sample reporting form. Also note if it is raining or snowing during sample collection.

9.2.2 Inspect the equipment for any damage and to see that all connections are secure. Remove any snow from top of lid. Operation of the rain sensor and lid will be checked during Section 1.4.4. Check operation of the heater or fan. Check for interferences (Section 1.1.3)

9.2.3 Record minimum and maximum temperatures from inside enclosure and reset thermometer.

9.3 Removal of Bottle from the Previous Week

9.3.1 Put on a clean pair of plastic gloves.

9.3.2 Unscrew the bottle, lower the jack, and recap the exposed collection bottle with the stored cap. (Last week the cap was placed in a plastic bag and stored in the enclosure. Do not put the cap down inside the enclosure unless it is inside a bag.) Place capped bottle inside a plastic bag. Put the label on the out side of the bag.

9.3.3 Remove the tube assembly and place in the plastic bag which was stored inside enclosure last week.

9.3.4 Close door to enclosure, leaving used bottle and tubing in bags inside enclosure. Bottle and tubing will be transferred to shipping box in Section 1.4.4.

9.4 Changing of Bottle for Overflow (During Sampling Period)

Heavy precipitation may result in bottle overflow. To prevent this the bottle may be changed during the sampling period as follows:

9.4.1 Bring one of the extra Teflon bottles in polyethylene bags to field site.

9.4.2 Wearing polyethylene gloves, unscrew the bottle cap, lower the jack, and recap the exposed collection bottle with the cap that was stored in the enclosure. Place the capped

bottle inside a plastic bag and leave inside enclosure until Tuesday sampling.

9.4.3 Place the new bottle on the overflow dish. Place the cap inside a polyethylene bag. Raise the jack to position the collection bottle so that Teflon tube is about ½ inch into the collection bottle. Screw on the cap which is part of the tubing assembly. Store the cap in bag inside the enclosure for use at the end of the week.

9.4.4 Both bottles will be shipped to BUF at the end of the sampling period. Indicate on the field report form and in the field notebook that two bottles were shipped.

9.5 Removal and Replacement of the Funnel

9.5.1 Replace the polyethylene bag in the dry side bucket and secure it with a bungee cord. Discard the old bag.

9.5.2 Standing downwind of the sampler, apply enough DI water to the sensor grid for the lid to remain open while changing funnels. Watch as the lid moves over. The lid should move freely with little motor noise. Wipe the underside of the lid with a damp (DI) Kimwipe.

9.5.3 Without leaning over the funnel, note any contamination on the funnel and record this on the site reporting form.

9.5.4 Using the bag as a second glove, remove the exposed funnel and place it in a polyethylene bag.

9.5.5 Retrieve the new funnel from the shipping box and place the used funnel in the shipping box in the same position.

9.5.6 Holding the new funnel through the bag, open the bag, and position the funnel on the wet-side sampler. Do not touch the funnel except when using the bag as a second glove. After the funnel has been properly seated, place the bag inside the enclosure for next week.

9.5.7 Blow any remaining water off the sensor, allowing the lid to close on the wet-side. After the sensor plate has been open, check to see that the sensor plate is warm. Clean any accumulated dirt off the sensor.

9.5.8 Check for a good seal between the lid and funnel.

9.6 Installation of Bottle and Tubing for Next Week

9.6.1 Open the sample enclosure. Put the used bottle and tubing in the shipping box and retrieve the new bottle and tubing.

9.6.2 Copy the weight written on the top of the capped bottle into the log book and onto the sample report form to be submitted *next* week. The dates of the new sampling period should be included with the weight.

9.6.3 Put on a new pair of polyethylene gloves. Using the polyethylene bag as a second glove,

remove the new tubing assembly from its bag and slip it onto the bucket nipple from inside the enclosure.

9.6.4 Remove the bottle from the bag and place on the overflow dish. Remove the cap and place it inside a polyethylene bag. Raise the jack to position the collection bottle so that the Teflon tube is about ½ inch into the collection bottle. Screw on the cap which is part of the tubing assembly. Store the bottle cap in a bag inside the enclosure. Place the bags for the bottle and funnel inside the enclosure for next week.

9.7 Waste Disposal and Clean up

Check the site for waste materials such as plastic gloves and Chem wipes prior to leaving site. Take an inventory of equipment and consumables. Notify ISWS of any equipment need repair or replacement of if any supplies are needed.

9.8 Sample Shipping

Once the bottle is detached from the funnel and capped it is not opened again by field personnel. Ensure that sampling train is properly packaged in polyethylene bags and in proper locations in shipping box. Send the contents to: Stephen Vermette, ESSE, Buffalo State University College, 1300 Elmwood Ave., Buffalo, NY 14222. Samples and the sample report form should be sent via UPS or U.S. priority mail to the laboratory no later than the day after collection. Photocopy paperwork so that a copy remains with the site operator. Notify ISWS if any equipment needs repair or replacement or if any supplies are needed.

10.0 Quality Assurance Samples

Occasionally the protocol will require collection of quality assurance samples. Travel blanks are bottles which are shipped with the regular sample trains and stored unopened in the enclosure during the sample period. They should be returned to BUF unopened after the specified period.

The operator will receive a box labeled "system blank" which contains a new sampling train and 250 mL bottle containing DI water. The sampling train should be installed as usual; however, the precipitation sensor is unplugged from the motor box so that the lid remains closed throughout the sampling period. At the end of the sampling period (the following Tuesday), the operator should reconnect the sensor and open the lid by wetting the sensor. The operator should then pour the DI water from the 250 mL bottle into the funnel in circular motions, wetting the sides of the funnel. The lid is then allowed to close. The sampling train is collected according to the procedures for weekly samples, with the exception that the field sheet is labeled "system blank" and the 250 mL bottle is returned.

11.0 Equipment Maintenance

Site operators will maintain equipment in good working order at the original location. Site operators should also maintain the area around the collector. Any changes to site conditions should be recorded and reported to ISWS. Modifications at the site or to its equipment must be approved by the ISWS Contact. This includes placing other equipment in close proximity to the existing

samplers.

11.1 Check Power Supply

Check all power connections at each visit.

11.2 Routine Cleaning

The housing and top of the lid should be washed periodically with water (distilled water is best) and a clean sponge to remove any residues (i.e. bird feces or accumulated dirt). Also the sensor grid should be scrubbed with a wetted toothbrush to remove accumulated minerals or other contaminants.

11.3 Check Foam Pad Insert

The foam pad should maintain a good seal with the funnel. If there are any gaps blowing dust may enter and contaminate the sample. Over time, the pad will tear and break down and may fall into the sample and cause contamination. This has been the most common maintenance problem. The pad should be replaced at least once a year.

11.4 Enclosure Filter

The enclosure filter is replaced at least once a year.

11.5 Troubleshooting

If the sampler fails to operate when you wet the sensor (lid does not move and motor does not start) there may be an existing power failure. Check that all the line power connections are secure, and that the fuses (found on the motor box) are good (check fuses with a volt meter or spare fuses, as you can't always see that they are blown). A voltage meter or appliance (i.e. radio or light bulb) can be used to check the power supply from the outlet.

If the sampler fails to operate when temperatures are below freezing (the lid does not move and motor is running) the collector lid may be frozen to the bucket, or the support arm pivots may be frozen to the housing, or the weight of snow on the collector lid may prevent the lid from opening. Gently pull at the lid or lid arms to break the ice, or remove the snow from the collector lid. A peaked roof and heating pads can be used to prevent freezing if this problem occurs often.

If the precipitation sampler fails to operator properly, aside from a power failure and freezing, there are three components which can fail: the sensor unit, the motor box (containing the drive motor, fuses, and circuitry), or the clutch unit. Common signs of these failures are the continuous cycling of the collector lid, the lid remains on the wet (even when the sensor is wet) or dry-side bucket, or the collector lid stays open long after the precipitation event ends. Signs of these failures well be evident from the event recorder trace on the Belfort raingage drum chart.

11.5.1 Sensor Unit

When the sensor unit is faulty the following symptoms may be observed: The collector lid oscillates non-stop between buckets, or remains on either the wet- or dry-side with the

motor running. A quick way to check if the sensor is faulty is to unplug it from the motor box. If the collector lid moves to cover the wet bucket the sensor needs to be replaced.

When the sensor's heater is faulty the lid stays over the dry-side long after precipitation stops and the sensor dries slowly. A faulty heater will not allow the sensor to evaporate water or melt snow, and the collector lid is not triggered to cover the "wet" bucket in a timely manner. This can be checked by feeling the sensor for heat. A properly operating sensor will feel warm to the touch. If the sensor has cooled the heater probably has failed. If this is the problem, the sensor should be replaced, even though the sensor may continue to activate the lid as the sensor will dry through natural evaporation. If a replacement is not available the sensor may still be used, although the sample may be more susceptible to contamination from dry deposition. Note this on report forms and notify ISWS of the need of a replacement sensor.

11.5.2 Motor Box Unit

When the motor box unit is faulty the collector lid oscillates non-stop between buckets, or rests on the wet- or dry-side without the motor running. If unplugging the sensor (discussed in previous section) doesn't move the lid over to the wet bucket, or if the fuses are found to be good, the motor box will require replacement or repair. ISWS should be contacted. A diagram of the fuse arrangement in the motor box is shown in Figure 2.

11.5.3 Clutch Unit

When the clutch unit is faulty the motor will run but the lid mechanism will not move. In this case the clutch needs to be examined for wear. To do this, remove the clutch arm bolt to separate the clutch from the lid mechanism, and then loosen the thrust collar screw and gently pry the clutch off the motor box. If the thrust collar indent or the clutch tooth appear significantly worn then the clutch should be replaced. If they do not, the tension spring needs to be stretched. To do this, move the tension plate away from the thrust collar. The further away from the thrust collar the plate is pushed, the more tension is produced. Note: the clutch spring should not be stretched so far as to "freeze" the clutch -- it should still be able to pull away ("pop-out") from the motor box. If the clutch cannot be repaired at the site, notify ISWS.

LM/LS Metals Network

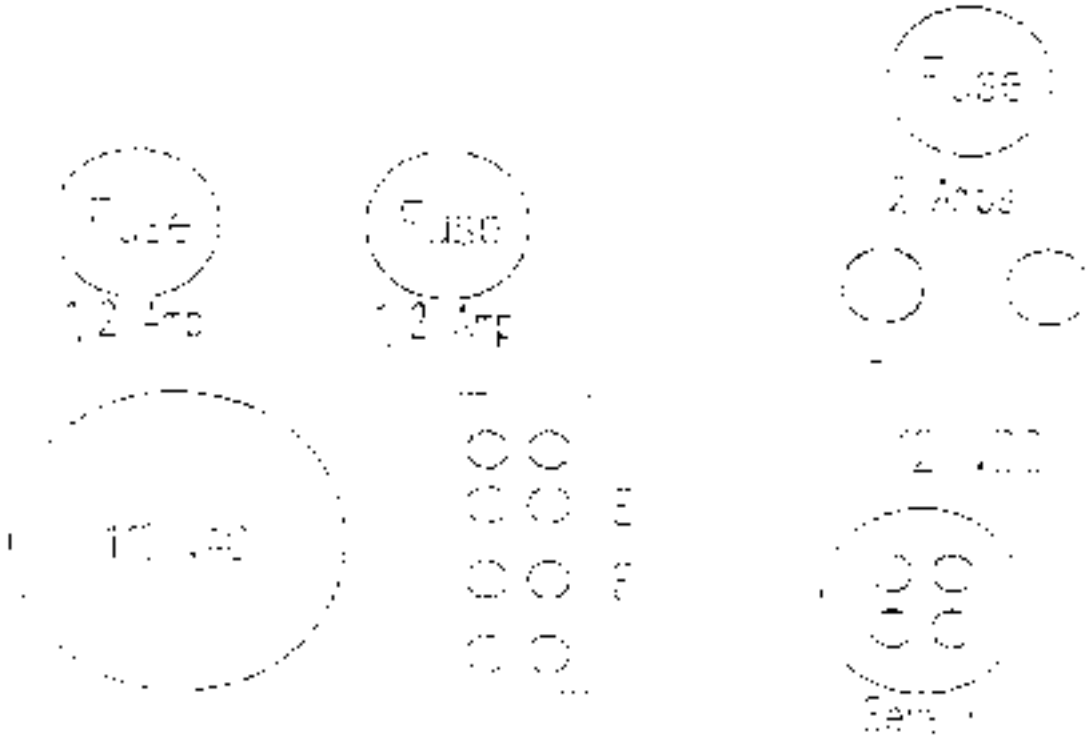

Figure 2. Aerochem Motor Box

Appendix A

SAMPLE REPORTING FORM

1. STATION

Name_____

ID ☐ ☐ ☐ ☐

2. OBSERVER

Name_____

Initials ☐ ☐ ☐

3. SAMPLE INTERVAL

Start ☐☐/☐☐/☐☐ (☐☐☐☐)
yr/mo/day/hr(0000-0000)

End ☐☐/☐☐/☐☐ (☐☐☐☐)
yr/mo/day/hr(0000-0000)

4. SAMPLE TYPE

Wet-deposition ☐

System-blank ☐

5. SAMPLE WEIGHT (laboratory use)

Collection Bottle & Sample	☐☐☐☐☐	grams
Collection Bottle	☐☐☐☐☐	grams
Sample Weight	☐☐☐☐☐	grams
Sample Volume	☐☐☐☐☐	mL
Rain Gage Volume	☐☐☐☐☐	mL

6. SAMPLE APPEARANCE

Clear ☐

Cloudy ☐

Floating Material ☐

Settled Out ☐

Other _____

7. REASON FOR BOTTLE CHANGE

End of Sampling Period ☐

To Prevent Overflow ☐

Did Bottle Overflow ☐

8. REMARKS

_____

_____

_____

_____

_____

9. LABORATORY CUSTODY (laboratory use) Ultrapure Acid added _____ mL

Sample Acidified Yes ☐ (if yes, Date ☐☐/☐☐/☐☐) No ☐

Aliquots: Lab I.D. Volume Routing

_____

_____

_____

_____