Standard Operating Procedure for Sampling of Mercury in Precipitation

Gerald J. Keeler and Matthew S. Landis
University of Michigan
Air Quality Laboratory
109 South Observatory Street
Ann Arbor, MI 48109-2029

June 1, 1994

Version 2.0

Standard Operating Procedure for Sampling of Mercury in Precipitation

1.0 Introduction/Overview

The objective of the Lake Michigan Loading Study is to assess the contribution of atmospheric deposition to the concentration of mercury and other toxic trace species found in Lake Michigan. The atmosphere has been implicated as one of the dominant sources of mercury and trace elements to bodies of water and it is clear from investigations in remote regions of the globe that long range transport of mercury and other toxics from source regions is occurring. By quantifying the wet deposition and ambient concentrations of mercury it will be possible to determine the relative importance of precipitation and dry deposition in accounting for the atmospheric loading of mercury to Lake Michigan. In addition, investigating other ambient trace species will aid in the identification of significant mercury sources.

2.0 Preparation for Precipitation Sampling

Acid Cleaning Procedure

All field sampling and analytical supplies which will come into contact with the samples are cleaned according to the following procedure.

Supplies to be acid cleaned are first rinsed in reagent grade acetone under a fume hood, then washed in hot tap water and diluted Alconox. Supplies are rinsed five times in cold tap water then rinsed three times in DI water. The supplies are then heated in 3M hydrochloric acid (EM Science Tracepur HCl in Milli-Q water (18.2 MÙ/cm)) for six hours at 80°C. One liter of 3M HCl is prepared by adding 750 mL of Milli-Q water to 250 mL of concentrated EM Science Tracepur HCl. The 3M HCl can be used several times and is stored for reuse in a polyethylene carboy dedicated for this purpose. The supplies are placed into clean polyethylene tubs which are then filled with the 3M HCl, making sure that all of the surfaces are submersed in the HCl. The tubs are covered and placed in a water bath which is heated to 80°C in a fume hood. The water in the bath is maintained at the level of the acid inside the tubs. After the water in the bath reaches 80°C, the supplies in the tubs are allowed to soak for six hours.

After the six hour, 80°C soak, the tubs are removed from the water bath and allowed to cool in the fume hood. When cool, the 3M HCl is poured back into its polyethylene carboy. The supplies are rinsed in the tubs three times with Milli-Q water. The supplies are then soaked in a 0.56M nitric acid solution (Baker Instra-Analyzed HNO_3 in Milli-Q water) for 72 hours at room temperature in the same polyethylene tubs in which they were heated with HCl. The nitric acid solution is made by adding 35 mL Baker Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. Nitric acid is reused for up to six months and is stored in a carboy dedicated for HNO_3. At the end of the three day soak, the supplies being cleaned are rinsed three times with Milli-Q water and transferred into a Class 100 Clean Room.

Inside the clean room, the supplies are again rinsed three times with Milli-Q water. The tubs containing the supplies are filled with 0.56M Baker Instra-Analyzed HNO_3 that is kept in the clean room and is dedicated for this final step only. The supplies are then allowed to soak in this acid for seven days. This acid is prepared by adding 35 mL of the Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. At the end of the seven day acid soak inside the clean room, the supplies are rinsed five times with Milli-Q water and allowed to air dry on a clean surface. When the supplies are dry, they are triple bagged in new polyethylene bags and removed from the clean room, ready for use in sampling.

The Teflon precipitation sampling bottles are not allowed to dry. After the seven day HNO_3 soak, the Teflon bottles are rinsed three times with Milli-Q water and are filled with 0.05M Hydrochloric acid (EM Science Suprapur HCl in Milli-Q water) and allowed to soak in the clean room until needed. When needed, the Teflon bottles are emptied, rinsed with Milli-Q water five times and 20 mL of HCl preservative is added. The bottles are then weighed, sealed with Teflon tape and triple bagged in new polyethylene bags.

3.0 Preparation and Set-up of the MIC-B Precipitation Collector

3.1 Summary

The automatic precipitation collector works by detecting precipitation on a sensor grid. During precipitation the sensor grid energizes a relay which switches on the motor-relay and, in turn, the motor. The motor acts through a chain sprocket drive system to move the cover from the funnel to the wet cover support. The motor is stopped by micro switches which trip as soon as the cover is properly seated on the cover support. When precipitation stops, the sensor grids dry out and the cover returns to seal the collector. This wet only collection prevents dry deposition from contaminating the collection funnel.

A heater is laminated to the underside of the sensor board to accelerate evaporation at the end of precipitation. The temperature of the heater is controlled so that the grid dries at the same rate independent of ambient temperature. To prevent excessive back and forth movement of the lid during extremely light precipitation, a time delay for return of the cover is incorporated into the control circuit.

During sample collection the screen to the right of the funnel reduces rain/snow splash-off into the precipitation collector. The sensor array is mounted two feet away from the collection funnel for the same reason.

The University of Michigan Air Quality Laboratory (UMAQL) has developed a new modified MIC-B collector that enables the installation of up to four discrete precipitation sampling systems. This configuration allows for two mercury sampling trains and two trace element & nutrient sampling trains. A mercury sampling train consists of a Borosilicate glass collection funnel with an effective collection area of 181 cm^2, a Teflon adapter, a glass vapor lock and a 1 L Teflon sample bottle. A trace element sampling train consists of a polypropylene funnel with an effective collection area of 167 cm^2, a polypropylene adapter and a 1 L polypropylene sample bottle (Figure 1). This new sampling configuration allows for the discrete collection and preservation of four independent precipitation samples using one MIC-B sampling instrument.

Figure 1. Modified MIC-B1 Sampling Trains for the Collection of Hg(a) and Trace Elements (b)

3.2 Sampler Set-up

The MIC-B collector is placed on a 1 meter tall wooden platform in a location free from obstruction in every direction. The collector cannot be located within 2 meters of other pieces of equipment or splash off may result and contaminate the sample. The sensor grid must also free of any obstruction.

3.3 Sampler Start-up

Connect the instrument to a grounded receptacle. Switch on the main power toggle located on the front of the instrument (only when the hood is in the closed position over the collection funnel insert). Touch one of the sensor grids with a wetted finger. The cover will lift up from the collection funnel insert and over to the rest bar. The motor will then turn off (be sure that you can hear the motor turn off, so that in the event it does not turn off, corrective measures can be taken). Wait one to two minutes and the hood will move back to cover the funnels and the motor will turn off. If the motor does not turn off after seating on the collection funnel insert then refer to the trouble-shooting guide (Section 4.3).

Note: The sampler hood must always be over the collection funnel insert when turning on the instrument's main power!

A space heater and heat tape funnel nests are placed inside the precipitation collector during cold months to melt snow and slush that lands in the funnel and to prevent freezing of the collected sample. The space heater is plugged into the outlet provided inside the sampler cabinet and is maintained on the setting required to keep the cabinet at approximately 10°C.

3.4 Installing the Collection Funnels

The acid-cleaned collection funnels are shipped with the adapters and vapor lock system pre-assembled and packaged in protective polyethylene wrapping. To keep the collector hood open during installation of the funnels into the MIC-B insert, place a wet towel or cloth onto the sensor grid. Open the sampler cabinet, and put on a pair of particle free gloves. Carefully remove the polyethylene wrapping and place each funnel system into the corresponding hole on the funnel support base (Figure 2). Be sure funnels are properly seated into the support base to insure a tight seal. Once all the sampling trains have been installed, cover any unused funnel support bases with the sealing caps provided to prevent water intrusion into the interior of the sampling instrument. Remove the wet towel and allow the collector hood to close.

In order to minimize evaporative loss of mercury from the sample bottle in the collector, a vapor lock system and hydrochloric acid preservative have been incorporated into the new collection system. Each Teflon sample bottle is shipped from UMAQL containing 20 mL of 0.08M HCl preservative. Extreme care is exercised when handling these bottles to avoid spilling the acid and causing personal injury. In the unlikely event that acid does come into contact with exposed skin, the area is immediately flushed with water. Wearing gloves and safety glasses, remove one Teflon sample collection bottle from the three polyethylene bags, unscrew the cap and place it in the inner bag from which you removed the bottle. Reseal the bags to keep the cap clean. Thread the 1 L bottle into the Teflon funnel adapter to complete the mercury sampling train setup. The sample bottles must be snug, however, care must be taken to avoid over tightening. Teflon threads on the sample bottles and the adapters are easily stripped.

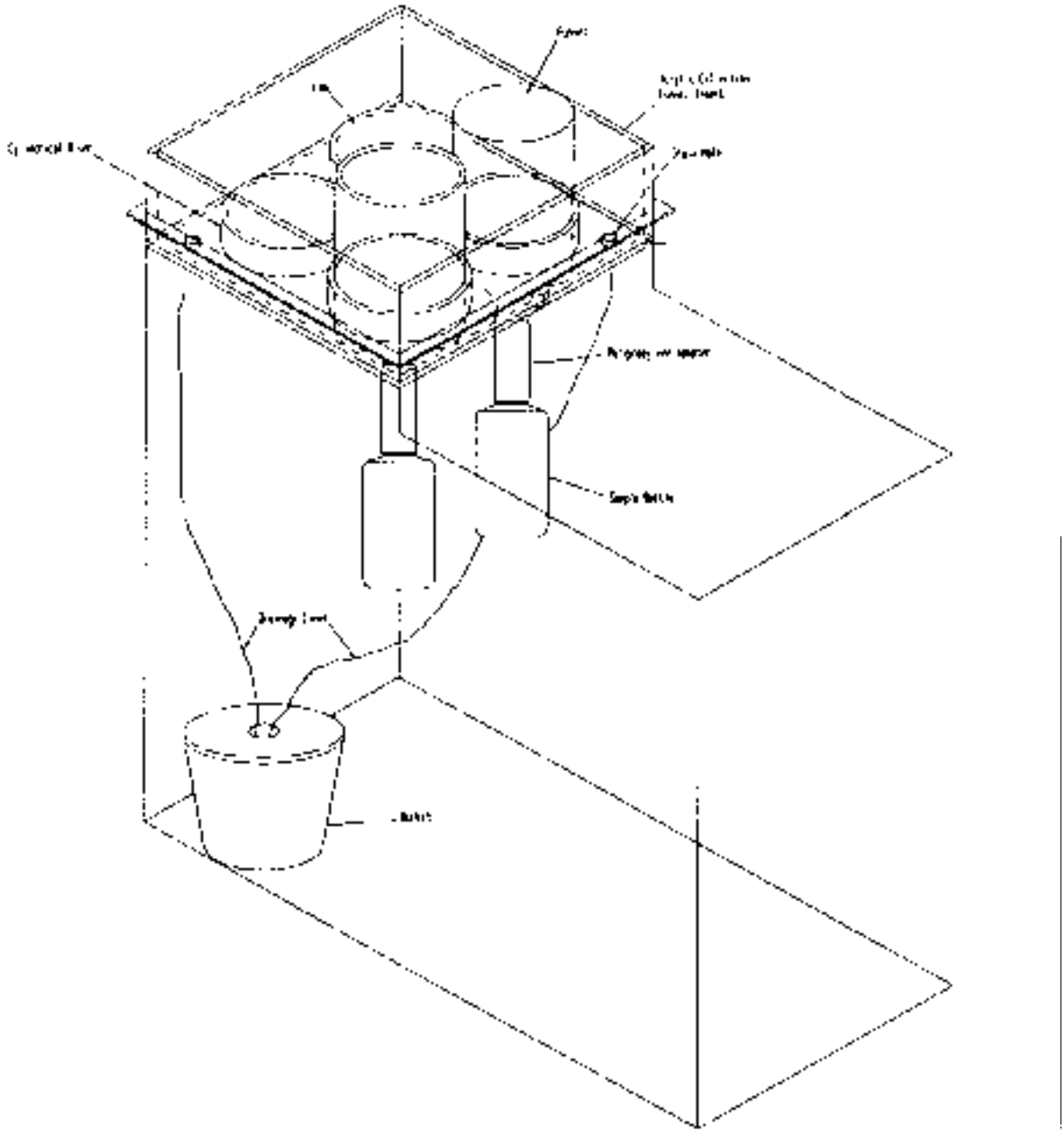

Figure 2. The University of Michigan Custom Acrylic Insert (UM-B)

The other trace elements collected are not volatile, therefore, the sampling train does not utilize a vapor lock or acid for preservation in the field. Wearing particle free gloves, remove one polypropylene sample collection bottle from the three polyethylene bags, unscrew the cap and place it in the inner bag from which you removed the bottle. Reseal the bags to keep the cap clean. Thread the 1 L polypropylene sample collection bottle into the polypropylene funnel adapter to complete the metals sampling train setup.

Note: The funnels and sample bottles have been acid-cleaned in a laborious 11-day procedure and packaged to ensure no particle contamination. Extreme care is exercised when handling the funnels and open sample bottles to prevent anything from falling in or contacting them during installation.

4.0 Sample Collection Procedure

4.1 Daily Site Visit

The operator must arrive at the sampler every morning at 8:00 a.m. local time to perform the following tasks:

1) Check the polypropylene sample bottle for any collected precipitation.
2) Check the Belfort rain gauge for any precipitation and record amount for each event.
3) Fill in information in the daily Sampler/Site Log Book.
4) Check the sampler to make sure, if appropriate, that the heater is working, the funnels are free of obvious contamination and the sampler is operating (by tripping the sensor grid).

If it is raining or snowing when the operator visits the site in the morning, the sample is not collected until the next morning, unless it appears that the sample bottle is going to overfill. If it is still raining the following morning, the site operator collects the sample as usual and replaces the sampling trains. The duration of the rain event is recorded by the operator on the sample log sheet. If it appears that the sample bottle is going to overfill then the operator removes the sample bottle while it is raining/snowing and collects the sample according to the procedure below. If the operator is unclear about what should be done, they are instructed to call Matthew Landis at UMAQL to determine if the sample should be collected.

4.2 Sample Collection

Supplies necessary to collect a sample: (quantities may vary depending on configuration)

1) One triple-bagged acid-cleaned Teflon bottle
2) One triple-bagged acid-cleaned polypropylene bottle
3) Two log books: samples and meteorological data
4) Particle-Free Gloves
5) Teflon Tape
6) Sample Label Stickers

Open the sampler cabinet, put on a pair of particle-free gloves. If there is evidence that precipitation has overflowed the sample bottle, put the two gallon white plastic bucket underneath the funnel before unscrewing the sample bottle from the funnel adapter. Unscrew the bottle from the funnel adapter, screw the cap on tightly and seal it to the bottle using the Teflon tape provided. Place the appropriate sample number label on the vinyl tape that is on the bottle *(This tape will have the bottle weight and a batch number to identify the bottle, avoid placing the sample label over these numbers)*. Seal the sample bottle into three successive polyethylene bags.

Fill out a tracking form (Appendix B) to send with each sample, funnel rinse and control. Please note if the sample overflowed. Fill out the Sample Log and Collector Log sheets. Use the note column for important and/or unusual observations/notes (e.g., pesticide spraying nearby, road construction near site, leaves found in collector funnel, etc.). Do not fill in 'Sample Volume' - this is for lab use.

The samples are shipped to UMAQL in Ann Arbor the day they are collected. If the operator is unable to do so, the samples are refrigerated until they can be shipped the next day. Do not allow the samples to freeze.

Precipitation samples will be collected on an event basis during the intensive months of May through October and on a weekly basis for the remainder of the sampling period. During event precipitation sampling, collection funnels and funnel adapters will be replaced after every precipitation event or after a period of seven successive calendar days without a precipitation event, whichever occurs first. The old funnels and the funnel adapters are removed and replaced with freshly cleaned ones from UMAQL. The old funnels and funnel adapters are shipped back to UMAQL as soon as possible so they can be cleaned. Site operators log the date and time the funnels are replaced on the sample log (an entire line in the log is used).

4.3 Funnel Blank Collection

In order to confirm that the collection funnel assemblies are free of mercury and other contaminants, 'funnel blank' samples are collected. Particle-free gloves are worn by the operator for this procedure. Clean sample bottles with no HCl preservative are attached to each sampling train and are used to collect the funnel rinses. To keep the collector hood open during this procedure, a wet towel is placed on the sensor grid. An acid-cleaned 1 L Teflon sample bottle and an acid-cleaned 1 L polypropylene sample bottle are filled with Milli-Q water and Control identification sticker labels are affixed. The operators are instructed to positions themselves down wind of the sample before the bottles are opened, to prevent particles from their clothing from being shed into the sample. Each funnel is rinsed with approximately 0.5 L of the water making sure all the surfaces of the funnel are covered, the sample bottles are capped and sealed using the Teflon tape provided. The Teflon and polypropylene bottles are removed from the funnel adapters, the caps are threaded on, the bottles are sealed with Teflon tape and the Rinse identification sticker labels are attached. Care is taken to prevent the mouth of the sample bottles from contacting anything during this procedure. The Rinse and Control solutions are re-bagged and packed into a shipping box. The tracking forms are completed for the Rinses and Controls separately.

4.4 Shipping a Sample

It is very important that samples reach UMAQL as soon as possible after being collected. To ship a sample, wrap the triple bagged sample bottle in a layer of bubble-wrap and place it in a shipping container provided. Any extra space in the container is packed with additional bubble-wrap so the bottles will not move inside.

Sample tracking forms for each sample are completed and sent with the samples to UMAQL.

4.5 Maintenance of MIC-B Precipitation Collector

4.5.1 Routine Maintenance

The precipitation collector sensor array is cleaned every month with a damp cloth and mild detergent (1% Alconox), both of which are provided. The detergent film is rinsed off the sensor array with a second, clean, damp cloth.

An operational check on sampler performance is conducted daily. This is done by placing a wetted finger on one of the sensor grids and waiting to make sure the cover seats in the open rest position properly and that one and a one-half to two and a one-half minutes after the hood returns to cover the funnels the hood is seated properly and the motor turns off. If the cover does not seat properly on either side or if the hood drops over excessively when open, refer to the trouble-shooting guide for the appropriate remedy.

4.5.2 Trouble-Shooting

If a collector fails to operate properly or the operator has to replace a fuse or make adjustments, they are instructed to notify Matthew Landis at UMAQL as soon as possible. Some of the parts that can fail will need to be replaced by UMAQL personnel. These cases are noted below.

1. Collector Fails to Operate:

   a. No Power to Instrument

      Check to make sure the instrument is plugged in and the power source is on (no tripped fuses/breakers etc.).

   b. Blown Fuse

      Replace the blown fuse with appropriate fuse.

   c. Faulty Sensor Board or Faulty Power Control Board

      The sensor board will have to be replaced by UMAQL personnel or sent to the operator for replacement. If you have exhausted the two options above call Matthew Landis or Jerry Keeler as soon as possible so replacement parts can be shipped.

2. Motor Will Not Switch Off

   a. Limit switch adjusting screw and/or cam out of adjustment
   Read just the limit switch cam and/or actuating screw.
   This is done by:

      i) Switching off main power and unplugging the sampler (be sure to do this with the cover seated on the funnel).

      ii) While holding the nut still, loosen the set screw on the appropriate micro-switch cam and readjust it until the switch is depressed. Tighten the set screw and repeat the procedure on the right side. When both sides have been adjusted, test the collector by placing a slightly wetted finger on one of the sensor grids. Wait to see if the motor stops when the hood is seated on the hood support and after the hood returns to its resting position over the funnel.

   b. Limit switch may be broken - if this is the case the switch needs to be replaced.

3. Cover Drops Once It Moves Over Dead Center

   a. The set-screw on the motor sprocket may be loose. Locate the set-screw and tighten it.

   b. The chain may be loose and is tightened.

4. Cover Does Not Return To Collection Funnel Insert

   a. Clean the sensor array with a damp cloth and mild detergent - making sure to wipe the detergent off the sensor array.

   b. Heater on sensors may not be operating. If this is the case the heater element may be burned out in which case the sensor board needs to be replaced or there may be a faulty component on the power control board and the power control board needs to be replaced.

5.0 Clean Room Procedures

5.1 Entering the Clean Room

Shoes are taken off outside the clean room by all UMAQL personnel. Personnel then enter the outer vestibule (changing room). Once inside, the hood is put on followed by the clean room suit and clean room boots. The boots are snapped to the suit at the back of the leg (to hold up the boots) and are buckled in the front. Personnel then step over a dividing bench where they put on clean room gloves and snap the clean room suit at the wrist. Now fully clothed they enter the clean room making sure to securely close the door behind.

5.2 Taking Supplies into the Clean Room

All supplies to be taken into the clean room are double bagged in polyethylene. The supplies to be taken into the clean room are placed in the outer dressing room. Upon entering the clean room, the outer bag is removed and left in the entry room. All supplies that enter the clean room that have not been bagged are rinsed with MQ-water and wiped off with particle-fee wipes.

Appendix A. Facilities, Equipment and Reagents

Following is a list of the required facilities, equipment, supplies and reagents for sample preparation and sample collection that are outlined in this document. The make and model of the following items are those used at The University of Michigan Air Quality Laboratory. Many of these items are available from a variety of sources.

1. Preparation of Field Supplies

-Class 100 Clean Room, Work Stations
-Clean Room Gloves
-Particle-free Wipes
-Clean Room Cap, Gown and Boots
-Milli-Q Water (18.2MÙ/cm)
-Exhaust Hood
-Acetone
-Alconox
-Polyethylene Tubs
-EM Science Tracepur and Suprapur Hydrochloric Acid
-Polytherm Water Bath (Science/Electronics)
-Baker Instra-Analyzed or EM Science Suprapur Nitric Acid
-New Polyethylene Bags
-20 L Polyethylene Carboys

2. Sample Collection

-MIC-B Wet-Only Precipitation Collector (MIC)
-UMAQL Modified Acrylic Insert
-Digital Indoor/Outdoor Recording Thermometer
-BSG Collection Funnels
-Polypropylene Collection Funnels
-Teflon & Polypropylene Precipitation Adapters
-Glass P-trap Vapor Lock
-1 L Teflon & Polypropylene Sample Bottles
-Funnel Heat Tape Nests & Variable Transformer
-Ceramic Space Heater
-2 Gallon HDPE Bucket
-Particle-Free Gloves
-Teflon Tape
-Sample Labels
-Permanent Label Markers
-Field Operator Log Book
-Shipping Crates

Appendix B.

LAKE MICHIGAN LOADING STUDY
PRECIPITATION SAMPLE TRACKING FORM
I.I.T.-CHICAGO

Sample Number:_____ OPERATOR: _____

Date of Precipitation: _____

Date Sample Collected: _____

Time Sample Collected:_____

Date Shipped: _____

Comments: _____

FOR USE AT THE UNIV. of MICH. AIR QUALITY LAB:

Date Received at UMAQL: _____ Rec'd By: _____

Volume of Sample Received: _____

Sample Analyzed in the Following Fractions:

Type of Analysis	**Volume of Precip (mL)**	**Vol. Of HCl, HNO_3, or BrCl (mL)**	**Lot/Batch of BrCl, HCl or HNO_3**	**Date Filtered, Acidified, Oxidized**	**Date Analyzed**	**Analyzed By**
pH/i.c.						
ICP-MS (0.2%)						
Filtered						
Reactive Hg						
Total Hg						

Bottle Type (circle one): BSG Polypropylene Teflon
Bottle Batch: _____ Init. Wt. (g) _____
COMMENTS: _____

Appendix B. (Cont'd)

LAKE MICHIGAN LOADING STUDY

IIT-CHICAGO

Vapor Phase Mercury

DATE	TIME	Outdoor Min Temp (in last 24 hrs)	Cabinet Min Temp (in last 24 hrs)	Outdoor Max Temp (in last 24 hrs)	Cabinet Max Temp (in last 24 hrs)	PRECIP. TYPE	Notes	Initials