National Human Exposure Assessment Survey (NHEXAS)

Maryland Study

Quality Systems and Implementation Plan for Human Exposure Assessment

Emory University
Atlanta, GA 30322

Cooperative Agreement CR 822038

Standard Operating Procedure **NHX/SOP-F07**

Title: Collection, Storage, and Shipment of Drinking or Tap Water Samples for Metal and Pesticide Analysis

Source: Harvard University/Johns Hopkins University

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
Human Exposure Research Branch

1. Title of Standard Operating Procedure

   Harvard University/Emory University/Johns Hopkins University Standard Operating Procedures: **F07 Collection, Storage, and Shipment of Drinking or Tap Water Samples for Metal and Pesticide Analysis, Rev. 1.0**

2. Overview and Purpose

   This standard operating procedure describes the procedures necessary for collection of tap water and drinking water samples to be analyzed for metals, pesticides, and PAHs by an external analytical laboratory assumed to be EPA-EMSL Cincinnati.

3. Discussion

   Ingestion of drinking water can be responsible for a significant fraction of total exposure to certain pollutants. Soluble metals leached from waste streams and pesticides from farms and gardens are potentially responsible.

4. Personnel Responsibilities

   4.1 Sampler Preparation

   Sampler preparation is the responsibility of the Field Coordination Center (FCC) Supervisor (FCC-S).

   The FCC Clerk is responsible for preparing Field Packets (including printing ID labels and affixing them to forms) before sampling.

   4.2 Appointments and Reminders

   Making appointments and sending reminder letters are the responsibility of the FCC staff.

   4.3 Sample Collection

   Field collection, including selection of the sampling location, and preparation of the storage container, is the responsibility of the Field Interviewer.

   4.4 Storage

   Immediate storage of the sample prior to return to the field coordination site is the responsibility of the Field Interviewer. Custody will be turned over to the Field Study Coordinator or his designate for storage at the field coordination site.

   4.5 Shipment

   Shipment to the analytical laboratory is the responsibility of the FCC-S or his designate.

   4.6 Analysis

Analytical laboratory personnel, presumed to be EPA-Cincinnati, will be responsible for all aspects of water sample analysis.

5 Required Equipment and Reagents

5.1 Field Coordination Center (before field sampling)

1 1-L plastic container (Cubitainer or equivalent) for metals sample, cleaned as per EPA *Handbook for Sampling and Sample Preservation of Water and Wastewater*, Sept. 1982.
1 1-L glass bottle with Teflon-lined cap for pesticides sample, supplied by Southwest Research Institute, cleaned as per EPA method 525.2.
ultra-high-purity water, Milli-Q or equivalent
sodium sulfite, 1 g
balance to weigh sodium sulfite [RAW -- precision? 0.1 g?]
weighing boat, small
buffer solution, pH 4.0
hydrochloric acid, pesticide quality [????], 6N
(If 6N pesticide quality HCl is not available: concentrated pesticide quality HCl, ultra-high-purity water, 100-mL graduated cylinder, 500-mL beaker)
bottle to take HCl to field: amber glass 100-mL bottle with red lid and label
glass funnel
powder-free gloves
safety glasses and apron

5.2 Field Sampling

1 1-L plastic container (Cubitainer or equivalent) for metals sample, labeled
1 1-L glass bottle with Teflon-lined cap for pesticides sample, with sodium sulfite, labeled
powder-free gloves
portable pH probe
disposable cup such as 250-mL plastic urine cup
tissues (Kimwipes or equivalent)
glass tray (see dermal wipe SOP)
bottle of 6N hydrochloric acid, sealed into plastic bag
disposable dropper sealed into plastic bag
safety glasses and apron
parafilm or electrical tape
cooler with cold pack to keep samples for pesticide analysis at 4°C or below

5.3 Sample Tracking and Paperwork

6 sample ID labels with sample type (digits 7 and 8) 45 for "water for metals" sample:
3 for logsheets, 1 for chain-of-custody form, 1 for sample container, 1 spare
6 sample ID labels with sample type 46 for "water for pesticides" sample:
3 for logsheets, 1 for chain-of-custody form, 1 for sample container, 1 spare
Field Packet for household: logsheet, 2 chain-of-custody forms
Field Manual (SOPs)
clipboard
pens, ballpoint

6 Procedure

6.1 Preparation for Collection

6.1.1 Preparation of Sampling Bottles for Pesticides Samples

The FCC Supervisor (FCC-S) will prepare enough bottles for a week's sampling:

- Weigh out 1.0 g of sodium sulfite to the nearest 0.1 g. Transfer it into a 1-L glass bottle. Put the lid on securely.
- Store prepared bottles in a specified and clearly marked location.

6.1.2 Identification Labels

The FCC Clerk will:

- Print ID labels and inspect them to make sure that they are correct for the household, Cycle, and sample types.
- Affix a "45" ID label and a "46" label to each of the three parts of a logsheet.
- Affix a "45" ID label to one chain-of custody form, and a "46" label to the other.
- Obtain a plastic water container and a glass container containing 1 g of sodium sulfite (section 6.1.1). Affix a "45" ID label to the plastic container and a "46" label to the glass container.

6.1.3 Testing of pH Probe

The FCC Technician will: [RAW -- how often? Before each week of sampling?]

- Test the pH probe against a pH 4.0 buffer solution.
- If the probe does not read between 3.9 and 4.1, adjust it as specified in the manual.

6.1.4 Preparation of Acid Bottle and Dropper

The FCC-S will:

- Seal a disposable dropper into a 3" x 5" plastic bag. Prepare enough for at least a week's sampling and keep them in a specified and clearly marked location.

If 6N pesticide grade hydrochloric acid is available:

- Wear safety glasses, gloves, and an apron.
- Get a 100-mL amber glass bottle with a red cap and an ACID label.

- Pour acid into the bottle [RAW -- OK to use a funnel?] until the bottle is about half full.

- Tighten the lid of the bottle. Put the bottle into a plastic bag and seal the bag.

If 6N pesticide grade hydrochloric acid is not available:

- Wear safety glasses, gloves, and an apron.

- Use the graduated cylinder to measure 100 mL of ultra-high-purity water. Pour it into the beaker.

- Use the graduated cylinder to measure 100 mL of concentrated HCl. Pour it slowly into the beaker. The mixture is approximately 6N. [RAW -- stir?]

- Distribute the acid into bottles to go to the field, as described above.

6.1.5 Transfer and Inspection of Equipment

At the Field Coordination Center, the Interviewer will:

- Make sure that all equipment and paperwork is present and that the ID labels are correct. If the bottle of acid is less than half full, get another bottle.

- Pack the tote boxes to go to the field.

6.2 Sampling Location

The Baseline Questionnaire asks the respondent to point out the primary water supplies used for drinking and cooking. The Interviewer will take the samples from these supplies. If they use tap water, use the kitchen tap (cold water).

If either water supply is a well, the Interviewer will: [Is this necessary?]

- In Cycle 1, ask the respondent the location of the well. Ask Field Technician 2 to mark the well on the yard plan that is done for soil collection.

- In Cycles 2-8, ask the respondent whether the household has been using water from the well for drinking or cooking since before the previous Cycle began. If they started using water from the well since the previous Cycle, ask the location of the well and ask Field Technician 2 to mark it on the yard plan. Otherwise, proceed as in Cycle 1.

6.3 Sample Collection Procedure

At the residence, the Interviewer will:

- On the logsheet, note your name and signature, the date and time, water sources, presence of an aerator or purification device, and characteristics (cloudiness, color, or odor) of the water.

- Put on gloves.

- If the main supply is tap water, remove any aerators. Leave any water purification devices, including household water softeners and at-the-tap purifiers, in place. If there are dishes or other objects in the sink, ask permission and move them aside so that the drain is clear. Open the cold tap (on full) and allow the water to run for a minimum of two minutes.

- If bottled water is the primary source, do not flush the system. Half fill the disposable cup with bottled water, measure the pH, and record it on the logsheet.

- Measure the pH of the water:
  → Half fill the disposable cup with water.
  → Take the pH probe out of its plastic bag, remove the cap, and put the cap in the bag.
  → Set the pH probe in the cup and turn it on.
  → Leave the pH probe in the water for about two minutes until the reading stabilizes.
  → Record the pH on the logsheet. If the pH probe is alternating between two numbers, record them both.
  → If both tap water and bottled water are used, measure and record the pH of both types of water.
  → After measuring the pH, set the cup of water in the glass tray.
  → Dry the pH meter with a tissue, replace the cap, and seal the pH probe into the bag.
  → If the pH probe appears to be malfunctioning, write a note on the logsheet that the pH of the water should be tested at the FCC immediately after it is delivered there.

- If both drinking and cooking water are taken from the same source, fill both containers. Use a gentle flow to avoid splashing.

- If water for drinking and cooking are taken from different sources, half fill each container from one source. Then fill the containers from the other source.

- Cap the plastic container securely.

- Replace any aerators that were removed.

- Acidify the sample in the glass bottle (pesticide sample) as follows. (Do not acidify the metals sample in the plastic container.)
  - → Put the bottle of water into the glass tray.
  - → Put on safety glasses and an apron.
  - → Remove the bottle of acid from its plastic bag. Set the bottle in the glass tray. Remove the lid and put it upside down in the glass tray.
  - → Remove the dropper from its plastic bag. Half fill the narrow part of the dropper with acid.
  - → Transfer the acid into the glass bottle. Do not let the tip of the dropper touch the bottle or the water.
  - → Fill the dropper with water from the cup and return the water to the cup. Repeat this several times. Put the dropper back into its plastic bag and seal the bag. Put it into the trash bag.
  - → Close the acid bottle and seal it into its plastic bag.
  - → Cap the glass bottle securely.
  - → Carefully pour the water from the cup down the drain. Rinse the cup with cold tap water and pour this water down the drain. Put the cup into the trash bag.

- Remove the gloves and discard them in the trash bag. Remove the safety glasses and apron.

- Cap the two bottles of water and seal them with parafilm or electrical tape. Place them in the cooler withthe cold pack.

6.4 Labeling of Samples

A unique ID number will be assigned for each sample (see SOP G03 "Identification Numbers"). Printed labels will show the ID number in bar-code and human-readable format. The Interviewer will affix identical labels to the sample container, the logsheet, and the chain-of-custody form.

6.5 Preservation and Storage

Upon return to the Field Coordination Center, transfer custody of the samples to the Field Coordinator. Both Interviewer and Field Coordinator will sign a chain-of-custody form recording the transfer.

Samples awaiting shipping will be kept in a refrigerator at 4°C.

6.6 Handling and Shipping

For shipping, bottles should be packed in styrofoam or bubble pack to prevent leakage. The shipping container should contain sufficient ice or cold packs to ensure maintenance of 4°C temperature throughout shipment, and should have labels showing the UP direction.

Arrangements will be made with EPA-EMSL Cincinnati (or other cooperating laboratory) for timely shipments of samplers. It is expected that shipments will occur at least weekly.

6.7 Laboratory Analysis

Laboratory analysis will be performed by the cooperating laboratory. Metals analysis will be in accordance with EPA Method 200.8 (see reference). Samples to be analyzed for metals will be acidified at the laboratory. Holding time is up to six months after acidification.

Pesticide analysis will be by EPA method 525.2. Samples to be analyzed for pesticides will be extracted within seven days and completely analyzed within 40 days of extraction.

6.8 Data Workup

Field and laboratory data will be returned to Harvard in both magnetic and hardcopy format. Data will be coded and checked, computer entry verified, and discrepancies resolved. Analytical results will then be merged with questionnaires and other data, using the ID number as the merge parameter.

6.9 Sample Tracking

The ID number will allow tracking of each sample. A data base management system will ensure knowledge of the status and location of any sample at any time including retrospectively.

The chain-of-custody form will accompany the sample wherever it goes. Anyone who receives, transfers, or ships the sample will sign and date it, and keep a photocopy. It must clearly contain all necessary information so that the custody of the sample can be determined at any time. Airbills, bills of lading, etc., are acceptable substitutes when a commercial or government carrier is used; copies of such bills will be attached to the chain-of-custody form.

A copy of the chain-of-custody form will be sent to:

NERL-CI
c/o Lisa Jo Melnyk
26 W. Martin Luther King Drive
Cincinnati, OH 45268

Phone: 513-569-7497
Fax: 513-569-7115
Email: melnyk.lisa@epamail.epa.gov

7 Quality Assurance Procedures

7.1 Laboratory Blanks

Laboratory blanks will comprise 10% of the analyzed samples. A laboratory blank will consist of a 1-L container filled with ultra-high-purity water and handled in a manner consistent with the above protocol.

Shipping to the analysis laboratory and analysis itself will be performed identically to all other samples. Such laboratory blanks will be assigned a unique identifying number. The analyzing laboratory will have no knowledge of which samples are laboratory blanks.

7.2 Field Blanks

Field blanks will not be utilized in this study. The laboratory blanks described in section 7.1 will serve the quality assurance purposes normally attributable to field blanks.

7.3 Duplicate Samples

Duplicate sampling will be undertaken in 10% of the residences. At each Cycle, a random 10% of the homes will be designated for duplicate sampling of tap water. The duplicate sample will be taken as is the primary sample. A unique identifying number will be assigned and the sample will be handled as any other. Duplicate sample data will be handled in accordance with the standard operating procedure for duplicate analysis.

7.4 Tolerance Limits, Detection Limits, and Sensitivity Limits

The tolerance limits, detection limits, and sensitivity limits for the method will be determined through analysis of blank values and duplicate samples. According to Lobring, the minimum detection limit for lead by this method is 0.0006 mg/L (0.6 µg/L). Similar detection limits are found for arsenic (1.4 µg/L), cadmium (0.5 µg/L), and chromium (0.9 µg/L).

The table below shows expected concentrations and equivalent limits of detection given the sampling protocol.

Category	Pollutant	Expected Concentration	Expected Limit of Detection Given Sampling Protocol
Metals	Arsenic	< 10. ng/g	1.0 ng/g
	Cadmium	< 5.0 ng/g	0.05 ng/g
	Chromium	< 50. ng/g	0.10 ng/g
	Lead	< 50. ng/g	0.7 ng/g
Pesticides	Chlordane		1.5 ng/g
	Chlorpyrifos		3 ng/g
	Chlorpyrifos-methyl		5 ng/g
	4,4'-DDD		5 ng/g
	4,4'-DDE		2 ng/g
	4,4'-DDT		3 ng/g
	Dieldrin		1.5 ng/g
	Heptachlor		1.5 ng/g
	Malathion		3 ng/g

8 References

Maurice Berry. Memorandum, "Shipping Acidified Drinking Water Samples for Phase I Studies" to Principal Collaborators. August 17, 1994.

J. W. Eichelberger, J. W. Munch, and J. A. Shoemaker. *EPA Method 525.2 Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry.* Revision 1.0, March 1994. Environmental Monitoring Systems Laboratory, Office of Research and Development, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268.

Environmental Protection Agency. *Handbook for Sampling and Sample Preservation of Water and Wastewater.* EPA-600/4-82-029, September 1982.

Harvard University/Emory University/Johns Hopkins University Standard Operating Procedures:

G03 Identification Numbers for Samples and Forms
G04 Chain-of-Custody and Sample Tracking
G05 Storage and Shipping of Samples
L02 Cleaning of Glass and Plastic Containers
L13 Extraction of Neutral Pesticides from Drinking Water
L14 Determination of Pesticides, Acid Herbicides, and PAHs by GC/MS

Stephen E. Long and Theodore D. Martin. *EPA Method 200.8 Determination of trace elements in waters and waste by inductively coupled plasma-mass spectrometry.* Revision 4.4 April 1991. Environmental Monitoring Systems Laboratory, Office of Research and Development, United States Environmental Protection Agency, Cincinnati, Ohio 45268.

Larry Lobring. Memorandum on Drinking Water Issues to Tim Buckley, Karen Hammerstrom, and Jim Quackenboss. December 23, 1993.

Research Triangle Institute Analytical and Chemical Sciences. *Procedure for collection , storage, and shipment of drinking water samples by EPA method 200.8.* Lower Rio Grande Valley Environmental Pilot Study. RTI/ACS-AP-207-2.