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-F05**

Title: Collection, Storage, and Shipment of Soil Samples for Metal, Pesticide, and PAH 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

Notice: *The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), partially funded and collaborated in the research described here. This protocol is part of the Quality Systems Implementation Plan (QSIP) that was reviewed by the EPA and approved for use in this demonstration/scoping study. Mention of trade names or commercial products does not constitute endorsement or recommendation by EPA for use.*

1 Title of Standard Operating Procedure

Harvard University/Emory University/Johns Hopkins University Standard Operating Procedures: **F05 Collection, Storage, and Shipment of Soil Samples for Metal, Pesticide, and PAH Analysis, Rev. 1.0.**

2 Overview and Purpose

This standard operating procedure outlines the necessary steps for sampling soil from the yard, the food garden, and the foundation of the respondent's home. The samples will be composited and sent to Southwest Research Institute (SwRI) to be sieved and divided. One fraction will be analyzed for metal content at HSPH. In Cycles 1, 3, 5, and 7, another fraction will be extracted by SwRI for pesticide analysis by SwRI and PAH analysis by EPA NHEERL.

3 Discussion

Soil samples will be taken every Cycle (weather permitting), by Field Technician 2 during the first visit to the home. Samples will be taken in order to evaluate what exposure from bare soil and play areas might be. If the household has a garden where food is grown, the garden soil will be analyzed to evaluate this possible food exposure pathway. The foundation soil will be sampled to evaluate the potential for exposure from past use of exterior paint with possible lead content, pesticides for termite control, etc.

4 Personnel Responsibilities

4.1 Sampler Preparation

Sampler preparation is the responsibility of the Field Technician 2 (FT2).

Syringes and skewers will be prepared at HSPH. Sampling jars and lids will be acid washed at SwRI as per HSPH SOP L02 “Cleaning of Glass and Plastic Containers.”

The Field Coordination Center (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

Sample collection is the responsibility of the Field Technician 2.

4.4 Storage

Immediate storage of the sample prior to the return to the field coordination site is the responsibility of the Field Technician 2. Custody will be turned over to the Field Coordinator (FC) or his designate for storage at the field coordination site.

4.5 Shipment

Shipment to the analytical laboratory is the responsibility of the Field Coordinator or his designate.

4.6 Sieving and Division

Sieving and division of the samples is the responsibility of SwRI.

5 Required Equipment and Reagents

5.1 Field Coordination Center (before field sampling)

disposable plastic syringe, 50 cc, with the tip cut off, marked at 15 cc (~1" length)
2 jars, glass, 1-liter, with Teflon-lined lids, acid washed
(1 primary, 1 spare unless there is already a spare in the "general" tote box)
transparent tape
plastic bags, sealable, 3-quart (Ziplok or equivalent)

5.2 Field Sampling

disposable plastic syringe with tip cut off, marked at a standard length (in bag)
2 jars, glass, 1-liter, with lids (labeled, in bags)
(1 primary, 1 spare unless there is already a spare in the "general" tote box)
1 package wooden barbecue skewers, about 12" long, with half of each spray-painted orange
tape measure, approximately 25 feet long (8 m), Craftsman recommended
plastic electrical tape
flashlight
cooler with cold packs

5.3 Sample Tracking and Paperwork

12 sample ID labels with sample type 31 for soil sample:
3 for logsheet, 1 for chain-of-custody form, 1 for yard plan, 1 for foundation plan,
1 for collection jar, 5 spare
Field Packet for household: logsheets (3-part carbonless), chain-of-custody form,
yard plan sheet (Cycle 1: blank sheet; Cycles 2-8: copy of plan from previous Cycle),
foundation plan sheet (Cycle 1: blank sheet; Cycles 2-8: copy of plan from previous Cycle)
Field Manual (SOPs)
clipboard
pens, ballpoint, 2 black or blue for logsheet, plus (in Cycles 2-8) 2 red or green for writing
on the copies of the yard and foundation plans (to distinguish new writing from old)

6 Procedure

6.1 Preparation for Collection

6.1.1 Preparation of Sampling Equipment

At HSPH:

Syringes: Use a saw to cut the tip off each syringe so that the cylinder is open. File off any rough edges. Use a marker to mark the syringe at a volume of 15 cc (1 inch).

Skewers: Spread out skewers on a sheet of plastic. Cover half of each skewer with newspaper. Spray with bright orange paint. When the paint is dry, rotate the skewers and paint again. Repeat if necessary.

At SwRI (after removing soil for sieving):

Jars: Acid wash and dry jars and lids as specfied in HSPH SOP L02 "Cleaning of Glass and Plastic Containers."

6.1.2 Permission from Property Owner

Before the first visit, FCC staff will ask the respondent whether s/he owns the property and, if not, who does. The property owner will be asked for permission to take soil samples.

6.1.3 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 an ID label to a chain-of custody form and 3 identical labels to the three parts of a logsheet. Affix one label to the yard plan sheet and one to the foundation plan sheet. (If this is Cycle 1, place the label in the box. If this is a later Cycle, place the label covering the previous label on the photocopy.)

6.1.4 Collection Equipment

At the FCC, the FT2 will:

- Affix a strip of transparent tape to each collection jar. Affix an ID label to the tape on the primary jar. If unused labeled jars are available, remove the labels and treat them like clean jars.
- Place each jar and lid, a cut-off syringe, and the spare ID labels in a plastic bag. Seal the bag.

- Place the jar with the ID label in the tote box for the household. Place the unlabeled jar in the "general" tote box if there is not already one there.

6.1.5 Transfer and Inspection of Equipment

At the Field Coordination Center, FT2 will:

- Make sure that all equipment and paperwork is present and that the ID labels are correct. Pack the tote boxes to go to the field.

6.2 Selection of Sampling Location(s)

The soil will be sampled as indicated below, with the exception that if there are no areas of the property that meet the criteria, no samples will be taken. For example, if there is no food garden, no garden samples can be taken.

A total of 24 cores (syringefuls) of soil will be collected. If all three areas (foundation, yard, and garden) are sampled, 8 cores will be taken from each area. If two areas are sampled, 12 cores will be taken from each area. If only one is sampled, 24 cores will be taken from that area.

If soil is frozen too hard for sampling, samples will not be taken in that Cycle.

6.2.1 Cycle 1 -- General

The interviewer will:

- Ask the respondent to point out the boundaries of the property, and areas where household members play or participate in sports.

- If the household has no yard, ask if there is a place where household members play near the home. This area will be sampled if (1) the target individual plays there, (2) the location is within one block of the home, (3) the area is not locked, and (4) no additional permission must be obtained.

- Ask if there are any gardens where food is grown to be eaten by members of the household. Include fruit trees. If there will be a garden but it is not yet planted, sampling will be done where the garden will be. If they have a plot in a community garden, it will be sampled if (1) the location is near the home, (2) the area is not locked, and (3) no additional permission must be obtained.

- If there are potential problems such as a dog run or other fenced-in area, ask the respondent whether it is all right to sample there, and (if so) how to enter the area.

6.2.2 Cycle 1 -- Foundation

Field Technician 2 will:

- On the foundation plan form, sketch the shape of the house. Mark walks, decks, chimneys, bushes, mulch, roof drain spouts, etc. Note if the house is on pilings or

stilts. Mark measurements on the form, but the sketch need not be exactly to scale. See example.

- If the foundation is unavailable or nonexistent (e.g., if the entire area from house to boundaries is paved), check the appropriate box on the logsheet.

- The foundation soil is within one meter of the house. (Sampling will be done 10 cm from the side of the house where possible, but if the surface close to the house is paved, soil up to 1 m away will be acceptable.) Accessible areas on all sides of the building will be sampled. Mark areas where the foundation is inaccessible because of decks, mulch, bushes too close to walk behind them, etc.

- If all 3 areas (foundation, yard, and garden) will be sampled, 8 cores will be taken from the foundation. Mark 8 sampling points as follows:

  → On each side of the house, mark the ends of the accessible area with skewers. If the house has four sides, place two more skewers at the 1/3 and 2/3 points of this length, 10 cm from the foundation. The skewers that are not at the ends mark the sampling locations. If the house has more than four sides, distribute the sampling points as evenly as possible. Choose points near entrances if possible.

  → If the available area is limited, mark sampling points where possible; they can be close together if necessary but there should be 8. If the house is on pilings or stilts, mark sampling locations near the pilings or stilts.

- If only 1 or 2 areas will be sampled, so 12 or 24 cores will be taken from the foundation, mark points as above, but mark more sampling points, distributed around the house as evenly as possible.

- If any sampling point is paved, make a note on the foundation plan, and mark another point near it if possible. If the entire side is paved, mark 5 cm from the edge of the paved surface if this is less than one meter from the house.

- Remove the skewers that do not mark sampling points. Count the sampling points and make sure the number is correct.

- Write the sampling points as (F) on the foundation plan with distance measurements. If points are close together, be careful to distinguish them on the plan.

6.2.3 Cycle 1 -- Yard

- On the yard plan form, sketch a plan of the property. Note buildings and other built structures, their general condition, boundaries, paved areas, bare soil, evident uses of the property including play and gardens, and nature of adjacent property. Mark measurements on the form, but the sketch need not be exactly to scale. See example.

- The yard is defined as the property that is not paved nor built upon that begins 1 m away from any built structure and ends at the boundary, crossing any paved areas.

- Consult with Field Technician 1 about where the outdoor air sampler will be placed.

Mark this location on the yard plan sheet as (A).

- If the yard is unavailable or nonexistent, check the appropriate box on the logsheet.

- If the household includes children but has no yard, soil samples will be taken from the area near the home where the children go to play, if this is convenient.

- Choose four areas to sample, e.g., two side yards, a back yard, and a front yard. Choose play areas and other heavily used locations, e.g., near a picnic table or other lawn furniture. Try to find exposed soil; soil covered with thick grass, thatch, or mulch will not be sampled. Decide how many cores to take from each area to total 8, 12, or 24.

- In one of the sampling areas, use a skewer to mark a point where there is exposed soil. Measure distances in two directions to landmarks such as the house or a fence.

- Use skewers to mark other points where there is exposed soil in the same area. If possible, and if several cores will be taken, choose points in a grid about 2 m apart.

- Repeat the procedure at other areas until the number of marked points is the same as the number of foundation points sampled and the points are well distributed. Write these points as (Y) on the yard plan, with distances and any other information needed to find the same location in later Cycles.

6.2.4 Cycle 1 -- Garden

- Mark any area of the property where food eaten by members of the household is grown. If there is more than one garden plot, all plots will be sampled. Soil covered with mulch or fabric, or soil in pots, will not be sampled. If the garden is unavailable or nonexistent, check the appropriate box on the logsheet.

- Walk around each food garden area to locate suitable sampling points. The number of sampling points should be the same as for foundation and yard soil. Sampling points should be about 25 to 50 cm in from the edge of the garden.

- If the residence has a fruit tree or fruit or vegetable bush that is not in a garden area, mark at least one sampling point. If there is bare soil under the tree or bush, estimate the distance from the trunk to the outer branches, and mark the sampling point(s) half the distance from the trunk.

- On the yard plan form, mark and measure each garden area as for yard soil.

- Note sampling locations as (G) on the yard plan and soil characteristics on the logsheet.

6.2.5 Cycles 2-8

- Identify the areas marked on the yard and foundation plans from the previous Cycle. If there are any changes that make it impossible to sample a previously sampled area (such as thick grass where there was exposed soil before), note the changes on the

logsheet. If another area can be sampled instead, mark this area on the yard plan.

- Mark all sampling points with skewers. Make sure there are 24 points.

6.3 Sample Collection Procedure

6.3.1 Conditioning Sampling Syringe

- Put on gloves.
- In a location that will not be sampled, insert the syringe into the soil and pull it out, tilting it if necessary to keep the soil inside. Discard the soil nearby.
- Repeat the process twice more. Smooth the soil.

6.3.2 Foundation Soil Samples

- Take a sample at each marked sampling point by inserting the syringe into the soil to the depth mark and pulling it out, tilting it if necessary to keep the soil inside. Open the collection jar and let the soil slide into the jar. If the syringe cannot be inserted at a sampling point because of a rock or other obstacle, take a sample as close to the point as possible.
- Cap the jar. Remove the skewers, replace them in the package, and smooth the soil.
- When all sides have been sampled, put the lid tightly on the jar and shake it to mix the soil.
- On the logsheet, write soil characteristics and the number of samples taken.

6.3.3 Yard Soil Samples

- At each marked point, take a sample as for foundation soil. Remove the skewer and smooth the soil. Put the lid tightly on the jar and shake it to mix the soil.
- Note on the logsheet the characteristics of the soil, e.g. sand or humus, wet or dry. Note the number of samples taken.

6.3.4 Garden Soil Samples

- At each marked point, take a sample as for foundation soil. Remove the skewer and smooth the soil. Put the lid tightly on the jar and shake it to mix the soil.
- Note on the logsheet the characteristics of the soil, e.g. sand or humus, wet or dry. Note the number of samples taken.

6.3.5 Completion of Sampling

- Place the jar in the plastic bag with the spare ID labels. Seal the bag. Place the jar in a cooler with cold packs.

- Remove the gloves and put them into the trash bag.

- Check the logsheets and yard plans. Fill in any missing information.

- At the FCC, transfer custody of the sample to the Field Coordinator or his designate.

6.4 Labeling of Samples

A unique ID number will be assigned for each sample (see SOP G03 "Identification Numbers for Samples and Forms"). Printed labels will show the ID number in bar-code and human-readable format. For each sample the field technician will affix identical labels to the sample container, the logsheet, and the Chain-of-Custody form. Any remarks regarding the sampling conditions and the soil type, color, wetness, etc., will be noted on the logsheet.

6.5 Preservation and Storage

Samples will be kept in a refrigerator until shipment according to SOP G05 "Storage and Shipping of Samples." All samples will be stored in a locked room at the Field Coordination Center until weekly shipment for analysis.

6.6 Handling and Shipping

Samples will be shipped to SwRI weekly according to SOP G05 "Storage and Shipping of Samples." Samples will be kept cold with cold packs during shipping.

6.7 Laboratory Analysis

6.7.1 Sieving and Division

Samples will be sieved and divided at SwRI. See HSPH SOP L05, "Sieving and Division of Dust and Soil Samples."

6.7.2 Metals

Samples will be prepared at HSPH using EPA Method 200.8 as a guideline. This will involve extended digestion in one or more concentrated or diluted mineral acids followed by a dilution to an optimal volume for analysis by either GF-AAS or ICP-MS or both. See HSPH SOPs L06 "Extraction of Metals from Sampling Media," L07 "Analysis of Metals by GF-AAS, and L08 "Analysis of Metals by ICP-MS."

Any analyses by another laboratory will be done according to EPA Method 200.8 or a documented equivalent.

6.7.3 Pesticides and PAHs

In Cycles 1, 3, 5, and 7, samples will be extracted at SWRI for pesticide analysis by SwRI and PAH analysis by EPA NHEERL. See HSPH SOPs L09 "Extraction of Neutral Pesticides and PAHs from House Dust and Soil" and L14 "Determination of Pesticides, Acid Herbicides, and PAHs by GC/MS."

If a sample cannot be taken in an odd-numbered Cycle (e.g. because ground is frozen), the sample from the next Cycle will be extracted for pesticide and PAH analysis.

6.8 Data Workup

Field and laboratory data will be returned to Harvard in both magnetic and hard copy 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.

7 Quality Assurance Procedures

7.1 Laboratory Blanks

Laboratory blanks will be prepared and analyzed according to the schedule set up by the laboratory and the laboratory quality assurance measures as outlined in the extraction and analysis SOPs. See section 6.7.

7.2 Field Blanks

The field blank will consist of a jar of clean quartz sand at 10% of households. It will be opened in the field, handled in a manner similar to the sample handling, closed, sealed, and placed in a plastic bag. It will be transferred to the field coordination site and to the analysis site with the rest of the samples.

7.3 Duplicate Sampling

Duplicate samples will be collected at 10% of the households at all sampling points. Replicate analysis will be done in the lab by splitting the composite samples and then analyzing them.

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 and replicate analytical measurements.

The table shows expected concentrations (% detected and maximum range in 24 surface soils)

and equivalent limits of detection given the sampling protocol.

Category	Pollutant	Expected Concentration (ng/g)	Expected Limit of Detection* (ng/g)
Metals	Arsenic	500-25,000	350.
	Cadmium	100-5,000	12.5
	Chromium	5,000-250,000	62.5
	Lead	10,000-500,000	75.
Pesticides	Chlordane-α	600.	0.81
	Chlordane-γ		0.95
	Chlorpyrifos	18	1.71
	4,4'-DDD	5	4.92
	4,4'-DDE	50	0.91
	4,4'-DDT	1-100	1.22
	Dieldrin	2-10	4.35
	Heptachlor	1-10	2.88
	Malathion	7	1.38
PAHs	Anthracene	10-1,000	100.
	Benzo(a)pyrene	2-1480	130.
	Chrysene	2-1600	100.
	Phenanthrene		100.

*Expected Limit of Detection Given Sampling Protocol

8 References

Ashengrau, Ann, Robert Bornschein, Merrill Brophy, *et al*. *Three City Urban Soil-Lead Demonstration Project: Protocols for Sampling and Analysis of Soils, Dust, and Handwipes*. Internal EPA document, October 1991.

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
G06 Problem Management
L02 Cleaning of Glass and Plastic Containers
L05 Sieving and Division of Dust and Soil Samples
L06 Extraction of Metals from Sampling Media
L07 Analysis of Metals by GF-AAS
L08 Analysis of Metals by ICP-MS
L11 Extraction of Neutral Pesticides and PAHs from House Dust and Soil
L14 Determination of Pesticides, Acid Herbicides, and PAHs by GC/MS

SwRI: Expected pesticide and PAH concentration from 24 surface soil samples from yards in the Childhood Leukemia Study (9 states in Great Lakes region) (data not yet published)

Foundation Plan Form
NHEXAS Phase I Study

Sample ID Label
31 -- soil field sample

Yard Plan Form
NHEXAS Phase I Study

Sample ID Label
31 -- soil field sample