

# National Human Exposure Assessment Survey (NHEXAS)

## *Arizona Study*

## Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona  
Tucson, Arizona 85721

Cooperative Agreement CR 821560

**Standard Operating Procedure**

**SOP-UA-F-17.1**

**Title:** Collection, Storage, and Shipment of Drinking and Tap Water  
Samples for Pesticides and Carbaryl Analysis

**Source:** The University of Arizona

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.

## **Collection, Storage, and Shipment of Drinking and Tap Water Samples for Pesticides and Carbaryl Analysis**

### **1.0 PURPOSE AND APPLICABILITY**

The procedures in this SOP describe how to collect, store and ship tap and drinking water samples for analysis by EPA Method 525.2 (revision 1.X) and EPA Method 531.1 (revision 3) for the NHEXAS Arizona Project, AZ Border project, and other Health and Environment projects. This SOP provides a brief description of the sample containers, collection, preservation, storage, shipping, and custody procedures.

### **2.0 DEFINITIONS**

- 2.1 AZ BORDER = The US border region is defined as 100 km north of the border. In this study, we define the border as 40 km north of the border. The Arizona Border Study or "Border AZ" is an alias for "Total Human Exposure in Arizona: A Comparison of the Border Communities and the State" conducted in Arizona by the University of Arizona / Battelle / Illinois Institute of Technology Consortium.
- 2.2 BUCKET = A plastic container with a buckle top. One bucket is assigned to each household to be visited. Household identification and stage numbers are listed on the outside of the container. The bucket contains all paperwork to be completed by field staff or household respondents. It serves as the primary vehicle for securing and transporting forms, data and room temperature tolerant samples to and from the field.
- 2.3 DPD TEST KIT = Commercially available and used to indicate the presence of chlorine in a water sample.
- 2.4 DRINKING WATER = Any water used for drinking. This includes tap water that is treated, or filtered, and water brought into the home from an outside source and used for drinking.
- 2.5 FIELD COORDINATOR = The employee of the research project who supervises field data collection and operations. The Field Coordinator collates individual data into HH packets, and upon completion of all visits, sampling and QA checks, forwards the packet to the Data Coordinator.
- 2.6 FIELD STAFF = The Field Coordinator, the Team Leader and the Team Members.
- 2.7 HCl = Hydrochloric acid, Ultrex II, Ultrapure Reagent, 36.9%.

- 2.8 LAB SUPERVISOR = The employee of the research project who supervises laboratory analyses.
- 2.9 MATERIALS TECHNICIAN (Materials Tech) = The employee of the research project who is responsible for assembling and assigning field forms, questionnaires and equipment for field use.
- 2.10 NHEXAS Arizona = Acronym for National Human Exposure Assessment Survey, a research project conducted in Arizona by the University of Arizona/Battelle/Illinois Institute of Technology consortium.
- 2.11 QUALITY ASSURANCE (QA) = All those planned and systematic actions necessary for ensuring the accuracy, validity, integrity, preservation and utility of collected data.
- 2.12 QUALITY CONTROL (QC) = Those quality assurance actions providing a means to control and measure the characteristics of a datum, process or the adherence to established parameters.
- 2.13 RESPONDENT = A person in the study population of NHEXAS Arizona, AZ Border project, and other Health and Environment projects.. Each household is assigned an HHID. All respondents are assigned an Individual Respondent Number (IRN). Each respondent can be uniquely identified by an HHID, IRN combination.
- 2.14 SAMPLE = The water collected from the household for pesticide or Carbaryl analysis.
- 2.15 SAMPLE IDENTIFICATION NUMBER = A numeric code that uniquely identifies every sample. It is generated through the NHEXAS tracking system by the Materials Technician.
- 2.16 TAP WATER = Untreated or softened water passing through the kitchen tap after removal of aerators, filters, or other attachments at the tap.
- 2.17 TEAM LEADER = The member of the field team who is primarily responsible for respondent contact, data collection, field form and questionnaire completion, and site QC checks of all data.
- 2.18 TEAM MEMBER = Member of a field team responsible for assisting the Team Leader in the collection of data and quality control checks in the field.
- 2.19 TRACKING SYSTEM = A database system containing information about the custody, transfer and storage of hard copy data, electronic data, field samples, and field sample

aliquot.

- 2.20 VISIT = A scheduled appointment with participating respondents at their place of residence (HH) for the collection of samples, questionnaires and other data.

### **3.0 REFERENCES**

- 3.1 Eichelberger, J.W., Munch, J.W., and Shoemaker, J.A. 1994. Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (Method 525.2, Revision 1.X). Environmental Monitoring Systems Laboratory Office of Research and Development, U.S. EPA.
- 3.2 Graves, R. L. 1989. Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in Water by Direct Aqueous Injection HPLC with Post Column Derivatization (Method 531.1, Revision 3.X). Environmental Monitoring Systems Laboratory Office of Research and Development, U.S. EPA.
- 3.3 Lebowitz, M. D. 1993. Study Design (Revision of 31 Dec. 1993). EPA NHEXAS Cooperative Agreement.

### **4.0 DISCUSSION**

- 4.1 If a house has one single untreated water source, only one tap water sample will be collected. If separate tap and drinking water sources are used, tap water and a sample from the most frequently consumed drinking water source will be collected. Presence of chlorine interferes with analysis of the sample. Therefore chlorine in the water is chemically quenched during the collection procedure.
- 4.2 Samples will be transported from the field on blue-ice and stored at 4°C immediately upon return to the UA Lab.
- 4.3 The relative timing of water sample collection to other sampling types by stage is shown in Fig. 2.

### **5.0 RESPONSIBILITIES**

- 5.1 The Field Coordinator is responsible for:
- (a) knowing the procedures described in this SOP and insuring that they are followed by the Field Staff,
  - (b) supervising the set-up and collection of water samples in one out of every ten

- houses sampled as a field audit for QA,
- (c) coordinating with the Materials Technician to insure that water sample containers have been logged in to the Tracking System and assigned to HH as appropriate,
- (d) QA checks of the Water Sampling Field Sheet within 24 hours of collection.

5.2 The Team Leader is responsible for:

- (a) knowing the procedures described in this SOP and insuring that they are followed by the Team Members,
- (b) arranging sampling dates and times with the HH,
- (c) obtaining the water containers from the Materials Technician, and acid bottles from the Lab Supervisor
- (d) collaborating with the Team Member(s) to select the appropriate sampling site at each HH,
- (e) insuring the integrity and custody of the water sample and field forms collected,
- (f) quality control (QC) checks in the field,
- (g) properly storing the water samples in the dark at 4°C to and from the Field site in a cooler,
- (h) forwarding individual QC checked field forms to the Field Coordinator for QA check within 24 hours of collection.

5.3 All Team Member(s) are responsible for:

- (a) knowing and following the procedures described in this SOP,
- (b) receiving the water containers from the Team Leader,
- (c) collaborating with the Team Leader to select the appropriate sampling site at each HH,
- (d) obtaining the water samples according to this SOP,
- (e) completing the Water Sampling Sheet and the Chain of Custody Record,
- (f) quality control (QC) checks in the field.

5.4 The Materials Technician is responsible for:

- (a) the proper assignment of water containers to selected HH,
- (b) accepting custody of the water containers from the Team Leader and annotating the receipt in the Chain of Custody Record that accompanies the sample,
- (c) properly storing the water containers in the dark at 4°C after receipt, and forwarding the water samples to the Lab Supervisor for preservation if it was not done in the field,
- (d) stocking the HH Bucket with appropriate field sampling forms,
- (e) including Field Blanks with water assignment as appropriate.

- (f) Shipping the samples collected to the analyzing laboratory at room temperature and documenting shipment on the Chain of Custody Record and on the NHEXAS Arizona (or other project) Shipment Log (Fig.5).

## **6.0 MATERIALS AND EQUIPMENT**

### **6.1 Materials:**

- (a) 1 Liter I-Chem Certified Amber (NM BR) glass bottles with Teflon lined septa in the screw caps (pesticides). I-Chem certified for use in the analysis of semi-volatiles, pesticides/PCBs and metals.
- (b) 60 ml trace clean, pre-cleaned amber glass vials (Carbaryl). Short amber SS WM glass with Teflon lined closure.
- (c) 1/2 dram glass vials
- (d) Nalgene plastic 30 ml drop dispenser bottles
- (e) DPD type chlorine test kit
- (f) Electrical tape or parafilm
- (g) latex gloves
- (h) paper towels
- (i) plastic funnel
- (j) 'Type 1' high purity, high resistivity water purchased from VWR for Field Blanks.

### **6.2 Reagents:**

- (a) Ultrex Ultrapure HCl 30% min.
- (b) Exsiccated purified sodium sulfite
- (c) Suprapur Sodium Thiosulfate 5-hydrate
- (d) Monochloroacetic acid
- (e) Potassium acetate.

## **7.0 PROCEDURE**

### **7.1 Preparation**

#### **7.1.1 Containers (pesticides and carbaryl)**

- (a) The sample bottles (1L and 60 ml amber glass) are purchased pre-cleaned meeting EPA specifications for the use of water containers in pesticide sampling. The bottle caps contain Teflon septa.
- (b) 1/2 dram vials contain the reagents used to quench chlorine within the sampled water. The vials are cleaned (UA-L-5.X) and then burned at approximately 500

degrees C for at least one hour. The vials are sealed in a clean environment with cleaned caps (UA-L-5.X). Once filled, the vials are labeled and a color coded piece of tape is affixed to the container. The tape color matches the color of the water sampling container lids and is used in the field as a double-check for the field teams. The vials are then released for field use.

1. Turn on the scale in the laboratory and follow the calibration guidelines (UA-L-1.X). Place a piece of weighing paper on to the scale and tare to 0.0000. Sodium Sulfite is used as the chlorine quenching agent for water pesticide samples and is obtained as a fine granular powder. Weigh  $45 \pm 1$  mg of Sodium Sulfite on to the weighing paper and place into a clean vial. Set aside, place the weighing paper on to the scale pan, tare if necessary, and repeat the procedure.
  2. Sodium thiosulfate 5-hydrate, the chlorine quenching agent for water carbaryl samples, is obtained as large crystals, thus initial grinding must occur to obtain fine granular powder suitable for weighing. The material is placed into a mortar (cleaned and burned at approx. 500 degrees °C) and a pestle (cleaned and burned at approx. 500 degrees °C) is used to grind the crystals to a fine powder suitable for weighing. Turn on the scale in the laboratory and follow the calibration guidelines (UA-L-1.X). Place a piece of weighing paper on to the scale and tare to 0.0000. Weigh  $4.8 \pm 1$  mg of Sodium thiosulfate 5-hydrate on to the weighing paper and place into a clean vial. Set aside, place the weighing paper on to the scale pan, tare if necessary, and repeat the procedure.
- (c) Nalgene plastic 30 mL drop dispenser bottles contain Ultrex II, Ultrapure HCL for addition to samples in the field. The bottles are cleaned according to UA-L-5.X prior to their being filled with HCL. The bottles are labeled and the cap taped shut.
- (d) The carbaryl sample containers have monochloroacetic acid buffer added prior to release to the field teams. It consists of Monochloroacetic acid and Potassium acetate. The buffer is mixed using apparatus cleaned to specifications listed in UA-L-5.X. the chemicals are weighed on the scale in the laboratory (calibrated in accordance with UA-L-1.X).
1. 2.5 Molar Monochloroacetic acid solution is made by mixing 236.2 mg of crystalline monochloroacetic acid with one liter of distilled/deionized water.
  2. 2.5 Molar Potassium Acetate solution is made by mixing 245.4 mg of crystalline potassium acetate with 1 liter of distilled/deionized water.
  3. The buffer is mixed by adding 156 mL of the monochloroacetic acid

solution with 100 mL of the potassium acetate solution. The solutions are measured in a graduated cylinder with  $\pm 1$  mL accuracy.

4. Once the solution is mixed,  $1.8 \pm 0.2$  mL is measured into each carbaryl sample container using a bottle dispenser. The bottle dispenser is cleaned with distilled water and the amount dispensed is checked using a graduated cylinder prior to use. A large "B" is marked on the top of the container with a wax pencil to denote the addition of the buffer. The containers are then released to the Materials Technician for use by the Field Teams.

### 7.1.2 Identifying water sources

Have the participants identify the primary drinking water source that the Primary Respondent uses. If multiple drinking water sources are used by the Primary Respondent identify secondary sources and prepare to sample.

## 7.2 Sample Collection

### 7.2.1 Water Delivery System

- (a) For tap water samples, run the water at high flow for at least three minutes before collecting. The temperature of the water should stabilize before sampling.
- (b) Remove any aeration devices before collecting tap water samples. Be sure to line the outer edge of aeration device with electrical or Teflon tape before removal to prevent damage to outer surface of aerator housing.
- (c) Collect a second sample if there is a second "source" of water for dish washing, drinking, cooking, or bathing. A second source would include any water delivery system which contains a separate in-line filter.
- (d) If modified tap water is used for drinking, do not remove any filters present at the tap (do not bypass any water softening systems). Run water for at least 3 minutes before collecting sample.
- (e) If the water source is bottled, do not run water prior to sample collection.
- (f) If the water source is hand pumped from a well, pump for at least three minutes before sample collection.

### 7.2.2 Chlorine Detection using DPD test kit. (Test water once prior to collecting sample.)



- (a) The DPD test kit contains the equipment and chemicals needed to test for total residual chlorine.
- (b) Rinse one of the clean test tubes from the kit with the test sample, then fill to the top line on the test tube.
- (c) Add one DPD #4 tablet or equivalent "powder pop", cap the test tube, and shake to dissolve. The provided stirring rod may be used to crush the tablet to aid total dissolution.
- (d) Compare the resulting color with the color standards. This reading represents the total residual chlorine content. The test kit allows a range of readings from 0.1 PPM to 6 PPM. If the reading is above 3 PPM Chlorine, repeat Chlorine Tests using a 5 ml sample (bottom line of the test tube).
- (e) Record the results on the "Water Collection and Chain of Custody Record" (fig. 1).

#### 7.2.3 Collection of the Pesticide sample (EPA Method 525.2)

- (a) Don a pair of non-powdered disposable latex gloves.
- (b) If any color appears during the DPD test, residual chlorine is present, and the contents of the 1/2 dram vial containing 50 mg of sodium sulfite is added to the 1 L bottle. If the DPD test remains clear, then residual chlorine is **not** present and nothing is added prior to sample collection.
- (c) Note the addition of the chlorine quencher on the "Water Sample Collection" form (figure 1).
- (d) Reduce the flow rate of the water to avoid introducing bubbles in the sample (or pour slowly from a drinking storage container).
- (e) Fill the bottles slowly with water, do not pre-rinse. During the initial filling swirl the water to dissolve the sodium sulfite. **Do not flush the quenching chemicals.** Bottles do not need to be completely filled, and air bubbles will not ruin this sample.
- (f) Use the plastic funnel to guide the stream of water into the collection container as necessary. Clean up any spills with paper towels as necessary.

#### 7.2.4 Collection of the Carbaryl sample (EPA Method 531.1)

- (a) Don a pair of non-powdered disposable latex gloves.
- (b) If any color is present during the DPD test, residual chlorine is present, and the contents of the 1/2 dram vial containing 6 mg of sodium thiosulfate is added to the 60 ml bottle. If the DPD test remains clear, then residual chlorine is **not** present and nothing is added prior to sample collection.
- (c) Note the addition of the chlorine quencher on the "Water Collection and Chain of Custody Record" (fig. 1).
- (d) Reduce the flow rate of the water to avoid introducing bubbles in the sample (or pour slowly from a drinking water storage container).
- (e) Fill the bottles slowly with water, do not pre-rinse. During the initial filling swirl the water to dissolve the sodium thiosulfate (if added). **Do not flush the quenching chemicals** (if added).
- (f) Use the plastic funnel to guide the stream of water into the collection container as necessary. Clean up any spills with paper towels as necessary.

#### 7.3 Preservation

##### 7.3.1 Pesticide sample (EPA Method 525.2) preservation

- (a) Test the pH of the sample (7.6.2 below) and if  $\text{pH} > 2$  then add, from the drop dispenser bottle, enough hydrochloric acid to the 1 L bottle to reduce the water samples to a  $\text{pH} < 2$  ( $\approx 40$  drops).
- (b) Place the cap on the bottle and invert slowly to mix the preservative.
- (c) Test the pH with pH paper (7.6.2 below), and if necessary add more HCl in small increments until the pH is  $< 2$ .
- (d) Once the water has achieved the proper pH, seal the cap with electricians tape or parafilm and transport to the field office in a cooler on blue ice.

##### 7.3.2 Carbaryl sample (EPA Method 531.1) preservation

The addition of the chlorine quenching agent to the buffered vial is typically sufficient to

lower the pH below 3 for preservation. However, you must test the pH of each sample and acidify as necessary.

- (a) Test the pH of the sample (7.6.2 below) and if  $\text{pH} > 3$  then add, from the drop dispenser bottle, enough hydrochloric acid to the vial to reduce the water samples to a  $\text{pH} < 3$  ( $\approx 10$  drops).
- (b) Place the cap on the bottle and invert slowly to mix the preservative.
- (c) Test the pH with pH paper (7.6.2 below), and if necessary add more HCl in small increments until the pH is  $< 3$ .
- (d) Once the water has achieved the proper pH, seal the cap with electricians tape or parafilm and transport to the field office in a cooler on blue ice.

#### 7.4 Sample Storage

- 7.4.1 Immediately place each sample in a darkened storage area at  $4^{\circ}\text{C}$ . The samples must be kept out of the light at  $4^{\circ}\text{C}$  at all times until analysis.

#### 7.5 Sample Delivery or Shipment

##### **Caution:**

**The shipped water has a pH of 2 or less. This could create a hazard if shipping bottles leak or break. Use care in preparing samples for shipment.**

- 7.5.1 All samples should be chilled to  $4^{\circ}\text{C}$  prior to shipping.
- 7.5.2 Complete the NHEXAS AZ (or other project) Shipment log and document shipment on the Chain of Custody Record. Retain a copy of the Chain of Custody records and Shipment Log. Forward a second copy of the Chain of Custody Record and Shipment Log to U.S. EPA Labs in Cincinnati. The original Chain of Custody Record and shipment log remains with the sample(s).
- 7.5.3 Ship or transport the sample in insulated shipping containers with sufficient cold packs to maintain a sample temperature of  $4^{\circ}\text{C}$  for 24 hours.
- 7.5.4 Wrap each container in bubble wrap or other protective cover to prevent breakage. Specific instructions for the packaging and preparation of samples for shipment are given

in Figure 6.

7.5.5 Transport samples using the quickest possible method conforming to all DOT (Department of Transportation), express mail packaging and shipping regulations.

## 7.6 Analysis and Calculations

7.6.1 In the field the presence of residual chlorine in the water to be sampled must be determined using a DPD chlorine test kit. Refer to section 7.2.2 for the procedure.

7.6.2 In the field the pH must be determined for the pesticide and carbaryl sample using pH paper strips by;

- a. tearing off a small piece of pH paper.
- b. holding the pH paper with a pair of clean tweezers, dip it into the water after the HCl has been added.
- c. compare the color of the pH strip with the scale on the side of the pH paper box to determine the acidity.

## 7.7 Quality Control

7.7.1 5% of all samples will be accompanied by a Field Blank. A sample container filled with high purity Type 1. water purchased from VWR will be taken to and returned from the field and sent with actual samples for analysis. The blank will undergo quenching and preservation as other samples.

7.7.2 Duplicate samples will be collected in 5% of the homes sampled.

7.7.3 10% of all samples collected/analyzed are for QC/QA purposes.

7.7.4 Samples must be stored in the dark at 4°C.

7.7.5 Samples must be analyzed within 14 days.

7.7.6 The pH paper has a measurable range of 1.2 to 2.4

7.7.7 All weighing and measuring apparatus used in chemical preparation follow standard laboratory protocols (UA-L-1.X, UA-L-5.X). The lot number and date of opening are recorded for each chemical and kept in a notebook in the laboratory. All mixed chemicals are labeled with the appropriate Tech ID and date of creation.

## 8.0 RECORDS

- 8.1 The Water Collection and Chain of Custody Record must be completed for all samples (Figure 1).
- 8.2 The original of each form remains with the sample at all times.
- 8.3 A photo copy of each form is retained with the household sampling packet.

Figure 1. Water collection sampling sheet and chain of custody record.

Sample Protocol and Chain of Custody Sheet NHEXAS Arizona Water Sample				
Sample ID# : _____		HHID: _____		
Collection Date: ____/____/____		Collection Time ____:____		
Water Source : Municipal, surface _____ Municipal, well _____ Private _____ Bottled water _____ Other _____				
Collection Location: Kitchen Tap: _____ Other _____				
Water sample type: Drinking(only) _____ Tap(only) _____ Drinking=Tap _____				
Sample type: Pesticides _____ Carbaryl _____ VOCs _____ Metals _____ (525.2) (531.1) (524.2) (200.8)				
Residual chlorine measurement: Residual chlorine = _____ ppm				
Quencher: Sodium Sulfite (pests) : # vials added = _____ or N/A Ascorbic Acid (VOCs) : # vials added = _____ or N/A Sodium Thiosulfate (carb): # vials added = _____ or N/A				
Preservative added: HCl Yes [ ] or No [ ] pH less than 2 Yes [ ] or No [ ]				# Containers = [ ]
Storage Conditions : Field: _____ Lab: _____				
Collection Comments: _____ _____ _____				
Custody Record				
Relinquished or Recieved	Signature	Date mo./day/yr.	Time	Action
[Rel] [Rec]		____/____/____	____:____	
[Rel] [Rec]		____/____/____	____:____	
[Rel] [Rec]		____/____/____	____:____	
[Rel] [Rec]		____/____/____	____:____	
[Rel] [Rec]		____/____/____	____:____	
[Rel] [Rec]		____/____/____	____:____	
[Rel] [Rec]		____/____/____	____:____	
[Rel] [Rec]		____/____/____	____:____	

Other Comments:

FORM = UA-F16.0-1.0

Figure 2. Relative Timing of Sample Collection by Stage (page 1 of 3).

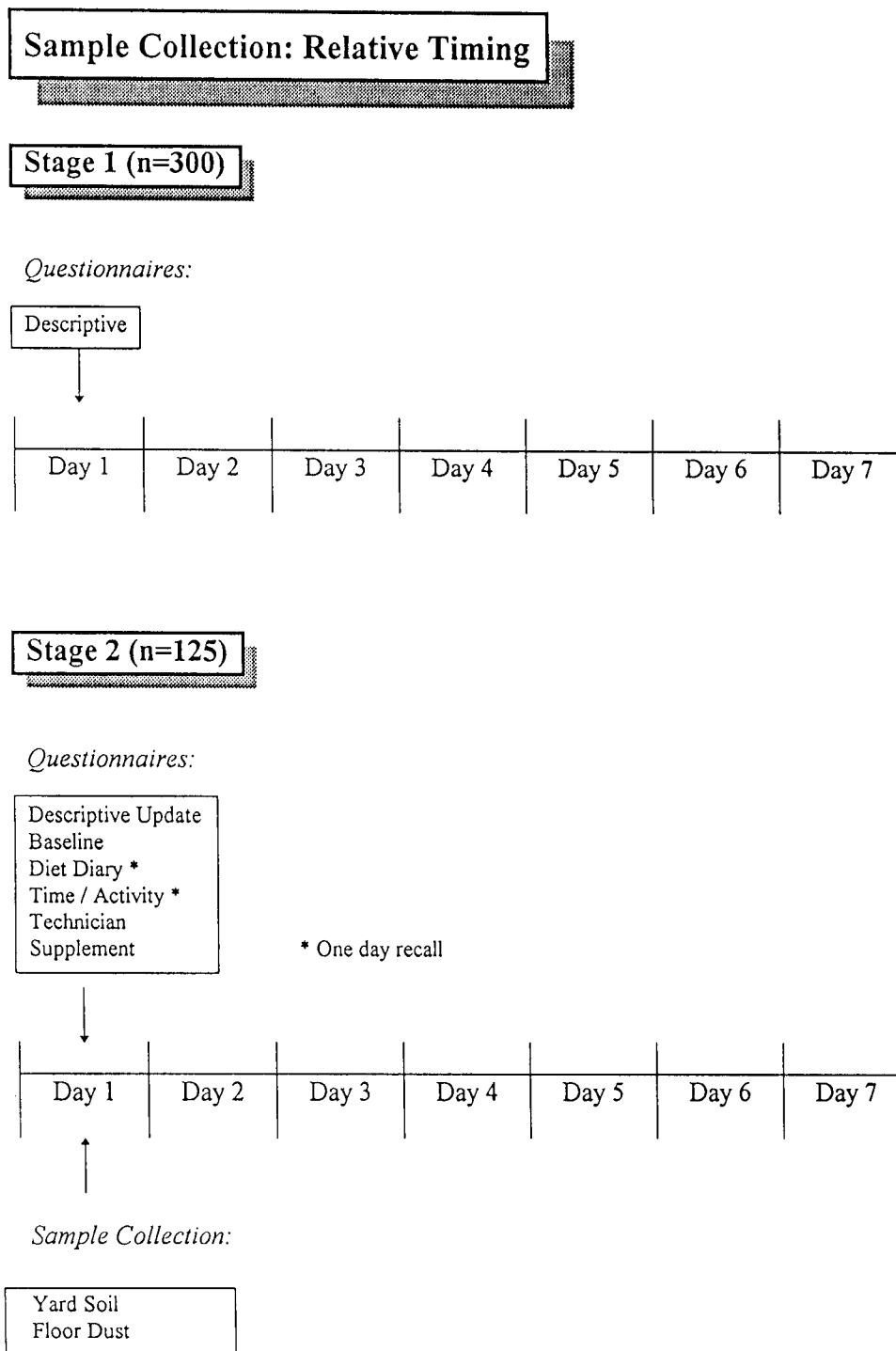
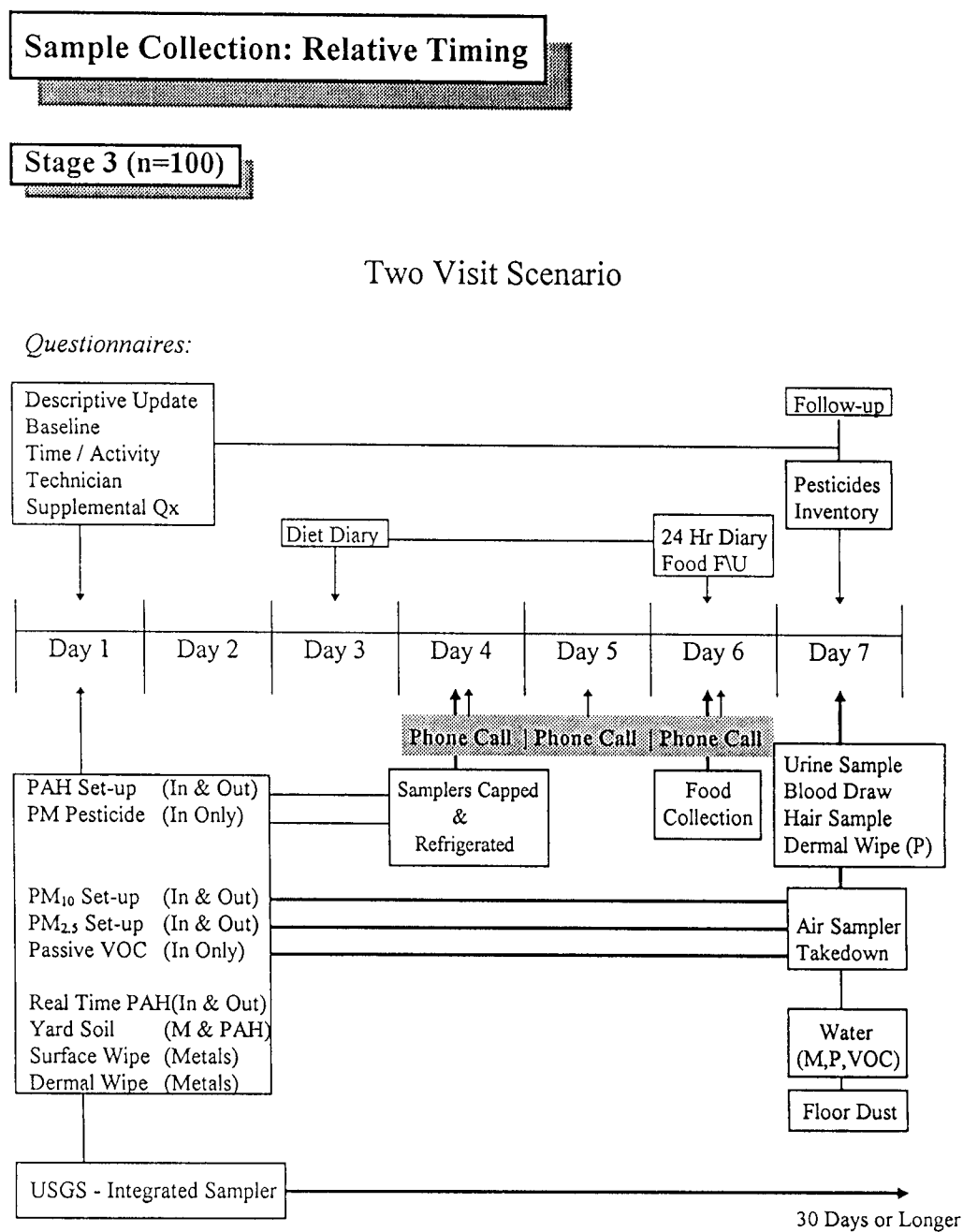


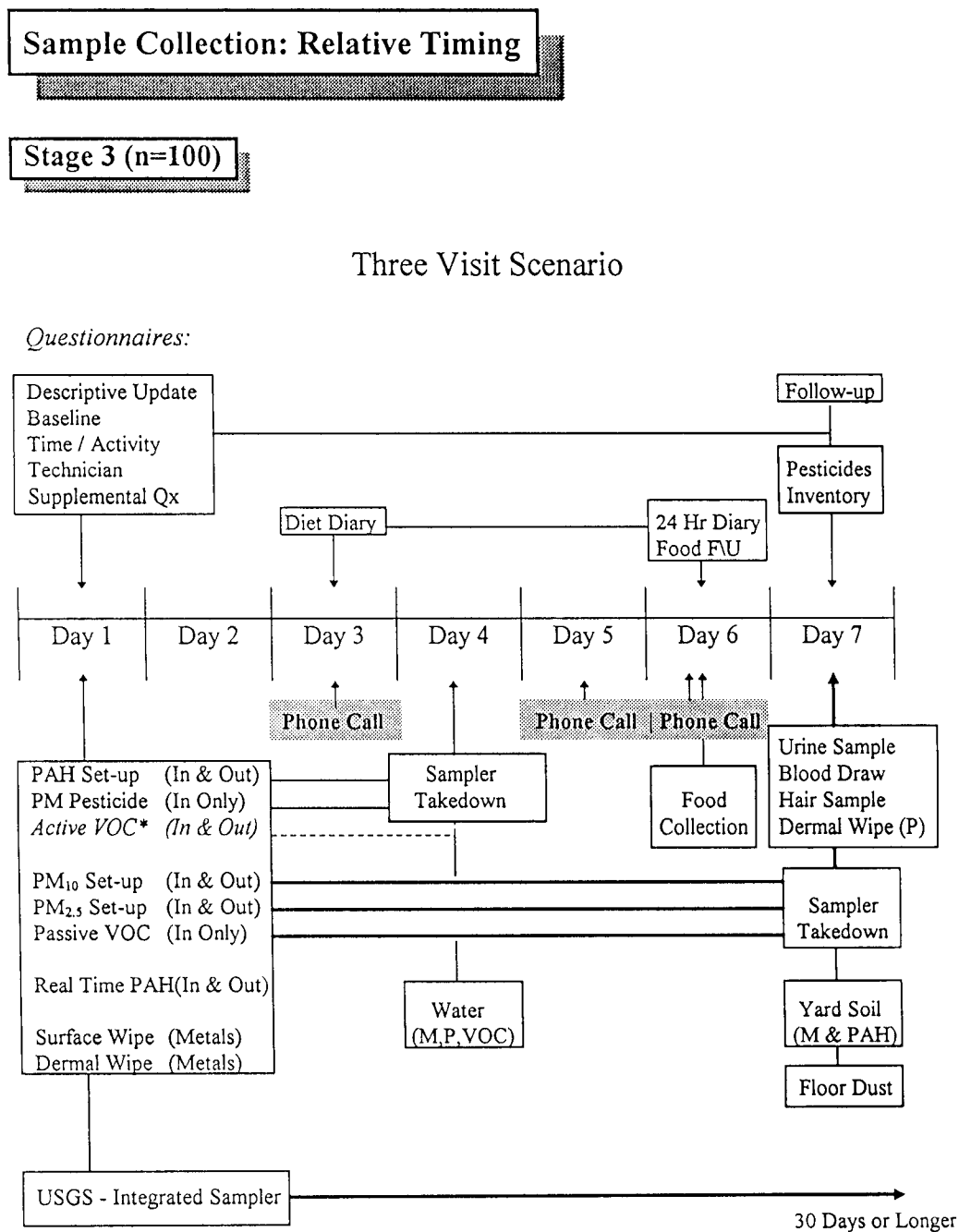
Figure 2. Relative Timing of Sample Collection by Stage (page 2 of 3).



\* Active VOC is collected in a subset of 25 homes only



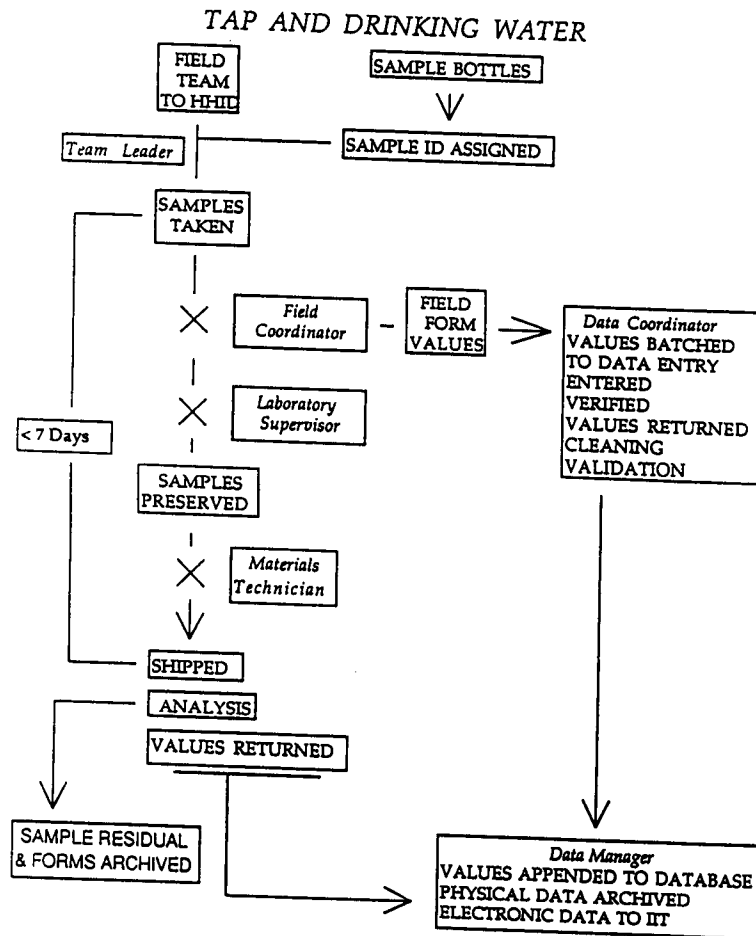
Figure 2. Relative Timing of Sample Collection by Stage (page 3 of 3).



**Figure 3. Field Notes and Trouble Shooting Guide.**

No field notes or Troubleshooting guides are currently on record for UA-F-17.X. Additions will be appended and the SOP reviewed and updated in accordance with UA-G-1.X as appropriate.

Figure 4. Handling Water Samples.



FORM ID = UA-F20-1.0

**Figure 6. Specific Instructions For Sample Packaging and Preparation for Shipment.**

1. Wrap EACH sample in small bubble wrap individually.
2. In a large Ziploc bag place the following items:
  - a. Each of the pre-wrapped samples,
  - b. Custody sheets in a small separate Ziploc for protection in case of breakage.
3. Seal the Ziploc bag with the contained articles
4. Find a biomailer of the appropriate size.
5. Place cold packs in the bottom of the container.
6. Sprinkle in Styrofoam "Peanuts" until cold pack is covered.  
Note: These should be "free", unconstrained peanuts not those contained in a plastic bag.
7. Place the sample bag described above on top of the peanuts.
8. Cover the sample bag with peanuts (see note in 3).
9. Place additional cold pack on the top.
10. Seal and mail the package.