# Drinking Water Sampling Protocols

# for

# Benton Harbor Water Study

Version 2.5 12/10/21

# Contents

Filter Screening Study

Drinking water will be sampled for lead before and after passing certified POU devices and pitcher filters that are properly installed and maintained. Two water samples will be collected at each home, a filtered and unfiltered sample. Samples should be digested in the laboratory before analysis (even if turbidity is <1 NTU) and analyzed according to Table 1:

*Table 1: Samples to be collected and analyzed during the filter screening study*

| **Type of Sample** | **Number of Samples per Residence** | **Analytes** |
|---|---|---|
| Filtered Water (5 second flush through certified POU filter) | 250[1] mL wide mouth HDPE sample bottle | Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sn, and Zn (EPA methods 200.7 and 200.8 (Pb, Cu, and Zn only)) |
| Filtered Water (passed through certified POU or pitcher filter) | (2)[2] 1 L wide mouth HDPE sample bottles | Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sn, and Zn (EPA methods 200.7 and 200.8 (Pb, Cu, and Zn only)) |
| Unfiltered Water | (2)[3] 1 L wide mouth HDPE sample bottles | Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sn, and Zn (EPA methods 200.7 and 200.8 (Pb, Cu, and Zn only)) |
| Fully Flushed Water | 1 measurement (SL1000 sample cup) | Field collected background water quality parameters: total chlorine and free chlorine |

**1.1 Site Selection and Scheduling:**
The Operations Section leadership and/or sampling group lead will provide the proposed list of sampling locations to the project lead for approval and then communicate the approved site locations to scheduling and sample teams.

To assess filter efficacy under challenging conditions, sampling will be prioritized at single-family homes likely to have or known to have a lead service line (LSL), based on documentation from Benton Harbor (e.g., water main age map) and/or historical water sampling results with elevated Pb levels and consistent with the statistical analysis plan. EPA anticipates sampling will be conducted at a subset of the ~2,500 homes which have received water filters from the Berrien County Health Department (BCHD). BCHD's records track the brand (e.g., PUR, Brita, ZeroWater) and type (e.g., Pitcher, Faucet mount) that was distributed to each house.

During scheduling (EPA Community Involvement Group), residents should be asked about the following items to evaluate if a home is a candidate for sampling and if a new filter cartridge is needed from BCHD prior to the sampling visit. [A separate script has been developed based on these questions.]

[1] Or similar 500 mL or 1 L wide mouth HDPE sample bottle.
[2] One 1L for the first-liter sample (e.g., PF or FF) and one 1L for the 7th-liter service line sample (i.e., PFL or FFL).
[3] One 1L for the second-liter sample (e.g., UF) and one 1L for the 8th-liter service line sample (i.e., UFL).

- Does the residence have a whole house filter (including Reverse Osmosis) and/or a water softener on the cold-water line or does the kitchen faucet have an RO unit attached upstream under the sink? [Residences with either a whole house filter, water softener, or kitchen faucet with RO unit inline/upstream should not be sampled; kitchen faucet with RO unit routed to a separate tap would not be impacted by the RO unit and could be sampled.]
- Has the resident(s) run hot water through the pitcher or faucet filter? [This question helps with planning the number of bottles to be sampled; filters with hot water used would be sampled for research purposes. Hot water should only be run at the faucet when the filter is in the off/bypass mode, and hot water should not go through a pitcher filter.]
- When is the filter cartridge replacement due? [This question helps with planning the number of bottles to be sampled; filters with red lights would be sampled for research purposes. Instruct the resident about following manufacturer instructions i.e., replace if filter indicator is red for the faucet-mount filters; or for ZeroWater the Total Dissolved Solids (TDS) reading on a glass of filtered water is above 006[4].]
- If the resident notes that hot water has been through the filter, or that the filter is due for replacement (e.g., red light indicator), the resident should be asked to schedule TWO site visits (first visit to collect existing filter samples and install a new cartridge, second visit a day or two later to collect proper functioning filter samples), unless (1) the resident prefers to install the replacement cartridge themselves or (2) their filter (e.g., ZeroWater) does not have a replacement filter cartridge preconditioning step (soaking the cartridge or running water through it) in the manufacturer instructions.

Based on preliminary data collected during the filter study (samples collected through 11/18/2021) 48 resident reported stagnation times are 1 hour or less, whereas only 12 have had a stagnation time of 1.5-6 hours. Having samples collected after a range of stagnation times is key to a strong statistical sampling design as higher Pb levels can be associated with longer stagnation times.

- Therefore, a new strategy for scheduling will be employed for homes already scheduled for the week of 11/29. When schedulers call to confirm appointments, they should request/encourage the residents to not use any water from faucets, appliances, showers, toilets for several hours (2-6+ hours) prior to the visit, if possible. Residents should be reminded that they can still use bottled water for drinking and cooking during that time.
- For residents who have not yet received a date/time for a sampling visit as of 11/29, during the scheduling call the scheduler will request that the resident stagnate their water for 6+ hours prior to the sampling visit. If the resident is unable to accommodate a stagnation time, the scheduler will make a note and will move on to the next priority site to schedule. For all sampling visits that are scheduled (resident is contacted by a scheduler and a date/time is determined for a sampling visit) on 11/29 or later the goal is to sample high priority sites with longer stagnation times.

[4] https://zerowater.com/pages/frequently-asked-questions

Based on preliminary data reported during the filter study (preliminary results reported through 11/24/2021), unfiltered lead levels in the second liter "UF" grab samples were fairly low (30 "UF" results <0.5 ug/L, 33 "UF" results between 0.5 ug/L and 5 ug/L, and 5 "UF" samples between 5 ug/L and 15 ug/L, whereas only one unfiltered water "UF" sample (30.1 ug/L) was above 15 ug/L). In order to improve chances of finding higher lead, starting on 12/2/2021, additional filtered and unfiltered water samples will be collected from water estimated to represent the service line, as water that has stagnated within a lead service line is more likely to have higher Pb levels.

**1.2 Field Team:** Estimated 2–3 person team (at least 1 sampler and possibly one Community Involvement Coordinator (CIC) or person to engage with the homeowner). Training will be documented using Attachment No. 7.

**1.3 Supply list for filter screening study:**

- Booties for entering homes
- COVID-required safety supplies (e.g., face coverings, hand sanitizer),
- HDPE pre-certified clean wide-mouth 1-L and 250 mL single use rigid plastic bottles for all metals analysis (to be field preserved to pH<2 with nitric acid ($HNO_3$)),
- At least (3) 1 L bottles marked for volume measurement use only (these can be used in multiple homes),
- Trace-metal free nitric acid ($HNO_3$) dropper bottles,
- Filter replacement cartridges (e.g., PUR, Brita, ZeroWater),
- ZeroWater TDS meter (for ZeroWater pitcher filter life checks, in case resident has lost theirs),
- NIST Traceable Thermometer,
- pH paper,
- Hach SL1000 meter and chemkeys (free chlorine and total chlorine),
- Weatherproof bottle labels,
- Chain-of-custody forms,
- Sturdy coolers and, if third-party shipping, shipping packing materials (e.g., bubble wrap, trash bags, zip-type plastic bags, shipping tape, and shipping labels),
- Milli-Q water,
- UPS Shipping labels from EPA R5 Mail Room (if third-party shipping),
- Nitrile Gloves (for field preservation),
- Safety glasses (for field preservation),
- Bound field logbook and field forms or electronic field note recorder (e.g., iPad with Survey 123 software) with Charging cables.
- Photograph labels (e.g., dry erasable board or sheet of paper),
- Indelible ink pen/marker, and
- Camera.

**1.4 Pre-sample Preparation**

1. Check that all equipment is charged and that there are back up batteries.

2. Verify Hach SL1000 and note verification in equipment log book - The Hach system verification key will be used on all four chemkey slots at the beginning of each day that monitoring occurs using the procedure outlined in the manual (see Attachment 2).
3. Prepare Chain of Custody, sample bottles, cooler, safety supplies to take to sample locations. Ensure each sampling team has field blanks to take with them into the field.
4. Verify safety equipment and procedures for the day – see Health and Safety Plan.
5. Obtain field blanks these will be provided by field team lead for every 20 samples collected or one per day.

**1.5 Procedure for filter screening study:**

Samples will be taken from the kitchen sink faucet in increments of 1 L. Aerators, both on filter units and on taps without filters, are to remain, and should be unaltered, during sampling. Only cold water is to be sampled.

1. Before entering the home, pre-label the sample bottles using standardized nomenclature. Four bottles will be needed for faucet filter sites and six bottles will be needed for pitcher filter sites, plus at least three 1 L bottles marked for volume measurement use only. If the sampling is rescheduled, unopened bottles may be re-labeled.

- "BH" for Benton Harbor sampling
- Four-digit (####) house identifier unique to the address (i.e., from a master list developed with a random number generator provided to sampling teams on sampling schedule). This allows protection of personal identification information in subsequent data analysis.
- Then include a sample type identifier:
    - "-5FF" for the first 5 seconds flow through the faucet filter,
    - "-FF" for the next 1L through the faucet filter,
    - "-PF" for pitcher filter,
    - "-UF" if sample is unfiltered water,
    - Targeted service line samples, "-FFL" and "-PFL", faucet filtered and pitcher filtered liter (respectively) collected as approximately the 7$^{th}$ liter through the filter. And associated "-UFL" unfiltered targeted sample of approximately the 8$^{th}$ liter.
    - If a filter is found to have a red light or the light is malfunctioning, or if ZeroWater filtered water TDS is found to be >006 mg/L, a qualifier will be added to the sample ID for the samples collected from the existing filter, "e" for existing (e.g., -5FFe, -FFe, -PFe, and -UFe). **If this is realized after the samples are collected, a new label may be prepared and affixed to the bottle(s); do not transfer sample water from one bottle to another.**
    - Similarly, if the resident indicates they have filtered HOT water through the existing filter, a qualifier will be added to the sample ID for the samples collected from the existing filter, "h" for hot water (e.g., -5FFh, -FFh, -PFh, and -UFh).
- After the sample type ID (-5FF, -FF, -PF, or -UF) numbers will be used to indicate unique samples in the order they are collected (i.e., 01, 02, 03, 04, 05).

Labeling Examples:

- For home identified as 0001, BH0001-5FF01 (5 second faucet filtered sample, collected first), BH0001-FF02 (1 L faucet filtered sample, collected second), BH0001-UF03 (unfiltered sample, collected third). Then 4 L of water is measured and wasted using marked 1 L bottles, then BH0001-FFL04 (1 L faucet filtered sample, collected fourth) and BH0001-UFL05 (unfiltered sample collected fifth).
- For home identified as 9999, BH9999-PF01 (pitcher filtered sample) and BH9999-UF02 (unfiltered sample, collected second). Then 4 L of water is measured and wasted using marked 1 L bottles, then BH9999-PFL03 (1 L pitcher filtered sample, collected third) and BH9999-UFL04 (1 L unfiltered sample, collected fourth)
- For home identified as 2222, BH2222-5FFe01 (5 second faucet filter red light sample collected first), BH2222-FFe02 (1 L faucet filter red light sample collected second), BH2222-UFe03 (Unfiltered red-light sample collected third). No "-FFL" or "-UFL" samples will be collected when a filter is classified as a red light, but these samples should be collected at a different time after the new cartridge is installed.

See quick summary of sample IDs in Table 2.

*Table 2: Sample IDs for Filter Screening Study*

| **Filter Screening Study** | |
|---|---|
| **Sample ID** | **Description** |
| BH####-5FF## | Faucet Filtered Sample, initial 5 second flush |
| BH####-FF## | Faucet Filtered Sample, next 1L |
| BH####-PF## | Pitcher Filtered Sample of the first 1L from tap (no 5-second flush) |
| BH####-UF## | Unfiltered Sample |
| BH####-FFL## | Faucet Filtered Sample collected at ~7$^{th}$ Liter |
| BH####-PFL## | Pitcher Filtered Sample collected at ~7$^{th}$ Liter |
| BH####-UFL## | Unfiltered Sample collected at ~8$^{th}$ Liter |
| BH####-5FFe## | Faucet Filtered Sample through red lighted/malfunctioning filter, initial 5 second flush |
| BH####-FFe## | Faucet Filtered Sample through red lighted/malfunctioning filter, next 1L |
| BH####-PFe## | Pitcher Filtered Sample through red lighted/malfunctioning filter (no 5-second flush) |
| BH####-UFe## | Unfiltered Sample associated with red lighted/malfunctioning filter |
| BH####-5FFh## (or BH####-5FFeh##) | Faucet Filtered Sample through filter in which hot water has been used, initial 5 second flush (or "eh" if filter has both red lighted/malfunctioning AND hot water usage) |
| BH####-FFh## (or BH####-FFeh##) | Faucet Filtered Sample through filter in which hot water has been used, next 1L (or "eh" if filter has both red lighted/malfunctioning AND hot water usage) |
| BH####-PFh## (or BH####-PFeh##) | Pitcher Filtered Sample through filter in which hot water has been used (no 5-second flush) (or "eh" if filter has both red lighted/malfunctioning AND hot water usage) |

| | |
|---|---|
| BH####-UFh## (or BH####-UFeh##) | Unfiltered Sample associated with filter in which hot water has been used (or "eh" if filter has both red lighted/malfunctioning AND hot water usage) |
| MMDDYYYY## | Field blank to be brought out while sampling and preserved with other samples and shipped back in cooler at least once a day or with every 20th sample |

####- House identifier unique number
-##- sequential number representing order sample type was collected

2. Before entering home, samplers should ask resident COVID screening and pre-sampling questions and record answers in iPad. If COVID screening does not pass, samplers should inform resident they will be contacted to reschedule sampling.
3. When first entering the home, samplers should ask the resident if the samplers can check the service line material, and if there is whole-house filter or softener, and record data.
4. Request permission from the resident and if approved take photographs of the sample tap(s), filters, and underlying fixtures and components.
5. If a faucet-mount water filter is installed at the kitchen sink, follow the instructions for *Faucet Filter Sampling*, if a pitcher-style water filter is in use at the home, follow the instructions for *Pitcher Filter Sampling*. If both styles are in use at the home, samplers can collect both Faucet Filter (-5FF##, -FF##) and Pitcher Filter (-PF##) samples (e.g., 5 seconds and then 1st L through faucet filter, 2nd L through pitcher filter, 3rd L for unfiltered analysis).
6. Ask Resident when the water was last used in the home and also at the kitchen faucet specifically, and record data.
7. Ask the resident how the filter is typically used and record data (e.g., checking to see if hot water has been used through the filter). If the resident indicates HOT water has been used through the filter, the filter should be sampled as a malfunctioning filter, replaced, and resampled.
    a. Faucet filter – collect "FFh" (or FFeh if it is also a red light/malfunctioning filter) samples the same day. Change cartridge and reschedule the resident for a second sampling event if possible.
        i. Ex.: BH1234-FFh01
        ii. Ex.: BH1234-FFeh01
    b. Pitcher filter – collect "PFh" (or PFeh if it is also a red/malfunctioning filter) samples the same day, change cartridge, and then sample the same day if the replacement filter cartridge does not have a preconditioning step (soaking the cartridge or running water through it) in the manufacturer instructions.
    c. The sampling teams will remind residents of the importance of following manufacturer guidance, including only filtering COLD water through the faucet and/or pitcher filters.

8. During the sampling visit if a filter is found to have a red light or the light is malfunctioning, or the resident indicates HOT water has been used through the filter, a qualifier(s) will be added to the sample ID for the samples collected from the filter:
    a. "e" for existing (e.g., -5FFe/-FFe, -PFe, and -UFe) if red light or the light is malfunctioning

b. “h” for hot water (e.g., -5FFh/-FFh, -PFh, and -UFh) if HOT water has been used through the filter
c. “eh” if both issues are found for the existing filter (e.g., -5FFeh/-FFeh, -PFeh, and -UFeh).

A new filter cartridge will be installed during the sampling visit (see PUR and Brita User Manuals in Attachment No. 8) and the filter will be prepared according to the manufacturer instructions. For filter models (e.g., PUR FF and Brita FF) which require flushing to condition the filter, a second sampling event will be scheduled with the resident to return and collect samples associated with the newly replaced cartridge. For pitcher models (e.g., ZeroWater) that does not have a replacement filter cartridge preconditioning step (soaking the cartridge or running water through it) in the manufacturer instructions, the second set of samples may be collected during the same sampling visit. The second set of samples, including the service line targeted samples, will be labeled according to the nomenclature used for samples with proper functioning indicator lights and no hot water usage (-5FF, -FF, -PF, and -UF and -FFL/-PFL and UFL). Relabel bottles as needed, making sure not to reuse bottles. Additionally, if a sampling visit is scheduled to install a new filter, the filter will be installed and prepared according to the manufacturer instructions. No samples will be collected directly after the installation if flushing/conditioning is required, but a second sampling event will be scheduled with the resident to return and collect samples associated with the newly installed filter.

### 1.5.1 Faucet Filter Sampling

1. While one sampler is collecting water the other should be timing the collection in order to calculate the filtered and unfiltered flow rates and record data.

2. Verify label and place a 500 mL [or 250mL, pending availability] “-5FF##” sample bottle under the kitchen faucet. [Have the second “-FF##” and third “-UF##” 1 L sample bottles ready.]

3. Place the filter in the “on” position and turn on the cold-water faucet (fully open, maximum flow). Use a timer and collect the first 5 seconds of filtered water flow into the “-5FF##” sample bottle. Hand the bottle off for the second person to cap.

4. Sampler should note filter light color during operation and record that information in Survey 123, if red or malfunctioning sample IDs should be adjusted to add an “e” suffix using a new label after sample collection is complete.

5. Immediately following the first sample without turning off the water and taking care not to spill, collect a 1 L sample in the “-FF##” labeled bottle (fill to the neck of the bottle). Hand the bottle off for the second person to cap.

6. Immediately following the second sample without turning off the water, turn the filter “off” (to bypass mode) and collect a 1 L sample in the “-UF##” labeled bottle (filled to the neck). Hand the bottle off for the second person to cap.

7. If a filter is found to have a red light, or the resident reports HOT water usage through the filter, a new filter cartridge will be installed during the sampling visit and prepared according to the manufacturer instructions (see PUR and Brita User Manuals in Attachment No. 8). No further laboratory samples (which includes "-FFL##" and "-UFL##" samples) will be collected that day. A second sampling event will be scheduled with the resident to return and collect samples associated with the newly replaced cartridge following the previously described steps. Specifically, these new-filter samples will be labeled according to the nomenclature used for samples with properly functioning indicator lights (-5FF, -FF, -FFL, and -UFL).

8. If filter is functioning properly (green or yellow light) and the resident did not report any HOT water usage through the filter, then immediately following the "-UF##" sample, continue to run the water with the filter "off" (in bypass mode) and fill and waste FOUR (4) 1 L bottles marked for volume measurement only (one sampler fills the second person wastes and returns an empty bottle to the sampler). If the filter is found to have a red light or the resident reports HOT water usage through the filter, skip to step 11.

9. At the 7th L the sampler should place the filter in the "on" position and run the filtered water for 5 seconds to clear out first draw filtered water, then collect a 1 L filtered water sample in a "-FFL##" labeled bottle (fill to the neck of the bottle). Hand the bottle off for the second person to cap.

10. Immediately following the "-FFL##" sample without turning off the water, turn the filter "off" (to bypass mode) and collect a 1 L sample in the "-UFL##" labeled bottle (filled to the neck). Hand the bottle off for the second person to cap.

11. The first home sampled of the day and every 20$^{th}$ sample will have a field blank. Field blank bottles are prelabeled and filled with milli-Q water. Open the field blank bottle, remove lid then place back on and store in cooler with other samples. Record the field blank collection in Survey123. Record the field blank information on forms or 123Survey.

12. Run the water for an additional 5 minutes. Rinse Hach SL1000 sample cup 3 times with tap water from the faucet. Then collect a sample to the sample cup fill line for field analysis using free chlorine and total chlorine chemkeys, or an equivalent method (instrument/method used to be noted in field records). Using the SL1000 sample cup or another container, collect a sample of running water and measure the temperature with a NIST traceable thermometer.

    - Record chlorine and temperature results in Survey123 and share results with resident. See Attachment No 2 for further information on proper calibration and operation of the Hach SL1000.

    - If the free chlorine residual is <0.2 mg/L, EGLE and MDHHS representatives in the Unified command structure will be notified immediately and the sampling team will

then run the water for 5 more minutes and re-sample for free chlorine. Record 10-minute flushed free chlorine and temperature results in Survey123 and share results with resident. Michigan will provide necessary follow-up activities for protection of public health.

13. Record chlorine and temperature results in Survey123 and share results with resident. Turn the water off and leave the faucet filter in the "on" position.

14. Before you leave the house, make sure the Field Notes sheet (i.e., Survey 123 electronic form) is completed and all materials/sample bottles are retrieved.

1.5.2 Pitcher Filter Sampling

1. Ask the resident to empty their pitcher filter into another glass or container; this may require waiting for any water in the unfiltered portion to pass through the filter. Sampler should note filter light color during operation. If a ZeroWater filter, sampler should pour out some filtered water to take a reading on the filtered water with the TDS meter, results >006 indicate a "red light"; if no filtered water is available upon arrival, the TDS reading should be on a separate filtered water sample after the sample is collected for laboratory analysis. This information is recorded in Survey 123. If the filter light is red or malfunctioning or elevated TDS is found for a ZeroWater filter, bottles with sample IDs containing "e" should be prepared for the initial sample collection ("-PFe" and "-UFe"), "-PFL" and "-UFL" samples will only be collected on the same sampling visit for pitcher filters that do NOT require a preconditioning step. In other cases, these samples should be collected at a different time with the -PF samples after the new cartridge is installed.

2. While one sampler is collecting the water the other should be timing the collection in order to calculate the unfiltered flow rate and record data.

3. Verify label then place a 1 L "-PF##" (marked for eventual disposal) sample bottle under the kitchen faucet. [Have the second 1 L sample bottle labeled "-UF##" ready to go.]

4. Turn on the cold water (fully open, maximum flow).

5. Collect a first draw 1 L sample (i.e., to pass through the pitcher for the first draw, filtered sample), fill to the neck of the bottle. Cap and set aside for use in Steps 13-14 below.

6. Without turning off the water, collect a "-UF##" 1 L sample immediately after the first sample (filled to the neck). Cap the bottle, this "-UF##" sample should not be filtered through the pitcher as it represents unfiltered water.

7. If filter is functioning properly (green or yellow light) and the resident did not report any HOT water usage through the filter, then immediately following the "-UF##" sample, continue to run the water and fill and waste FOUR (4) 1 L bottles marked for volume measurement only (one sampler fills, and the second person wastes and returns an empty bottle to the sampler).

a) If the filter is found to have a red light or the resident reports HOT water usage through the filter, and the replacement cartridge REQUIRES a conditioning step, no additional laboratory samples will be collected; skip to step 12 ("-PFL" and "UFL" samples will not be collected with the "e" or "h" set of samples).
b) If the filter is found to have a red light or the resident reports HOT water usage through the filter, and the replacement cartridge DOES NOT REQUIRE a conditioning step, collect the 3rd liter and 4th liter as noted below then waste only the 5th and 6th liters.
   - Verify label then place a 1 L "-PF##" (marked for eventual disposal) sample bottle under the kitchen faucet. [Have the next 1 L sample bottle labeled "-UF##" ready to go.]
   - Collect the 1 L "-PF##" (marked for eventual disposal) sample (i.e., to pass through the pitcher for the filtered sample) as the third liter, fill to the neck of the bottle. Cap and set aside for use, after replacing the filter, as described in Step 16b.
   - Without turning off the water, collect a "-UF##" 1 L sample as the 4th liter, immediately after the third sample (filled to the neck). Cap the bottle, this "-UF##" sample should not be filtered through the pitcher as it represents unfiltered water.
   - Immediately following the "-UF##" sample, continue to run the water and fill and waste TWO 1 L bottles marked for volume measurement only (one sampler fills, and the second person wastes and returns an empty bottle to the sampler).
   - Continue below with Step 8.

**8.** Verify label then place a 1 L "-PFL##" (marked for eventual disposal) sample bottle under the kitchen faucet. [Have the next 1 L sample bottle labeled "-UFL##" ready to go.]

**9.** Collect the targeted 7th liter "-PFL##" 1 L sample (i.e., to pass through the pitcher for the targeted, filtered sample), fill to the neck of the bottle. Cap and set aside for use in Steps 13-14 below [or in Step 16 if the filter is found to have a red light or the resident reports HOT water usage through the filter].

**10.** Without turning off the water, collect an 8th liter "-UFL##" 1 L sample immediately after the first sample (filled to the neck). Cap the bottle, this "-UFL##" sample should not be filtered through the pitcher as it represents unfiltered water.

**11.** If the pitcher filter is a ZeroWater unit and no filtered water was available in the pitcher at the time of sampler arrival, collect another water sample, pass it through the filter, empty the pitcher filter into another glass or container and measure TDS of the filtered water. Then discard the water.

**12.** Turn the water off.

**13.** Take the first "-PF##" (marked for eventual disposal) labeled bottle and "turn end over end" five times to mix. Then pour the contents of the bottle into the pitcher filter and filter the entire sample. Take care to ensure the unfiltered water from the bottle goes into the top part of the pitcher filter without any splashing or overfilling. Discard the bottle, which will be marked to distinguish that the bottle is to be discarded. [The ZeroWater User Manuals

do not indicate any initial filtered water is wasted after a period of non-use, see Attachment No 8.]

**14.** After the sample passes completely through the filter, pour the filtered water into a **new** "-PF##" labeled 1 L bottle. Cap the bottle.

**15.** Repeat steps 13 and 14 for the targeted "-PFL##" (marked for eventual disposal) sample. Pour the filtered water into a **new** "-PFL##" labeled 1 L bottle. Cap the bottle.

**16.** If a filter is found to have a red light or elevated filtered water TDS, or the resident reports HOT water usage through the filter, a new filter cartridge will be installed during the sampling visit (see Attachment No. 8) and prepared according to the manufacturer instructions. A second set of samples will be collected the same day (if the cartridge DOES NOT require a conditioning step; if the cartridge requires conditioning a second sampling event should be scheduled with the resident to return and collect samples) to be associated with the newly replaced cartridge following the previously described steps with an exception detailed in the sub-steps below. Specifically, this second set of samples will be labeled according to the nomenclature used for samples with proper functioning indicator lights (-PF, -UF, -PFL, and -UFL).

a) While the "-PFe" [or "-PFh"] sample is filtered through the existing filter, the "-PF" and "-PFL" samples will be filtered through the pitcher only after replacing the cartridge.
b) After replacing the filter cartridge,
   - Take the first "-PF##" (marked for eventual disposal) labeled bottle and "turn end over end" five times to mix. Then pour the contents of the bottle into the pitcher filter and filter the entire sample. Take care to ensure the unfiltered water from the bottle goes into the top part of the pitcher filter without any splashing or overfilling. Keep this bottle until the sample is completely filtered through the pitcher, as some additional volume may need to be collected. [The ZeroWater User Manuals do not indicate any initial filtered water is wasted after a period of non-use, see Attachment No 8.]

   - After the sample passes completely through the filter, pour the filtered water into a **new** "-PF##" labeled 1 L bottle. Cap the bottle.

c) If the replacement filter cartridge does not have a preconditioning step (soaking the cartridge or running water through it) in the manufacturer instructions, there may be void spaces present within the cartridge. If the sampler finds that after pouring in the first 1 L ("-PF##", marked for eventual disposal), the filtered water does not fill the new "-PF##" 1 L bottle to the neck of the bottle, then an additional sample of water needs to be collected.

- Ready the "-PF##" (marked for eventual disposal, saved from Step 16b) bottle at the kitchen tap.
- Turn on the cold water (fully open, maximum flow).
- Fill the "-PF##" (marked for eventual disposal) bottle one quarter of the way full
- Immediately pour the contents of the bottle into the filter pitcher and filter the entire sample. Take care to ensure the unfiltered water from the bottle goes into the top part of the pitcher filter without any splashing or overfilling.
- Once completely filtered pour the filtered water into the "-PF##" labeled 1 L bottle.
- Ensure the "-PF##" labeled bottle is filled up to the neck of the bottle with water that has passed through the pitcher filter.

– If additional volume is still needed repeat these steps, until there is 1 L of filtered water that has passed through the newly installed pitcher filter cartridge.
– Once the new "-PF##" 1 L bottle is filled to the neck with filtered water the "-PF##" 1 L bottle (marked for eventual disposal) can be discarded.
– Filtered water in excess of what is needed to fill the "-PF##" labeled bottle up to the neck of the bottle should also be discarded before the next step.

d) Ensure no filtered water is in the pitcher from a previous sample (pour out and discard). Repeat step 16b above for the targeted "-PFL##" sample. Pour the filtered water into a **new** "-PFL##" labeled 1 L bottle. Cap the bottle.

**17.** Turn the water back on and run the water for an additional 5 minutes. Rinse Hach SL1000 sample cup 3 times with tap water from the faucet. Then collect a sample to the sample cup fill line for field analysis using free chlorine and total chlorine chemkeys, or an equivalent method (instrument/method used to be noted in field records). Using the SL1000 sample cup or another container, collect a sample of running water and measure the temperature with a NIST traceable thermometer.

a) Record chlorine and temperature results in Survey123 and share results with resident. See Attachment No 2 for further information on proper calibration and operation of the Hach SL1000.

b) If the free chlorine residual is <0.2 mg/L, EGLE and MDHHS representatives in the Unified command structure will be notified immediately and the sampling team will then run the water for 5 more minutes and re-sample for free chlorine. Record 10-minute flushed free chlorine and temperature results in Survey123 and share results with resident. Michigan will provide necessary follow-up activities for protection of public health.

**18.** Before you leave the house, make sure the Field Notes sheet (i.e., Survey 123 electronic form) is completed and all materials/sample bottles are retrieved.

### 1.6 Sample Preservation, Storage and Transportation

1. The sampling team will return samples to the field office, and the EPA Field lab team (or sampling team as directed) will field preserve all samples for metals analysis following the instructions below and place all bottles into the cooler for transport back to the specified laboratory. Ensure the sample bottles are securely packed. If needed, field preservation may be completed the day after sampling.

   a) Use Nitrile gloves, safety googles and absorbent pads on workbench and follow necessary safety precautions when preserving samples with nitric acid.
   - Each day preserve the first 1 L sample by adding ~30 drops of nitric acid. Recap bottle and turn "end over end" five times, then use a pH strip to see if the pH is less than 2. If the pH is greater than 2, incrementally add more drops of nitric acid (capping and mixing) until a pH strip indicates that the pH is less than 2. Once a number of drops have been determined for the sample volume for the day, use that number of drops to preserve all water samples of the same volume collected in the day.

   b) Add an appropriate number of drops (as determined in the previous step) of the nitric acid preservative to each 1 L bottle collected, except for any "-PF##" [including "PFe##", "PFh##", "PFL##"] samples that were collected from a ZeroWater unit or "-5FF" samples. Samples collected from ZeroWater units are expected to need less nitric acid (ZeroWater units lower the pH of the water as it passes through the filter). "-5FF" samples will vary in volume depending on the water pressure at each individual house.
   c) Recap bottle and turn "end over end" five times.
   d) Pour out a few drops of the sample onto pH paper held over another container (to catch any spilled water from the pour), DO NOT dip anything into a sample. If the pH is less than 2 then the sample is properly field preserved, if pH is greater than 2 add additional drops of acid, mix and recheck pH as previously described.
   e) One field blank (1 L bottle containing laboratory Milli-Q water) will be provided to field samplers to take out in the cooler with the samples. These field blanks should be field preserved (following the same steps as the samples) per every 20 bottles to confirm that field collection and preservation is not a source of metals contamination. If 20 bottles are not collected in one day, then there should be at least one field blank per sampling team per day, field preserved with the sample bottles collected that day. Field blanks will be labeled with the date in MMDDYYYY format and a sequential number at the end (MMDDYYYY##). If additional field blanks are needed to meet the 1 per 20 samples requirement, they can be created at the field office with the same naming convention with an additional suffix "FP" to indicate those field blanks were created during the field preservation process (MMDDYYYY##FP).
   f) All sample bottles and blanks should be put into zip-type bags then placed in a cooler lined with a heavy-duty garbage bag (Attachment No 6).

2. Make sure the Chain-of-Custody form is completed and checked by a team leader against cooler content and secured within the cooler in a zip-loc bag. You should also have a scan or copy for tracking purposes. See example in Attachment No 3.

3. Seal the garbage bag, tape the cooler closed and label with the lab it is destined to (e.g., tape with lab name on it) if transported, or complete shipping label if it is being overnighted. Ship/transport samples to the specified laboratory as soon as possible (e.g., within 24 hours of sampling for shipping or 72 hours if transported). See packing protocols and addresses in Attachment No 6.

## 2. Concurrent Lead Assessment Study

This study will speciate lead (soluble and particulate) and examine the properties of lead-containing particles as well as other co-present particles present in conjunction with filter assessments. Size fractionation filtrations will be performed on a subsection of water samples collected from homes in Benton Harbor to assess the relative presence of particulate and soluble lead using multiple size fractions down to ultrafiltration.

Water will be sampled for lead (and other important metals) using different approaches to understand lead sources in the home, state of corrosion control and provide an approximation of filter loading. Complete water quality analyses will also be necessary to fully assess distribution system water in the home/distribution water quality zone to completely understand the lead observations. Ion balance calculations will be performed on the background water quality parameters, and if significant discrepancies exist, additional analytes may need to be added.

*Table 3: Samples to be collected and analyzed for the sequential sampling and particle characterization portions of the concurrent lead assessment study*

| | **Type of Sample** | **Number of Samples per Residence** | **Analytes** |
|---|---|---|---|
| Sequential Sampling | Sequential Profile | Two 125 mL and 20-40<br>500 mL wide mouth HDPE sample bottles | Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sn, and Zn (EPA methods 200.7 and 200.8 (Pb, Cu, and Zn only)) |
| | Fully flushed | Sample collection detail in Table 4 below | Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Si, Sn, and Zn (EPA methods 200.7 and 200.8 (Pb, Cu, and Zn only))<br><br>Laboratory background water quality parameters: total alkalinity, $Cl^-$, $F^-$, sulfate, orthophosphate, nitrate (or nitrate+nitrite (as N)), and total organic carbon |

| | | | |
|---|---|---|---|
| | | | Field collected background water quality parameters: total chlorine, free chlorine, alkalinity, pH, and temperature |
| Particle Characterization | Unfiltered Water | One 1 L wide mouth HDPE bottle sample collected and aliquoted into smaller volume bottles (aliquots from: 0.45µm filter (60 mL bottle), 0.2µm filter (60 mL bottle), ultrafiltration (125 mL bottle), and total metals without any filtrations) | Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sn, and Zn (EPA methods 200.7 and 200.8 (Pb, Cu, and Zn only)) |
| | Ultrafilter Surfaces | 1 ultrafilter disc, 1 SEM stub, 1 TEM grid | Material trapped on ultrafilters will be analyzed in Cincinnati by ORD by electron microscopy, energy dispersive spectroscopy, and other solids analysis approaches as warranted. |

*Table 4: Fully flushed sample collection detail*

| **CRL** | | | |
|---|---|---|---|
| ***Sample Bottle*** | ***Analytes*** | ***Preservation*** | ***Label*** |
| (1) 500 mL HDPE wide mouth bottle | Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Si, Sn, and Zn (EPA methods 200.7 and 200.8 (Pb, Cu, and Zn only)) | Nitric acid ($HNO_3$) preserved in field | -DS01 |
| (1) 500 mL HDPE wide mouth bottle | total alkalinity, $Cl^-$, $F^-$, sulfate, orthophosphate, nitrate, nitrite | Cool (≤6°C) (orthophosphate, nitrate, and nitrite have a 48 hr hold time) | -DS02 |
| (1) 500 mL HDPE wide mouth bottle | total organic carbon (TOC) and, if needed, nitrate+nitrite (as N) | Cool (≤6°C); Sulfuric acid ($H_2SO_4$) preserved in the field to pH <2 | -DS03 |
| (1) 500 mL HDPE wide mouth bottle | Total chlorine, free chlorine, and low range alkalinity (if meter is not available for analysis in the home) | Cool (≤6°C) | -DS04 |
| (4) 50 mL or 125 mL Glass | pH | Zero Headspace | N/A |

| | | | |
|---|---|---|---|
| Erlenmeyer flasks | | | |

**2.1 Field Team:** Estimated 2–3-person team (2 samplers at the sampling tap and possibly one Community Involvement Coordinator (CIC) or person to engage with the homeowner). Training will be documented using Attachment No. 7.

**2.2 Site Selection:**

The Operations Section leadership and/or sampling group lead will provide the proposed list of sampling locations to the project lead for approval and then communicate the approved site locations to scheduling and sample teams.

To assess lead sources and particles present, sampling will be prioritized at single-family homes likely to have or known to have a lead service line, based on documentation from Benton Harbor (e.g., water main age map) and/or historical water sampling results with elevated Pb levels. EPA anticipates sampling will be conducted at some of the homes that have been previously sequentially profiled by the Michigan Department of Health and Human Services (MDHHS).

During scheduling, residents should be asked about the following items to evaluate if a home is a candidate for sampling.

- Is there a whole-house water softener or whole-house water filter (including reverse osmosis) on the cold-water line?
- Is there a RO unit under the kitchen sink upstream of the kitchen faucet? [Residences with a kitchen faucet with RO unit inline/upstream should not be sampled; however, a kitchen with RO unit routed to a separate tap would not be impacted by the RO unit and could be sampled.]
- Are there any known water leaks in the home (e.g., running toilets or dripping faucets)? [Ideally, Resident should check for water leaks by comparing water meter readings before and after a period of 15 minutes where no one is using water in the house.]

**2.3 Supply list for sequential sampling, particle characterization and fully flushed sampling activities:**

- Booties for entering homes,
- COVID-required safety supplies (e.g., face coverings, hand sanitizer),
- HDPE pre-certified clean wide-mouth 60 mL, 125 mL, 500 mL, and 1 L single use rigid plastic bottles (method-specific preservations, see table 4 above)
- Trace-metal free nitric acid ($HNO_3$) dropper bottles,
- Dropper bottle of sulfuric acid ($H_2SO_4$),
- Glass 50 mL or 125 mL Erlenmeyer flasks with polyseal caps (for field pH analysis),
- Thermo Scientific Orion Star A211 pH meter, including calibration solutions (Buffer 4,7,10) and electrode (Thermo Scientific™ Orion™ ROSS Ultra™ Glass Triode™ pH/ATC Combination Electrode) or equivalent,

- Colorimetric kits for chlorine residual measurement or Hach SL1000 and associated chemkeys (total chlorine, free chlorine, alkalinity)
- NIST Traceable Thermometer,
- Timer (e.g., on ipads if Survey 123 is used)
- Weatherproof bottle labels,
- Chain-of-custody forms [see example in Attachment No 3],
- Sturdy coolers and packing materials (e.g., ice packs, ice, absorbent material, bubble wrap, trash bags, zip-type plastic bags, shipping tape, and shipping labels),
- UPS shipping labels from EPA R5 Mail Room (if third-party shipping),
- Amicon® Stirred Cell (ultrafilter),
- Anodisc™ Ultracel® 30 kDa ultrafiltration discs,
- $N_2$ tank, regulator and tubing,
- Magnetic stir plate,
- TEM grids and self-closing tweezers,
- TEM storage boxes with labeling sheet,
- Disposable plastic pipettes (to hold approximately 5ml)
- SEM stubs and carbon sticky tabs,
- Plastic petri dishes,
- SEM stub boxes,
- 50 mL luer lok syringes,
- 0.45 µm PTFE filter,
- 0.2 µm PP filter,
- Caulk gun,
- Kemio heavy metals analyzer, (See Attachment 5)
- Kemio lead sensors,
- Milli-Q water,
- Gloves (for field preservation),
- Safety glasses (for field preservation),
- Bound field logbook and field forms or electronic field note recorder (e.g., iPad with Survey123 software),
- Charging cables,
- Photograph labels (e.g., dry erasable board or sheet of paper),
- Indelible ink pen/marker, and
- Camera (e.g., on tablet/iPad).

**2.4 Pre-Sample Preparation**

1. Check that all equipment is charged and that there are back up batteries.
2. Verify Hach SL1000 and note verification in equipment logbook - The Hach system verification key will be used on all four chemkey slots at the beginning of each day that monitoring occurs using the procedure outlined in the manual (see Attachment No 2).
3. Calibrate pH meter using a three-point calibration with high precision pH buffers (4,7,10) daily prior to sample analysis. Calibration checks should be performed after

calibration, after every 3 sets of four flasks and after all sample analyses have been completed for the day (See Attachment No 4).

4. Prepare Chain of Custody, sample bottles, cooler, safety supplies to take to sample locations. Ensure each sampling team has field blanks to take with them into the field.
5. Verify safety equipment and procedures for the day – see Health and Safety Plan.
6. Make sure that sample collection allows for the particulate characterization filtering to be started within one hour of sample collection and completed within 2 hours of sample receipt in the field office otherwise the sample will need to be discarded.

**2.5 Procedure for Sequential Sampling and Particle Characterization Event:**

2.4.1 Instructions to be provided to residents prior to sequential sampling event:

**Flushing**

1) At least 6 hours prior to scheduled sampling, go to the kitchen faucet and turn any faucet-mounted filter to bypass/off mode (whole house filters or water softeners should not be bypassed), then turn on the cold water (fully open, maximum flow) and let it run for 5 minutes, then turn it off.

2) Write down the date/time you turned the water off. If home has an accessible water meter, please write down (or take a picture of) the meter reading after the flushing is completed.

*Flushing the system will allow the sequential sampling to provide representative information on the sources of lead for each specific volume of water that is sampled later.

**Stagnation**

Do not use **ANY** water from the home plumbing, after completing the 5-minute flushing, for the 6+ hours until the sampling visit. Specifically, do not shower, flush toilets, wash laundry, or use other water taps. Any automatic lawn sprinkler systems, ice makers, plumbed humidifiers etc. should also be turned off. It may help to tape a sign in the kitchen and bathrooms with a reminder not to use the water, in case people forget. If water is accidentally used, please notify sampling coordinator.

2.4.2 Procedure for samplers:

All bottles should be labeled and numbered using standardized nomenclature before entering the home, and it is very important to collect them in order (Sample "-SS01" first, Sample "-SS02" second, etc.). The number of sequential sample bottles will be approximately 16 liters (32, 500 mL bottles), unless it needs to be adjusted either based on previous sampling (e.g., MDHHS data) or field observations (e.g., house set back far

from the road). EPA will collect a targeted 1 L "PC##-TM" sample for particle characterization during the sequential sampling visit. See step #7 in "Drinking Water collection for sequential profile samples (lead sources)" regarding specifics on how to collect this targeted 1 L at each individual residence.

Samples will be taken from the kitchen sink cold-water faucet. Ensure any point-of-use filters on the kitchen faucet are in bypass mode. Aerators, both on filter units and on taps without filters, are to remain, and should be unaltered, during sampling. Only cold water is to be sampled.

Prior to entering the house, determine the targeted sample volume (provided by the Environmental Unit leader, based on estimated LSL location or highest sequential sample) and pre-label sample bottles using standardized nomenclature.

- "BH" for Benton Harbor sampling
- House identifier unique to the address (i.e., from a master list developed with a random number generator provided to sampling teams on sampling schedule). This allows protection of personal identification information in subsequent data analysis.
- Then "-SS" for sequential samples, "-PC##-TM" particle characterization, (unfiltered, total metals), and "-DS" for fully flushed samples (distribution system background water quality samples).
- After the sample type ID (-SS, -PC##-TM, or -DS) numbers will be used to indicate unique samples in the order they are collected (e.g., 01, 02, 11).
- For the fully flushed 500 mL "-DS" sample bottles, pre-label with DS01 for "metals", DS02 for "alk+WQ", DS03 for "TOC". If there is insufficient time/space to complete the SL1000 field water quality analyses in the home, a fourth bottle may be needed, labeled DS04, for field WQ analysis at the Field Office.

Labeling Examples:

- Benton Harbor, house identifier 0001, the first and second 125 mL samples would be labeled BH0001-SS01 and BH0001-SS02, then subsequent sequential 500 mL sample bottles would be labeled BH0001-SS03, BH0001-SS04…..BH0001-SS26. Then the fully flushed water sample would be labeled BH0001-DS01.
- Benton Harbor, house identifier 9999: the first and second 125 mL samples would be labeled BH9999-SS01 and BH9999-SS02, then subsequent sequential 500 mL sample bottles would be labeled BH9999-SS03, BH9999-SS04….. BH9999-SS14. Then the fully flushed water sample would be labeled BH9999-DS01.

See quick summary of sample IDs in Table 5.

*Table 5: Sample IDs*

| **Sequential Sampling** |
|---|

| | |
|---|---|
| BH####-SS## | Sequential Samples |
| BH####-DS## | Fully Flushed Water Quality Sample |
| **Particle Characterization** | |
| BH####-PC##-TM | Unfiltered Sample (field collected) |

####- House identifier unique number
-##- sequential number representing order sample type was collected

2.4.3 Drinking Water collection for sequential profile samples (lead sources)

1. Prior to entering the home, sampler should ask resident COVID screening questions and pre-sampling questions to determine if sampling can take place that day. If COVID screening does not pass or water was not stagnated correctly, notify resident they will be contacted to reschedule sampling.

2. The sampler shall record information in Survey 123 or field sheets listed in Attachment No 1B. It is important to ensure no one has used the water since the flushing occurred and at least 6 hours have passed from when the flushing was completed. If the homeowner took a photo of their water meter after the preflush ask if you can take a photo of their photo for record.

3. Request permission from the resident and if they approve take photographs of the sample tap(s) and underlying fixtures and components

4. Place the sample bottles (two 125 mL, one 1 L, and rest 500 mL) near the kitchen faucet in order by sample number (e.g., -SS01, -SS02, -SS03,…. -PC07-TM, -SS08, etc.) and ensure two samplers are ready to undertake the sampling.

5. Remove the caps from all bottles so that they are ready to fill.

6. Record the beginning sample date/time on the Chain-of-Custody form [see example in Attachment No 3].

7. Begin by placing the "-SS01" bottle under the kitchen faucet and open the cold water slowly, to fill the first two smaller volume bottles. While one bottle is filling, grab the next bottle (-SS02) so that you are ready to move it under the faucet quickly. Samples will be collected without shutting off the water in between bottles and try to not let any water spill in between samples.

8. Once the bottle is filled to the neck, quickly place the "-SS02" bottle under the faucet.

9. When you start filling the first 500mL bottle "-SS03" increase the flow so that the faucet is fully open (maximum flow) and continue at that flow rate to collect the remaining "-SS" and "-PC##-TM" sample bottles allocated for the site. The "-PC##-TM" sample should be filled to the very top of the bottle, "-SS##" bottles should only be filled to the neck of the

bottles. To the extent that the maximum flow results in spilling or loss of water, the sampler will use a lower flow rate as necessary for maximum water collection. The sampling flow rate will be measured as detailed below and noted in field notes.

- EPA will collect the targeted 1L "PC##-TM" sample for particle characterization while also collecting the sequential samples. **The specific volume to be targeted will be specific to individual homes, based on previous sampling results (e.g., MDHHS sequential sampling).** For example, if the 8.25 Liter is the targeted sample volume for the "PC##-TM" sample at an individual home, the following would be the order of samples collected:
    - "SS01" and "SS02" as noted above (125 mL each, totaling 0.25 L), then
    - As noted above faucet flow is increased and samples "SS03", "SS04", "SS05", "SS06", "SS07", "SS08", "SS09", "SS10", "SS11", "SS12", "SS13", "SS14", "SS15", and "SS16" are collected (500 mL each, totaling 7 L for a cumulative sequential volume of 7.25 L), then
    - "PC17-TM" (1 L bottle, for a cumulative sequential volume of 8.25 L), then
    - Back to 500 mL bottles for "SS18", "SS19", etc. until the remaining sequential samples are collected.
- If the targeted 1 L "PC##-TM" sample for particle characterization is the first liter (Liter 1 is the targeted sample volume) sample, the following would be the order of samples collected:
    - "SS01" and "SS02" as noted above (125 mL each, totaling 0.25 L), then
    - As noted above faucet flow is increased as the "PC03-TM" (1 L bottle, for a cumulative sequential volume of 1.25 L) sample is collected,
    - Then back to 500 mL bottles for "SS04", "SS05", etc. until the remaining sequential samples are collected.

**10.** A field blank is brought to each sequential home. The bottle is prelabeled and filled with milli-Q water. Open the field blank bottle, remove lid then place back on and store in cooler with other samples. Record the field blank collection in 123 survey. Record the field blank information on forms or 123survey.

**11.** Leave the faucet running and record the date and time when the final sequential sample was filled on the Chain of Custody form. Tightly place the caps back on all the filled sequential sample bottles.

**12.** Using a 1 L container (reusable; marked for flow rate use only), determine the amount of time needed to fill the bottle, also measure the temperature of the water with a NIST traceable thermometer. Discard that water.

2.4.4 Drinking Water collection for fully flushed (background water chemistry samples)

- As the faucet continues to run, remove the caps from the three 500 mL fully flushed "-DS" sampling bottles.
    - If water is not running at maximum flow (because you had to turn it down for the sequential sample collection) then make sure you increase the flow to maximum flow at this step. Measure the flow rate again if increased.
- After the faucet has been on and flowing for an additional 5 minutes at maximum flow (beyond the time taken to fill the sequential samples), record the time on the Chain-of-Custody form.
- Fill the three bottles to the neck and recap tightly.
    - One 500 mL bottle ("-DS01" for metals) to be later field preserved with $HNO_3$
    - One 500 mL bottle for laboratory water quality analyses ("-DS02" for alk+WQ).
    - One 500 mL bottle ("-DS03" for TOC) to be later field preserved with $H_2SO_4$
    - Place fully flushed bottles for background water quality ("-DS02" for alk+WQ and "-DS03" for TOC) into a cooler with frozen ice packs (or bagged ice); these will be field-preserved at the Field Office as discussed below.
- Rinse Hach SL1000 sample cup 3 times with tap water from the faucet. Then collect a sample to the sample cup fill line for field analysis using free chlorine, total chlorine, and alkalinity chemkeys, or an equivalent method (instrument/method used to be noted in field records). Record results in Survey123 and notify resident of results. See Attachment No 2 for further information on proper calibration and operation of the Hach SL1000. pH may be analyzed at this time in the future if the equipment becomes available. If analysis in the home is not feasible, a fourth 500 mL sample bottle identified for field collected water quality analyses ("-DS04" for field WQ) can be collected and packed with ice for analysis of these parameters outside the home but within 2 hours of receipt at the field office.

g) Record chlorine and temperature results in Survey123 and share results with resident. See Attachment No 2 for further information on proper calibration and operation of the Hach SL1000.

h) If the chlorine residual is <0.2 mg/L, EGLE and MDHHS representatives in the Unified command structure will be notified immediately and the sampling team will

then run the water for 5 more minutes and re-sample for chlorine. Record 10-minute flushed chlorine and temperature results in Survey123 and share results with resident. Michigan will provide necessary follow-up activities for protection of public health.

- Remove the caps from the four glass Erlenmeyer flasks (pH analysis), reduce the flow of water to the width of a pencil and fill the four Erlenmeyer flasks. Ensure they are filled to no-headspace and recap tightly.
- Turn the water off. Return any faucet mount point-of-use filters to the "on" position.
- Before you leave the house, make sure the Field Notes sheet (i.e. Survey 123 electronic form) is completed and all materials/sample bottles are retrieved.

**2.5 Sample Storage and Transportation for Concurrent Study Samples**

1. Place all bottles and glass Erlenmeyer flasks into a cooler for transport back to the field office for processing. Ensure the sample bottles are securely packed, particularly the glass flasks. Ice is not needed for metals samples. Place fully flushed bottles for background water quality ("-DS02" for alk+WQ, "-DS03" for TOC, and "-DS04" for field WQ (if collected)) into a cooler with frozen ice packs (or bagged ice).
2. The sampling team will return samples to the field office, and particle size fractionation filtrations should begin **immediately on arrival at the field office (no more than 1 hour) after sample collection**. The EPA Field lab team will follow the instructions for this in the following "Particle Fractionation" Section 2.7 below. Because ultrafiltration can take 30-60 minutes per sample, be sure to begin the ultrafiltration process as soon as possible after arrival at the field office and then proceed with the syringe filters and other tasks. All filtrations should be completed within 2 hours of sample receipt at the field office, if a sample is not filtered within 2 hours it should be discarded.
3. The sampling team will return samples to the field office, and the EPA Field lab team (or sampling team as directed) will preserve all samples for metals analysis following the instructions below:

    - Use Nitrile gloves, safety googles and absorbent pads on workbench and follow necessary safety precautions when preserving samples with nitric acid.
    - For each sample, add nitric acid:
        - ~2 drops for 125 mL (SS01 and SS02)
        - ~10 drops for 500 mL (SS03, SS04, etc. and DS01)
        - DO NOT acidify -PC##-TM until after particle fractionation (Section 2.7) is completed

    Recap bottle and turn "end over end" five times, then use a pH strip to see if the pH is less than 2. If the pH is greater than 2, incrementally add more drops of nitric acid (capping and mixing) until a pH strip indicates that the pH is less than 2. Once a number of drops have been determined for the sample volume for the day, use that number of drops to preserve all water samples of the same volume collected in the day.

- Add an appropriate number of drops (as determined in the previous step) of the nitric acid preservative to each "-SS" and "-DS01" (for metals) bottle.
- Recap bottle and turn "end over end" five times.
- Pour out a few drops of the sample onto pH paper held over another container (to catch any spilled water from the pour), DO NOT dip anything into a sample. If pH is less than 2 then the sample is properly field preserved, if pH is greater than 2 add additional drops of acid, mix and recheck pH as previously described.
- One field blank (1 L bottle containing laboratory Milli-Q water) will be provided to field samplers to take out in the cooler with the samples. These field blanks should be field preserved (following the same steps as the samples) per every 20 bottles to confirm that field collection and preservation is not a source of metals contamination. If 20 bottles are not collected in one day, then there should be at least one field blank per sampling team per day, field preserved with the sample bottles collected that day. Field blanks will be labeled with the date in MMDDYYYY format and a sequential number at the end (MMDDYYYY##). If additional field blanks are needed to meet the 1 per 20 samples requirement they can be created at the field office with the same naming convention with an additional suffix "FP" to indicate those field blanks were created during the field preservation process (MMDDYYYY##FP).

4. The EPA Field lab team (or sampling team as directed) will also field preserve the sample for Total Organic Carbon ("-DS03" for TOC) following the instructions below:

   - Use Nitrile gloves, safety googles and absorbent pads on workbench and follow necessary safety precautions when preserving samples with nitric acid.
   - For each 500 mL ("-DS03") TOC sample, add ~2 drops of sulfuric acid. Recap bottle and turn "end over end" five times, then use a pH strip to see if the pH is less than 2. If the pH is greater than 2, incrementally add more drops of sulfuric acid (capping and mixing) until a pH strip indicates that the pH is less than 2. Once a number of drops have been determined for the sample volume for the day, use that number of drops to preserve all water samples of the same volume collected in the day.
   - Add the sulfuric acid preservative (as determined in the previous step) to each "-DS03" TOC bottle.
   - Pour out a few drops of the sample onto pH paper held over another container (to catch any spilled water from the pour), DO NOT dip anything into a sample. If pH is less than 2 then the sample is properly field preserved, if pH is greater than 2 add additional drops of acid, mix and recheck pH as previously described.
   - Field preservation is unlikely to substantially impact TOC; no field blanks will be required for TOC samples.

5. Place all field preserved sequential samples (-SS) and fully flushed samples (-DS01) for metals analysis (which do not require ice) in a secure container for transportation to the lab. Place fully flushed bottles for background water quality ("-DS02" for alk+WQ and "-DS03" for TOC) into a cooler with frozen ice packs (or bagged ice) for transport back to the specified laboratory. Ensure the sample bottles are securely packed and sent to Chicago Regional Laboratory (Attachment No 6). .

6. Make sure the Chain-of-Custody form is completed and checked by a team leader against cooler content and secured within the cooler in a zip-loc bag. You should also have a scan or copy for tracking purposes. See example in Attachment No 3.

7. Seal the garbage bag, tape the cooler closed and label with the lab it is destined to (e.g., tape with lab name on it) if transported, or complete shipping label if it is being overnighted. Ship/transport samples to the specified laboratory within 24 hours. See addresses and specific shipping protocols in Attachment No 6.

**2.6 Field Water Quality Analyses**

1. Transport the fully flushed Erlenmeyer flasks identified for field pH analysis to the field office. Field pH with the Erlenmeyer flasks will be analyzed following instructions in Attachment No 4. These field analyses should be completed as soon as possible, within 6 hours of sample receipt at the field office, if analyses are not in process or complete within 6 hours of receipt the sample should be discarded.

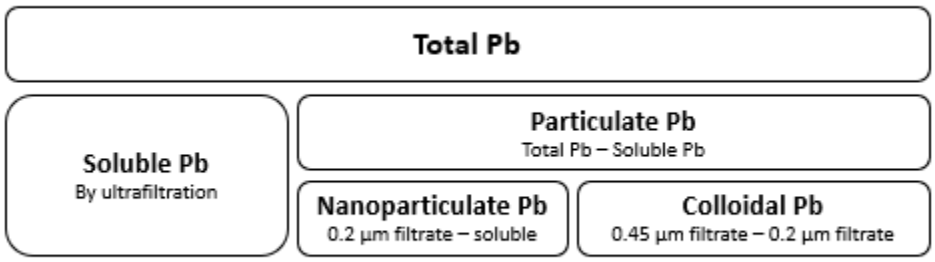
2. If analysis in the home is not feasible and a fourth 500 mL sample bottle identified for field collected water quality analyses ("-DS04" for field WQ) is collected, water quality analyses (total chlorine, free chlorine, and alkalinity) will be analyzed using a Hach SL1000 or equivalent within 2 hours of sample receipt at the field office. If analyses are not in process or complete within 2 hours of receipt, the sample should be discarded. Sparingly rinse the Hach SL1000 sample cup 3 times with water from the "-DS04" bottle. Then pour water from the "-DS04" (for field WQ) bottle to the sample cup fill line (~100 mL) for field analysis using free chlorine, total chlorine, and alkalinity chemkeys, or an equivalent method (instrument/method used to be noted in field records). See Attachment No 2 for further information on proper verification and operation of the Hach SL1000.

    - If the chlorine residual is 0.2 mg/L, EGLE and MDHHS representatives in the Unified command structure will be notified immediately. Michigan will provide necessary follow-up activities for protection of public health.

**2.7 Particle Fractionation:**

Three particle size fractionations will be performed at the field office on the 1 L sample (-PC##-TM) collected: 0.2 µm, 0.45 µm, and ultrafiltration (Figures 1 & 2). Particle size fractionation filtrations should begin immediately on arrival at the field office which will be no more than 1 hour after sample collection. All filtrations should be completed within 2 hours of sample receipt at the field office, if a sample is not filtered within 2 hours it should be discarded.

*Figure 1: Lead particle fractions to be collected and calculated.*




Prior to beginning the filtrations pre-label sample bottles using standardized nomenclature.

- "BH" for Benton Harbor sampling
- House identifier unique to the address (i.e., from a master list developed with a random number generator provided to sampling teams on sampling schedule). This allows protection of personal identification information in subsequent data analysis.
- Then "-PC##-20" for the 0.2 µm filtration (60 mL bottle), "-PC##-45" for the 0.45 µm filtration (60 mL bottle), and "-PC##-UL" for the ultrafiltration (125 mL bottle).

See quick summary of sample IDs in Table 6.

*Table 6: Sample IDs*

| **Particle Characterization** | |
|---|---|
| BH####-PC##-20 | 0.2 µm Filtration (60mL, prepared in field office) |
| BH####-PC##-45 | 0.45 µm Filtration (60mL, prepared in field office) |
| BH####-PC##-UL | Ultrafiltration (125mL, prepared in field office) |

####- House identifier unique number
##- sequential number representing order sample type was collected

Prior to beginning the filtrations check the pH of the "-PC##-TM" sample with a strip to ensure it wasn't accidentally preserved. Pour out a few drops of the sample onto pH paper held over another container (to catch any spilled water from the pour), DO NOT dip anything into a sample. Record this in the pH logbook with the sample data.

2.7.1 TEM grid procedure:

1. Take the 1 L (-PC##-TM) bottle and "turn end over end" five times to mix.

2. Using a Kemio heavy metals analyzer, check the concentration of Pb in the 1 L "-PC##-TM" bottle (~40 mL, see instructions in Attachment No. 5). Record the measurement result and proceed to the next step.

3. Take the 1 L (-PC##-TM) bottle and "turn end over end" five times to mix.

4. Using self-closing tweezers, pick up a TEM grid at the edge and sit the tweezers on a benchtop so that the shiny side (brighter) of the TEM grid is facing up.

5. Using a disposable pipette draw up <5 mL of sample water from the 1 L "-PC##-TM" bottle.

6. Pipette one drop of sample water onto the shiny side of the TEM grid, cover with a plastic Petri dish and let dry under ambient conditions. If time allows once the drop dries place another drop on the TEM grid (be sure to shake the bottle prior to pipetting). When completely dry transfer grid to labeled TEM grid box. Be sure to record the TEM grid box location for the sample on the TEM grid record keeping card associated with the box. The TEM grid sample ID will follow the standard nomenclature (-PC##-TM-01).

7. Repeat steps 3-6 to prepare a second TEM grid from the "-PC##-TM" bottle, so there are two TEM grids per site (-PC##-TM-02, for the duplicate TEM grid)).

2.7.2 0.2 µm and 0.45 µm syringe filtration procedure:

1. Take the 1 L (-PC##-TM) bottle and "turn end over end" five times to mix.

2. Using a 50 mL syringe draw up approximately 5 mL of sample water (from the 1 L "-PC##-TM" bottle) and rinse the inside of syringe, then waste this portion.

3. Fill the 50 mL syringe with sample water (from the 1 L "-PC##-TM" bottle). Attach a 0.45 µm PTFE syringe filter. Using a caulk gun (Figure 3), syringe pump, or your hands slowly push approximately 10 drops of water through the filter and waste this water. The remaining water should be collected in a labeled 60 mL HDPE bottle (-PC##-45) and preserved with nitric acid ($HNO_3$) for metals analysis (see instructions in Field Preservation, Sample Storage, and Transportation below).

4. Take the 1 L (-PC##-TM) bottle and "turn end over end" five times to mix.

5. Using a new 50 mL syringe draw up approximately 5 mL of sample water (from the 1 L "-PC##-TM" bottle) and rinse the inside of syringe, then waste this portion.

6. Fill the 50 mL syringe with sample water (from the 1 L "-PC##-TM" bottle). Attach a 0.2 µm PP syringe filter. Using a caulk gun (Figure 3), syringe pump, or your hands slowly push approximately 10 drops of water through the filter and waste this water. The remaining water should be collected in a labeled 60 mL HDPE bottle (-PC##-20) and preserved with nitric acid ($HNO_3$) for metals analysis (see instructions in Field Preservation, Sample Storage, and Transportation below).

7. New syringes and filters should be used for each individual aliquot of water for filtration.

2.7.3 Ultrafiltration
See Amicon Stirred Cell Start Guide for assembly, and operation (Figures 4 and 5)

1. Place Anodisc™ Ultracel® 30 kDa ultrafiltration disc in Amicon® Stirred Cell shiny side up (as the discs are oriented in the packaging).
2. Assemble stirred cell using the start guide for guidance (Figures 4 and 5). Leave the top of cell off until you add your sample water.
3. Take the 1 L (-PC##-TM) bottle and "turn end over end" five times to mix.
4. Pour 250 mL of the 1 L sample bottle (-PC##-TM) water into the stirred cell and turn on magnetic stir plate (low setting) and allow the cell to stir for 5 minutes. Preliminary studies observed that the cell adsorbs up to 20 µg of soluble lead. This rinse steps allows the cell to saturate with lead prior to filtration.
5. Take the 1 L (-PC##-TM) bottle and "turn end over end" five times to mix.
6. Turn off the stir plate. Waste the rinse water and quickly replace with 250 mL of the remaining sample water from the 1 L bottle (-PC##-TM).
7. Attach the lid of the stirred cell.
8. Turn on the stir plate and set mixing speed at low to medium.
9. Connect stirred cell to a pressurized nitrogen gas tank using the tubing provided by the manufacturer (Figure 6). Set pressure to 10 psi.
10. Turn on nitrogen gas at the cylinder and waste the first 100 ml and then collect 125 mL of the filtered water into a labeled 125 mL HDPE bottle (-PC##-UL). Preserve with nitric acid ($HNO_3$) for metals analysis see instructions in Field Preservation, Sample Storage, and Transportation below.
11. After collecting the 125 mL of filtered water continue to run the ultrafilter to a waste container until all water has been filtered. Once water has been completely filtered, turn off stir plate and nitrogen gas at the cylinder.
12. Release pressure of the cell by removing the pressure inlet tubing assembly.
13. Unscrew cap of stir cell and remove stir bar. Unscrew cell body to access the ultrafilter.
14. Collect Ultrafilter using tweezers and store filter in a labeled (date in MMDDYYYY format plus the sample ID for the site "-PC##-UL") Petri dish (orientation of the filter

should be the same in the Petri dish as it was in the stirred cell, so particles remain on the "up" side).

15. Affix a carbon sticky tab to a labeled (-PC##-UL) aluminum SEM stub (label should be written along the side of the SEM stub with a permanent marker, not on the base).

16. Dab the carbon sticky tab onto the ultrafilter in the Petri dish a few times.

17. Place the labeled SEM stub in a SEM sample box labeled with the date of collection in MMDDYYYY format. Be sure to record the SEM storage box location for the sample on the SEM record keeping card associated with the box.

18. TEM grids, ultrafilters, and SEM stubs with the retained particulate lead will be shipped to ORD in Cincinnati for analysis.

19. Rinse all materials of Ultrafiltration sample cell with DI water.

20. The remaining water (~230 mL) in the 1 L sample bottle (-PC##-TM) should be preserved with nitric acid ($HNO_3$) for metals analysis, see instructions in Field Preservation, Sample Storage, and Transportation below. This sample will represent total metals present at the site with no filtration.

### 2.8 Preservation, Sample Storage, and Transportation for Particle Fractionation Samples

1) Preserve all particle fractionation samples for metals analysis prior to shipping following the instructions below:

   a) Use Nitrile gloves, safety googles and absorbent pads on workbench and follow necessary safety precautions when preserving samples with nitric acid.
   b) For the first of each bottle size for the day, add drops of nitric acid:
      i) ~1 drop for 60 mL (PC##-20 or PC##-45),
      ii) ~2 drops for 125 mL (PC##-UL), and
      iii) ~3 drops for ~230mL (remaining in -PC##-TM after particle fractionation)
      Recap bottles and turn "end over end" five times, then use a pH strip to see if the pH is less than 2. If the pH is greater than 2, incrementally add more drops of nitric acid (capping and mixing) until a pH strip indicates that the pH is less than 2. Once a number of drops have been determined for the sample volume for the day, use that number of drops to preserve all water samples of the same volume collected in the day.
   c) Add an appropriate number of drops (as determined in the previous step) of the nitric acid preservative to "-PC##-20", "-PC##-45", "-PC##-UL" and "-PC##-TM" bottles.
   d) Recap bottle and turn "end over end" five times.
   e) Pour out a few drops of the sample onto pH paper held over another container (to catch any spilled water from the pour), DO NOT dip anything into a sample. If pH is less than 2 then the sample is properly field preserved, if pH is greater than 2 add additional drops of acid, mix and recheck pH as previously described.
   f) One field blank (1 L bottle containing laboratory Milli-Q water) should be field preserved (following the same steps as the samples) per every 20 bottles to confirm that field

collection and preservation is not a source of metals contamination. If 20 bottles are not collected in one day, then there should be at least one field blank per sampling team per day, field preserved with the sample bottles collected that day. Field blanks will be labeled with the date in MMDDYYYY format and a sequential number at the end (MMDDYYYY##). If additional field blanks are needed to meet the 1 per 20 samples requirement, they can be created at the field office with the same naming convention with an additional suffix "FP" to indicate those field blanks were created during the field preservation process (MMDDYYYY##FP).

**2)** Place all field preserved fully flushed samples (-PC##-) for metals analysis (which do not require ice) in a secure container for transportation to the lab (see Attachment No 6).

**3)** For solids samples:

a) All TEM grids should be placed in TEM grid boxes labeled with the date of sample collection in MMDDYYYY format. TEM grid boxes will be taped shut before shipping. There should be a record keeping card associated with each TEM grid box that has the date of sample collection, in MMDDYYYY format and also the placement of all of the grids and associated sample IDs (e.g. slot A3 has a grid for sample BH0001-PC##-TM or slot B2 has a grid for sample BH0001-PC##-TM-2).

b) All labeled SEM stubs should be placed snugly in SEM storage boxes labeled with the date of sample collection in MMDDYYYY format (can put double sided sticky tape on the bottom of the SEM stub before securing in storage box). There should be a record keeping card associated with each SEM storage box that has the date of sample collection, in MMDDYYYY format and also the placement of all of the stubs and associated sample IDs. The storage box will be taped shut before shipping.

c) All petri dishes containing ultrafilter discs labeled with the date of sample collection in MMDDYYYY format and sample ID will be individually parafilmed shut, and then rubber banded together in small stacks of 3 or 4 dishes.

Solids samples should be carefully packed with bubble wrap. TEM and SEM record keeping cards and Chain of Custody forms should be completed and secured within the container in a zip-loc bag. Samples should be shipped to ORD in Cincinnati once accumulated; see address in Attachment No 6.

**4)** Make sure the Chain of Custody forms are completed and secured within the container in a zip-type bag. See examples in Attachment No 3. Separate Chain of Custody forms should be completed for each cooler/container, particularly if shipping UPS/FedEx. For solids sample collection a separately formatted Chain of Custody is required for shipment to ORD in Cincinnati (Attachment No 3). Security seals will be provided to field sampling teams to be used as necessary to ensure appropriate chain of custody.

*Figure 2: Flowchart of particle fractionation sample collection.*

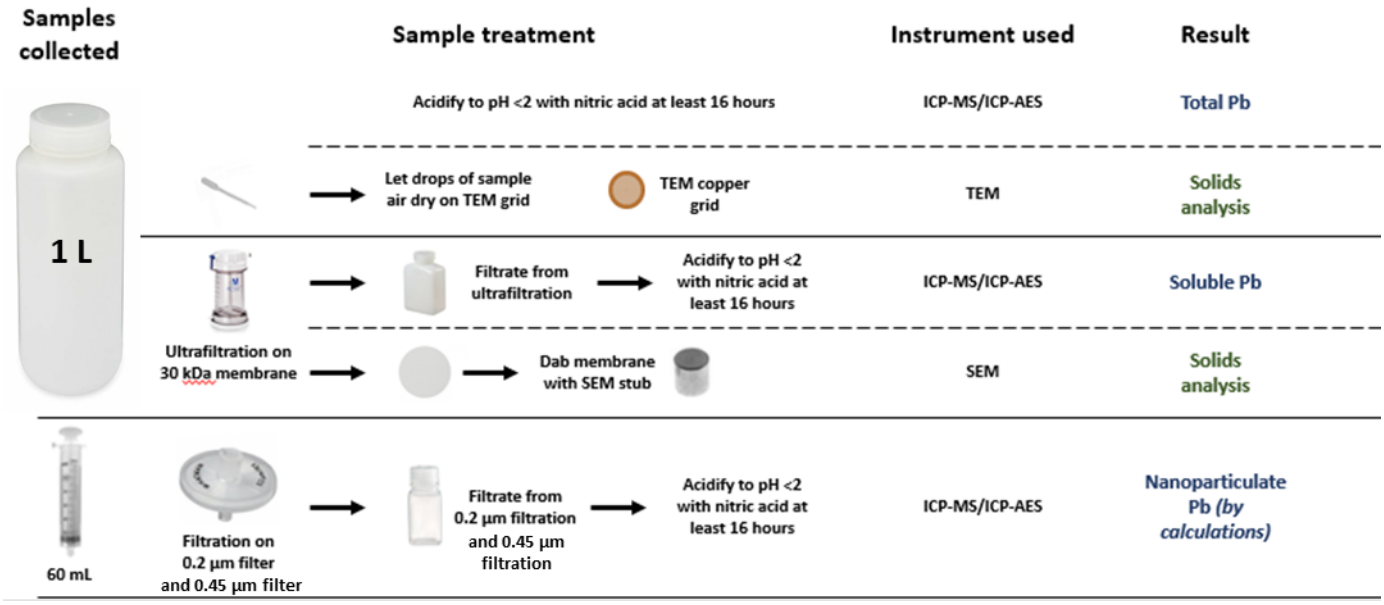



*Figure 4: Manufacturer instructions.*

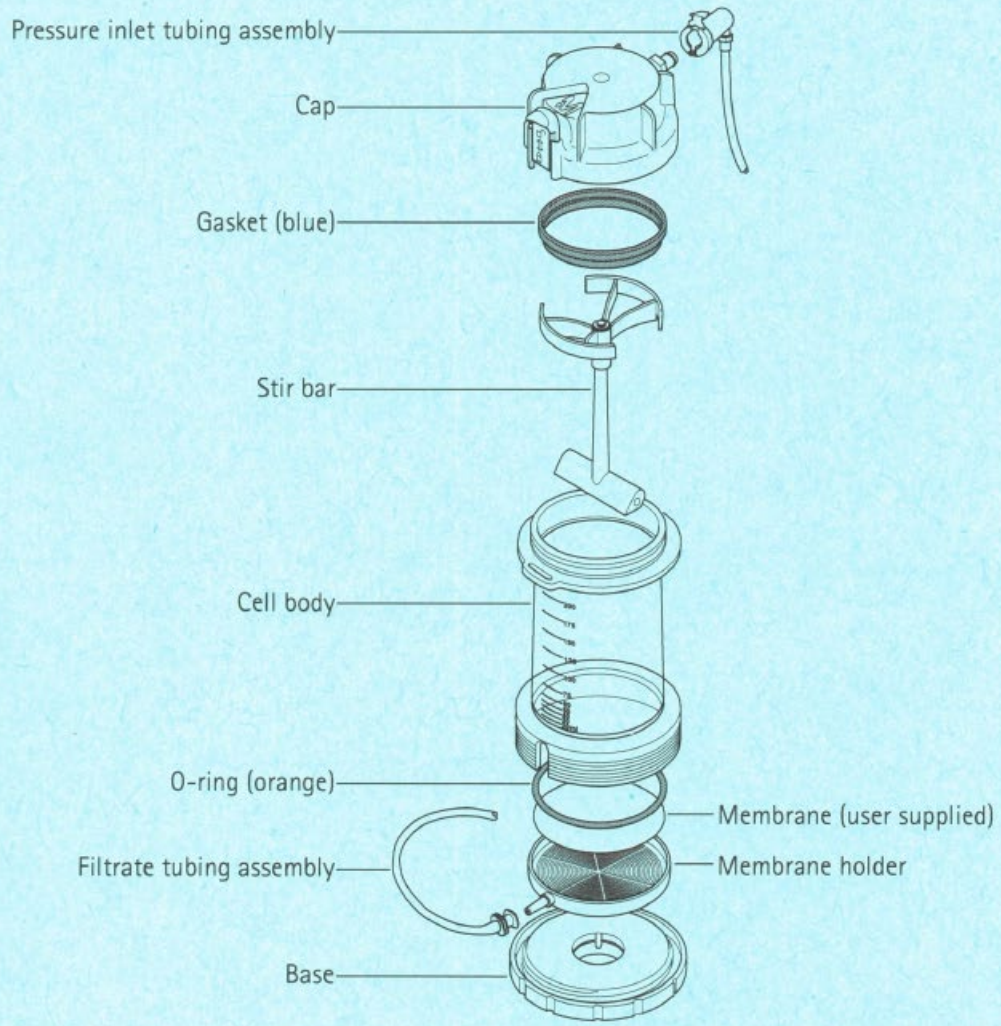
Quick Start Guide

# Amicon® Stirred Cell

**Caution: Not intended for medical purposes or for use in diagnostic procedures.**

*Before using the Amicon® Stirred Cell, please read the full-length user guide available at www.millipore.com/amiconstirredcell.*

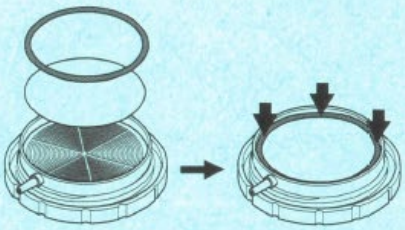
## Amicon® Stirred Cell Components



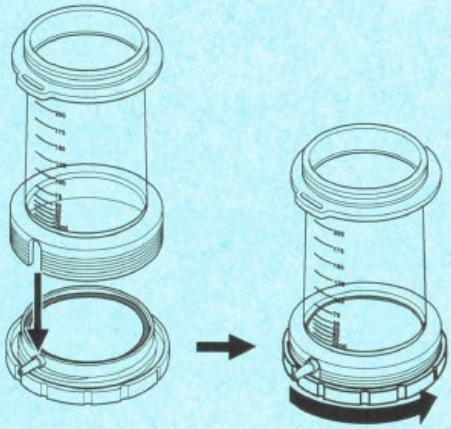
## Assembly and Operation

1. Snap membrane holder onto base.

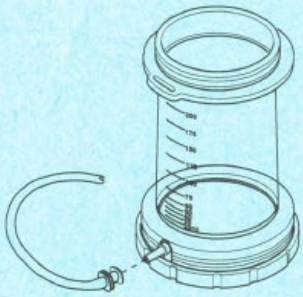
2. Place membrane into membrane holder, oriented as indicated in membrane instructions. Place O-ring on top of membrane and push down gently to seat membrane in holder.



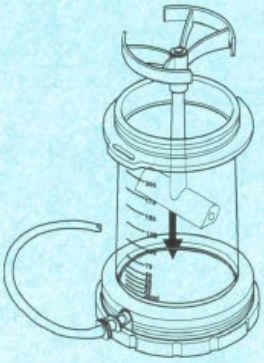
3. Align filtrate port on membrane holder with slot in bottom of cell body. Screw base into cell body.



4. Attach filtrate tubing assembly to filtrate port on membrane holder.

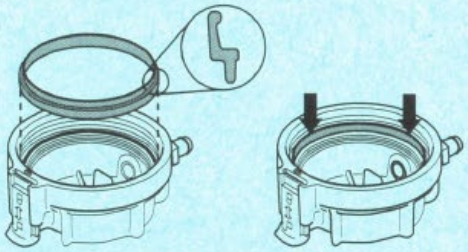


5. Insert stir bar into cell body until support ring is seated on ridge inside the top of cell body.



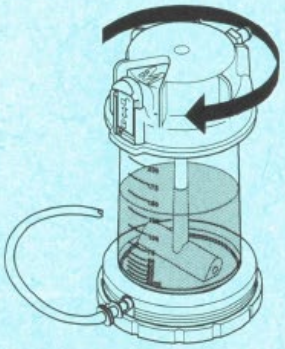
6. Pour desired sample into cell.

7. With cap oriented as shown, seat large diameter of gasket in gasket groove. Gently push the gasket down to seat it fully.

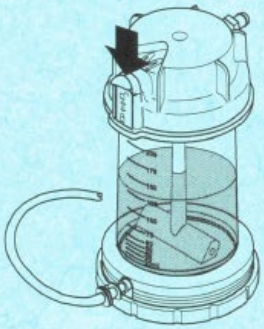


**IMPORTANT!** To avoid leakage between cap and cell body, make sure that the gasket is free of dirt/debris and oriented correctly in the cap.

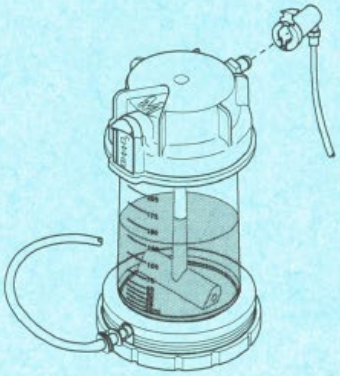
8. Screw cap onto cell body until it stops.



9. Move blue slide-lock downward to close pressure relief valve and lock cap in place.

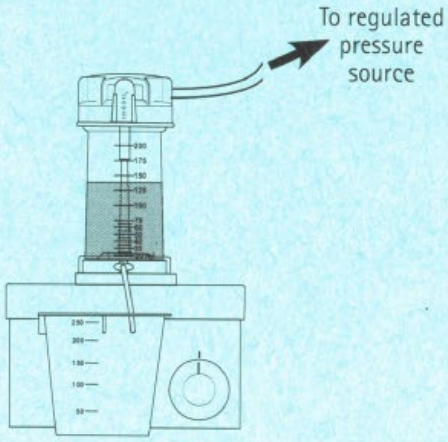


10. Attach pressure inlet tubing assembly by inserting female connector onto quick-connect fitting on cap until it clicks.



11. Place stirred cell on magnetic stirrer.
12. Insert filtrate tubing into an appropriate collection container.
13. To concentrate, connect free end of pressure inlet tubing to a pressure source.
14. Initiate stirring and pressurize stirred cell to desired pressure. Refer to membrane instructions for optimal operating pressures.

    **WARNING:** Do not exceed pressure limit of 5 bar (75 psi).
15. Collect filtrate until desired concentration factor is achieved.



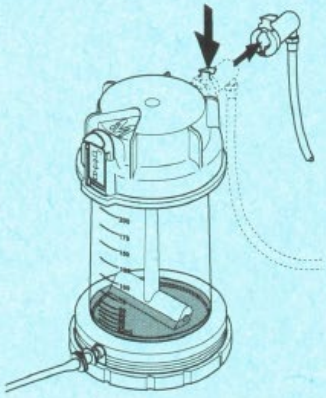
## Shut down and disassembly

1. Once filtration is complete, turn off pressure at the source, then turn off magnetic stirrer.

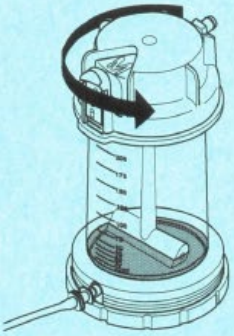
   **WARNING:** Do not disconnect pressure inlet tube until stirred cell is depressurized.

2. Move blue slide-lock upward to vent residual pressure and disengage cap lock.


3. Disengage the quick-connect fitting by pressing down on the metal tab and pulling the fitting away from the cap.



4. Unscrew cap and remove from cell body.



5. Remove stir bar and recover concentrated sample. Save filtrate sample if required.

## Notice

The information in this document is subject to change without notice and should not be construed as a commitment by EMD Millipore Corporation, ("Millipore"), or an affiliate. Neither EMD Millipore Corporation nor any of its affiliates assumes responsibility for any errors that may appear in this document.

## Technical Assistance

For more information, contact the office nearest you. In the U.S., call 1-800-221-1975. Outside the U.S., go to our web site at www.millipore.com/offices for up-to-date worldwide contact information. You can also visit the tech service page on our web site at www.millipore.com/techservice.

## Standard Warranty

The applicable warranty for the products listed in this publication may be found at www.millipore.com/terms ("Conditions of Sale").



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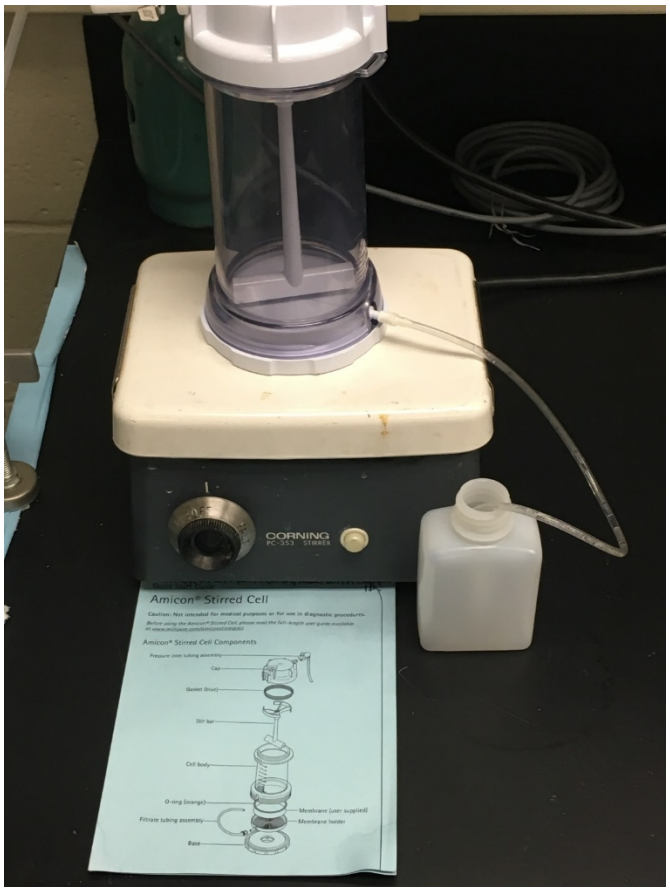

CORNING
PC-353 STIRRER
Amicon® Stirred Cell
Caution: Not intended for medical purposes or for use in diagnostic procedures.
Amicon® Stirred Cell Components
Pressure inlet tubing assembly
Cap
Gasket (blue)
Stir bar
Cell body
O-ring (orange)
Filtrate tubing assembly
Base
Membrane (user supplied)
Membrane holder

*Figure 6: Example of $N_2$ tank, regulator, and tubing.*

## Attachment No. 1A – Field notes (list of fields for Survey 123) for Filter Screening Study

Owner/Occupant name and contact phone number/email address will be maintained separately from the water quality data. For all applicable data points where resident input is needed there should also be two options "resident declined" and "did not ask").

- Address (connect to GIS)
- House identifier code (from scheduler/master list)
- Building type (Options: Single Family Residential, multi-family residential, commercial)
- Year Built (from the county's Parcel dataset)
- Whole house water treatment? (Options: None per resident/visual, water softener, whole-house filtration; in-line reverse osmosis; Unknown) [Describe any whole house water treatment in Remarks]
- Time since the POU/pitcher filter cartridge was installed (weeks) – Enter ("0") if EPA installs the filter during the sampling visit.
- How does the resident use the POU/pitcher filter? (Options: Cold water only, Hot and cold water, Not used, Other- describe) [add "h" qualifier if hot water has been run through the filter]
- Brand of the POU/pitcher filter (Options: PUR, Brita, ZeroWater, Other-describe)
- Model of POU/pitcher filter if available from original product packaging (such as: SAFF-100, FM-2000B, FM-3333B, ZD-018; Other - describe; could not find)
- Model of POU/pitcher replacement cartridge if available from original product packaging (such as: FR-200, RF-3375, ZR-001, ZF-201; Other - describe; could not find)
- Sample type (Options: PF = Through Pitcher Filter; 5FF= 5 second flush through Faucet-mount filter, FF = Through Faucet-mount filter, or UF = Bypassing Filter)
- Status of the POU/pitcher filter indicator (red/yellow/green) or filtered water TDS reading for ZeroWater [add "e" qualifier for "red" or filtered water TDS >006]
- Upload photo of filter as installed; if available, upload photos of filter product box and replacement cartridge box [if photos stored outside of Survey123 be sure the House Identifier code e.g. BH0001 is in the camera view when photo is taken]
- Sampling location (e.g., kitchen sink faucet (preferred); Other – bathroom sink faucet; Other - describe)
- Floor of sampling location (Options: main/1st floor, 2$^{nd}$ floor, basement)
- Time since resident last used water in house (hours)
- Time since resident last used water at sampling location (kitchen sink) (hours)
- Sample ID, date, and time
- Flow rate (separate for unfiltered and filtered) Liters per minute [based on time to fill 1L bottle)
- Remarks (other notes)

Field records should also include the following, to the extent information is provided by the resident or observed in the field. The list of observations recorded may include, but is not required to include, the following with a focus on not overly burdening the residents and sampling teams:

- Interior plumbing materials observed (Select all that apply: crosslinked polyethylene (PEX), PVC, galvanized iron, copper, and/or lead; not observed)
- Approximate length (feet) of interior plumbing from tap to the service line (e.g., estimated as straight-line horizontal distance plus 10 ft per floor)
- Any known leaking faucets/fixtures in residence (Options: Yes – describe; No per resident/visual; not observed)
- Any plumbing work completed in the home in the past 6 months (Options: Yes – describe; No per resident/visual; not observed)
- Service line including material observed coming into home (e.g., PVC, galvanized iron, copper, and/or lead; not observed)
- Service line including diameter observed coming into home (e.g., inches or not observed)
- Estimated distance (or pipe length) between the sample tap and the distribution water main (feet; not observed)
- Estimated service line length (feet to the nearest quarter, e.g., estimated as straight-line distance between the back of the home and the far side of the street OR not observed)
- Known physical disturbances such as recent road work or utility work that could disturb the service line near the sampling location [Yes-Describe or none reported/observed]
- Other relevant field observations such as activities completed at the home (e.g., flushing, aerator cleaning) and color, odor, or debris in the water
- Photographs of the sample tap(s), filters, and underlying fixtures and components (through Survey 123) [if photos must be stored outside of Survey123 be sure the House Identifier code e.g., BH0001 is in the camera view when photo is taken]

Another 'daughter' form may be needed to collect field water quality analysis results, such as:

- Address (connect to GIS?)
- House identifier code (from scheduler/master list)
- Sampling location (e.g., kitchen sink faucet (preferred); Other – bathroom sink faucet; Other - describe)
- Floor of sampling location (Options: main/1st floor, 2$^{nd}$ floor, basement)
- Sample date, and time
- Sample type (e.g., UF= Bypassing Filter)
- Sampled Volume (e.g., 5 min fully flushed or 10min fully flushed)
- Water temperature (degrees Celsius- to the nearest degree- whole number)
- Total Chlorine (mg/L) (record as shown on Hach SL1000)
- Free chlorine residual (mg/L) (record as shown on Hach SL1000)
- Remarks (other notes)

## Attachment No. 1B – Field notes (list of fields for Survey 123) for Particle Fractionation and Sequential Sampling

For all applicable data points where resident input is needed there should also be two options "resident declined" and "did not ask"). Specifically, the list of observations regarding plumbing materials recorded may include, but is not required to include, information as described below, with a focus on not overly burdening the residents and sampling teams. However, effort should be made to attempt to collect plumbing material information for the sequential sampling study. Pipe materials will correspond with the water samples collected.

- Address (connect to GIS)
- House identifier letter (from scheduler/master list)
- Year Built (from county Parcel dataset)
- Building type (e.g. Single Family Residential (preferred), multi-family residential, commercial)
- Whole house water treatment? (Options: None, water softener, whole-house filtration; in-line reverse osmosis; Unknown) [Describe any whole house water treatment in Remarks]
- Sampling location (e.g., kitchen sink faucet (preferred); Other – bathroom sink faucet; Other - describe)
- Floor of sampling location (e.g., main/1st floor, 2$^{nd}$ floor, basement)
- Time since resident last used water in house (hours)
- Time since resident last used water at sampling location (kitchen sink) (hours)
- Did resident complete the pre-flush?
- Water meter reading by resident after pre-flush (incl units)
- Photograph of the image captured by the resident of the water meter after pre-flush
- Water meter reading by field team prior to sampling (incl units)
- Sample ID, date, and time
- Sample type (Bypassing any Faucet Filter)
- Liter of water sampled (example- 3.25, 7.25, 14.25) for PC sample
- Flow rate (liters per minute)
- Water temperature (degrees Celsius- to the nearest degree- whole number)
- Interior plumbing materials observed (Select all that apply: crosslinked polyethylene (PEX), PVC, galvanized iron, copper, and/or lead; not observed) and associated:
    - Length of that plumbing material (feet, to the nearest quarter of a foot)
    - Outside diameter of that plumbing material observed (inches, to nearest quarter of an inch)
- Approximate length of interior plumbing from tap to the service line (e.g., estimated as straight-line horizontal distance plus 10 ft per floor) (feet, to the nearest quarter of a foot)
- Any known leaking faucets/fixtures in residence (Options: Yes – describe; No per resident/visual; not observed)
- Any plumbing work completed in the home in the past 6 months (Options: Yes – describe; No per resident/visual; not observed)

- Service line including material observed coming into home (e.g., PEX, PVC, galvanized iron, copper, and/or lead; not observed)
- Service line including diameter observed coming into home (e.g. inches, to nearest quarter of an inch or ; not observed)
- Estimated service line length (e.g. estimated as straight-line distance between the back of the home and the far side of the street, in feet, to the nearest quarter of a foot OR not observed)
- Known physical disturbances such as recent road work or utility work that could disturb the service line near the sampling location [Describe or none reported/observed]
- Other relevant field observations such as activities completed at the home (e.g., flushing, aerator cleaning) and color, odor, or debris in the water
- Photographs of the sample tap(s) and underlying fixtures and components (through Survey 123) [if photos must be stored outside of Survey123 be sure the House Identifier code e.g. BH0001 is in the camera view when photo is taken]
- Remarks (other notes)

Another 'daughter' form may be needed to collect field water quality analysis results, such as:

- Address (connect to GIS)
- House identifier code (from scheduler/master list)
- Sampling location (e.g., kitchen sink faucet)
- Floor of sampling location (Options: main/1st floor, 2$^{nd}$ floor, basement)
- Sample date, and time
- Sample type (Options: Bypassing Filter)
- Sampled Volume (e.g. 5 min fully flushed or 10-min fully flushed)
- Flow rate of water collected for fully flushed samples (liters per minute)
- Water temperature (degrees Celsius- to the nearest degree- whole number)
- Total Chlorine (mg/L) (record as shown on Hach SL1000)
- Free chlorine residual (mg/L) (record as shown on Hach SL1000)
- Alkalinity (mg/L) (record as shown on Hach SL1000)
- pH (std units), determined at field "lab"
- Remarks (other notes)

## Attachment No. 2 – SL1000 Field Reference Guidance


HachSL1000_5ed.pdf

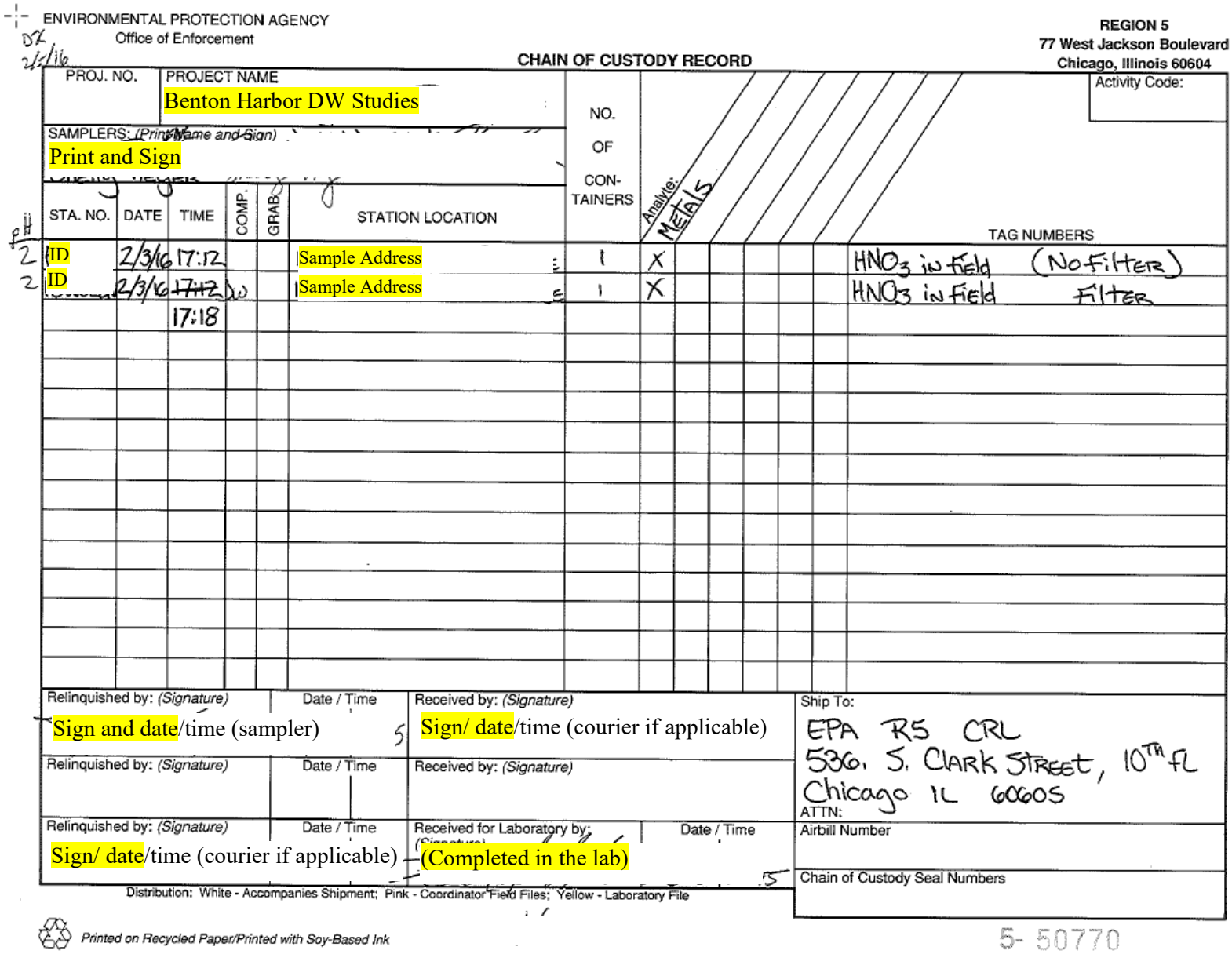

Hach Free Chlorine Method 10260 6th Ed


Hach Total Alkalinity LR Method 10280 4th


Hach Total Chlorine Method 10260 6th Ed

## Attachment No. 3 – Example Chains of Custody Forms

**For CRL (water samples)**



ENVIRONMENTAL PROTECTION AGENCY
Office of Enforcement

REGION 5
77 West Jackson Boulevard
Chicago, Illinois 60604

CHAIN OF CUSTODY RECORD

DX 2/5/16

| PROJ. NO. | PROJECT NAME | NO. OF CONTAINERS | Analyte: METALS | Activity Code: |
|---|---|---|---|---|
| | Benton Harbor DW Studies | | | |

SAMPLERS: (Print Name and Sign)
Print and Sign

| STA. NO. | DATE | TIME | COMP. | GRAB | STATION LOCATION | NO. OF CONTAINERS | Analyte: METALS | TAG NUMBERS |
|---|---|---|---|---|---|---|---|---|
| pH 2 ID | 2/3/16 | 17:12 | | | Sample Address | 1 | X | $HNO_3$ in field (No Filter) |
| 2 ID | 2/3/16 | 17:17 17:18 | | | Sample Address | 1 | X | $HNO_3$ in field Filter |

| Relinquished by: (Signature) | Date / Time | Received by: (Signature) | Ship To: |
|---|---|---|---|
| Sign and date/time (sampler) | | Sign/ date/time (courier if applicable) | EPA R5 CRL<br>536. S. Clark Street, 10TH FL<br>Chicago IL 60605<br>ATTN: |
| Relinquished by: (Signature) | Date / Time | Received by: (Signature) | |
| Relinquished by: (Signature) | Date / Time | Received for Laboratory by: (Completed in the lab) | Date / Time |
| Sign/ date/time (courier if applicable) | | | Airbill Number |
| | | | Chain of Custody Seal Numbers |

Distribution: White - Accompanies Shipment; Pink - Coordinator Field Files; Yellow - Laboratory File

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5- 50770

ENVIRONMENTAL PROTECTION AGENCY
OK
2/5/16
Office of Enforcement

**CHAIN OF CUSTODY RECORD**

REGION 5
77 West Jackson Boulevard
Chicago, Illinois 60604

| PROJ. NO. | PROJECT NAME | Activity Code: |
|---|---|---|
| | Benton Harbor DW Studies | |

SAMPLERS: *(Print Name and Sign)*
Print and Sign

| pH | STA. NO. | DATE | TIME | COMP. | GRAB | STATION LOCATION | NO. OF CONTAINERS | Analyte: Total Organic Carbon | Anions + WQ + Alk | TAG NUMBERS |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ID | 805 | 2/3/16 | | X | Sample Address | 1 | X | | •$H_2SO_4$ + Ice |
| 6 | ID | 805 | 2/3/16 | | X | Sample Address | 1 | | X | Ice |

| Relinquished by: *(Signature)* | Date / Time | Received by: *(Signature)* | Ship To: |
|---|---|---|---|
| Sign and date/time (sampler) | | Sign/ date/time (courier if applicable) | RS CRL 10th floor<br>536 S. Clark<br>Chicago, IL 60605 |
| Relinquished by: *(Signature)* | Date / Time | Received by: *(Signature)* | ATTN: |
| Relinquished by: *(Signature)* | Date / Time | Received for Laboratory by: | Date / Time |
| Sign/ date/time (courier if applicable) | | (Completed in the lab) | Airbill Number |
| | | | Chain of Custody Seal Numbers |

Distribution: White - Accompanies Shipment; Pink - Coordinator Field Files; Yellow - Laboratory File

Printed on Recycled Paper/Printed with Soy-Based Ink

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**For ORD (solid samples)**

**CHAIN OF CUSTODY RECORD**

| CONTACT INFORMATION | PROJECT INFORMATION | **USEPA**<br>Center for Environmental Solutions and Emergency Response<br>26 West Martin Luther King Drive<br>Cincinnati, OH 45268 |
|---|---|---|
| Sampler : | Project Name: Benton Harbor, MI Particulate Characterization | |
| Sampler Contact Info (phone and email): | SharePoint Site: | Sampler Notes: |
| | QAPP #: | |
| | USEPA Contact: Steve Harmon<br>Phone: 513-569-7184<br>Fax: 513-569-7172<br>Email: Harmon.Stephen@epa.gov | |

| Date Sampled | Time Sampled | Sample Description (SEM stub, TEM grid, ultrafilter) | Sample ID | TEM grid box location | Duplicate? | Sampler | Remarks |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
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**Special Instructions:** Ensure petri dishes are sealed around the edges with parafilm and TEM grid boxes are taped shut. Include liter collected for each Sample ID in the notes section

| SAMPLE RECEIPT | Relinquished By: | SAMPLE DISPOSAL |
|---|---|---|
| Total # of Containers: | Date: | Total # of Containers: |
| Chains of Custody in Container Y/ N/ NA | Company: | Disposal Date: |
| Samples intact: Y/ N/ NA | Received By: | Special Instructions: |
| Condition of Samples: | Date: | |
| | Company: | |

## Attachment No. 4- pH Measurement Protocol

pH measurement protocol_R1

## Attachment No. 5- Kemio User Instructions

Kemio User Instructions .docx

# Attachment No. 6- Packing and Shipping Instructions

## Sample Packing Instructions

Supply list:

- Sturdy cooler(s)
- Heavy-duty, 30-gallon trash bags
- Bubble-wrap style materials, suggested (required if any glass sample bottles are to be shipped)
- **For shipment of sample bottles for analysis of TOC/anions/alkalinity:** Fresh ice, approximately 15-25 pounds of ice per large cooler – at least 1/3 of the airspace of the cooler should be ice-filled during moderate weather; more ice should be used if weather is hot (80 F or hotter). Sample containers should be stored on ice as soon as possible after collection. If samples must be held more than a few hours before shipping, fresh ice may be needed for shipping.) **– not required for metals sample bottles**
- Filled and labeled sample bottles, with all lids tightly closed
- Sampling form(s) and chain-of-custody form(s)
- Zip-type plastic bags (Freezer style is best) such as Ziploc (1 per sample)
- Shipping tape
- Completed shipping labels, with pouches if needed (1 per cooler)
- Paper towels

Cooler Packing Instructions:

1. Begin with a dry, sturdy cooler. If the cooler has a drain, the drain should be closed and taped shut.
2. If available, place dry bubble wrap in the bottom and along the sides of the cooler.


3. Open trash bag. Place the trash bag inside the cooler as a liner.

4. **If the cooler will contain sample bottles for analysis of TOC/anions/alkalinity:** Place ice inside Zip type bags then place those in the cooler lined with trash bag along the bottom of the cooler. **Ice may be omitted for coolers containing only metals samples.**
5. Place each sample bottle in Zip type bag then place upright in the bottom of the cooler. Depending on the number of sample bottles, additional cooler(s) may be needed.

6. Double check the chain-of-custody form against the labels and number sample bottles in the specific cooler. If more than one cooler is used, the chain-of-custody form(s) should match the contents of the individual cooler.

8. **If the cooler will contain sample bottles for analysis of TOC/anions/alkalinity:** Place ice in zip type bags on top of the samples, inside the trash bag. Take care to avoid getting any ice in the bottom of the cooler outside the trash bags.
9. After confirming the contents of the cooler, tie the trash bag shut, taking care to press out excess air from the bag. Do not use drawstrings, use the sides of the trash bag to tie the bag shut securely. Check that the cooler lid is able to close (rearrange samples or remove excess air as needed).
10. If the cooler is not full, use additional packing materials (i.e., bubble wrap) to fill remaining airspace.


11. Shut the cooler lid (there should be no gap) and use packing tape to bind the cooler shut. Packing tape should make two to three full passes around the cooler at two different places.

12. Affix the shipping form to the outside of the cooler if it is to be shipped otherwise write on tape the lab it will be delivered to.

*If the cooler will contain sample bottles for analysis of TOC/ anions/alkalinity: If the last pick-up is missed, the cooler should be repacked with fresh ice.

Photo credit: https://www.youtube.com/watch?v=iSO7gjD5KF0 (Pace Analytical Services: How to Pack a Cooler)

## Sample Delivery and Shipment Addresses:

Water Samples (to be analyzed for metals and TOC/anion/Alkalinity) to CRL should be addressed to:

Robert Snyder
US EPA Region 5
Chicago Regional Laboratory
536 South Clark Street, 10th Floor
Chicago, IL 60605

Before shipping samples, please notify the CRL Sample Custodian, Rob Snyder, (312-353-9083, Snyder.robert@epa.gov) to arrange for sample receipt.

Solid Samples (to be analyzed for particulate characterization) to Andrew W. Breidenbach Environmental Research Center (AWBERC) should be addressed to:

Steve Harmon
US EPA

ORD, CESER, WID, DWMB
26 W. Martin Luther King Dr.
Cincinnati, OH 45268
When samples are shipped please send the tracking number to: Steve Harmon, Christina Bennett-Stamper, and Mike DeSantis (Harmon.Stephen@epa.gov, bennett-stamper.christina@epa.gov, desantis.mike@epa.gov).

## Attachment No. 7- Field Training Log

FieldTrainingLog_211028.docx

## Attachment No. 8- User Manuals for the filter types distributed by BCHD

PUR fm3333b and FM-2000b.pdf

Brita_SAFF-100_Users Guide.pdf

ZeroWater guidance.pdf

ZeroWater guidance sheet.pdf