Bottle Washing
LDPE bottles must be acid washed prior to use in trace element analyses. The process should take two weeks.
• Rinse bottles three times with “house” DI water.
• One week in 3M HCl (ACS Plus) bath.
• Rinse three times with Milli-Q.
• One in 0.5M distilled HCl bath.
• Rinse three times with Milli-Q then fill with Milli-Q. Acidify to 0.1M HCl with 6M distilled HCl and place in Ziploc bags for storage.

Falcon tubes do not need to be cleaned as extensively as they are not used for trace element analyses.
• Rinse three times with “house” DI water.
• One week in 3M HCl (ACS Plus) bath.
• Rinse three times with “house” DI water and place in Ziploc bags for storage.

Filter Types/Cleaning Methods
1. Polycarbonate/Teflon filters
   These can be washed in large batches (~100 filters) using the blue lidded plastic bins. Each of the baths should be made to 2 liters total volume. The volumes can be reused several times.
   • 4M HNO₃ (ACS Plus) for 1 week
   • Transfer to Milli-Q bath and batch rinse 5 times (you can also use a pH strip to check that the rinse water pH has risen to 5-6 but it is not necessary)
   • Transfer to 3M HCl (ACS Plus) for 1 week.
   • Repeat batch rinse with Milli-Q.
   • Transfer to 0.5M distilled HCl for 1 week.
   • Repeat batch rinse.
   • Using plastic forceps and Milli-Q squeeze bottle, individually rinse filters and lay them in the large, white plastic bin with plastic grating lining the bottom. When all filters are rinsed, place the bin inside the flow bench overnight or until filters are dry. Once dry, place the filters shiny side up in petrislides. The petrislide do NOT need to be acid washed.

2. Polyether sulfone/Metricel membrane/Pall GN-6
   • 3M HCl (ACS Plus) for 1 week.
   • Transfer to Milli-Q bath and batch rinse 5 times (you can also use a pH strip to check that the rinse water pH has risen to 5-6 but it is not necessary)
   • Repeat 3M HCl (ACS Plus) for 1 week.
   • Repeat batch rinse with Milli-Q.
   • Transfer to 0.5M distilled HCl for 1 week.
   • Repeat batch rinse.
   • Using plastic forceps and Milli-Q squeeze bottle, individually rinse filters and lay them in the large, white plastic bin with plastic grating lining the bottom. When all filters are rinsed, place the bin inside the flow bench overnight or
until filters are dry. Once dry, place the filters shiny side up in petri slides. The petri slide do NOT need to be acid washed.

3. Whatmann GFF/Millipore Quartz
   • Place filters on top of a glass Petri dish in furnace
   • Set the temperature to 450 degree for 5 hours
   • Once cooled, place filters in 3M HCl (ACS Plus) for 1 week.
   • Transfer to Milli-Q bath and batch rinse 5 times (you can also use a pH strip to check that the rinse water pH has risen to 5-6 but it is not necessary)
   • Transfer to 0.5M distilled HCl for 1 week.
   • Repeat batch rinse.
   • Using plastic forceps and Milli-Q squeeze bottle, individually rinse filters and lay them in the large, white plastic bin with plastic grating lining the bottom. When all filters are rinsed, place the bin inside the flow bench overnight or until filters are dry. Once dry, place the filters shiny side up in petri slides. The petri slide do NOT need to be acid washed.

Aerosol Filter Extraction

Clean nitrile gloves are worn at all times when handling filters and conducting the filter leaching. Use a pair of clean plastic tweezers to handle the filters. It is best to lay some large Kimwipes down on the counter to provide a clean work surface. All work should be done inside a flow bench or hood.

It is best to rinse the 125 mL LDPE sample bottles ahead of time (three times each with Milli-Q water), as this is a time consuming process. Falcon tubes do not require rinsing. Label each bottle and tube with the same information from the petri slide (generally the data and soluble/insoluble). Record the LDPE bottle numbers and their corresponding filter data in your log book. Write the bottle number of the leach on the bottom of the corresponding Petri slide, i.e. DI #1498. The Falcon tubes can be labeled with the collection date.

100 mL Ultrapure (Milli-Q) Water Leaches – 18.2MΩ:
   • The Milli-Q should be allowed to equilibrate with the air so that the pH is about 5.6.
   • Fill the labeled 1-L LDPE bottle with DI, leaving some head space. Cap and shake the bottle, open the cap to allow the head space air to exchange, then re-cap the bottle and shake again. Do this five times then check the pH on a 10 mL subsample of the Milli-Q (poured into a clean, rinsed 25mL LDPE bottle) using the pH meter. Repeat the air equilibration until the pH is between 5.5 and 5.7.
   • Rinse the filtration rig 3 times with Milli-Q and shake out the excess water prior to the first use and between each subsequent filter leach.
   • Pour 100mL Milli-Q into a clean plastic graduated cylinder.
   • Place a mixed cellulose ester backing filter in the rig and wet slightly with Milli-Q water. This will aid in laying the polycarbonate sample filter flat in the rig. Tightly seal the filter rig.
• Connect the length of tubing from the vacuum pump to the “Pump” port on the shoulder of the bottom reservoir and turn on the pump.
• Cover the opposite hole in the rig with a clean, gloved finger and gently pour the volume of Milli-Q onto the filter within a few seconds, making sure that the entire filter is covered with solution. Allow the filter to suck dry for 5-10 seconds, then slowly remove the pump tubing from the rig to allow the vacuum to dissipate smoothly.
• Turn off the pump and carefully pour 25mL of the leach solution out of the filtration rig (through the finger plug hole, not the Pump hole!) and into a Falcon tube. Pour the remainder into a pre-labeled 125 mL LDPE bottle.
• Freeze the Falcon tube sample. The trace element sample can be acidified at this time by adding 300µL of 6M Teflon distilled HNO₃.
• Rinse filtration rig. The backing filter can be retained for multiple samples. We have used this same technique for filtering ocean samples with much lower dissolved metal concentrations without any evidence of cross contamination.

**Teflon Filter Extraction**

- Milli-Q will not flow through a Teflon filter; therefore sonication, following Ying Chen’s method, must be used to extract soluble elements.
- Cut the filter in half.
- Fill a polypropylene jar with 50mL of Milli-Q, add filter and seal. Seal lid of jar with Parafilm
- Sonicate for 30 minutes.
- Filter resulting solution through an acid-washed 0.4µm filter.
- Subdivide for ICP and IC analyses.

**Ion Chromatography** (consult with Rob Franks regarding IC use)

The frozen, unacidified aerosol extracts are analyzed for major anions and oxalate in two separate analytical runs. Major anions are measured using a 25µL sample loop and oxalate with the 200µL sample loop.

**ICP-MS** (consult with Rob Franks regarding ICP use)

Samples for ICP analysis are transferred by pipette to acid washed 7mL scintillation vials. Sample volume is 2mL. There is an ICP sequence specifically designed for analysis of soluble and digested aerosols.

1. **Standard Preparation (see excel sheet “ICPMS Standards 060409”)**
   - There are two primary standards used to calibrate. Each is made through several steps using stock solutions. Standards should be made gravimetrically but the following are in nominal volumes.
   - Standardization is completed using 5 solutions: Acid Blank, “Low” standard, “High” standard, 50% “Low”, and 50% “High”. The 50% standards are made by dilution with the Acid Blank. These standards should be spiked with the same volume ratio as the samples, e.g. 200µL spike per 2mL.
• Other stock solutions made in 2% HNO₃ were 1000ppb Ti, 10ppm Fe, and 10ppm Al
  o “Low” mixed standard – contains low concentrations of most of the trace elements and is derived from SPEX Multi-element Solution 2 (10ppm).
    ▪ 100µL SPEX Multi-element Solution 2 – Final=10ppb
    ▪ 10mL 2ppm P standard (in Falcon tube) – Final=200ppb
    ▪ 10µL 1000ppb Ti – Final=1ppb
    ▪ 90mL Milli-Q
    ▪ 2mL 6M distilled HNO₃
  o “High” mixed standard – contains several alkalis from SPEX Custom Ion Standard as well as higher concentrations of Fe and Al
    ▪ 1mL SPEX Custom Ion Standard
    ▪ 1mL 10ppm Fe
    ▪ 2mL 10ppm Al
    ▪ 93mL Milli-Q
    ▪ 3mL 6M distilled HNO₃
  o 2% HNO₃/Acid Blank
    ▪ 96.76 mL Milli-Q
    ▪ 3.24mL 6M distilled HNO₃

2. Spike Solution Preparation
• Samples are spiked with an internal standard to monitor instrument drift during analysis - 200µL spike per 2mL sample
  o Spike = 100ppb Rh, 1ppm Sc
  o To make 50mL of spike
    ▪ 5mL Sc stock solution (10µg/mL)
    ▪ 0.2mL of 1ppm Rh
    ▪ 43.69mL Milli-Q
    ▪ 1.44mL distilled HNO₃

Aerosol Sample Digestion

Digesting the insoluble aerosol fraction requires the use of concentrated hydrofluoric acid (HF). HF is extremely dangerous and potentially lethal; therefore users should receive specific safety training and follow lab safety guidelines.

1. Microwave – Polycarbonate/HPWP
• This method can be used to dissolve the entire filter or a fraction of the original.
• Step 1: Microwave program “Chen PC”
  o 3mL conc. HCl + 3mL conc. HNO₃ + 1mL conc. HF
• Step 2: Program “W41 Step 2”
  o Add 2mL 5% Boric Acid
• Decant the digest solution from the digestion vessels into a wide-mouth 60mL LDPE bottle.
• Rinse the inside of the vessel three times with Milli-Q and pour into the 60mL bottle.
• Place bottles on ~70°C hotplate with caps off and evaporate to dryness.
• Rehydrate with 50mL Milli-Q and acidify with 200µL 6M HNO3.

2. Microwave – Teflon
   • Digest half the filter. This filter section will not have been extracted and therefore represents the “total” aerosol fraction (insoluble + soluble).
   • Step 1: Microwave program “Teflon”
     o 2mL conc. HNO3
   • Step 2: Microwave program “Teflon St2”
     o Add 0.1 mL conc. HF
   • Rinse, evaporate, and rehydrate following above.

3. Microwave – Vessel Cleaning
   • Rinse vessel five times with Milli-Q.
   • If there is filter residue stuck in vessel, a pipette tip can be used to scrape off as much as possible.
   • Fill vessel with 40-50mL of 1M HNO3.
   • Run program “Clean”
   • Pour off 1M HNO3 (this can be retained for reuse) and rinse five times with Milli-Q.

4. Hotplate – HA/GN-6
   • Digest half the filter in 15mL Teflon jars.
   • Step 1: Add 8mL Milli-Q, 0.5mL HNO3, 0.4mL HF
   • Place on 80°C hotplate and take to dryness.
   • Step 2: Add 2mL Milli-Q, 0.3mL HNO3, 0.3mL HCl, 0.1mL HF
   • Place on 80°C hotplate and take to dryness.
   • Fill graduated cylinder with 50mL with Milli-Q and use to rinse Teflon jar into narrow-mouth 60mL LDPE bottle. Acidify with 200µL 6M HNO3.
   • To Clean: Rinse jar five times with Milli-Q.
   • Use a Kimwipe to wipe out any residue and fill with 1M HNO3. Seal jar and place on 80°C hotplate overnight.
   • Pour off 1M HNO3 (this can be retained for reuse) and rinse five times with Milli-Q.