

Advanced Institute on Health Investigation and Air Sensing for Asian Pollution

PM sampling procedures for source samples

Dr. Kin-fai Ho and Dr. Fabienne Reisen

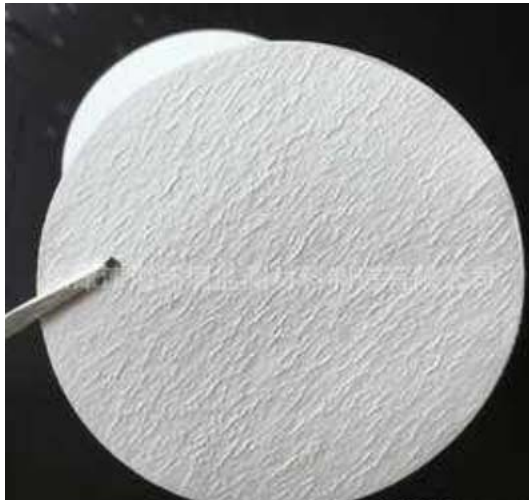
5 September, 2019

Taipei

Filter preparation

Quartz filter

(47mm, Whatman QMA;
47mm, PALL)



Burn in muffle furnace:
at 600 °C for 4 hours

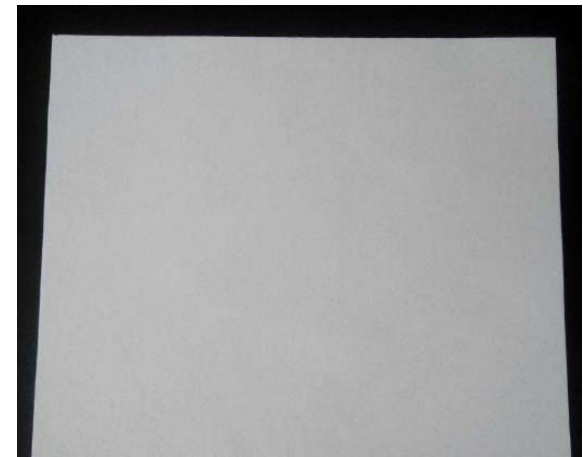
Teflon filter

(47mm, Whatman PTFE;
47mm, PALL)



Quartz filter for Hi-vol

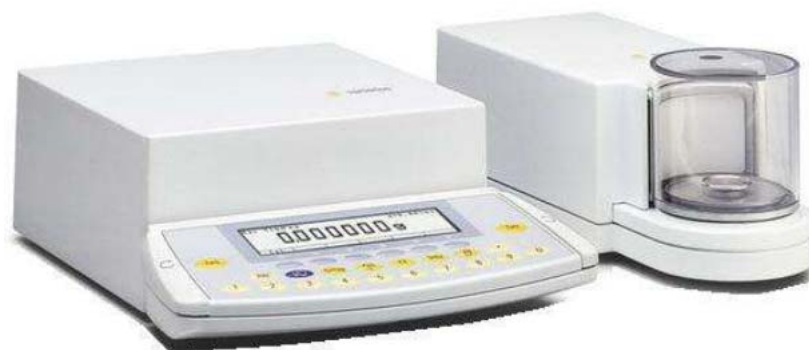
(Whatman QMA)



Burn in muffle furnace:
at 600 °C for 4 hours

Filter weighting

- Equilibrated at a controlled temperature (20~23 °C) and relative humidity (35~45%) for 24 h
- Each filter should be weighed twice before and after sampling
- Precision: <15 µg per filter before sampling and <20 µg after sampling



M5 electronic microbalance (± 1 µg sensitivity, Sartorius, Gottingen, Germany)

Filter storage

Petri Dish



Cleaning before use:

- Soak in acid solution (2% nitric acid) for 24h
- Cleaning with deionized water three times
- Ultrasonic 30 min and wash three times again
- Drying with oven at $\sim 40^\circ\text{C}$

Aluminium foil



Before use:

- Burn in furnace at 350°C for 3 hours

Outdoor sampling

- Instruments installed at ~ 1.5 m from ground level
- The location should be located near the selected source and have no interferences from other sources
- Do not install near the wall or corner (at least 1.5 m away)
- Shelters for the instruments inlet in case of rains



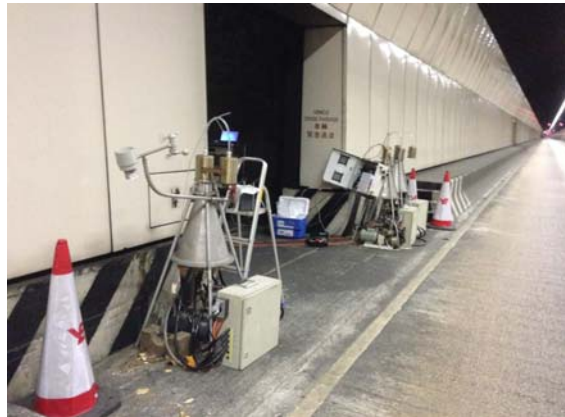
Outdoor source sampling

Vehicular emissions: including diesel, gasoline and nature gas etc.

Biomass emissions from woods, straw, garbage etc.



Roadside sampling site



Tunnel sampling



Wildfire sampling

Indoor source sampling

- PM_{2.5} can be collected near the chimney or near the combustion process

Cooking

Near the stove



Near the Chimney



Residential combustion

Near the stove



Near the Chimney



Mini-vol operation

1. Power on

- Connect the power supply;
- Install the battery into the instrument battery slot



Mini-vol operation

2. Install a filter

- Clean the tweezers with clean paper;
- Carefully cover the filter holder cover after installing the filter membrane; (pay attention to the front and back of the filter membrane)
- Tighten sampling head, and insert the sampling head into the mini host and press it down until it doesn't move (Remember not to push it too hard, just press it down)



Mini-vol operation

3. Switch on and off the instrument

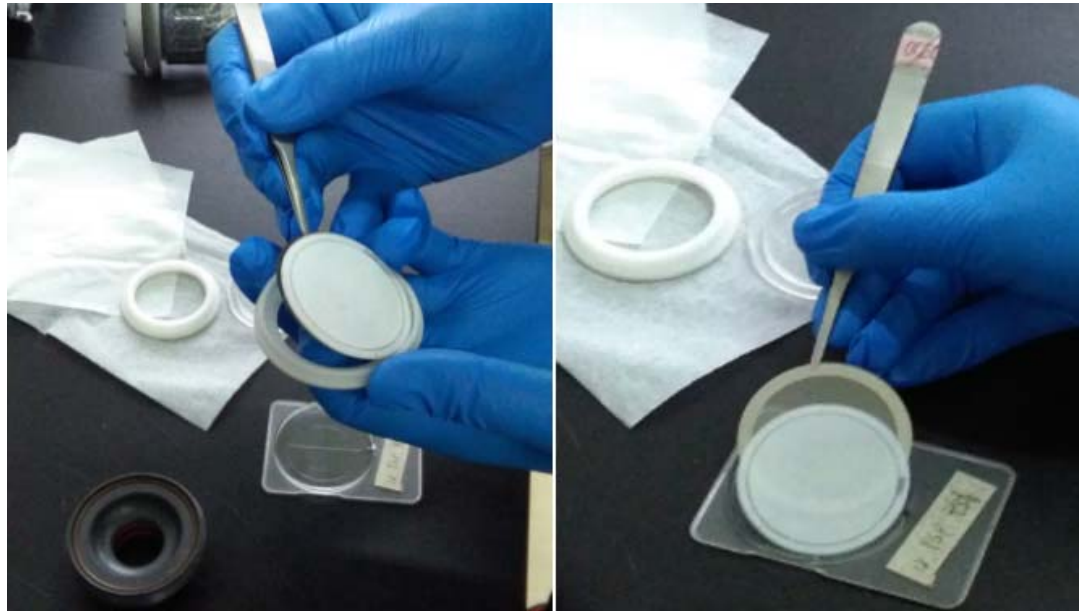
- Press button “ON/AUTO/OFF” to “ON” position to switch on Mini-Vol.
- The flowrate on the flowmeter should be “5”.
- Press button “ON/AUTO/OFF” to “OFF” position to switch on Mini-Vol.



Mini-vol operation

4. Collect after-sampling filter

- Unscrew the base of sampling head, take out the filter holder, and place the membrane holder cover on the dust-free paper.
- Use the fingers of your left hand to push out the side of the mesh, and then clamp the mesh with tweezers and slowly put the filter film back into the clip.



Hi-Vol operation

1. Filter loading

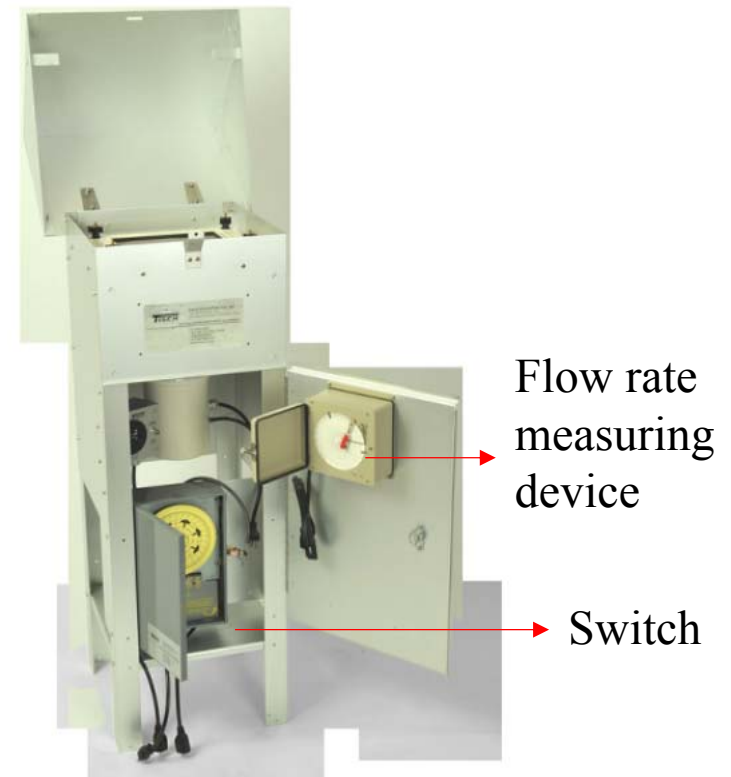
- Open the filter cover;
- Clean the tweezers with clean paper;
- Put the filter on the sampling area (pay attention to the front and back of the filter);
- Close the cover carefully



Hi-Vol operation

2. Switch on and off the instrument

- Put the recoding paper on the pressure recorder to record the flow rate ($\sim 1\text{m}^3/\text{min}$).
- Turn on the instrument
- Turn off the instrument after sampling

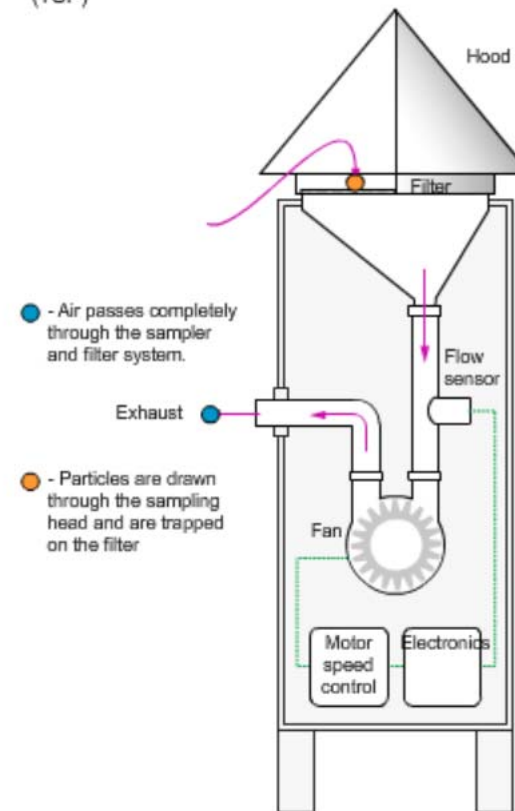


Hi-Vol operation

3. Filter collection

- Remove the filter cover carefully;
- Remove the sampled filter without tearing or touching the collected surface;
- Put the filter in prepared aluminium foil

High volume sampler
for Total Suspended Particulates
(TSP)



Quality control

- Triplicated samples should be collected for each source
- Field blank filter should be collected for each source

Sampling log sheets

Sampling date: _____
Site ID: _____

Field Log Sheet for Mini Sampler

A) Sampling Preparation:
(mark ✓ as appropriate)

ice bag	memory stick	gloves	kimwipes	forcep	key	DryCal and Tubes
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

B) Pre-sampling:
Pre-sampling Worked By: _____
Date of Visit: _____ Arrival Time: _____ Departure Time: _____

Operation Procedures:
(mark ✓ as appropriate)

1. Check the clock on the Mini ☐
2. Change the battery for Mini ☐
3. Sampling date: _____
4. Record the sampling information as follow ☐

Sample ID ^a (Description)	Sampler ID	Initial Flow (LPM) Q_{net}/Q_{int} ?	Start Time (hh:mm)	Stop Time (hh:mm)	Initial Elapsed Time (Mini Only)	Pressure Temp

5. Set the cursor at "Auto" position for Mini ☐
6. Collect the filter pack of BGI and put it in aluminum foil immediately ☐

C) QA Checklist:
Checked by: _____

(mark ✓ as appropriate)

1. Recheck the timer ☐
2. Set the cursor at "Auto" position for Mini ☐

D) Post-sampling:
Post-sampling Worked By: _____
Date of Visit: _____ Arrival Time: _____ Departure Time: _____

Operation Procedures:
(mark ✓ as appropriate)

1. Check final flow rates for each Mini & record them in the following table ☐
2. Collect the samples and put it in respective petrislide ☐
3. Ensure the petrislide is tied by rubber band ☐
4. Put samples in a new zip lock bag and put in ice bag ☐

Sample ID ^a (Description)	Sampler ID	Fin. Elapsed Time (Mini)/ Fin. Vol. (BGI) V_{net}/V_{int} ?	Final Flow (LPM) Q_{net}/Q_{int} ?	Broken samples? (Y/N)	Pressure Temp

Remarks: _____

Appendix A

- Pre-sampling
- Check list
- Data recording

- Post-sampling
- Check list
- Data recording

Sample storage and transportation

- Blank samples before sampling should be stored and transported under sealed and dark conditions. If possible, they can be placed in a 0°C constant temperature refrigerator or in an ice box with blue ice.
- Filters after sampling are loaded into the film clip, aluminum foil shall be used to avoid light packaging, and then put into a self-sealing bag for preservation. The filter sample shall be stored in the refrigerator at -20°C as soon as possible, and the transportation shall be carried out in the ice box with blue ice.
- All collected samples shall be analyzed chemically within one month after collection. If the analysis cannot be done in time, they shall be stored in a refrigerator at -20°C to reduce the loss of volatilization. Before analysis, it shall be put into the normal temperature thermostat and raised to room temperature.

Data collected finally

- Details of the sampled source
- Filter type and filter ID
- Sampling date and time
- Sampling flowrate
- Temperature and weather at sampling date for reference

in vitro experiments for cytotoxicity

➤ **Reactive oxidative species (ROS):**

oxidative potential of PM_{2.5} from different sources

- Free for first 20 samples and \$150 per sample for additional samples

➤ **8-hydroxy-2'-deoxyguanosine (8-OHdG):**

DNA damage to cells caused by PM_{2.5}

- Free for first 20 samples and \$150 per sample for additional samples

➤ **Interleukin-6 (IL-6):**

Inflammatory responses caused by PM_{2.5}

- Free for first 20 samples and \$120 per sample for additional samples

Teflon Filter - Analysis

Analysis	Instrument	Type	Cost (USD)
Gravimetric mass	Microbalance	Non-destructive	
Elemental composition	X-ray fluorescence (XRF)	Non-destructive	\$40 (GNS)
	Ion beam analysis (IBA)	Non-destructive	\$120 (GNS)

Elements analysed		
Hydrogen (H)	Calcium (Ca)	Nickel (Ni)
Sodium (Na)	Titanium (Ti)	Copper (Cu)
Aluminium (Al)	Vanadium (V)	Zinc (Zn)
Silicon (Si)	Cobalt (Co)	Selenium (Se)
Sulfur (S)	Chromium (Cr)	Bromine (Br)
Chlorine (Cl)	Manganese (Mn)	Lead (Pb)
Potassium (K)	Iron (Fe)	Phosphorous (P)



Teflon Filter - Analysis

Analysis	Instrument	Type	Cost (USD)
Water-soluble ions	Ion Chromatography	Destructive	\$170 (CSIRO)
Anhydrous sugars	High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD)	Destructive	

Sample preparation

- extracted in 10 ml of 18.2 mΩ de-ionized water
- preserved using 0.1 ml of chloroform

30 samples at no cost for water-soluble ions and anhydrous sugars

For any collaborative work (e.g. being involved in the science and not solely providing analytical services), this cost can be reduced to 60% of the full-recovery cost.

Ion Chromatography & HPAEC-PAD

Ion Chromatography	
Sodium (Na^+)	Nitrate (NO_3^-)
Ammonium (NH_4^+)	Sulfate (SO_4^{2-})
Potassium (K^+)	Oxalate (C_2O_4^-)
Magnesium (Mg^{2+})	Phosphate (PO_4^{3-})
Calcium (Ca^{2+})	Formate (HCOO^-)
Chloride (Cl^-)	Acetate (CH_3COO^-)
Bromide (Br^-)	Methanesulfonate (MSA^-)
Fluoride (F^-)	



HPAEC-PAD	
Levogluconan	Arabitol
Mannosan	Mannitol
Galactosan	Sorbitol
Glucose	

Quartz filter - analysis

Analysis	Instrument	Type	Cost (USD)
Elemental composition	ICP-MS XRF	Destructive Non-destructive	\$40(GNS)
Water-soluble ions	Ion Chromatography	Destructive	\$170 (CSIRO)
Anhydrous sugars	High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD)	Destructive	

Sample size – 1/8 to 1/4 of quartz filter (depending on loading)

Sample preparation

- extracted in 10 ml of 18.2 mΩ de-ionized water
- preserved using 0.1 ml of chloroform

Quartz filter - analysis



Analysis	Instrument	Type	Cost (USD)
Organic & elemental carbon	Thermal/optical carbon analyser	Small punch (1cm ²)	\$100 (CSIRO)
Organic compounds (e.g. PAHs)	TD-GC/MS	Destructive	\$250 (CUHK)

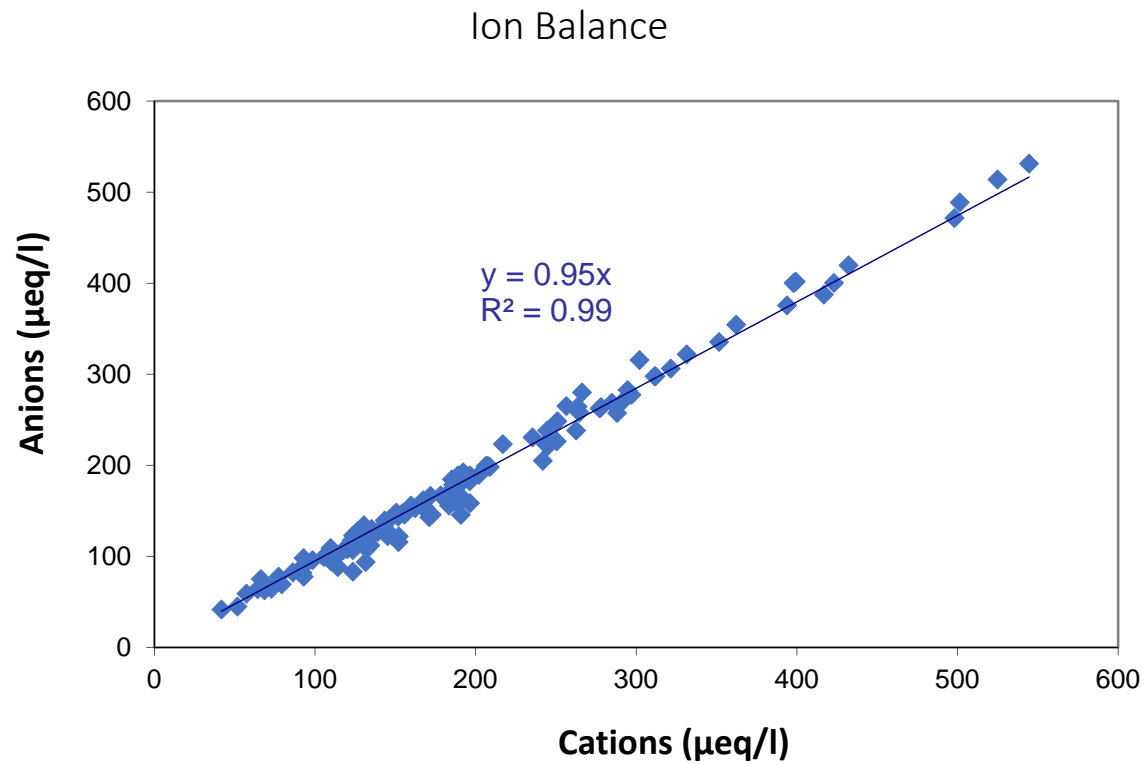
Multi-wavelength Carbon analyser

- Distinguish black carbon from brown carbon
- effectively measure carbon concentrations between 0.05 – 750 $\mu\text{g C cm}^{-2}$, with uncertainties in OC and EC of $\pm 10\%$.

CSIRO can offer 30 samples for OC/EC analysis at no cost

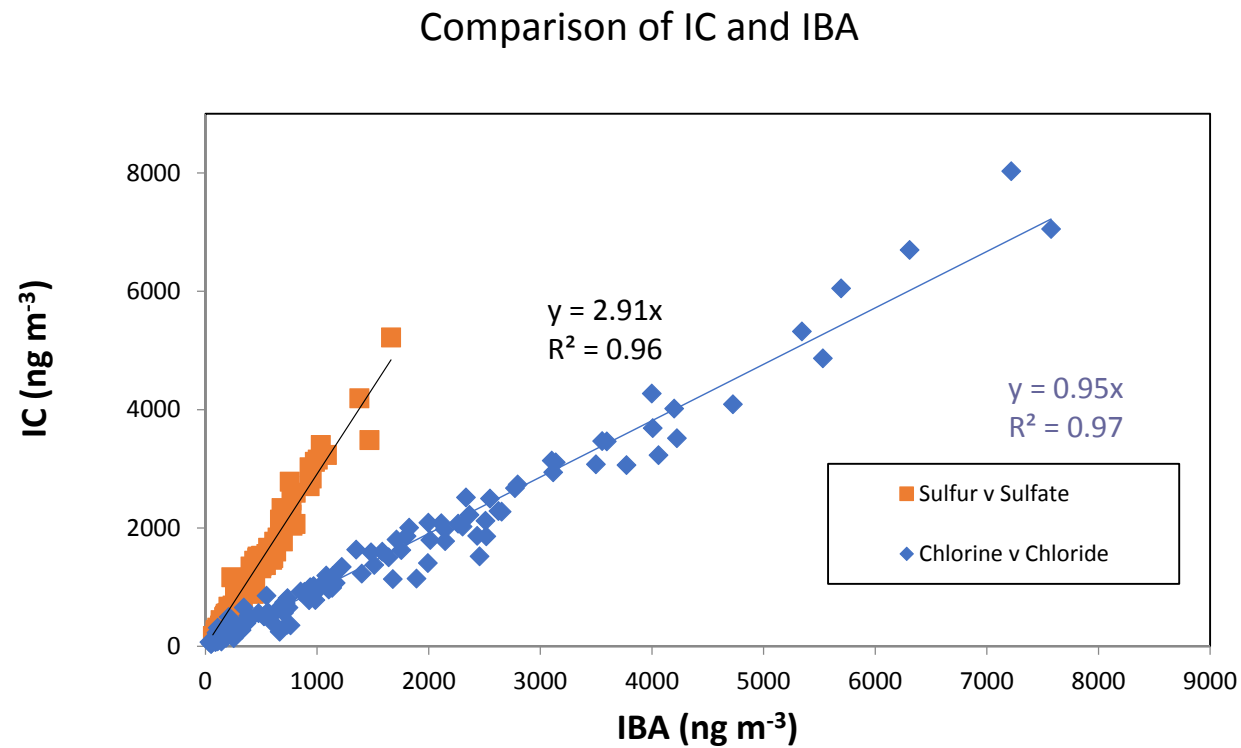
CUHK can offer 20 samples for PAHs at no cost

Data quality



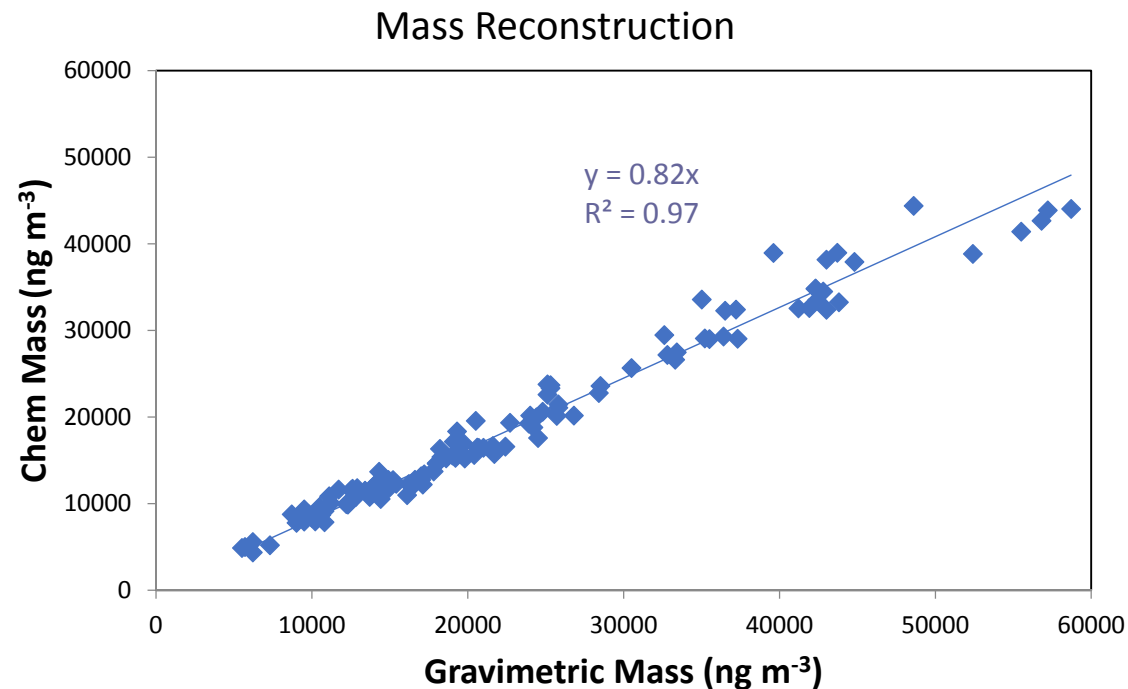
Ion Balance is close to electroneutrality.

Data quality



Chlorine should equal chloride and sulfate should be 3 times sulfur

Data quality



82% of the gravimetric mass accounted for.

- Filters weighed at 40-50% RH
- Mass difference could be water uptake by the aerosol on the filter

Identifying/naming sources using chemical composition

Chemical composition of PM:

- source of the particles (or precursor gases)
- chemical transformations in the atmosphere or within the particles themselves



Use it to indicate the source of the particles

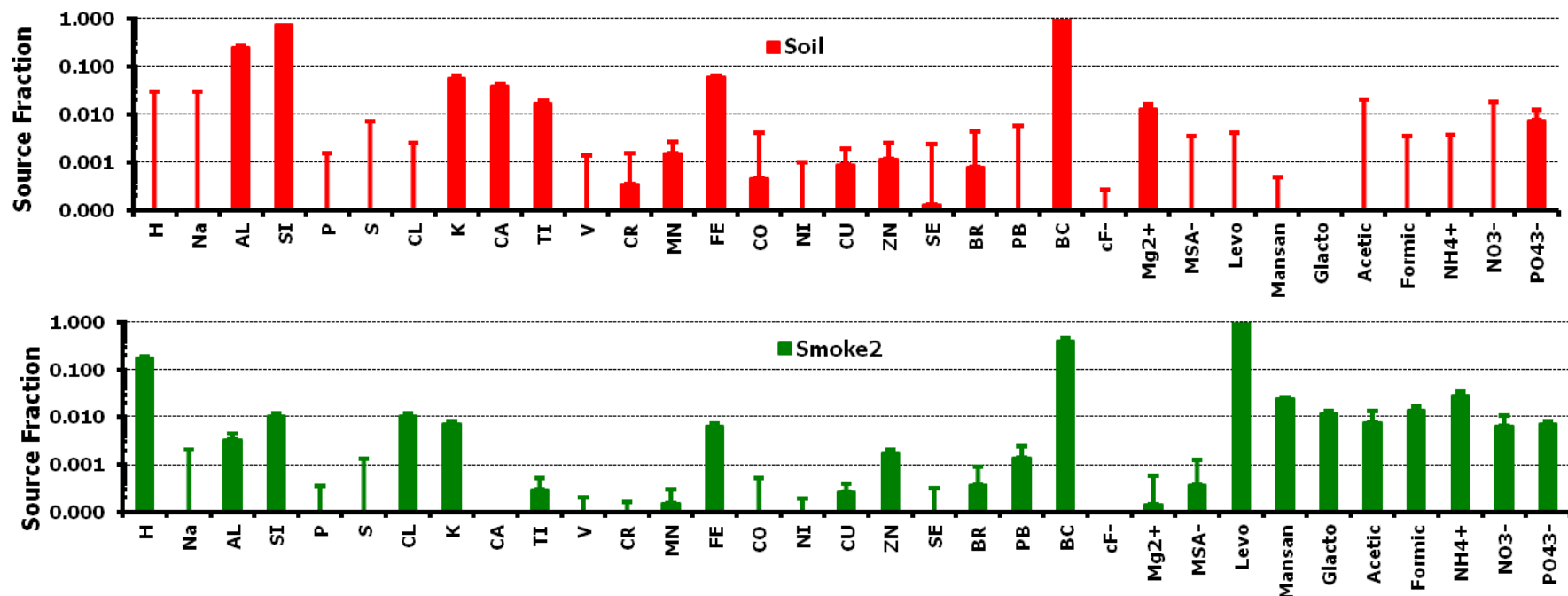
- unique tracer (e.g. levoglucosan)
- ratios of species, e.g. $[\text{Na}^+/\text{Mg}^{2+}]$ for sea salt and $[\text{Si}/\text{Al}]$ for crustal dust source.

Many compounds may have a number of different sources

e.g. EC from biomass burning, industrial emissions, and vehicle emissions

Characterising sources

- Data series – diurnal and seasonal variations
- Unique tracers (e.g. levoglucosan)
- Species ratios
- Fingerprinting



Sources and markers

Dominant sources	Marker species
Soil	Non sea-salt calcium (Ca), Silicon (Si), Iron (Fe), Aluminium (Al), Titanium (Ti), Si to Al ratio
Sea salt	Sodium (Na), Chloride (Cl), Magnesium (Mg), Na to Mg ratio
Biomass burning	Levoglucosan, OC1 (fresh wood smoke), Potassium (K), Black carbon (BC)
Industry/vehicles	BC, Sulfate (SO_4^{2-}), Iron (Fe), Zinc (Zn), Manganese (Mn), Copper (Cu)
Secondary sulfate (power stations)	Ammonia (NH_4^+) and SO_4^{2-}
Secondary nitrate	NO_3 and includes some NH_4^+ , Cl, Na, OC
Industry aged sea salt	Na, Mg, SO_4^{2-} and with almost no Cl
Bioaerosol	Arabitol, Mannitol, Cl, SO_4^{2-} , Fe, Mg