

Aerosol and Rainfall Sampling and Analysis for GEOTRACES

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NSF/OCE funding to acquire and validate aerosol and rain sampling equipment for use on all US-sponsored GEOTRACES cruises

GEOTRACES Hi-Vol Aerosol Samplers: Tisch-5170VBL (equipped with brushless motors) on RSMAS roof in September 2008 for 1st GEOTRACES Aerosol intercalibration experiment.

Shipboard deployment would be on 03 or 04 decks (as high as possible). Sampling (ON/OFF) is controlled by wind speed and sector.



1st and 2nd Aerosol samplers use 20cm x 25cm filters:
Whatman-41 (pre-cleaned) for inorganic TEIs and quartz
microfiber (pre-baked) for N isotopes and organics.

Flow rates are 1.2 m³/minute; 24-hour integrated sampling

Filters can be subsampled for many groups and TEIs;
Remaining filter will be archived (frozen).



3rd Aerosol sampler accepts a “Sierra-style” slotted impactor for size-fractionation studies (needed for modeling dry deposition and studies of particle chemistry as a function of particle size).

>7.2, >3.0, >1.5, >0.95, >0.49, and <0.49 μm particle cut-offs.

Filters can be subsampled; archived.



Event-based rainfall sampling with modified N-CON rain samplers. Lid design and movement minimizes splash into the bucket.

One sampler for unfiltered rain; 2nd sampler equipped with in-line filtration (47 mm, 0.45 μ m Millipore HA) for filtered rain samples.

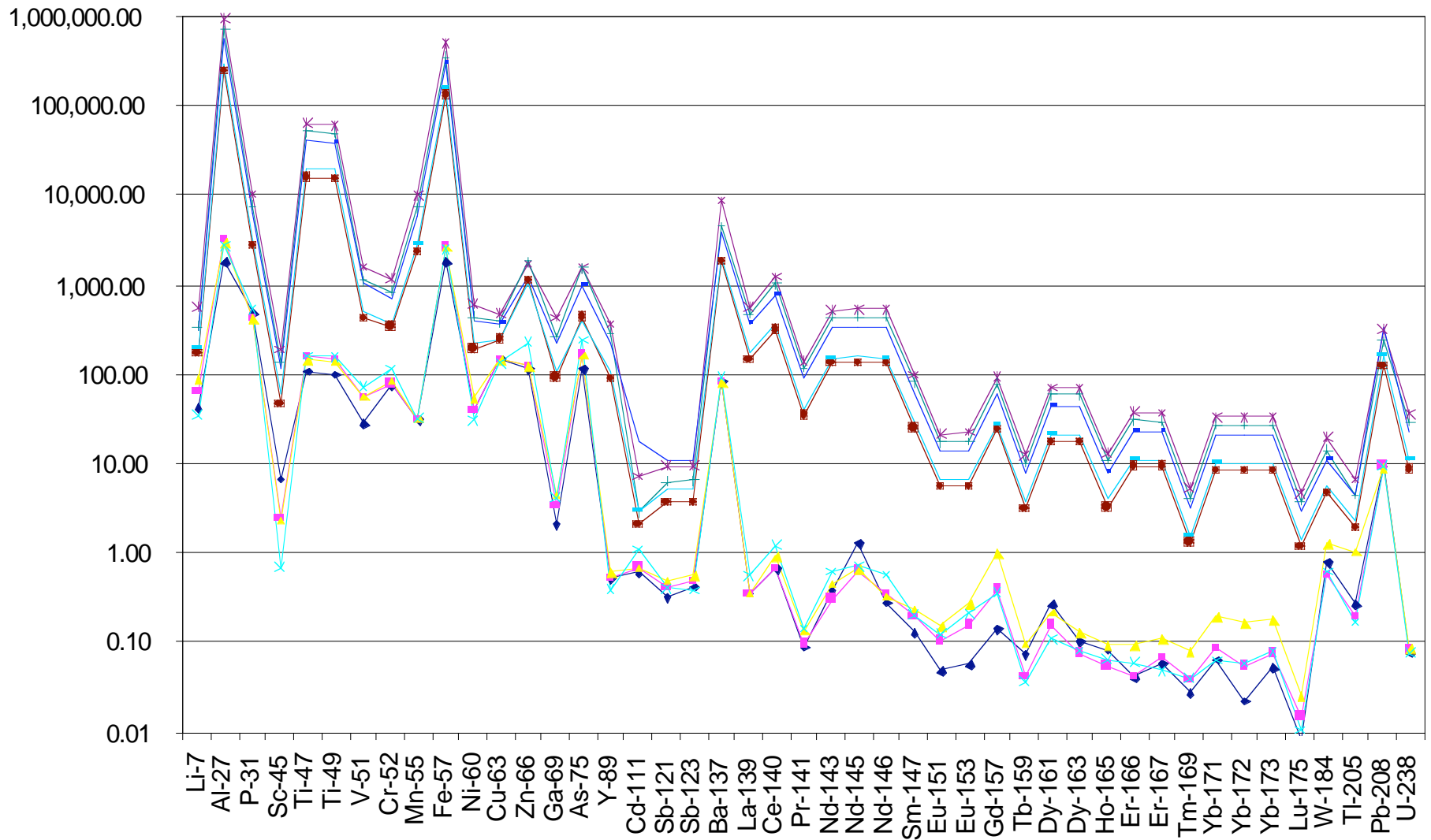
Pre-cleaned HD polyethylene funnels (attached to 500mL Nalgene receiving bottles) are inserted into the buckets.

25 cm funnel diameter; 1 cm rain yields 490 mL.

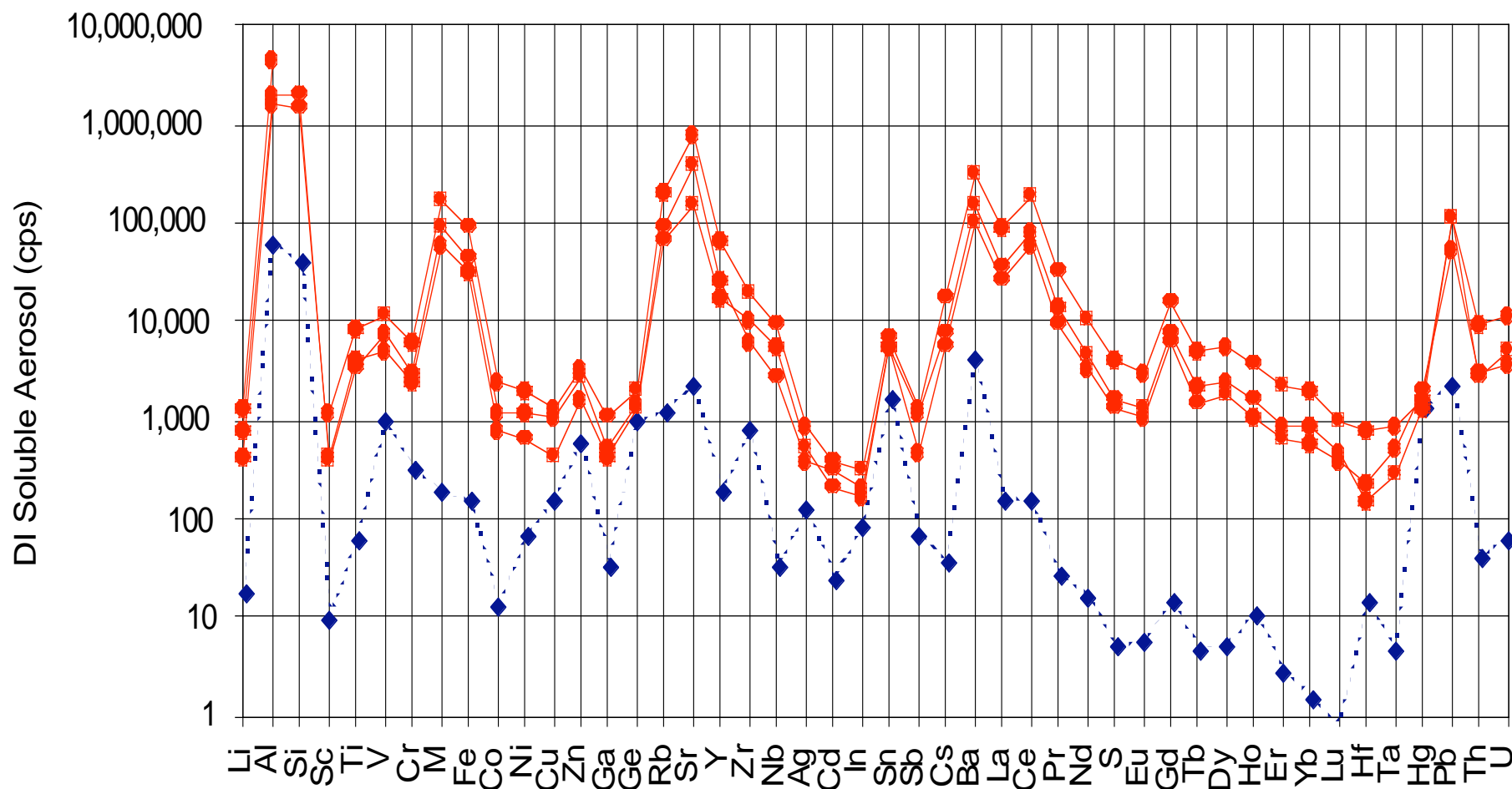


Many elements are detectable in aerosol samples from Barbados (Prospero) on hi-vol Whatman-41 filters vs. blank filter digestions.

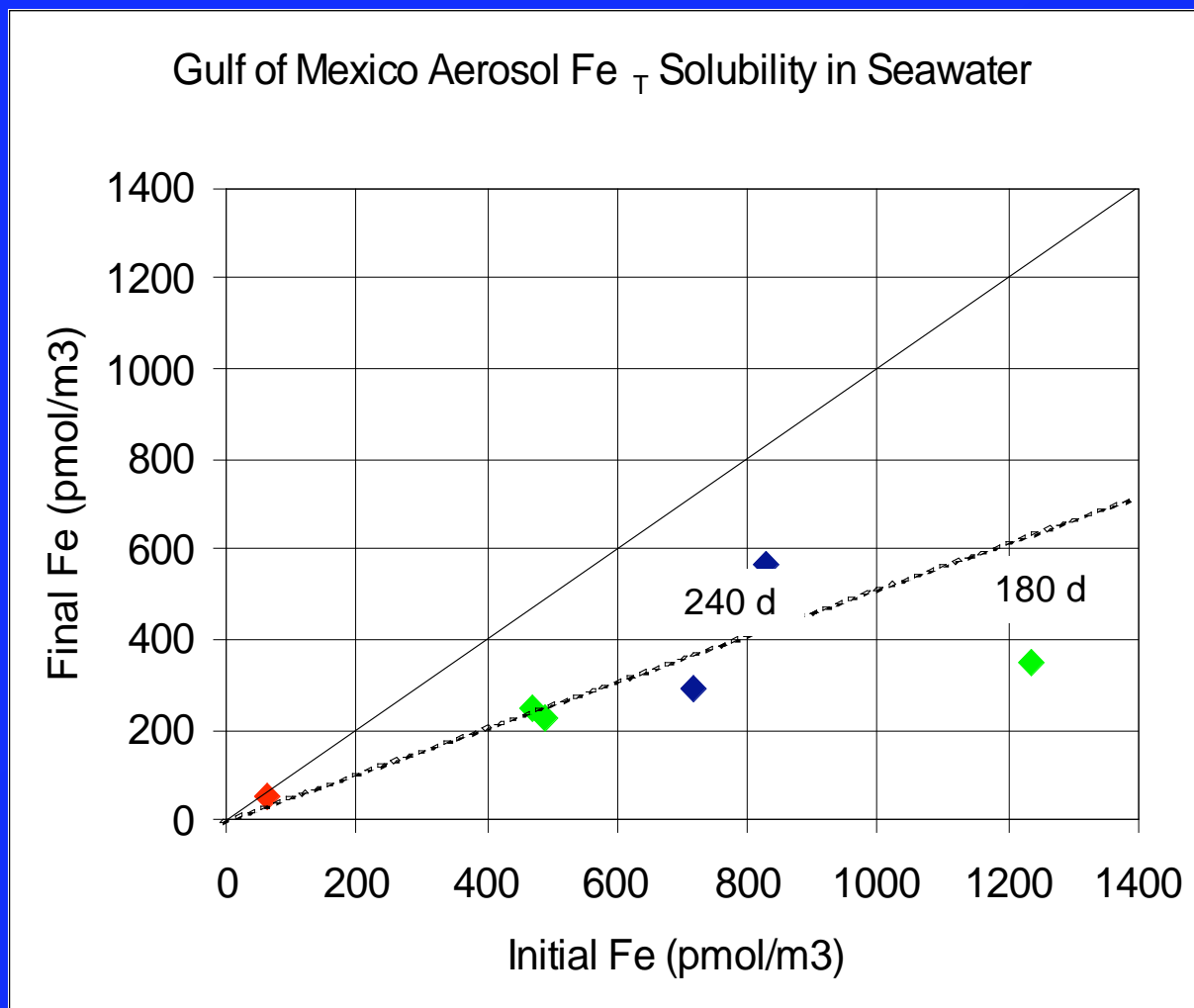
Pre-cleaning filters lowers blanks for most TEIs.



High-resolution ICPMS analysis of DI water-soluble trace elements in Saharan dust samples shows many elements well above the detection limits (excepting Ge, In, Sn, and Hg).



Unfrozen aerosol samples lose up to 50% of their total soluble Fe after 180-240 days of dry storage.



Two intercalibration experiments are planned where aerosol and rainfall subsamples will be distributed to the community for testing and validation of analytical methods. The first experiment was conducted in early September 2008 on the roof at RSMAS/University of Miami. For the second experiment, the aerosol and rain sampling equipment will be deployed on the 2nd GEOTRACES intercalibration cruise in May 2009.

Results:

11 daily-integrated samples were collected from Sep. 11-22, 2008.

The total air volume filtered was ~1400 cubic meters per filter, yielding ~10 mg of dust.

Each quartz fiber and Whatman-41 filter is sub-sampled into 28 equal segments (2.54 cm x 11.43 cm), yielding ~400 µg dust per segment.

The slotted impactor filters yield 9 strips per filter, with dust loading of ~1,400 µg dust per strip.

Subsamples still available: email wlanding@fsu.edu

Results:

Precision:

Filter edges are not significantly different from filter centers.

Precision test:

Whatman-41; 28 subsamples 2.54cm x 5.5cm

DI water solubility (100mL, <10 seconds exposure)

4-6% chloride, nitrate and sulfate

5-9% P, Mn, Fe, Cu, Zn

13-18% Al, Co, Nd, Pb

Iron dissolution control

- Why a reference material is needed
 - For intercomparison and method validation
- Linked with reference method:
 - Is a “reference” leaching method required?
- To produce (or identify) a sample large enough, and stable enough, to be shared for a long time.

Some Possibilities

- Collect dust from heavily-loaded filters?
- Invert and beat, like a rug.
- Nuclepore, or Nylon, or Zefluor-Teflon?
- Slotted Impactor with Nuclepore?
- Cyclonic samplers? Dyson?

Some Possibilities

- SRMs: kilogram quantities from Major dust-producing areas, loess
- Sieved to small size (20 μm or smaller?)
- Stored dry.
- Several recommended leaching protocols to quantify Fe solubility and long-term stability:
 - DI water
 - Mild reducing agents ($\text{NH}_2\text{OH}\cdot\text{HCl}$; sulfite?)
 - Added ligands: desferrioxamine-B, protoporphyrin-IX

Temporal Stability

- Must be stable
- Storage: dry or frozen?
- Chemical stability
 - Stable = not soluble ?
 - Unstable = soluble = evolves over time?

Additional Possibilities

Intercalibration Samples plus Standard Reference Materials

Intercalibration: short-term (<1 month) sampler deployment to collect samples to share

US GEOTRACES cruises

other opportunities: Cape Verde, Barbados, Hawaii, southern hemisphere (Patagonia, Australia, Indian Ocean)

Deploy multiple high-volume collectors for simultaneous sampling

Leaching solutions

- Must also be stable, simple, easy to reproduce in any lab
- Ultrapure water: short (10 sec) vs. Long (hours?) exposure.
- Dilute acetic acid/ammonia mixtures: Can we use a very dilute solution that will have a stable pH during leaching but is more easily analyzed using ICPMS?