Sampling particles in the ocean: Go-Flo bottles vs. in situ pumps

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Why fight to measure particulate TE on 5-10L from GoFlo bottles?

- Need to quantify and model particulate TEI inputs and exchanges with the dissolved pool !
- Alternative is *in situ* pumping - pumps may not be available for all future international GEOTRACES cruises.
- Depth coverage and resolution same as diss. TEI.
- No extra wire time needed on long sections.
- Deep samples not exposed to upper water column.
- Cost - seagoing hardware and supplies.
- History: bottle particulate sampling attempted during GEOSECS - largely unsuccessful.

What are the issues to think about for sampling and analysis of particulate TEs?

1. Filter material and pore size
2. Filter performance (flow rate, clog?, *effective* pore size etc.)
3. Digestion or leaching procedures
4. Analytical methodology
5. Filter blanks - (major blank source - depends on digest)
6. Filtration from GOFIos - avoiding artifacts
7. GOFIo vs. in situ pump sampling
8. Intercalibration - Interlaboratory, solutions and filters
9. Oceanographically consistent and reproducible profiles?

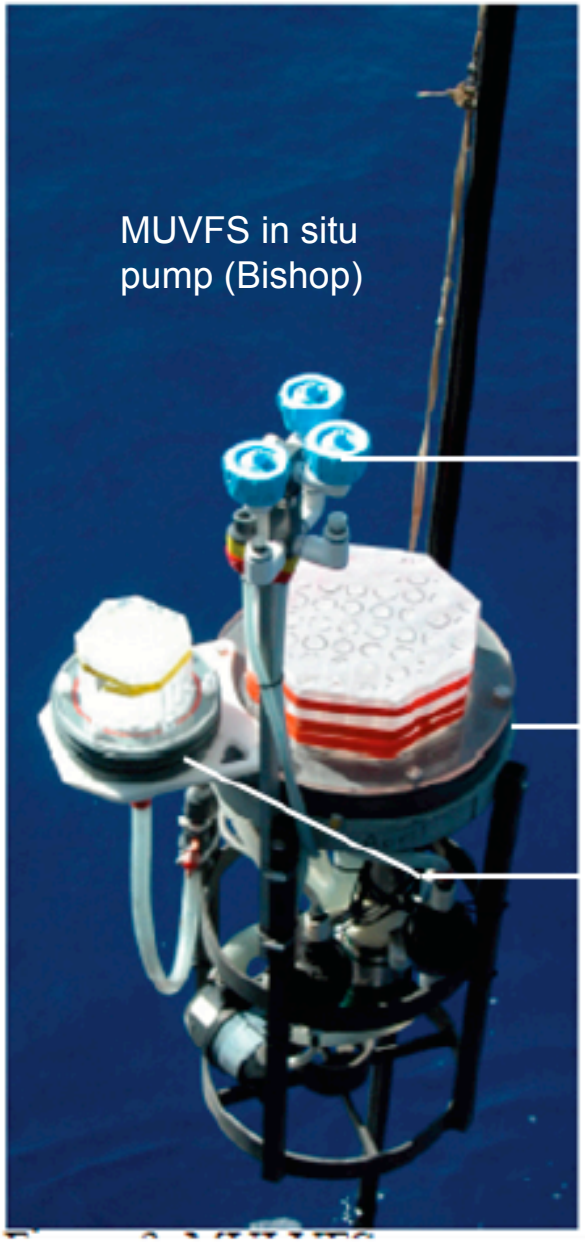
Outline:

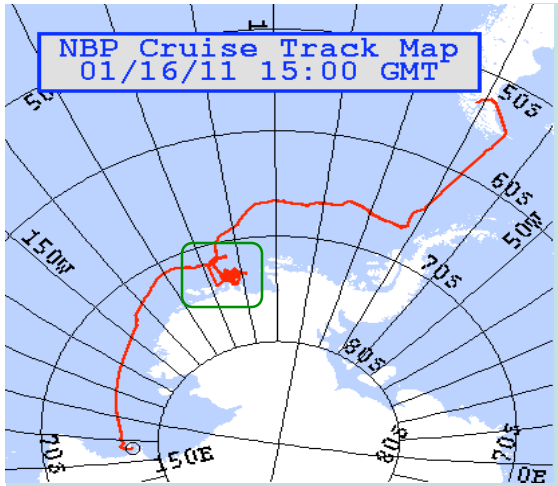
1. Filter choice - criteria
2. Blanks
3. Digestion methods
4. Reproducibility and filter type
5. Artifacts - particle settling
6. Bottles vs. in situ pumping (!)
7. Example results
8. Conclusions

NOTES before beginning.

1. All analyses from the Sherrell lab at Rutgers - No conflation of pump-bottle comparison with interlaboratory biases.
2. All data are 0.45-51 μm size fraction. Large sinking particles difficult to determine using bottle-sized volumes.
3. Results here focus largely on the GEOTRACES IC2 cruise in the NW Pacific.
4. Much of this presentation is in a submitted manuscript (Planquette and Sherrell, L&O Methods, submitted).

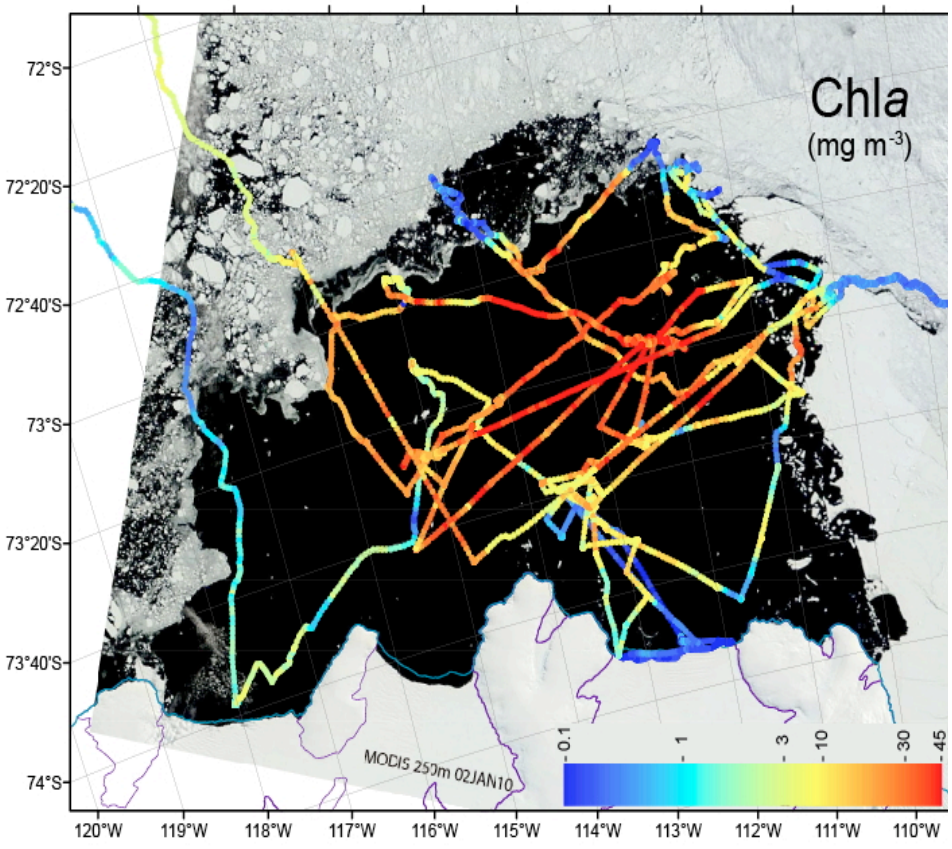
SAMPLING METHODS

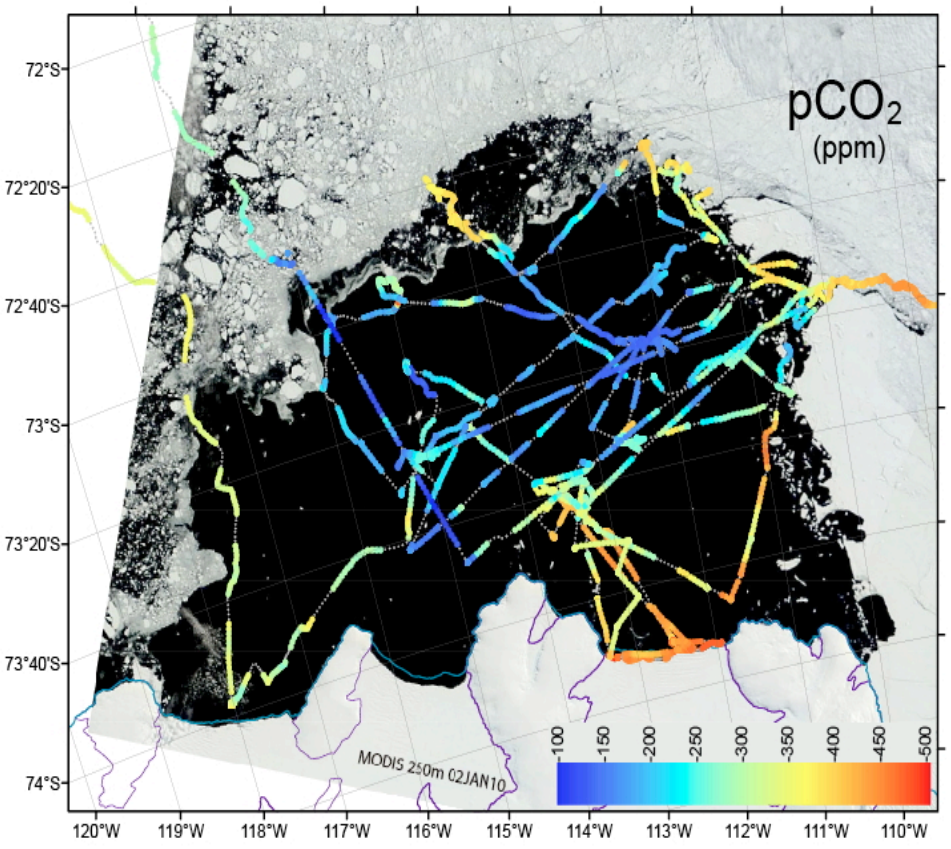




ASPIRE

Amundsen Sea
Polynya International
Research Expedition





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Characteristics of filter types evaluated

1=good, 2=fair, 3=bad

FILTERS>	Pall GN-6 cellulose	Millipore MF c'lose	Whatman Polycarb.	Whatman QMA	Gellman Supor
Material->	Mixed cell-ulose ester	Mixed cell-ulose ester	Polycarbon-ate etched	quartz	polysulfone
Flow Rate	2	2+	3	1	2
Clogging	2	2	3	1	2
Handling	2	1	2	2	1
Blanks	2	2	2	3	2
Digestion flexibility	1	1	2	3	2
POC OK?	3	3	3	1	3
Cost	2	2	2	1	2

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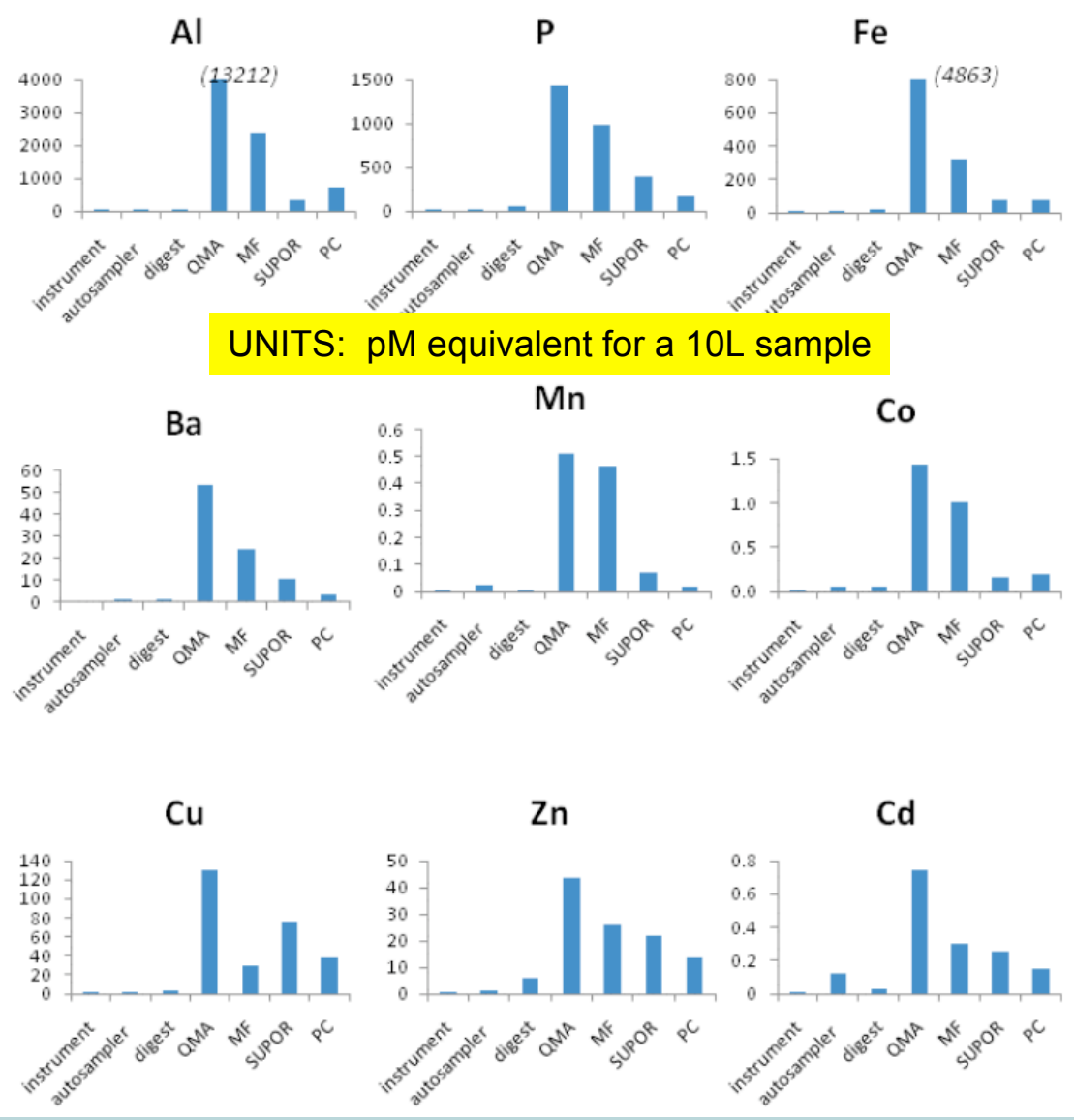

Process filter blank corrections generally <10%. (Up to 25% for Cu and Zn in euphotic zone)

Important: use full process blanks, not dipped or unused blks

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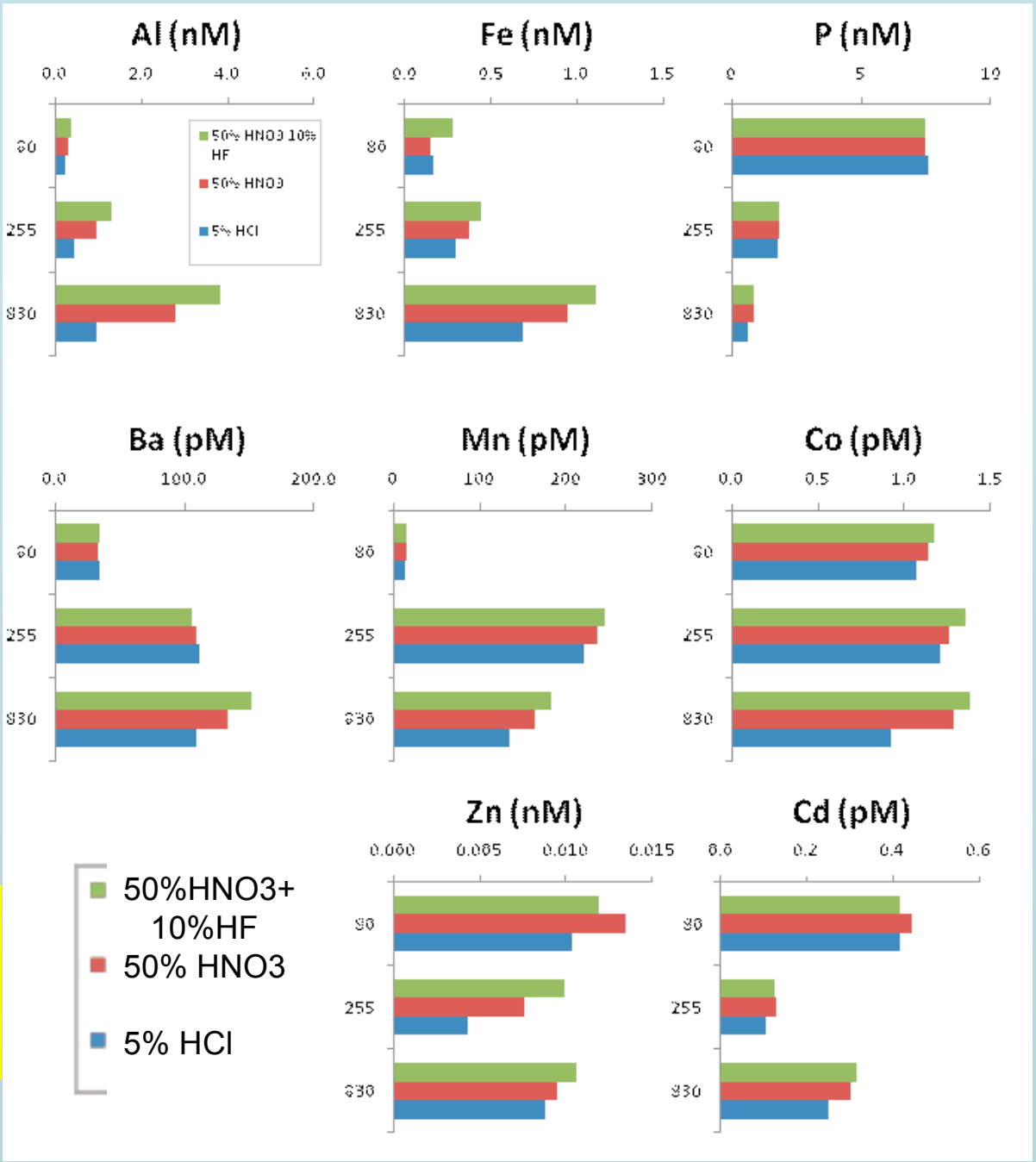
3 digest/leach recipes compared

BATS station 80, 255, 830m

MULVFS large volume filter subsamples used

Remainder of this talk shows results of complete particle digestions using hot HNO_3+ HF (after Cullen and Sherrell, 1999).

Note: Digest optimization expts are ongoing.



The GEOTRACES SYSTEM: Sampling with a 'clean' rosette of 24 10-liter GO-Flo bottles

As part of the intercalibration program, Greg Cutter built a GEOTRACES system that has 24 sample bottles and 8000 meters of Kevlar conducting cable. It will be a community resource.

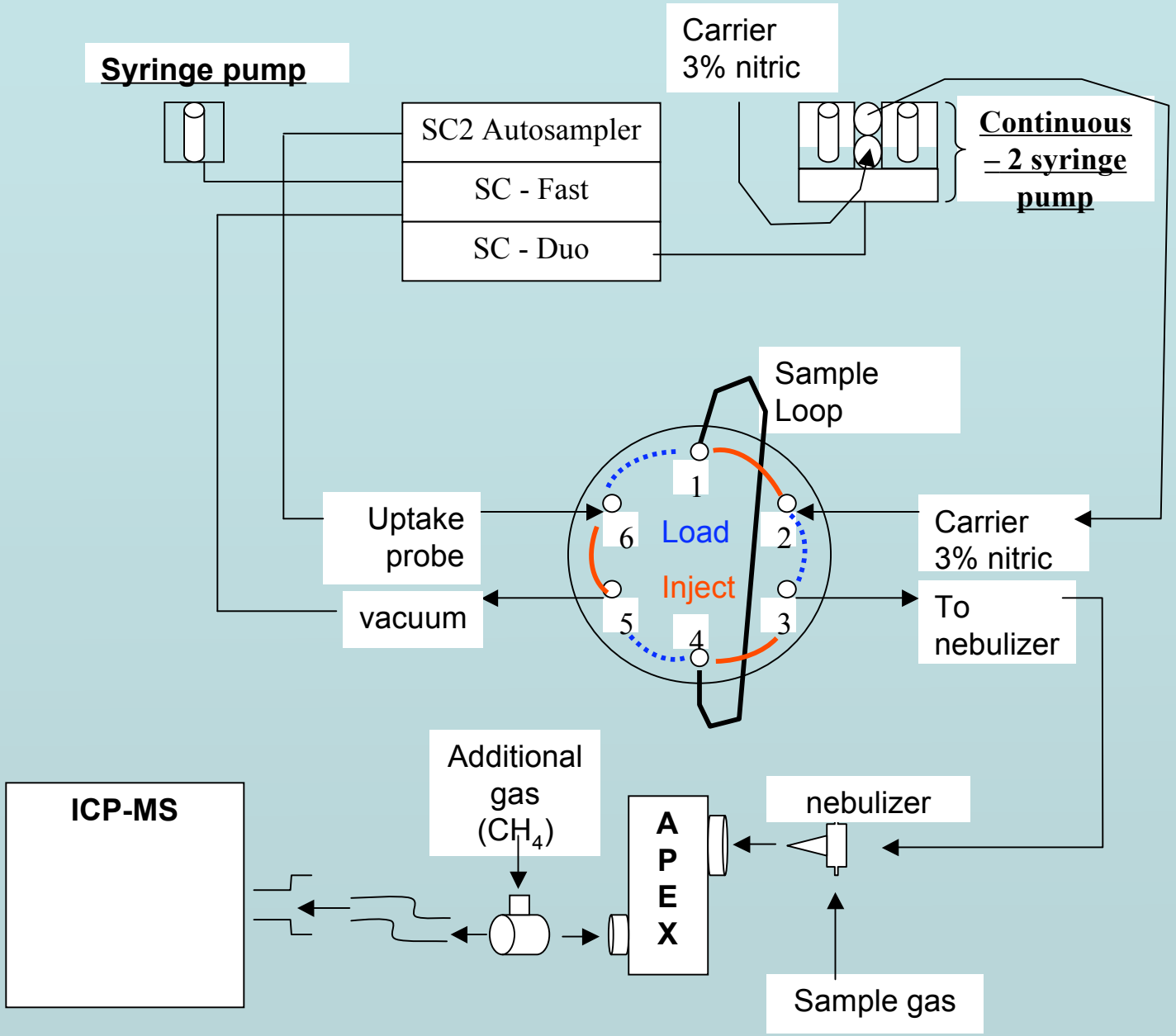
We are making a smaller version of this system for USAP.

Now carry bottles to the clean van and start filtration.

Result of a 24 bottle rosette cast at Bermuda - many filters!

Processing and analysis:
Filters from ~10L SW are digested,
Dried down, taken up in 3mL dilute acid,
~0.5 mL analyzed by HR-ICP-MS for ~35 elements.
Take-up recovery and drift monitors are used.

ICP-MS setup and introduction system



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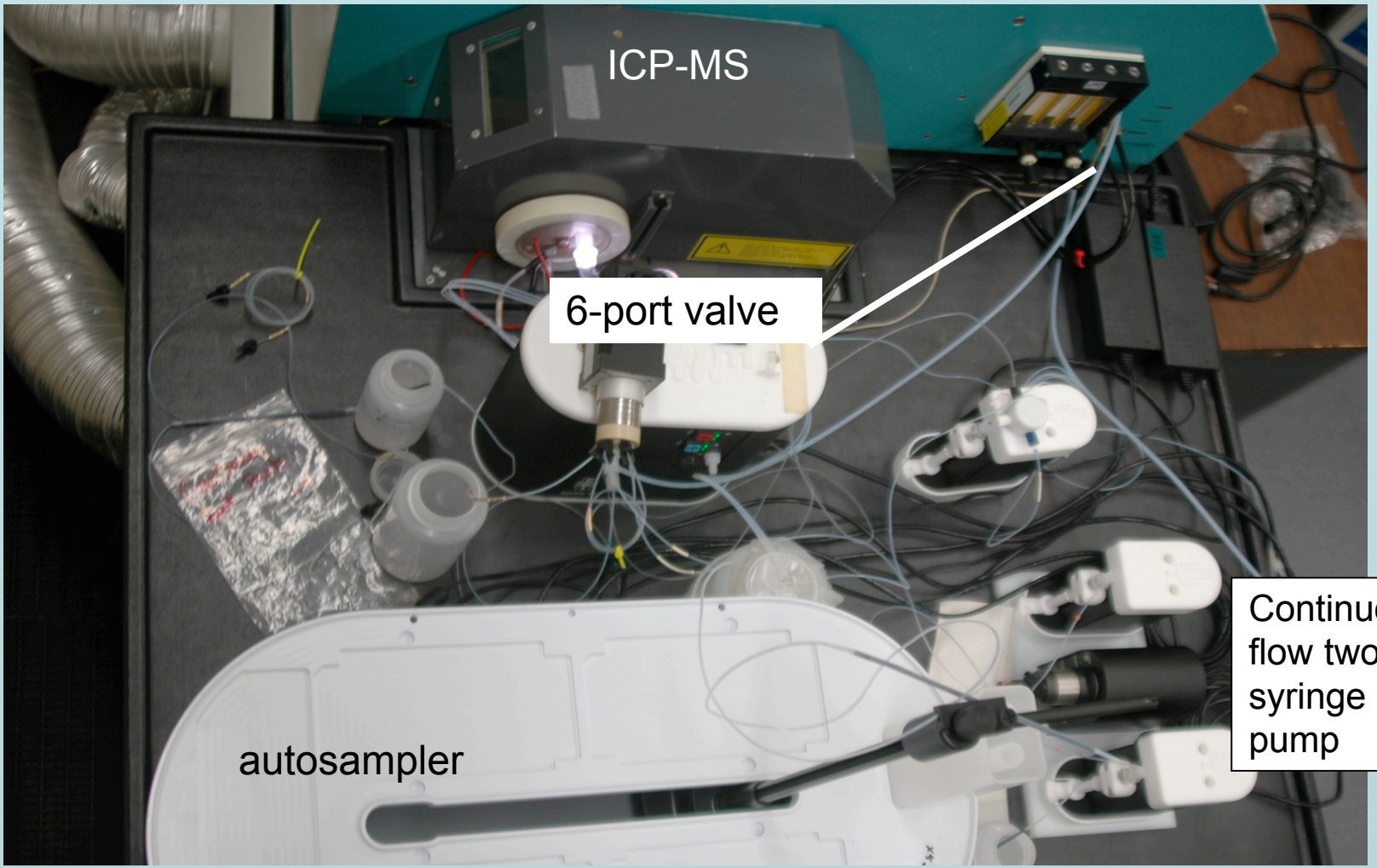

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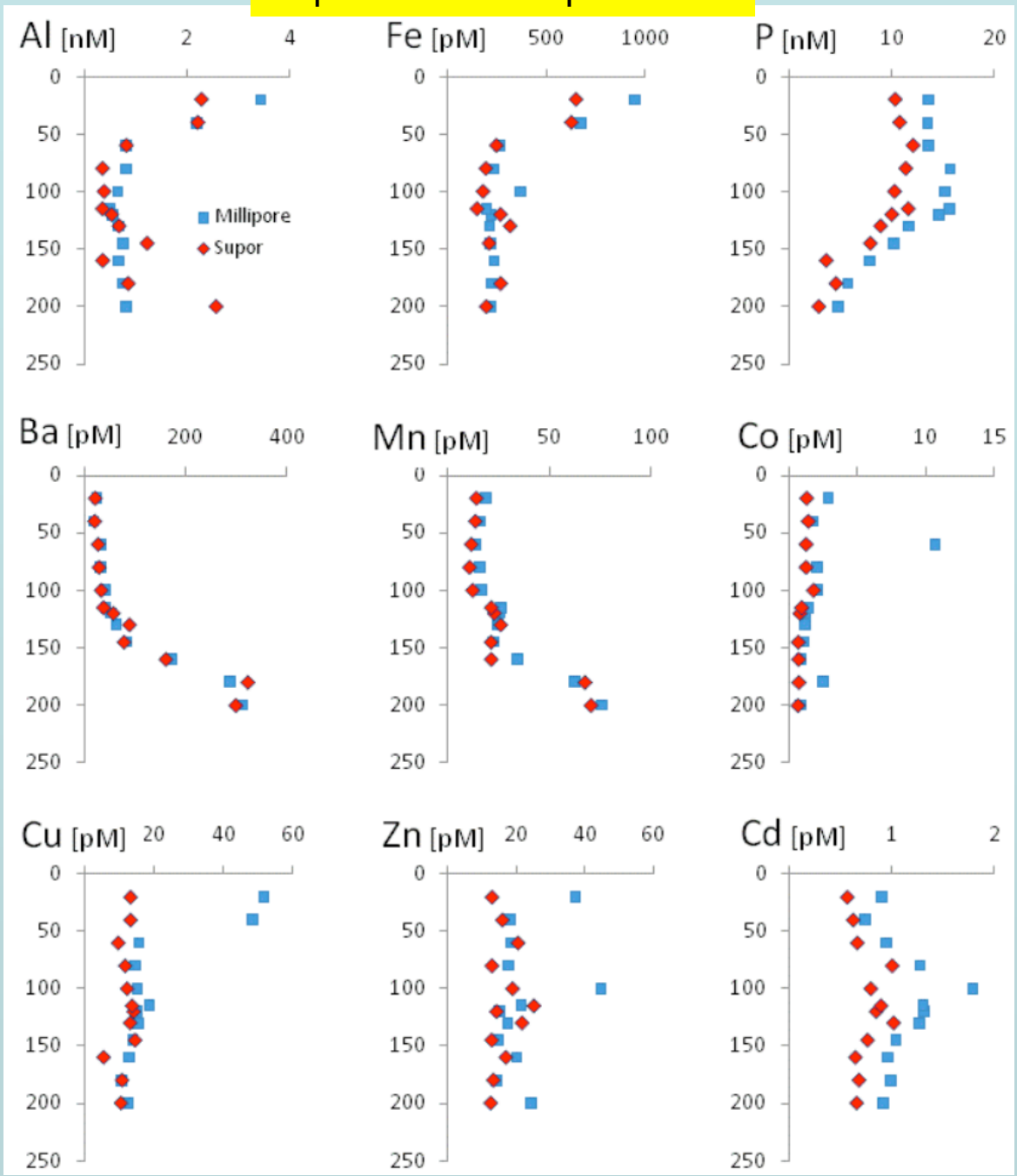
SAFe Station - NW Pacific
Upper 200m
GO-FLO bottles

Filters:
MF-Millipore mixed cellulose 0.45µm
Pall Gelman Supor polysulfone 0.45µm

Supor vs. MF-Millipore filters



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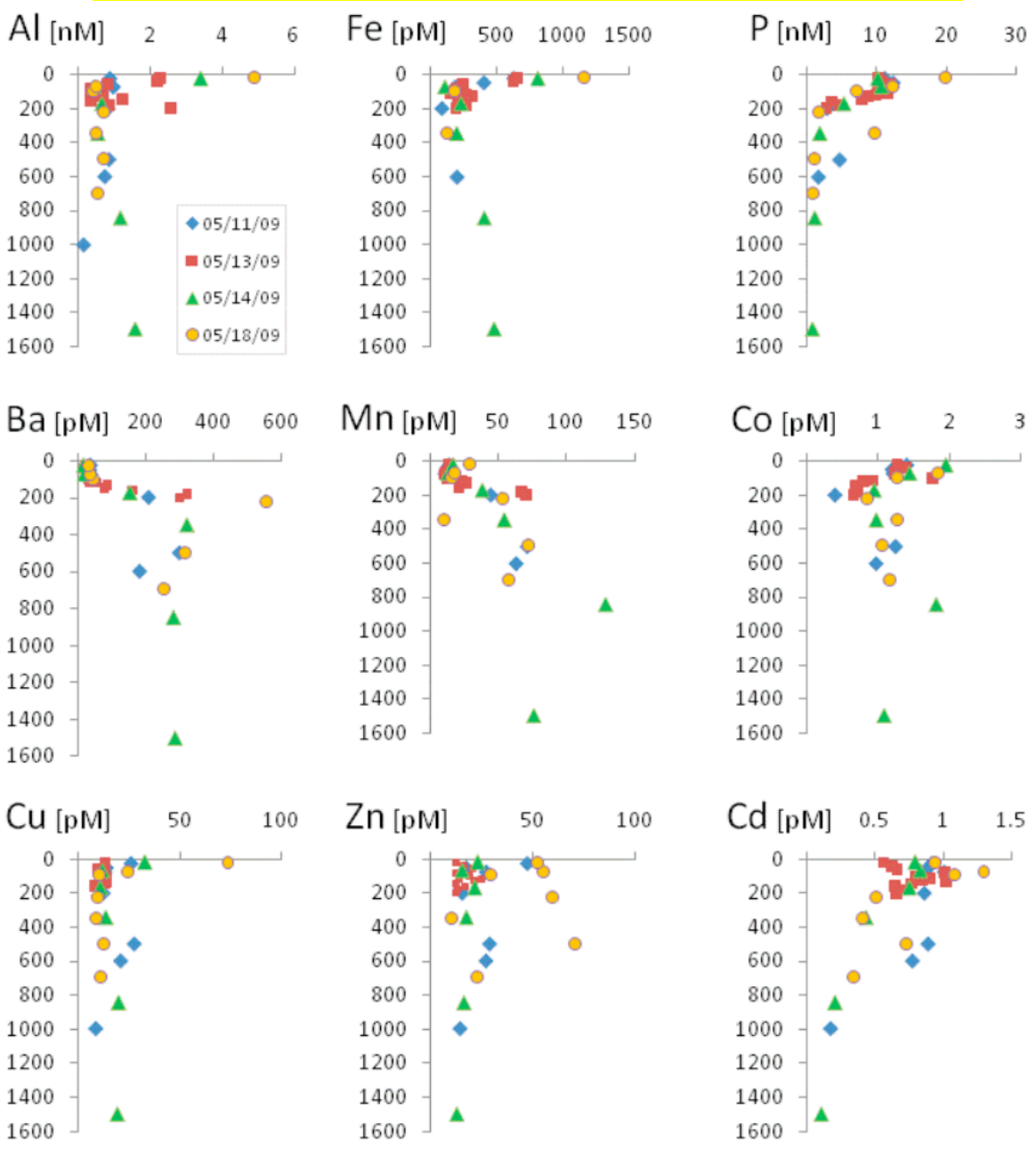
Sampling reproducibility over one week on station



SAFe Station - NW Pacific

4 GO-FLO profiles over 7 days.

All Supor polysulfone filters.

Hydrographic shifts?

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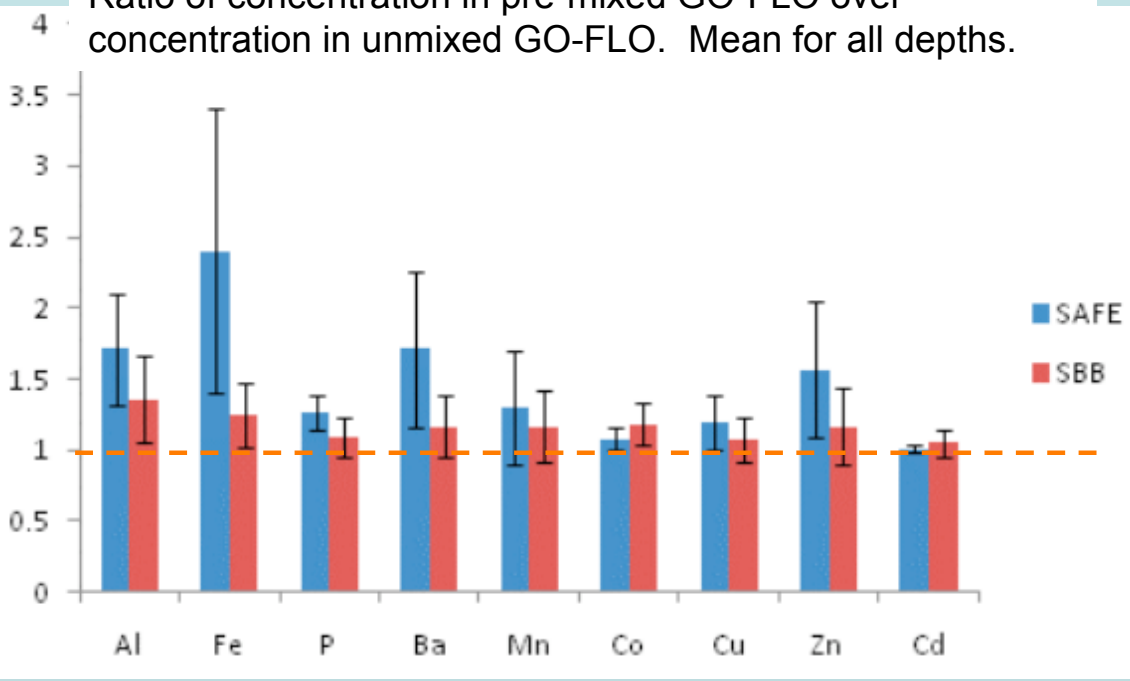
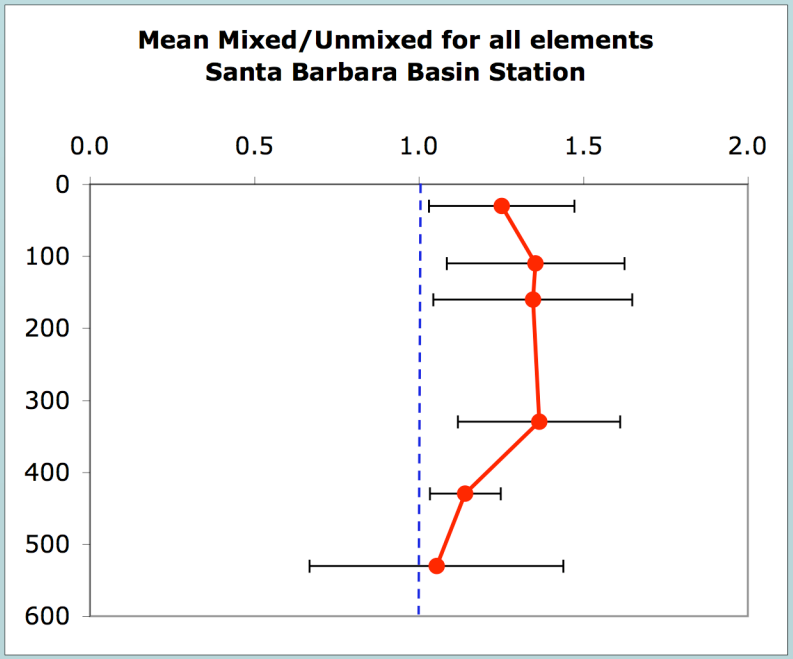
Ratio of concentration in pre-mixed GO-FLO over concentration in unmixed GO-FLO. Mean for all depths.



Elements affected by particle settling:

Most affected: Al, Fe, Ba, (Zr, Th)

Least affected: P, Cd



Rob Sherrell,GEOTRACES 3rd Data-Model Synergy Workshop, Nov. 2011

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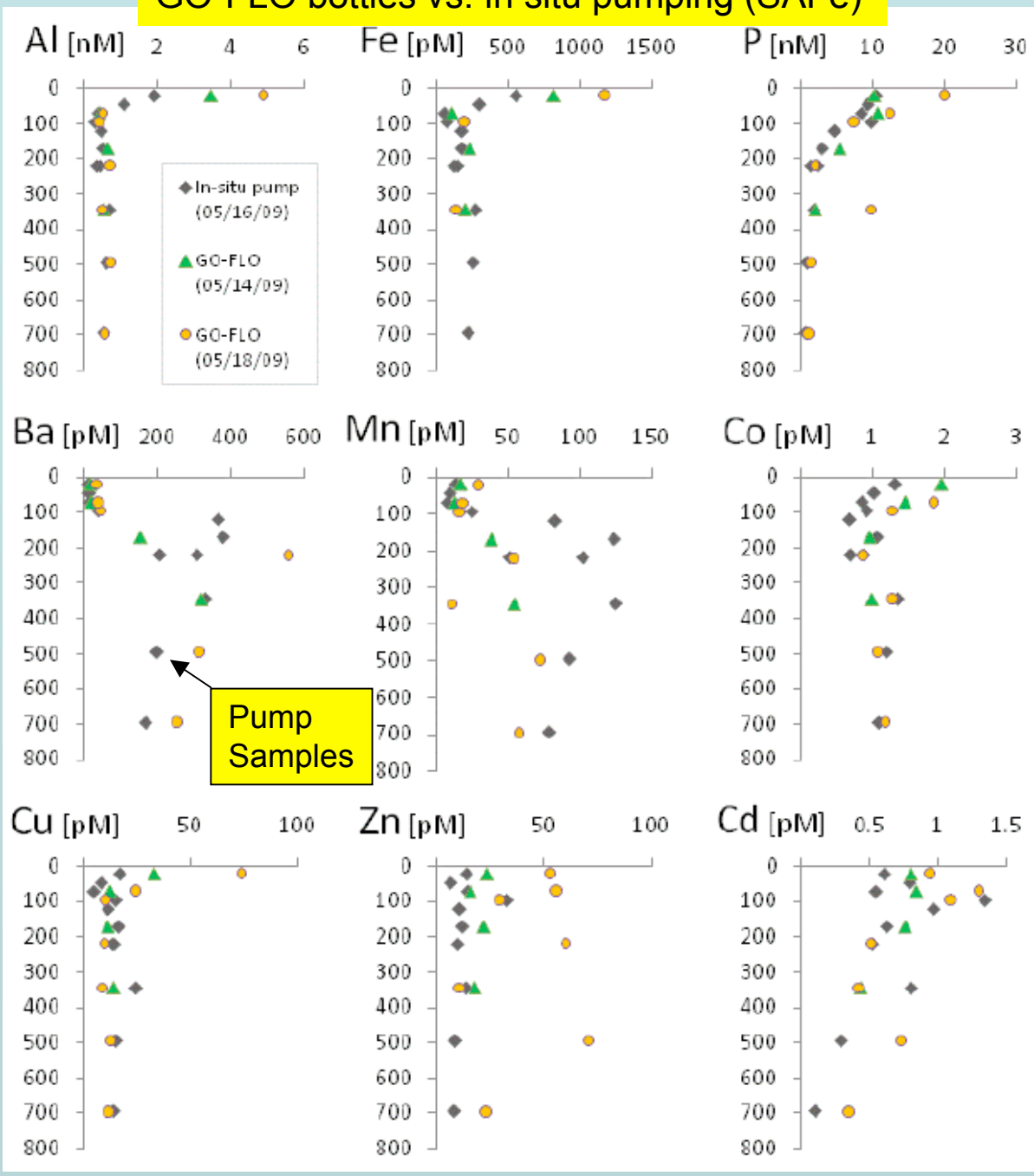
SAFe Station - NW Pacific

2 GO-FLO deployments
1 MULVFS pump deployment
Over 4 days.
Same Supor filters.

GO-FLO bottles vs. in situ pumping (SAFe)



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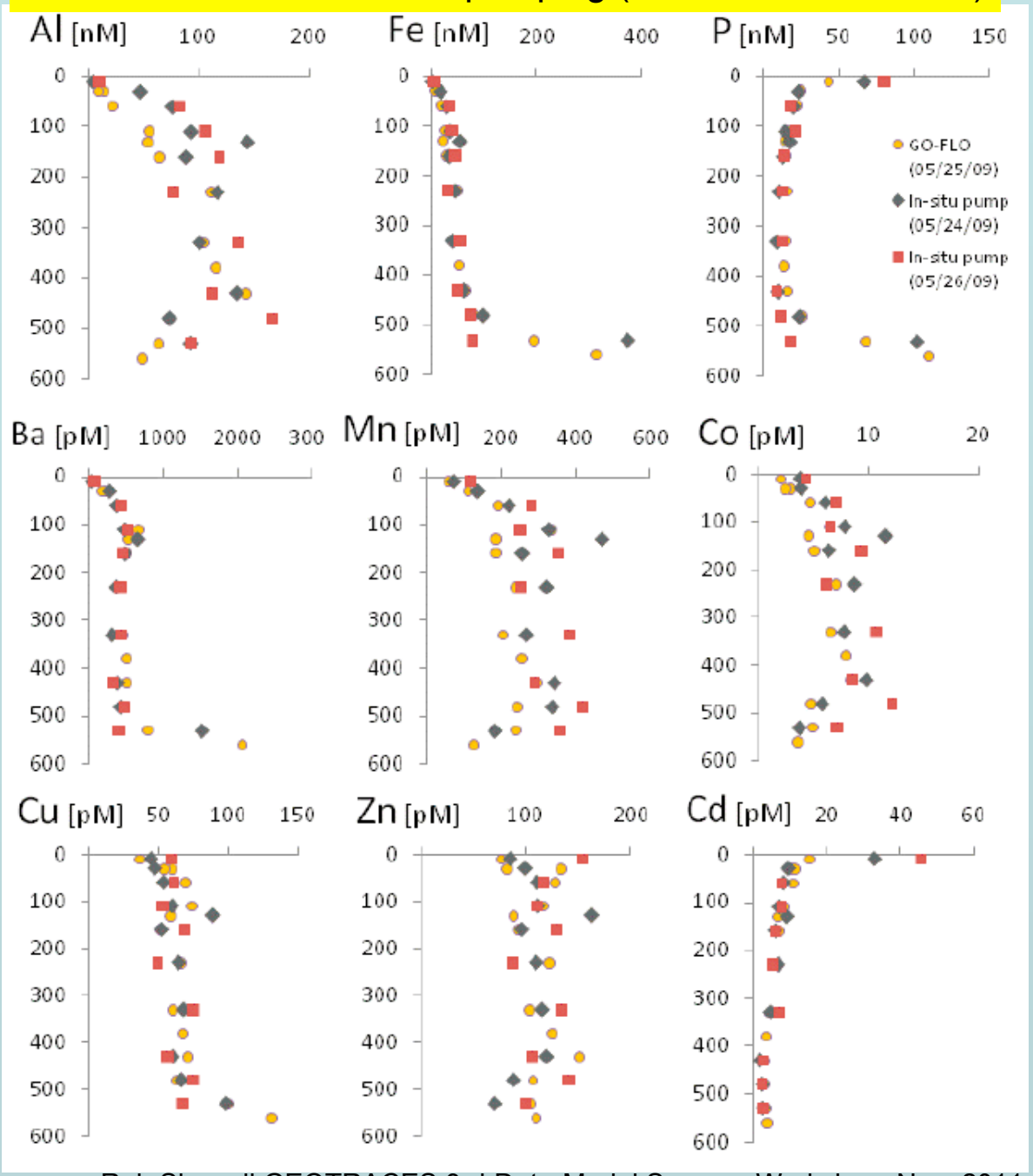
GO-FLO bottles vs. in situ pumping (Santa Barbara Basin)

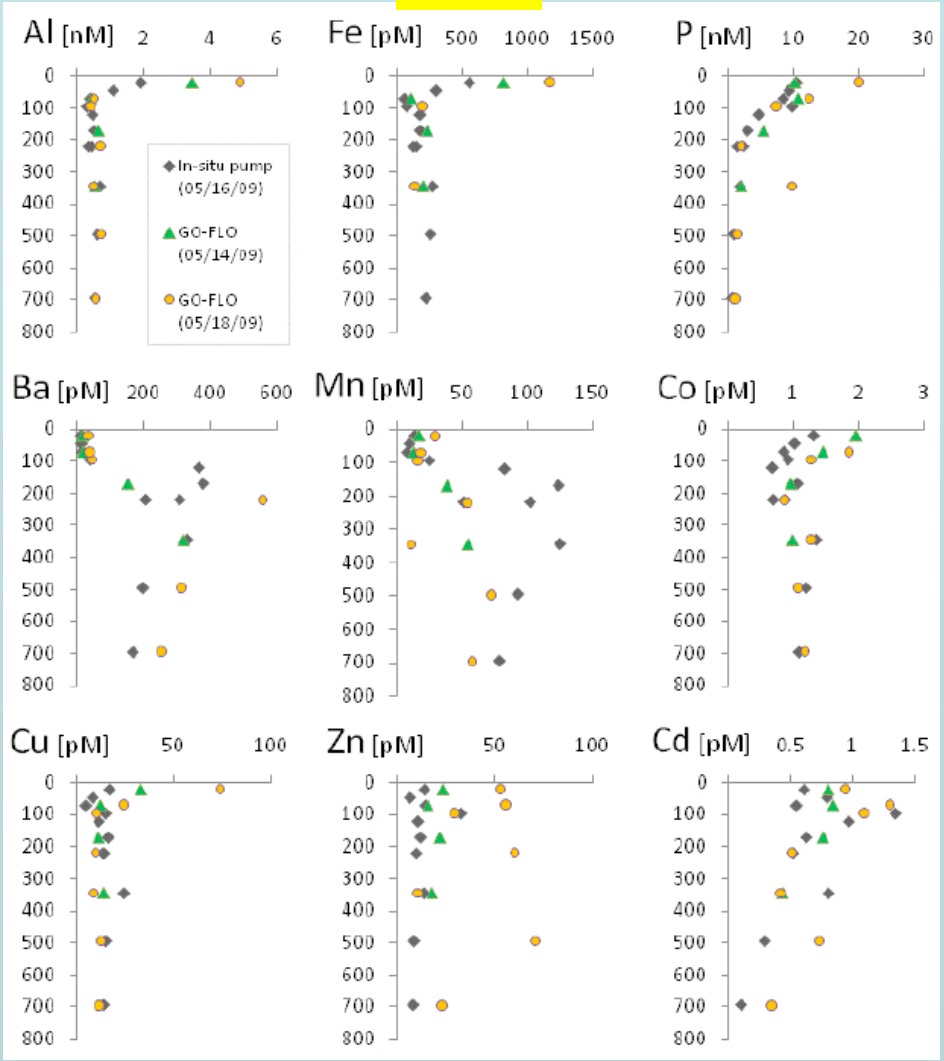


Santa Barbara Station - California Coast

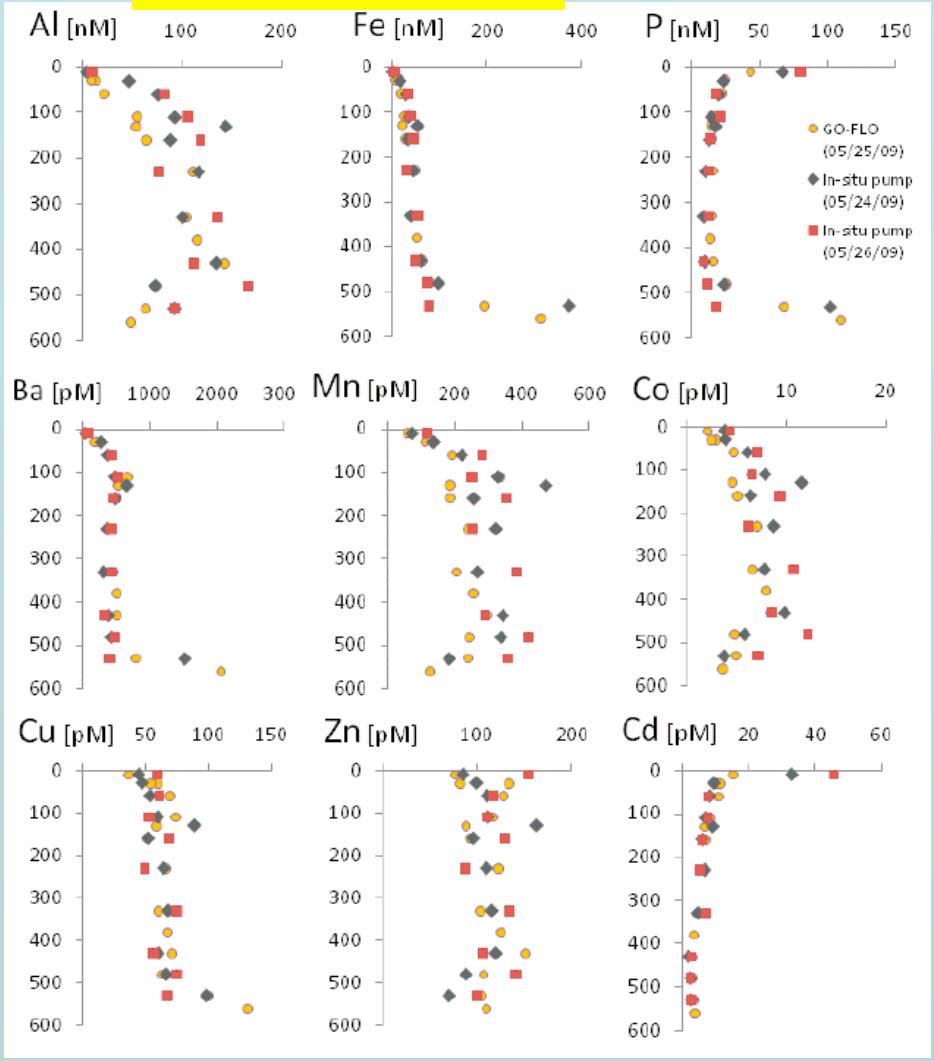
1 GO-FLO deployment
2 MULVFS pump deployments
Over 3 days
Same Supor filters

GO-FLO bottles vs. in situ pumping

SAFe



Santa Barbara Basin



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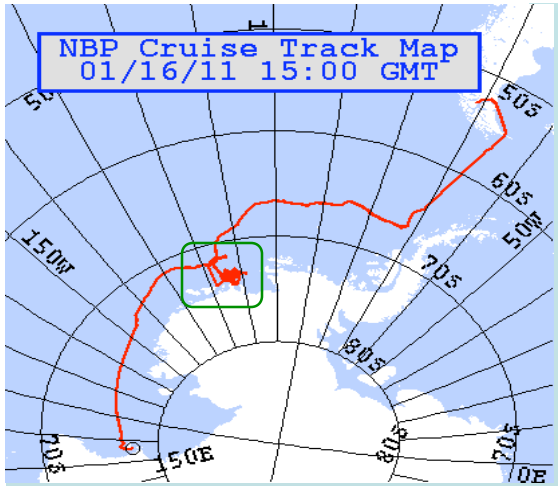
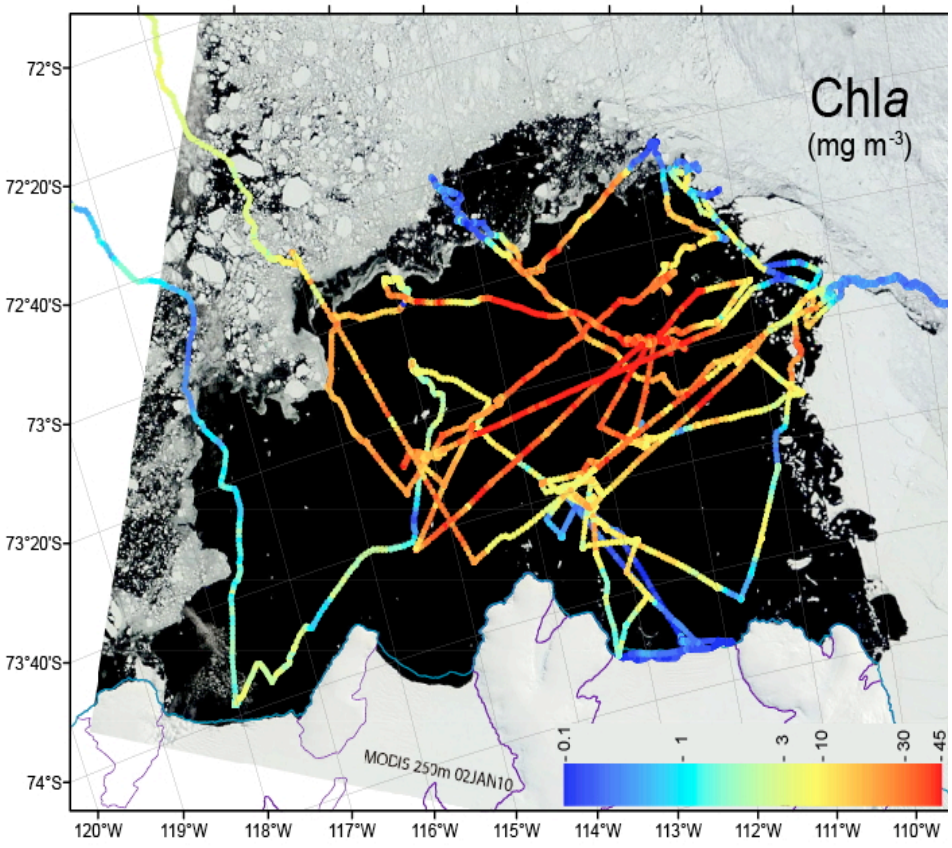
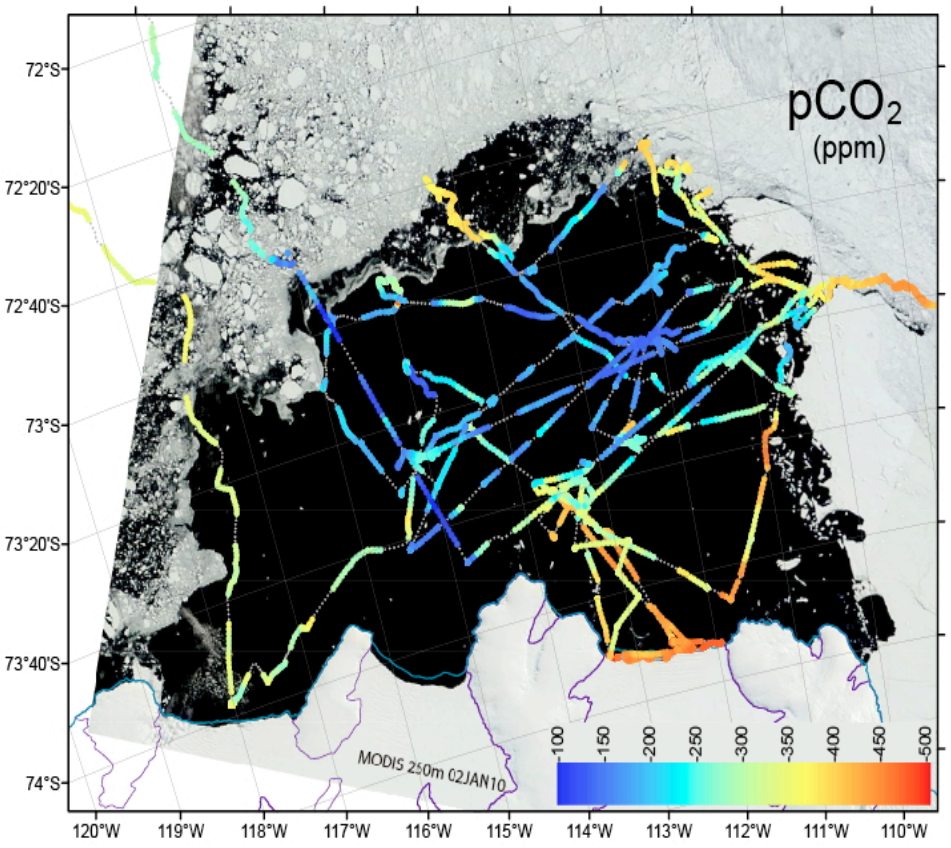


ASPIRE

Amundsen Sea Polynya International Research Expedition

Tish Yager, Univ. of Georgia, lead PI





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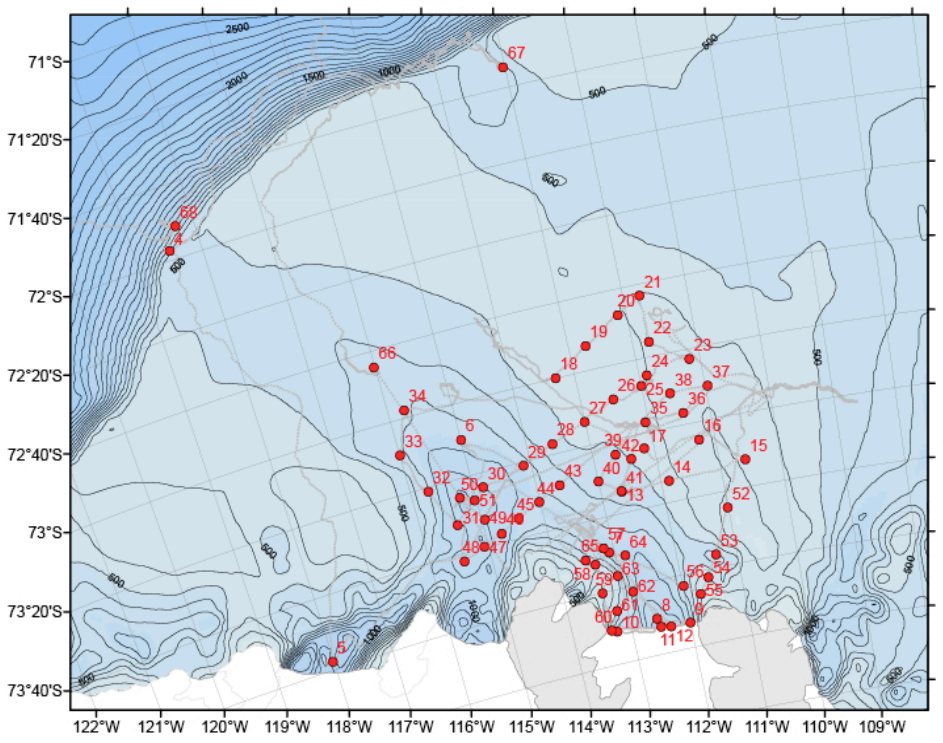
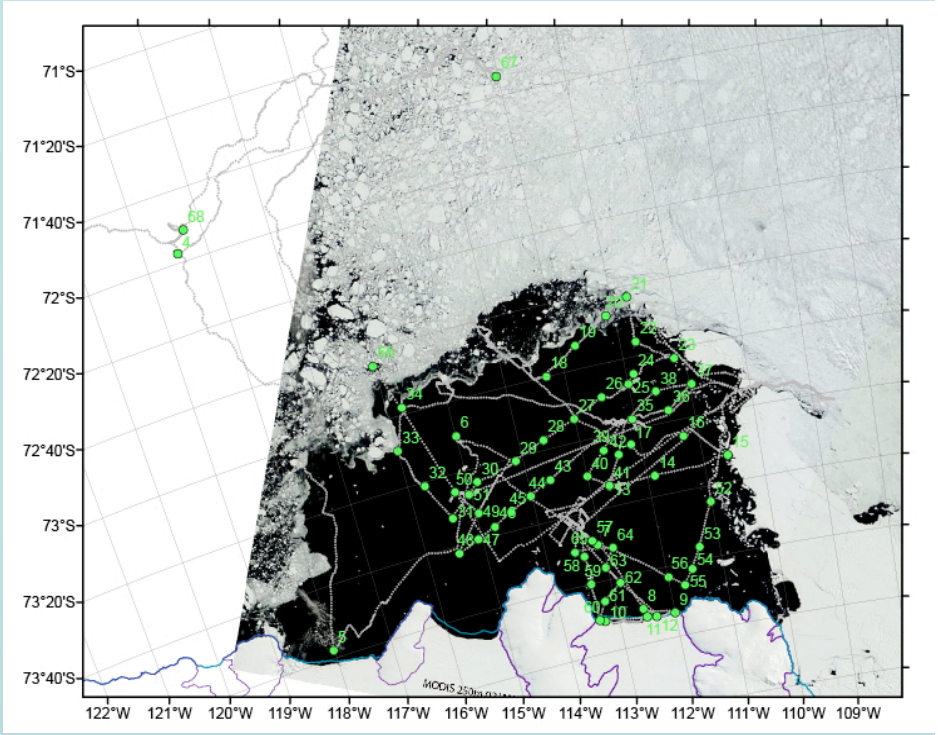
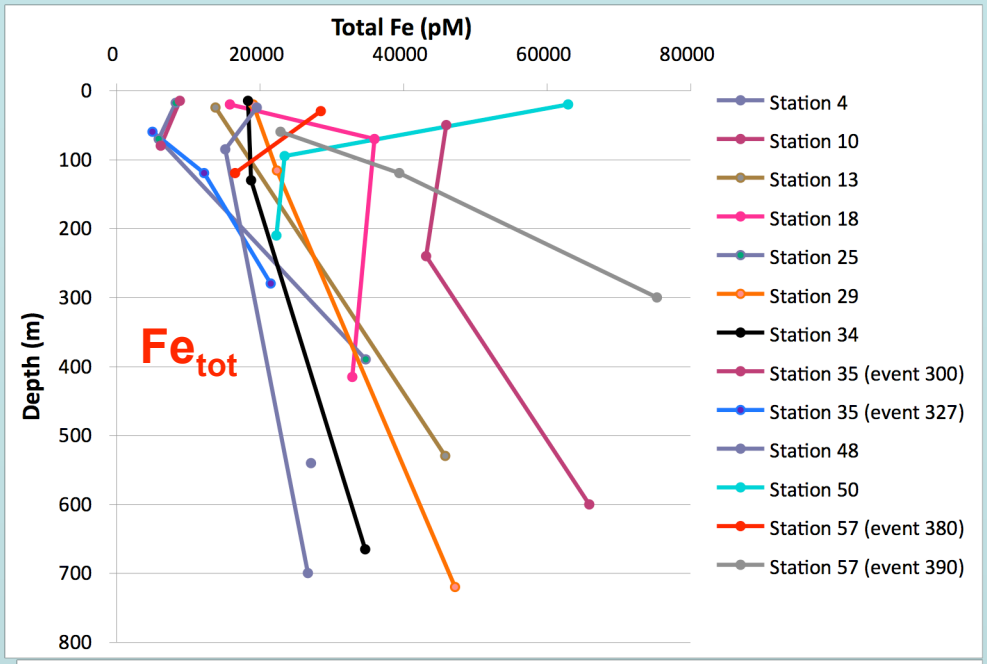
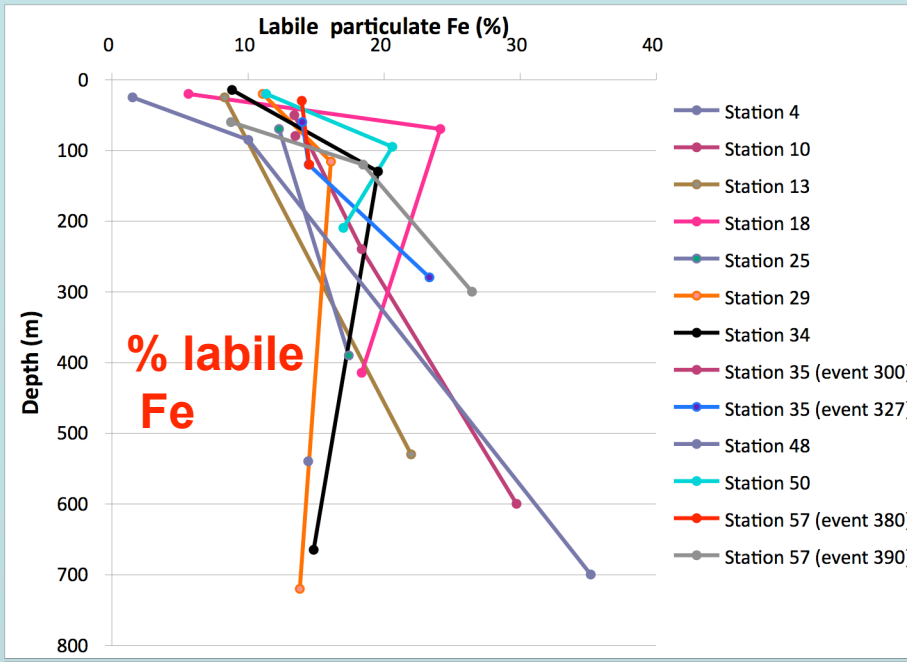
35 stations samples for particulate and dissolved trace metals

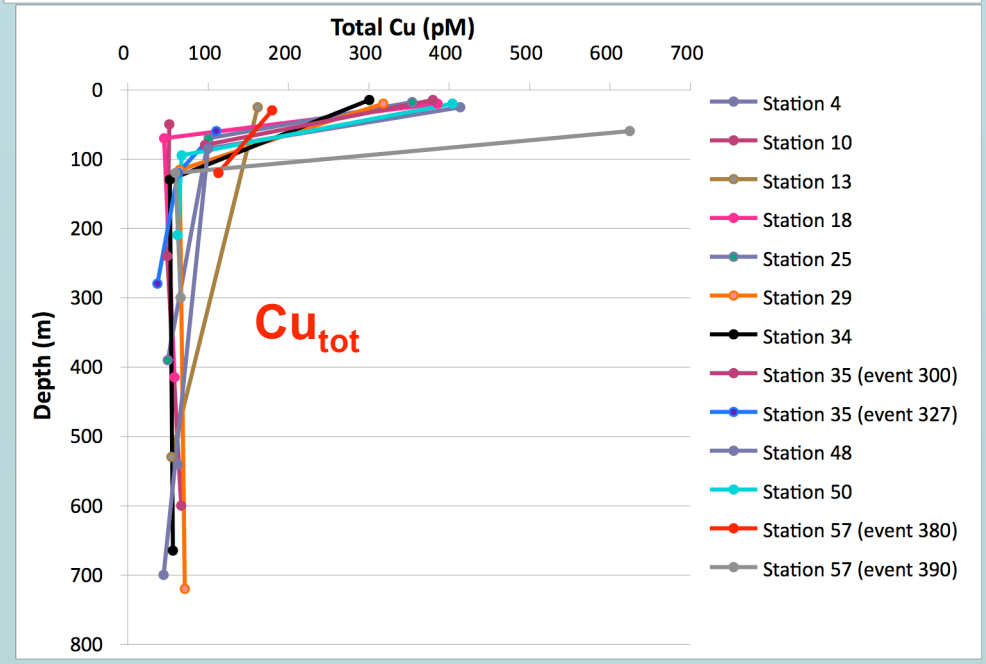


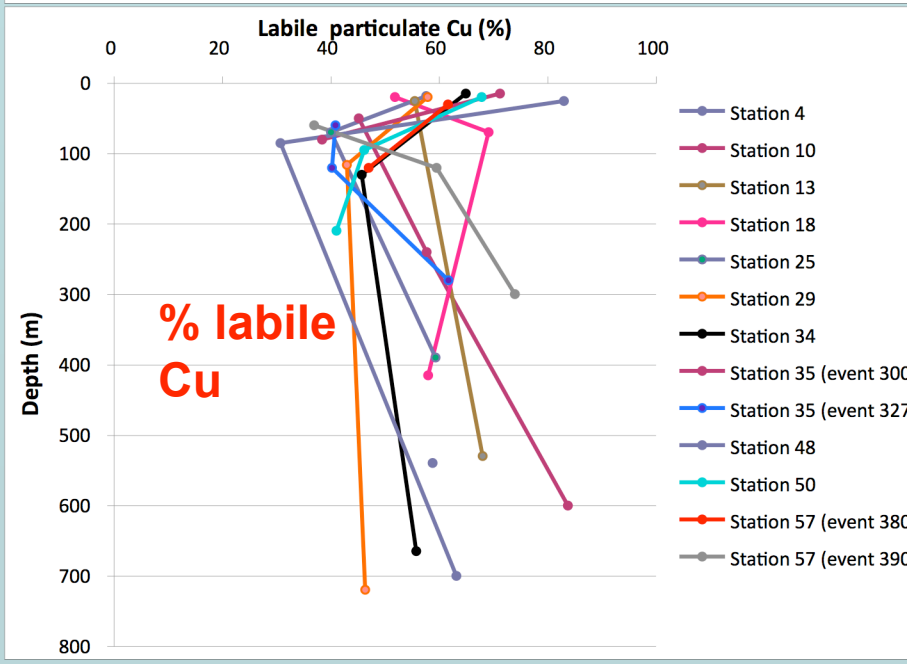


Example Application: Amundsen Sea Polynya pump profiles (S. Severmann samples)



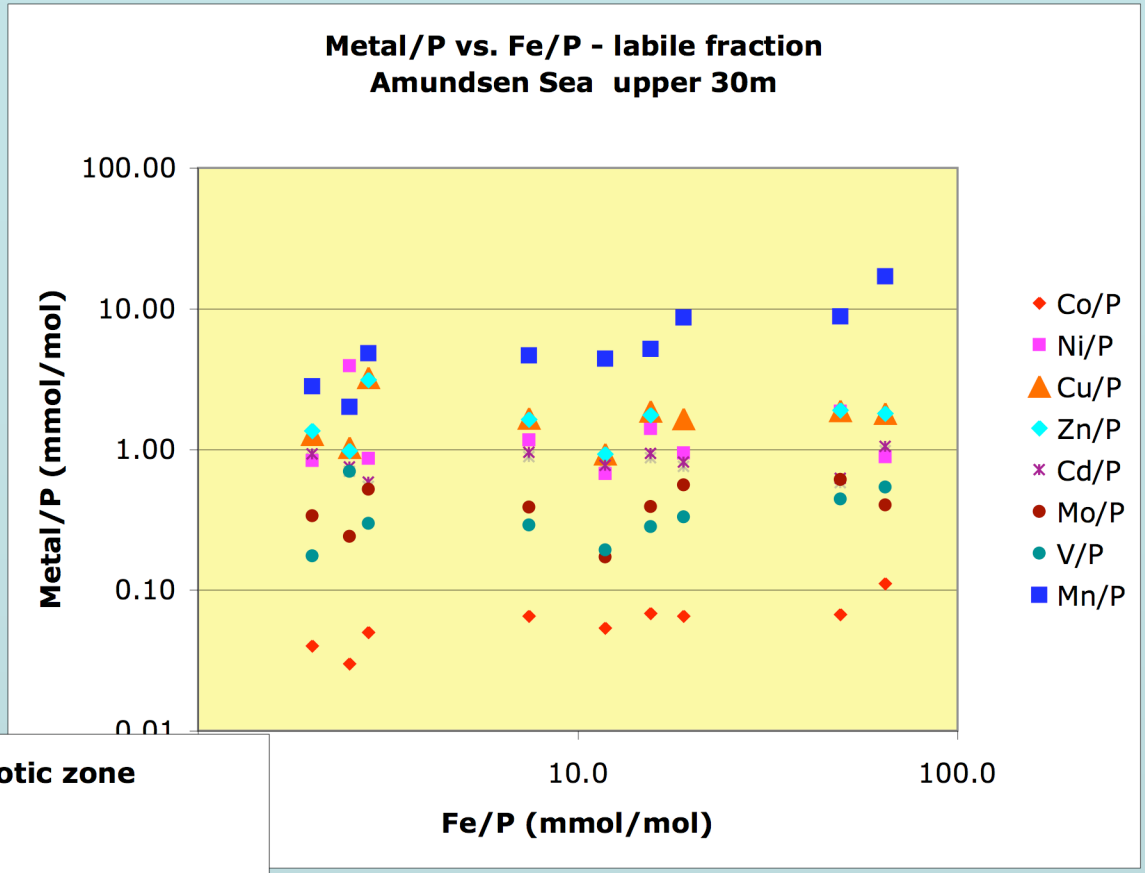


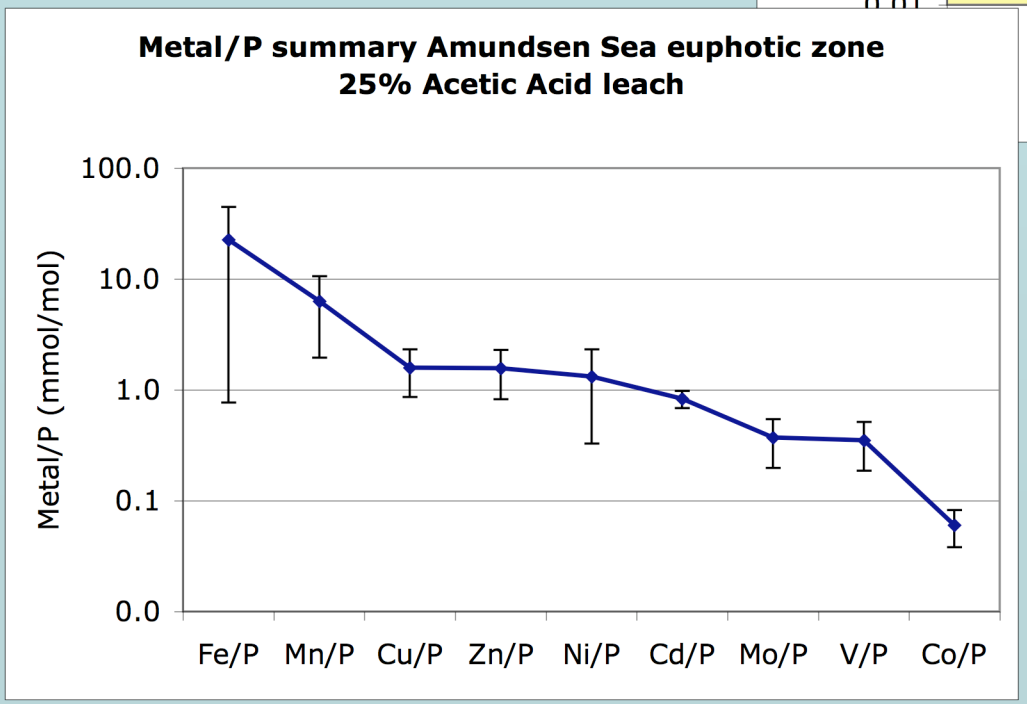




Trace metal "quotas" (Me/P) in upper 30m euphotic zone particles - Amundsen Sea

- Derive micronutrient uptake ratios
- Determine dependencies of Me/P on extra-cellular Fe
- Compare to lab incubations
- Explore gradients in photic zone
- Incorporate into biogeochemical models





GOAL: Expand these pump results (one euphotic zone sample per station) using 12-point profiles from Go-Flo bottles.

CONCLUSIONS

1. Reproducible particulate TM profiles can be determined from 5-10L from GO-FLO bottles, with care.
2. Recommended filters: #1 Gellman Supor; #2 MF-Millipore. Supor now in use on Atlantic GEOTRACES cruise.
3. Blanks: Generally <10%. Cu, Zn are biggest % blank correction. Flow-through process blanks should be investigated further.
4. Digestion: HNO_3 & HF, needed to digest crustal elements Al, Fe, Ti, Th. "Piranha" for total Supor dissolution?
5. Filter choice defines "particulate TE". Accuracy?
6. Particle settling in sampling bottles is a significant problem. Mixing before filtration gives higher values.
7. Pumps vs. Bottles: Very good agreement with GoFlo bottle mixing, no systematic offsets. Need "simultaneous" sampling.
8. Recommendations:
   - continue pump-bottle comparisons in various oceanic regimes - samples being collected on Atl. GEOTRACES
   - mixing Go-Flos and limiting filtration time seems to work.
   - think hard about procedural blanks!
   - refine digestion and analytical methods - underway now.

THANKS FOR LISTENING