

Refinement of Atmospheric Ar/N₂ Techniques: Implications for O₂/N₂ (and trace gas) Measurement



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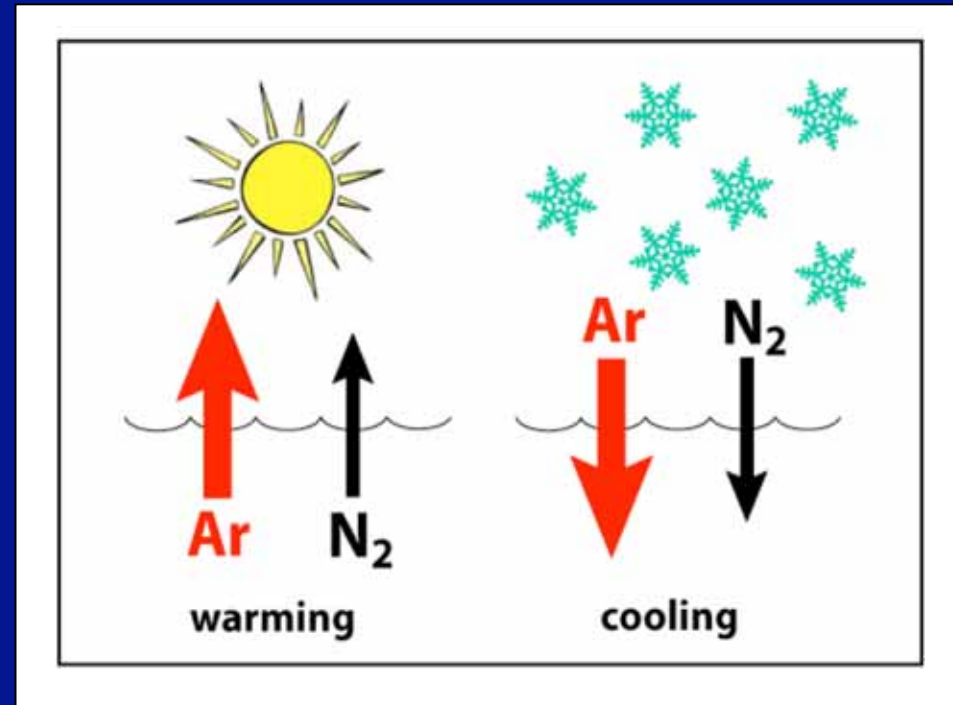
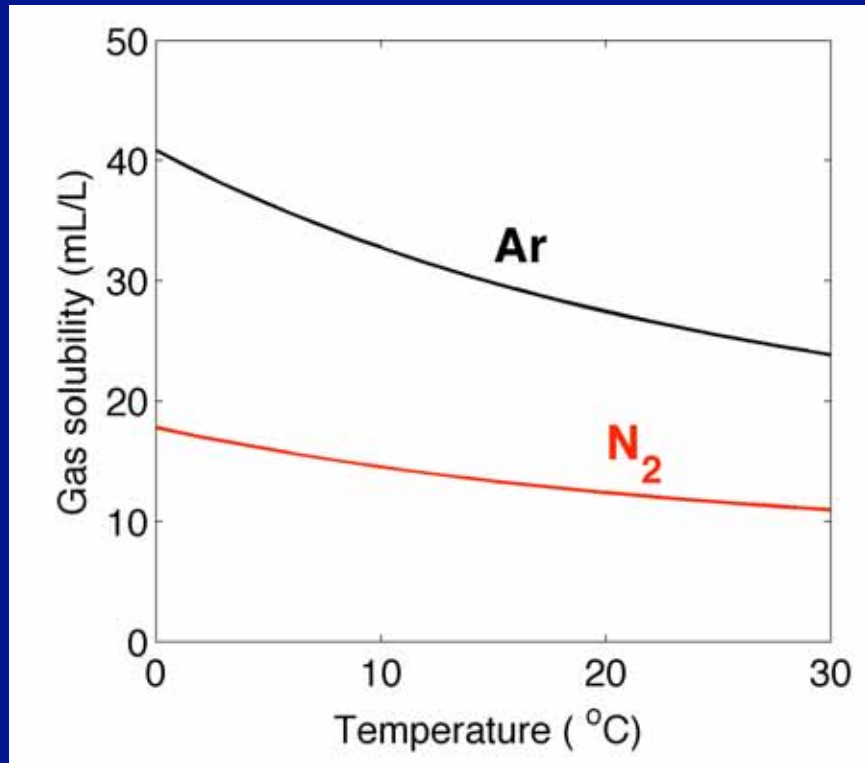
Scripps Institution
of Oceanography

Thanks to: US NSF, NOAA Office of Global Programs,
Comer Foundation, the staff of the air sampling stations



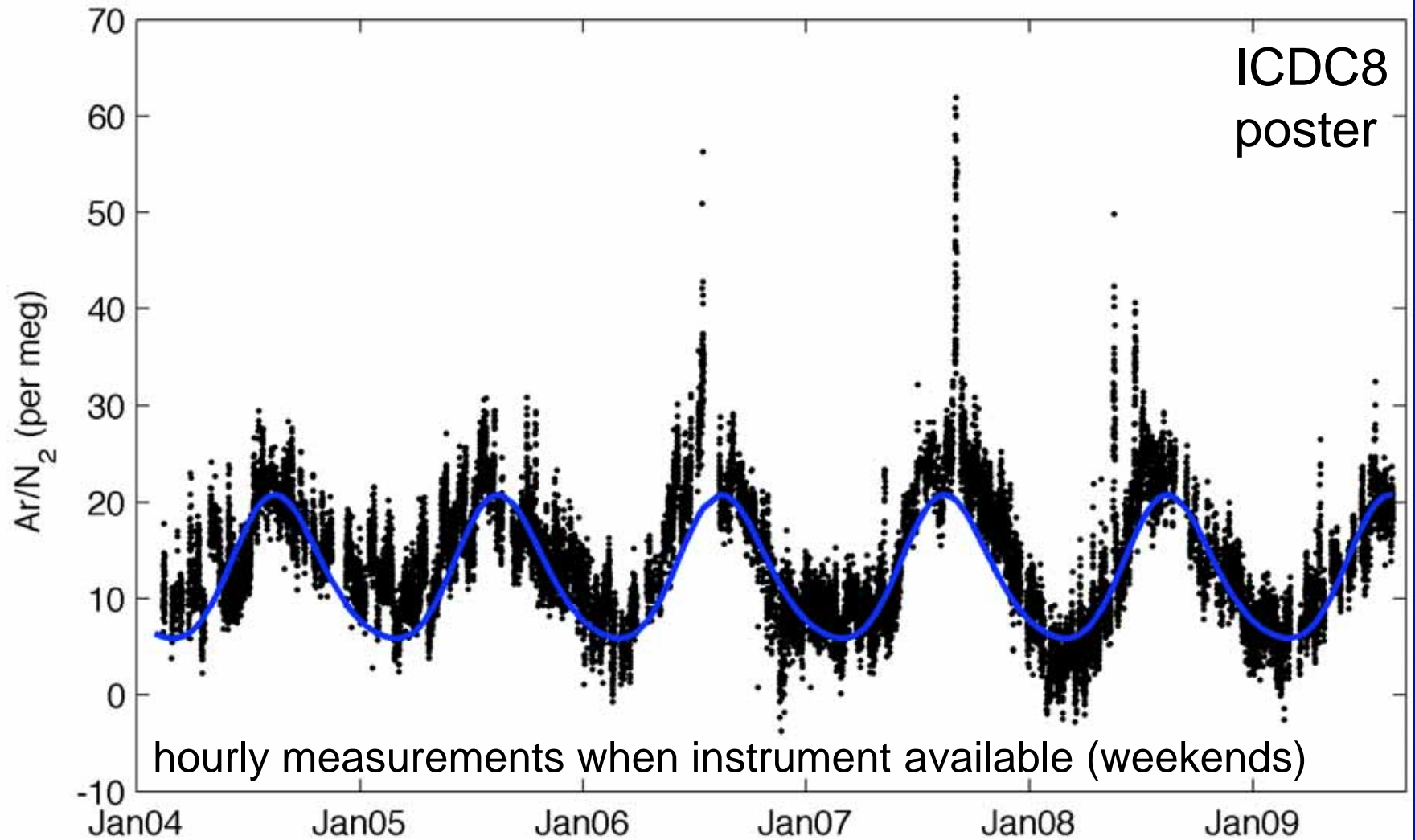
Atmospheric Ar/N₂ = tracer of ocean heat content

- Ar is about twice as soluble as N₂ in seawater
- Warming ocean increases atmospheric Ar/N₂, cooling opposite



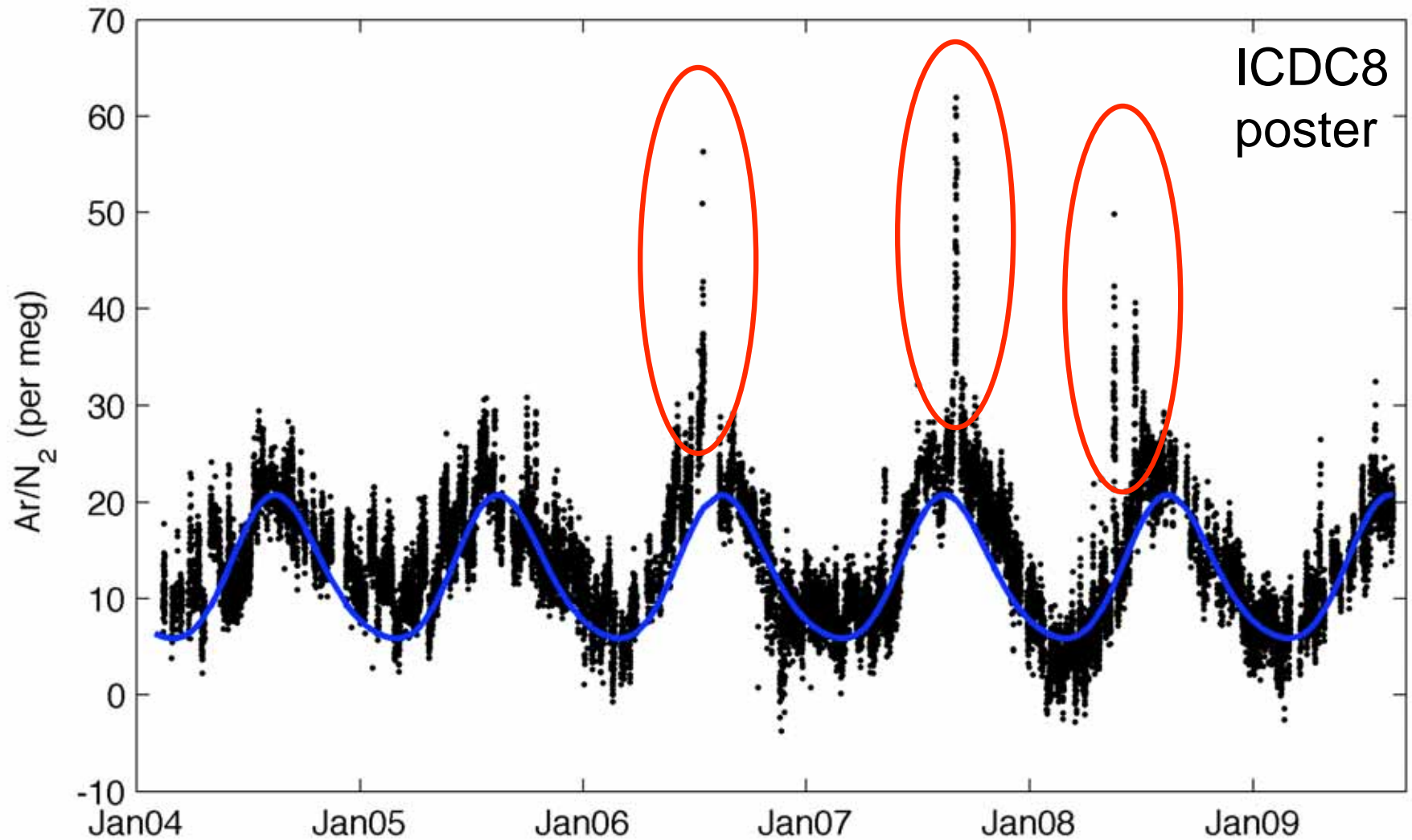
Semi-continuous measurements of Ar/N₂ at La Jolla

Mean seasonal cycle shows ~20% of ocean O₂/N₂ fluxes driven by air-sea fluxes; constraint on ocean / atm models

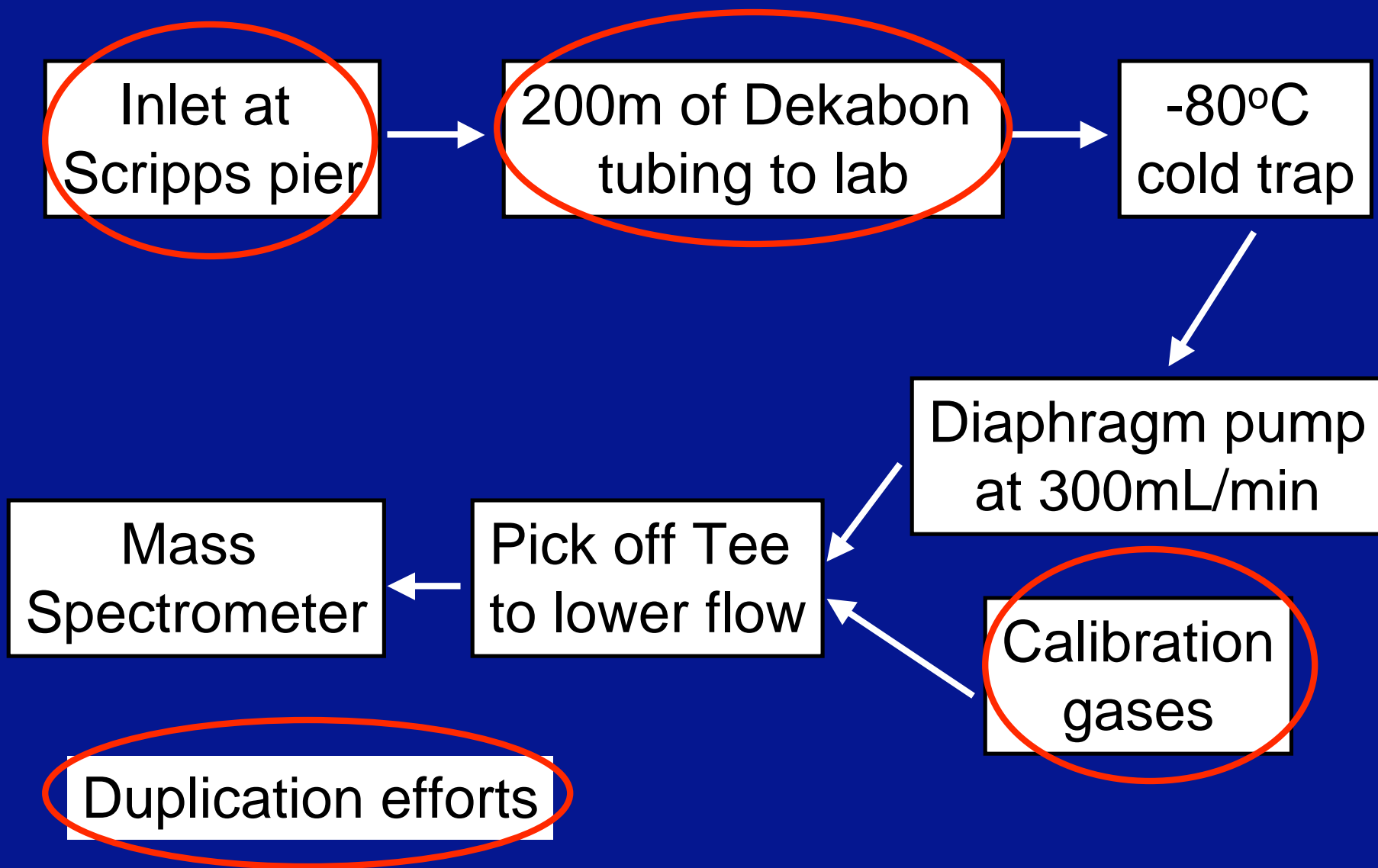


Semi-continuous measurements of Ar/N₂ at La Jolla

Days-long, high Ar/N₂ events observed in summer



Simplified continuous sample processing



Ar/N₂ issues diagnostic of problems in O₂/N₂,
high precision CO₂,
or other trace gases at 5 significant figures

Thermal fractionation affects Ar/N₂ 2.5-4 times more than O₂/N₂,
Ar/N₂ fractionation effect similar to CO₂/N₂
pressure and temperature dependent

Mass-based fractionation affects Ar/N₂ more than O₂/N₂
CO₂/N₂ will fractionate even more by mass

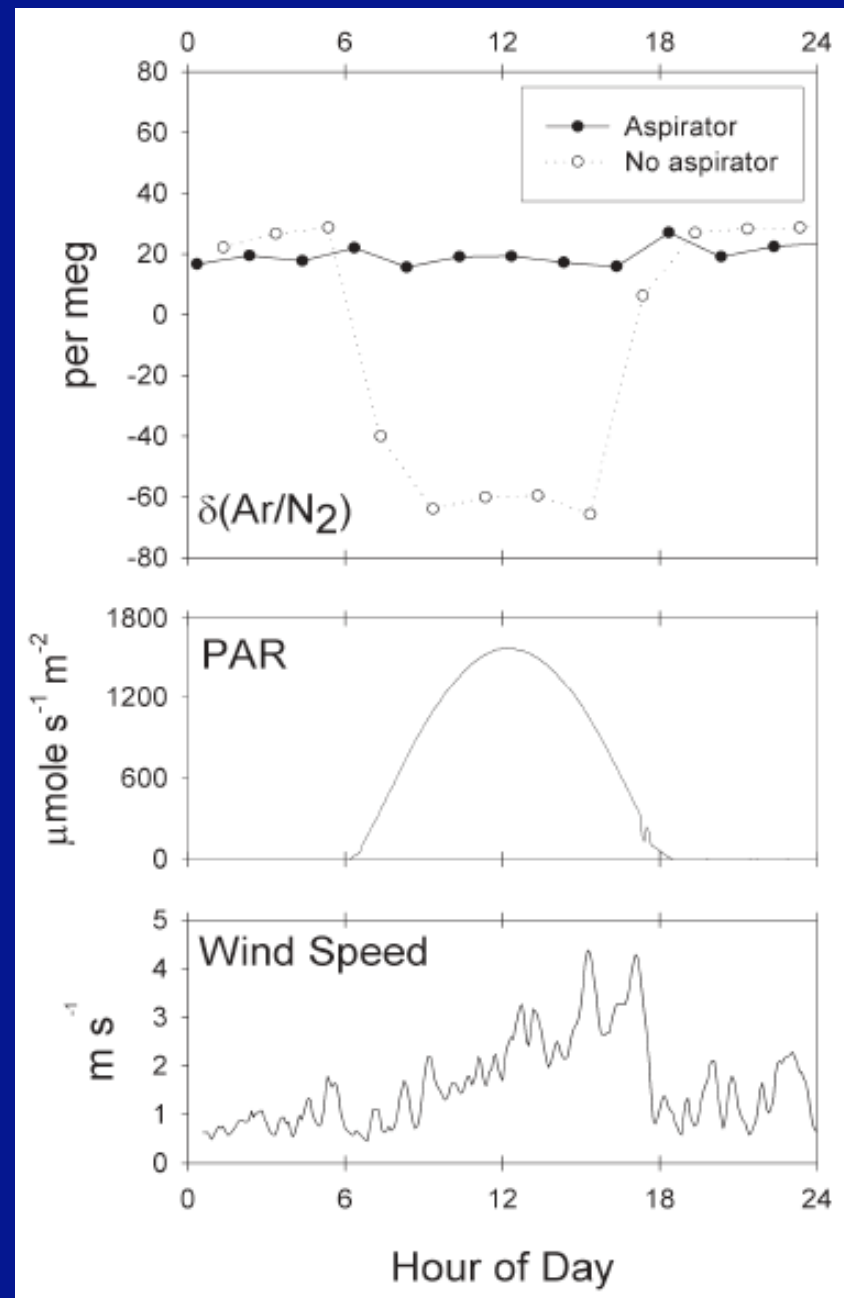
Less environmental variability in Ar/N₂ highlights methodological offsets

Preventing thermal fractionation at the inlet



Heating of unshielded inlet drives thermal fractionation of Ar/N_2

Aspirator fan provides 5m/s flow past tubing intake

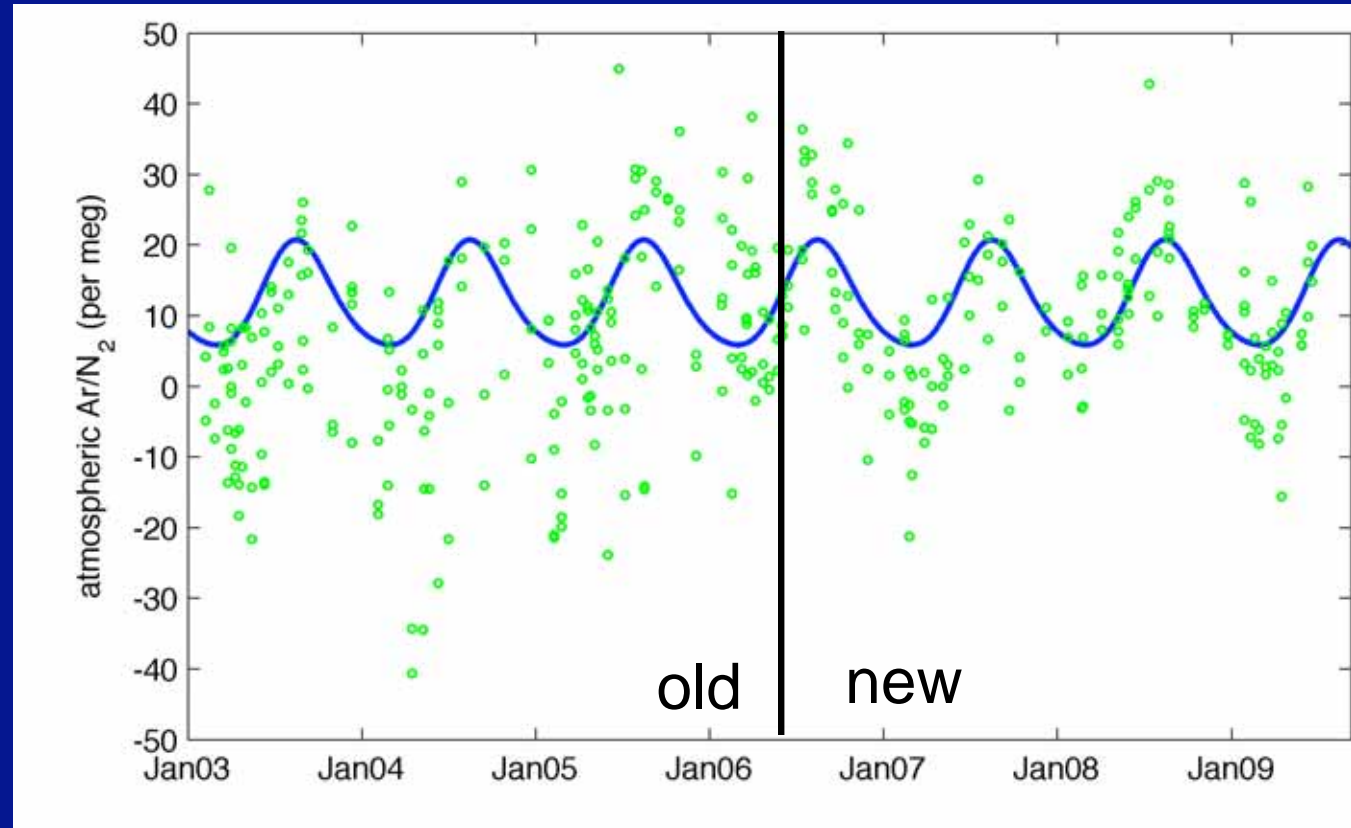


(Blaine et al., 2006)

Aspirator inlet improves flask-sampled measurements

Aspirators installed at all Scripps flask stations

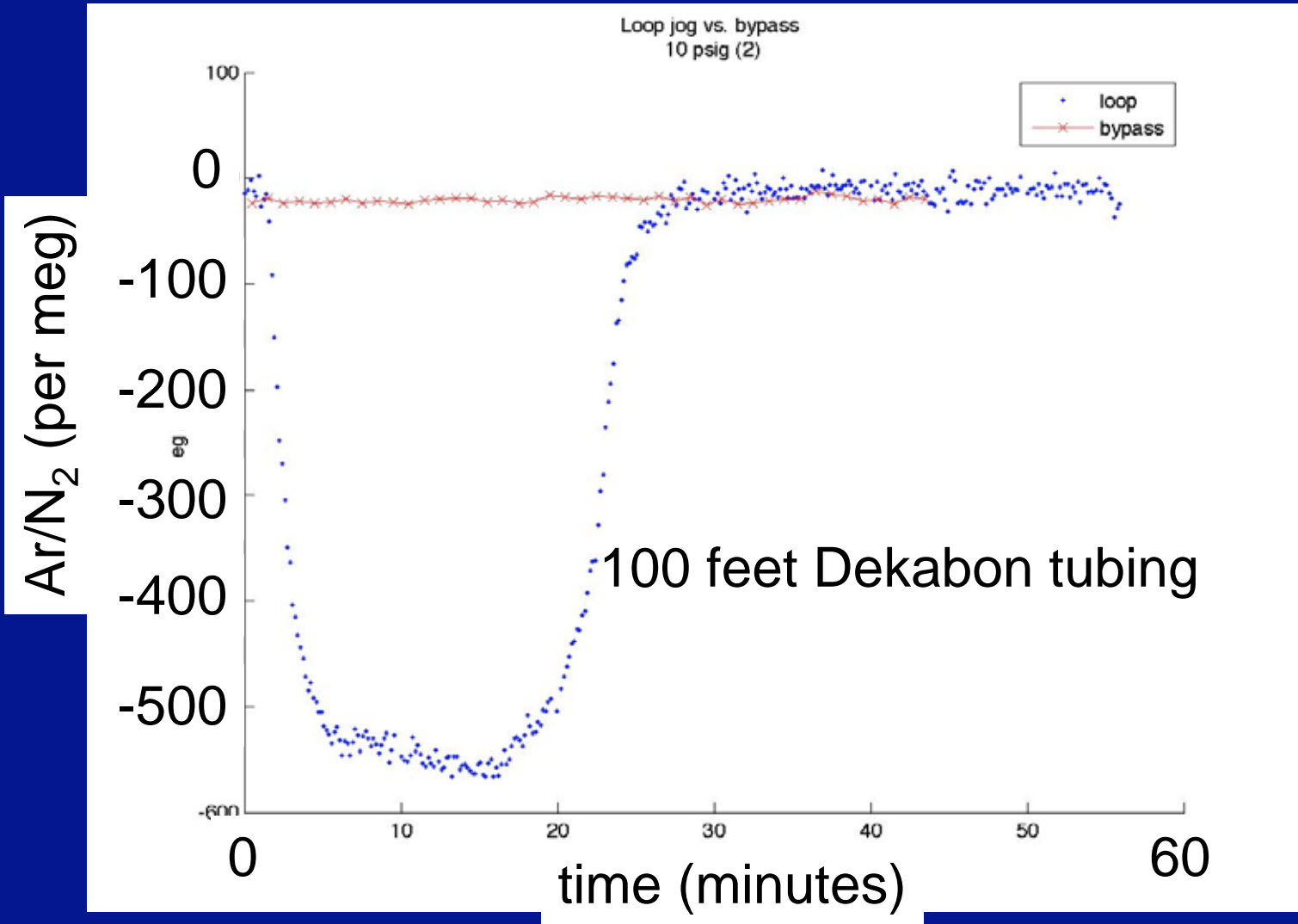
Requires periodic check of fan operation



Dekabon / Dekaron / Synflex (polyethylene-lined) tubing effects

Pressure in 100 foot loop of tubing increased 5 to 10 psig

Lining preferentially absorbs Ar compared to N₂ for 20 min

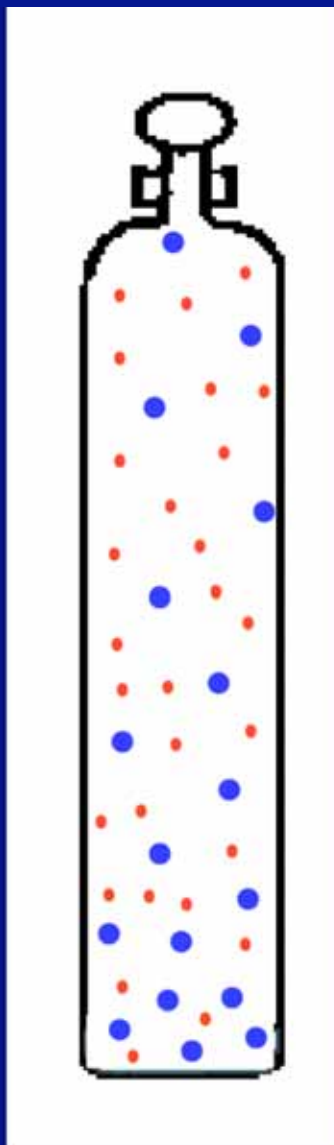


Fractionation within gas standard cylinders

Warmer

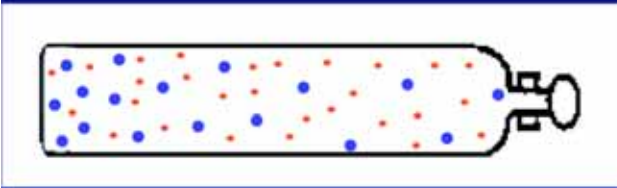
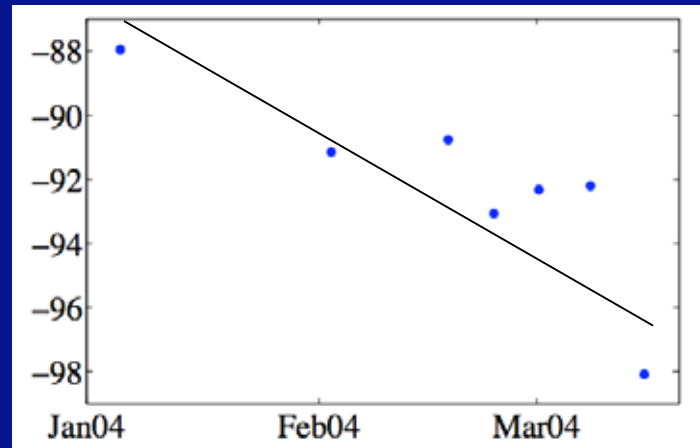
Typical thermal gradient & gravity concentrates heavier molecules downward

Cooler



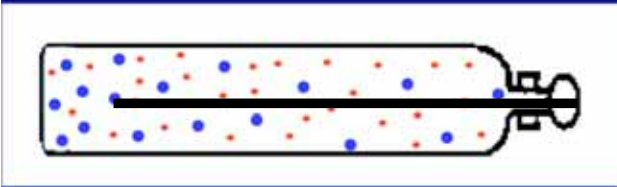
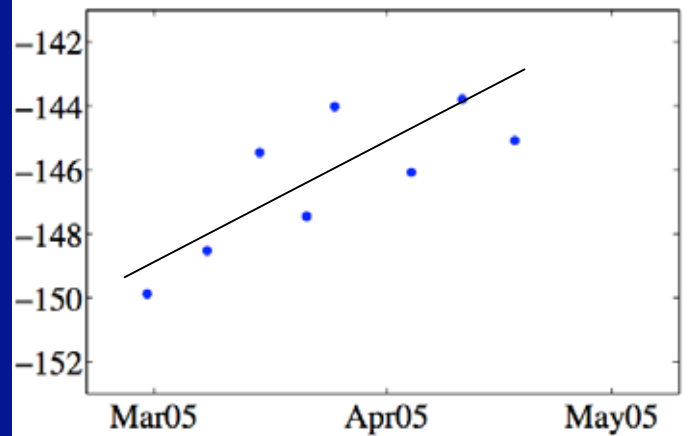
For O_2/N_2 , Ar/N_2 : must dispense standard gases from horizontal position in insulated enclosure

Working standard Ar/N₂ concentrations



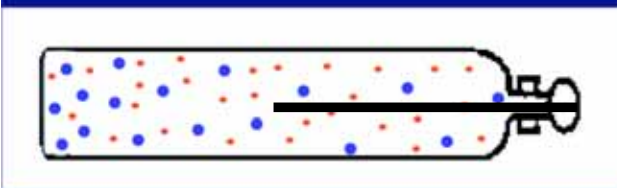
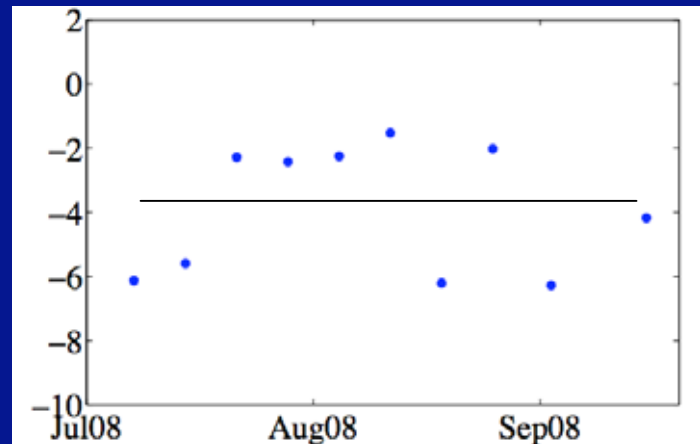
No diptube

Lateral gradients still exist in horizontal cylinders



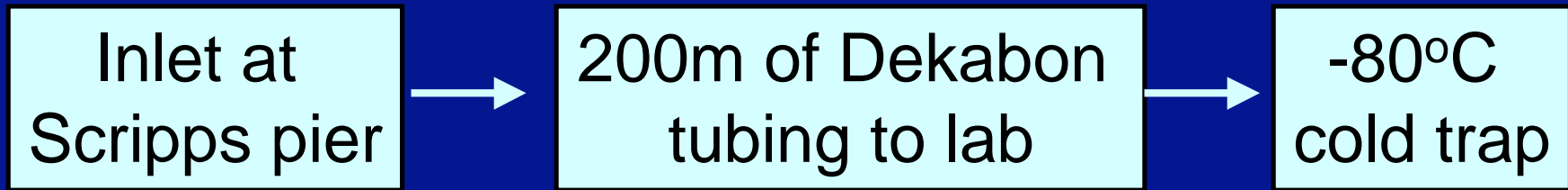
Too long diptube

Adding diptubes to remove gas from exact center of cylinder improves standard stability

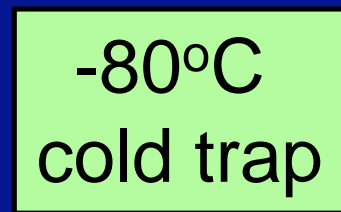
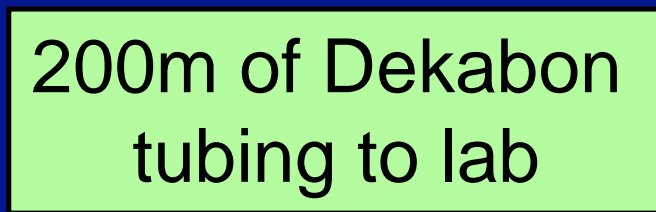
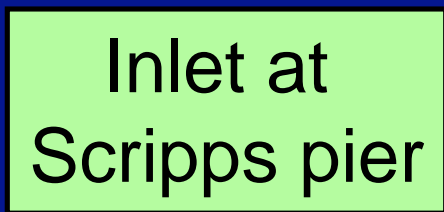
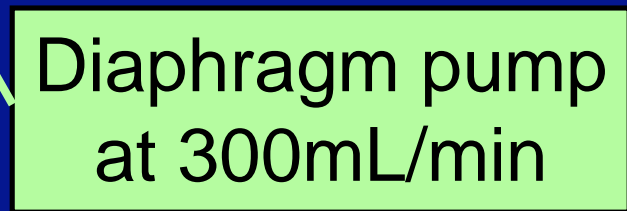
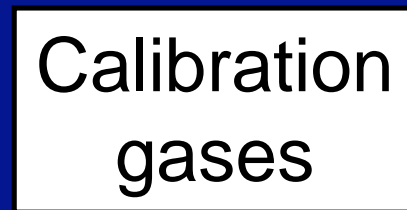
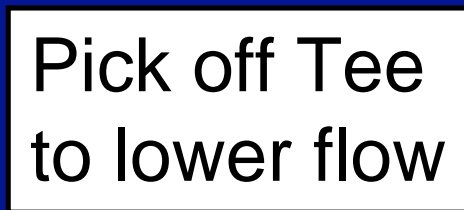
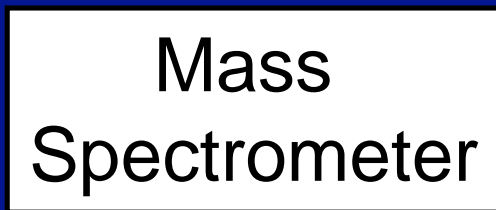
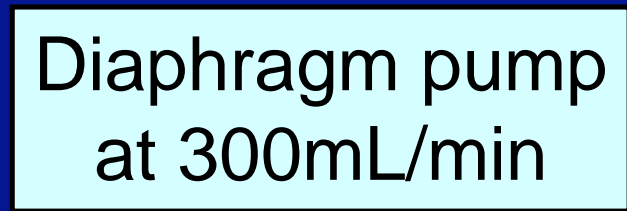


Just right

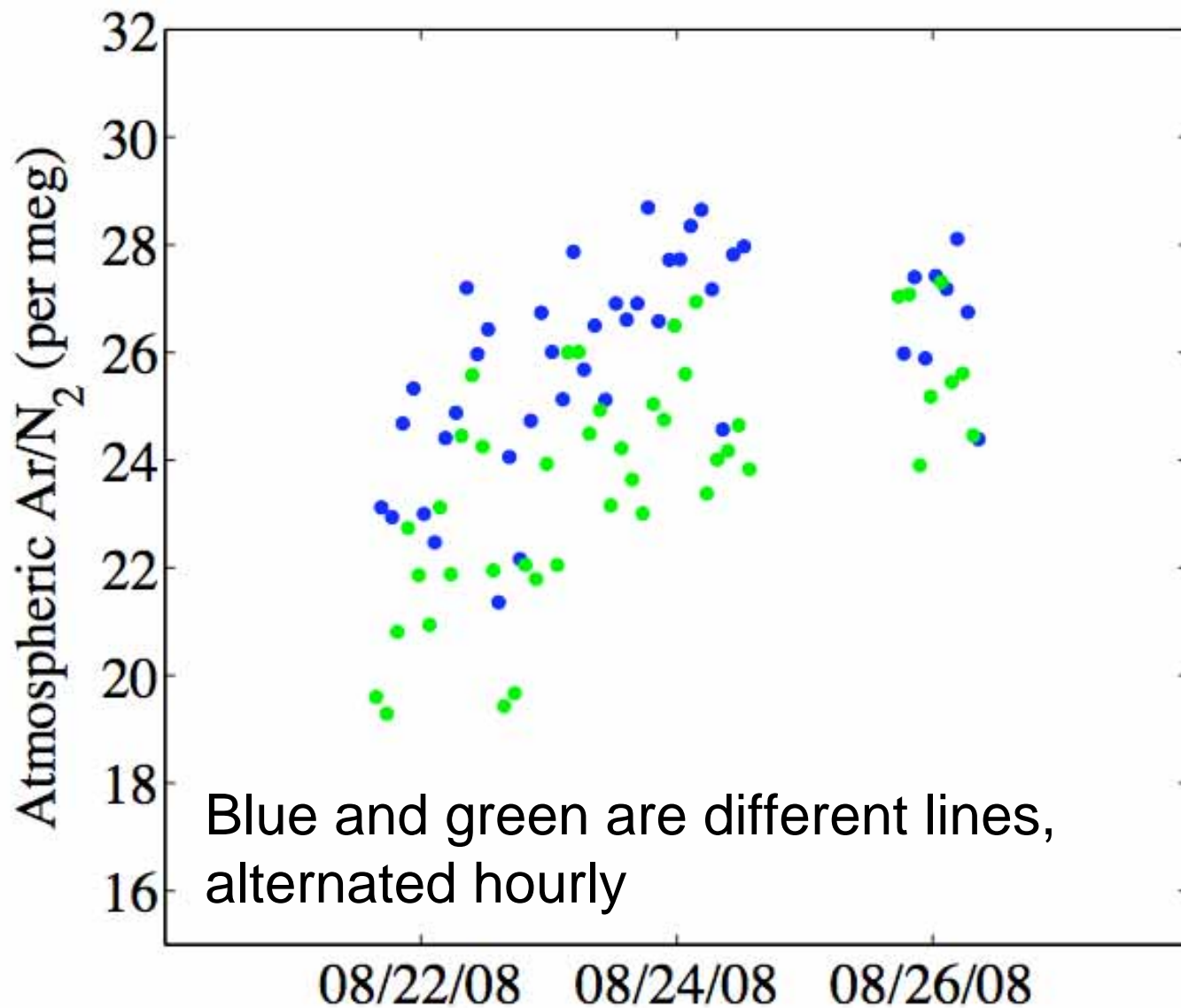
Diptubes may improve stability of vertical cylinders

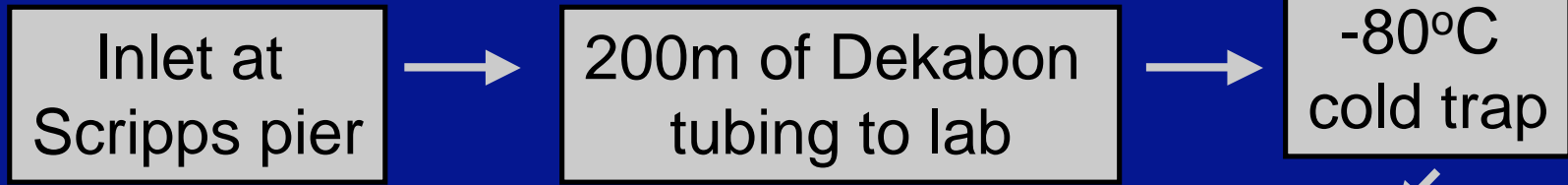


Duplication of inlet system helps diagnose arising problems

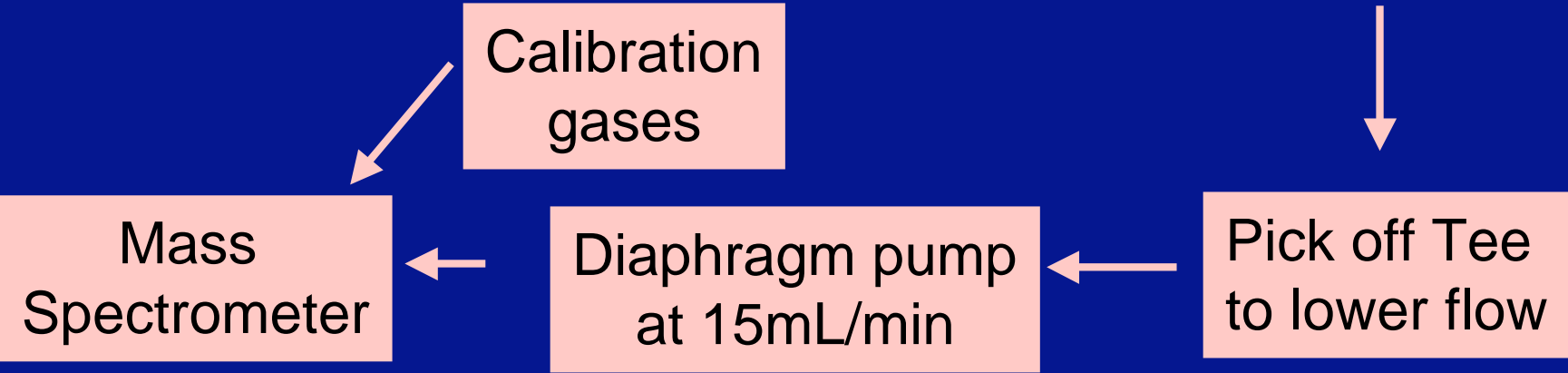
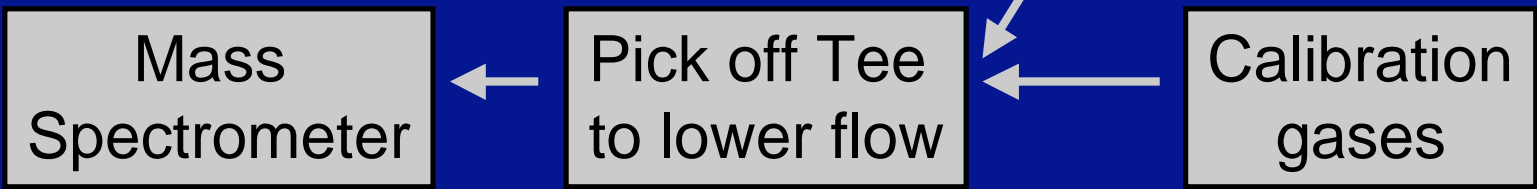
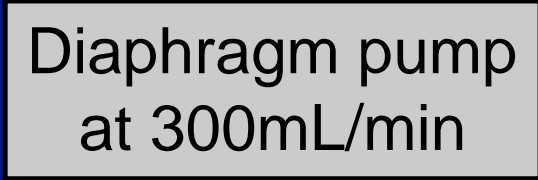


Example of leak-related line differences





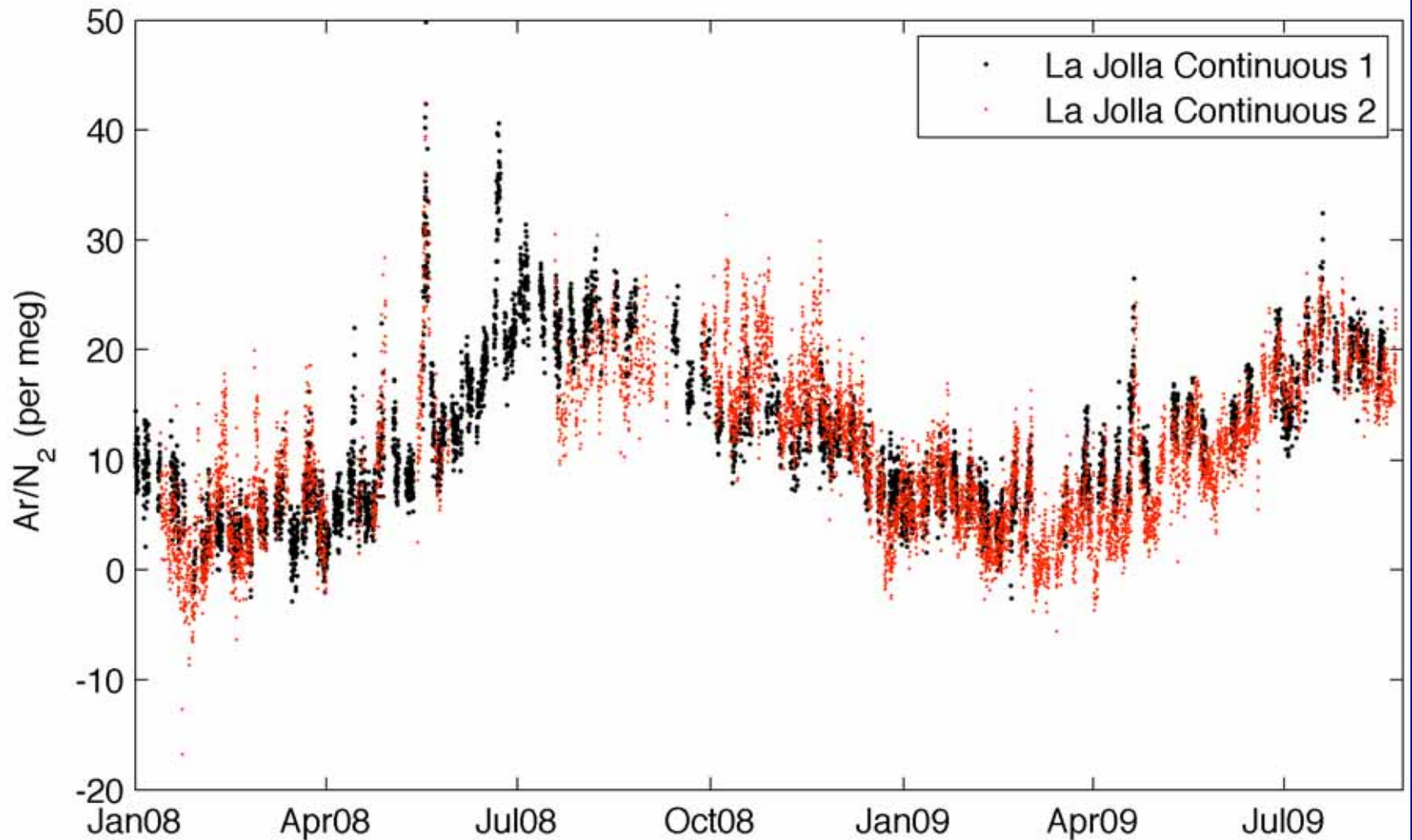
Duplication of entire system with some analytic differences



Independent instrument comparison

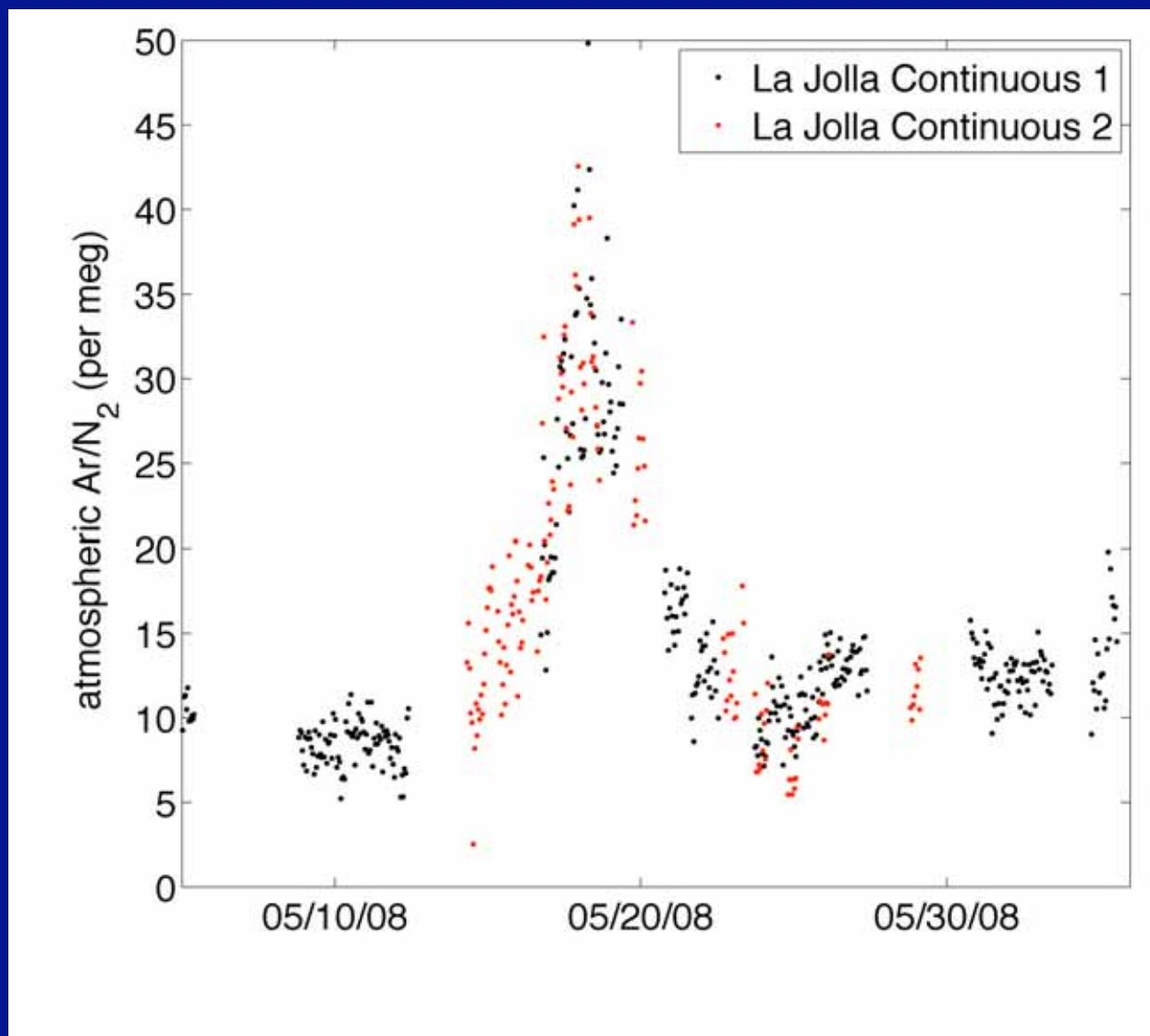
Good duplication at many times, but not all

Second instrument needs gain and CO₂ interference calibration



High Ar/N₂ events duplicated between instruments

May be driven by coastal upwelling & thin boundary layers



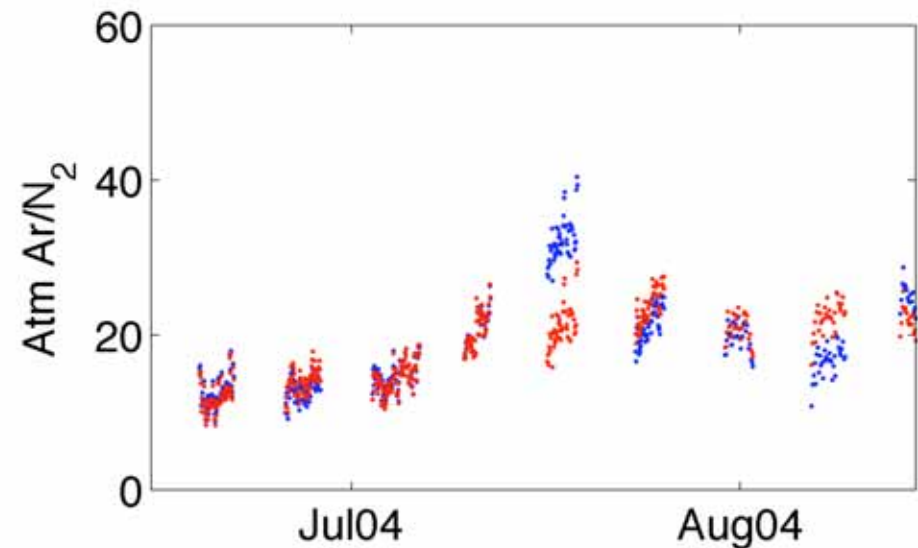
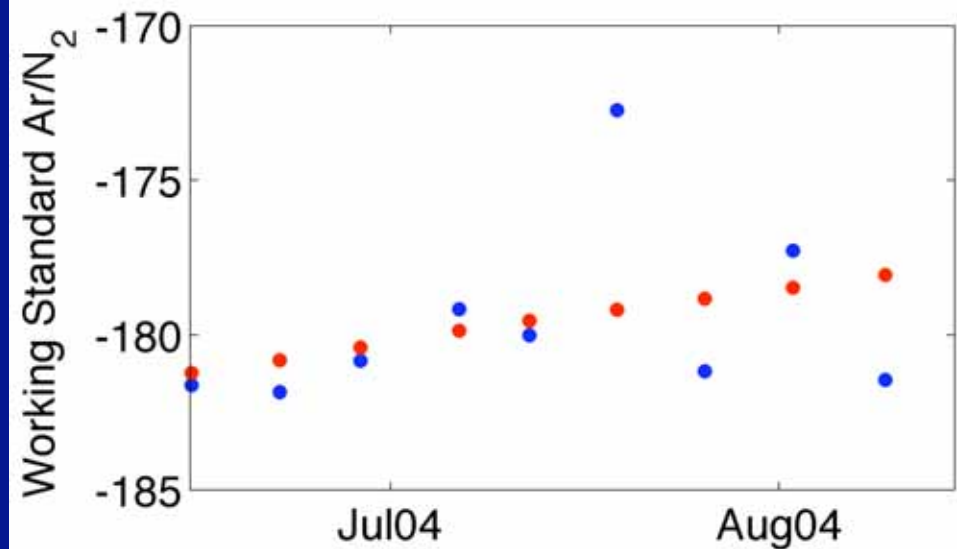
Summary

- Atmospheric Ar/N₂ responds to air/sea heat flux with potentially interesting long-term, seasonal and short-term variations
- Aspirators correct thermal fractionation at inlet
- Polyethylene-lined tubing absorbs some gases preferentially
- Diptubes in horizontal standard cylinders reduce drift (likely lateral temperature gradients) - **May help in vertical standards**
- System duplication reveals subtle bias

Avoid propagation of working standard calibration errors into dataset

blue data assumes real changes in working standard concentration

red data assumes noise in working standard determinations should be averaged out



Semi-continuous measurements of Ar/N₂ at La Jolla

Unclear whether seasonal variability is real environmental change or unresolved calibration problems

