Underwater Membrane Introduction Mass Spectrometers: Recent Developments and Deployments

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Need for In-water Chemical Monitoring and Profiling

- Oceans and coastal regions
  - Biogeochemical studies
  - Hydrothermal vent analysis
  - Pollution monitoring and tracking
  - Bloom and plume diagnostics
  - Energy source discovery
    - Methane and natural gas
    - Oil reservoirs

- Harbors and internal waterways
  - Port safety and security
    - Inadvertent chemical release
    - Deliberate chemical release
  - Water supply monitoring
  - Ecosystem health (global climate change)

NASA
C 98-2815

National Aeronautics and Space Administration
Lewis Research Center

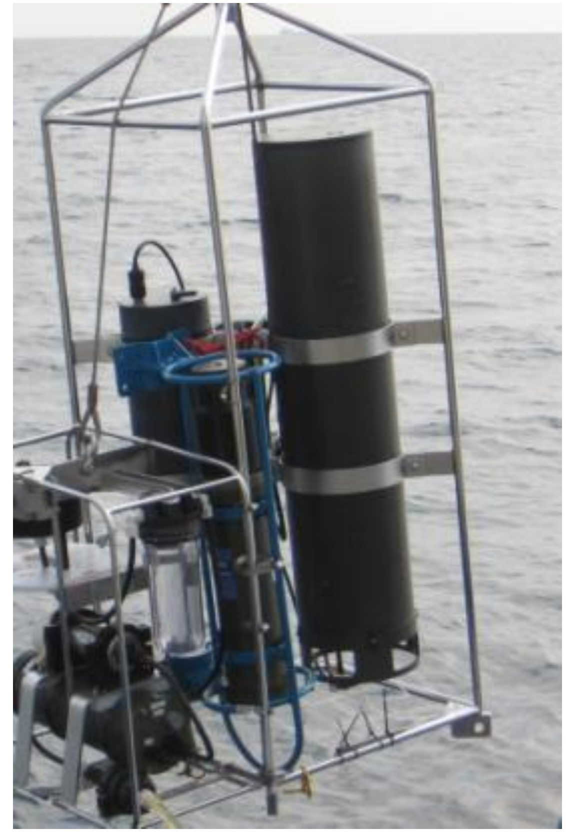
Approach of In Situ Analysis Provides Benefits

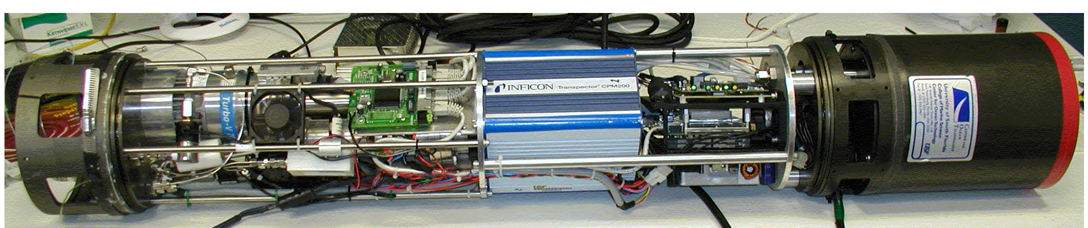
- Reduced sample contamination
- Increased sampling speed/density
- Real-time feedback
  - Rapid response
  - Adaptive sampling
  - Gradient mapping
- Self-directed sensors

Mass spectrometry allows sensitive simultaneous detection of multiple chemical species with high specificity

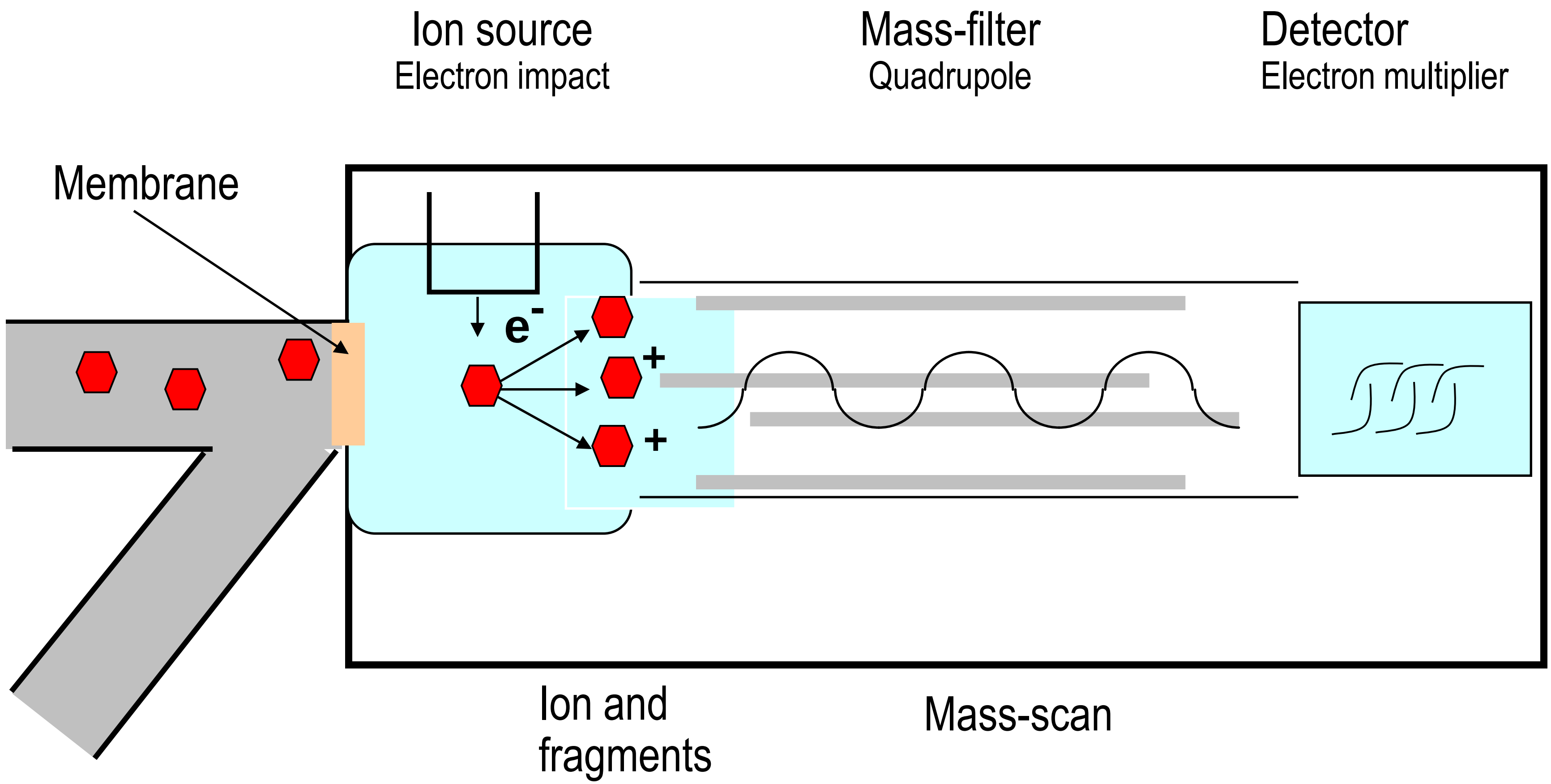
Portable Underwater Mass Spectrometry (UMS)

- Membrane introduction mass spectrometry (MIMS)
  - Simultaneous in situ detection of multiple analytes
  - Dissolved gases
  - Volatile organic compounds (VOCs)
  - Light hydrocarbons
- Recent developments
  - Dissolved inorganic carbon (DIC) measurements
  - Effect of salinity on MIMS measurements
- Recent deployments
  - Santa Barbara (SB) Channel: 2-D mapping
  - Gulf of Mexico: MC118 gas hydrates research
  - Gulf of Mexico: MC252 deep tow surveys



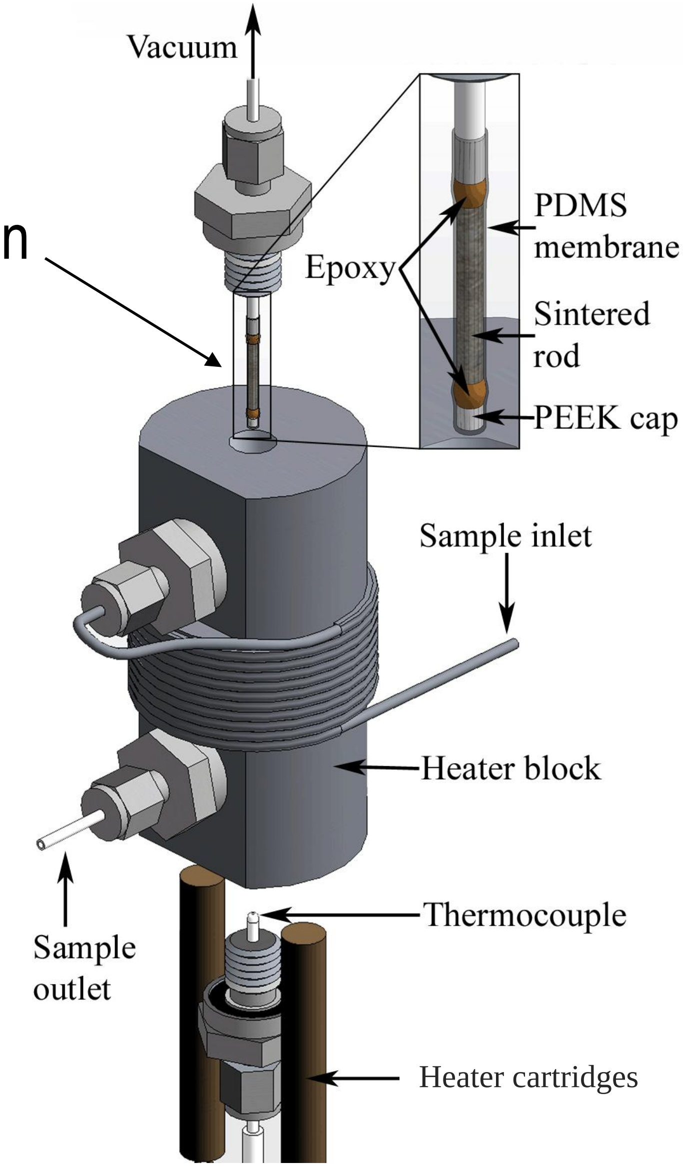


Membrane Introduction Mass Spectrometry (MIMS)



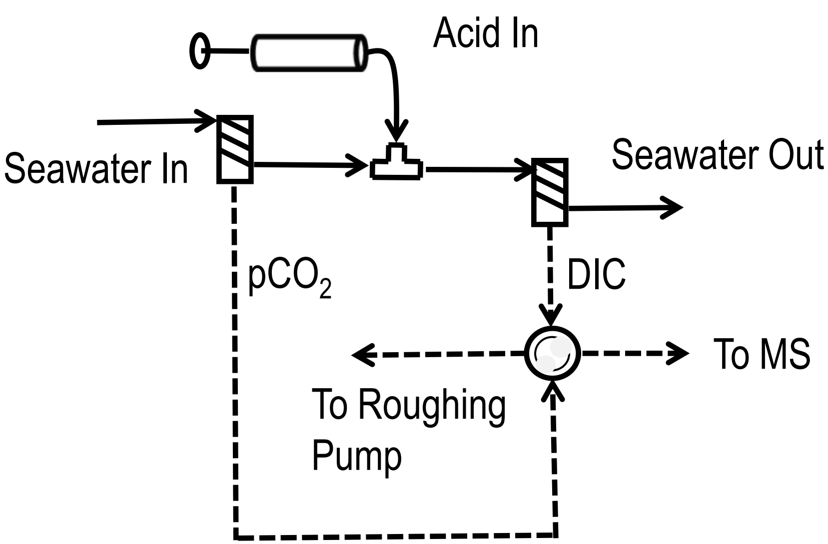
High Pressure Membrane Assembly

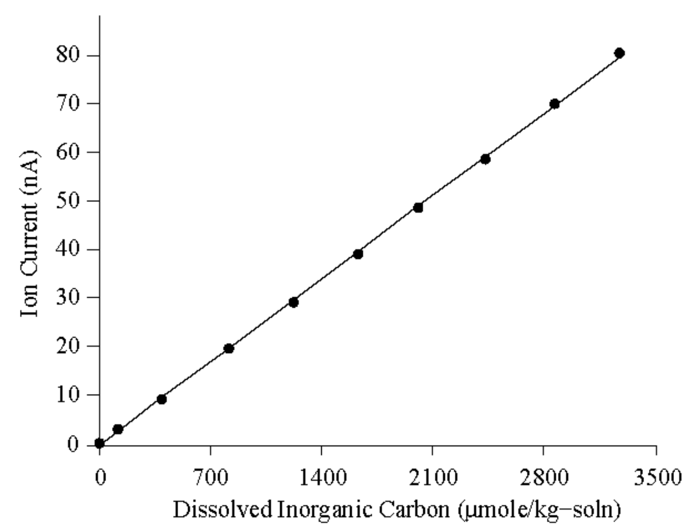
- Flow-over membrane interface design
  - Polydimethlysiloxane (PDMS)
- Temperature regulated
- Pressure tested to 200 bar (2000 m depth)



Oceanic Carbon System Measurements Using Underwater Mass Spectrometry

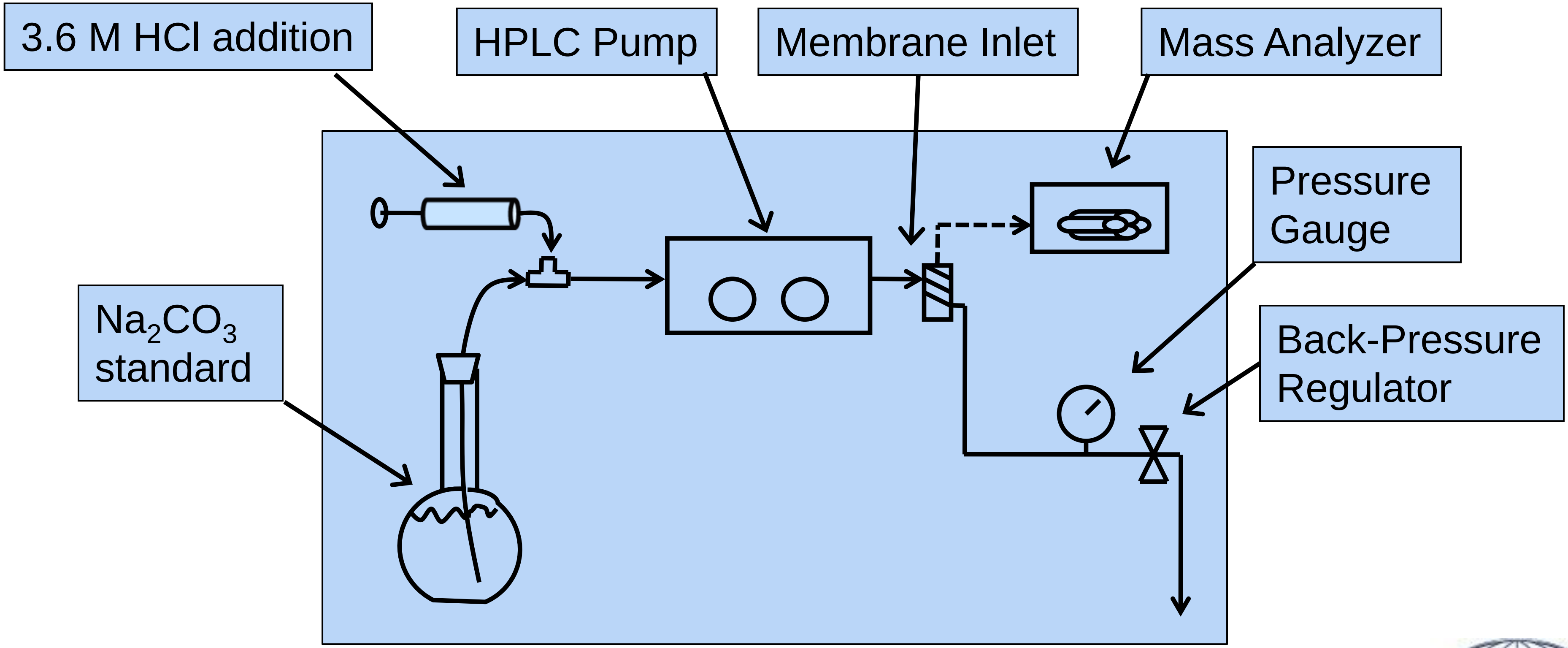
- Method for measuring gaseous dissolved carbon dioxide (pCO_2) and total dissolved inorganic carbon (DIC) with UMS
  - Calculate total alkalinity and pH
- Dual membrane probe system (also possible with single membrane)
- Switching valve for rapid changing between acidified and non-acidified samples (DIC/ pCO_2)



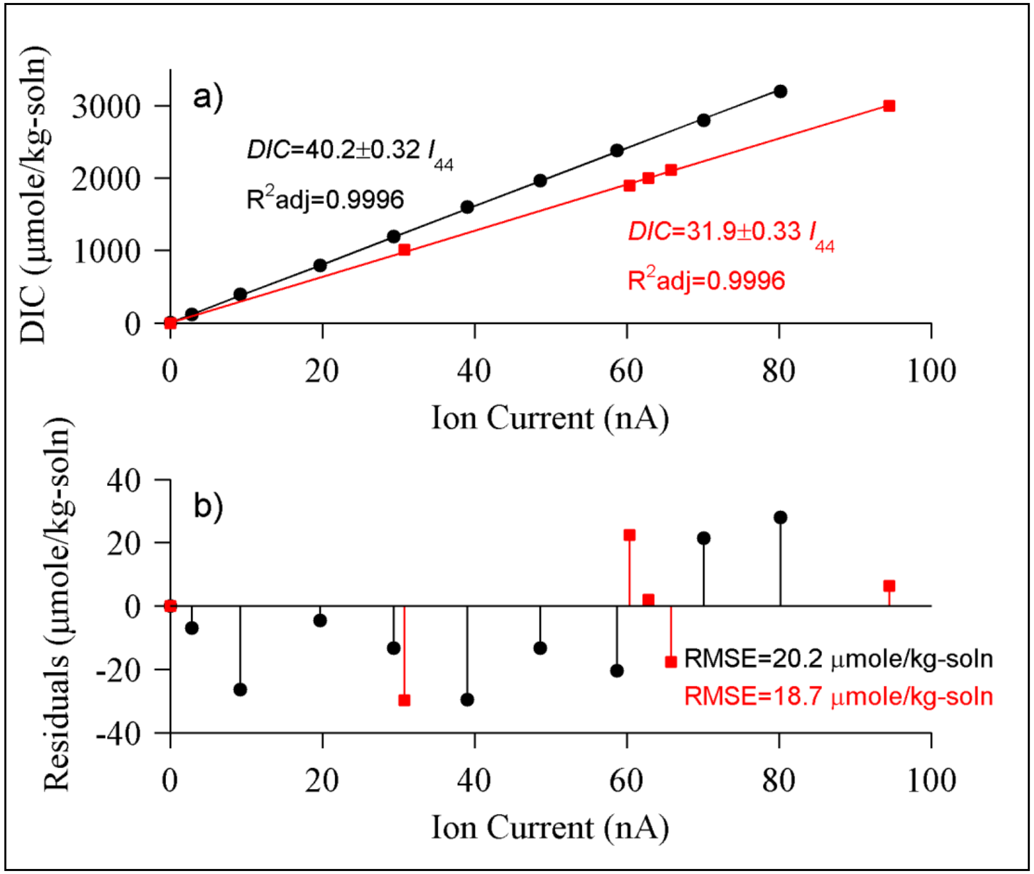


DIC Linearity Experimental Setup

- Na_2CO_3 standards for DIC were infused with acid and analyzed by MIMS to determine instrumental linearity and precision



MIMS Response to DIC is Linear over Expected Range



$$DIC = \beta_1 I_{44}$$

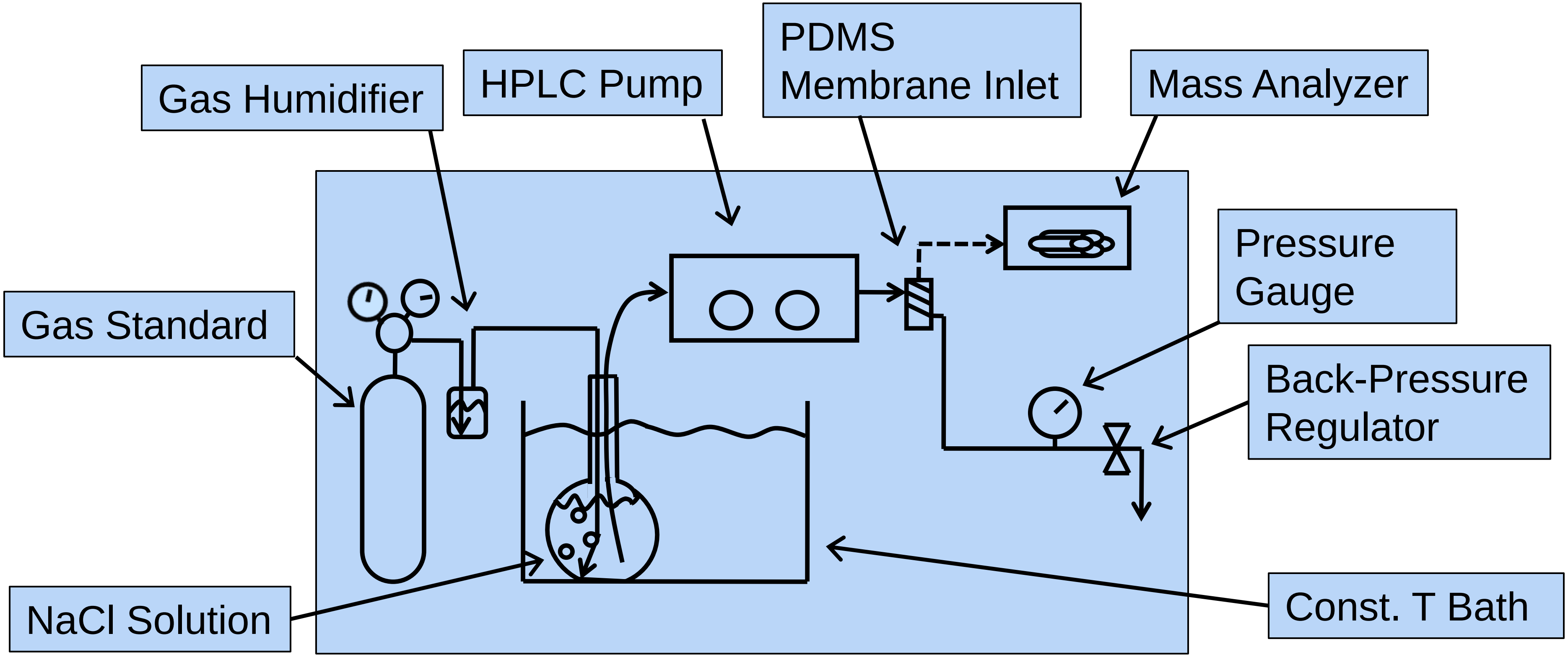
@ 35° C, $\beta_1 = 31.9 \pm 0.3$

@ 30° C, $\beta_1 = 40.2 \pm 0.3$

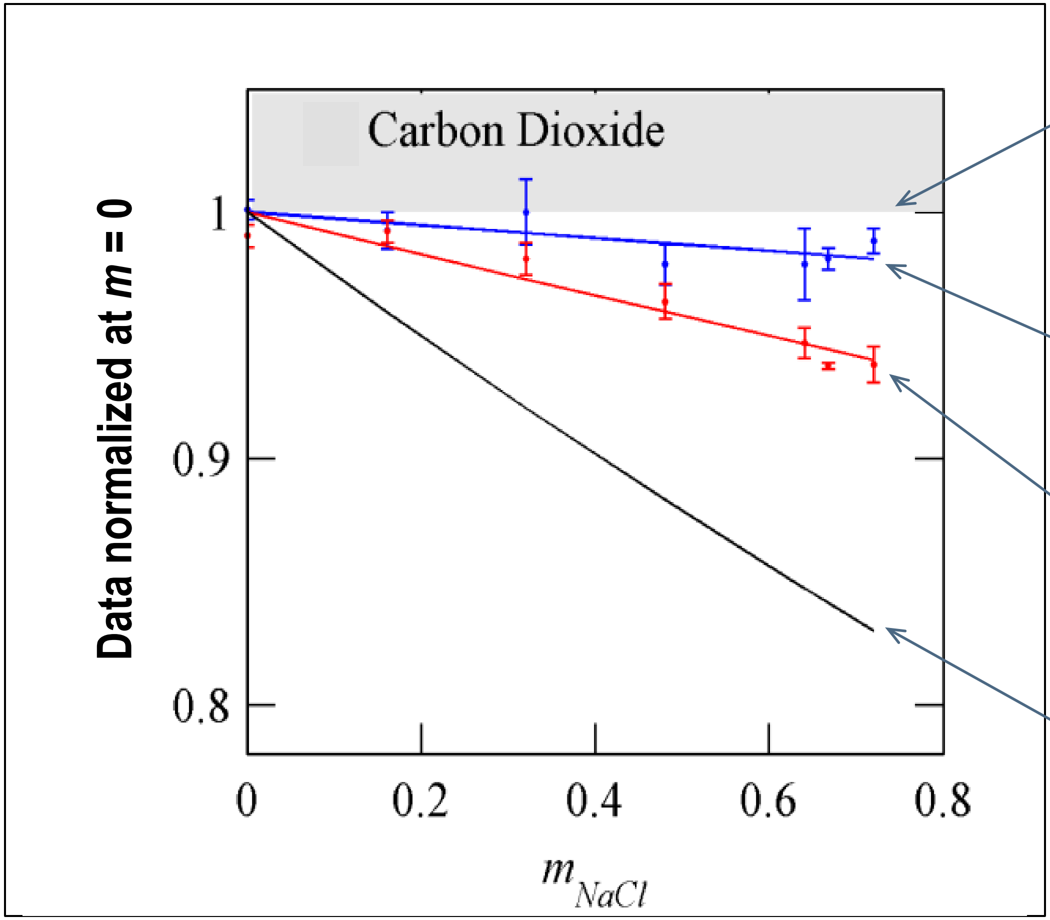
- Baseline was subtracted prior to linear fit
- Residuals indicate a possible small quadratic component

Salinity Dependence Experimental Setup

- Acidified NaCl solutions of various ionic strength were simultaneously equilibrated with a gas standard (1% CO_2 in N_2)
  - Each sample was of equal fugacity, but varied in concentration



Salinity Dependence Results (PDMS Membrane)



Expected response if signal were proportional to fugacity (no variation)

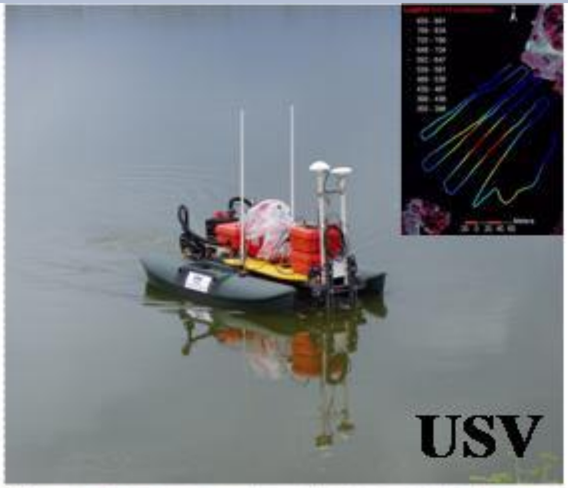
Actual response at 184 atm

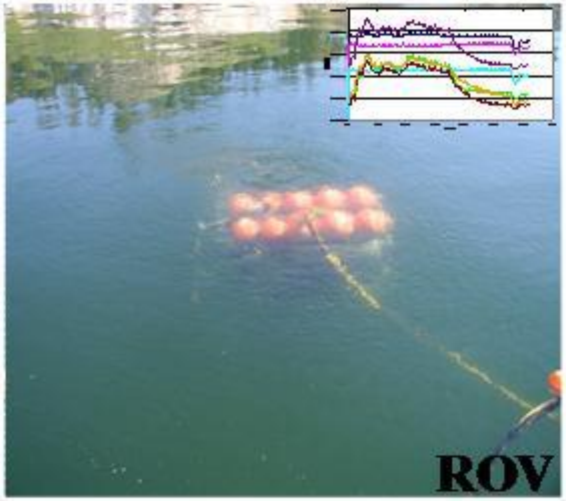
Actual response at 1 atm

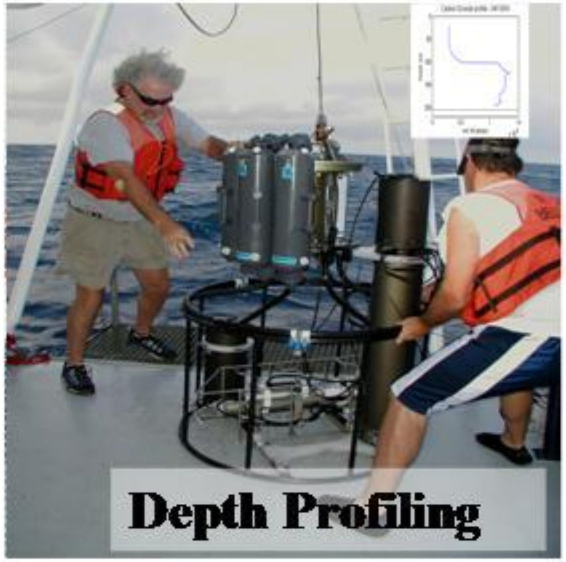
Expected response if signal were proportional to concentration

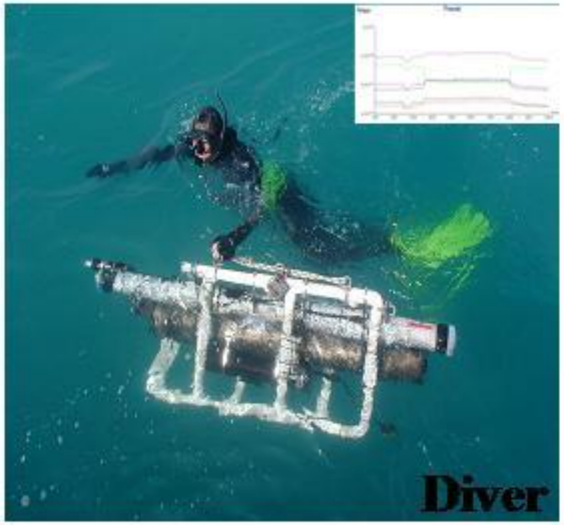
- MIMS response is salinity-dependent and the degree of dependence changes with hydrostatic pressure (two diffusion mechanisms?)

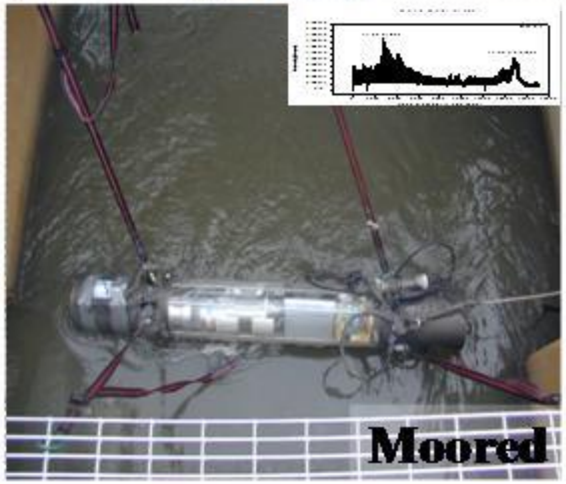
Deployment Methods



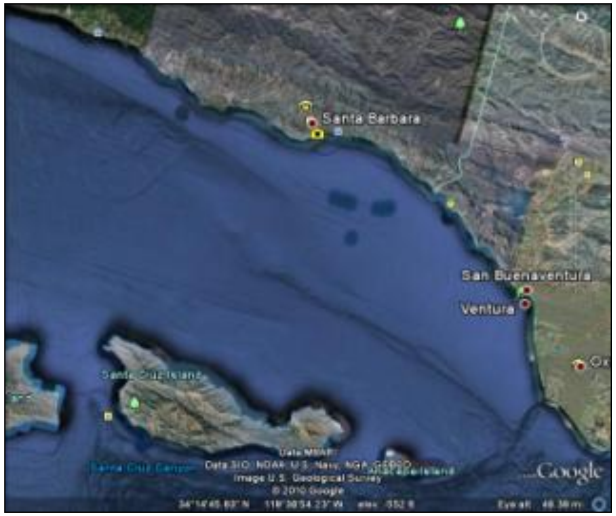


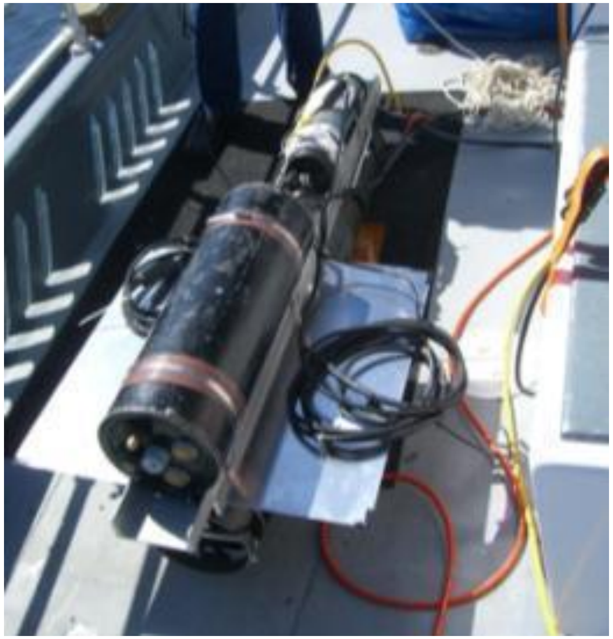






In Situ Methane Measurements in the Santa Barbara Channel Using UMS Analyses (Sept. 2009)

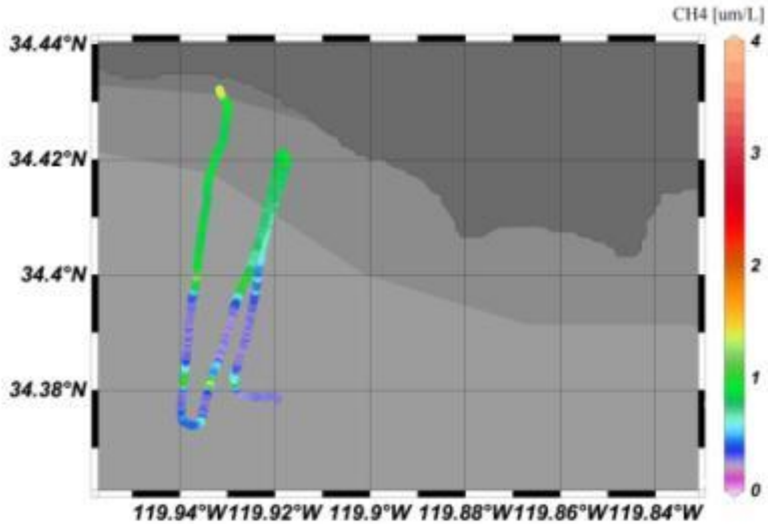


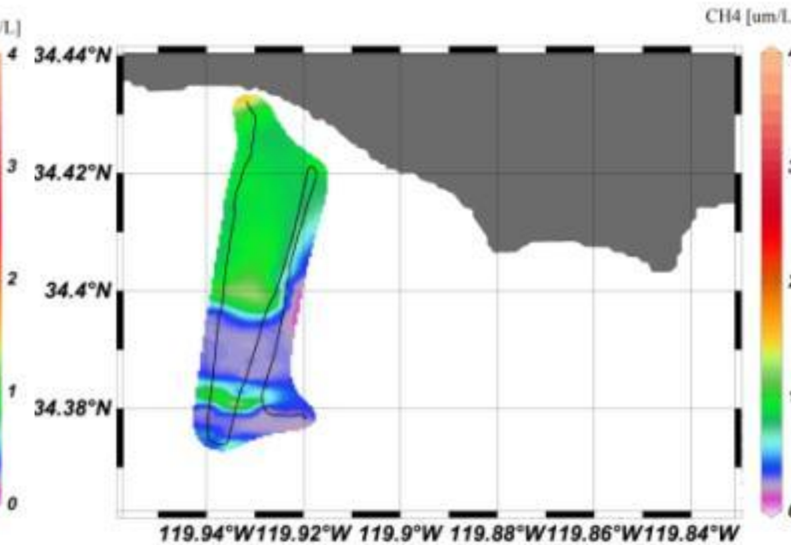


- Surface tow surveys of dissolved gases and VOCs with UMS in SB Channel
- UMS mounted on custom towfish along with conductivity, temperature, and depth (CTD) sensor and battery vessel
- Communicated with instrument through a tethered Ethernet connection

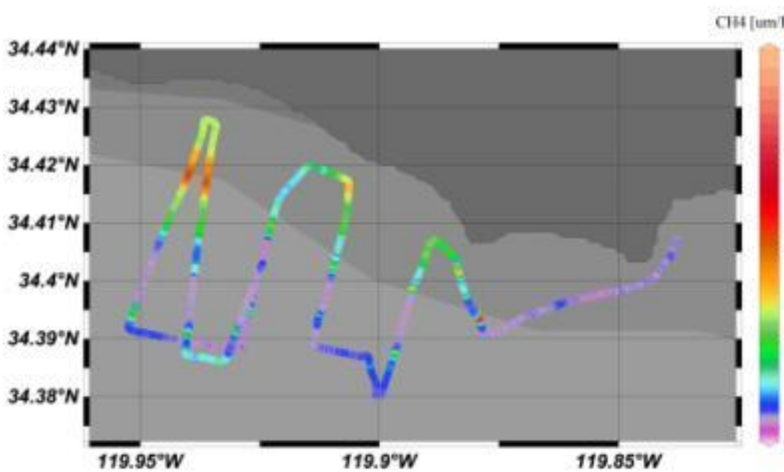
Transects and Interpolated UMS Data in SB Channel

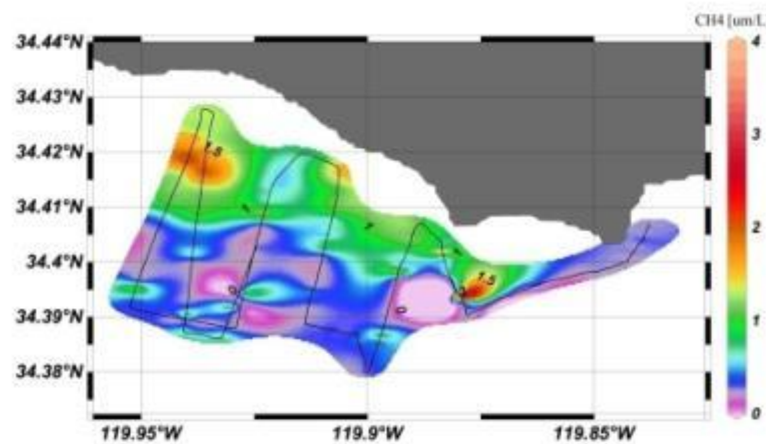
Day 1, Sept. 28, 2009





Day 3, Sept. 30, 2009

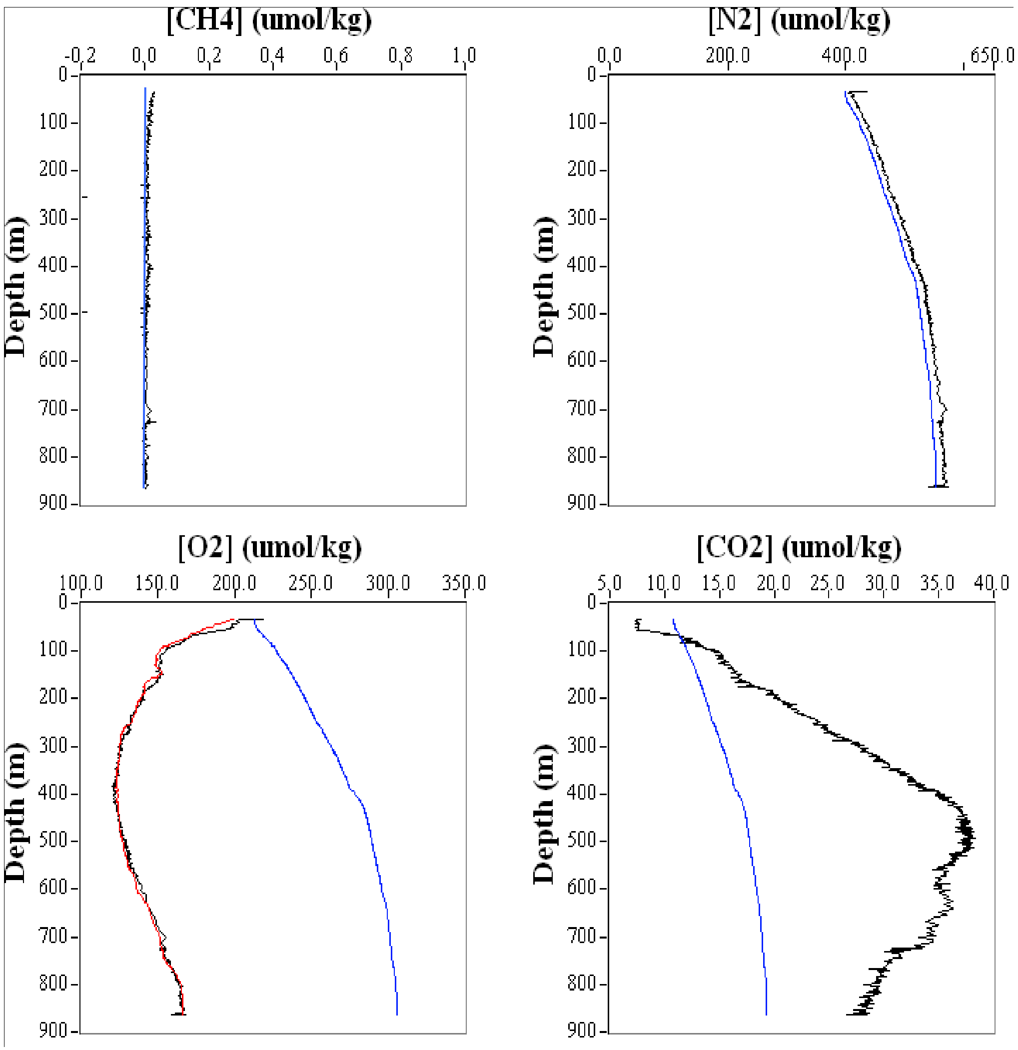




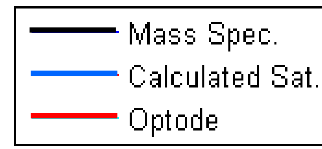
UMS for Hydrates Research in the Gulf of Mexico (March 2009)

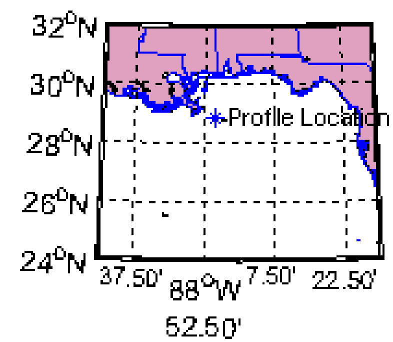
- Vertical profiles of dissolved gases with UMS in Gulf of Mexico (MC118)
- UMS mounted on custom frame along with CTD, dissolved oxygen (DO), and pH sensors
- Communicated with instrument through standard UNOLS CTD tether using Seabird modem
- Determined dissolved gas concentrations from UMS data with the aid of a portable calibration unit

Depth Profile Data – Gulf of Mexico



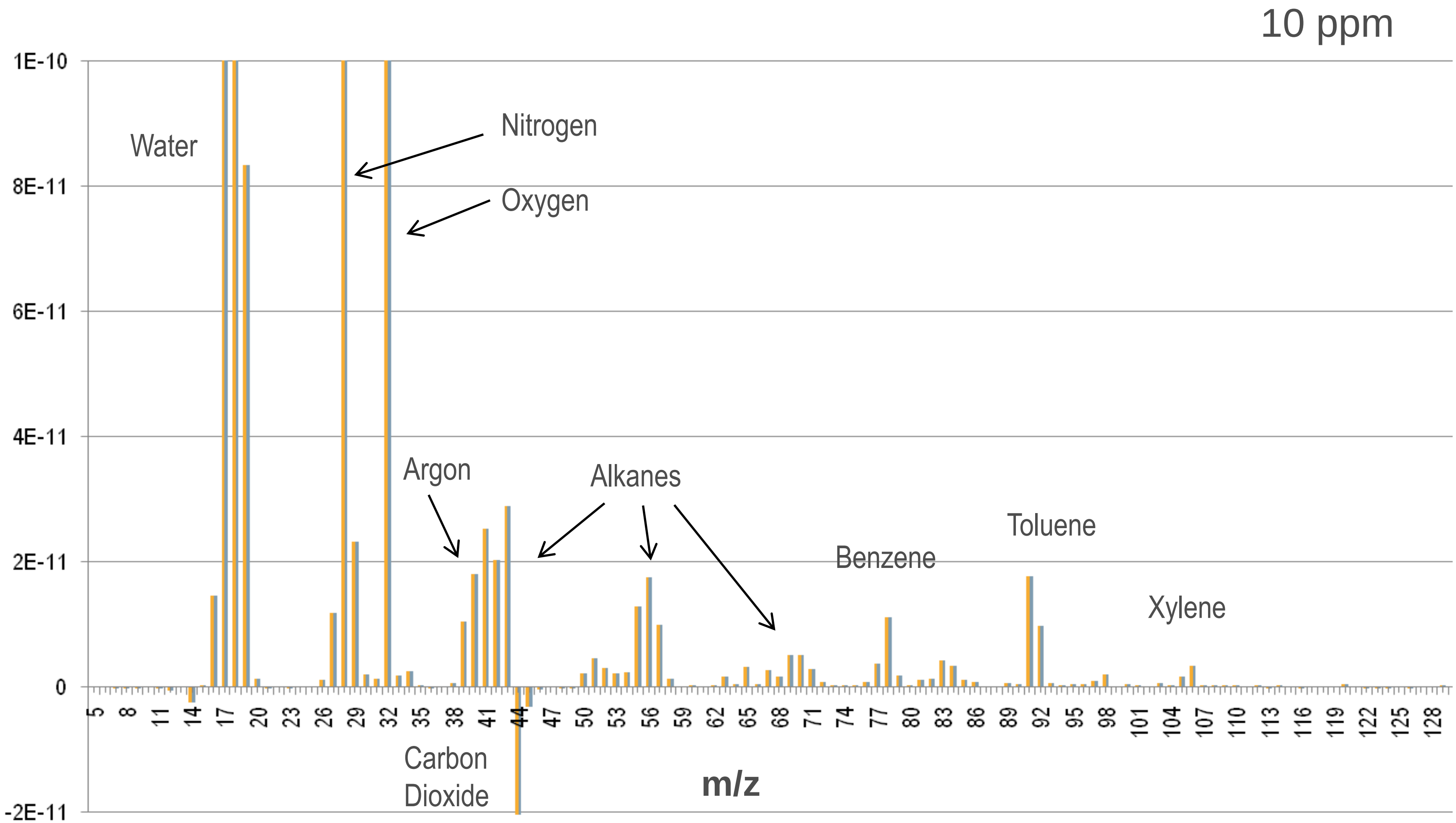
Argon Corrected





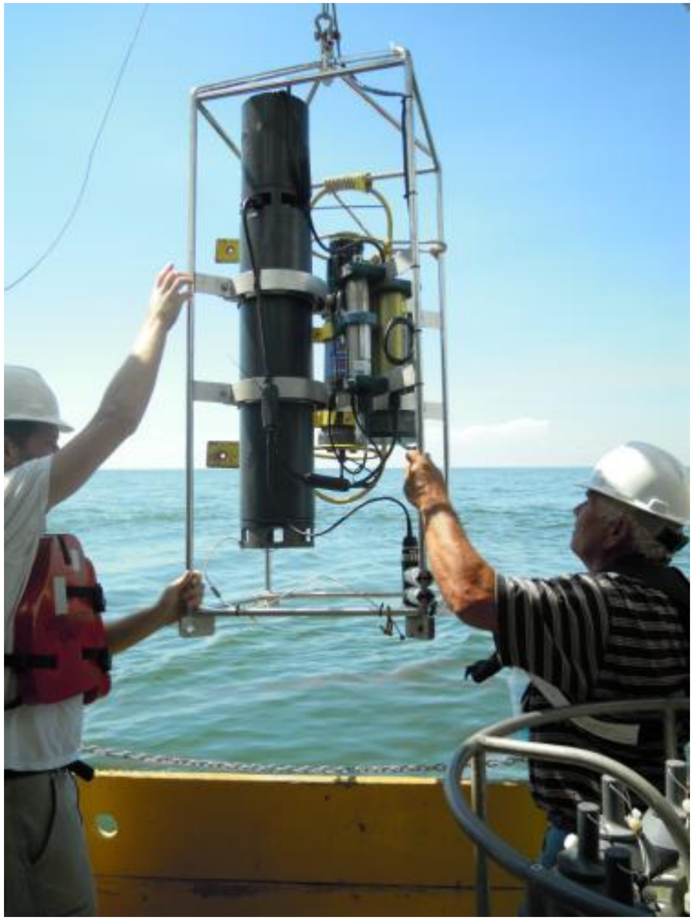
Deepwater Horizon Incident – Subsurface Oil

Louisiana Crude Reference Oil Dissolved in Water



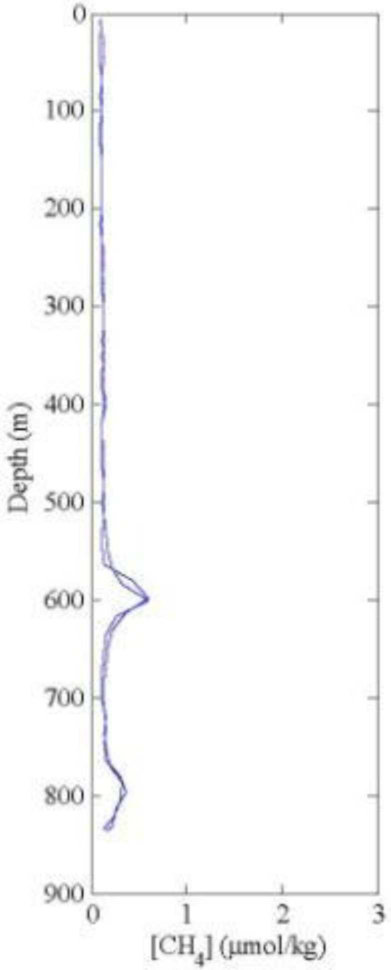
Background Subtracted Mass Spectrum

UMS Deployment at MC118 (June 2010)

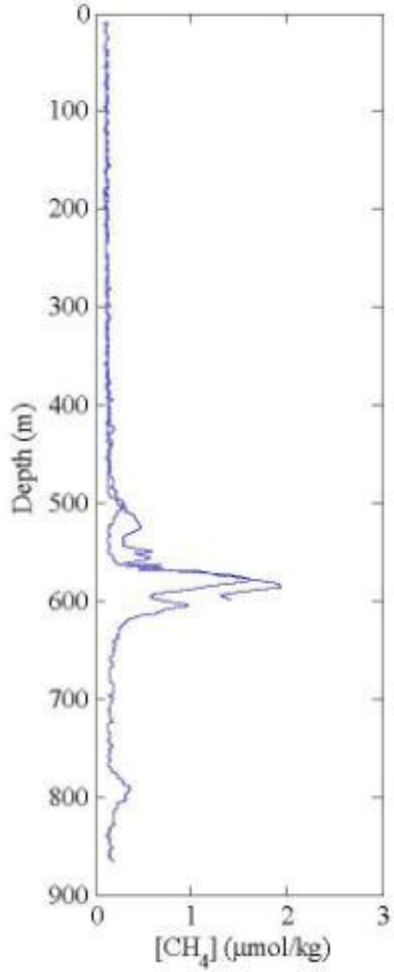


- Vertical profiles of dissolved gases with UMS in Gulf of Mexico (MC118)
- UMS mounted on custom frame along with CTD, DO, and pH sensors
- Communicated with instrument through standard UNOLS CTD tether using Seabird modem

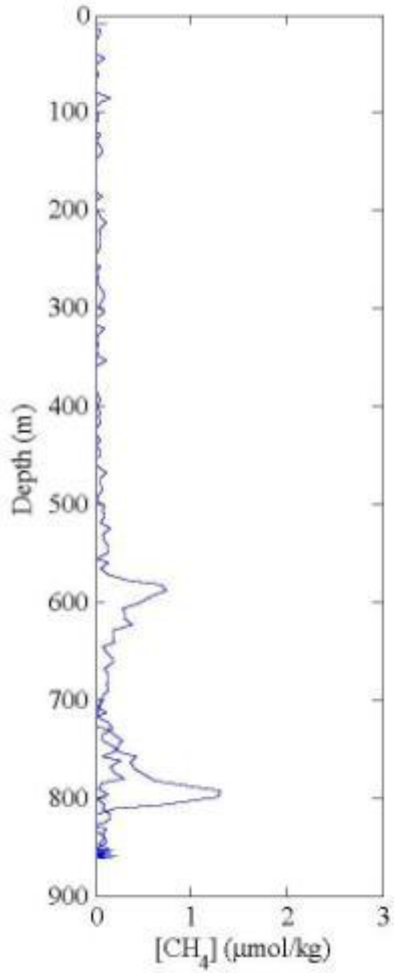
Vertical Methane Concentration Profiles at MC118



Cast 1

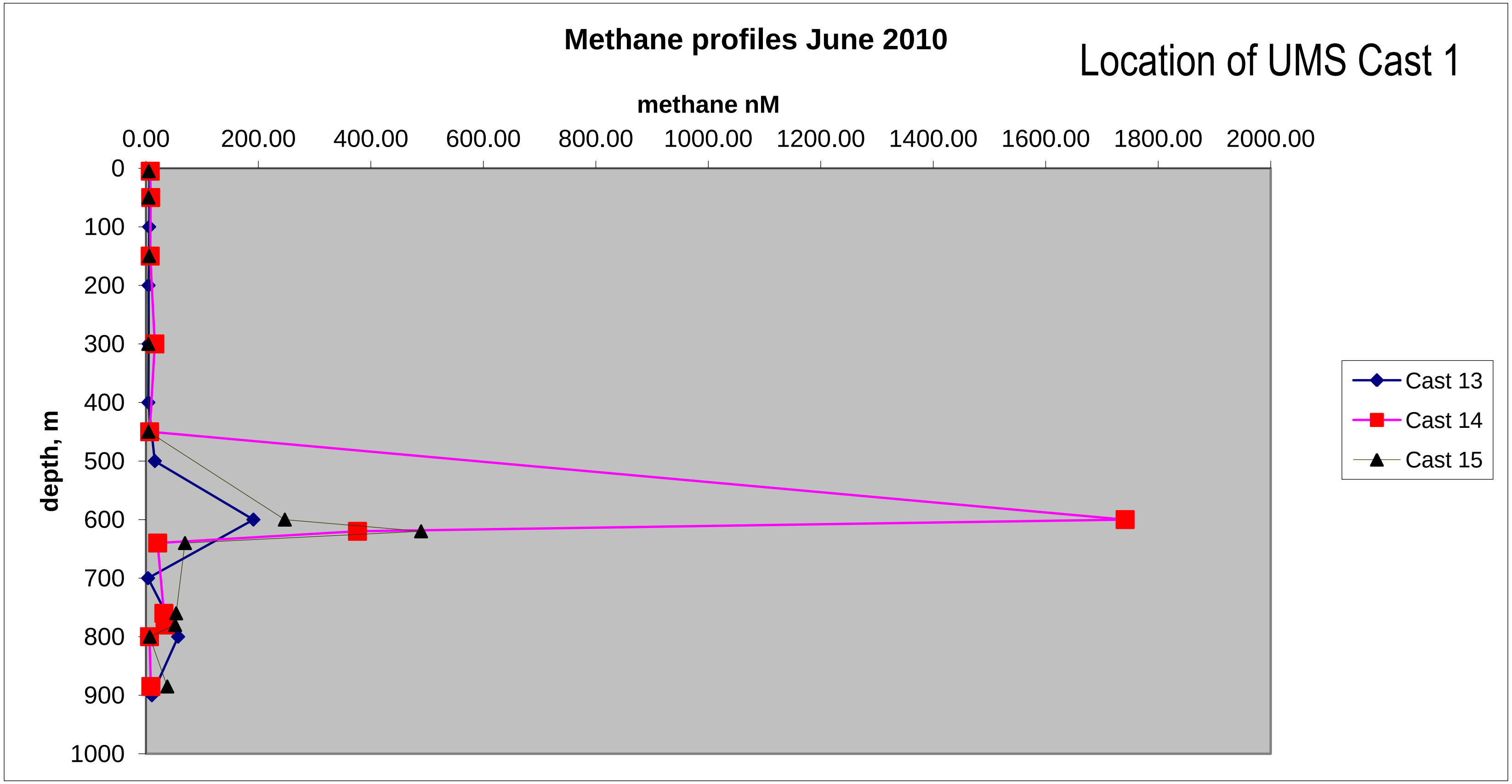


Cast 2



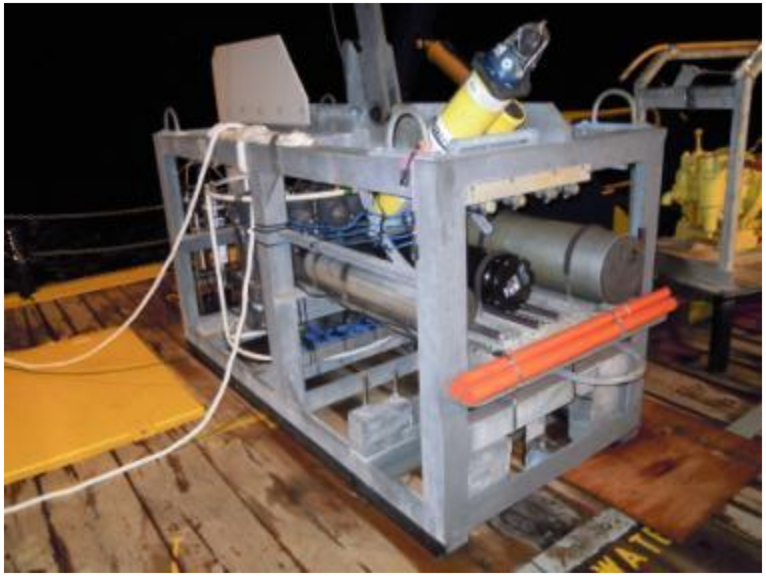
Cast 3

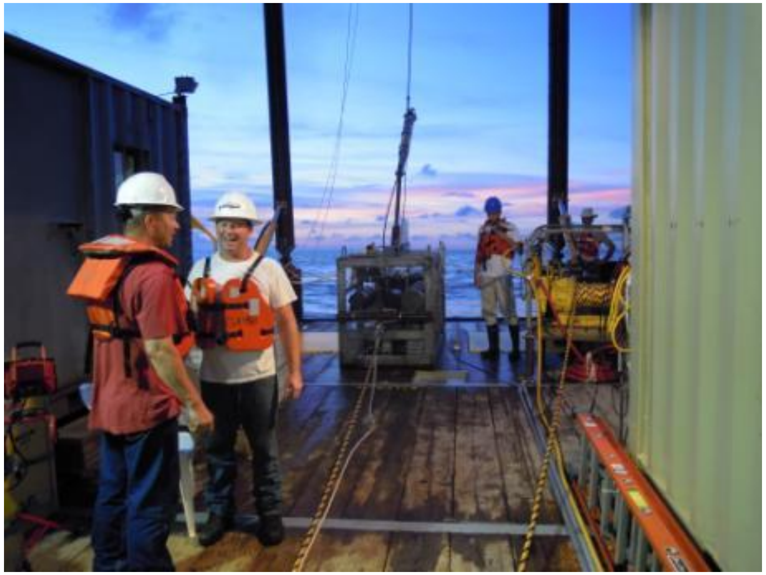
Analysis of Collected Samples at MC118



Provided by Jeff Chanton, Florida State University

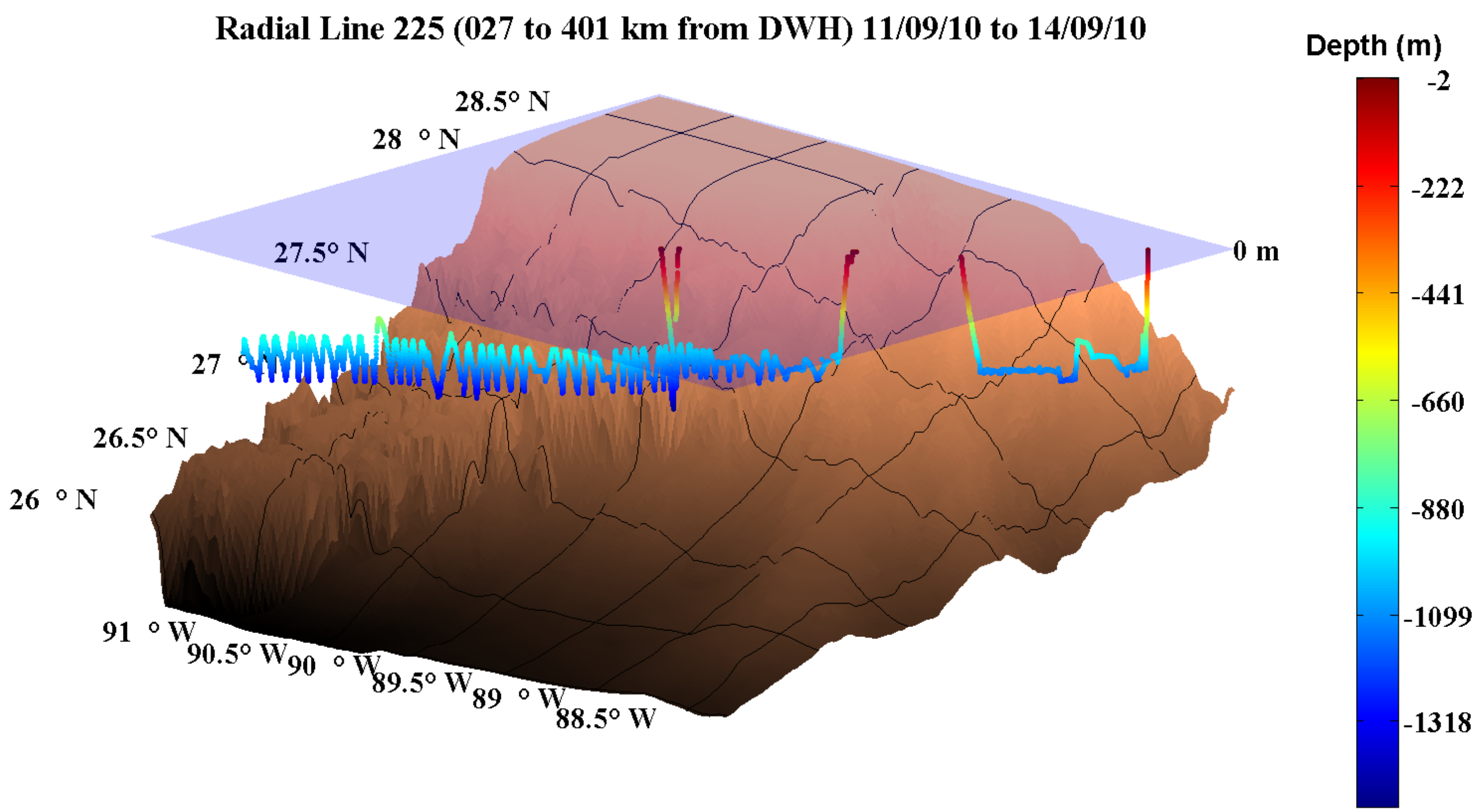
Deep Tow Surveys Southwest of MC252 (Sept. 2010)





- Deep tow surveys of dissolved gases and VOCs with UMS in Gulf of Mexico
- UMS mounted on deep tow sled with CTD, sampling rosette, USBL, and multiplexer vessel to provide communication and power
- Sled deployed from A-frame of M/V *Arctic* for deep tow operations as part of Broader Gulf of Mexico Survey Cruises

Tow-yo Between 900 and 1500 m Along 225° Heading



Plot of tow sled depth during deep tow transect

Conclusions

- Need for in-water chemical monitoring and mapping
  - Wide variety of motivations
- In situ MIMS analysis
  - Simultaneous detection of dissolved gases and VOCs
  - Real-time information on chemical distributions
- DIC measurements possible with in-line acidification
- Salinity dependence of MIMS response is pressure dependent
- Deployment methodologies
  - Towed (2-D or 3-D)
  - Vertical profiling (1-D)
- Application to subsurface spills
  - Real-time mapping of dissolved gases, methane, and volatile organics
  - Adaptive sampling
  - Guide water sampling strategies

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