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Recent Scientific Applications of Underwater Mass Spectrometry

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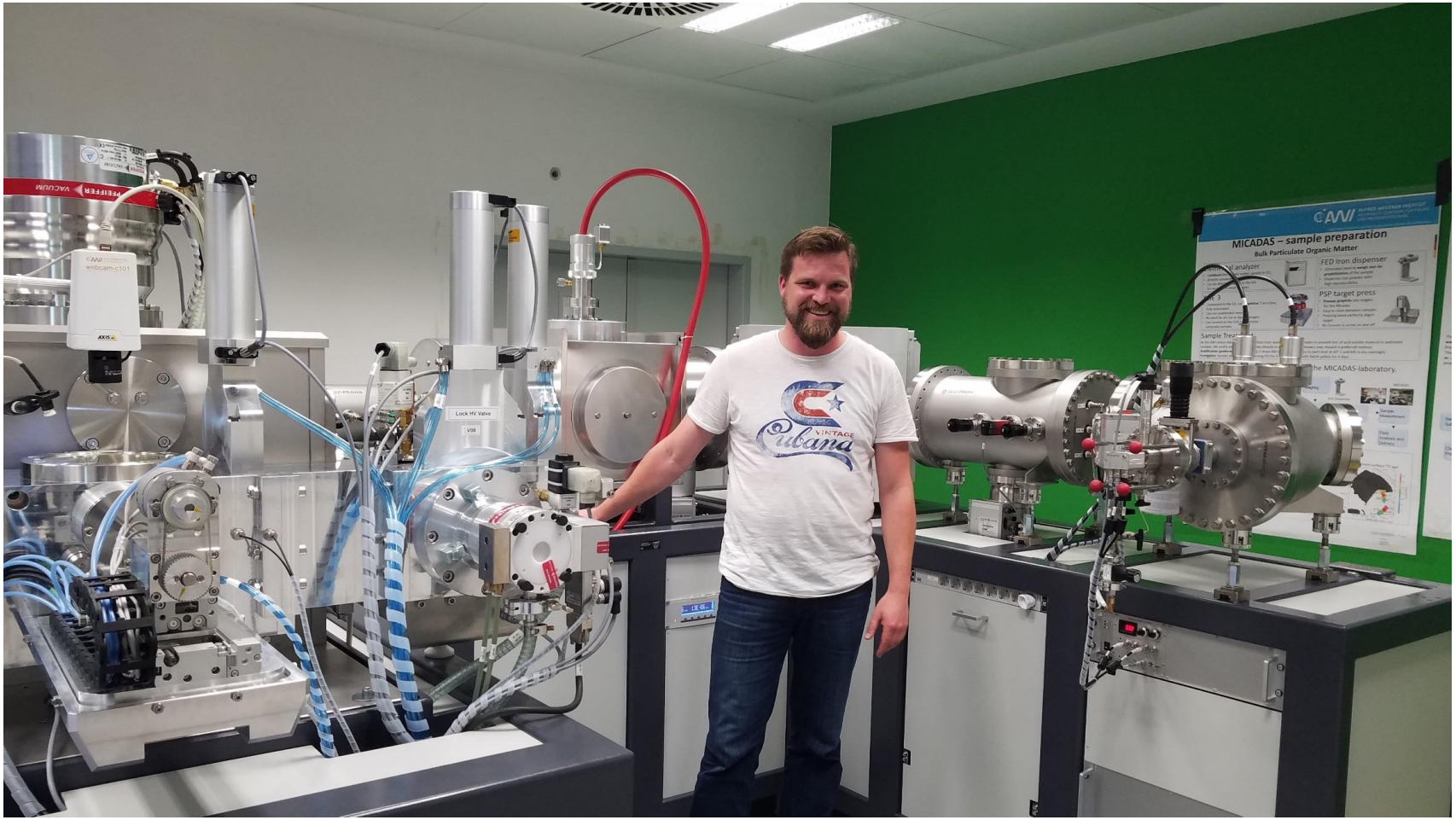
11th Workshop on Harsh Environment Mass Spectrometry

20 September 2017

Dr. Torben Gentz and his Mini Accelerator Mass Spectrometer at AWI

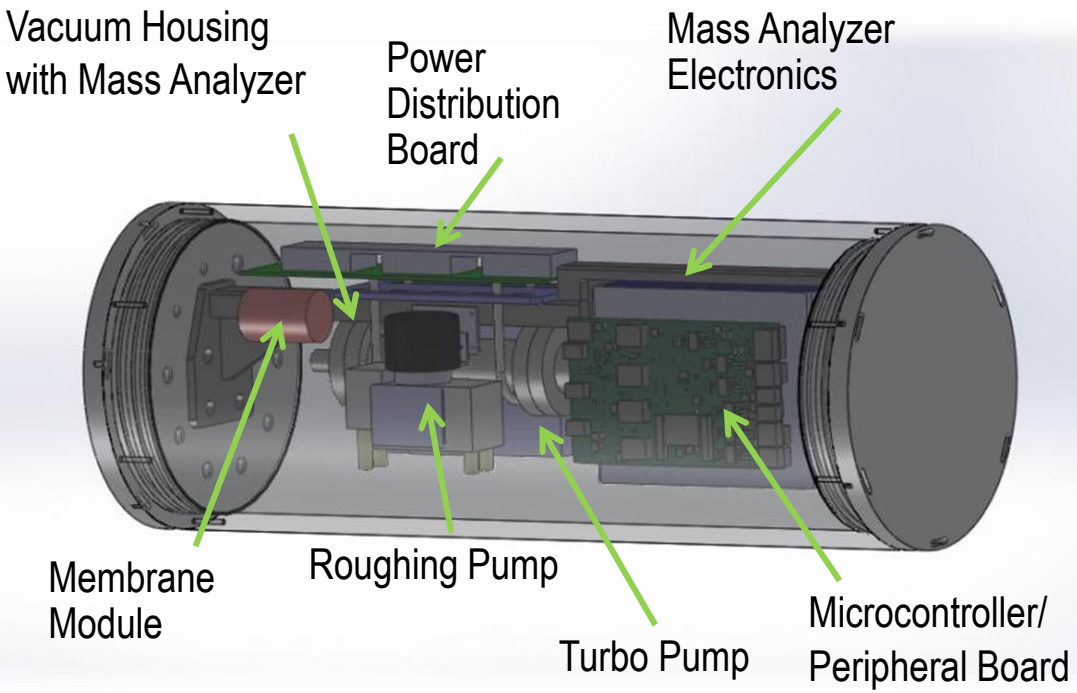


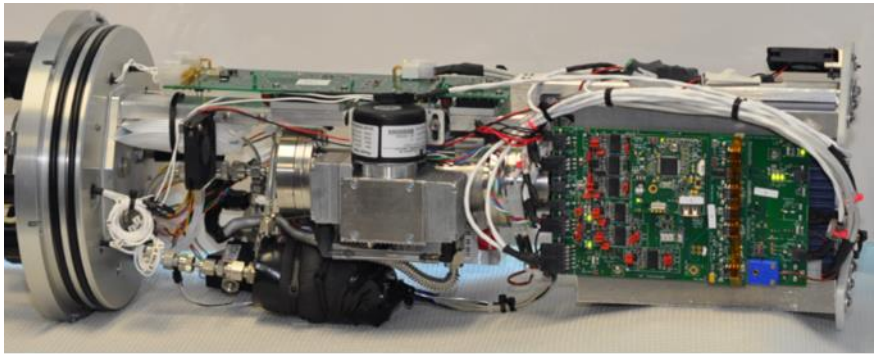
Ionplus AG (Ionplus.ch) from Switzerland

SRI's Membrane Inlet Mass Spectrometer

Specifications

- Power: 60-80 Watts
- Voltage: 24 VDC
- Dimensions:
  - Length: 64 cm
  - Diameter: 24 cm
- Weight:
  - In air: 35 kg
  - In water: 5 kg neg.
- Depth rating: 2000 m



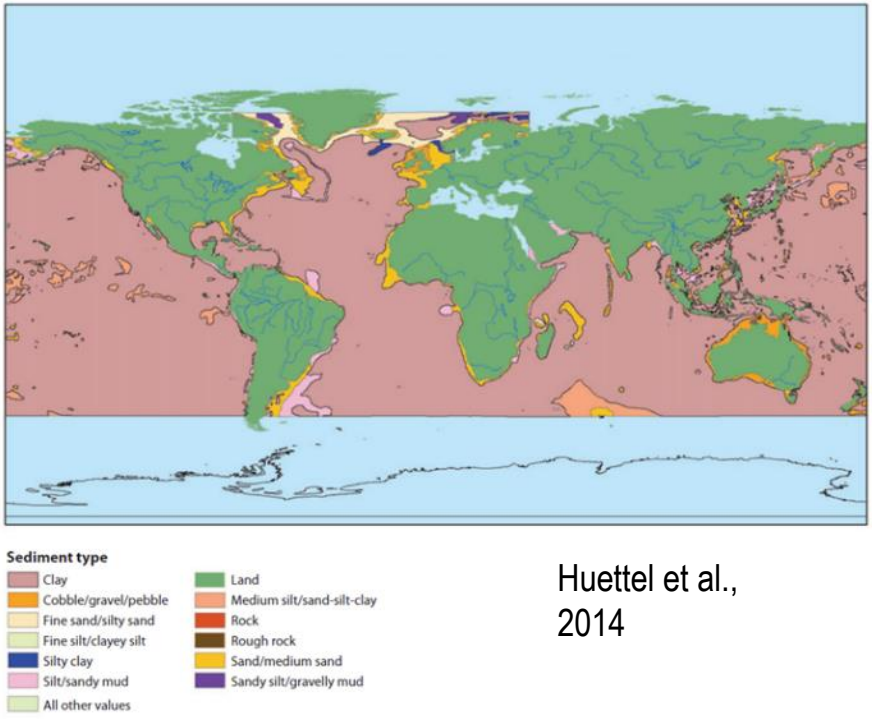


MIMS without pressure housing

Collaborative Research

Development of an in situ porewater sampler coupled to an underwater mass spectrometer for high-resolution biogenic gas measurements in permeable sediments

R. W. Fulweiler (PI), E. J. Chua, W. Savidge, A. M. Cardenas-Valencia, S. K. Toler, and R. T. Short



Huettel et al., 2014

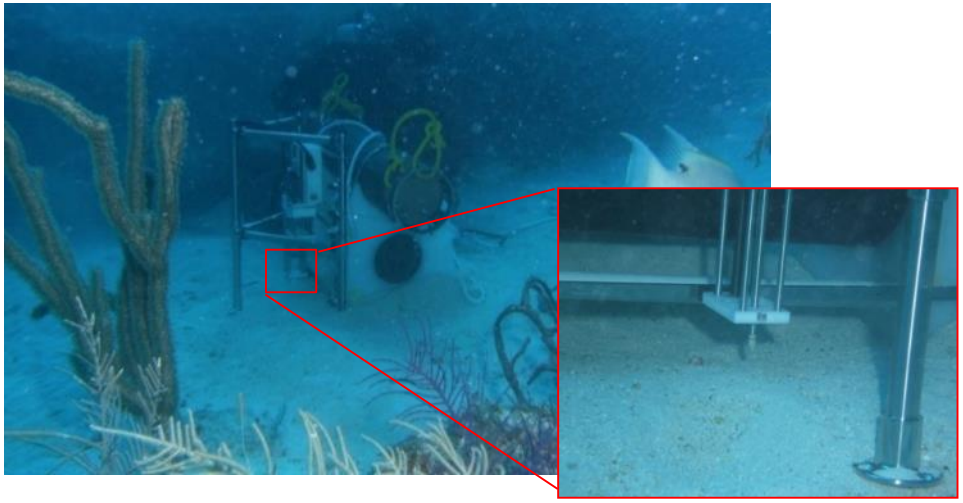
Problem: Approximately two-thirds of continental shelf seafloors consists of permeable sediments that are important in biogeochemical cycling, but sampling difficulties in permeable sediments have inhibited accurate measurements of chemical fluxes.

Objective: Provide a reliable tool to measure dynamic biogeochemical processes in the field to gather more realistic, high-resolution data for models.

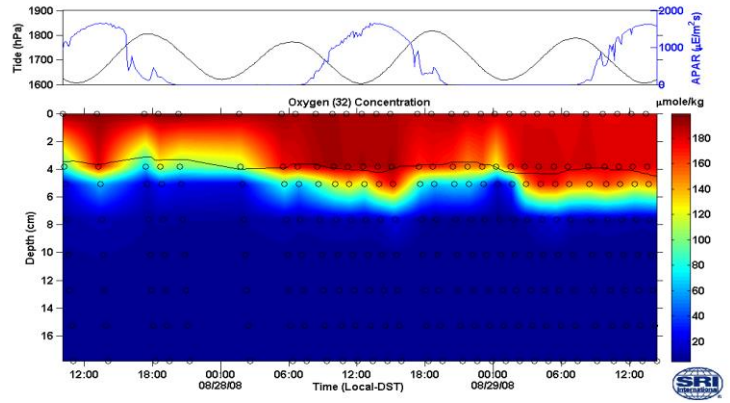
Approach: Develop a porewater sampling system that introduces minimal sampling artifacts, and deploy it with an underwater mass spectrometer (UMS) to collect high temporal resolution data from various sediment depths over periods of days to weeks.

Previous Porewater Analysis by SRI and SKIO (NSF)

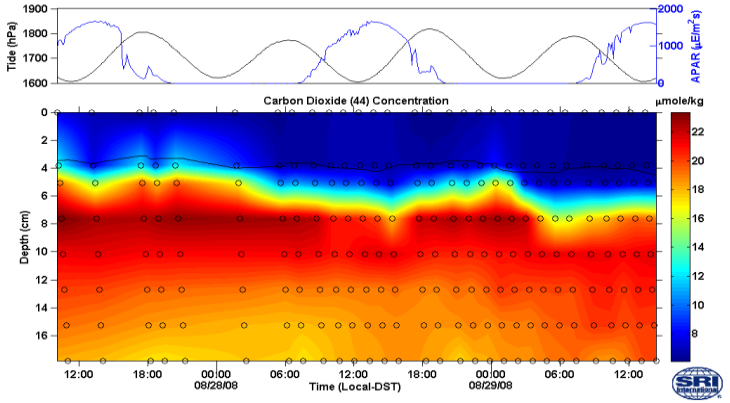
- Programmable profiling probe for analysis of sediment porewater (Bell et al., 2012)
- Water pumped from various depths (< 20 cm) in the sediment (and water column above the sediment) to UMS for analysis of dissolved gases
- Data collected continually over periods of several days and transmitted to shipboard laptop



Sediment water probe in the Florida Keys



O_2



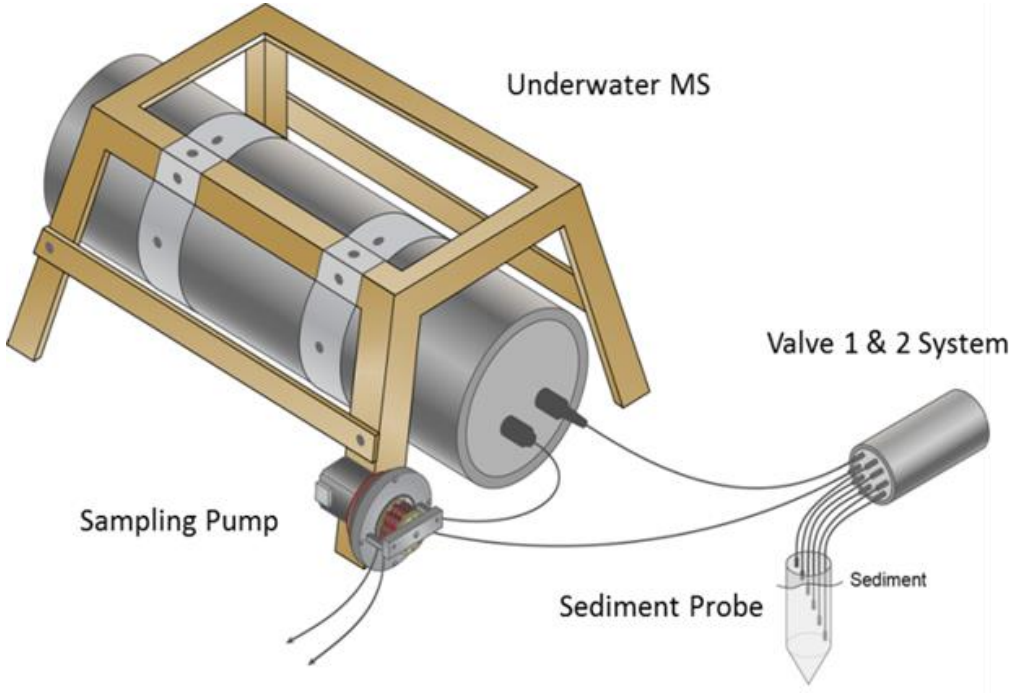
CO_2

Two-day time series of sediment dissolved gas concentrations on the Georgia continental shelf

New Porewater Analysis System Concept

Key modifications to improve accuracy and reduce sampling artifacts:

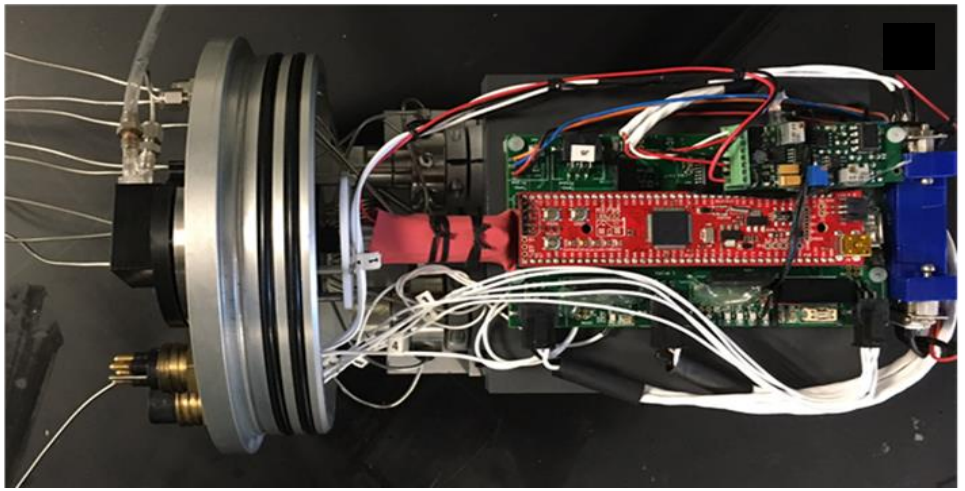
- Separate sampling process and UMS analyses using a two-valve system
  - Different flow rate regimes for sampling and analysis
  - UMS farther from sampling location to reduce environmental interferences
- Use a flow-injection analysis approach to improve reproducibility and accuracy
  - Integrate flow injection peak for improved statistics rather than quantifying on a steady-state signal level

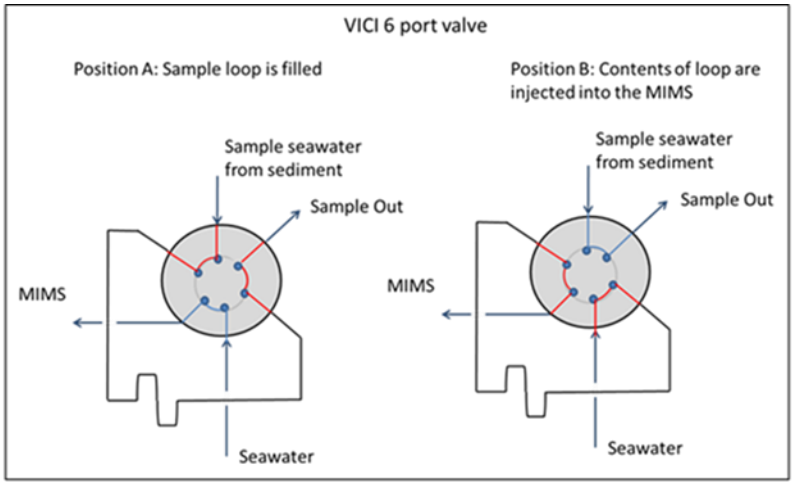


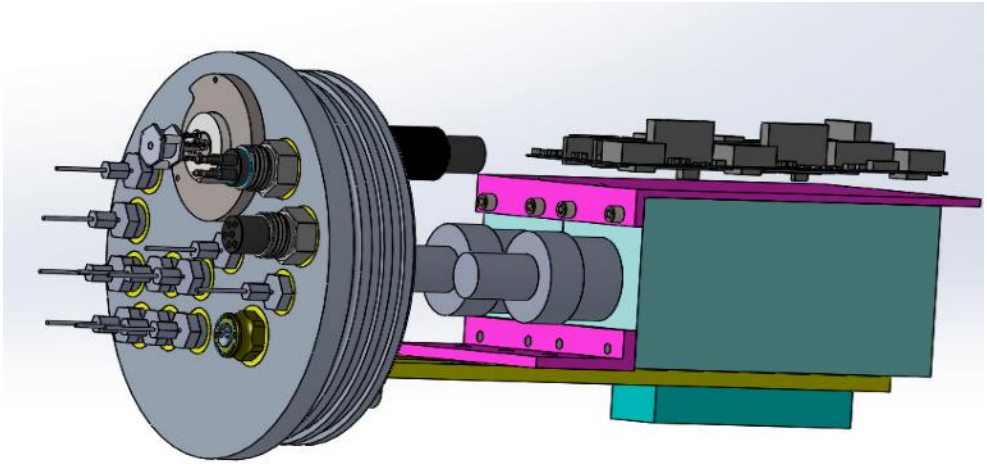
Dual Valve System for Porewater Sampling

- Two-valve system used for sample collection and analysis
- 8-port valve selects sediment depth
- 6-port valve contains a sample loop (2 mL) to be filled from each depth
- Valve is switched after loop is filled to direct contents to UMS
- UMS samples water column while the sample loop is filled

Patent Pending



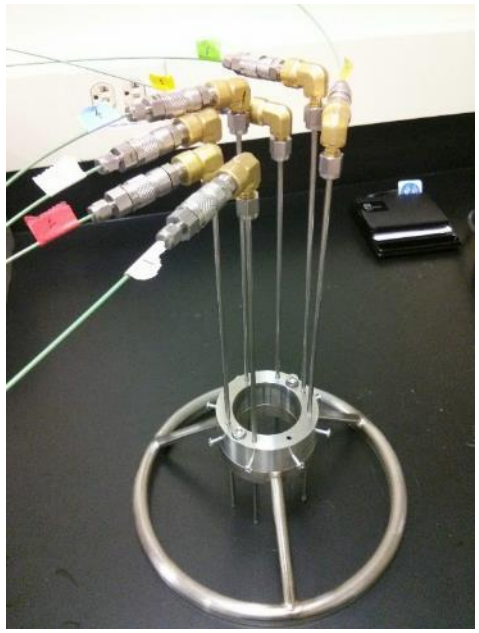


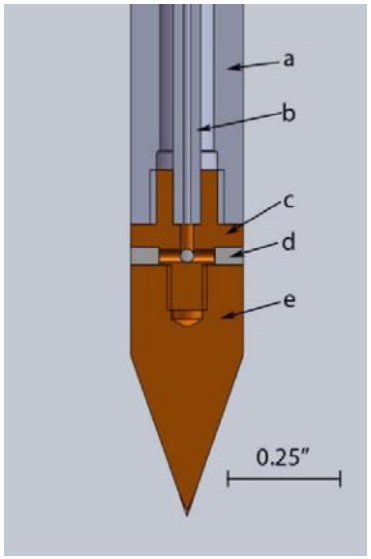


New Porewater Sampling Probe Systems

Concept 1 (SRI):

- Array of 7 sediment probes, each at a fixed depth
- Water is pumped through a porous frit (d) to valve system
- 3D sampling profile (difficult to model)
- Surface expression produces sediment artifacts

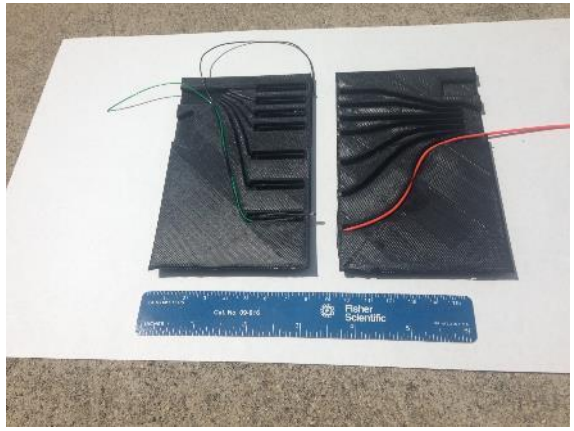




Bell et al., 2012

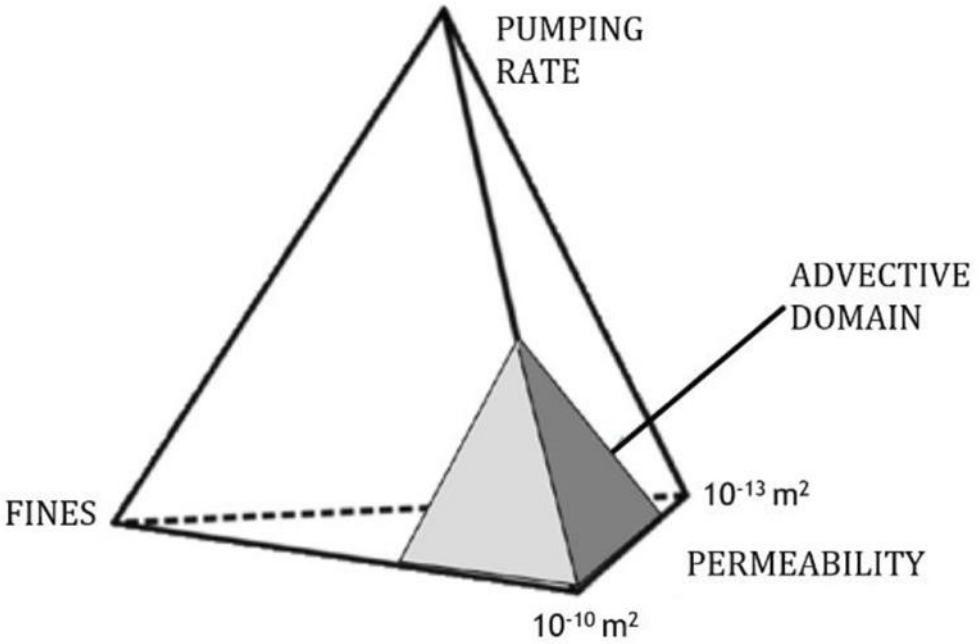
Concept 2 (SKIO):

- Linear array in a “printed” plate holder for insertion into sediment
- Water pumped through a porous frit at the end of each sampling tube
- 1D sampling profile (easier to model) and no surface expression



Evaluation of Appropriate Sediments and Field Deployment

- Inlet system being tested at BU to determine appropriate sediment porosities
- Goal is to establish practical lower limits of sediment permeability, fines content, and optimum sampling flow rate
- A quaternary diagram will be developed from tests
- Results will determine range of natural environments suitable for deployments
- A field deployment of the porewater sampling system and UMS scheduled for the summer of 2018

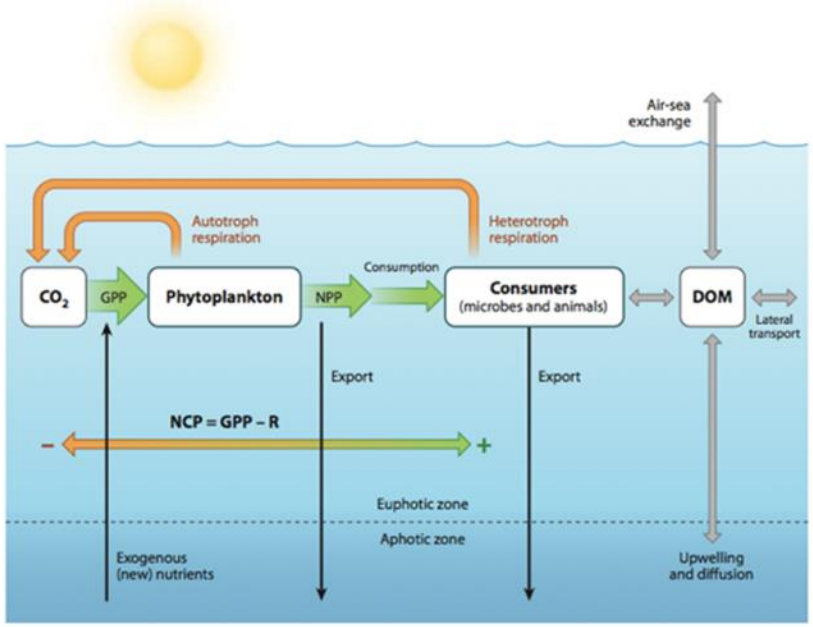


See HEMS Workshop Poster:
Development Suitable Sediments for Deployment of a Novel Porewater Sampling Underwater Mass Spectrometer, E. J. Chua et al.

Collaborative Research

Inventories of Primary Productivity by In Situ Mass Spectrometry in the Upper Ocean (ZIPP MS)

B. Loose (PI), S. Gartzman, S. K. Toler, and R. T. Short



Carbon cycle of biological pump in euphotic zone

Problem: Insufficient data on primary productivity in the upper ocean. Most measurements are made by collecting water samples yielding poor spatial and temporal resolution

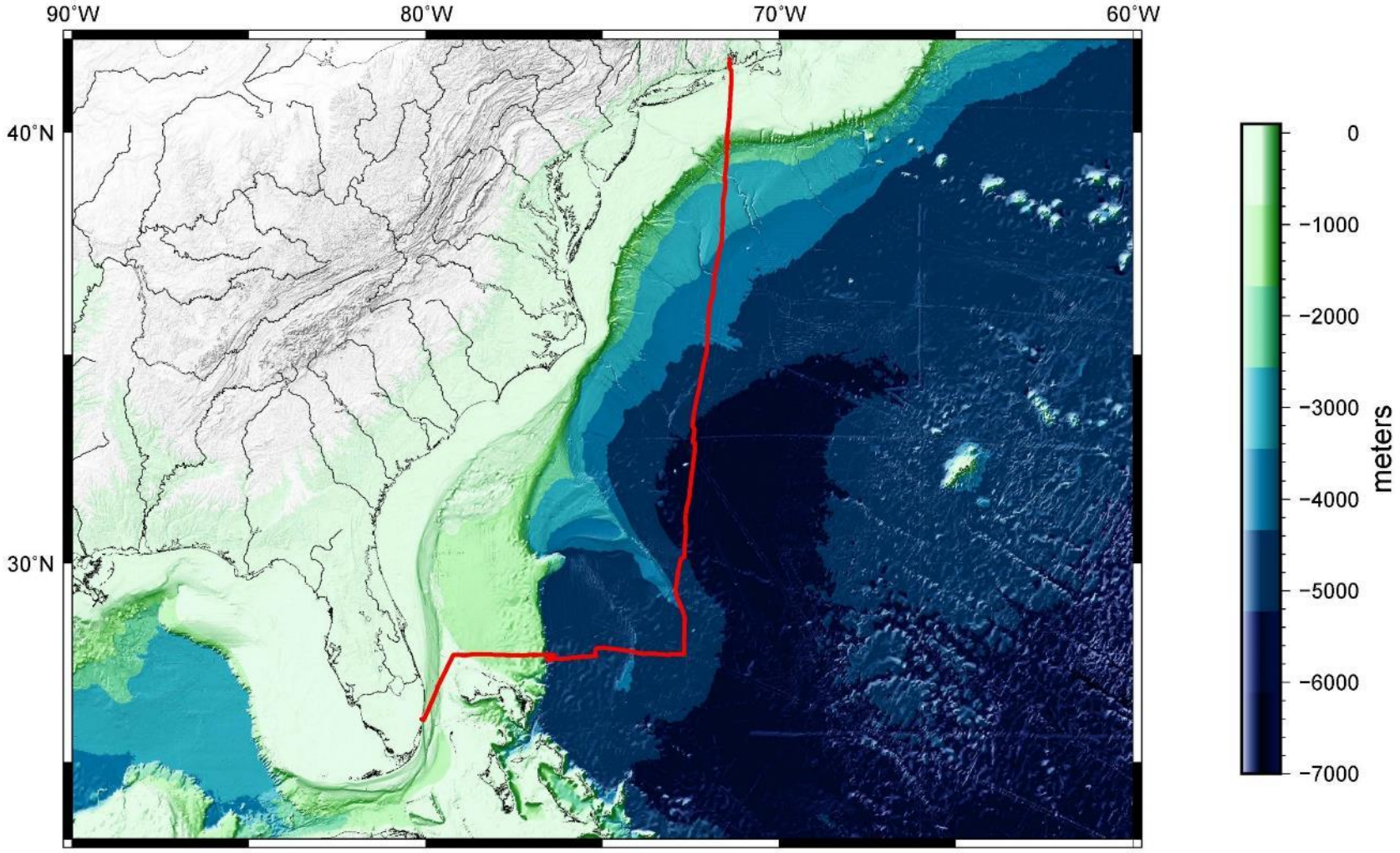
Objective: Provide a means to collect high spatial resolution measurements of concentrations of O_2 and Ar to evaluate net community production (Ar measurements account for variations from physical parameters)

Approach: Deploy the SRI membrane introduction mass spectrometer (MIMS) on a towed platform to obtain high resolution vertical (Z) inventories of primary productivity (ZIPP) in the upper 200 m of water column

Deployment Vessel

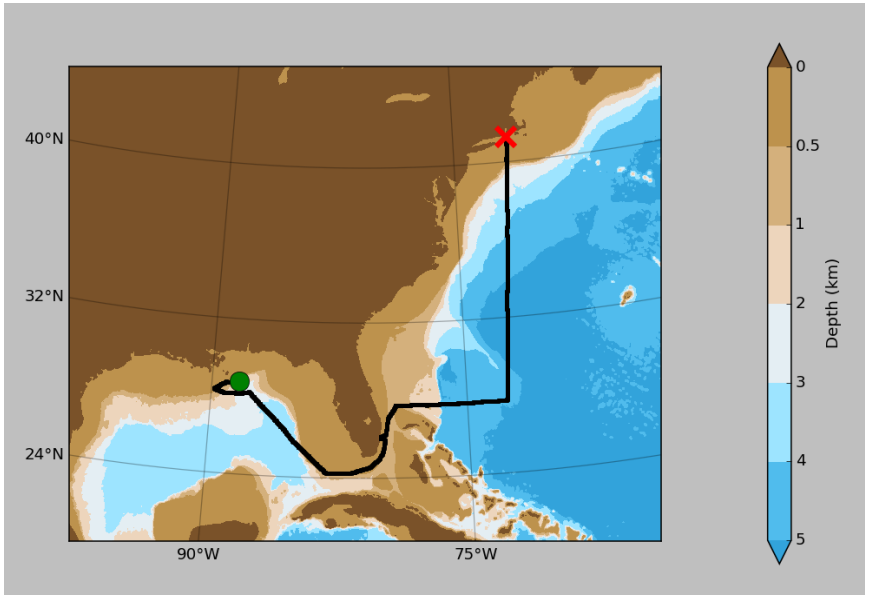
Actual Deployment Vessel
R/V Endeavor, URI Graduate School of Oceanography

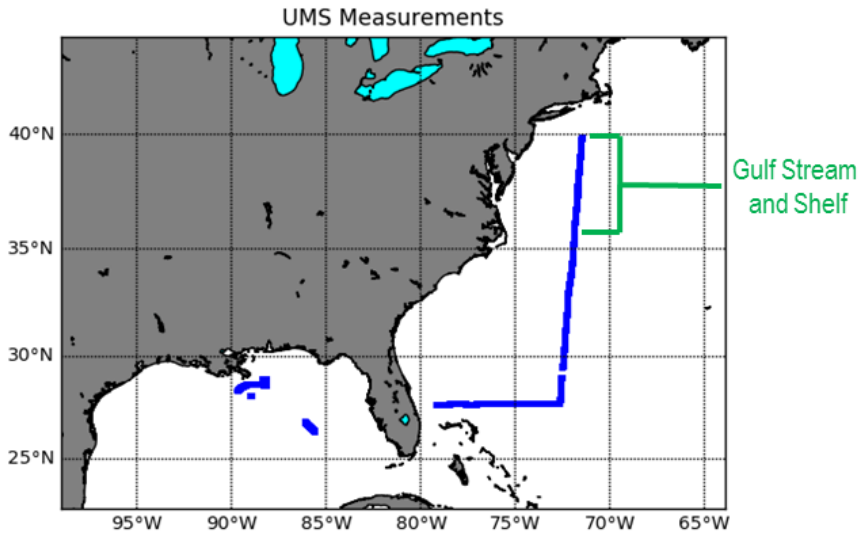
R/V Endeavor ZIPP MS Cruise 1 Route



Transects from Port Everglades, FL to Port Senesco, RI
March 3 -11, 2016

R/V Endeavor ZIPP MS Cruise 2 Route

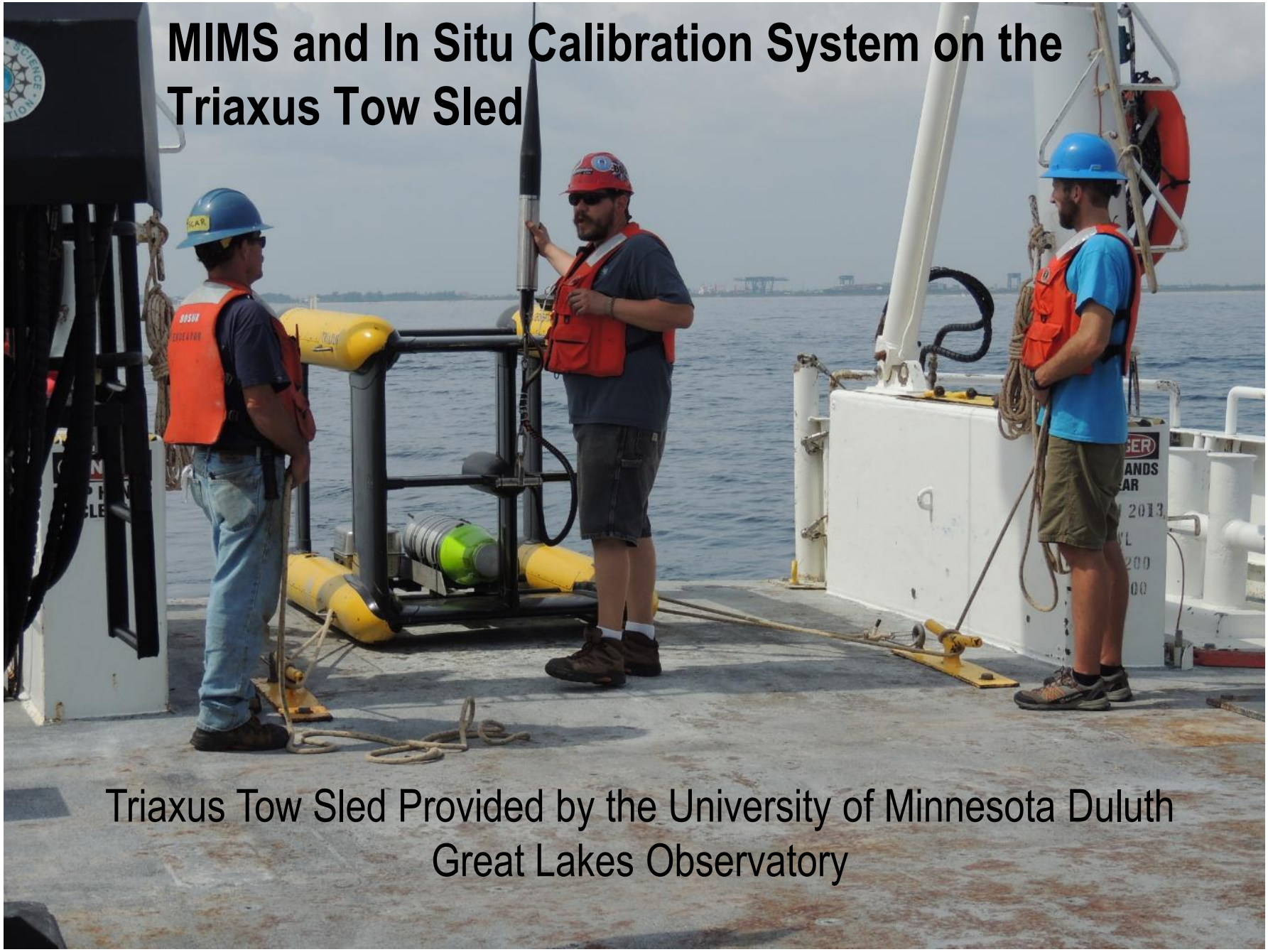




Over 400 Tow-Yos

Transects from Gulfport, MS to Narragansett, RI
July 7 -18, 2017

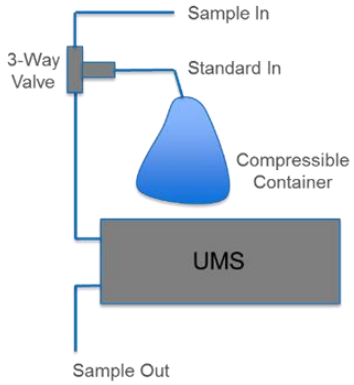
MIMS and In Situ Calibration System on the Triaxus Tow Sled

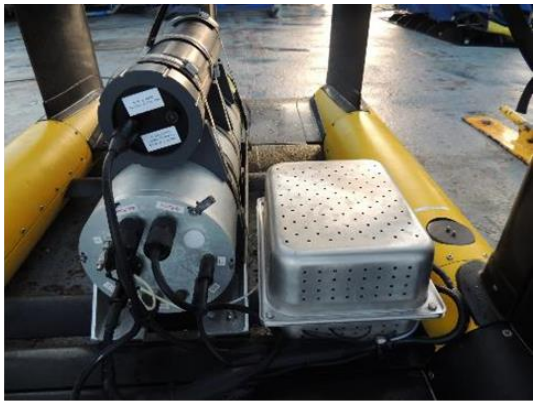


Triaxus Tow Sled Provided by the University of Minnesota Duluth Great Lakes Observatory

In situ Calibration Device to Improve Accuracy

- A dissolved gas standard is deployed in a gas-tight compressible bag.
- Gas standard in the bag is subjected to the same hydrostatic pressure and temperature as the water column.
- A valve is used to switch UMS sampling between the water column and the bag
- Bag analyses are to normalize UMS data for effects of temperature and pressure

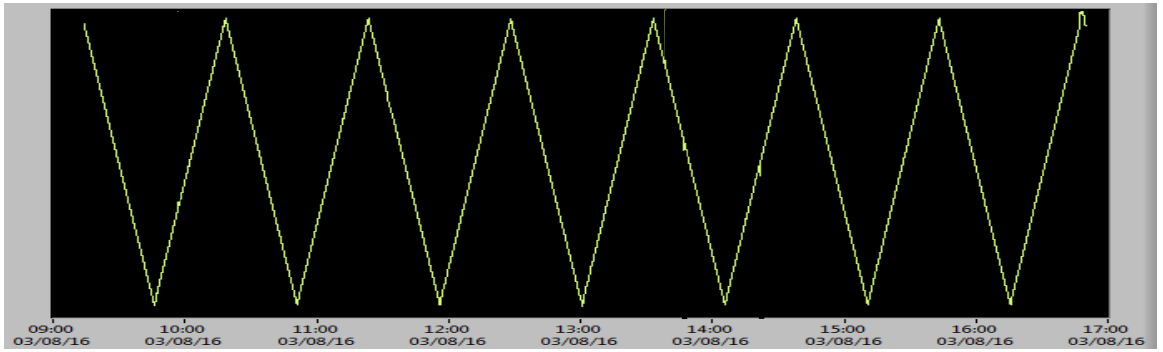




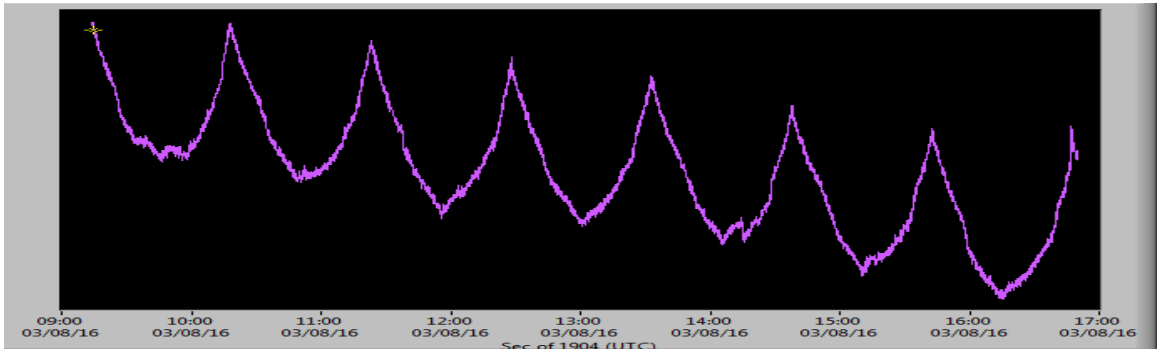
Triaxus Deployment

MIMS Tow-Yo Data for Oxygen and Argon – Cruise 1

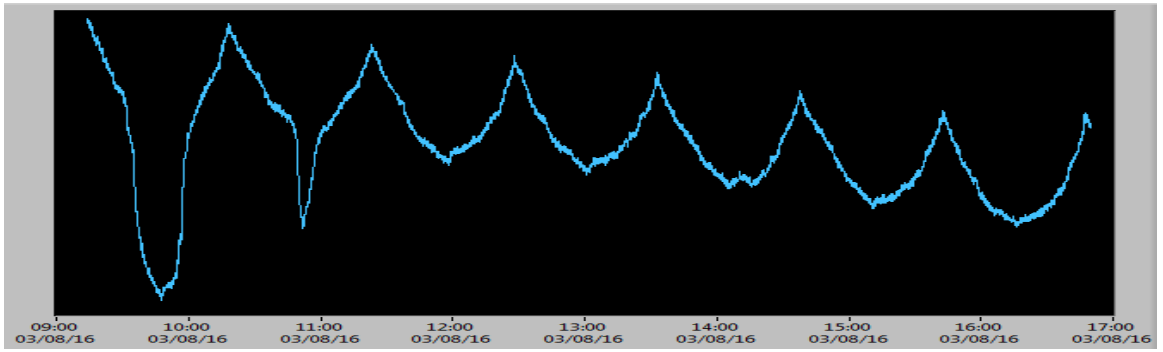
Depth (0 – 200 m)



m/z 40 (Ar)

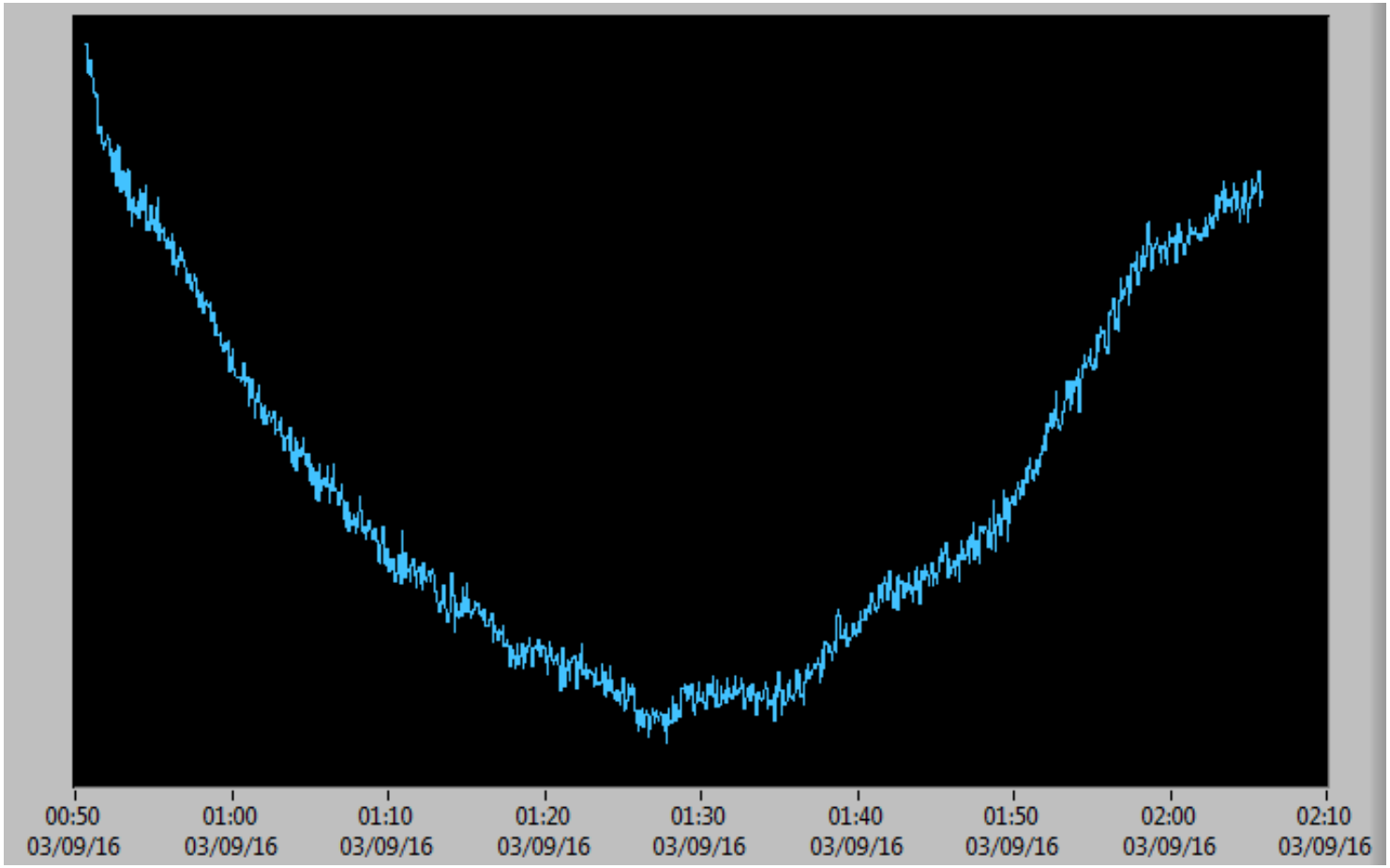


m/z 32 (O_2)



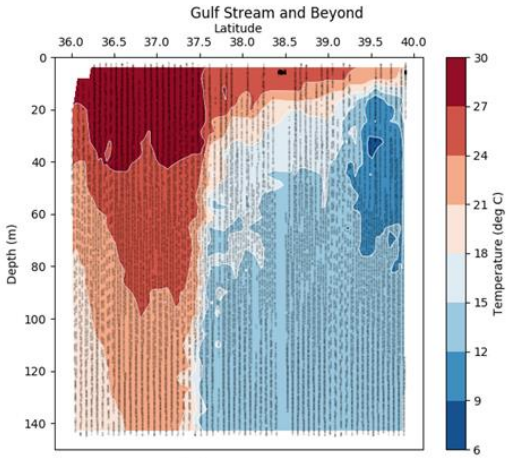
(~8 hours)

MIMS data for *m/z* 32 (O_2) from in situ calibration standard during one Tow-Yo

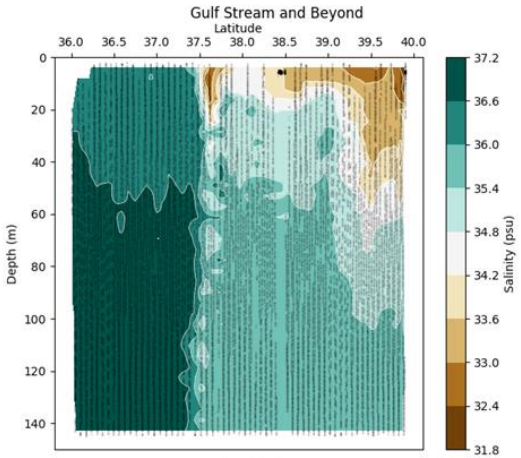


Data from ZIPP MS Cruise 2 – Gulf Stream and Shelf

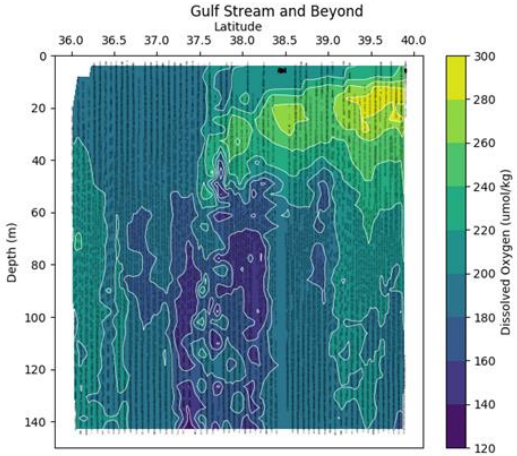
- Interpolated plots of in situ data from Tow-Yo deployments
- Black dashes show locations with data
- Transition from the Gulf Stream to the continental shelf at approximately latitude 37.5 deg N
- Warmer, more saline water in the Gulf Stream
- Surface water on the shelf is less saline, with increased oxygen and decreased carbon dioxide



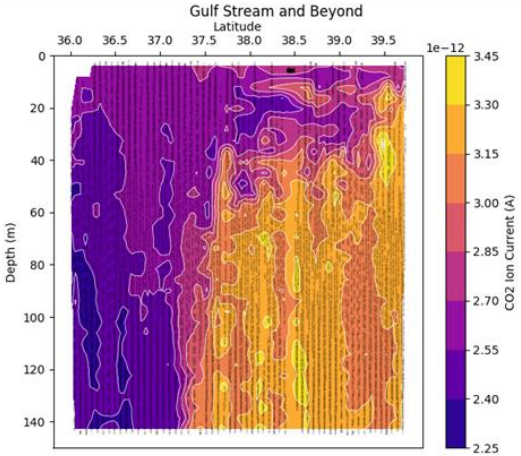
Temperature



Salinity



Dissolved Oxygen

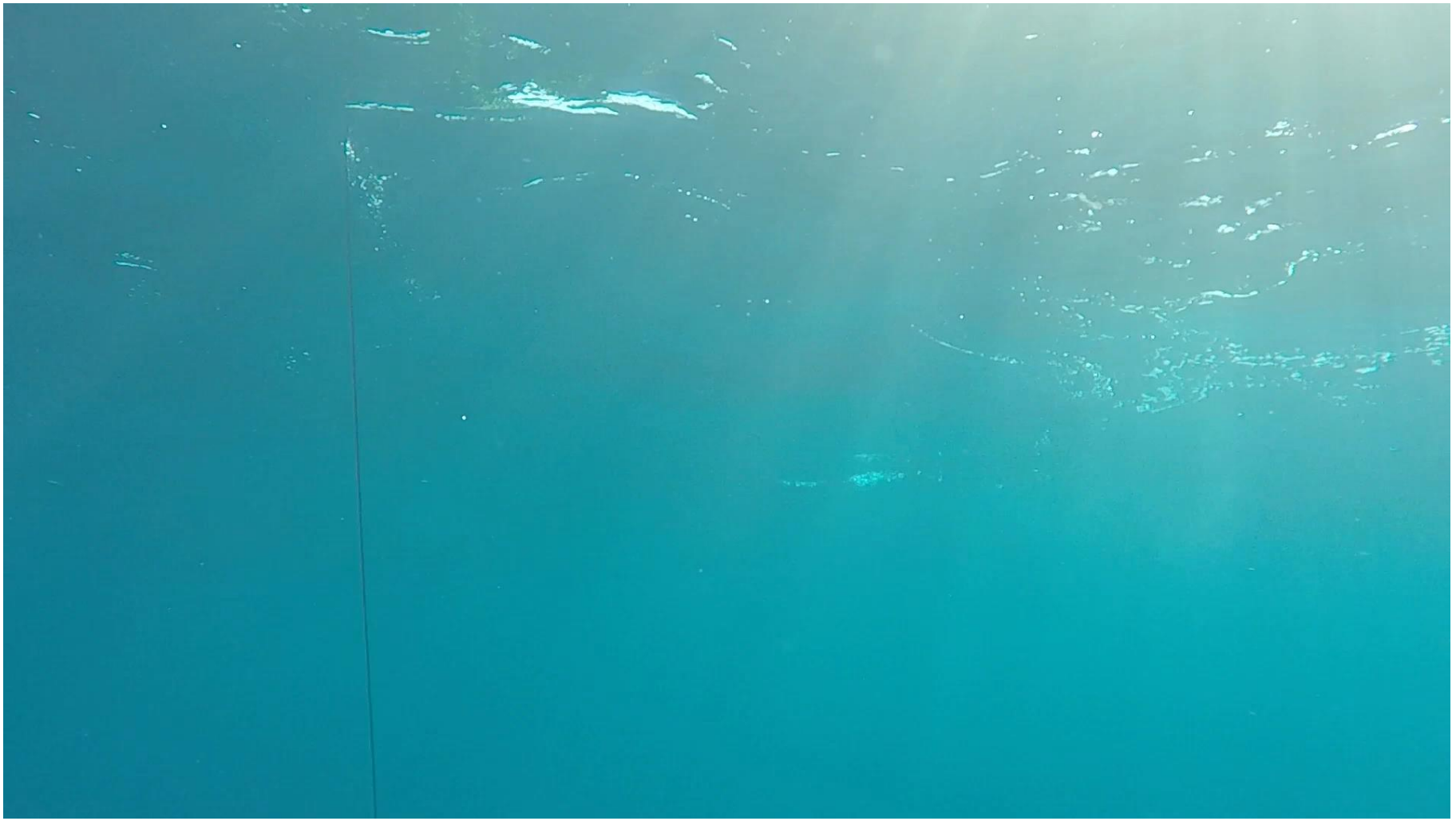


UMS CO_2 (uncalibrated)

Triaxus Deployment

Triaxus Point of View

Triaxus Recovery



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- Funding from National Science Foundation Grant OCE-1429952 to SRI for the ZIPP MS Project (PI, B. Loose, University of Rhode Island)
- Funding from the National Science Foundation through Sub Agreement 2500-1158-00-A to SRI from the University of South Florida Award #0536345 (PI, W. B. Savidge, Skidaway Institute of Oceanography)
- Patent Pending: US Provisional Patent SRI-US-7421-2P "Flow Injection Apparatus for the In Situ Analysis of Multiple, Successive Samples in Fluidic Interfaces with an Integrated Calibration Scheme"

- References

  - M. Heuttel, P. Berg, J. E. Kostka, Benthic Exchange and Biogeochemical Cycling in Permeable Sediment, *Annu. Rev. Mar. Sci.* 2014, 6:23-51
  - R. J. Bell, W. B. Savidge, S. K. Toler, R. H. Byrne, R. T. Short, In Situ Determination of Porewater Gases by Underwater Flow-Through Membrane Inlet Mass Spectrometry, *Limnol. Oceanogr.: Methods* 10, 2012, 117-128

Thank You!

Questions?

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