SRI International

In-Water Mass Spectrometry for Characterization of Light Hydrocarbon Seeps and Leaks

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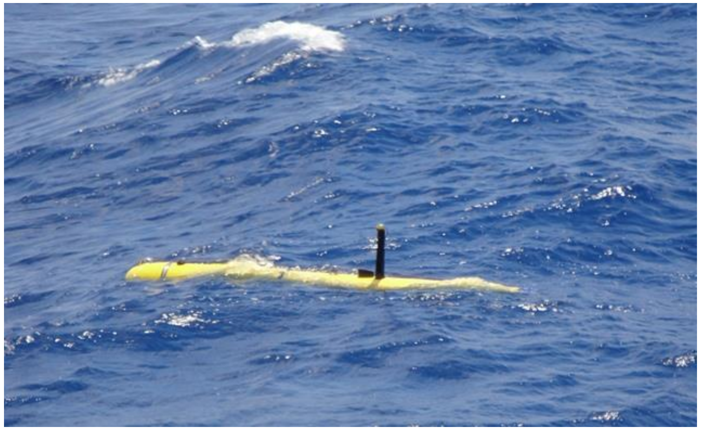
Outline

- Need for in-water detection and quantification of hydrocarbons (HCs)
- Membrane introduction mass spectrometry (MIMS)
  - Underwater MIMS systems
  - Detection of light hydrocarbons
- Integration of sensor suite with autonomous underwater vehicle (AUV)
  - SRI's underwater MIMS
  - Blueview MBS 1350 multi-beam sonar
  - Turner Design C7 fluorometer



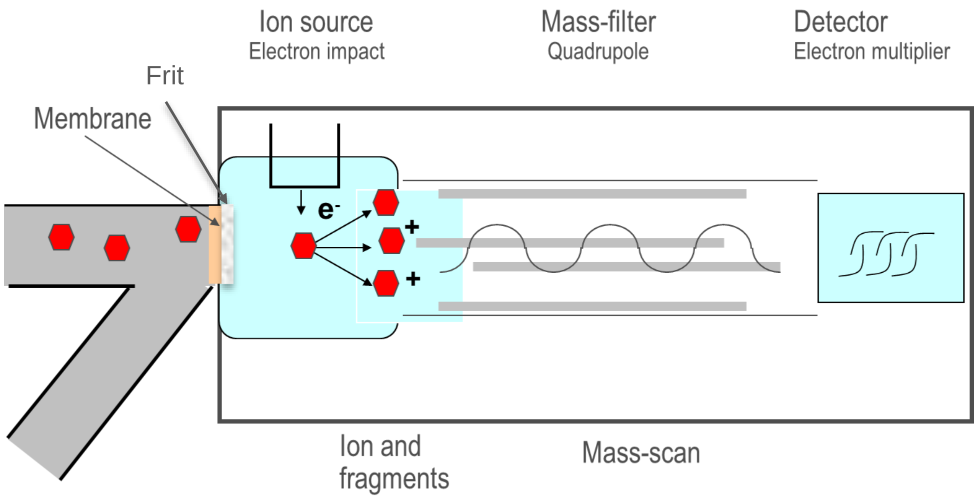
- Gas and dye plume generator
- AUV operations in Tampa Bay
- AUV operations in Santa Barbara Channel
- Summary

Challenges for the Expanding Oil and Gas Industry

- Improved exploration and environmental monitoring in the open ocean and coastal regions
  - Cost-effective mapping of HCs over large areas
  - Differentiation of hydrocarbon sources (thermogenic vs. biogenic)
- Environmental assurance protocols for operations
  - Reliable methods for establishing HC background concentrations (liability)
  - Sensitive leak detection for disaster management

MIMS: Ideal for In Situ Detection of Light HCs and Gases

- Simultaneously monitor multiple analytes
  - Dissolved gases (oxygen, nitrogen, carbon dioxide), light HCs (methane, ethane, propane, butane), and volatile organic compounds (benzene, toluene, xylene)
  - Full mass scans or selected ion monitoring
  - Up to 45 m/z values with a cycle time of ~5 seconds
- Introduce analytes from the water column
  - Passive (except for sample pumping and heating, if desired)

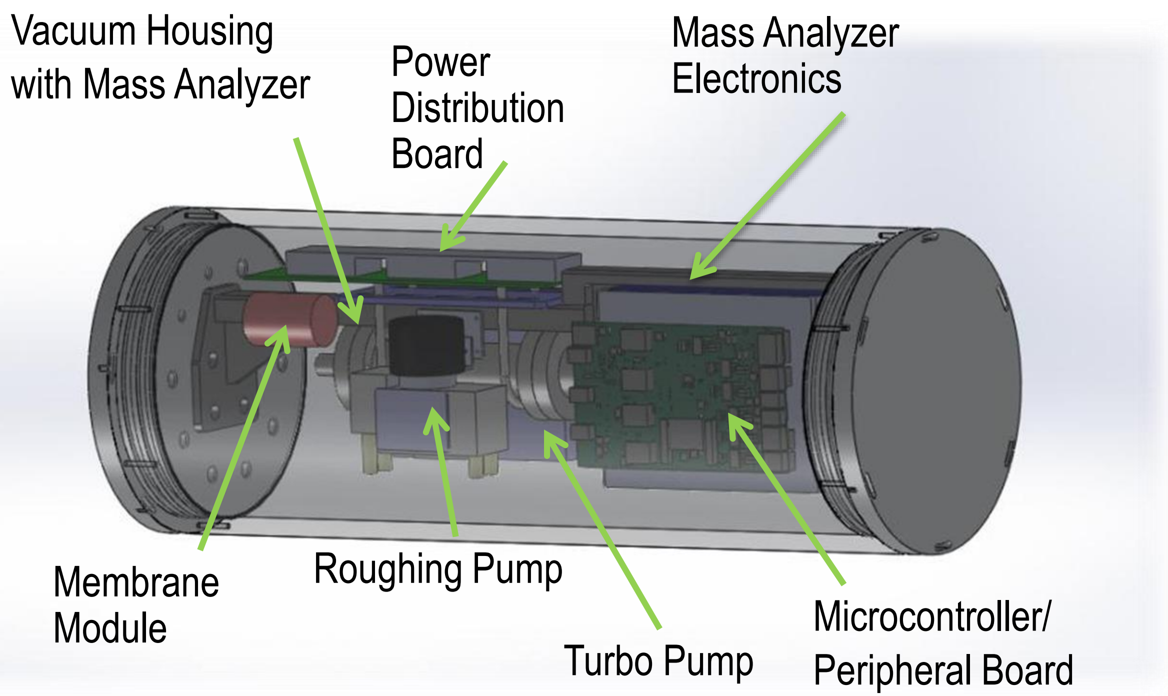


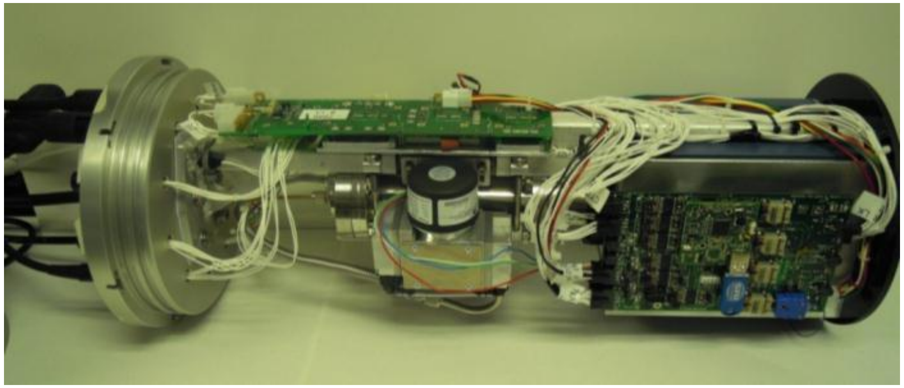
A porous metal or ceramic frit is used to mechanically support the membrane (hydrostatic pressure)

SRI's MIMS Instrument is AUV Deployable

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





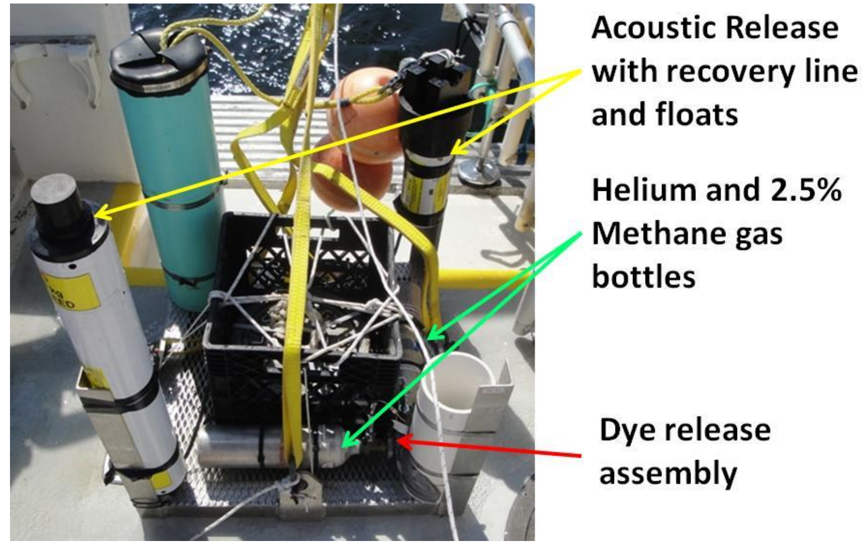
Typical MIMS Diagnostic Ions

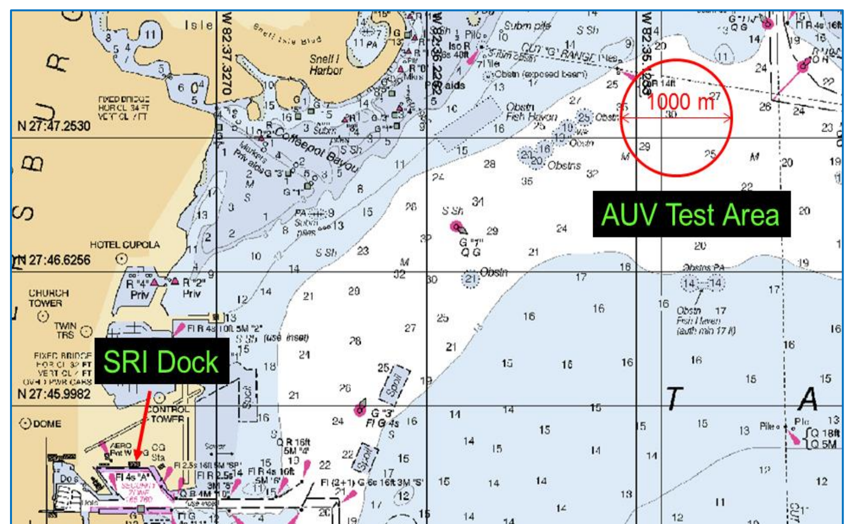
M/Z VALUE	COMPOUND	ISOTOPIC FORM
4	Helium (He)	^{4}He
15	Methane (CH_4)	$^{12}CH_3$ Fragment
28	Nitrogen (N_2)	$^{14}N^{14}N$
30	Ethane (C_2H_6)	Various
32	Oxygen (O_2)	$^{16}O^{16}O$
34	Oxygen (O_2) Hydrogen Sulfide (H_2S)	$^{16}O^{18}O$ $H_2{}^{32}S$
39	Propane (C_3H_8)	Various
40	Argon (Ar)	^{40}Ar
44	Carbon Dioxide (CO_2)	$^{12}C^{16}O^{16}O$
58	Butane (C_4H_{10})	Various
78	Benzene (C_6H_6)	Various
92	Toluene (C_7H_8)	Various
106	Xylene (C_8H_{10})	Various
128	Naphthalene ($C_{10}H_8$)	Various

Characterization of an Artificially Generated Seep in Tampa Bay, FL

Artificial Plume Generator Designed and Constructed

- Device constructed to generate an artificial “seep” to allow local testing of the AUV sensor suite
- Helium gas (and at times 2.5% methane in air) released from two small compressed gas cylinders – *proxy for light HCs*
- Fluorescein dye released from compressible bags – *proxy for larger oil compounds*
- Deployment time ~1 hour
- Acoustic release system used for generator recovery

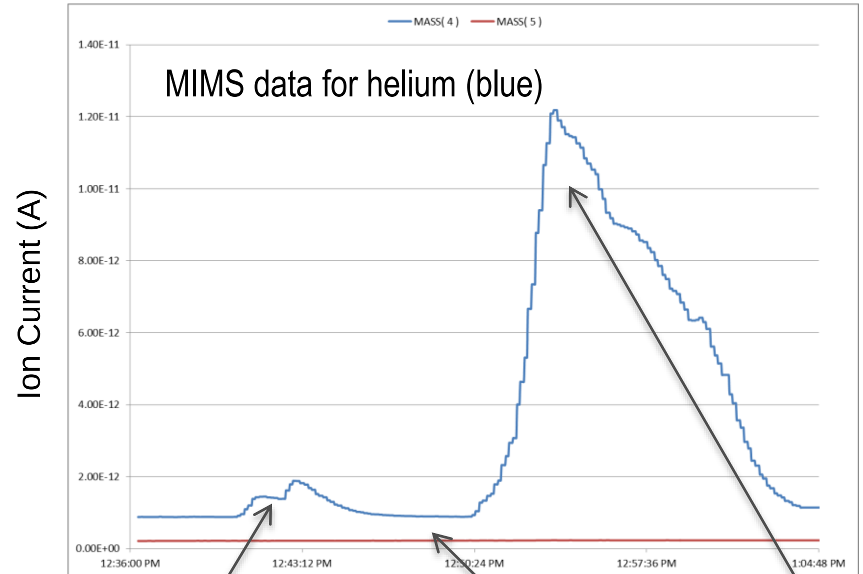




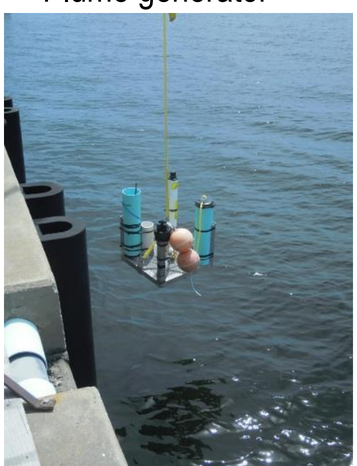
SRI St. Petersburg

Helium Plume Generator Test

- Used the seawall crane in St. Petersburg to deploy the instruments
  - Lowered the plume generator to seafloor (~10 m depth)
  - Lowered the MIMS
  - Moved the MIMS ~2 m upstream from the plume, then pulled the MIMS through the plume

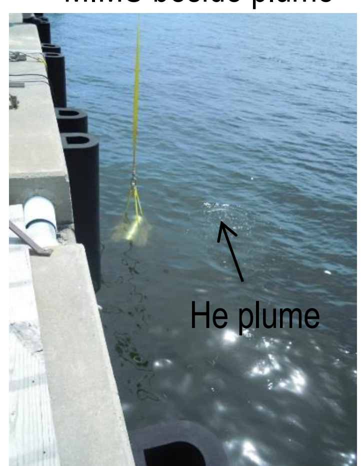


Plume generator

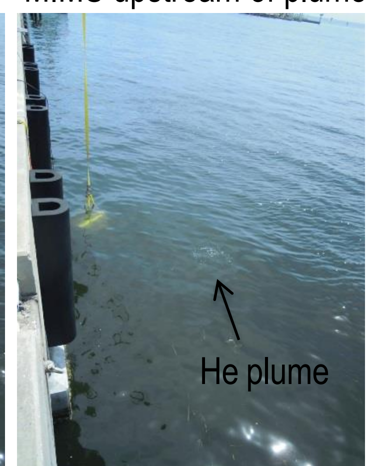


MIMS

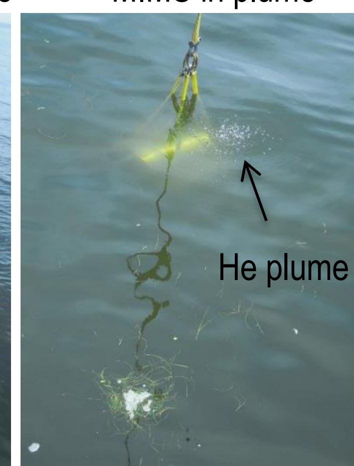
MIMS beside plume



MIMS upstream of plume

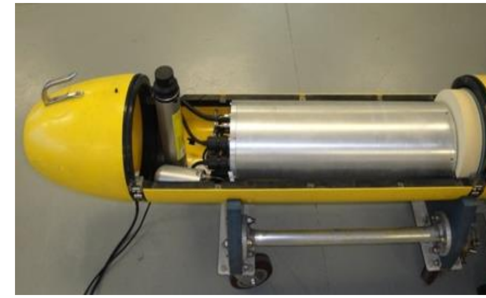


MIMS in plume



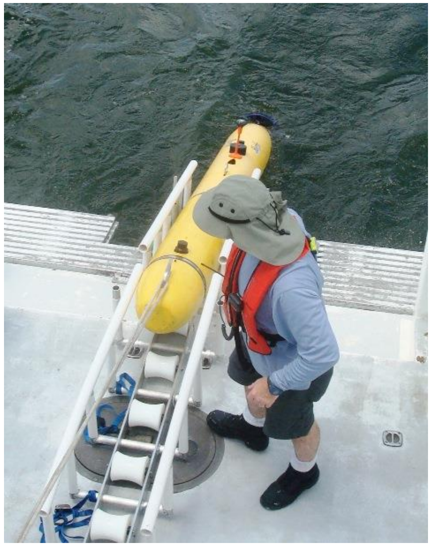
Bluefin AUV Equipped with MIMS-based Sensor Suite

- Custom payload shell designed and constructed for sensor integration into SRI's Bluefin BF-12 AUV
- MIMS detects light HCs, dissolved gases, and volatile organic compounds
- Turner Design C7 fluorometer detects fluorescein (can be interchanged with a version to detect oil)
- Blueview MBS 1350 multi-beam sonar provides bathymetric maps and images of bubble plumes
- Custom data logger integrates and assimilates multi-sensor data
- Inertial navigation system provides accurate 3D geo-referencing of multi-sensor data



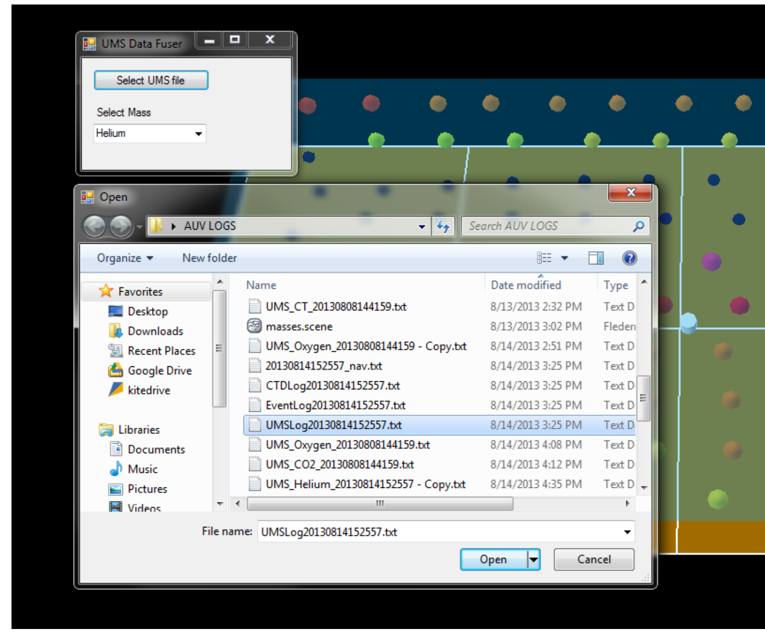
AUV Operations with Plume Generator

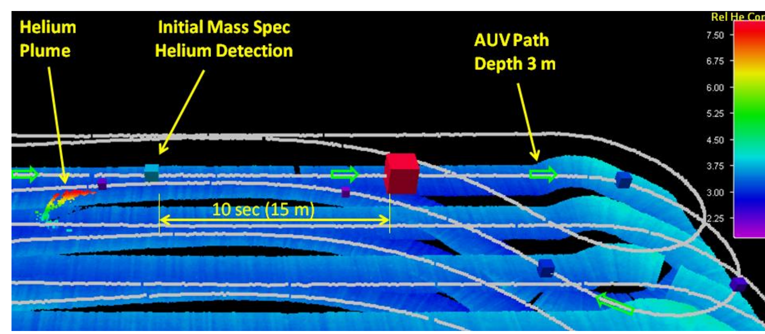
- Designed the basic survey pattern and programmed it to be downloaded to the AUV
- Deployed the plume generator near the center of the survey pattern (opened the gas cylinders and started the dye flow)
- Moved out of the survey pattern and deployed the AUV
- Downloaded the survey pattern to the AUV, and completed one or two surveys (~30 – 45 min)
- Retrieved the AUV and recovered the plume generator (total deployment ~1 hour)
- Downloaded sensor data from the AUV and devised a new mission plan



Post-processing Software Allows Rapid Data Display

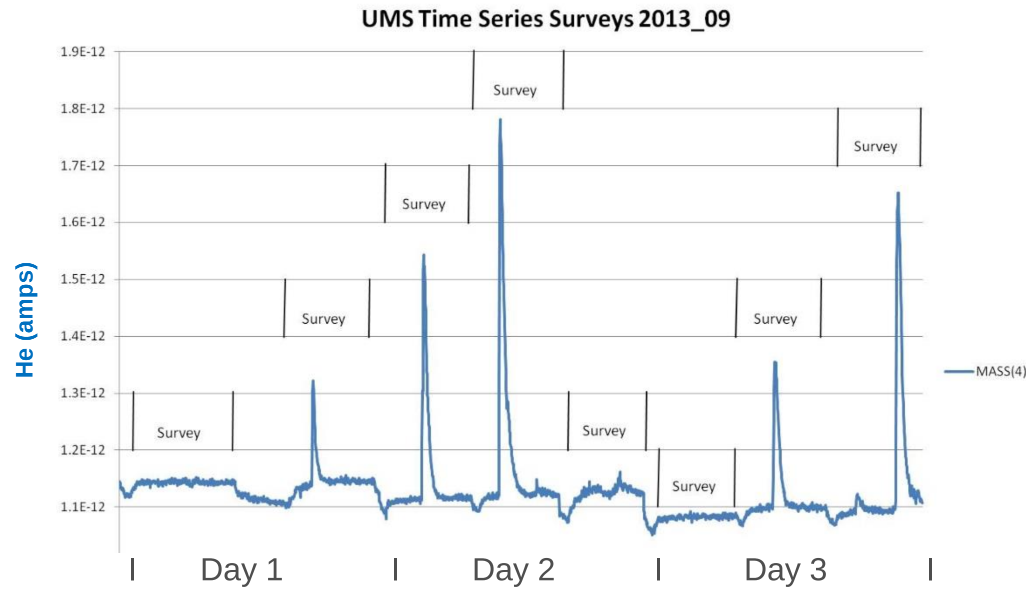
- Software fuses AUV navigation, MIMS, C7, conductivity, temperature, and Blueview sonar data into geo-referenced files/layers viewable in 3D viewer, Fledermaus
- Specific analytes can be selected from MIMS data and multiple layers of intensities displayed in 3D, along with fluorometer and sonar data
- Data from multiple dives can be displayed simultaneously
- Future processing can include calibrated concentration calculations

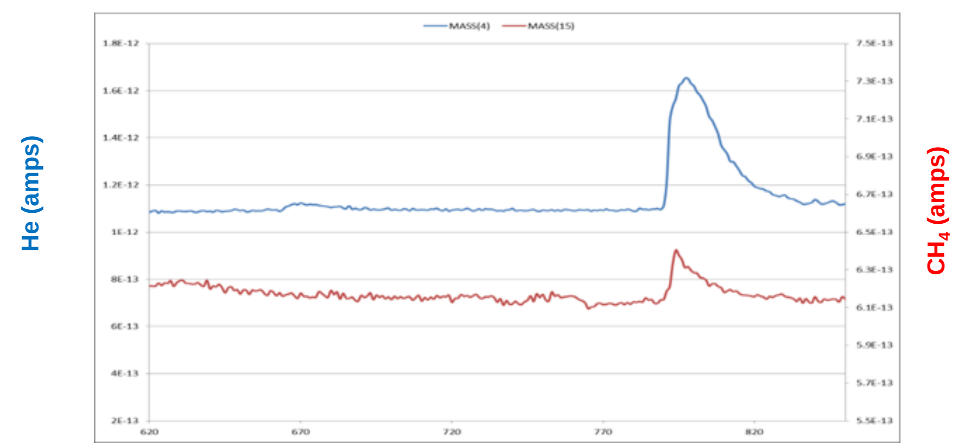




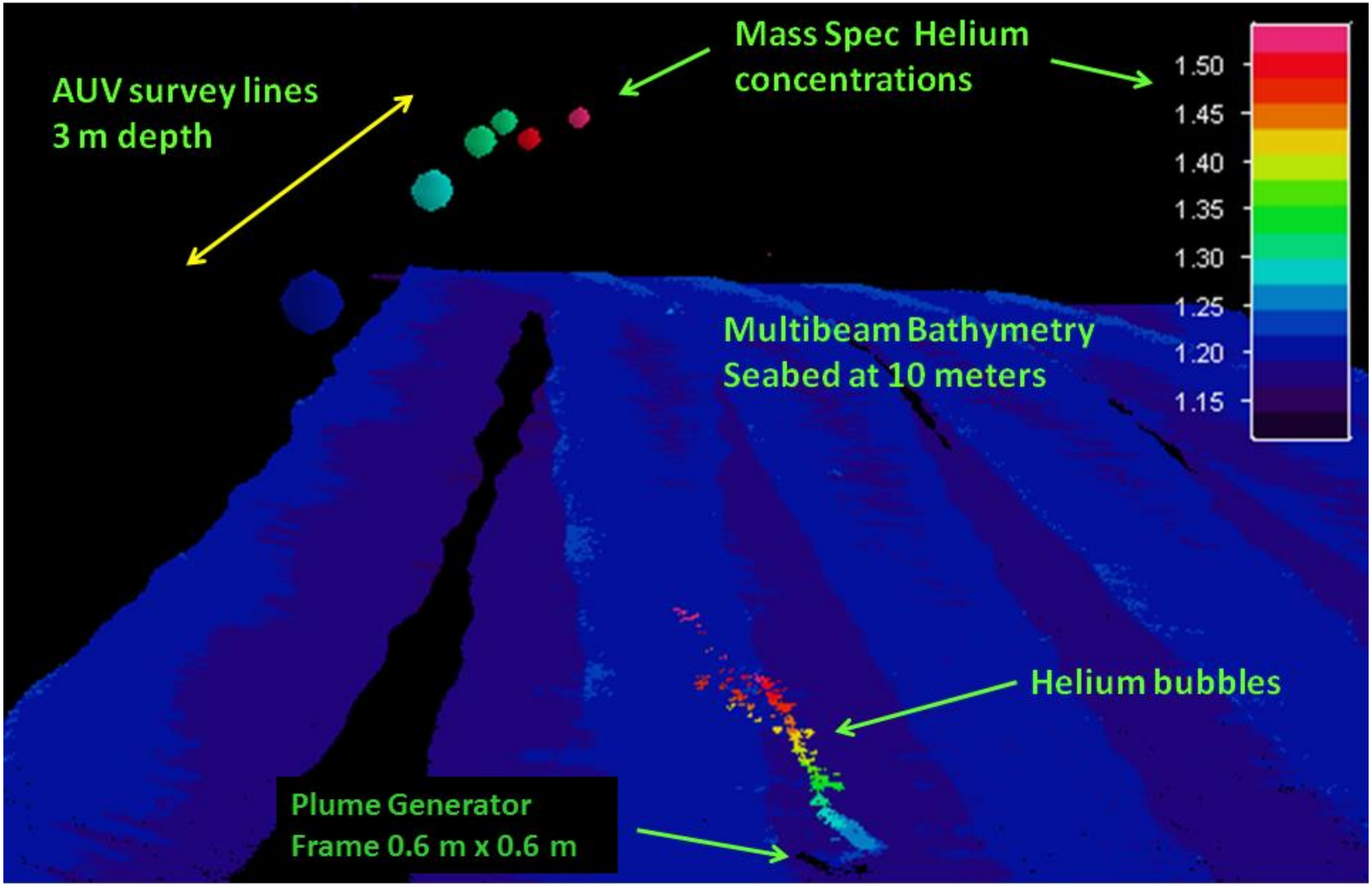
Successfully Detected Helium on Multiple Surveys

- Three days of AUV "lawnmower" surveys with the plume generator
  - Released helium from both gas cylinders on days 1 & 2 (except the first survey on day 1)
  - Detected helium on most surveys
  - Released helium and 2.5% methane in air on day 3; detected both helium and methane on the last survey
  - Fluorescein was not detected by the C7 fluorometer



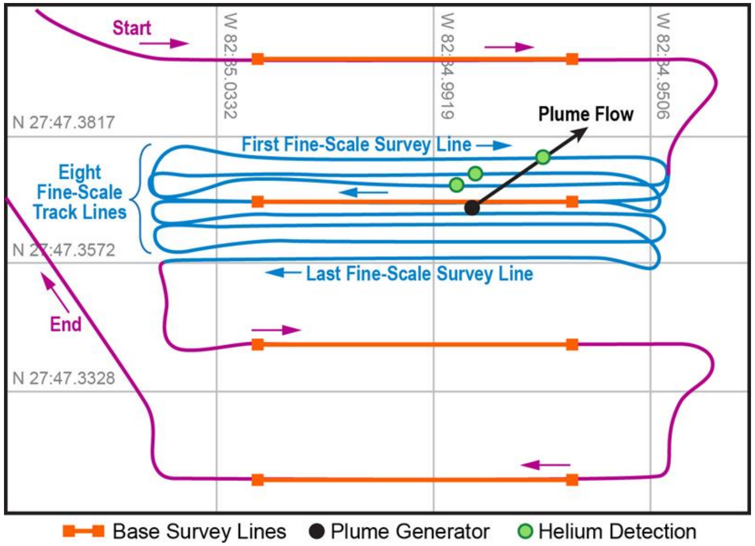


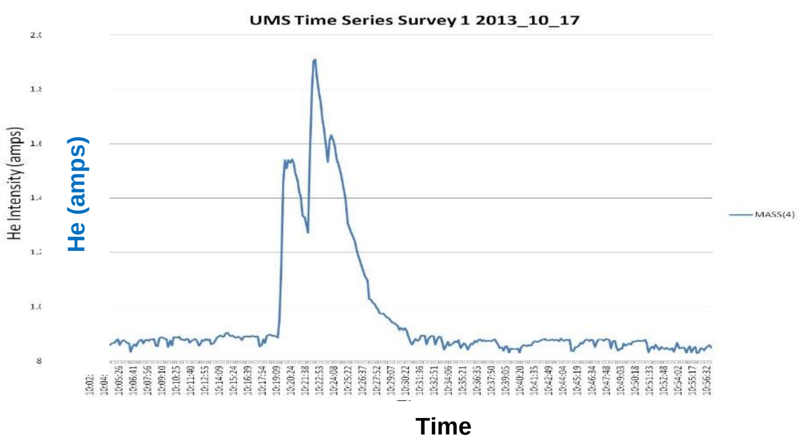
Fledermaus 3D Viewer Display of Multi-sensor Data

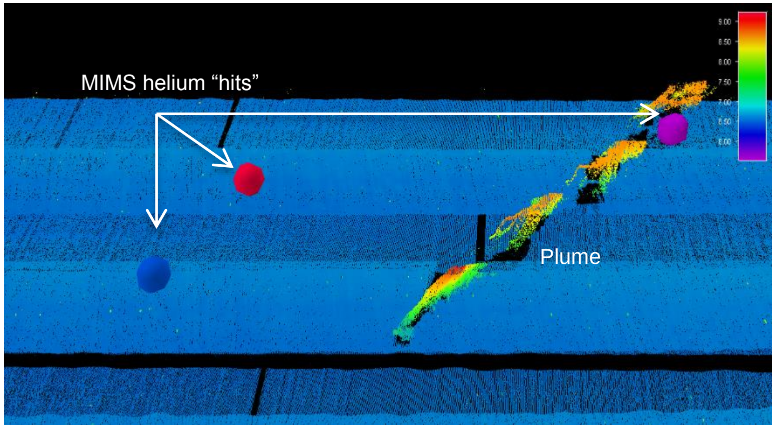


Embedded Fine-scale Survey Finds Helium Plume

- Base survey
  (100-m lines, 50-m spacings)
- Fine-scale survey
  (100-m lines, 3-m spacings)
- Detected helium on three lines of the fine-scale survey
  (time shift may need to be adjusted)





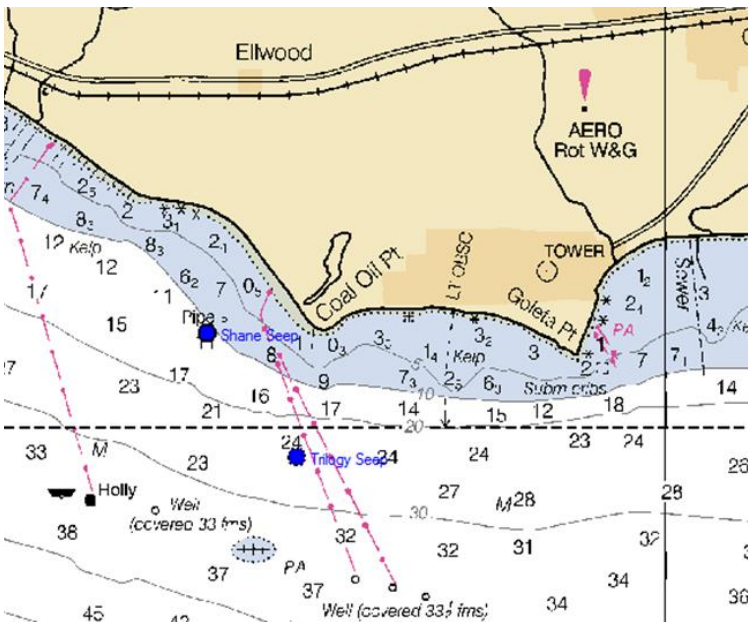


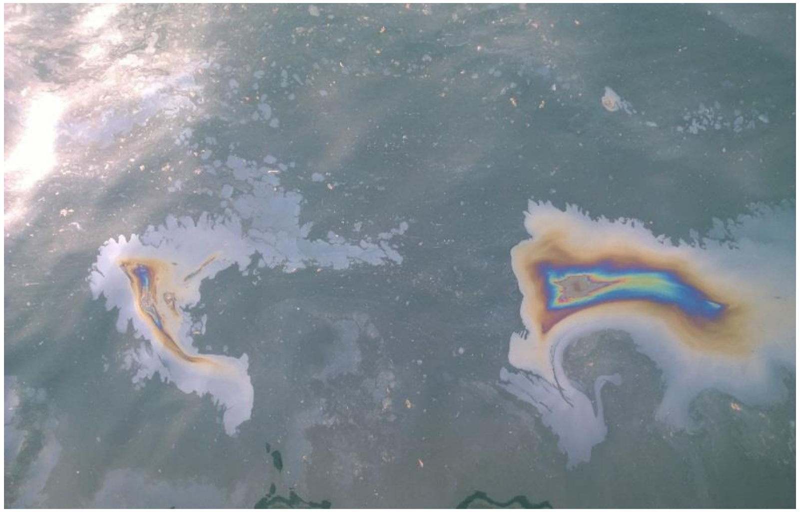
Fledermaus 3D Plot

Characterization of Natural Hydrocarbon Seeps in Santa Barbara Channel, CA

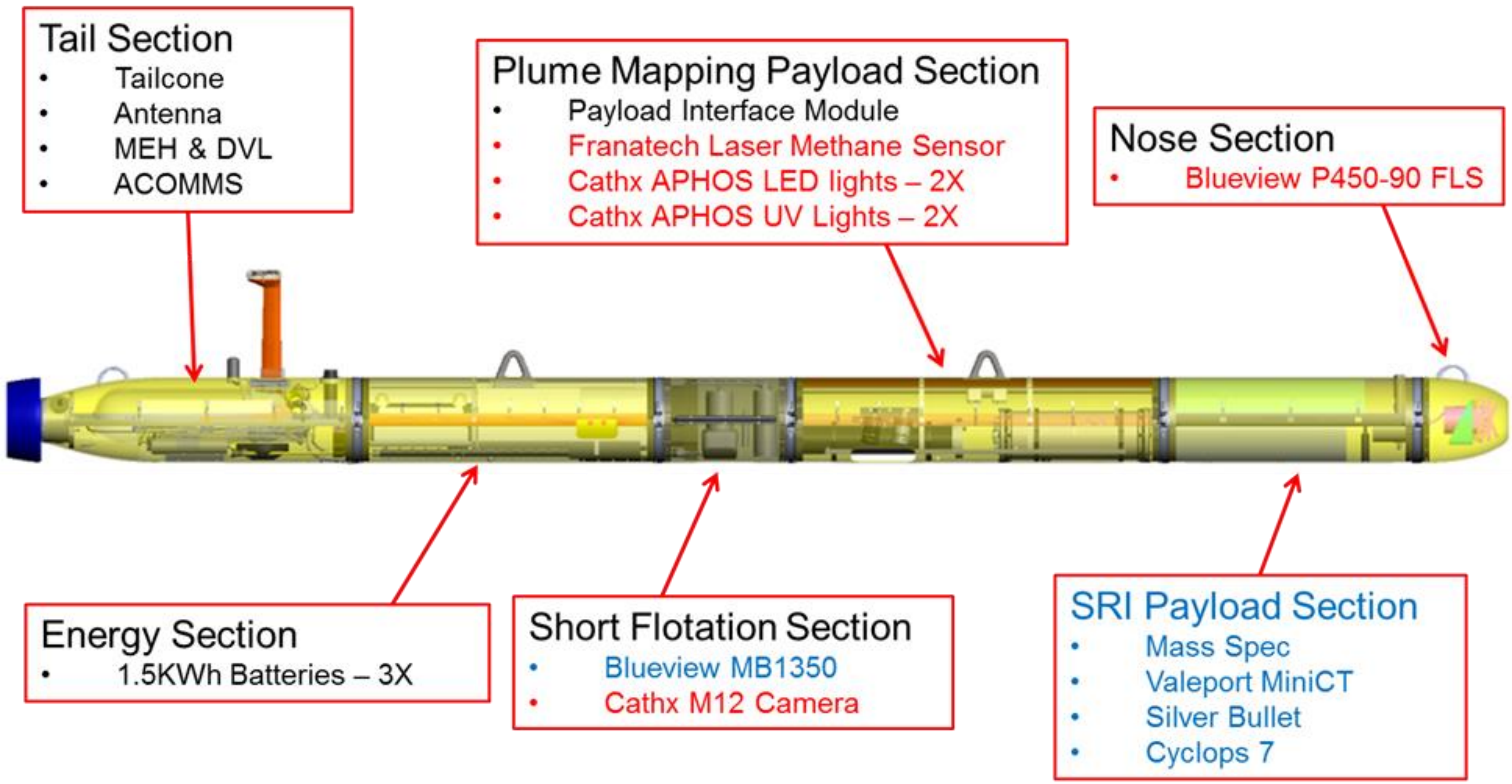
Natural Hydrocarbon Seeps in Santa Barbara Channel

- AUV operations with Bluefin Robotics to characterize natural hydrocarbon seeps
- Test site near Coal Oil Point
- Shane and Trilogy seeps

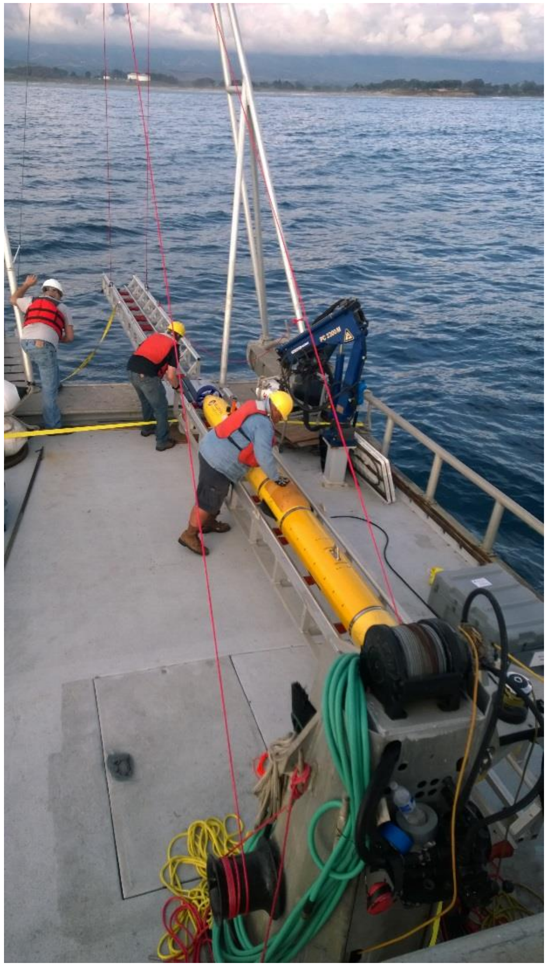




Bluefin-12 AUV Equipped with Multi-sensor Payload



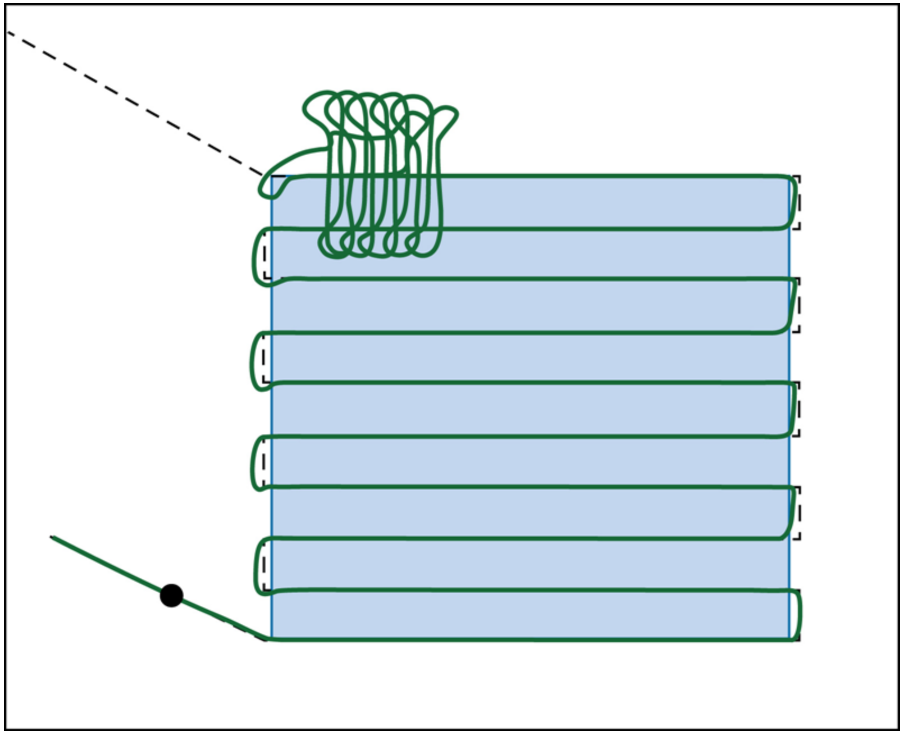
AUV Operations in Santa Barbara Channel on *R/V Lightning*



AUV Deployment and Recovery

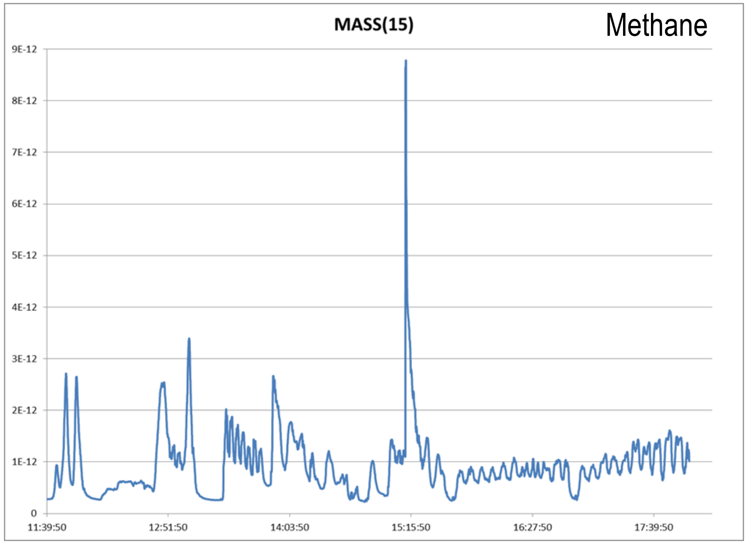
Typical AUV Survey Pattern for Seep Characterization

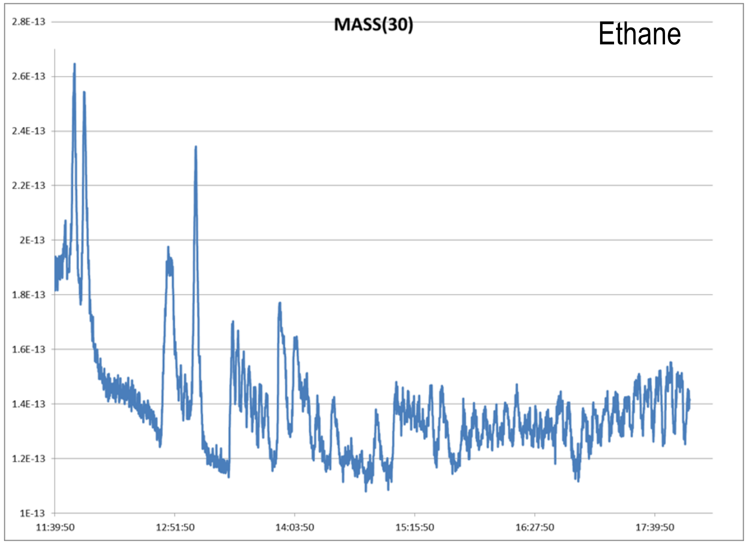
- Blue box shows the planned survey area for the Trilogy Seep
- Dotted line indicates the planned large-scale survey
- Green line shows the actual AUV path with embedded smaller-scale survey
- Smaller-scale survey was performed for better characterization of detected seep

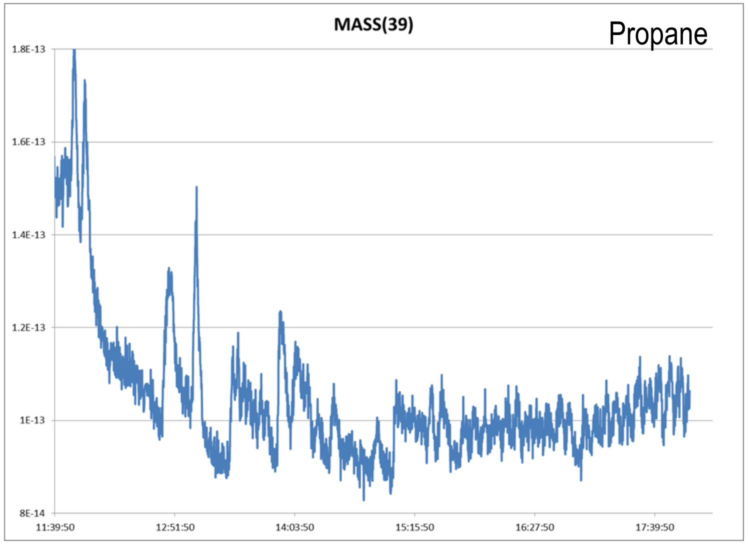


MIMS Light Hydrocarbon Data from Trilogy Seep

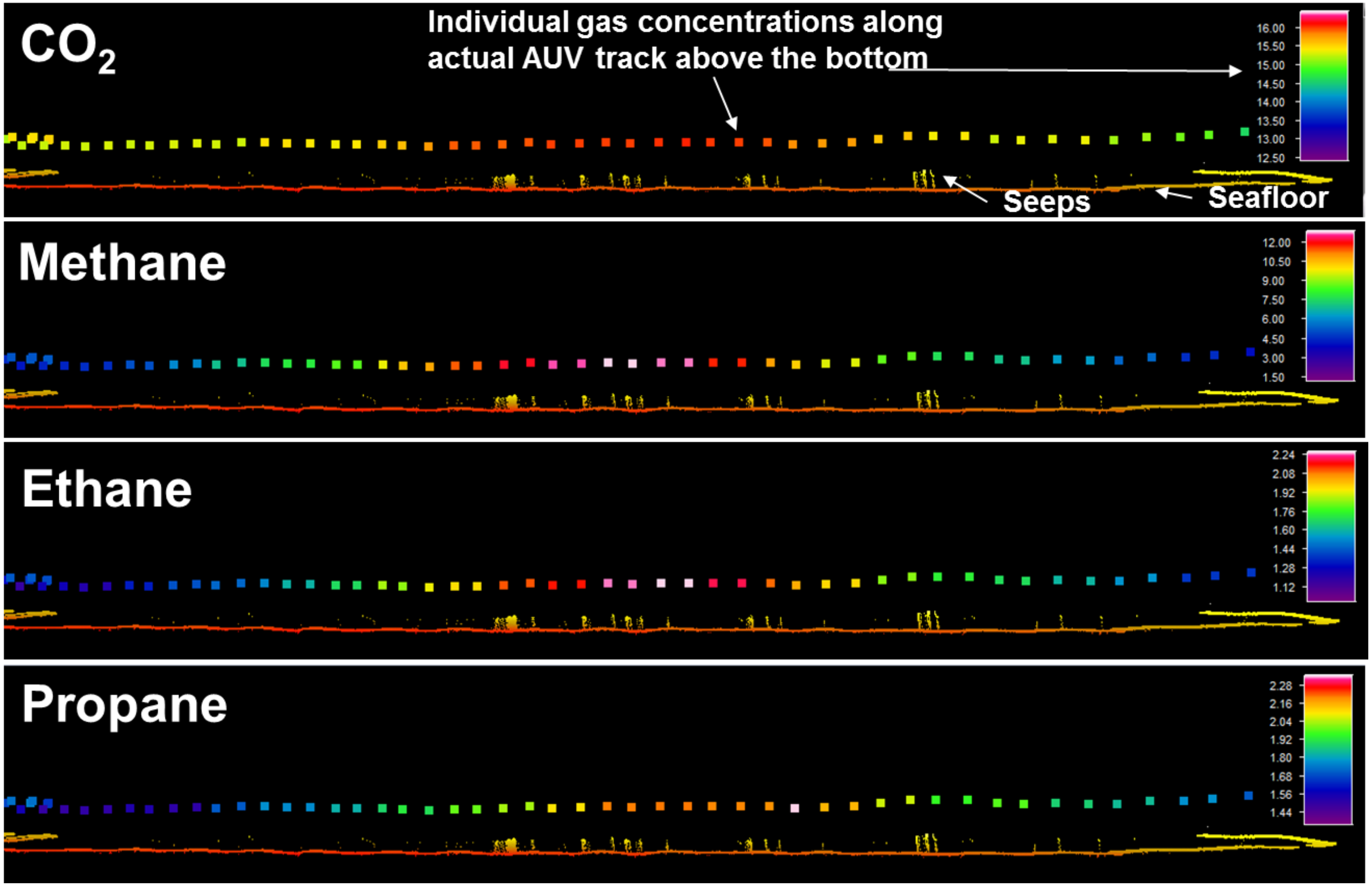
- MIMS raw data from six AUV surveys (over 5 hours)
- Similar time-series data profiles for all three analytes
- One exception at 15:15:50 is still under investigation







MIMS and Multi-beam Sonar Data for one AUV Line



MIMS data correlated with location of seep bubble streams

Summary

- Bluefin BF-12 AUVs were equipped with a state-of-the-art MIMS-based sensor suite for wide-area surveys of HCs
- An artificial plume generator was used as a proxy for natural HC seeps or leaks from pipelines or during drilling operations
- The AUV MIMS-based sensor suite was tested in Tampa Bay, FL to validate operation and survey strategies
  - MIMS detected helium from the plume generator on most surveys
  - Blueview sonar images of the bubble stream were valuable for locating gas plumes and interpreting MIMS data
- AUV operations in the Santa Barbara Channel demonstrated use of the multi-sensor suite's ability to characterize natural hydrocarbon seeps
  - MIMS hydrocarbon data and multi-beam sonar data are highly correlated
  - A similar approach can be used for early leak detection and characterization from pipelines and rigs

Acknowledgements

- Mote Marine Lab *R/V Eugenie Clark* for deployments in Tampa Bay
- *R/V Lightning* and crew for deployments in Santa Barbara Channel
- Funding and operational support from Bluefin Robotics Corporation for deployments in Santa Barbara Channel

Thank You!

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