Development of a Mass Spectrometer for Deployment on Moorings and Cabled Observatories for Long-Term Unattended Observation of Low-Molecular Weight Chemicals in the Water Column (2007 Annual Report)

Richard Camilli
Woods Hole Oceanographic Institution, MS#7 Woods Hole, MA 02543
Phone: (508) 289-3796 FAX: (508) 457-2191 E-mail: rcamilli@whoi.edu

Award Number: (#0537173)
http://www.monitorinstruments.com

LONG-TERM GOALS

The goals of this project are to address the need for advanced chemical sensing in the ocean environment through development of a new mass spectrometer for long-term unattended deployment. The TETHYS (TETHered Yearlong Spectrometer) mass spectrometer is based on Monitor Instruments' miniature cycloidal mass analyzer technology and oceanographic components developed by WHOI.

OBJECTIVES

The TETHYS design is being optimized for long-term measurement of low molecular weight dissolved biogenic, atmospheric, and noble gases as well as light hydrocarbon compounds. Building upon the capabilities achieved in 2006, this past year's work has focused on the following items:

1. Extended spectral range
2. Increased sensitivity
3. Long-term unattended operation
4. Autonomous real-time analysis

APPROACH AND WORK PLAN

During this past year of the program the working TETHYS prototype has been refined and is now routinely used for scientific and industry deployment onboard human occupied submersibles, ROVs, AUVs, ship-towed platforms, SCUBA operations, and cabled observatories.

Overall direction and technical leadership is being provided by the Principal Investigator, Richard Camilli of Woods Hole Oceanographic Institution. Dr. Camilli is in charge of engineering development and deployment. Development of many hardware components is being carried out by Monitor Instruments. Mr. Anthony Duryea, president of Monitor Instruments, is in charge of all aspects of Monitor Instruments involvement in the TETHYS development program.
During this past year's effort the TETHYS prototype was integrated onboard AUVs using a newly developed AUV communications protocol, allowing low bandwidth real-time communications. In addition, a lightweight 1,000 meter variant was successfully utilized in a scientific expedition to characterize reef ecology in the Pacific coast of Panama, north of the Panama Canal Zone. The success of the 1,000 meter design has also lead to the development an even lighter 100 meter design that is approximately neutrally buoyant, that is appropriate for SCUBA diver-based deployment. The 100

meter design has bee successfully used for long-term cabled deployment at the Aquarius Habitat, near Key Largo Florida. These Aquarius deployments were carried out using SCUBA divers.

WORK COMPLETED

During this third year effort we have completed the following objectives:

1) Expanded spectral range from 2-150 to 2-200 AMU

2) Improved mass resolution, increasing resolution by approximately 30% (Figure 1).

3) Successfully completed multiple long-term unattended deployments at a time at cabled observatories, with continuous operation of up to a month.

4) Integrated complimentary sensors with TETHYS, including fluorometers, CTD, navigation, and sonar systems.

5) Integrated and operated the TETHYS instruments onboard an increasing range of human occupied submersibles, ROVs, AUVs, and towfish (e.g. DSV Alvin, ROV Jason, AUV PUMA).

6) Collected scientifically useful data, including long-term time series data that has proven useful for various lines of scientific enquiry

7) Expanded use for real-time mapping of environments for spill assessment (i.e. petroleum and other toxic industrial chemicals).

RESULTS

The first working TETHYS prototype was completed in August 2006. Since then, the TETHYS operational capabilities have been significantly expanded and improved, among these modifications are: 1) integration of fail-safes for deep operation onboard human occupied submersibles, 2) integration of external sensors (i.e., CTD, pH, ORP, fluorometers, and navigation sensors), 3) development of a high energy-density rechargeable battery pack for up to 2 ½ days of continuous operation (this enables continuous operation on cabled observatories, despite power interruption which often occurs during large storms [i.e. hurricanes and nor'easters]). Software developments include 4) a low bandwidth serial protocol is also available for transmitting processed data and receiving parameterized mission control commands. This low bandwidth protocol is useful for AUV operations or deployments utilizing acoustic communications (i.e., where intermittent connectivity

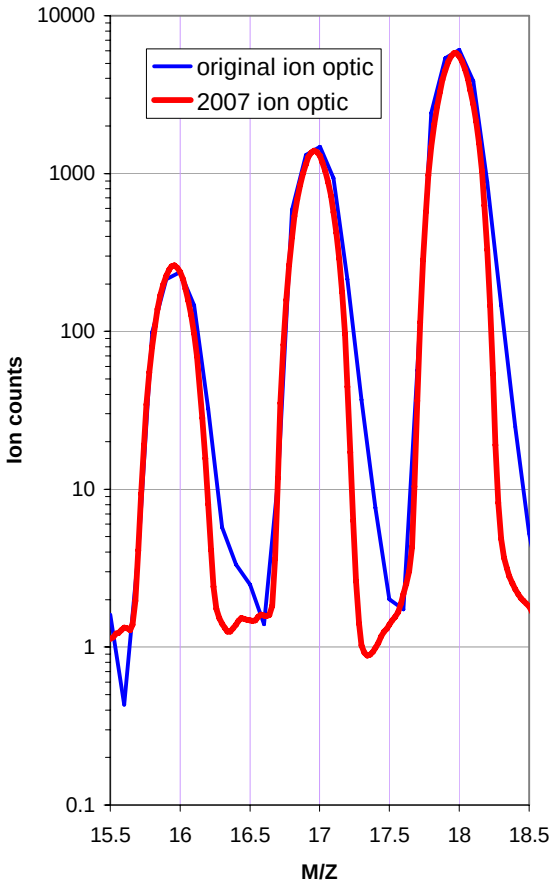

Figure 1: Comparison of mass resolution using original TETHYS ion optic and new ion optic.

is likely). 5) Finally, a software controlled differential sensing capability has been added, allowing the instrument to control valve systems by autonomously selecting and measure different sample streams. This capability has enabled the direct measurement of the metabolic activity (i.e. productivity and respiration) of marine organisms in-situ.

IMPACT AND APPLICATIONS

Over the past year four general categories of research deployments have been successfully undertaken, represented by the following programs:

- Human-occupied submersible survey of Pacific cold seeps aboard the DSV Alvin. During this expedition a TETHYS prototype was successfully operated on 8 Alvin dive missions, and 8 nights of CTD casts and tow-yos. These Alvin and CTD operations were used to characterize numerous biogenic and thermogenic cold seeps to depths of 2,000 meters.

- Mega-transect (>100 km) survey. This expedition successfully mapped the water column chemistry of large coastal areas along the Pacific coast of Panama, including reef ecosystems, using a TETHYS-fluorometer towfish and a chemical imaging SCUBA diver sled.

- Environmental survey/cleanup in the Gulf of Mexico. The TETHYS instrument has been integrated onto various work class ROVs and has been successfully used in several environmental cleanup programs to rapidly identify hydrocarbon leaks from offshore oil&gas platforms and pipelines destroyed in natural disasters (hurricanes and seafloor subsidence events). TETHYS data has been instrumental in identifying the locations of leak sources. Along with localization TETHYS has been used to fingerprint the composition of leaks, enabling positive identification of the source.

- Tethered long-term deployments at cabled observatories in the coastal waters of Cape Cod, Massachusetts and the Florida Keys. These deployments have successfully measured, in-situ, the magnitude and types of temporal variability in biologically active gases due to respiration, tidal forcing, and storm events.

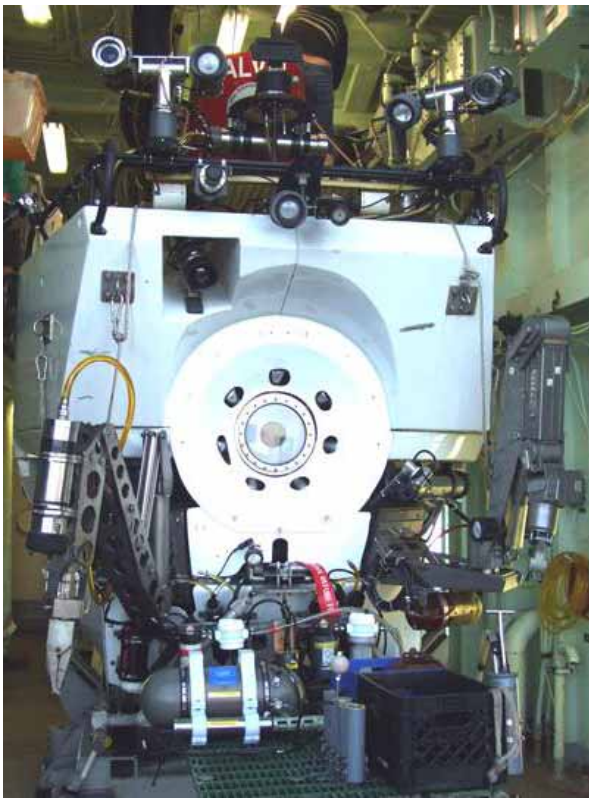

Figure 2: Above, a TETHYS 5,000 meter unit mounted to the DSV Alvin science basket prior to a series of deployments in the Pacific Ocean. Below, photo of TETHYS taken during investigation of a methane hydrate site off the coast of California.

National Security

The broad spectrum sensitivity and low limits of detection (typically on the order of 1 part per billion) show great potential for National Security or Homeland Defense in detecting explosives and toxic chemicals.

Economic Development

The TETHYS prototype has already demonstrated its utility as a survey. The information provided by TETHYS has also been useful for characterizing natural hydrocarbon seeps. This information is useful for oil and gas exploration and assessment of mineral lease rights by the Minerals Management Service.

Quality of Life

TETHYS has been successfully used as a tool to aid in the cleanup of numerous oil and gas leaks emanating from offshore structures damaged in hurricanes Katrina, Rita, and Ivan. The instrument has also proven useful for identifying groundwater discharge into costal areas and for characterizing coastal pollution. All of these capabilities are useful for quality of life issues involving public and ecosystem health, coastal resource management, such as the surveys carried out in Panama, Cape Cod, and the Florida Keys.

Science Education and Communication

Several cabled observatory networks, including the proposed Neptune array can potentially integrate this instrument into their architectures to rapidly collect data across wide spatial domains, providing synoptic coverage of large-scale transient chemical phenomena. Preliminary data from long-term cabled observatory deployment in Massachusetts and Florida indicate that the TETHYS instrument can resolve variability in biologically active gas concentrations and isotopic ratios on time scales ranging from minutes to several weeks. In addition TETHYS is useful for chemical exploration of dynamic regions within the deep ocean such as hydrothermal vent and cold seep activity (i.e. detecting and monitoring hydrogen sulfide, oxygen, hydrogen, helium, carbon dioxide, and methane), as well as investigation of ocean-mediated green house and environmental gas dynamics.

Figure 3: Above, photo of a TETHYS 100 meter unit during cabled observatory deployment at the Aquarius Habitat near Key Largo, Florida.

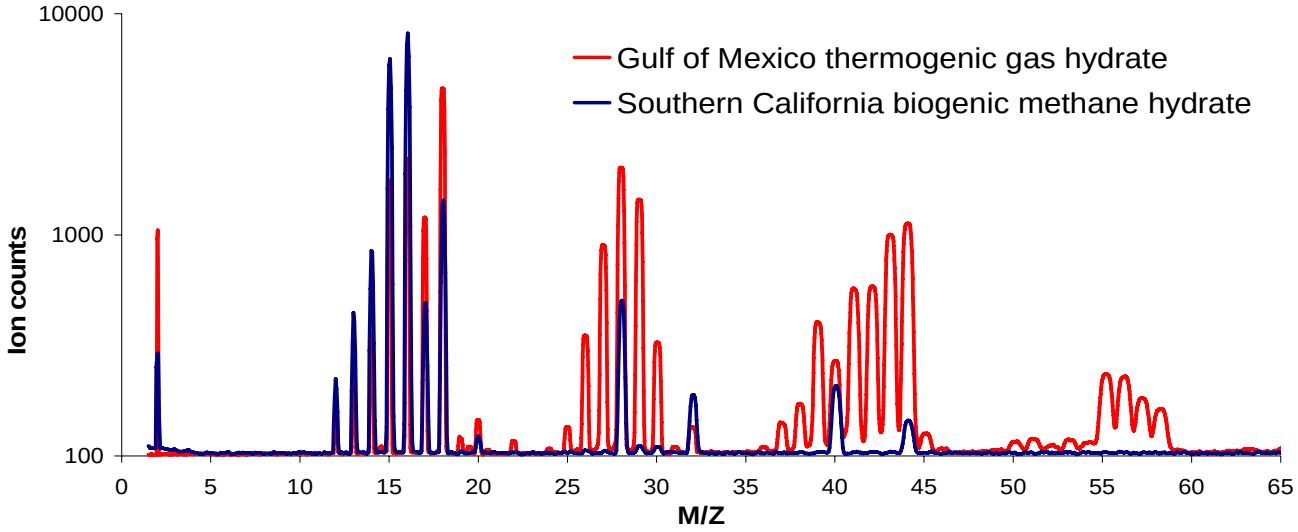

Figure 4: Comparison of TETHYS mass spectra gas hydrate data from the Gulf of Mexico (2006) and along the continental margin of Southern California (2007). Spectral peaks from the Gulf of Mexico data suggest a homologous series of alkanes (methane through pentane) along with other higher hydrocarbons, indicating that the hydrate is thermogenic in origin. In contrast, the spectral data from Pacific hydrates indicate the presence of methane, but no higher hydrocarbons, suggesting that these hydrates are biogenically derived.

RELATED PROJECTS

The TETHYS prototype and technologies have been used in the following scientific research programs and expeditions:

- NOAA Office of Ocean Exploration PHAEDRA Expedition June-July 2006
- NOAA National Undersea Research Program coastal reef survey August 2006
- U. Miss Gulf of Mexico Hydrates Consortium cruise Sept 2006
- Scripps R/V Revelle Santa Barbara Basin geotechnical cruise November 2006
- WHOI Coastal Ocean Institute study of groundwater discharge survey Dec 2006
- Rapid swath mapping of reef ecology and associated water column chemistry Gulf of Chiriquí, Panamá, February 2007.
- UNC SCUBA diver-based deployment Florida Keys, March 2007
- WHOI cabled observatory deployment, May 2007
- WHOI AGAVE Arctic Ocean cruise to explore the Gakkel Ridge with PUMA AUV, June 2007.
- NOAA Aquarius Habitat cabled observatory deployments June and September 2007.
- UCSB Pacific biogenic and thermogenic cold seeps cruise using the DSV Alvin, July 2007.

In addition, the following research programs have utilized the TETHYS instrument for related scientific research:

NSF SST: PIs H. Singh, R. Camilli, J. Whelan of WHOI and B. Bingham of Olin College, explored new methods for integrating mass spectrometer data for closed-loop AUV control. This project developed a means by which an AUV can utilize the chemical data in real time to refine search strategies and dynamically re-task its mission planning. The TETHYS instrument is now being extensively used in integrated deployments as a result of this sensor networking development program.

Tropical Research Initiative: PI R. Camilli This ongoing research program utilizes the TETHYS technology along with other novel methods to rapidly map characterize pristine and degraded coral reef habitats and associated water column chemistry in the Gulf of Chiriquí, Panamá. In February 2006 a TETHYS instrument was deployed in a towfish configuration in the Western Isthmus of Panamá. Over the course of two weeks, chemical (CTD, fluorometry, and *in-situ* mass spectrometry) and acoustic bathymetric transects mapped approximately 300km, collecting over 25,000 chemical samples, with spatial resolution on the order of 10 meters. The results from these surveys provide insight into reef structure, bathymetry, spatial heterogeneity of marine organisms, and fundamental metabolic processes of photosynthesis and respiration. This information has proven useful for understanding both natural and human dynamics affecting tropical reef systems within the eastern Pacific Ocean. Results of this survey also provide baseline ecological information for identifying priority conservation areas in the Veraguas and Chiriquí marine provinces that are biologically linked, although outside Panamá's Coiba National Park.

US Coast Guard heavy oil spill detection : This program utilizes a TETHYS instrument in combination with a high-precision acoustic navigation system to rapidly detect and map submerged heavy oil spills. The system's compact size and real-time updates permit geo-referenced estimation of source location at spatial scales of less than 30 meters when surveying at speeds of 5 kts. This combined survey speed and spatial resolution enables rapid identification of source areas (full coverage of a $1nm^2$ area with 30 meter trackline spacing within 12 hours). When a high probable target has been identified, a nested survey grid can be undertaken at lower speed to pinpoint the spill location and fingerprint its hydrocarbon composition.

PUBLICATIONS

R. Camilli, A. Duryea, J. Buchner, and J K Whelan, "TETHYS: an in-situ mass spectrometer for Cabled Observatories" In: *Proceedings of the Fourth International Workshop on Scientific Use of Submarine Cables and Related Technologies*. Dublin, Ireland Feb 2006.

R. Camilli, T. Duryea, M. Wilson, "Underwater Vacuum Technology", *Vacuum Technology & Coating Magazine* pp.34-39, December 2005.

R. Camilli, D. Sakellariou, B. Foley, et al. "Real-time characterization of submarine hydrothermal vents with an in-situ mass spectrometer operating aboard a human occupied submersible". AGU fall Meeting, San Francisco CA, Dec 2006.

R. Camilli, J. Whelan, C. Martens, et al. "Coordinated mapping and characterization of ocean floor methane sources with manned submersibles, AUVs and modular observatory arrays". AGU fall Meeting, San Francisco CA, Dec 2006.

R. Camilli, D. Sakellariou, B. Foley, C. Anagnostou, A. Mallios, B. Bingham, R. Eustice, J. Goudreau, and K. Katsaros. "Investigation of Hydrothermal Vents in the Aegean Sea using an Integrated Mass Spectrometer and Acoustic Navigation System onboard a Human Occupied Submersible." In *Rapport*

du 38^e Congrès de la Commission Internationale pour l'Exploration Scientifique de la Mer Méditerranée. Vol. 38 page 79, 2007

Mau, S., D. L. Valentine, J. F. Clark, J. Reed, R. Camilli, and L. Washburn (2007), Dissolved methane distributions and air-sea flux in the plume of a massive seep field, Coal Oil Point, California, *Geophys. Res. Lett., 34*, L22603, doi:10.1029/2007GL031344.

R. Camilli and A. Duryea. "Characterizing marine hydrocarbons with in-situ mass spectrometry", in proceedings of *IEEE OCEANS Vancouver 2007*

R. Camilli, O. Pizarro, L.Camilli. "Rapid Swath Mapping of Reef Ecology and Associated Water Column Chemistry in the Gulf of Chiriquí, Panamá", in proceedings of *IEEE OCEANS Vancouver 2007.*

ADDITIONAL FIGURES

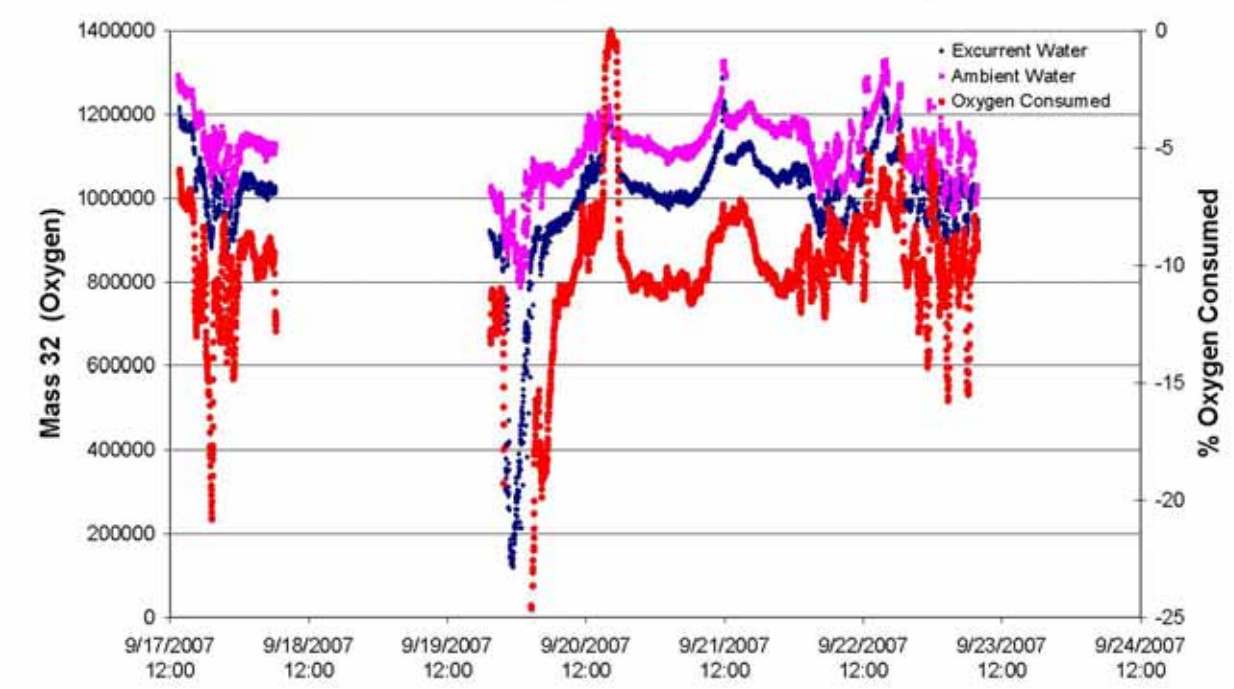

Figure 5: TETHYS in-situ time series data, using differential sampling to identify temporal variability in respiration rates of various marine organisms near the Aquarius Habitat in Key Largo, Florida. (Figure courtesy of C. Martens, UNC Chapel Hill).

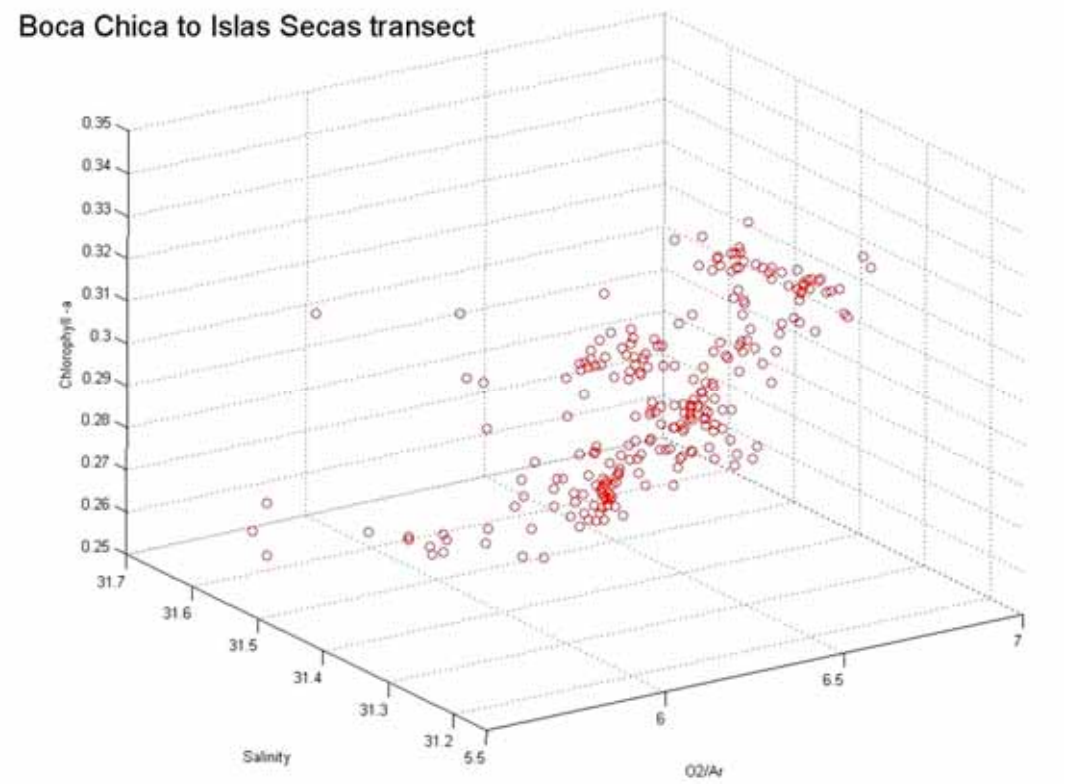

Figure 6: Correlation of chlorophyll-a and salinity with oxygen/argon ratios measured using a TETHYS mass spectrometer, CTD and fluorometer during a towed transect from Boca Chica to Islas Secas, in the Gulf of Chiriquí, Panamá.

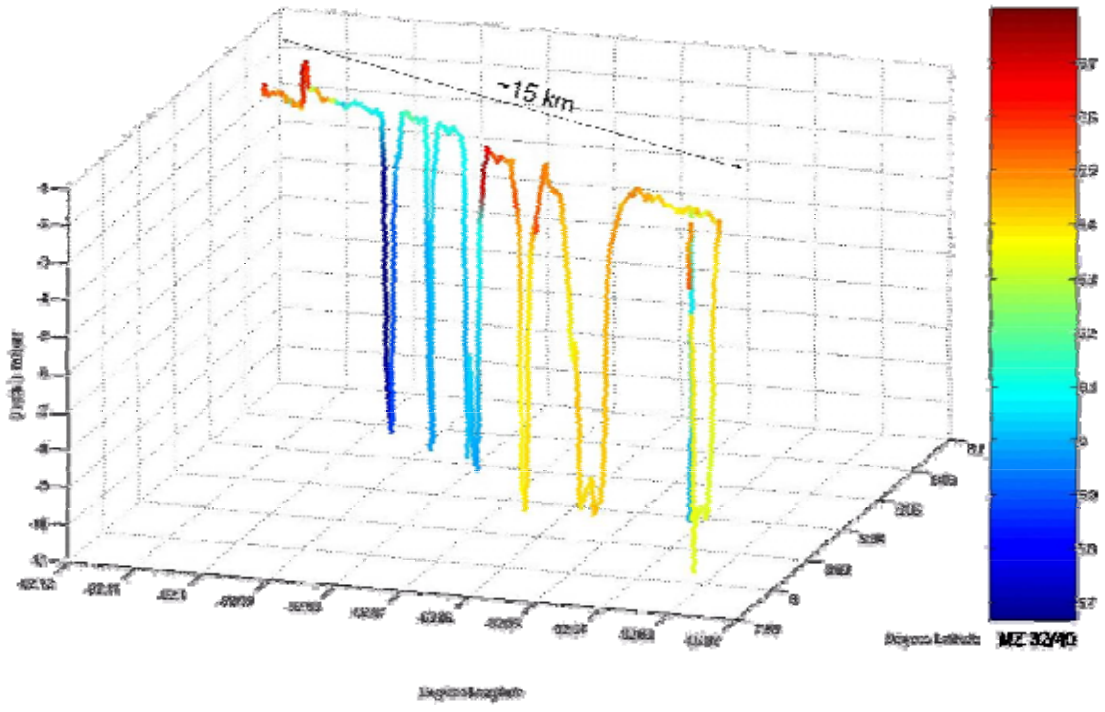

Fig. 7: TETHYS tracklog data indicating horizontal variability in dissolved oxygen/argon levels during a towed transect from Boca Chica to Islas Secas, in the Gulf of Chiriquí, Panamá. (Oxygen/argon units are dimensionless, red indicates higher dissolved oxygen levels, blue indicates lower levels).