PAPER

Recent Development in IR Sensor Technology for Monitoring Subsea Methane Discharge

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ABSTRACT

Recently developed methane sensors, based on infrared (IR) absorption technology, were successfully utilized for subsea methane release measurements. Long-term investigation of methane emissions (fluid flux determination) from natural methane seeps in the Hikurangi Margin offshore New Zealand were performed by using seafloor lander technology. Small centimeter-sized seep areas could be sampled at the seafloor by video-guided lander deployment. *In situ* sensor measurements of dissolved methane in seawater could be correlated with methane concentrations measured in discrete water samples after lander recovery. High backscatter flares determined by lander-based Acoustic Doppler Current Profiler (ADCP) measurement indicate bubble release from the seafloor. Highest methane concentrations determined by the IR sensor coincided with periods of high ADCP backscatter signals. The high fluid release cannot be correlated with tidal changes only. However, this correlation is possible with variability in spatial bubble release, sudden outbursts, and tidal changes in more quiescent seepage phases.

A recently developed IR sensor (2,000 m depth-rated) with a detection limit for methane of about 1 ppm showed good linearity in the tested concentration range and an acceptable equilibration time of 10 min. The sensor was successfully operated offshore Santa Barbara by a small work-class ROV at a natural methane seep (Farrar Seep). High background methane concentration of 50 nmol L^{-1} was observed in the coastal water, which increases up to 560 nmol L^{-1} in dissolved methane plumes south of the seepage area. ROV- and lander-based sensor deployments have proven the applicability of IR sensor technology for the determination of subsea methane release rates and plume distribution. The wide concentration range, low detection limit, and its robust detection unit enable this technology for both subsea leak detection and oceanographic trace gas investigations.

Keywords: methane, sensor development, natural hydrocarbon seeps, subsea leak detection

Introduction

Natural marine hydrocarbon seeps are important sources of methane (CH_4) to the surface sediments, the benthic boundary layer, and eventually to the water column and atmosphere. CH_4 is a potent greenhouse gas that warms the Earth about 23 times more than carbon dioxide (CO_2) when averaged over 100 years. Quantifying the discharge of CH_4 from the seabed, its fate in the water column and its flux to the atmosphere has been the subject of ongoing research on many different fronts (e.g., Clark et al., 2000; McGinnis et al., 2006; Judd & Hovland, 2007; Westbrook et al., 2009; Faure et al., 2010). Furthermore, a natural subsea hydrocarbon seep can serve as an ideal analogon for studying gas leakage scenarios from subsea constructions like gas/oil transport lines, active or abandoned wellheads, etc. (Leifer et al., 2006). Moreover, the dissolution behavior and transport of gas in the water column at variable oceanographic conditions, like currents, horizontal/vertical eddies, tidal changes, or stratified water columns can be studied at natural seepage sites (e.g., Leifer et al., 2006; McGinnis et al., 2006, 2011; Schneider von Deimling et al., 2010). Here, we report on the development and deployment of novel methane sensors, based on infrared absorption technology, which were tested in two different subsea settings. The first setting was a long-term multisensor deployment with a benthic lander, which was placed for 41 h at a 670-m-deep CH_4 cold-seep at the seafloor in the Hikurangi Margin, New Zealand. The second one was a shallow water test of ROV-operated sensor measurement at a natural hydrocarbon seep offshore Santa Barbara, California.

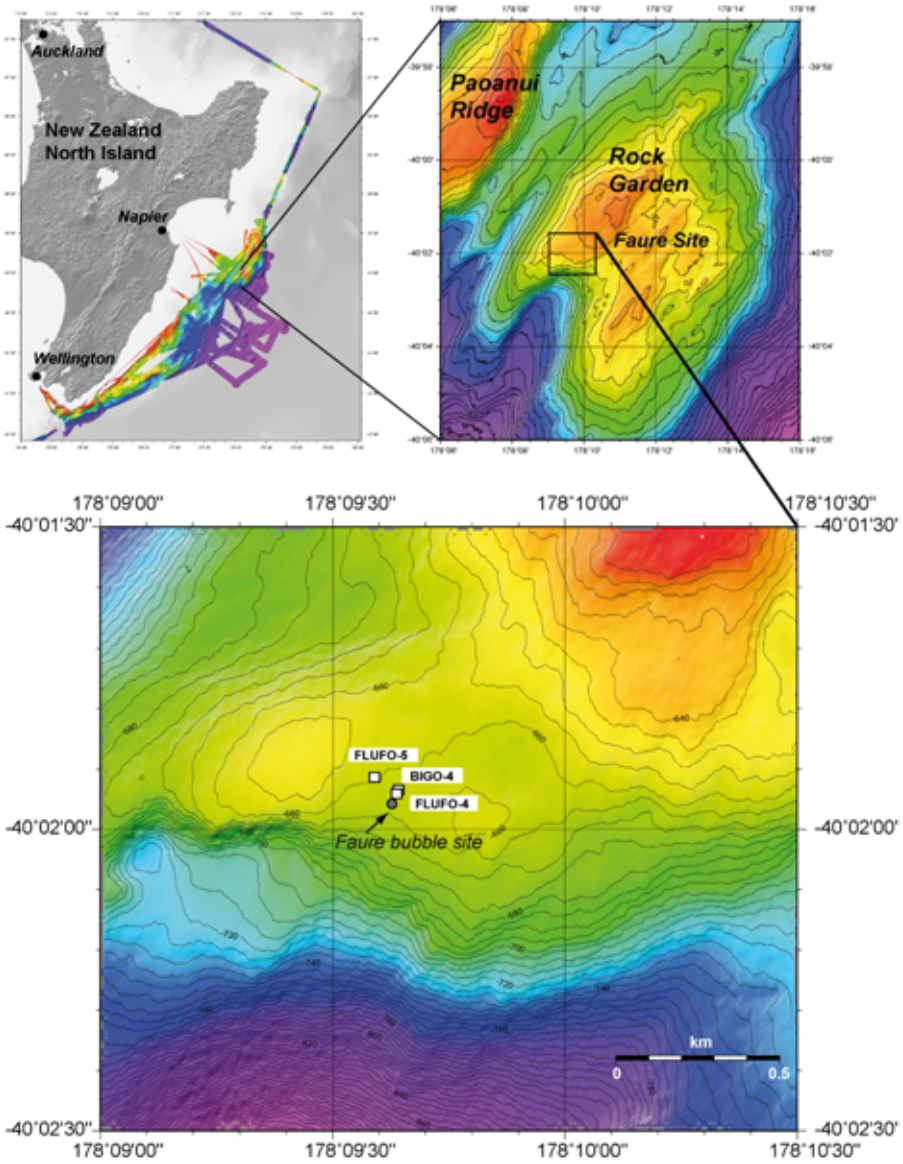
CH_4 Sensor Deployment on a Deep Sea Lander

A novel methane sensor HydroC™ of CONTROS System & Solutions

GmbH, Germany, was deployed on a benthic lander equipped with a wide range of instrumentation to study the role of physical parameters on exchange processes in the benthic boundary layer. Benthic landers provide a stationary study platform decoupled from the movement of the ship and simultaneously measure several physical, chemical, and biological parameters across the sediment water interface. The Fluid Flux Observatory (FLUFO) was deployed for *in situ* flux measurements of methane and oxygen in about 670-m water depth at a methane seep setting known as Rock Garden by local fishermen (Figure 1). This area is situated at the southern termination of Ritchie Ridge and is uplifted by the subduction of a seamount beneath the outer Hikurangi Margin at the east coast of New Zealand's North Island. Townend (1997) estimated that more than 20 m^3 of fluids are being squeezed from accreted and subducted sediments along each meter of the Hikurangi Margin every year, which results in abundant evidence of escaping gas offshore (Faure et al., 2010; Linke et al., 2010; Naudts et al., 2010) and onshore (Campbell et al., 2008). The deployment was part of a large campaign involving a large range of equipment and scientific disciplines to study the methane seeps at the Hikurangi Margin (Greinert et al., 2010).

FIGURE 1

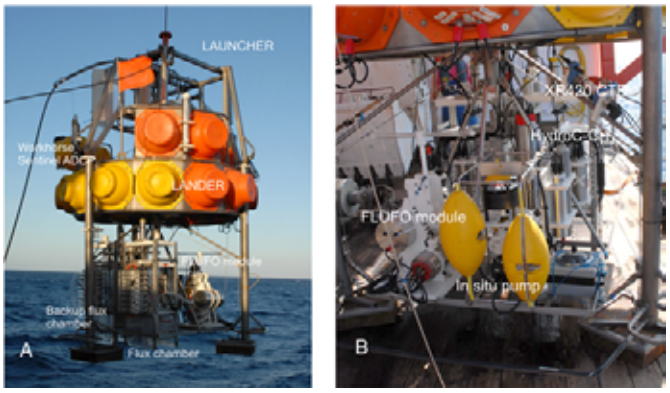
Overview map showing the bathymetry of the Hikurangi Margin at the east coast of New Zealand, mapped during R/V SONNE cruise SO191 in 2007 (modified from Linke et al., 2010). The enlarged bathymetric maps depict the Rock Garden area with stations relevant for this paper; for example, the site of vigorous gas discharge (Faure bubble site) discovered during a ROV dive (Naudts et al., 2010) and two other lander stations (FLUFO-4 and BIGO-4) described in Linke et al. (2010).



The observatory consists of a titanium tripod frame that carries 21 Benthos glass spheres for buoyancy and ballast weights attached to each leg (Figure 2a). The release of the ballast weights is controlled by two acoustic releasers. FLUFO is equipped with two circular benthic chambers, each covering a sediment area of 651.4 cm^2. A video-guided launching system (LAUNCHER) allowed smooth placement of the observatory on a selected site at the seafloor (Pfannkuche & Linke, 2003). Two to three hours after deployment, the benthic flux chambers were slowly driven into the sediment. Seabed methane emission was monitored with eight sequentially water samples taken from each chamber by means of glass syringe samplers. Sampling (monitoring) periods were about 34 (FLUFO-5) and 40 h (FLUFO-4, BIGO-4), respectively. After the *in situ* incubation, the bottom of the chambers was closed with a shutter to recover the sediments for further analyses. After recovery, syringe water samples retrieved during lander deployment were immediately transferred into the cold room, where

FIGURE 2

Launch of the Fluid Flux Observatory (FLUFO) with the video-guided launcher on top showing the different scientific modules integrated in the back (a) and in the front (b) of the lander (modified from Linke et al., 2010).



subsamples were obtained for the determination of oxygen and methane (Linke et al., 2010).

Next to the chambers, the lander carried the HydroC™ methane sensor for *in situ* measurements up to 4,000 m water depths (Figure 2b). The high-pressure seawater side is separated by a permeable membrane from the internal infrared detection unit. An internal pump system increases equilibration of internal partial pressure of, for example, methane with the dissolved methane in seawater. Concentrations of methane were determined by using optical NDIR absorption technique. Large quantities of methane accumulated in the internal gas circuit can actively be removed with a patented exhaust system. The sensor was calibrated to detect CH_4 concentrations as low as approximately 100 nmol L^{-1}, and data were logged by a 24-bit SmartDI controller.

The HydroC™ methane sensor was mounted upright at the lander frame to avoid any trapping of gas bubbles in front of the membrane inlet. Beside the methane sensor, FLUFO was equipped with an upward-looking Acoustic Doppler Current Profiler (ADCP; 300 kHz Workhorse Sentinel ADCP, Teledyne RD Instruments, USA) and a small stand-alone memory CTD (Conductivity, Temperature, Depth; XR420, RBR Ltd., Ottawa, Canada). The CTD was also equipped with an optical backscatter sensor (SeaPoint), which measures light scattered by particles suspended in water.

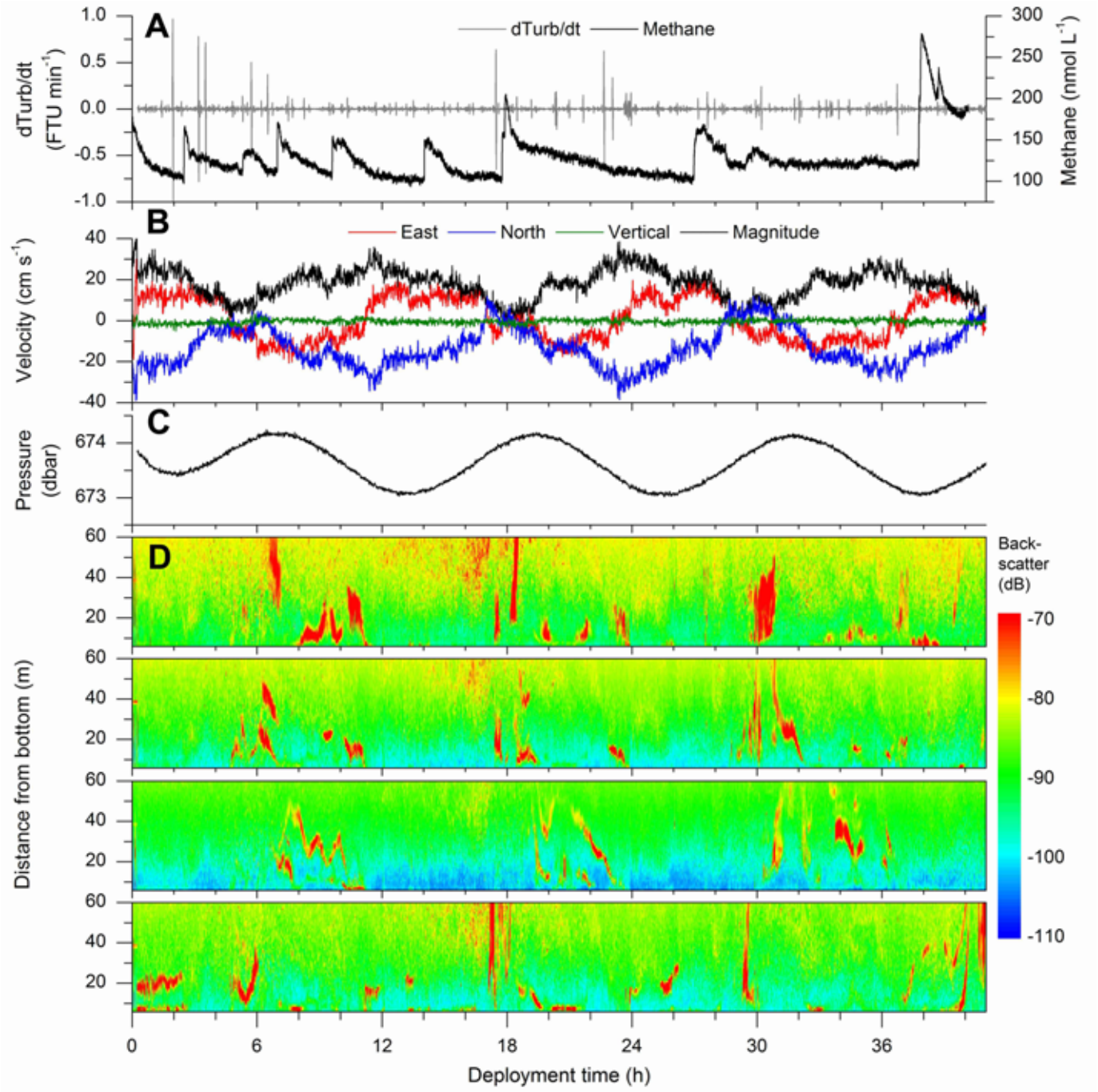
The lander was deployed in the vicinity of a methane gas vent named Faure bubble site (FLUFO-5; Figure 2). Here, bubble release occurs from differently sized depressions, which are often aligned in NW-SE direction; the largest depression observed by a ROV was 50 cm in diameter and 15 cm deep (Naudts et al., 2010). These observations clearly showed that the depressions are formed by the often violent release of bubbles. Naudts and coworkers observed that the bubbles entrained sediment particles, which then get carried away by the water currents, creating the depressions and a sediment outfall away from the venting hole. The data obtained with the HydroC™ sensor depict pulses of CH_4 emission (Figure 3a), ranging between 150 and 200 nmol L^{-1}. Water samples obtained from the ambient bottom water during a parallel deployment of another lander (BIGO-4; Figure 2) at the same height above the sediment water interface like the sensor showed two distinct peaks with CH_4 concentrations of 189 and 190 nmol L^{-1}, respectively (Linke et al., 2010), which are in the same range of the measurements obtained with the HydroC™ sensor. On the other hand, the data shown here depict that the sensor needed some time of relaxation after it had experienced high a peak of CH_4 before it was able to record another sudden increase.

However, the pulses seen in the HydroC™ sensor data correspond with increases in the backscatter strength detected in all four beams of the upward-looking ADCP (Figure 3d). The "flares" (presumed to be bubbles) persisted for 10–60 min, and some of them covered almost the whole acoustic depth range (100 m) of the ADCP. No associated signal was observed in the turbidity data obtained from the CTD (Figure 3a). The occurrence of the flares does not seem to be related to a sudden or tidal hydrostatic pressure drop (Figure 3c). In fact, some of the outburst occurred during high tide and at maximum current velocities of more than 20 cm s^{-1} (Figure 3b). This is in agreement with results of Linke et al. (2010) from another lander deployment next to the Faure Site (FLUFO-4; Figure 2). They found CH_4 concentration fluctuations in both the ambient bottom water and the chamber water, which coincided with tidally induced fluctuations of currents and acoustic backscatter flares in the ADCP record.

Furthermore, these measurements agree very well with ROV observations in the area reporting highly variable spatial bubble release rates and bubble sizes, with periods of low activity, alternating with periods of violent outbursts (Naudts et al., 2010).

FIGURE 3

Physical measurements obtained simultaneously to the changes in CH_4 concentration during deployment of FLUFO-5. Top to bottom: (a) turbidity changes and CH_4 concentration, (b) depth-averaged velocity time series, (c) local hydrostatic pressure, and (d) ADCP backscatter (all four beams).



High-Sensitive Methane Sensor (HISEM) Development

A new methane sensor, which should fulfill the needs for scientific trace gas (i.e., CH_4) investigations in the oceans and for subsea leak detection, is currently under development (www.martec-era.net). The sensor technology is based on laser diode IR absorption technology that provides excellent detection limits at good signal-to-noise ratios. The actual configuration is a 2,000-m depth-rated version with a (Contros HydroC™) membrane-inlet configuration. The system was tested in the laboratory

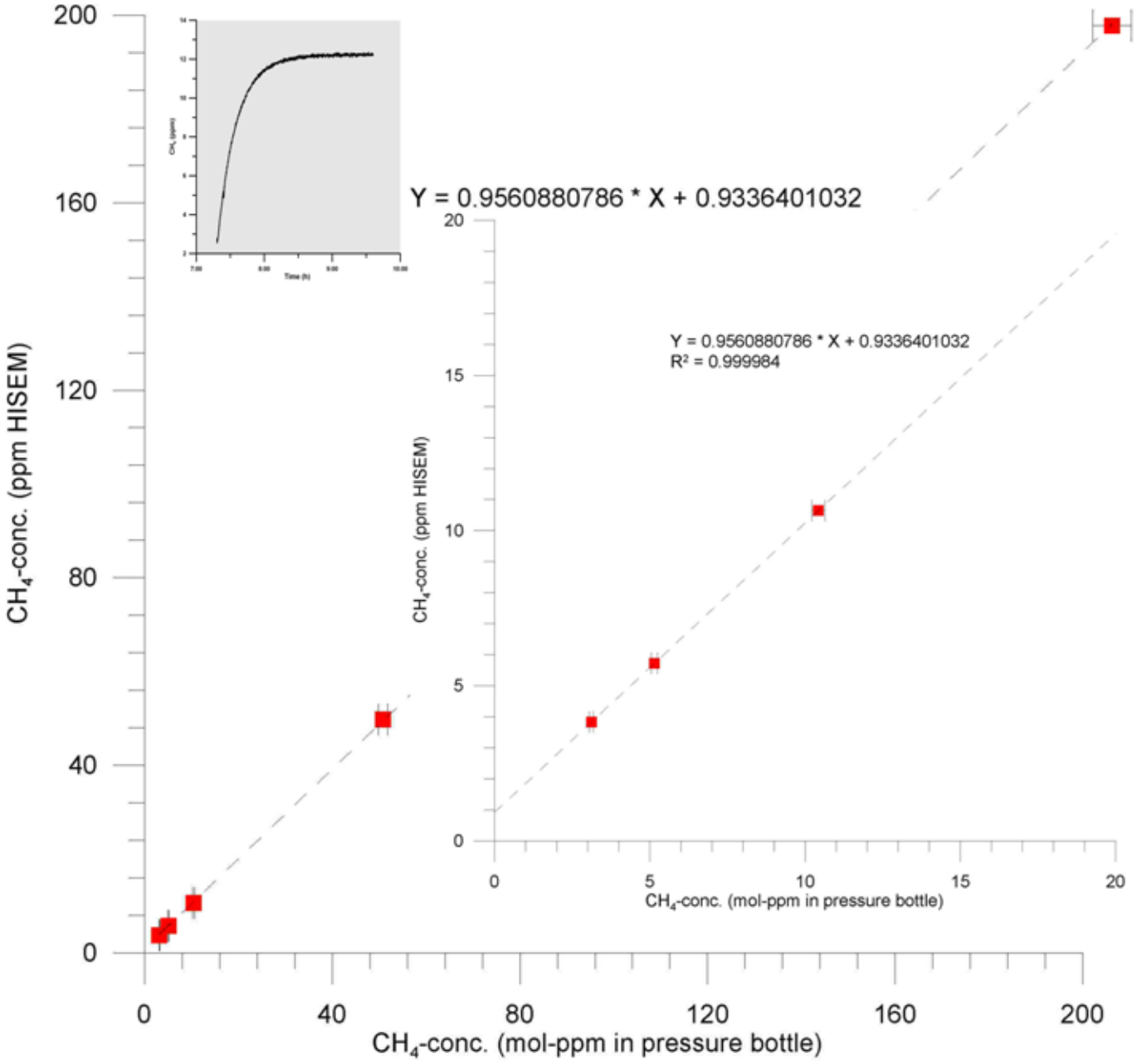
against various partial pressures of methane dissolved in water in a temperature controlled (4–15°C) water-filled calibration tube. The water is continuously equilibrated at atmospheric pressure with standard gas mixtures of methane (3–200 mol-ppm) in synthetic air pressure bottles (~200 bar). Gas exchange with atmosphere is prevented in the semiclosed system. The response of the sensor signal is continuously recorded during testing, and equilibration of the signal is established with a response time (t_{65}) of about 10 min after partial methane pressures have been changed in the tube (Figure 4).

The detection limit of the HISEM of about 1 ppm could be determined with a signal-to-noise ratio of 5.

The sensor output (ppm unit) shows good linearity (R^2 = 0.99998) against the known pressure bottle concentrations given in mol-ppm with an offset of ~1 ppm (Figure 4). The correlation

FIGURE 4

Methane concentrations determined with the HISEM system, which was placed in a water-filled calibration tube at 4°C. The water is equilibrated with methane by using different gas mixtures (3, 5, 11, 50, 100, and 200 mol-ppm CH_4 in pressure bottles).



was confirmed by parallel determination of dissolved methane concentrations sampled from the calibration tube. These methane analyses were conducted by using head space sampling technique and subsequent gas chromatographic analysis.

HISEM Offshore Test Site

To test the sensor performance for methane plume detection and its offshore practicability in operating the system with a small work-class remotely operated vehicle (i.e., HYSUB 20 ROV), a 3-day offshore campaign was performed in November 2012 near Santa Barbara, Southern California. The offshore test site that was chosen is named *Farrar Seep* and is located within the Coal Oil Point seep area in the inner Santa Barbara Channel (Figure 5a) about 1,300 m east of the University of California, Santa Barbara area (Figure 5b). The Farrar Seep is a natural hydrocarbon seep that is indicated by gas bubble release from the seafloor at about 22 mbsl. Natural gas seeps in the area of the inner Santa Barbara Channel can be characterized by low seepage activity, and the gas composition of bubbles emanating from the seafloor consists of up to 90% of methane and 10% of higher hydrocarbons (e.g., Leifer et al., 2006). As gas bubbles dissolve and exchange their gas content during uplift in seawater, dissolved gas plumes are formed in the water column and the initial hydrocarbon content of the bubbles decreases (e.g., Leifer & Patro, 2002; Clark et al., 2003; McGinnis et al., 2006). Numerous natural gas and oil seeps exist in the inner Santa Barbara channel, which lead to general high background concentrations of dissolved methane in the area (e.g., ~20–100 nmol L^{-1}; Clark et al., 2000).

To measure dissolved methane concentrations during ROV dives, the HISEM system was mounted parallel behind the upper bumper bar of the HYSUB 20 (Figure 6). The head (membrane inlet) of the HISEM prototype was connected with a plastic tube to a suction inlet at the front of the ROV. A metal filter was mounted to the suction inlet, and the inlet area was monitored permanently by cameras. A second tube connected the suction inlet by a y-adapter with a CTD and a commercial leak detection device (Combination of HydroC-CH4, Fluorometer). A constant water flow through the tubing was guaranteed by two Seabird pumps, which operated inline the tubes.

FIGURE 6

(a) Deployment of the $2ROV from the starboard site of M/V *Danny C.* (b) The HISEM prototype (marked by white rectangle) was mounted behind the bumper bar of the ROV.

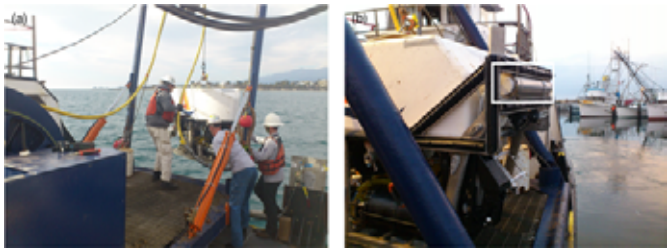
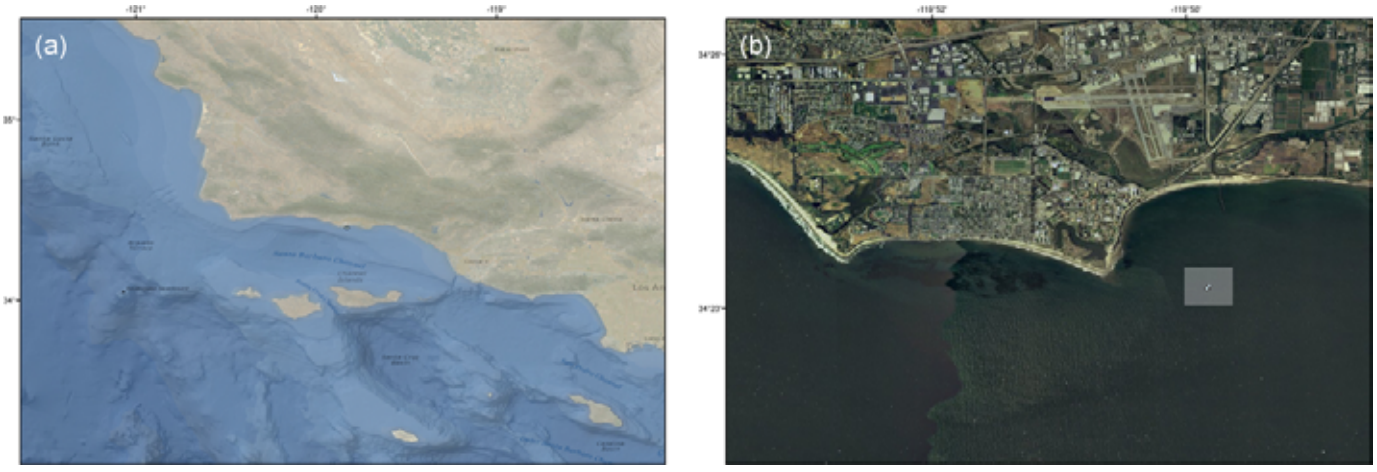


FIGURE 5

(a) Map of the overall area of the Santa Barbara channel in Southern California. The test site is marked as a small open circle. (b) Farrar Seep offshore test site (shaded rectangle), about 1,300 m east of the University of California Santa Barbara area.



ROV-Based Sensor Measurements

Two N-S and four W-E ROV dives were conducted at the 28th and 29th of November 2012 at the estimated location of the Farrar Seep (Figure 5b). The average length of a ROV dive track was about 250 m. Furthermore, one vertical dive track was conducted at the estimated center of the seep (Figure 5b). During all dives, water depth, temperature, conductivity (SV48 CTD, Sea and Sun Technology) and methane sensor data (HISEM) were recorded continuously. However, the ROV stopped every 15 m for 1–2 min to increase the total measuring time. The homogeneous temperatures of about 15.8°C and salinities of about 33.4 PSU measured during the ROV dives indicate a well-mixed water column in this coastal area during November 2012. The water depth of the test area is about 16–30 mbsl and ROV dive tracks plotted in Figure 7 were performed above seafloor at elevations of 2 and 12 m, respectively. Due to strong currents in the area and especially a current direction and current speed change between the 28th and 29th of November 2012 (Goleta Point buoy data, SCCOOS.org), navigating the ROV was challenging and deviations from predefined track lines were about 15 m. The Farrar Seep location could be verified at 119°49.836′W and 34°24.157′N (WGS84) by measuring a CH_4 concentration maximum (up to 260 ppm and 334 nmol L^{-1}, respectively) while crossing the central seepage site with the ROV at 2 m elevation above seafloor (Figure 8). The minimum concentration of dissolved methane, which was determined in water masses in the test area, was ~50 nmol L^{-1}.

The center of the main seepage activity of the Farrar Seep was also

FIGURE 7

ROV dive tracks conducted in the test area "Farrar Seep."

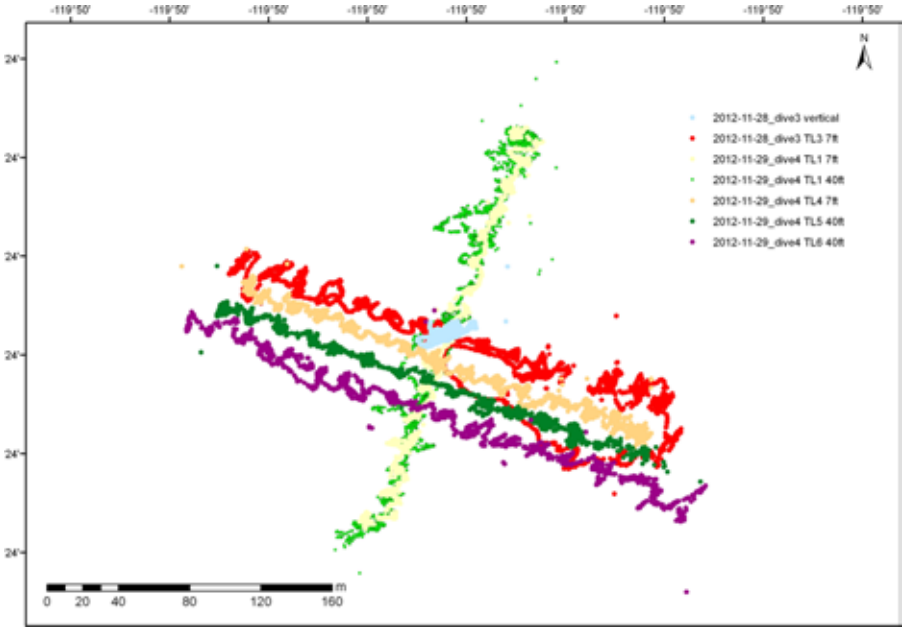


FIGURE 8

Methane sensor signal recorded with HISEM about 2 m above the seafloor during ROV track line 1 at the 28th and 29th of November 2012. Track line 1 is the N-S profile and crosses the Farrar Seep (Figure 3).

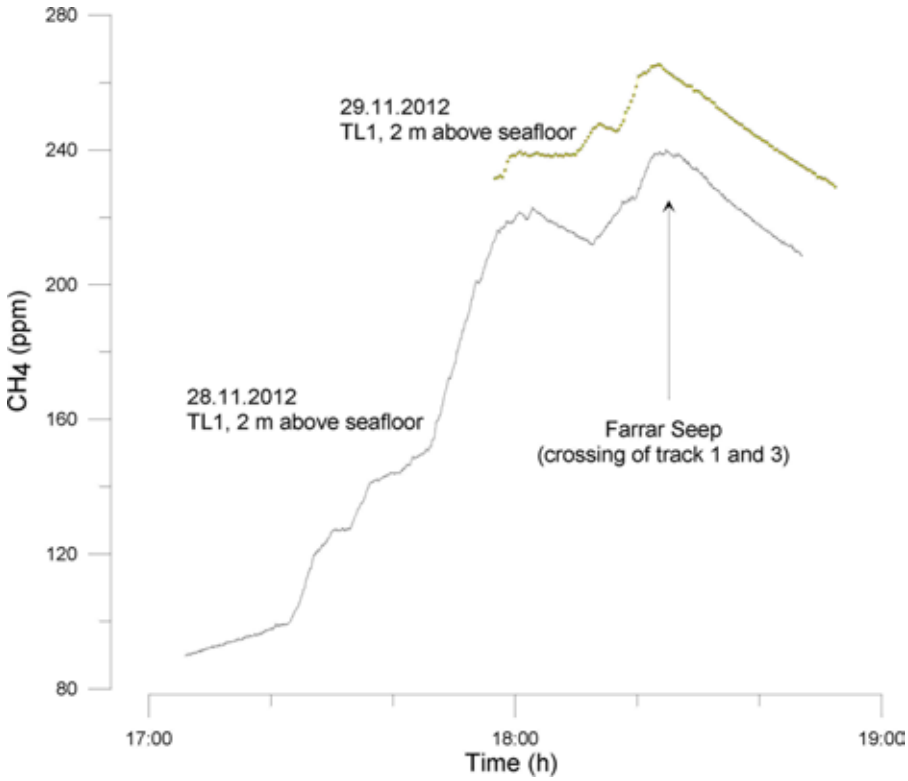
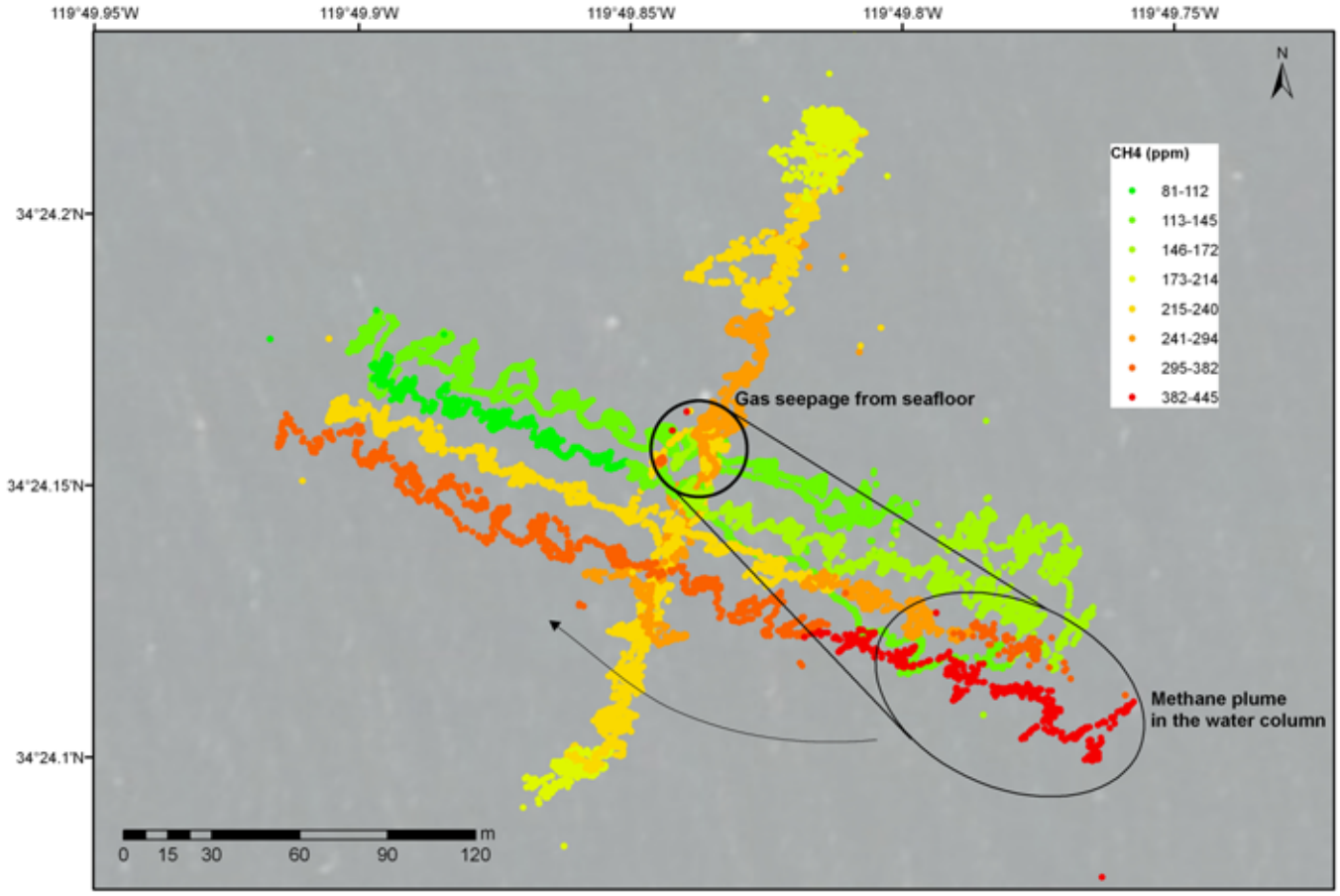


FIGURE 9

Spatial methane concentrations at Farrar Seep measured by HISEM during ROV dives. The concentration of methane is given in ppm. The total range measured by HISEM corresponds to dissolved methane concentrations of 50–560 nmol L^{-1} in the test area.



indicated by the ship's echo-sounder (acoustic blankening by gas bubbles) and ground-truthing by ROV (video observations). Note that measuring the dissolved gas content within the bubble streams emanating from the seafloor did not increase the HISEM sensor concentration signal. The concentration pattern of November 28th could be verified by following the same track on the 29th (Figure 8). The deviation of methane concentration data of about 25 nmol L^{-1} measured within the central seep area is possibly related to a weakening of the local current regime on the 29th (http://sccoos.org/).

The dimensions of the main (dissolved) methane plume were about 50–150 m around the seepage site (Figure 9). However, dissolved gas plumes with high methane concentrations (up to 560 nmol L^{-1}) were also examined towards the east and south at about 12 m above the seafloor (Figure 9). In general, the dissolved methane concentrations are highest towards the south, which could indicate a preferred rotation of the methane plume direction from east to south and then west (Figure 9).

Conclusions

Subsea determination of dissolved methane concentration can be conducted by using infrared absorption technology. The technology, measuring the partial pressure of methane in a separated gas chamber, is combined with a membrane inlet, which separates high-pressure conditions of the deep sea from the gas chamber at normal pressure. Recent advances in laser diode technology led also to cost-effective and high-sensitive infrared absorption units. The newly designed high-sensitive methane sensor (HISEM), which combines laser diode infrared absorption with membrane inlet technology, closes a gap between the needs of small and less sensitive methane sniffers used for offshore leak detection (Oil & Gas Industry) and oceanographic trace gas

determinations down to 1–2 nmol L^{-1} of CH_4 (equilibrium concentration of seawater with the atmosphere).

Membrane-inlet IR absorption sensors can be used for long-term measurements at the seafloor (e.g., lander-based deployment). The determination of, for example, varying methane concentrations in the vicinity of a methane seep have to be combined with determination of temperature, salinity, and pressure variations, as well with current measurements (i.e., using ADCPs). This combination is the basic information used to determine (dissolved) gas fluxes from natural seeps or leaking constructions at the seafloor.

Focused release of methane from subsea seeps and of rising plumes of dissolved methane can be monitored with ROV-based IR sensor technology. However, the quantification of methane release also needs some basic oceanographic information about the local current regime and physical parameters (T, S, P) along the ROV dive tracks. This could be realized during onboard CTD measurements and an upward-looking ADCP deployed at the seafloor. A miniaturization of the recently developed high sensitive methane sensor (HISEM) is prerequisite to use this technology onboard inspection class ROVs.

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AUTHOR QUERIES

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Q1: Please check Figure 2 and 3 if labels in image should be lowercase to be consistent with the captions.

Q2: Please provide first name of Schneider von Deimling in Faure et al., 2010 reference.

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