

## Measuring Methane Venting Fluxes in Extreme (Arctic) Conditions

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**What:** Ongoing program of studying escaping methane plumes from Arctic Shelf sea sediments including numerous ship and helicopter-supported surveys using two LGR methane analyzers. Massive quantities of stored CH<sub>4</sub> are found to be leaking and venting into the atmosphere via supersaturated ocean water.

**Relevant Publications:** *"Extensive Methane Venting to the Atmosphere from Sediments of the East Siberian Arctic Shelf,"* SCIENCE, 5 March 2010 Vol. 327.

**Which LGR Analyzer:** Two Fast Methane Analyzers (908-0001)

**Key Analyzer Benefits:** Small, lightweight packaging, rugged, portable operation, low power consumption, immunity to temperature extremes, high absolute precision, real-time (seconds) measurement.

### Introduction

Compared to the economic/political hot potato of global warming due to carbon dioxide (CO<sub>2</sub>), the impact of methane (CH<sub>4</sub>) on climate change generally receives much less attention and publicity outside the world of environmental science. However, methane has a four times stronger "greenhouse effect" than CO<sub>2</sub>, and the result of large methane generation sources, including bovine agriculture, waste landfills and naturally formed bio-geological sediments, cannot be omitted from any detailed climate model. Now, recent studies by a collaborative team of Russian, American and Swedish

researchers have revealed the significant extent of methane leakage from a massive undersea reserve trapped in East Siberian Arctic Shelf (ESAS) sediments, bringing worldwide and web wide attention to yet another possible negative consequence of continued ocean warming. These measured venting rates are already unprecedented, and on a par with the total methane venting flux from the entire World Ocean (see for example SCIENCE, 5 March 2010 Vol. 327 and <http://news.yahoo.com/blogs/sideshow/giant-plumes-methane-bubbling-surface-arctic-ocean-163804179.html>).

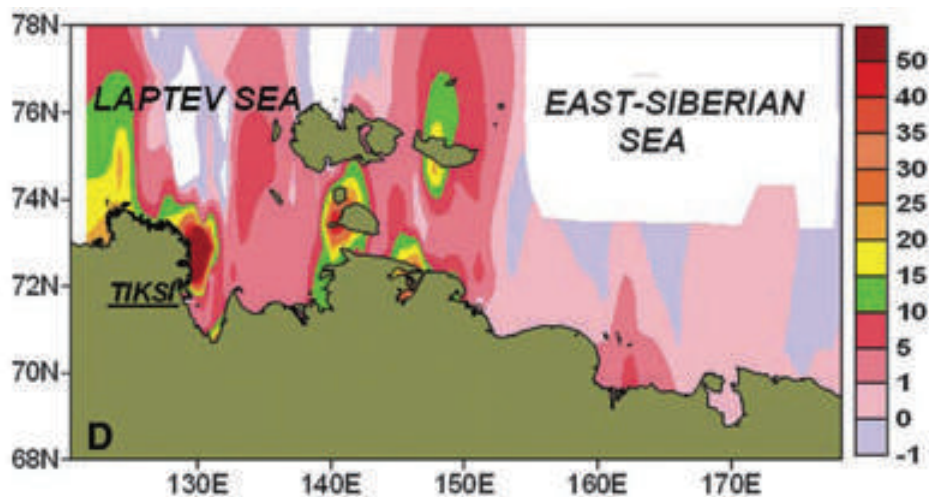


Figure 1. Summertime data showing fluxes of  $CH_4$  venting to the atmosphere over ESAS.

## Methane Trapped in Sediments

Global surface temperatures are predicted to increase  $1.4^{\circ}\text{C} - 5.8^{\circ}\text{C}$  over the period from 1990 to 2110. Published studies by various groups have already identified the potential positive feedback problem of methane being released from the resultant thawing of frozen (permafrost) wetlands by continued warming of the Arctic region [1,2] But until the studies reported here, the permafrost and frozen sediments trapped under ESAS (encompassing the Laptev, East Siberian, and Russian part of the Chuckchi seas) have not been strategically investigated as a possible major methane source, even though ESAS occupies an area of  $2.1 \times 10^6 \text{ km}^2$ , three times as great as that of terrestrial Siberian wetlands – see figure 1. Moreover, ESAS is a shallow seaward extension of the same Siberian tundra except, unlike these terrestrial wetlands, it was flooded with seawater during the Holocene transgression [3].

The scientists involved in the ongoing study suspected that there might be significant methane releases from the ESAS for several reasons. First, it was already known that the ESAS sub-sea permafrost contains comparable amounts of carbon as land-fast permafrost, as well as more recently formed permafrost-related seabed deposits of  $CH_4$  [4]. Moreover the original permafrost has already experienced drastic change in its thermal regime because of the seawater inundation that is estimated to have occurred 7,000 to 15,000 years ago [3]. This is a consequence of the annual average temperature of ESAS

bottom seawater ( $-1.8^{\circ}$  to  $1^{\circ}\text{C}$ ) being  $12^{\circ}\text{C}$  to  $17^{\circ}\text{C}$  warmer than the annual average surface temperature over onland permafrost [5]. The team postulated that a possible bottom line result of upward geothermal heat flux and this downward heating from warmer seawater would be failure of sub-sea permafrost. This could result in an increased permeability for gases, potentially leading to methane release on a very large scale.

## Multi-pronged Approach

Beginning in 2003, the team began a systematic approach to investigate the extent of methane leakage from the shallow ESAS sea region. This multi-pronged approach targeted both analyses of methane concentrations and distribution in the seawater [6,7], plus methane concentrations in the atmosphere above the ESAS. This included six (annual) ship-based surveys that captured over 5000 seawater samples from different depths over a large grid of locations, and then analyzed their methane content using standard chromatography methods. Air samples were simultaneously analyzed on several of these cruises in real-time over the entire cruise grid; this was accomplished using a LGR Fast Methane Analyzer (model 908-0001). More importantly, this portable analyzer was a key, real-time, atmospheric  $CH_4$  monitoring tool used in an over-the-ice winter expedition (April 2007) and a comprehensive airborne (helicopter) survey undertaken in September 2007. And, in 2010, another LGR analyzer was acquired by the team and

installed at a remote atmospheric monitoring station in Tiksi to provide additional continuous methane and carbon dioxide mole fraction data.

One of several overall goals of this study, now achieved and published [SCIENCE, 5 March 2010 Vol. 327], was to acquire sufficient dense mapping and profiling of methane venting to eventually obtain a statistically accurate total value for the methane venting flux from the entire ESAS, taking full account of any locally measured variations and year to year to fluctuations.

### **Role of the LGR Analyzer**

Traditionally, trace atmospheric gases were measured using captured samples which were returned for laboratory analysis using gas chromatography. This precludes measuring data at site and/or in real-time. And for practical reasons, it also limits the density of sampling. And while very accurate and sensitive, this approach has a relatively high direct and indirect cost per measurement in terms of skilled labor, time, chromatography consumables, chromatography calibration, the large number of baked and evacuated canisters that are required, transportation of these canisters, and so on.

In contrast, LGR trace gas analyzers such as the Methane Analyzer are self-contained and completely automated instruments based on ultra-precise optical absorption measurements. They deliver complete portability and real-time measurements with parts per billion (nmol/mol) precision in only 1 second of integration time. (Measurements can be continuous or via captured samples). Legacy absorption techniques, even those based on lasers, struggle to deliver sufficient signal to noise because of the low concentration and weak optical absorption at available laser wavelengths. But LGR analyzers utilize a fourth-generation cavity enhanced technology called off-axis cavity output spectroscopy (OA-ICOS). This unique approach delivers effective absorption pathlengths as long as 20 kilometers in an instrument smaller than a small suitcase. However, it does not suffer from the precision alignment problems, or sensitivity to temperature and pressure changes, associated with older optical techniques, such as those based on multi-pass cells or older first-generation

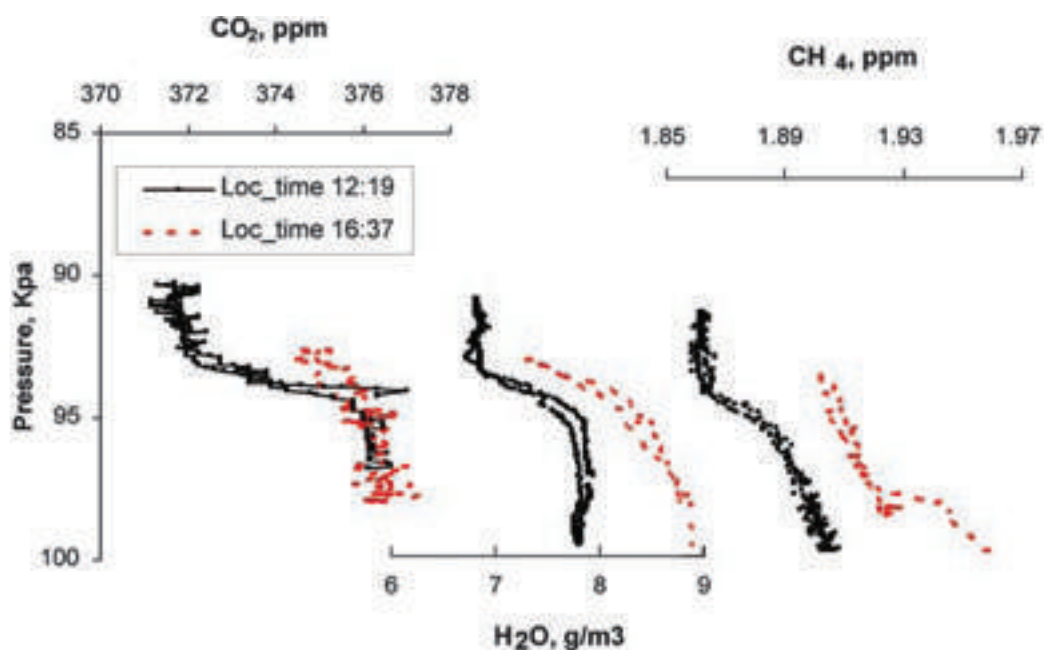
cavity ringdown spectroscopy (CRDS) methods. And LGR's cavity enhanced laser absorption technique (OA-ICOS) also offers much greater dynamic range than these previous techniques – from parts per billion to several percent.

The small, portable Methane Analyzer offers rugged immunity to vibration, motion, and temperature changes, as well as data archiving, low power consumption and remote operation capabilities. Together, these make it an optimum choice for continuous, real-time measurements in the helicopter survey used in this study, as well as for use at the remote Tiksi monitoring station. Its long, maintenance-free operating lifetime was obviously another factor in selecting its use for this location.

### **Results Summary**

Although the analysis of the summertime seawater samples revealed some spatial and vertical gradients in methane content, the authors found that most of the ESAS is supersaturated with methane in its near-bottom waters; over 50% of surface waters were also supersaturated. The median summertime supersaturation was 880% in background areas and 8300% in hotspot areas. In winter, the saturation in samples from under the ice was found to be even higher than in summer – by five to ten times. Collectively, these results demonstrate that the ESAS – the world's largest continental shelf sea – is perennially laden with CH<sub>4</sub> all the way up to the sea surface and that this CH<sub>4</sub> is virtually all of sedimentary origin. Clearly, the permafrost "lid" must be perforated.

Furthermore, the vertical concentration profiles indicate the leading role of a rapid transport process. This was deduced to be ebullition (bubbling), which is also supported by the observed presence of methane bubbles trapped everywhere throughout the ice. So the atmosphere over the ESAS would be expected to contain increased levels of methane as a result. This was completely borne out by the data obtained with the LGR analyzer used in the helicopter survey. Mole fractions of CH<sub>4</sub> were significantly elevated, relative to the latitude-specific monthly mean; typical vertical mole fractions obtained in this survey are shown in figure 2, which also shows corresponding CO<sub>2</sub> mole fractions, simultaneously recorded by the LGR analyzer.



*Figure 2. Vertical mole fraction of CH<sub>4</sub> in the atmosphere above southeast Laptev Sea (72.49°N, 130.51°E) as measured during a helicopter survey in September 2006 using the Methane Analyzer from LGR.*

## Conclusion

The researchers combined all the data to obtain a total annual flux of approximately 8Tg of methane vented from the ESAS. Amazingly, this is similar to the existing estimate for the vented methane flux from the entire world's ocean! Although large, this additional flux does not significantly change the global CH<sub>4</sub>

budget, but this work clearly indicates the vulnerability of the permafrost-trapped carbon. Future work by these same scientists should indicate whether this elevated flux is a steadily ongoing phenomenon or whether it heralds the start of a more massive CH<sub>4</sub> release period.

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