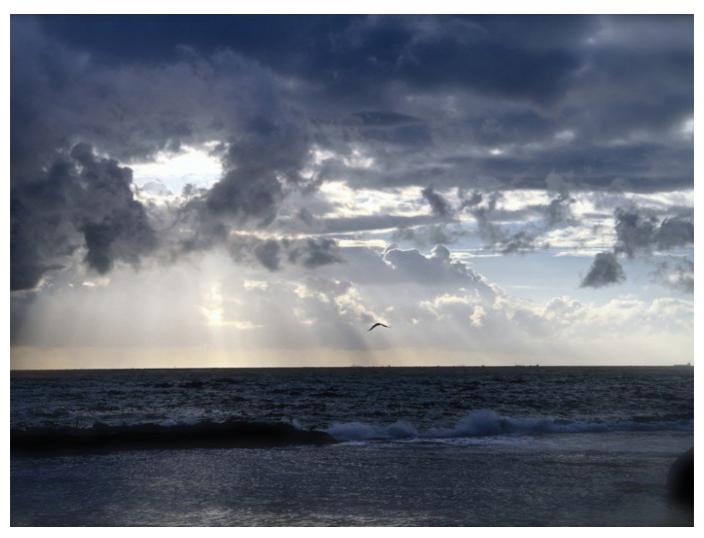
Marine Applications for a Promising New Spectroscopic Method

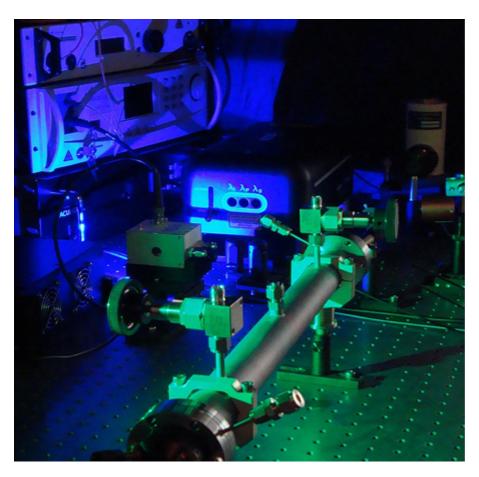
International Workshop: Applications and Perspectives of Cavity Enhanced Optical Detection Techniques in Ocean Sciences; Kiel, Germany, 20–21 April 2015



Cavity-enhanced absorption spectroscopy is an important new tool for quantifying trace gases in the oceans and atmosphere. This method aids in understanding biogeochemical cycles in the context of global change. Credit: <u>Dilan Ranjith</u>, <u>CCO 1.0</u>

By Gernot Friedrichs, Anke Schneider, and <u>Hermann W. Bange</u> **O** 1 December 2015

Understanding biogeochemical cycles in the context of global change requires us to understand and quantify the oceanic pathways and ocean-atmosphere exchange of climate-relevant trace gases, including carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4).



(https://eos.org/meeting-reports/marine-applications-for-a-promising-

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This cavity-enhanced absorption spectrometer setup is in the lab of the Institute of Physical Chemistry, Kiel University, Kiel,

Germany. Credit: Gernot Friedrichs

Absorption spectroscopy offers precise, accurate, and fast measurement capabilities that are a prerequisite for determining trace gas concentrations on small temporal and spatial scales. Cavity-enhanced absorption spectroscopy (CEAS) uses highly reflective mirrors at each end of a measurement cell in a resonant configuration to significantly extend the effective absorption path lengths to several kilometers (see photo). This enables us to detect gases at very low ambient concentrations.

In April 2015, more than 30 scientists from Australia, Canada, Denmark, Germany, the United Kingdom, and the United States came together for a 2-day workshop at Kiel University in Germany to review the progress in CEAS and to discuss future perspectives of this method in marine sciences.

Marine applications of CEAS have increased quickly since the first publication on the topic in 2010: CEAS-based instruments coupled to continuous seawater-gas equilibrators are now used frequently to determine dissolved trace gases (N₂O, CH₄, CO₂, carbon monoxide, and carbonyl

sulfide) from the surface layers of the open and coastal oceans.

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Workshop participants heard presentations on isotope measurements (including $\underline{\delta^{13}C}$ (https://en.wikipedia.org/wiki/%CE%9413C) in dissolved CO₂ and $\underline{\delta^{18}O}$ (https://en.wikipedia.org/wiki/ %CE%9418O)/ $\underline{\delta D}$ (https://en.wikipedia.org/wiki/Deuterium) in water), in situ deep-ocean measurements, and the analysis of discrete ice core samples, as well as five talks highlighting new developments beyond the currently available commercial CEAS-based instrumentation.

Participants concluded that CEAS has been established in a remarkably short time as a reliable technique in marine sciences. However, some scientists noted that temperature stabilization of the measurement cell needs to be improved to minimize instrumental drifts. Another common point of concern was the possibility for significant spectral interference and for gas matrix effects. In particular, the latter may occur when equilibrated water samples are supersaturated or undersaturated with respect to oxygen or when gas mixing ratios are extremely high, such as in coastal or riverine environments.

Attendees discussed long-term CEAS deployments on autonomous platforms, and they concluded that this seems to be technically feasible in the near future.

Participants agreed that there is an urgent demand for CEAS instruments that are able to measure small, discrete sample volumes (<10 milliliters) from Niskin bottle (http://www.coml.org/edu/tech/collect/niskin.htm) depth profile casts. Furthermore, to take advantage of the very high measurement frequency of the CEAS method, the commonly used seawater-gas equilibrators must be adapted to gases with slow equilibration times (i.e., gases with comparably low solubility, such as CH_4). Attendees discussed long-term CEAS deployments on autonomous platforms (e.g., moorings and gliders), and they concluded that this seems to be technically feasible in the near future when power consumption and the size of CEAS instruments are reduced.

An overview article summarizing the scientific results, the workshop discussions, and technical issues of marine CEAS applications is currently being compiled. The article will help to convey the scientific and technical demands for future CEAS instruments to the manufacturers. Additional contributions to the article are welcome.

The workshop was funded by <u>The Future Ocean–Cluster of Excellence (http://www.futureocean.org/)</u> of Kiel University. The list of participants, workshop agenda, and presentation abstracts for <u>this</u> workshop (http://www.futureocean.org/semester_topics/sose_2015/en/index.php) are also available online.

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