

In situ chemical analyses by underwater mass spectrometry

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Introduction

Manual collection and processing of seawater samples is the dominant methodology used by chemical oceanographers. However, as technologies have matured, *in situ* underwater chemical sensors and analyzers are increasingly being used to reduce costs and meet the goals of sustained, high-resolution ocean observing. Perhaps the most versatile *in situ* chemical analyzers under development are underwater mass spectrometer (UMS) systems [1].

Discussion and Results

Membrane introduction UMS systems developed by the University of South Florida and SRI have been deployed at study sites including hydrothermal vents, methane hydrate fields (Figure 1), anoxic basins, and hydrocarbon seeps.

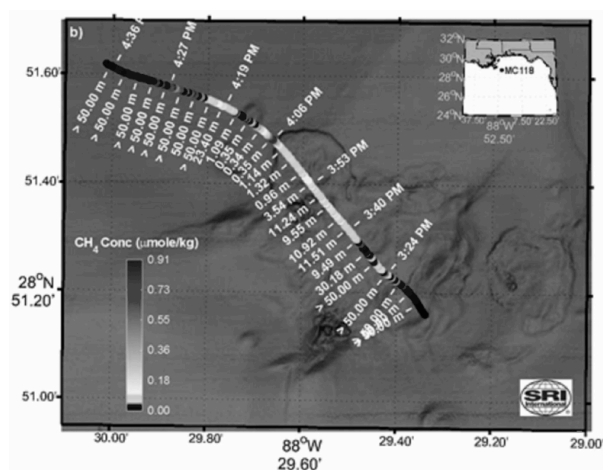


Figure 1: Methane concentrations above the MC118 hydrate field in the Gulf of Mexico at 880 m depth.

Expanding Applications

The UMS is capable of calibrated measurements of dissolved gases (CH_4 , N_2 , O_2 , H_2S , Ar, and CO_2) and volatile organic compounds to full ocean depth. Recent work has focused on expanding UMS applications to include reagent addition and sediment porewater sampling.

[1] Bell *et al.* (2007) *Environ. Sci. Technol.* **41**, 8123–8128.

Greenhouse gas emissions from a large metropolitan water reclamation plant

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Domestic and industrial wastewater treatment plants have been estimated to be the 7th and 8th highest contributors to atmospheric concentrations of N_2O and CH_4 , respectively [1]. N_2O is of particular interest because of its stronger greenhouse effect relative to CO_2 [2], and its high ozone-depleting potential [3].

To provide a more accurate basis for estimating the greenhouse gas contributions of wastewater treatment plants, we performed extensive sampling of fugitive greenhouse gas emissions throughout the entire treatment process at the Metropolitan Water Reclamation District of Greater Chicago's activated-sludge water reclamation plant at Stickney, IL (764 million gallons/day). Sampling was performed during June through December, 2009. Samples were analyzed for N_2O , CH_4 , and CO_2 concentrations. Total annual fluxes were determined: N_2O - 5.1×10^5 kg; CH_4 - 1.9×10^6 kg, and CO_2 - 1.1×10^8 kg. The aeration basins are the main source of N_2O . CH_4 emissions can occur in anaerobic pockets within dominantly aerobic processes. Preliminary isotopic data for CO_2 yields a range in $\delta^{13}\text{C}$ values of -19‰ to $+5\text{‰}$, with total CO_2 flux having $\delta^{13}\text{C}$ value near -18‰ . Isotopic measurements of N_2O and CH_4 are in progress.

[1] USEPA (2007) Washington DC, USEPA. [2] Doorn & Irving (2006) IPCC guidelines. [3] Ravishankara *et al.* (2009) *Science* **326**, 123–125.