In Situ Mass Spectrometry in Marine Science

Distribution and Quantification of Submarine Methane Sources

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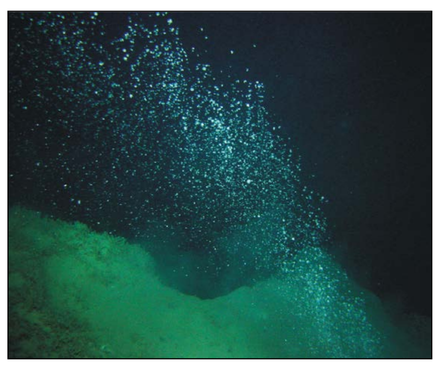
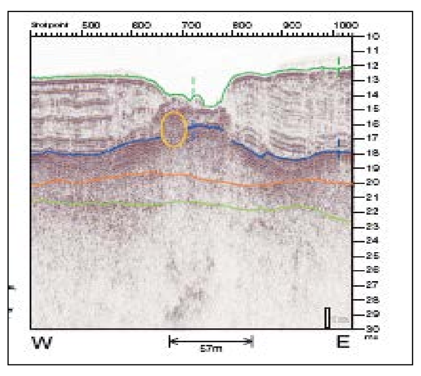
The motivation of our work is the spatial and temporal distribution analysis of methane around pockmarks and other CH_4 seeps.

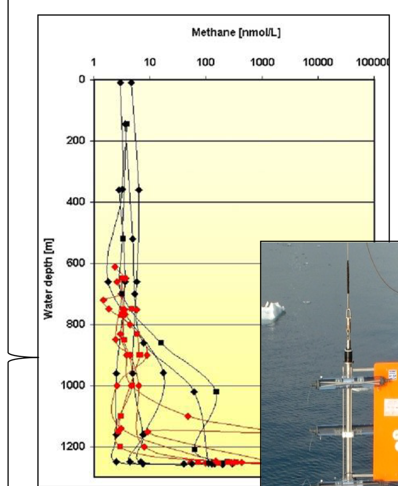
Worldwide, the release of methane from sediments of lakes, coastal regions as well as ocean margins is observed. The gas release is often associated with specific features like pockmarks (morphological depressions at the seafloor), mud volcanoes, cold seeps and occurrence of gas hydrates. This gas plumes were observed by underwater camera systems and acoustic techniques.



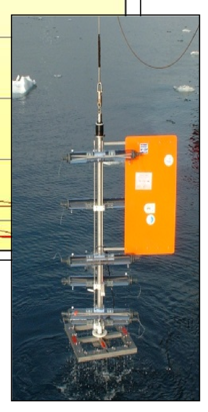
Visual observation of the release of gas bubbles from seafloor.



Acoustic blanking in surface sediments



Often the CH_4 concentrations around pockmarks are rather low.



Bottom Water Sampler Sauter et. al. (2005)

Why under water mass spectrometry (UWMS)?

Compared to such semi-quantitative information, rather little is known about the concentration field of CH4 as well as other gases around e.g., pockmarks. This is mainly due to the laborious sampling schemes and rather time consuming CH4 analysis by gas chromatography.

Established method

Water column and sediment sampling

Phase separation (gas phase from aqueous phase):

Headspace technique for analysis of discrete samples

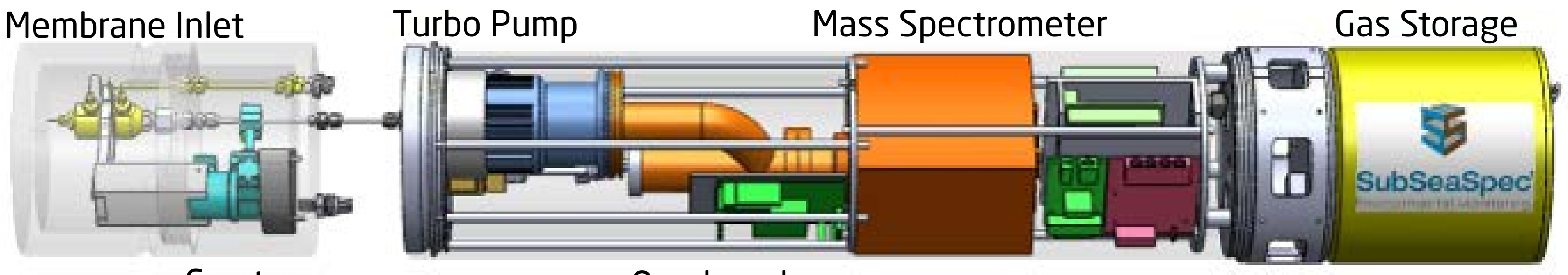
Gas analysis by gas chromatography

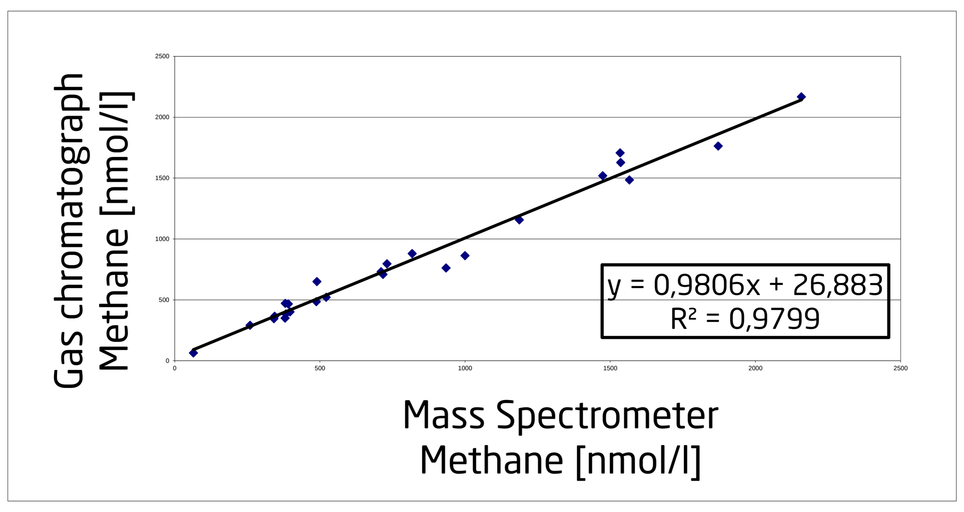
Advantage of UWMS compared to established methods:

- **NO sampling artifacts by e.g. de-pressurisation or sample warming due to in situ sampling**
- **Highest possible spatial and temporal resolution (up to 750 times higher than established techniques),**
- **online and realtime measurements**
- **simultaneous measurements of major and trace gases**

The application of UWMS is a step towards a more detailed investigation of spatial and temporal variations of methane in aquatic systems.

Underwater mass spectrometer:





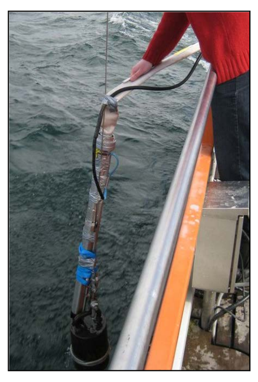
Comparison UWMS versus gas chromatography

Mass spectrometer:

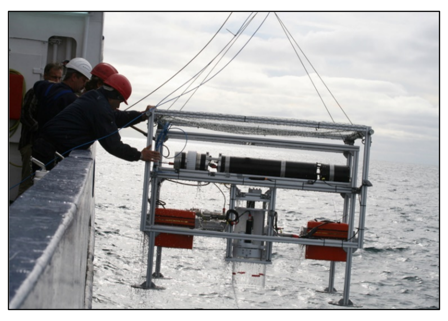
- Membrane introduction source
- Cryotrap to reduce water vapour
- Quadrupole based separation
- Varian turbo molecular with diaphragm backing pumps
- Embedded PC
- Online onboard visualization by ethernet connection

+ Detection limit of around 16nmol/l CH_4 by an implemented cryotrap
+ Results are comparable with established techniques like gas chromatography

Mode of operation



Ex situ

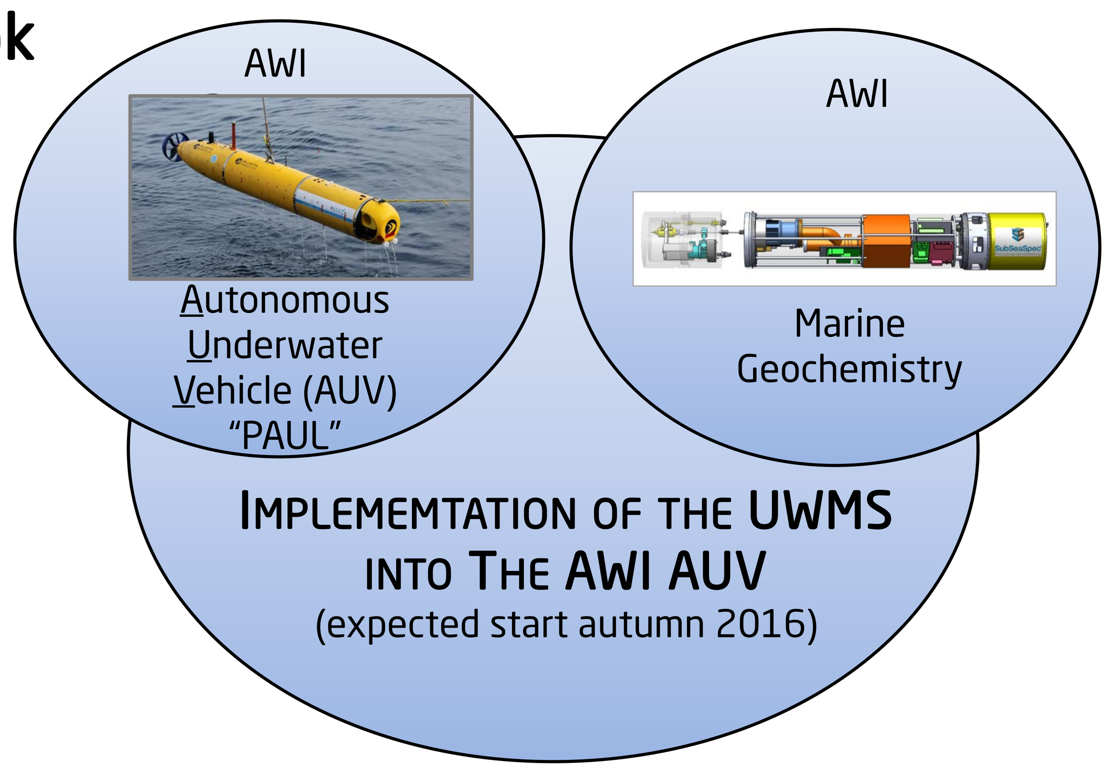


In situ in a frame including benthic chamber

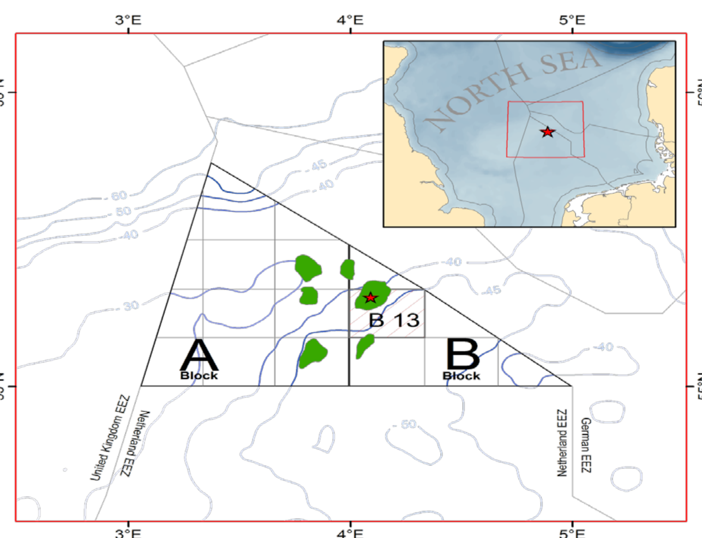
In situ at sediment-water-transition-zone

Laboratory measurements

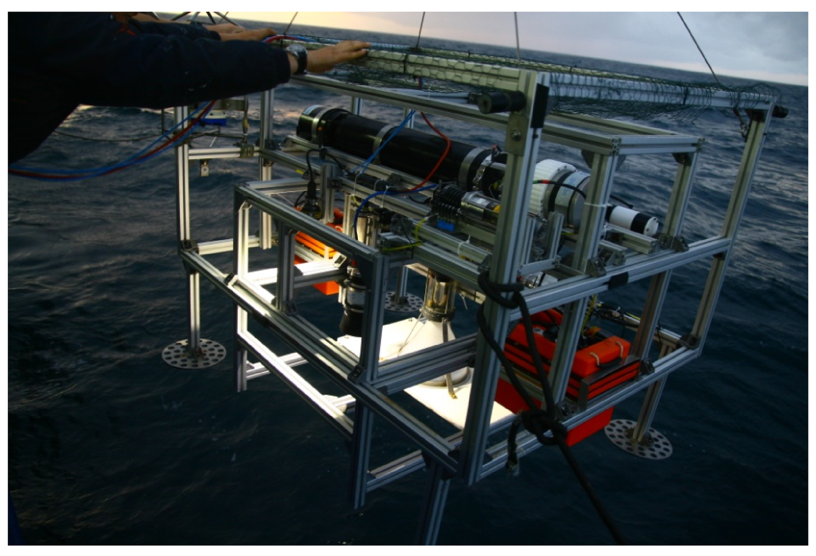
Outlook



Observation of a gas seep area (North Sea) in high resolution

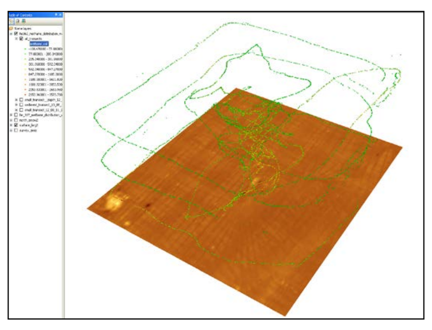


Working area (Modified after Schroot et al. 2005)

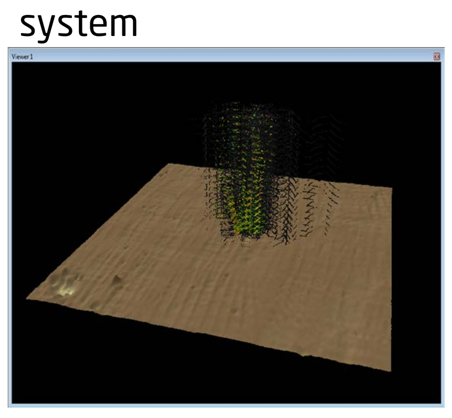


Under water gas analyser, sampler and observing system

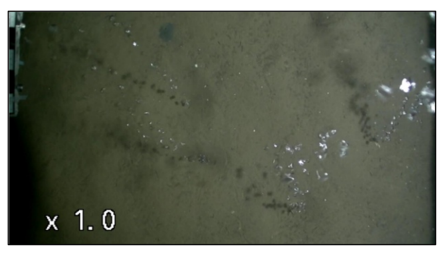
- UWMS; 11900 samples
- GC; discrete 154 samples
- Video observation; 12 h
- Hydroacoustic; 12 h
- Multibeam; 140000 m²
- CTD 14; vertical profiles
- Bubble sampler; 5 samples
- Multiple sediment corer; 5 cores



Transect of the observing system

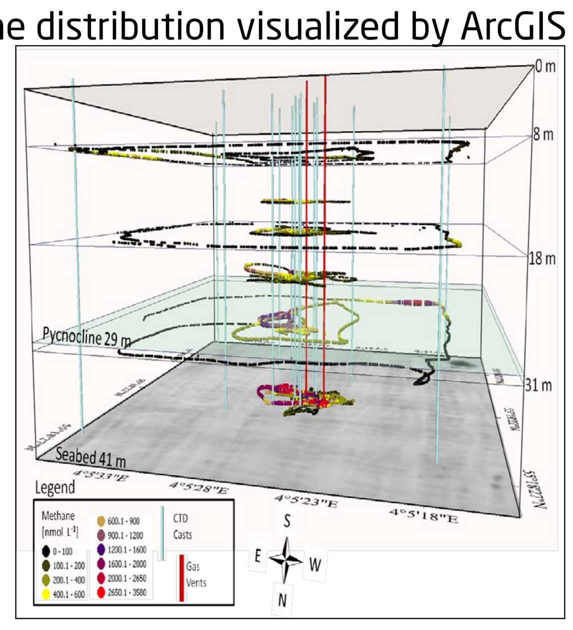


Echosounding during transect

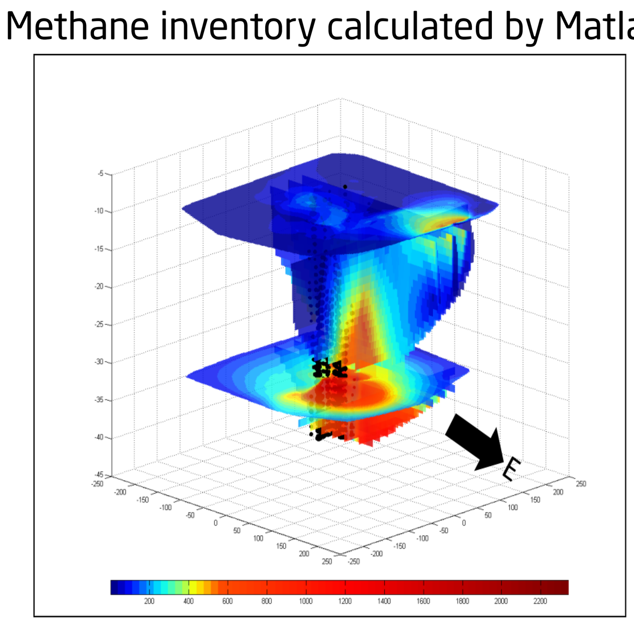


Video observation

Methane distribution visualized by ArcGIS



Methane inventory calculated by Matlab



(Gentz et al. unpublished data)

Results:

- A methane saturation of 23200 % was observed in 8 m water depth.
- The air sea exchange flux is calculated to ~210 ± 63 µmol m^{-2} d^{-1}.
- Methane flux: 28.27 L min^{-1}
- Methane release: 35.3 ± 17.65 t CH_4 yr^{-1}

Entire interpolated inventory of methane (6.410.000 m³):

- ~0.6 mol CH_4
- ~1.000.000 m³ (15.6 %) contaiin concentrations higher than 200 nmol L^{-1}
- 40 % of initial methane is dissolved above the pycnocline.

References:
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Sauter E.J., et al. (2005) Journal of Sea Research, Vol. 54: 204-210

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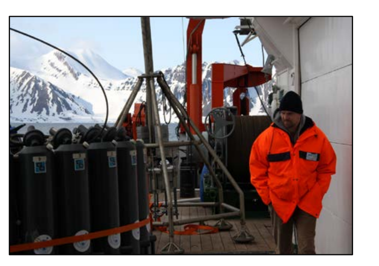
SubSeaSpec Environmental Monitoring

Beaver Creek Analytical



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