In Situ Mass Spectrometry in Marine Science: Distribution and Fate of Methane Released from Submarine Sources

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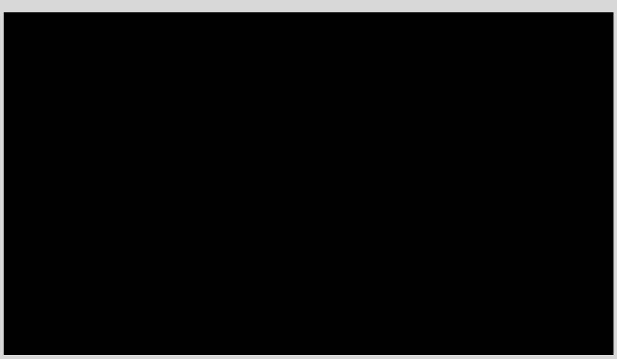
MARINE SCIENCE IS HARSH ENVIRONMENT !

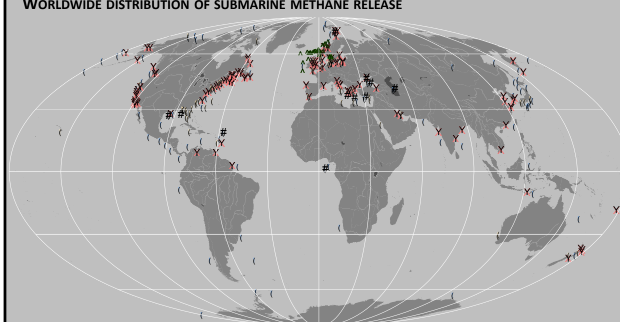
HE 337 NorthSea



Heincke 362

Submarine gas seeps

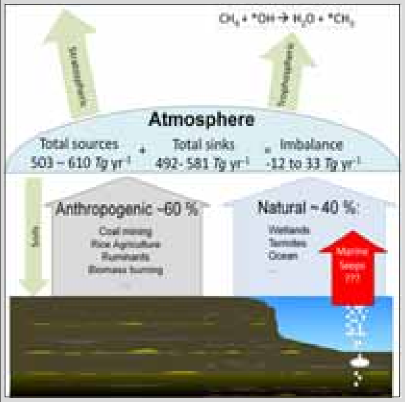
WORLDWIDE DISTRIBUTION OF SUBMARINE METHANE RELEASE



seepages
gas hydrates
methane related features
free gas / shallow gas
submarine mud volcanoes

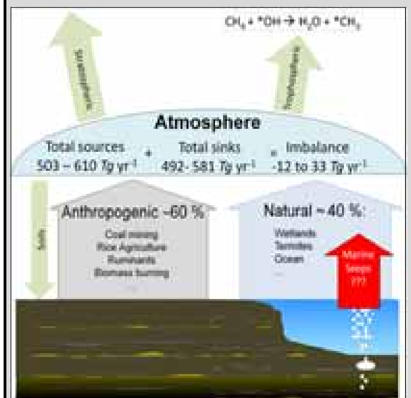
Free gas (Fleischer et al. 2001) Pockmarks (Hovland et al. 2002) Mud volcanoes (Milkov 2000) Gas hydrates (Kvenvolden et al. 2001)

Global relevance of methane



according to [Intergovernmental Panel on Climate Change](#) (IPCC,2007)

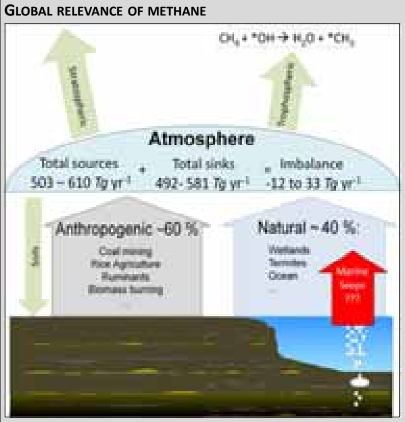
Global relevance of methane



according to IPCC (2007)

The average atmospheric concentration of methane has increased by 151 % since year 1750 (Houghton 2001).

Global relevance of methane



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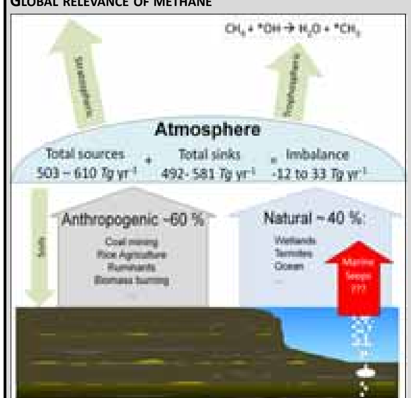
CH_4 acts beside CO_2 and water vapour as a greenhouse gas (Houghton 2001).

Global relevance of methane



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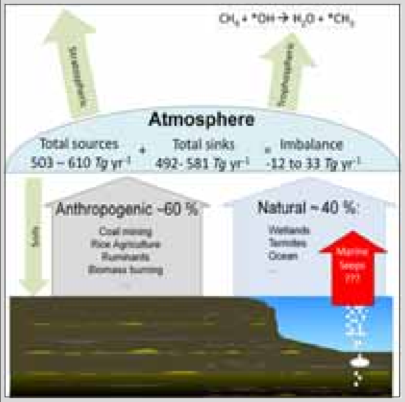
On a 100 year timescale the global warming potential (GWP) of CH_4 is 20 – 40 times higher than of CO_2 (Shindell 2009).

Global relevance of methane

4



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CH_4 represents the second largest contribution (about 15 %) to historical warming after CO_2 (Shindell et.al. 2009).

Global relevance of submarine sources

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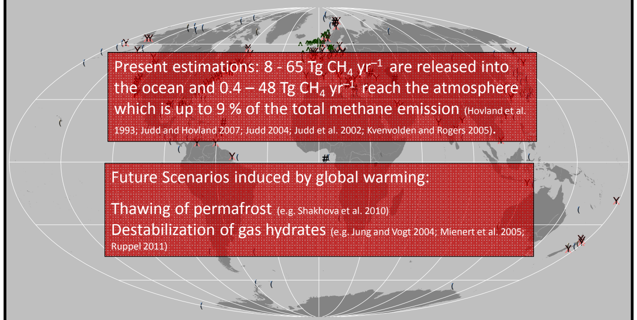

Present estimations: 8 - 65 Tg CH_4 yr^{-1} are released into the ocean and 0.4 – 48 Tg CH_4 yr^{-1} reach the atmosphere which is up to 9 % of the total methane emission (Hovland et al. 1993; Judd and Hovland 2007; Judd 2004; Judd et al. 2002; Kvenvolden and Rogers 2005).

Future Scenarios induced by global warming:

Thawing of permafrost (e.g. Shakhova et al. 2010)

Destabilization of gas hydrates (e.g. Jung and Vogt 2004; Mienert et al. 2005; Ruppel 2011)

(seepages
(gas hydrates
^ methane related features
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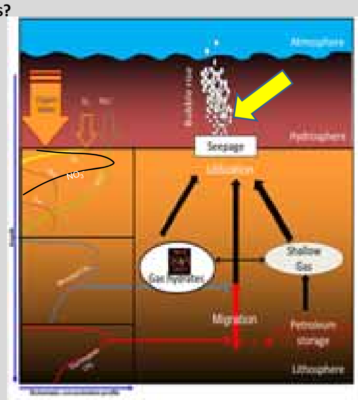
What are submarine gas seeps?

6



Schematic view of the formation (modified after Froelich et al. 1979) and the subsequent pathways of methane in the sediment (modified after Judd 2004). Crystallographic image of gas hydrates after Bohrmann and Torres (2006

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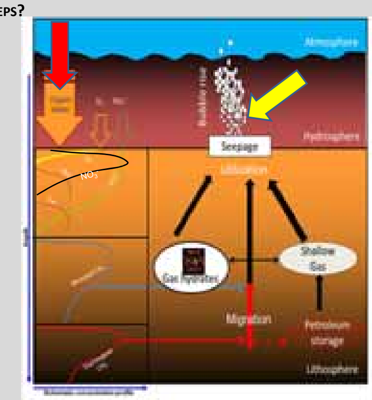

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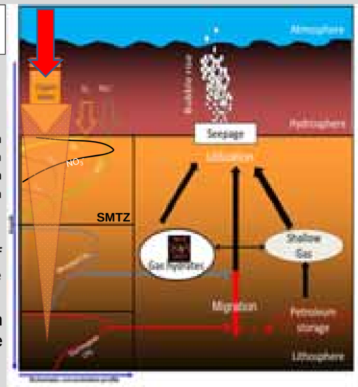
Formation of methane by degradation of organic matter

Aerobic respiration
Nitrate reduction
Manganese oxide reduction
Iron oxide reduction

Microbial formation of methane

Thermocatalytic formation of methane



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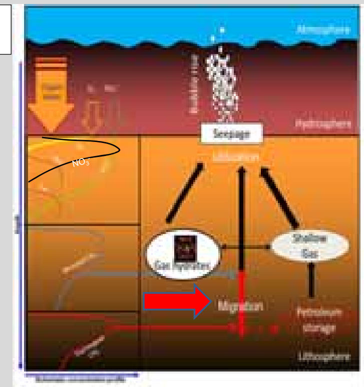
Storage and migration of methane



Schematic view of the formation (modified after Froelich et al. 1979) and the subsequent pathways of methane in the sediment (modified after Judd 2004). Crystallographic image of gas hydrates after Bohrmann and Torres (2006)

Utilization of methane in the sediment

Only if the rate of methane production in relation of migration exceeds the rate of microbial utilization, seepage into the water column occurs.

Aerobic oxidation
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

Anaerobic oxidation of methane (AOM)
$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$
(Boetius et al. 2000)

Sulfate / Methane Transition Zone (SMTZ)

Free methane gas

Schematic view of the formation (modified after Froelich et al. 1979) and the subsequent pathways of methane in the sediment (modified after Judd 2004).

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Heincke 362

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Introduction | Novel Instruments | Study Areas | Results and Interpretation | Conclusions

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Pathways of methane in the water column

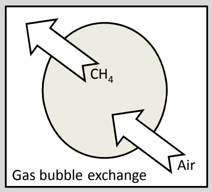
Air/Sea exchange

Vertical or horizontal transport of dissolved methane

Dilution

Microbial oxidation

Dissolution of methane from gas bubbles (Epstein and Plesset 1950; Leifer and Patro 2002; McGinnis et al. 2006)



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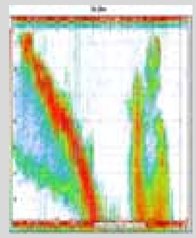
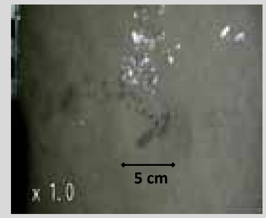
How to investigate the water column above gas seepage?



Hydroacoustic "image" of gas bubble plumes in the water column by Simrad EK60.



Gas release in the North Sea via video observation

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Gas analysis: State of the art

Water column sampling

Phase separation: gas phase from aqueous phase

Headspace technique for analysis of discrete samples

Gas analysis by gas chromatography

(Lammers and Suess 1994)

Problems:
-time consuming
-coarse spatial and temporal resolution

Need for new methods

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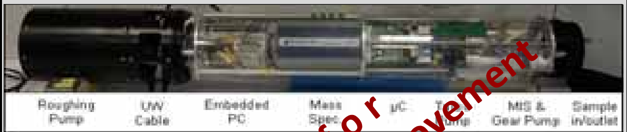
Requirements for in situ sensors:

- Robustness for the use in harsh environment
- The energy consumption needs to be low to allow long term measurements
- Sampling rates should be high and respond times correspondingly short for high temporal and spatial resolution
- Maintenance of the analyzer should be easy and short in time
- A low detection limit for trace gases.

INSPECTR200-200 FOR IN SITU, ONLINE, REAL TIME AND SIMULTANEOUS MEASUREMENTS:



(Short et al. 2001)

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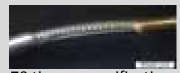
Need for detection limit improvement

IN SITU MASS SPECTROMETER MODE OF OPERATION


70 times magnification


320 times magnification

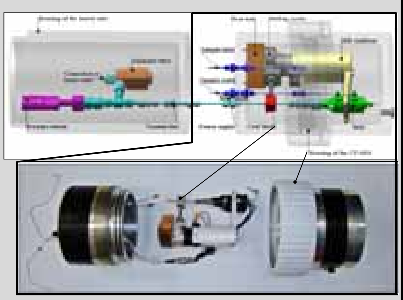
Water vapor

is the main gas that permeates through this membrane?

- Downgrades the detection limit
- Affects on the ionization effency
- Could cause condensation in the analytical line
- Downgrades the life time of the filament
- Indicate a high pressure in the analytical line

IMPLEMENTATION OF A CRYOTRAP


Micro Stirling Cooler, Ricor K508


(Gentz and Schlüter 2012)

Specifications:
Length: 290mm Max depth: 200m Weight: 5.1 kg Cooling area: 20mm
Outer diameter: 190mm Inner diameter: 180mm Material: Aluminum

IMPLEMENTATION OF A CRYOTRAP

Cooling of the capillary between sample inlet and sensor unit up to -90 °C

- Water vapour is reduced up to 98 % of initial
- Reduce the internal pressure significantly
- A higher ionization effency is observed

→Results in an obtimized detection limit

- Expand the lifetime of the analyser
- Secure the analyser for inflowing water

(Presented at the HEMS 2011, published in Gentz and Schlüter 2012)

Optimized and redesigned Inspectr200-200

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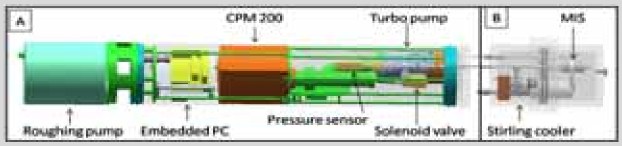

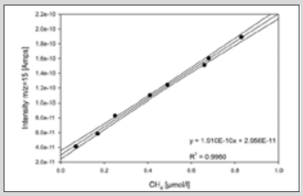

Calibration of the optimized Inspectr200-200

New detection limit of the optimized Inspectr200-200:

~16 nmol L^{-1}

Optimized and redesigned Inspectr200-200

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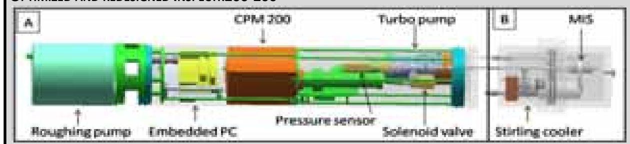

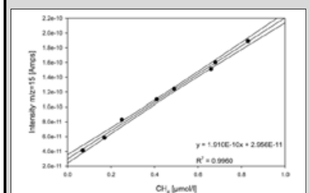

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~16 nmol L^{-1}

Low enough???

In situ mass spectrometer for field applications

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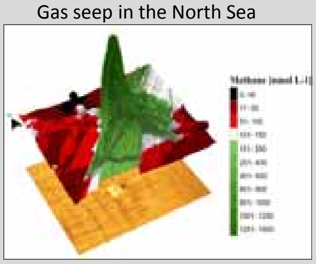
Gas seep in the North Sea



Concentration [nmol L^{-1}]	Area [%]
< 16	3.6
16 - 100	48.3
> 100	48.1

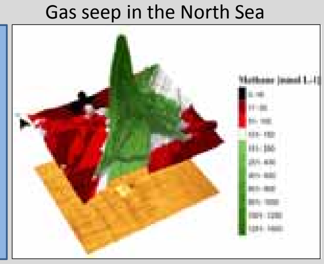
(Gentz and Schlüter 2012)

In situ mass spectrometer for field applications

20

Gas seep in the North Sea

without cryotrap: 48.1 %



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20

In situ mass spectrometer for field applications

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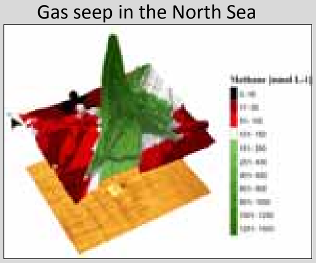

with cryotrap: 96.4 %

Concentration [nmol L-1]	Area [%]
< 16	3.6
16 - 100	48.3
> 100	48.1

(Gentz and Schlüter 2012)

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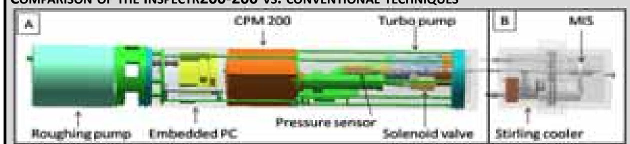
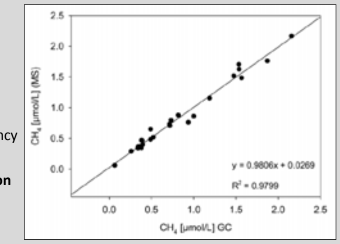
Comparison of the Inspectr200-200 vs. conventional techniques



- Both methods are comparable
- No sampling preparation
- Simultaneous measurement of the dissolved gases
- No artefacts during sampling
- Up to 750 times higher sampling frequency

→ **Higher temporal and spatial resolution**



Inspectr200-200 vs. GC

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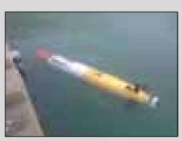

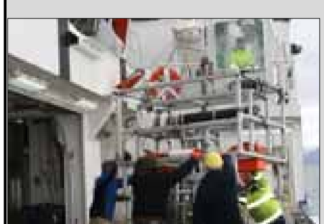

Deployments of the in situ mass spectrometer

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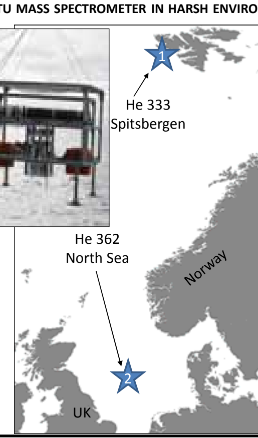
Application of the in situ mass spectrometer in harsh environments



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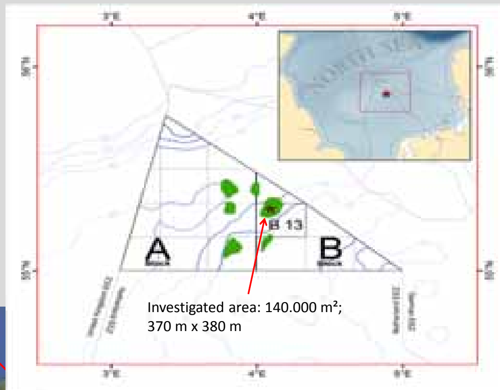
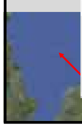
Observation of a gas seep area in the North Sea





Modified after Schroot et al. 2005

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Observation of a gas seep area in the North Sea

Under water gas analyser, sampler and observing system

- Inspectr200-200; 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

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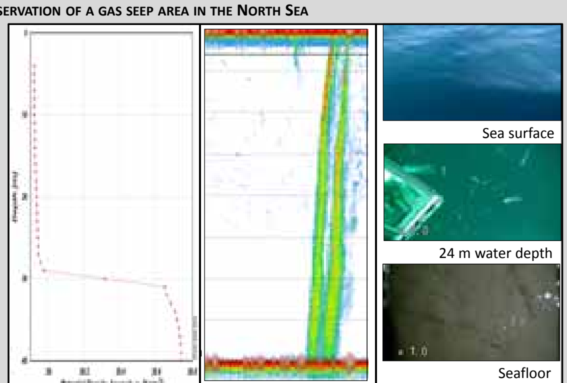
Observation of a gas seep area in the North Sea



CTD profiles | Hydroacoustic | Video observation

(Gentz et al. unpublished data)

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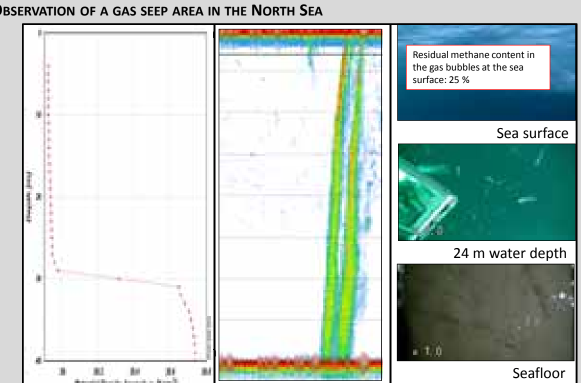
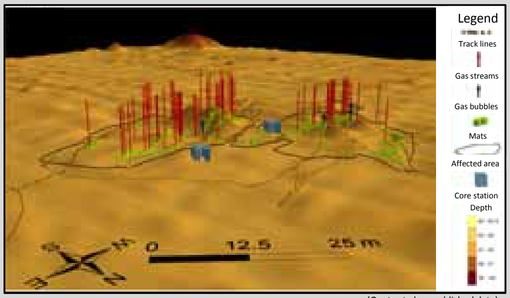
Observation of a gas seep area in the North Sea



CTD profiles | Hydroacoustic | Video observation

(Gentz et al. unpublished data)

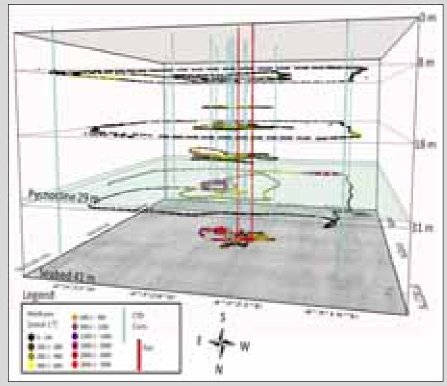
Video observation of the seafloor



(Gentz et al. unpublished data)

Affected area: ~3800 m²
Number of streams: 113
Bubble diameter: 4.5 to 16 mm (average 7 mm)
Release frequency: 0.3 – 40 bubbles s^{-1} (average 23 bubbles s^{-1})
Methane flux: 28.27 L min^{-1}
Methane release: 35.3 $\pm$ 17.65 t CH_4 yr^{-1}

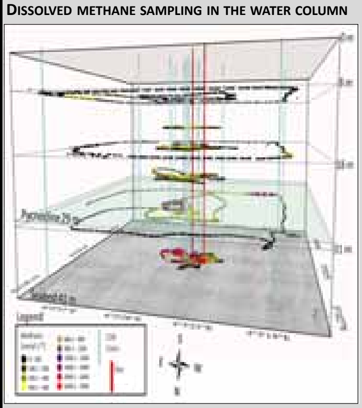
Dissolved methane sampling in the water column



11900 samples in various depth in between 24 hours

(Gentz et al. unpublished data)

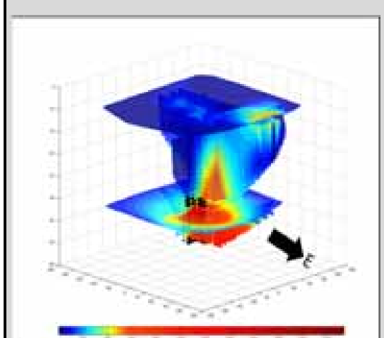
Dissolved methane sampling in the water column



- Discrete sampling: max 1.5 µmol L^{-1}
- In situ sampling: max 3.5 µmol L^{-1}
- A methane saturation of 23200 % was observed in 8 m water depth.
- The air sea exchange flux is calculated to ~210 $\pm$ 63 µmol m^{-2} d^{-1}.

(Gentz et al. unpublished data)

Interpolation of the Dissolved methane above the gas seep



Entire interpolated inventory of methane (6.410.000 m³):

~0.6 mol CH_4

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

Sibson, R., "A Brief Description of Natural Neighbor Interpolation", Kapitel 2 in *Interpolating multivariate data*, S. 21-36. John Wiley & Söhne: New York, 1981.

Main result North Sea 31

→ In total 65 % (23 ± 11.5 t CH_4 y^{-1}) of the released methane potentially reach the atmosphere, which is high compared to the Spitsbergen continental margin or the Tommeliten area.

Conclusions 32

This is the first study of methane above a gas seep in high resolution.

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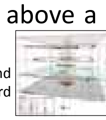

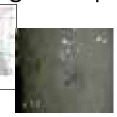

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- The investigated study area in the North Sea contributes to the global atmospheric methane budget.

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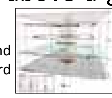
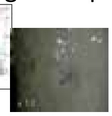

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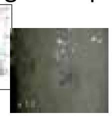
- The fate of methane as well as the contribution to the global atmospheric methane budget of each source depends on bubble size, the water depth, the water current and the water stratification.

	Spitsbergen	North Sea
Water depth [m]	245	40
Water stratification [m above seafloor]	25	10
Observed bubble rise [m above seafloor]	150	40
Estimated bubble diameter [mm]	< 5	7
Bubbles at seasurface	No	Yes
Direct methane transport	No	Yes
Indirect transport	???	Yes
Methane to atmosphere [% from origin]	???	~ 60

Introduction Novel Instruments Study Areas Results and Interpretation **Conclusions**

CONCLUSIONS 32

This is the first study of methane above a gas seep in high resolution.

- The inventory calculation is more accurate than before and shows that conventional methods tend toward underestimation.
- The investigated study area in the North Sea contributes to the global atmospheric methane budget.
- The fate of methane as well as the contribution to the global atmospheric methane budget of each source depends on bubble size, the water depth, the water current and the water stratification.

	Spitsbergen	North Sea
Water depth [m]	245	40
Water stratification [m above seafloor]	25	10
Observed bubble rise [m above seafloor]	150	40
Estimated bubble diameter [mm]	< 5	7
Bubbles at seasurface	No	Yes
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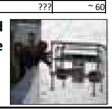
Indirect transport	???	Yes
Methane to atmosphere [% from origin]	???	~ 60

- **The use of the improved in situ mass spectrometry is one step forward to understand the pathways and potential global relevance of these methane sources.**



CURRENT AND FUTURE WORK

Implementation of the mass spec into an AUV

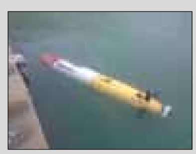
…

Thank you all for
developing new instruments as well as
your attention!

Torben.Gentz@awi.de

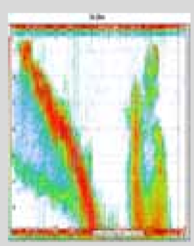
Backup

FUTURE WORK

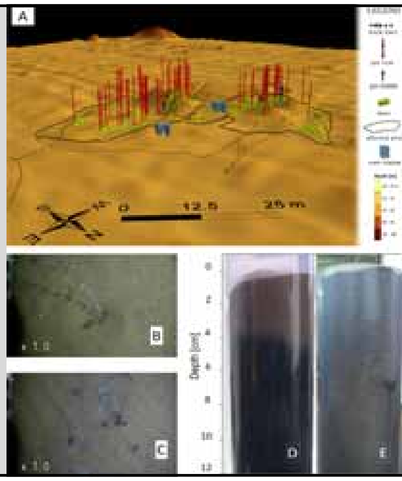


Implementation in new device holder

Benthic chamber measurements



Combining ydroacoustic with in situ mass spectrometry



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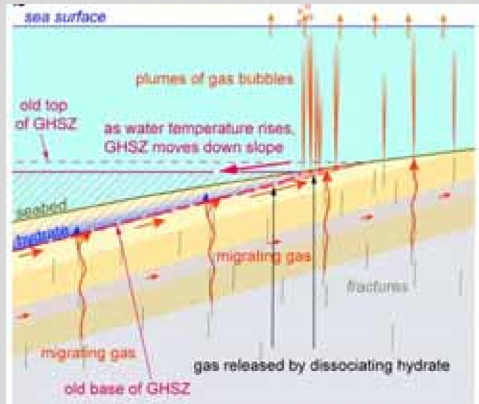
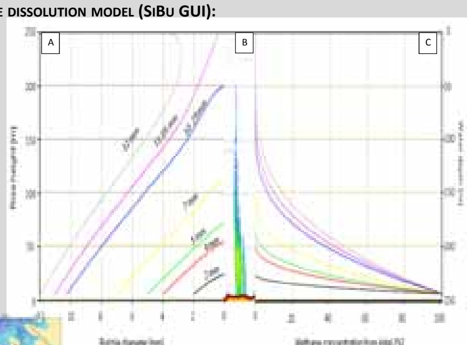
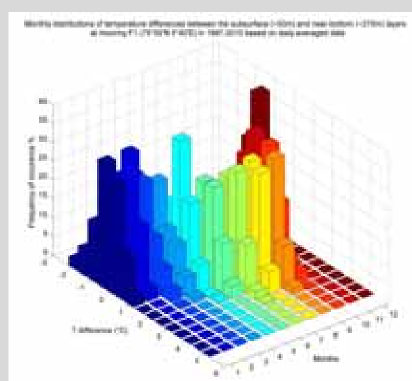


Westbrook et al. 2009

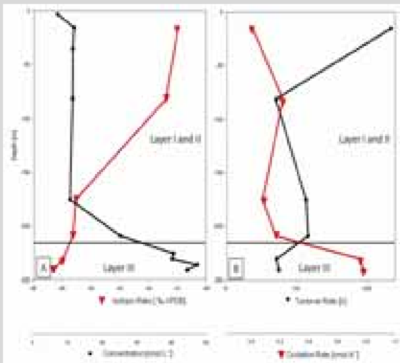
Gas bubble dissolution model (SiBu GUI):



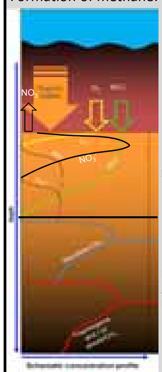
Decrease of the bubble diameter during the ascend from the seafloor for initial bubbles sizes of 2 mm to 12 mm (A) compared with the hydroacoustic image of the highest detected gas flare (B). Decrease of the initial CH_4 concentration in the bubbles during their rise in the water column (C). Data obtained by the model SiBu GUI (Greinert, J. and D. F. McGinnis 2009) *personally optimized by Dan McGinnis*



Personal communication Agnieszka Beszsynsky-Möller
28.26 km s-w direction



Formation of methane:



Degradation of organic matter by redox processes

Aerobic respiration $(CH_2O)x(NH_3)y(H_3PO_4)z + xO_2 \rightarrow xCO_2 + xH_2O + yNH_3 + H_3PO_4$

Nitrate reduction $5CH_2O + 4NO_3^- \rightarrow 4HCO_3^- + CO_2 + 2N_2 + 3H_2O$

Manganese oxide reduction $CH_2O + 2MnO_2 + 3CO_2 + H_2O \rightarrow 2Mn^{2+} + 4HCO_3^-$

Iron oxide reduction $CH_2O + 4Fe(OH)_3 + 7CO_2 \rightarrow 8HCO_3^- + 3H_2O + 4Fe^{2+}$

sulfate/methane transition zone (SMTZ)

Microbial formation of methane:

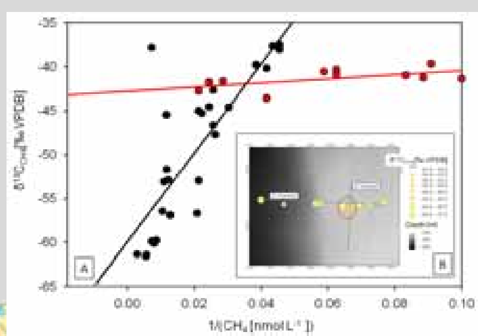
Hydrogenotrophic $CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$

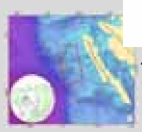
Acetotrophic $CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3$

Methylotrophic $CH_3\text{-}A + H_2O \rightarrow CH_4 + CO_2 + A\text{-}H$

Thermocatalytic formation of methane

Schematic view of the formation (modified after Froelich et al. 1979)





A) Inverse CH_4 concentration versus $d^{13}C_{CH4}$ values (Keeling plot). Layer III is presented by black dots and Layer II and I by red dots. (B) Distribution of $d^{13}C_{CH4}$ 2 m above the seafloor including the transect lines. The red circle indicates the crossing zone of the two transects.

Calculation:

Bubble diameter: 7 mm by ImageJ

$r_e = (a^2 b)^{1/3}$ (1)

$V = \frac{4}{3}\pi r_e^3$ (2)

Leifer and Patro 2002

Release frequency: 23 bubbles s^{-1}

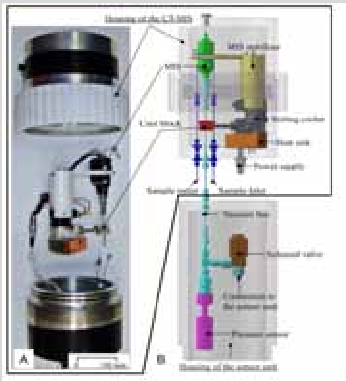
Methane flux: 28.27 L min^{-1}

$PVA = nRTZ$ (3)

Modified after Römer et al. 2012

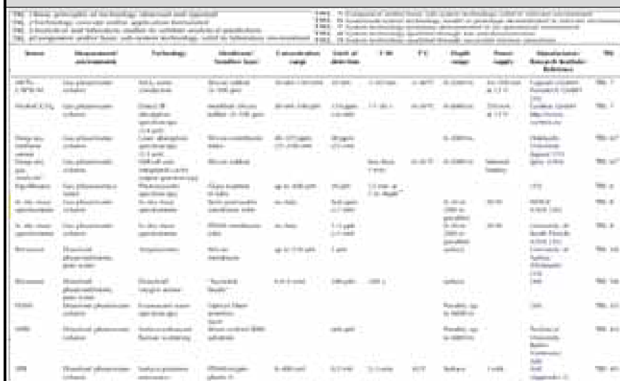
Seafloor methane release: 35.3 ± 17.65 t CH_4 yr^{-1}

Under water cryotrap

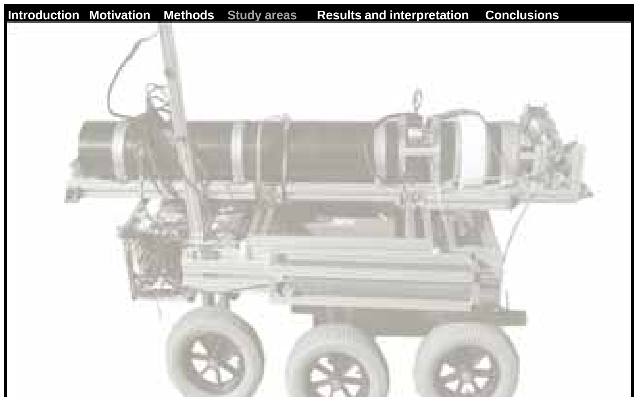


Gentz and Schlüter 2012

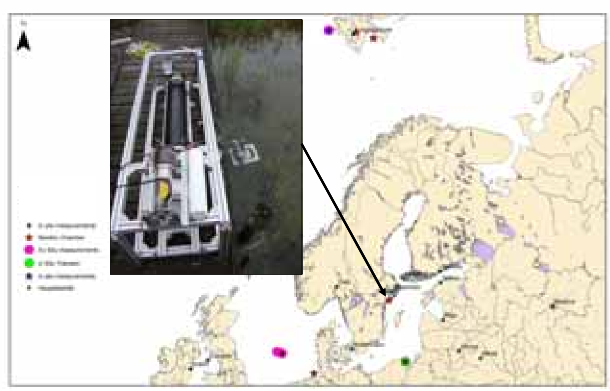
Gas analysis: New in situ sensors for high resolution mapping



Compilation of in situ methane sensors and technologies, modified after Boulart (2010) including the explanation of the TRL levels, modified from a UK Defence Procurement Agency version.



Working areas



Working areas