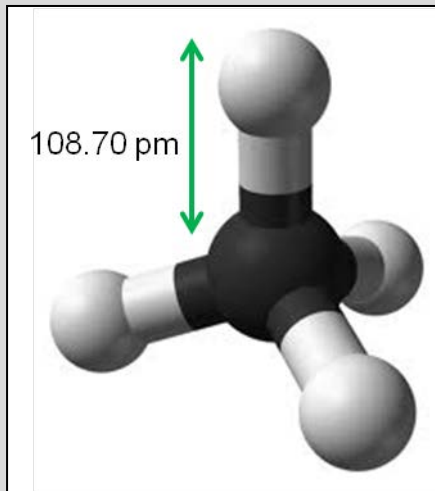


# Distribution and fate of methane released from submarine sources

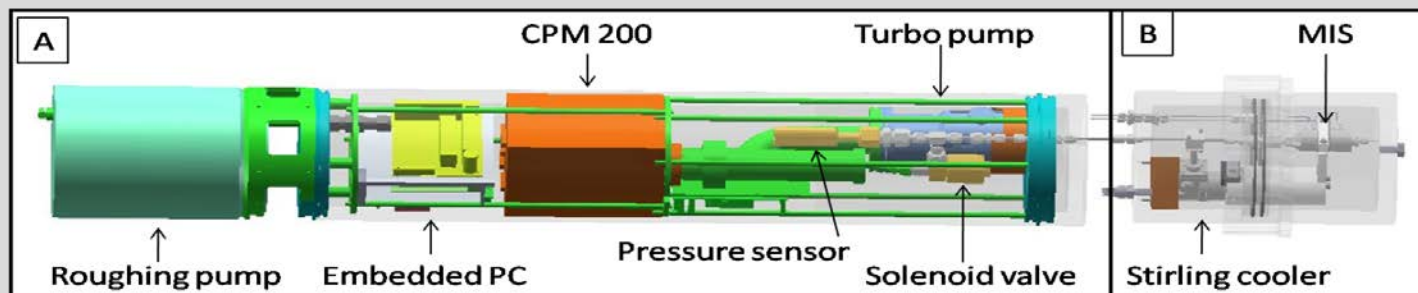
-

*Results of measurements using an improved in situ mass spectrometer*

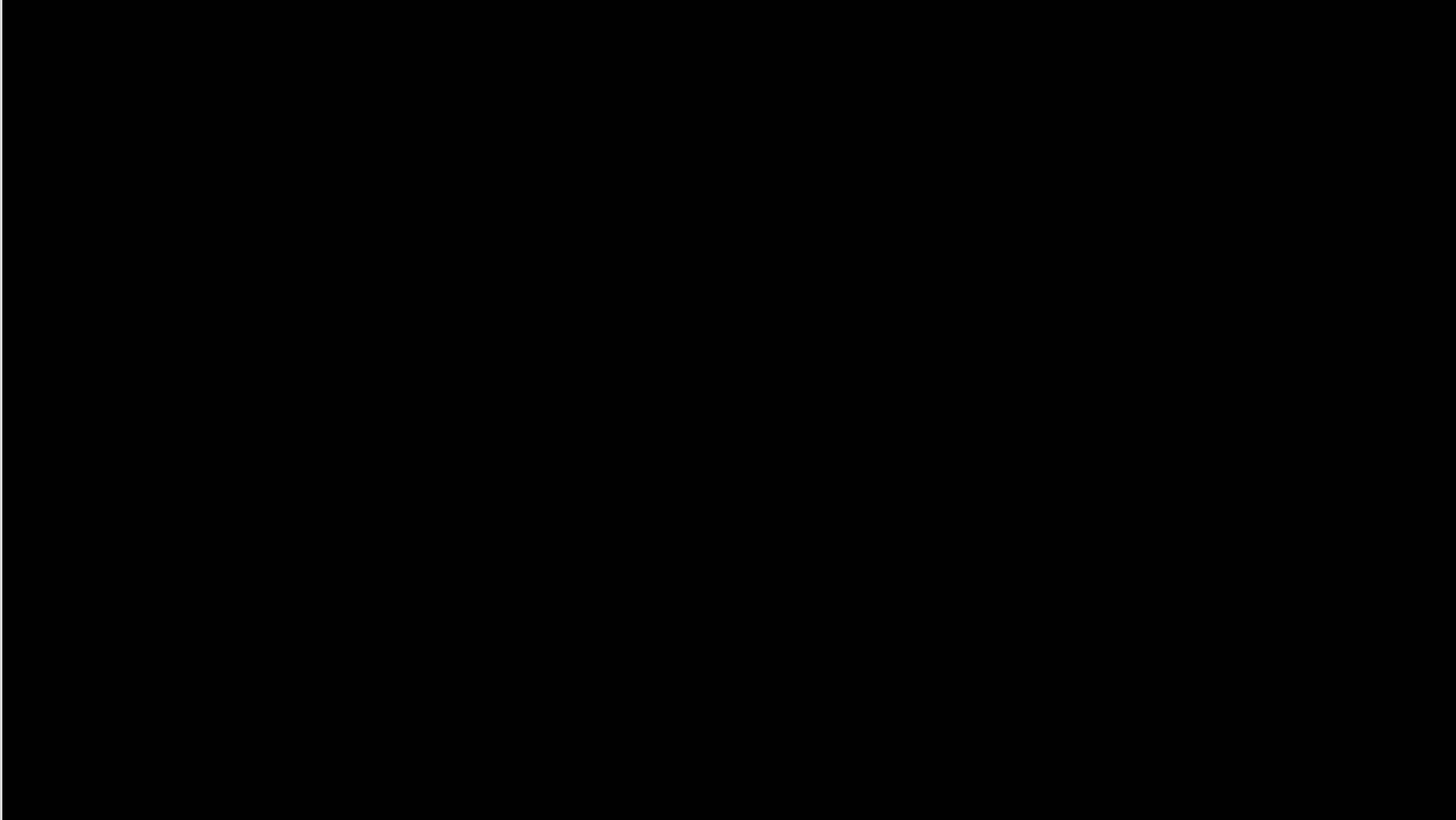


**Torben Gentz**

Universität Heidelberg  
29.10.2013



Torben.Gentz@awi.de



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Submarine gas seeps

## WORLDWIDE DISTRIBUTION OF SUBMARINE METHANE RELEASE

*Free gas (Fleischer et al. 2001)*

*Pockmarks (Hovland et al. 2002)*

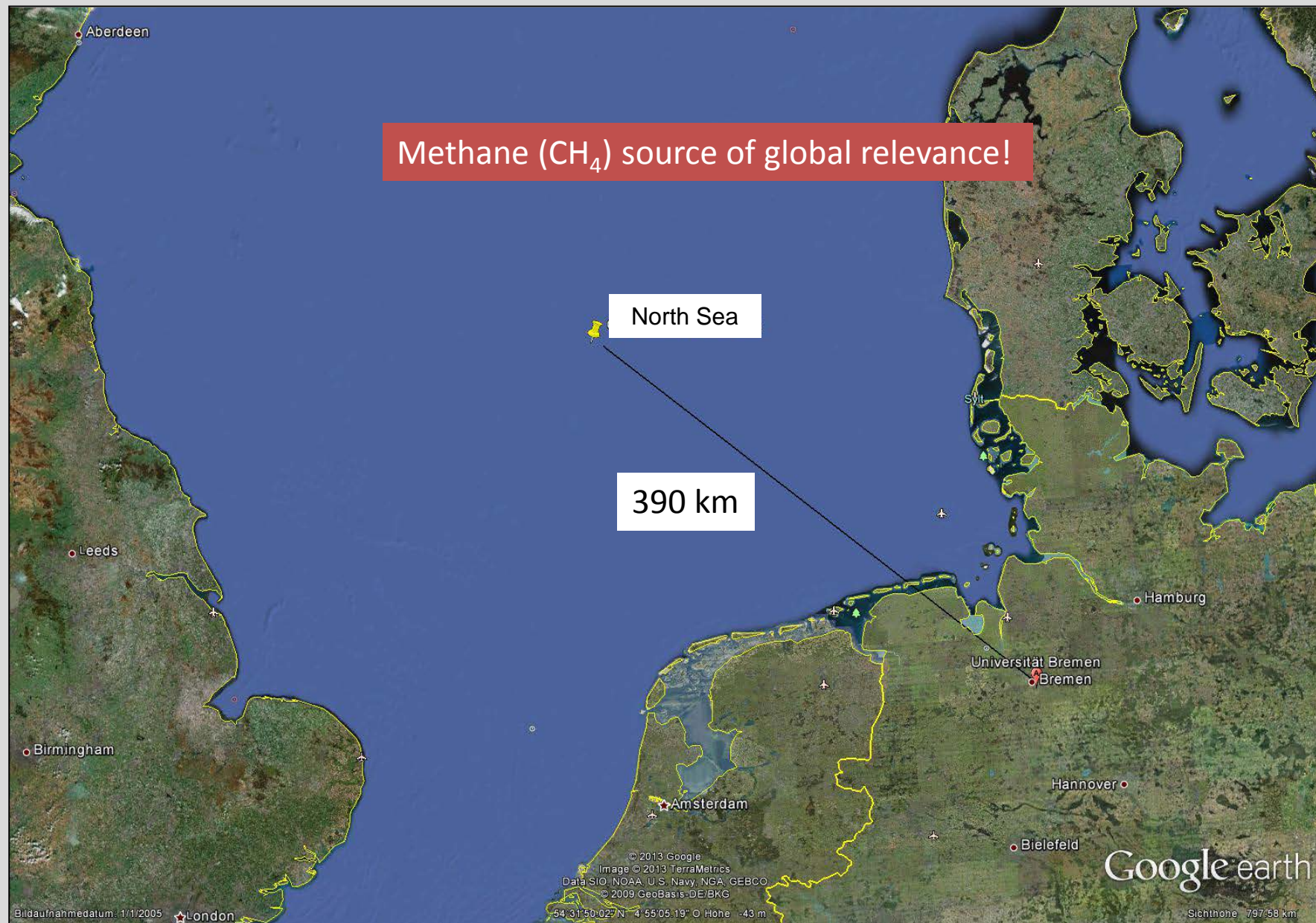
*Mud volcanoes (Milkov 2000)*

*Gas hydrates (Kvenvolden et al. 2001)*

Methane (CH<sub>4</sub>) source of global relevance!

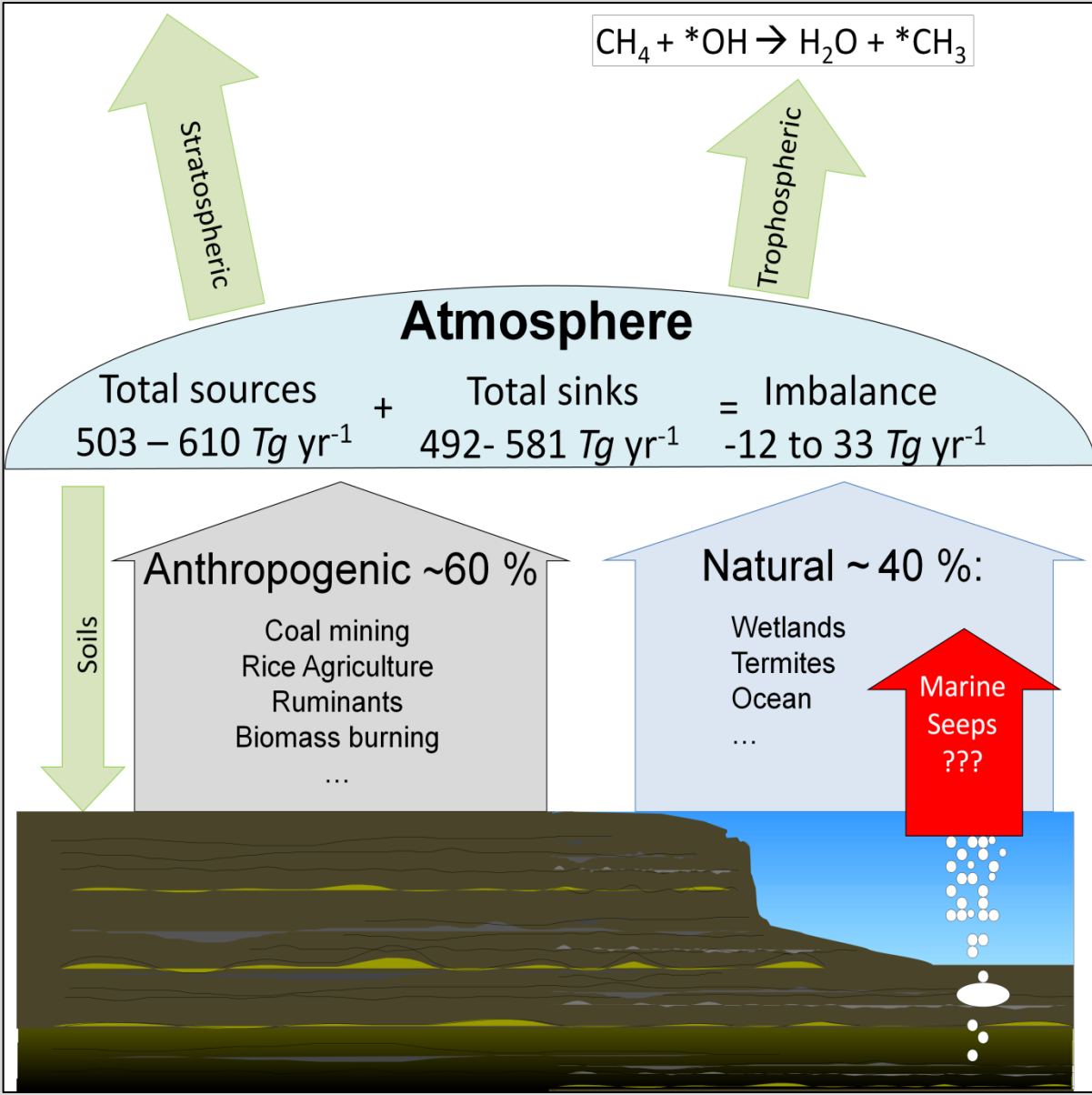
North Sea

390 km





# GLOBAL RELEVANCE OF METHANE



according to IPCC (2007)

## GLOBAL RELEVANCE OF METHANE



Stratospheric

Tropospheric

## Atmosphere

Total sources + Total sinks = Imbalance  
 $503 - 610 \text{ Tg yr}^{-1} + 492 - 581 \text{ Tg yr}^{-1} = -12 \text{ to } 33 \text{ Tg yr}^{-1}$

Soils

## Anthropogenic ~60 %

Coal mining  
 Rice Agriculture  
 Ruminants  
 Biomass burning  
 ...

## Natural ~40 %:

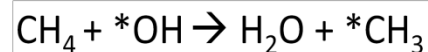
Wetlands  
 Termites  
 Ocean  
 ...

Marine  
 Seeps  
 ???

according to IPCC (2007)

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

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according to IPCC (2007)

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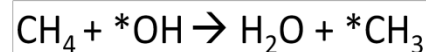
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On a 100 year timescale the global warming potential (GWP) of CH<sub>4</sub> is 20 – 40 times higher than of CO<sub>2</sub> (Shindell 2009).



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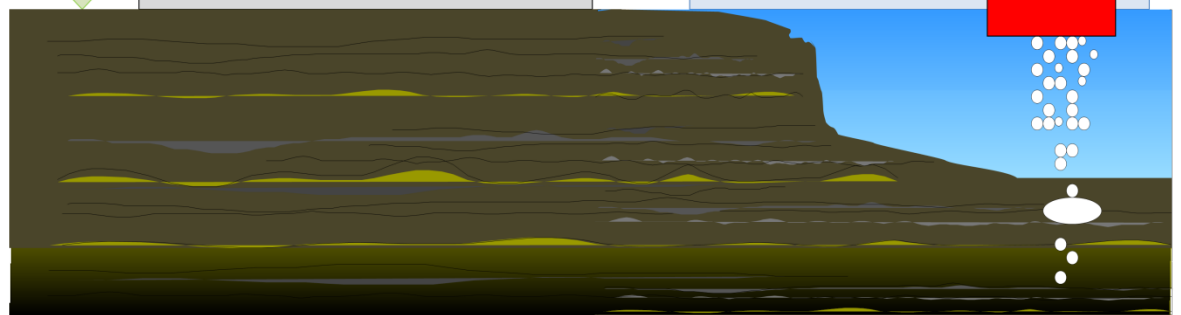
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Termites  
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...

Marine  
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???

Soils



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CH<sub>4</sub> represents the second largest contribution (about 15 %) to historical warming after CO<sub>2</sub> (Shindell et.al. 2009).

according to IPCC (2007)

## GLOBAL RELEVANCE OF SUBMARINE SOURCES

Present estimations: 8 - 65 Tg CH<sub>4</sub> yr<sup>-1</sup> are released into the ocean and 0.4 – 48 Tg CH<sub>4</sub> yr<sup>-1</sup> 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)

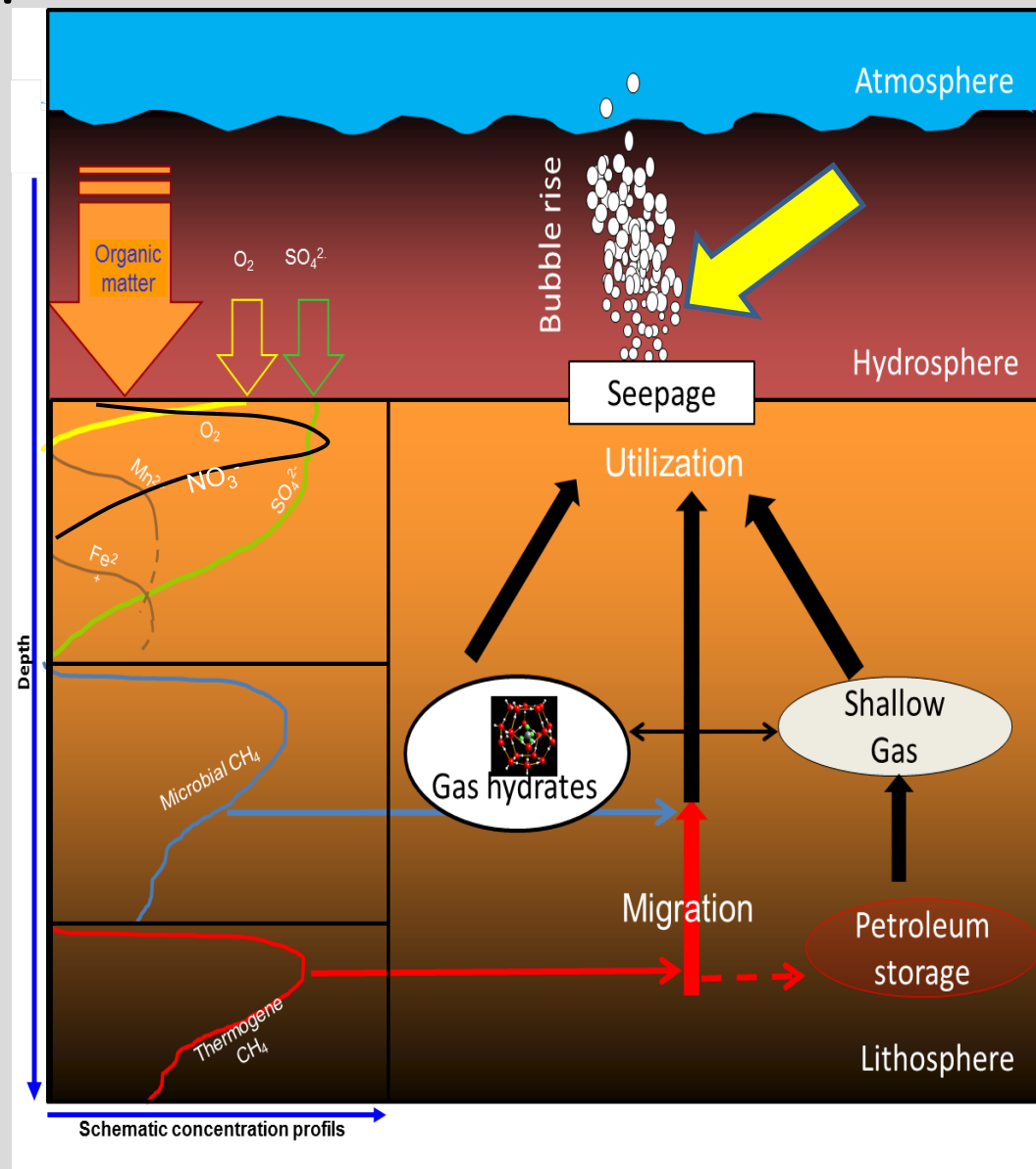
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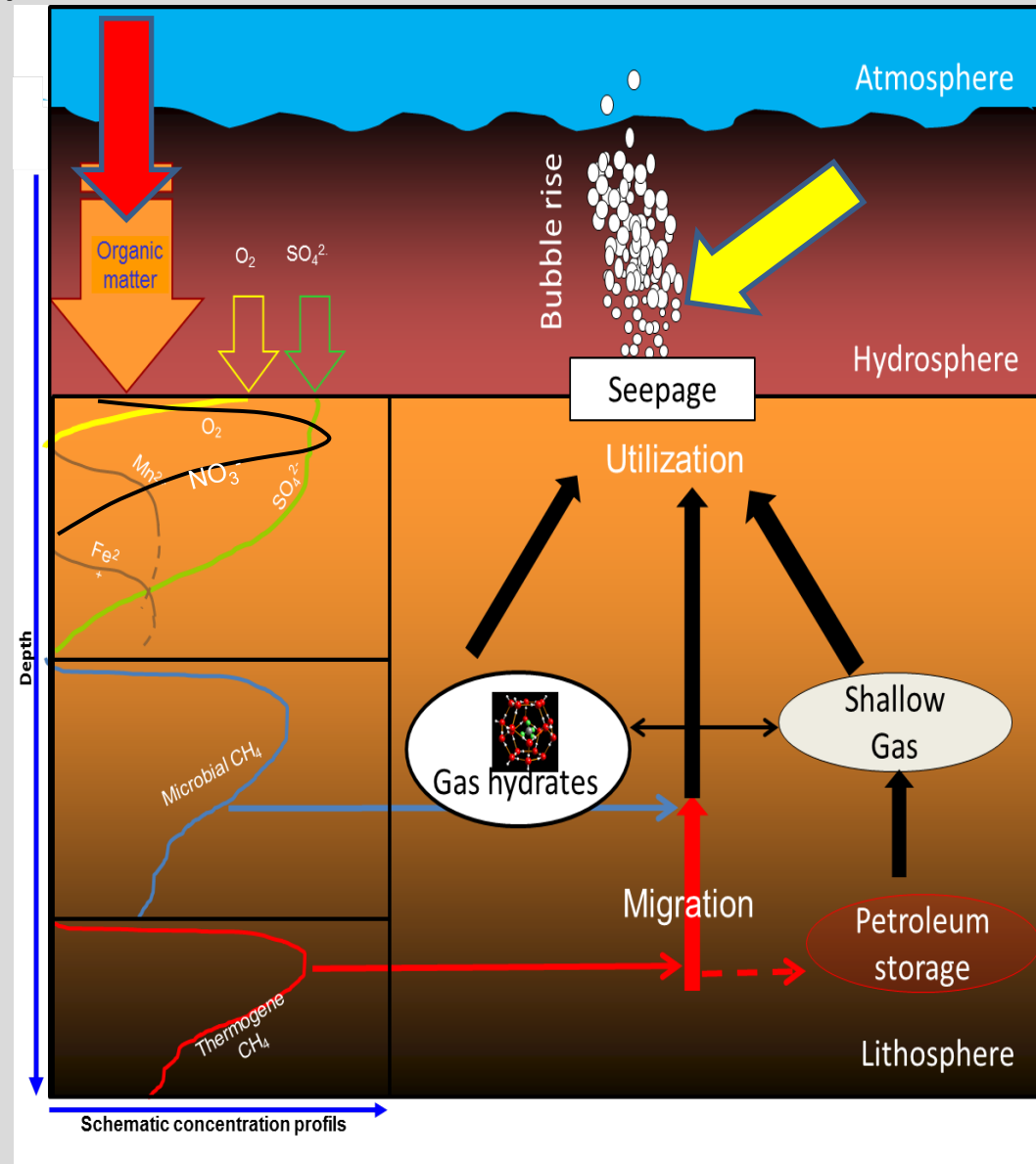
*Gas hydrates (Kvenvolden et al. 2001)*

# WHAT ARE SUBMARINE GAS SEEPS?



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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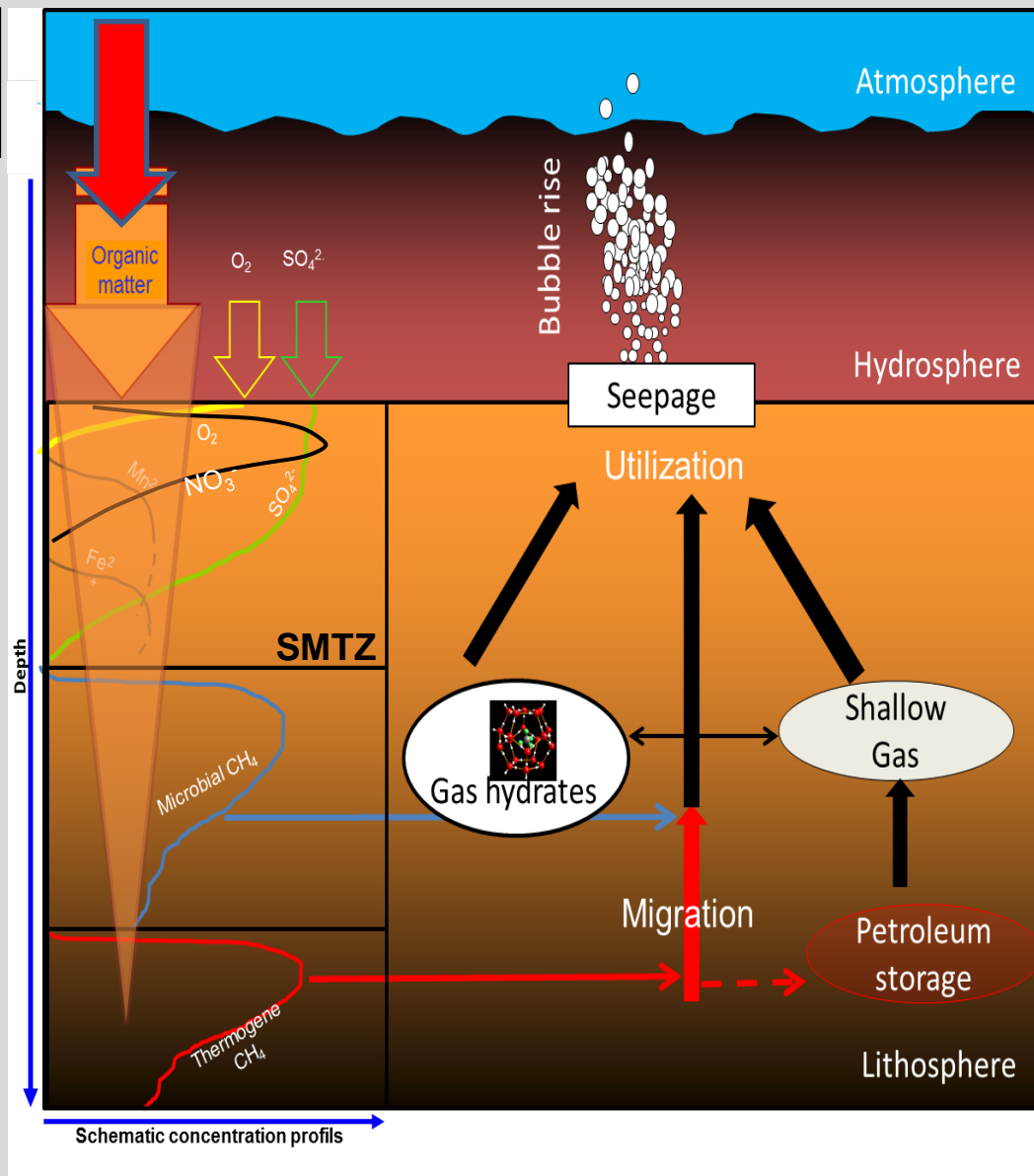


## Formation of methane by degradation of organic matter

Aerobic respiration  
Nitrate reduction  
Manganese oxide reduction  
Iron oxide reduction

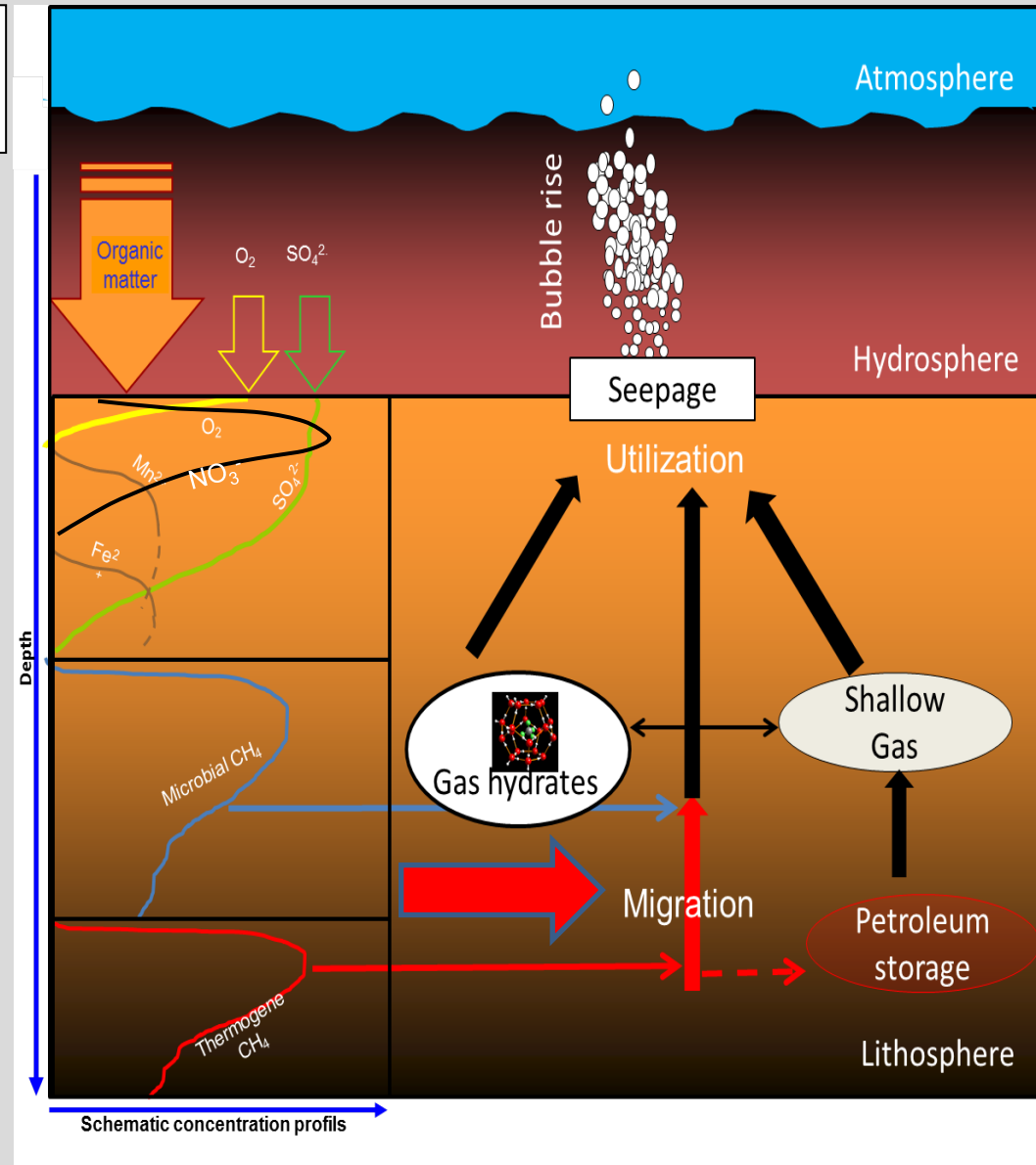
Microbial formation of methane

Thermocatalytic formation of methane



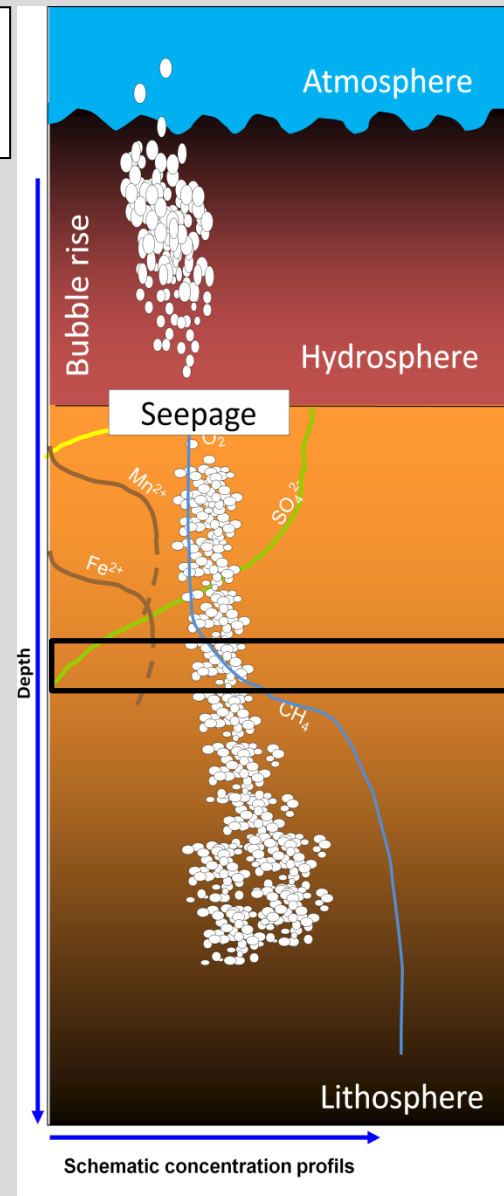
Schematic view of the formation (modified after Froelich et al. 1979) and the subsequent pathways of methane in the sediment (modified after Judd 2004). Crystallographic image of gas hydrates after Bohrmann and Torres (2006)

## Storage and migration of methane

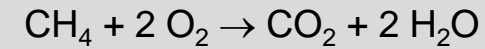


Schematic view of the formation (modified after Froelich et al. 1979) and the subsequent pathways of methane in the sediment (modified after Judd 2004). Crystallographic image of gas hydrates after Bohrmann and Torres (2006)

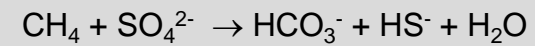
## Utilization of methane in the sediment



### Aerobic oxidation



### Anaerobic oxidation of methane (AOM)



(Boetius et al. 2000)

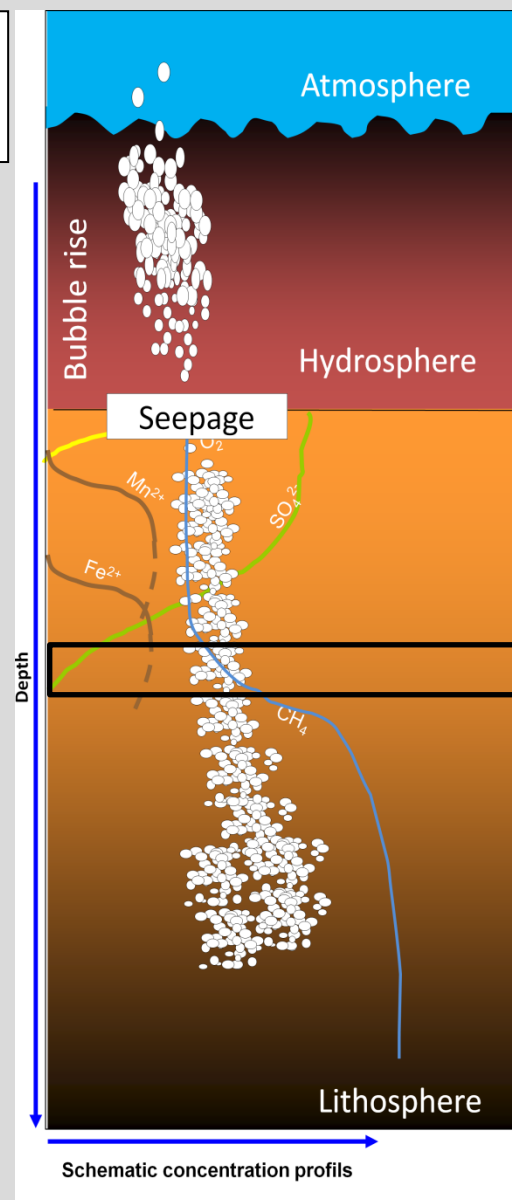
### Sulfate / Methane Transition Zone (SMTZ)

Free methane gas

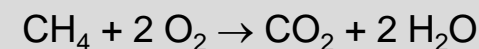
*Schematic view of the formation (modified after Froelich et al. 1979) and the subsequent pathways of methane in the sediment (modified after Judd 2004).*

## Utilization of methane in the sediment

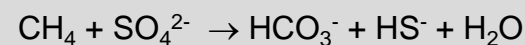
Only if the rate of methane production in relation of migration exceeds the rate of microbial utilization, seepage into the water column occurs.



### Aerobic oxidation



### Anaerobic oxidation of methane (AOM)



(Boetius et al. 2000)

Sulfate / Methane Transition Zone (SMTZ)

Free methane gas

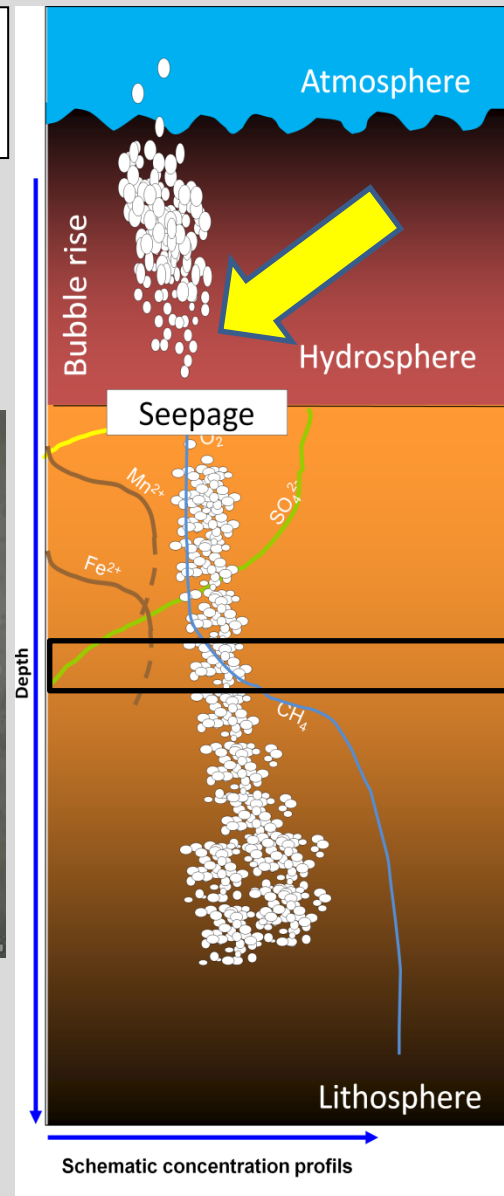
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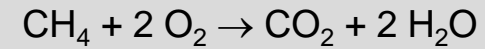
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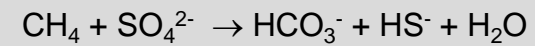
Heincke 362



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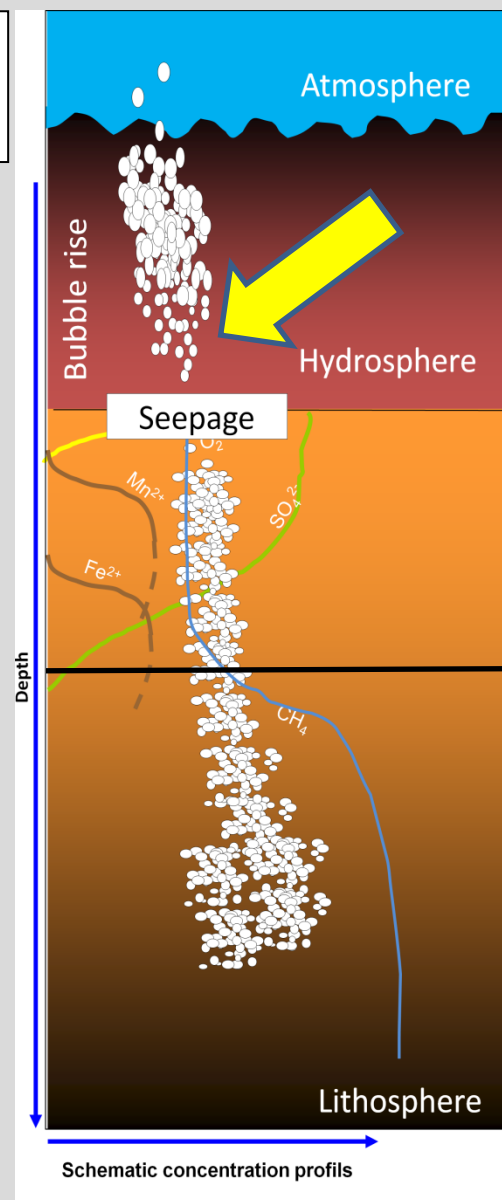
(Boetius et al. 2000)

### 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).*

## Pathways of methane in the water column



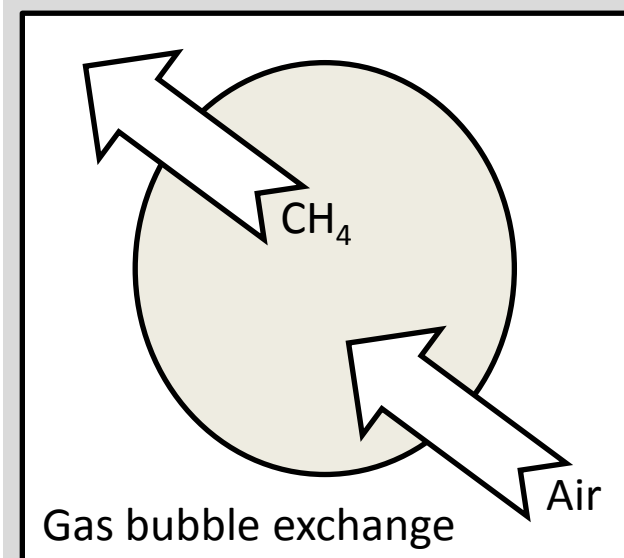
Air/Sea exchange

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)

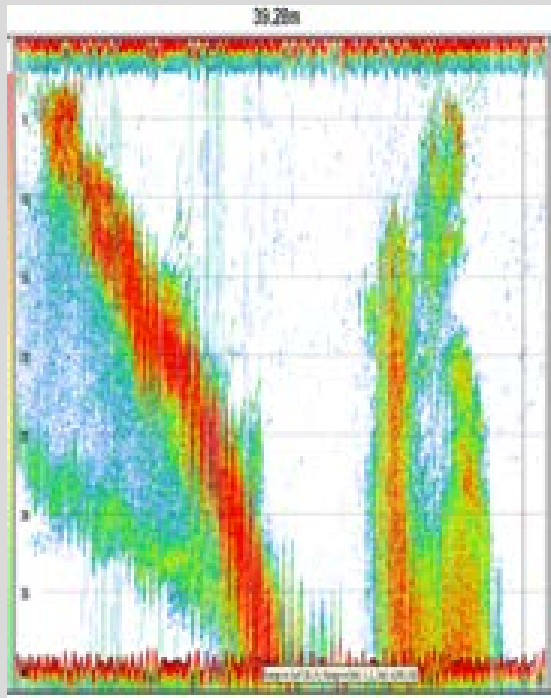


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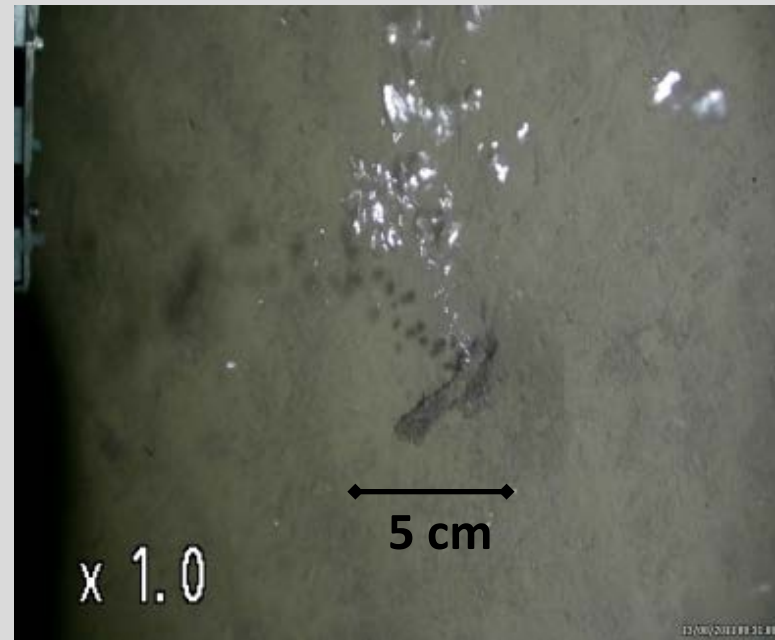
# SCIENTIFIC FRAMEWORK

1. Quantification of the dissolved methane above gas seeps in high temporal and spatial resolution.
2. Which are the main pathways of methane in the water column?
3. How much of the submarine released methane in the studied areas contribute to the global atmospheric budget?

# 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

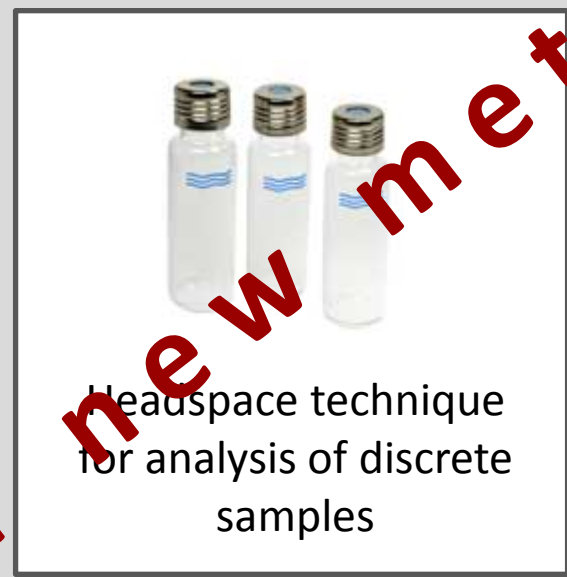


# GAS ANALYSIS: STATE OF THE ART

Water column sampling



Phase separation:  
gas phase from aqueous phase



Gas analysis by gas chromatography



(Lammers and Suess 1994)

**Need for new methods**

### Problems:

- time consuming
- coarse spatial and temporal resolution

## 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.
- Simultaneous measurement of the dissolved gases

## Mono-parameter instruments



HydroC, Contros

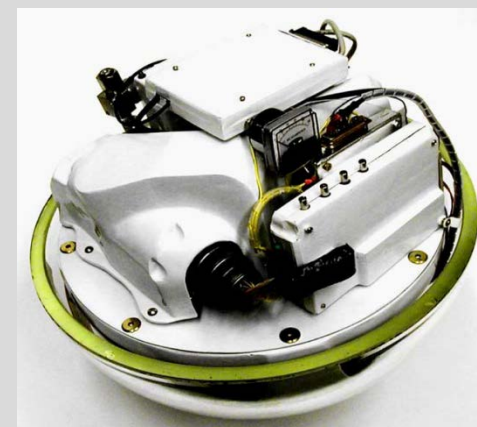


Mets, Franatech

## Poly-parameter instruments



Inspectr200-200, AML,  
by T. Short and G. Kibelka



Nereus/Kemonaut,  
by R. Camilli, H.F. Hemond

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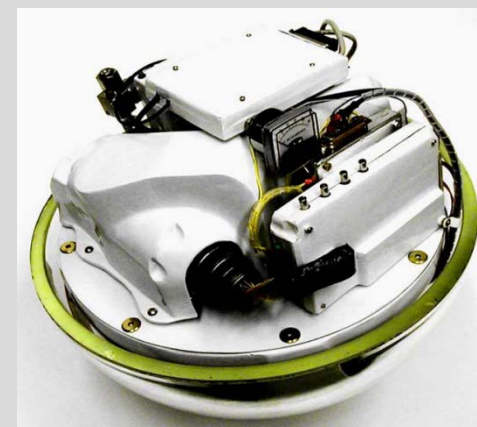


Mets, Franatech

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Nereus/Kemonaut,  
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## INSPECTR200-200 FOR IN SITU, ONLINE, REAL TIME AND SIMULTANEOUS MEASUREMENTS:



(Short et al. 2001)



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



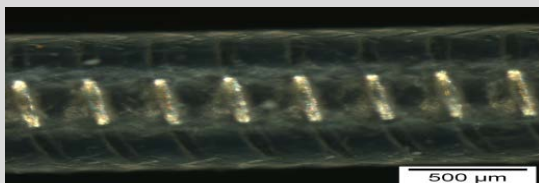
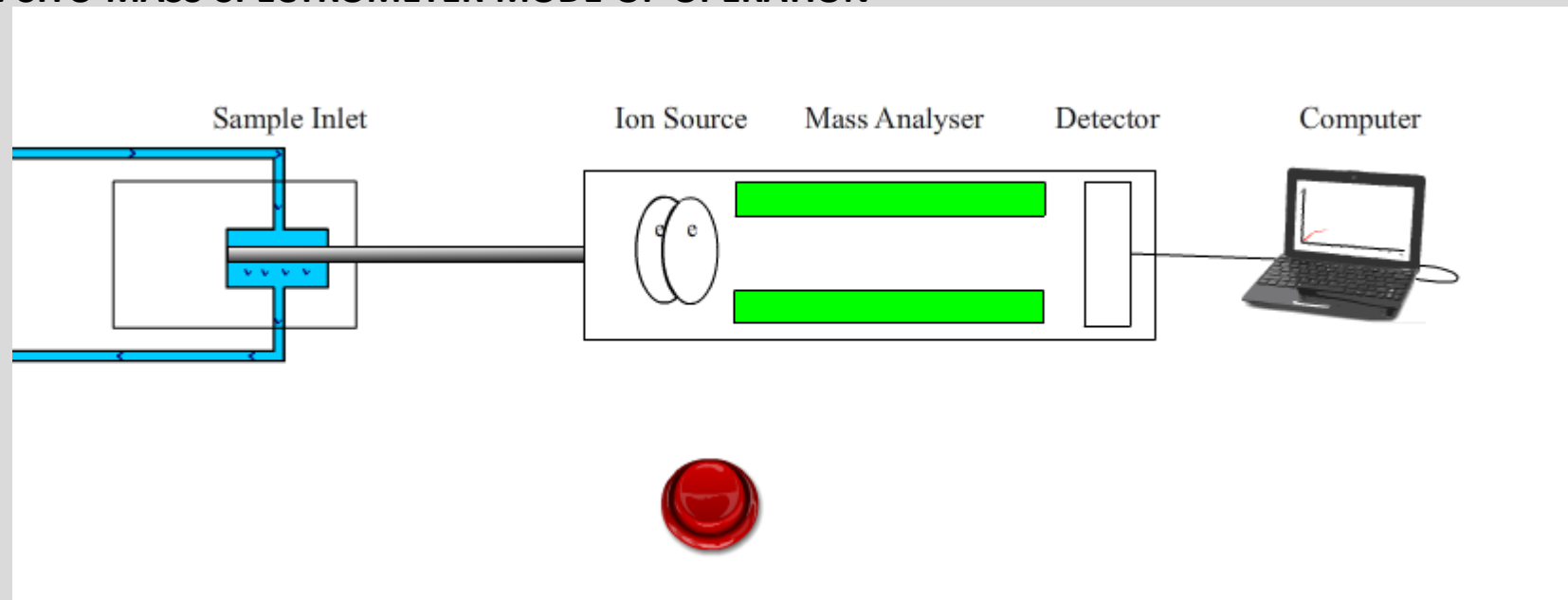
Allow detection limit for trace gases.



Simultaneous measurement of the dissolved gases

**Need for detection limit improvement**

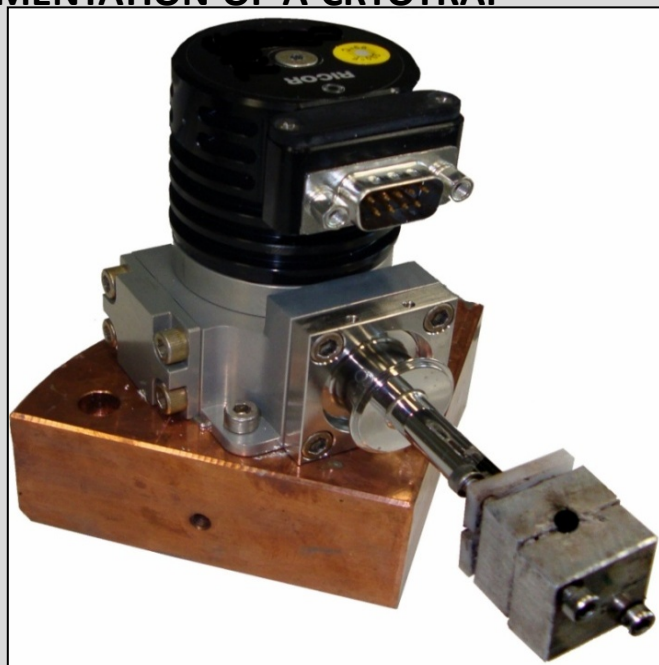
## IN SITU MASS SPECTROMETER MODE OF OPERATION



- Water vapour is the main gas that permeates through the membrane!
  - Affects on the ionization efficiency
  - Could cause condensation in the analytical line
  - Leads to a high pressure in the analytical line
- Downgrades the **detection limit** and the life time of the filament

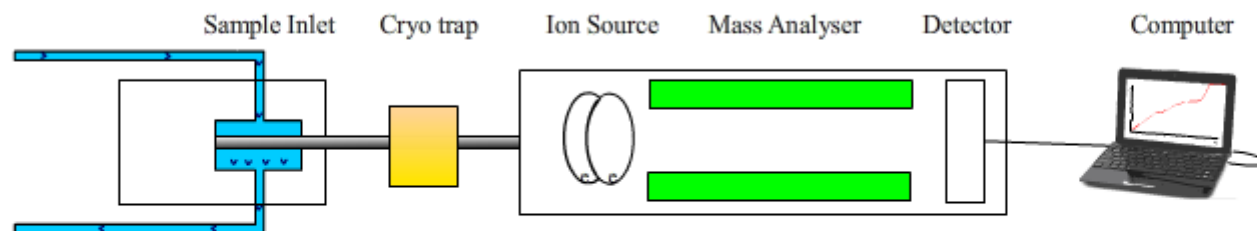


## IMPLEMENTATION OF A CRYOTRAP

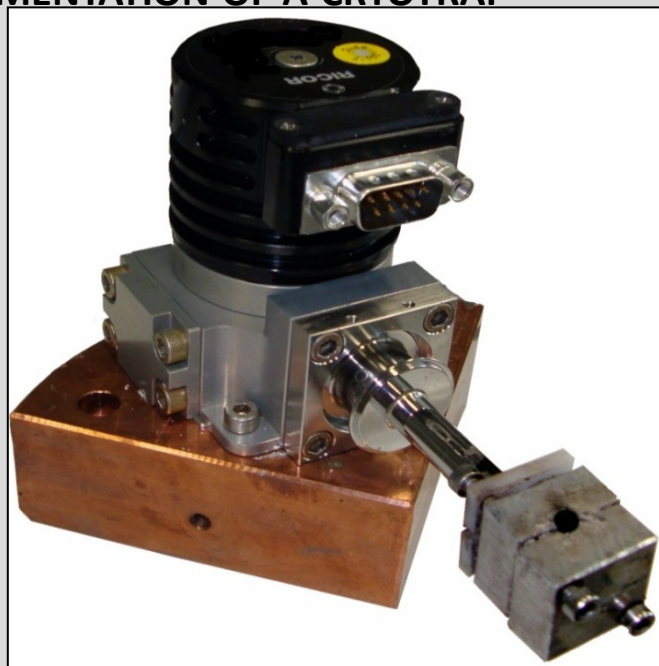


Micro Stirling Cooler, Ricor K508

Cooling of the capillary between sample inlet and sensor unit up to  $-90\text{ }^{\circ}\text{C}$



## IMPLEMENTATION OF A CRYOTRAP



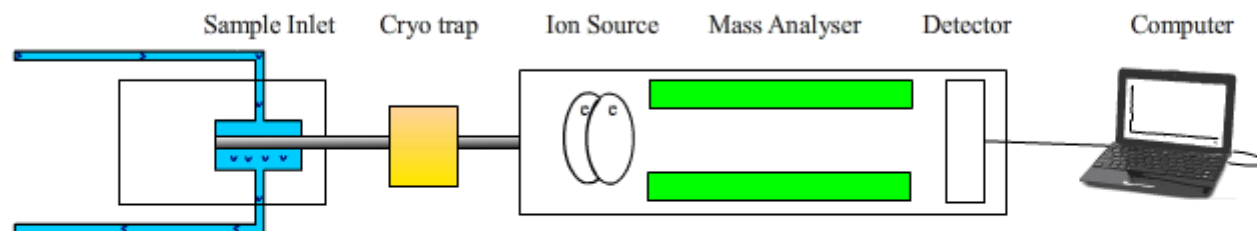
Micro Stirling Cooler, Ricor K508

**Cooling of the capillary between sample inlet and sensor unit up to  $-90\text{ }^{\circ}\text{C}$**

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

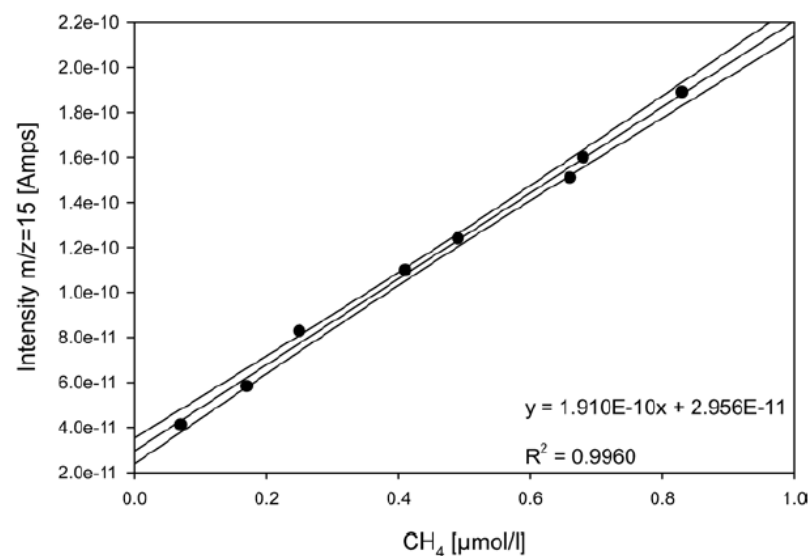
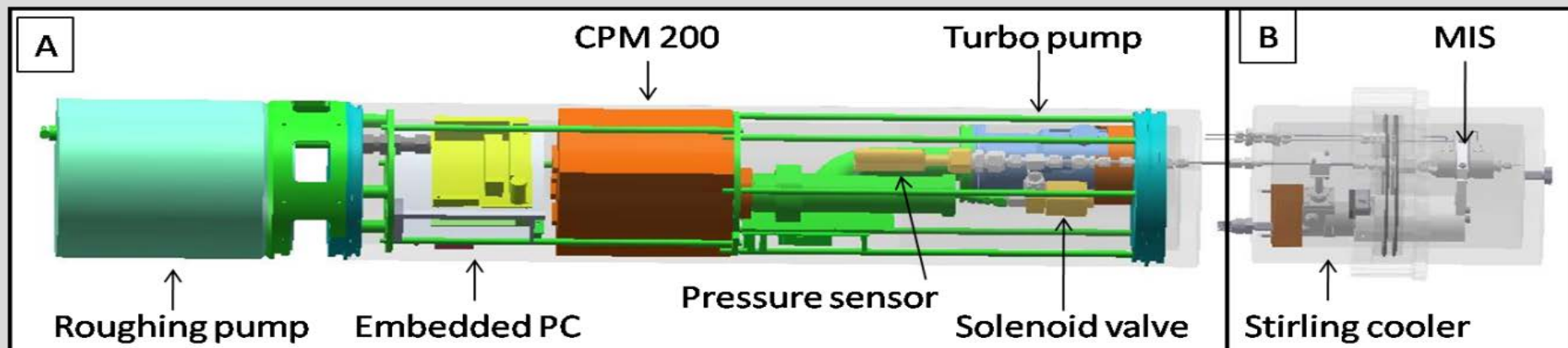
→ Results in an optimized detection limit

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





## OPTIMIZED AND REDESIGNED INSPECTR200-200

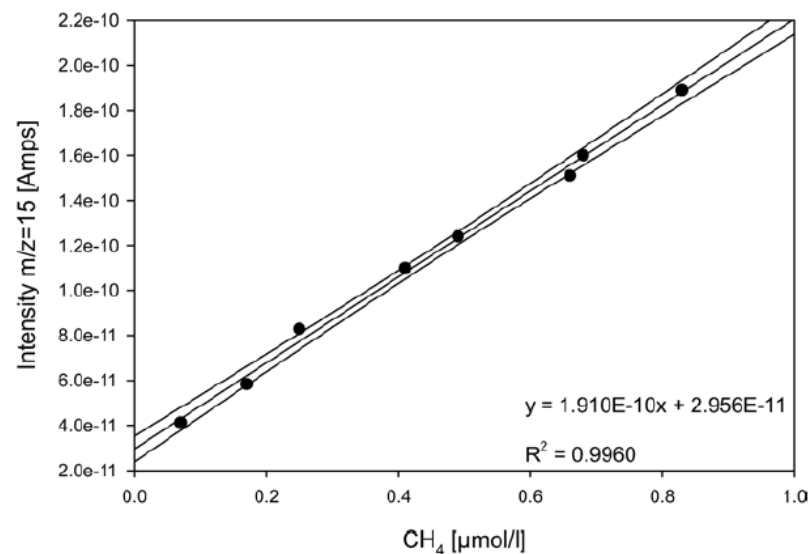
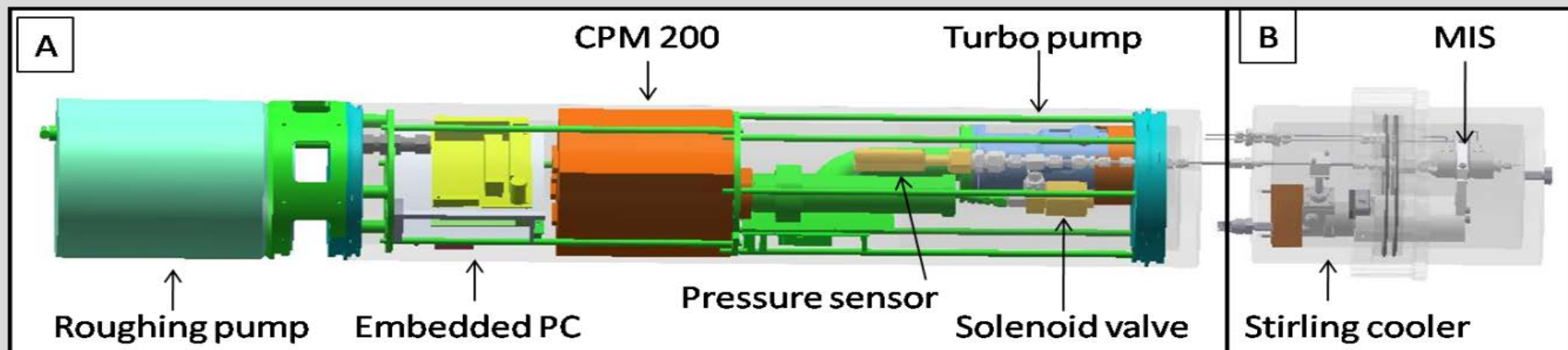


Calibration of the optimized Inspectr200-200

New detection limit of the optimized Inspectr200-200:

**$\sim 16 \text{ nmol L}^{-1}$**

## OPTIMIZED AND REDESIGNED INSPECTR200-200



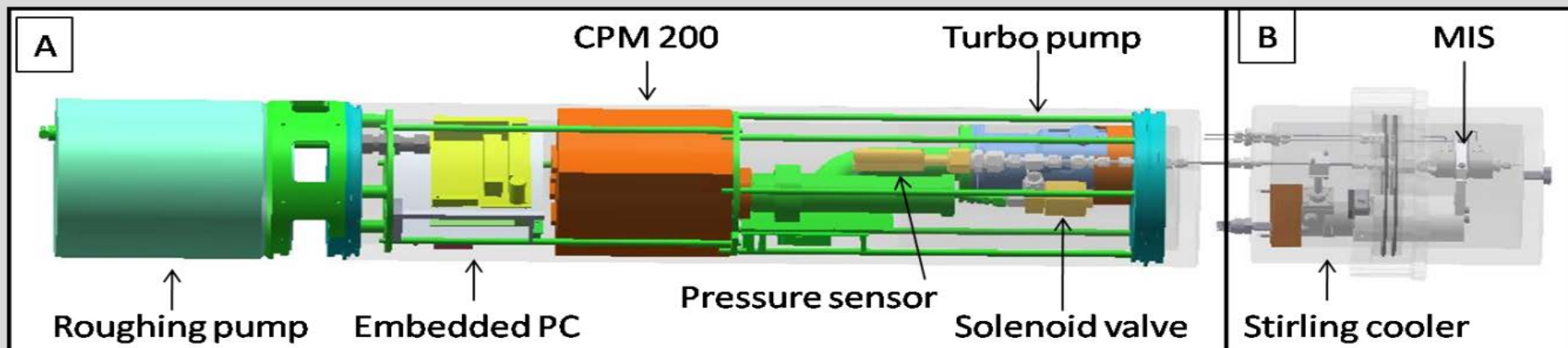
Calibration of the optimized Inspectr200-200

New detection limit of the optimized Inspectr200-200:

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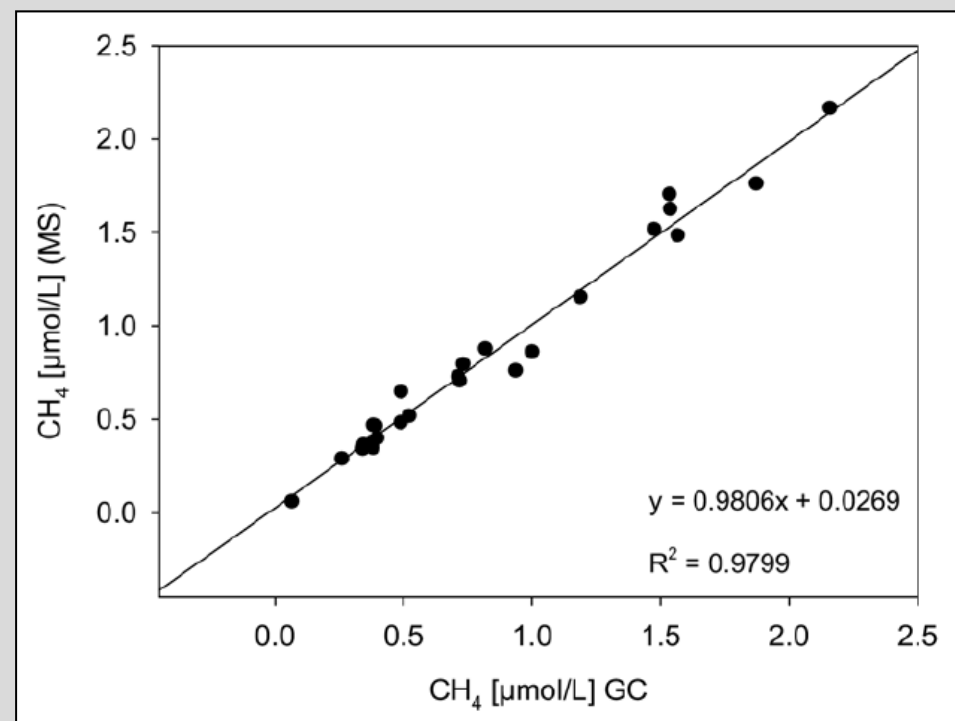


## COMPARISON OF THE INSPECTR200-200 VS. CONVENTIONAL TECHNIQUES



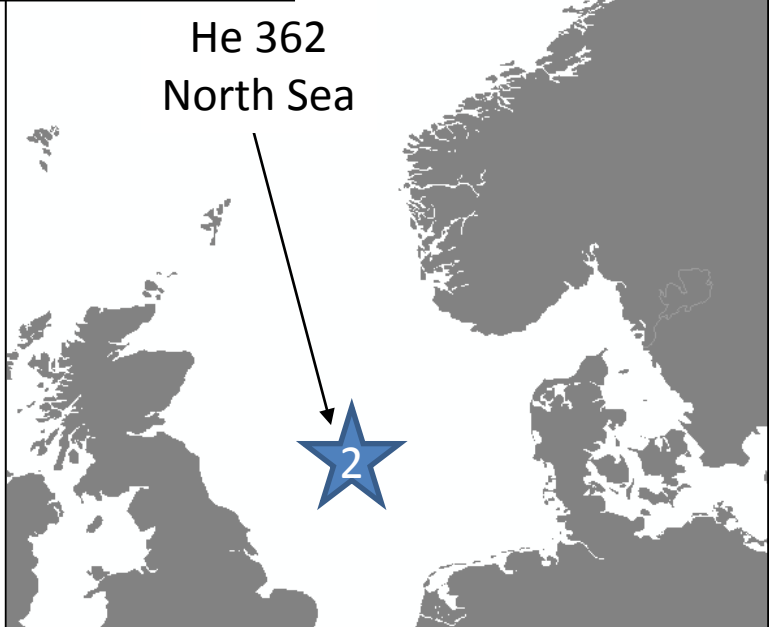
- Both methods are comparable
- No sampling preparation
- Simultaneous measurement of the dissolved gases
- No artefacts during sampling
- Up to 750 times higher sampling frequency

→ Higher temporal and spatial resolution



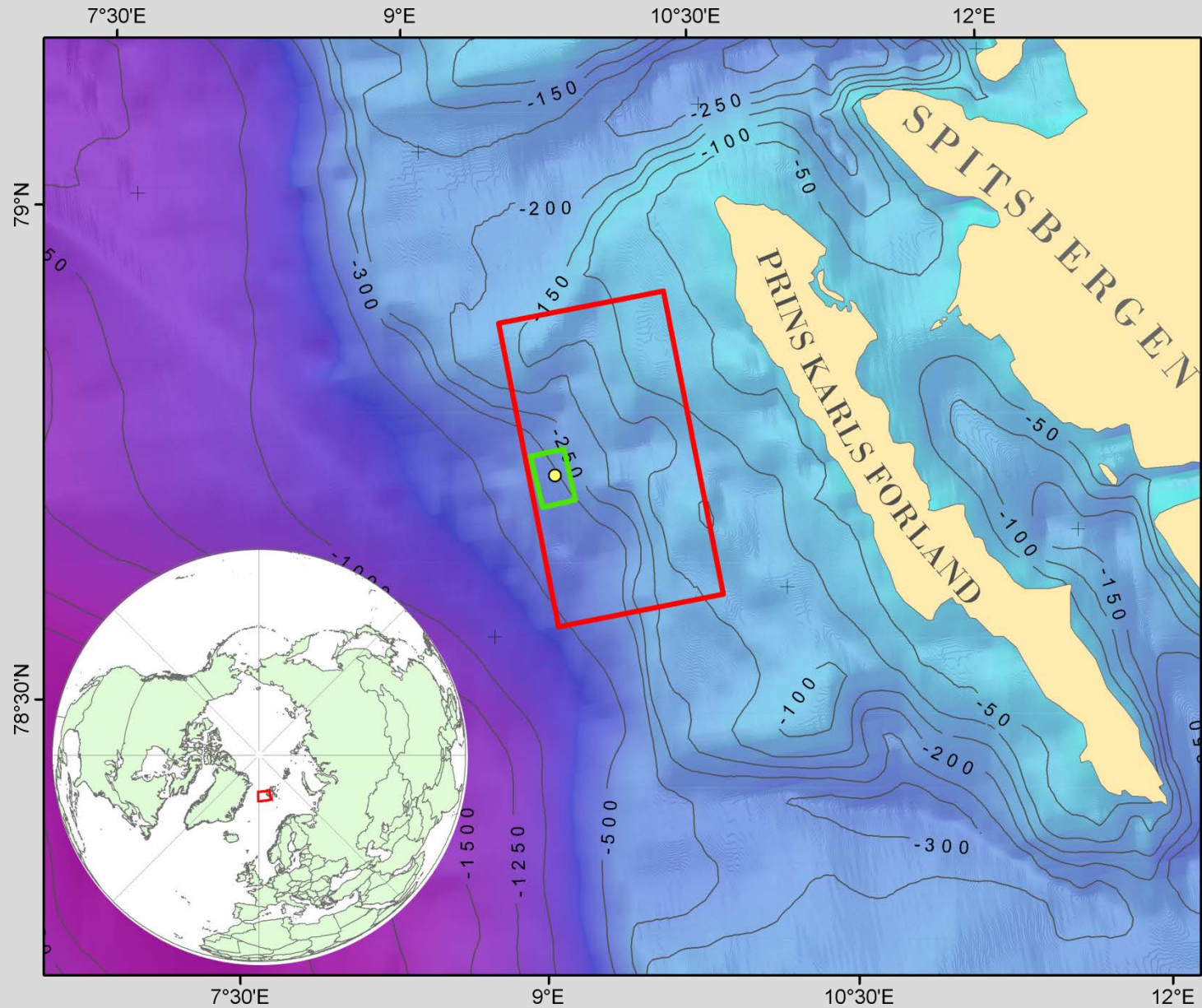
Inspectr200-200 vs. GC

# APPLICATION OF THE IN SITU MASS SPECTROMETER IN HARSH ENVIRONMENTS



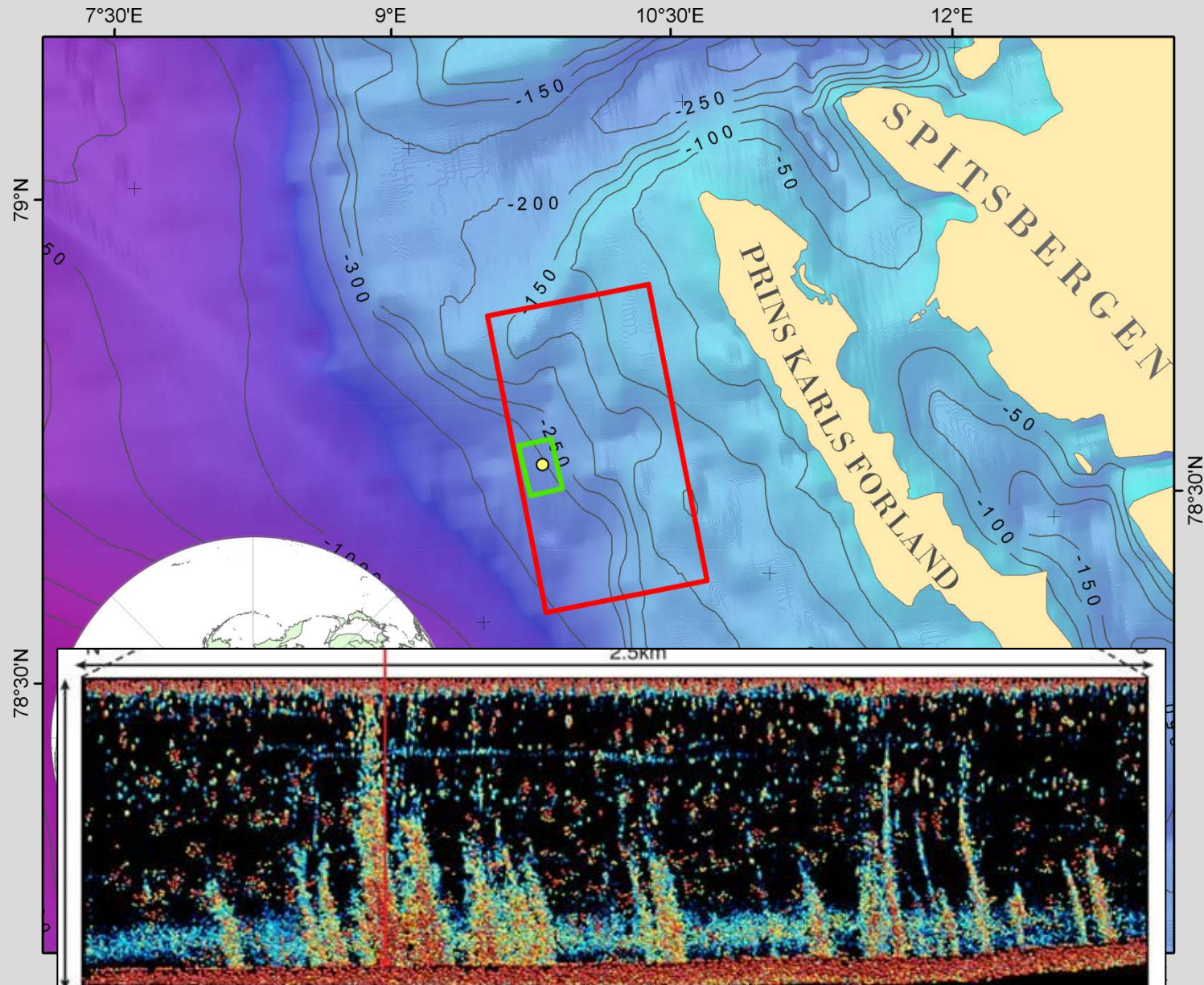


# STUDY AREA SPITSBERGEN



(Gentz et al. in press)

## STUDY AREA SPITSBERGEN

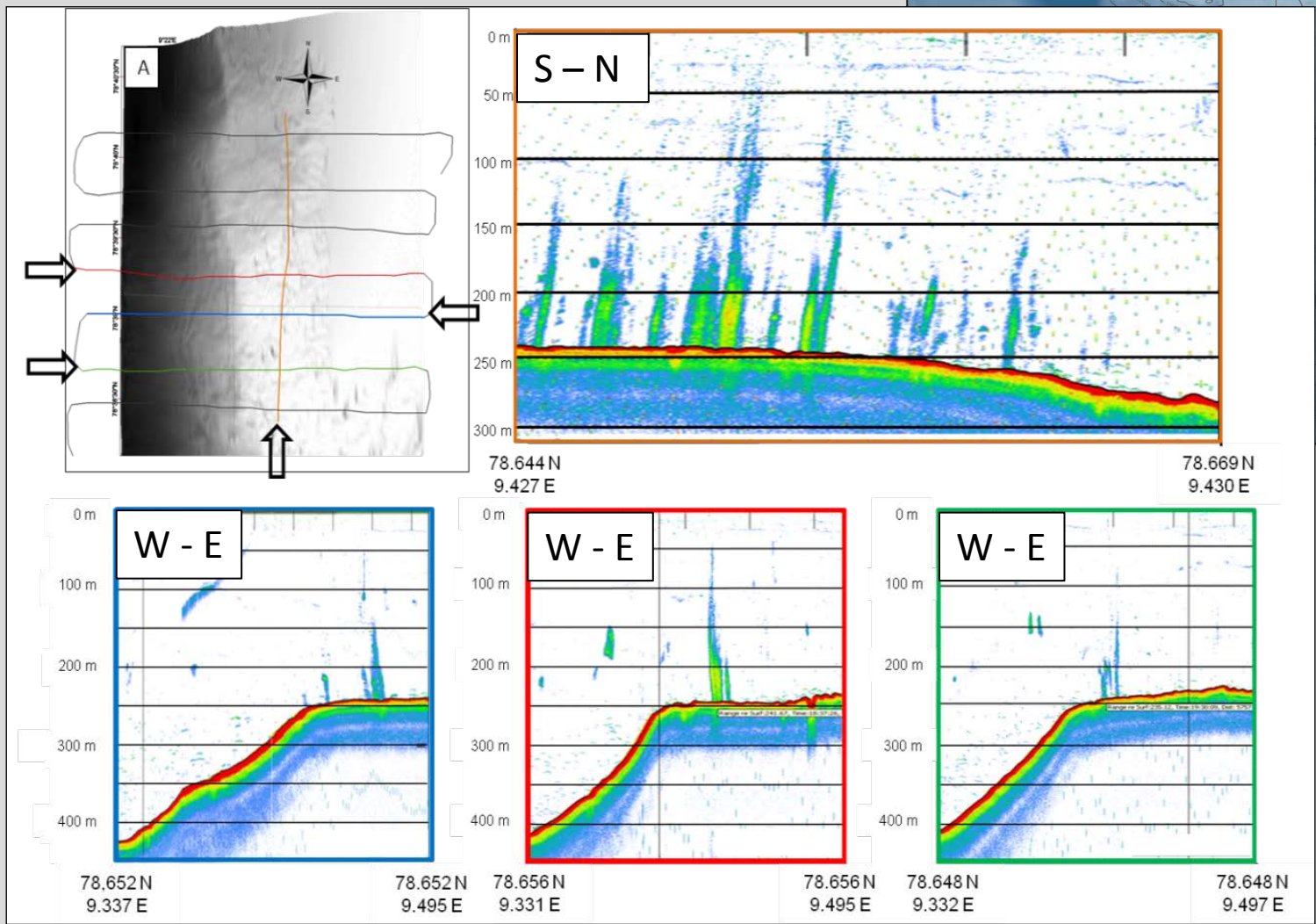
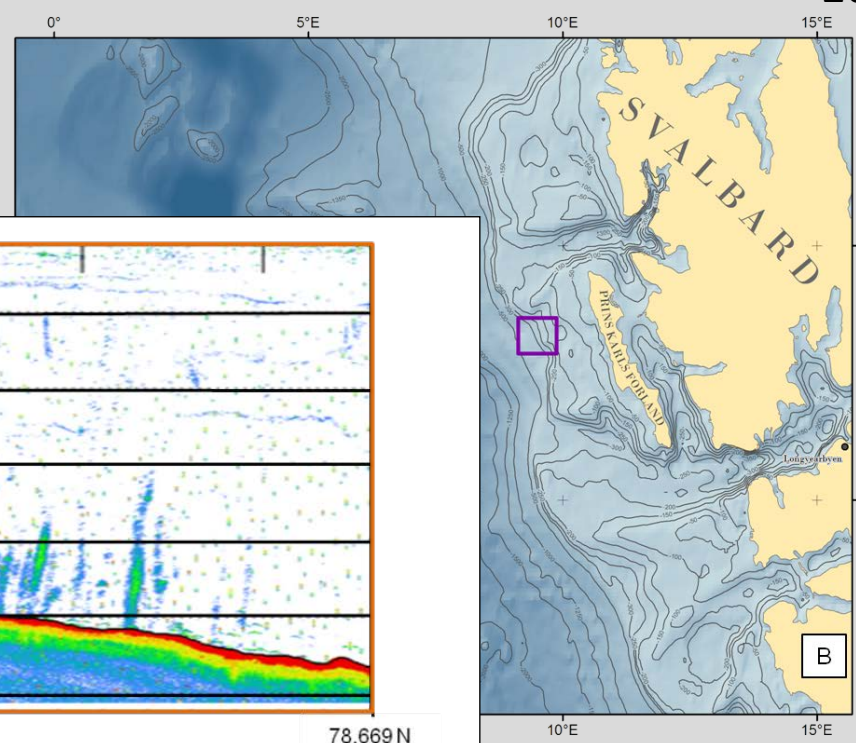


(Westbrook et al. 2009)



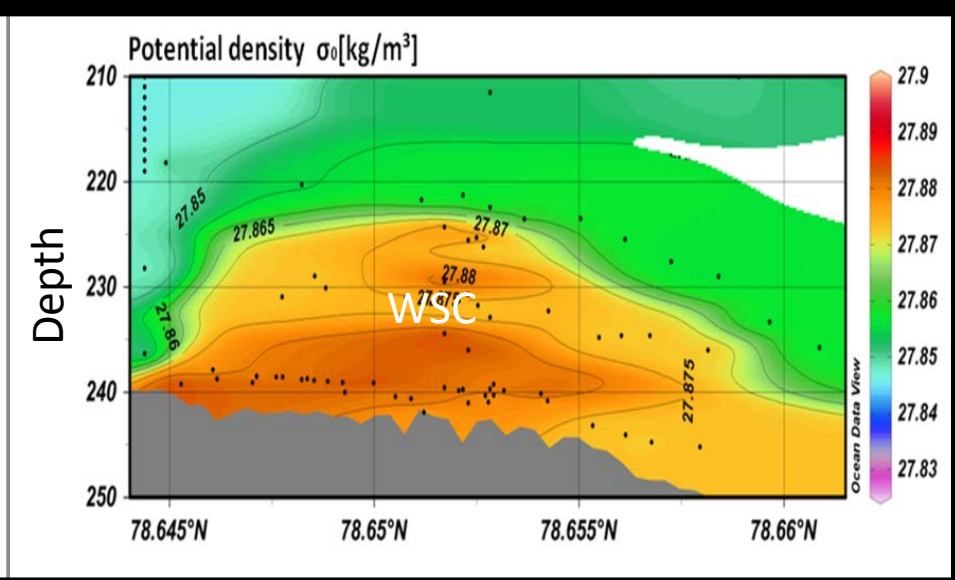
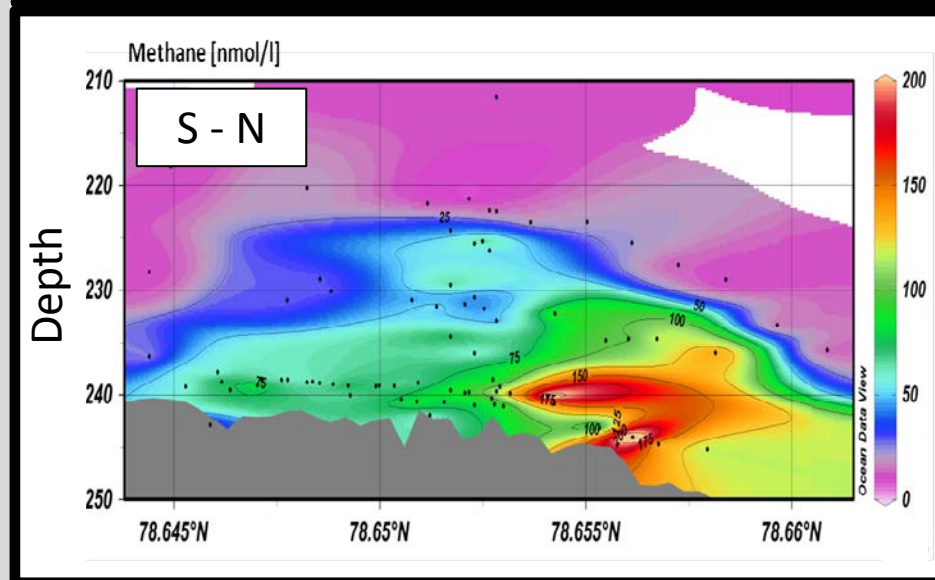
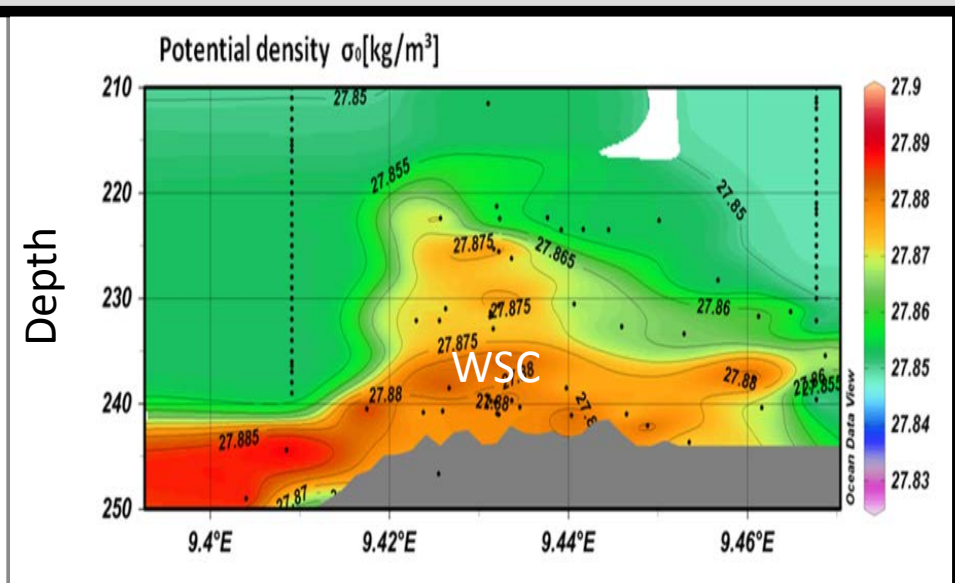
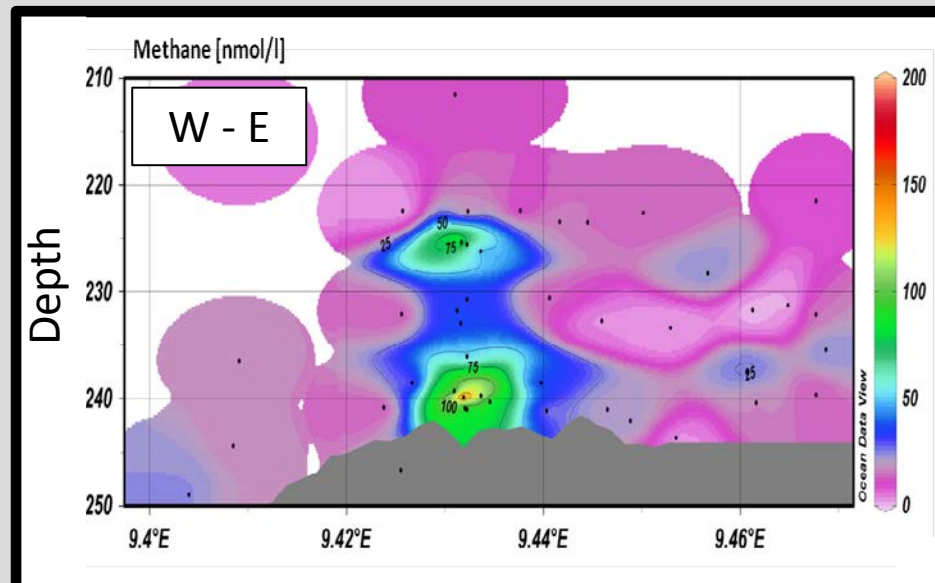
# HYDROACOUSTIC:

Ten gas flares lined up in S – N direction and max. rise height of up to 200 m were found.



(Gentz et al. in press)

## DISSOLVED METHANE AND HYDROGRAPHY

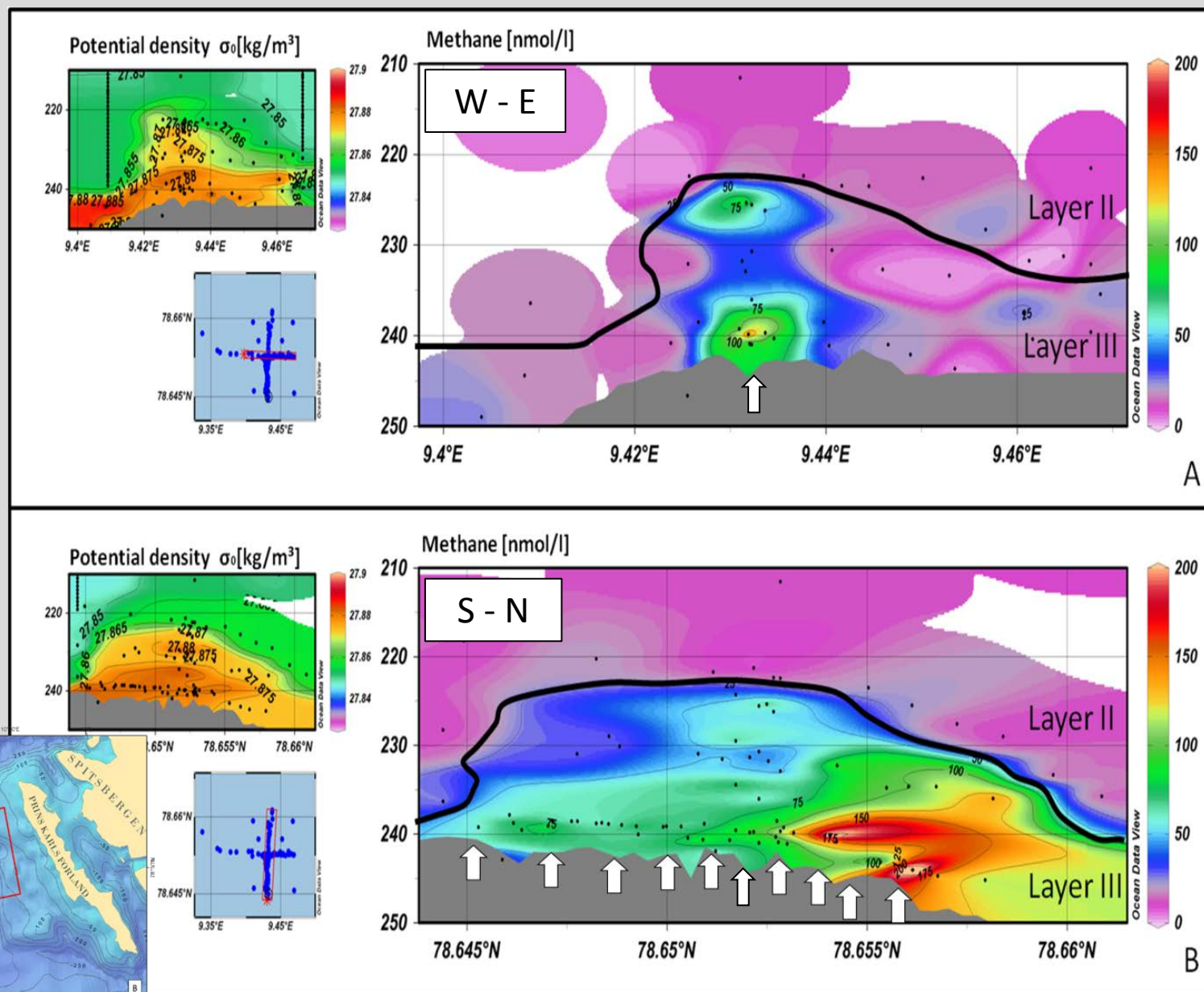


(Gentz et al. in press)

Graphic created by Ocean Data View  
 (R.Schlitzer, Ocean Data View, 2011, <http://odv.awi.de>)



## DISSOLVED METHANE AND HYDROGRAPHY

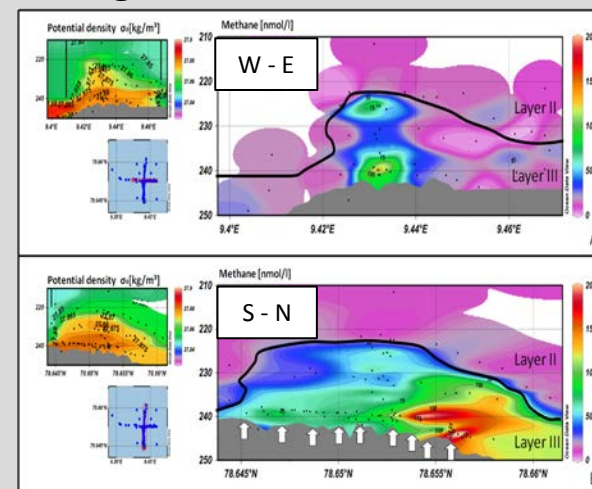


(Gentz et al. in press)

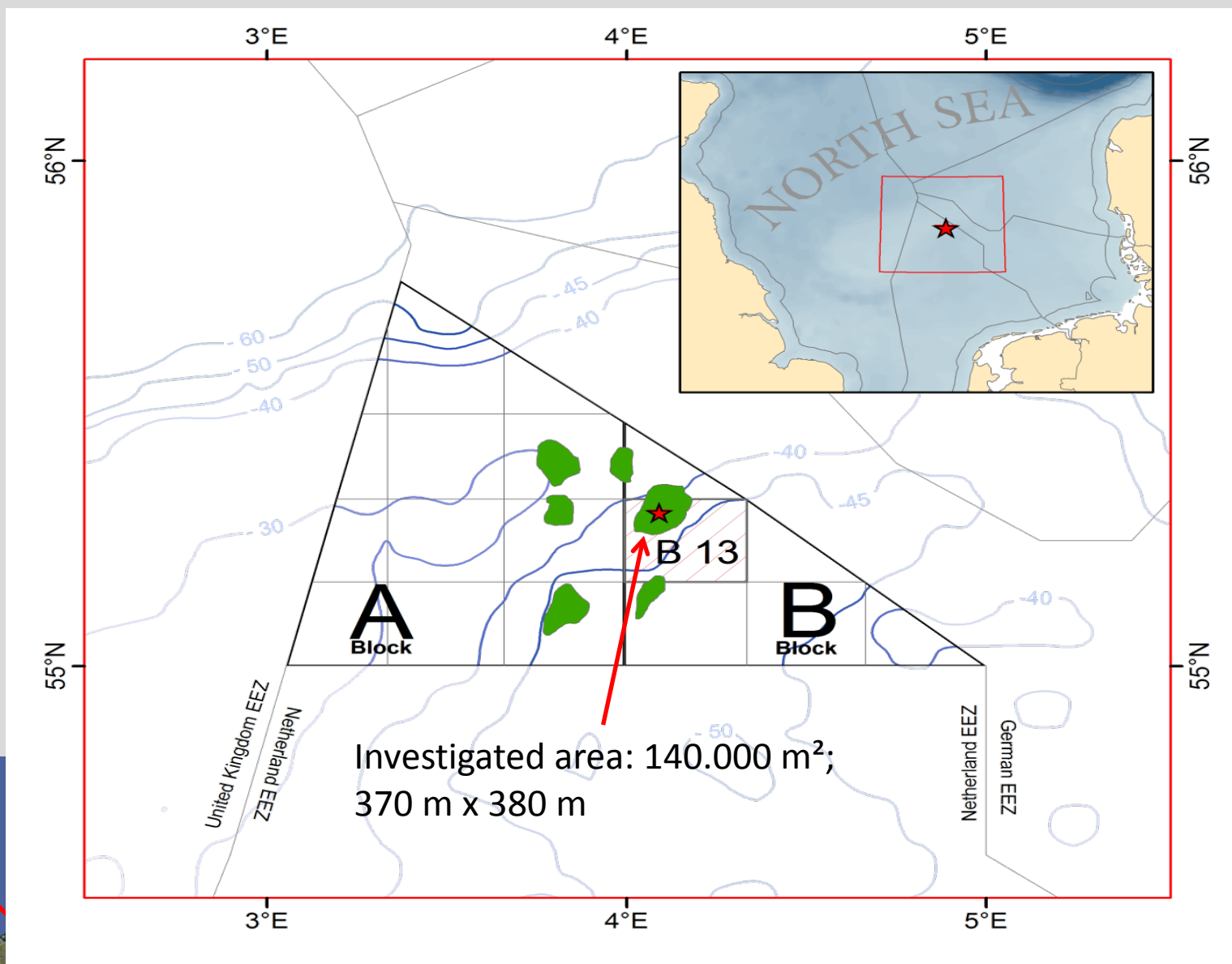
## MAIN RESULTS SPITSBERGEN

The pycnocline is a strong limitation for the vertical transport of methane released at the Spitsbergen continental margin.

- ~80 % of the methane will be dissolved and trapped below the pycnocline and horizontal transport in north direction to greater depth and subsequent oxidation occur.
- ~20 % could reach the water mass above the pycnocline.
- Due to dilution of dissolved methane in the upper water mass the contribution of the released methane to the global atmospheric methane budget could not be determined.
- Bubble transport can be excluded as direct pathway for methane to the atmosphere.
- In winter the stratification breaks down which could lead to methane release into the atmosphere.

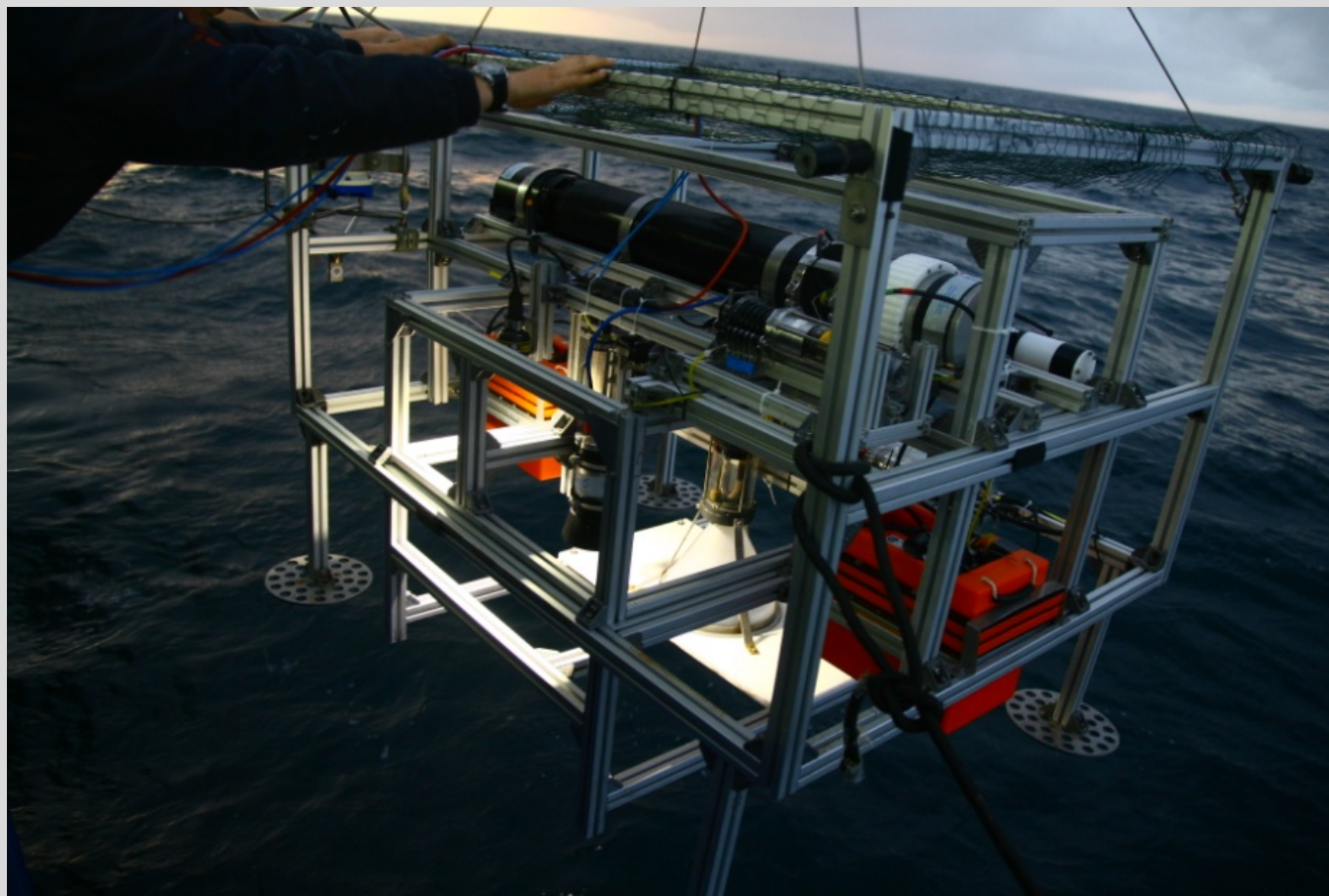


# OBSERVATION OF A GAS SEEP AREA IN THE NORTH SEA



Modified after Schroot et al. 2005

## OBSERVATION OF A GAS SEEP AREA IN THE NORTH SEA

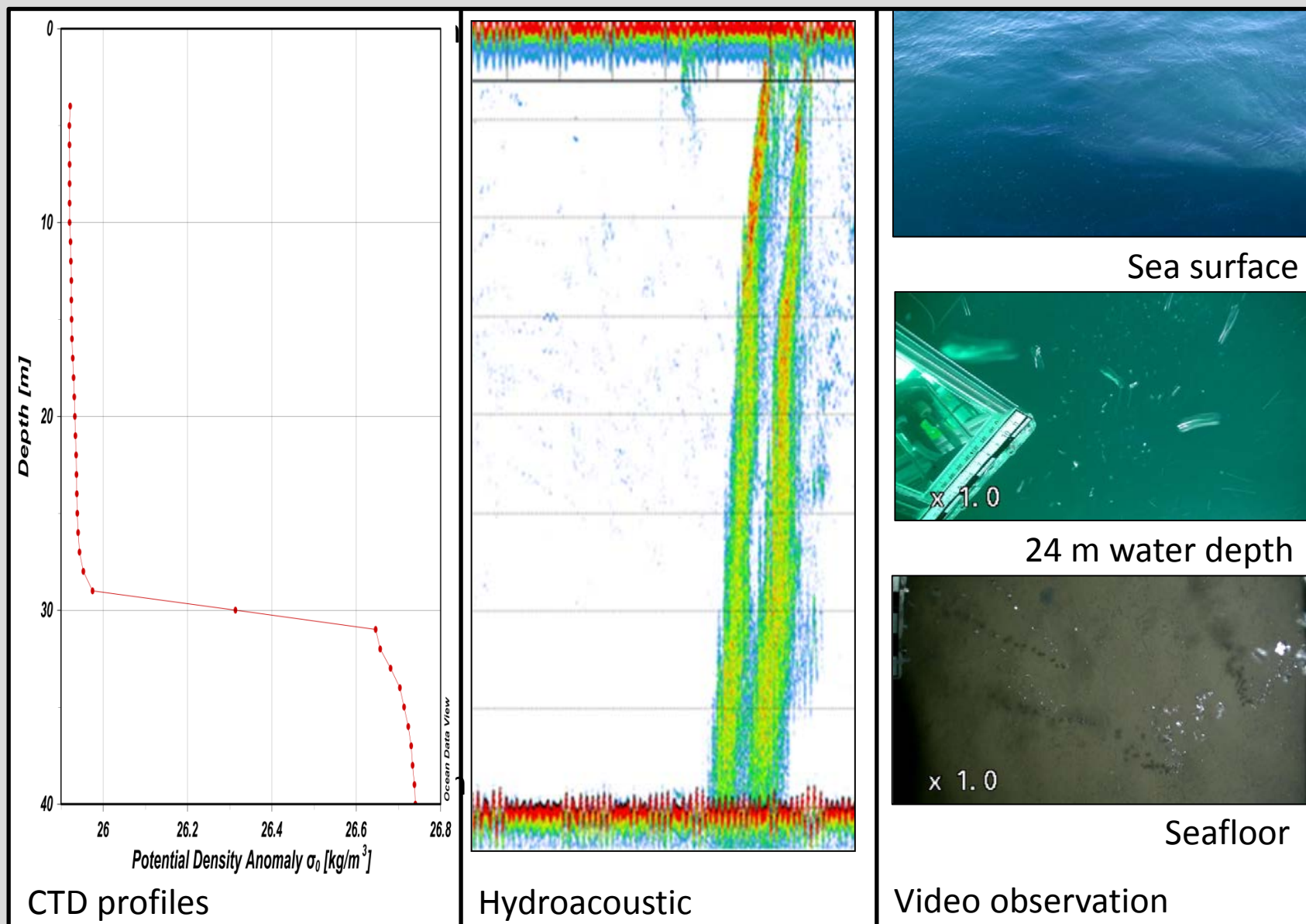


Under water gas analyser, sampler and observing system

- Inspectr200-200; 11900 samples
- GC; discrete 154 samples
- Video observation; 12 h
- Hydroacoustic; 12 h
- Multibeam; 140000 m<sup>2</sup>
- CTD 14; vertical profiles
- Bubble sampler; 5 samples
- Multiple sediment corer; 5 cores

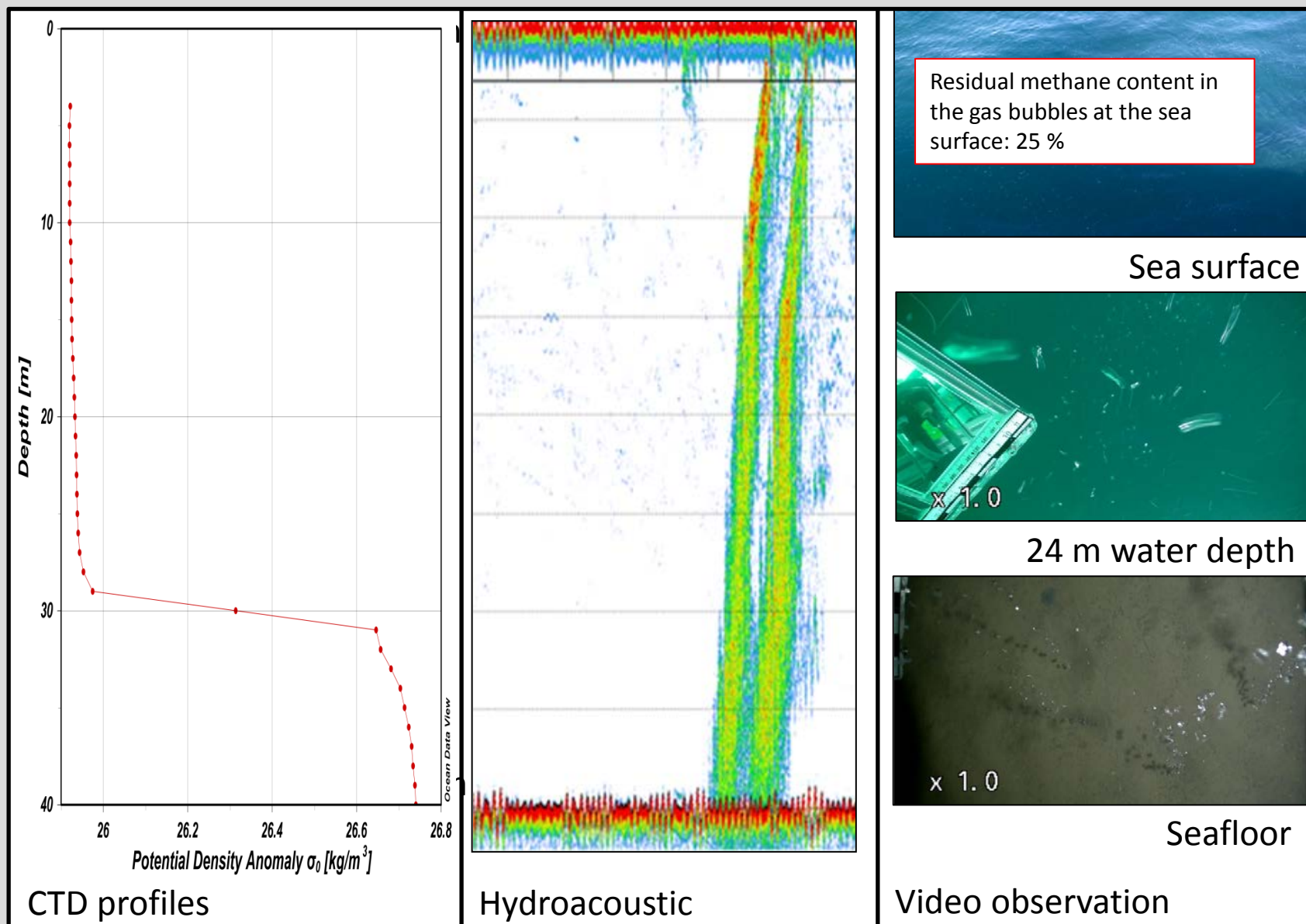


## OBSERVATION OF A GAS SEEP AREA IN THE NORTH SEA



(Gentz et al. unpublished data)

## OBSERVATION OF A GAS SEEP AREA IN THE NORTH SEA



Residual methane content in the gas bubbles at the sea surface: 25 %

Sea surface

x 1.0

24 m water depth

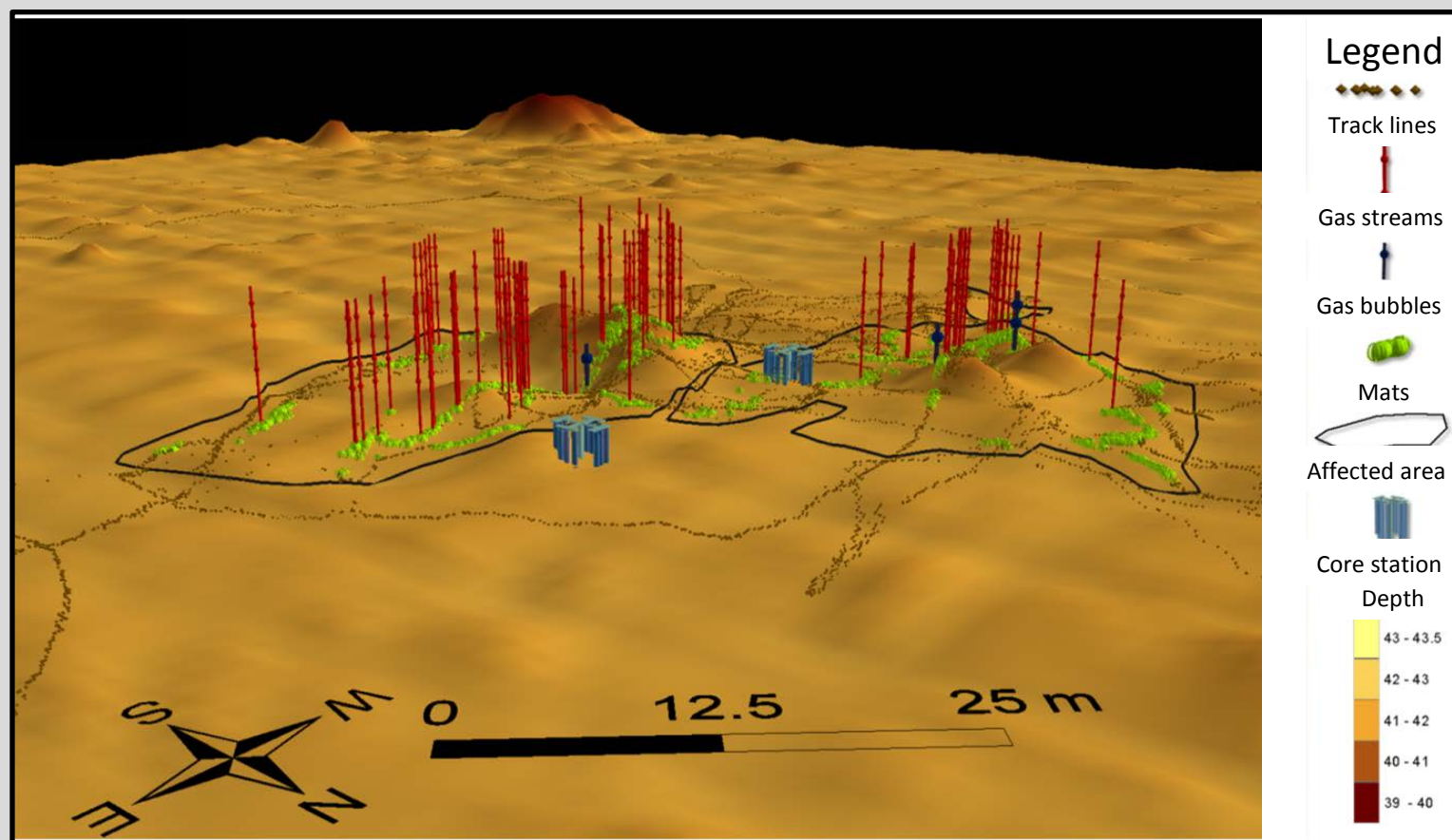
x 1.0

Seafloor

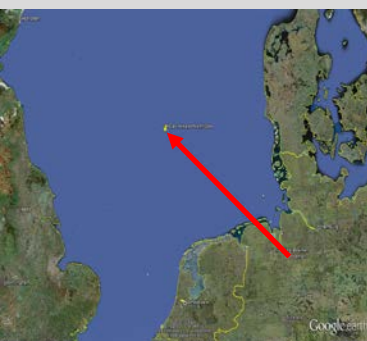
Video observation

(Gentz et al. unpublished data)

## VIDEO OBSERVATION OF THE SEAFLOOR



(Gentz et al. unpublished data)

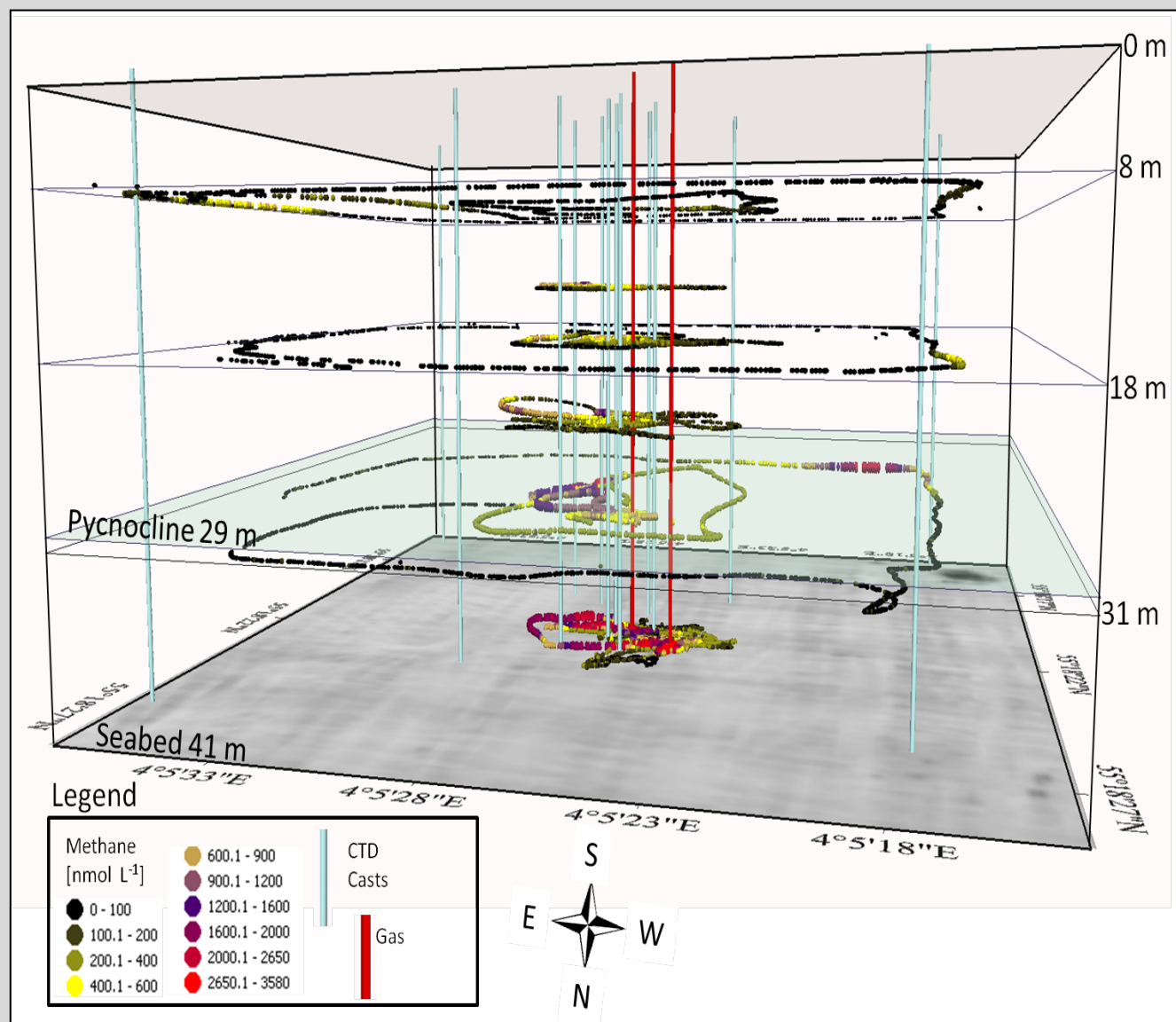
Affected area:  $\sim 3800 \text{ m}^2$ 

Number of streams: 113

Bubble diameter: 4.5 to 16 mm (average 7 mm)

Release frequency:  $0.3 - 40 \text{ bubbles s}^{-1}$  (average  $23 \text{ bubbles s}^{-1}$ )Methane flux:  $28.27 \text{ L min}^{-1}$ Methane release:  $35.3 \pm 17.65 \text{ t CH}_4 \text{ yr}^{-1}$

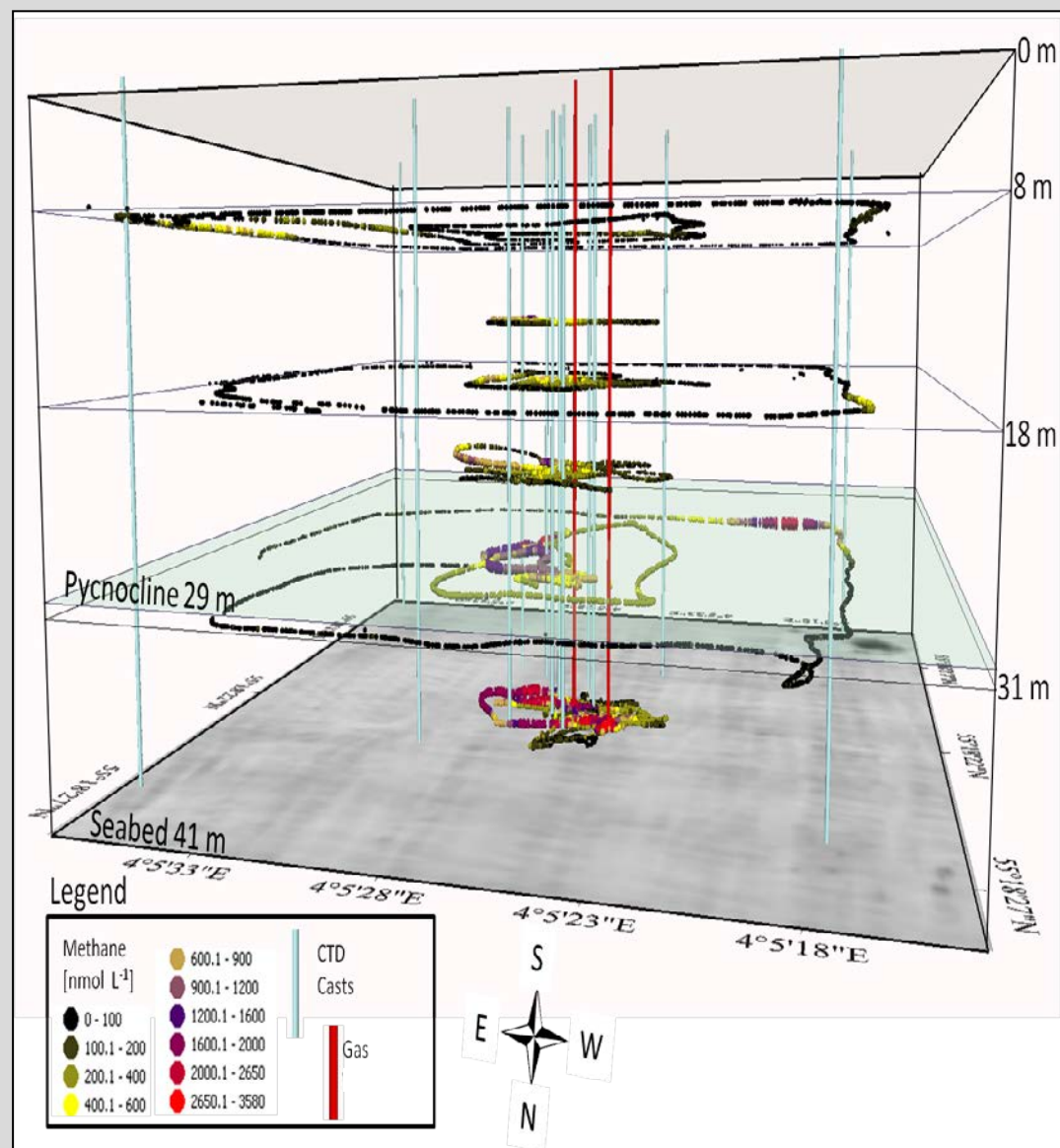
## DISSOLVED METHANE SAMPLING IN THE WATER COLUMN



11900 samples in various depth in between 24 hours

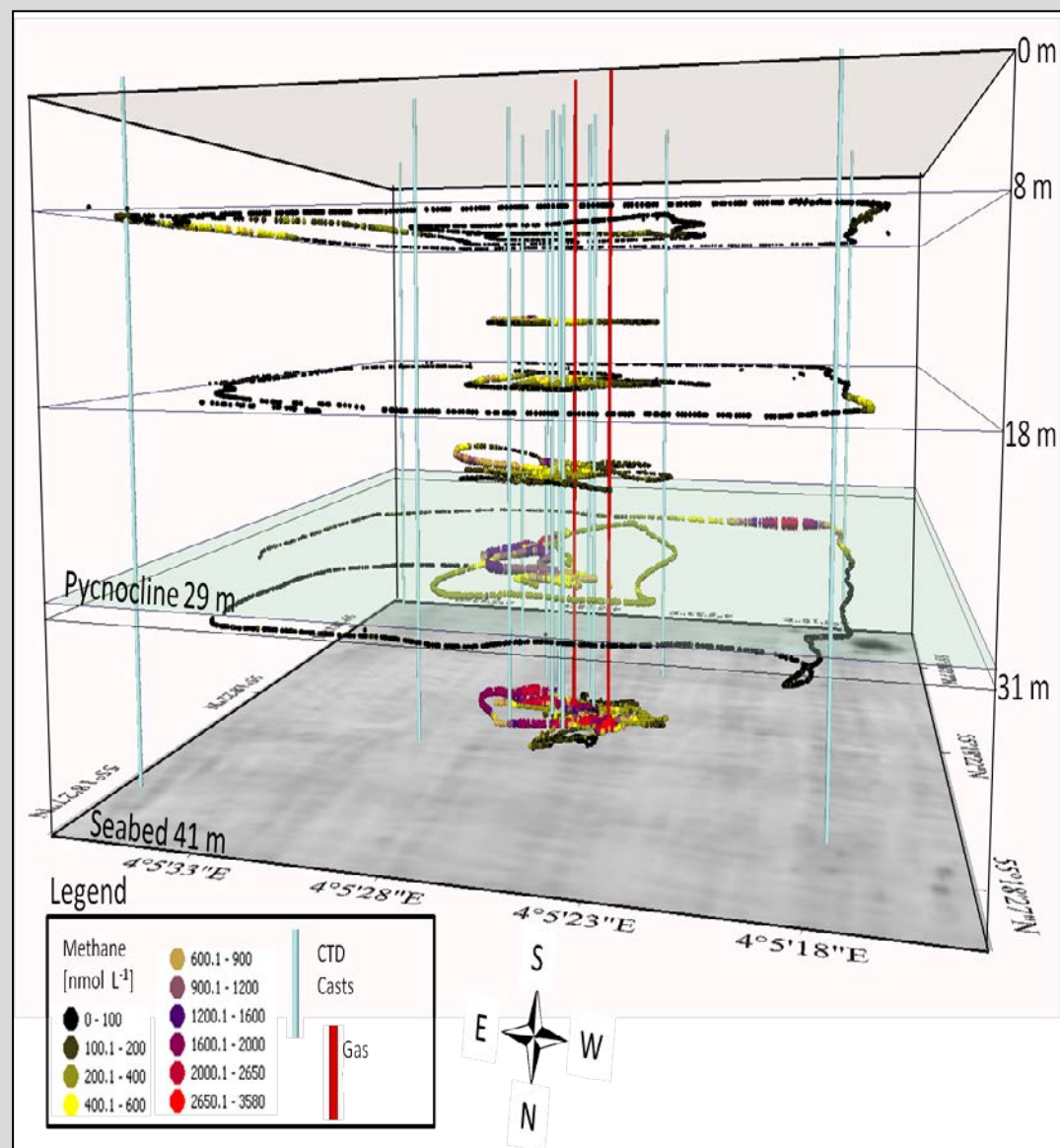


## DISSOLVED METHANE SAMPLING IN THE WATER COLUMN



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

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### Entire interpolated inventory of methane (6.410.000 m<sup>3</sup>):

$\sim 0.6 \text{ mol CH}_4$

- $\sim 1.000.000 \text{ m}^3$  ( 15.6 %) contain concentrations higher than 200 nmol L<sup>-1</sup>
- 40 % of initial methane is dissolved above the pycnocline.

## MAIN RESULTS NORTH SEA

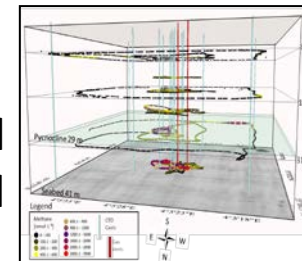
- Conservative estimation of methane release into the water column:  $35.3 \pm 17.65 \text{ t CH}_4 \text{ yr}^{-1}$  which is in the same order like the geographically close Tommeliten area (Schneider von Deimling et al. 2011).
- The total inventory of dissolved methane is calculated to  $\sim 0.6 \text{ mol}$ .
- The pycnocline is a limitation for the vertical transport of methane like at the Spitsbergen continental margin but only 35 % of the methane will be dissolved below the pycnocline.
- 40 % of the dissolved methane reaches the water mass above the pycnocline and could indirectly contribute to the atmospheric methane budget.
- 25 % of the released methane reaches the atmosphere via gas bubbles.
- In total 65 % ( $23 \pm 11.5 \text{ t CH}_4 \text{ y}^{-1}$ ) of the released methane potentially reach the atmosphere, which is high compared to the Spitsbergen continental margin or the Tommeliten area.

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

## CONCLUSIONS

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

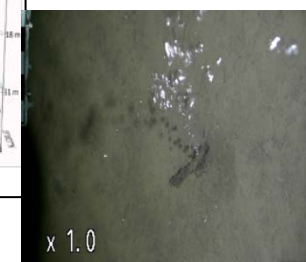
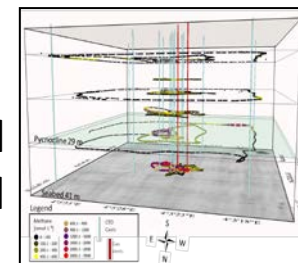
- The inventory calculation is more accurate than before and shows that conventional methods tend toward underestimation.



## CONCLUSIONS

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

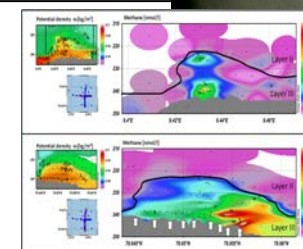
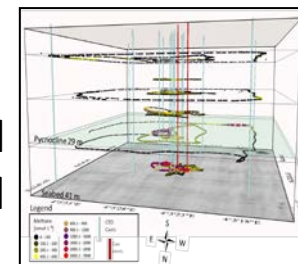
- The inventory calculation is more accurate than before and shows that conventional methods tend toward underestimation.
- The investigated study area in the North Sea contributes to the global atmospheric methane budget.



## CONCLUSIONS

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

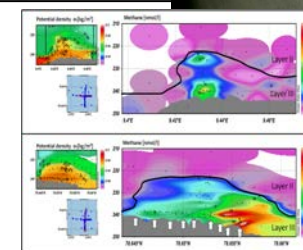
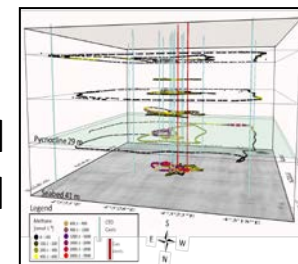
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## CONCLUSIONS

# 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.
- Pycnoclines are limitations for vertical transport of methane.
- 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.



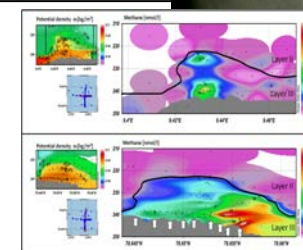
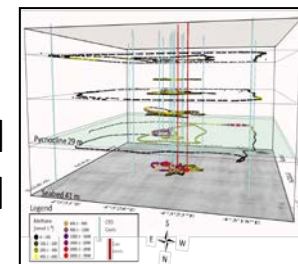
	Spitsbergen	North Sea
Water depth [m]	245	40
Water stratification [m above seafloor]	25	10
Observed bubble rise [m above seafloor]	150	40
Estimated bubble diameter [mm]	< 5	7
Bubbles at seasurface	No	Yes
Direct methane transport	No	Yes
indirect transport	???	Yes
Methane to atmosphere [% from origin]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



## CONCLUSIONS

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

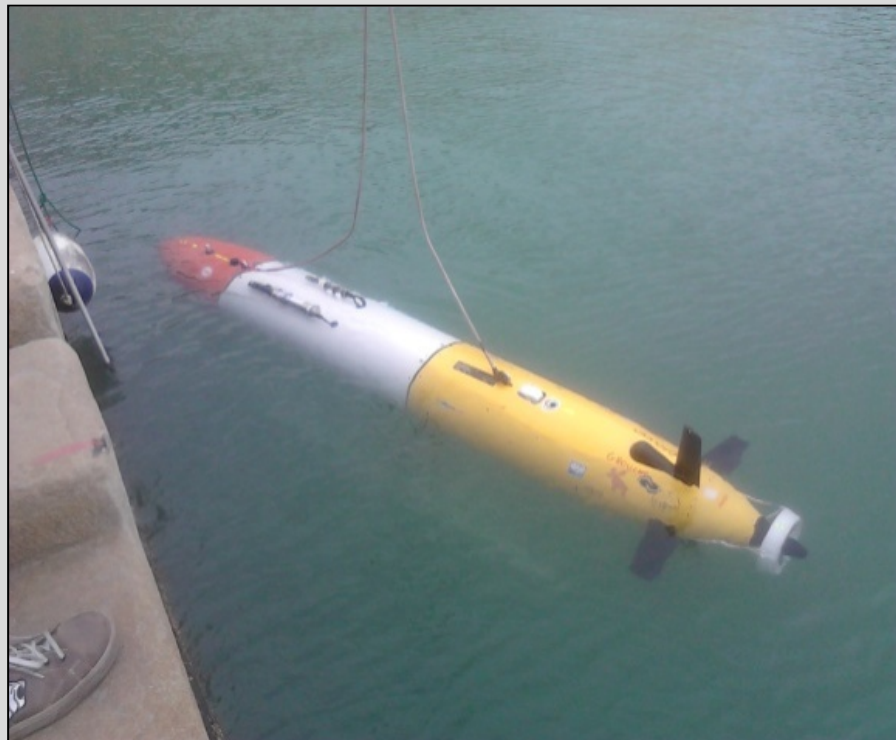
- The inventory calculation is more accurate than before and shows that conventional methods tend toward underestimation.
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- Pycnoclines are limitations for vertical transport of methane.
- The fate of methane as well as the contribution to the global atmospheric methane budget of each source depends on bubble size, the water depth, the water current and the water stratification.
- 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.



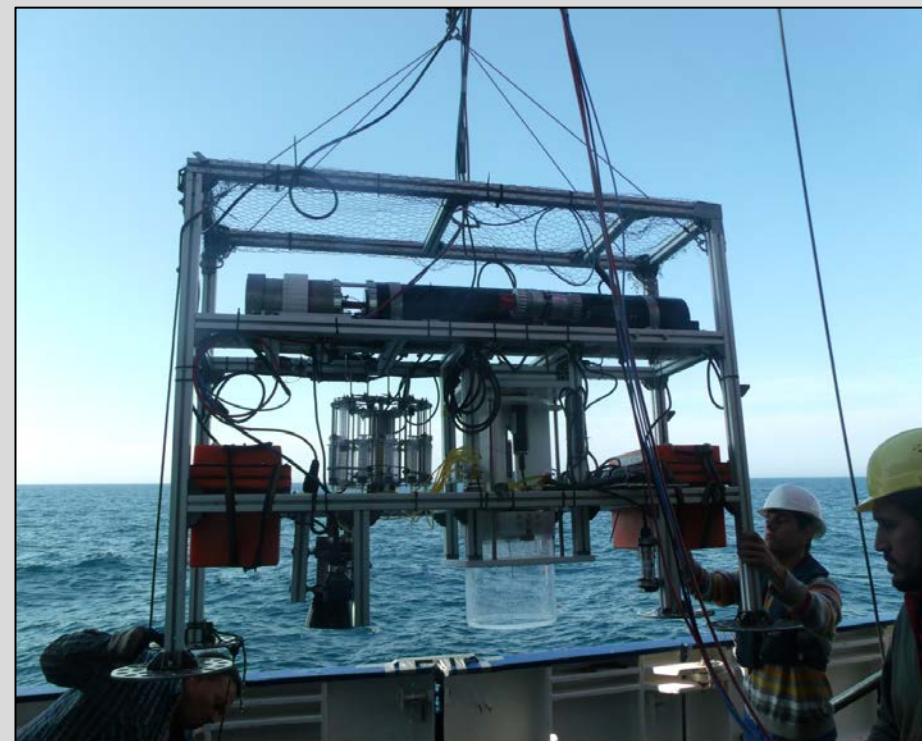
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# CURRENT AND FUTURE WORK



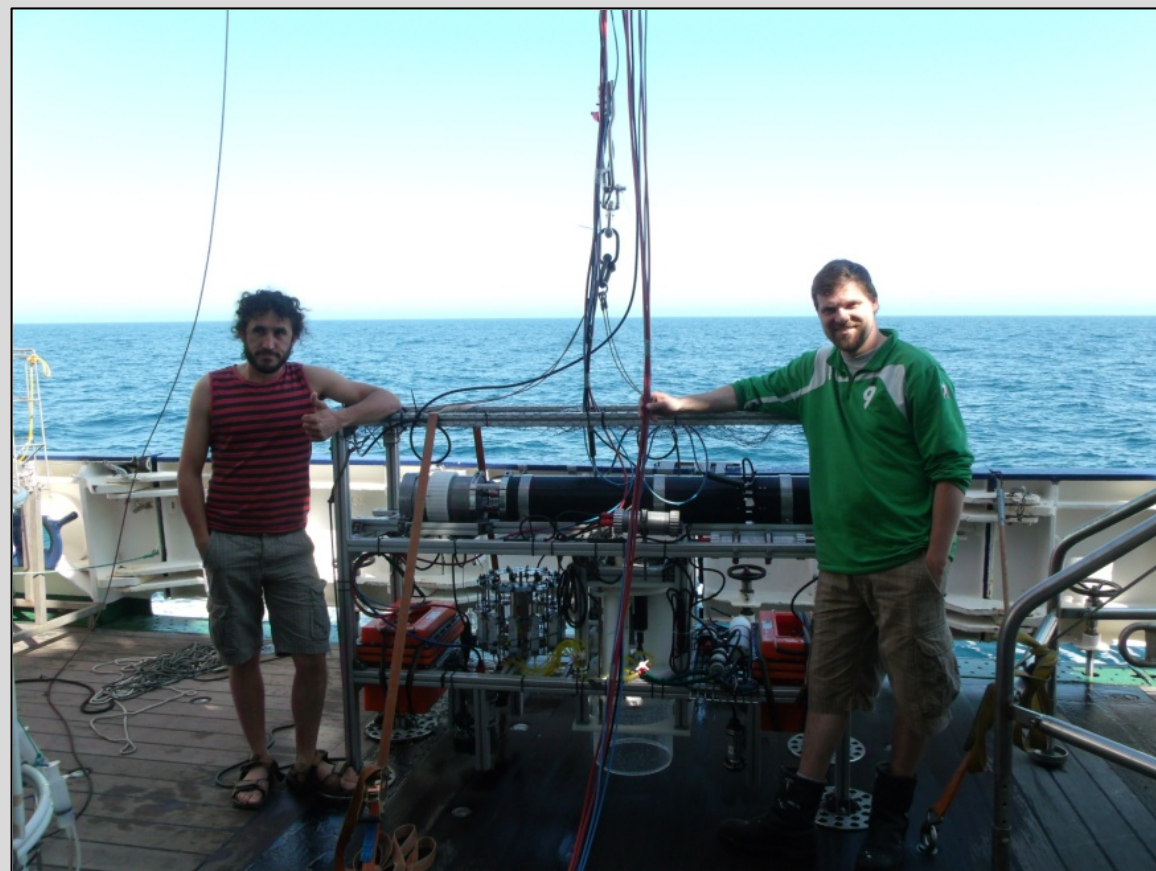
Implementation of the UWMS into an AUV



High resolution mapping of dissolved gases  
in a benthic chamber

# ACKNOWLEDGEMENTS

- Margot Isenbeck-Schröter
- Jan Hartmann
- Roi Martinez
- The captain and crew of the „Heincke“
- My Co-Authors



Thank you for your  
attention!





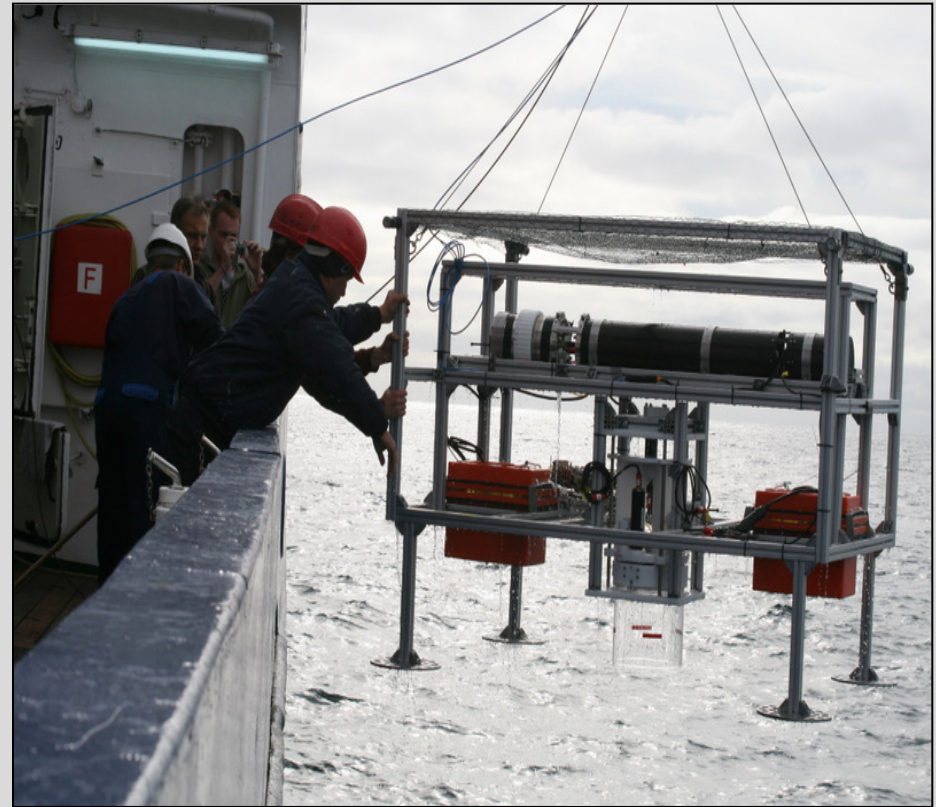
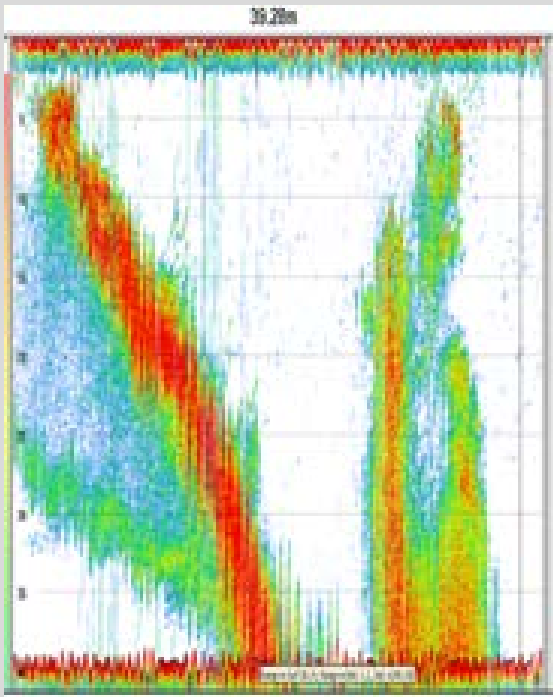
# Backup



## FUTURE WORK



Implementation in new device holder



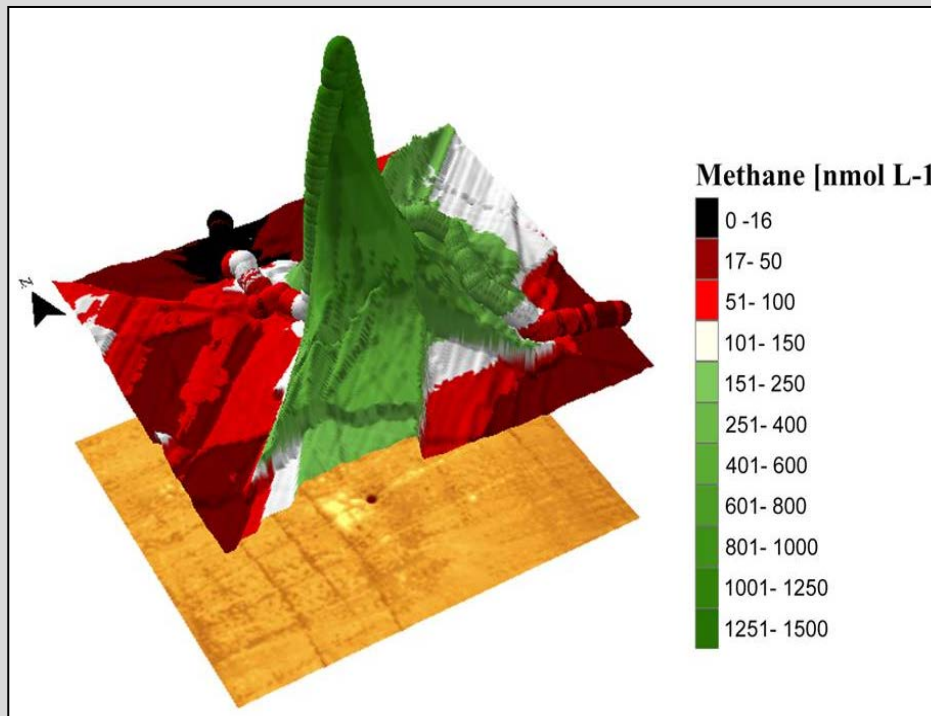
Benthic chamber measurements

Combining hydroacoustic with in situ mass spectrometry

## IN SITU MASS SPECTROMETER FOR FIELD APPLICATIONS

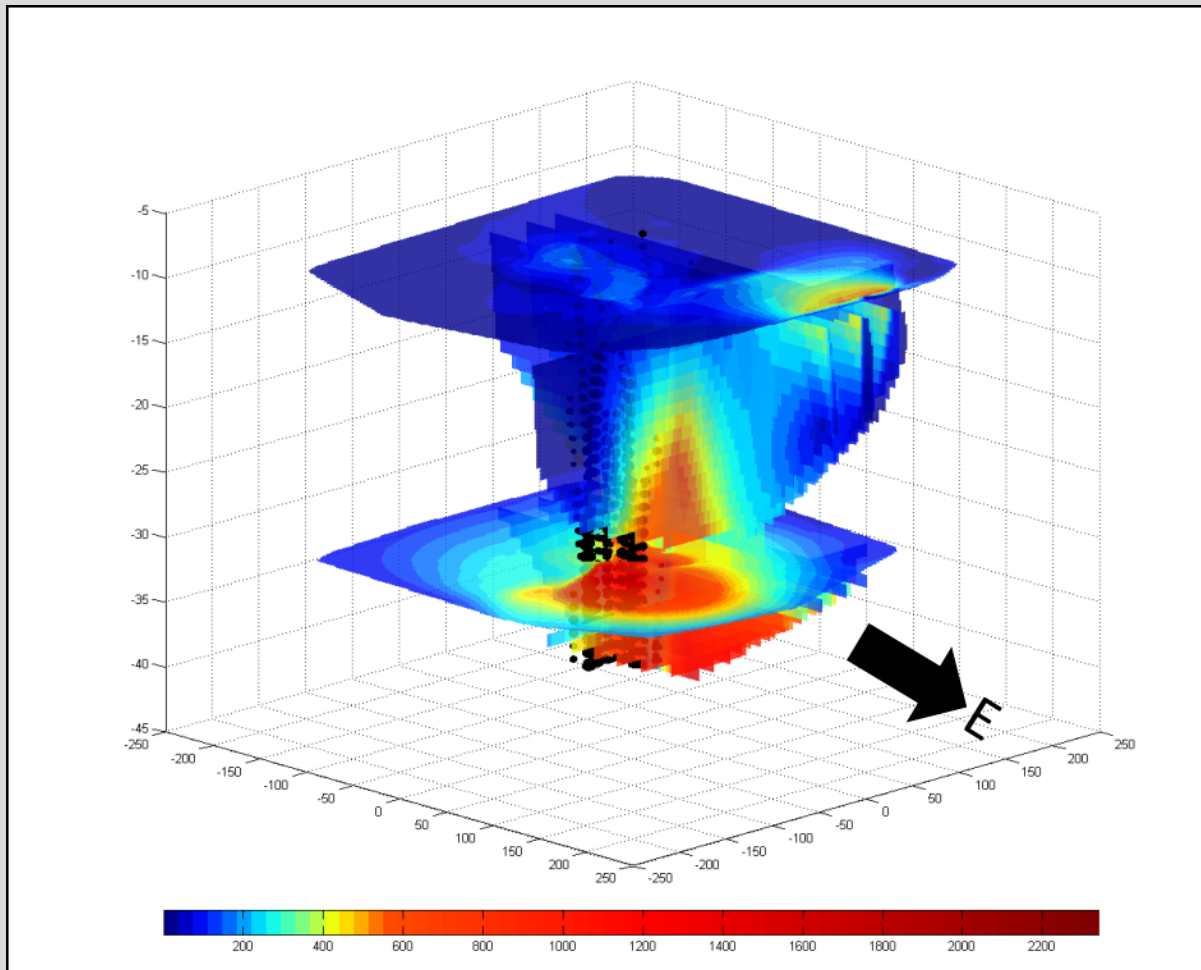
## Gas seep in the North Sea

without  
cryotrap:  
48.1 %



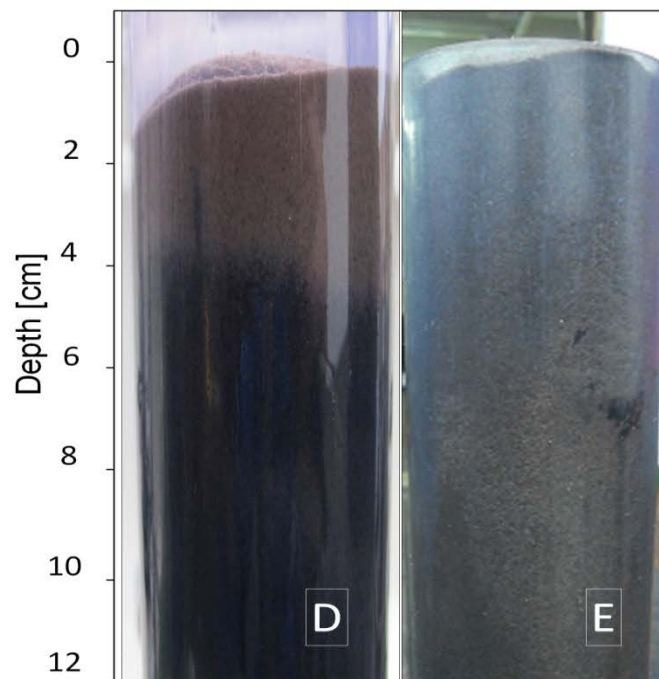
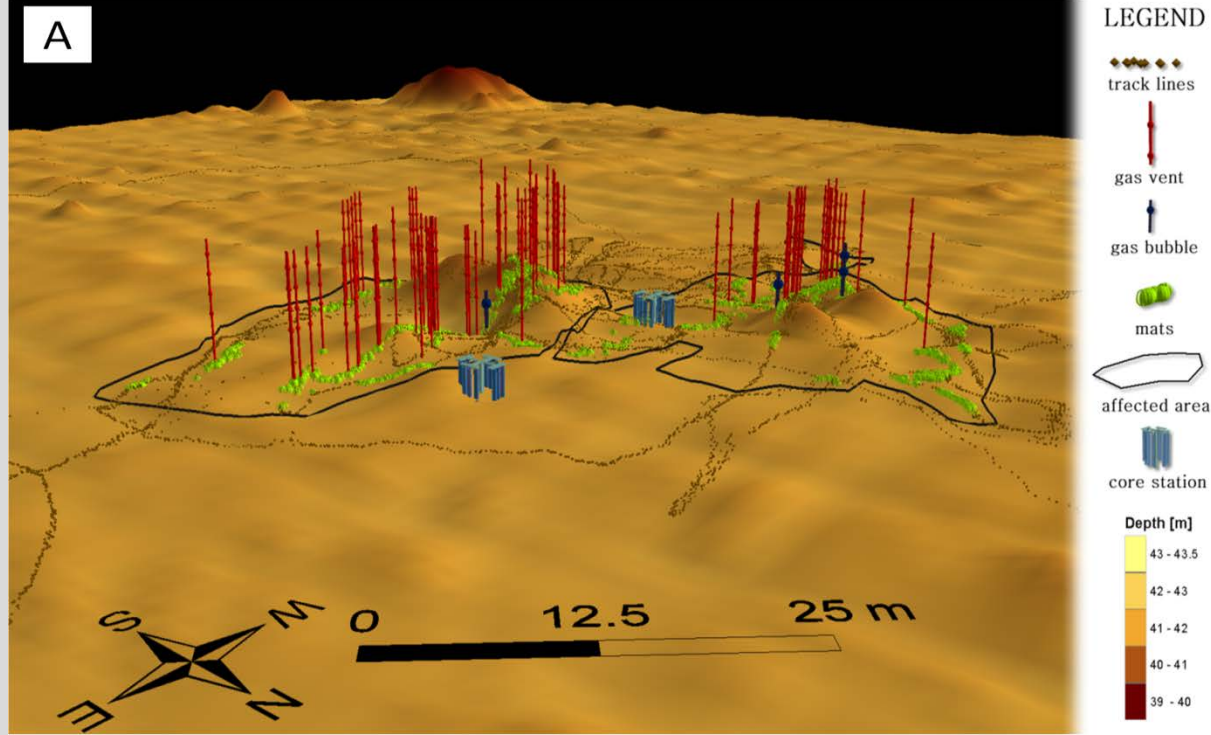
with  
cryotrap:  
96.4 %

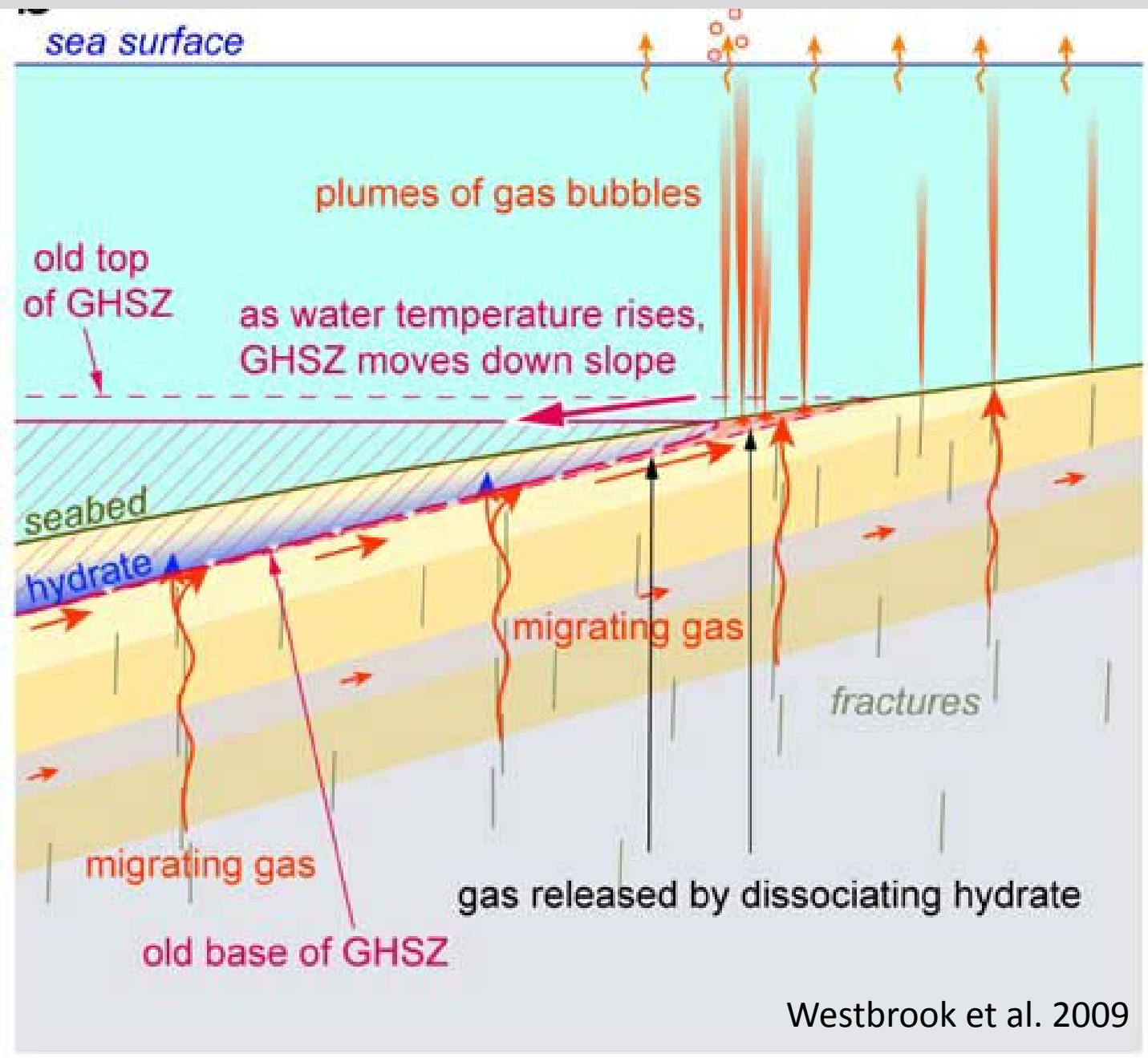
Concentration [nmol L <sup>-1</sup> ]	Area [%]
< 16	3.6
16 - 100	48.3
> 100	48.1



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



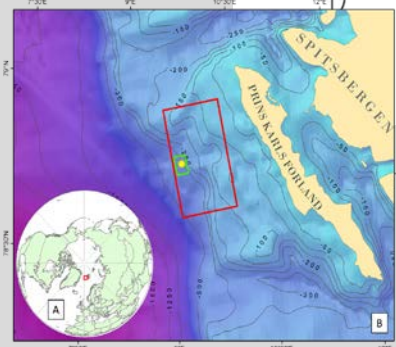
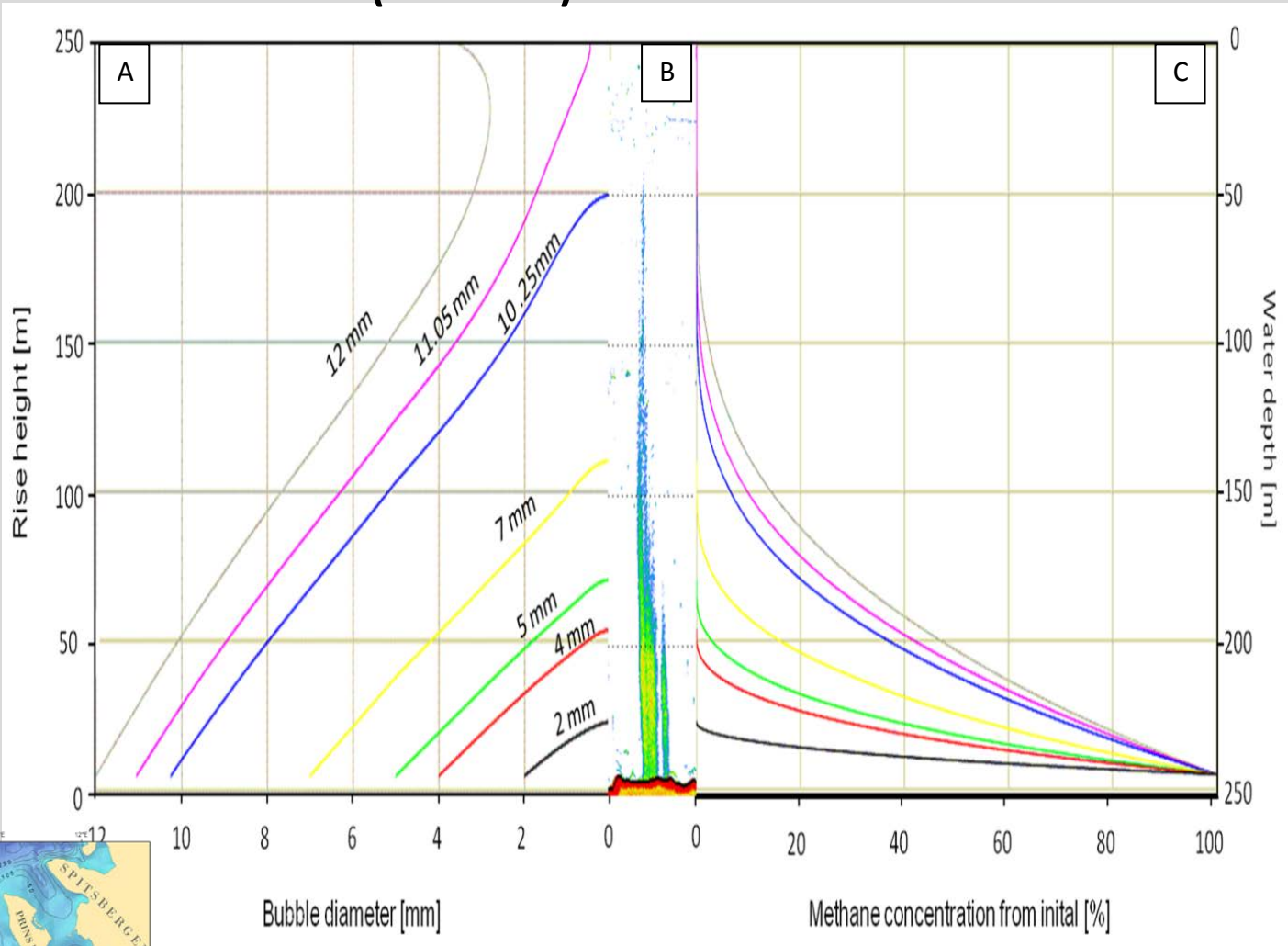




Westbrook et al. 2009

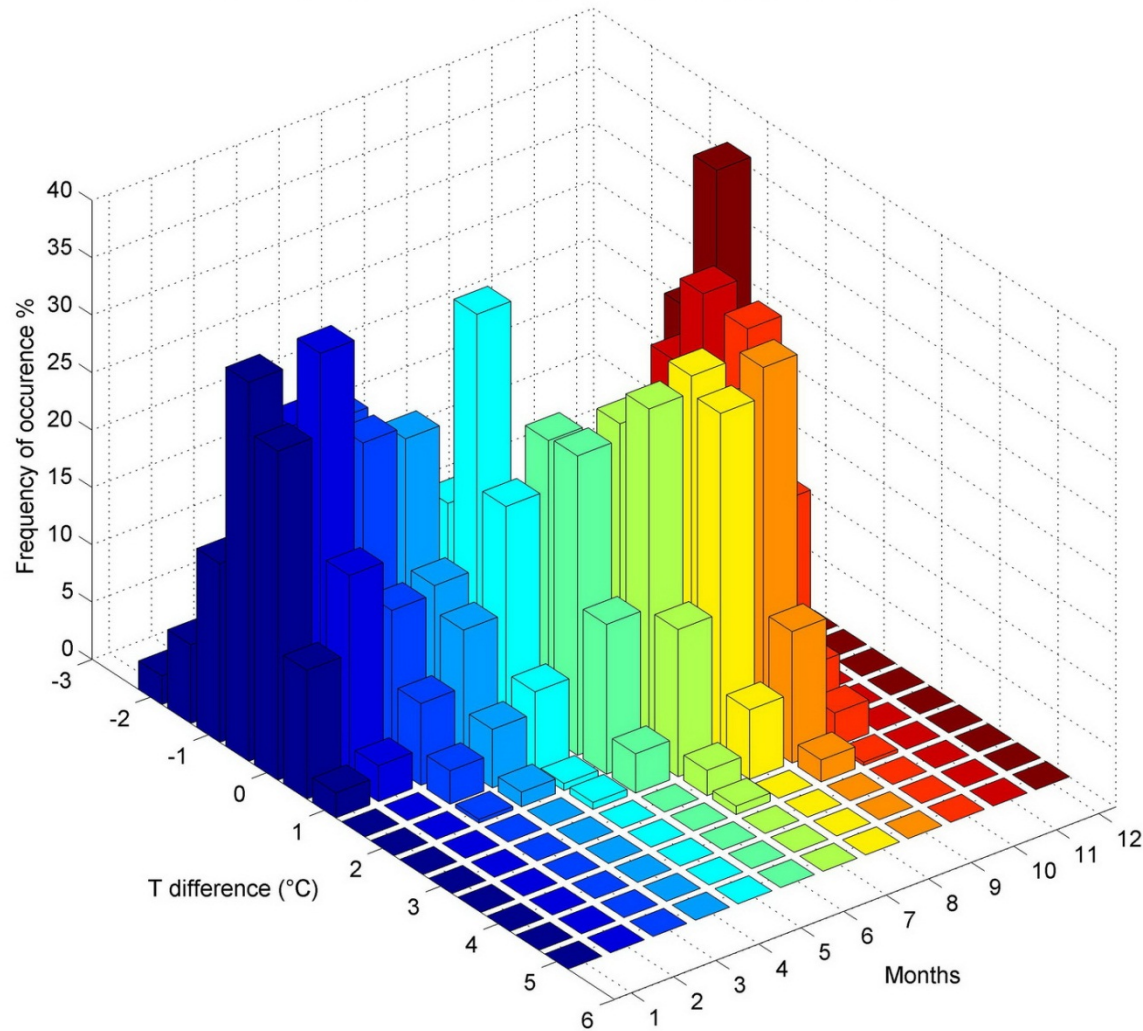


# GAS BUBBLE DISSOLUTION MODEL (SiBU GUI):

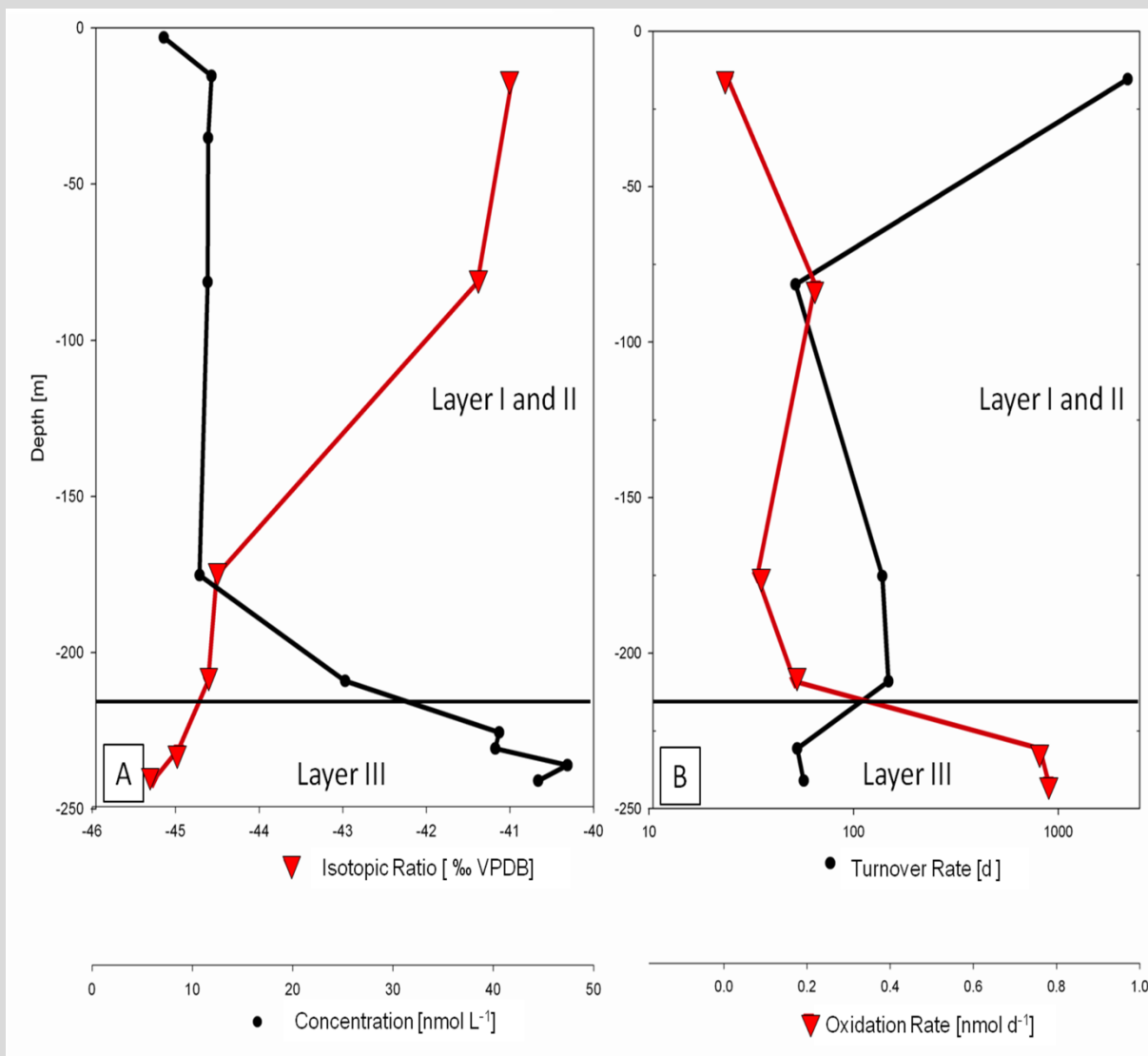


*Decrease of the bubble diameter during the ascend from the seafloor for initial bubbles sizes of 2 mm to 12 mm (A) compared with the hydroacoustic image of the highest detected gas flare (B). Decrease of the initial CH<sub>4</sub> concentration in the bubbles during their rise in the water column (C). Data obtained by the model SiBU GUI (Greiner, J. and D. F. McGinnis 2009) personally optimized by Dan McGinnis*

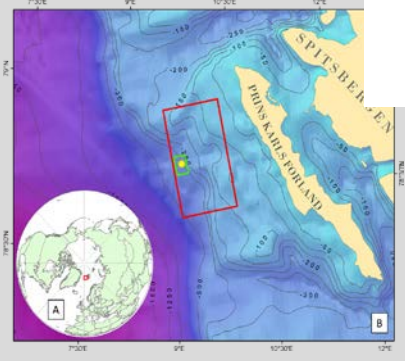
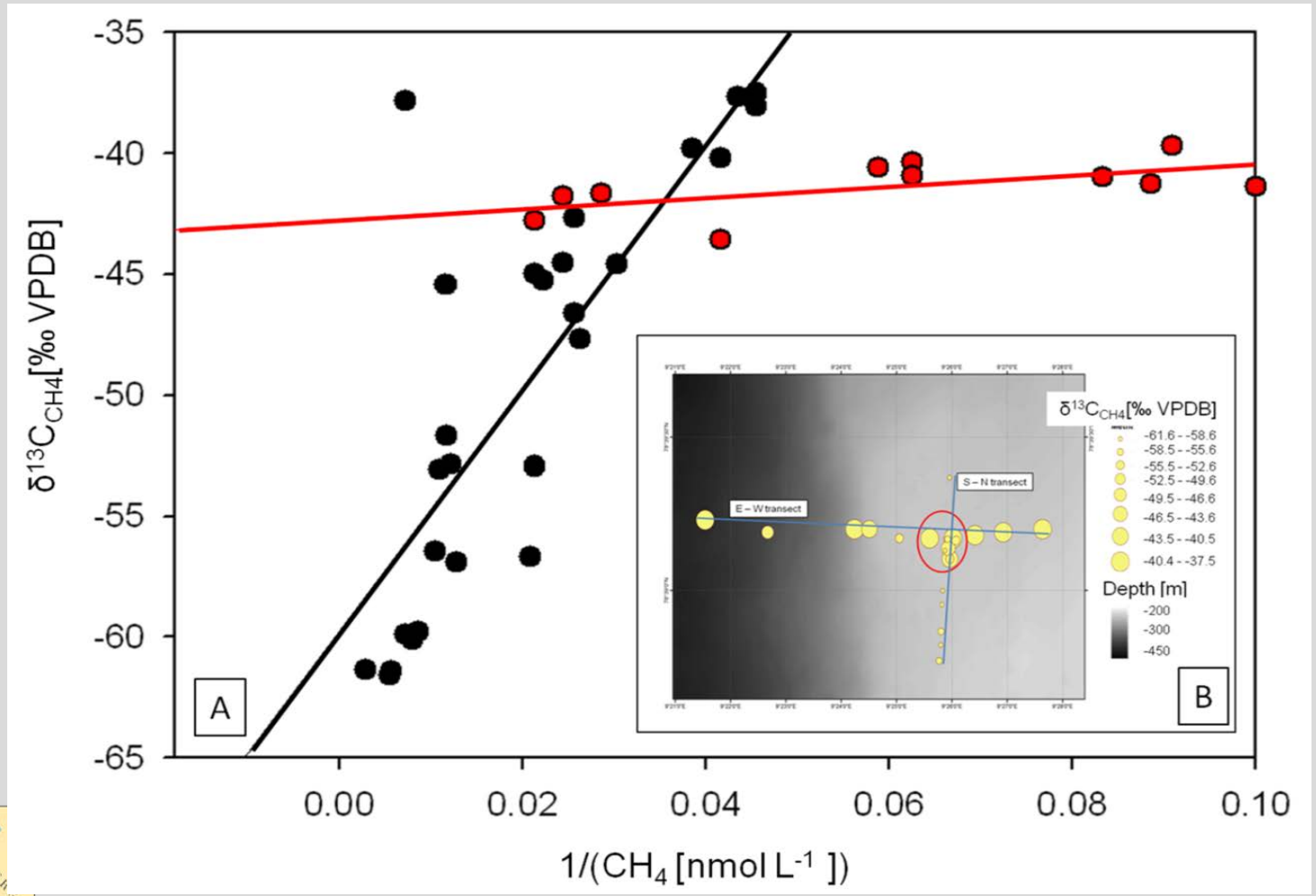
Monthly distributions of temperature differences between the subsurface (~50m) and near-bottom (~270m) layers at mooring F1 (78°50'N 8°40'E) in 1997-2010 based on daily averaged data



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







A) Inverse  $\text{CH}_4$  concentration versus  $\delta^{13}\text{C}_{\text{CH}_4}$  values (Keeling plot). Layer III is presented by black dots and Layer II and I by red dots.  
 (B) Distribution of  $\delta^{13}\text{C}_{\text{CH}_4}$  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

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

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

Leifer and Patro 2002

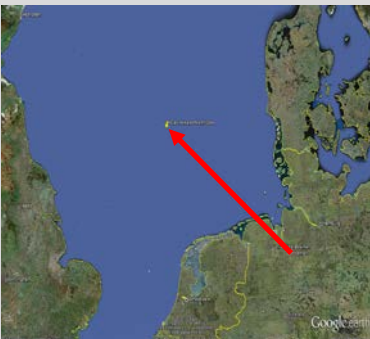
Release frequency: 23 bubbles  $s^{-1}$

Methane flux: 28.27 L  $min^{-1}$

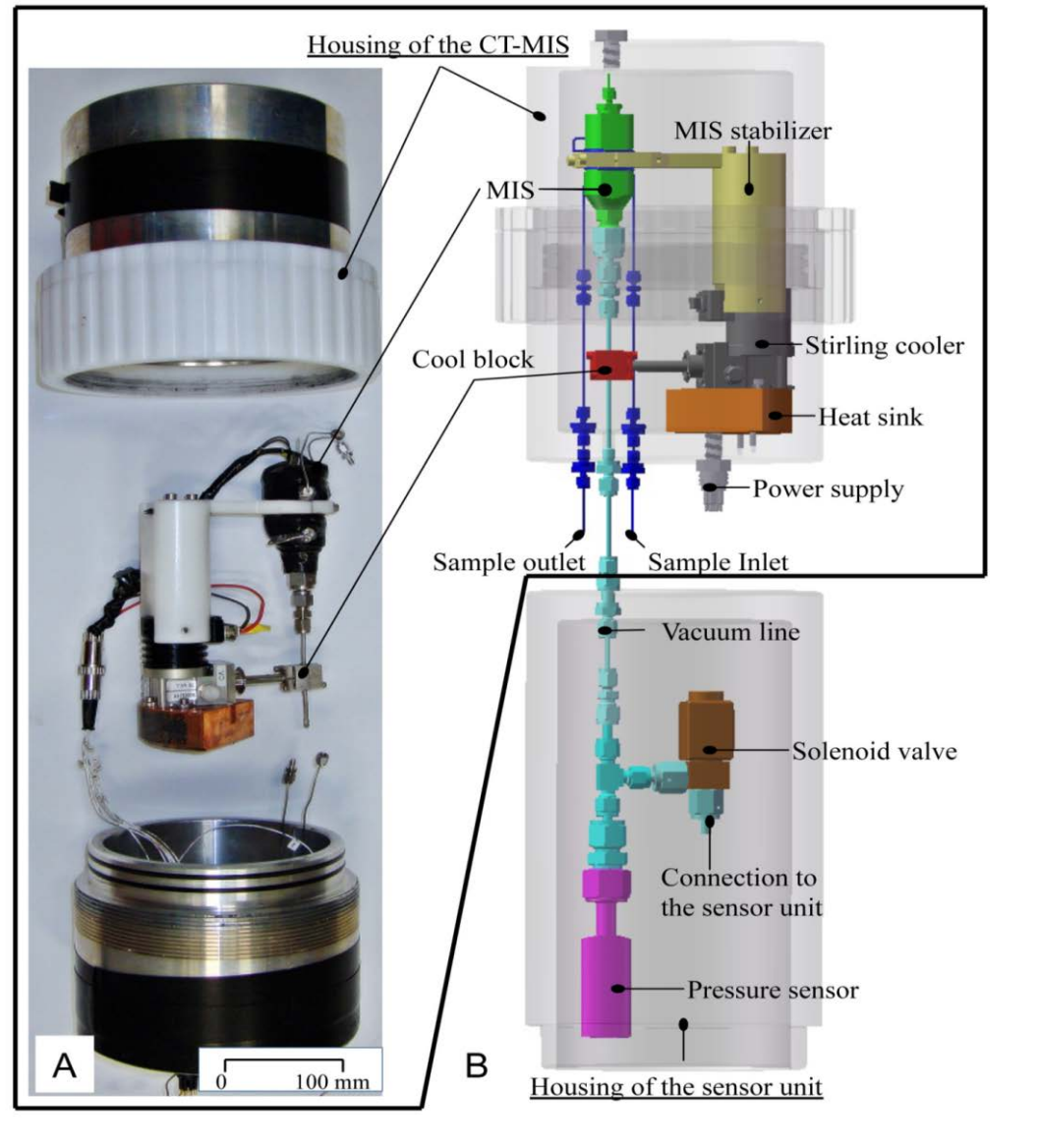
$$PVA = nRTZ \quad (3)$$

Modified after Römer et al. 2012

Seafloor methane release:  $35.3 \pm 17.65 \text{ t CH}_4 \text{ yr}^{-1}$



# Under water cryotrap

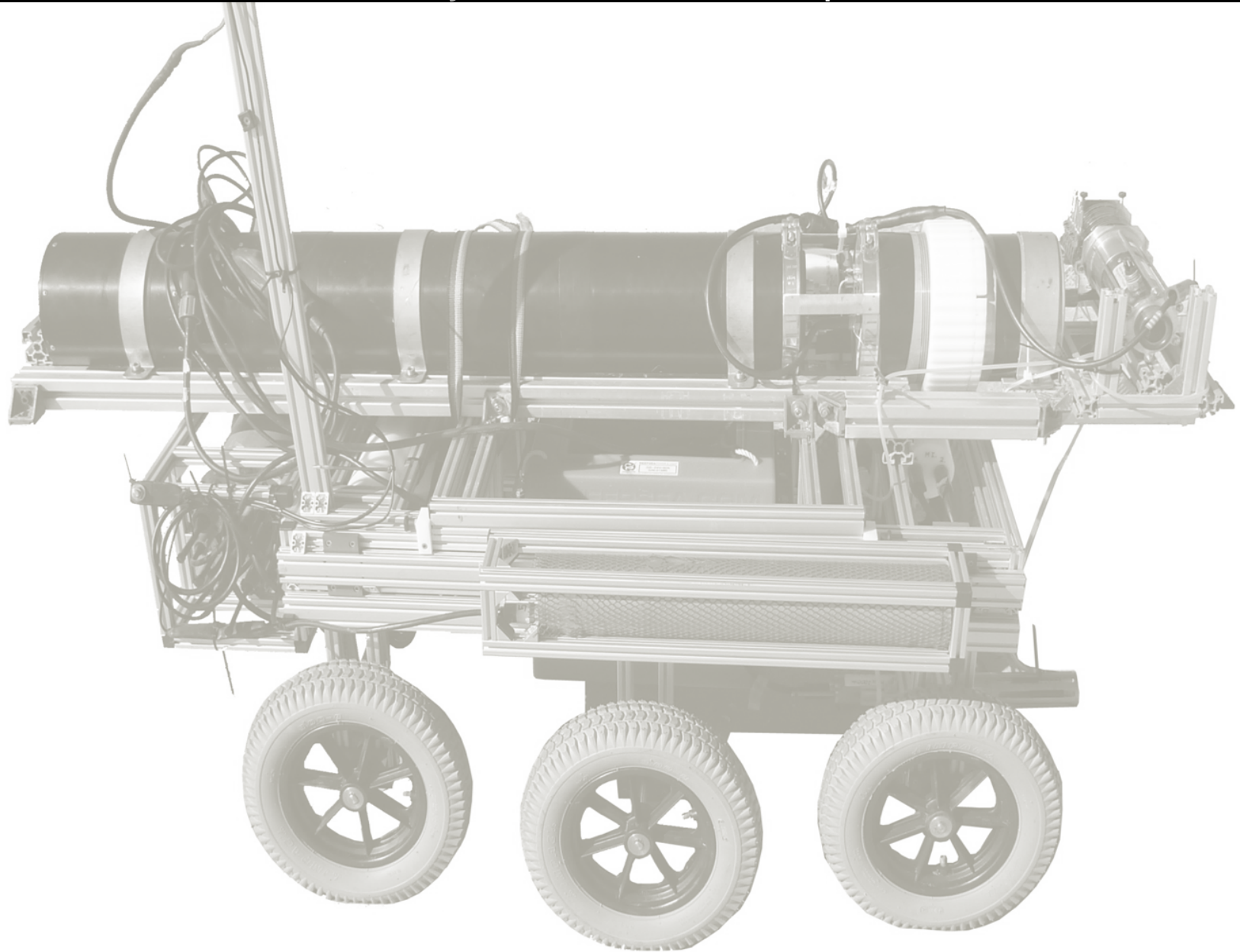




# Gas analysis: New in situ sensors for high resolution mapping

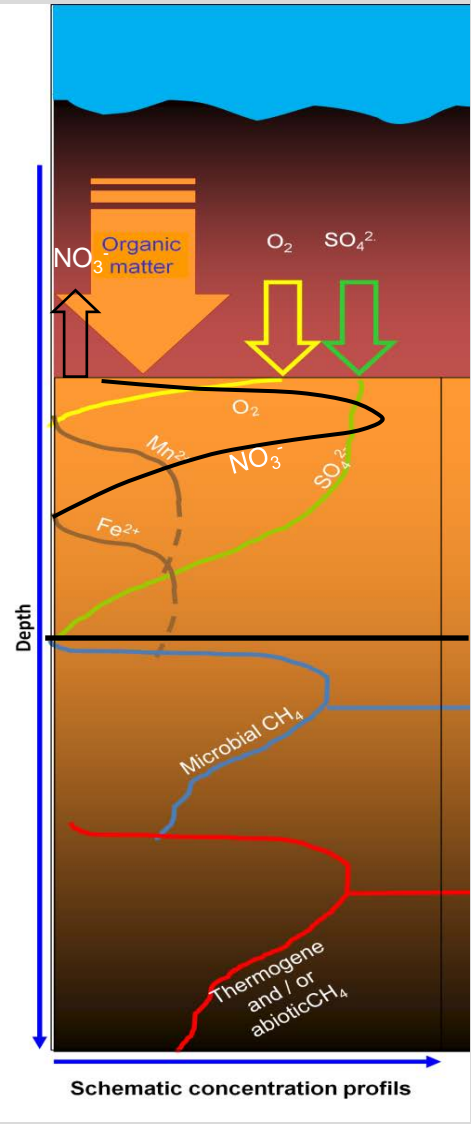
Sensor	Measurement/ environments	Technology	Membrane/ Sensitive layer	Concentration range	Limit of detection	T 90	T°C	Depth range	Power supply	Manufacturer/ Research Institute/ Reference	TRL
METS-CAPSUM	Gas phase/water column	SnO <sub>2</sub> semi-conductors	Silicon rubber (5–100 μm)	10 nM–150 mM	10 nM	1–30 min	2–40°C	0–3500 m	35–100 mA at 12 V	Capsium GmbH/Franatech GmbH [26]	TRL 7
HydroC/CH <sub>4</sub>	Gas phase/water column	Direct IR absorption spectroscopy (3.4 μm)	Modified silicon rubber (2–100 μm)	30 nM–500 μM	<10 ppm (<6 nM)	17–30 s	0–50°C	0–6000 m	250 mA at 12 V	Contros GmbH <a href="http://www.contros.eu">http://www.contros.eu</a>	TRL 7
Deep-sea methane sensor	Gas phase/water column	Laser absorption spectroscopy (3.3 μm)	Silicon-membrane tubes	40–320 ppm (25–200 nM)	40 ppm (25 nM)			0–2000 m		Hokkaido University (Japan) [15]	TRL 6/7
Deep-sea gas analyzer*	Gas phase/water column	NIR-off-axis integrated-cavity output spectroscopy	Silicon rubber			less than 1 min	0–45°C	0–2000 m	Internal battery	Iginc (USA)	TRL 6/7*
Equilibrator	Gas phase/surface water	Photoacoustic spectroscopy	Glass marbles in tube	up to 400 μM	20 μM	12 min at 7 m depth**				[33]	TRL 6
In situ mass spectrometer	Gas phase/water column	In situ mass spectrometer	Semi-permeable membrane inlet	no data	Sub-ppm (<1 nM)			0–30 m (200 m possible)	20 W	WHOI (USA) [36]	TRL 8
In situ mass spectrometer	Gas phase/water column	In situ mass spectrometer	PDMS membrane inlet	no data	1–5 ppb (<1 nM)			0–30 m (200 m possible) surface	20 W	University of South Florida (USA) [35]	TRL 8
Biosensor	Dissolved phase/sediments, pore water	Amperometry	Silicon membrane	up to 350 μM	5 μM					University of Aarhus (Denmark) [19]	TRL 5/6
Biosensor	Dissolved phase/sediments, pore water	Dissolved oxygen sensor	“bacterial beads”	0.4–2 mM	100 μM	100 s		surface		[44]	TRL 5/6
FEWS	Dissolved phase/water column	Evanescent wave spectroscopy	Optical fiber/sensitive layer					Possibly up to 6000 m		[50]	TRL 2/3
SERS	Dissolved phase/water column	Surface-enhanced Raman scattering	Silver-colloid SERS substrate		nM–μM			Possibly up to 6000 m		Technical University Berlin (Germany) [60]	TRL 4/5
SPR	Dissolved phase/water column	Surface-plasmon resonance	PDMS/crypto-phane-A	0–400 nM	0.2 nM	2–5 min	45°C	Surface	1 mW	[64] (Appendix 2)	TRL 4/5

*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.*



Formation of methane:

**Degradation of organic matter by redox processes**



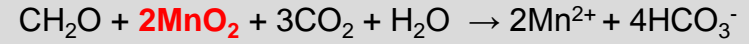
**Aerobic respiration**



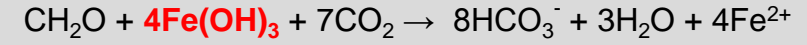
**Nitrate reduction**



**Manganese oxide reduction**



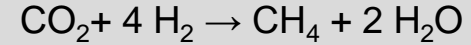
**Iron oxide reduction**



sulfate/methane transition zone (SMTZ)

Microbial formation of methane:

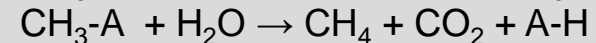
**Hydrogenotrophic**



**Acetotrophic**



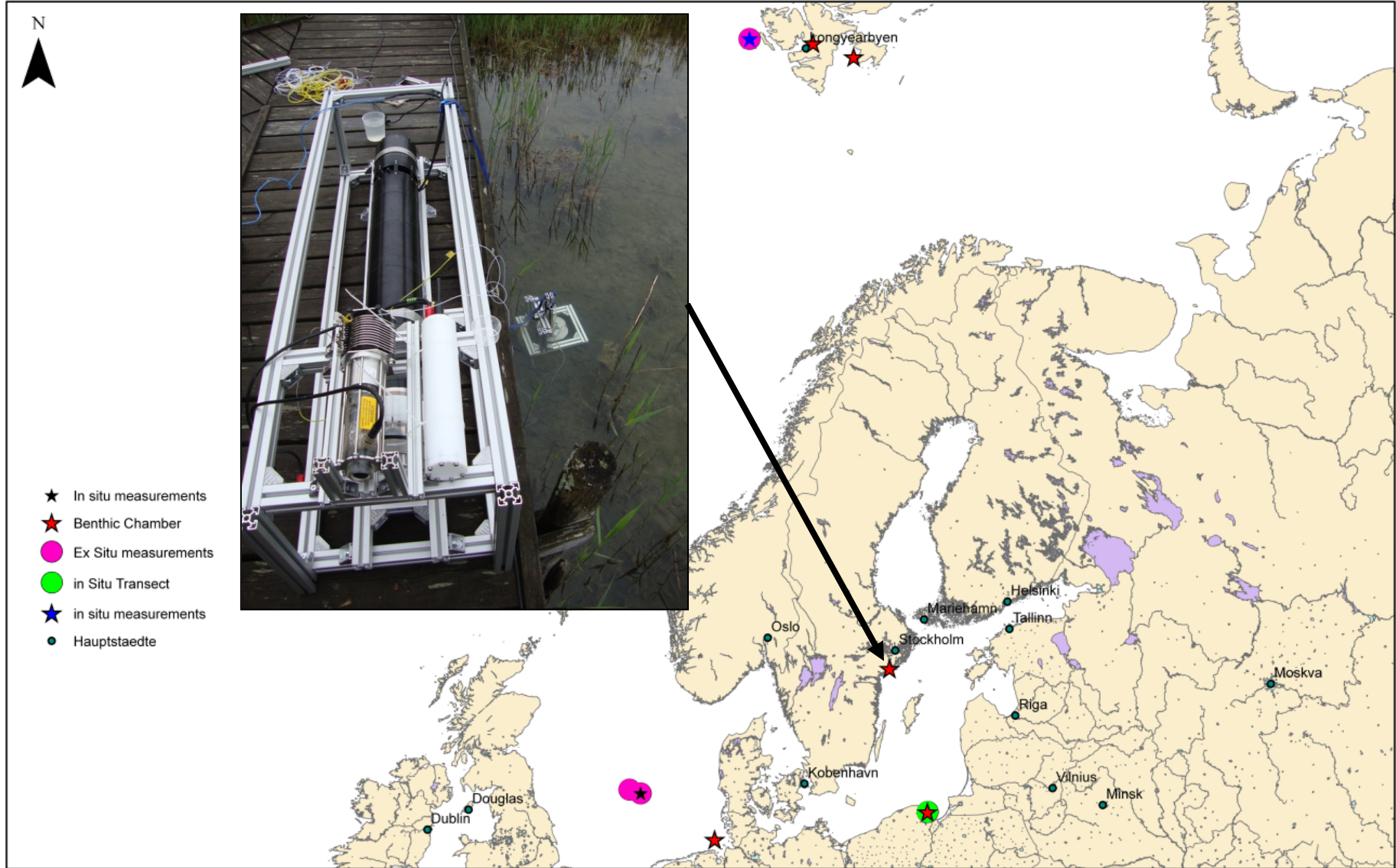
**Methylotrophic**



**Thermocatalytic formation of methane**

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

## Working areas





# Working areas

