# Distribution and fate of methane released from submarine sources

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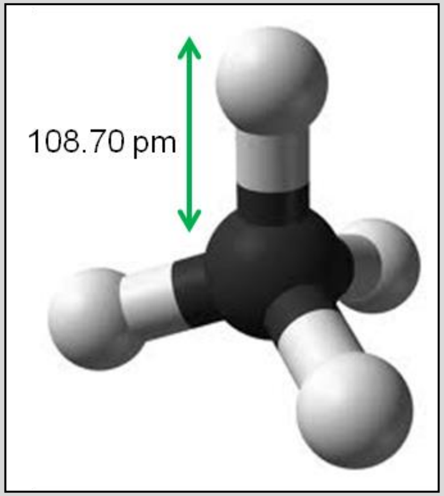
Results of measurements using an improved in situ mass spectrometer





**Torben Gentz**

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02.09.2013


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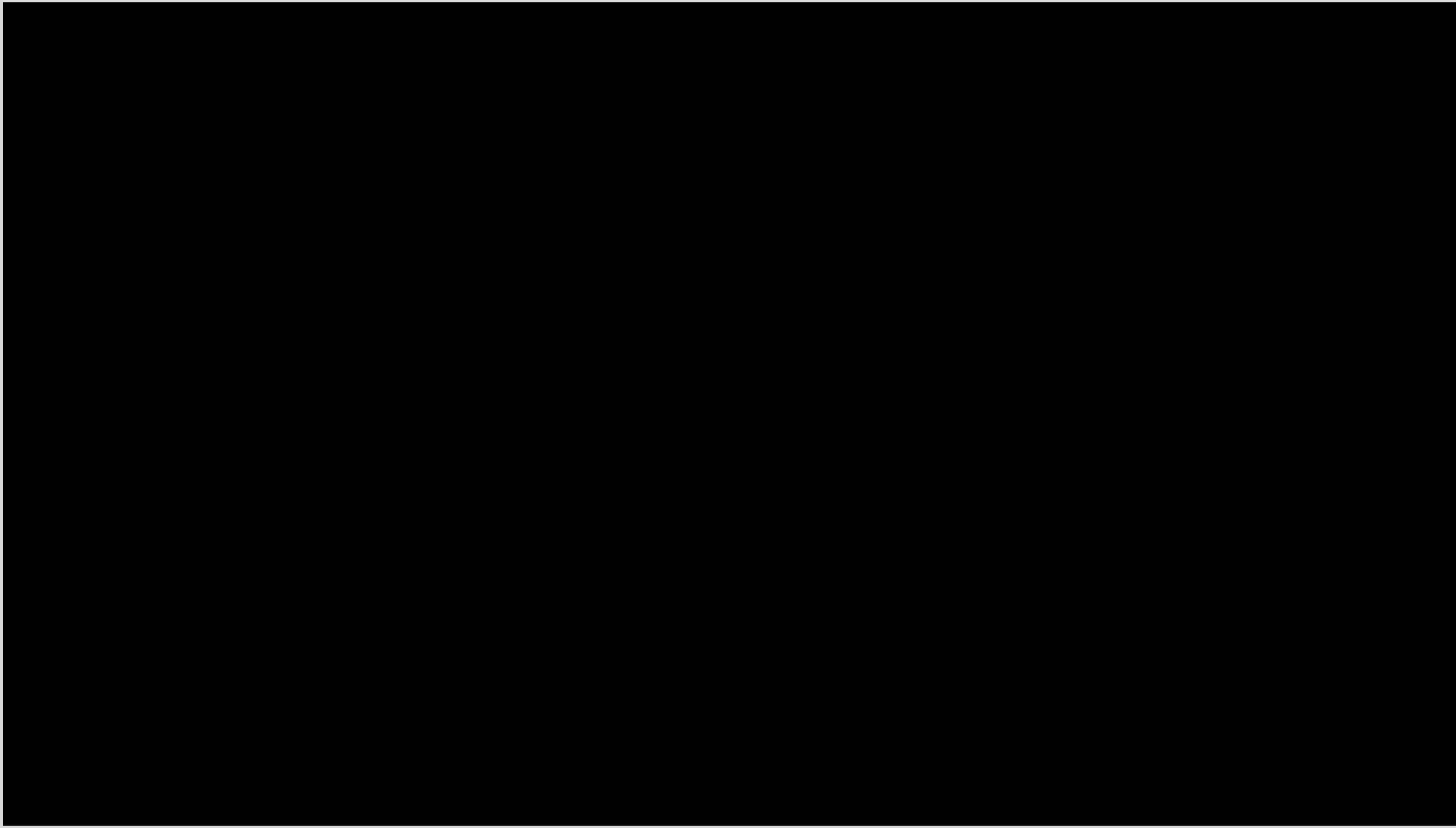
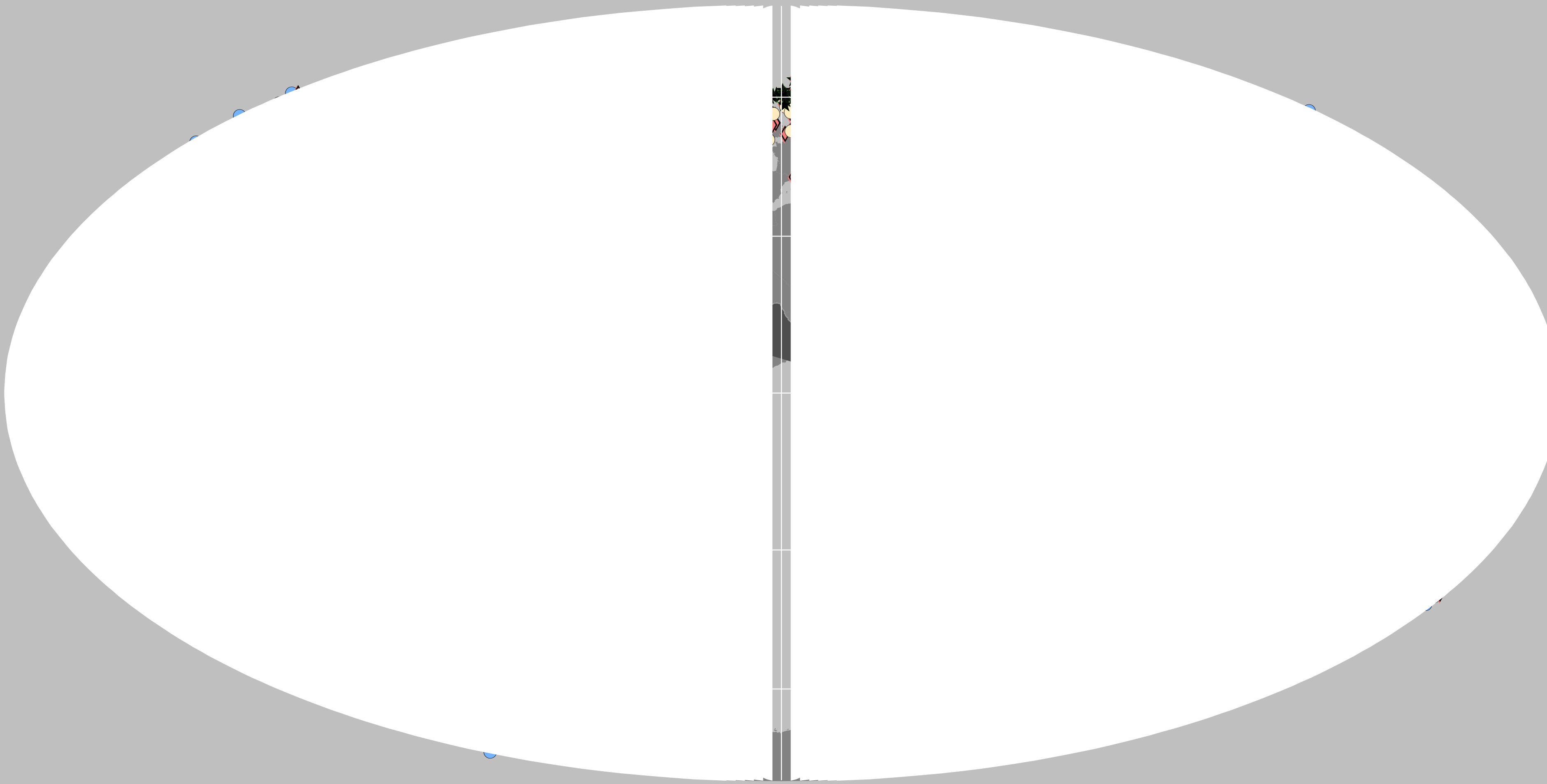


Heincke 362

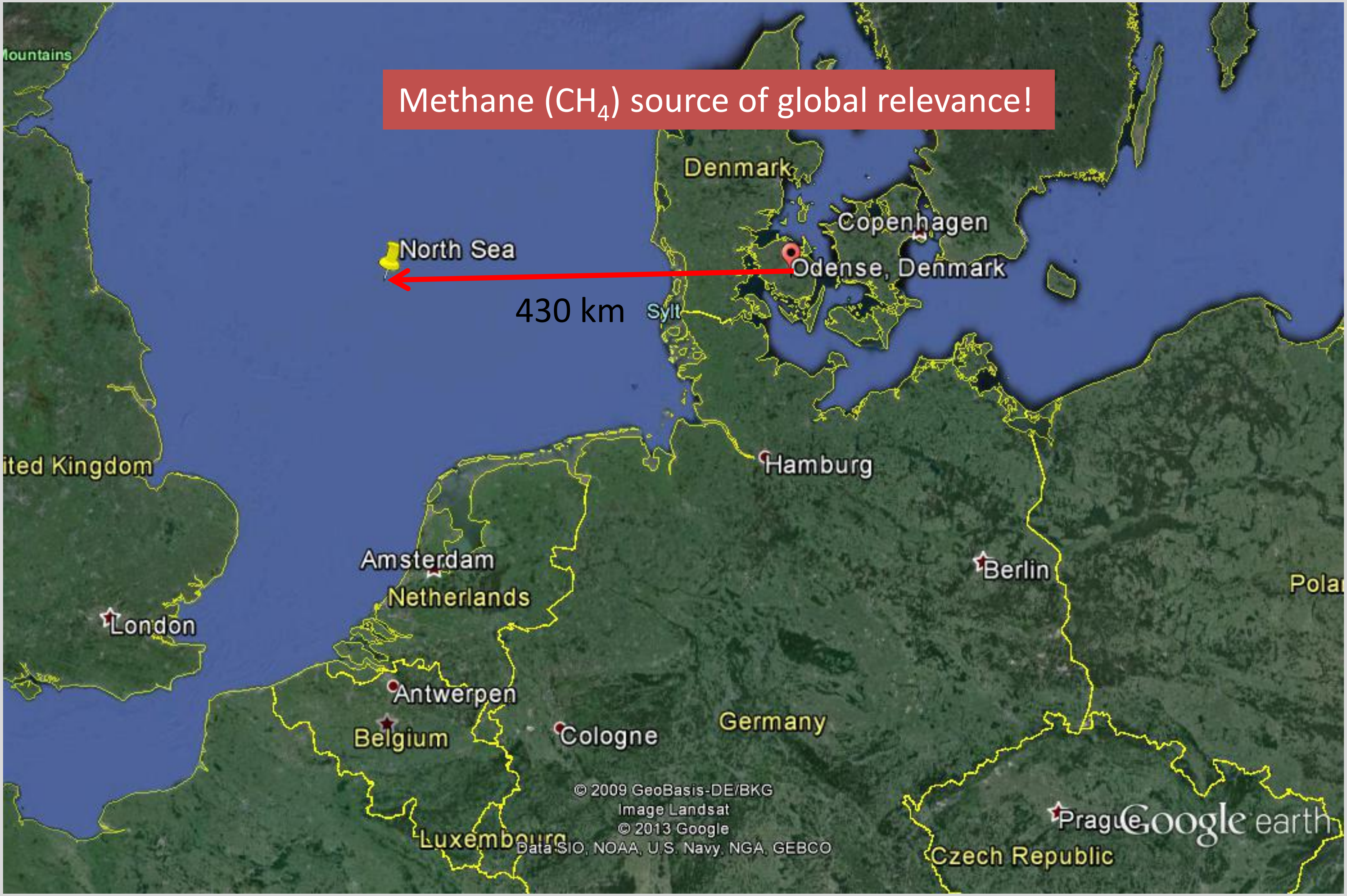
Submarine gas seeps

## WORLDWIDE DISTRIBUTION OF SUBMARINE METHANE RELEASE



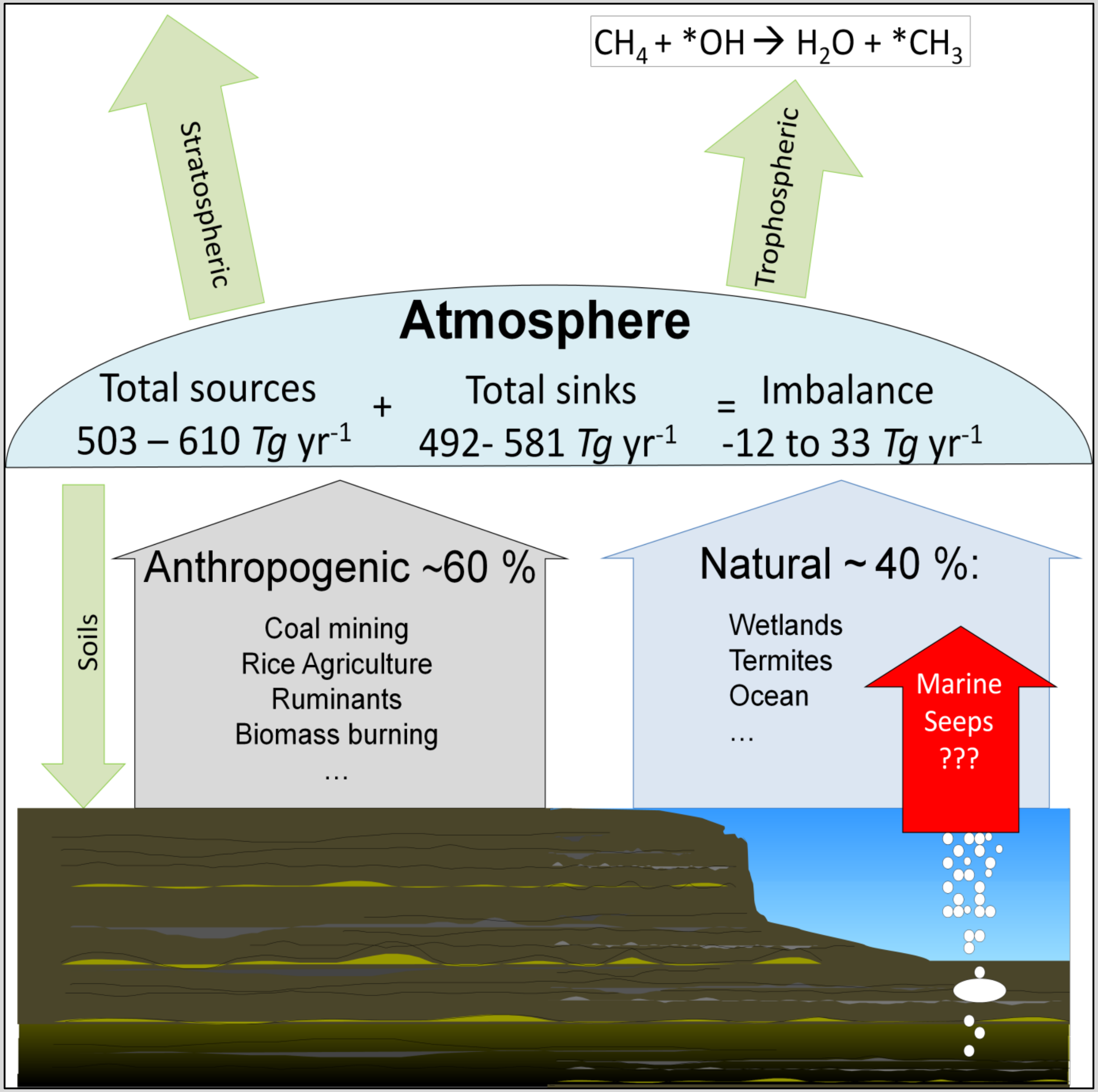
seepages
gas hydrates
methane related features
free gas / shallow gas
submarine mud volcanoes

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


Methane ($CH_4$) source of global relevance!
430 km
North Sea
Denmark
Copenhagen
Odense, Denmark
Sylt
Hamburg
Berlin
Amsterdam
Netherlands
London
Antwerpen
Belgium
Cologne
Germany
Luxembourg
Czech Republic
Prague
Polar
ited Kingdom
Mountains
© 2009 GeoBasis-DE/BKG
Image Landsat
© 2013 Google
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Google earth

# GLOBAL RELEVANCE OF METHANE

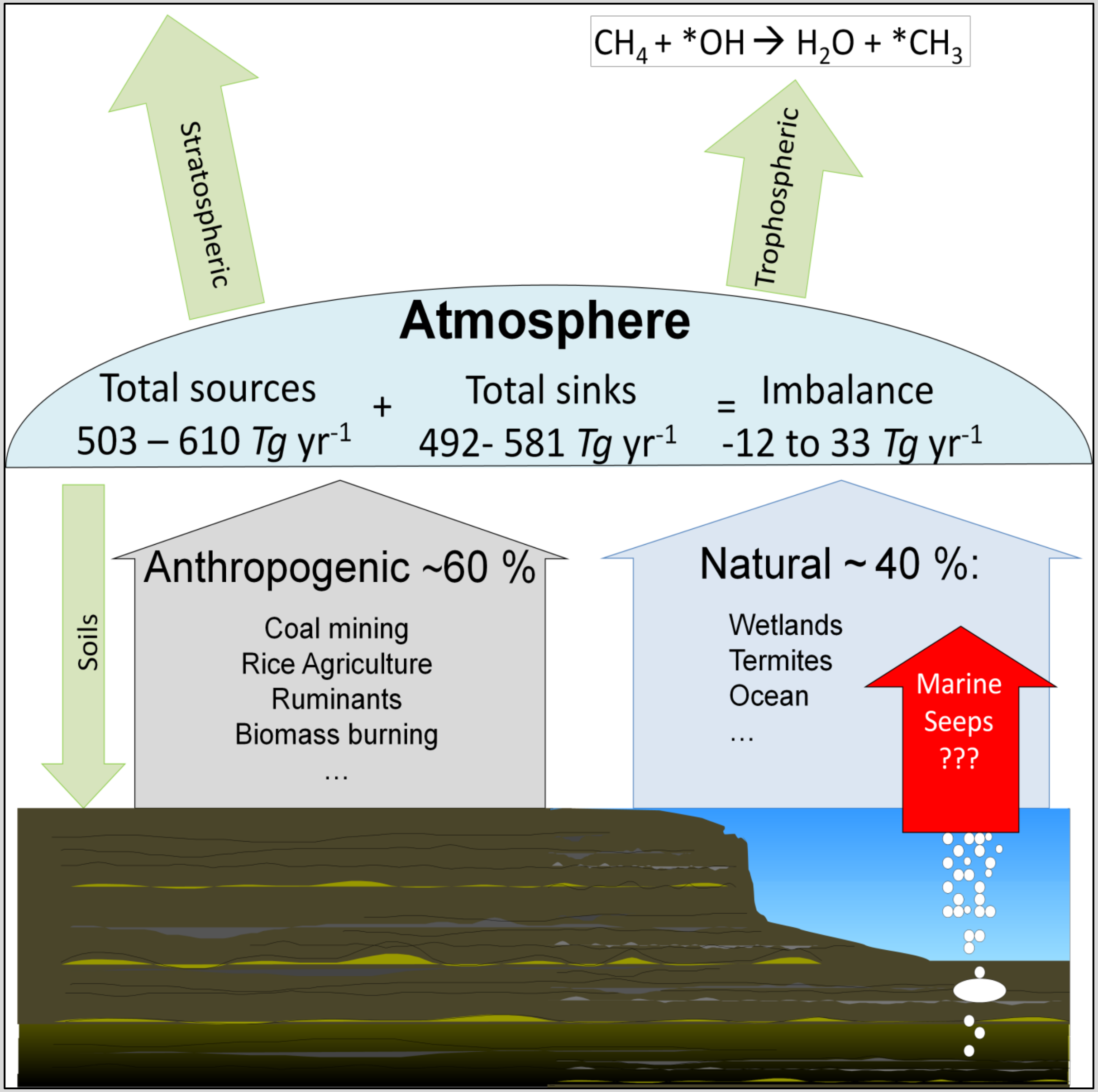





*according to IPCC (2007)*

## GLOBAL RELEVANCE OF METHANE



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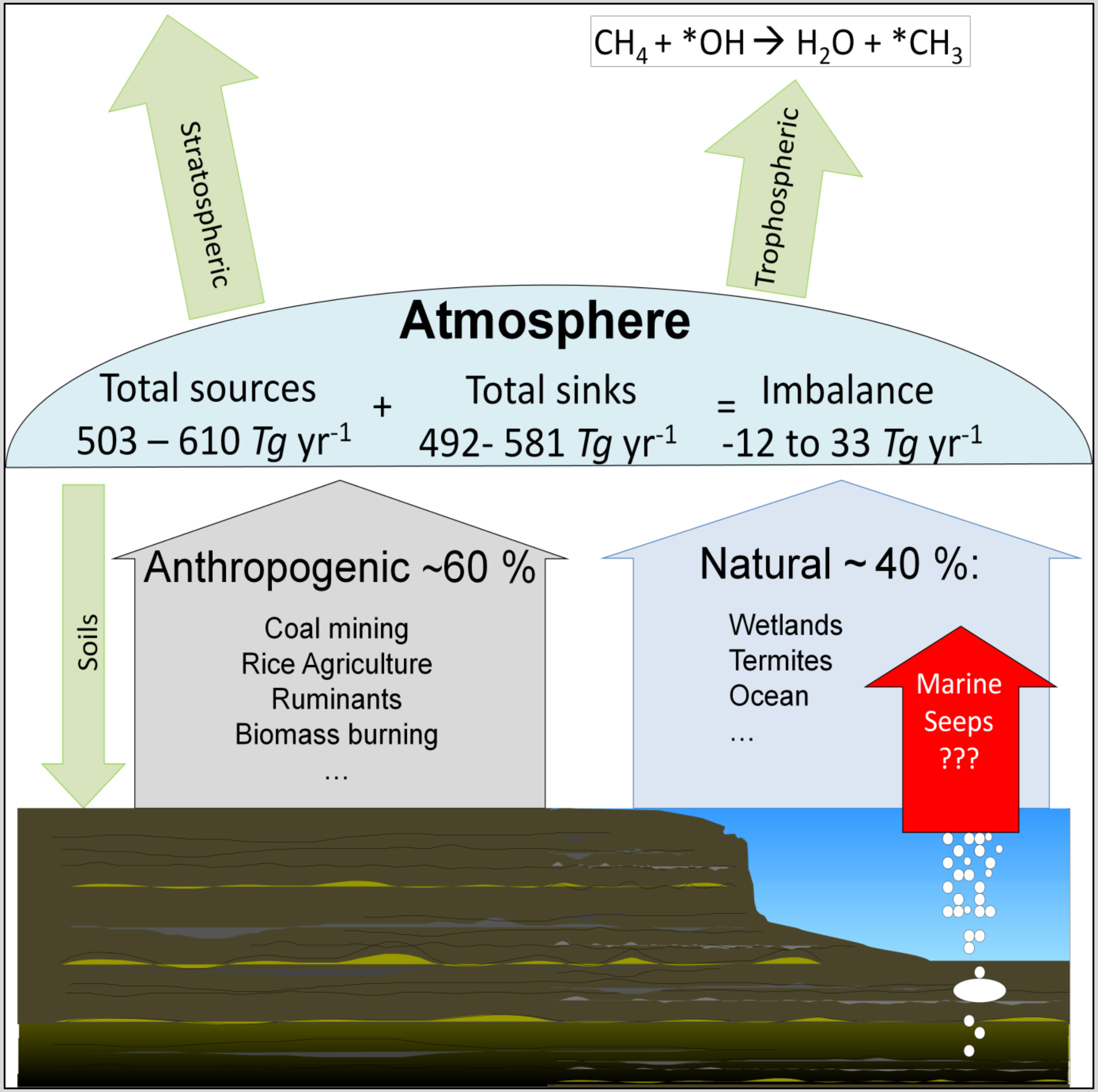
The average atmospheric concentration of methane has increased by 151 % since year 1750 (Houghton 2001).

## GLOBAL RELEVANCE OF METHANE



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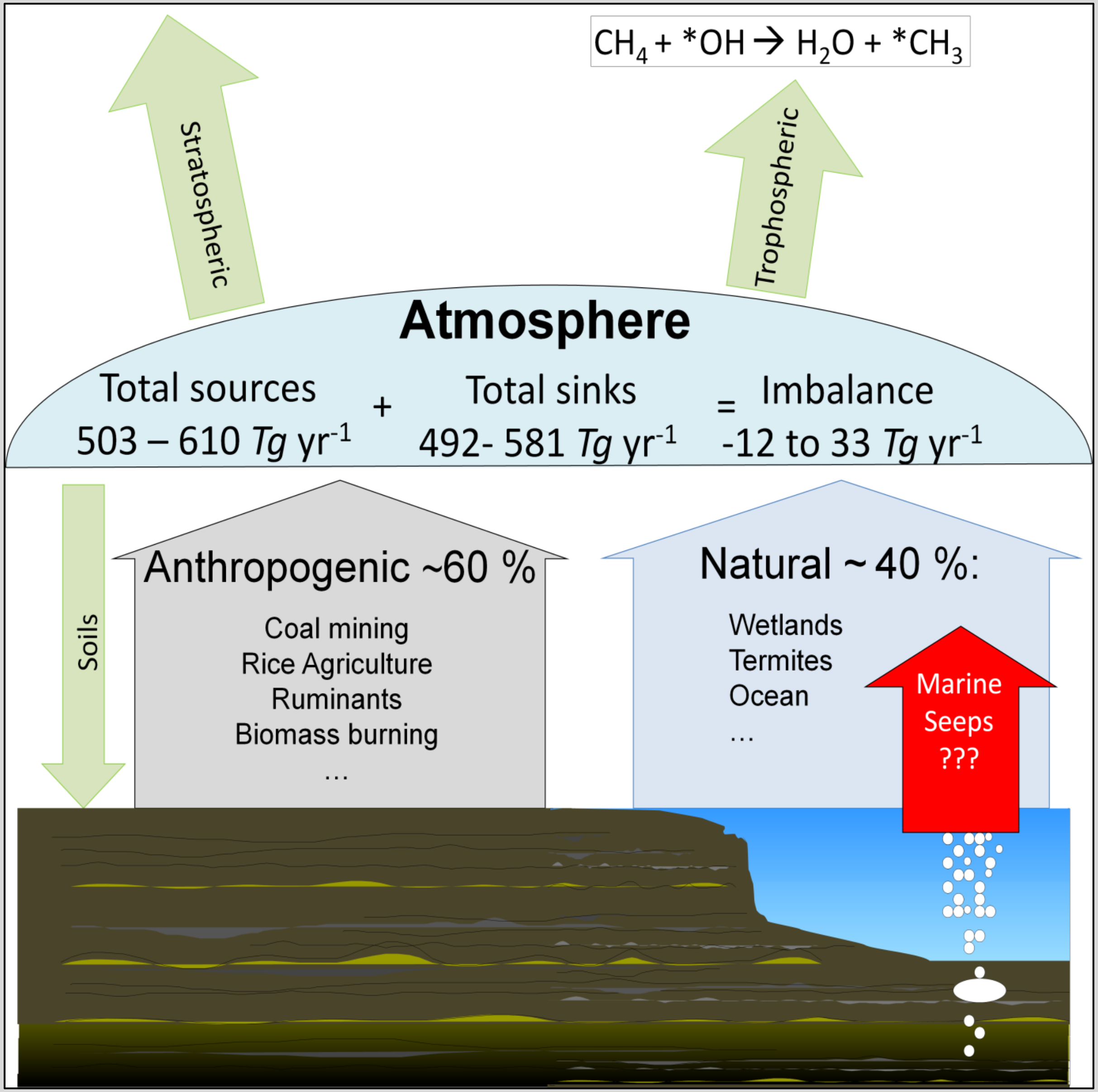


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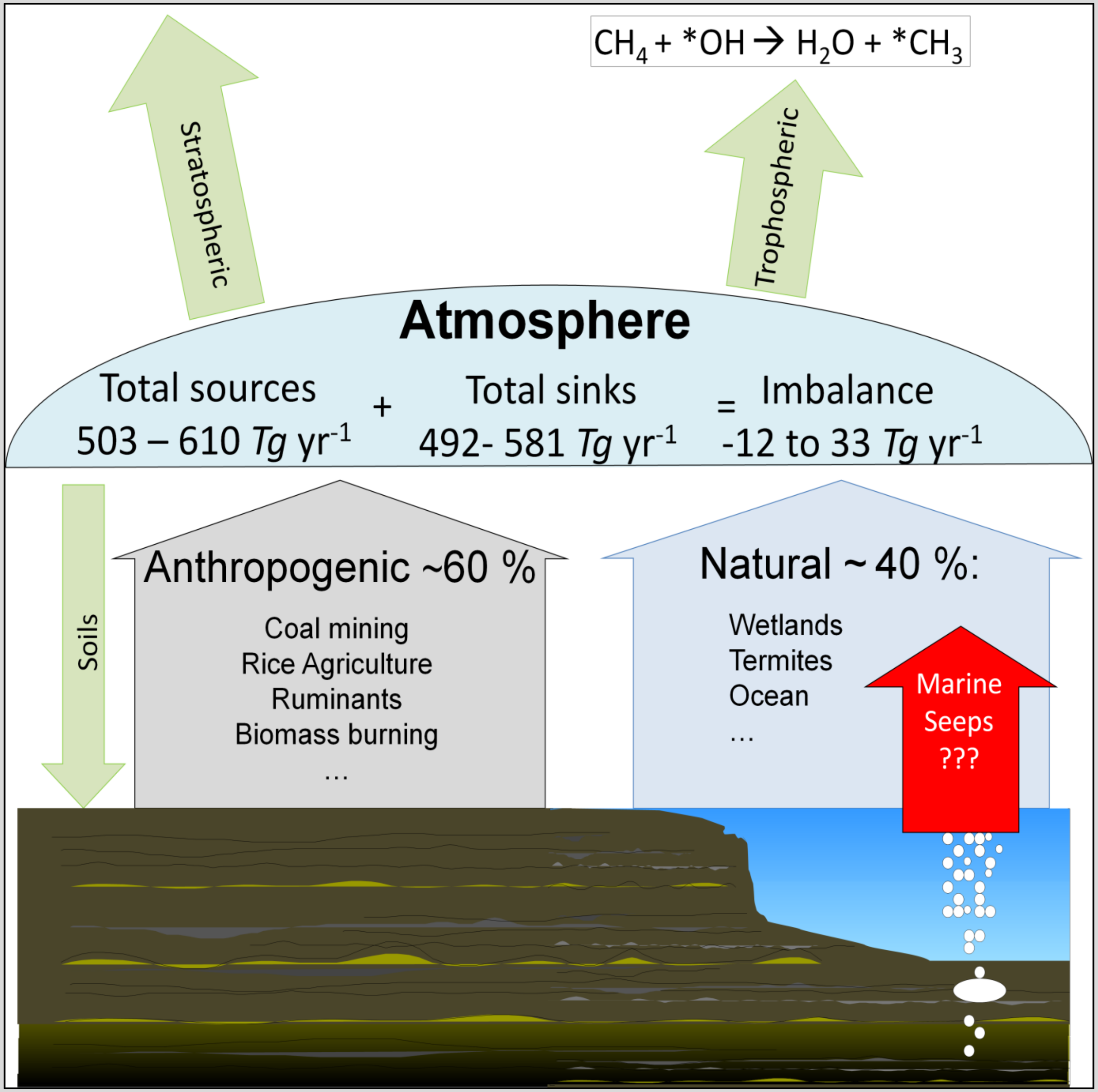


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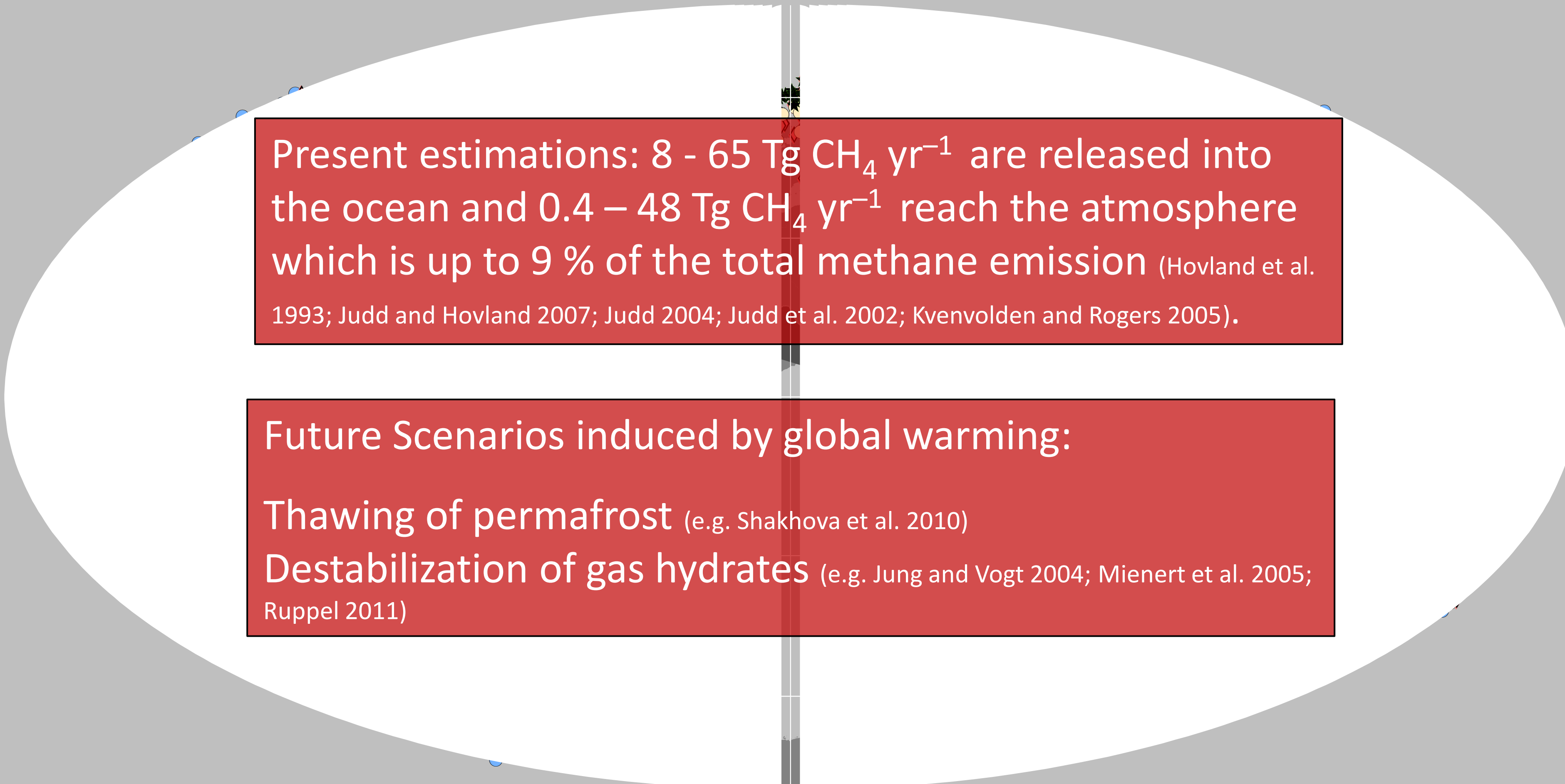
$CH_4$ represents the second largest contribution (about 15 %) to historical warming after $CO_2$ (Shindell et.al. 2009).

## Global relevance of submarine sources



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
- free gas / shallow gas
- submarine mud volcanoes

*Free gas (Fleischer et al. 2001)*
*Pockmarks (Hovland et al. 2002)*
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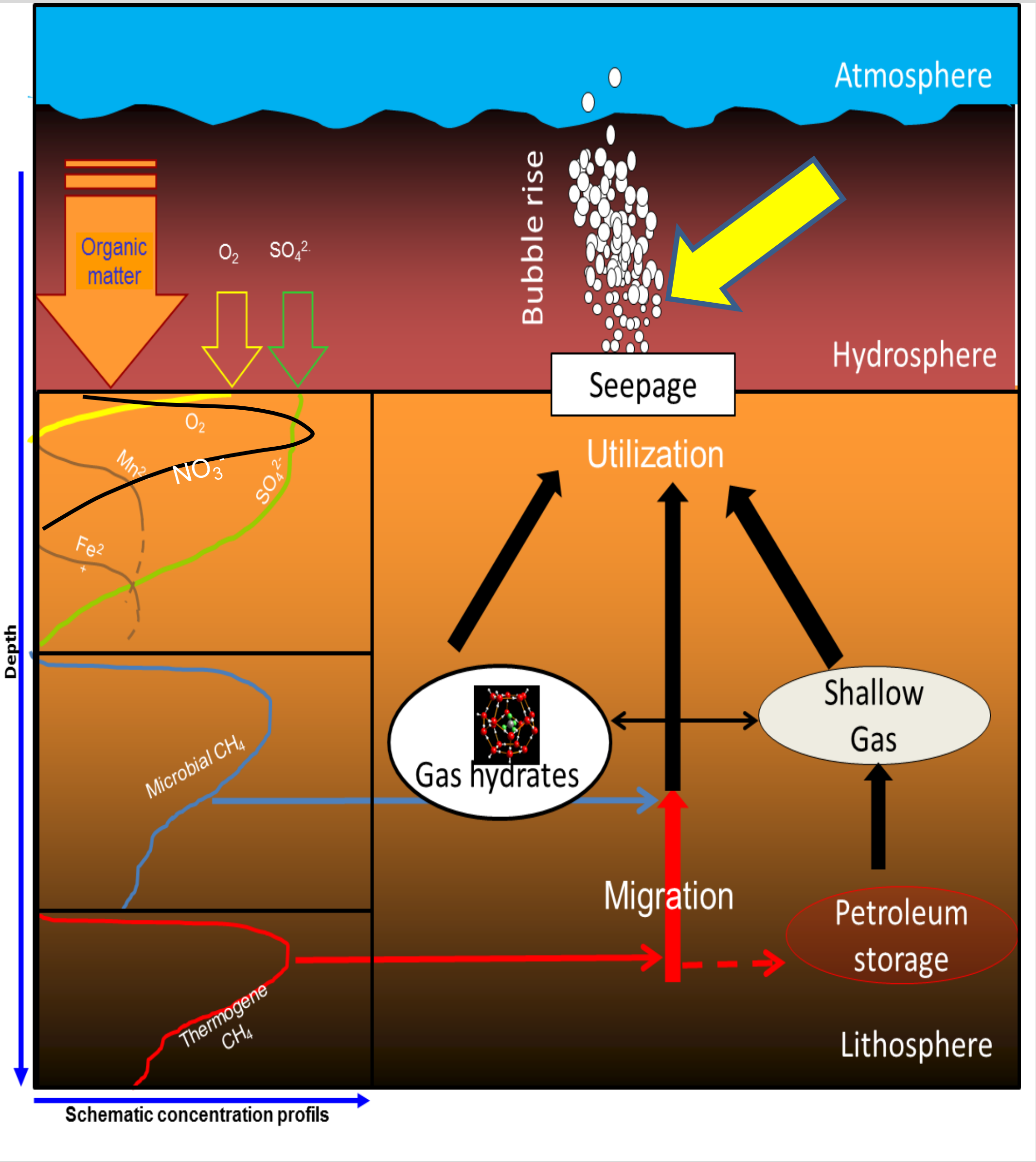
## WHAT ARE SUBMARINE GAS SEEPS?




*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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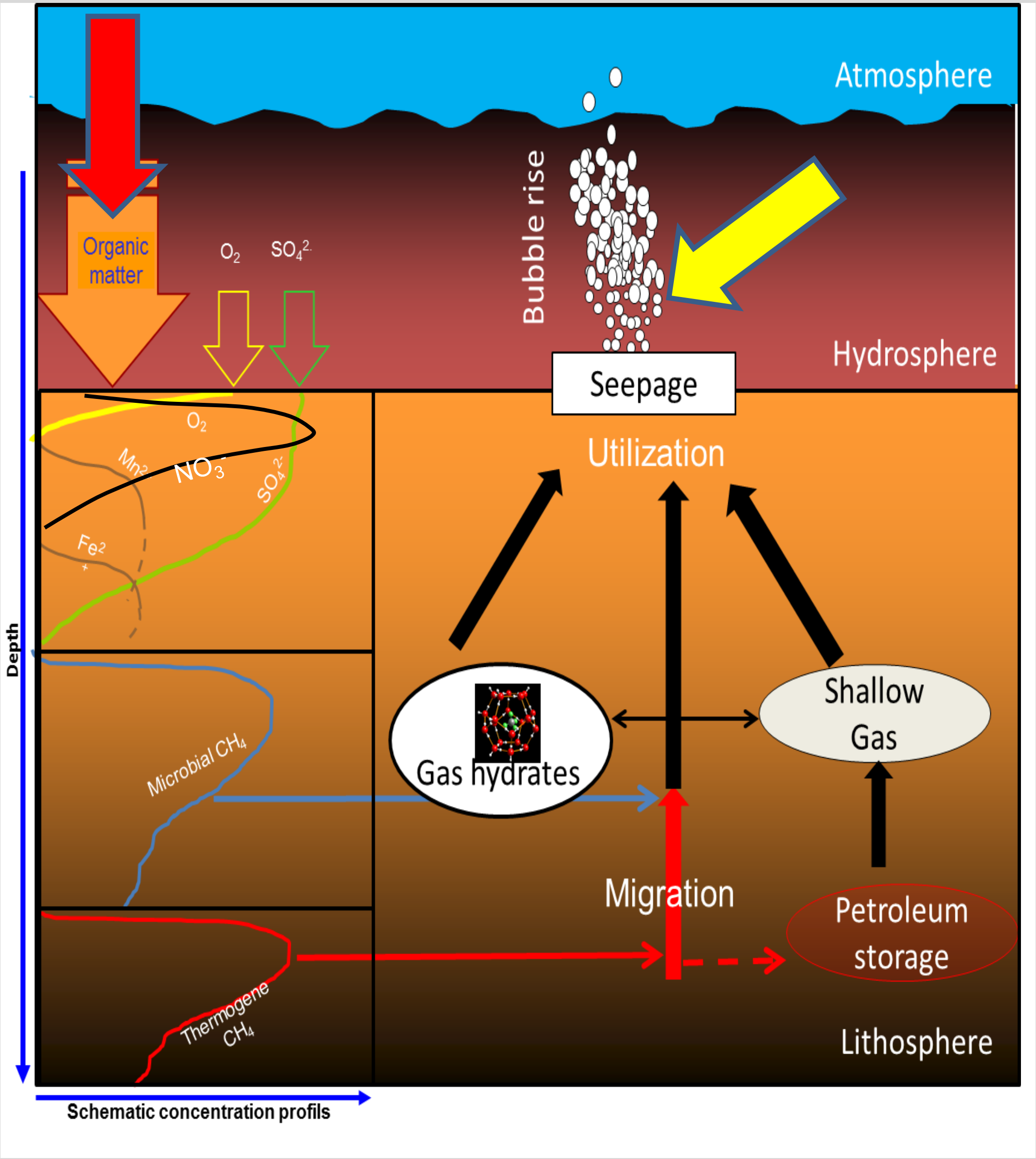



*Schematic view of the formation (modified after Froelich et al. 1979) and the subsequent pathways of methane in the sediment (modified after Judd 2004). Crystallographic image of gas hydrates after Bohrmann and Torres (2006)*

**Formation of methane by degradation of organic matter**

**Aerobic respiration**

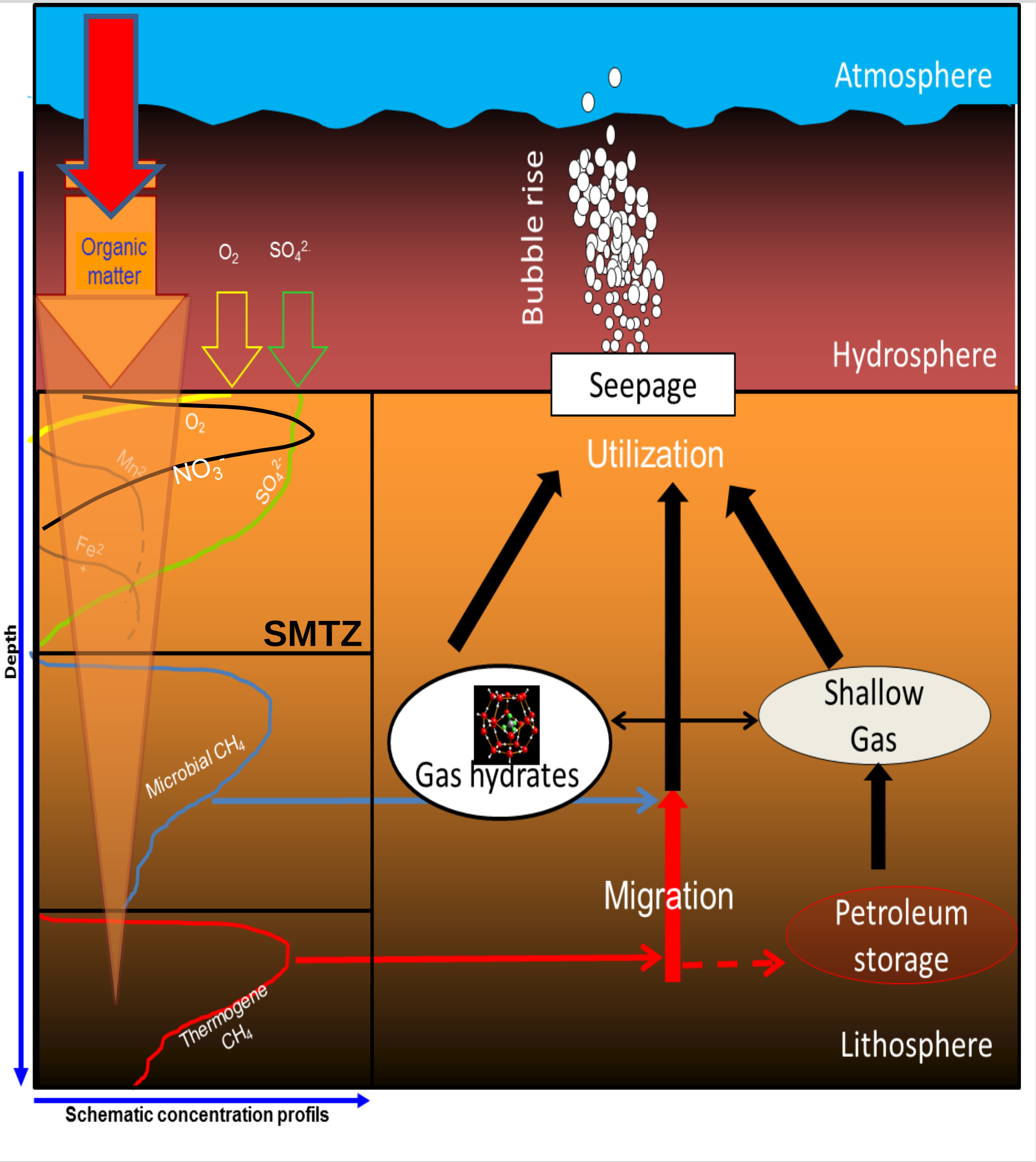
**Nitrate reduction**

**Manganese oxide reduction**

**Iron oxide reduction**

**Microbial** formation of methane

**Thermocatalytic** formation of methane

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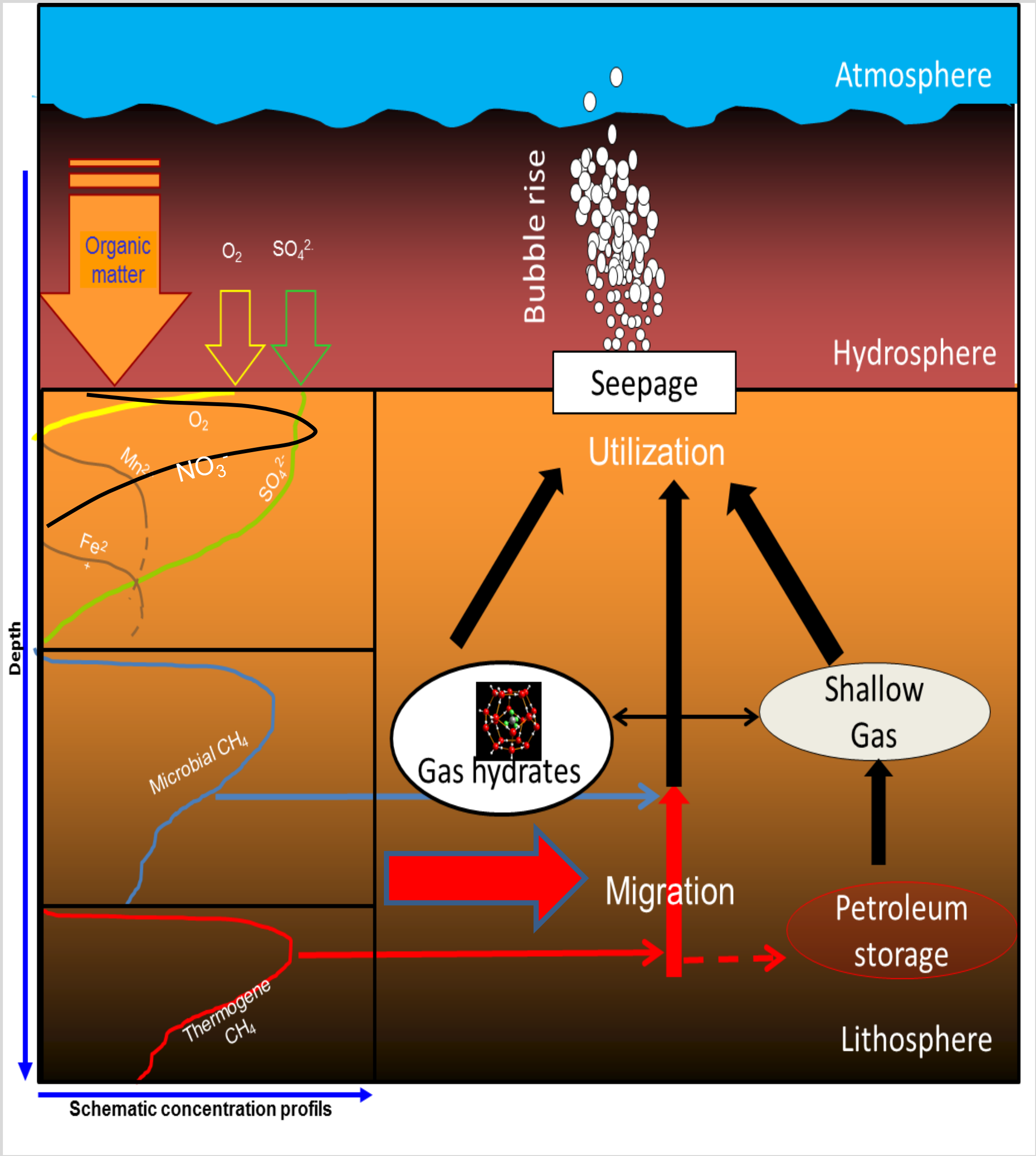
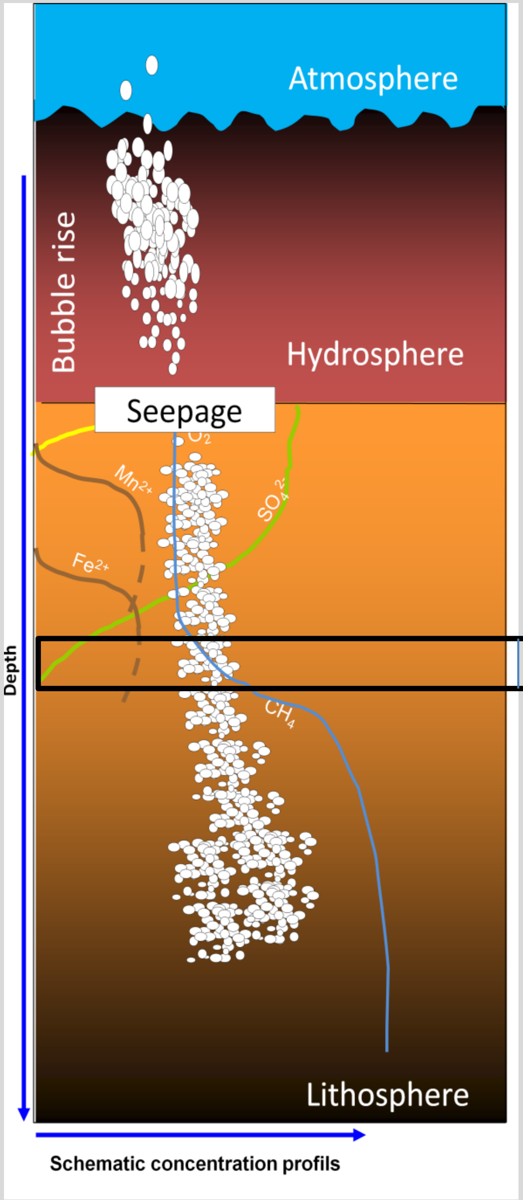
## Storage and migration of methane




*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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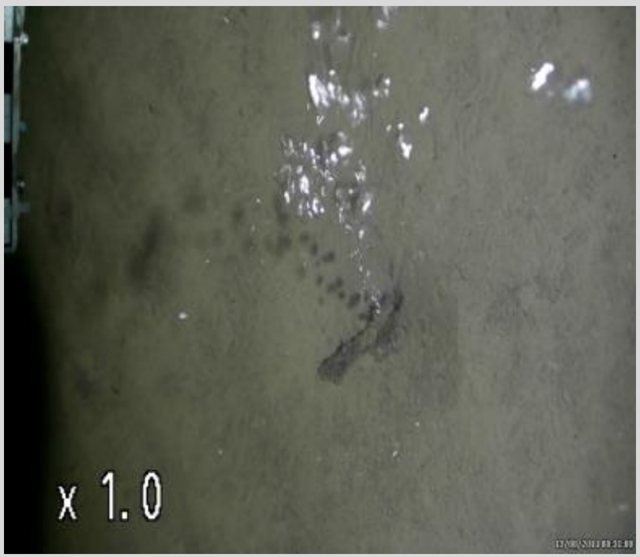
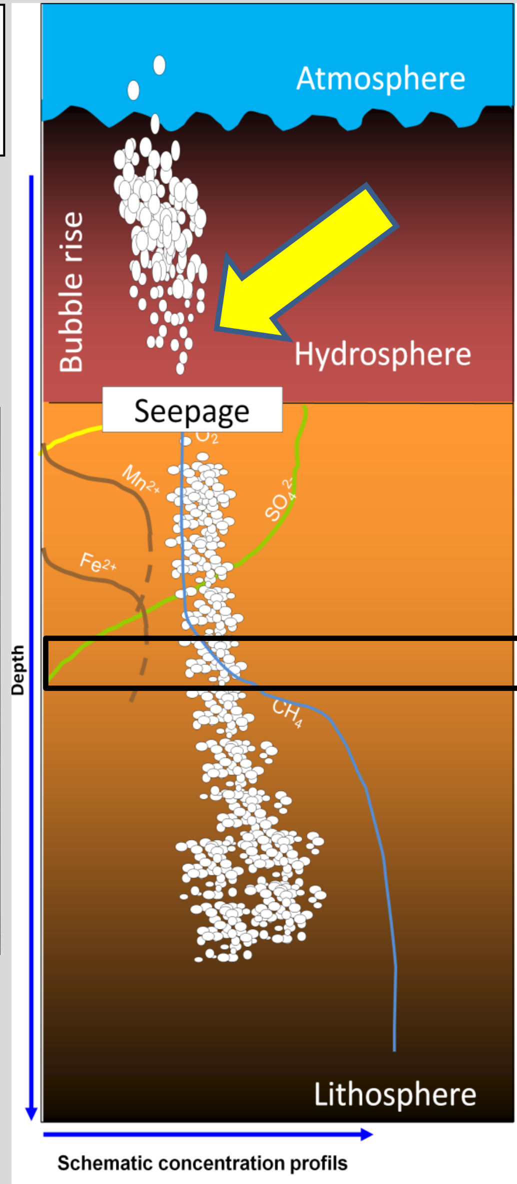



*Heincke 362*

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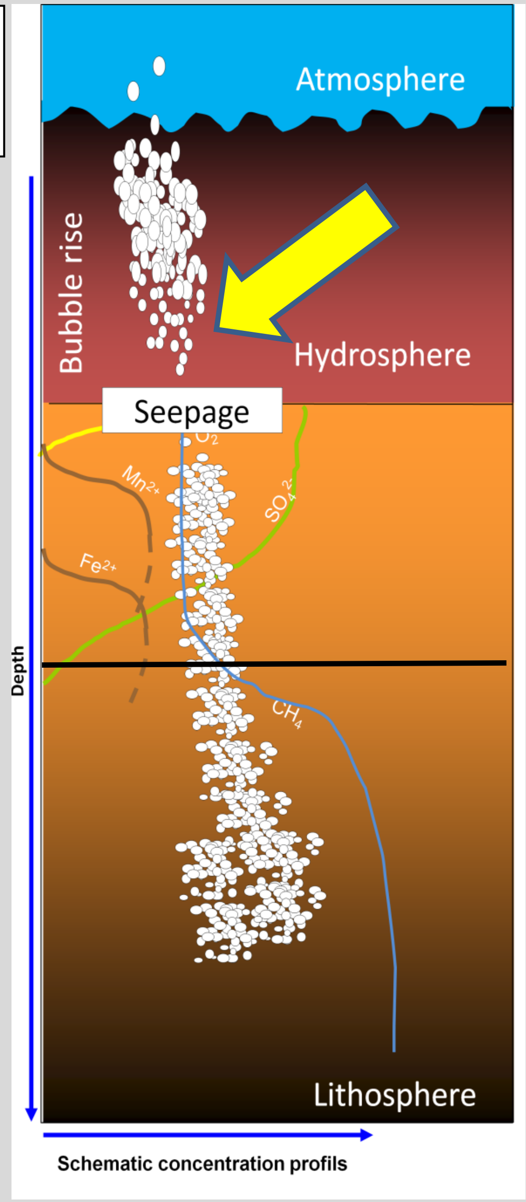
*Schematic view of the formation (modified after Froelich et al. 1979) and the subsequent pathways of methane in the sediment (modified after Judd 2004).*

**Pathways of methane in the water column**



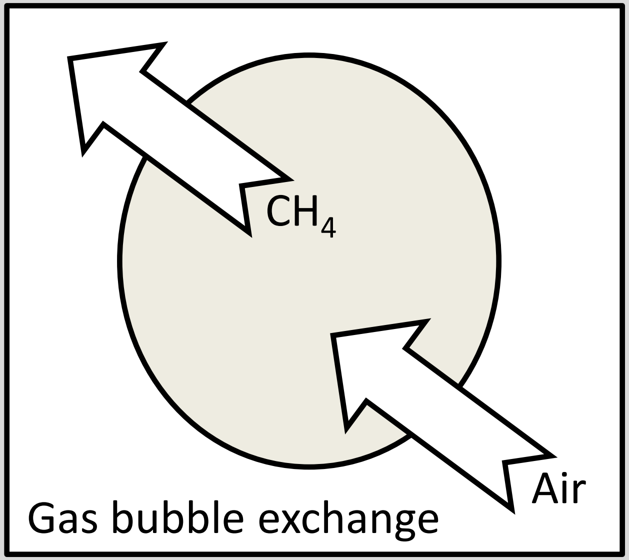

Air/Sea exchange

Vertical or horizontal transport of dissolved methane

Dilution

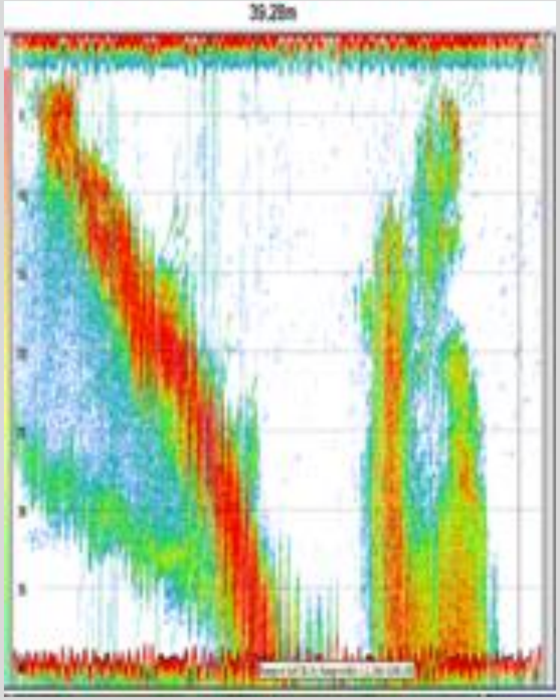
Microbial oxidation

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

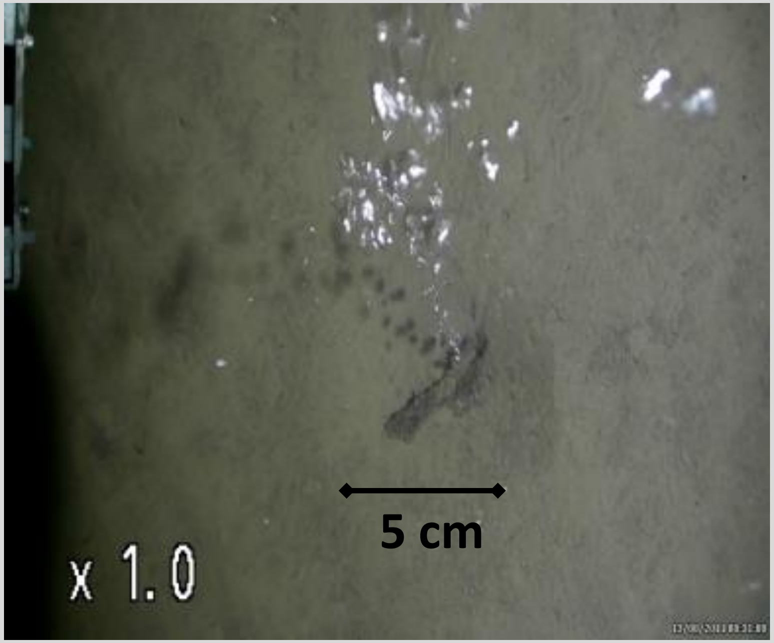



*Schematic view of the formation (modified after Froelich et al. 1979) and the subsequent pathways of methane in the sediment (modified after Judd 2004).*

## 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

Headspace technique for analysis of discrete samples

Gas analysis by gas chromatography

(Lammers and Suess 1994)

Need for new methods

**Problems:**

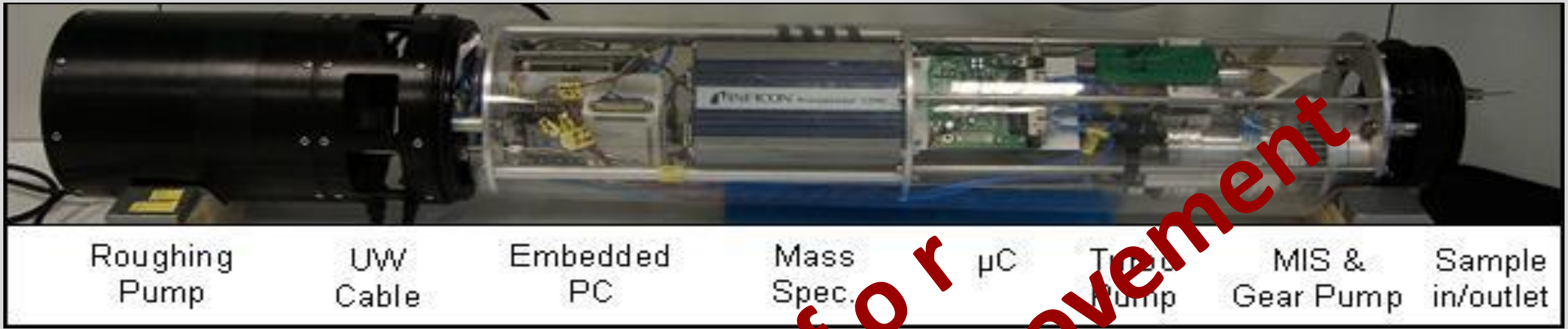
-time consuming

-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.

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




(Short et al. 2001)

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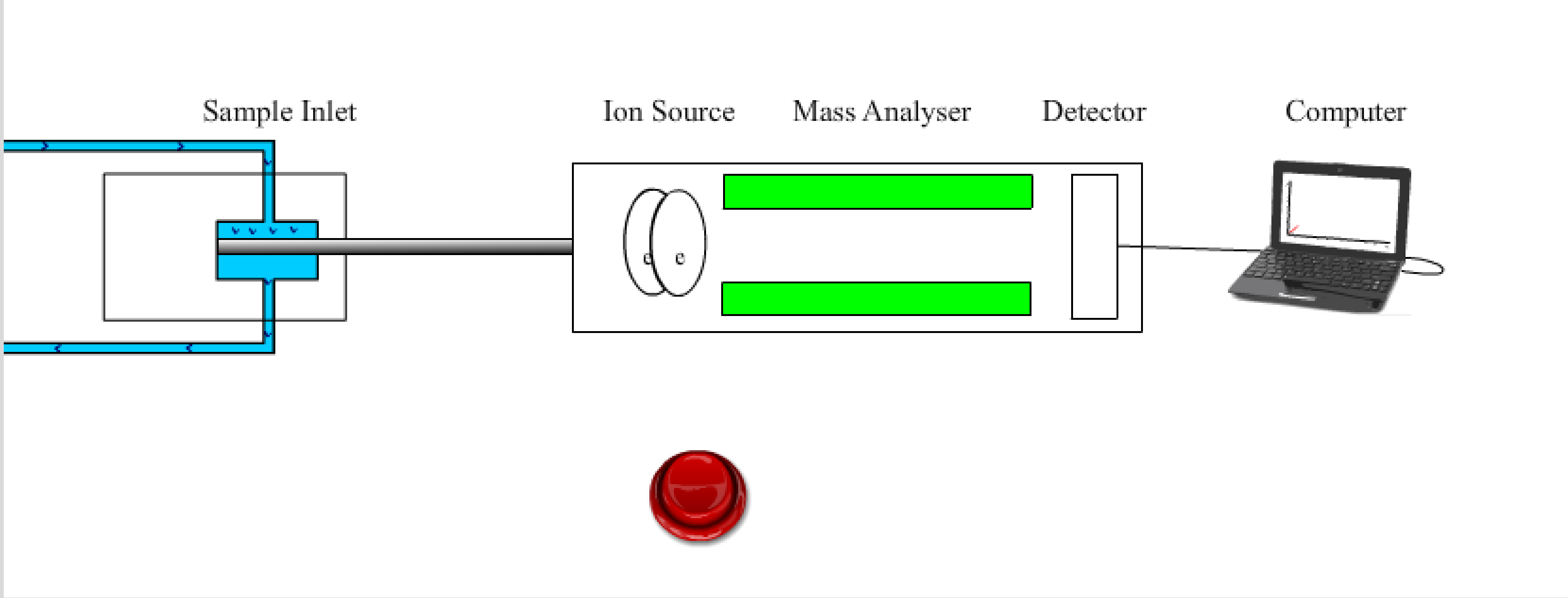
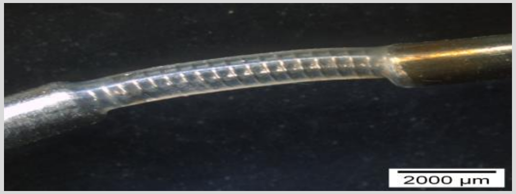
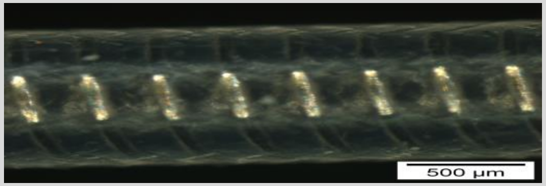
**Need for detection limit improvement**

## In situ mass spectrometer mode of operation




- Water vapour is the main gas that permeates through the membrane!

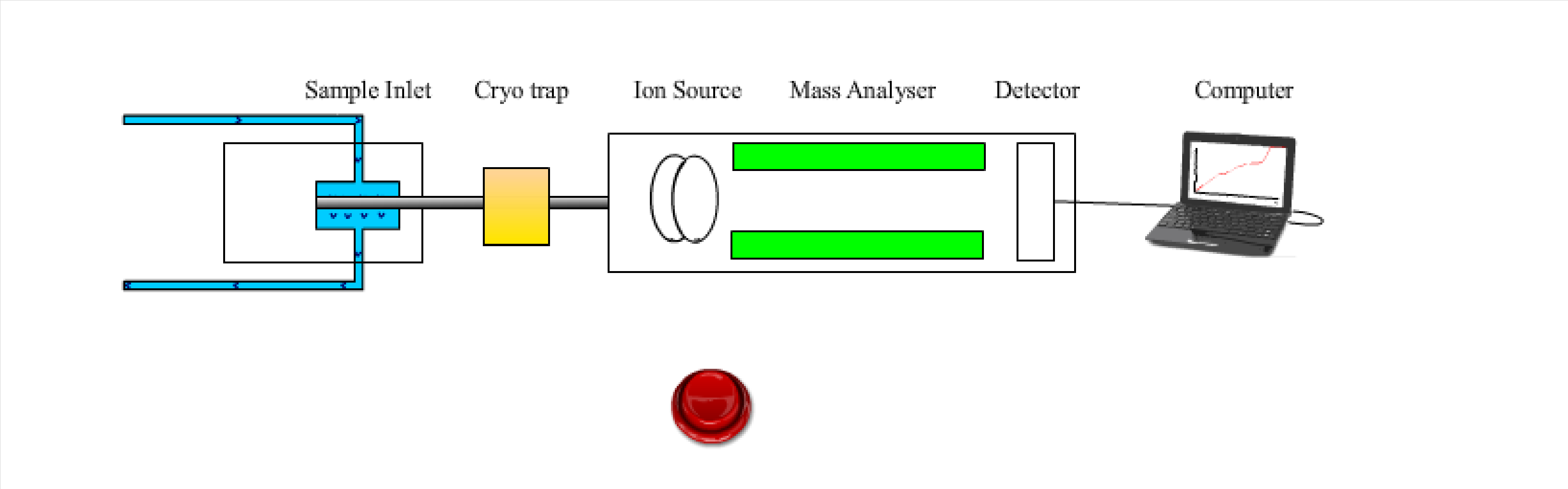
- Affects on the ionization effency
- Could cause condensation in the analytical line
- Leads to a high pressure in the analytical line

→ 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 °C**



## IMPLEMENTATION OF A CRYOTRAP

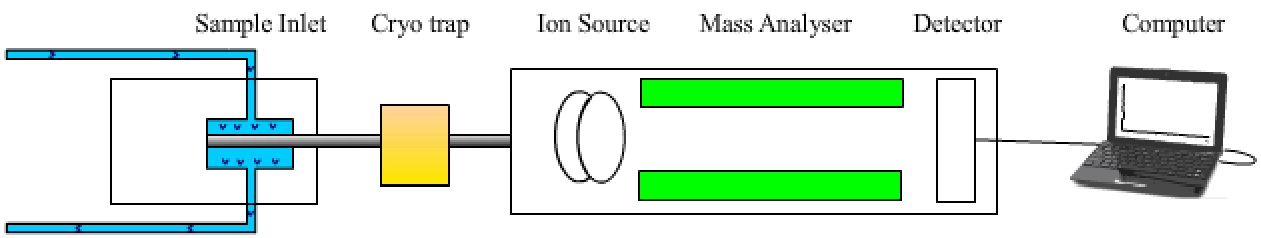

Micro Stirling Cooler, Ricor K508

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

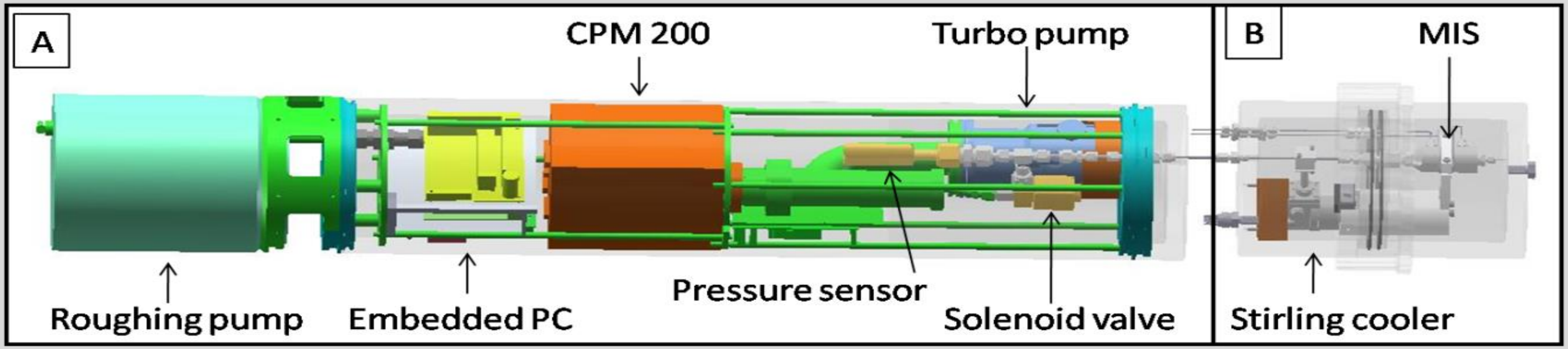
- Water vapour is reduced up to 98 % of initial
- Reduce the internal pressure significantly
- A higher ionization effency is observed

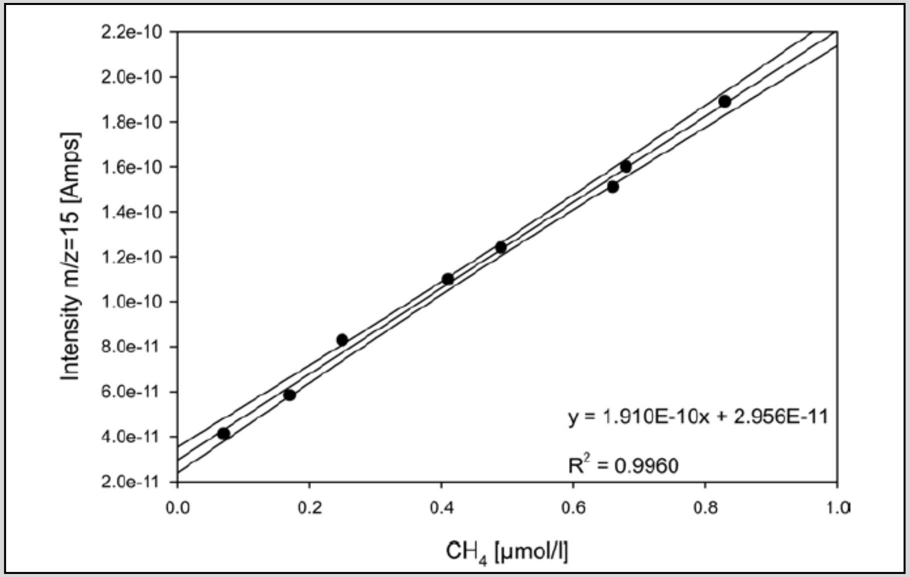
→Results in an obtimized detection limit

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



## OPTIMIZED AND REDESIGNED INSPECTR200-200



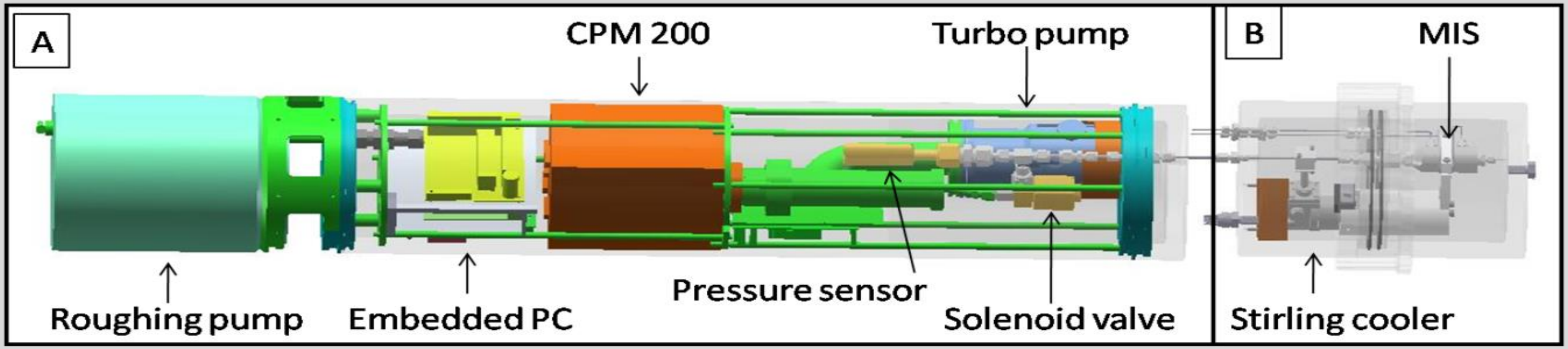



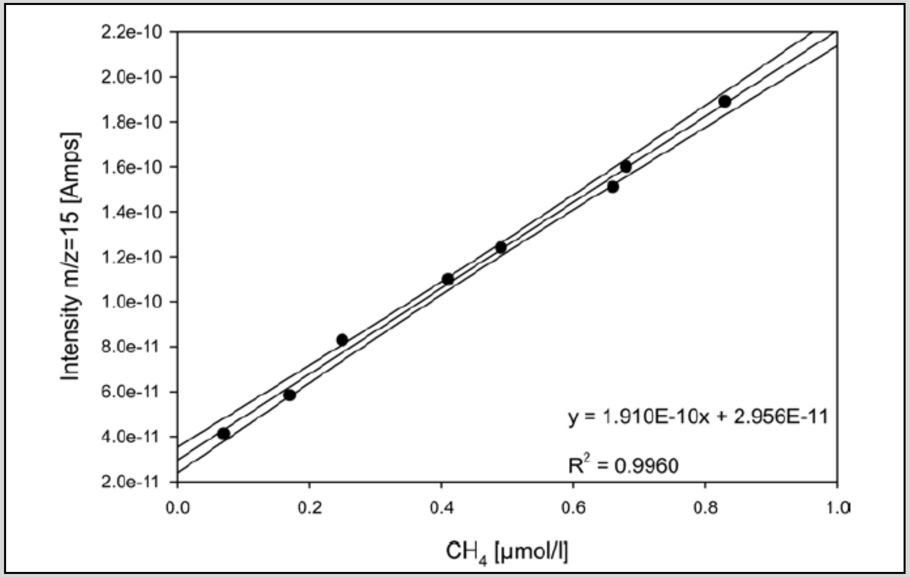

*Calibration of the optimized Inspectr200-200*

**New detection limit of the optimized Inspectr200-200:**

**~16 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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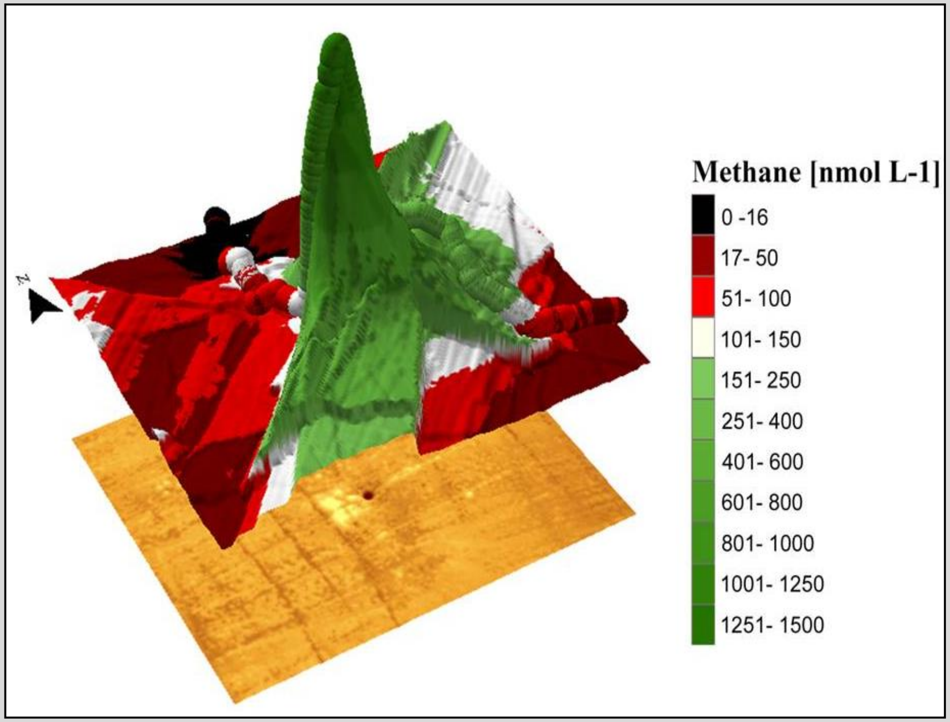
**Low enough???**

# In situ mass spectrometer for field applications

## Gas seep in the North Sea



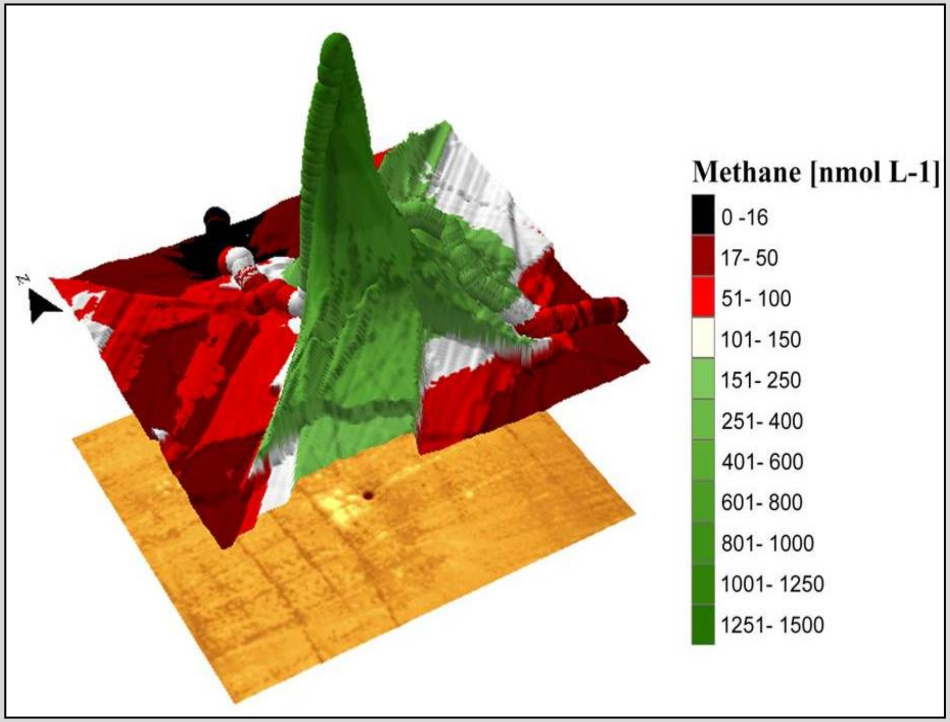

| Concentration [nmol L$^{-1}$] | Area [%] |
|---|---|
| < 16 | 3.6 |
| 16 - 100 | 48.3 |
| > 100 | 48.1 |

(Gentz and Schlüter 2012)

# IN SITU MASS SPECTROMETER FOR FIELD APPLICATIONS

## Gas seep in the North Sea

**without cryotrap:**
**48.1 %**

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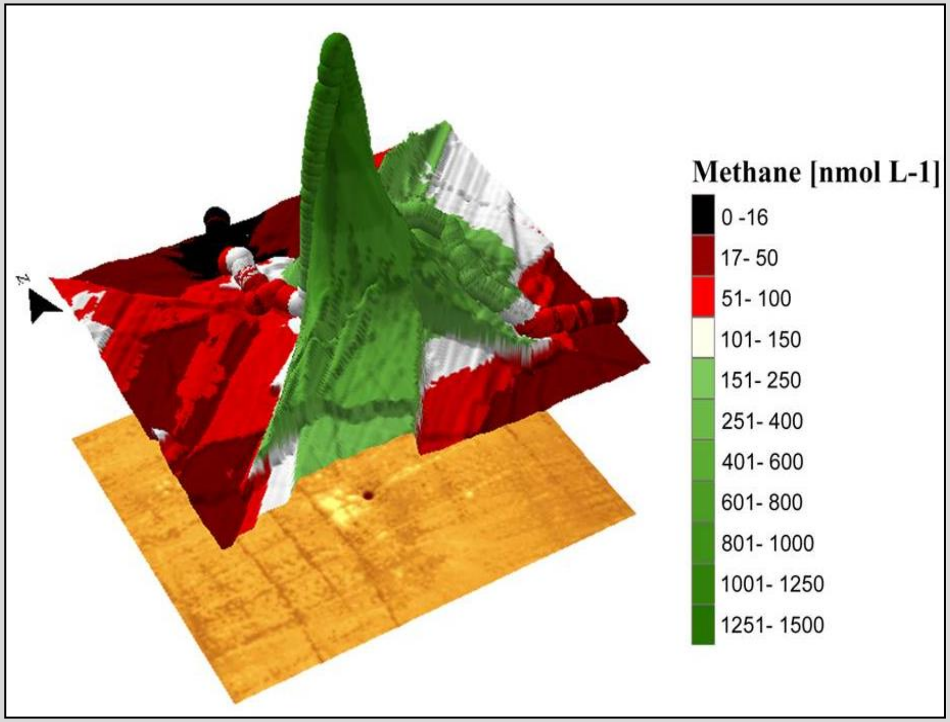
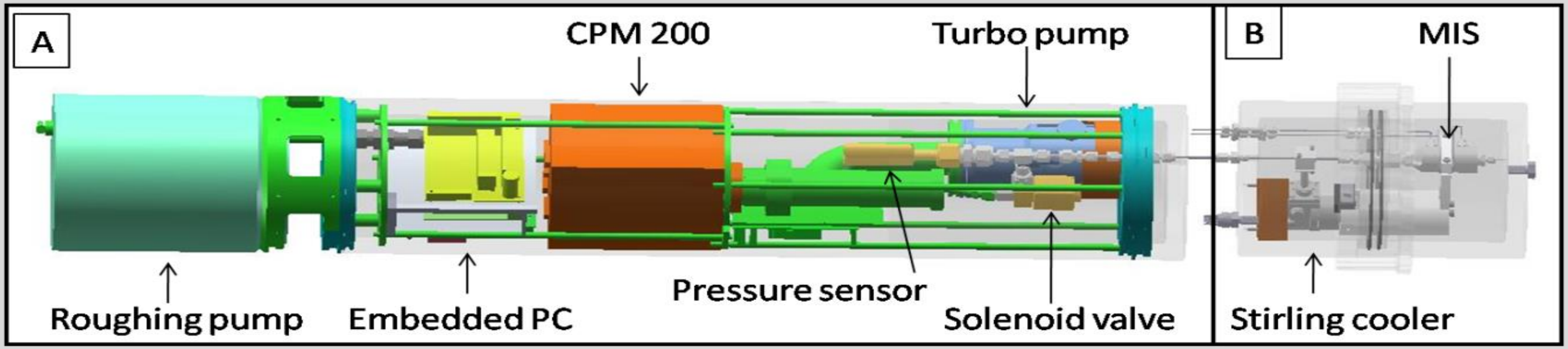



**with cryotrap:**
**96.4 %**

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

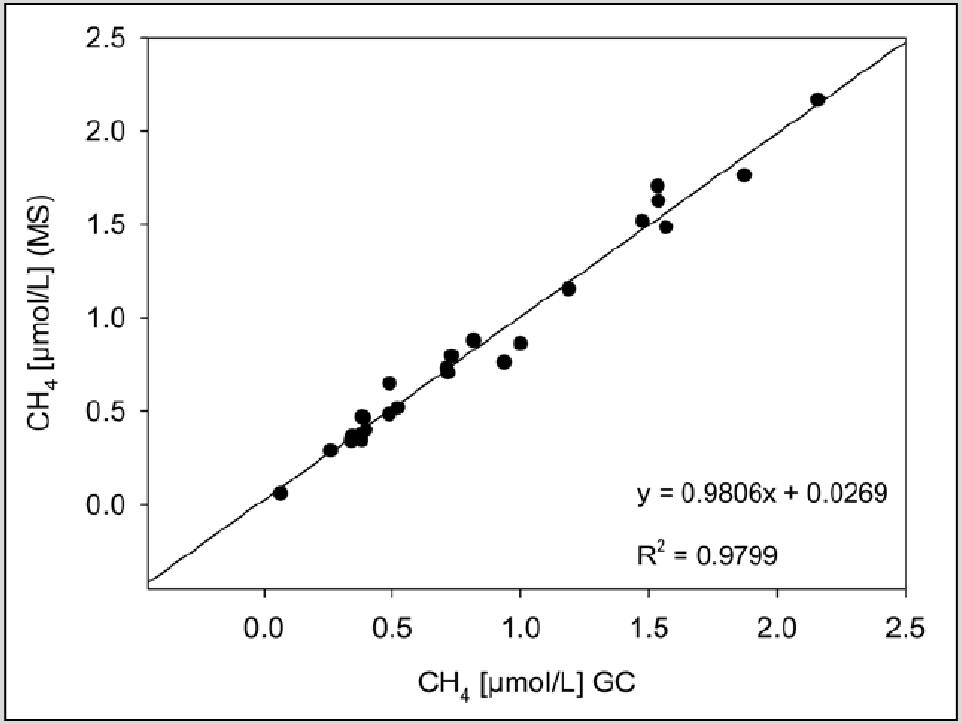
(Gentz and Schlüter 2012)

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



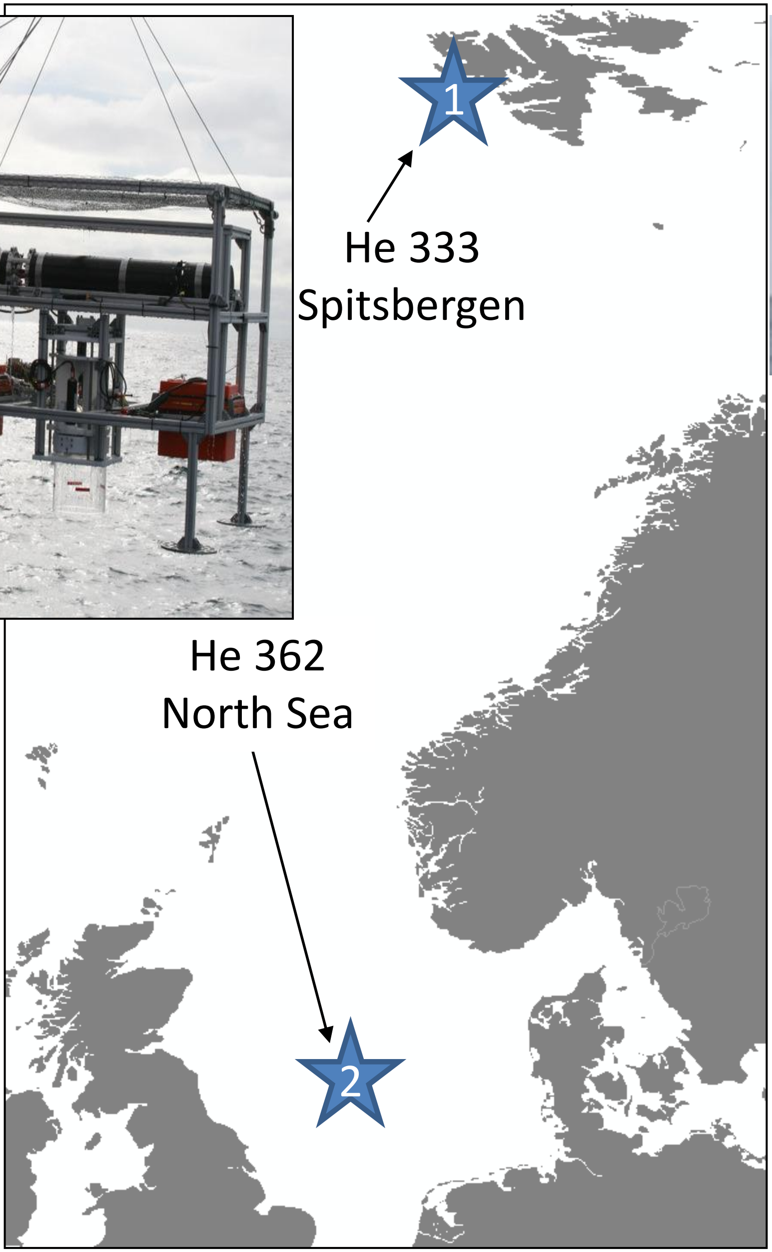

- Both methods are comparable
- No sampling preparation
- Simultaneous measurement of the dissolved gases
- No artefacts during sampling
- Up to 750 times higher sampling frequency

→ **Higher temporal and spatial resolution**

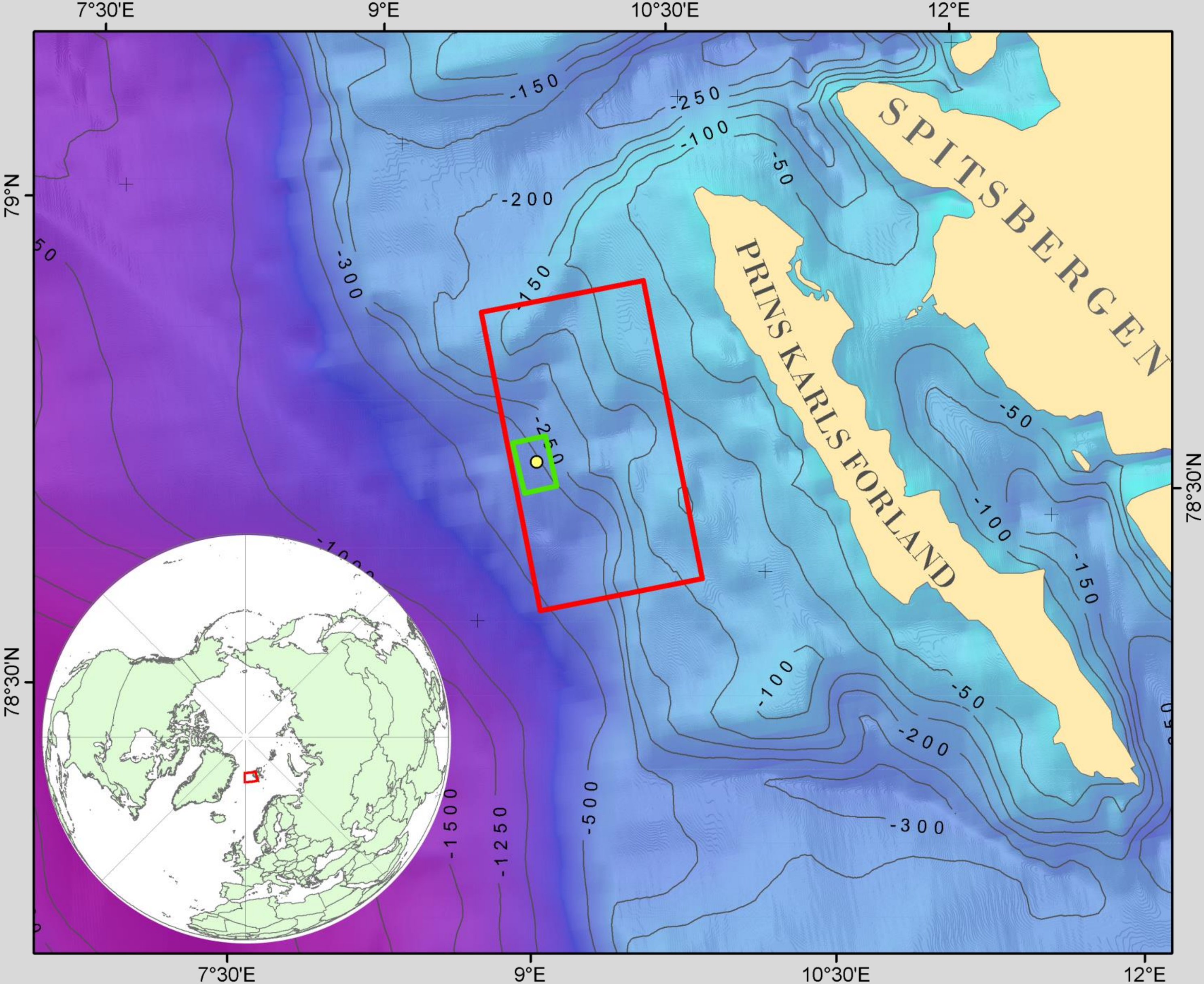



Inspectr200-200 vs. GC

# APPLICATION OF THE IN SITU MASS SPECTROMETER IN HARSH ENVIRONMENTS

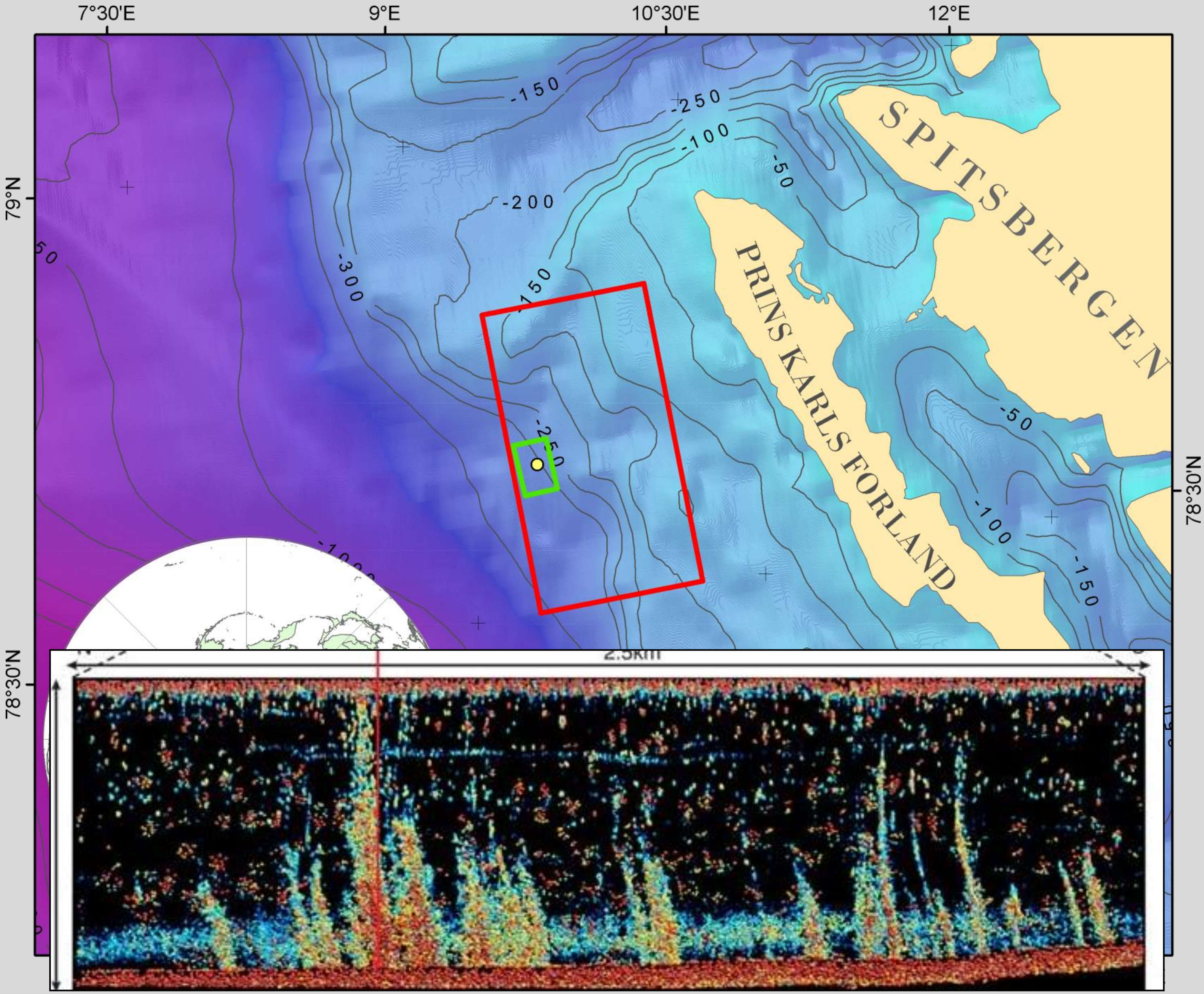



## Study area Spitsbergen




(Gentz et al. 2013)

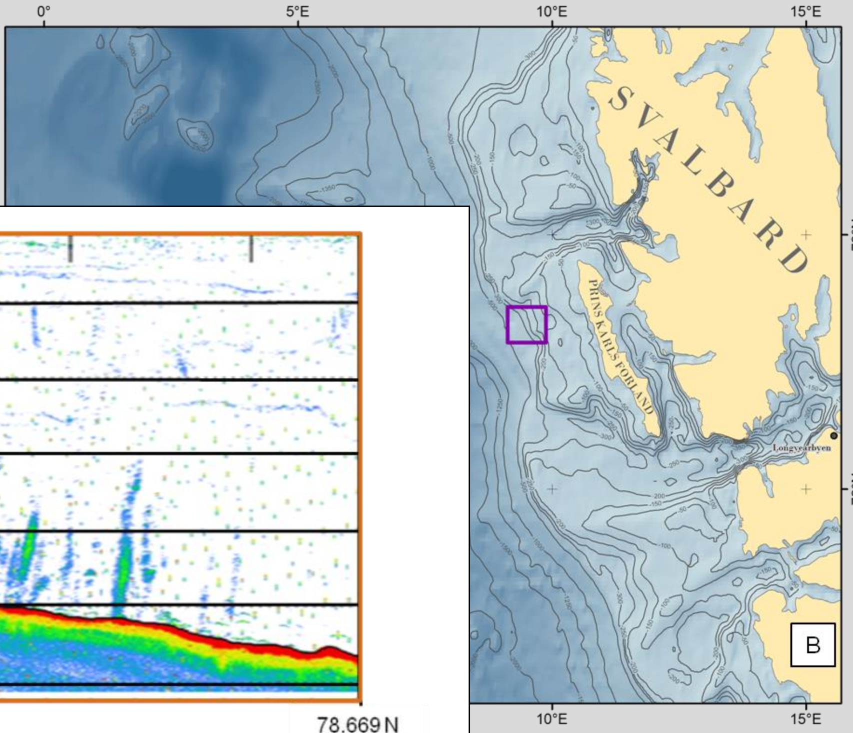
# STUDY AREA SPITSBERGEN

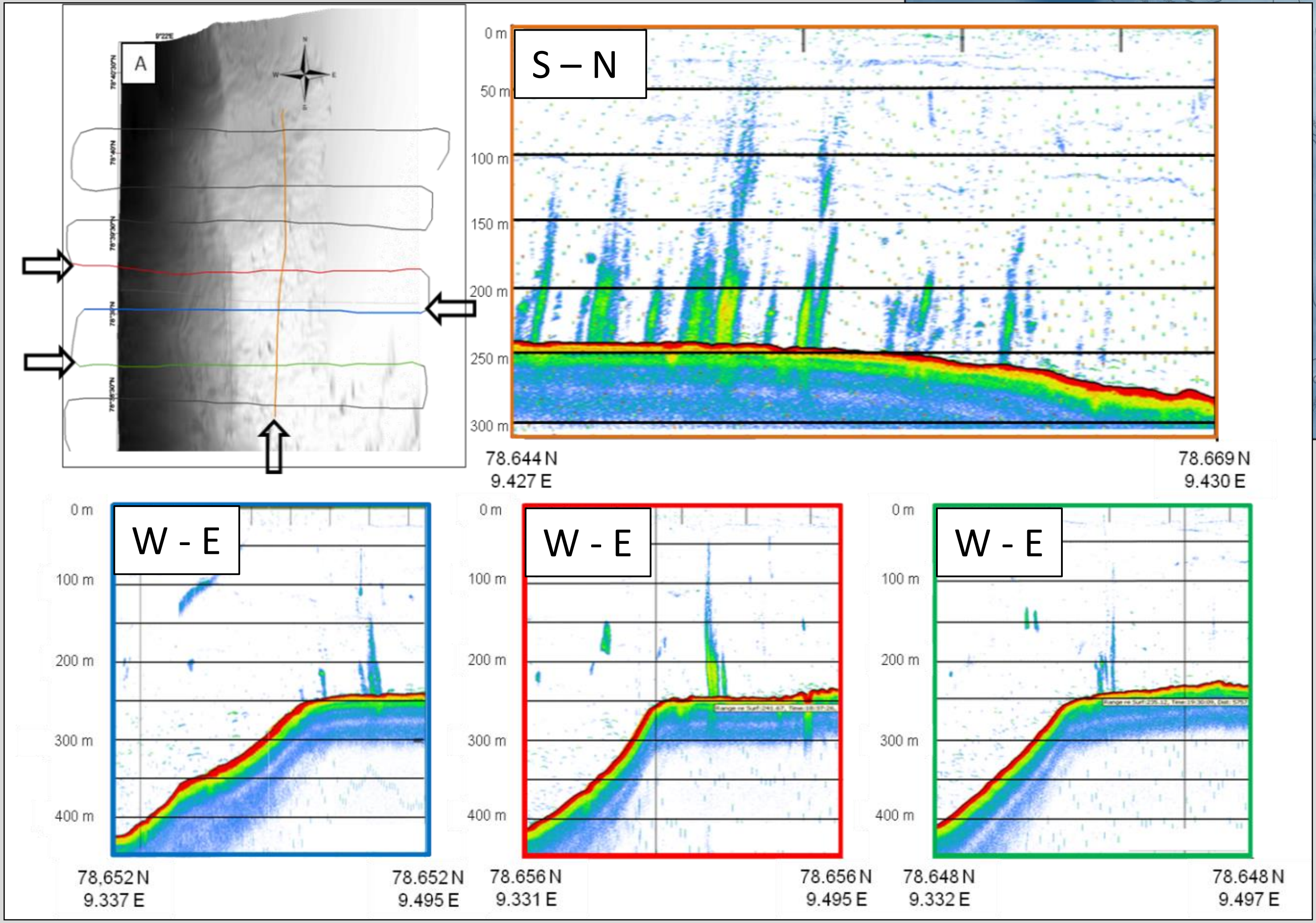



(Westbrook et al. 2009)

## HYDROACOUSTIC:

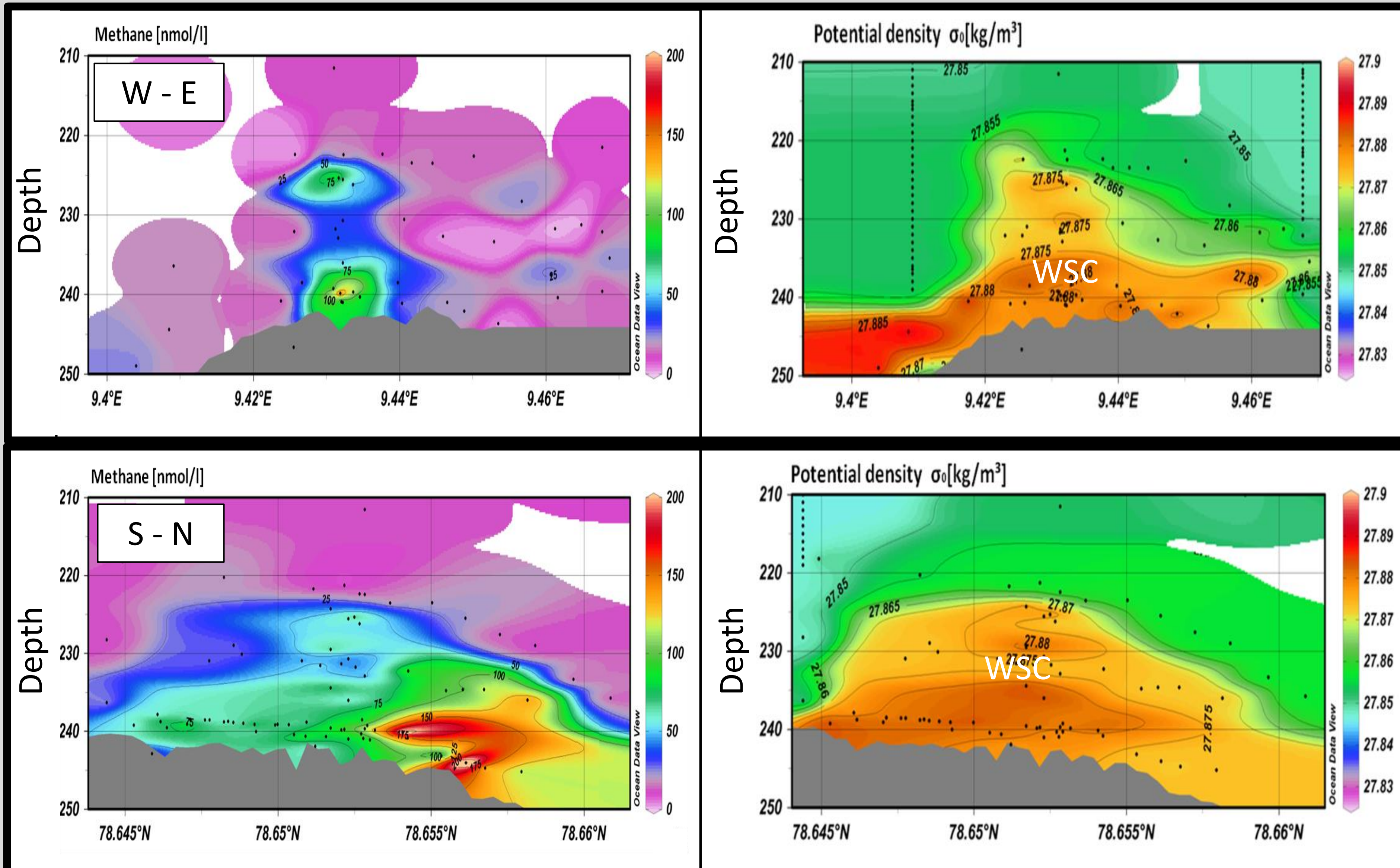
Ten gas flares lined up in S – N direction and max. rise height of up to 200 m were found.




(Gentz et al. 2013)

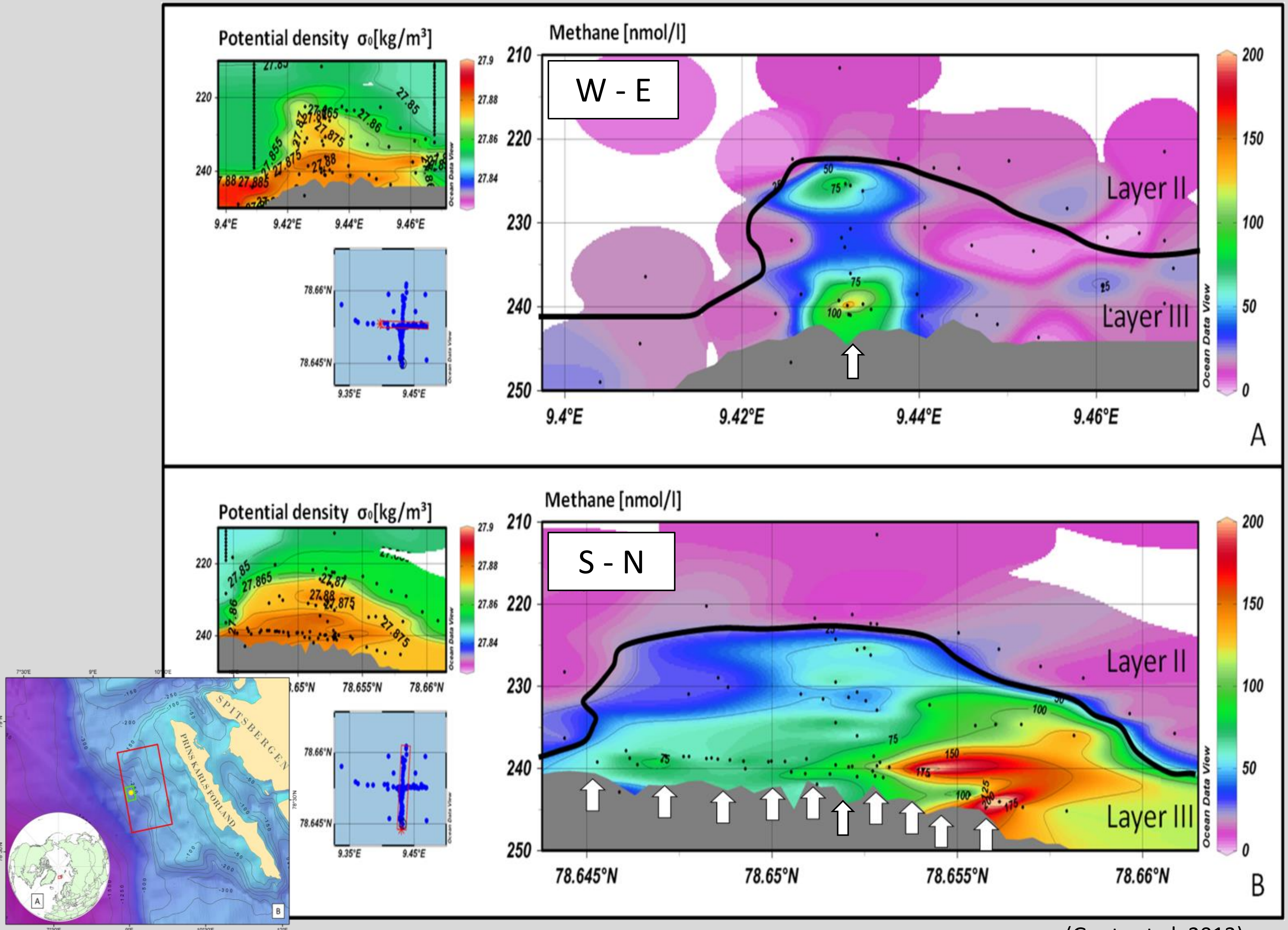
## Dissolved methane and hydrography




(Gentz et al. 2013)

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

## DISSOLVED METHANE AND HYDROGRAPHY




(Gentz et al. 2013)

# Main results Spitsbergen

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

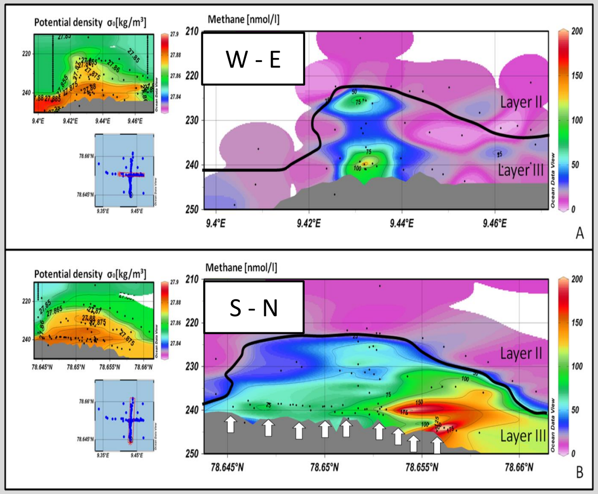
→ ~80 % of the methane will be dissolved and trapped below the pycnocline and horizontal transport in north direction to greater depth and subsequent oxidation occur.

→ ~20 % could reach the water mass above the pycnocline.

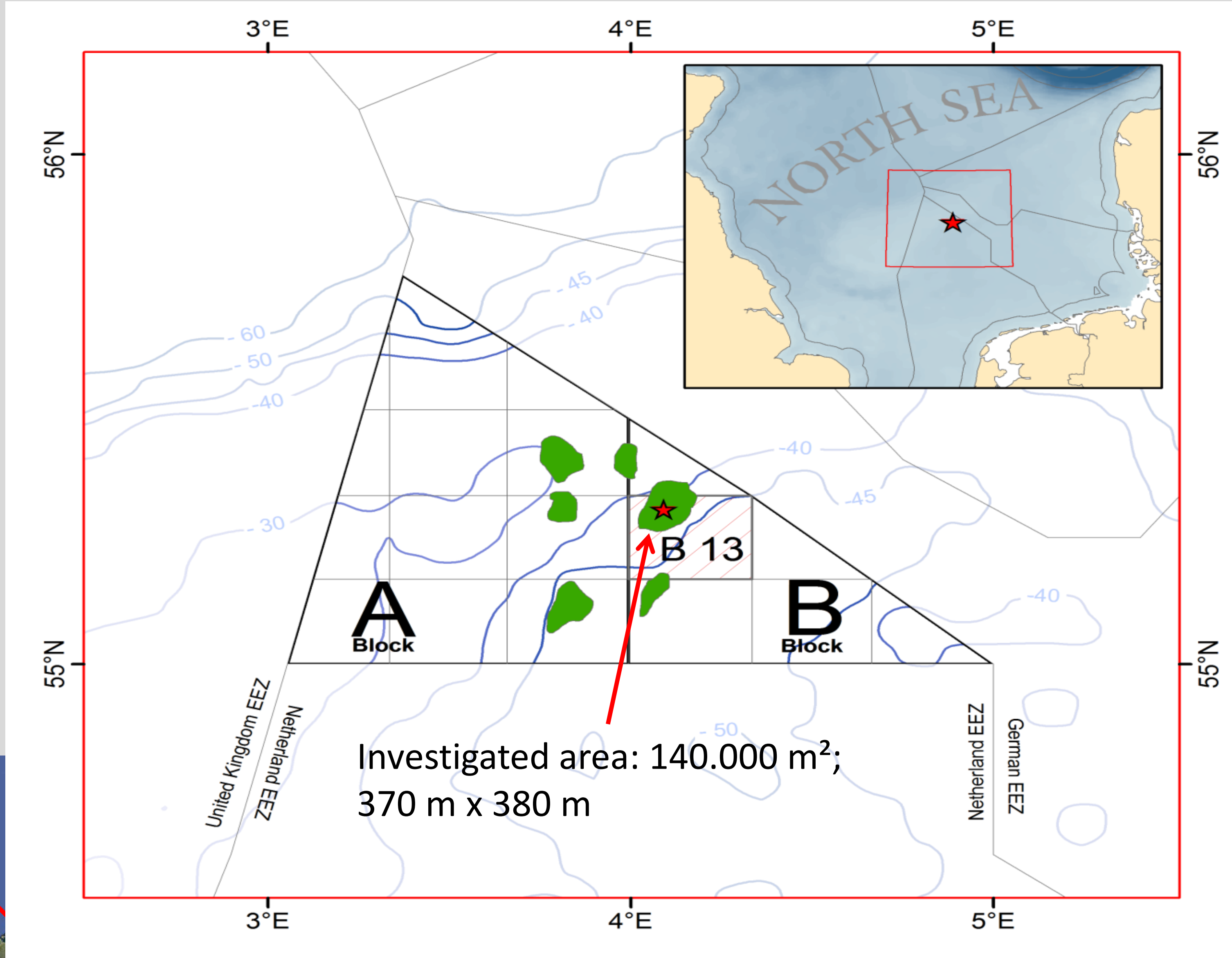
→ Due to dilution of dissolved methane in the upper water mass the contribution of the released methane to the global atmospheric methane budget could not been determined.

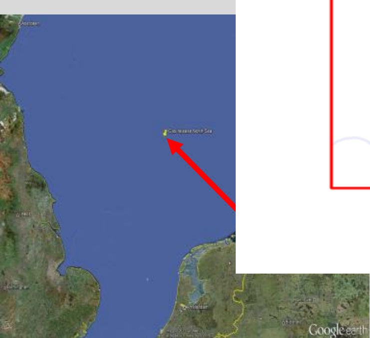
→ Bubble transport can be excluded as direct pathway for methane to the atmosphere.

→ In winter the stratification breaks down which could lead to methane release into the atmosphere.



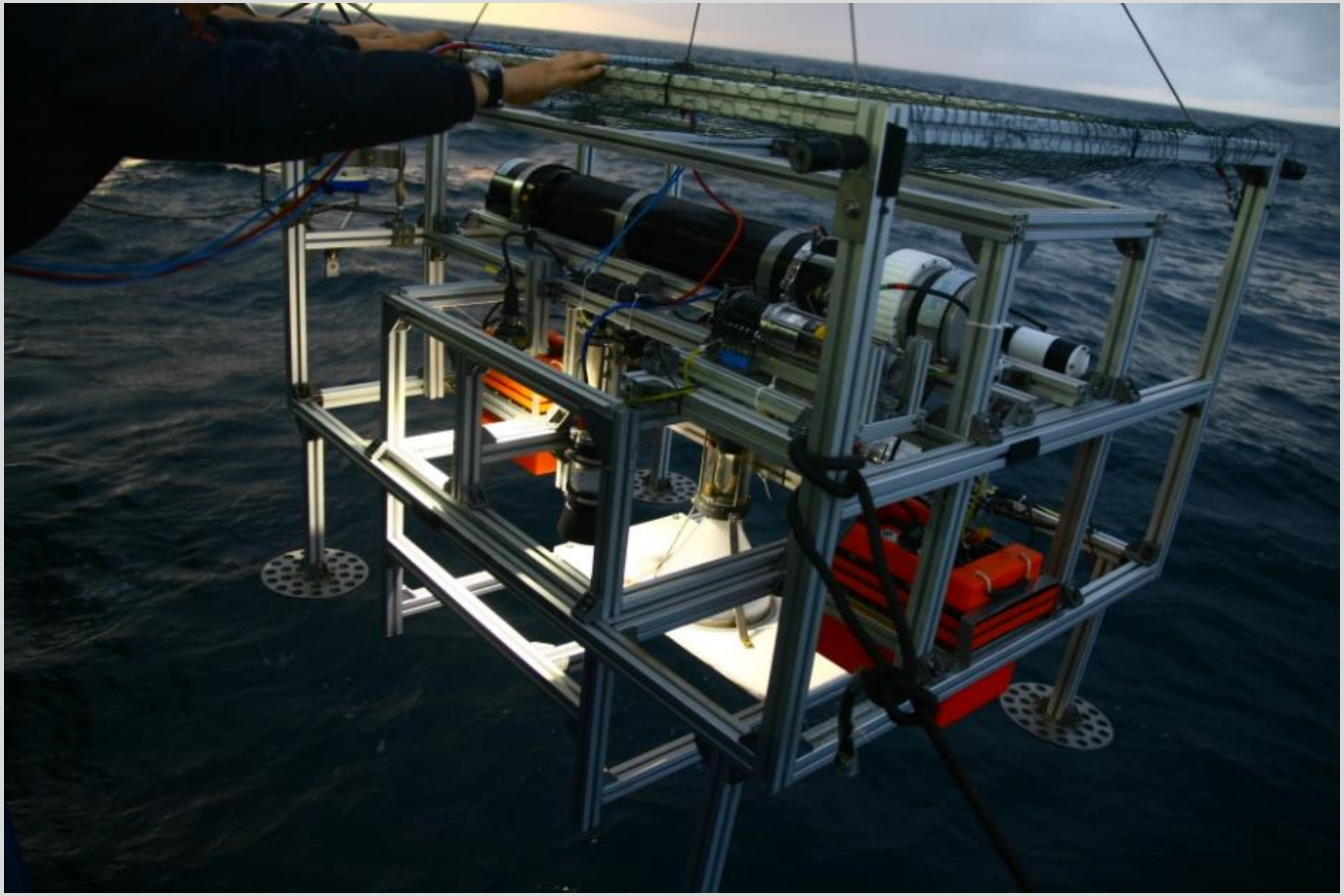
# Observation of a gas seep area in the North Sea



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 m²
- CTD 14; vertical profiles
- Bubble sampler; 5 samples
- Multiple sediment corer; 5 cores

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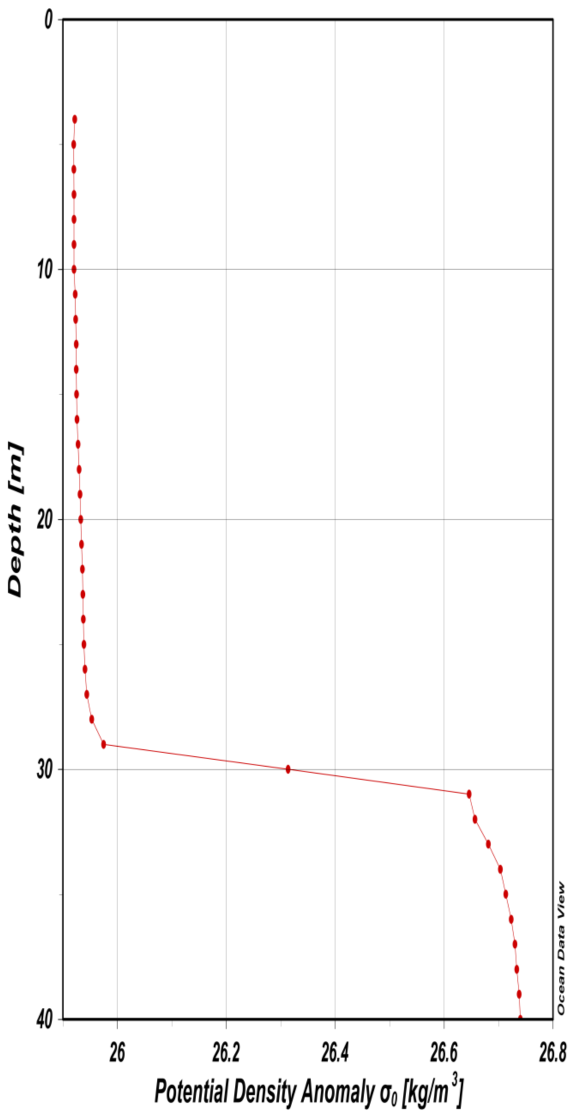
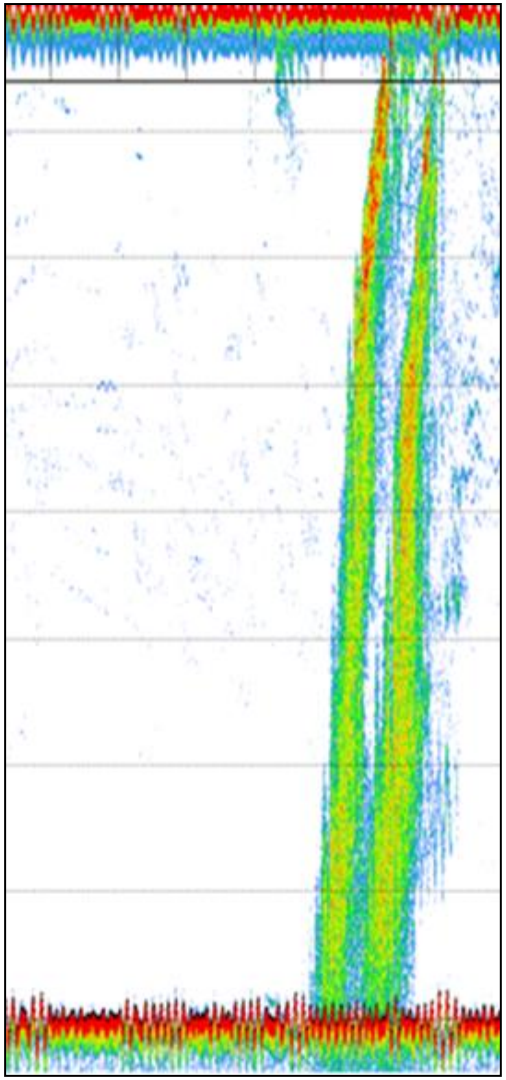
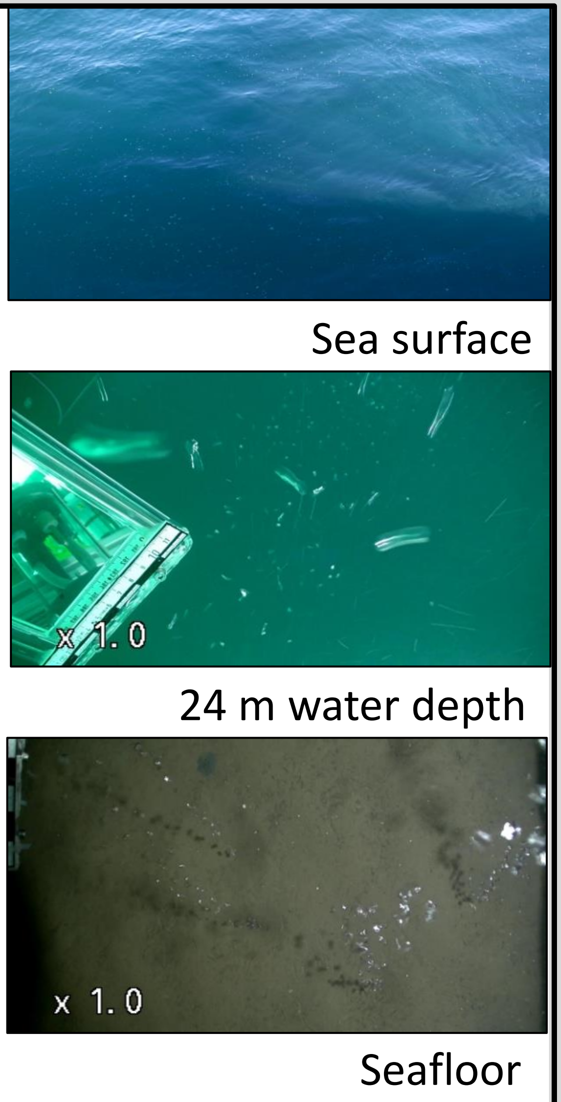



CTD profiles



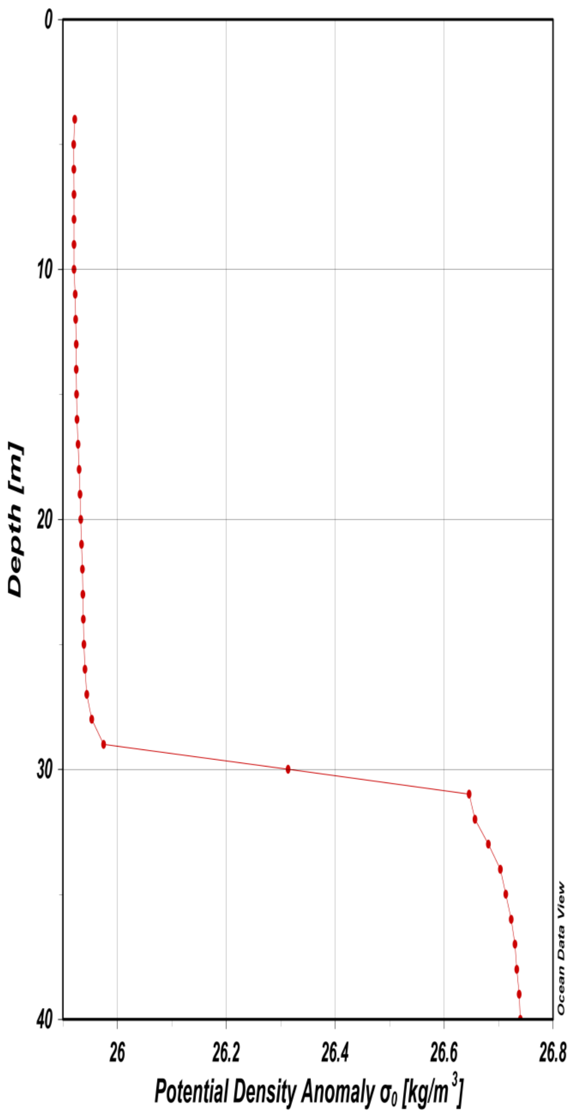
Hydroacoustic



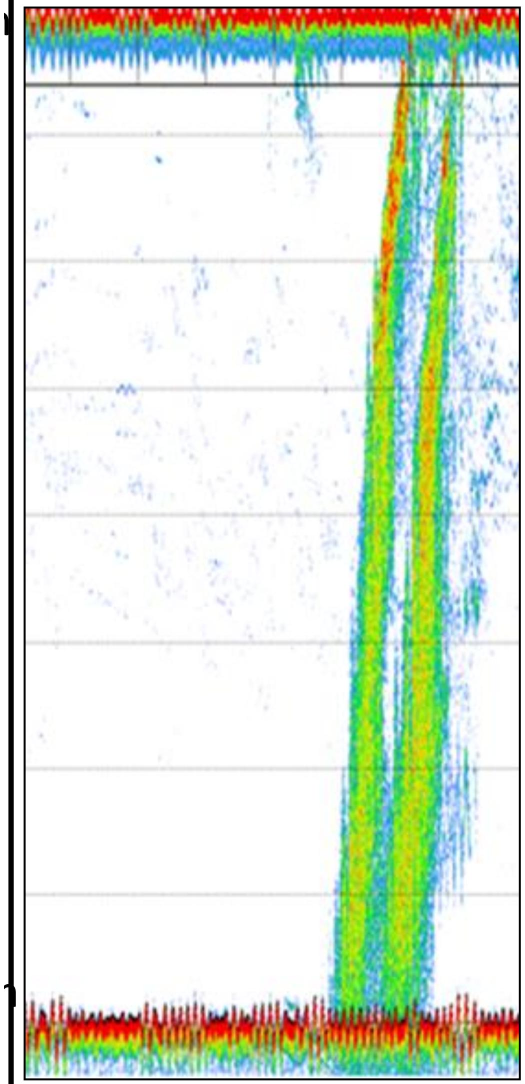

Video observation

(Gentz et al. unpublished data)

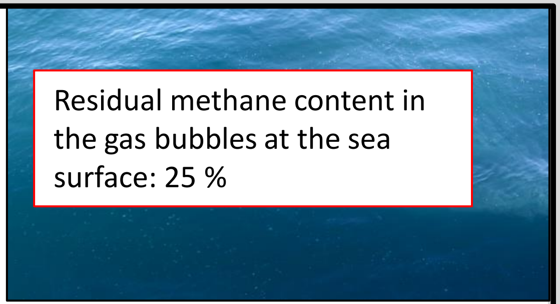
# Observation of a gas seep area in the North Sea




CTD profiles

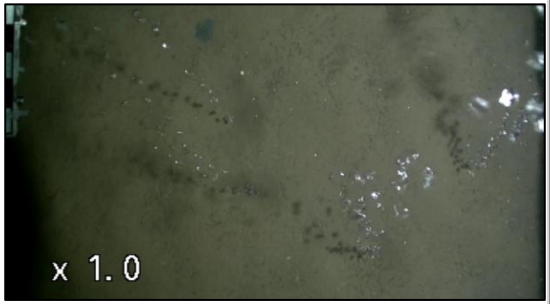


Hydroacoustic




Sea surface


24 m water depth

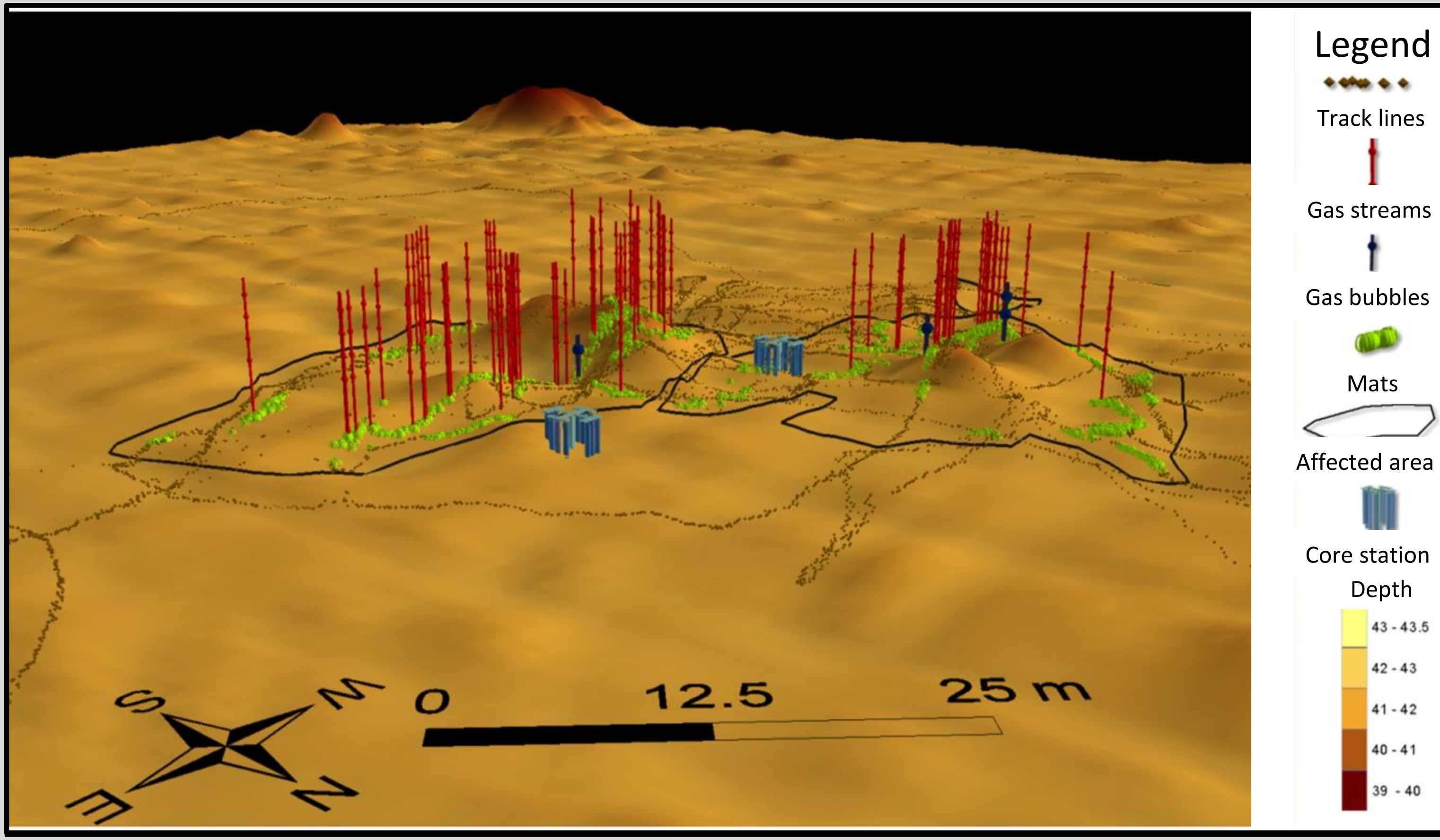



Seafloor

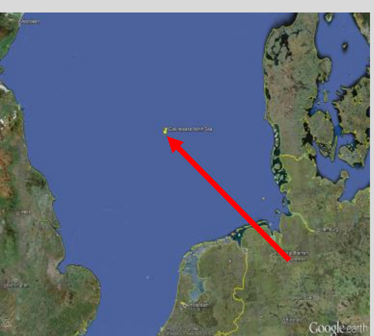
Video observation

(Gentz et al. unpublished data)

## VIDEO OBSERVATION OF THE SEAFLOOR

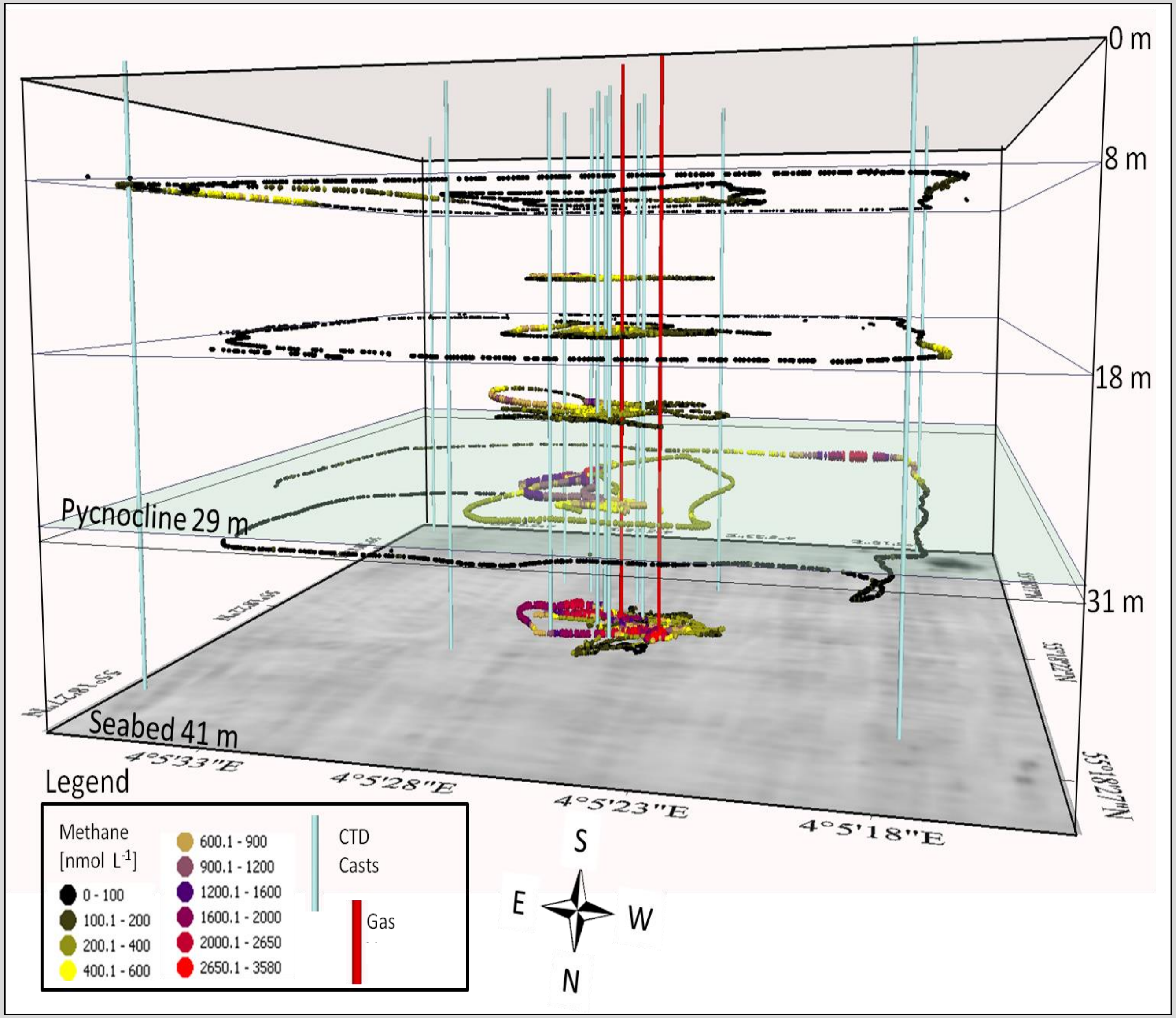



(Gentz et al. unpublished data)



Affected area: ~3800 $m^2$
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 $CH_4$ $yr^{-1}$

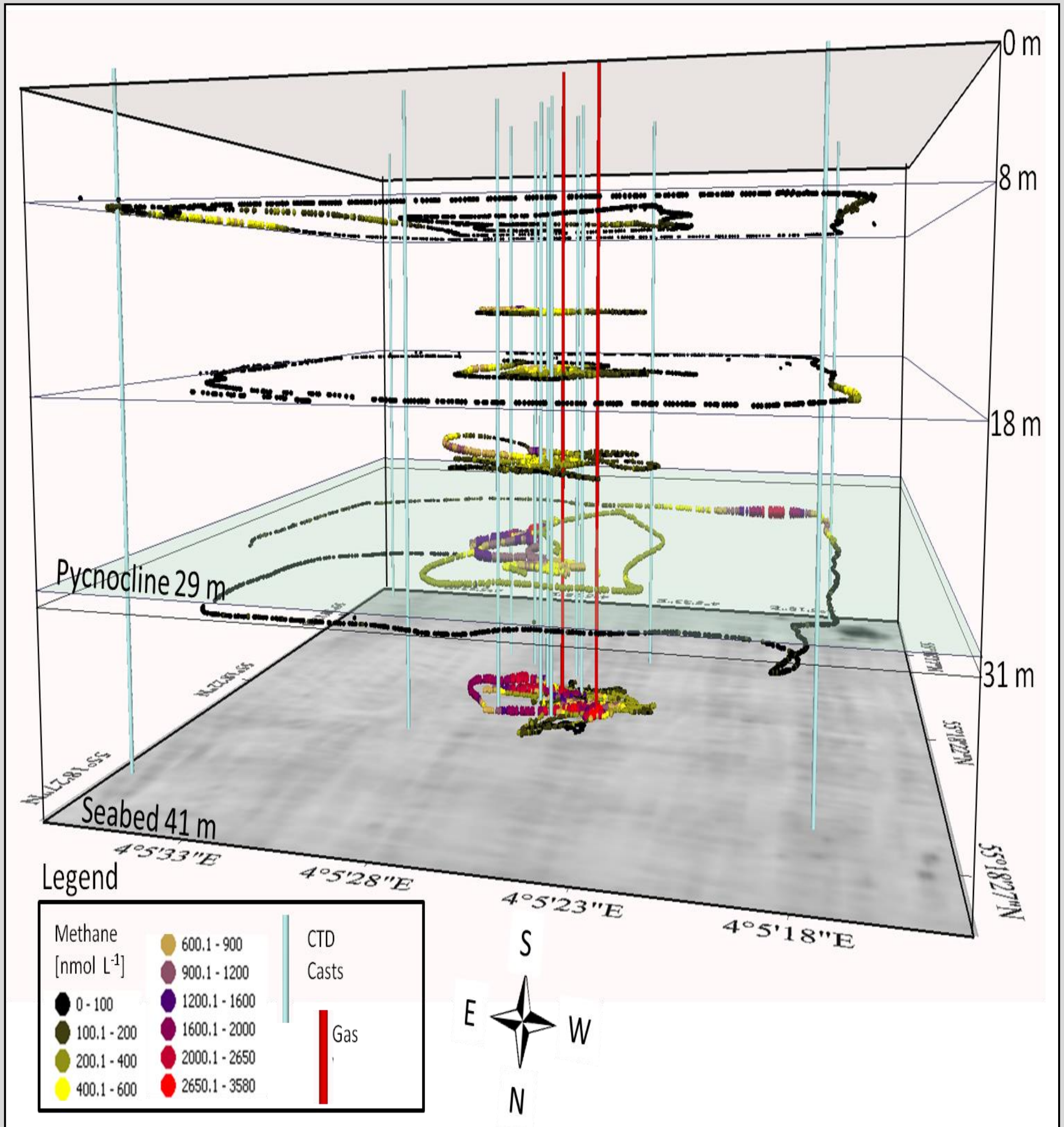
# DISSOLVED METHANE SAMPLING IN THE WATER COLUMN




11900 samples in various depth in between 24 hours

(Gentz et al. unpublished data)

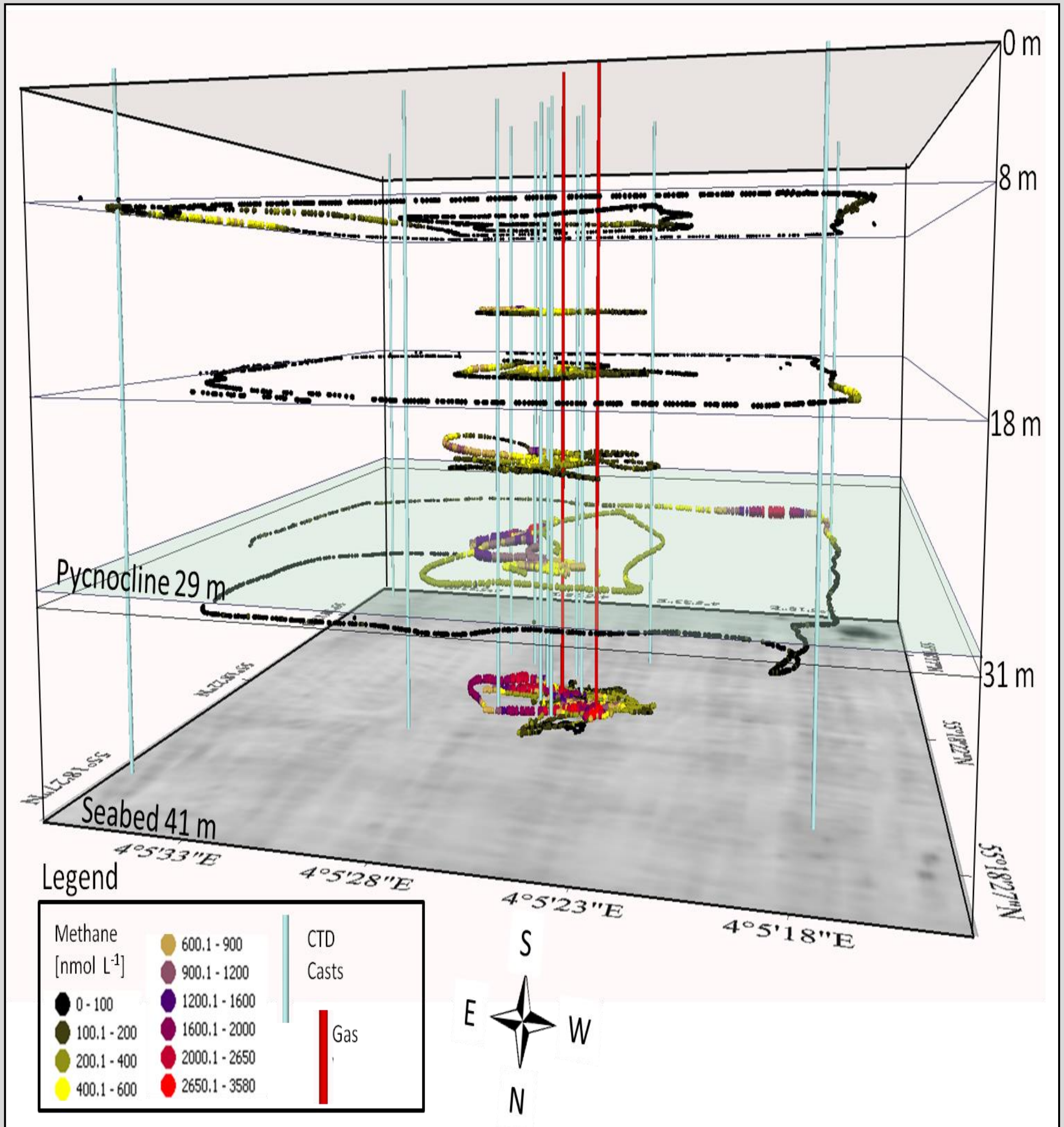
# DISSOLVED METHANE SAMPLING IN THE WATER COLUMN




- 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)

## Dissolved methane sampling in the water column

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

**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.

(Gentz et al. unpublished data)

## MAIN RESULTS NORTH SEA

→ Conservative estimation of methane release into the water column: 35.3 ± 17.65 t $CH_4$ $yr^{-1}$ which is in the same order like the geogragraphically close Tommeliten area (Schneider von Deimling et al. 2011).

→ The total inventory of dissolved methane is calculated to ~0.6 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 ± 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.

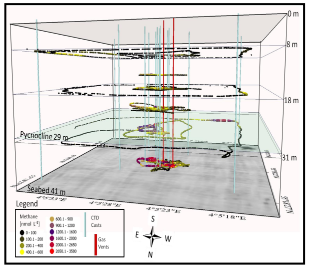
## Conclusions

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



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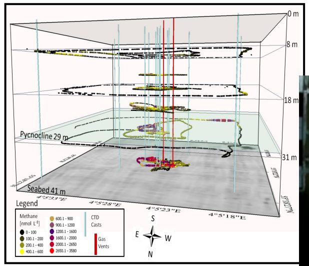


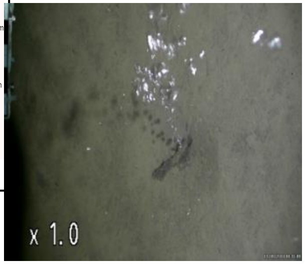


- The inventory calculation is more accurate than before and shows that conventional methods tend toward underestimation.
- The investigated study area in the North Sea contributes to the global atmospheric methane budget.

# CONCLUSIONS



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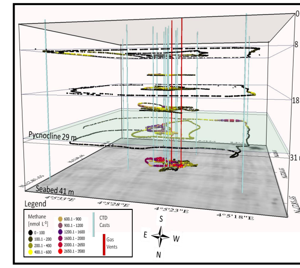


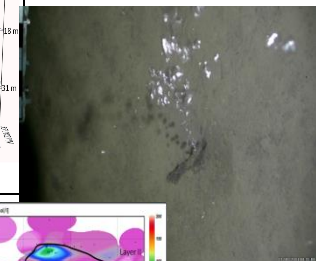

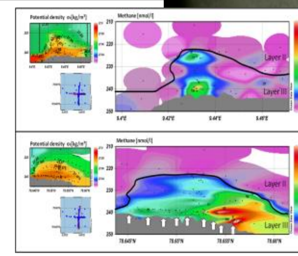

- The inventory calculation is more accurate than before and shows that conventional methods tend toward underestimation.
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## Conclusions

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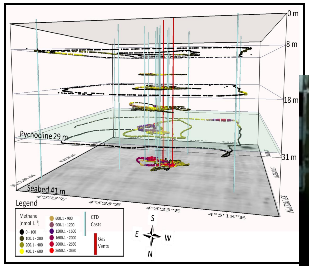


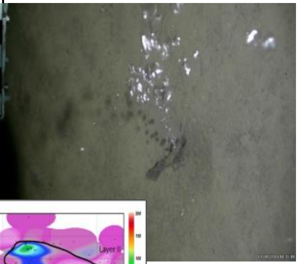

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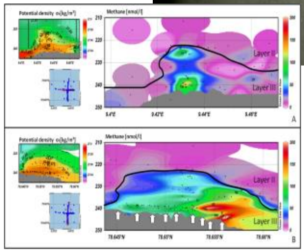


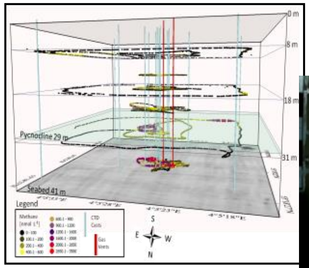
- Pycnoclines are limitations for vertical transport of methane.
- The fate of methane as well as the contribution to the global atmospheric methane budget of each source depends on bubble size, the water depth, the water current and the water stratification.

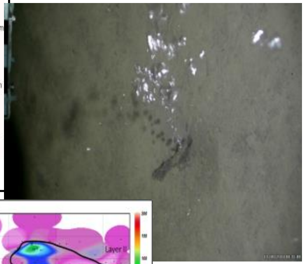
| | Spitsbergen | North Sea |
|---|---|---|
| Water depth [m] | 245 | 40 |
| Water stratification [m above seafloor] | 25 | 10 |
| Observed bubble rise [m above seafloor] | 150 | 40 |
| Estimated bubble diameter [mm] | < 5 | 7 |
| Bubbles at seasurface | No | Yes |
| Direct methane transport | No | Yes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

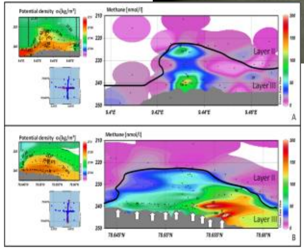
## CONCLUSIONS



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







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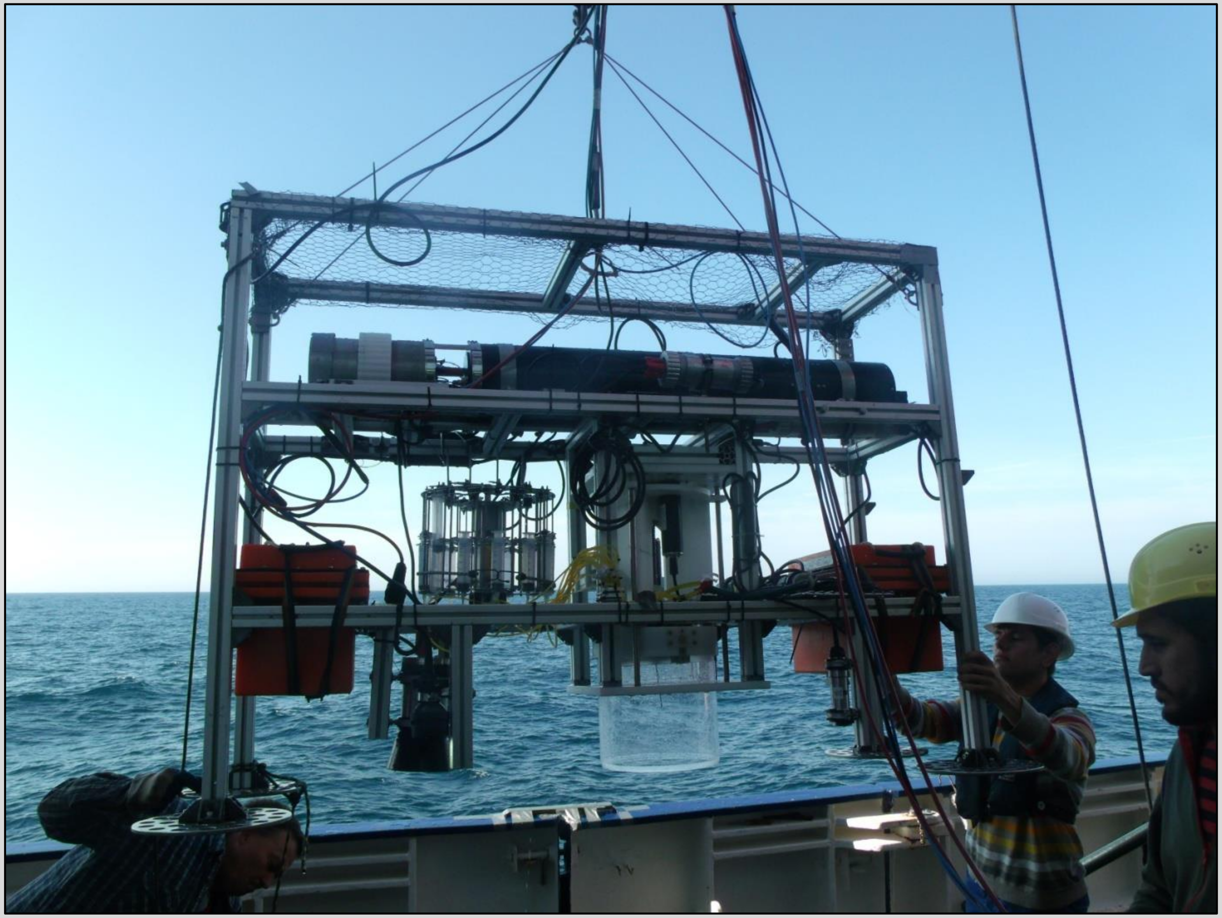
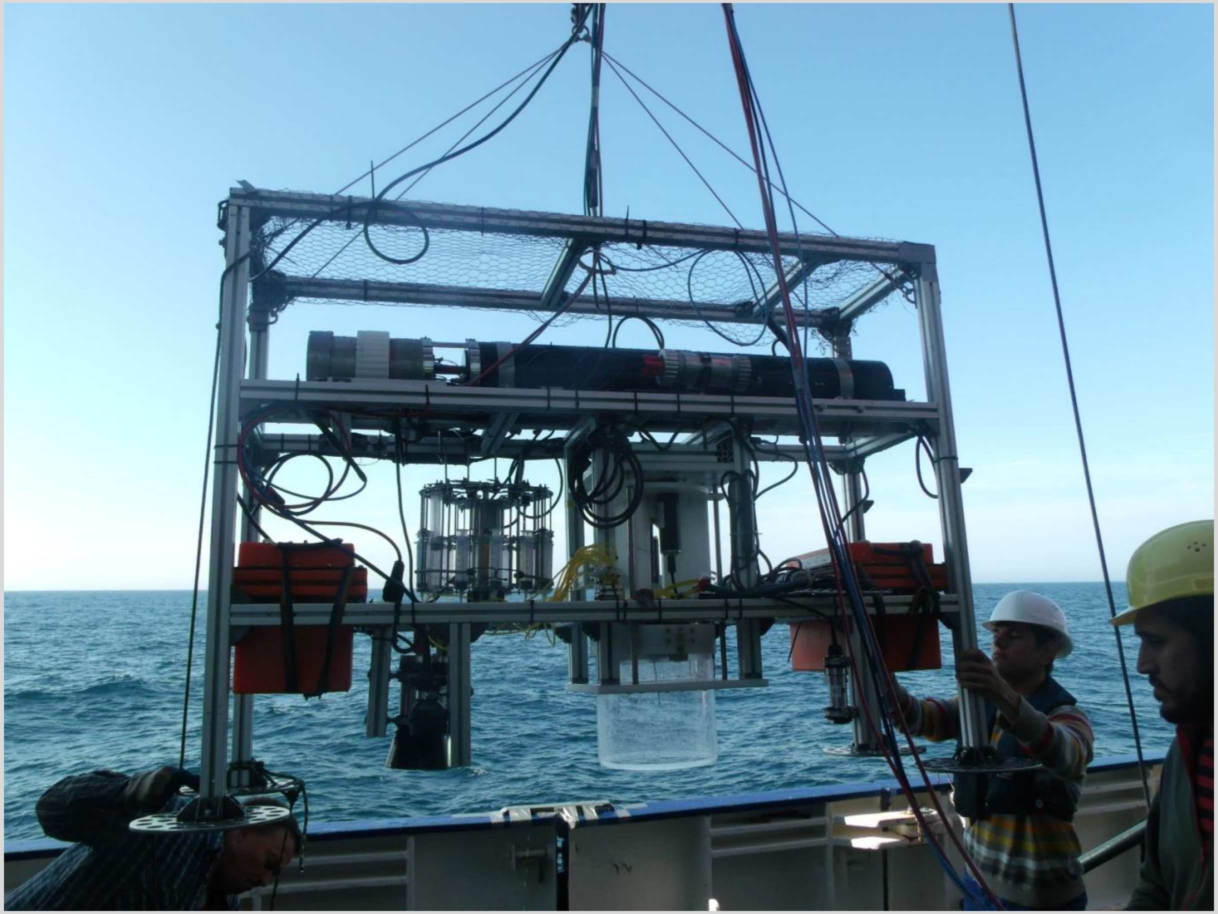
- The use of the improved in situ mass spectrometry is one step forward to understand the pathways and potential global relevance of these methane sources.

# Current and Future work

High resolution mappingof dissolved gases in a benthic  chamber



He 406; Aug 2013



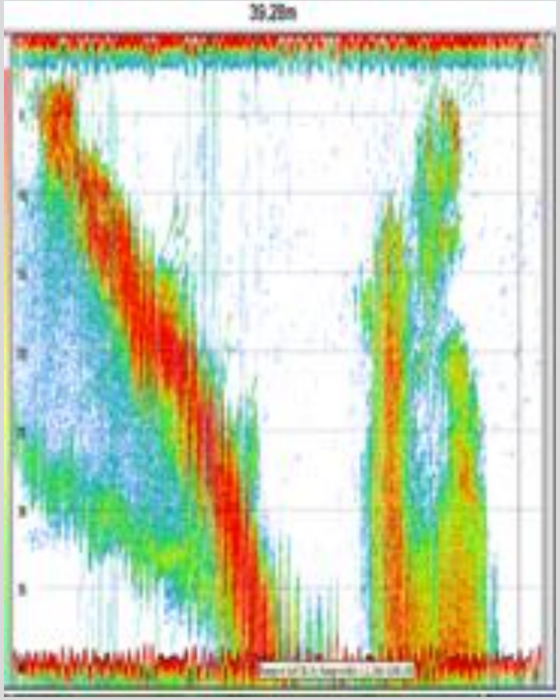
Thank you for your attention!

# Backup

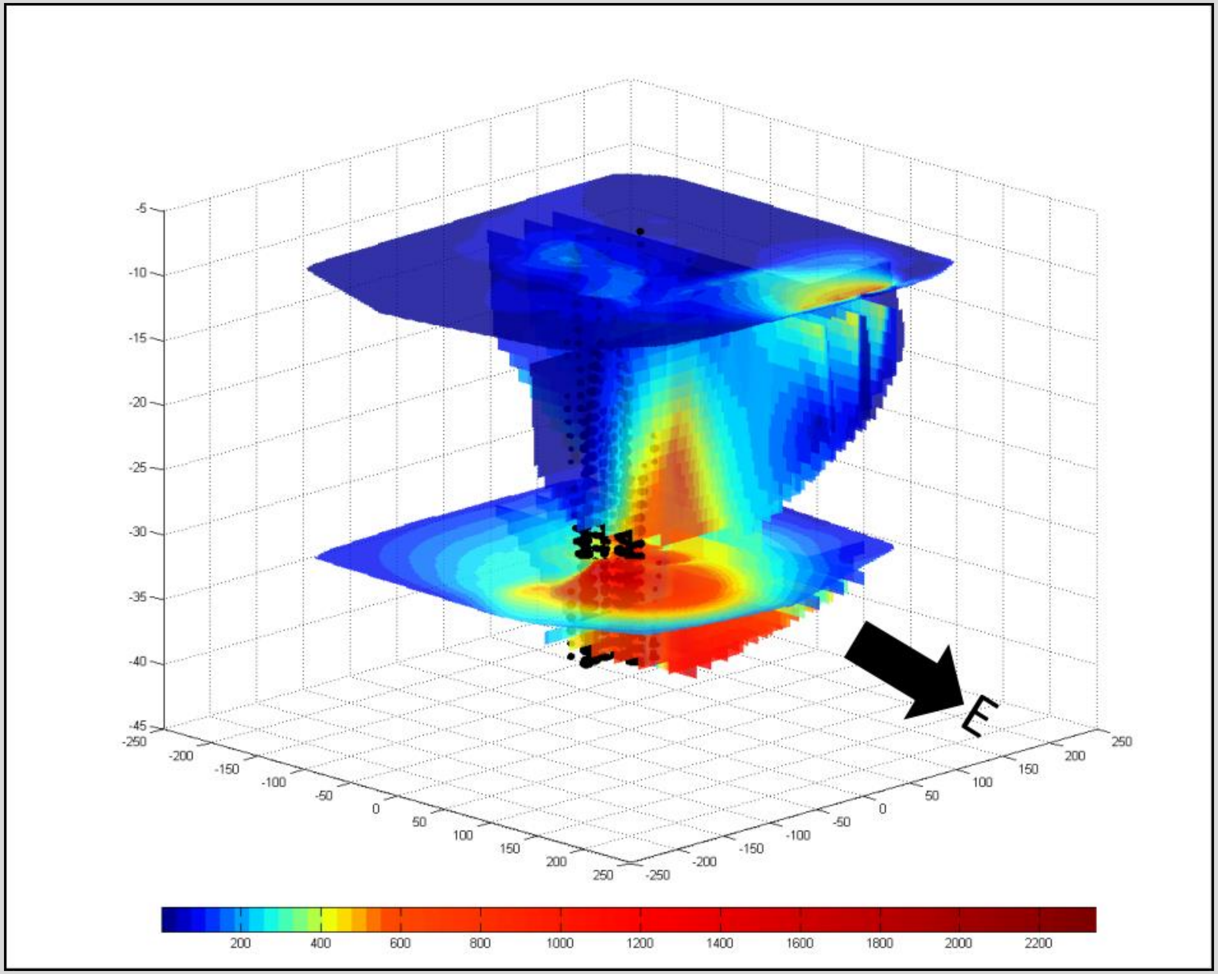
## FUTURE WORK

Implementation in new device holder

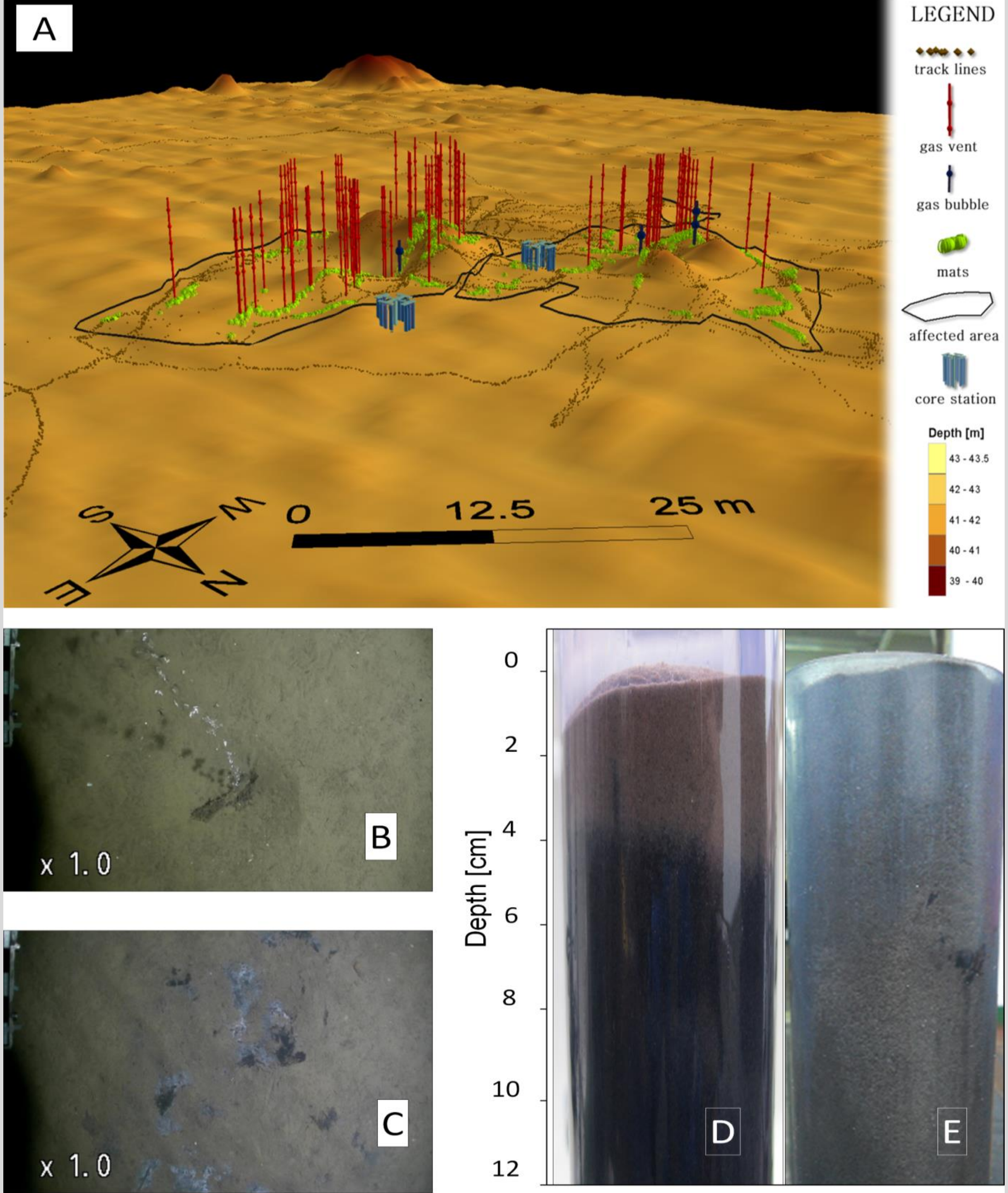
Benthic chamber measurements

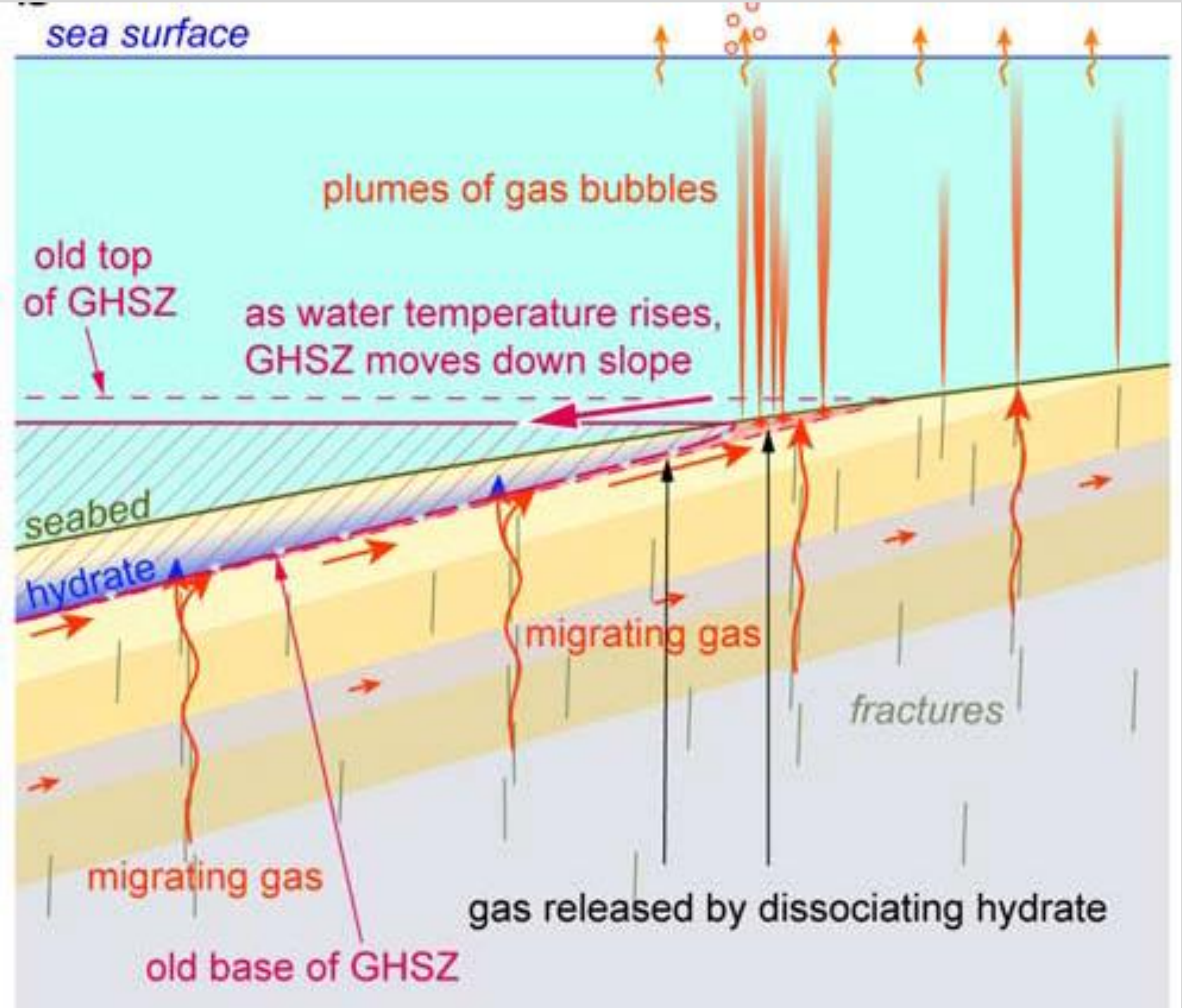


Combining ydroacoustic with in situ mass spectrometry



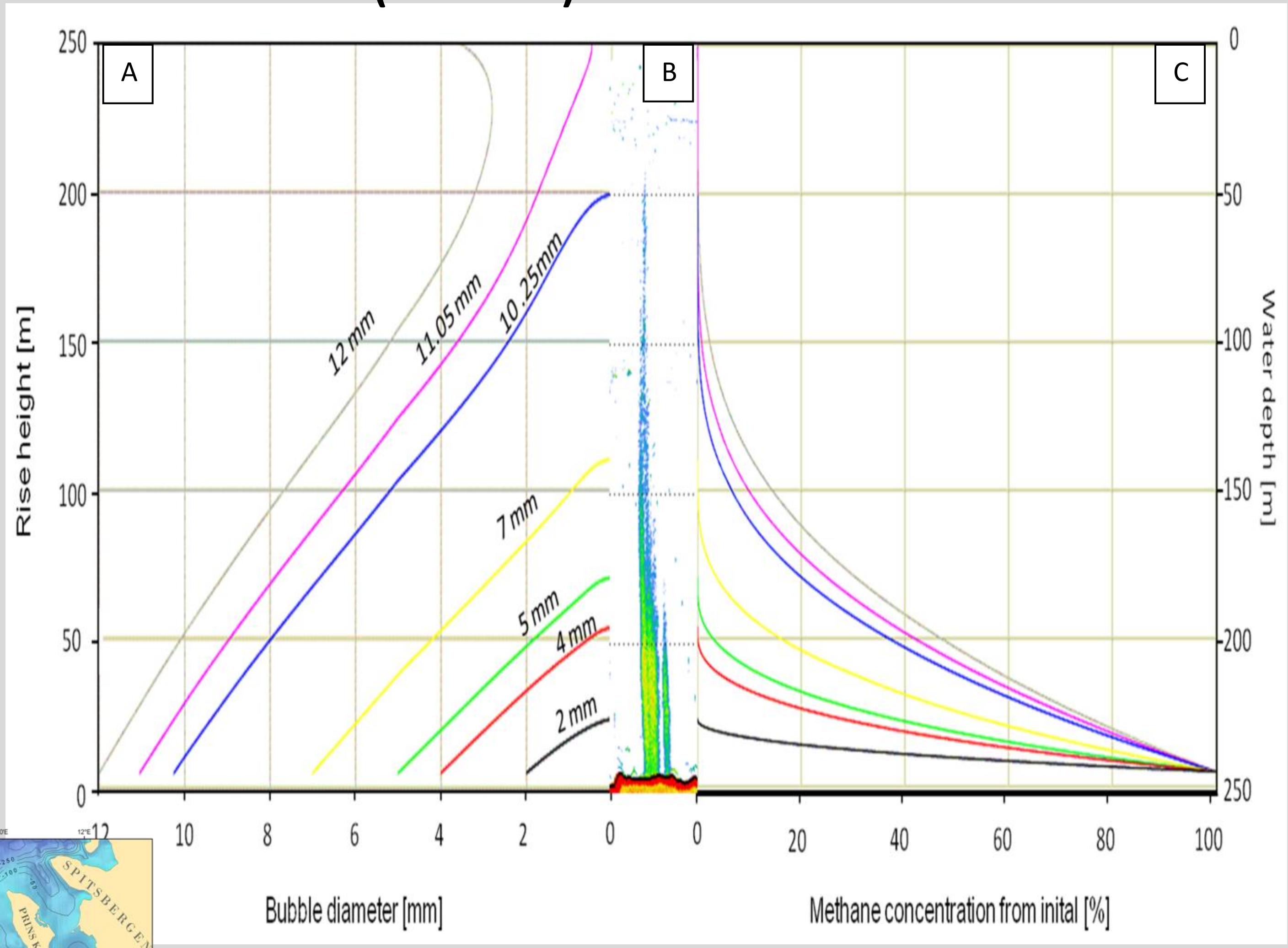

Sibson, R., "A Brief Description of Natural Neighbor Interpolation", Kapitel 2 in *Interpolating multivariate data*, S. 21-36. John Wiley & Söhne: New York, 1981.

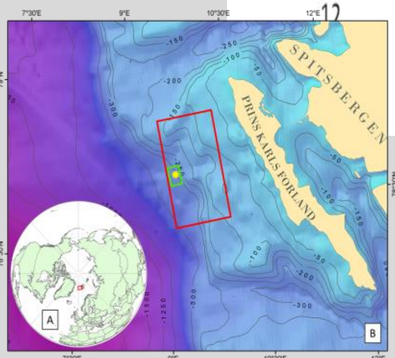

A
LEGEND
track lines
gas vent
gas bubble
mats
affected area
core station
Depth [m]
43 - 43.5
42 - 43
41 - 42
40 - 41
39 - 40
S
W
E
N
0
12.5
25 m
B
x 1.0
C
x 1.0
Depth [cm]
0
2
4
6
8
10
12
D
E



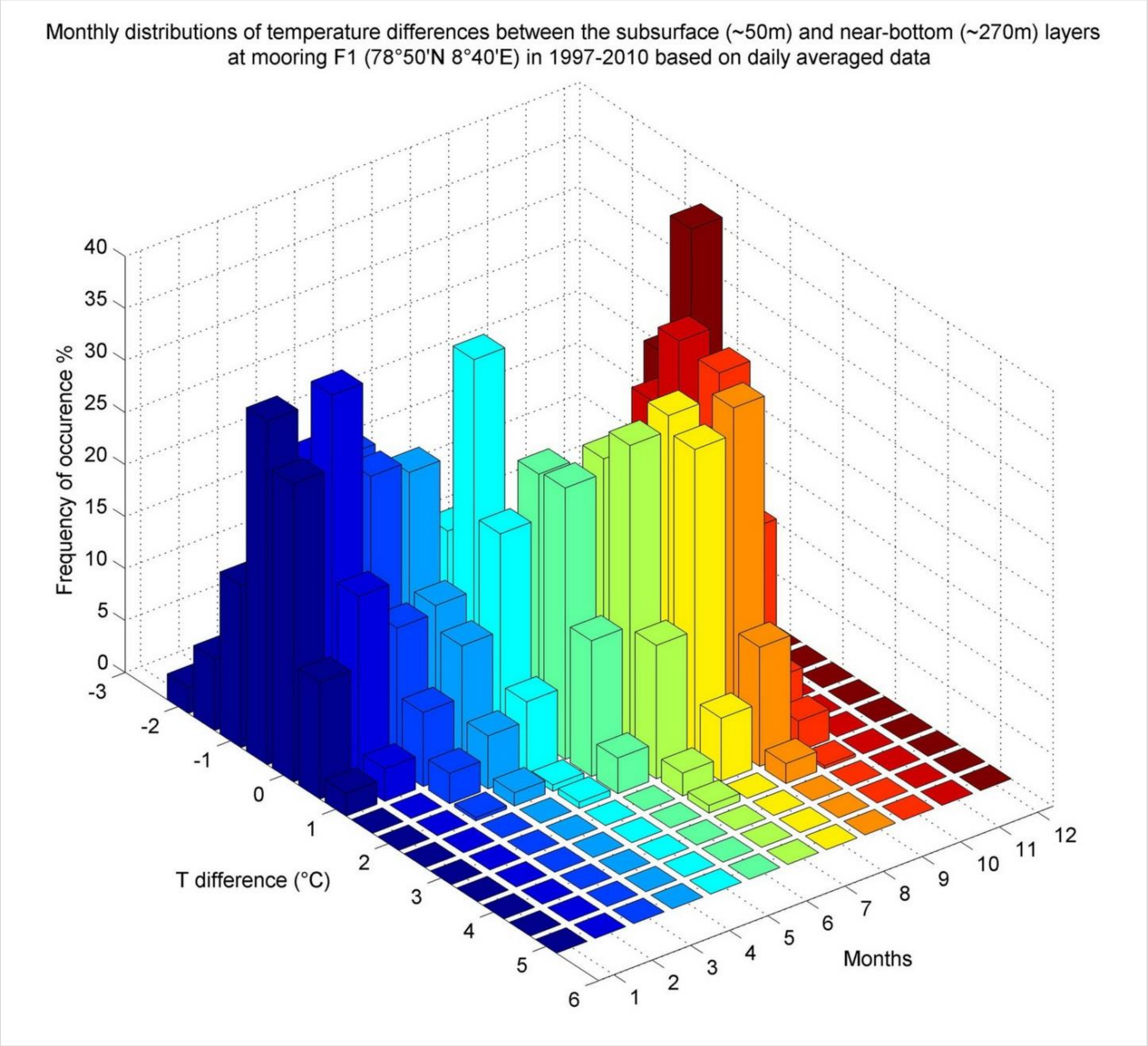

Westbrook et al. 2009

# GAS BUBBLE DISSOLUTION MODEL (SIBU GUI):

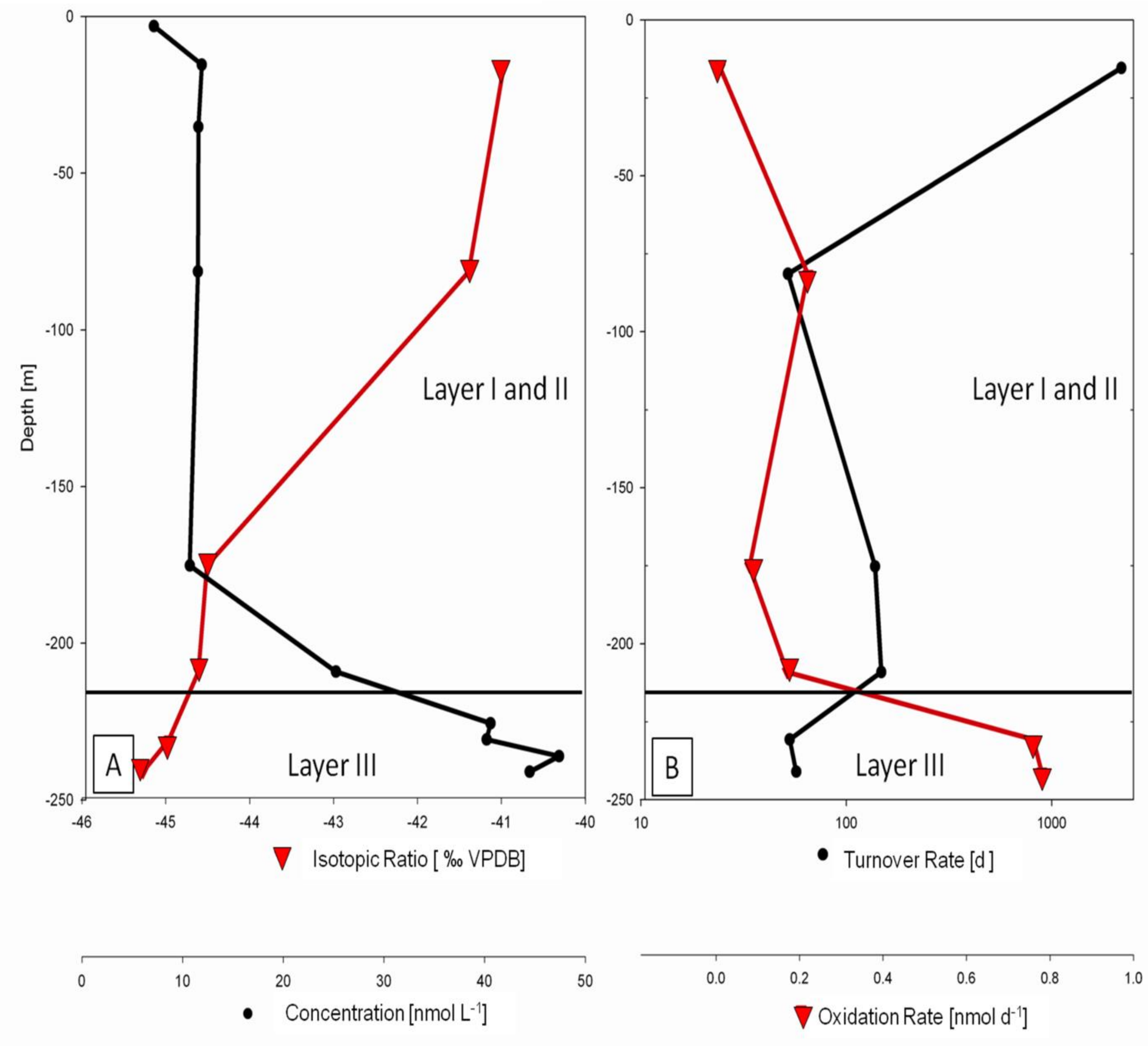


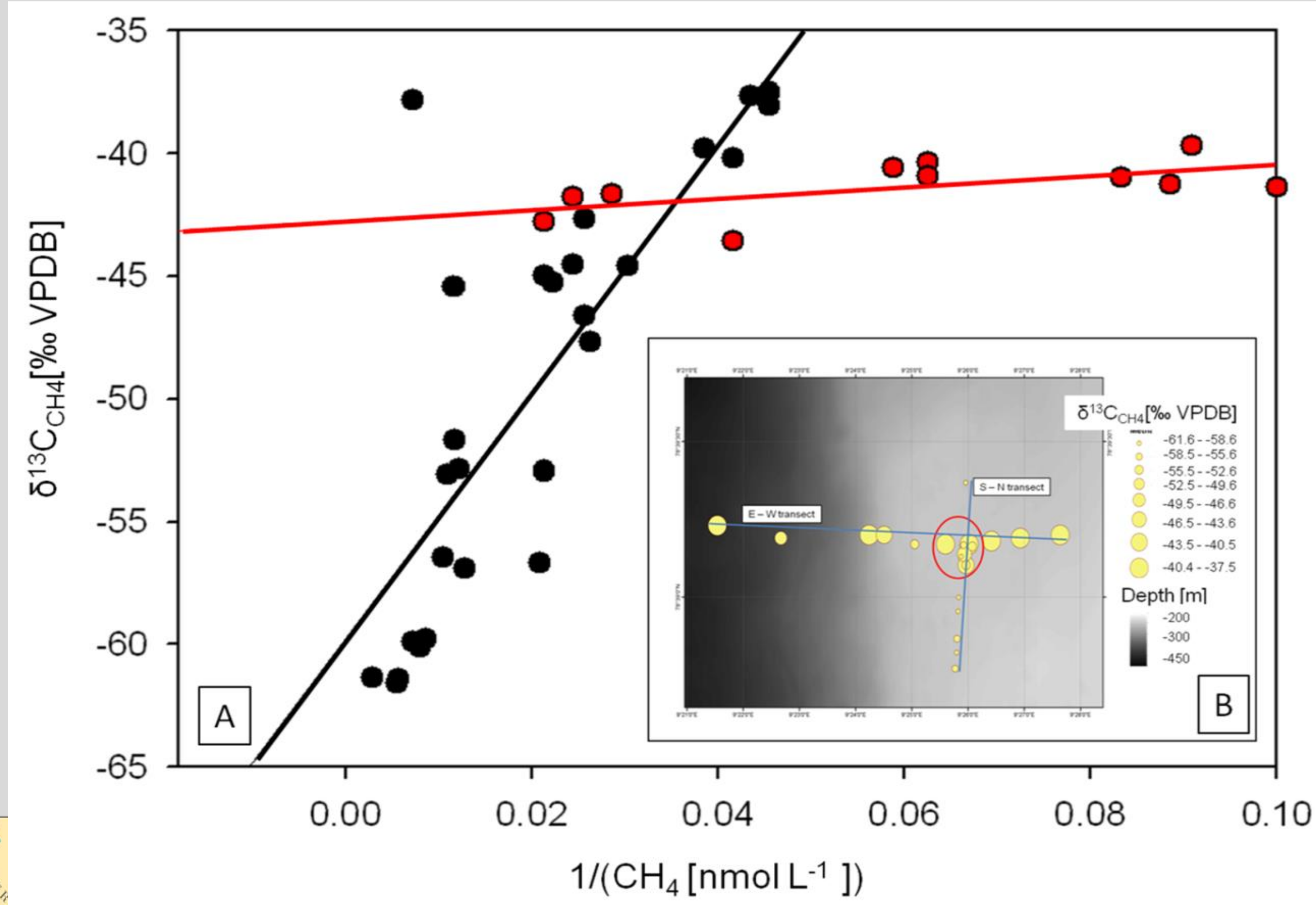

*Decrease of the bubble diameter during the ascend from the seafloor for initial bubbles sizes of 2 mm to 12 mm (A) compared with the hydroacoustic image of the highest detected gas flare (B). Decrease of the initial $CH_4$ concentration in the bubbles during their rise in the water column (C). Data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

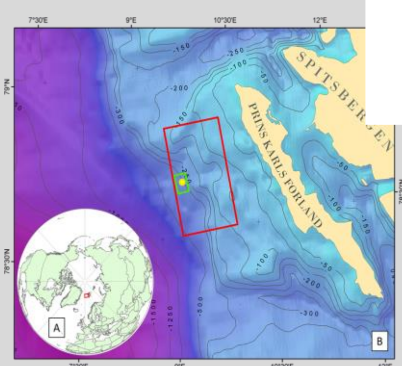



Personal communication Agnieszka Beszsynsky-Möller
28.26 km s-w direction



Depth [m]
Layer I and II
Layer III
A
Isotopic Ratio [ ‰ VPDB]
Concentration [nmol L-1]
B
Turnover Rate [d ]
Oxidation Rate [nmol d-1]




*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

$$r_e = (a^2 b)^{1/3} \quad (1)$$
$$V = \frac{4}{3}\pi r_e^{\,3} \quad (2)$$

Leifer and Patro 2002

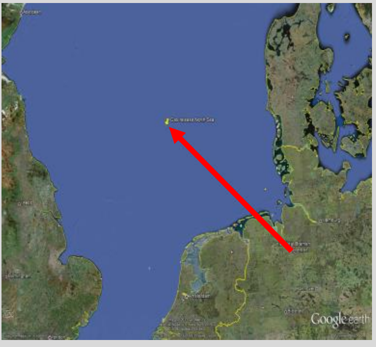
Release frequency: 23 bubbles $s^{-1}$

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

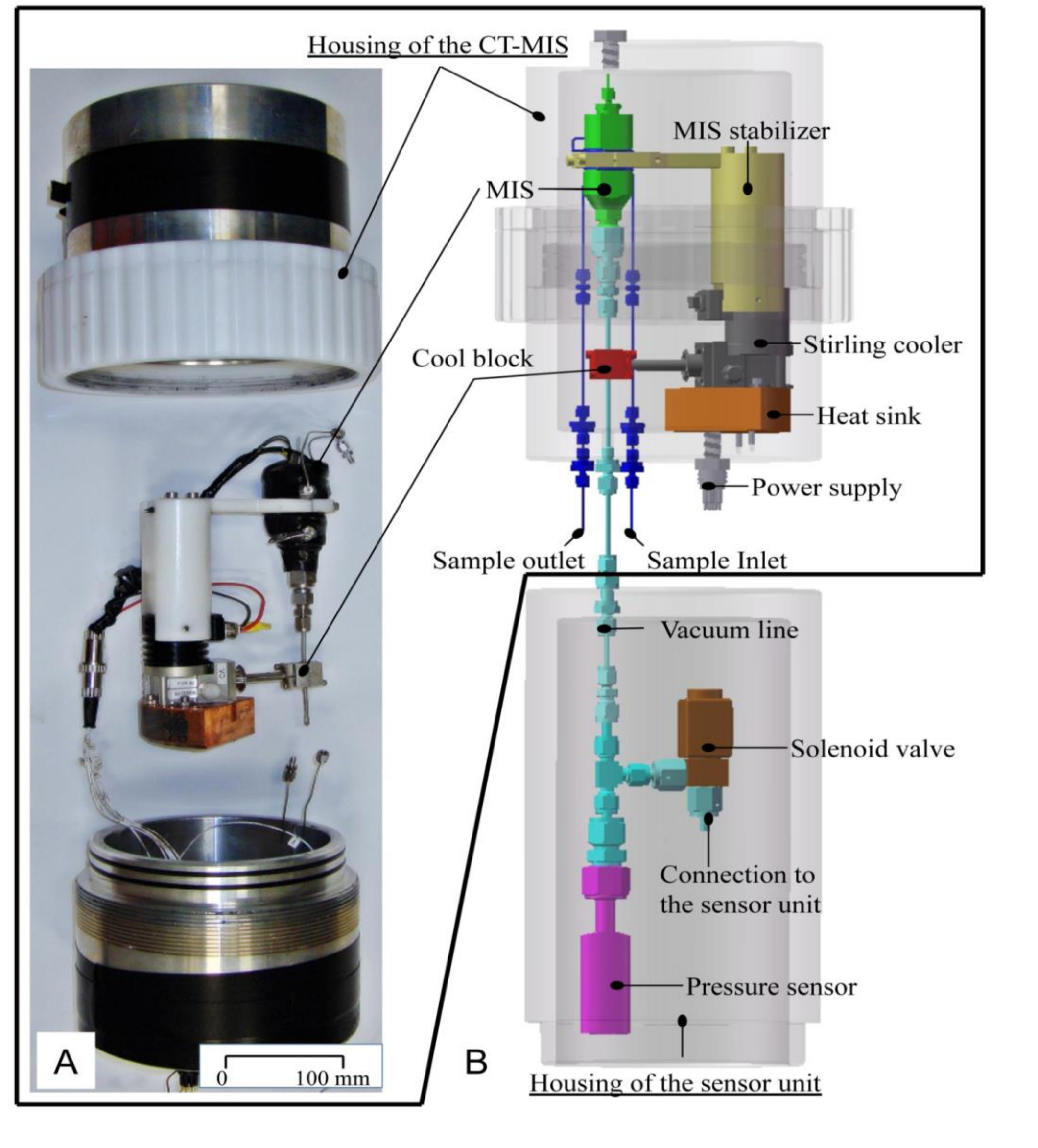
$$PVA = nRTZ \quad (3)$$

Modified after Römer et al. 2012

Seafloor methane release: 35.3 $\pm$ 17.65 t $CH_4$ $yr^{-1}$



# Under water cryotrap



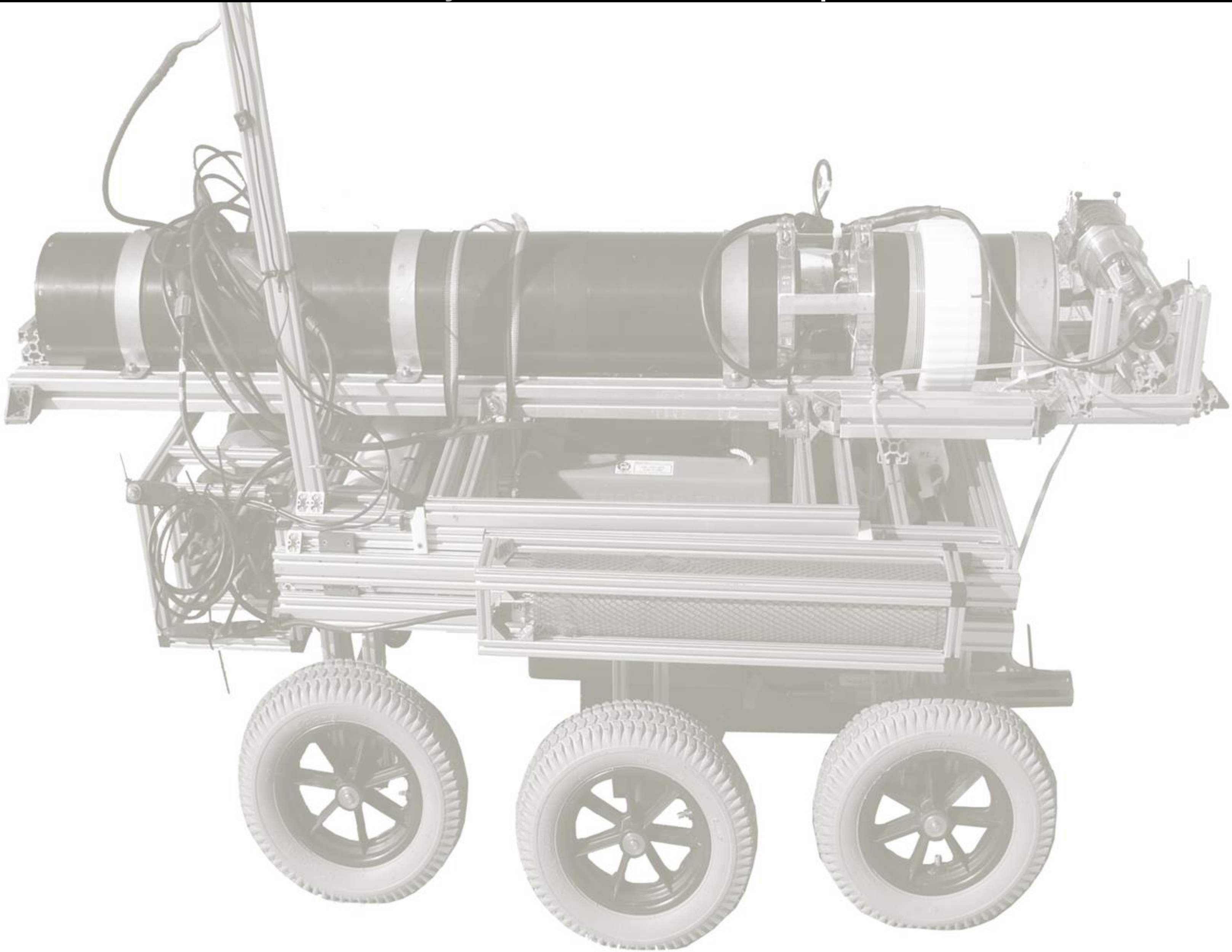

Gentz and Schlüter 2012

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

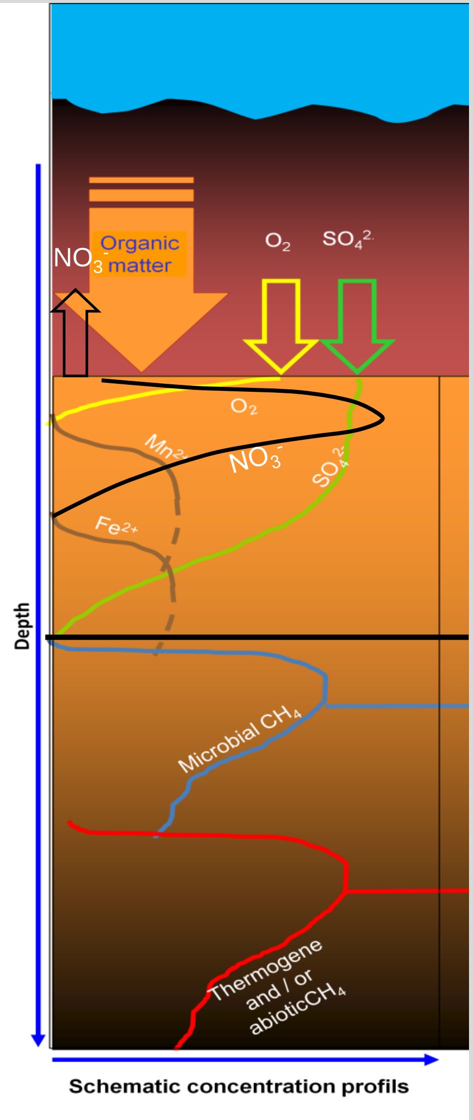
TRL 1 Basic principles of technology observed and reported
TRL 2 Technology concept and/or application formulated
TRL 3 Analytical and laboratory studies to validate analytical predictions
TRL 4 Component and/or basic sub-system technology valid in laboratory environment
TRL 5 Component and/or basic sub-system technology valid in relevant environment
TRL 6 System/sub-system technology model or prototype demonstrated in relevant environment
TRL 7 System technology prototype demonstrated in an operational environment
TRL 8 System technology qualified through test and demonstration
TRL 9 System technology qualified through successful mission operations

| 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 | $SnO_2$ 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 | Capsum GmbH/ Franatech GmbH [26] | TRL 7 |
| HydroC/$CH_4$ | 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 http://www.contros.eu | 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) | 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 | | | surface | | 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** $(CH_2O)x(NH_3)y(H_3PO_4)z + \mathbf{xO_2} \rightarrow xCO_2 + xH_2O + yNH_3 + H_3PO_4$

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

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

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

sulfate/methane transition zone (SMTZ)

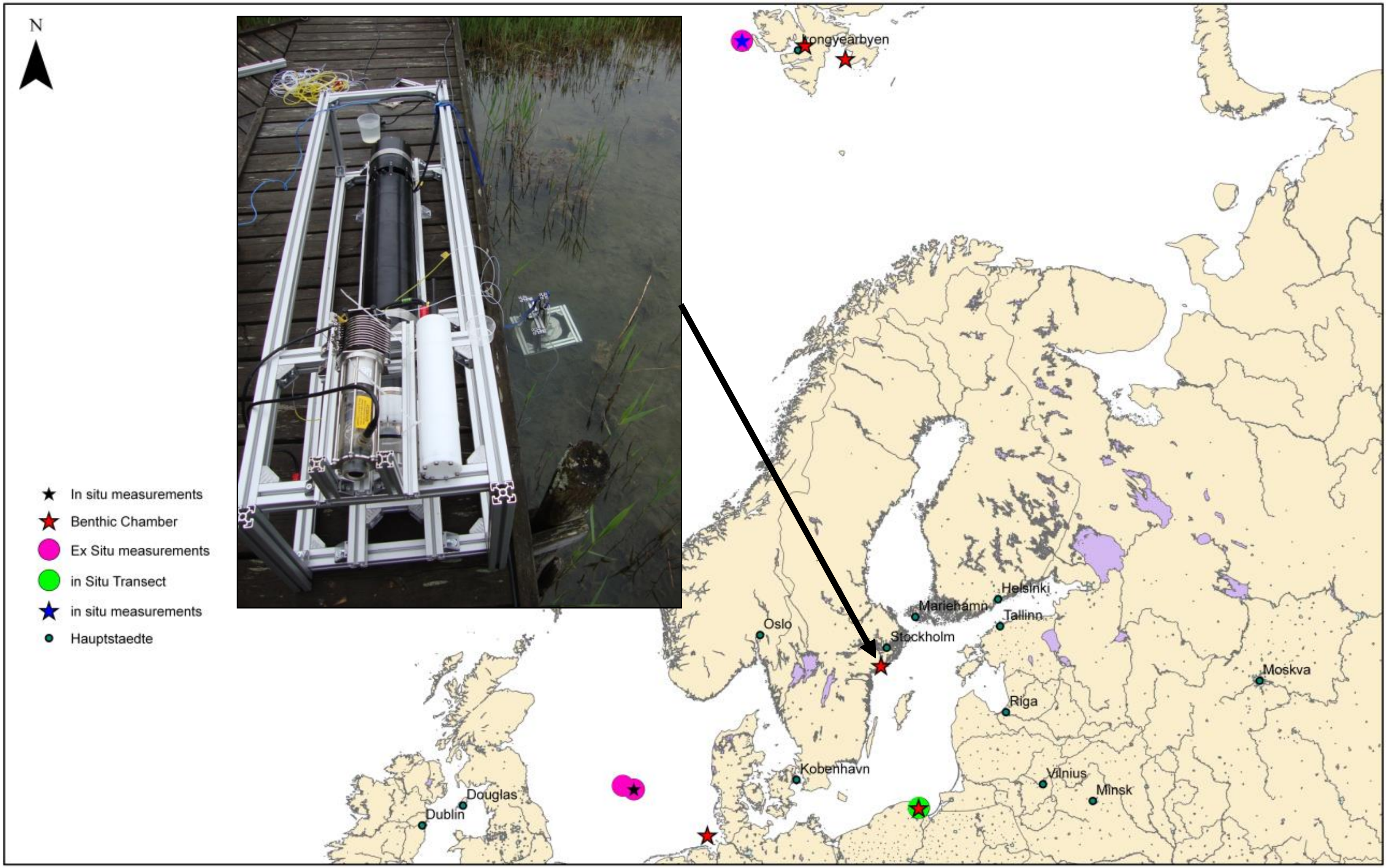
Microbial formation of methane:

**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)*

# Working areas



# Working areas