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

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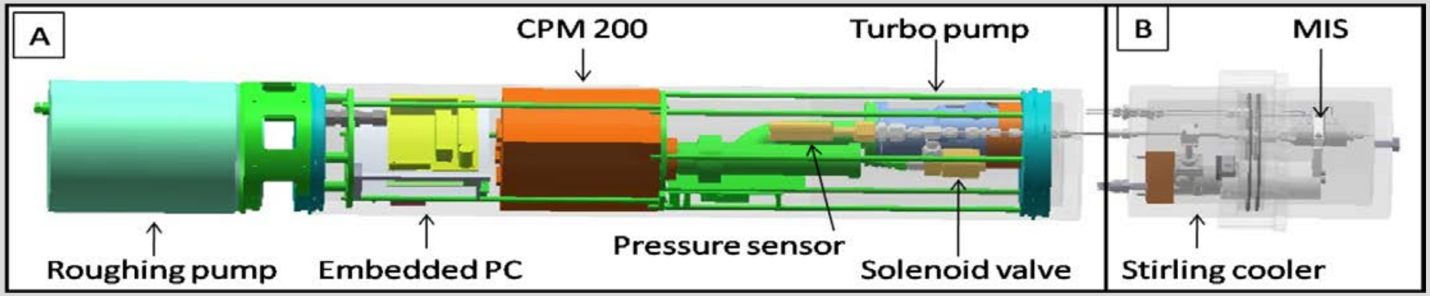
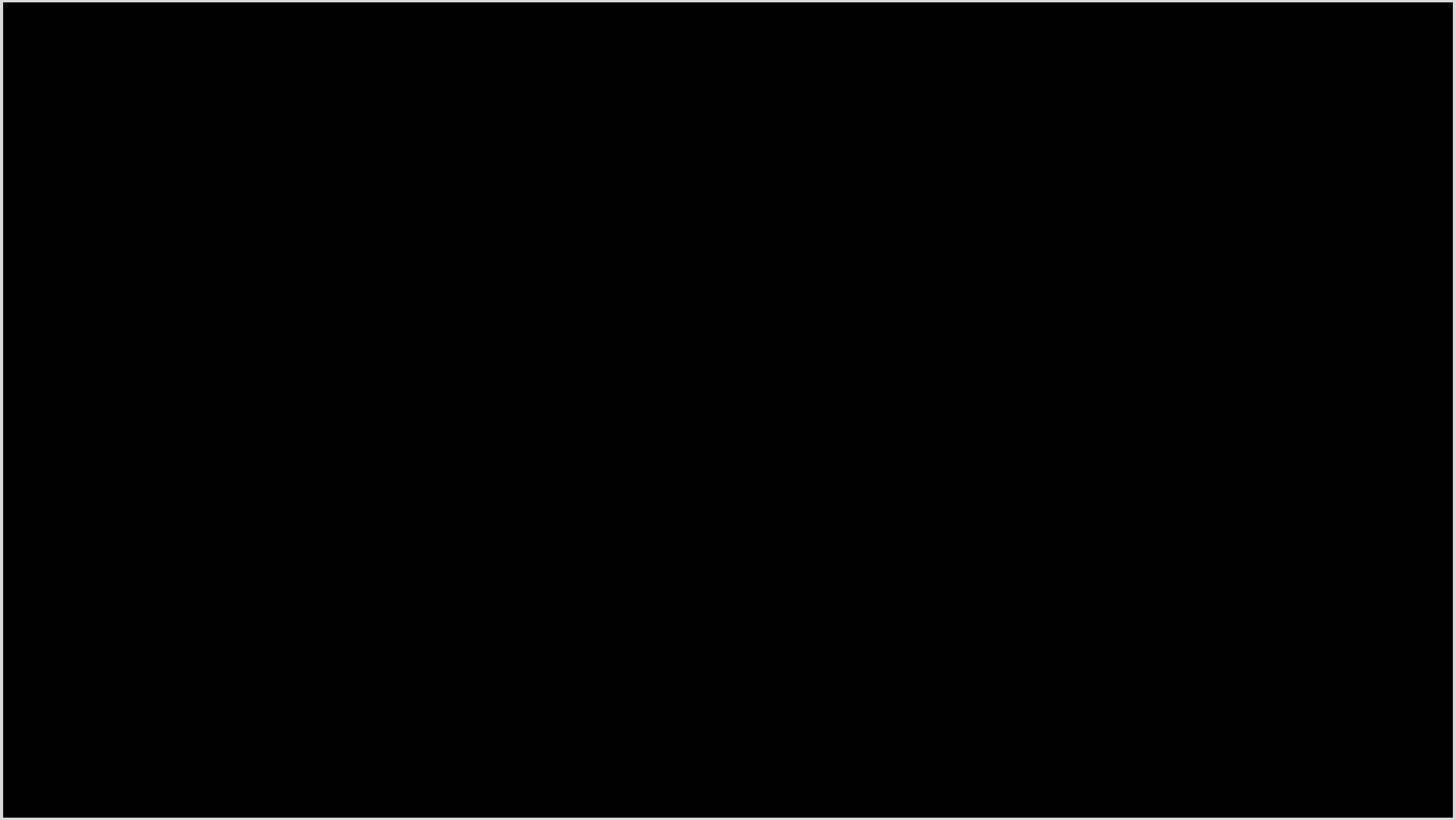


Presented at the 9thWorkshop on Harsh Environment Mass Spectrometry,
St Petersburg, FL September 17, 2013

MARINE SCIENCE IS HARSH ENVIRONMENT !

HE 337 NorthSea



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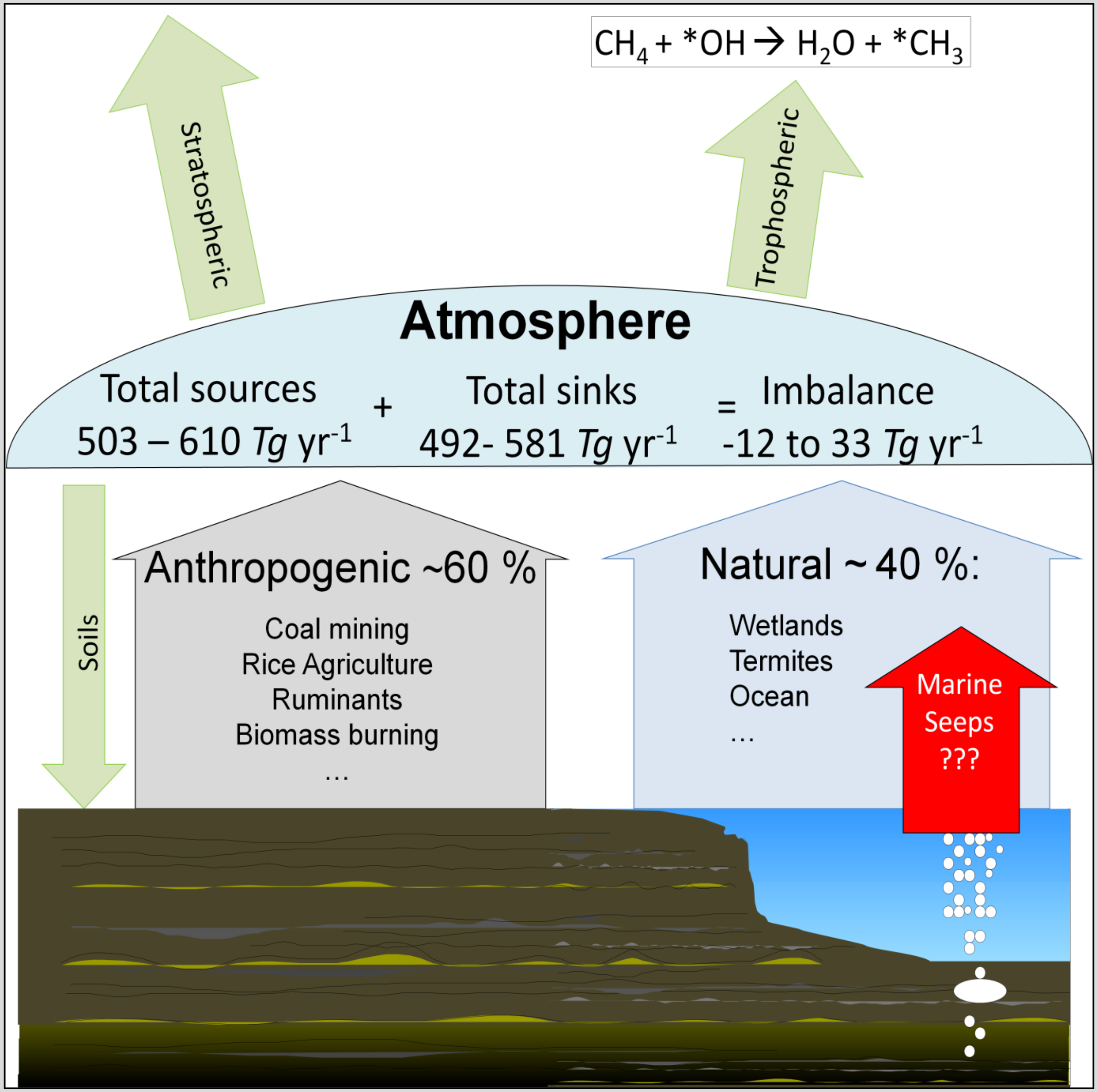
Submarine gas seeps

WORLDWIDE DISTRIBUTION OF SUBMARINE METHANE RELEASE

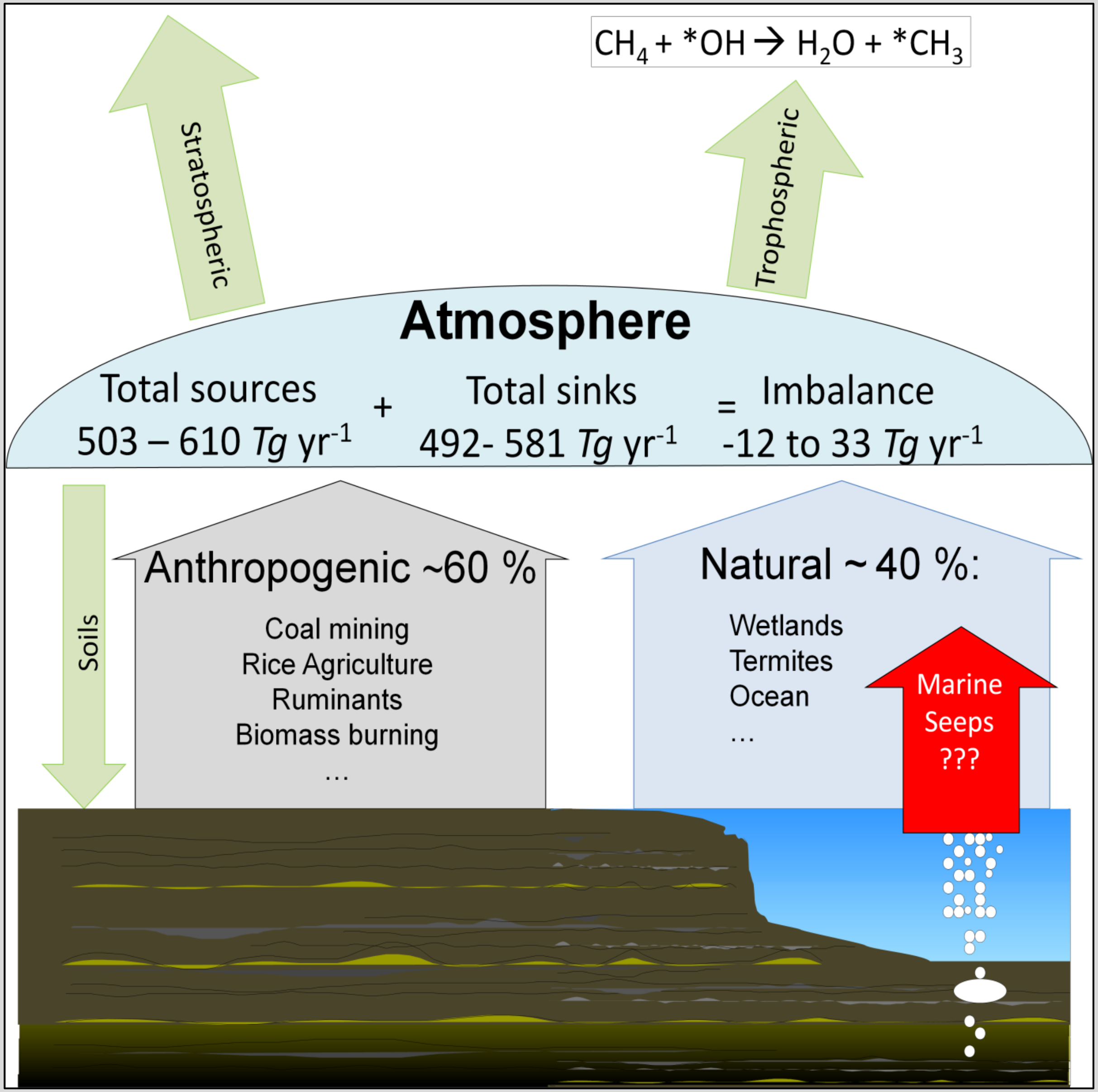
Free gas (Fleischer et al. 2001)
Pockmarks (Hovland et al. 2002)
Mud volcanoes (Milkov 2000)
Gas hydrates (Kvenvolden et al. 2001)

GLOBAL RELEVANCE OF METHANE



*according to **Intergovernmental Panel on Climate Change** (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).

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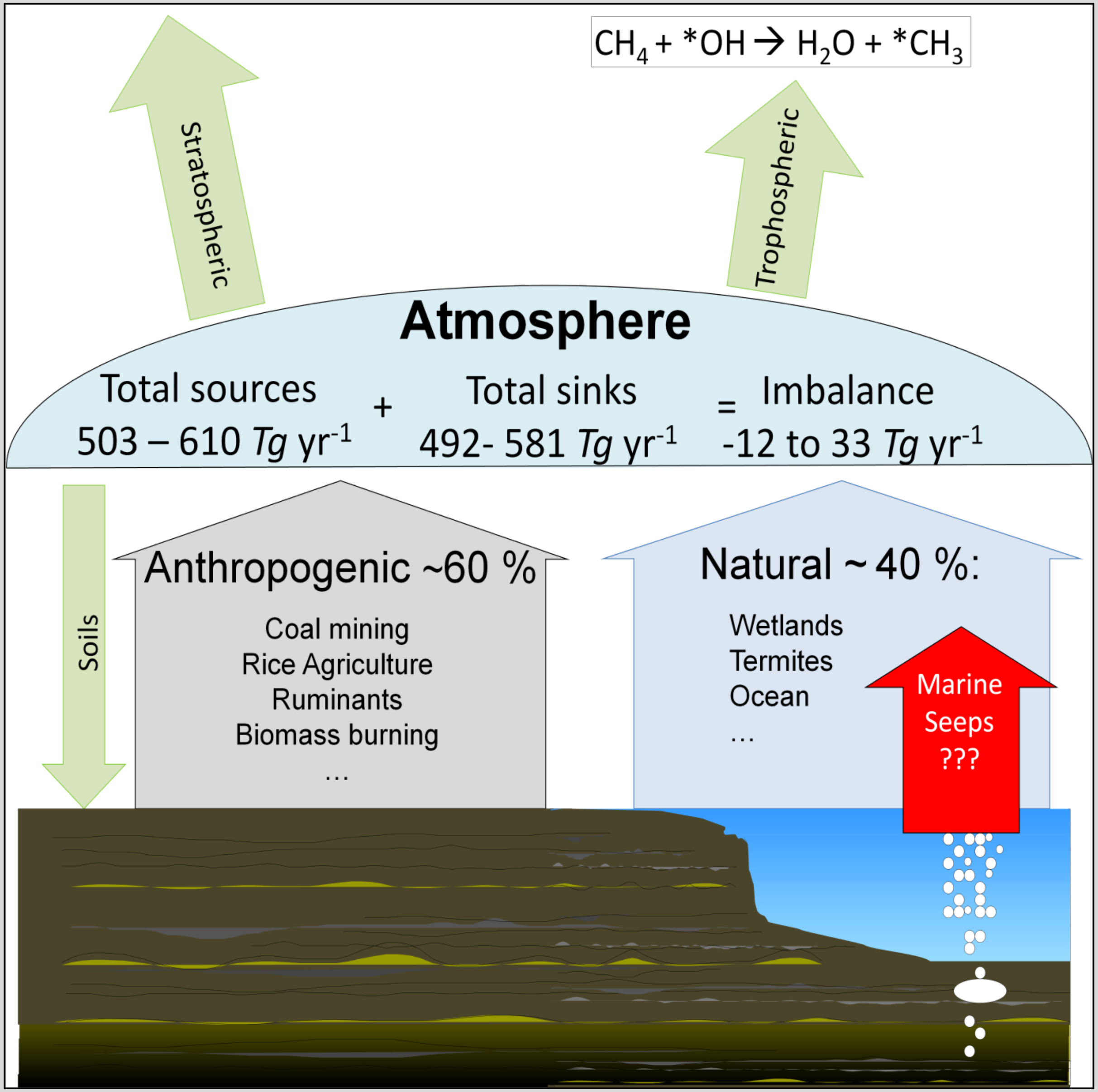

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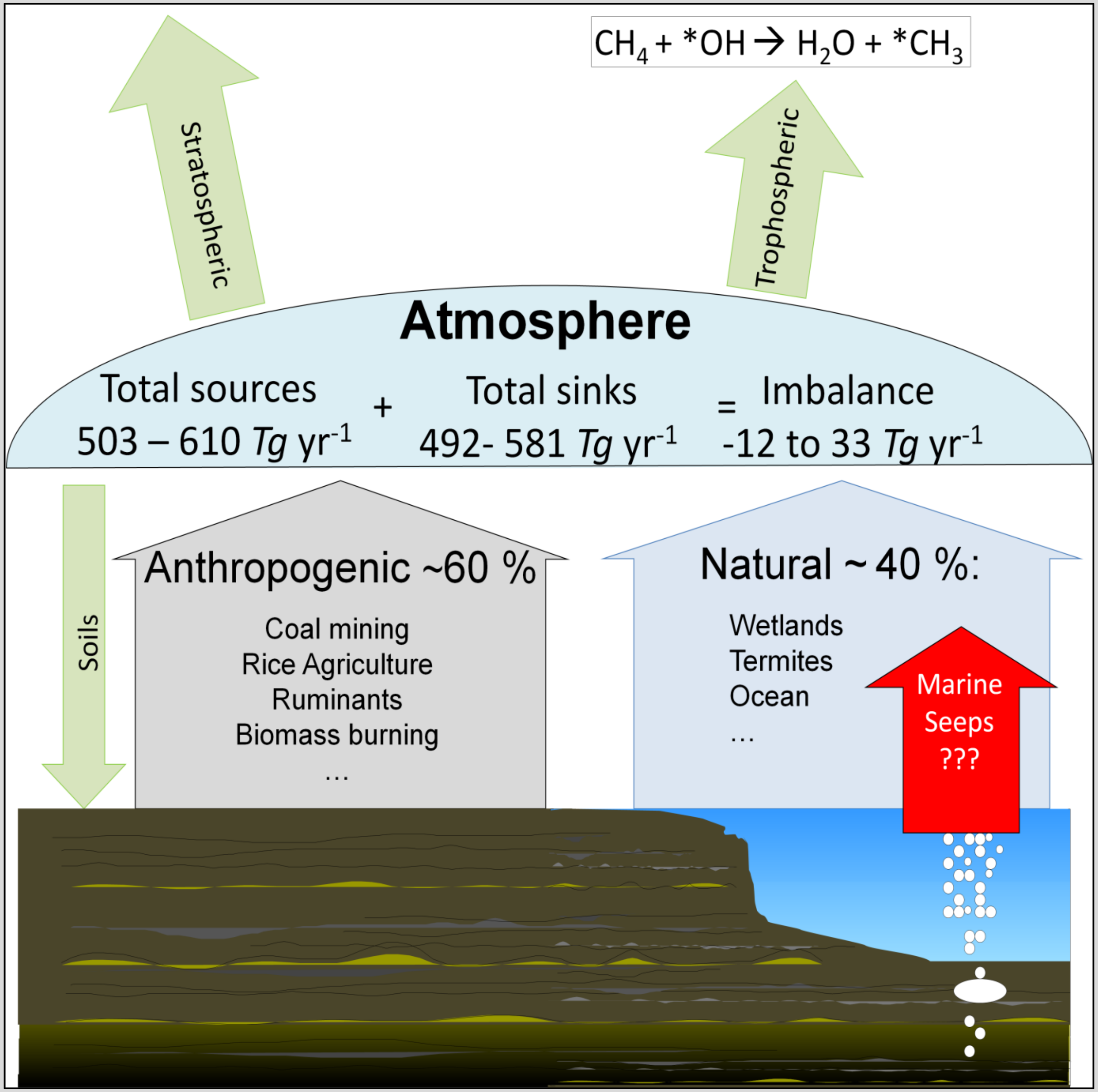

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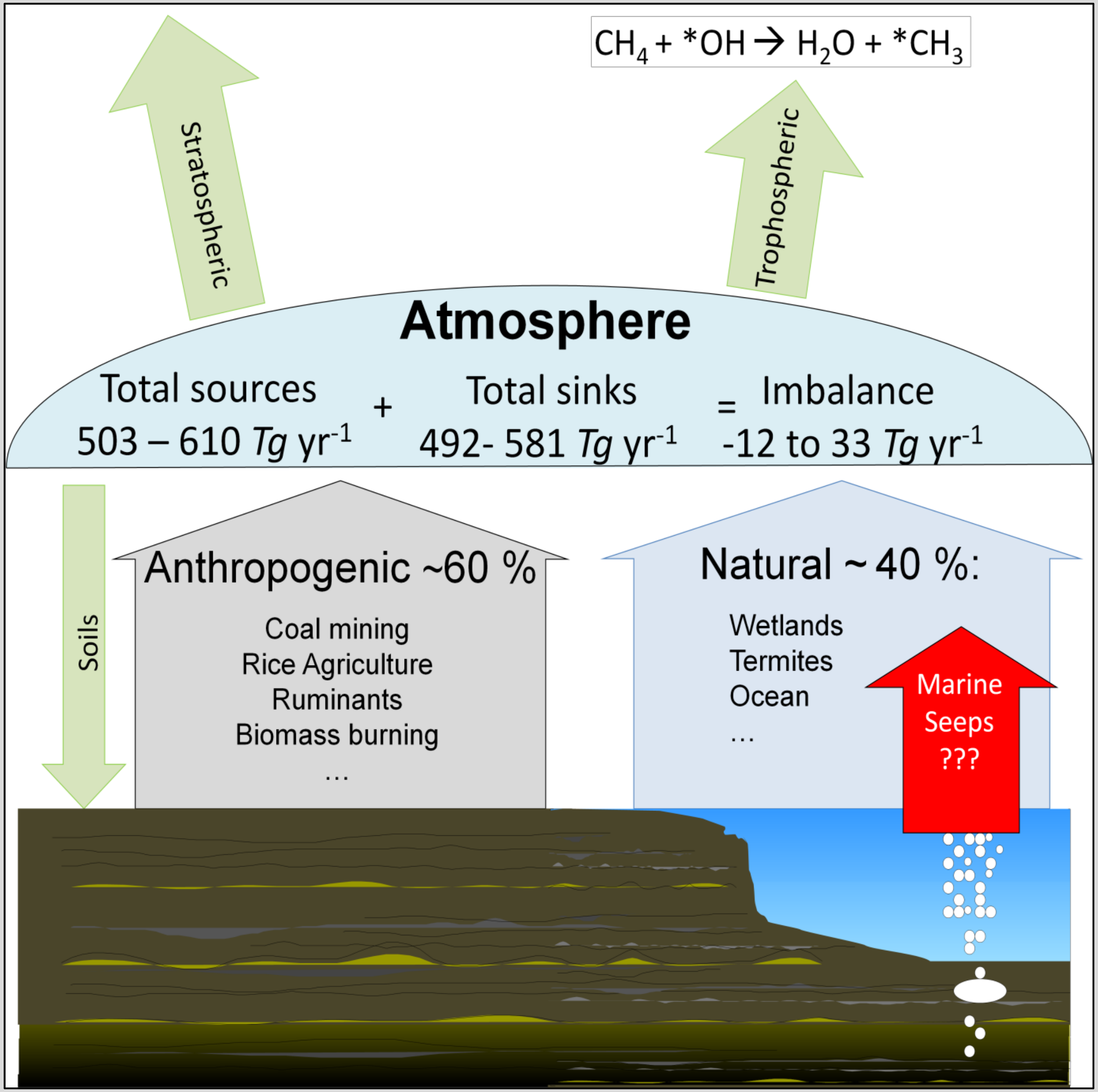

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CH_4 represents the second largest contribution (about 15 %) to historical warming after CO_2 (Shindell et.al. 2009).

GLOBAL RELEVANCE OF SUBMARINE SOURCES

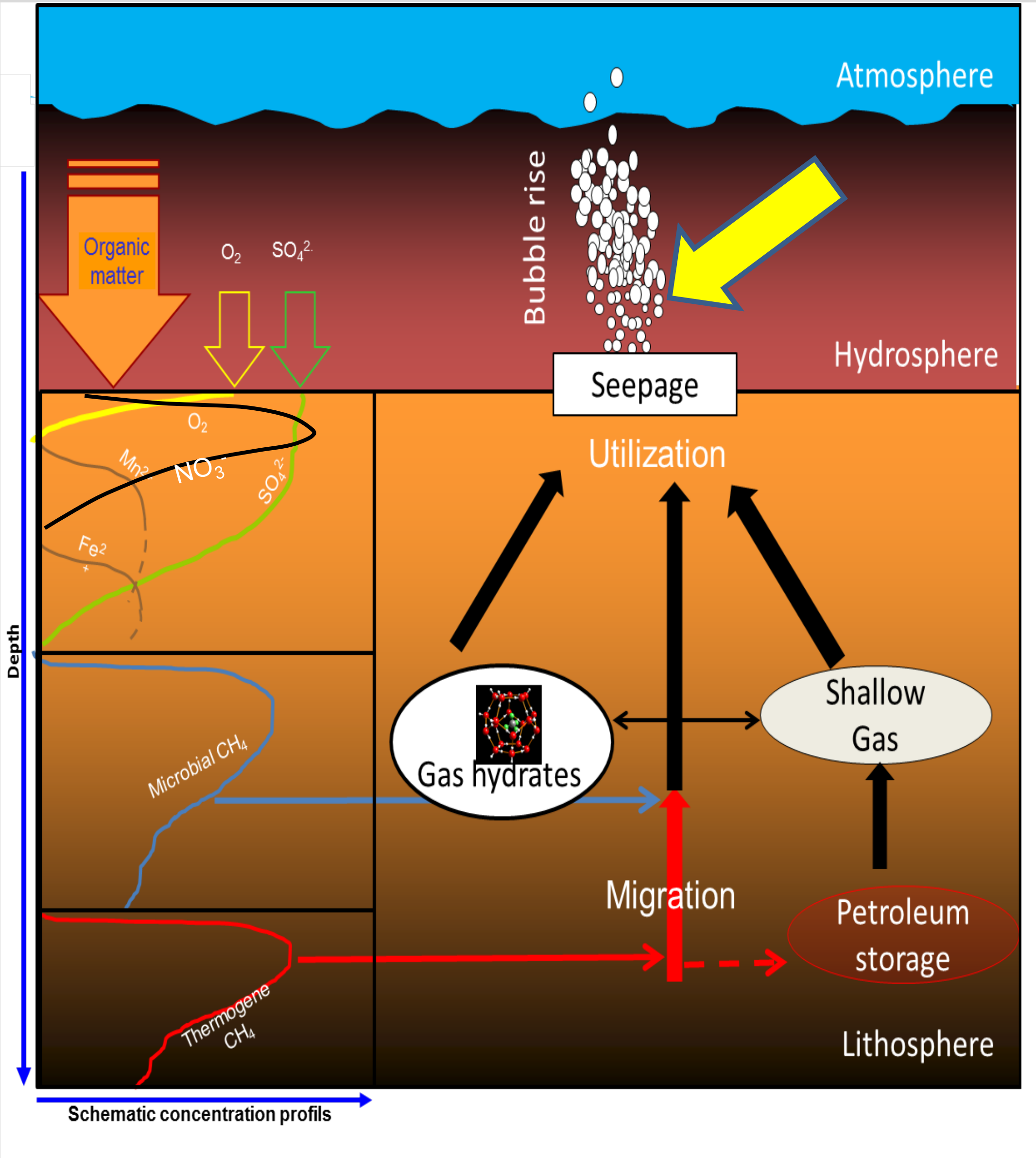
Present estimations: 8 - 65 Tg CH_4 yr^{-1} are released into the ocean and 0.4 – 48 Tg CH_4 yr^{-1} reach the atmosphere which is up to 9 % of the total methane emission (Hovland et al. 1993; Judd and Hovland 2007; Judd 2004; Judd et al. 2002; Kvenvolden and Rogers 2005).

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)

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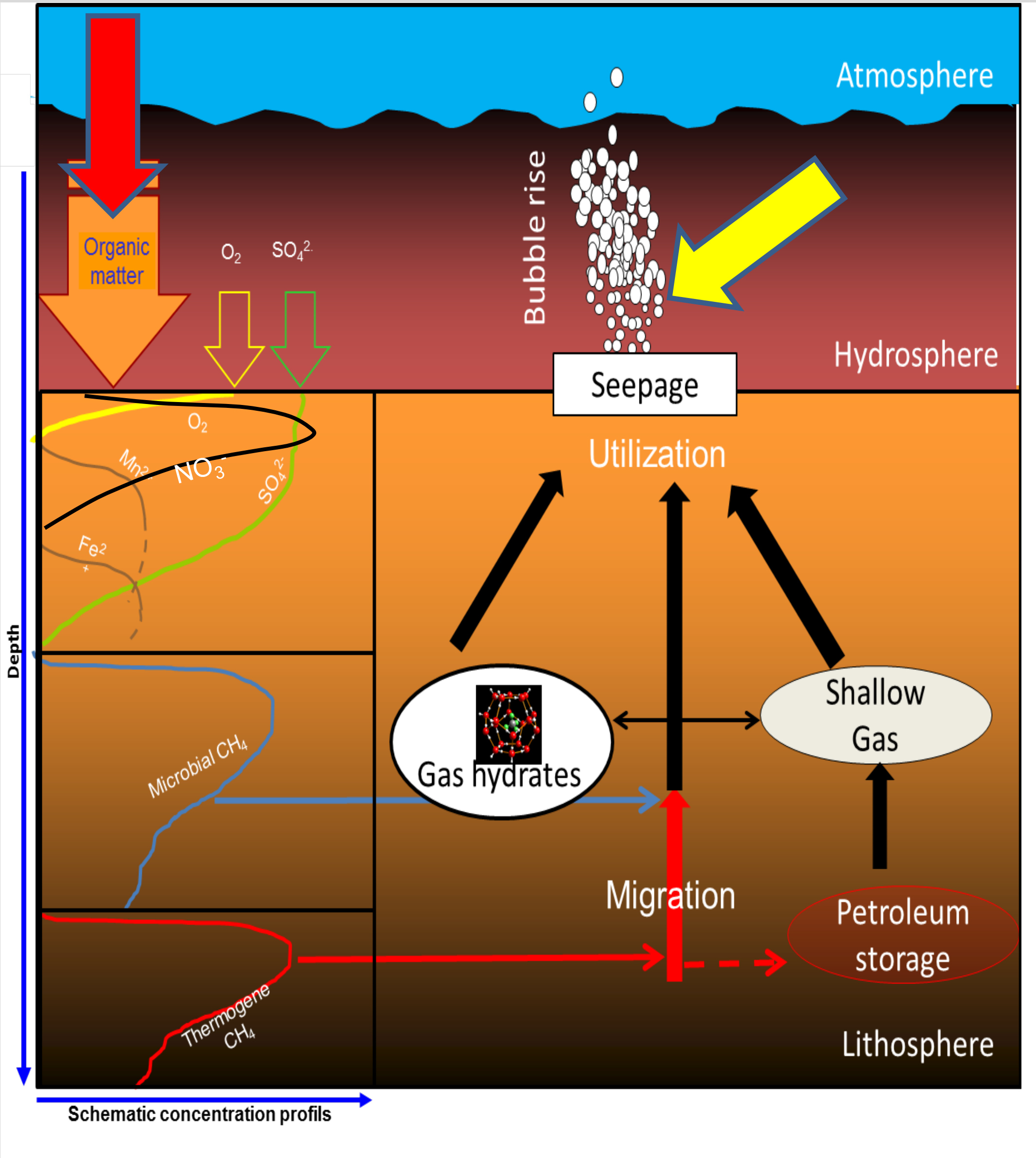

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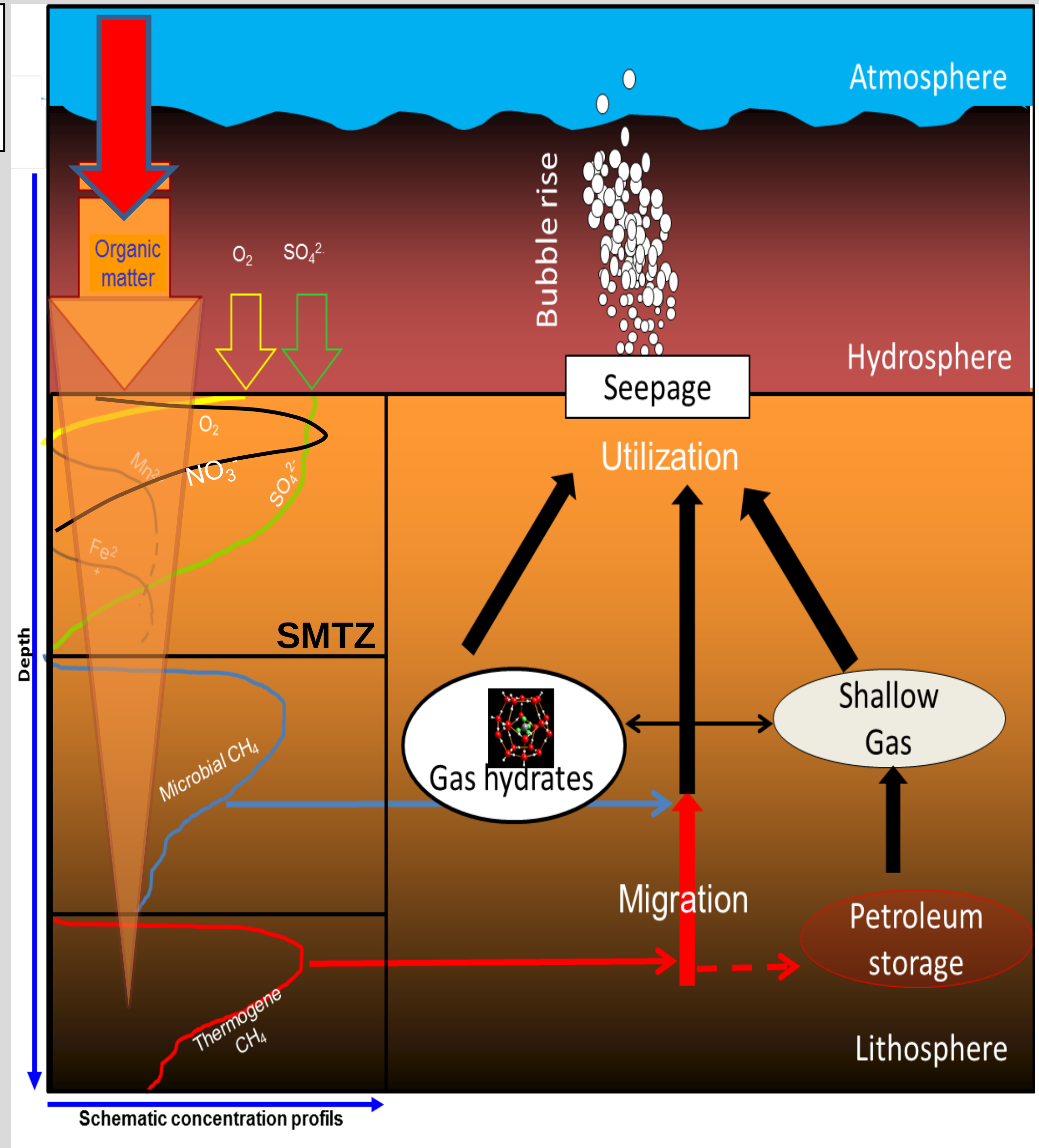
Formation of methane by degradation of organic matter

Aerobic respiration
Nitrate reduction
Manganese oxide reduction
Iron oxide reduction

Microbial formation of methane

Thermocatalytic formation of methane



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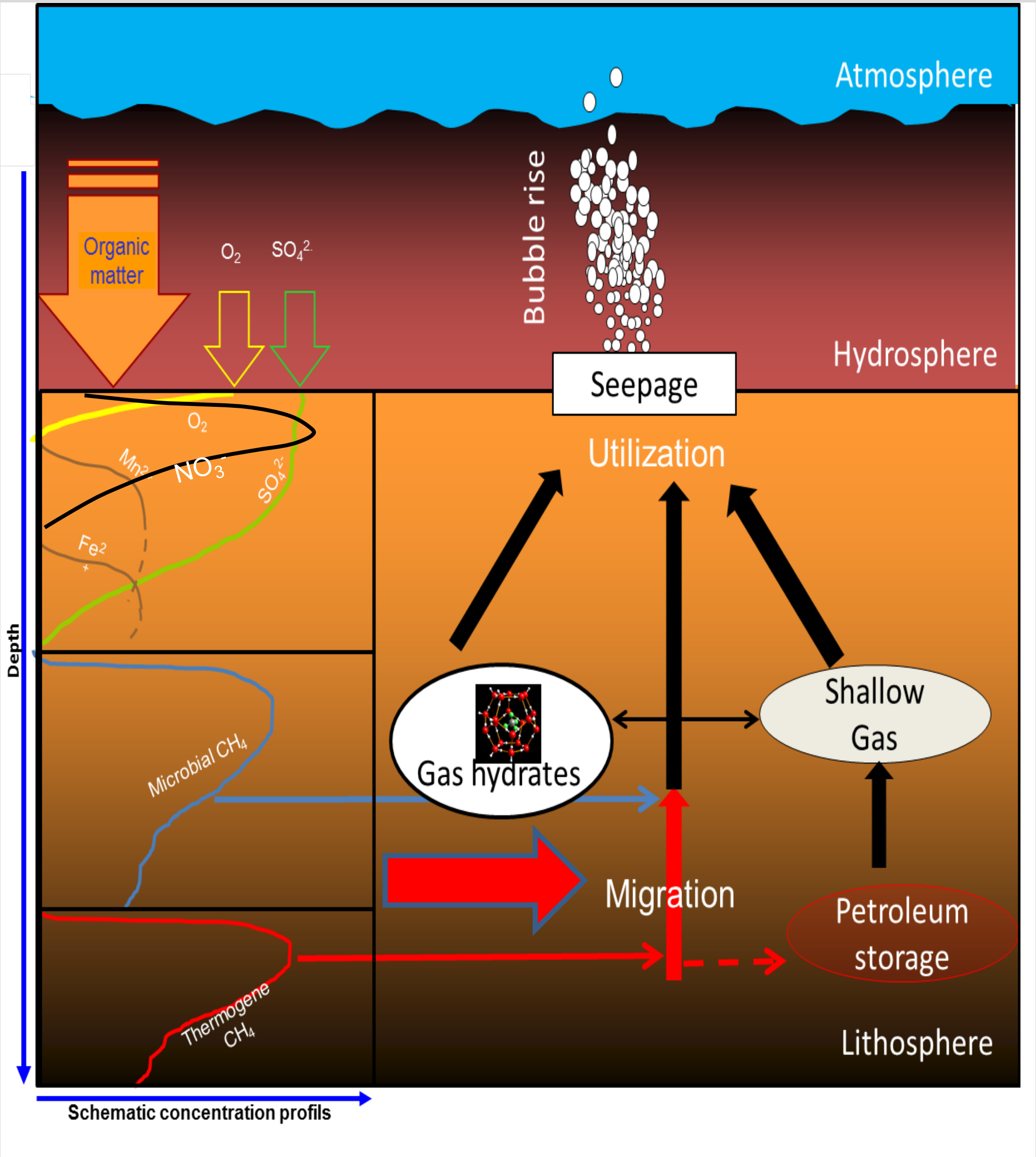
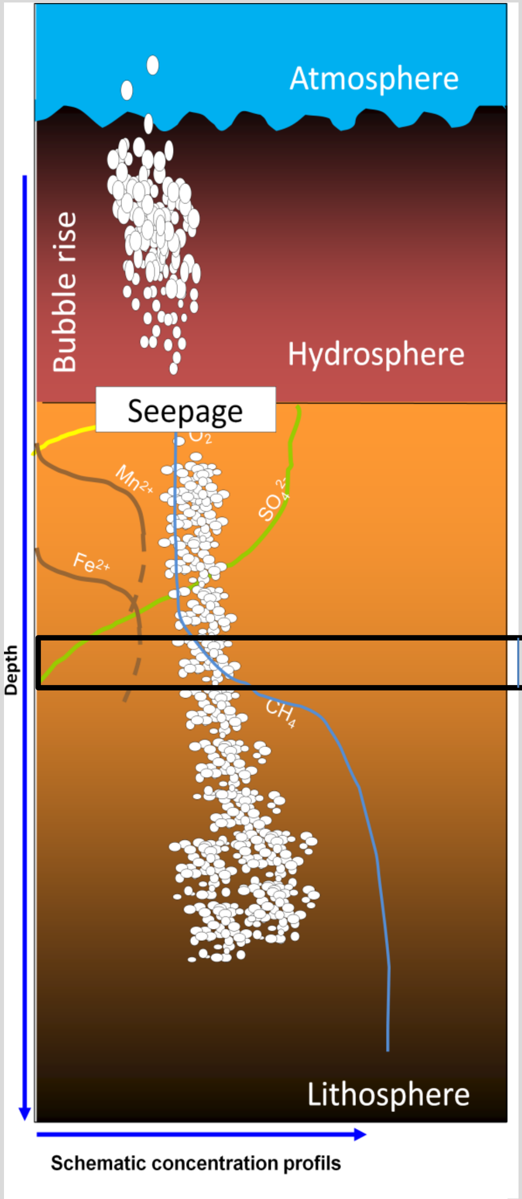
Storage and migration of methane



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).

Utilization of methane in the sediment

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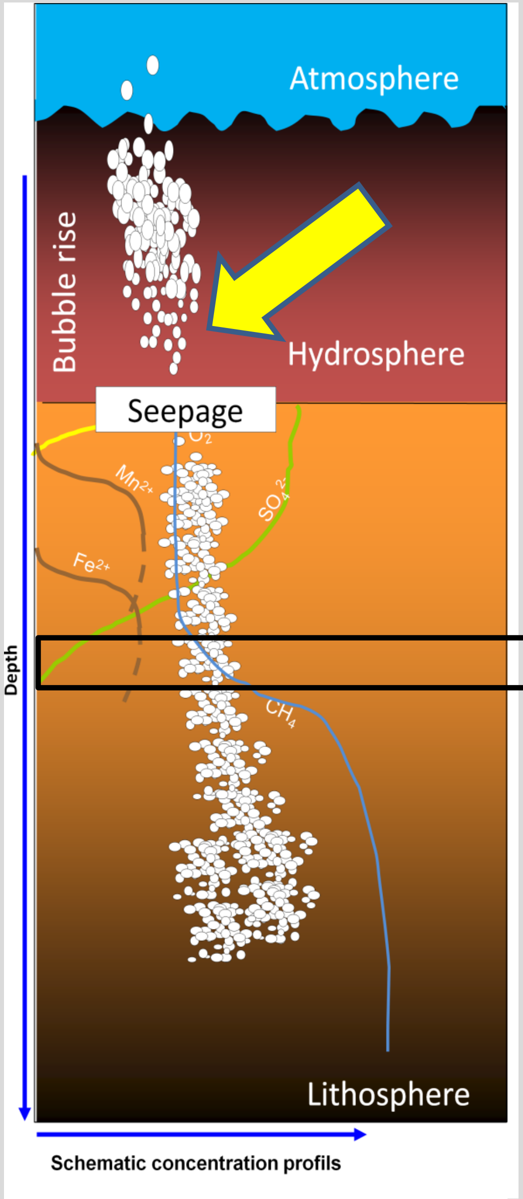

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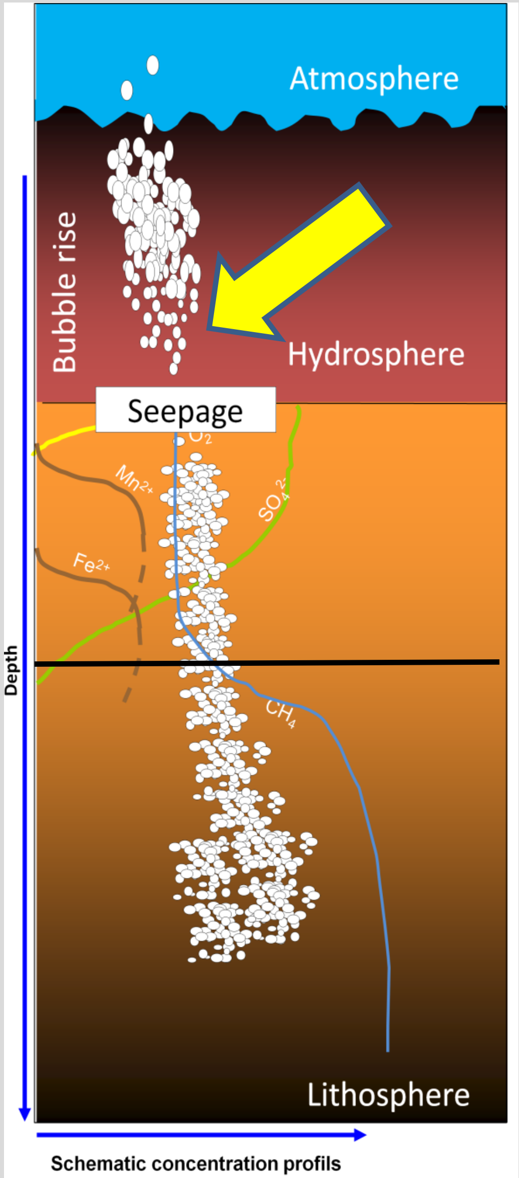
Pathways of methane in the water column



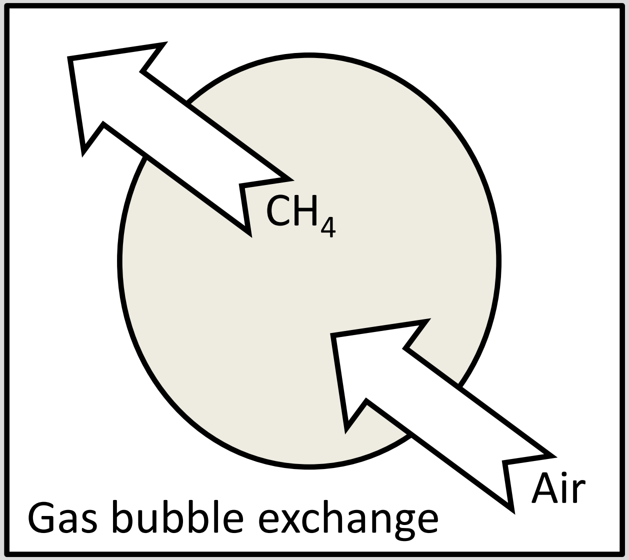
Air/Sea exchange

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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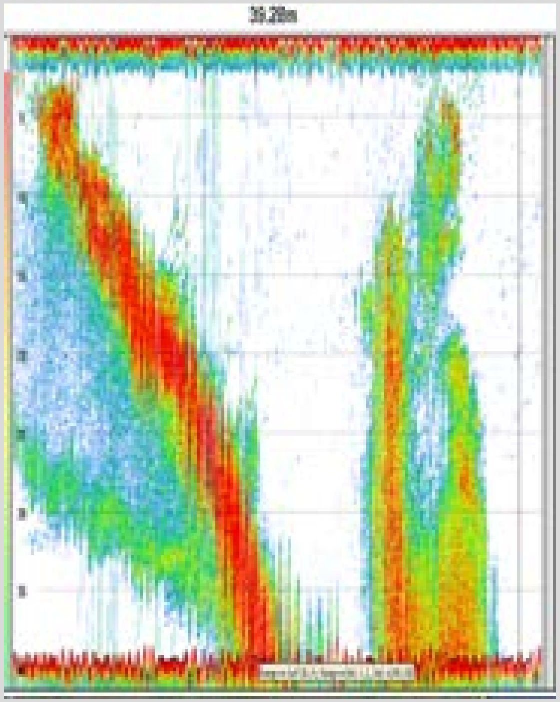
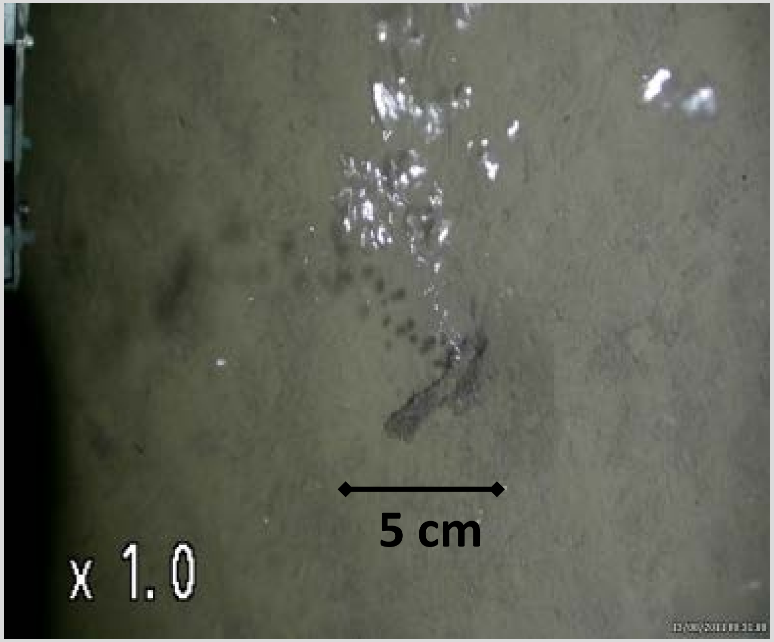
HOW TO INVESTIGATE THE WATER COLUMN ABOVE GAS SEEPAGE?



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



Gas release in the North Sea via video observation

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)

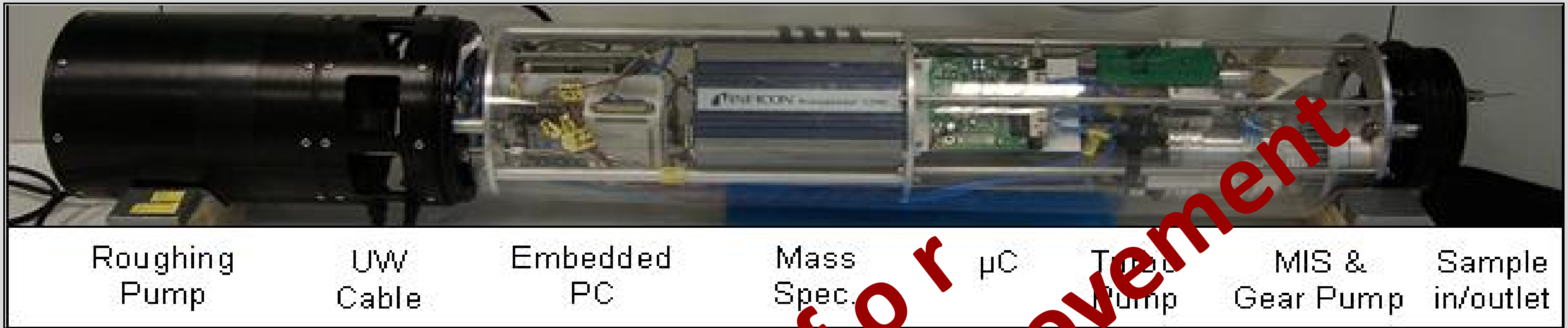
Need for new methods

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)

- Robustness for the use in harsh environment
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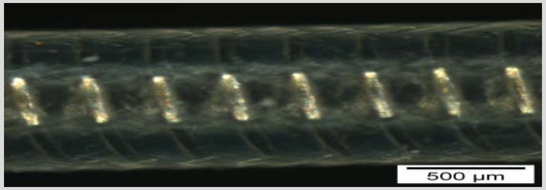
Need for detection limit improvement

IN SITU MASS SPECTROMETER MODE OF OPERATION

70 times magnification



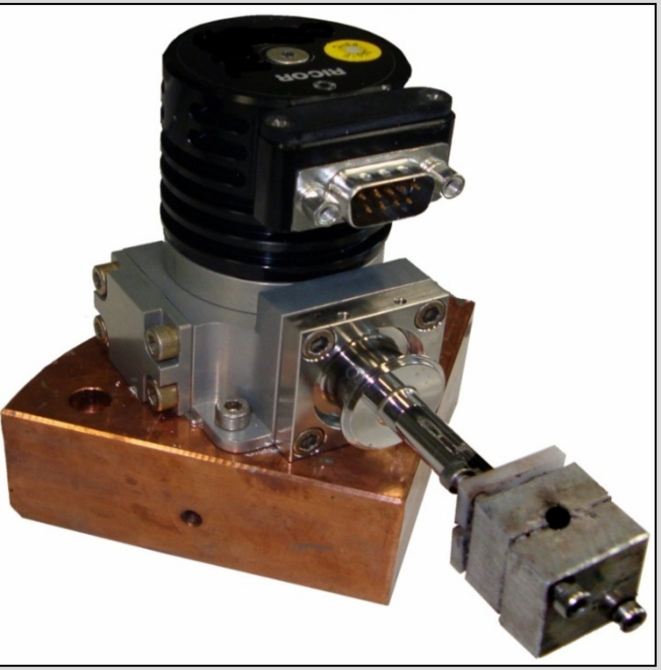
320 times magnification

Water vapor

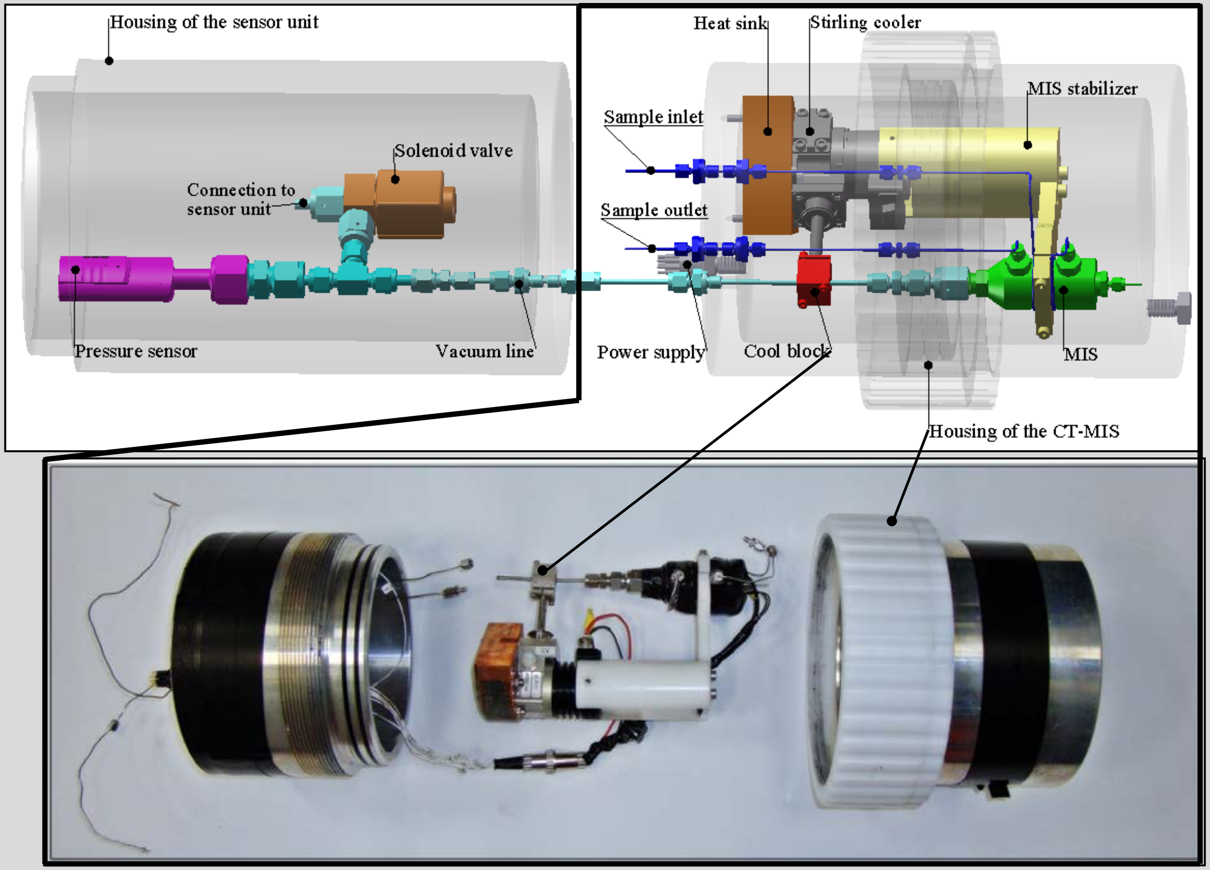
is the main gas that permeates through this membrane?

- 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

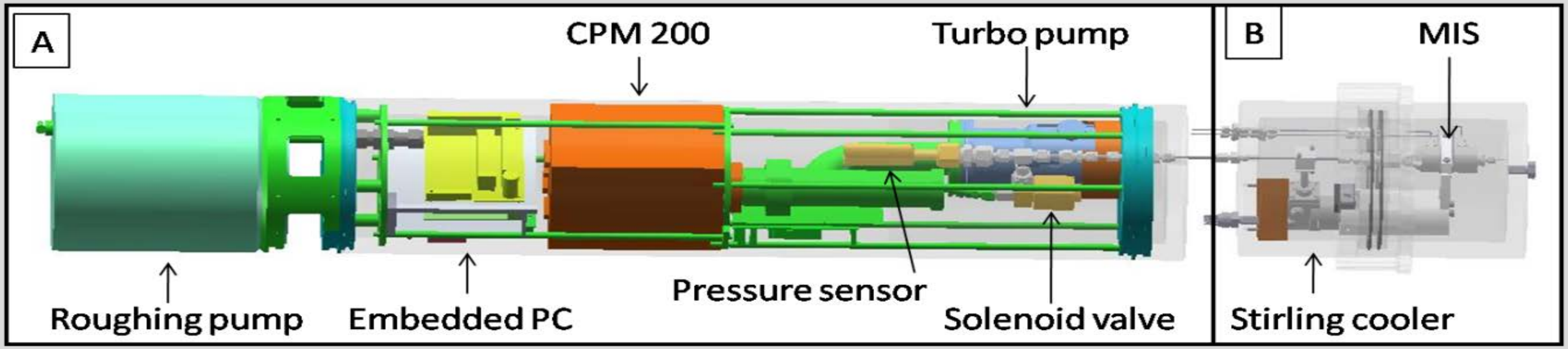
- Water vapour is reduced up to 98 % of initial
- Reduce the internal pressure significantly
- A higher ionization effency is observed

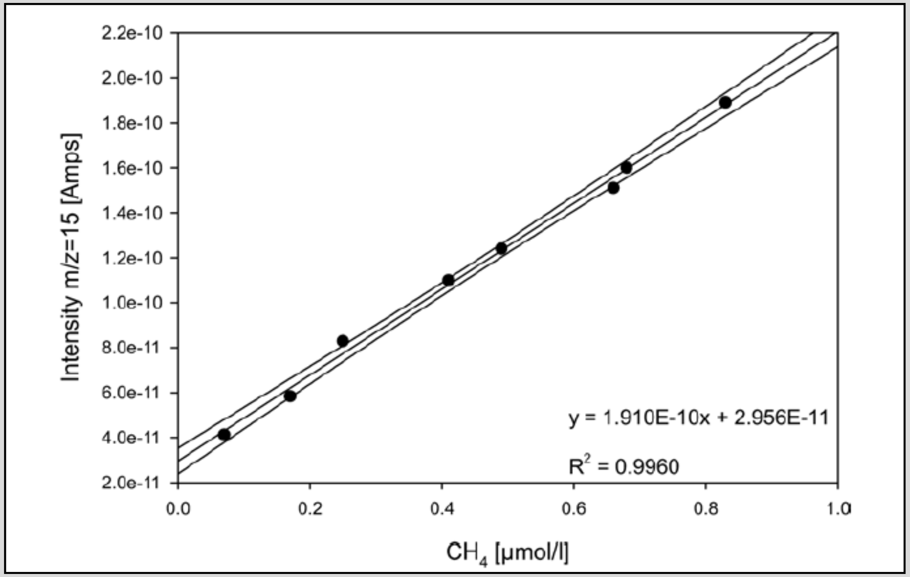
→Results in an obtimized detection limit

- 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



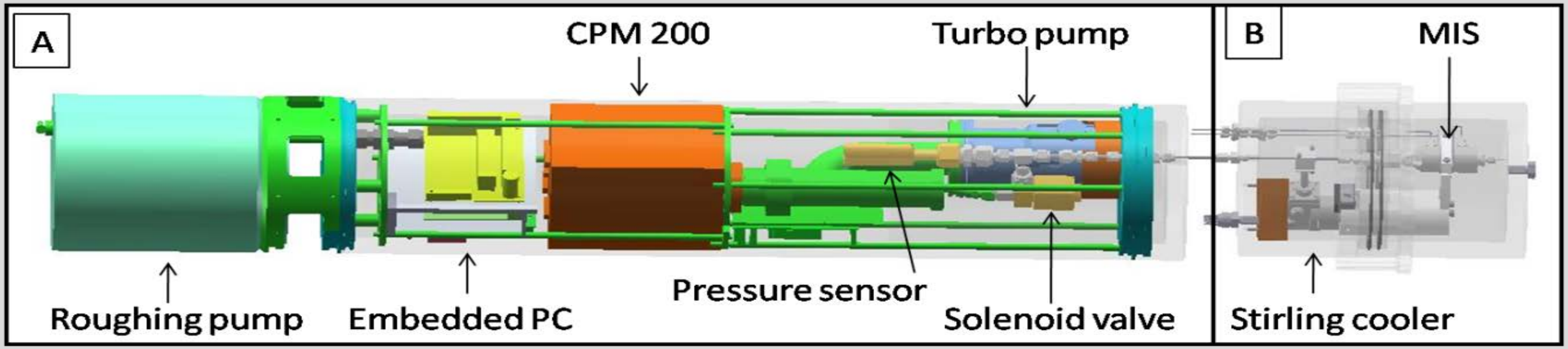


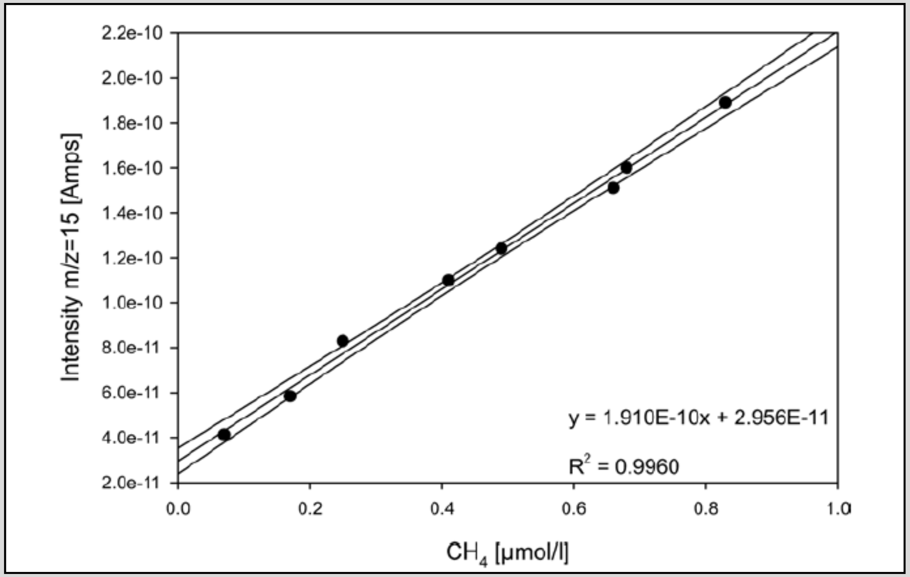
Calibration of the optimized Inspectr200-200

New detection limit of the optimized Inspectr200-200:

~16 nmol L^{-1}

Optimized and redesigned Inspectr200-200





Calibration of the optimized Inspectr200-200

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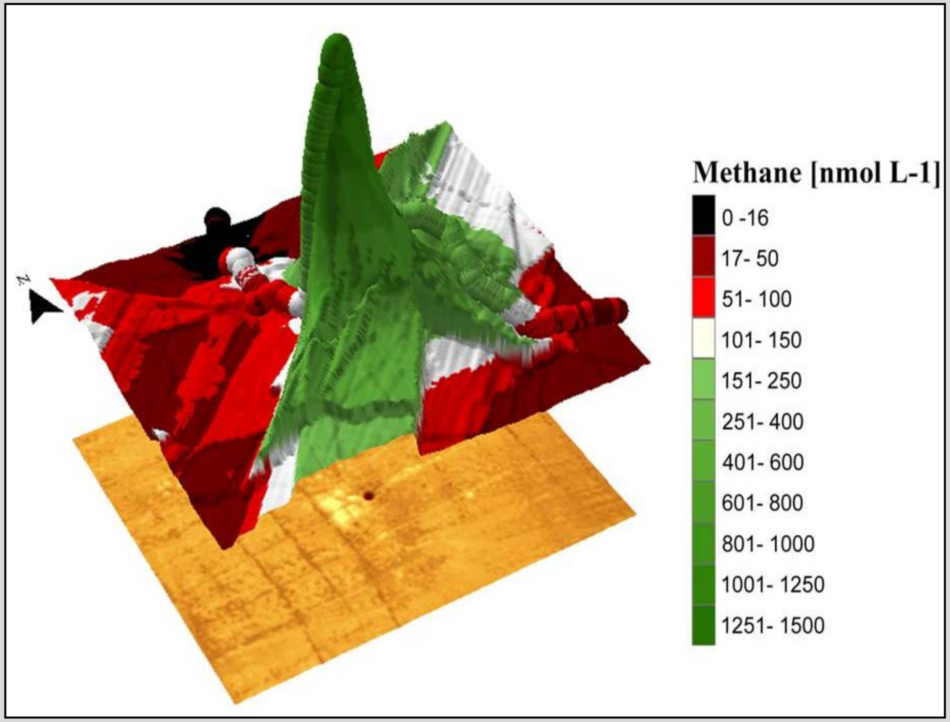
Low enough???

In situ mass spectrometer for field applications

Gas seep in the North Sea



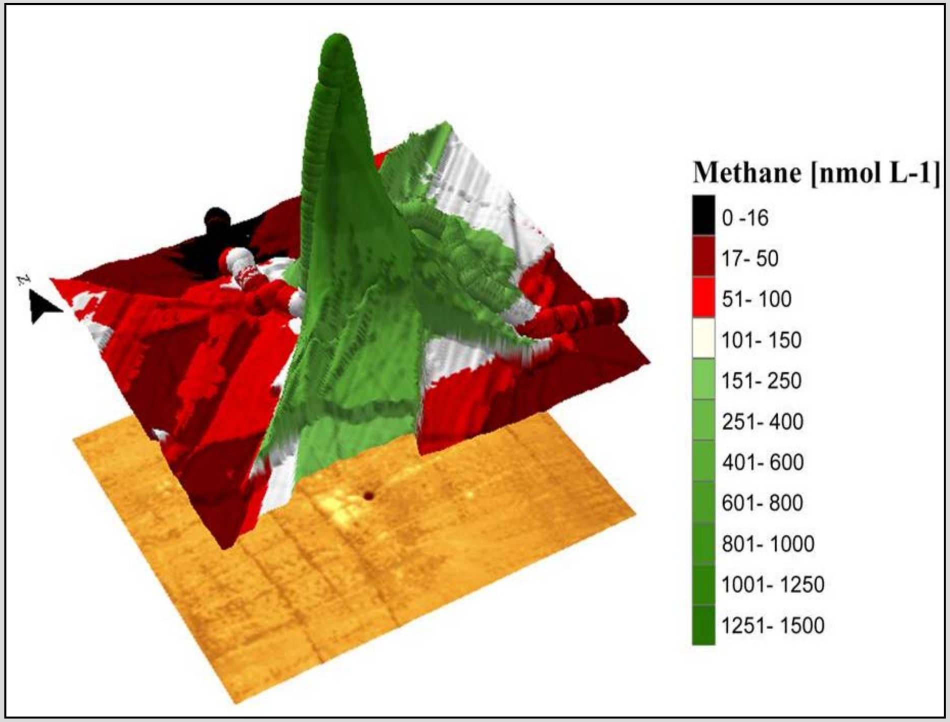
Concentration [nmol L^{-1}]	Area [%]
< 16	3.6
16 - 100	48.3
> 100	48.1

(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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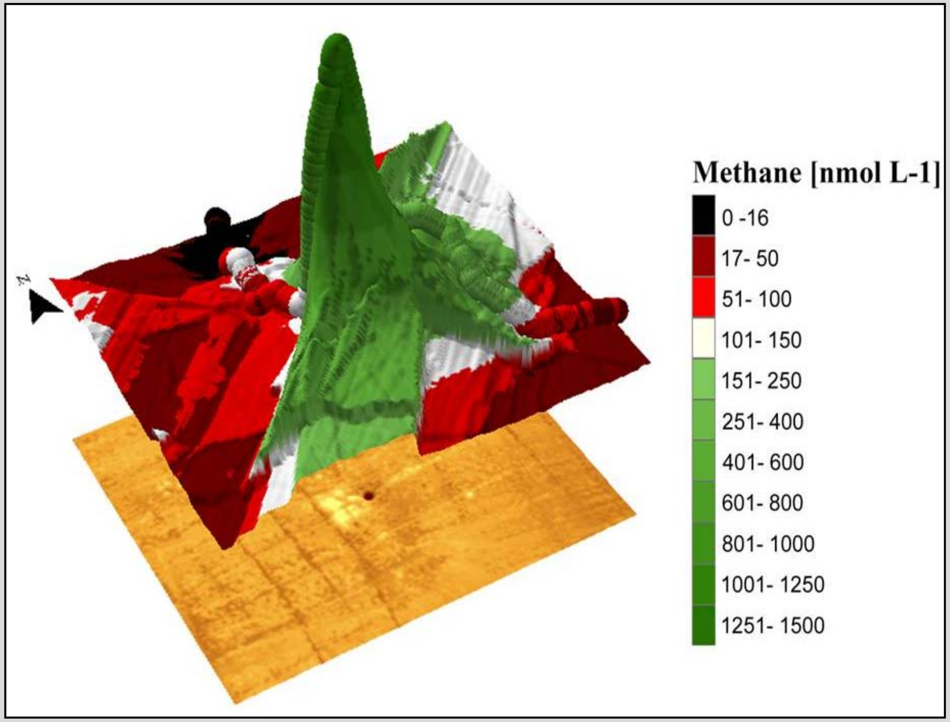

with cryotrap:

96.4 %

Concentration [nmol L^{-1}]	Area [%]
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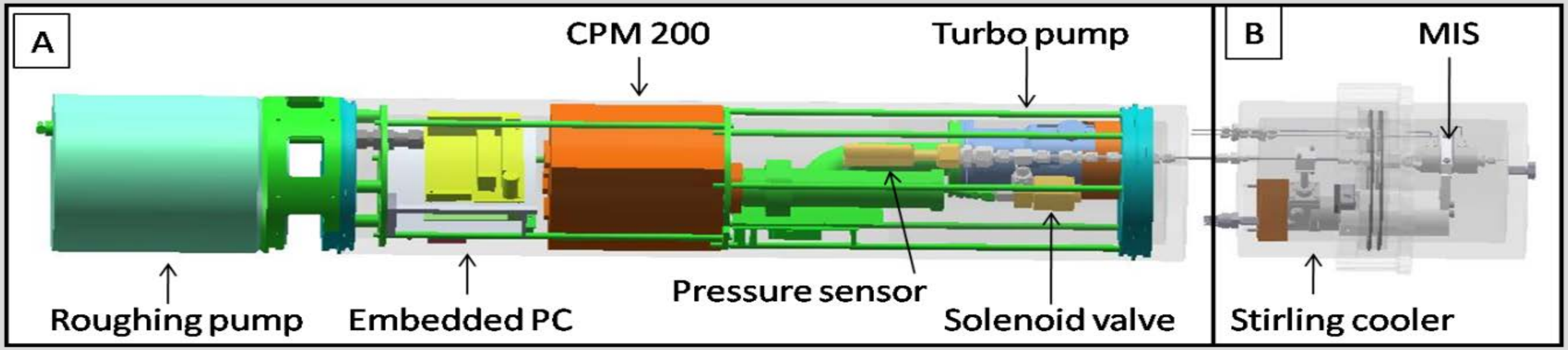
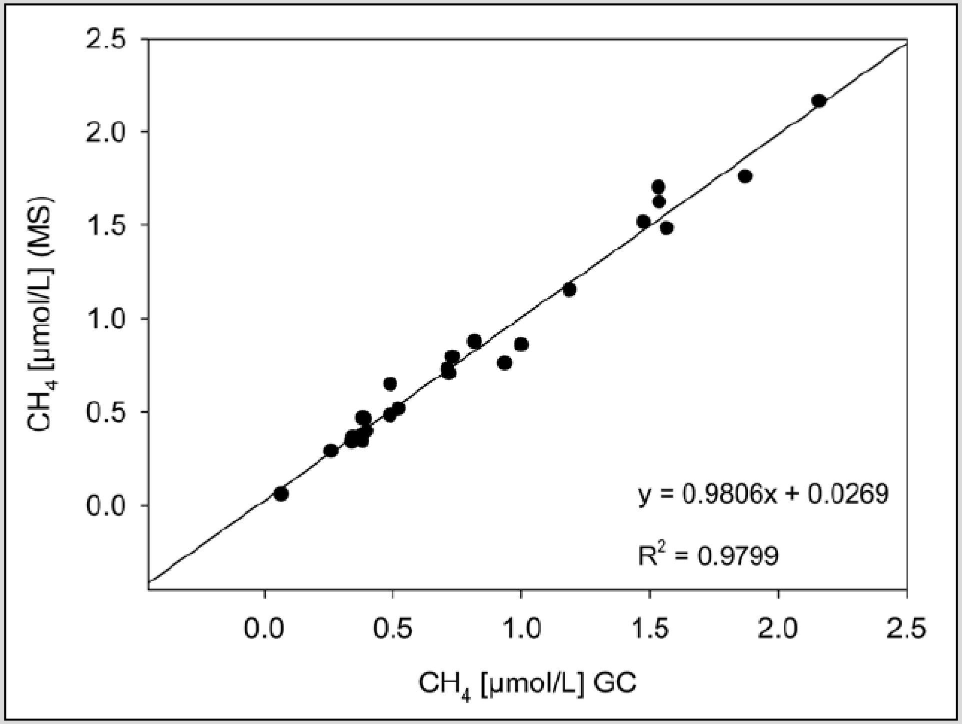
(Gentz and Schlüter 2012)

Comparison of the Inspectr200-200 vs. conventional techniques

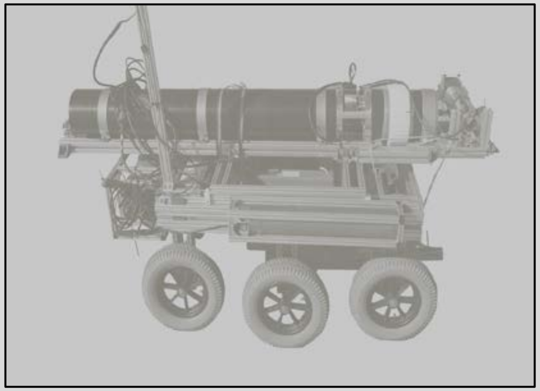


- Both methods are comparable
- No sampling preparation
- Simultaneous measurement of the dissolved gases
- No artefacts during sampling
- Up to 750 times higher sampling frequency

→ **Higher temporal and spatial resolution**

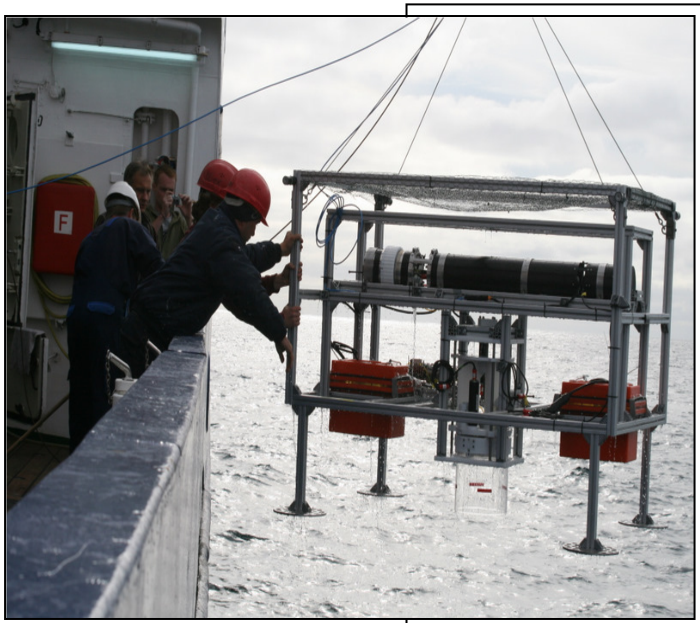


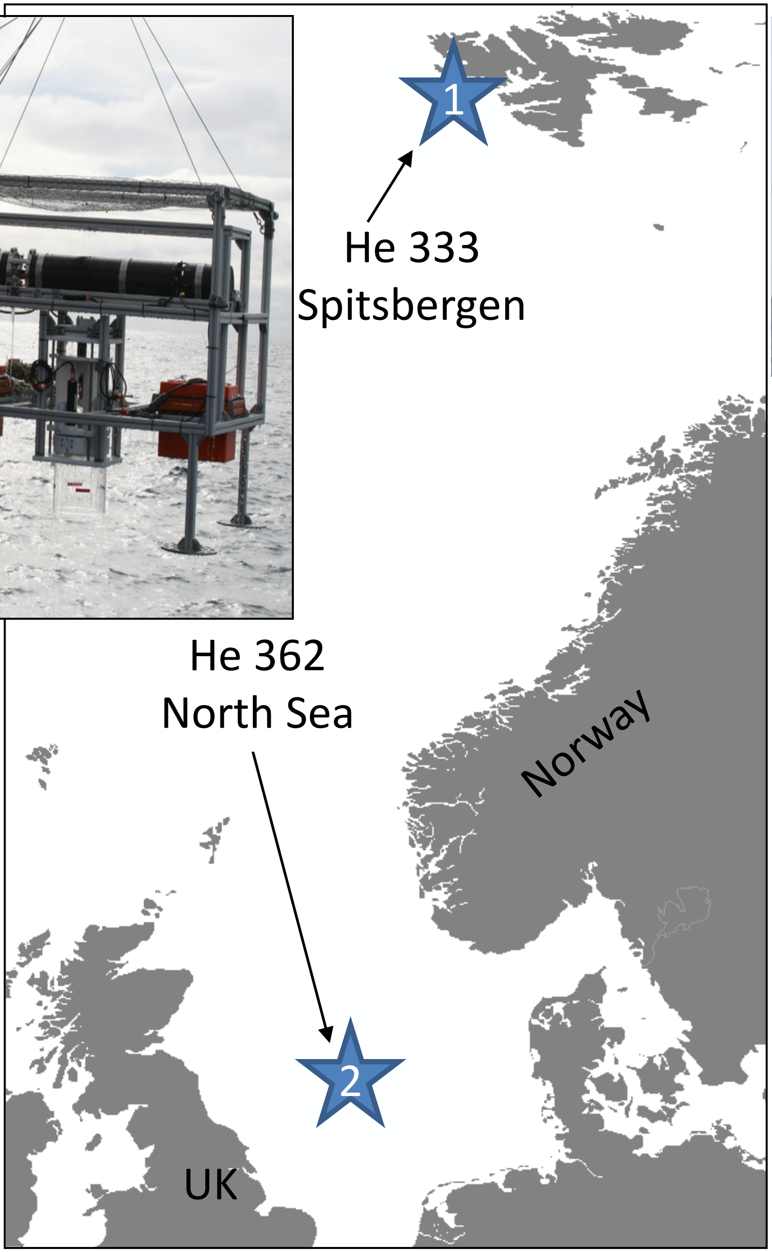
Inspectr200-200 vs. GC



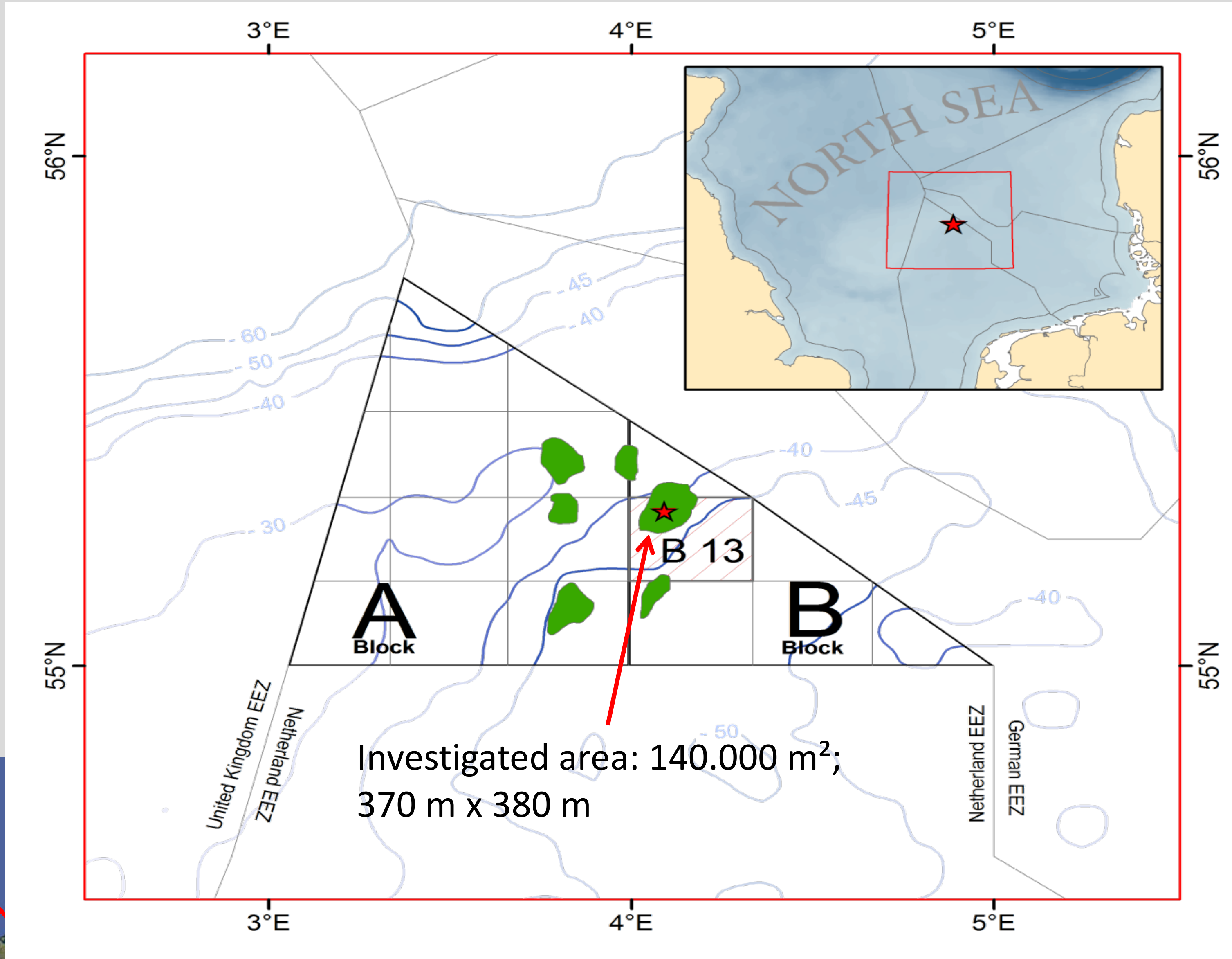
Deployments of the in situ mass spectrometer

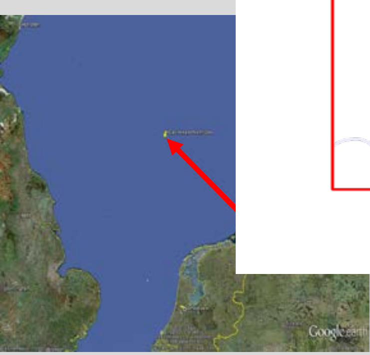
Application of the in situ mass spectrometer in harsh environments





Observation of a gas seep area in the North Sea





Modified after Schroot et al. 2005

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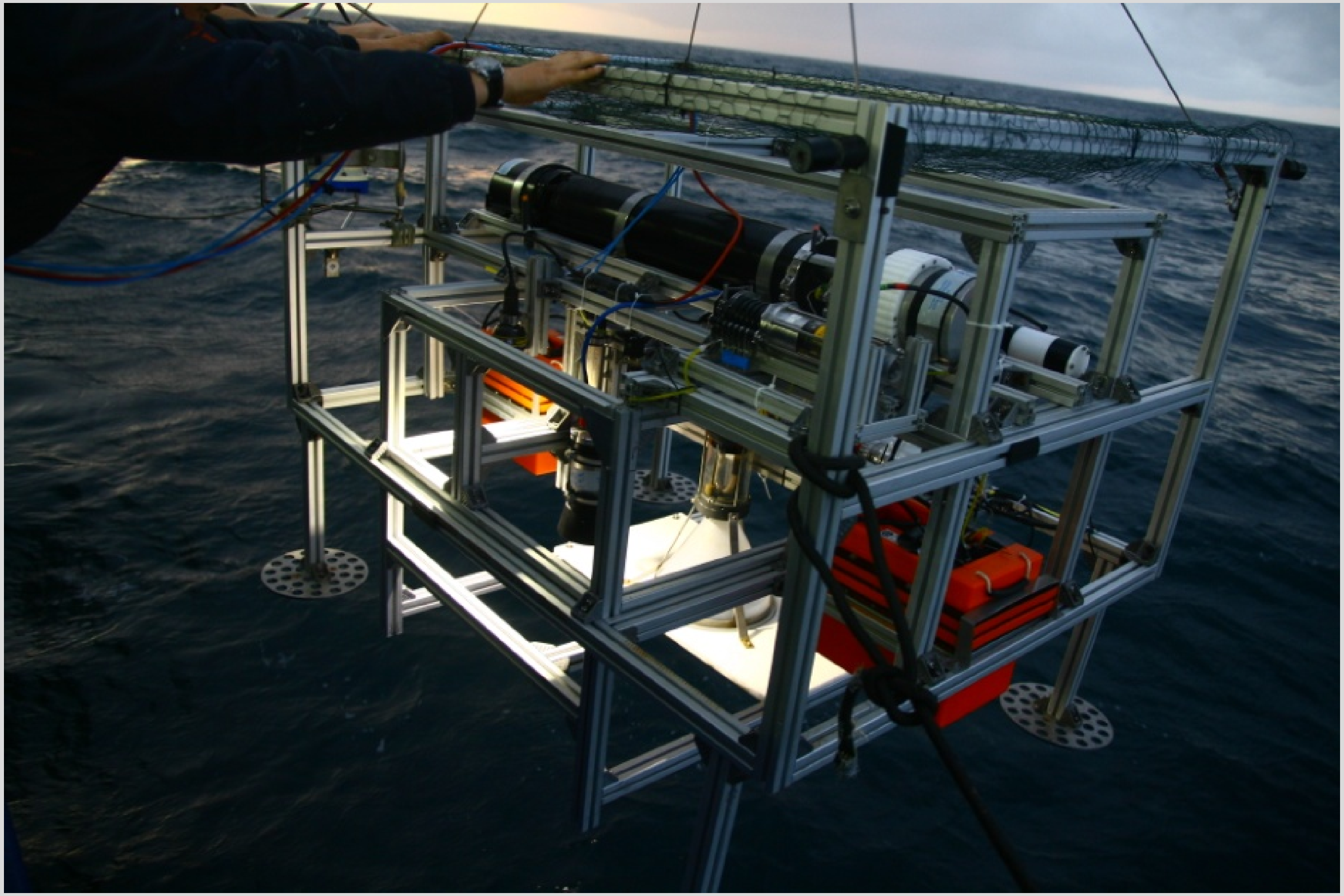
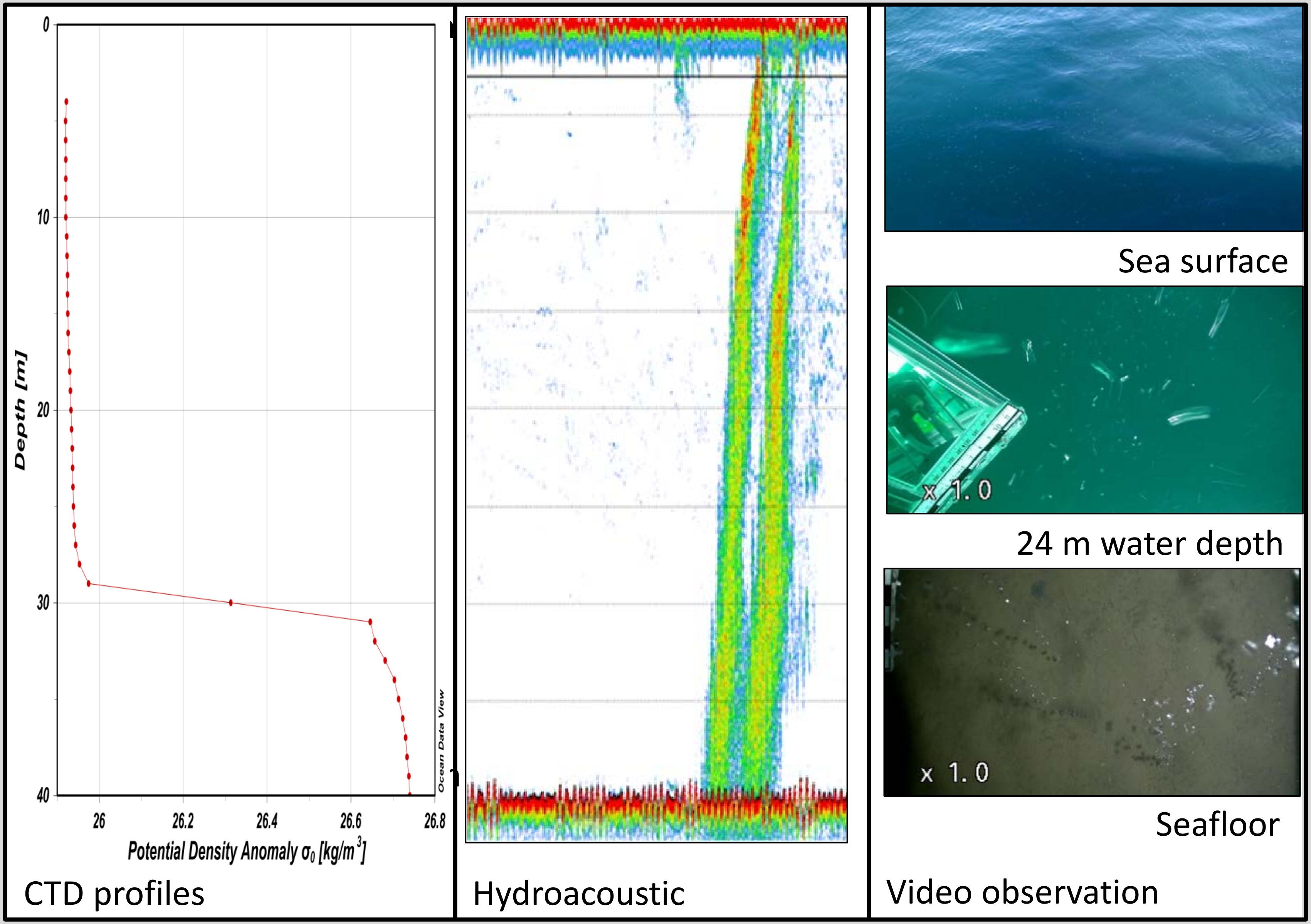


Under water gas analyser, sampler and observing system

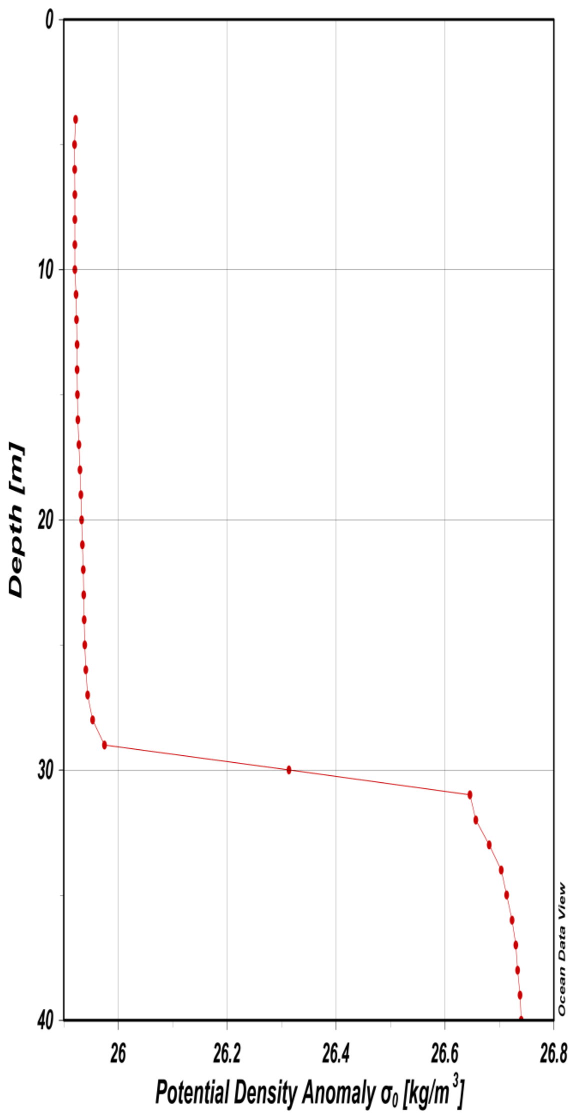
- Inspectr200-200; 11900 samples
- GC; discrete 154 samples
- Video observation; 12 h
- Hydroacoustic; 12 h
- Multibeam; 140000 m²
- CTD 14; vertical profiles
- Bubble sampler; 5 samples
- Multiple sediment corer; 5 cores

Observation of a gas seep area in the North Sea

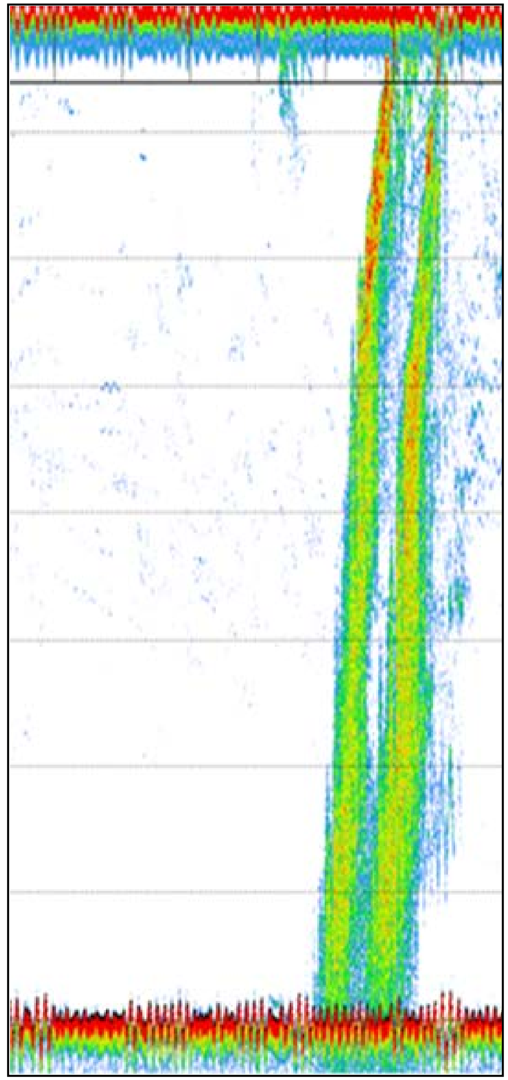


(Gentz et al. unpublished data)

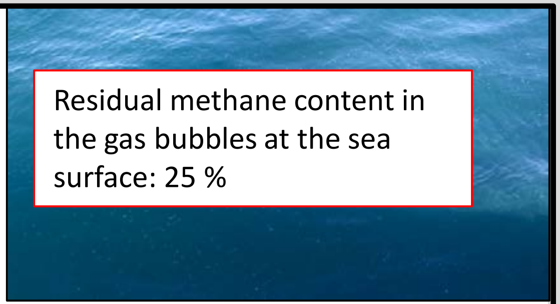
Observation of a gas seep area in the North Sea



CTD profiles

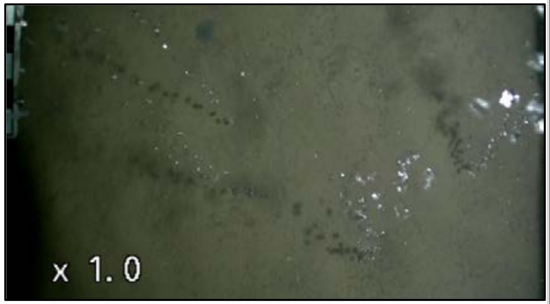


Hydroacoustic



Sea surface

24 m water depth

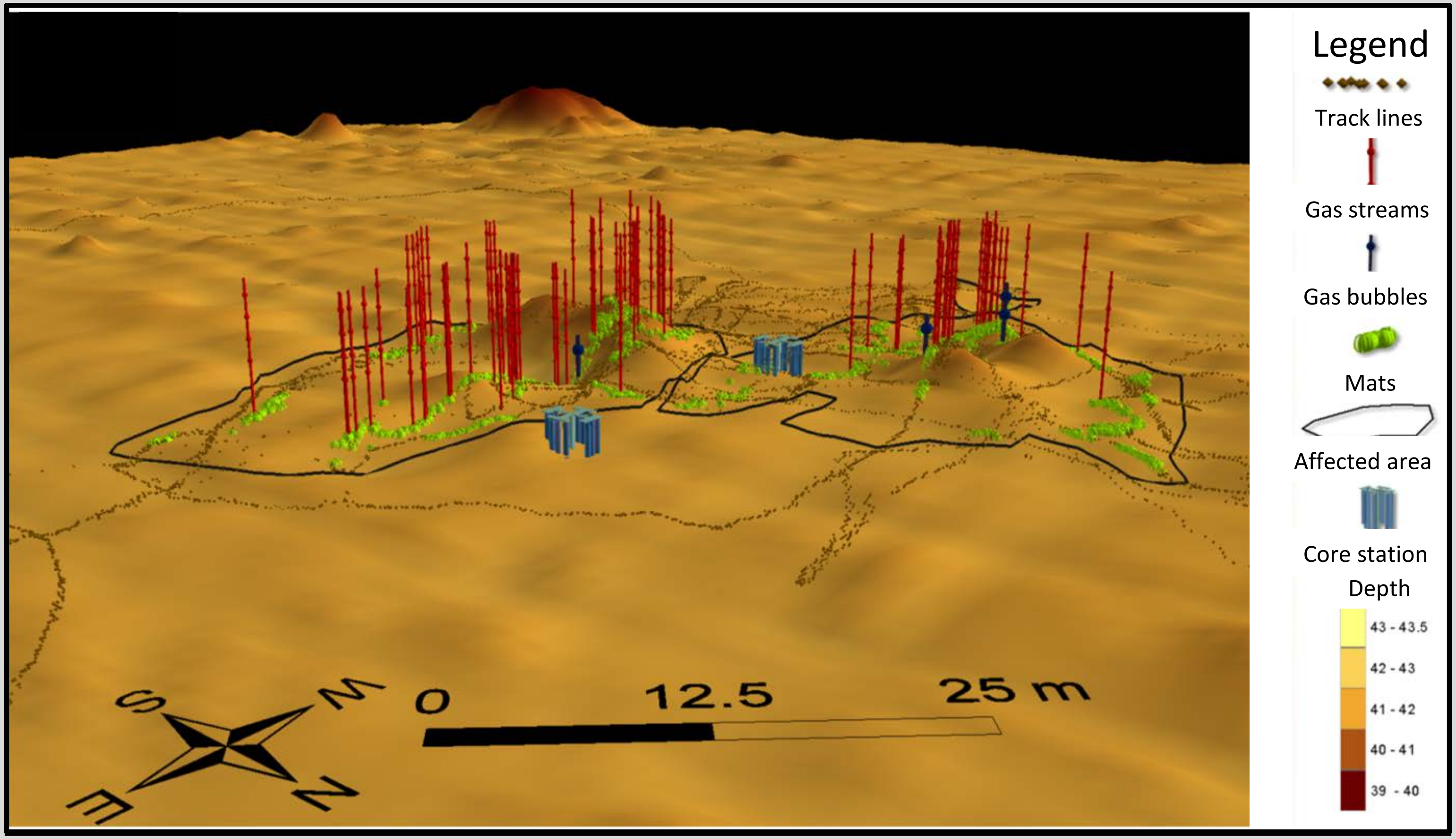


Seafloor

Video observation

(Gentz et al. unpublished data)

VIDEO OBSERVATION OF THE SEAFLOOR



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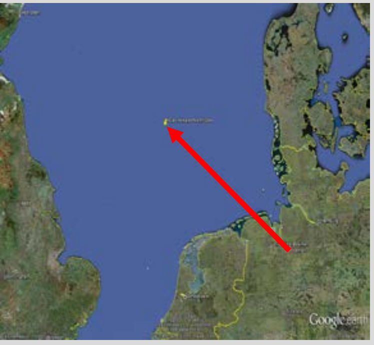


Affected area: ~3800 m²

Number of streams: 113

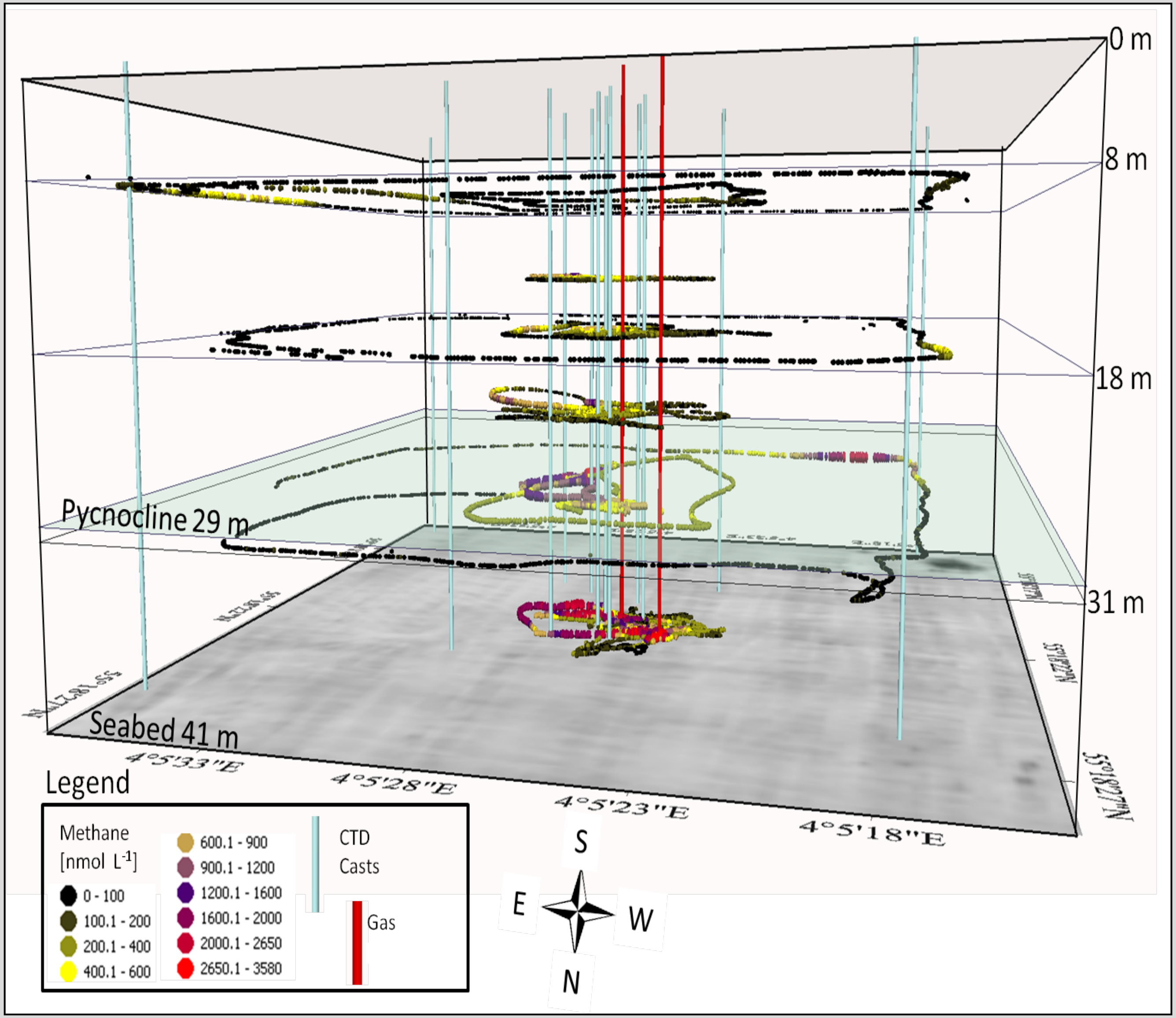
Bubble diameter: 4.5 to 16 mm (average 7 mm)

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}

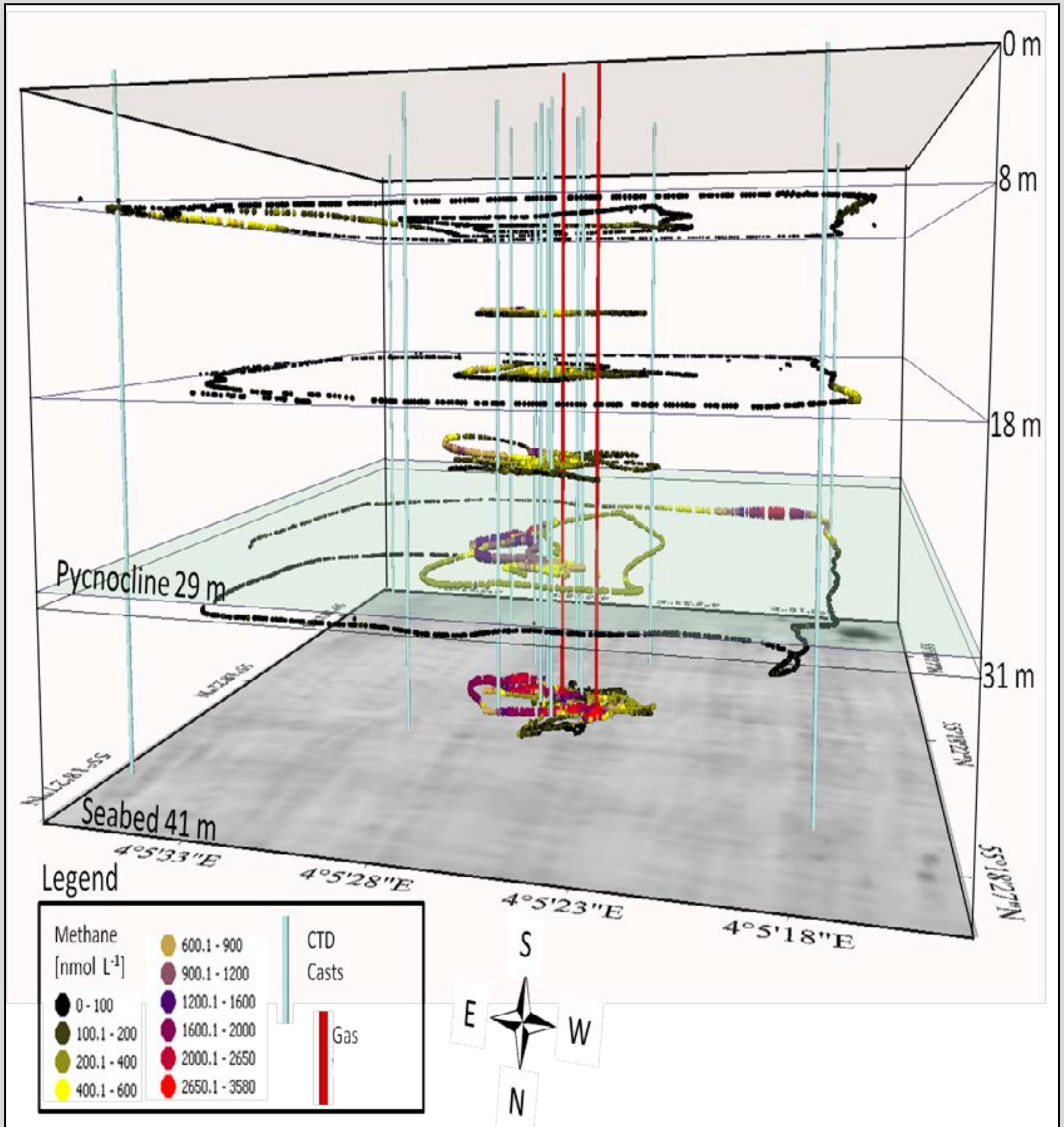
DISSOLVED METHANE SAMPLING IN THE WATER COLUMN



11900 samples in various depth in between 24 hours

(Gentz et al. unpublished data)

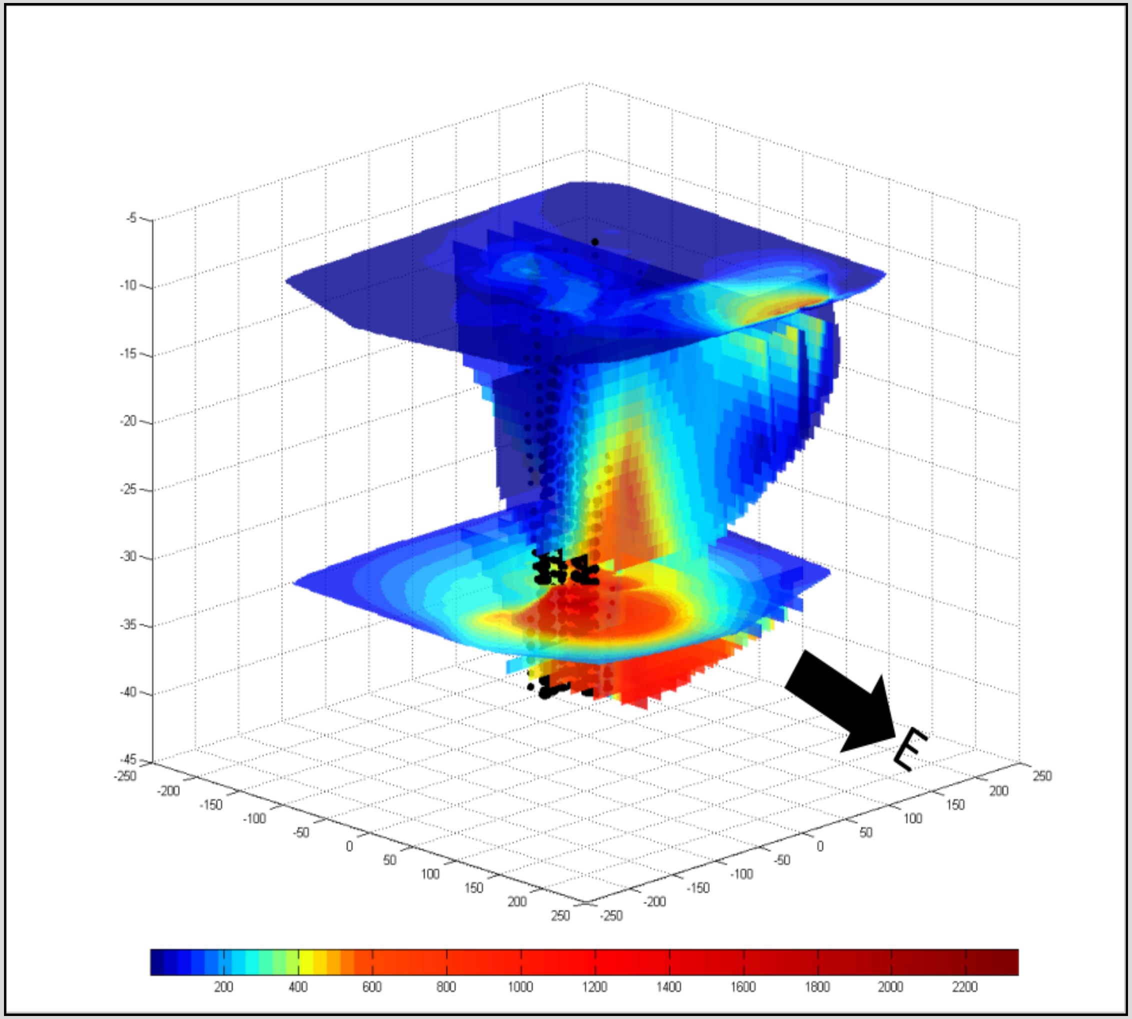
DISSOLVED METHANE SAMPLING IN THE WATER COLUMN



- 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 ± 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

→ 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.

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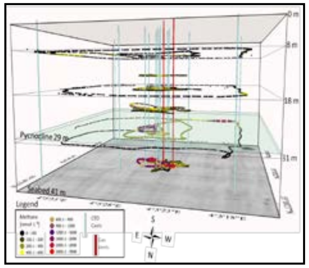
- The inventory calculation is more accurate than before and shows that conventional methods tend toward underestimation.



Conclusions

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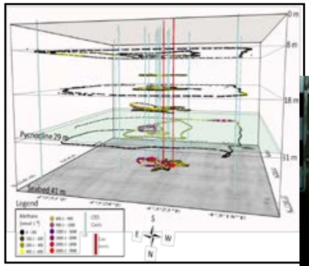

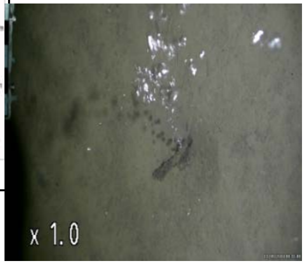

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CONCLUSIONS

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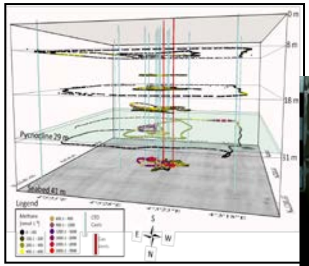

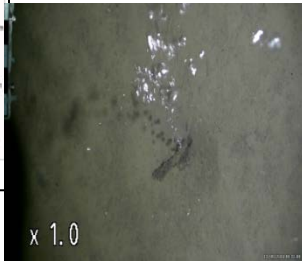

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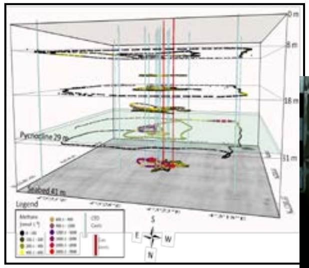

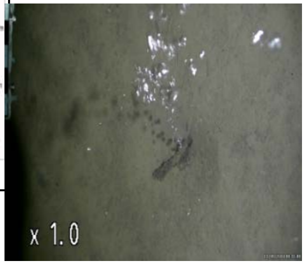

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- The investigated study area in the North Sea contributes to the global atmospheric methane budget.

- 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
Direct methane transport	No	Yes
indirect transport	???	Yes
Methane to atmosphere [% from origin]	???	~ 60

CONCLUSIONS

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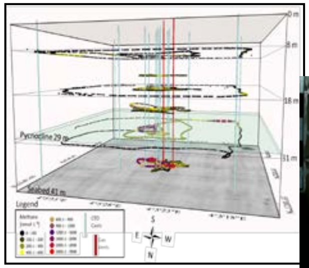

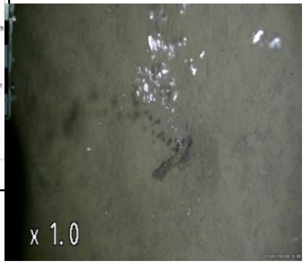

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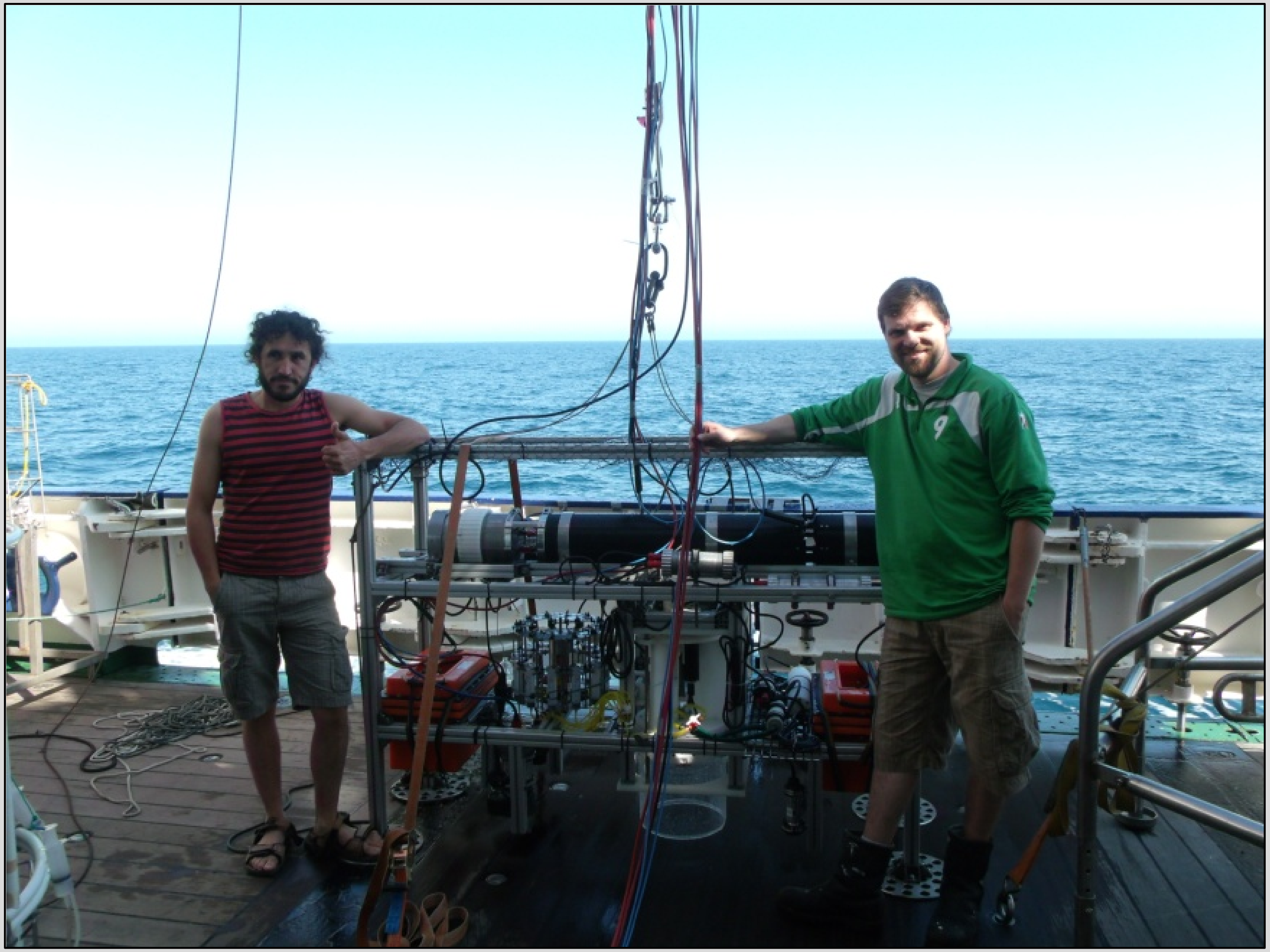
- **The use of the improved in situ mass spectrometry is one step forward to understand the pathways and potential global relevance of these methane sources.**

CURRENT AND FUTURE WORK

Implementation of the mass spec into an AUV

…



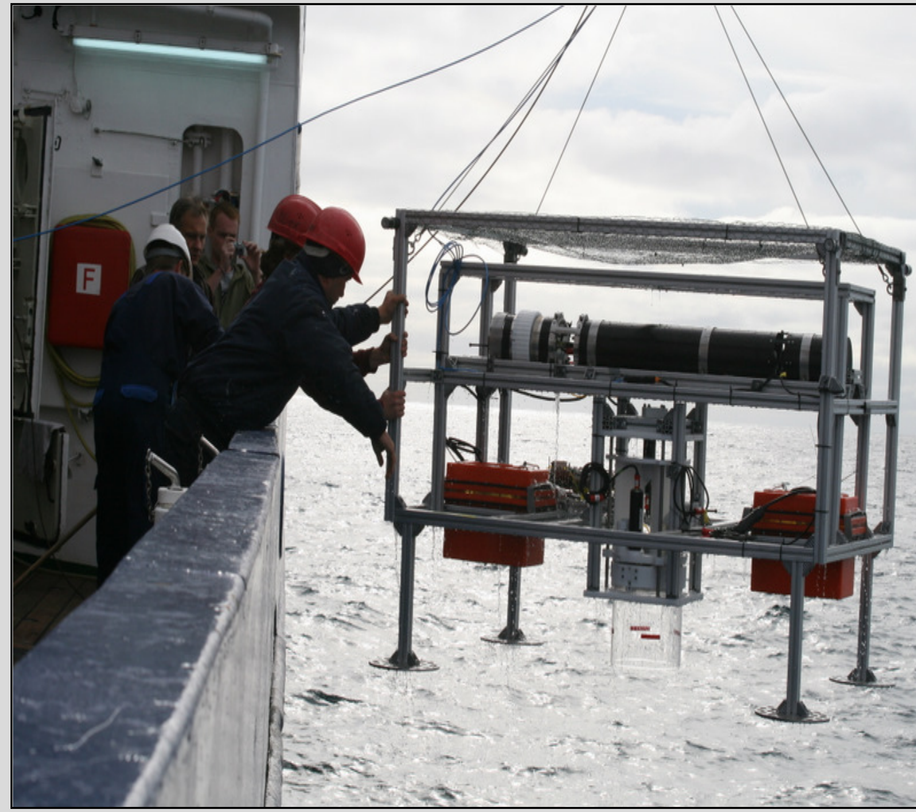
Thank you all for
developing new instruments as well as
your attention!

Torben.Gentz@awi.de

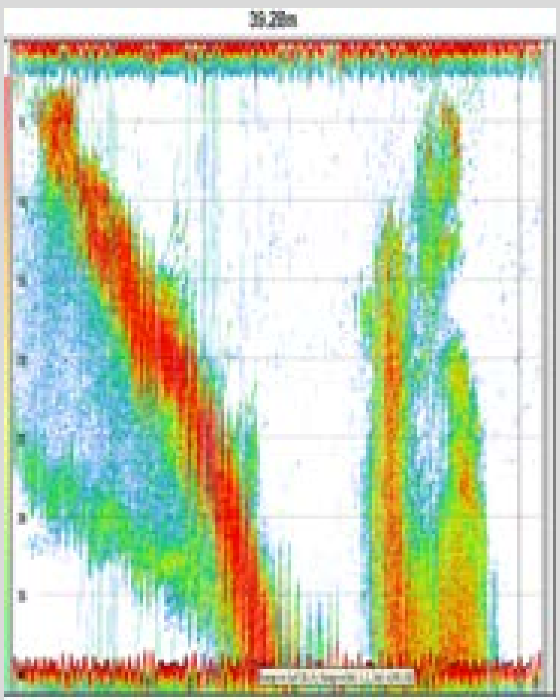
Backup

Future work

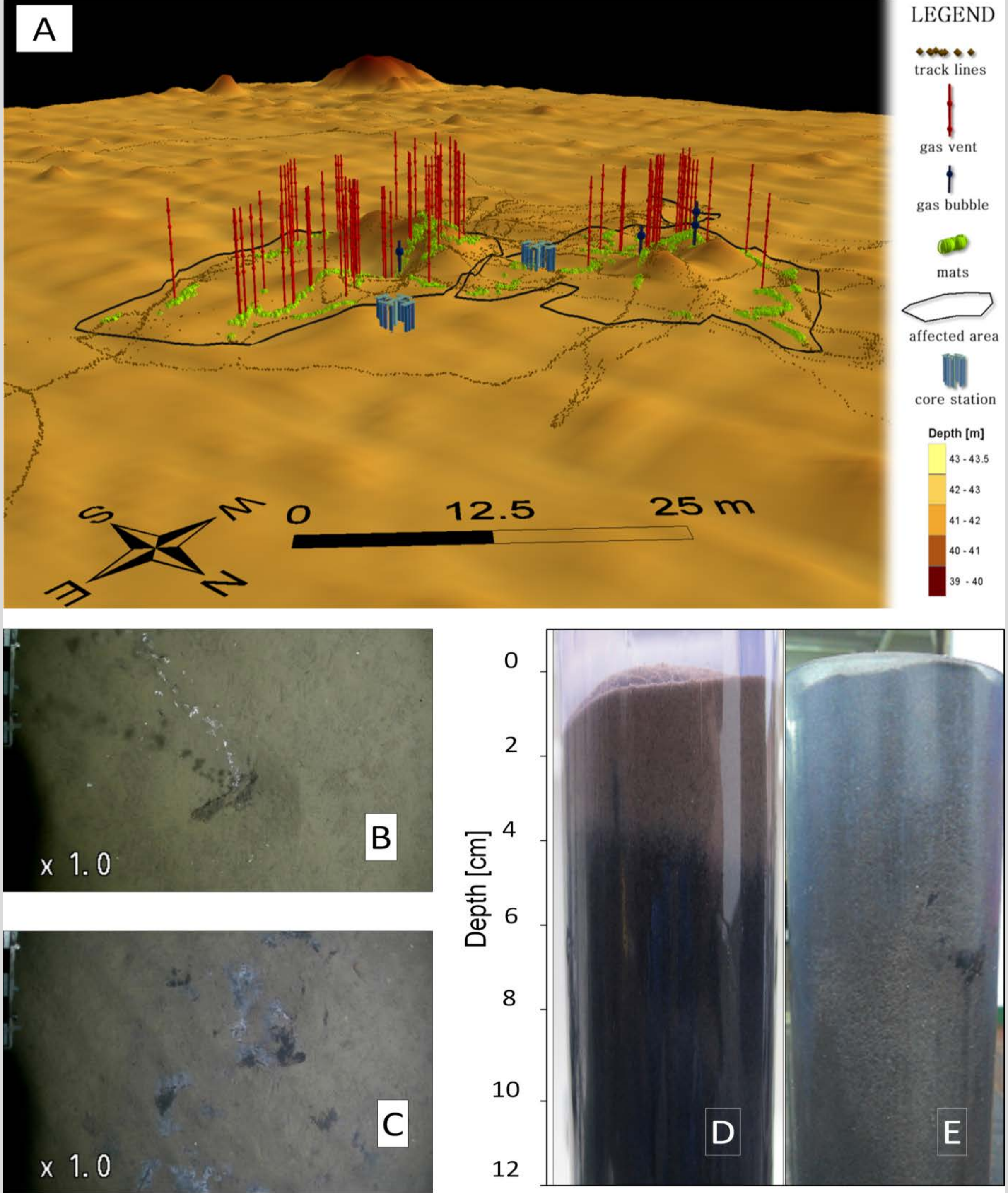
Implementation in new device holder

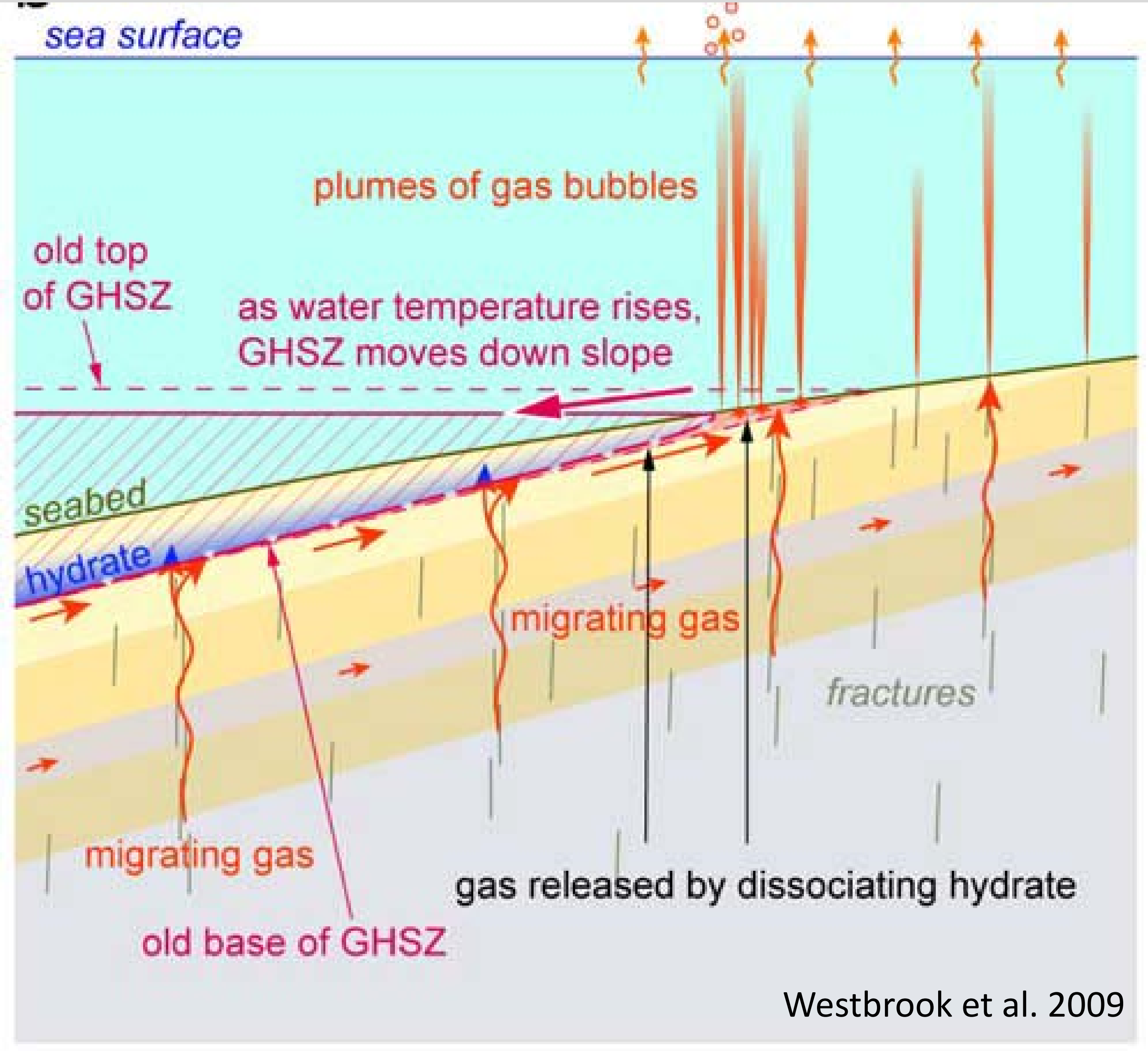


Benthic chamber measurements



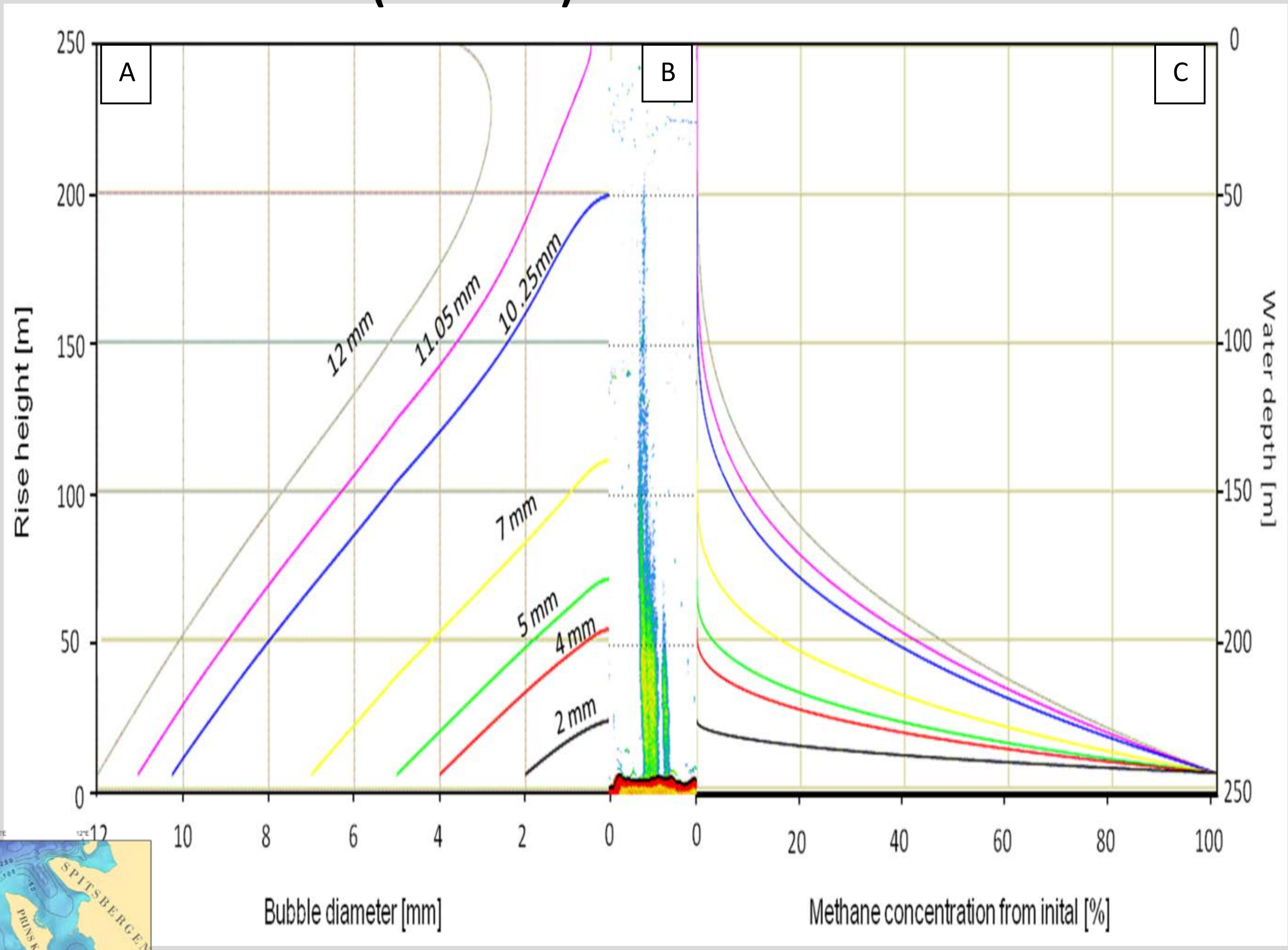
Combining ydroacoustic with in situ mass spectrometry

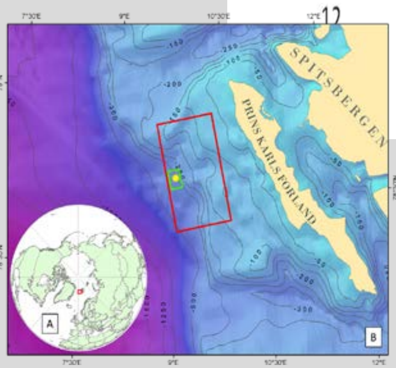

A
LEGEND
track lines
gas vent
gas bubble
mats
affected area
core station
Depth [m]
43 - 43.5
42 - 43
41 - 42
40 - 41
39 - 40
0
12.5
25 m
S
W
N
E
B
x 1.0
C
x 1.0
Depth [cm]
0
2
4
6
8
10
12
D
E



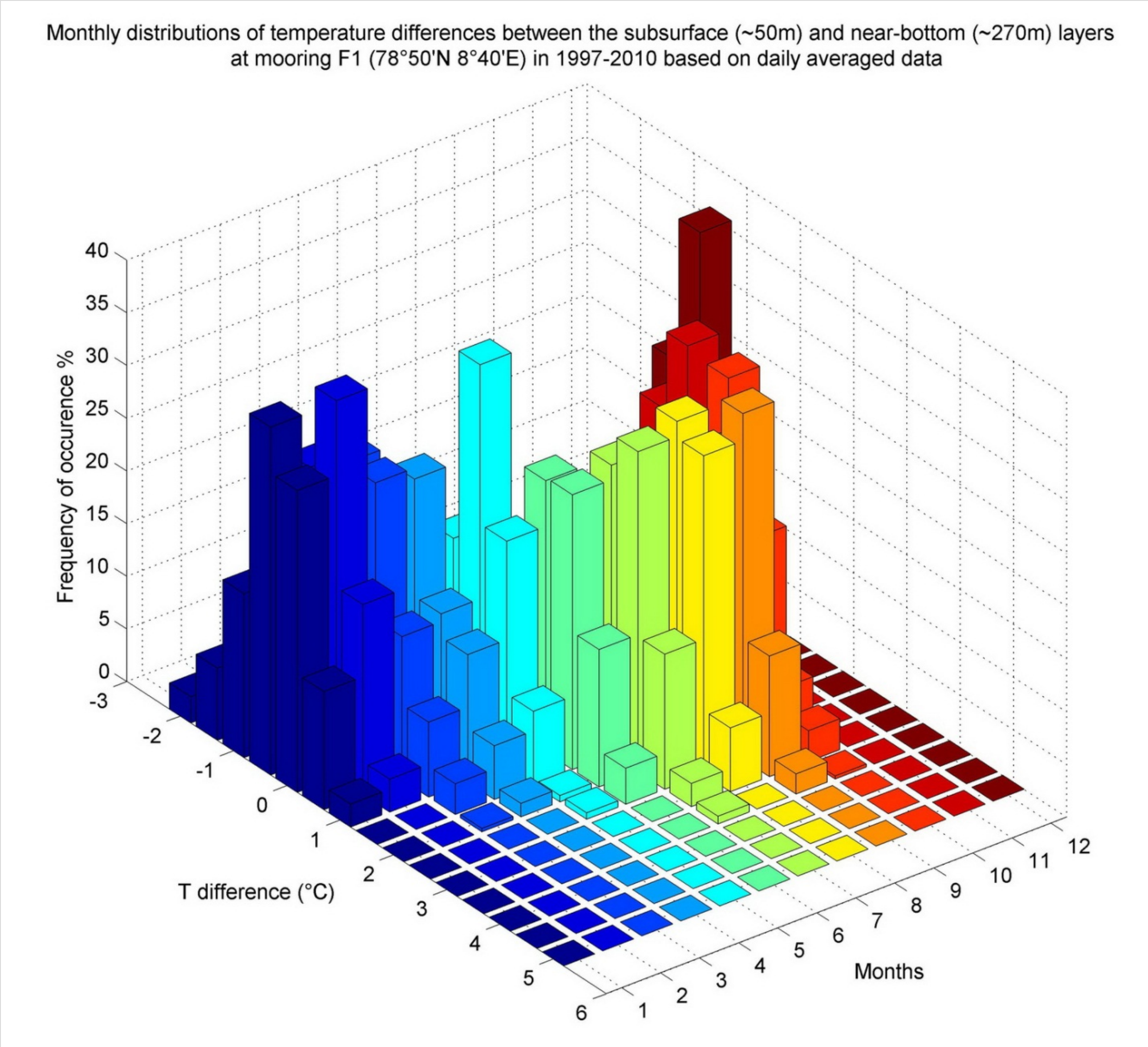
Westbrook et al. 2009

Gas bubble dissolution model (SiBu GUI):

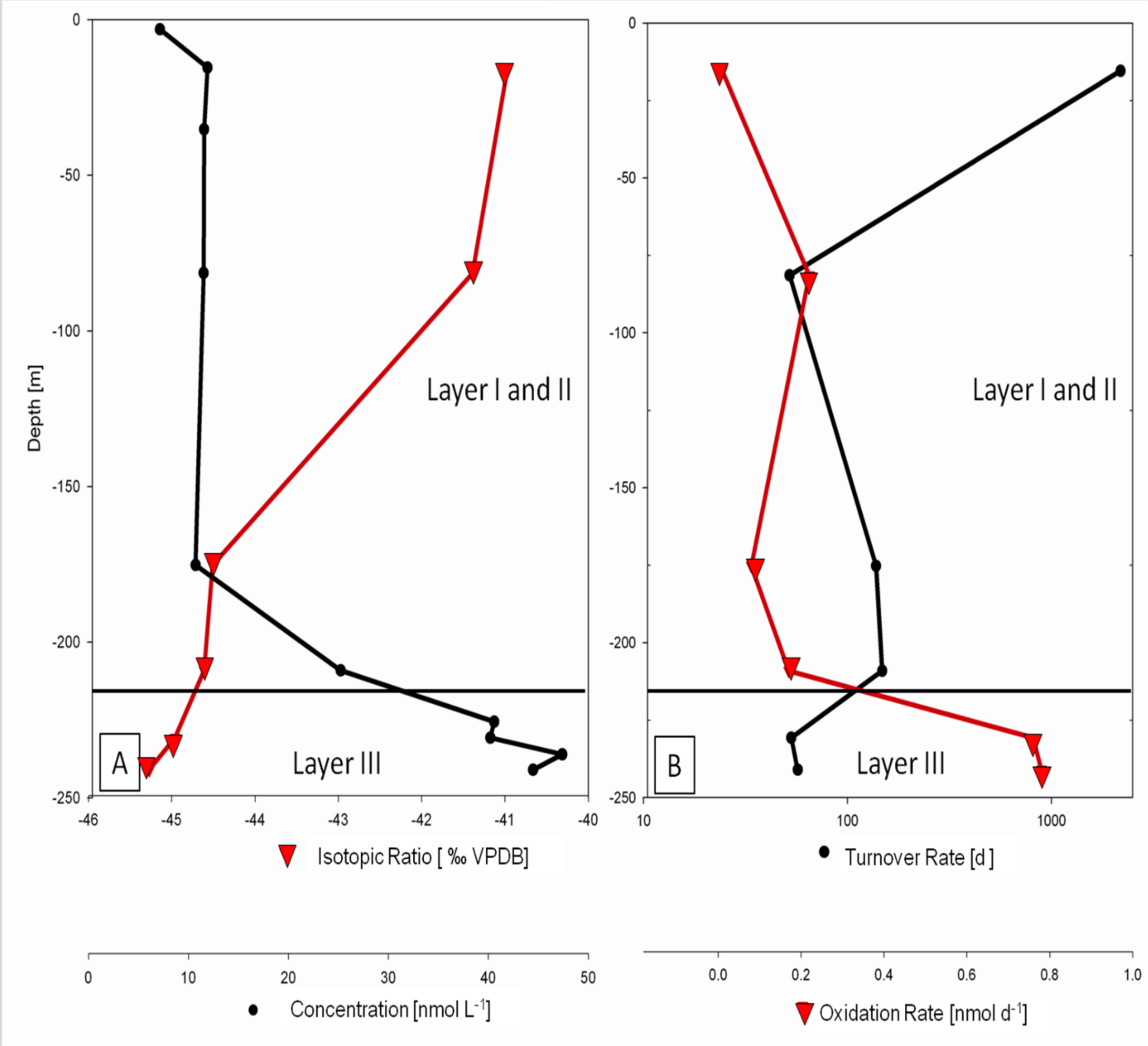




*Decrease of the bubble diameter during the ascend from the seafloor for initial bubbles sizes of 2 mm to 12 mm (A) compared with the hydroacoustic image of the highest detected gas flare (B). Decrease of the initial CH_4 concentration in the bubbles during their rise in the water column (C). Data obtained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

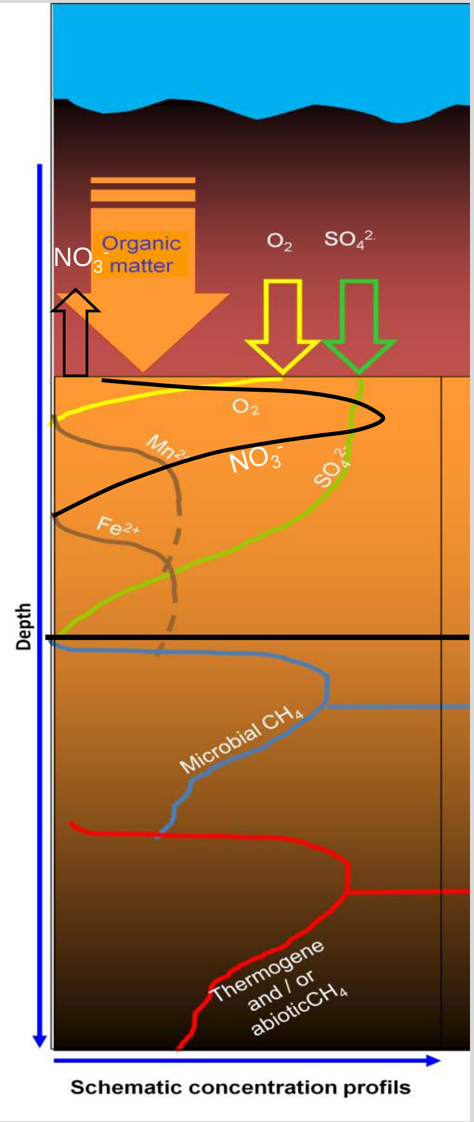


Personal communication Agnieszka Beszsynsky-Möller
28.26 km s-w direction



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

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

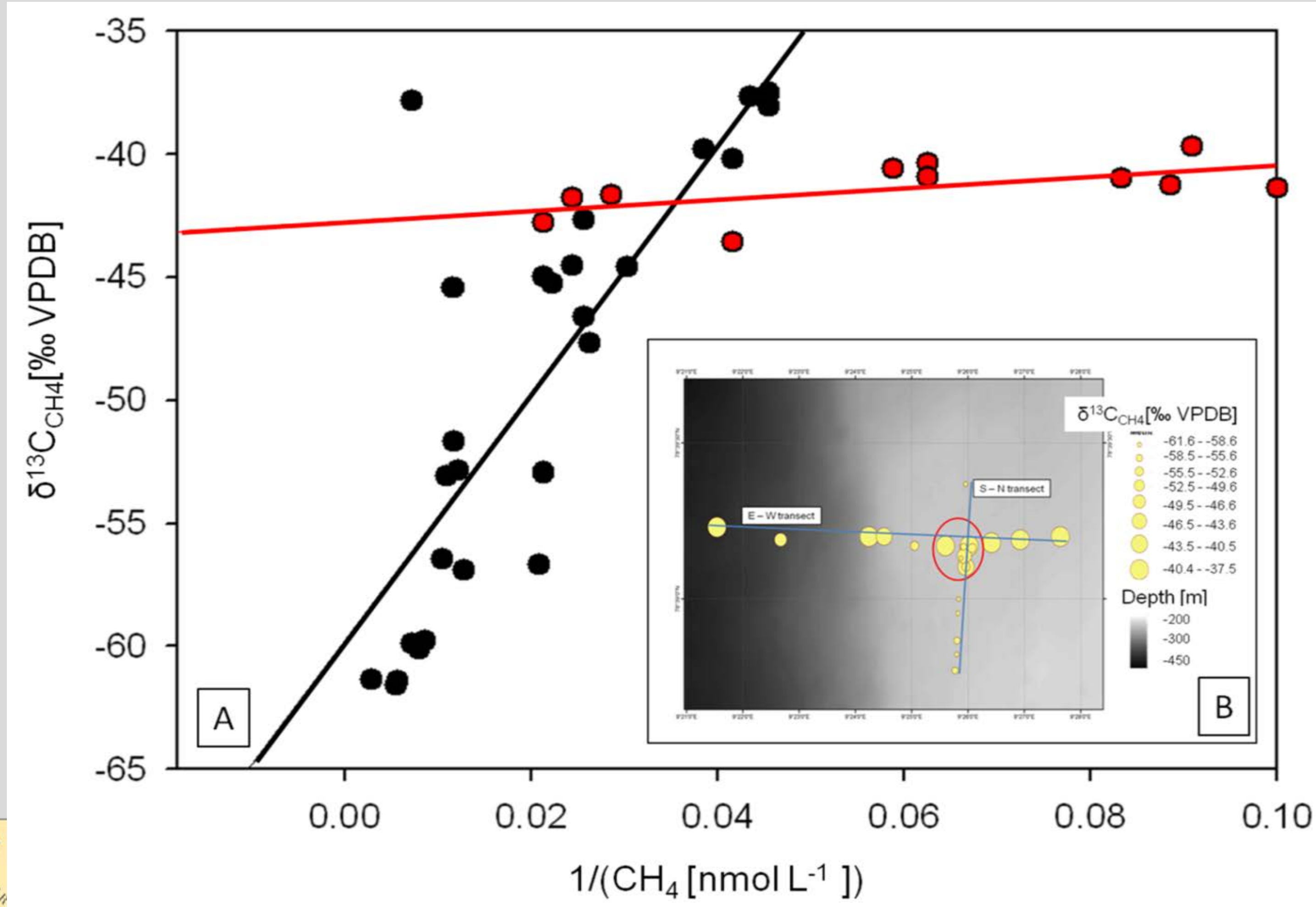
sulfate/methane transition zone (SMTZ)

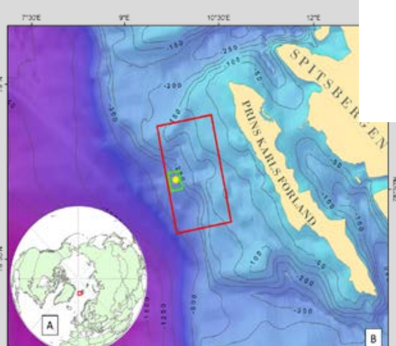
Microbial formation of methane:

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)





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

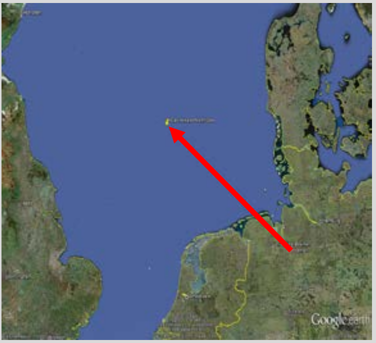
Release frequency: 23 bubbles s^{-1}

Methane flux: 28.27 L min^{-1}

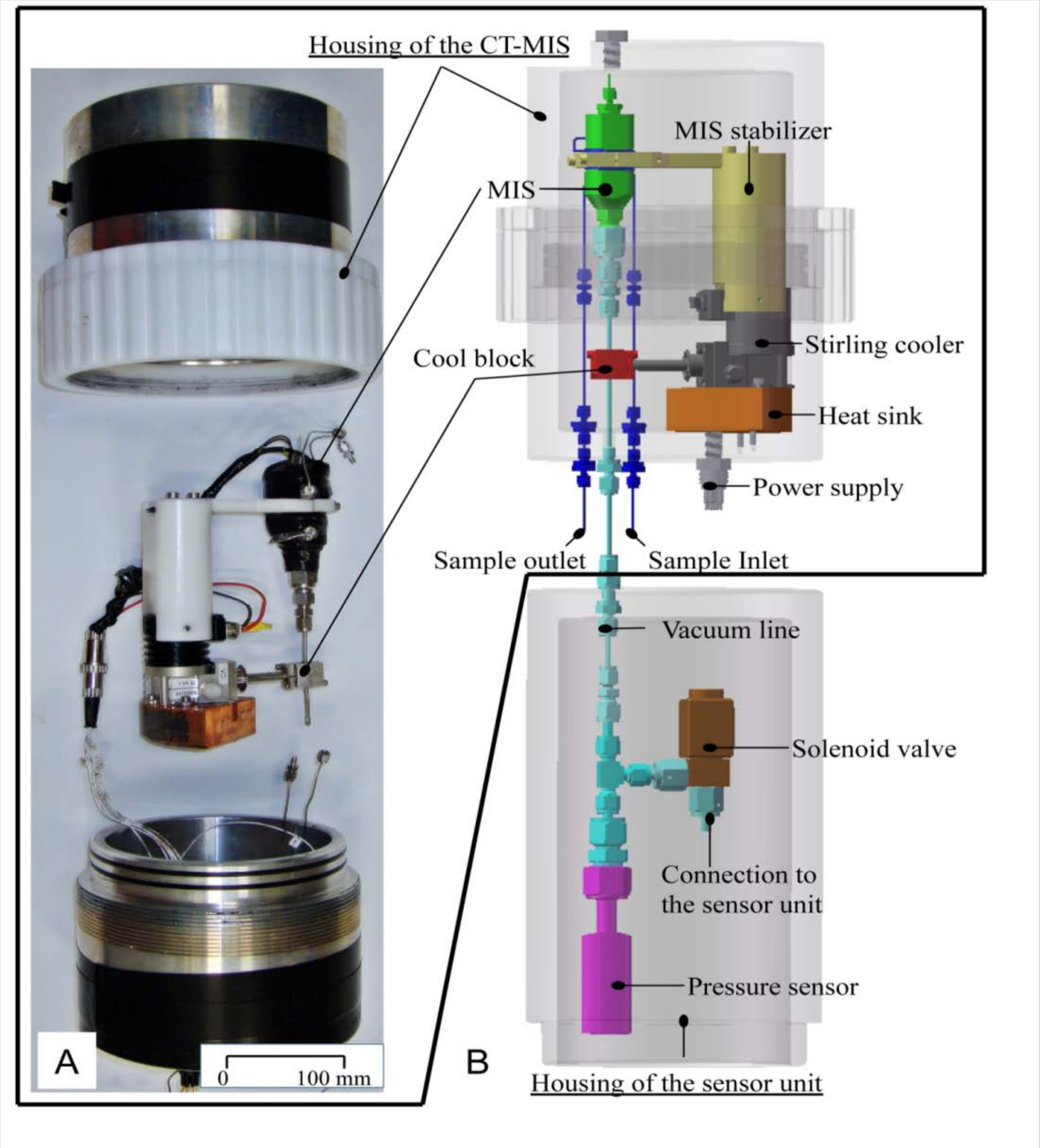
$$PVA = nRTZ \quad (3)$$

Modified after Römer et al. 2012

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



Under water cryotrap



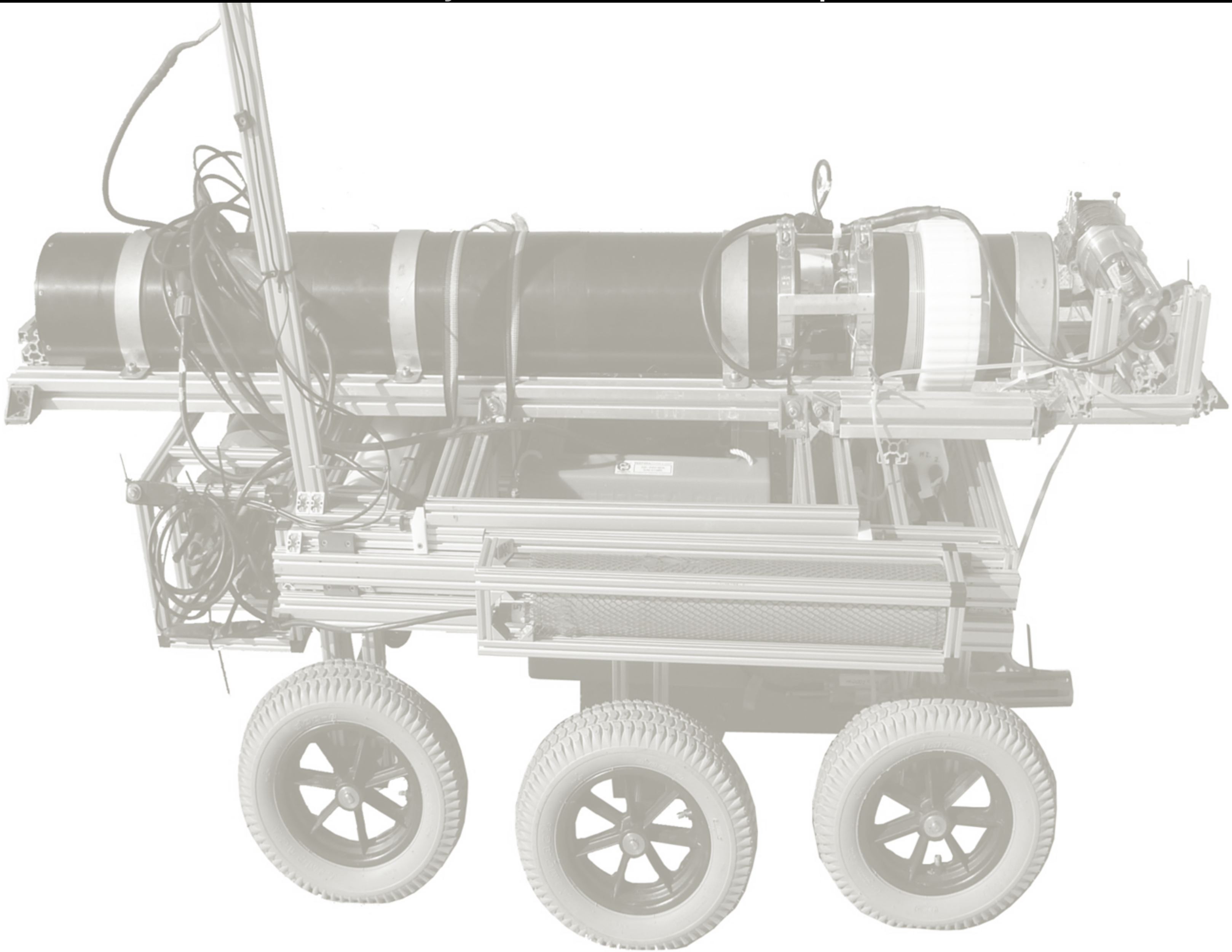
Gentz and Schlüter 2012

Gas analysis: New in situ sensors for high resolution mapping

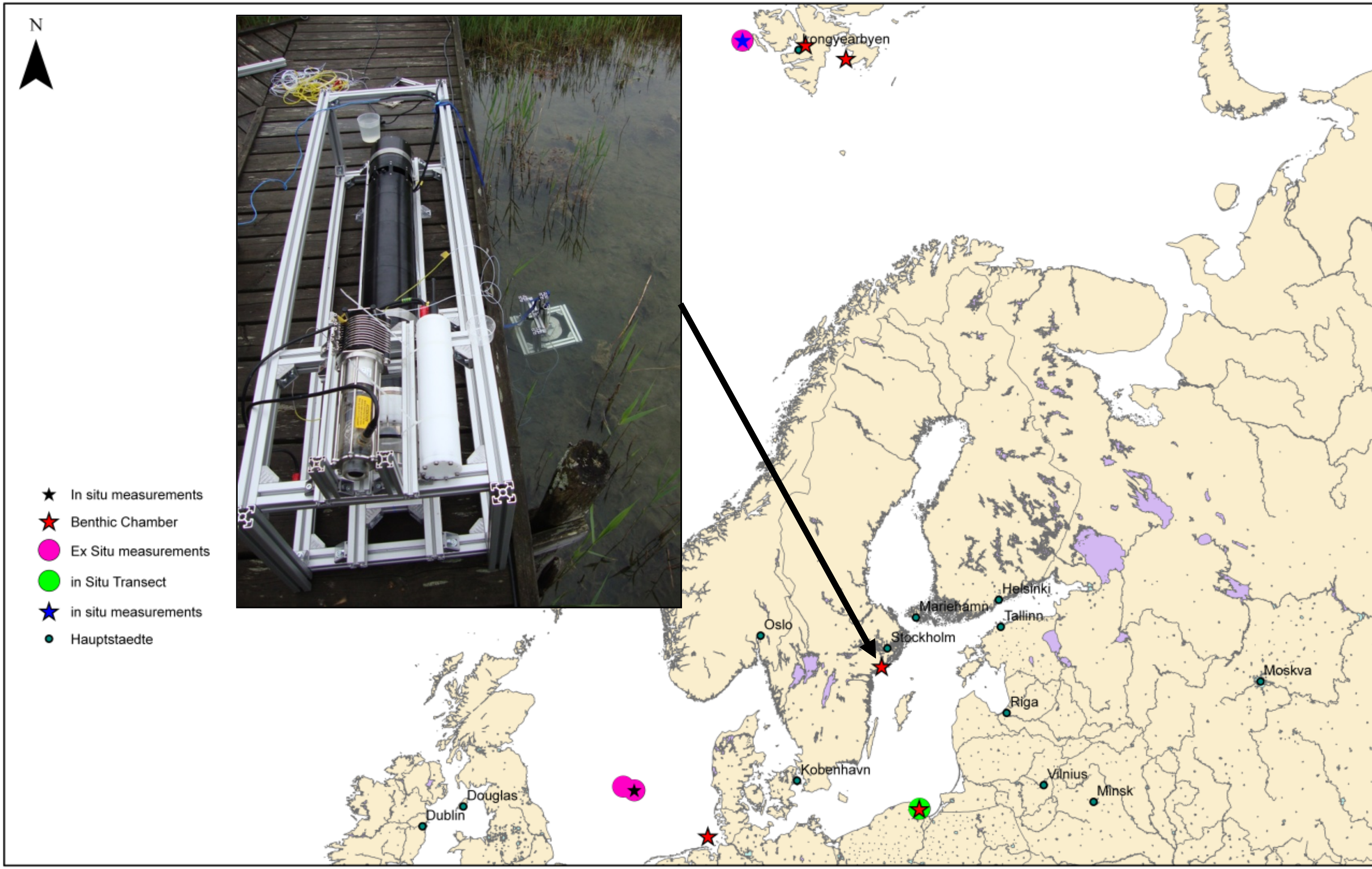
TRL 1 Basic principles of technology observed and reported
TRL 2 Technology concept and/or application formulated
TRL 3 Analytical and laboratory studies to validate analytical predictions
TRL 4 Component and/or basic sub-system technology valid in laboratory environment
TRL 5 Component and/or basic 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.



Working areas



Working areas