

# Continuous measurement of dissolved methane concentration in surface waters: a new method tested in the Scheldt Estuary

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## Biogeochemistry group

- Greenhouse gases in Polar Regions ( $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ )
- Physico-chemical characterization of different types of ice
- Interfacial processes
- Discrete/continuous sampling in water, ice and atmosphere



Colleagues from the glaciology lab drilling a core in Antarctic sea ice (Credit: Célia Sapart)

# HydroC™ HISEM CH<sub>4</sub>

Underwater sensor for continuous measurement of dissolved CH<sub>4</sub> concentration

- CH<sub>4</sub> diffuse through hydrophobic silicon membrane



Hydrophobic silicon membrane



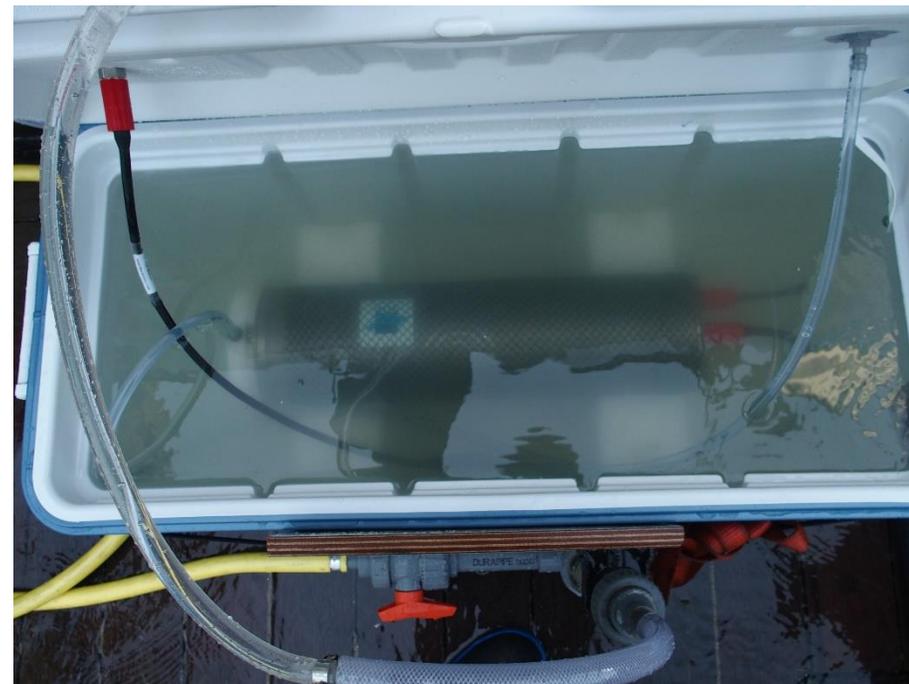
Picture of the underwater sensor

- pCH<sub>4</sub> measured by Tunable Diode Laser Spectroscopy (TDLS)
- High spatial and temporal resolution
- Accuracy of 1 nmol/l ± 0.3 nmol/l

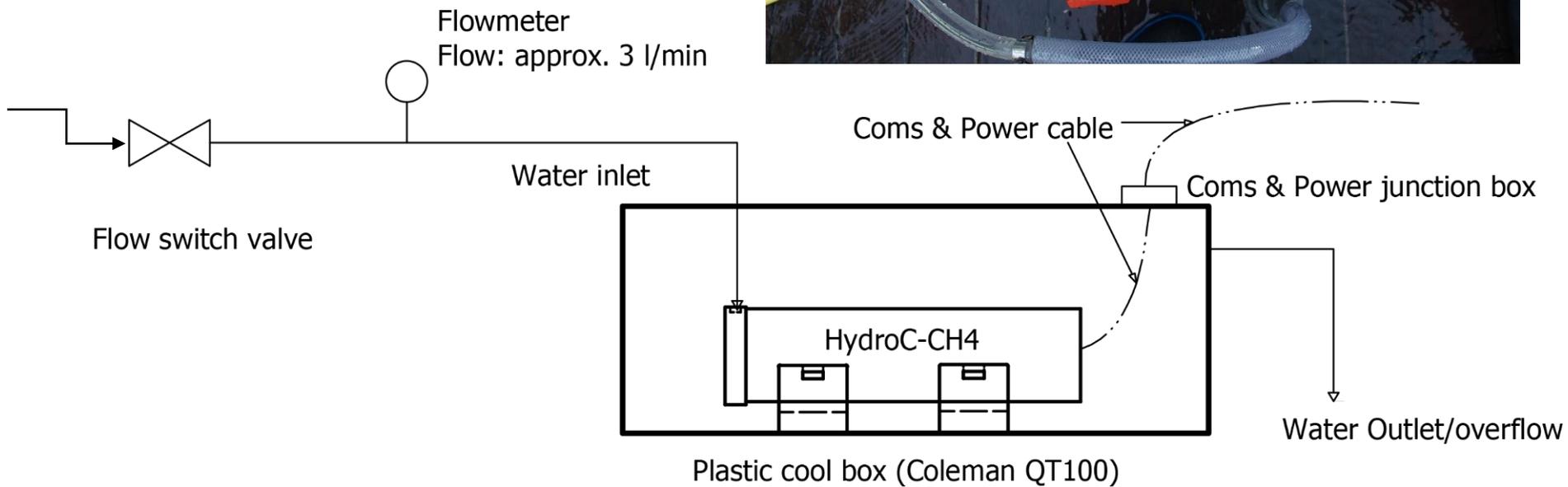
# HISEM set-up



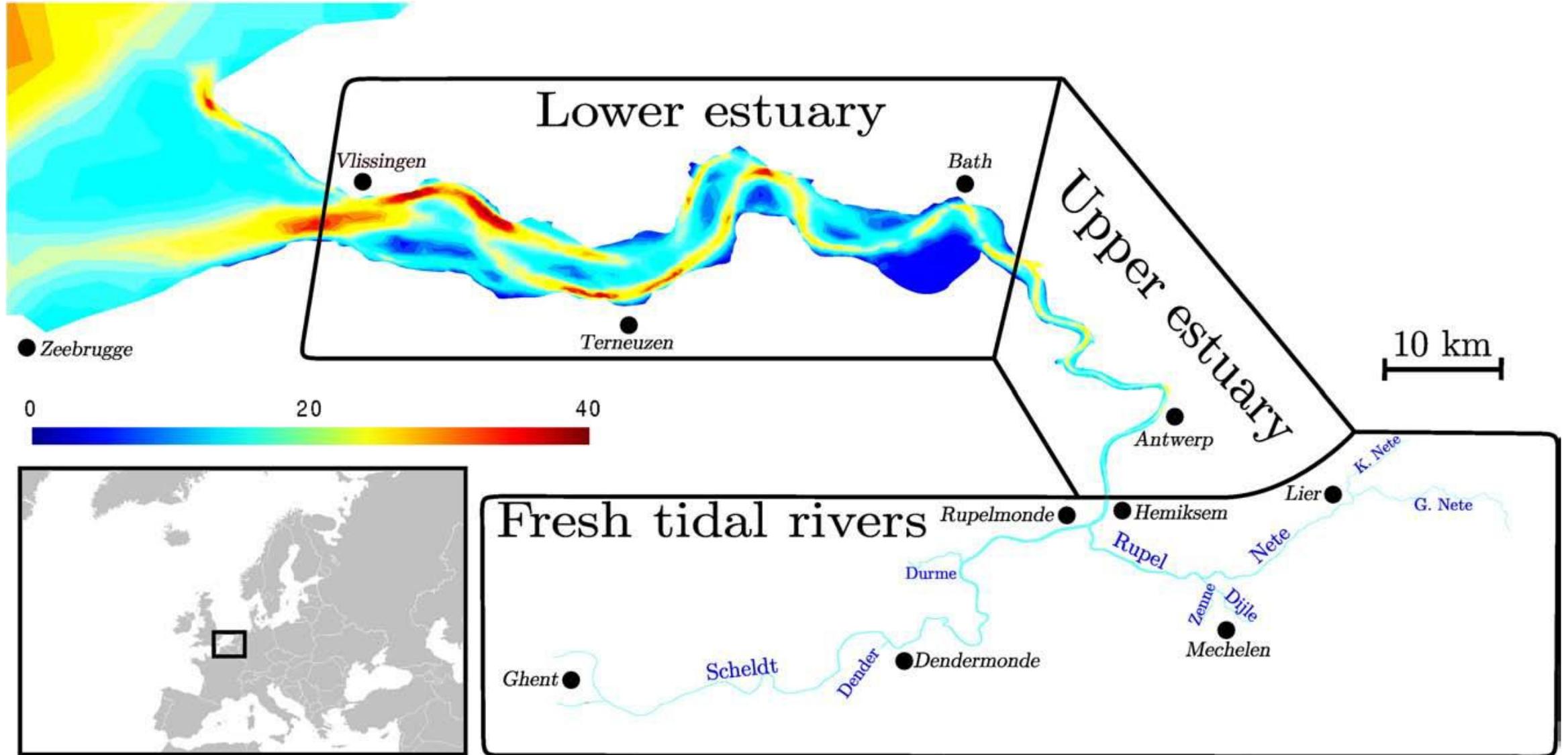
Seawater from vessel's Underway Non Toxic supply



Water intake at the bow of the ship



# The Scheldt estuary



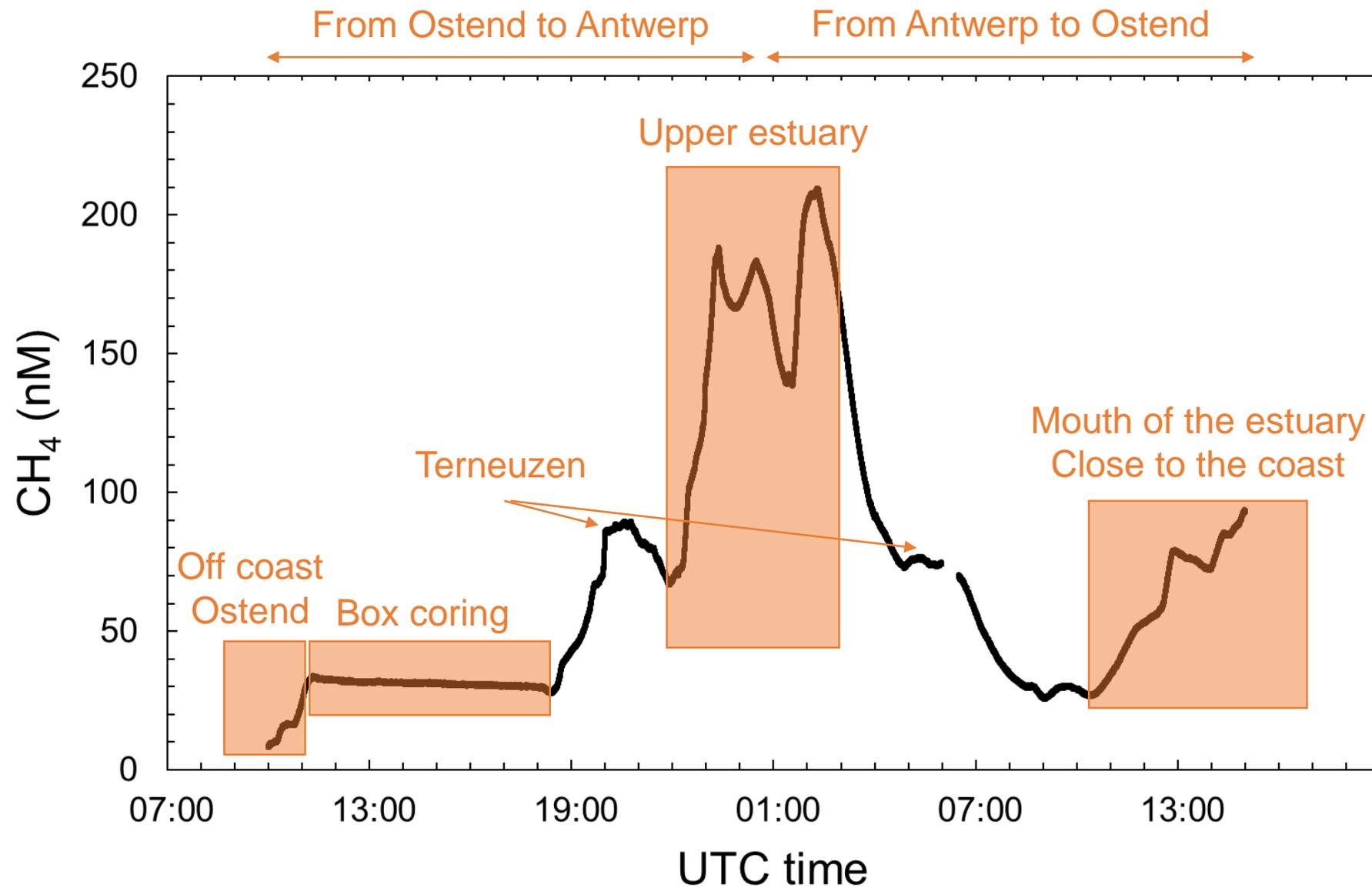
Map of the Scheldt estuary; colors refer to the bathymetry in meters (de Brye et al., 2010)

# CH<sub>4</sub> concentration measurements

Concentrations from 8nM along the coast to 209 nM in the port of Antwerp



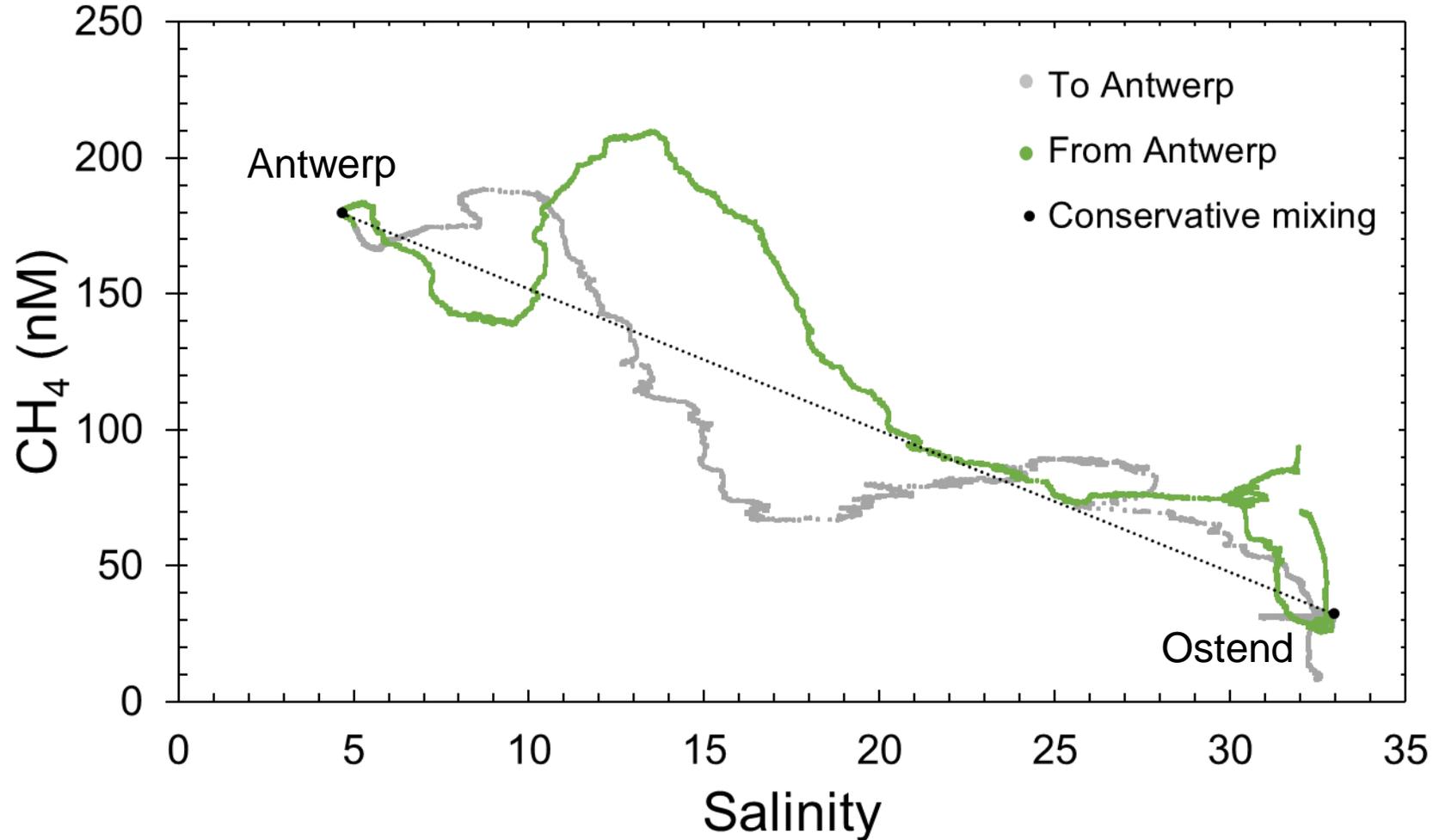
# CH<sub>4</sub> concentration measurements



Data uncertainty is comprised in the size of the dots

# Non-conservative behaviour of CH<sub>4</sub> concentrations

What are the sources of CH<sub>4</sub> in the estuary?



Potential sources:

- Riverine input
- Biogenic formation in the sediments
- Thermogenic degradation

# $\delta^{13}\text{C}\text{-CH}_4$ in surface waters

Enriched in heavy isotopes along the coast and in the upper estuary  
Depleted in most of the lower estuary



# $\delta D-CH_4$ in surface waters

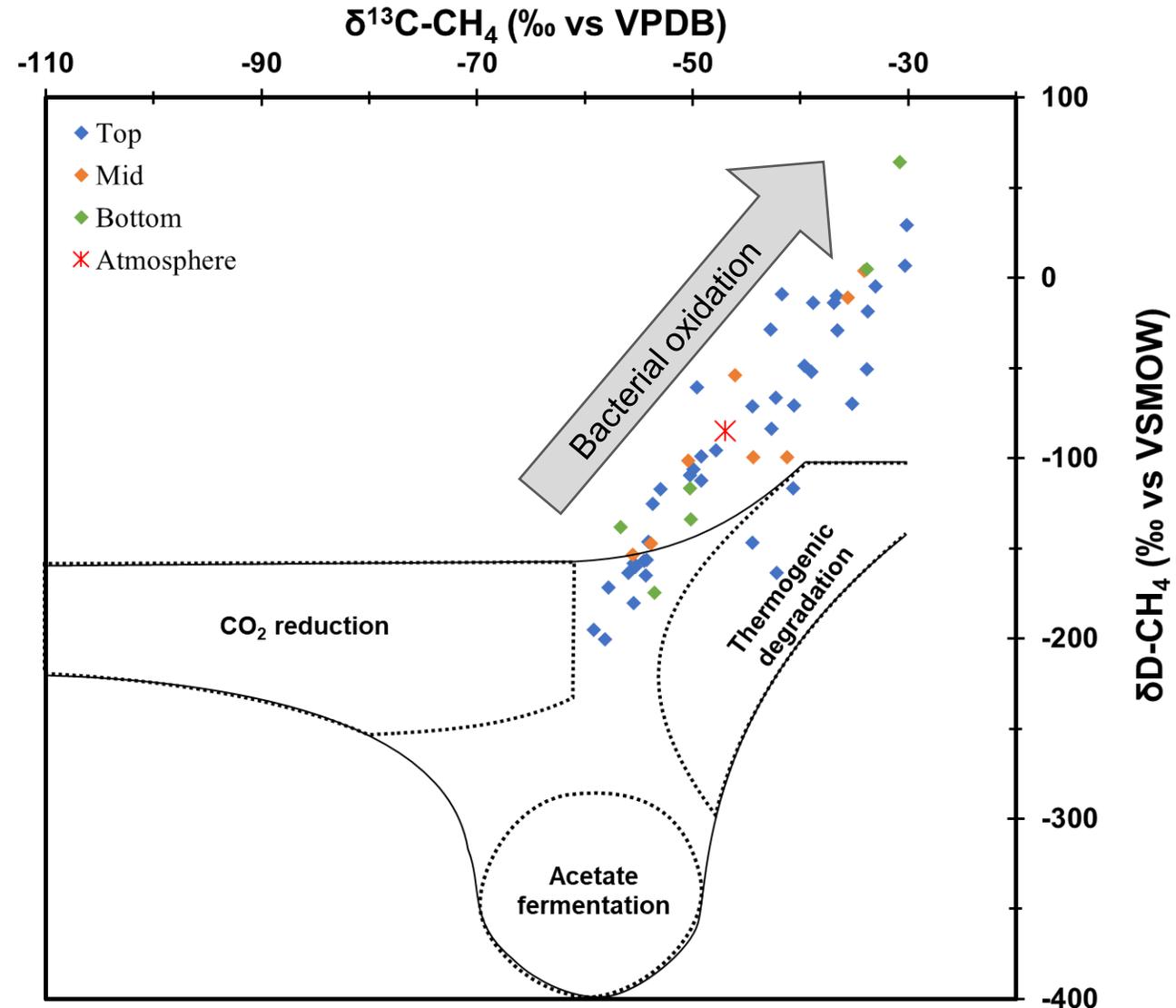
Same trend as  $\delta^{13}C$

Positive values in the port of Antwerp



# Dual isotope plot

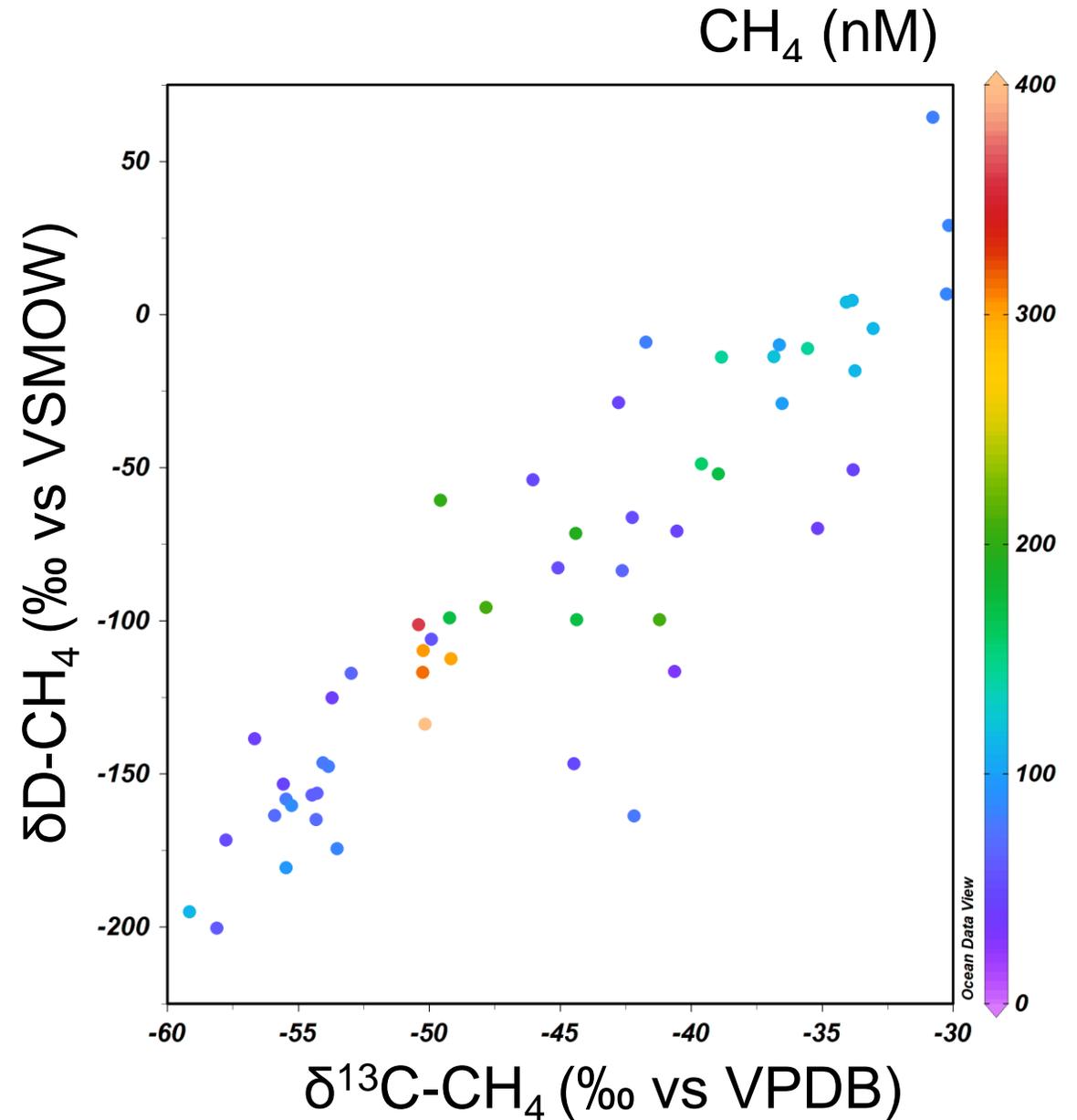
- Data fall in between the 3 domains
- Could be attributed to the mixing between a depleted source and a really enriched source
- Bacterial oxidation of a biogenic source is more likely



Typical isotopic signatures of the main  $\text{CH}_4$  formation pathways adapted from Whiticar, 1999

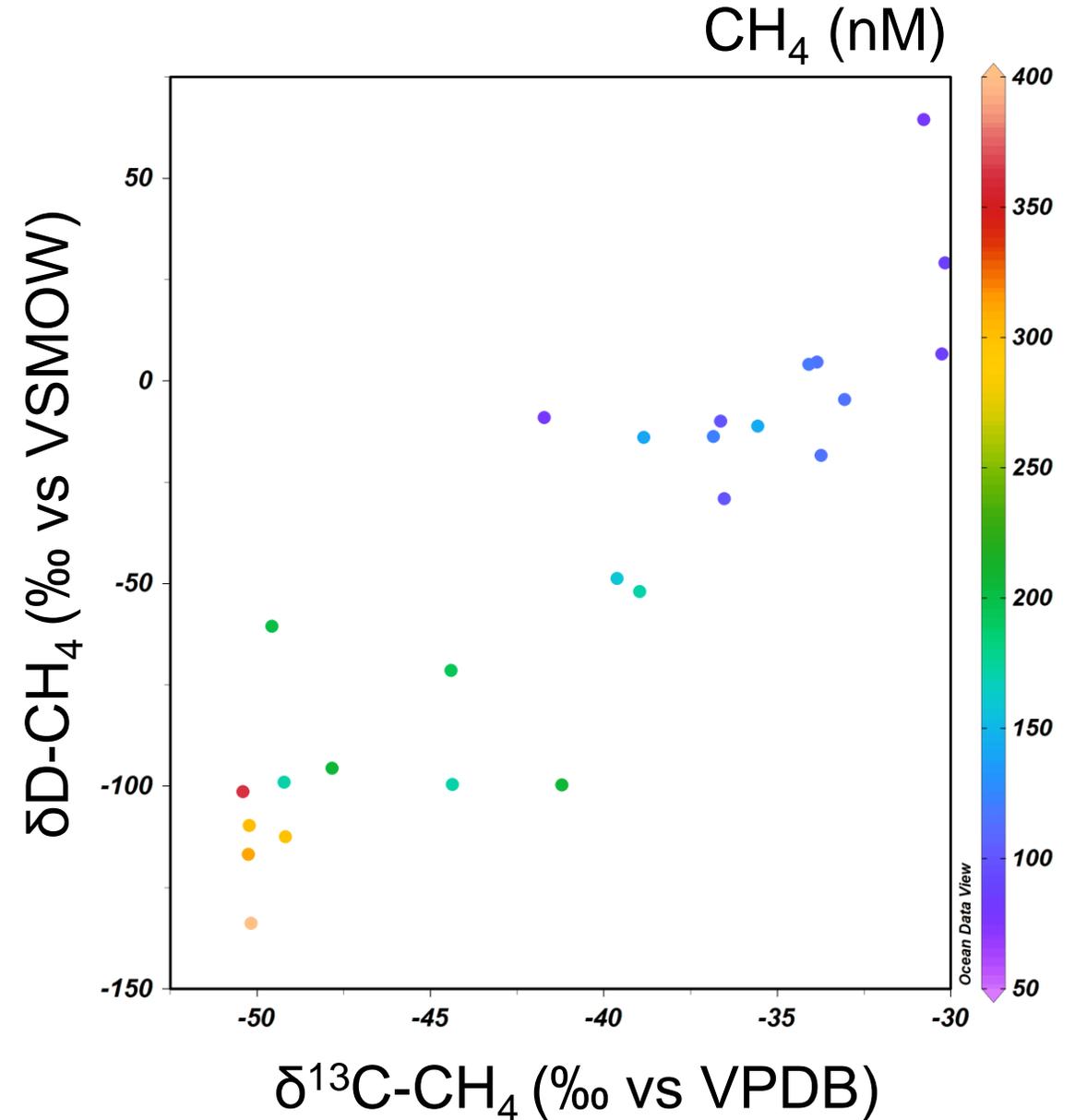
# Dual isotope plot

- Highest concentrations not necessarily associated with the most depleted signatures
- One hypothesis: organic matter underwent several oxidation cycles



# Dual isotope plot for the upper estuary

- Highest concentrations associated with the most depleted signatures
- Oxidation is probably the main factor driving this pattern



# Conclusion

- New method for continuous dissolved CH<sub>4</sub> concentration measurements, developed and tested successfully in the frame of ICOS
- The HISEM was deployed in the Ross Sea last spring; CH<sub>4</sub> concentrations were very stable, which is ideal for calibration
- The HISEM will be deployed in the Arctic in the summer 2018
- Some collaborators are willing to investigate the atmospheric CH<sub>4</sub> isotope composition in the estuary

# Aknowledgements

- Co-authors: Thanos Gkritzalis, André Cattijse, Thomas Hartley, Matthias Egger, Alberto V. Borges, Carina van der Veen, Jean-Louis Tison, Frank Dehairs, Jack J. Middelburg and Célia J. Sapart

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