Development of a Gas Equilibrium – Membrane-Inlet Mass Spectrometer (GE-MIMS) for continuous N_2, Ar and O_2 measurements to quantify nitrogen fixation in the Baltic Sea

DFG project – NArrFix
guided by Dr. Oliver Schmale and Dr. Bernd Schneider

PhD position supervised by Prof. Gregor Rehder

Thesis committee: Dr. Anke Kremp, Dr. Lars Umlauf

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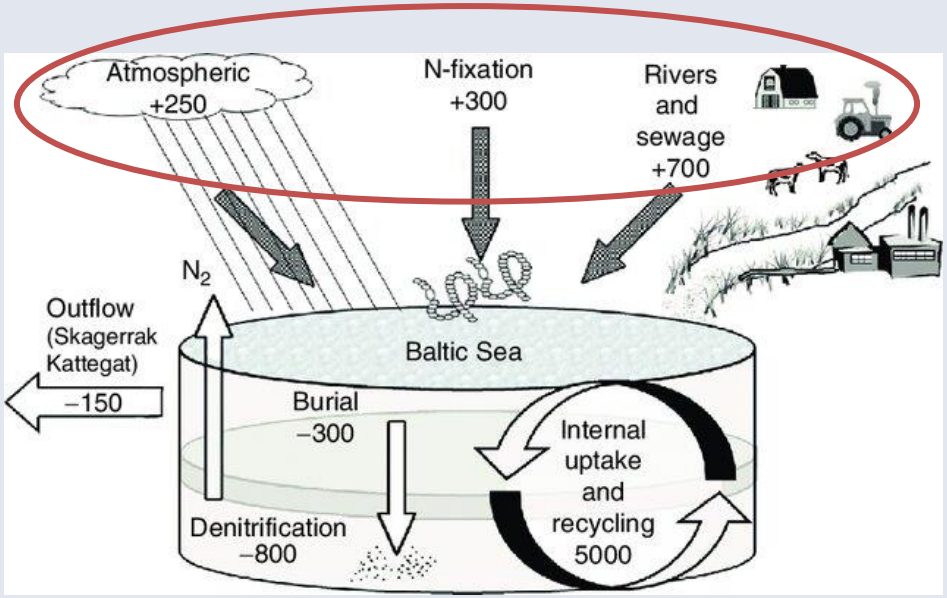
1. Motivation

nitrogen fixation

$|N \equiv N|$ ➢ bond dissociation energy ≈ 950 kJ/mol

$$\mathbf{N_2} + 8\ H^+ + 8\ e^- + 16\ MgATP \rightarrow \mathbf{2\ NH_3} + H_2 + 16\ MgADP + 16\ P_i$$

Baltic Sea: N budget [kt/yr]



Granéli (2008)

- biogeochemistry + ecological state of the Baltic sea are strong influenced by eutrophication

- N_2 fixation by cyanobacteria facilitates biomass production in the absence of dissolved inorganic nitrogen (DIN)

1. Motivation

methods for the quantification of N_2 fixation

- estimates for the Baltic Sea: 170 – 792 kt-N/yr

↓

interannual variability and serious methodological uncertainties

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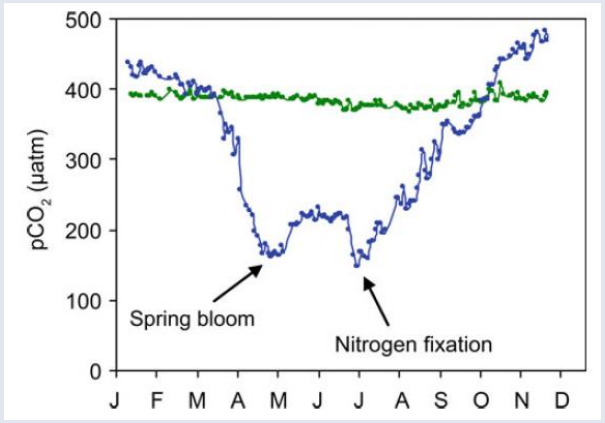
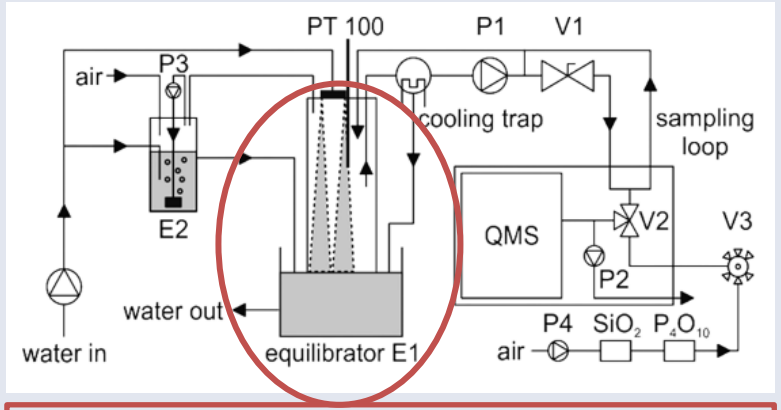
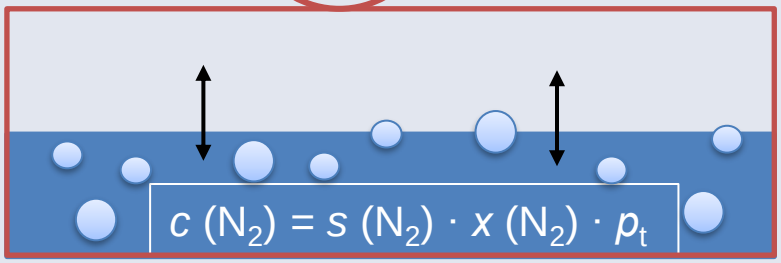
indirect method by continuous pCO_2 surface measurements (Schneider et al. 2017)

→ direct method by continuous measurements of N_2 concentrations in the surface water (Schmale et al. 2019)



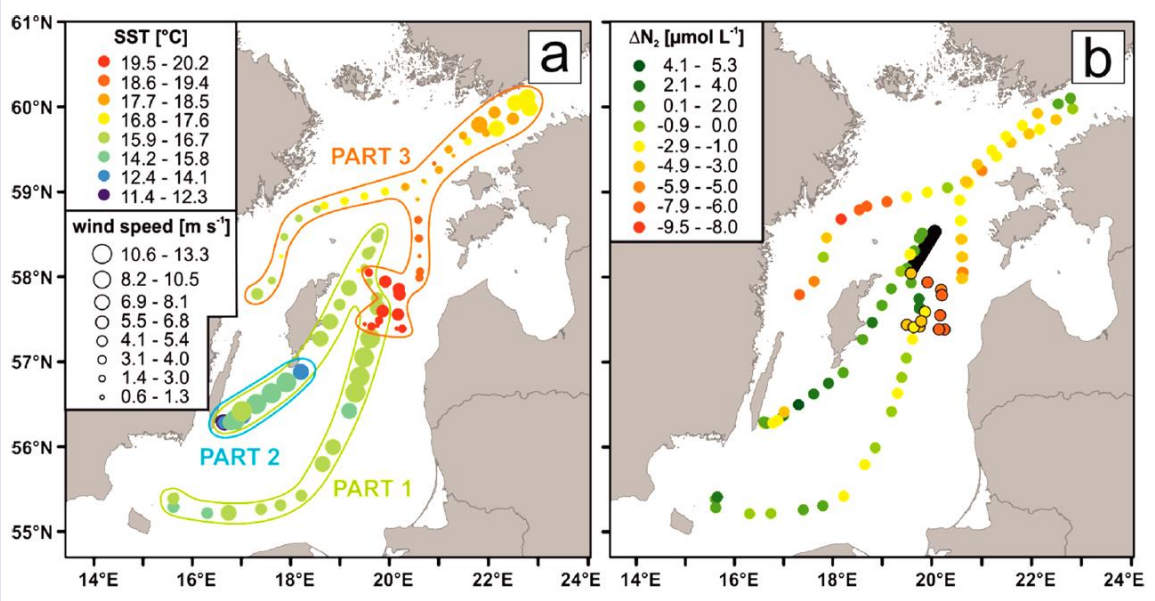


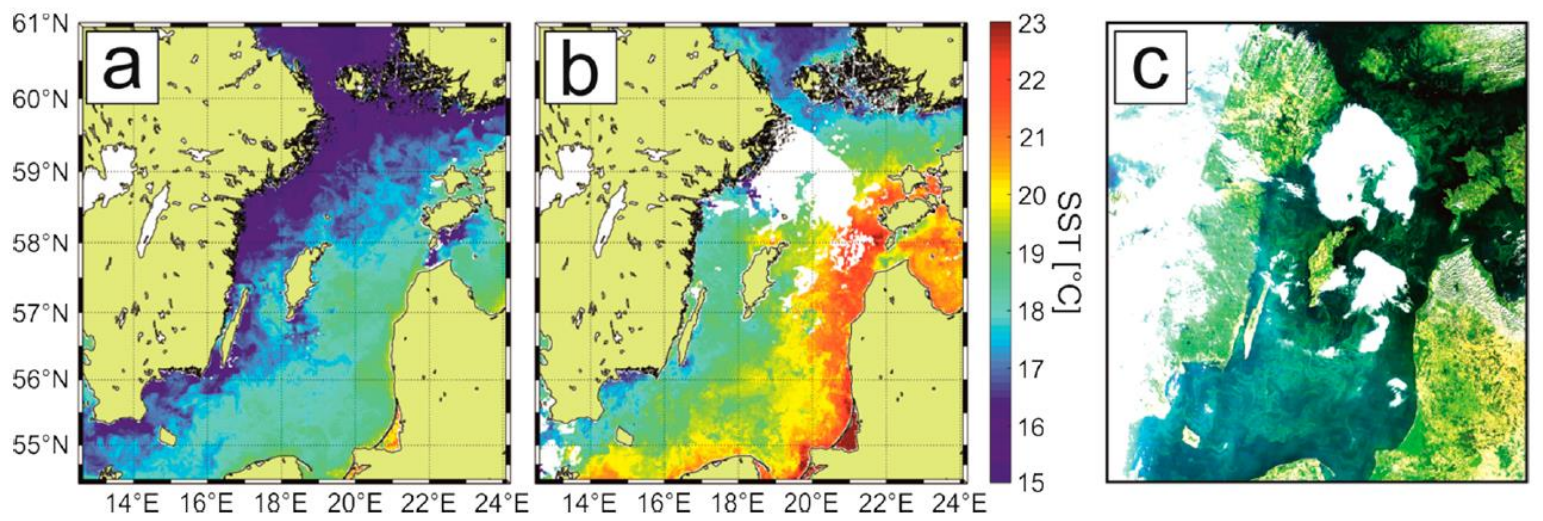


1. Motivation

Environmental Science & Technology

Schmale, Schneider et al. (2019).
Potential of nitrogen/argon analysis in surface waters in the examination of areal nitrogen deficits caused by nitrogen fixation





2. Experimental approach

methods for the quantification of N_2 fixation

- estimates for the Baltic Sea: 170 – 792 kt-N/yr

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interannual variability and serious methodological uncertainties

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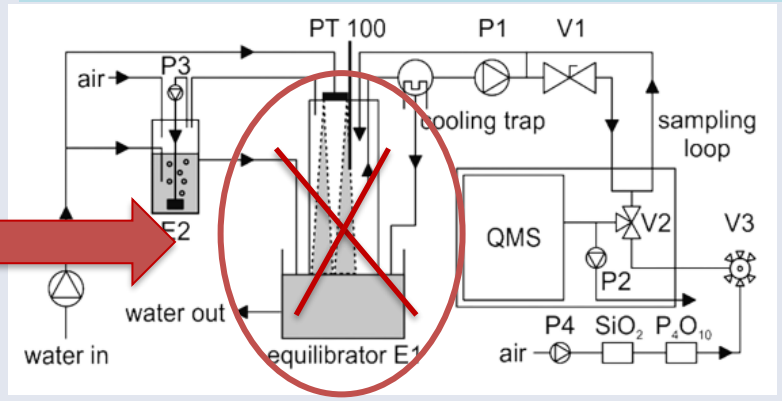
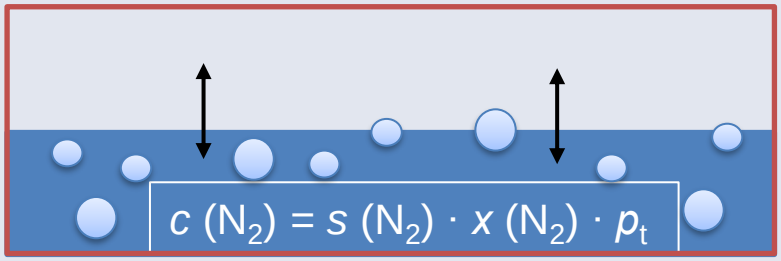
direct method by continuous measurements of N_2 concentrations in the surface water (Schmale et al. 2019)





2. Experimental approach

Integrating GE-MIMS into a VOS structure

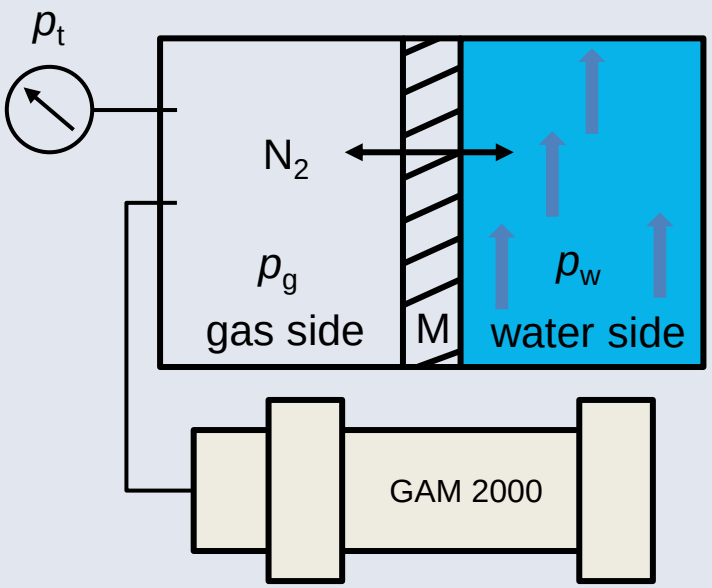
voluntary observing ship

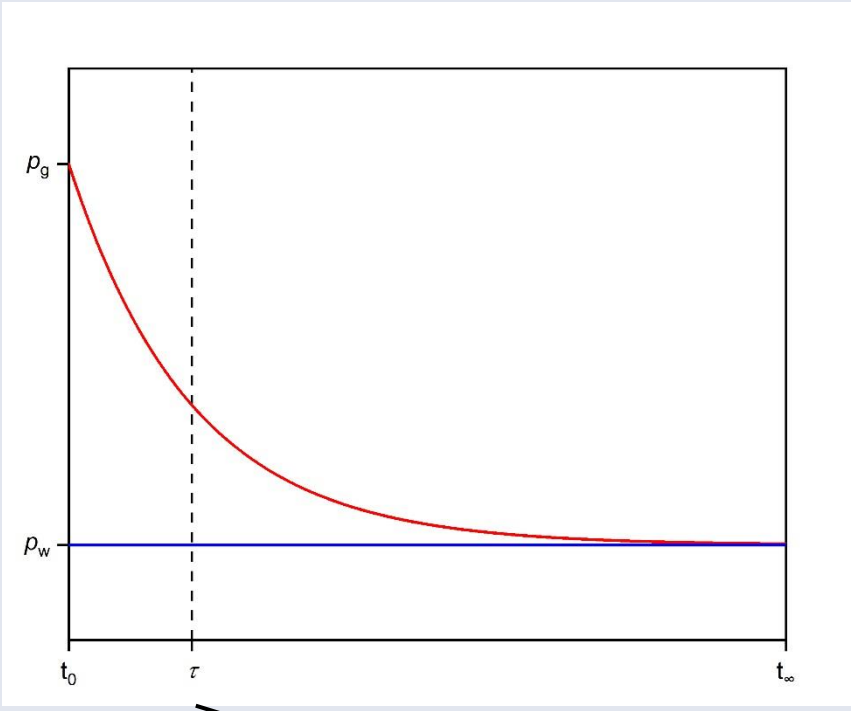
VOS „Finnmaid“

2. Experimental approach

membrane-equilibrator

- mass spectrometer determines **mole fraction *x*** of N_2, O_2 and Ar





- if **total pressure p_t** at gas side is known:

$$p\,(N_2) = x\,(N_2) \cdot (p_t - p_{H2O} - p_{CO2})$$

$$\downarrow$$

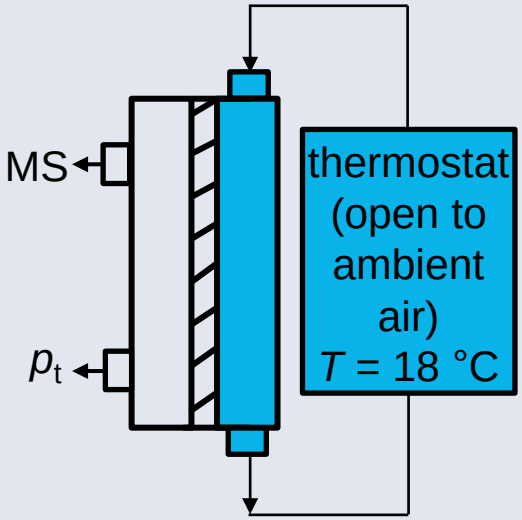
$$c\,(N_2) = p\,(N_2) \cdot s\,(N_2)$$

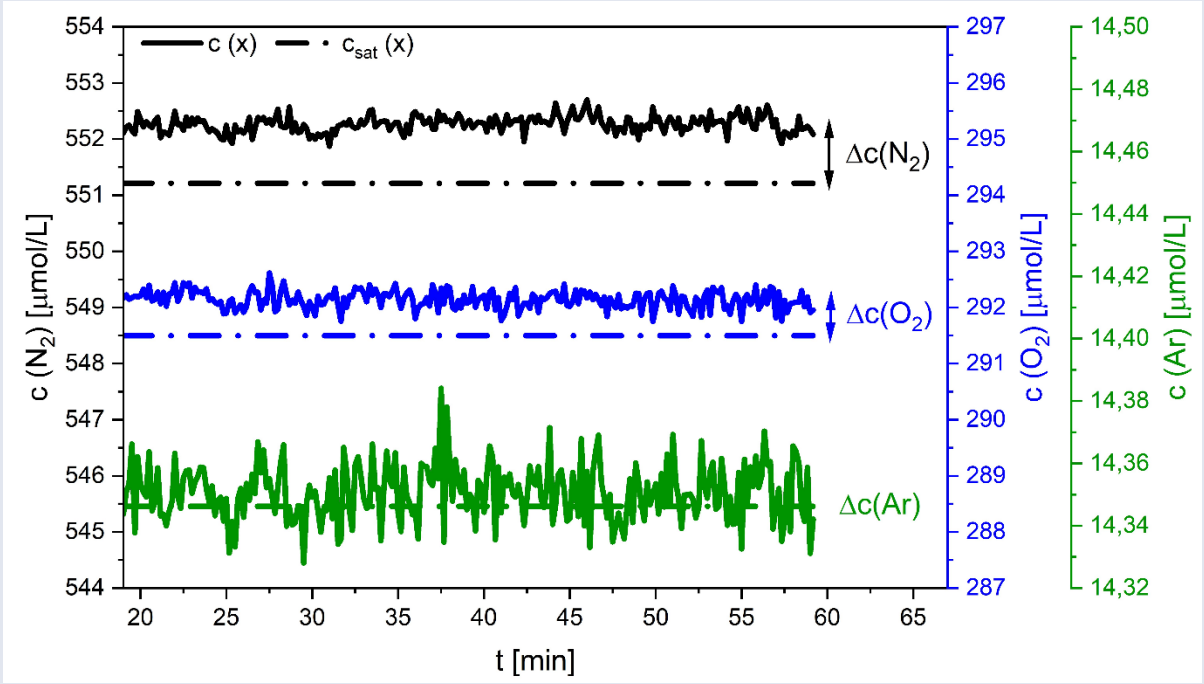
τ (N_2)

4,74 min ± 0,15 min

2. Experimental approach

completeness of the equilibration





accuracy

Δc (N_2) = 1,05 µmol/L **(~ 0,2 %)**

Δc (O_2) = 0,64 µmol/L **(~ 0,2 %)**

Δc (Ar) = 0,005 µmol/L **(~ 0,03 %)**

precision (limit of detection)

N_2 = 0,29 µmol/L

O_2 = 0,32 µmol/L

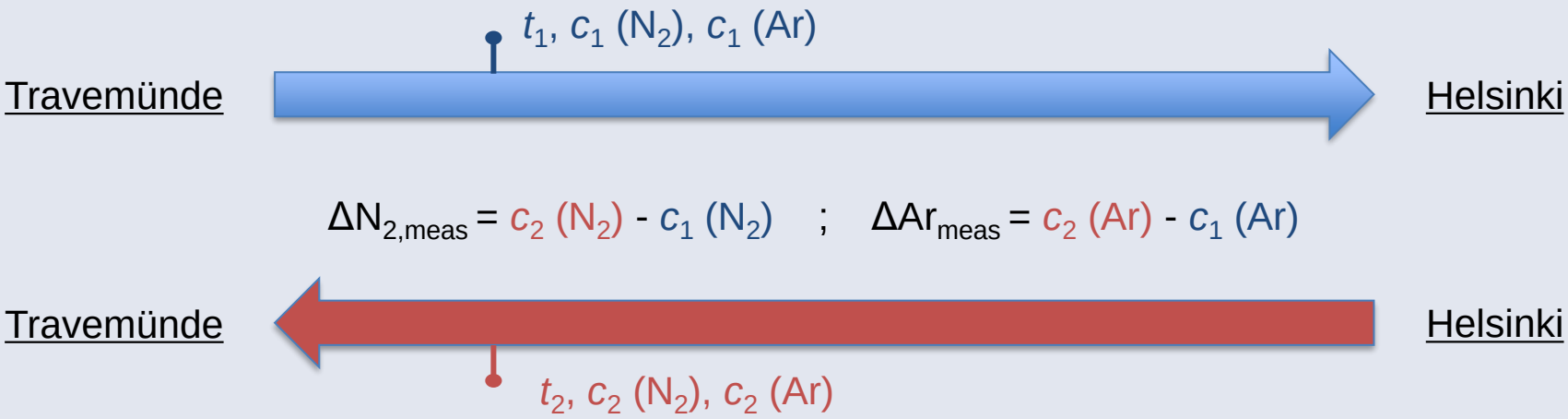
Ar = 0,02 µmol/L

2. Experimental approach

determination of the N_2 fixation

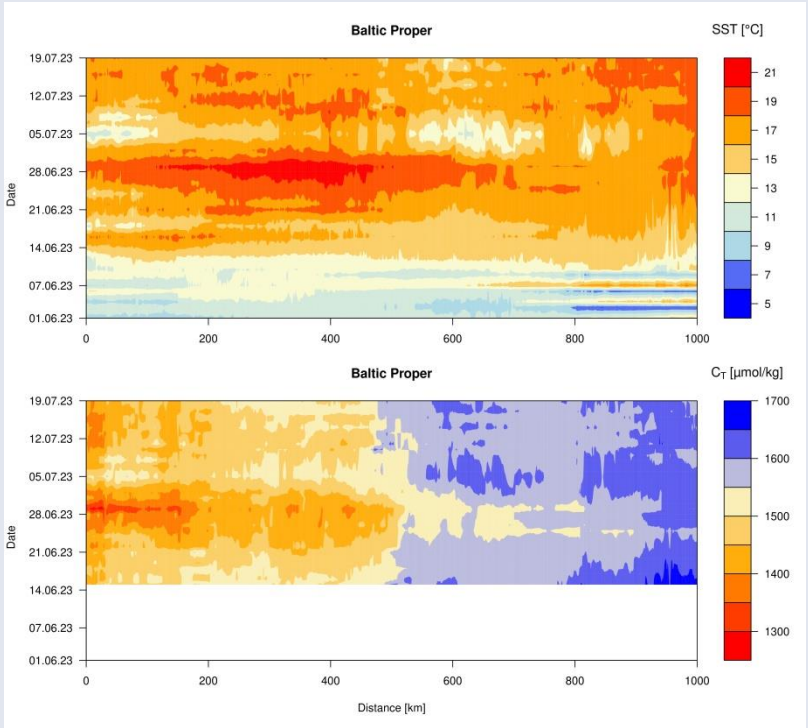
$$\delta N_{2,fix} = \Delta N_{2,meas} - \delta N_{2,gas}$$

- $\delta N_{2,gas}$ can be calculated by simultaneously measuring Ar
- ΔAr_{meas} is only influenced by gas exchange
- Temporal resolution: up to 3 days, spatial resolution: ~ 12 km

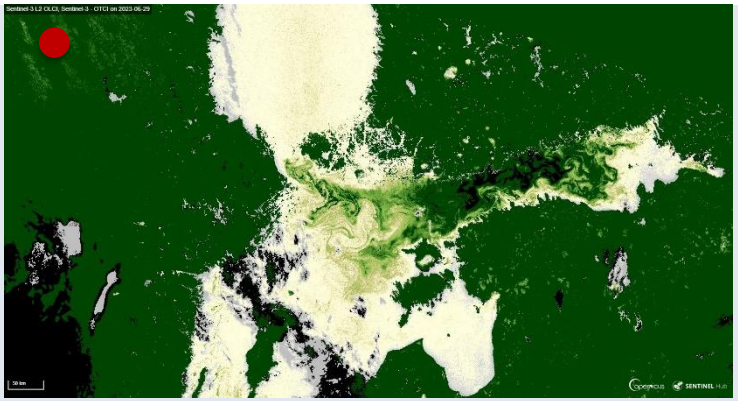


3. Field (VOS) data

cyanobacterial bloom 2023



- second production phase
- wind induced mixing
- high productivity period fueled by N_2 fixation
- sea surface temperature increases

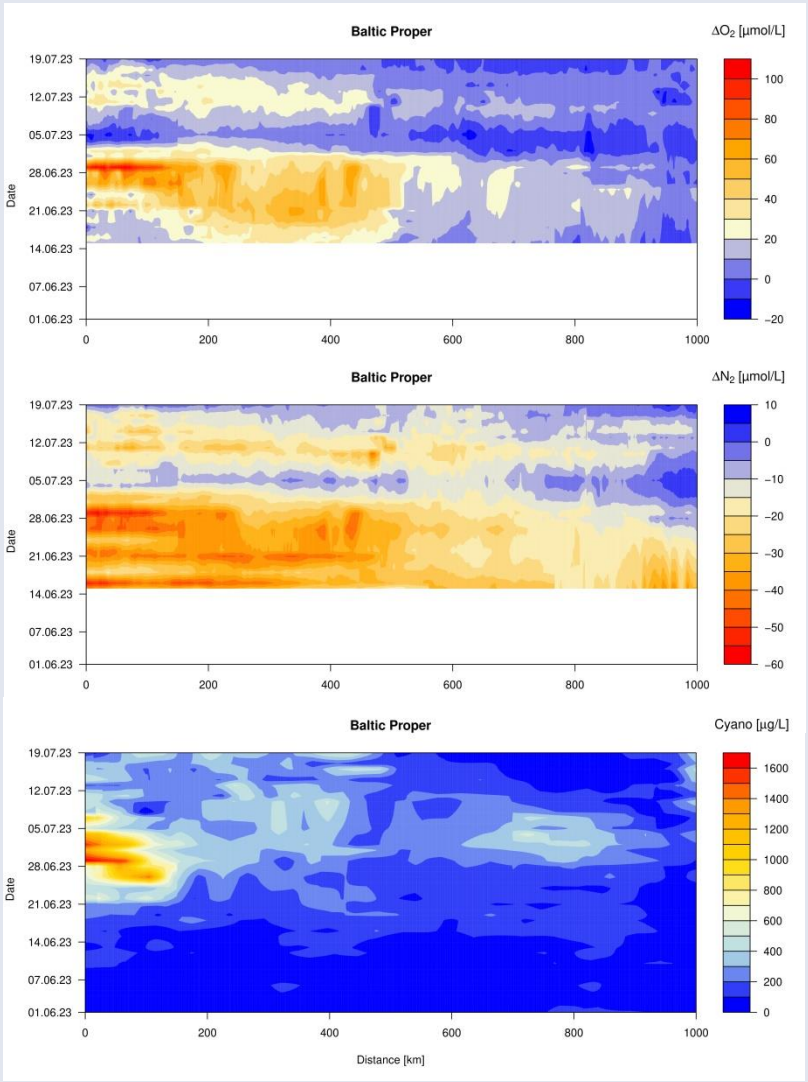


3. Field (VOS) data

cyanobacterial bloom 2023

$$\Delta X = \left[\left(\frac{X}{Ar}\right) - \left(\frac{X}{Ar}\right)_{sat}\right] \cdot Ar$$

X = N_2, O_2



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Acknowledgements

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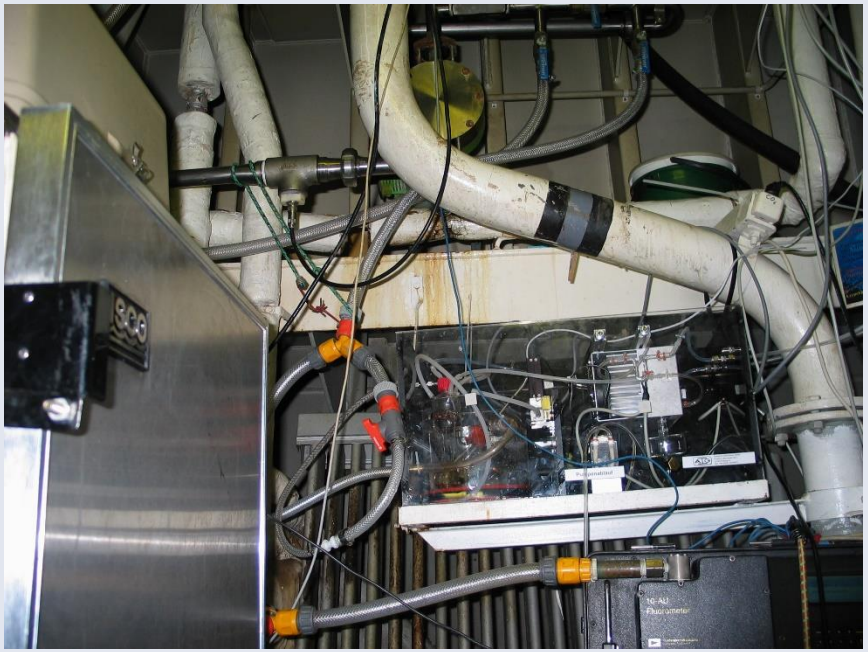
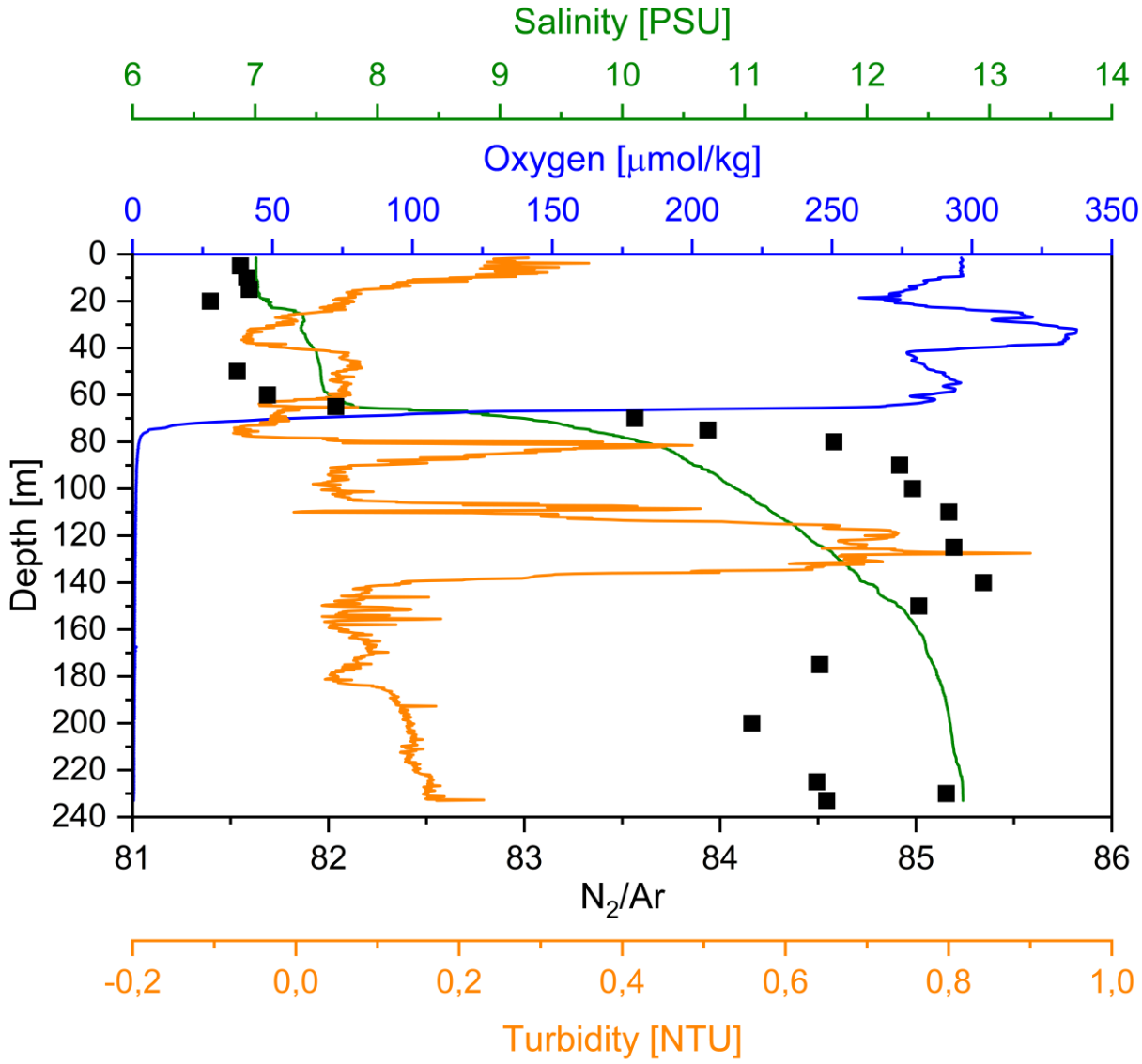
$$\Delta N_2 = \left(\left(\frac{N_2}{Ar} \right) - \left(\frac{N_2}{Ar} \right)_{sat} \right) Ar$$




Salinity [PSU]
6 7 8 9 10 11 12 13 14
Oxygen [µmol/kg]
0 50 100 150 200 250 300 350
Depth [m]
0 20 40 60 80 100 120 140 160 180 200 220 240
81 82 83 84 85 86
N2/Ar
-0,2 0,0 0,2 0,4 0,6 0,8 1,0
Turbidity [NTU]