# Biogeochemical process studies using VOS-based trace gas measurements in the Baltic Sea

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  - History
  - Basics
- **Results and Process Studies**
  - Overview
  - Case studies
- **Related activities**
  - PINBAL
  - The POSEC study
- **Outlook**
  - Setup for the next decade

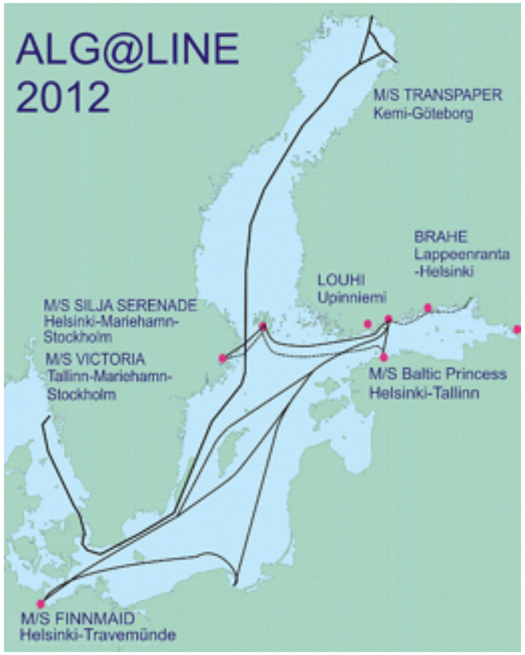

The "BALTIC VOS"
Voluntary observing ship M/S Finnmaid, run by Finnlines, equipped with systems for continuous trace gas measurements

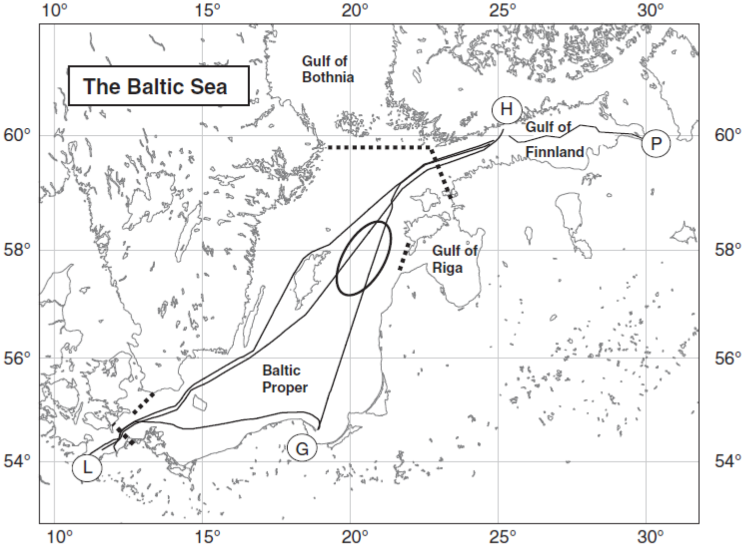
# History (IOW's view)

- **Amendment to the Alg@line Project**

- **Trace Gas Analytical Setup**
  - Originally installed on M/S Finnpartner in 2003
  - Completely renewed on M/S Finnmaid in 2007/2008
- **Trace Gas Surface Data**
  - $pCO_2$ since 2003
  - $O_2$ since 2003 (with interruptions)
  - $pCH_4$ since late 2009

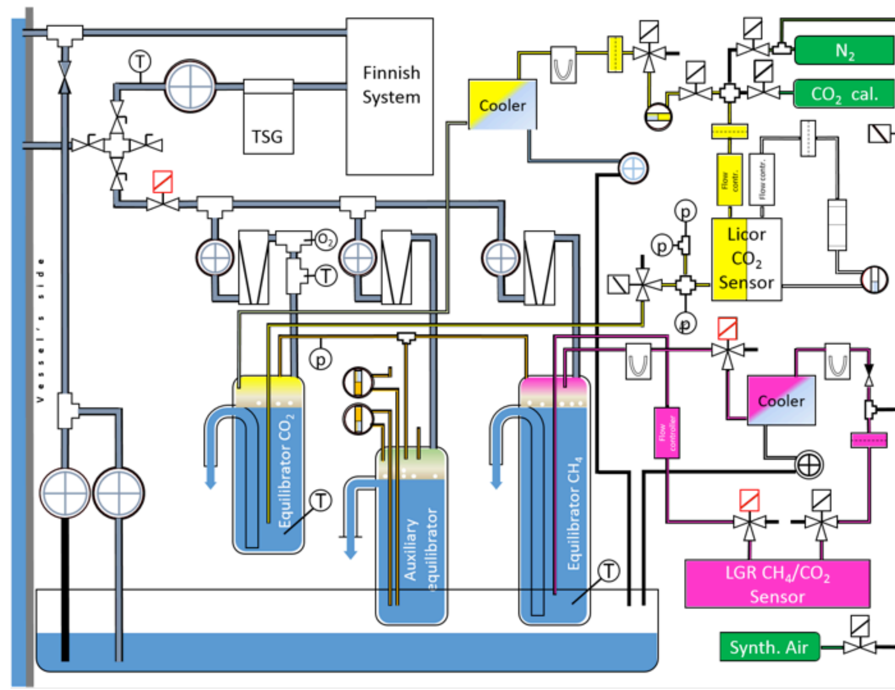
- **Since 2012 partly supported as German contribution to ICOS**



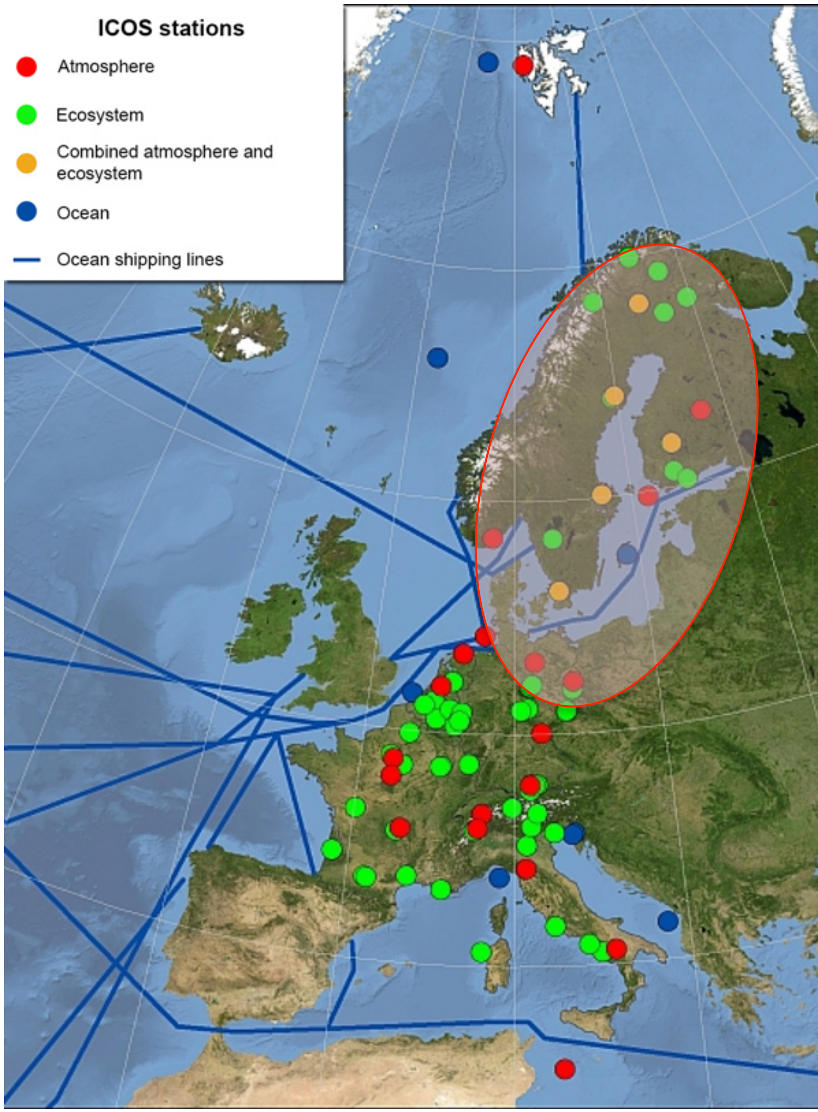
# IOW Ferrybox System

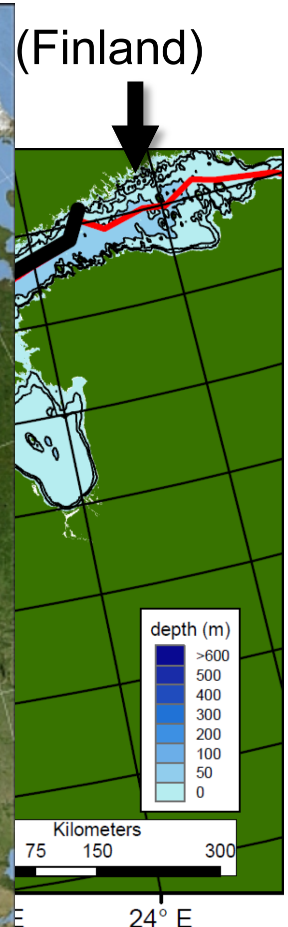

- Greenhouse gas measurements: **$pCO_2$** and **$CH_4$**
- Installed alongside preexisting Finnish Alg@line system (Real time algal monitoring in the Baltic Sea)




Bundesministerium für Bildung und Forschung
ICOS Integrated Carbon Observation System

# Spatial and temporal data coverage




- Good spatial coverage of the central Baltic Sea
- High repeat frequency: twice every three days
- 6 years of data ($CH_4$)
  - 800 (valid) transects,
  - 728 along main routes

# Rationale of Trace Gas measurements in the Baltic

- Carbon dioxide system

  As a key to quantify biogeochemical cycles

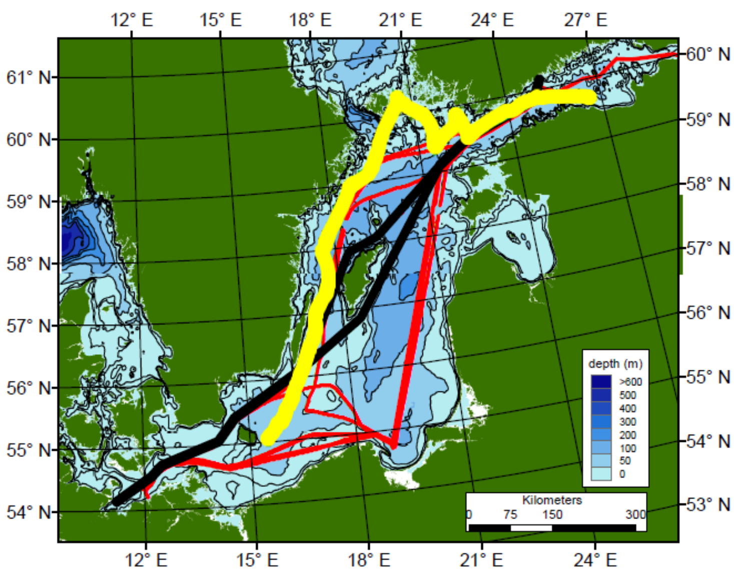
  - Affected directly by "ocean acidification"
  - Affected indirectly by eutrophication and climate change, including changes in run-off etc.
  - Direct indicator for carbon uptake and net primary production
  - Links eutrophication and hypoxia

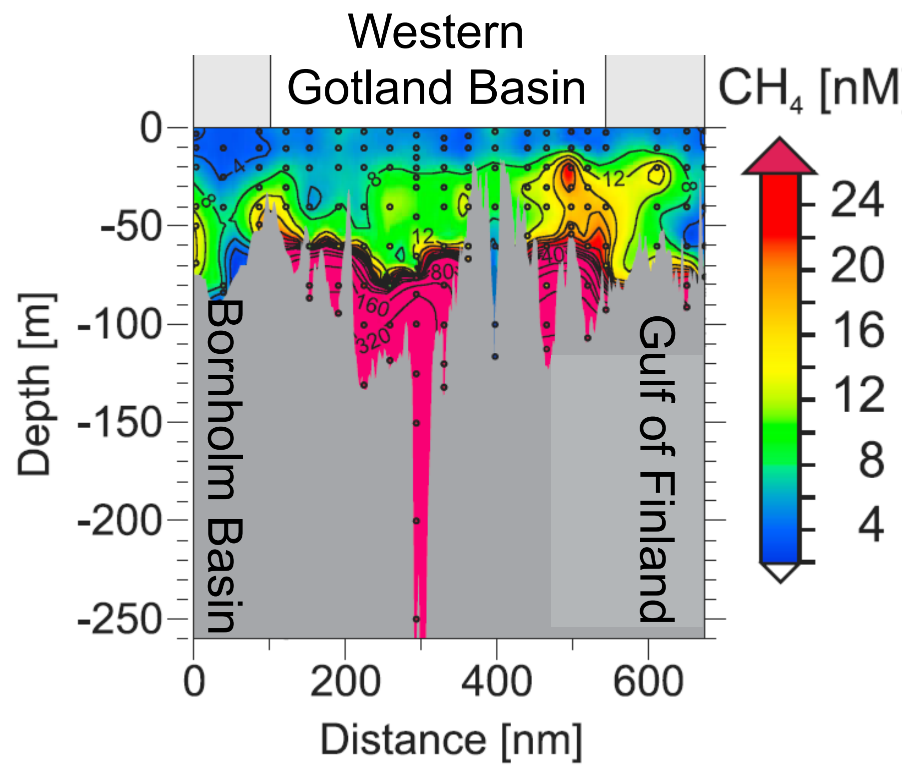
- Methane cycle
  - Ubiquitous in Baltic Sea sediments
  - Enhanced concentration in anoxic water bodies
  - Affected by eutrophication and climate warming
  - Main marine sources in shelf and marginal seas
  - Baltic as an ideal testfield because of its unique structure

- Excellent boundary conditions (models and long-term data series)

# Methane in the Baltic Sea





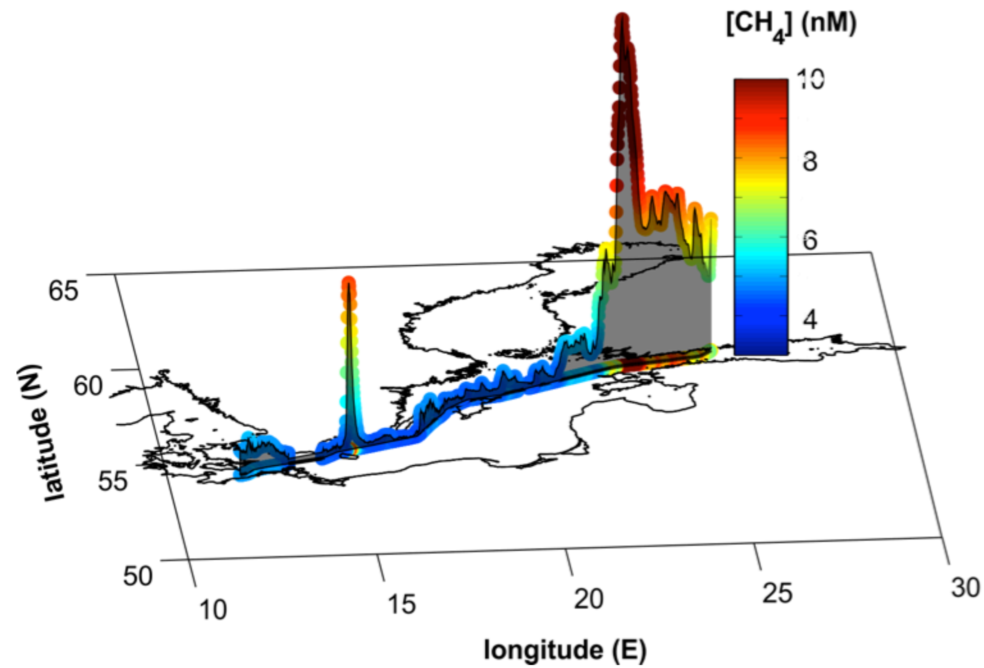




Modified from Schmale et al., (2010) Distribution of methane in the water column of the Baltic Sea.

# DATA OVERVIEW

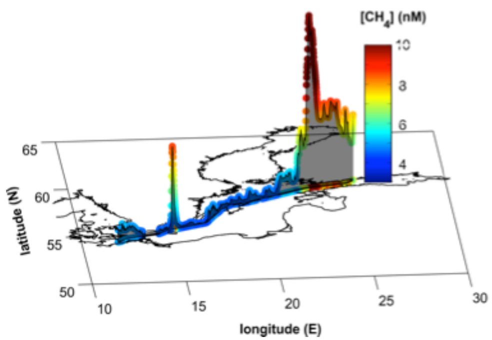
# One transect:

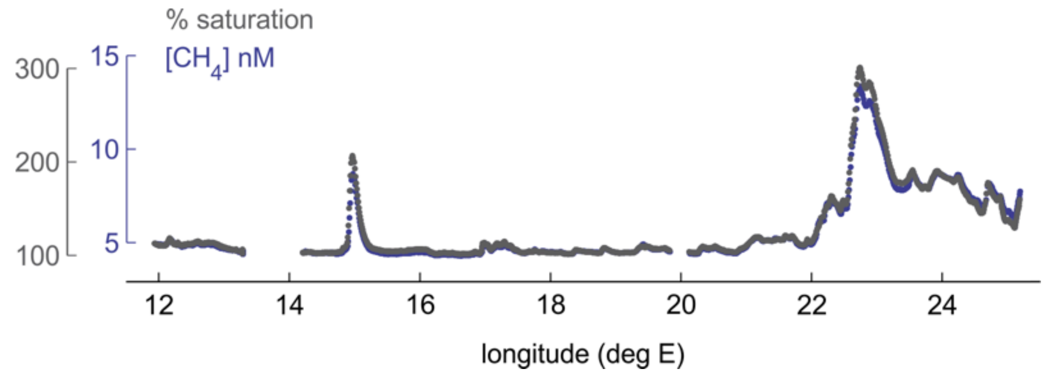
February 1st to 2nd 2014



# One transect:

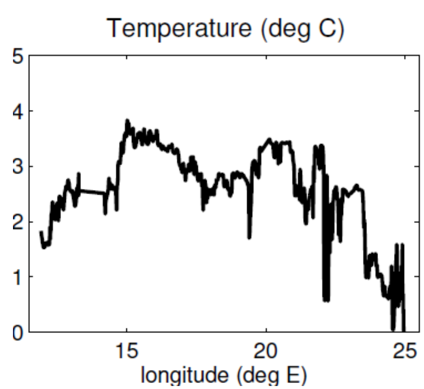
February 1st to 2nd 2014

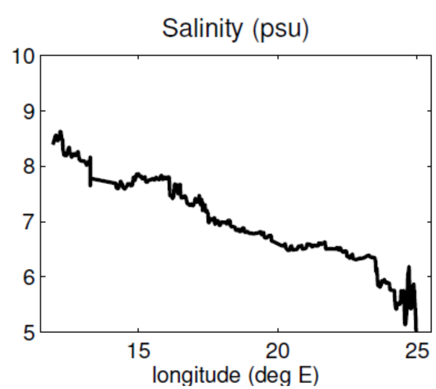



$$\%\ \text{saturation} = \frac{C_{\text{obs}} - \mathbf{C_{equilibrium}}}{C_{\text{equilibrium}}} \cdot 100\ \%$$

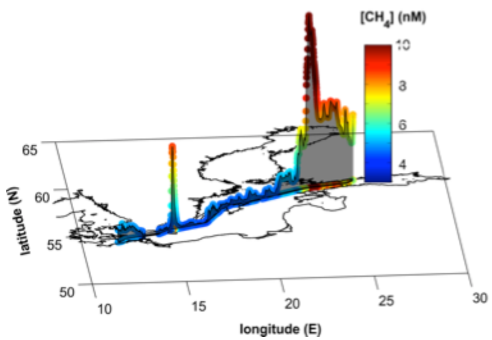
$$C_{\text{equilibrium}} = \mathbf{C_{atmosphic}} \cdot \text{Solubility} \longleftarrow \propto \mathbf{T}, \mathbf{S}$$

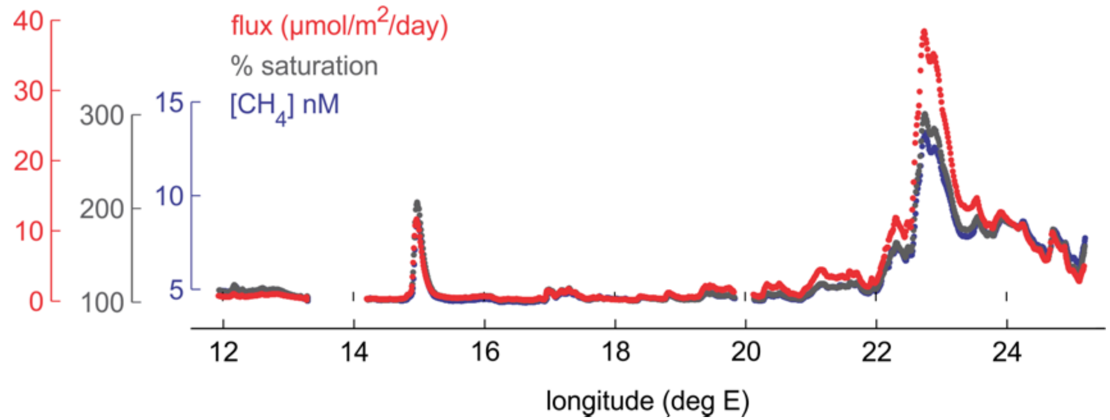


# One transect:

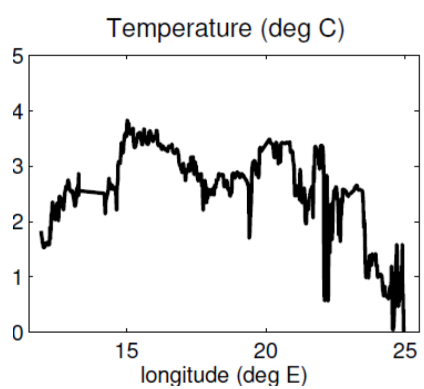
February 1st to 2nd 2014

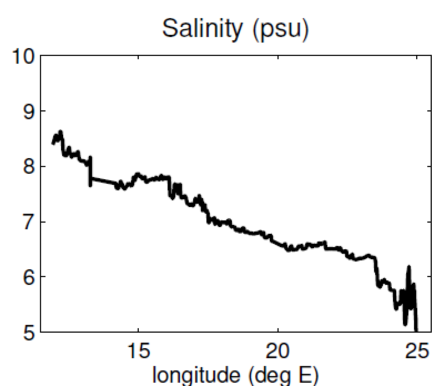


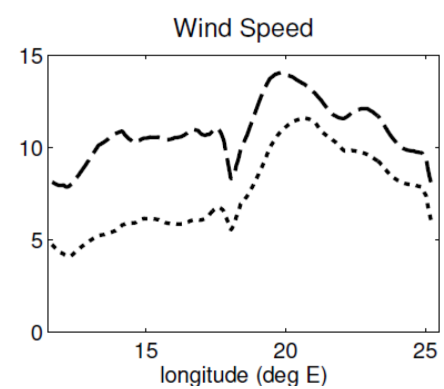




$$\text{sea} \rightarrow \text{air flux} = \left(C_{\text{obs}} - C_{\text{equilibrium}}\right) \cdot \textbf{exchange coefficient}$$

$$k = \left(\frac{\text{Schmidt number}}{660}\right)^{-0.5} \cdot (\text{wind speed})^2$$



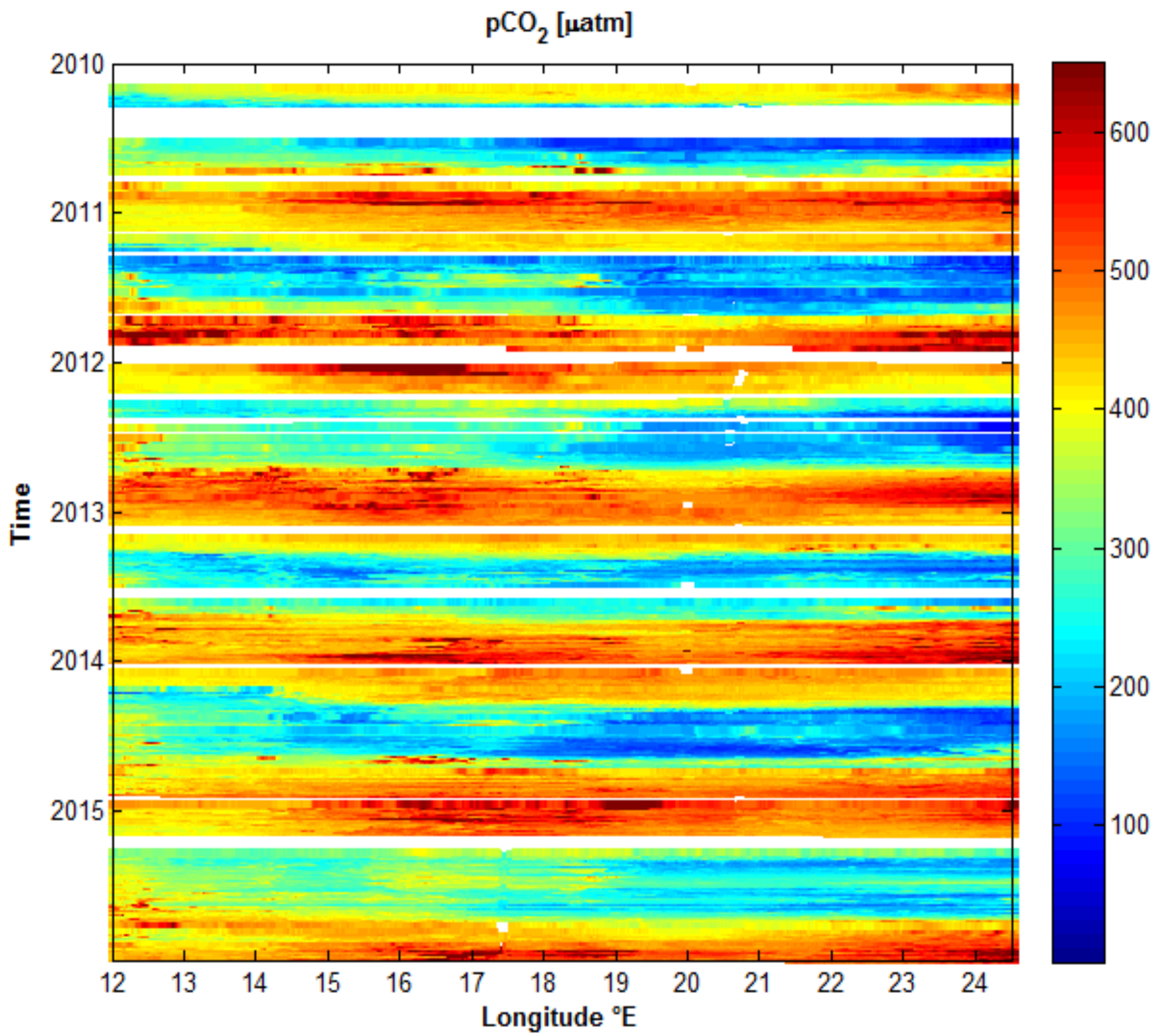



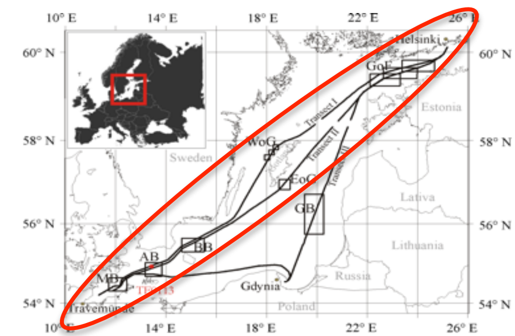

Meteorological data curtesy of Ulf Gräwe, IOW

Wanninkhof et al., (2009) Advances in Quantifying Air-Sea Gas Exchange and Environmental Forcing.

# Overview ($pCO_2$)




Surface $pCO_2$, all data 2010 to 2015 along main transect

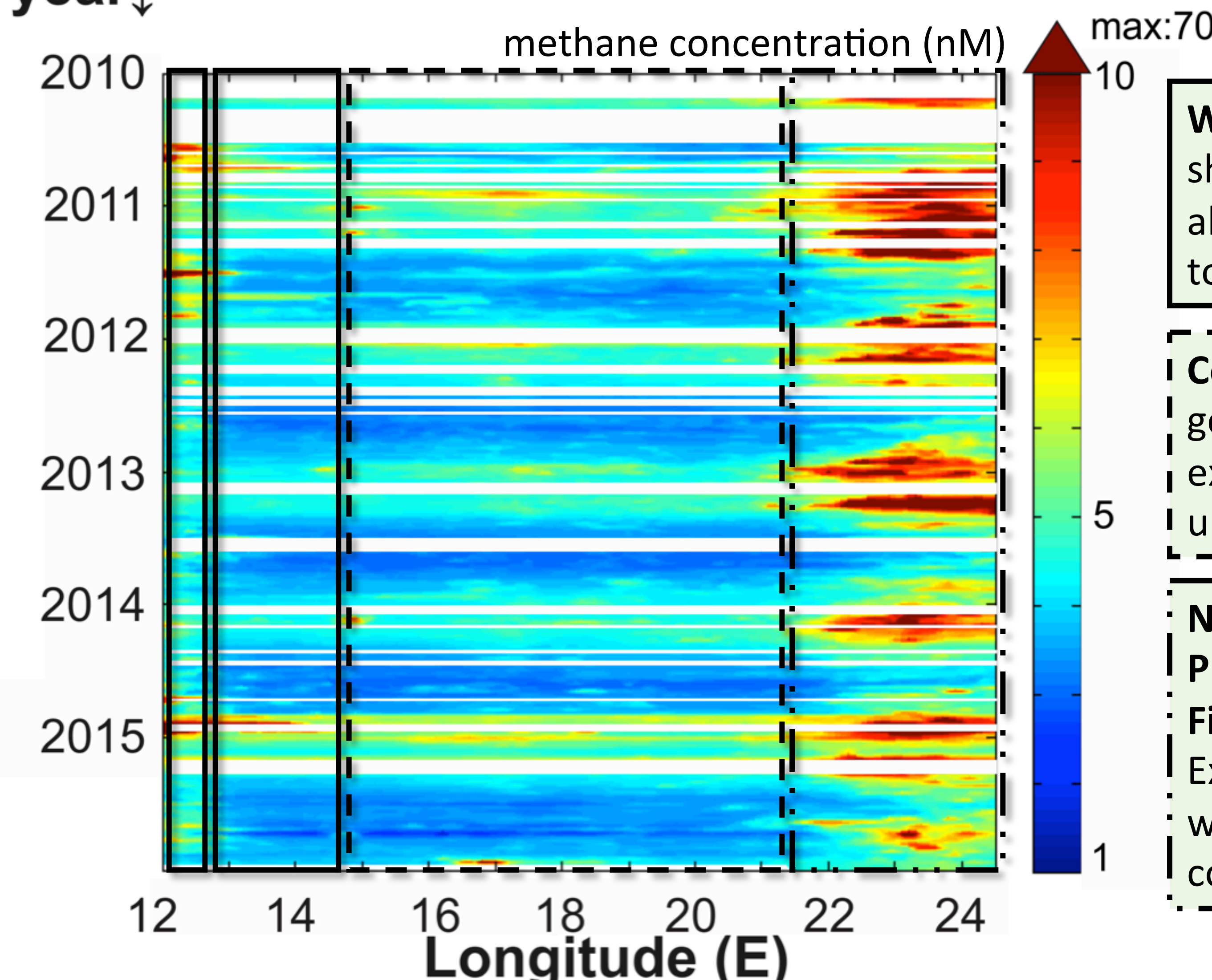



**Seasonality:**
Seasonal switch of atmospheric source-sink behavior, near-equilibrium phases are rare

**Lateral gradient:**
Highest and most robust amplitude in the (eutrophied) Gulf of Finland

**Biogeochemcal interpretation**
Allows quantification of productivity during different production phases

# Overview ($CH_4$)




Surface $CH_4$, all data 2010 to 2015 along main transect

**Western Basins:** shallow water allows mixing down to sediment surface

**Central Basins:** generally low $CH_4$ except for upwelling events

**Northern Baltic Proper and Gulf of Finland:** Extremely high wintertime surface concentrations

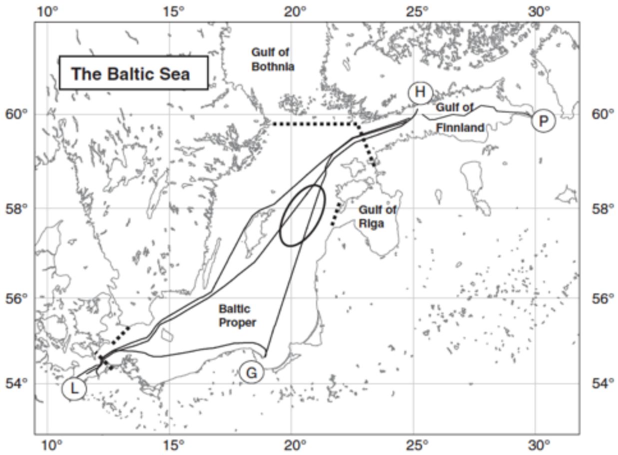
Gülzow et al. (2013) One year of continuous measurements constraining methane emissions from the Baltic Sea to the atmosphere.

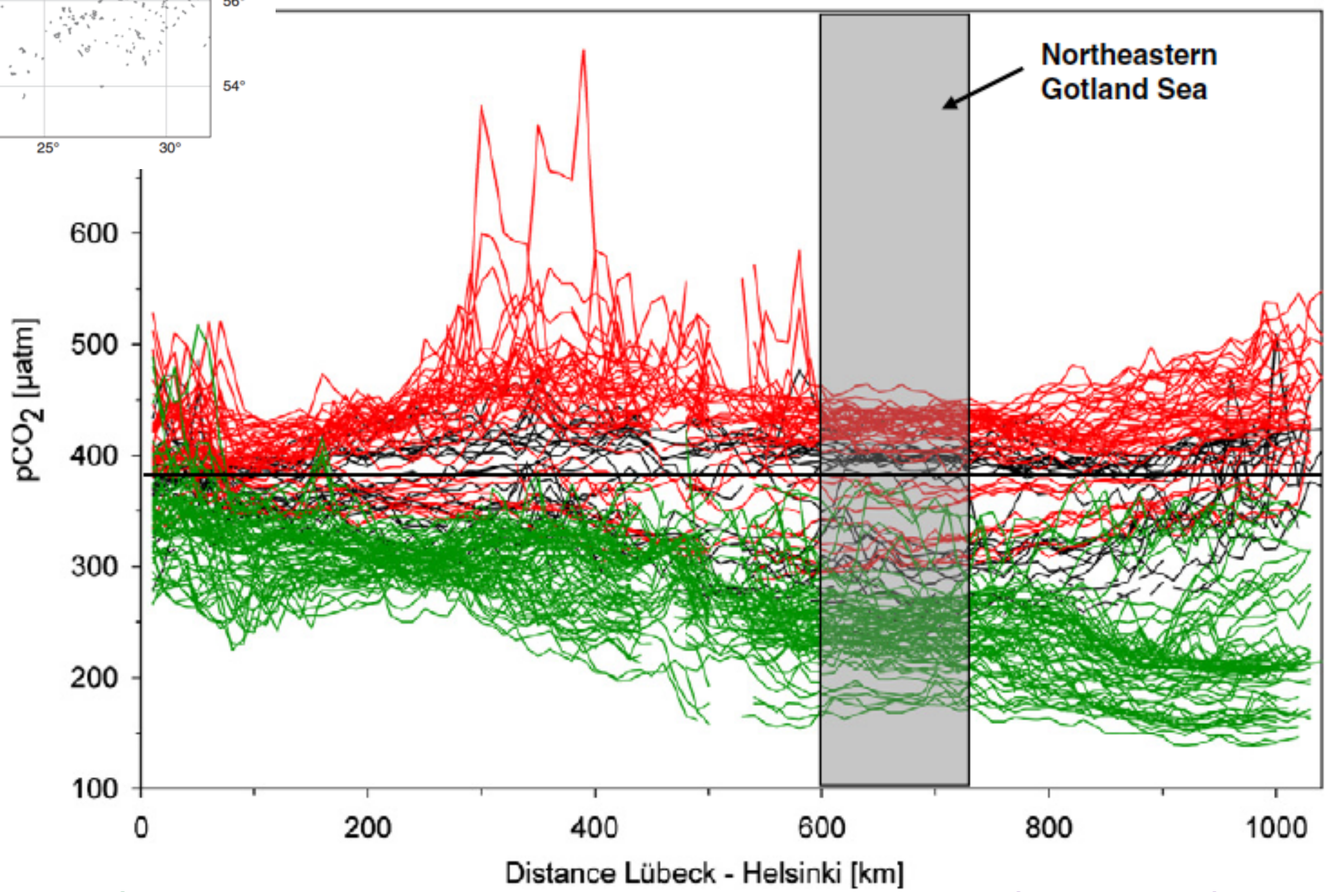
# Example 1:

# Constraints on the Annual Cycle of Net Primary Production

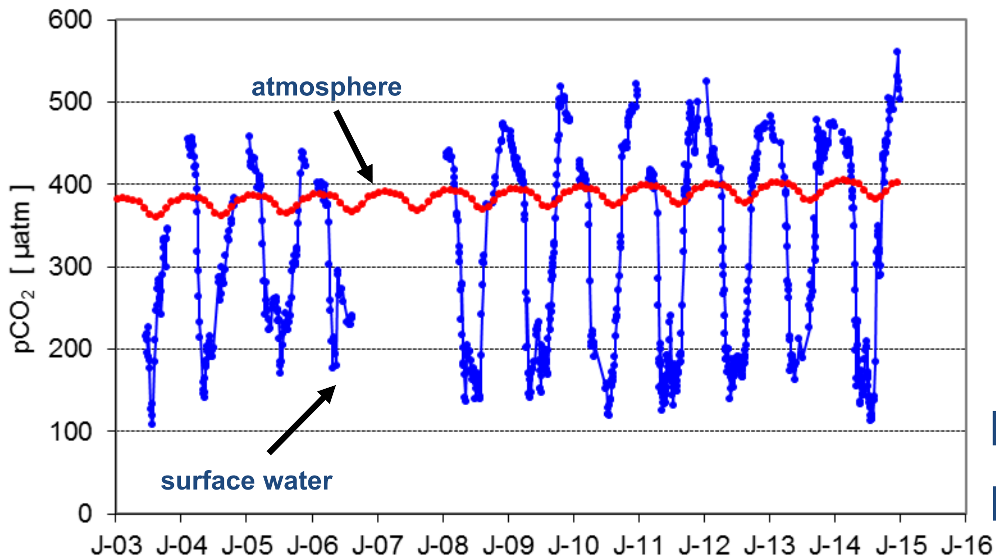
# Process Studies: Controls on $CO_2$ ASE fluxes

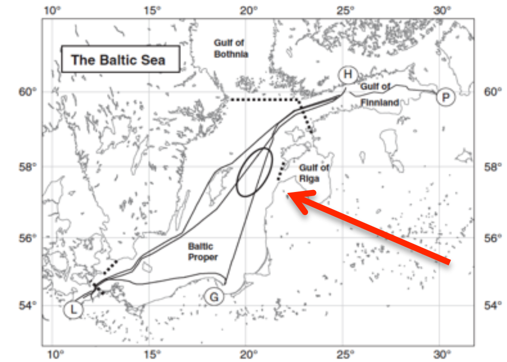
*Year 2005, along transect*
*Schneider et al.,J.Mar.Sys, 2014*



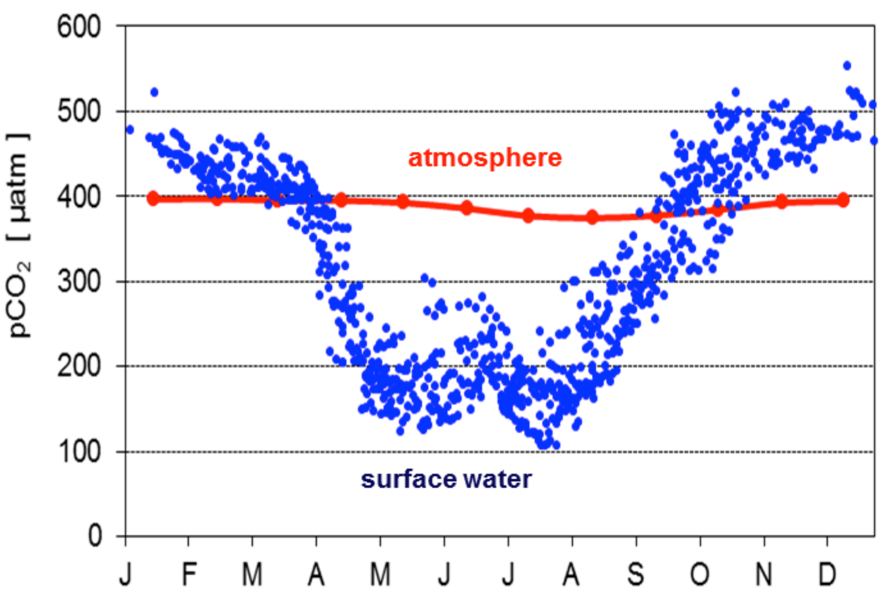




**Green: March – August, Red: November – February, Black: September - October**




**$pCO_2$ time series in the Eastern Gotland Sea**




**$pCO_2$ seasonality in the Eastern Gotland Sea**



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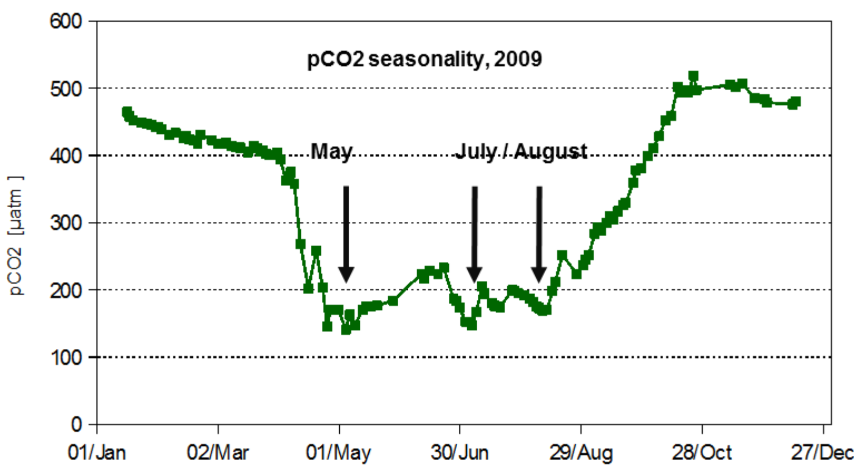
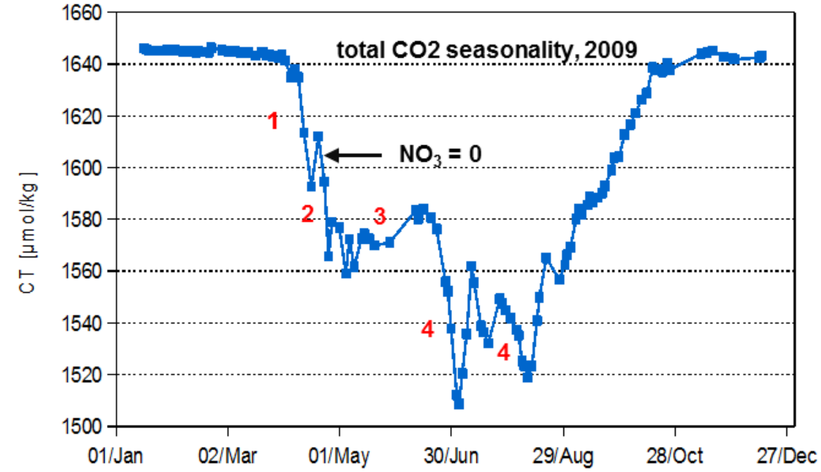
$$\Delta pCO_2 \xrightarrow[\text{T and S}]{\text{alkalinity}} \Delta C_T$$

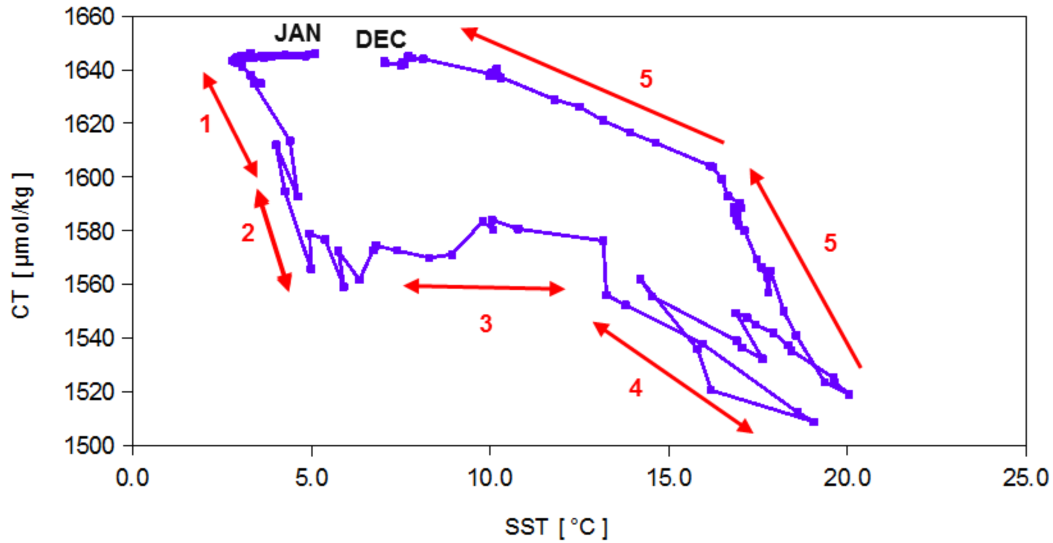
$C_T$ - total $CO_2$: $CO_2 + H_2CO_3 + HCO_3^- + CO_3^{2-}$




## Biogeochemical phases:

1. Spring „nitrate” bloom
2. „Post-nitrate” bloom
3. „Blue water” period
4. Mid/summer nitrogen fixation
5. Vertical mixing



# Productive Phases:

**Spring Bloom, Post Spring Phase, summer cyanobacterial bloom**

Calculation of changes in $C_T$ from cont. $pCO_2$ measurements and alkalinity.

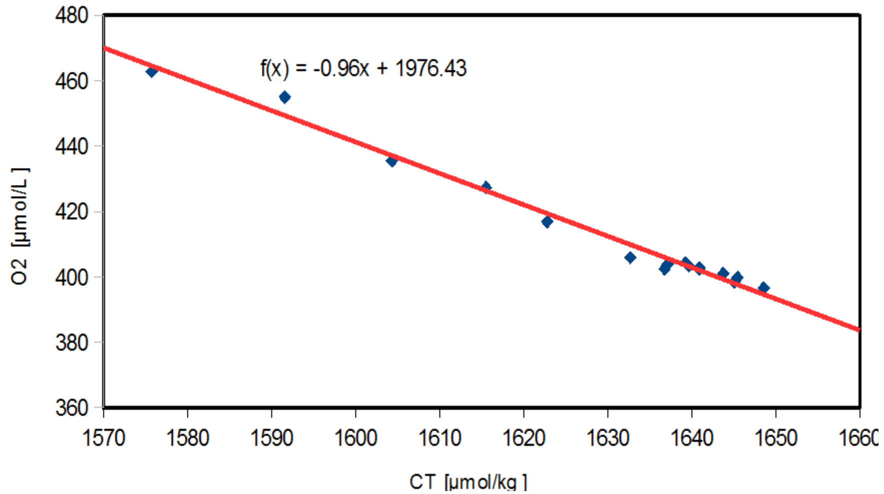
Correction for to the counteraction of $CO_2$ uptake by ASE during undersaturation by use of $O_2$ as a ASE tracer, and carbon uptake used for build up of biomass

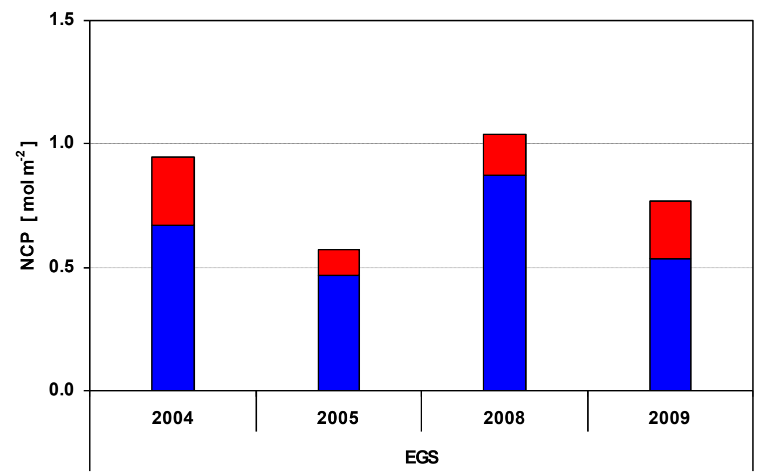
Allows for calculation of net production (carbon uptake)

Allows assessment of C/N/P stoichiometry

$$NCP = z_{mix} \bullet (\Delta C_t + C_t^{gasex}) \bullet 0.8$$

blue bars    red bars



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LEIBNIZ INSTITUTE FOR BALTIC SEA RESEARCH WARNEMÜNDE

# Spring bloom (1):

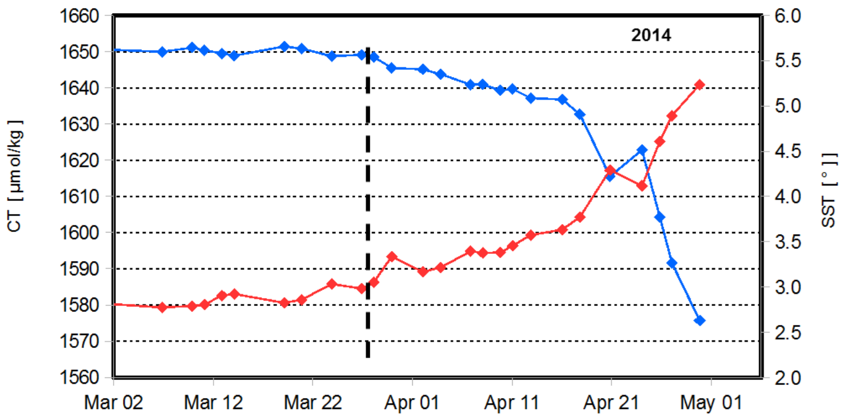
Continuous decrease of total $CO_2$ despite uptake of $CO_2$ from the atmosphere.

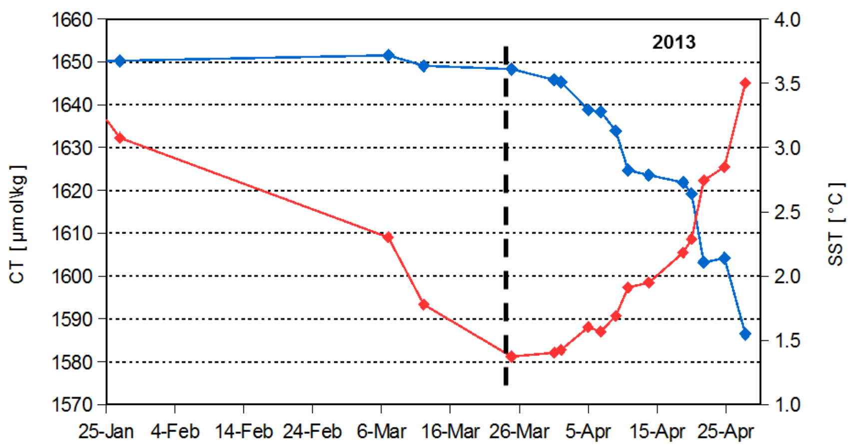
=>

Start of the spring bloom coincides with the increase of temperature.

The temperature as such does not trigger the start of the spring bloom.

Control by solar radiation in combination with low mixing depth (radiation dose)



# Post Spring bloom (2):

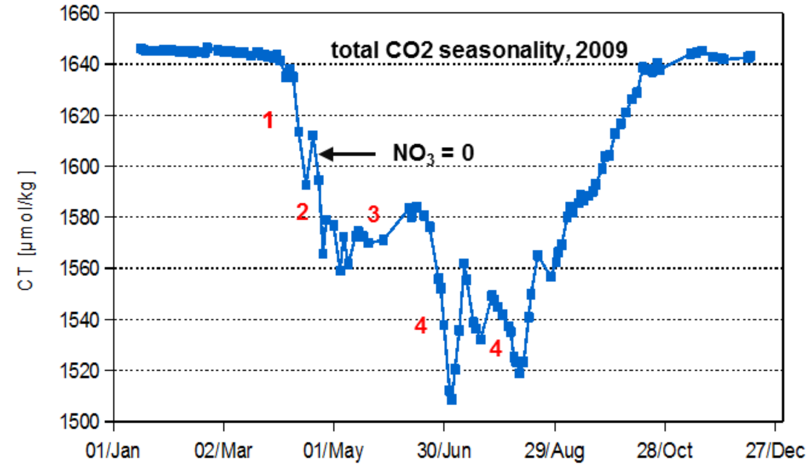
Continuation of net production after nitrate depletion

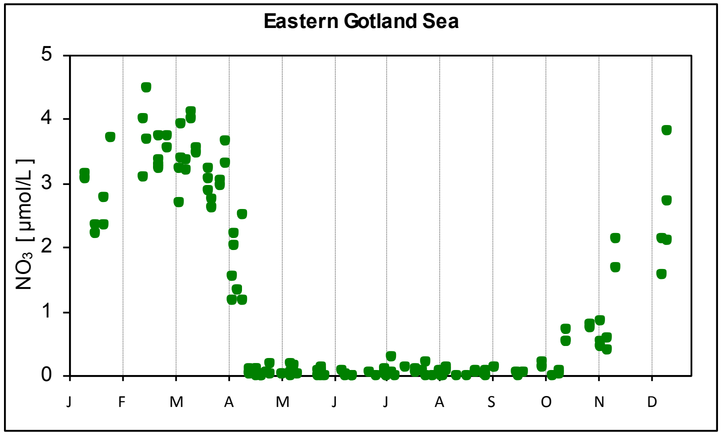
Nitrate usually completely depleted by mid-April

Base for theory of N-fixation at cold temperatures, and debate on potential missing N-source

=>

POSEC study and pending DFG proposal



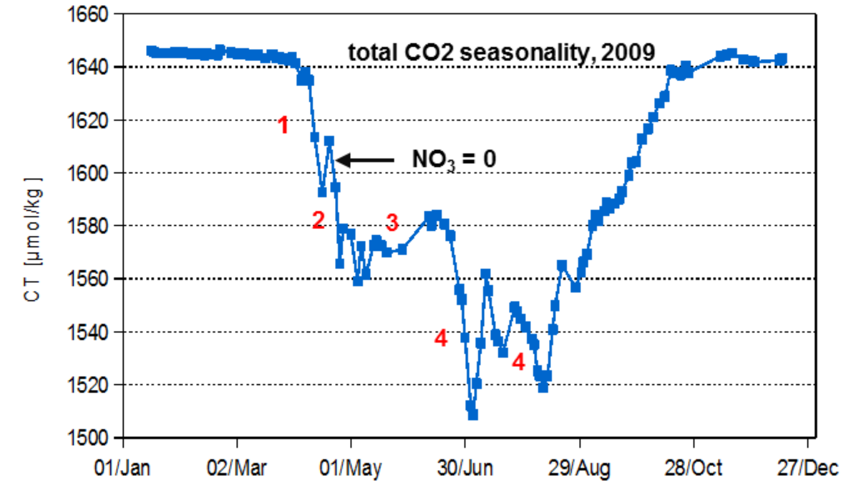
# Summer cyanobacterial bloom (4):

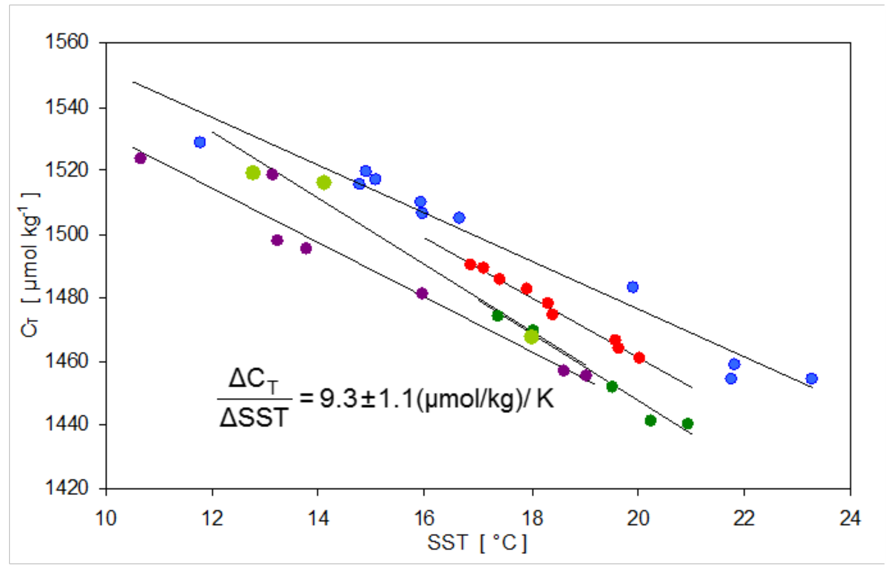
CT depletion (organic matter production) shows strong correlation to the increase of T

Combination of irradiation and low mixing depth control the dynamics biomass production !

Production rates correlate with the warming rate, both depend on radiation efficiency that increases at low mixing.

=> Improved parameterization of onset in biogeochemical models



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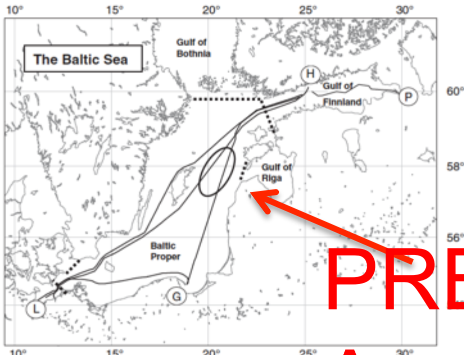
# Process Studies: Controls on $CO_2$ ASE fluxes

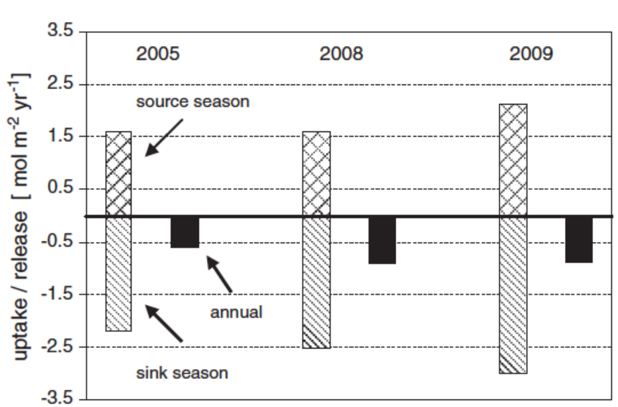
*Northeastern Gotland Sea*
*Schneider et al.,J.Mar.Sys, 2014*

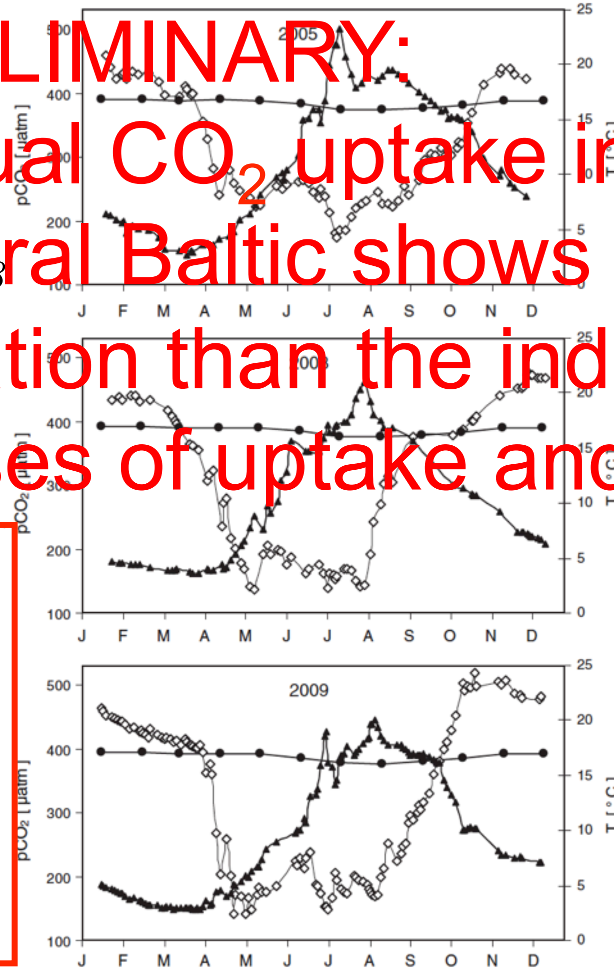


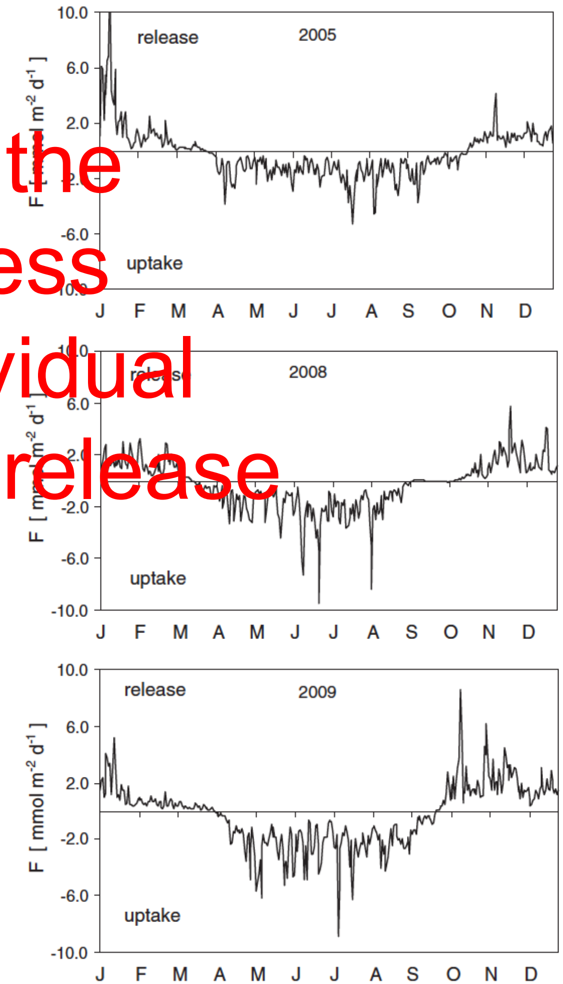

PRELIMINARY:
Annual $CO_2$ uptake in the Central Baltic shows less variation than the individual phases of uptake and release

$$NCP = z_{mix} \bullet (\Delta C_t + C_t^{gas-ex}) \bullet 0.8$$

blue bars
red bars

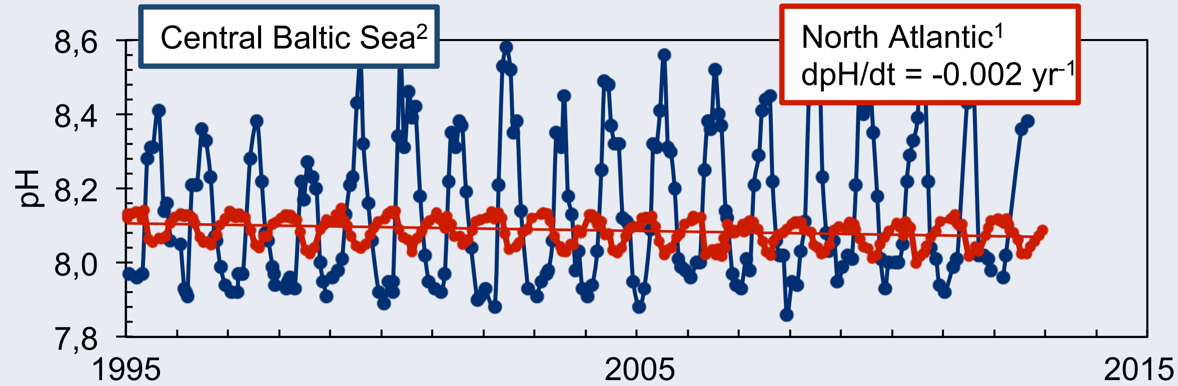


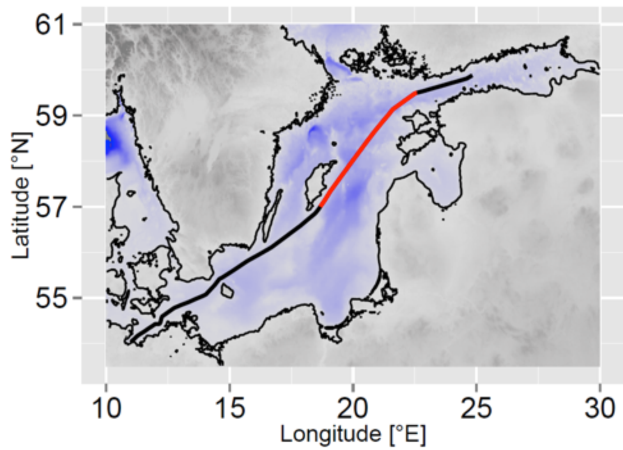



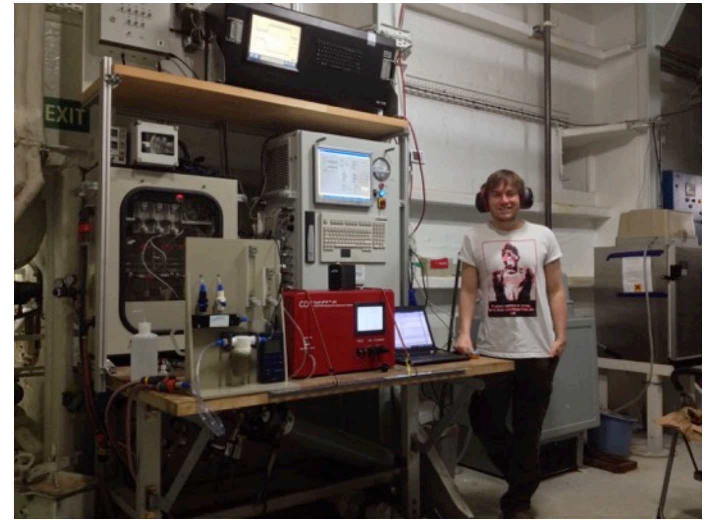
## BONUS PINBAL

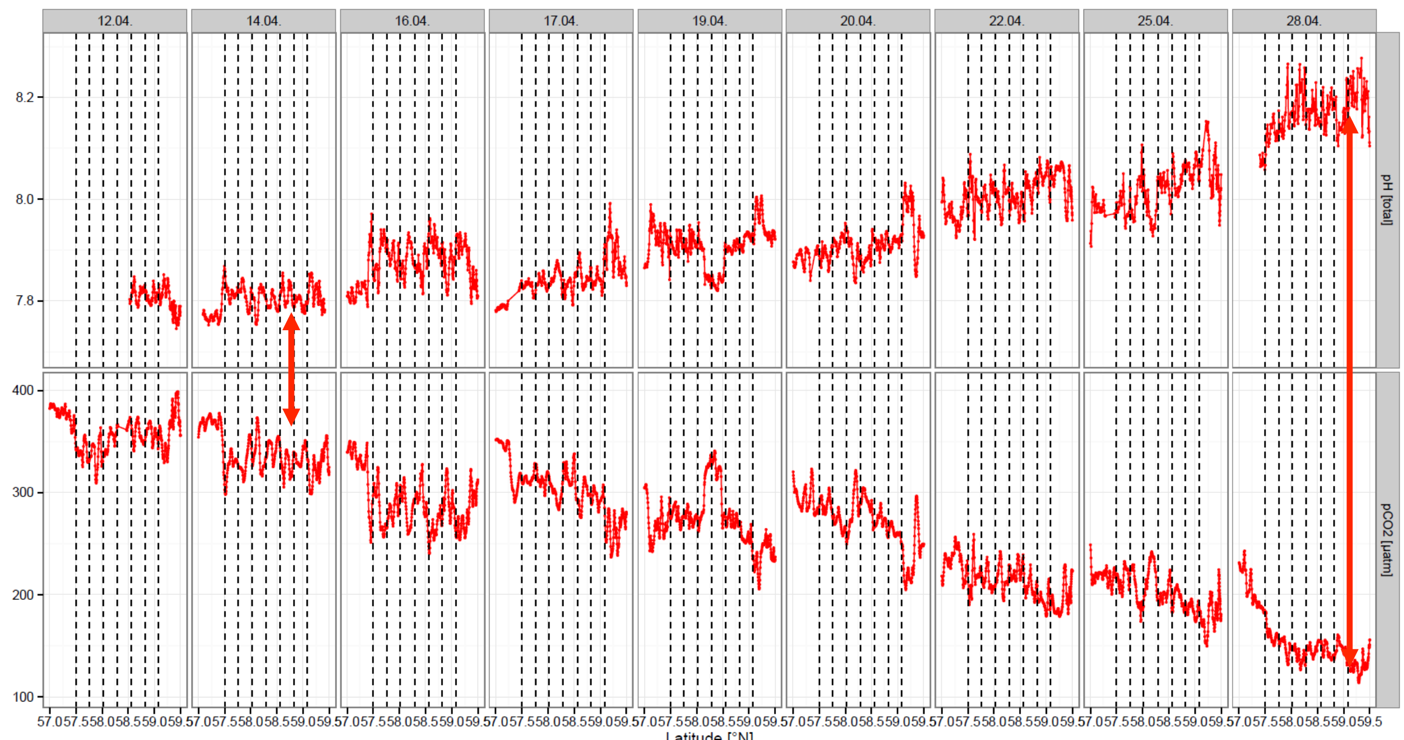
Development of a spectrophotometric **p**H measurement system for monito**rin**g in the **Bal**tic Sea






61
59
57
55
Latitude [°N]
10
15
20
25
30
Longitude [°E]

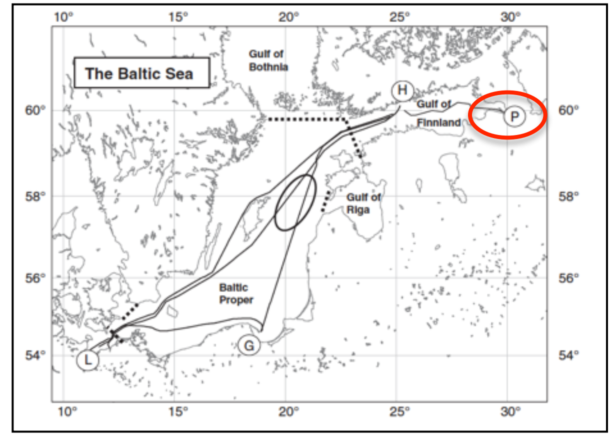

EXIT

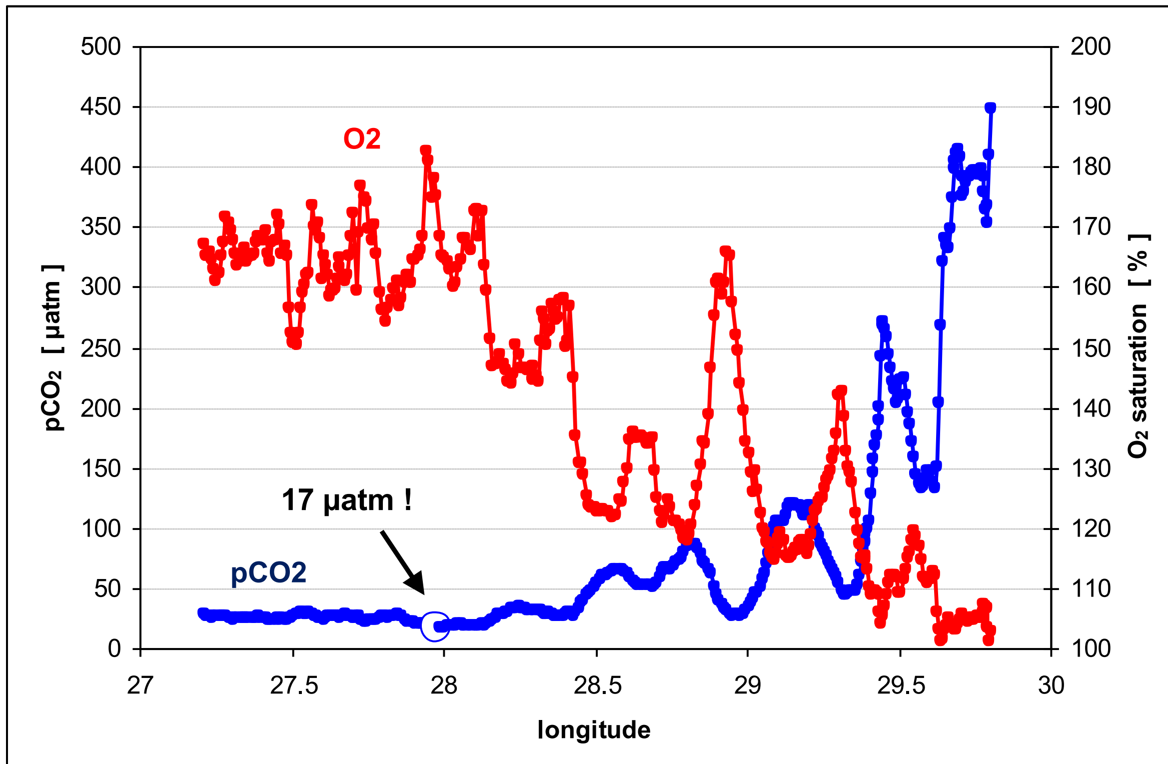

12.04.
14.04.
16.04.
17.04.
19.04.
20.04.
22.04.
25.04.
28.04.
8.2
8.0
7.8
pH [total]
400
300
200
100
pCO2 [µatm]
57.0 57.5 58.0 58.5 59.0 59.5
Latitude [°N]

PRODUCTIVITY IN THE BALTIC SEA

# EXTREMES 1:

## EUTROPHICATION EASTERN GULF OF FINLAND, INFLUENCE OF RIVER NEVA, SUMMER 2014





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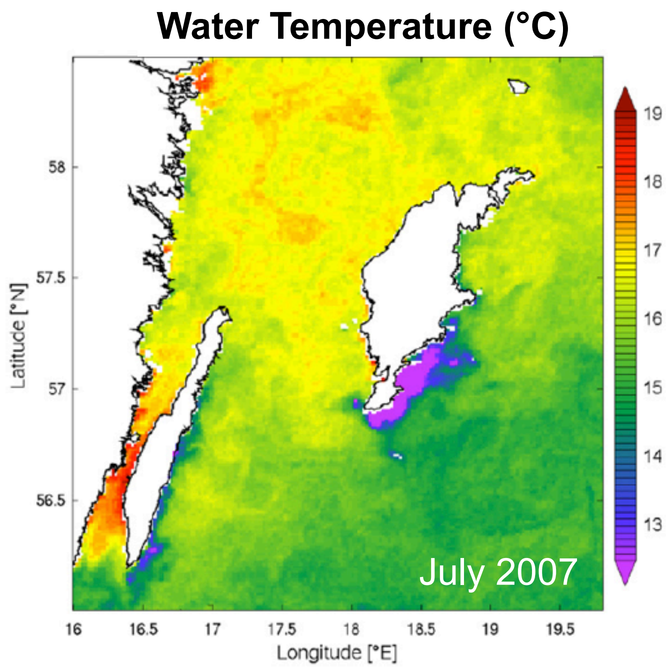
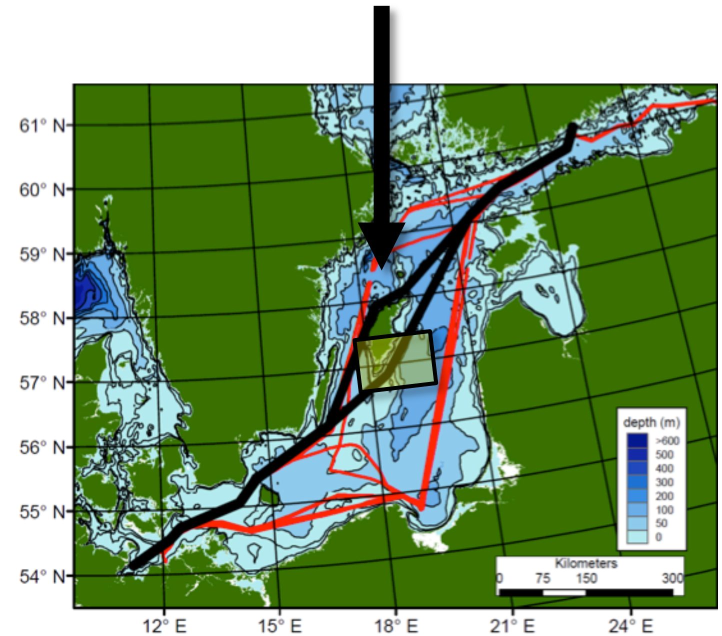
# Example 2:

# Upwelling Induced Trace Gas surface superation

# Summertime upwelling around Gotland




- Favorable wind forcing produces coastal upwelling events lasting days to weeks in the Baltic Sea
- In summertime upwelling transports cold water rich in methane and $CO_2$ from beneath the thermocline into the surface mixed layer

Adapted from Fennel et al., et al., (2010) Transient upwelling in the central Baltic Sea.

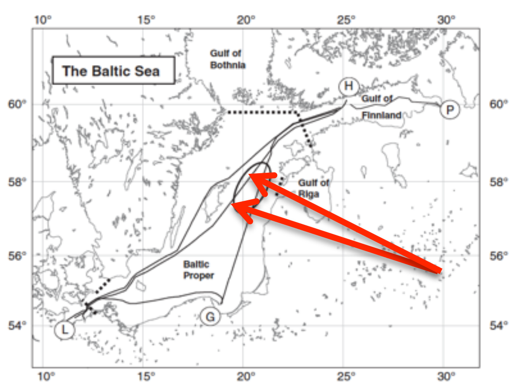
IMPORTANCE OF UPWELLING IN THE CENTRAL BALTIC

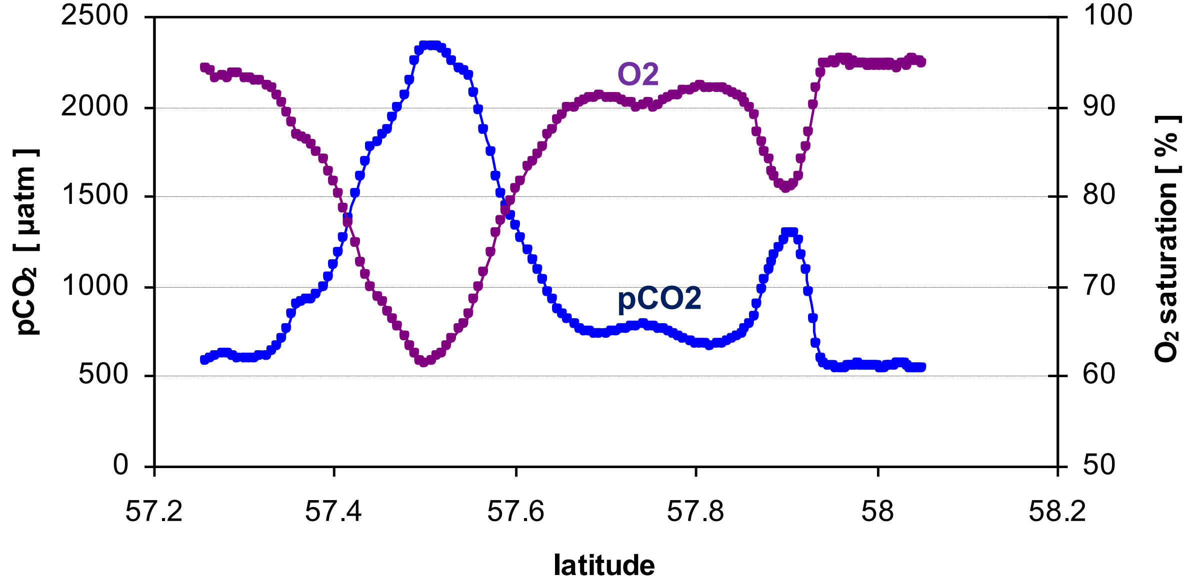
# EXTREMES 2:

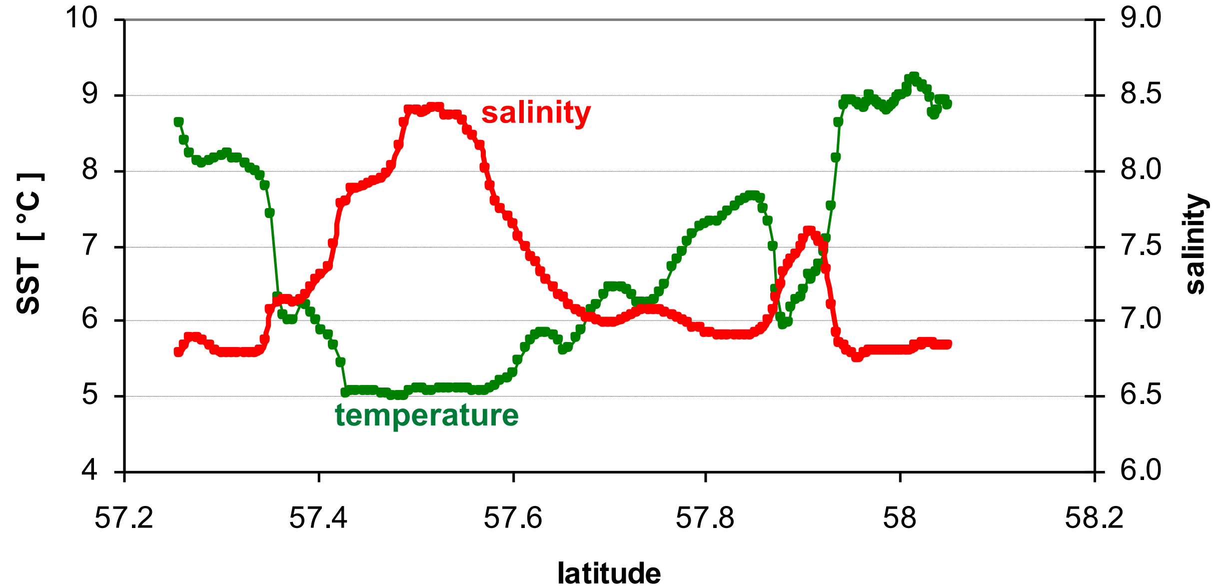
# UPWELLING INDUCED SURFACE SUPERATION

**Upwelling:**

**northwestern tip of Gotland, October 2009**

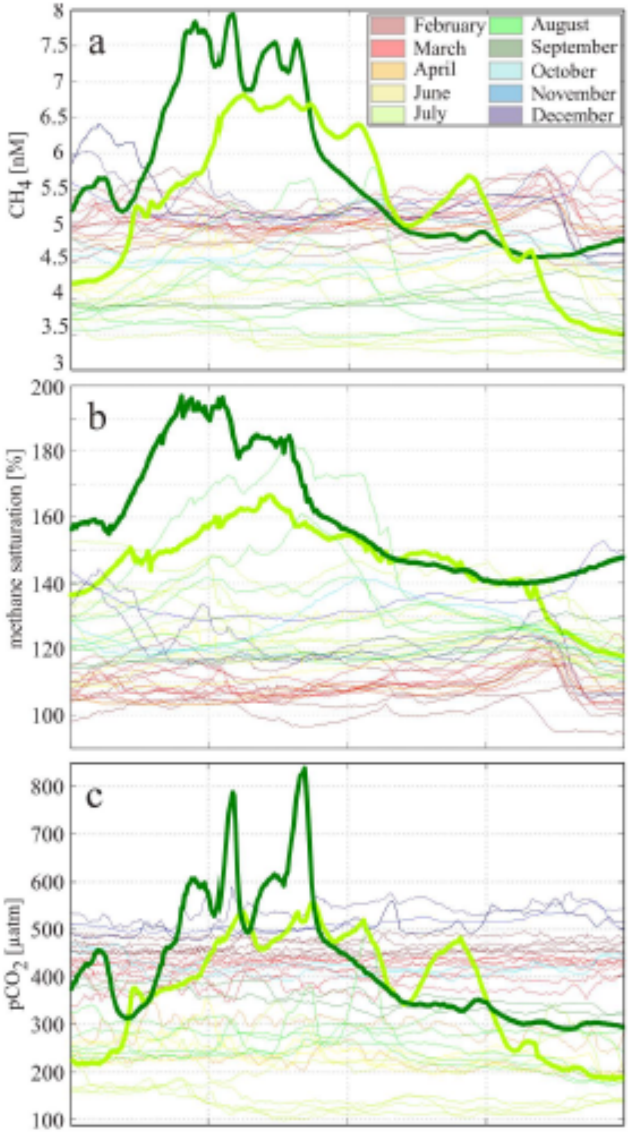


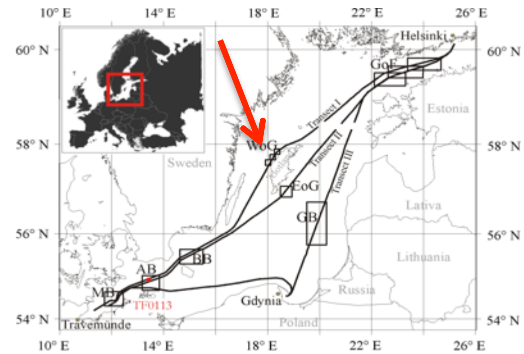



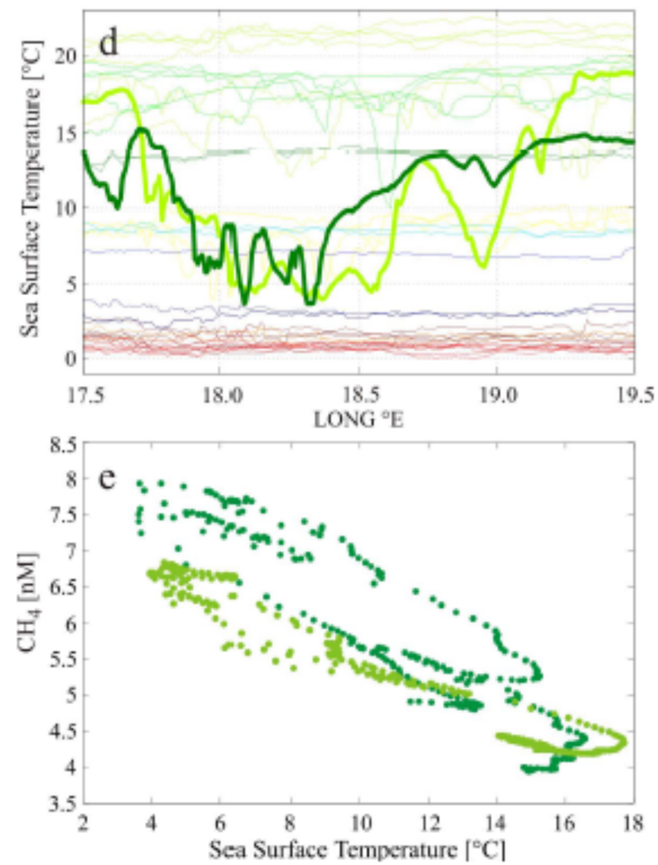



# Process Studies: Upwelling I

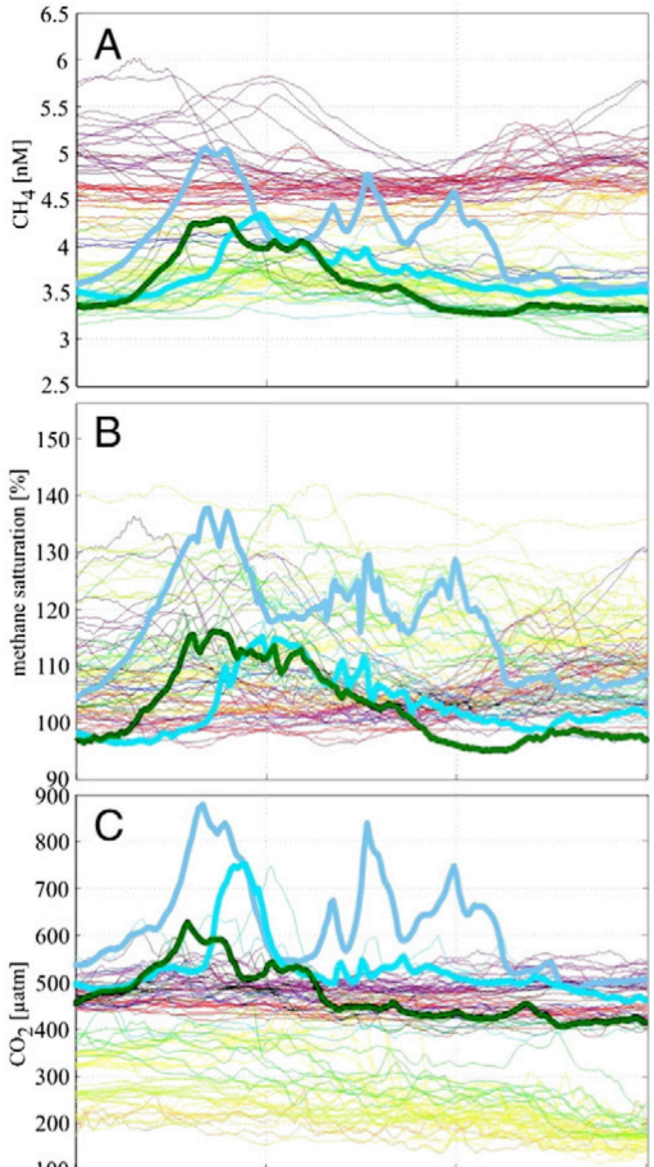
*North of Gotland, 2010*
*Gülzow et al.,BGS, 2013*



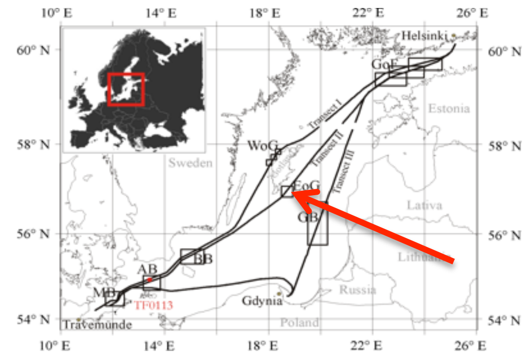



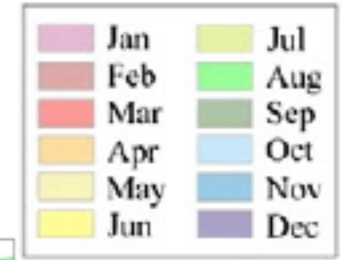



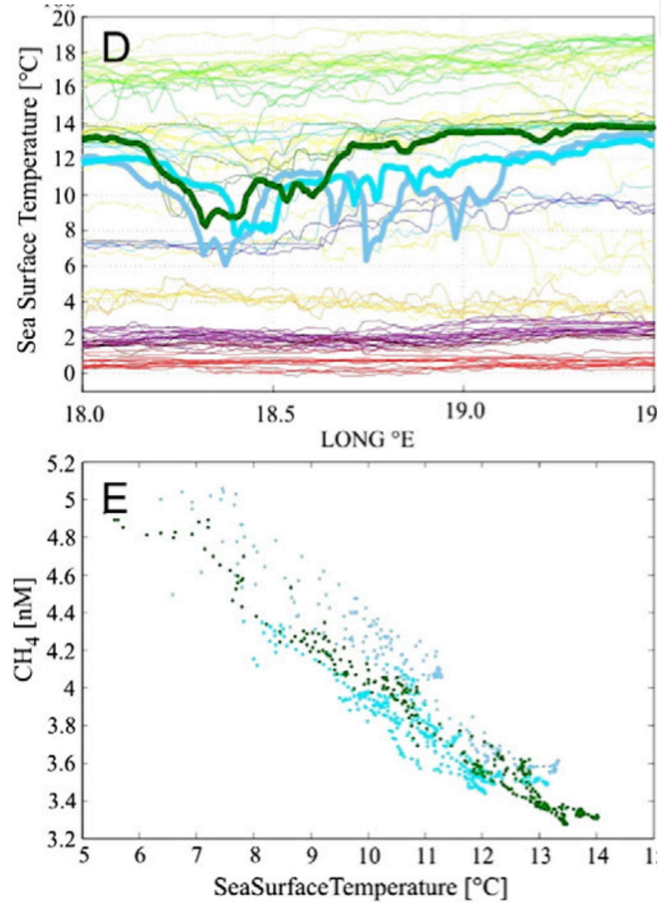
# Process Studies: Upwelling II




***South*** *of Gotland, 2011*
*Schneider et al.,J.mar.Sys, 2014*



# Temporal development of upwelling indicators



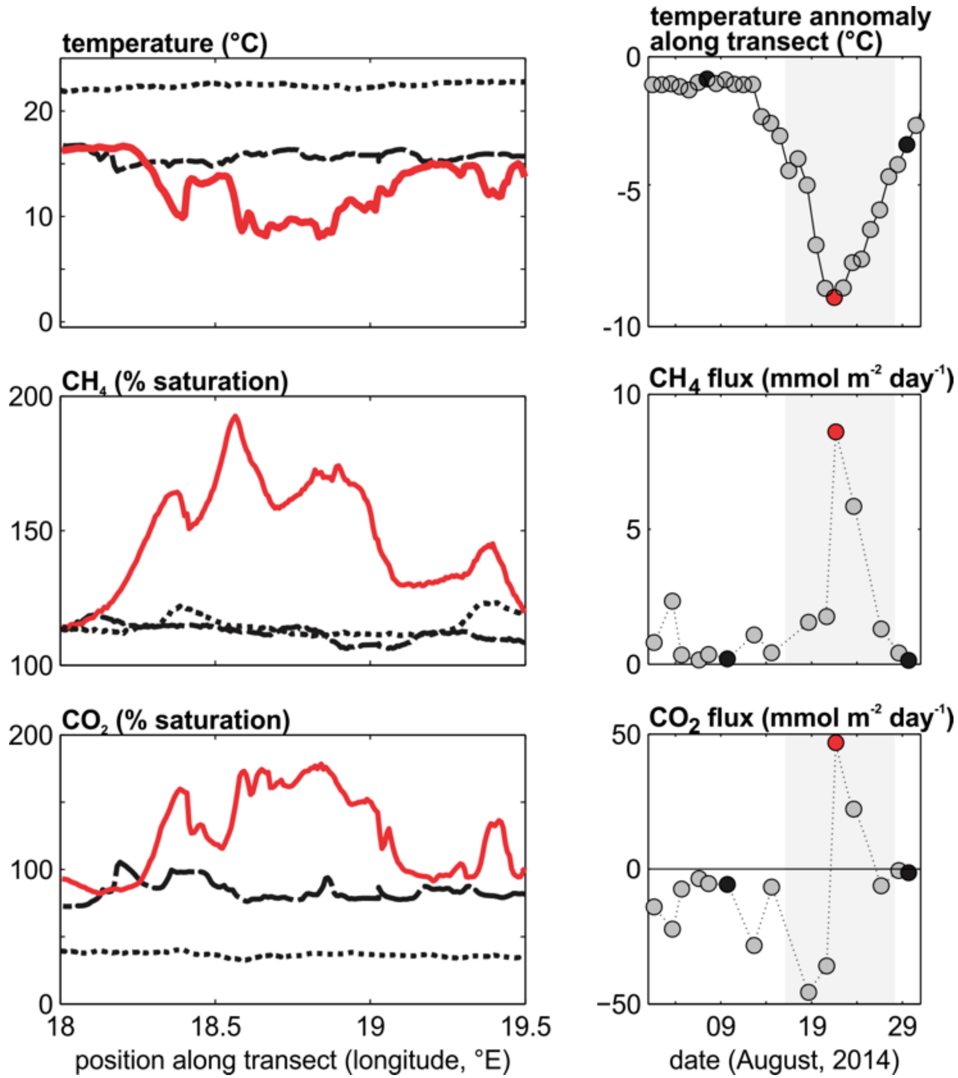
August 9th, 2014

**August 22nd, 2014**

August 29th, 2014

Different relaxation of T, $CH_4$, $pCO_2$, $O_2$ to allow for better ASE param. ????

How does interannual variability of upwelling intensity influence annual methane flux?

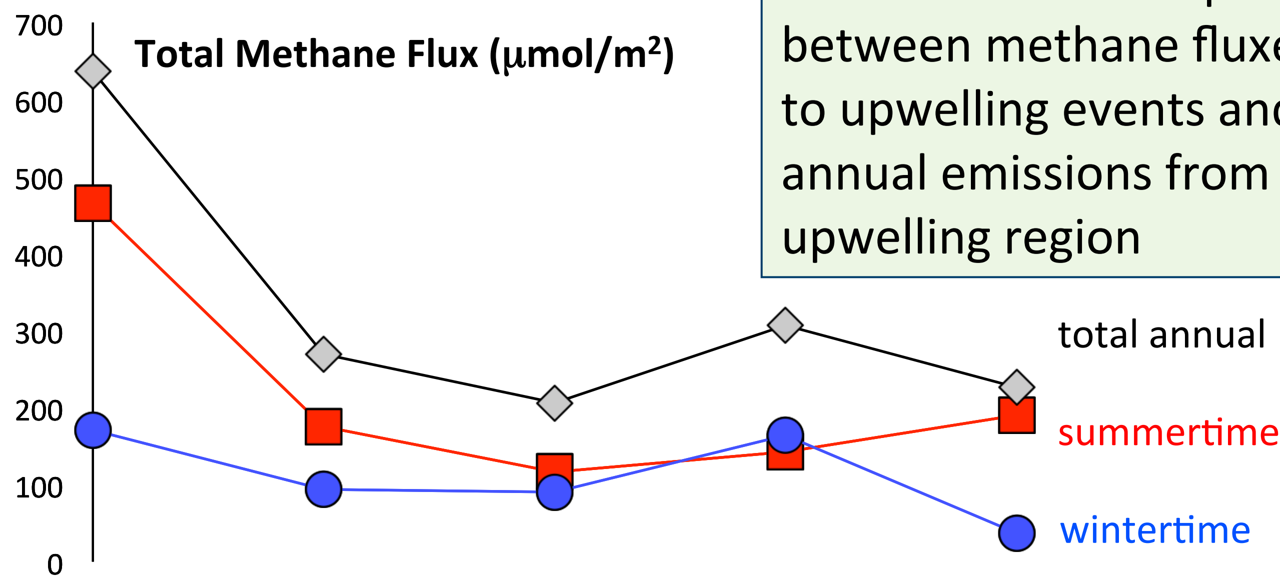


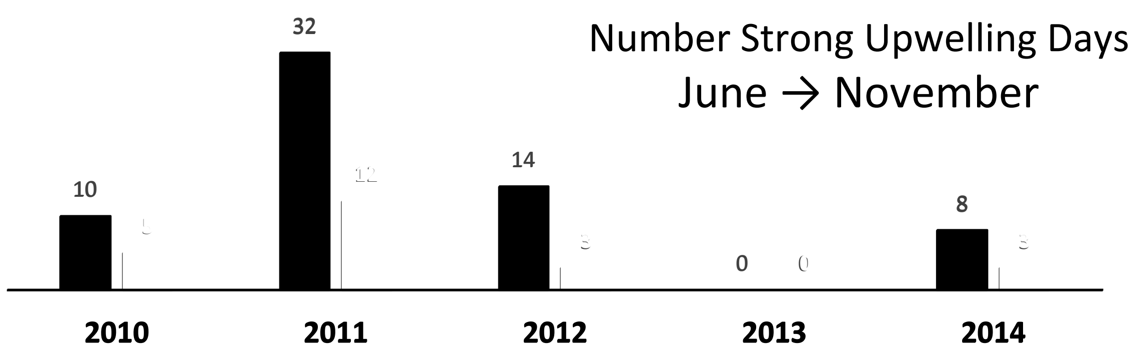

Daily temperature data derived from Baltic Sea model data, curtesy of Ulf Gräwe (IOW)

Gräwe, U., et al., Advantages of vertically adaptive coordinates in numerical models of stratified shelf seas. Ocean Model. 92, 56–68 (2015).

# Inter-annual variability of upwelling

No clear relationship between methane fluxes due to upwelling events and total annual emissions from the upwelling region




Daily temperature data derived from Baltic Sea model data, curtesy of Ulf Gräwe (IOW)

Gräwe, U., et al., Advantages of vertically adaptive coordinates in numerical models of stratified shelf seas. Ocean Model. 92, 56–68 (2015).

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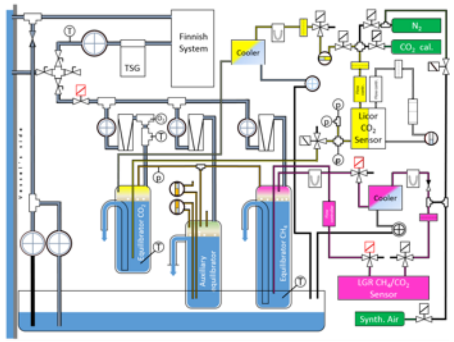
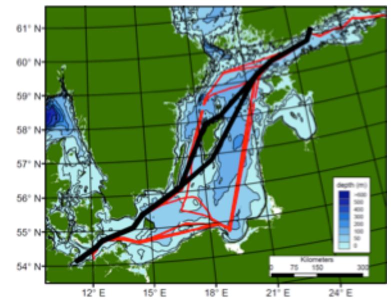
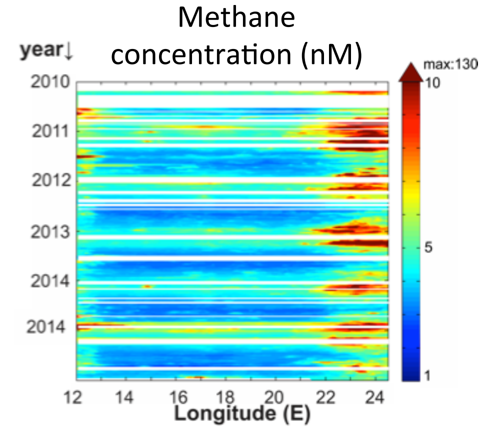
# Publications

- Identification and quantification of plankton bloom events in the Baltic Sea by continuous $pCO_2$ and chlorophyll a measurements on a cargo ship. Journal of Marine Systems 59: 238-248, (2006). **Schneider et al., with S. Kaitala and P. Maunula.**
- A new method for continuous measurements of $O_2$ in surface water in combination with $pCO_2$ measurements: Implications for gas phase equilibration. Mar. Chem., 103, 163 -171, (2007). **Schneider et al.**
- The annual cycle of carbon dioxide and parameters influencing the air-sea carbon exchange in the Baltic Proper. J. Mar. Sys., 74, 381 – 394, (2008). **– Schneider et al.**
- A nitrogen fixation estimate for the Baltic Sea based on continuous $pCO_2$ measurements on a cargo ship and total nitrogen data. Continental Shelf Research 29: 1535-1540, (2009). **Schneider et al., with S. Kaitala and M. Raateoja.**
- Inter-annual and seasonal variations in the air-sea CO2 balance in the central Baltic Sea and the Kattegat. Cont. Shelf Res., 30, 1511 – 1521, (2010). **Wesslander et al., with Schneider.**
- Processes regulating $pCO_2$ in the surface waters of the central eastern Gotland Sea: a model study. Oceanologia, 53, 745 – 770, (2011). **Kusnetzov et al., with Schneider.**
- A new method for continuous measurement of methane and carbon dioxide in surface waters using off-axis integrated cavity output spectroscopy (ICOS): An example from the Baltic Sea. Limnology Oceanography Methods, 9, 168-174, (2011). **Gülzow et al., with Rehder and Schneider.**
- One year of continuous measurements constraining methane emissions from the Baltic Sea to the atmosphere using a ship of opportunity. Biogeosciences 10, 81-99, doi:10.5194/bg-10-81-2013, (2013). **Gülzow et al., with Rehder.**
- Biogeochemical Control of the Coupled $CO_2$-$O_2$ System of the Baltic Sea: A Review of the Results of Baltic-C. AMBIO 02/2014; 43(1):49-59, (2014). **Omstedt et al., with Schneider.**
- Control of the mid-summer net community production and nitrogen fixation in the central Baltic Sea: An approach based on $pCO_2$ measurements on a cargo ship, Journal of Marine Systems, (2014). **Schneider et al.**
- Detecting sinks and sources of $CO_2$ and $CH_4$ by ferrybox-based measurements in the Baltic Sea: Three case studies. J. Mar. Sys., Doi:10.1016/j.jmarsys.2014.03.014, (2014). **Schneider et al., with Gülzow and Rehder.**
- Characteristics of the spring/summer production in the Mecklenburg Bight (Baltic Sea) as revealed by long-term pCO2 data , Oceanologia 57, 375—385 (2015), Schneider et al.

# Summary and Outlook




- IOW ferrybox system provides:
  - Good temporal and spatial sea surface concentration data
  - **Multi-year observations**
- Soon to be upgraded for additional parameters:
  - **p$CO_2$** (LI-COR)
  - **$O_2$** (PreSens)
  - **$CH_4$** and secondary **p$CO_2$** (Los Gatos Research)
  - **$\delta^{13}C$-$CO_2$** (PICARRO)
  - **$N_2O$** + **CO** (LGR)
  - **pH** (Bonus PINBAL project)
  - **Atmospheric concentrations** + **weather station**

SUMMARY AND CONCLUSIONS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# Questions?

.. funding from: ICOS INTEGRATED CARBON OBSERVATION SYSTEM | Bundesministerium für Bildung und Forschung

... thanks to " the team"

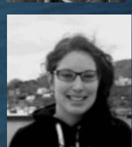

Ulf Gräwe


Wanda Gülzow


Michael Glockzin


Bernd Sadkowiak


Bernd Schneider


Carolyn Graves


**Thanks to our**
collegues from
SYKE
Petri Maunula
Seppo Kaitala

... and Finnlines