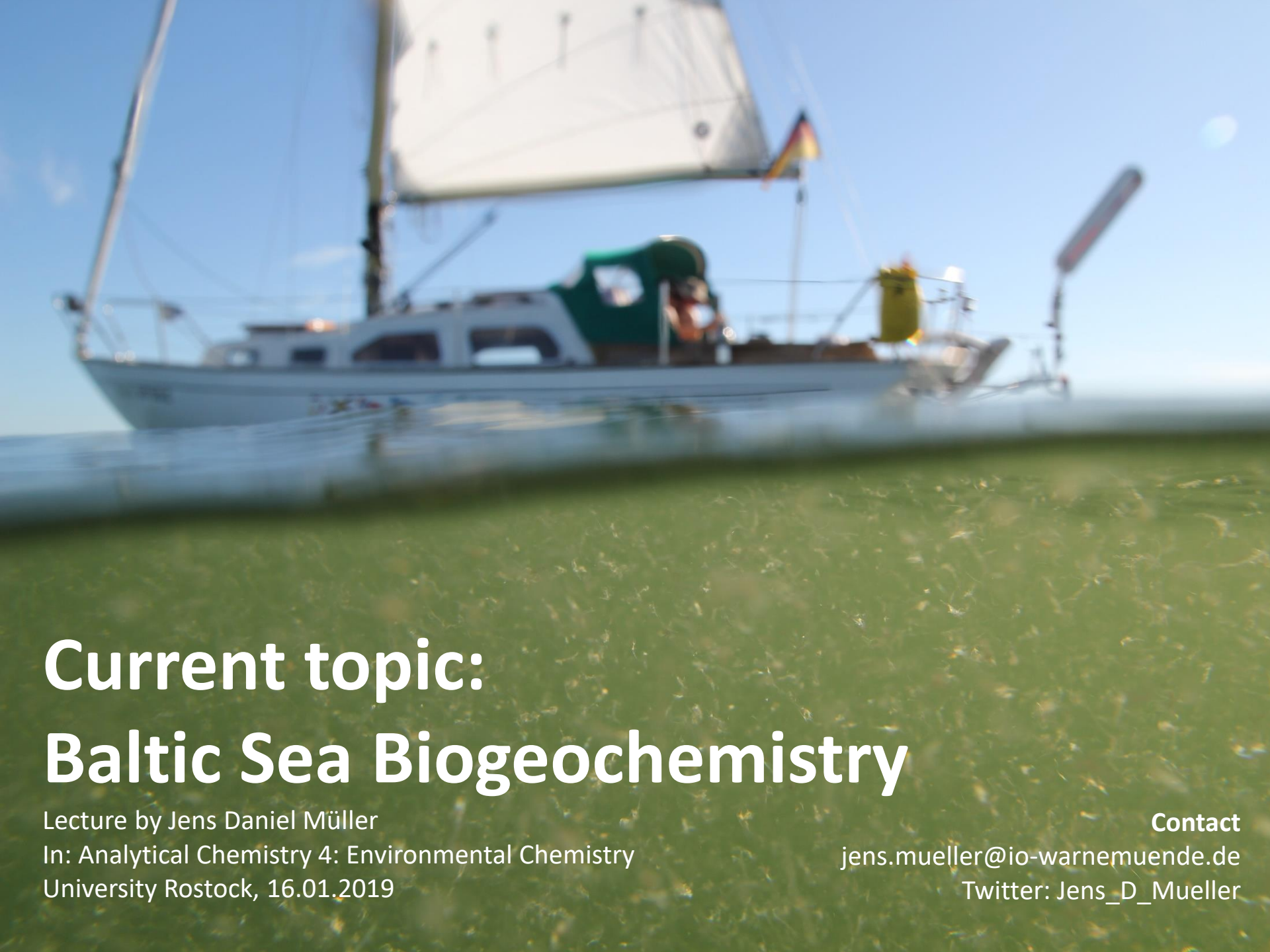
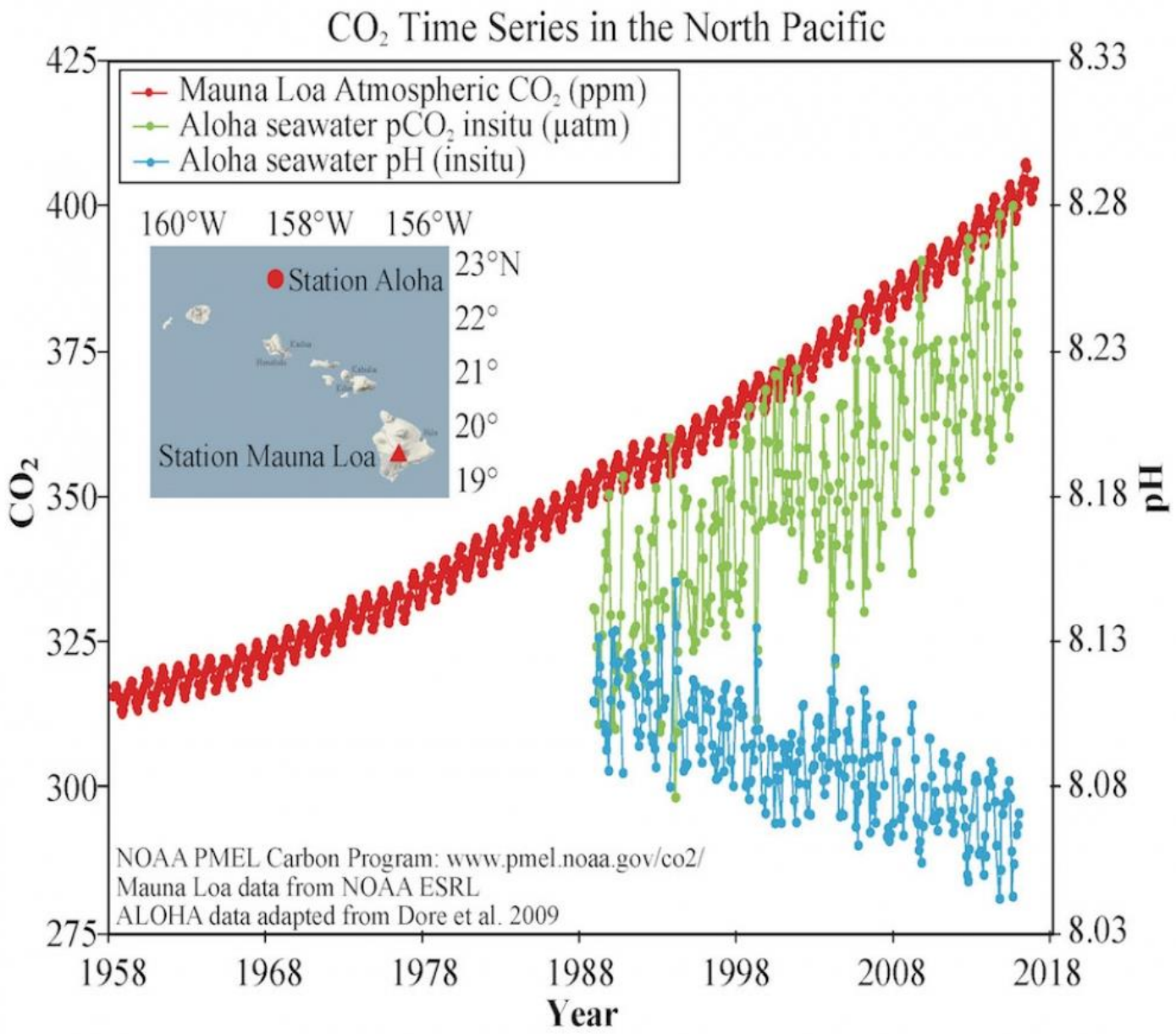


Current topic:
Baltic Sea Biogeochemistry

Lecture by Jens Daniel Müller
In: Analytical Chemistry 4: Environmental Chemistry
University Rostock, 16.01.2019

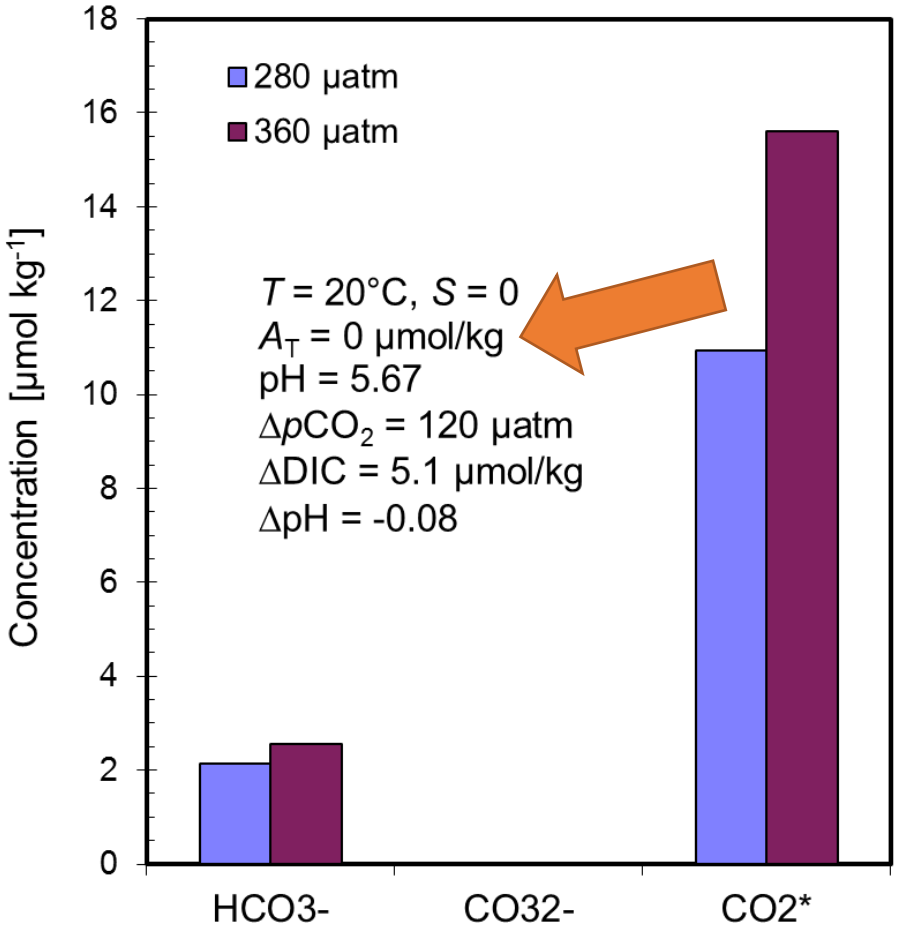
Contact
jens.mueller@io-warnemuende.de
Twitter: Jens_D_Mueller

Recap: Changes in Seawater Chemistry due to Uptake of Anthropogenic CO_2

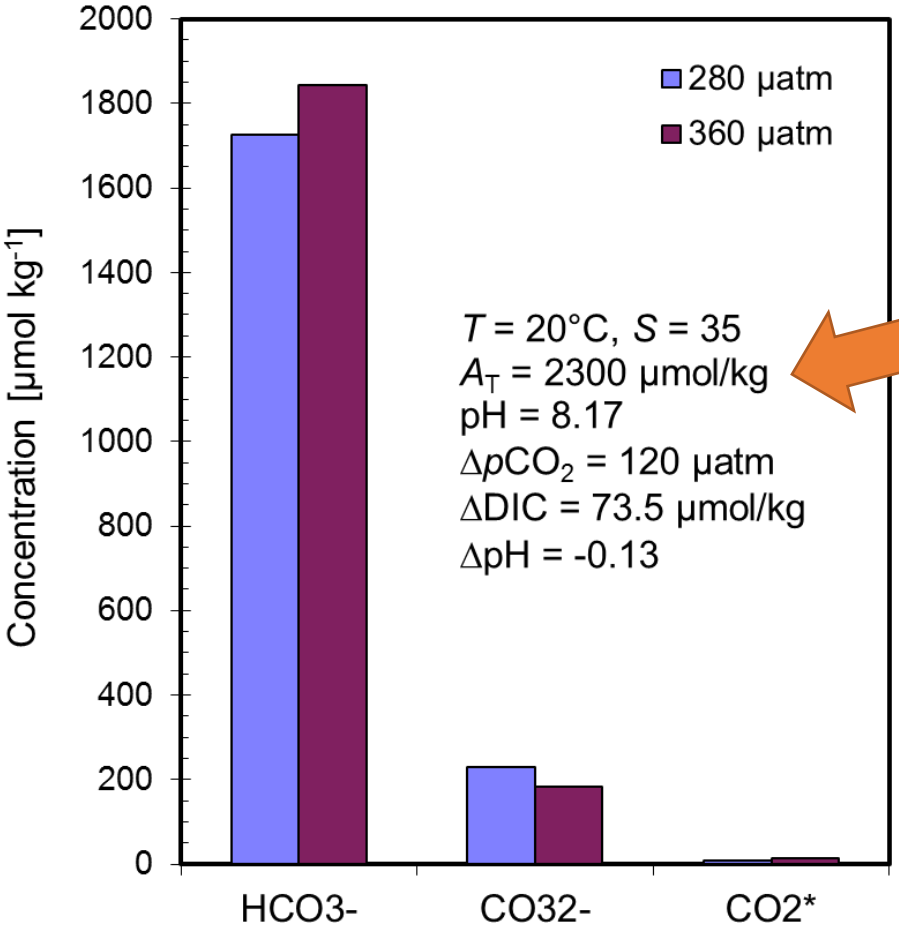


Dore et al. (2009)

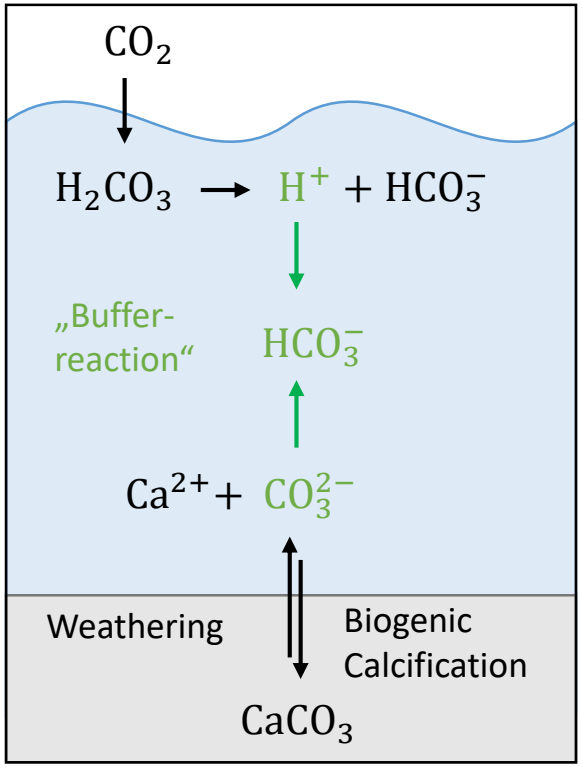
CO_2 system freshwater



CO_2 system seawater

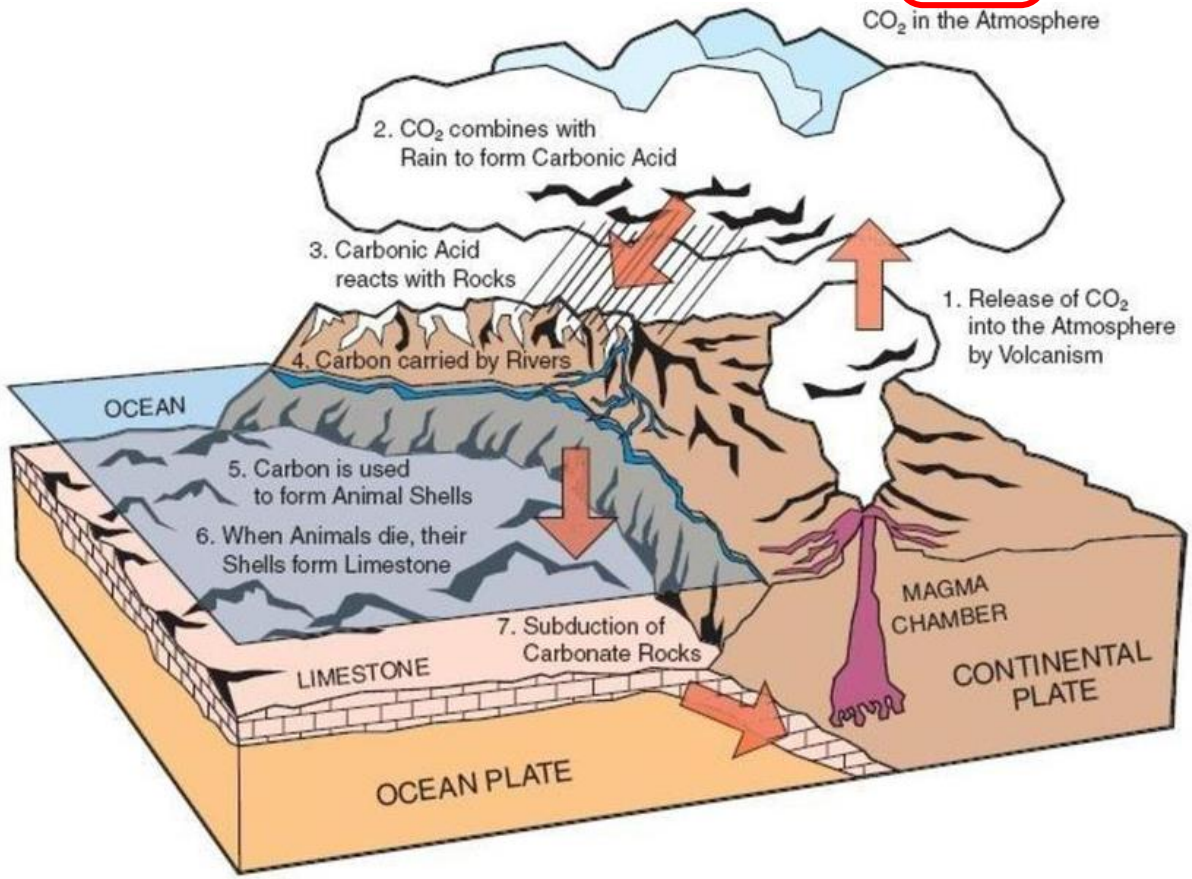


Recap: The Alkalinity Concept



Silicate weathering $CaSiO_3 + 2H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4$

Limestone weathering $CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$



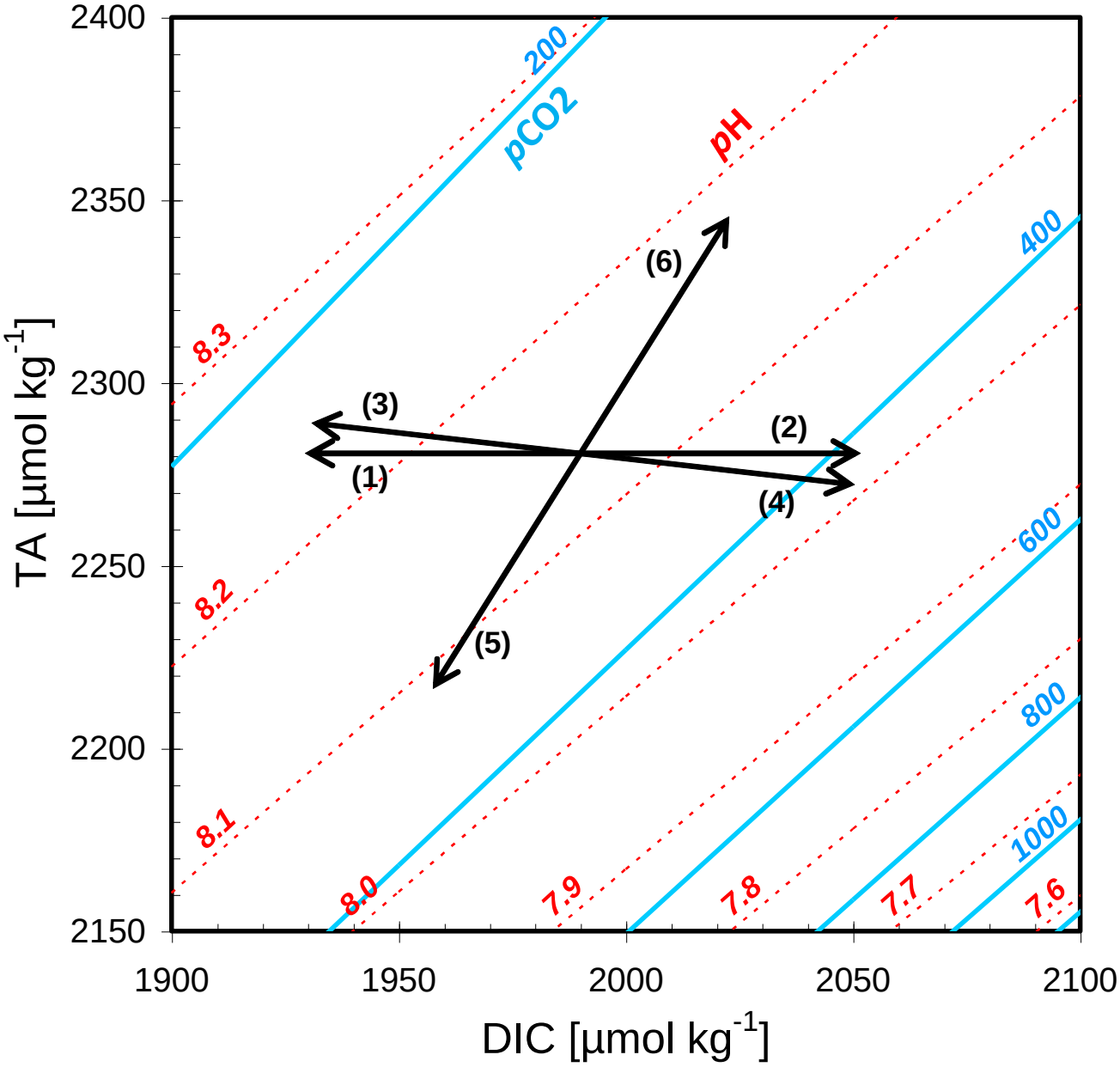
Alkalinity A_T

- Defined as the excess of pronton acceptors over proton donors
- Carbonate Alkalinity:

$$A_T \approx [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

- Buffer reaction controls the CO_2-uptake capacity of seawater

Recap: Biogeochemical processes in the parameter space of the marine CO_2 system



(1) CO_2 release to atmosphere

(2) CO_2 uptake from atmosphere

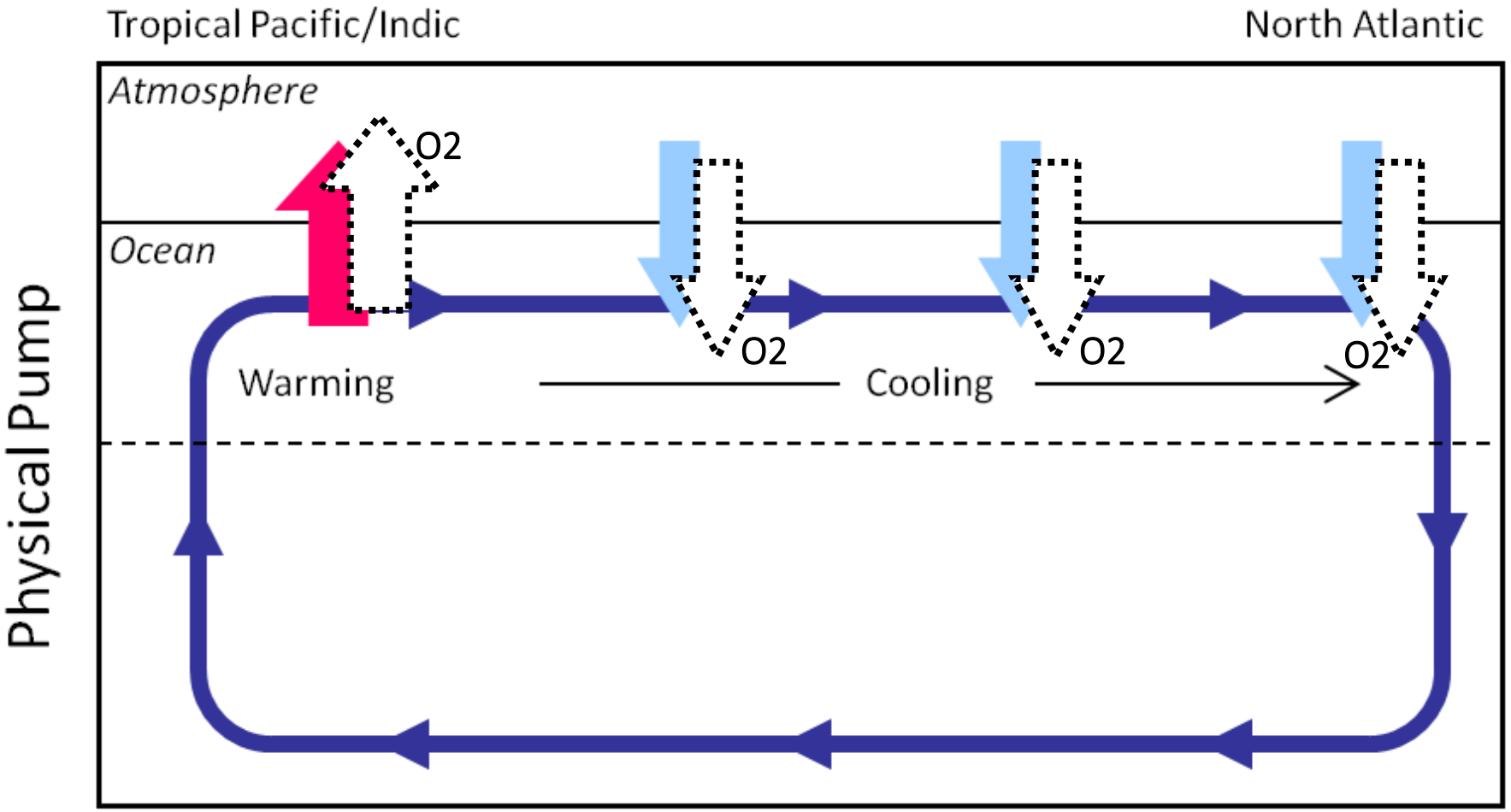
(3) Primary production

(4) Respiration

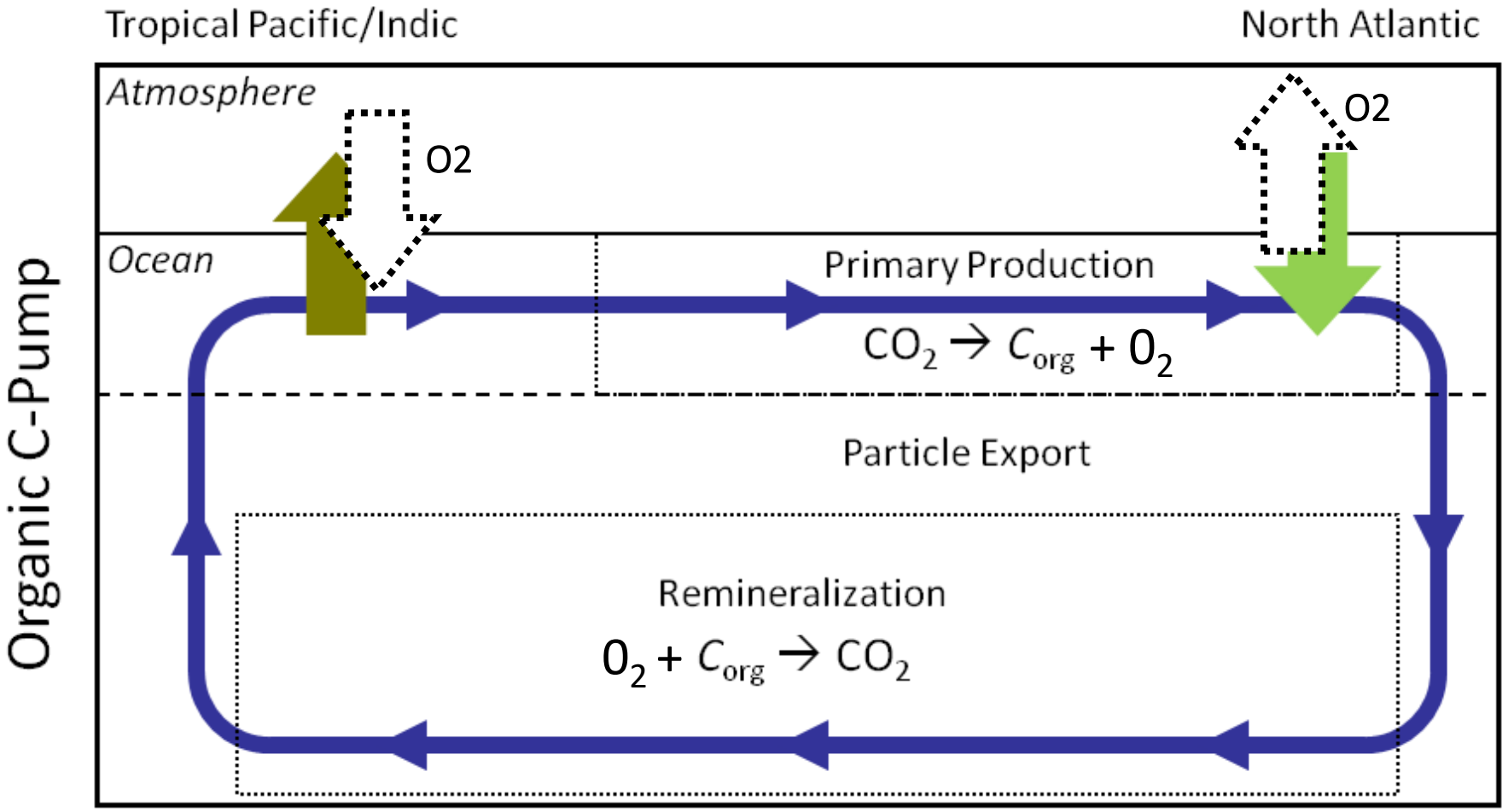
(5) Calcification

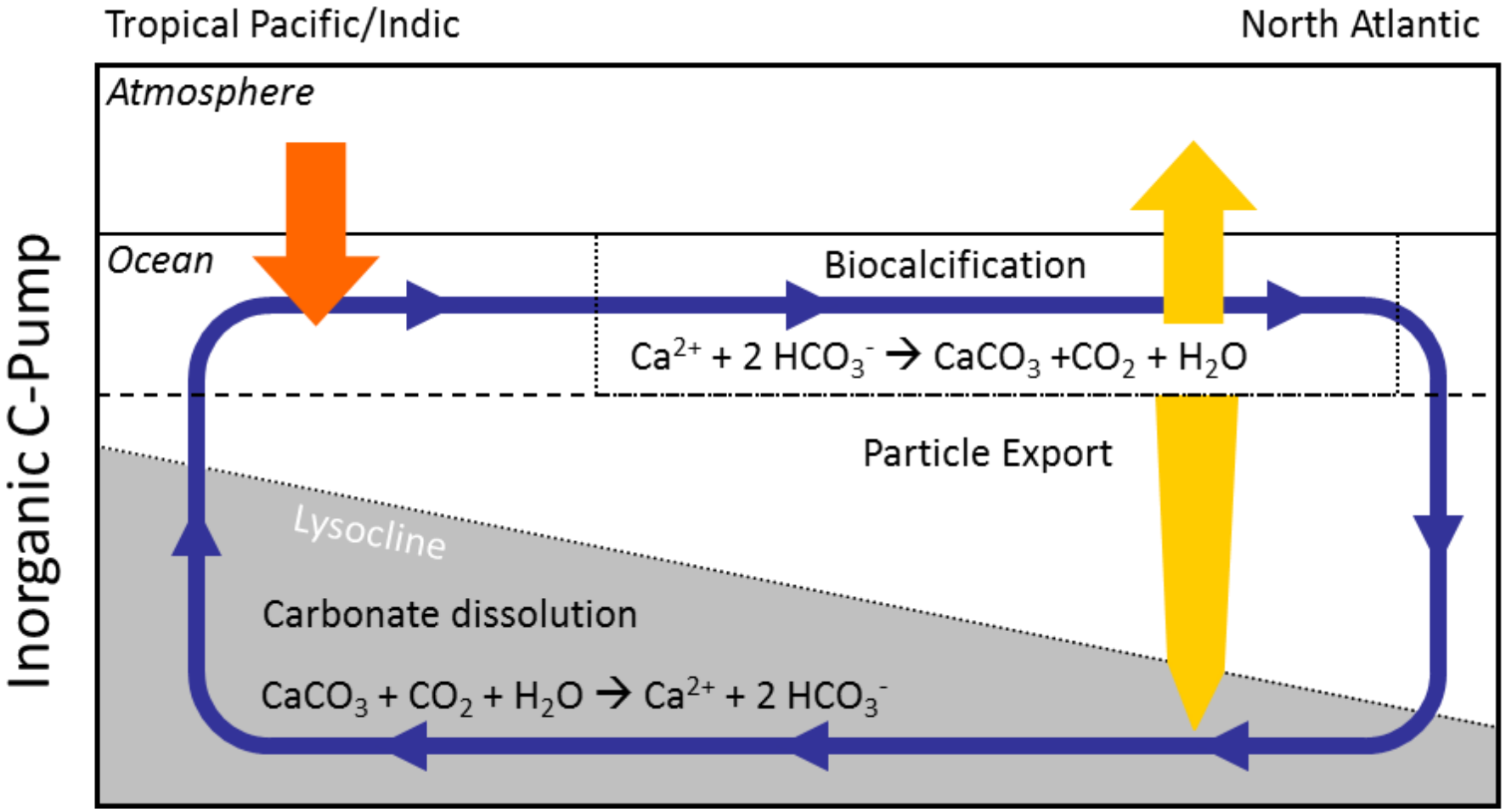
(6) Carbonate dissolution

- Decrease in SST favors O_2 solubility and increases density
- Downwelling in the North Atlantic (e.g. Labrador Sea) ventilates ocean interior

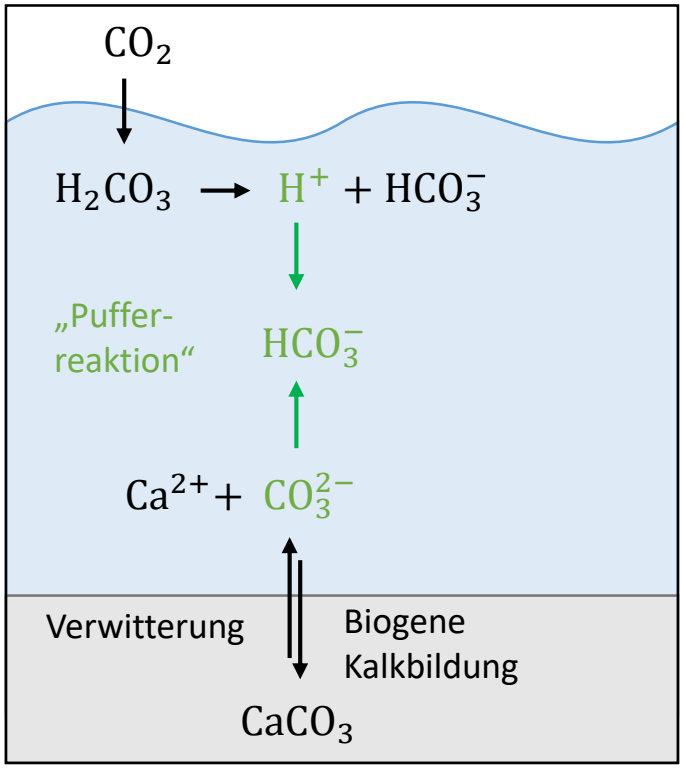


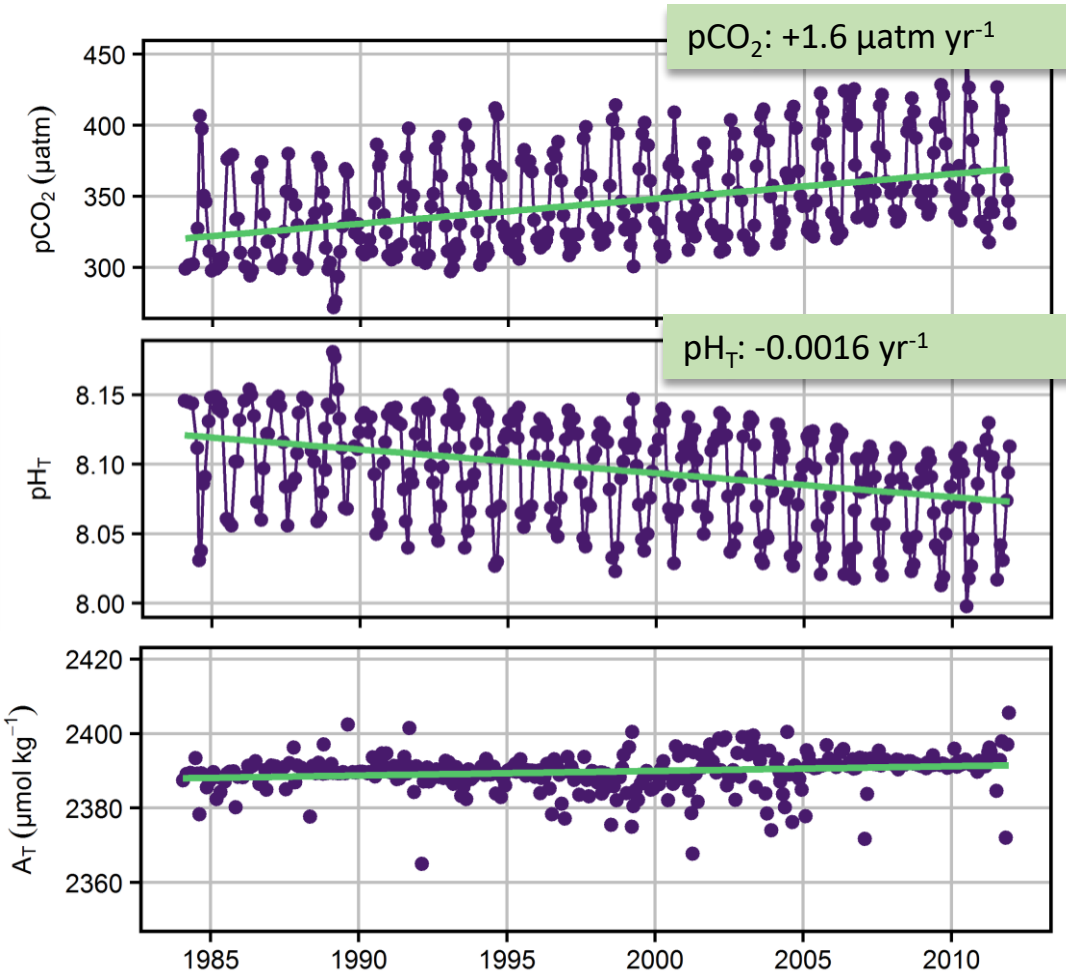
$$CO_2 + H_2O \underset{Mineralisation}{\overset{Production}{\rightleftharpoons}} O_2 + CH_2O$$




Tropical Pacific/Indic
North Atlantic
Inorganic C-Pump
Atmosphere
Ocean
Biocalcification
$Ca^{2+} + 2\ HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$
Particle Export
Lysocline
Carbonate dissolution
$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2\ HCO_3^-$

Globale Veränderungen des marinen CO_2-Systems: Beispiel Nordatlantik[1]





Alkalinität A_T

Überschuss an Protonenakzeptoren

$$A_T \approx [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

Je höher A_T, desto:

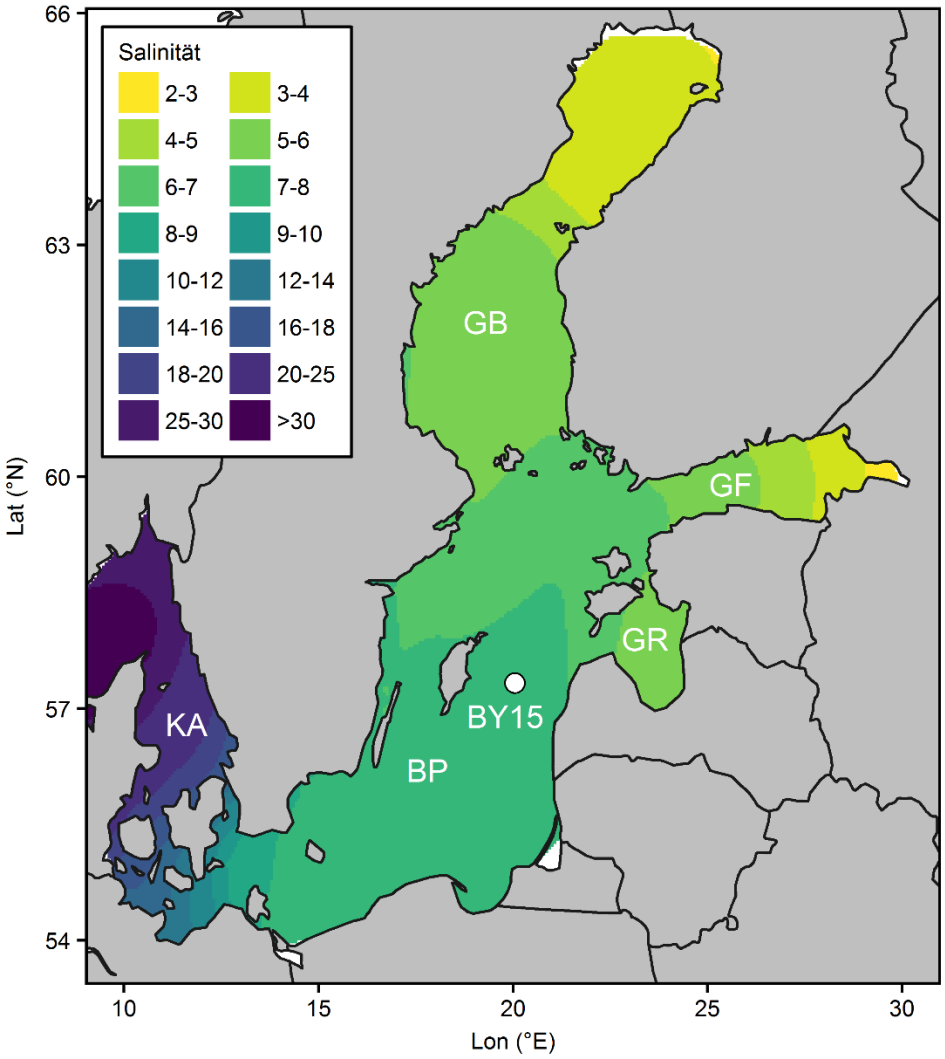
- geringer $|\Delta pH/\Delta pCO_2|$
- geringer $|\Delta \Omega/\Delta pCO_2|$

Voraussetzung für strikte Korrelation zwischen pCO_2 und pH: Gleichbleibende Alkalinität!

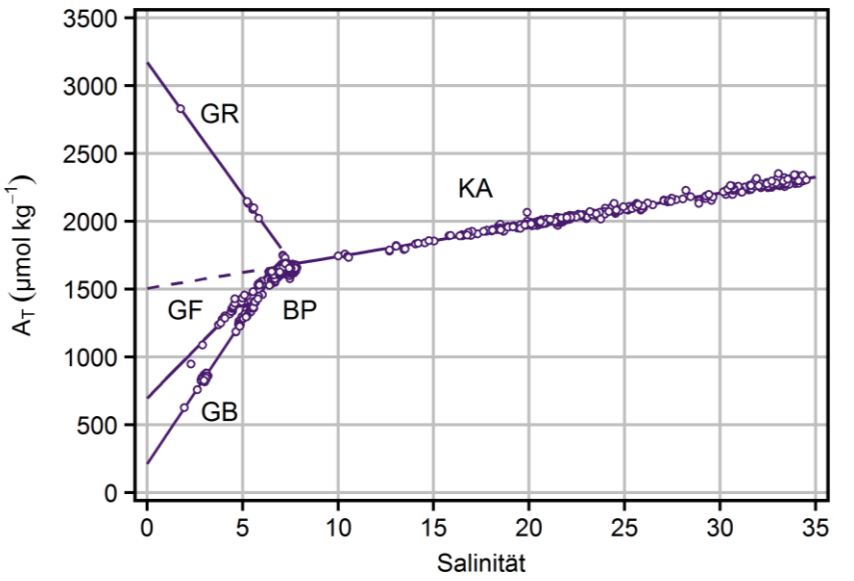
Gibt es auf Zeitskalen der Ozeanversauerung A_T-Änderungen in der Ostsee?

[1]Bates et al. (2012) – Zeitreihe „BATS“

Besonderheiten der Ostsee: Hydrographie und CO_2-System



Jahr: 2008

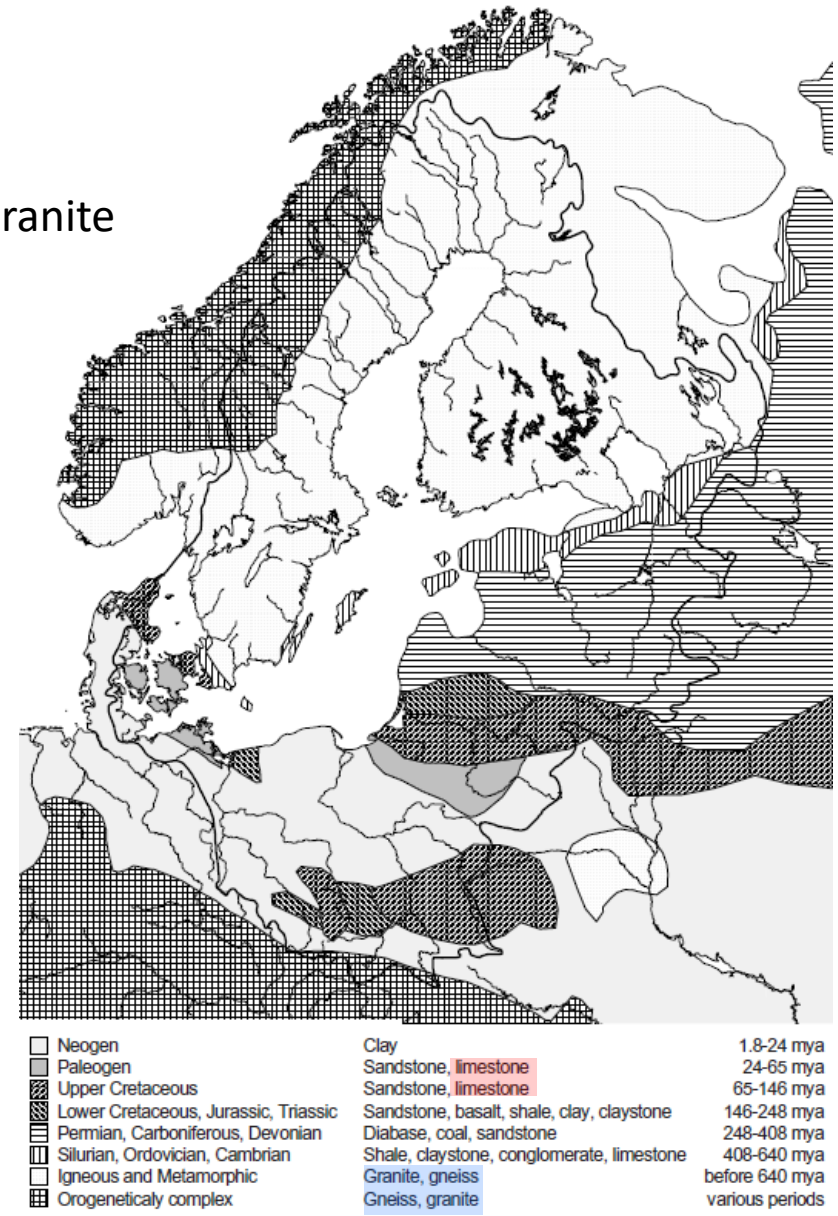


- Salinität und Alkalinität zeigen konservatives Mischungsverhalten
- Flusseinträge bestimmen A_T-S-Beziehung
- Wasserresidenzzeit
  - Ostsee ca. 30 Jahre[1]
  - Ozean ca. 10^4 Jahre[2]

[1]Helcom (1993); [2]Sarmiento und Gruber (2006); [3]Hjalmarsson et al. (2008); [4]SHARK data base (2015); [5]M. Pertilla (pers. comm.)

Exkurs: Geology of the Baltic Sea drainage basin

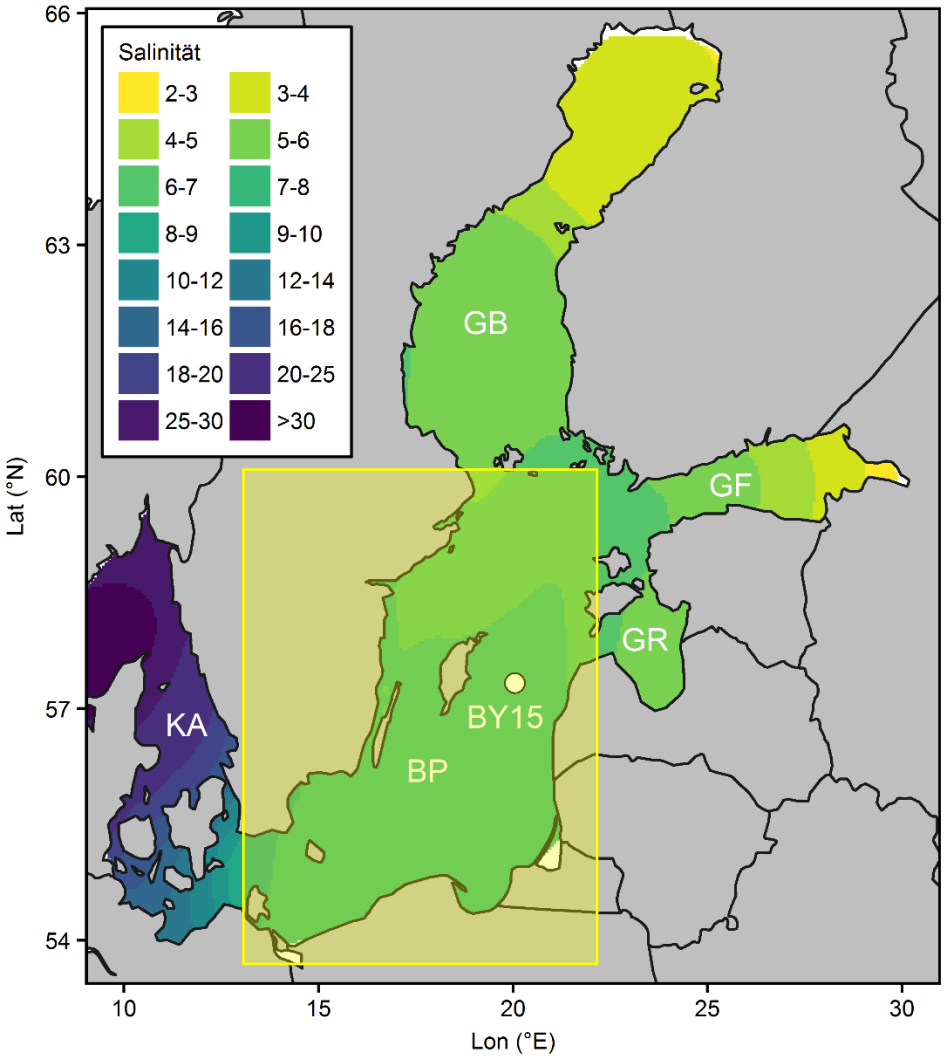
North: Granite



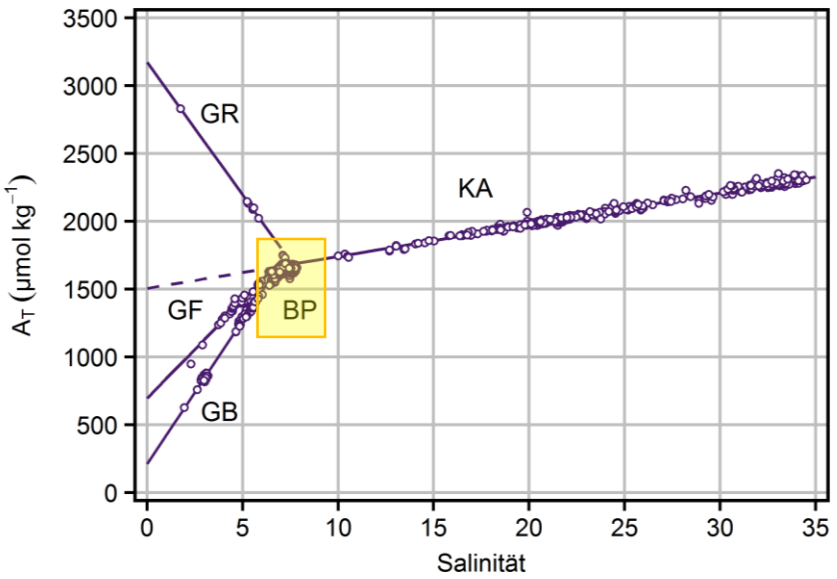
South: Limestone

Håkanson et al. (2003)

Besonderheiten der Ostsee: Hydrographie und CO_2-System



Jahr: 2008



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  - Ozean ca. 10^4 Jahre[2]

<u>Kompilierter Alkalinitäts-Datensatz</u>[3-5]

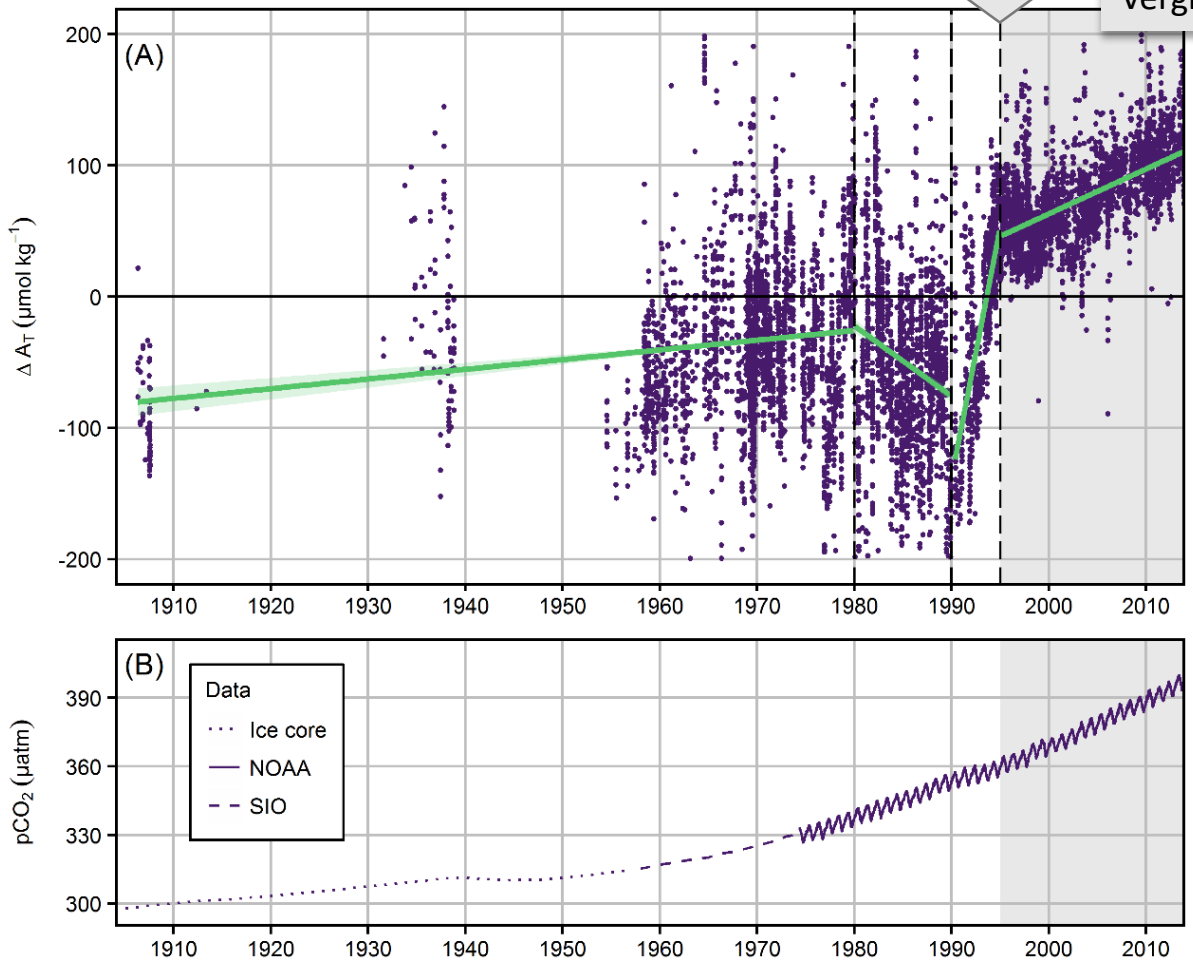
- Zeitraum: 1906 - 2015
- 31436 Messungen
- Oberflächenwasser <20 m

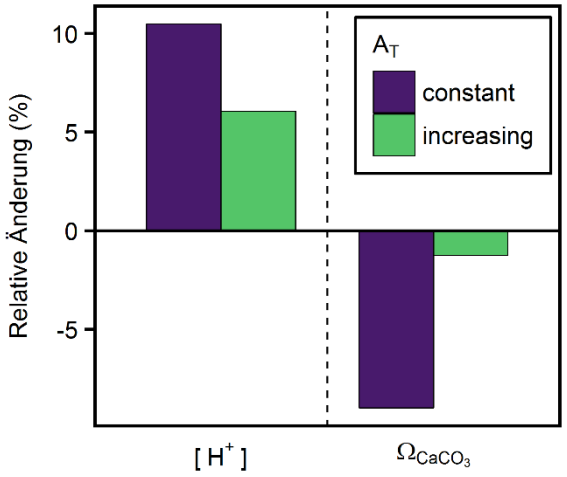
[1]Helcom (1993); [2]Sarmiento und Gruber (2006); [3]Hjalmarsson et al. (2008); [4]SHARK data base (2015); [5]M. Pertilla (pers. comm.)

Alkalinitätstrends in der zentralen Ostsee

Einführung von Referenzmaterialien!

1995 - 2014
Rate: +3.4 µmol kg^{-1} yr^{-1}
Relative Änderung: +5%
Vergl. Nordatlantik: +0.1%



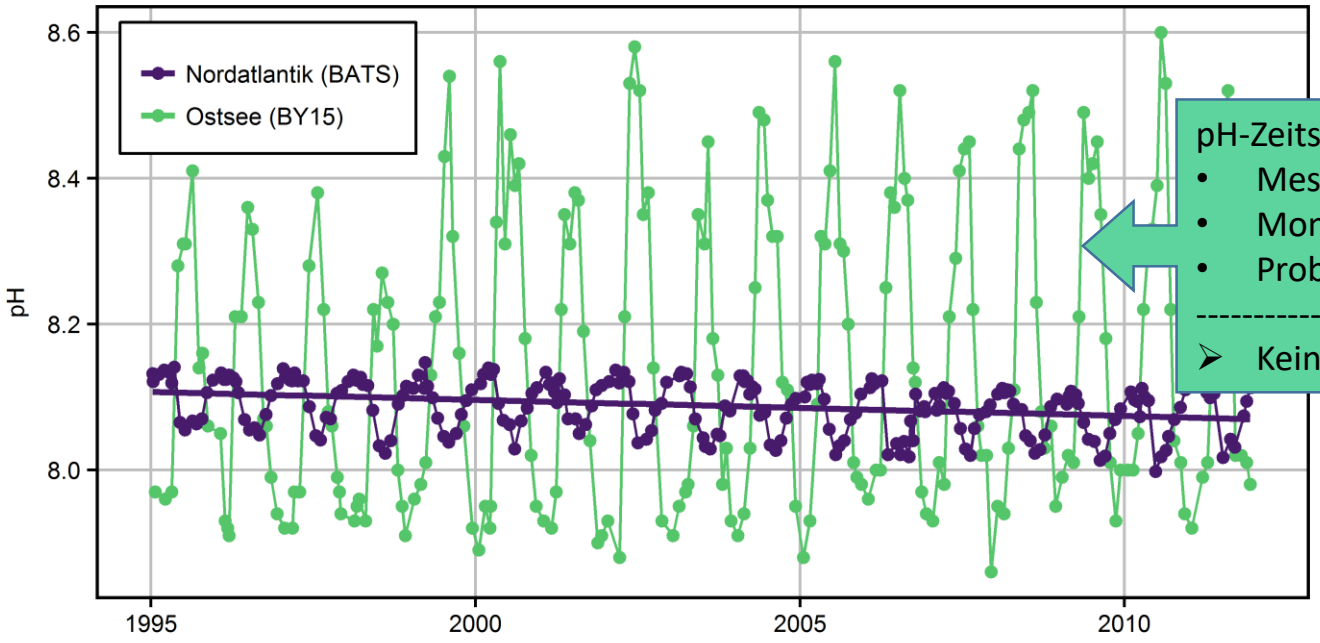


A_T-Anstieg wirkte Ozeanversauerung durch CO_2-Aufnahme entgegen!

[1]Müller et al. (2016)

pH Variabilität: Vergleich Ostsee (BY15) und Nordatlantik (BATS)

(1,2)



pH-Zeitserie Ostsee[2]
- Messung mit Glaselektrode
- Monatliche Ausfahrten
- Proben nur an Monitoring-Stationen

➢ Kein pH-Trend identifizierbar

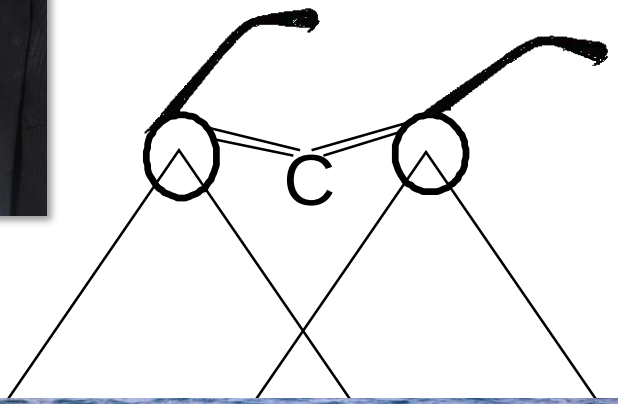
Fazit Ostsee

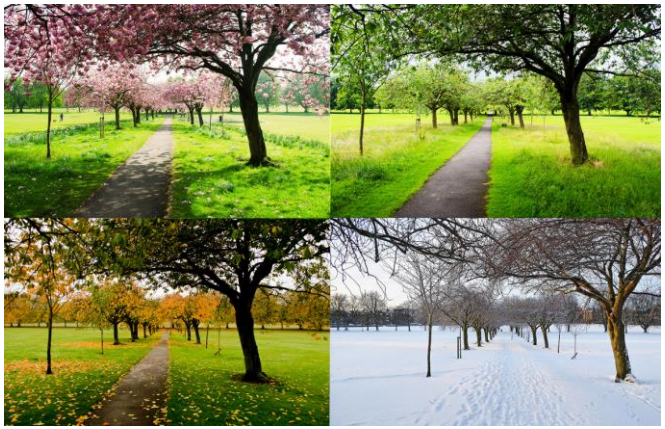
- Alkalinitätsanstieg pufferte Ozeanversauerung, Prognose unmöglich
- Starke pH-Schwankungen überlagern möglichen Langzeit-Trend
- Bisher keine adäquate pH-Messtechnik

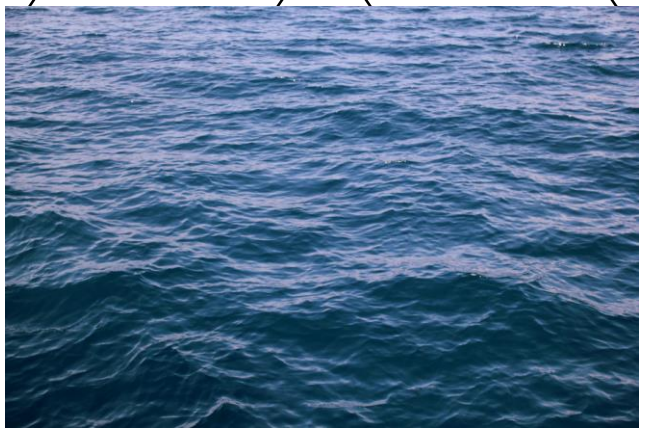
➢ Zeitlich und räumlich hochaufgelöste, genaue pH-Messungen erforderlich

[1]Bates et al. (2012); [2]SMHI Monitoring Daten

Biogeochemical transformations in the Baltic Sea: Observations through carbon dioxide glasses







Nutrients

- Small amounts
- Deviations from Redfield

$$106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122\ H_2O + 18\ H^+$$

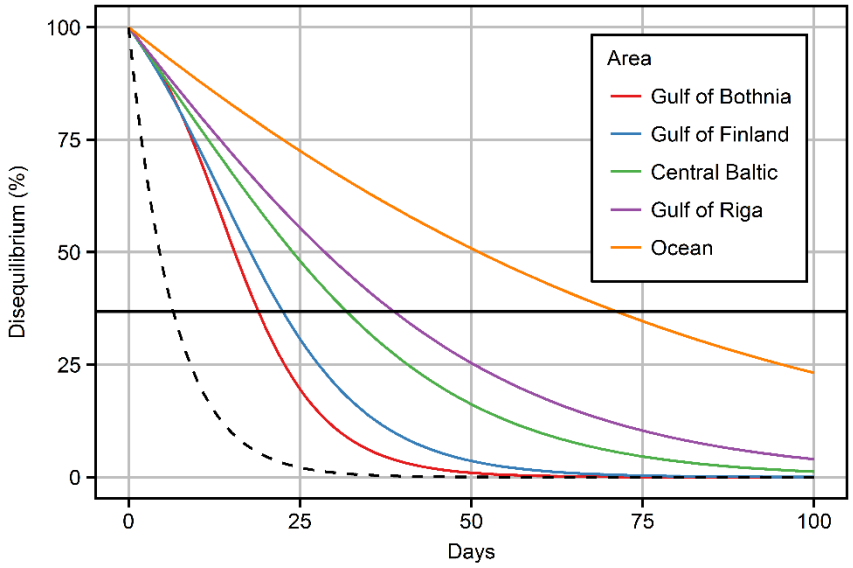
Organic matter production

Mineralization

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138\ O_2$$

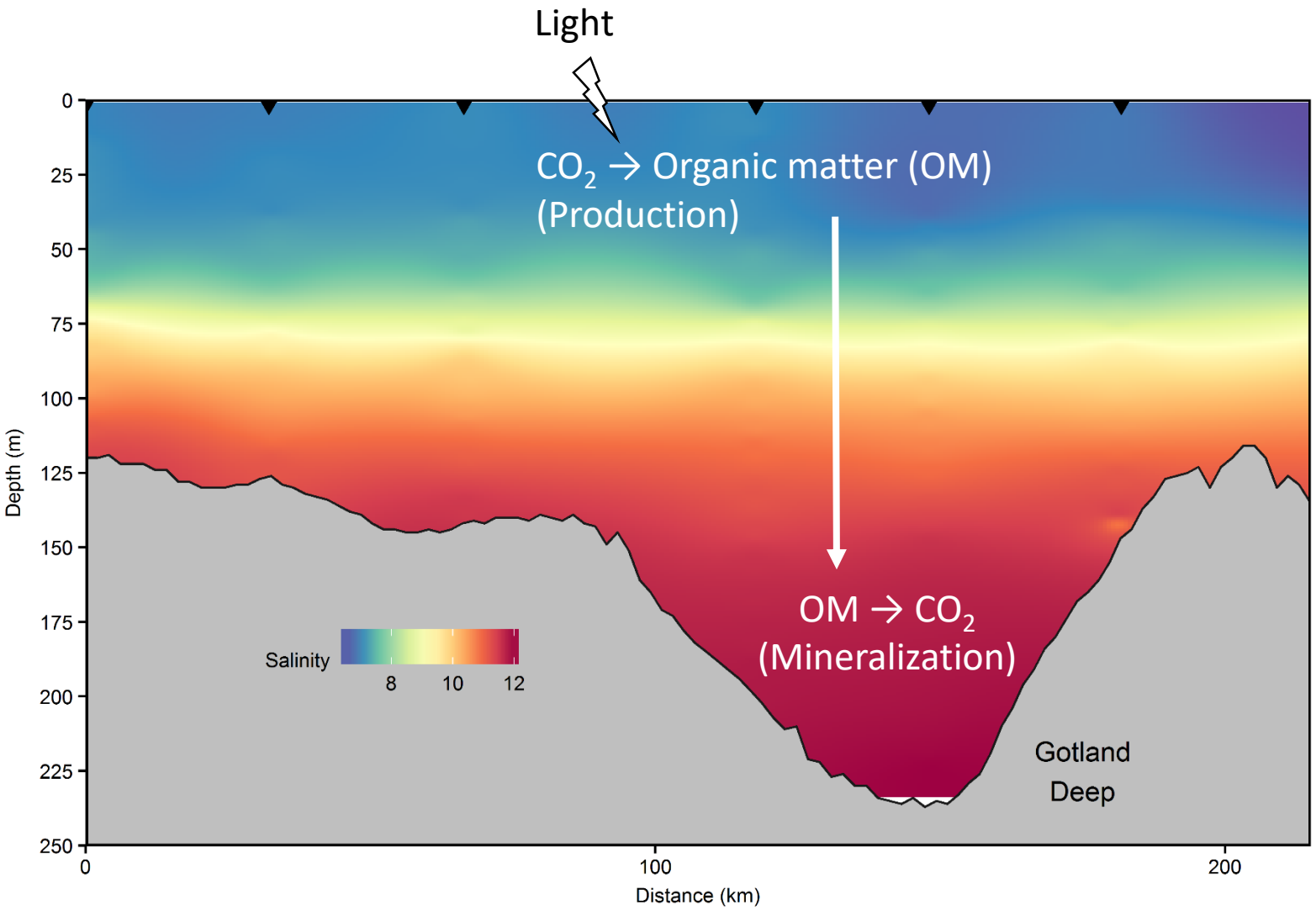
Carbon dioxide

- Retarded equilibration
- Inevitably involved in production/mineralization

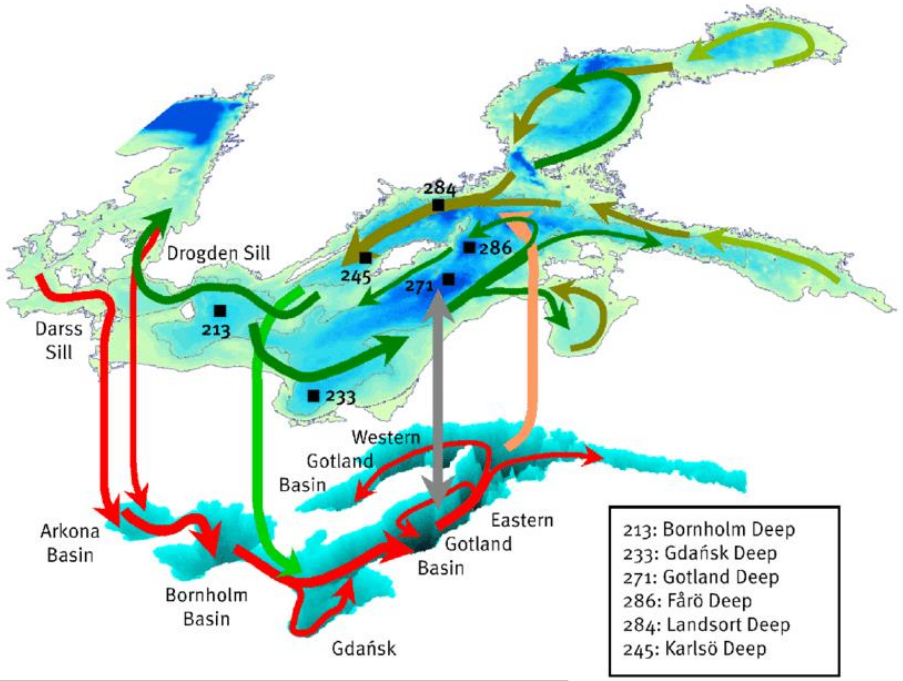


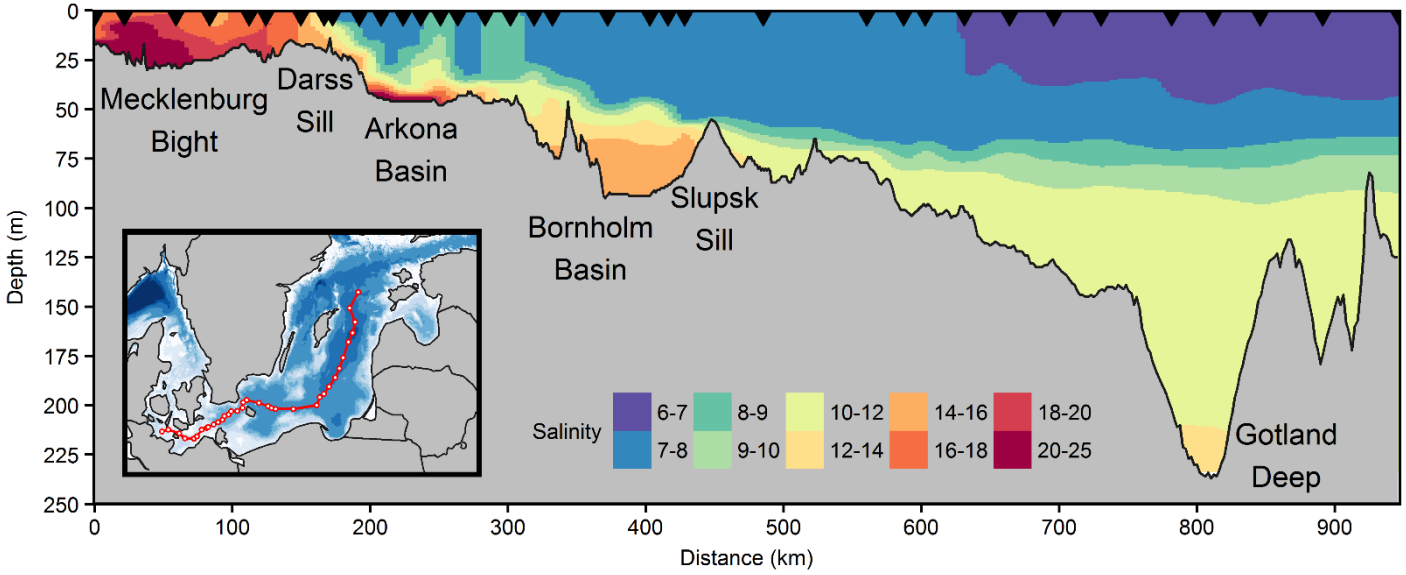
Oxygen

- Alternative e⁻-acceptors
  - Fast equilibration


Light
CO_2 → Organic matter (OM)
(Production)
OM → CO_2
(Mineralization)
Salinity
8
10
12
Gotland
Deep
Depth (m)
0
25
50
75
100
125
150
175
200
225
250
0
100
200
Distance (km)

- Salty and dense water from the North Sea fills the deep basins of the Baltic Sea
- A surplus of less saline surface water from river discharge flows out of the Baltic Sea

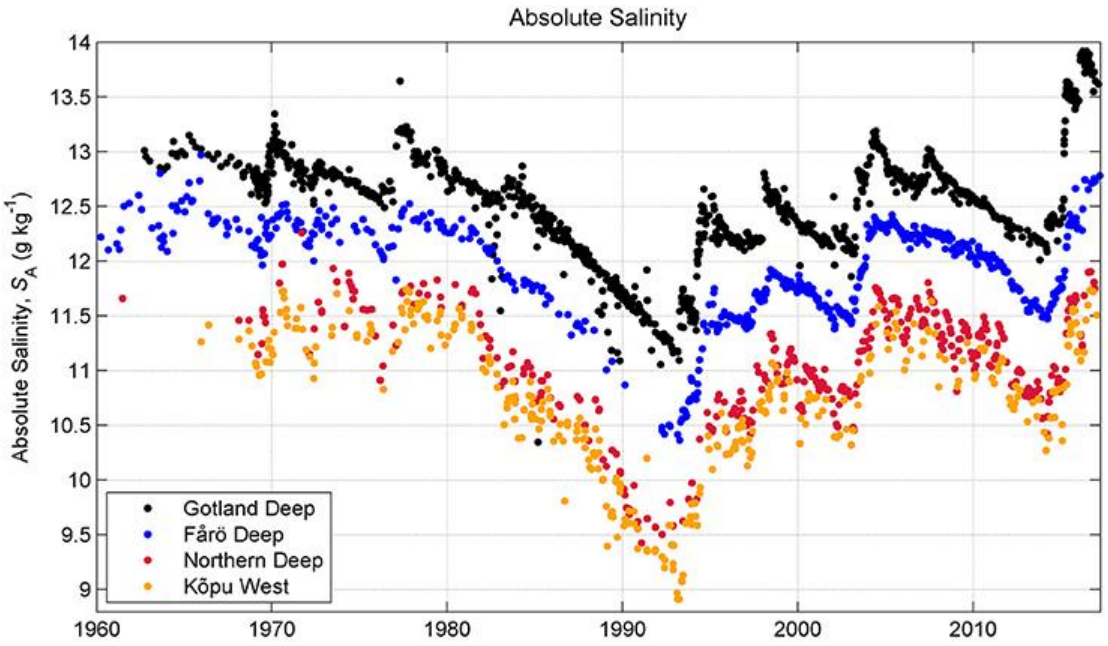


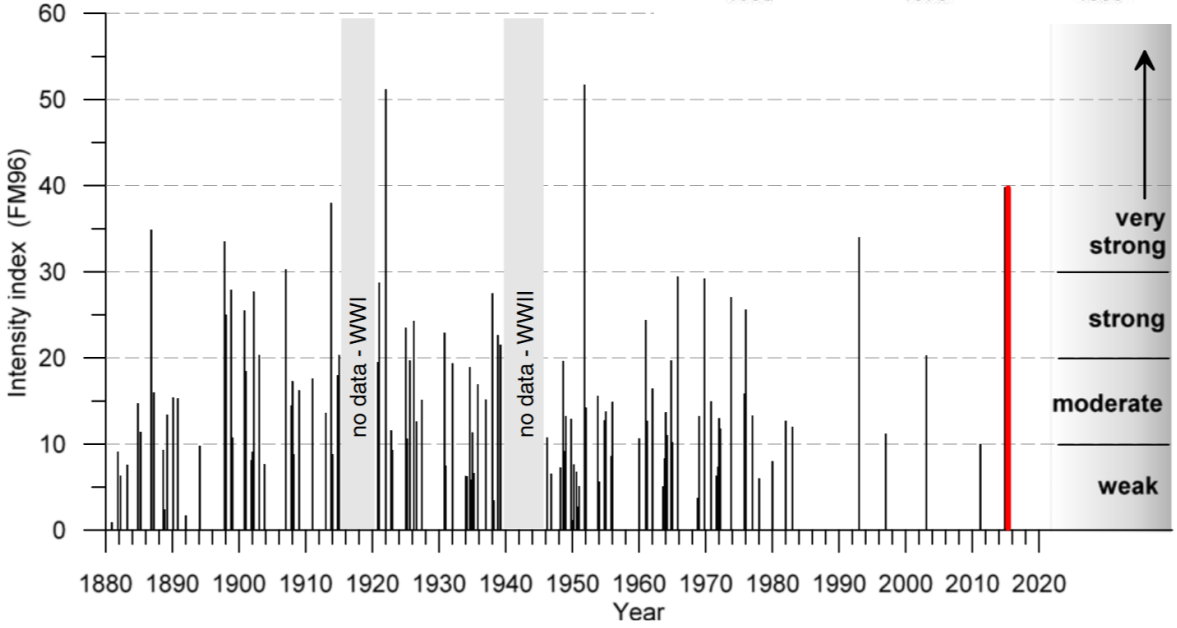


Elken & Matthäus (2008)

Majory Baltic Inflow (MBI) events

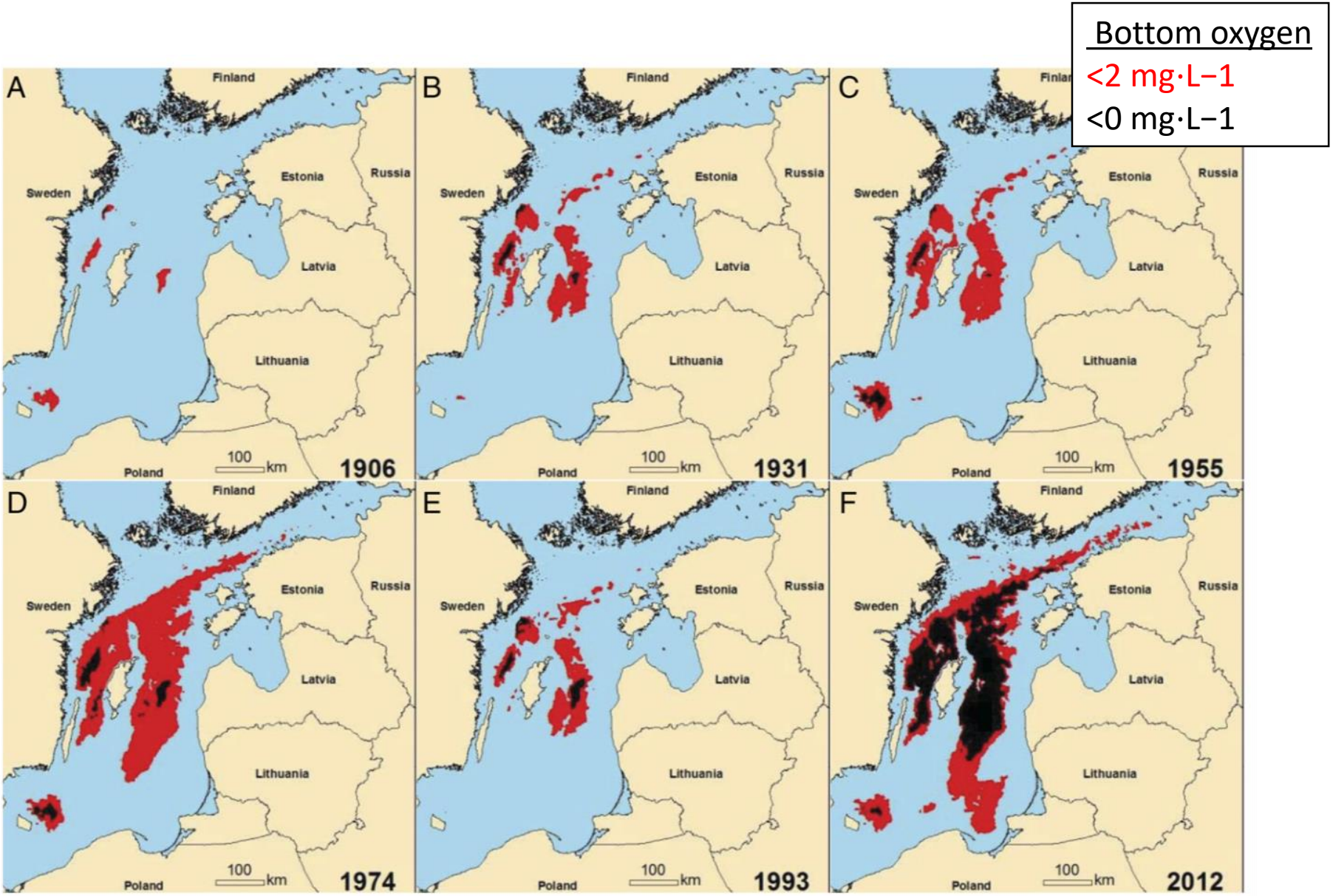
- Saltwater inflows happen in large inflow events



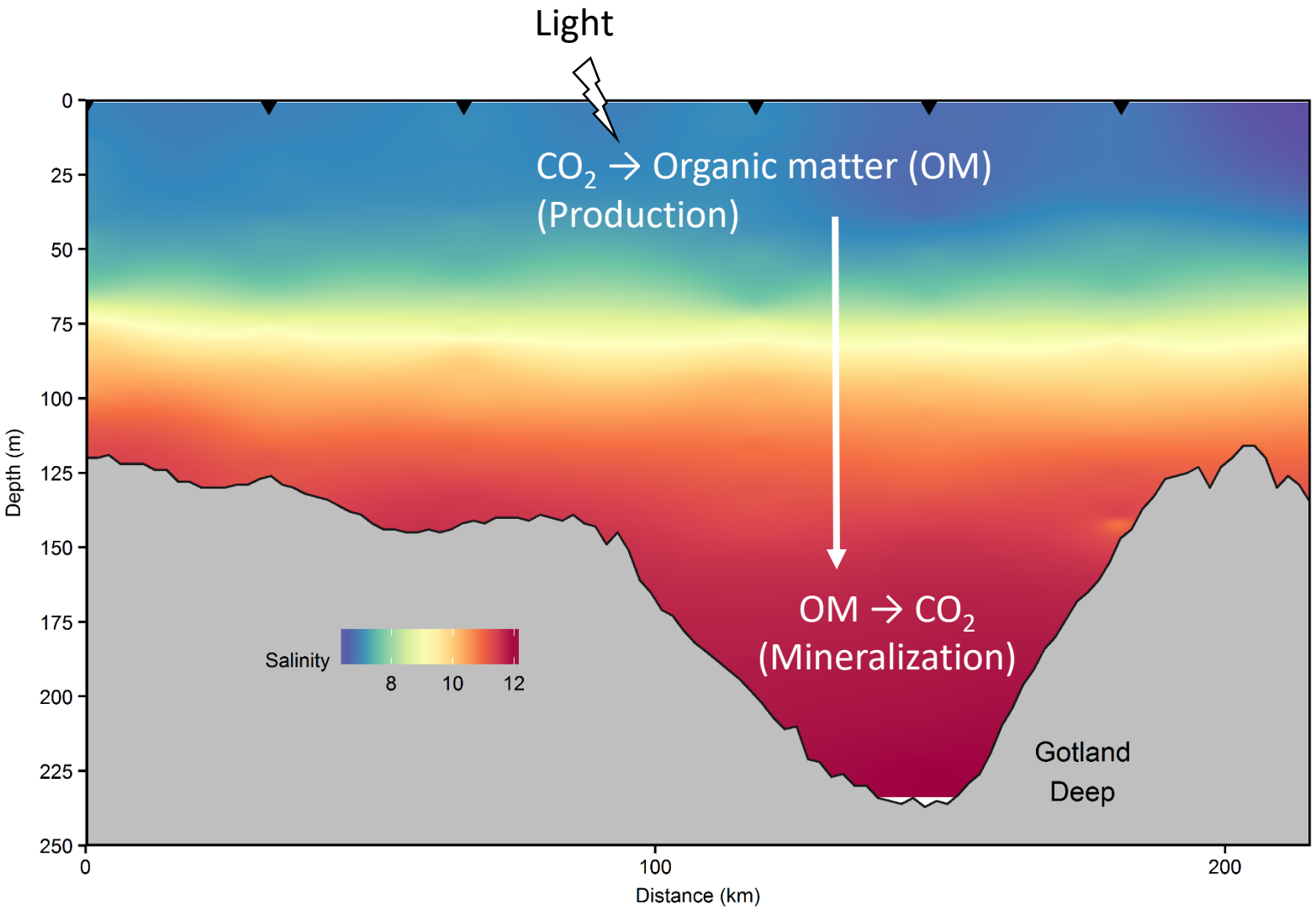


Liblik et al. (2018)

Increasasing hypoxic and anoxic areas (dead zones)



Carstensen et al. (2014)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OM → CO_2
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Gotland
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8
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Depth (m)
0
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50
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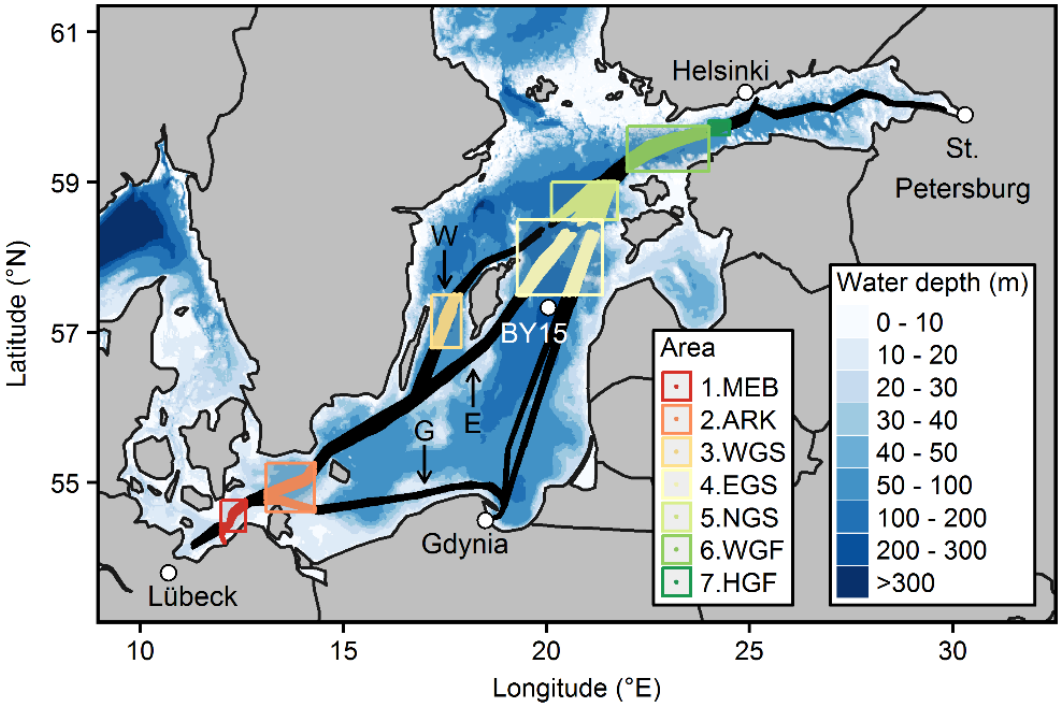
125
150
175
200
225
250
0
100
200
Distance (km)

Observation of the Baltic Sea CO_2-system since 2003



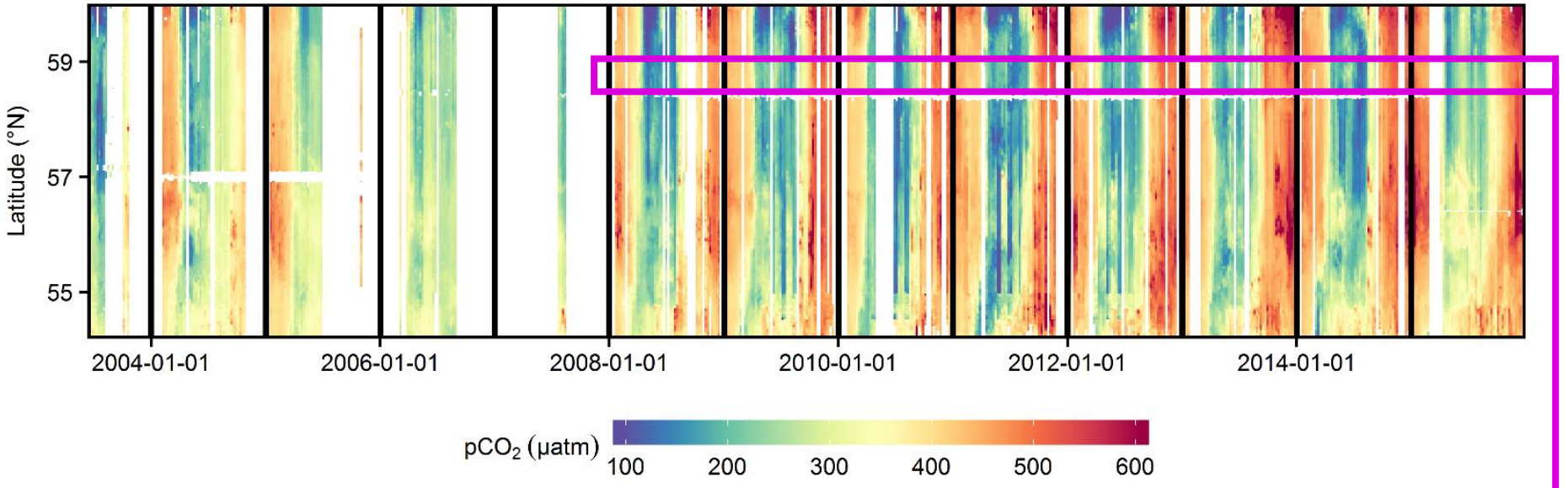
VOS Finnmaid

- Automated pCO_2 measurements
  - Up to 5 transects / week
    - Total: 1600 transects
  - Mainly eastern route (E)
    - Production studies

Monitoring BY15

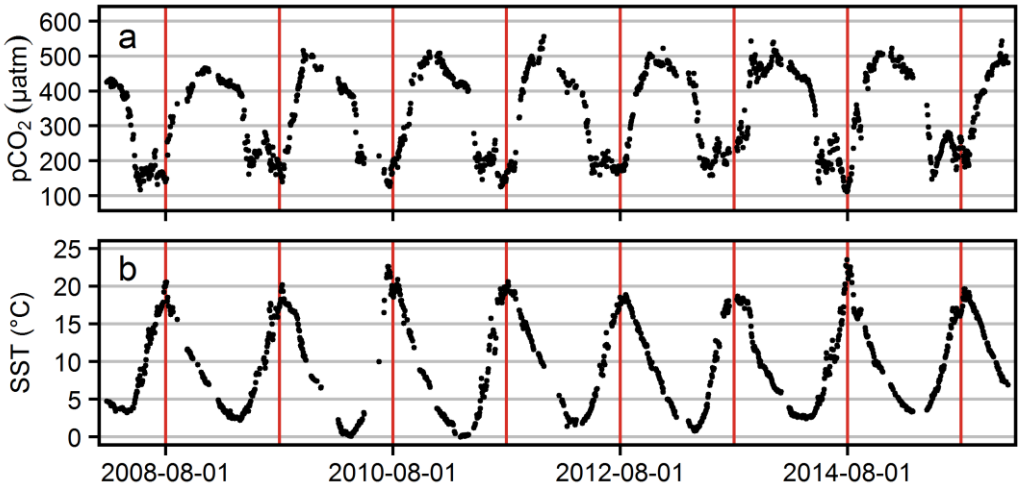
- Discrete C_T measurements
- 100 – 233m in steps of 25m
- Total: 58 profiles
- Mineralization studies

Surface water pCO_2 patterns

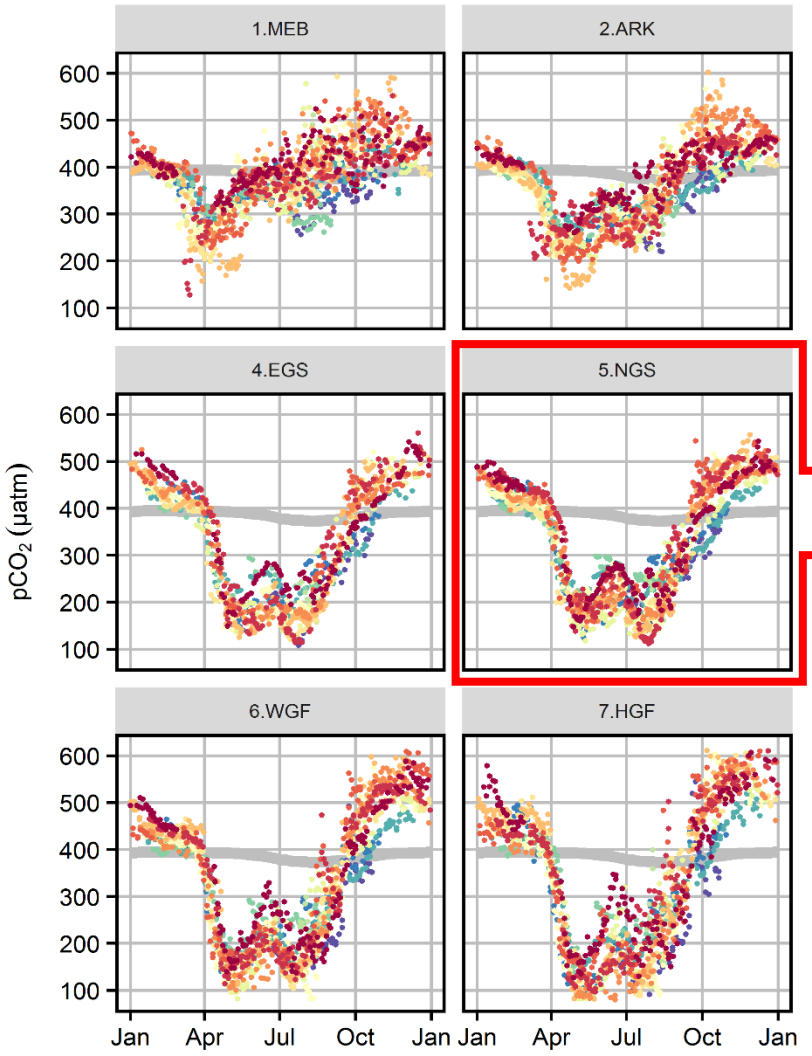


<u>Characteristics</u>

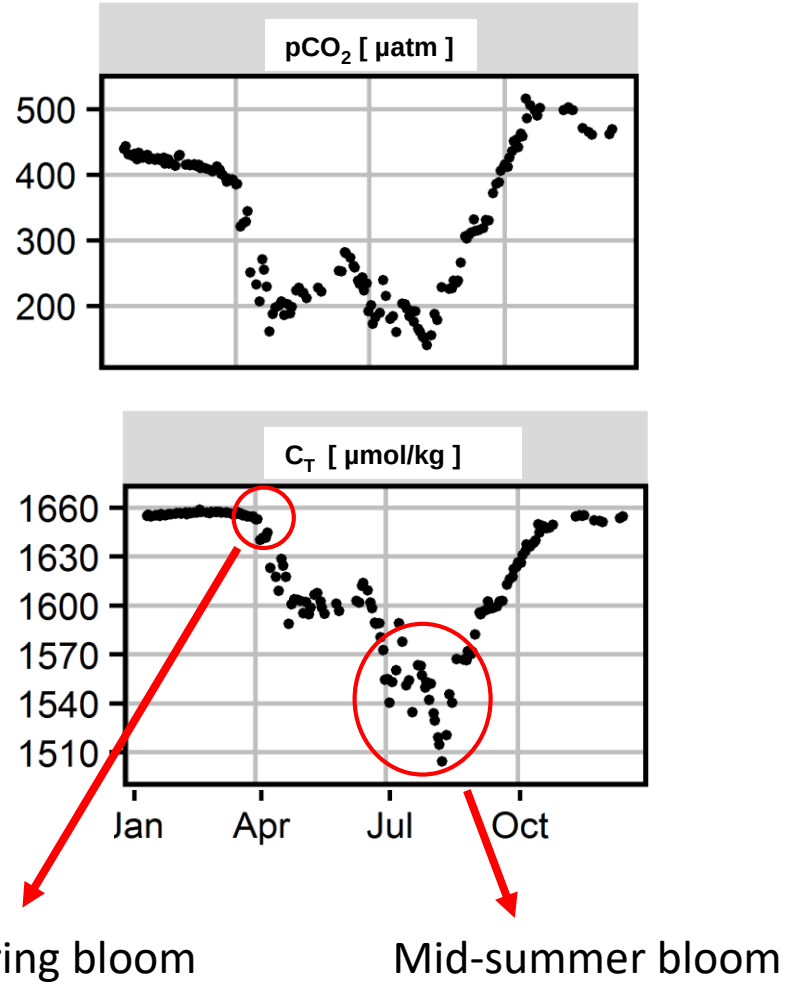
- Strong pCO_2 amplitude:
  - S->N gradient
- Anti-correlation with temperature:
  - Biological control



The seasonality of pCO_2, 2003 – 2014.



The fine structure of the CO_2 partial pressure (pCO_2) and total CO_2 (C_T) seasonality in the northern Gotland Sea (2009)



Spring bloom net community production, integrated over depth, iNCP [mmol-C/m^2]

Not available for mid-summer bloom!

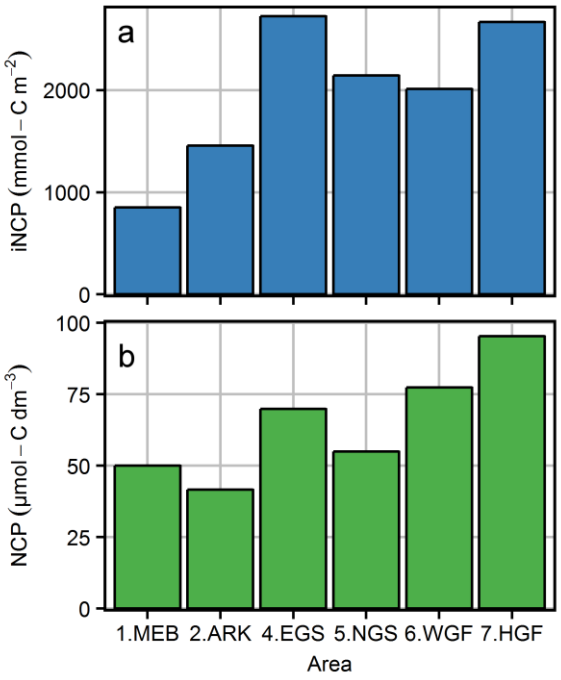
$$iNCP = (\Delta C_T \cdot z_{eff} + F_{AS} \cdot \Delta t) \cdot 0.8$$

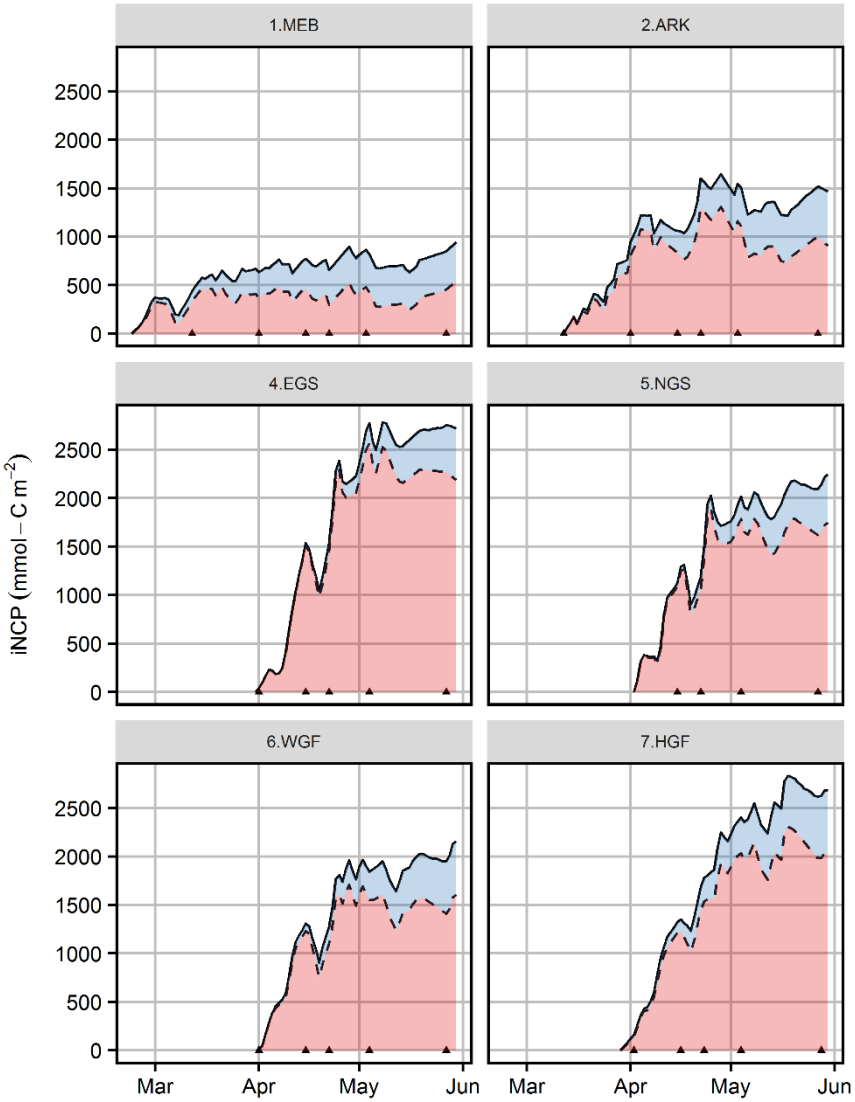
F_{AS} – CO_2 exchange with the atmosphere;

Z_{eff} – effective penetration depth;

Δt considered time intervall;

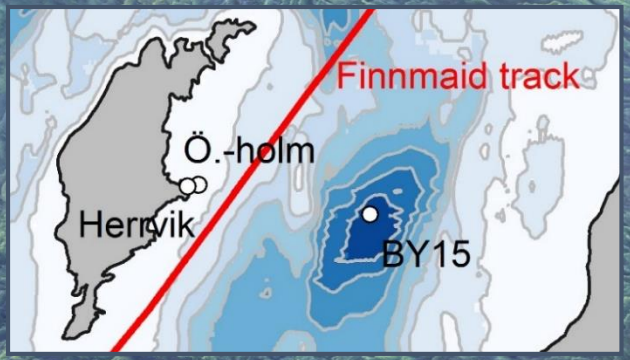
All sub-transects:





#BloomSail

Chasing Cyanobacteria Blooms
in the Baltic Sea with SV Tina V

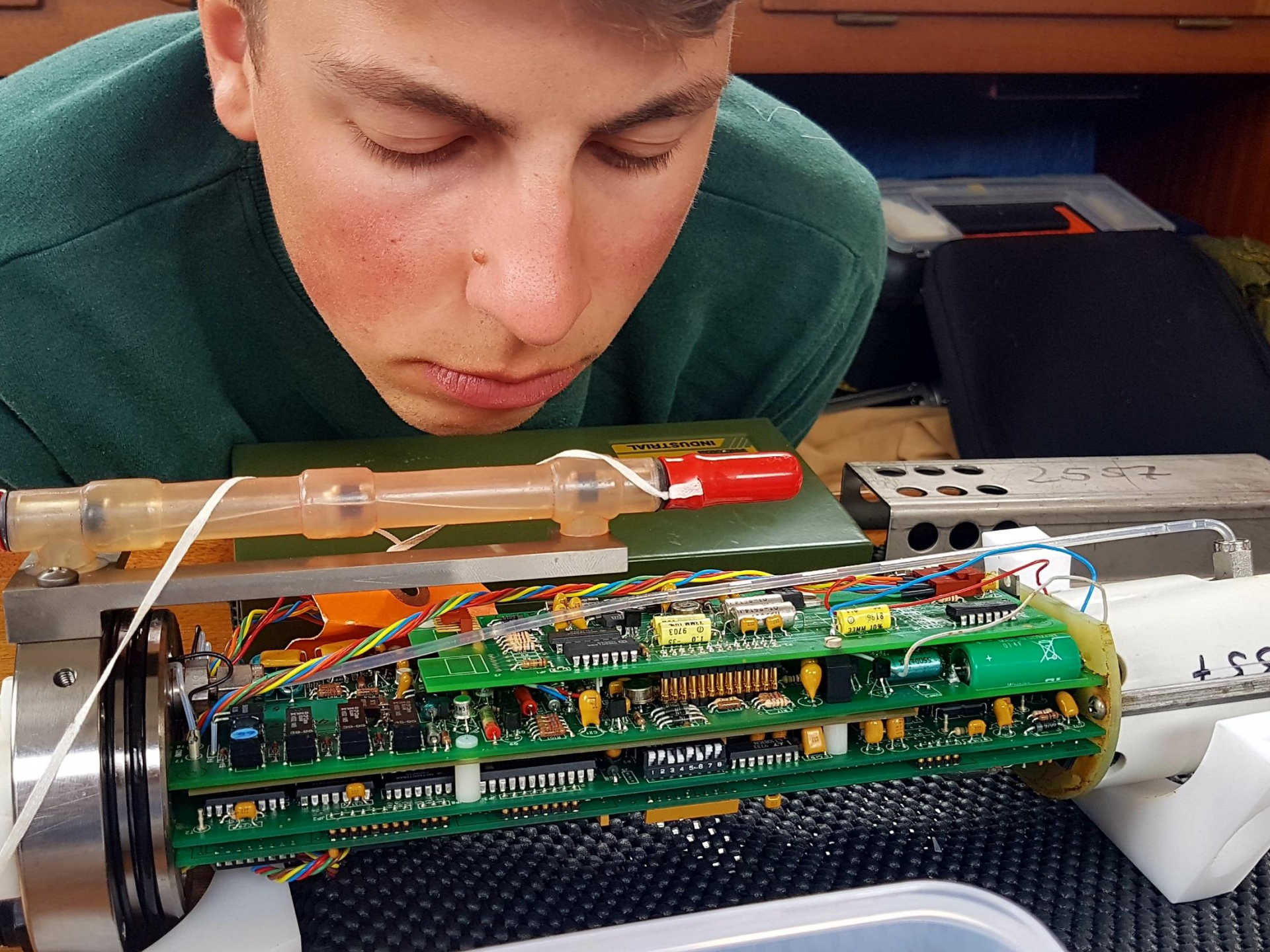


Vessel: 27 foot sailing vessel Tina V
Time: June – Aug 2018
Crew: Jens D. Müller + 6 x 2 sailors

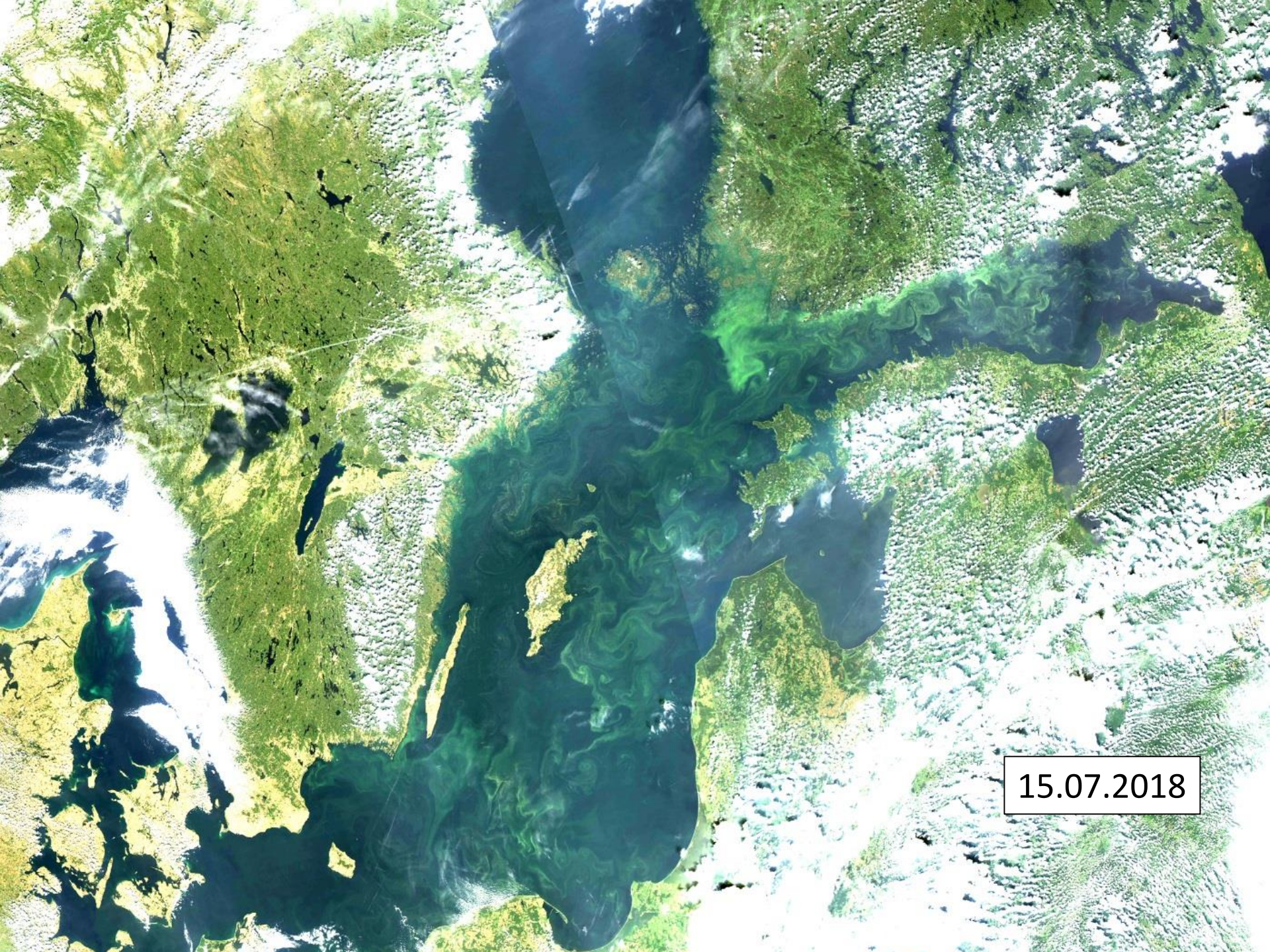
Sensor-package for
surface transects and profiles:
pCO_2, pH, O_2, Chla, CTD

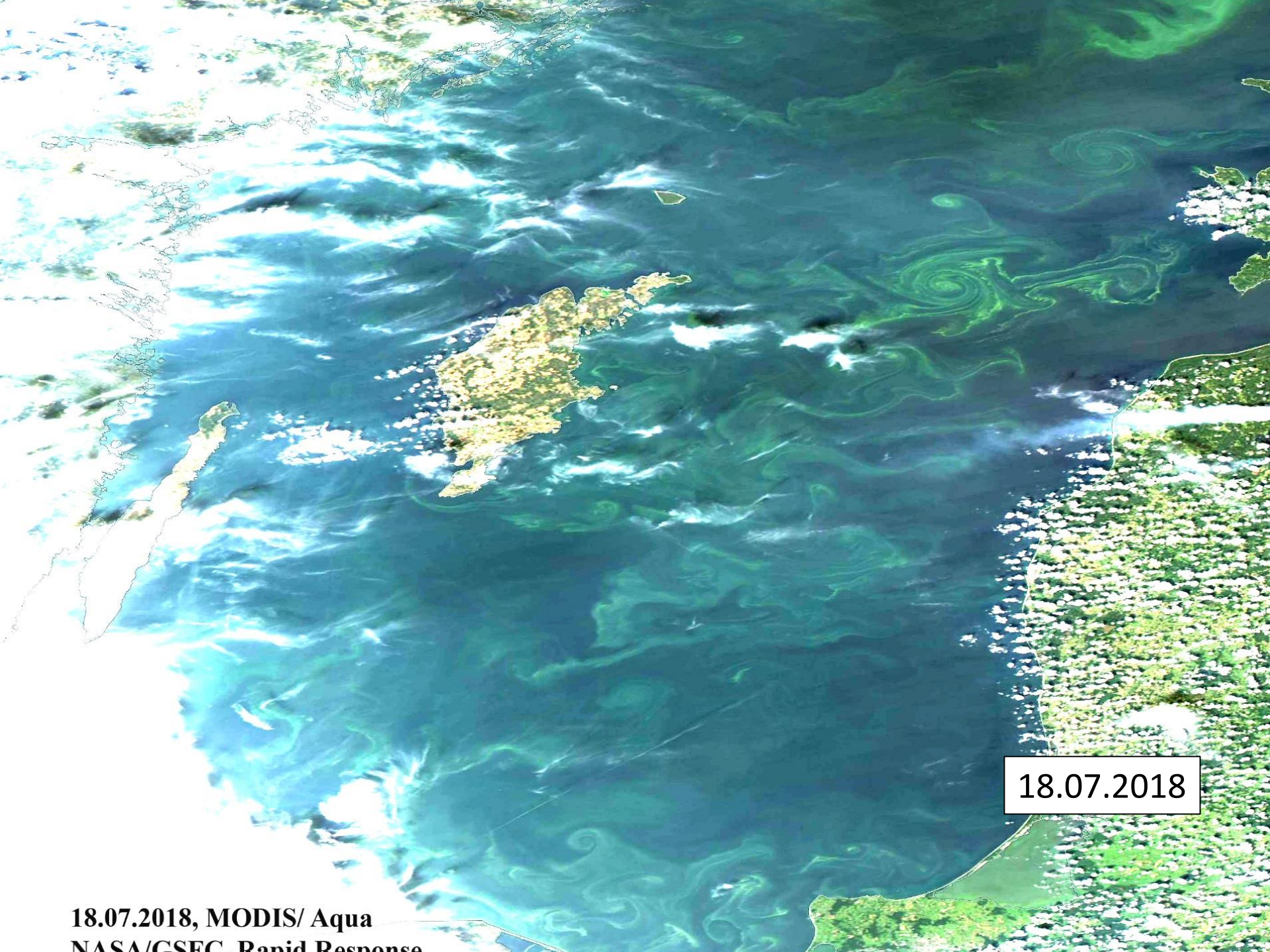
Discrete Sampling: Nutrients, POM, Phytoplankton


Café
Niedlich

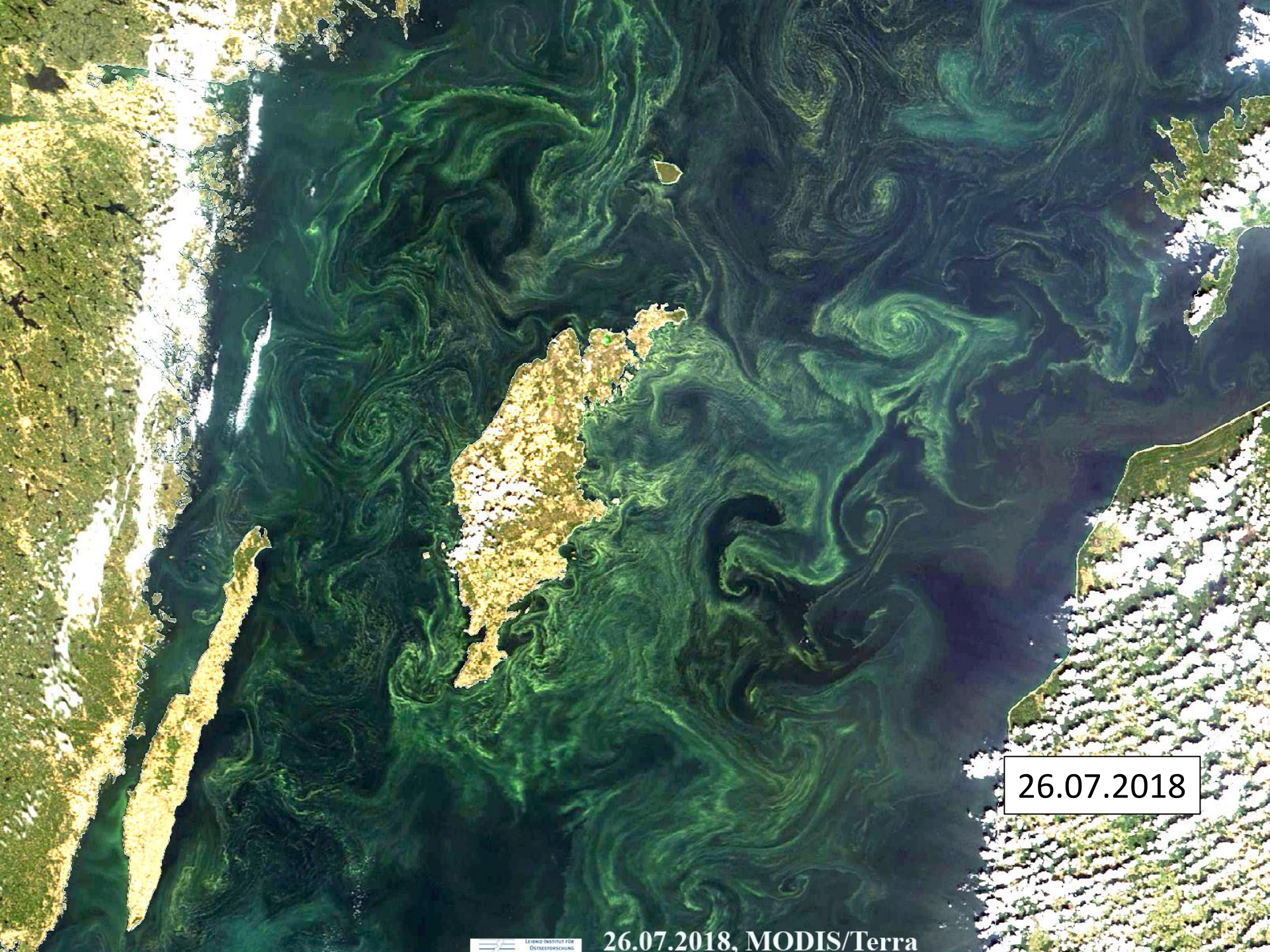

INDUSTRIAL

01.07.2018, MODIS/Aqua
NASA/GSFC, Rapid Response


15.07.2018



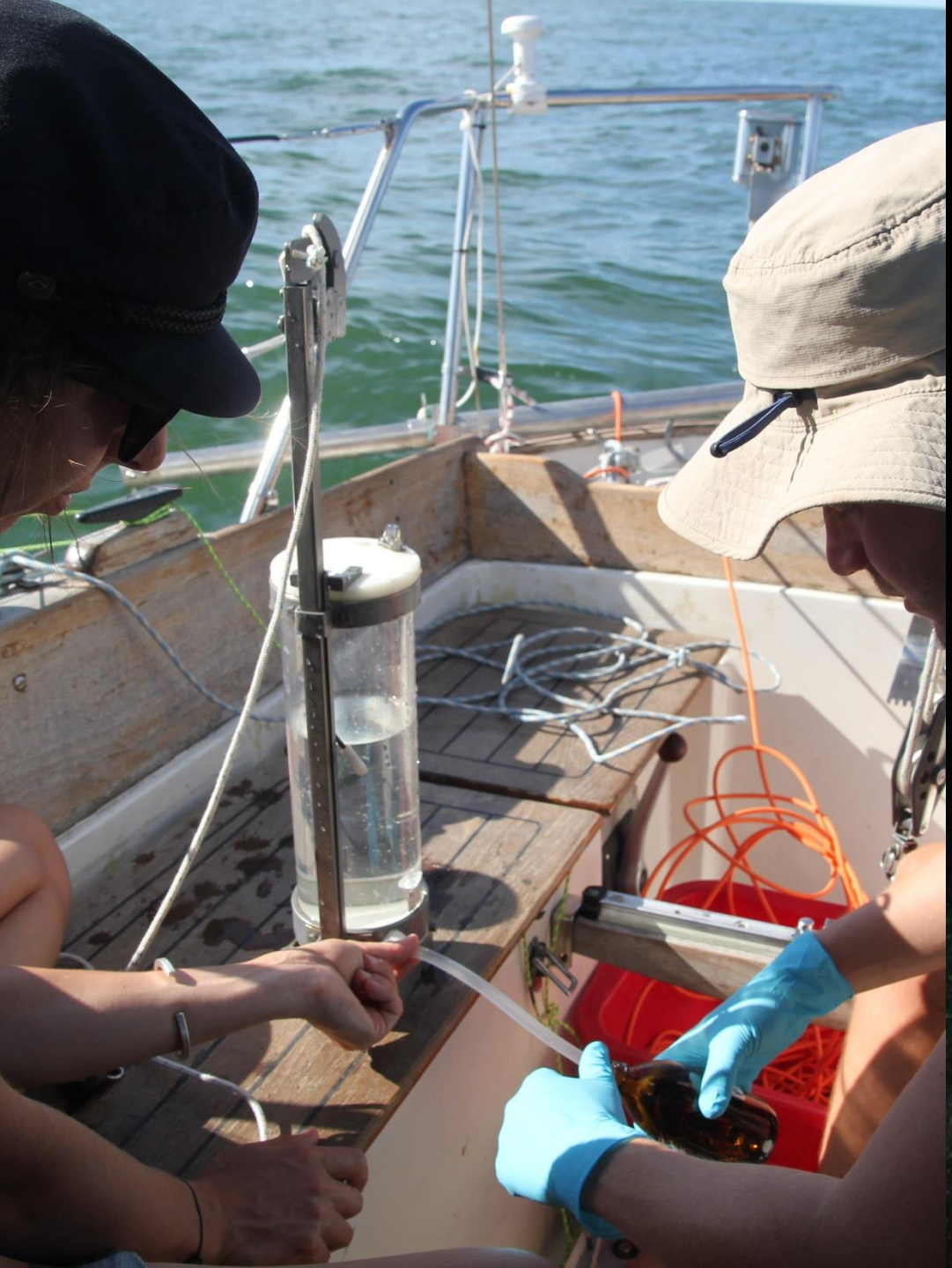
18.07.2018, MODIS/ Aqua
NASA/GSFC, Rapid Response



26.07.2018, MODIS/Terra

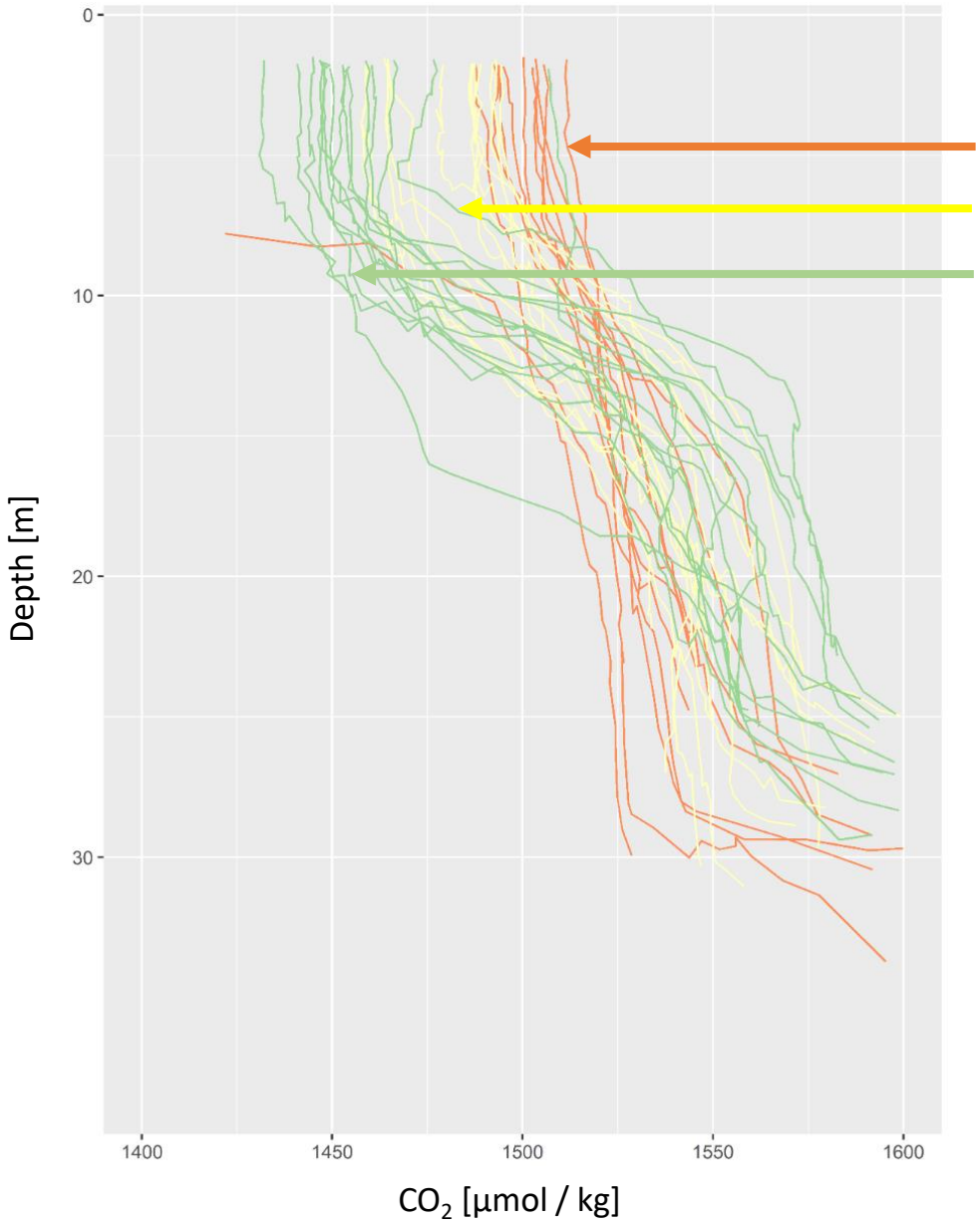
03.08.2018


Leibniz Institute for
Baltic Sea Research




LEIBNIZ
BALTIC SEA
WARNE

Vertical CO_2 distribution during Cyanobacteria bloom



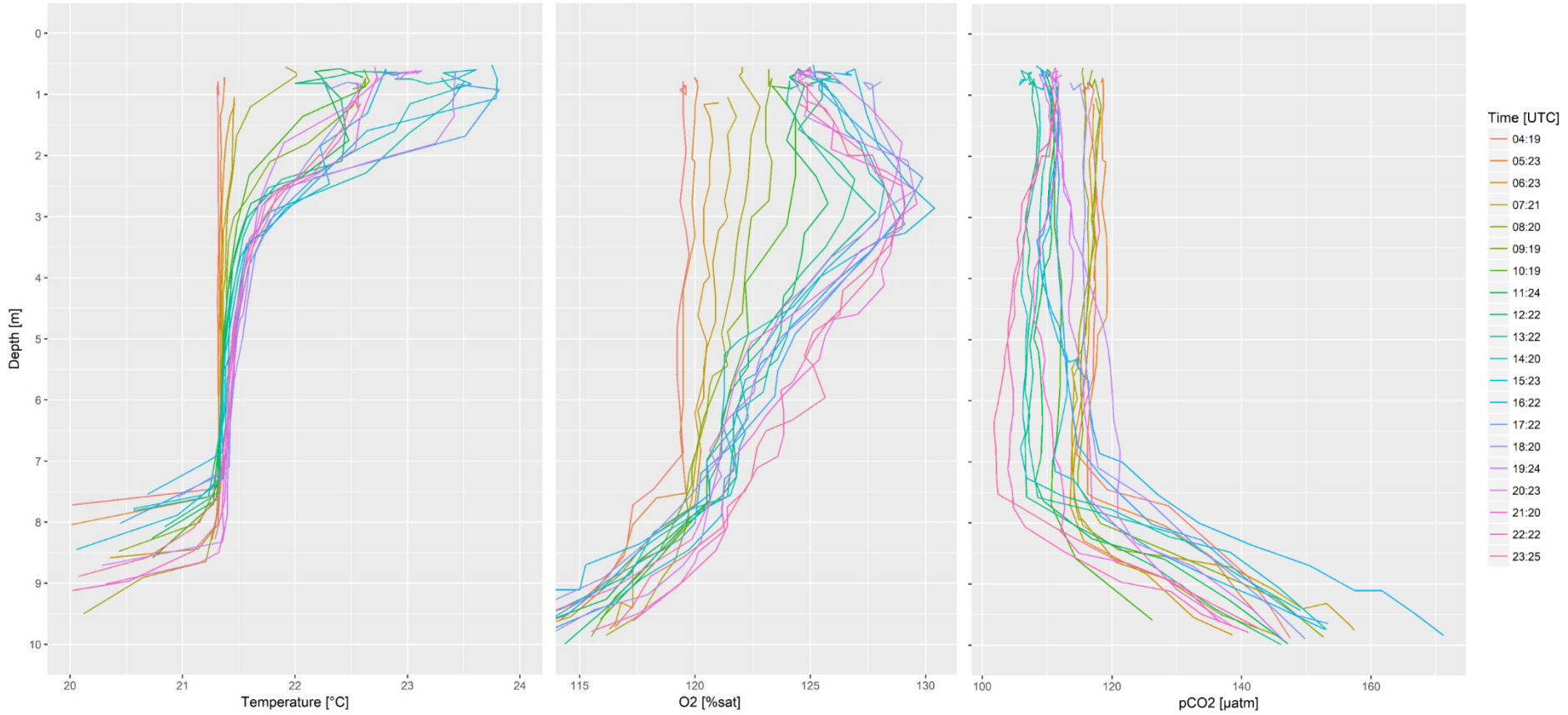
Before Bloom (July 5)

Start Bloom (July 9)

Developped Bloom (July 18)


24h experiment

Diurnal productivity cycle



N58°06'

N57°54'

N57°42'

N57°

Jens_Fron

N57°

E 19°15'

N57°06'


298
18

Thanks for your interest &
see you at sea!