INSTITUTE OF OCEANOLOGY
POLISH ACADEMY OF SCIENCES

The acid-base system of the Baltic Sea

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2nd Baltic Earth Conference
The Baltic Sea Region in Transition
Helsingor, Denmark, 11-15 June 2018

Baltic Earth
Earth System Science for the Baltic Sea Region

BONUS INTEGRAL
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BONUS SCIENCE FOR A BETTER FUTURE OF THE BALTIC SEA REGION
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Seawater acid-base system

Measurable parameters:

- C_T – total CO_2 concentration (DIC)

  $C_T = [CO_2]^* + [HCO_3^-] + [CO_3^{2-}]$

- A_T – total alkalinity

  $A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + \ldots - [H^+] - \ldots$

- pCO_2 – CO_2 partial pressure

- pH –spectrophotometric measurement with m-cresol purple, total scale

  $pH_T = -\log([H^+]_F + [HSO_4^-]) = -\log[H^+]_T$

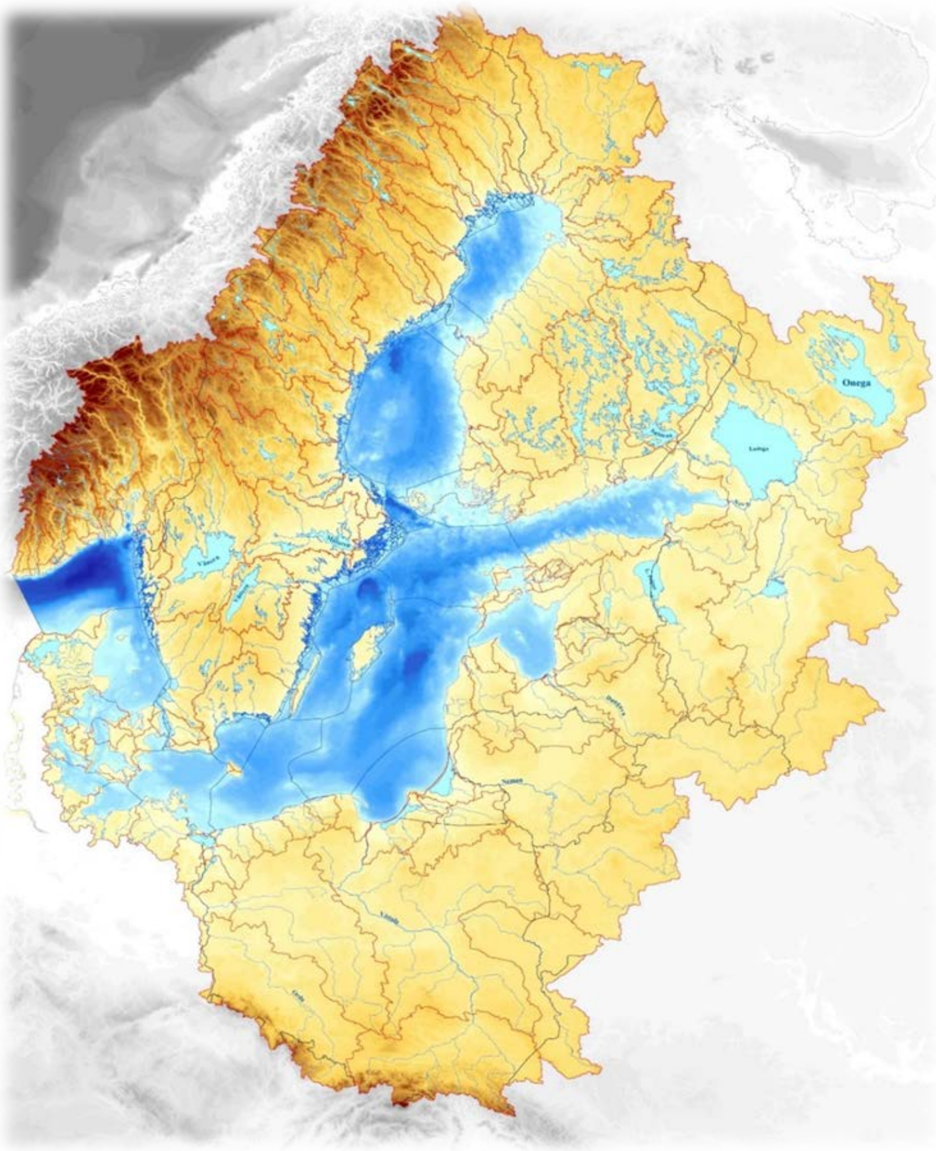
It is possible to calculate 2 parameters when the following is known:

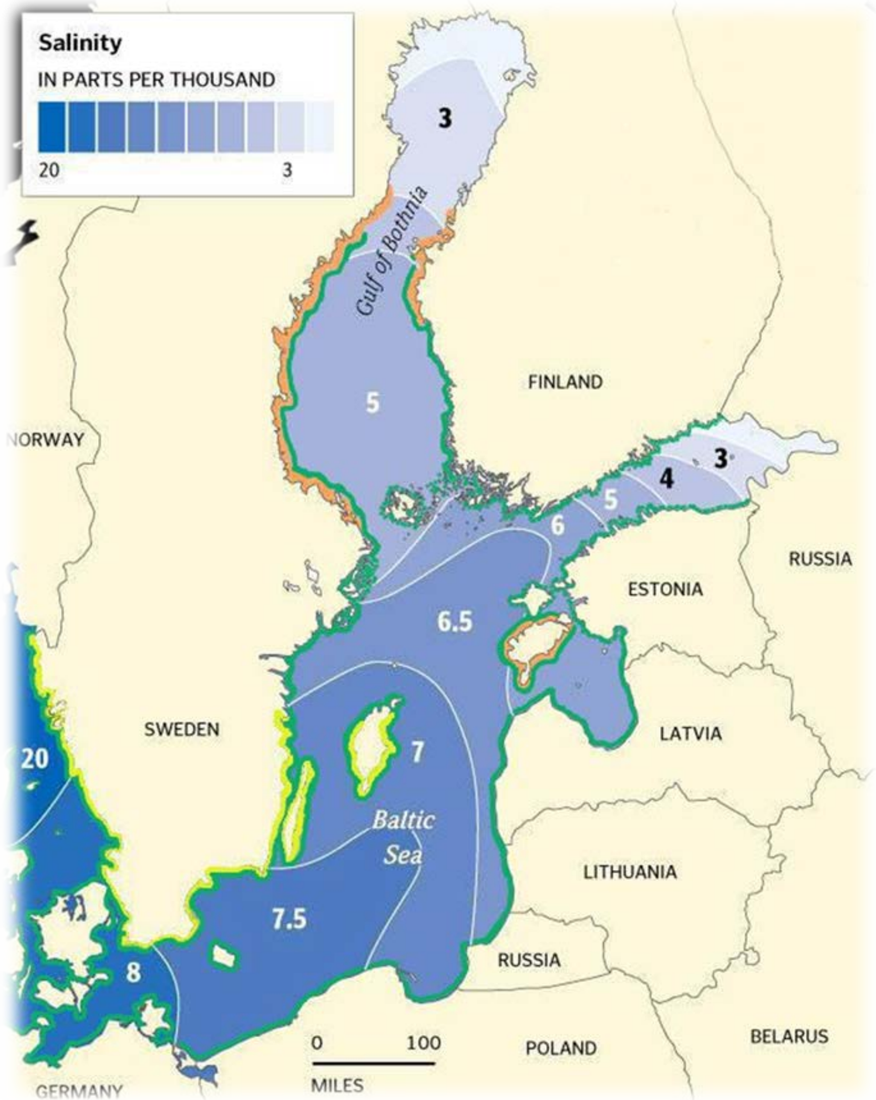
- other 2 parameters
- temperature & salinity
- equilibrium constants for each of the acid dissociation reactions
- total concentrations for each non-CO_2 substances

The pair used in the calculations:

- C_T & A_T – recommended, used in biogeochemical modelling

The Baltic Sea

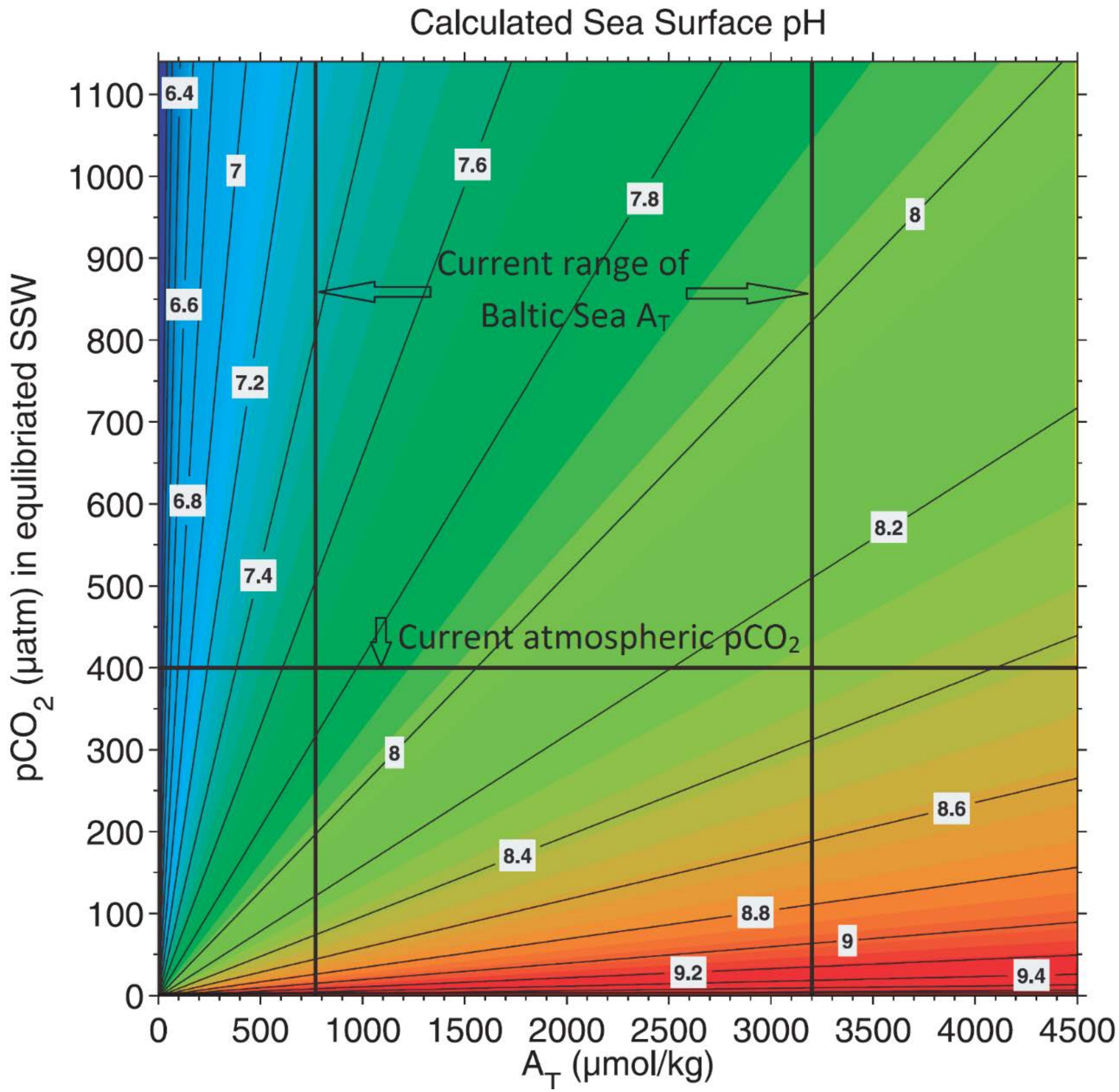




Source: SMHI

Source: balticseaweed.com

A_T variability in the Baltic Sea



Kuliński et al., 2017, Earth Syst. Dynam.
modified after Omstedt et al., 2010

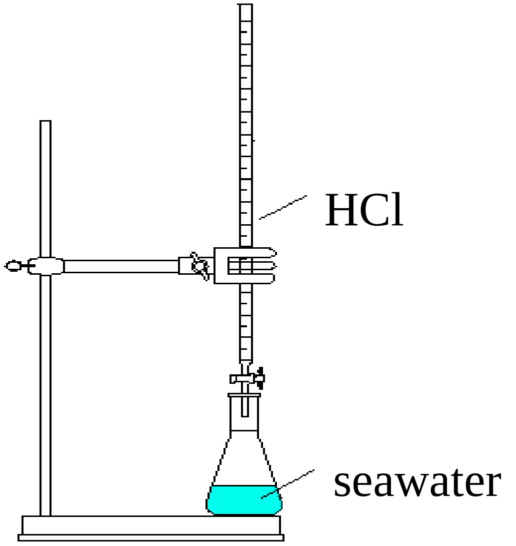
Total alkalinity

The total alkalinity of seawater is defined as the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25ºC) over proton donors (acids with $K > 10^{-4.5}$) and expressed as a hydrogen ion equivalent in one kilogram of sample (Dickson, 1981):

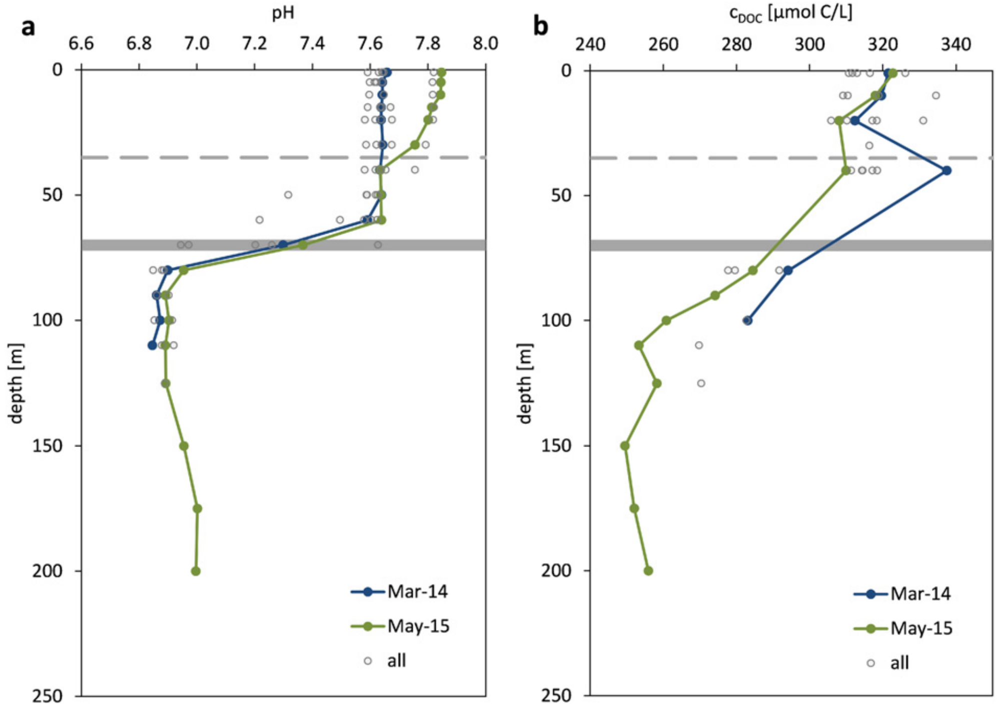
$$\mathbf{A_T} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots + \text{Organics}$$

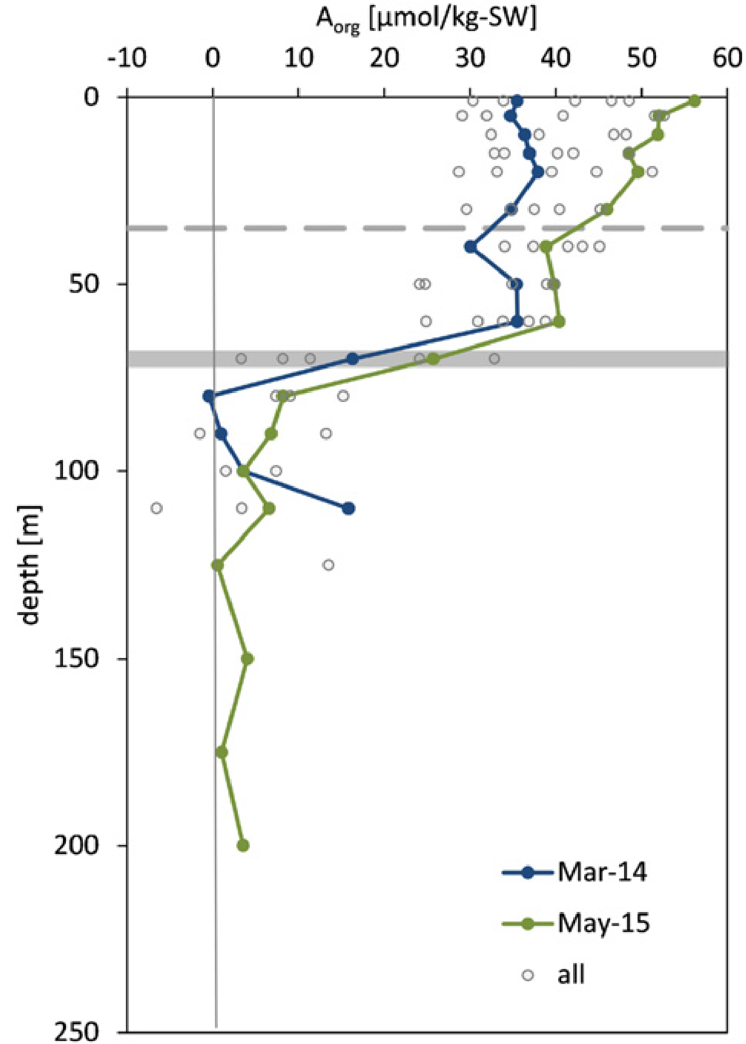
$$- [H^+]_{wolny} - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots$$

$$A_T = A_{inorganic} + A_{org}$$



Organic alkalinity





Hammer et al., 2017, J. Mar. Syst.

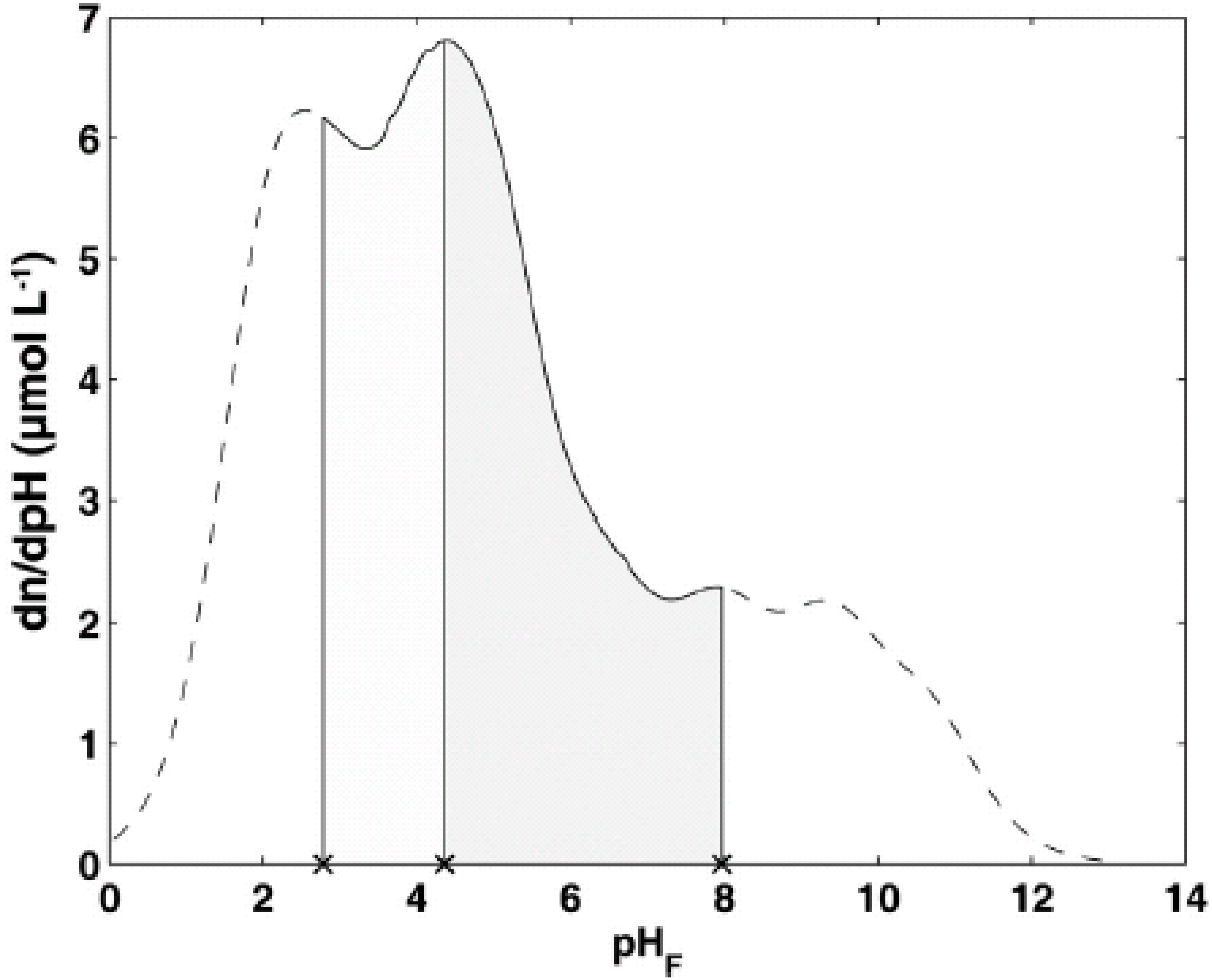
$$K_{DOM} = \frac{[H^+] \cdot A_{org}}{(f \cdot DOC) - A_{org}}$$

$f = 0.12$

$pK_{DOM} = 7.34$

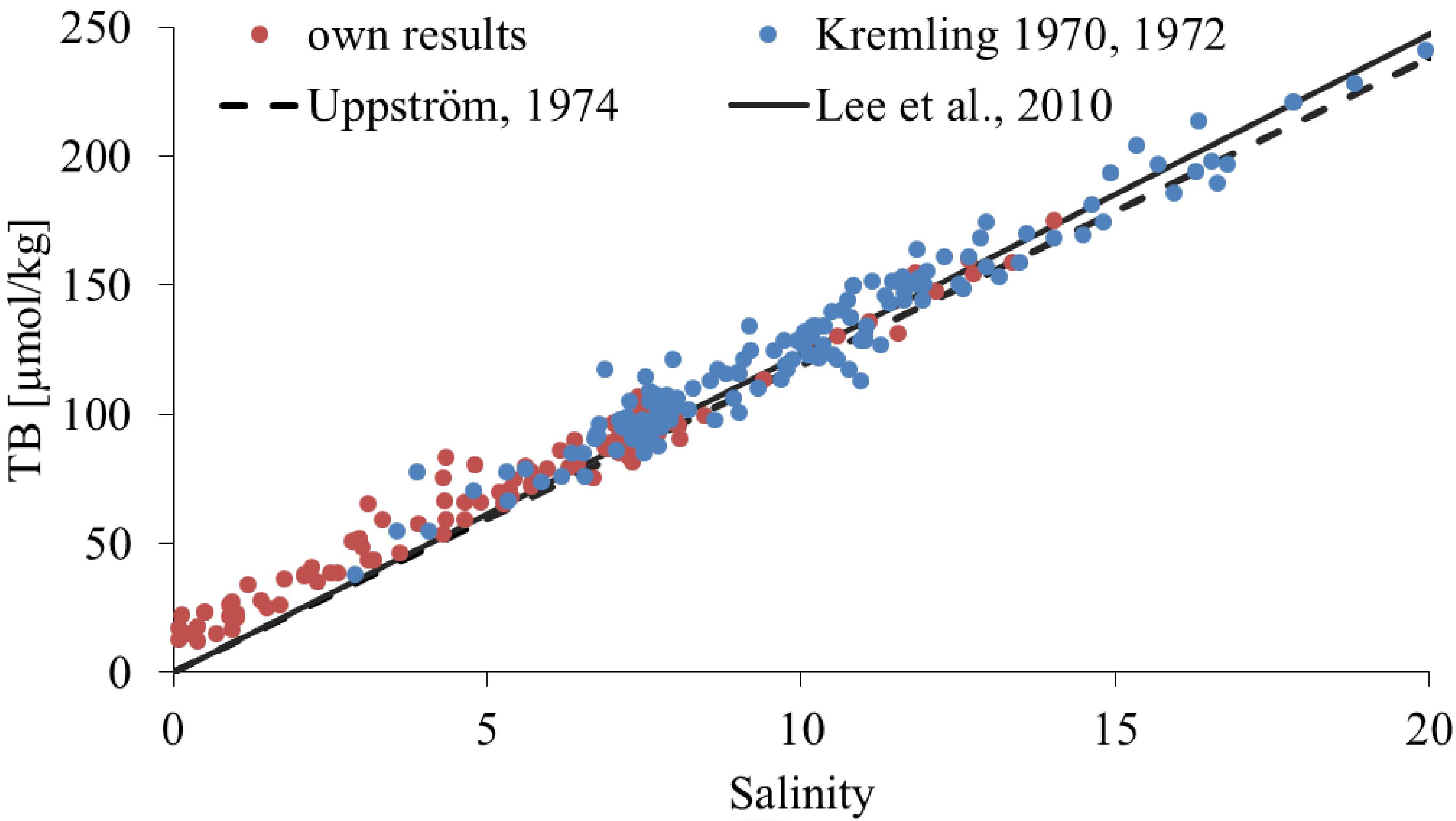
Kuliński et al., 2014, J. Mar. Syst.

Organic acids



Ulfsbo et al., 2015, Mar. Chem.

Boron anomaly

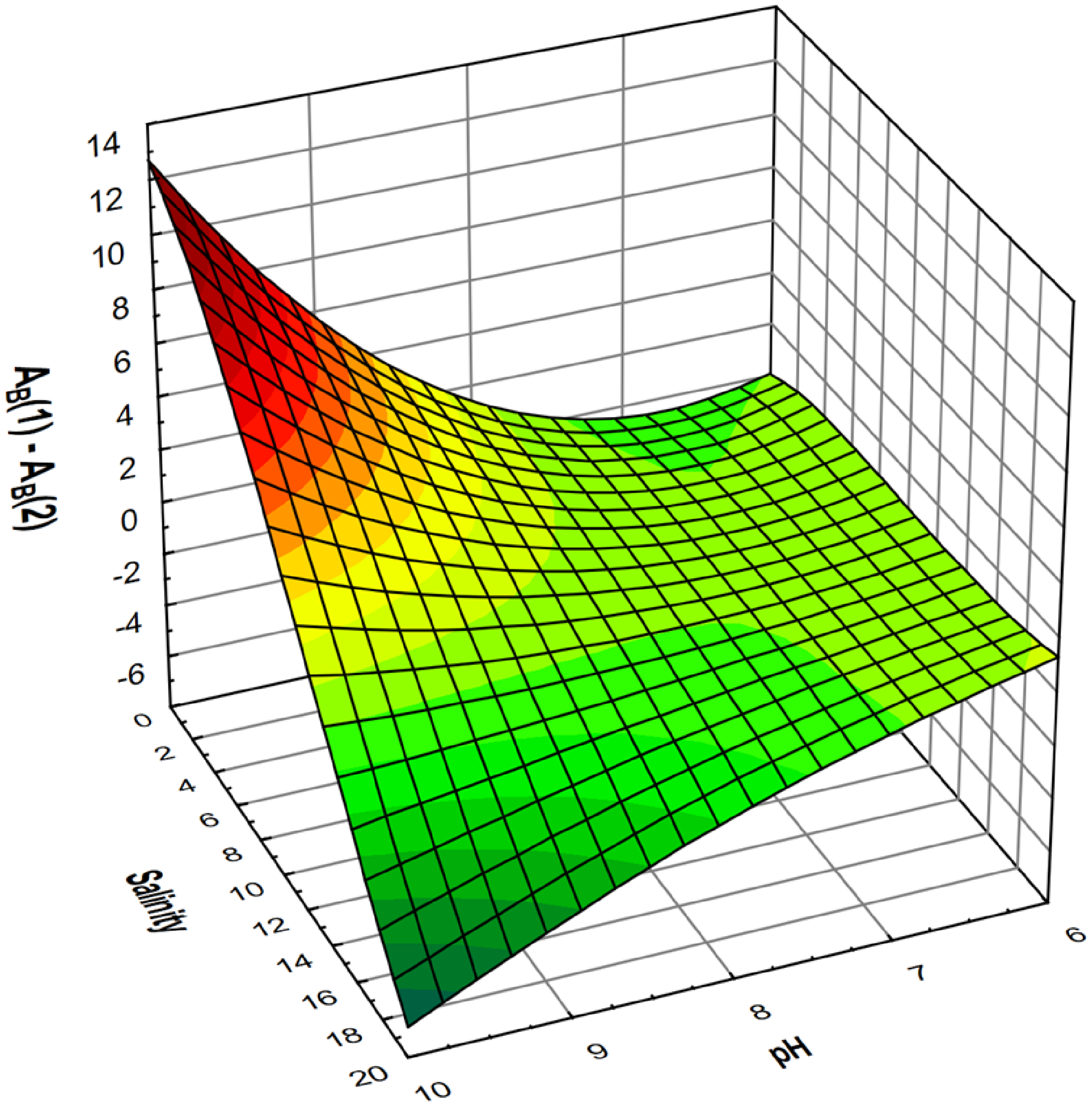


A_T = $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}]$
$+ 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots +$ Organics

$- [H^+]_{wolny} - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots$

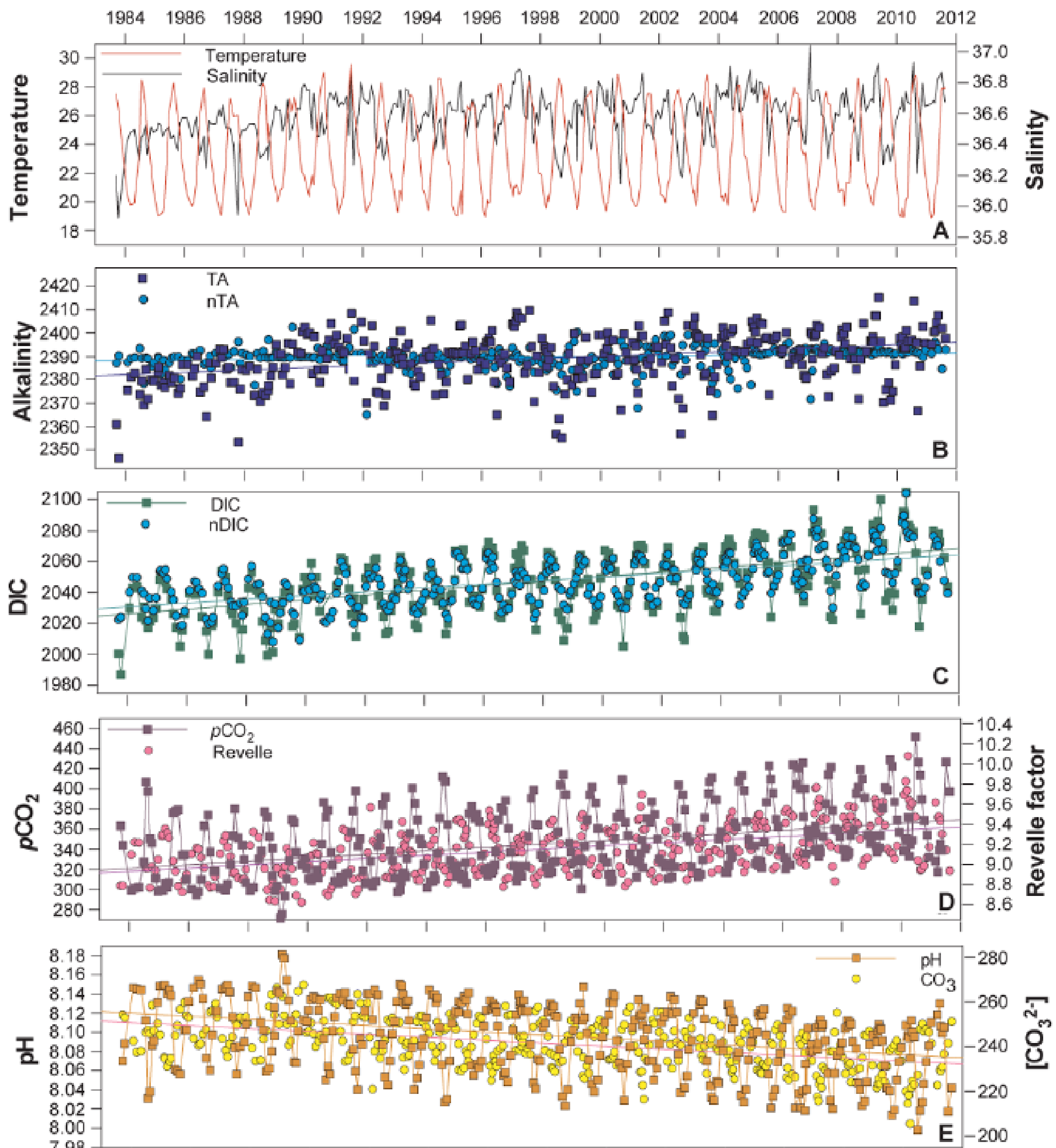
Kuliński et al., in print, Mar. Chem.

Boron anomaly



Kuliński et al., Mar. Chem. in print

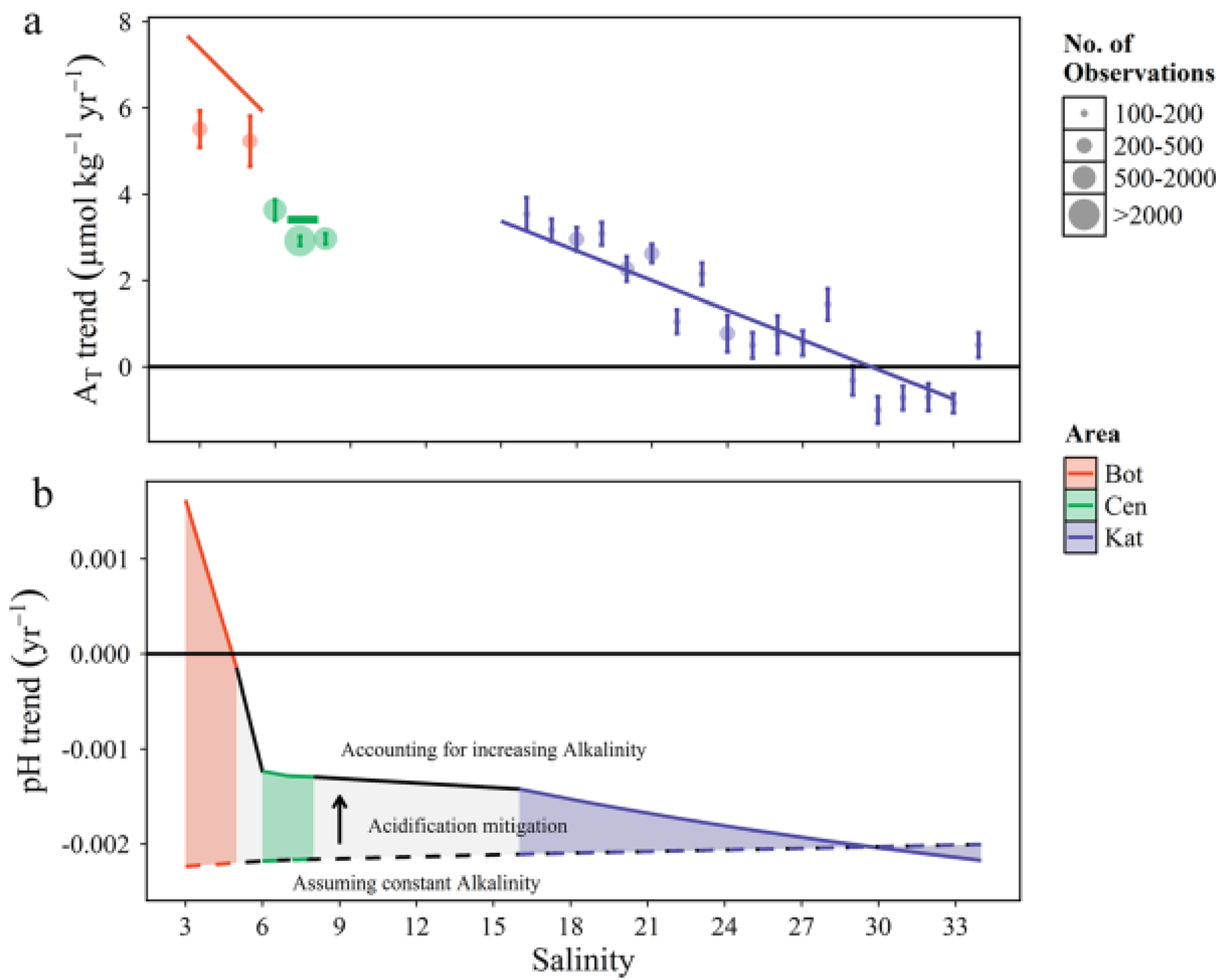
The oceanic CO_2 system



BATS - Bermuda Atlantic Time-series Study

Bates et al, 2012

Long-term A_T changes in the Baltic Sea



Müller et al., 2016, L&O

Sediments – source of alkalinity

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \rightarrow$$
$$106CO_2 + 16H^+ + 16NO_3^- + 122H_2O + H_3PO_4$$

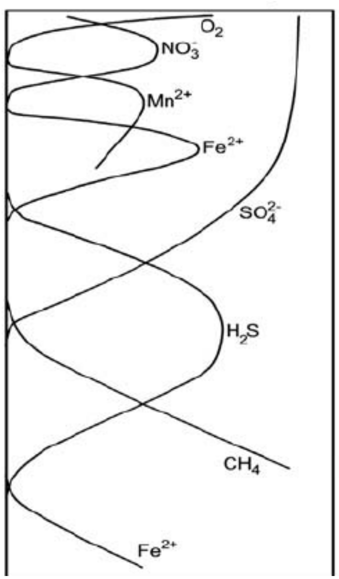
ΔA_T = -16

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236MnO_2 + 472H^+ \rightarrow$$
$$236Mn^{2+} + 106CO_2 + 8N_2 + 366H_2O + H_3PO_4$$

ΔA_T = +472

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8H^+ + 84.8NO_3^- \rightarrow$$
$$106CO_2 + 42.4N_2 + 16NH_3 + 148.4H_2O + H_3PO_4$$

ΔA_T = +100.8



$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212Fe_2O_3 + 848H^+ \rightarrow$$
$$424Fe^{2+} + 106CO_2 + 16NH_3 + 530H_2O + H_3PO_4$$

ΔA_T = +864

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} \rightarrow$$
$$106CO_2 + 16NH_3 + 53S^{2-} + 106H_2O + H_3PO_4$$

ΔA_T = +122

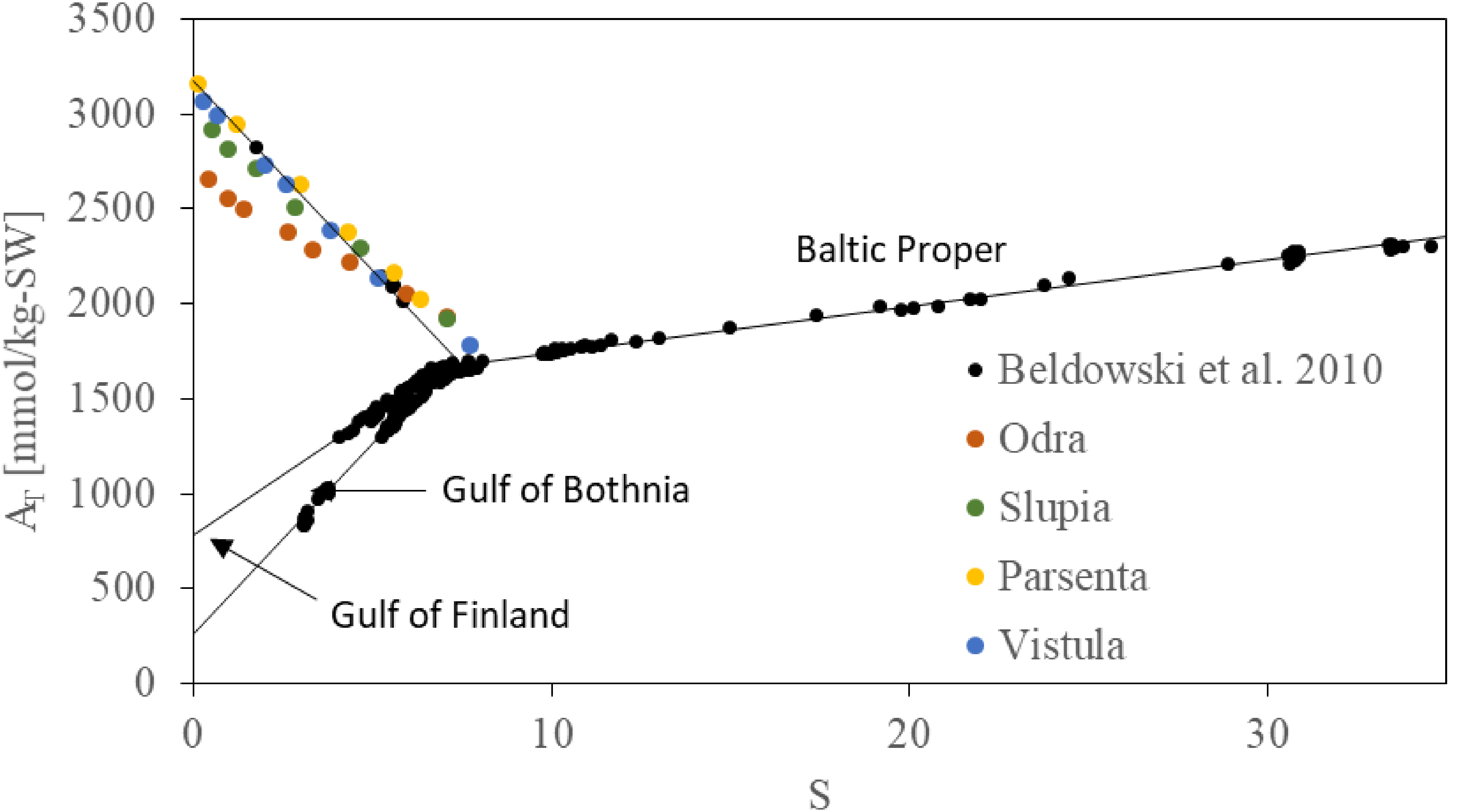
$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4$$

ΔA_T = +16

Kuliński et al., 2017, Earth Syst. Dynam.

A_T variability in the Baltic Sea

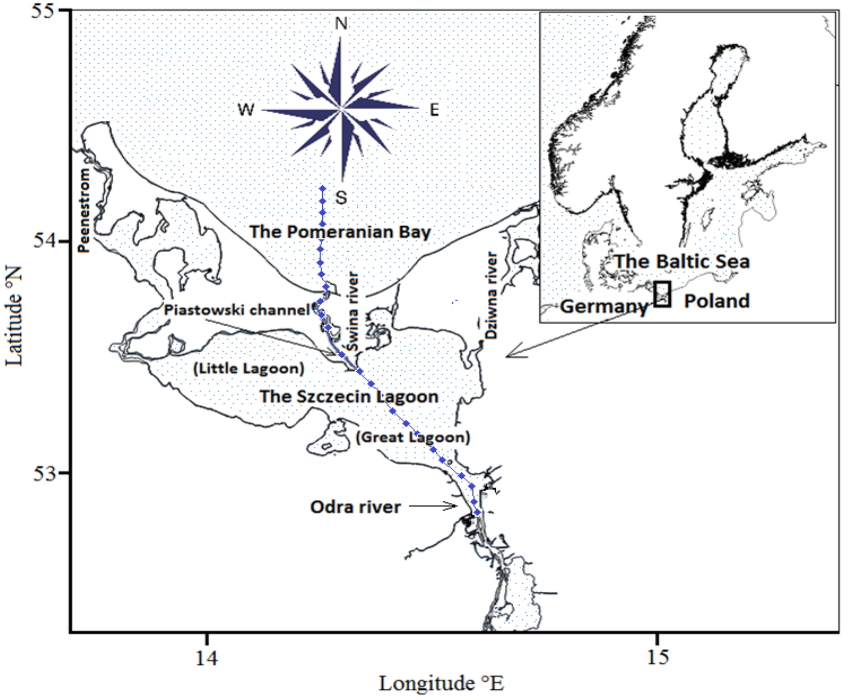
Poster B4

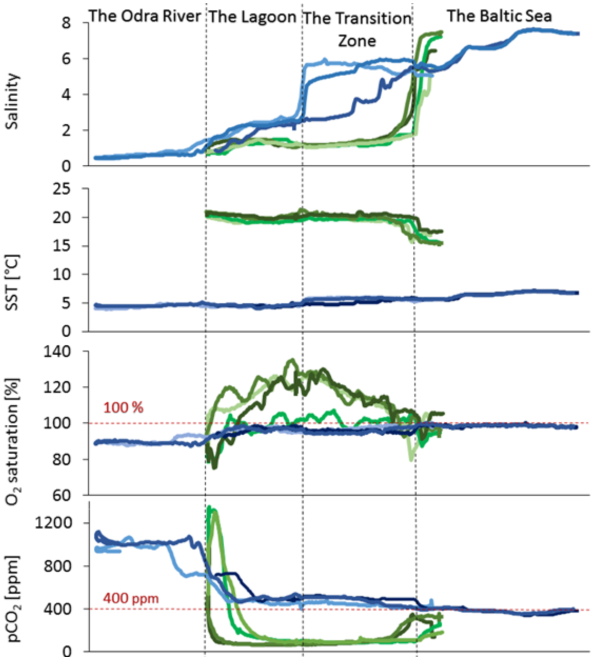


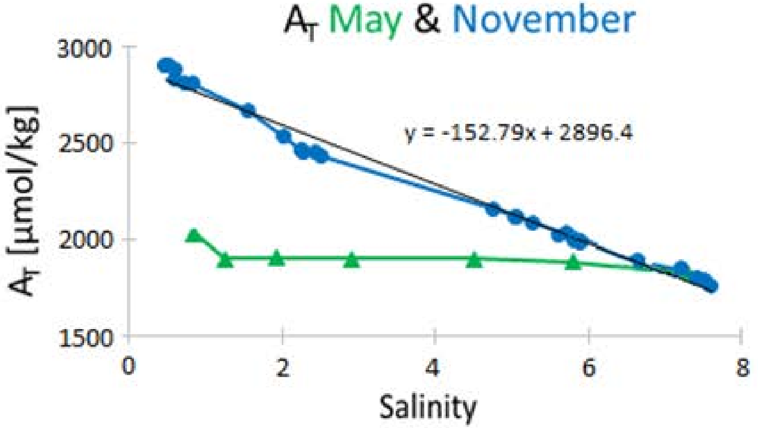
Hammer et al., in prep.

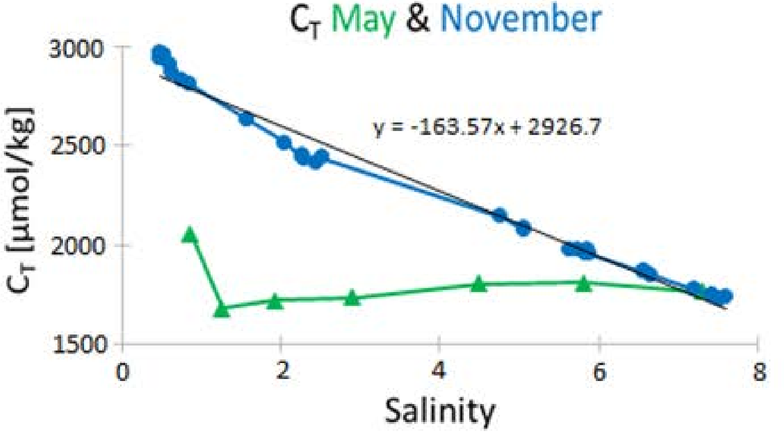
Poster B11

$CaCO_3$ precipitation in the Odra mouth



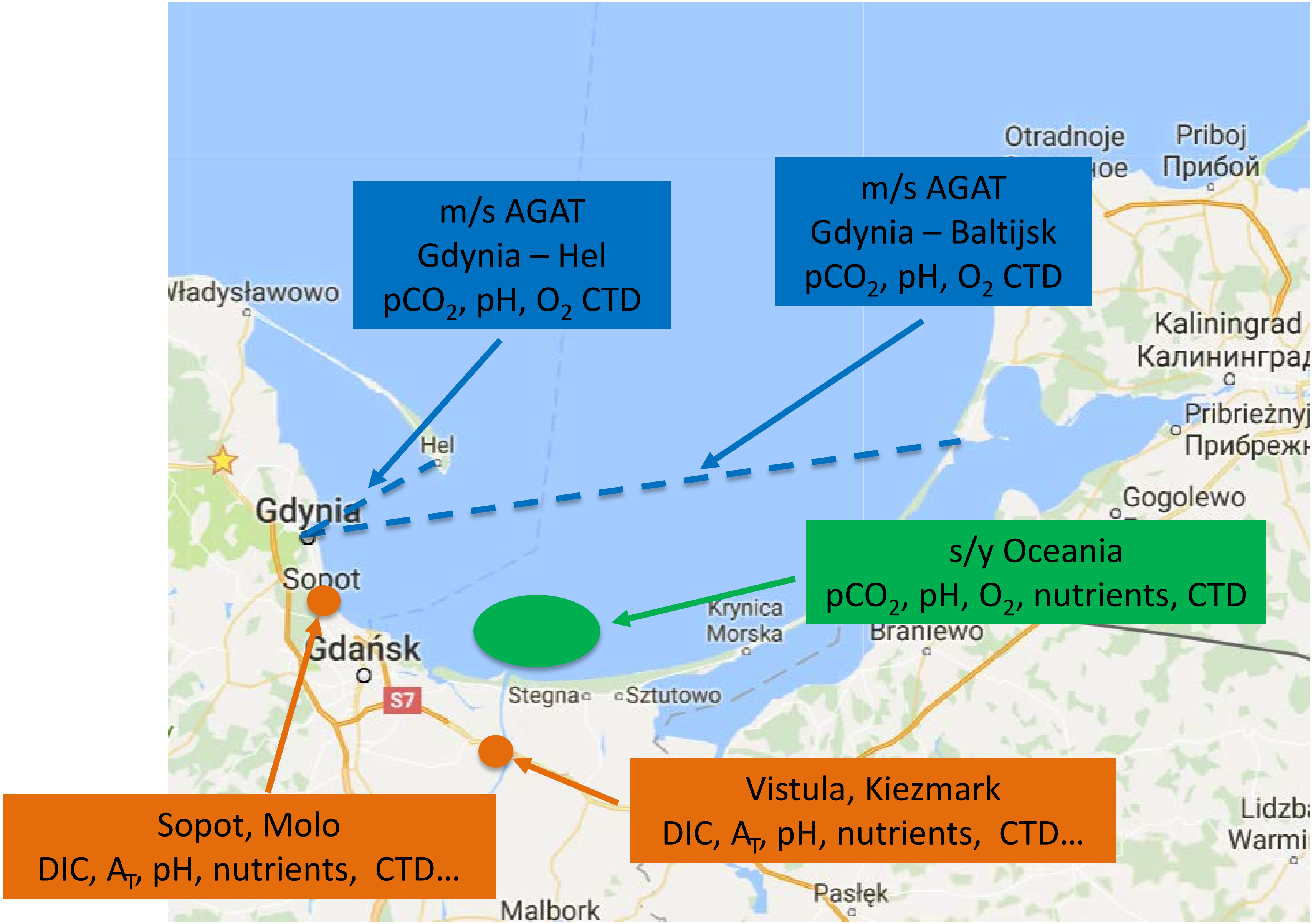






Stokowski et al., in prep.

CO_2 system studies in the Gulf of Gdansk

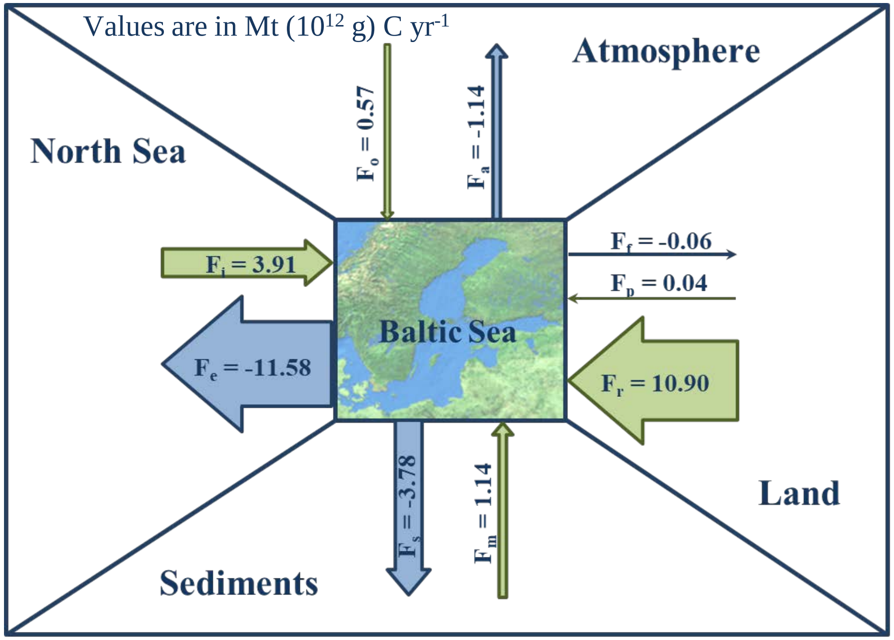


Conclusions

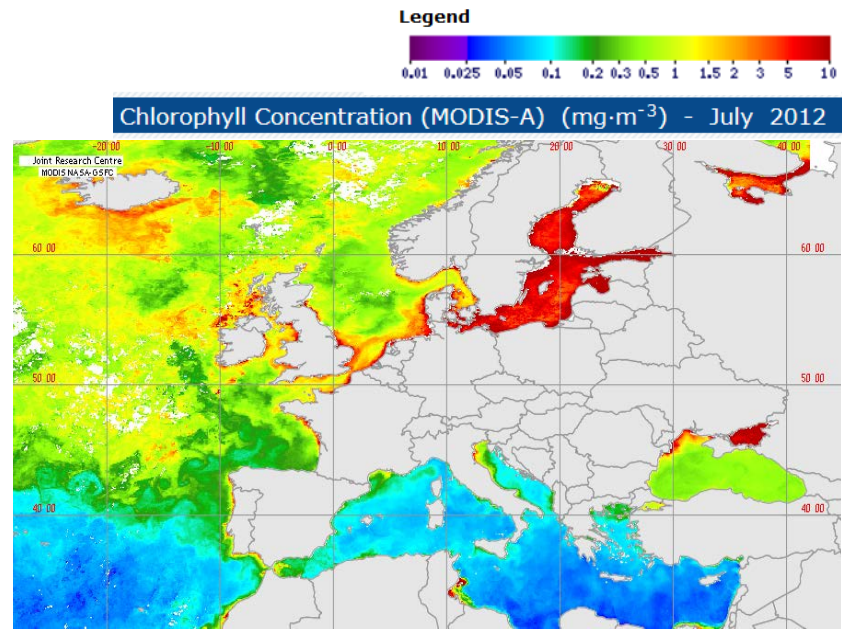
- The Baltic Sea acid-base system characterizes with high spatial and temporal variability
- A common thermodynamic model of the A_T does not work for the Baltic Sea (organic alkalinity, borate alkalinity….)
- There is a clear positive long-term A_T trend in the Baltic, higher in the north and lower in the south. What is the source of that increase?
- Role of sediments in A_T release?
- Transformations of the CO_2 (and acid-base) system in the mixing zone in estuaries can have significant impact on the A_T loads to the Baltic Sea.

Thank you

The Baltic Sea



Kuliński & Pempkowiak, 2011, Biogeosciences



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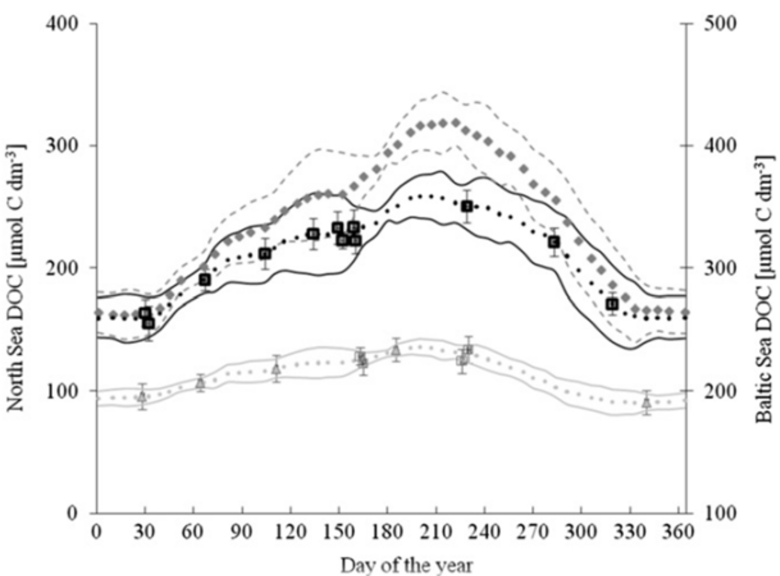
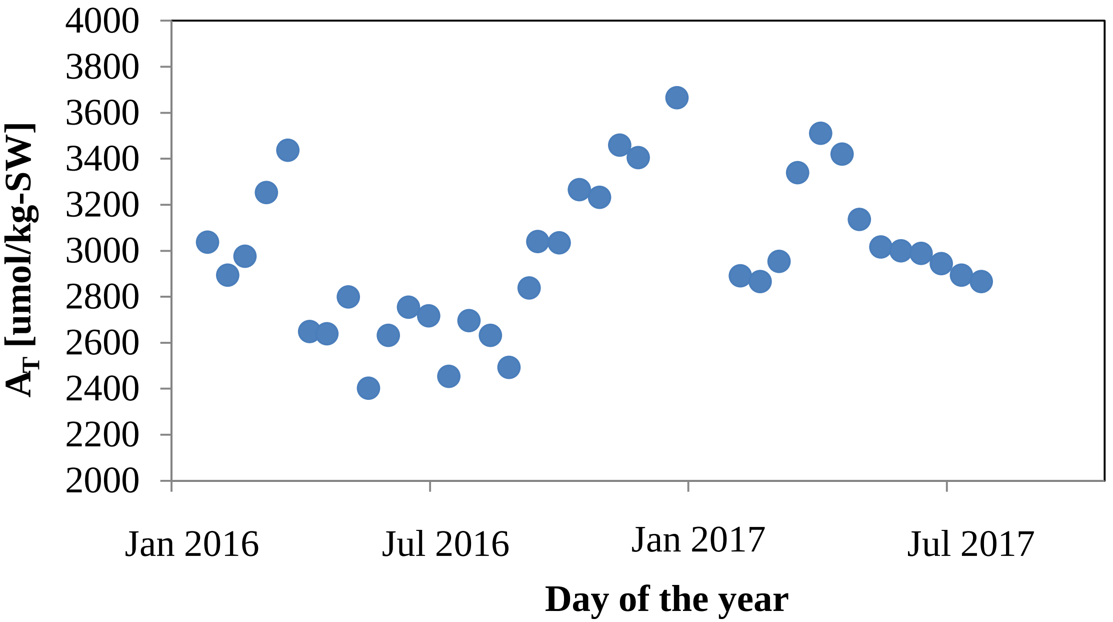
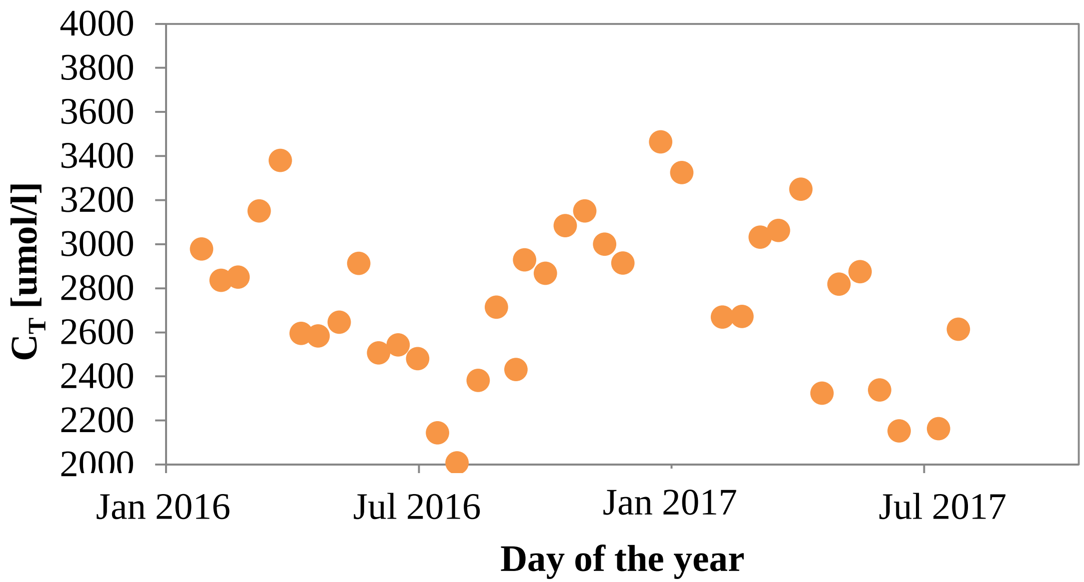


Kuliński et al., 2011, Cont. Shelf Res.

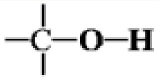
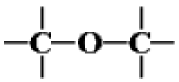
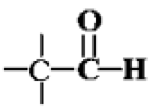
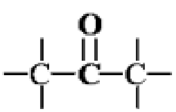
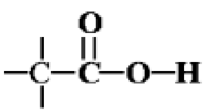
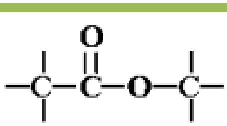
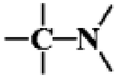
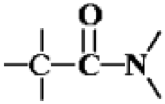
A_T and C_T seasonality in the Vistula River

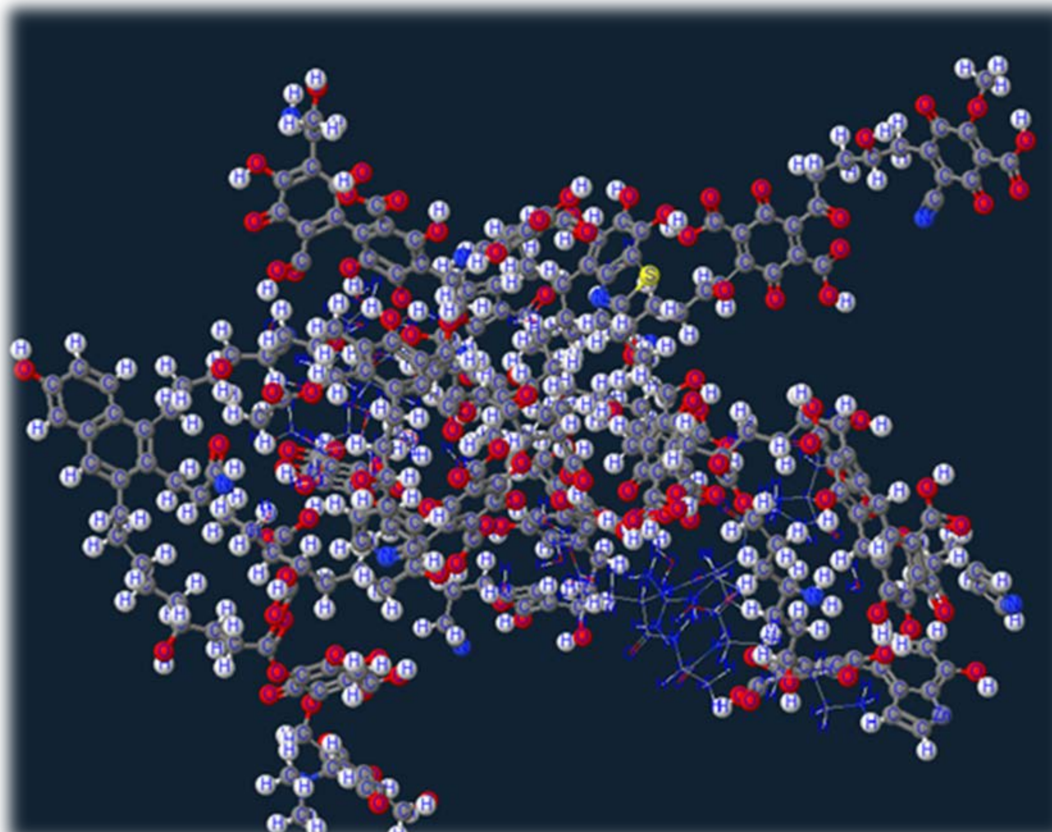




Kuliński et al., in prep.

Functional groups in DOM

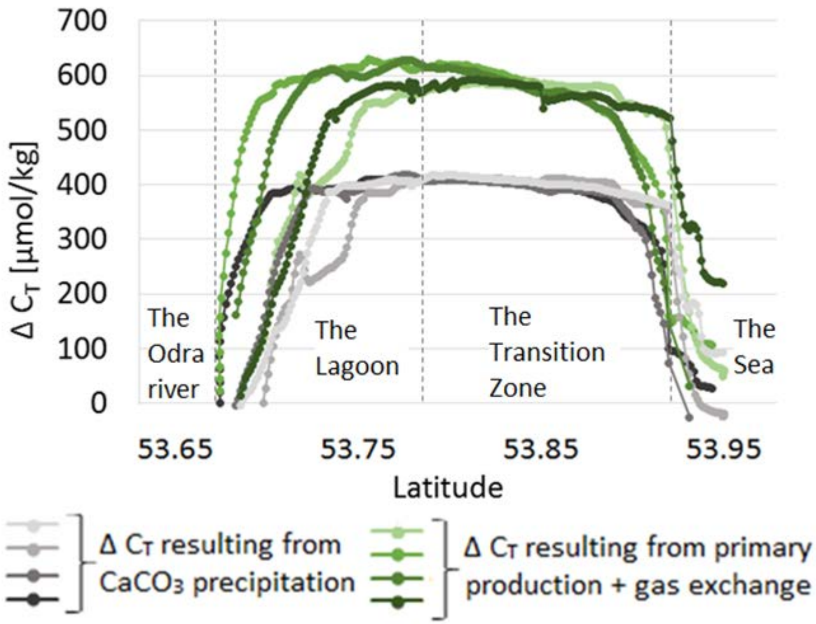
Group	Structure	Exchange H ?
Alcohol		Yes
Phenol		Yes
Ether		
Aldehyde		No
Ketone		
Carboxyl		Yes
Ester		
Amine		Yes
Amide		Yes

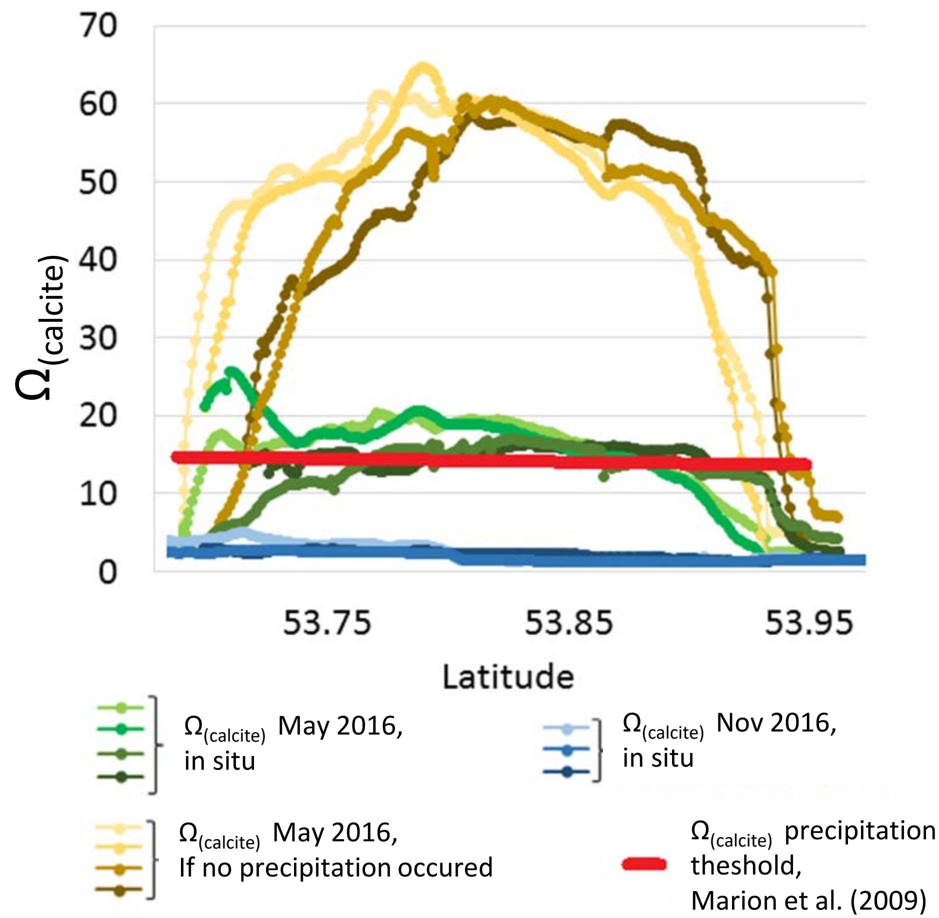


hypothetical structure of humic-like substances

$CaCO_3$ precipitation in the Odra mouth

Poster B11





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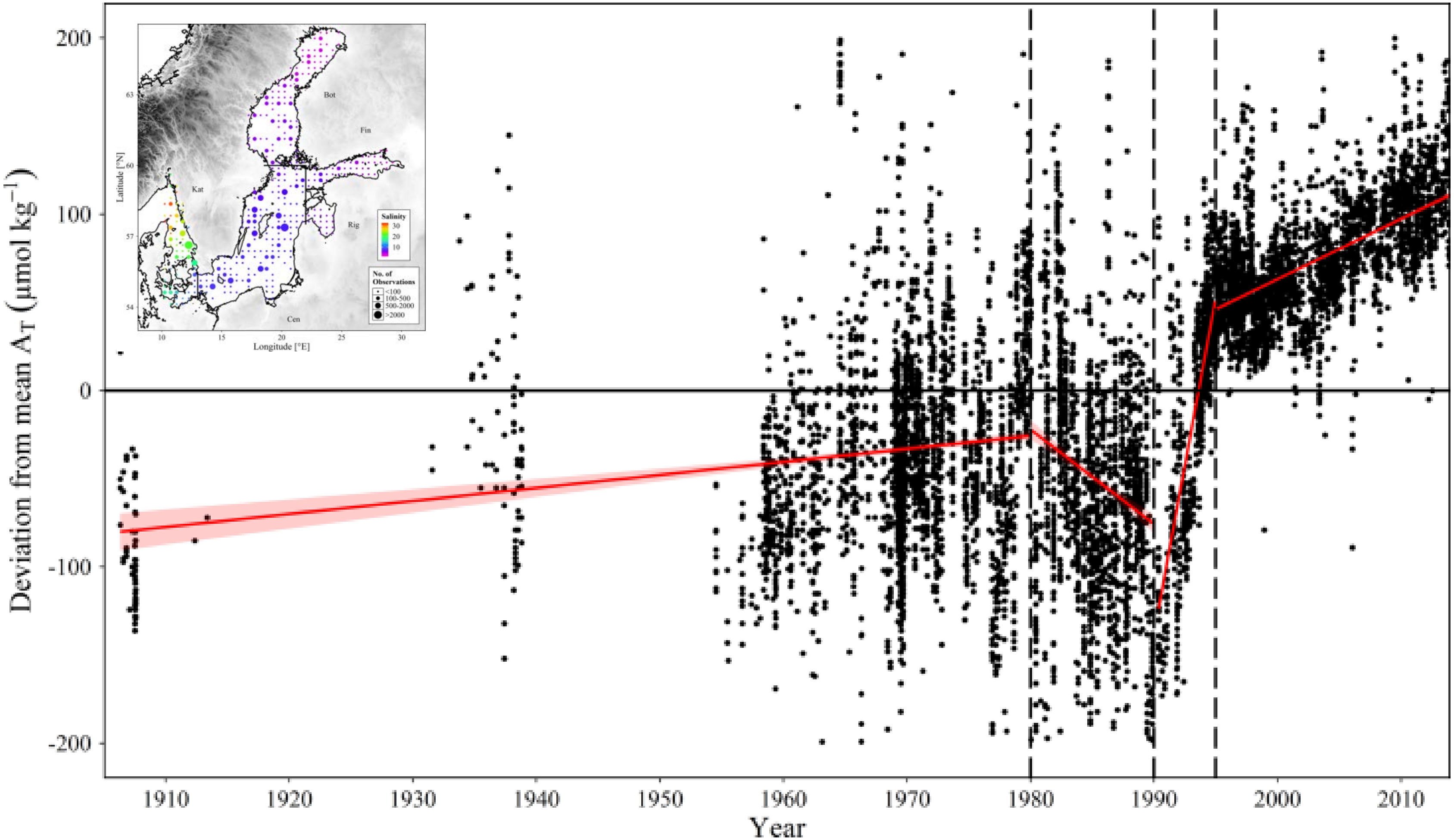
Long-term A_T changes in the Baltic Sea



Müller et al., 2016, L&O