Dissolved organic matter – a missing component in the acid-base system

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Baltic Earth workshop
13.11.2013
Sopot

Ministry of Science and Higher Education
Republic of Poland

Baltic Earth
Earth System Science for the Baltic Sea Region

Seawater acid-base system

The measurable parameters:

- C_T – total CO_2 concentration (DIC)
- A_T – total alkalinity
- pCO_2 – partial pressure of CO_2
- pH

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

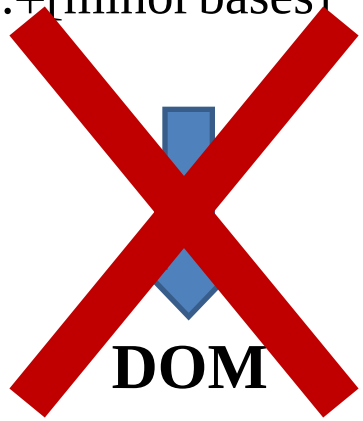
The pairs used in the calculations:

- C_T & A_T – recommended, used in biogeochemical modelling
- A_T & pH – measured within the monitoring programs

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):

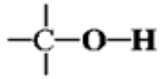
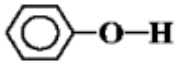
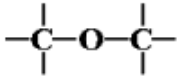
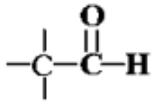
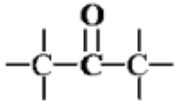
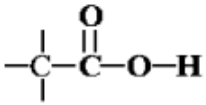
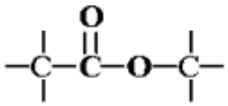
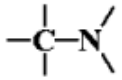
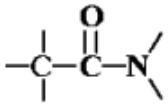
$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + \ldots + [\text{minor bases}]$$

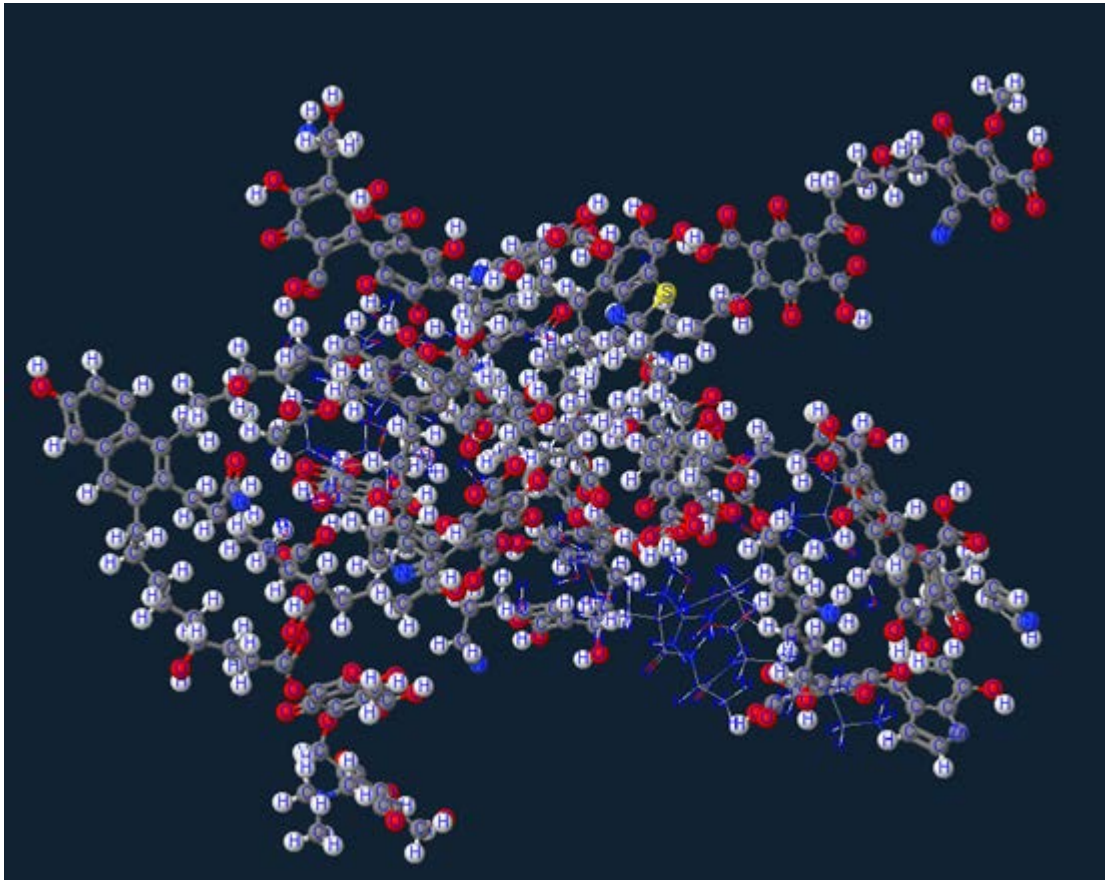
$$A_T = A_{inorganic} + A_{org}$$



Organic term is not included in the thermodynamic model of a seawater

Functional groups in DOM

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



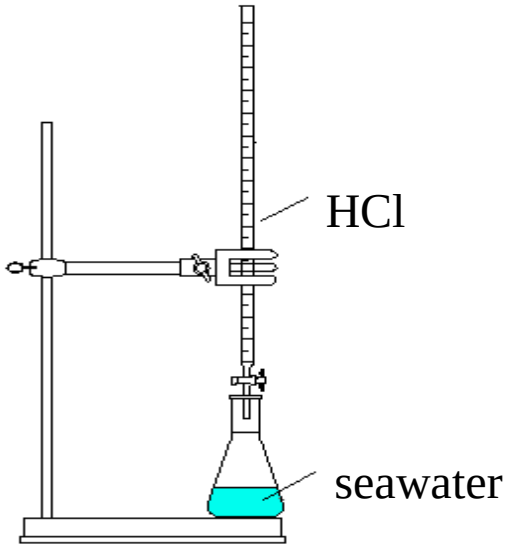
hypothetical structure of humic like substances

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):

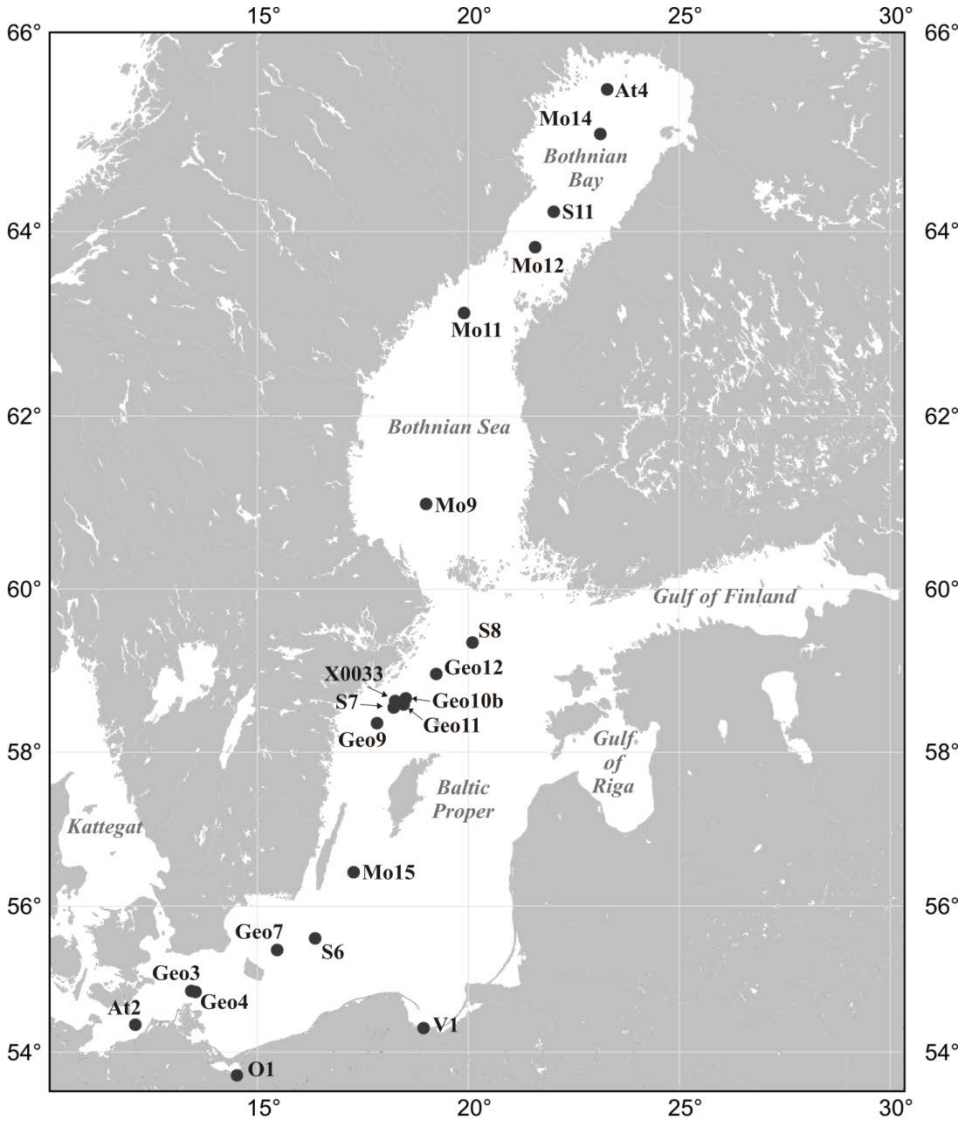
$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + \ldots + A_{org}$$

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

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



Influence of A_{org} on the calculations of pCO_2 and pH

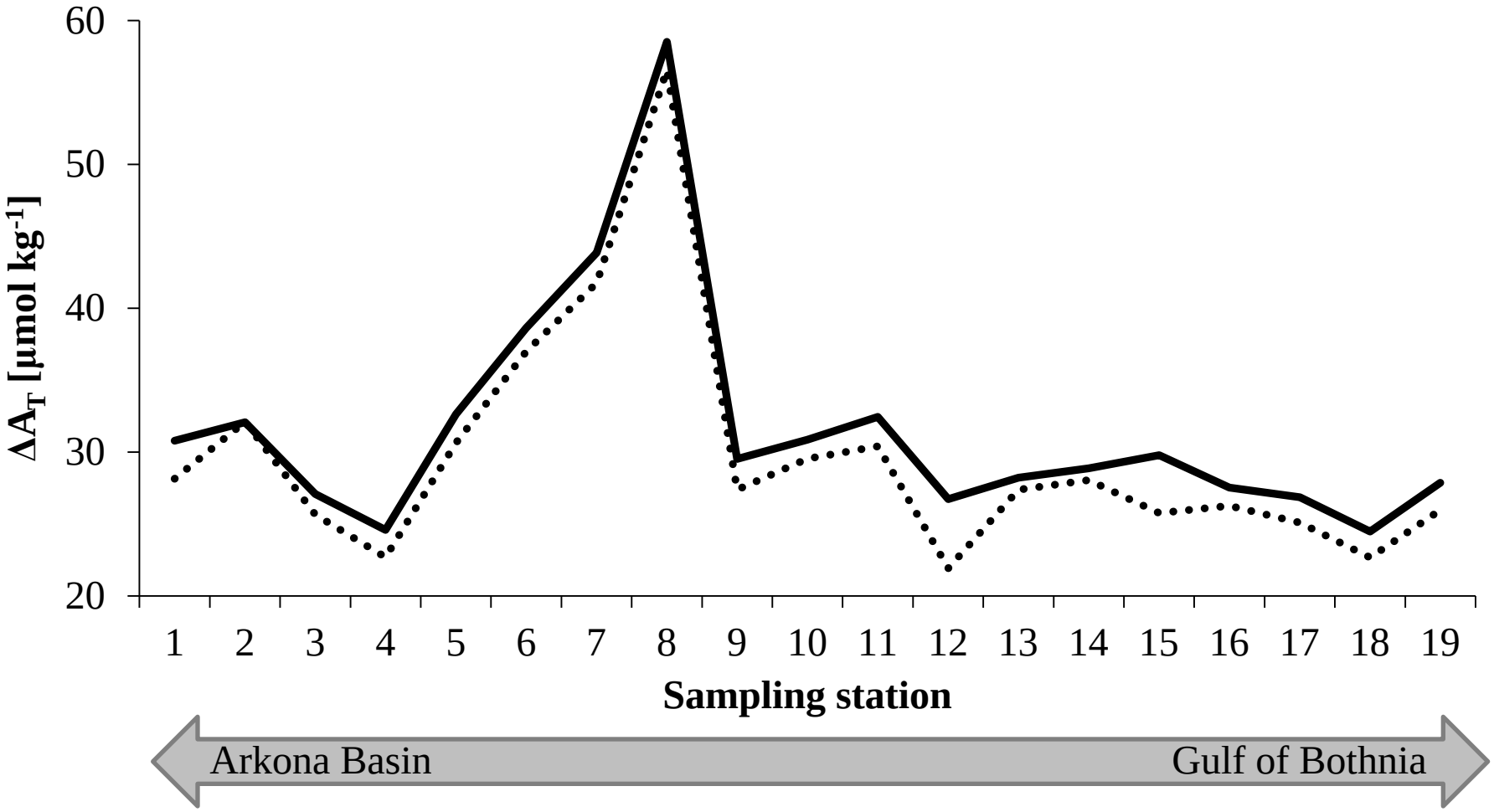


r/v Meteor cruise, November 2011

Database

- C_T, A_T, pH, pCO_2

Influence of A_{org} on the calculations of pCO_2 and pH



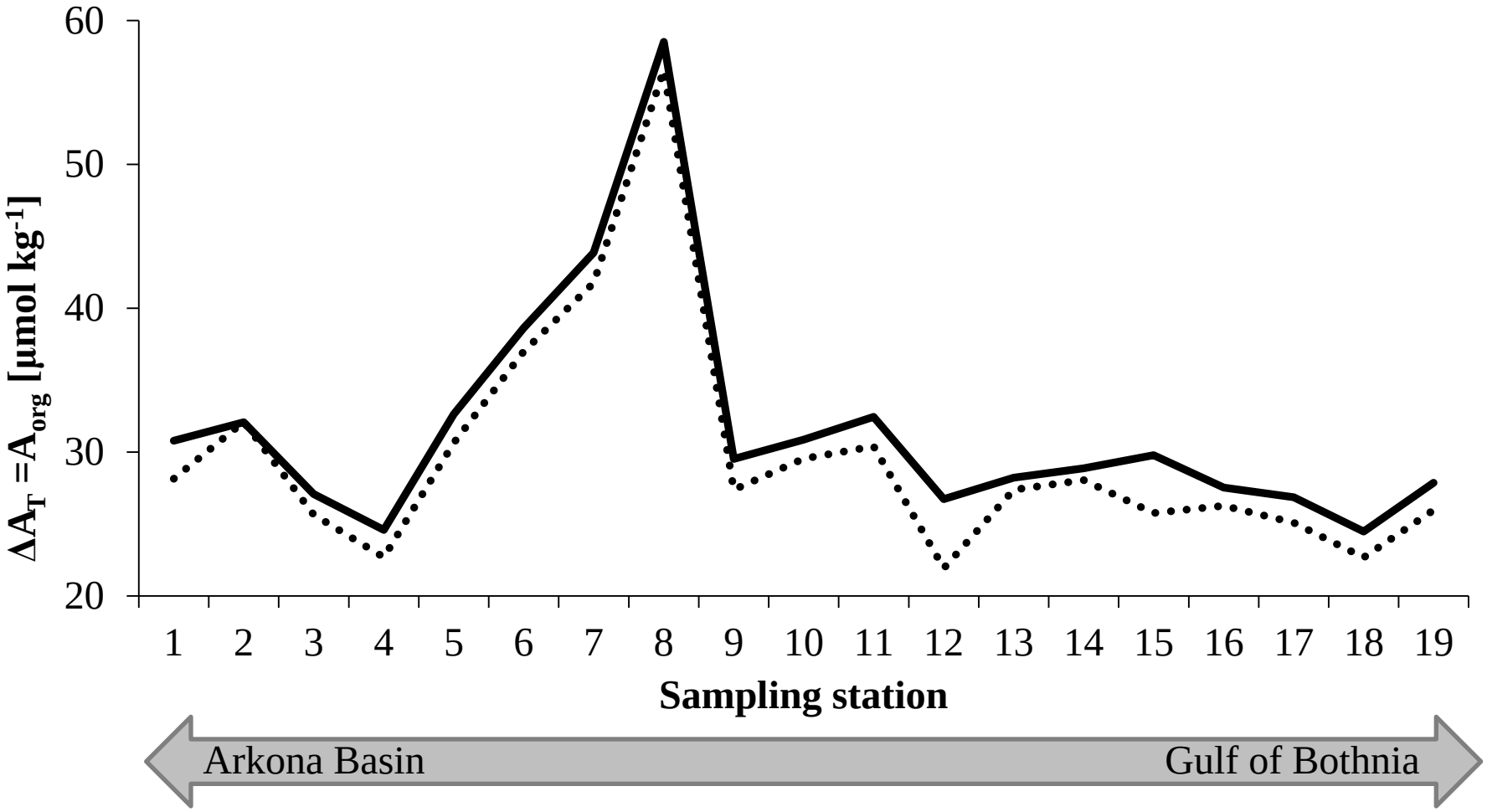
A_{org} is the difference between measured and calculated A_T (ΔA_T)

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

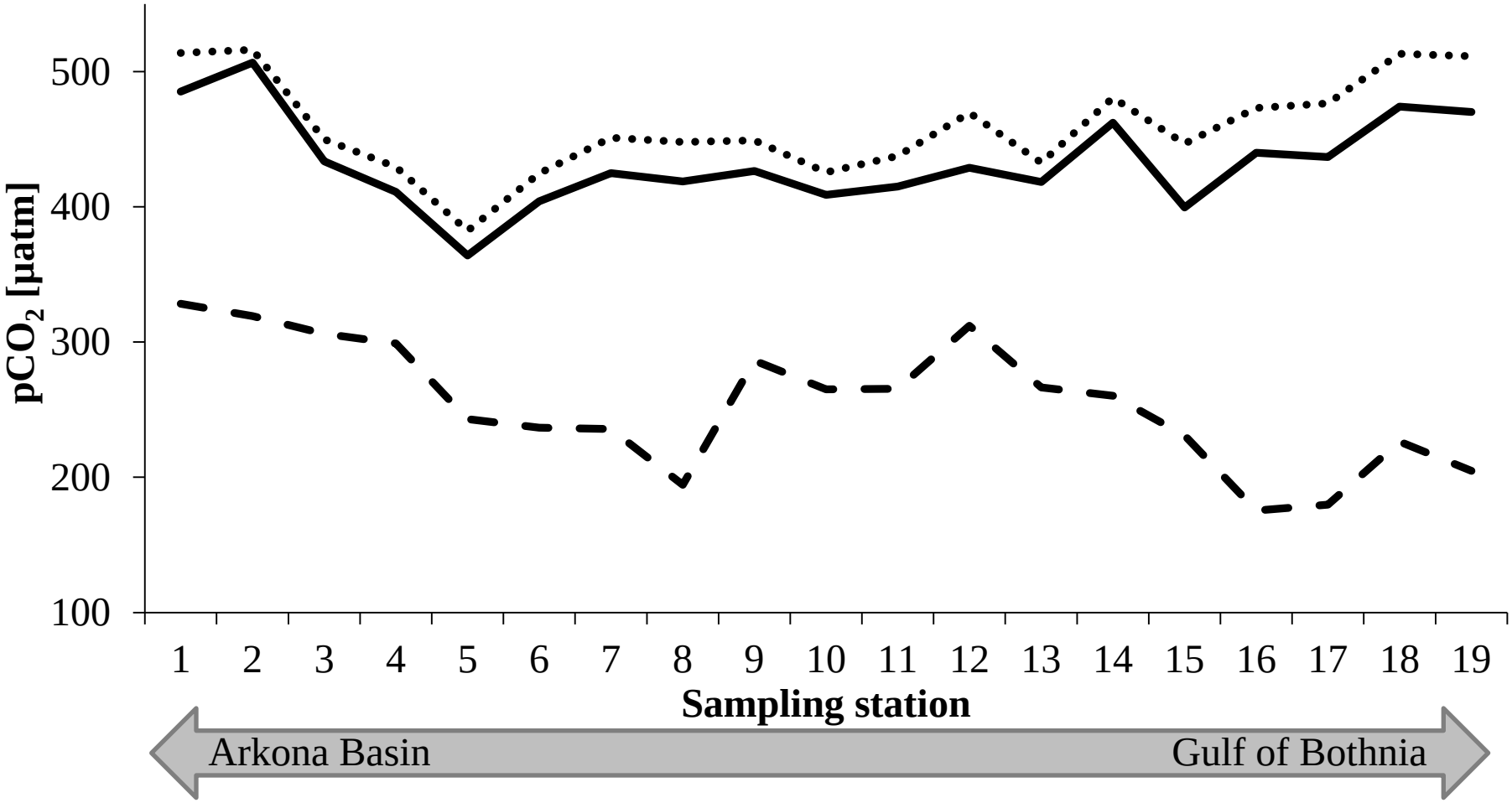
$$A_{org} = A_T - A_{inorganic}$$

$A_{inorganic}$ – A_T calculated from C_T and pH or C_T and pCO_2

Influence of A_{org} on the calculations of pCO_2 and pH



Influence of A_{org} on the calculations of pCO_2 and pH



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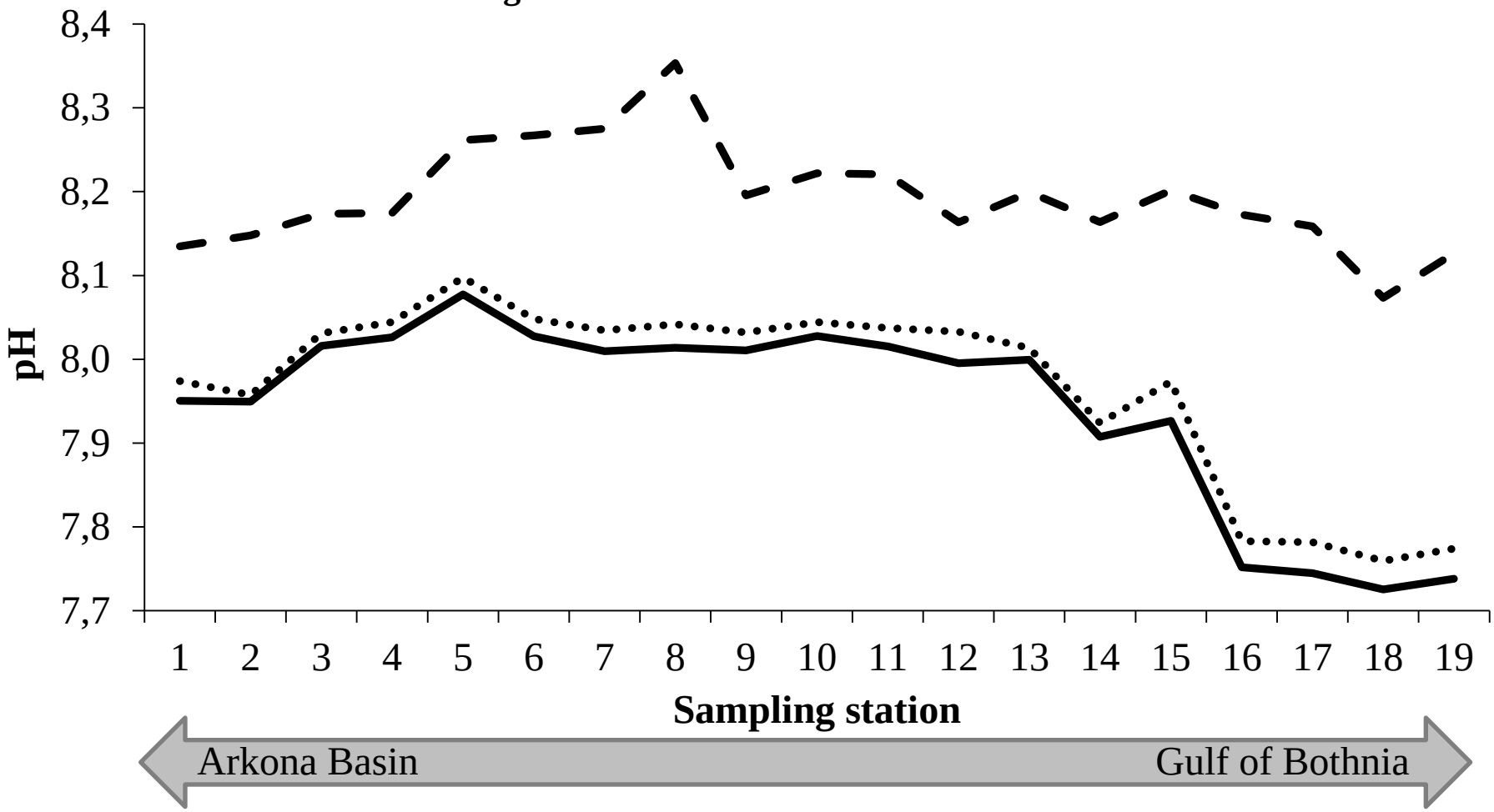
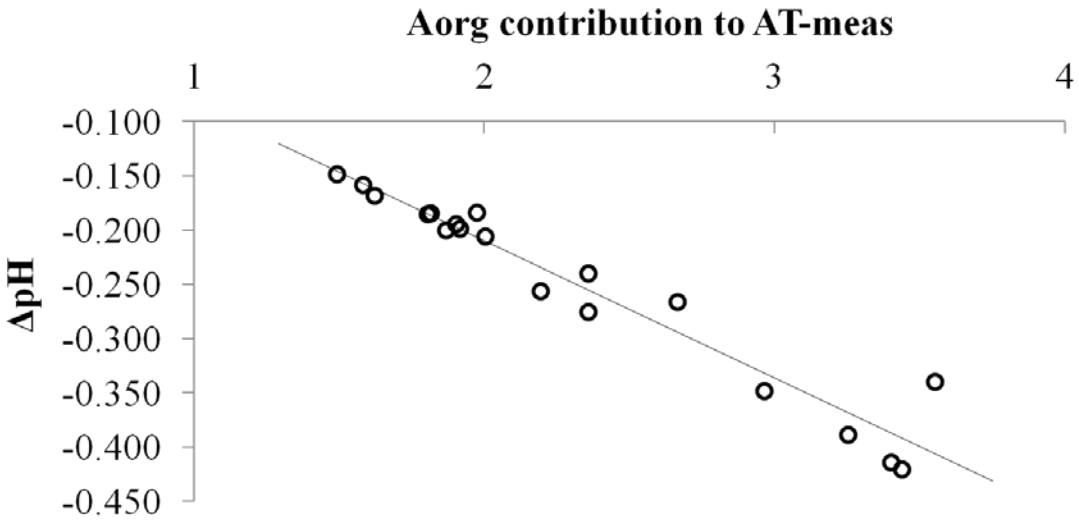
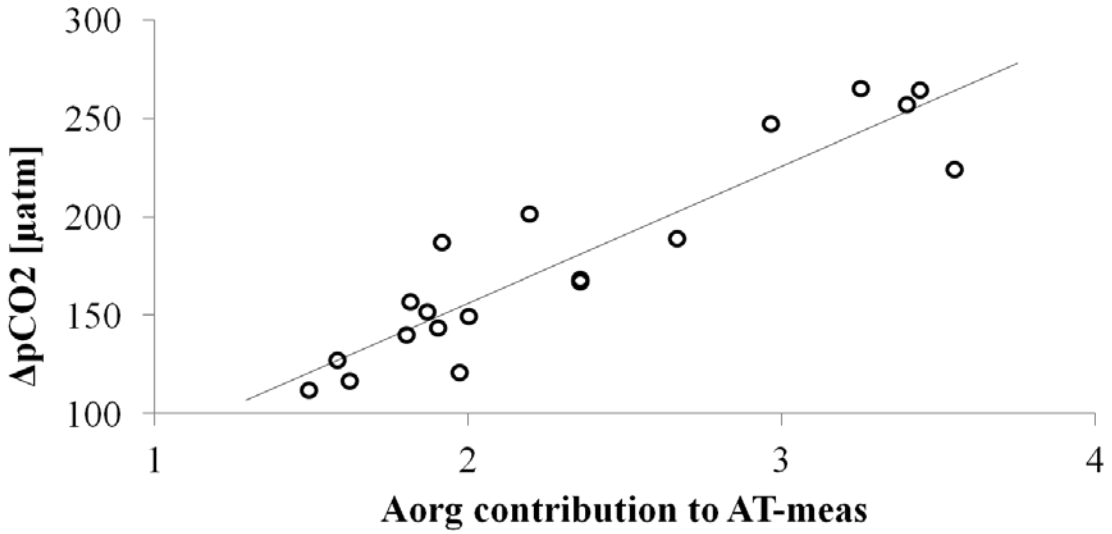


(In)consistency of the acid-base system parameters





Monoprotic acid dissociation

$$HOrg \leftrightarrow H^+ + Org^-$$

$$K_a = \frac{[H^+] \cdot [Org^-]}{[HOrg]}$$

The mean DOM dissociation constant – K_{DOM}

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

$[H^+]$ – calculated from pH

A_{org} – organic alkalinity

DOC – well described method

f – share of DOC providing functional groups

f = 0.14

pK_{DOM} = 7.53

Conclusions

- A_{org} term is missing in the A_T model
- A_{org} is the difference between measured and calculated A_T.
- A_{org} was found in the range 25-60 µmol kg^{-1} in the Baltic Sea water.
- Ignoring the DOM component in A_T model causes significant uncertainty of pH and pCO_2 in numerical studies, especially for the input data of A_T and C_T.
- Some 14% of DOC carry the functional groups dissociating in seawater. The pK_{DOM} in the Baltic Sea water amounts to 7.53
- Tests of „K_{DOM}" approach in numerical studies are required
- Further studies on DOM acid-base properties are required.

Thank you