The influence of the dissolved organic matter (DOM) on the acid-base system of the Baltic Sea

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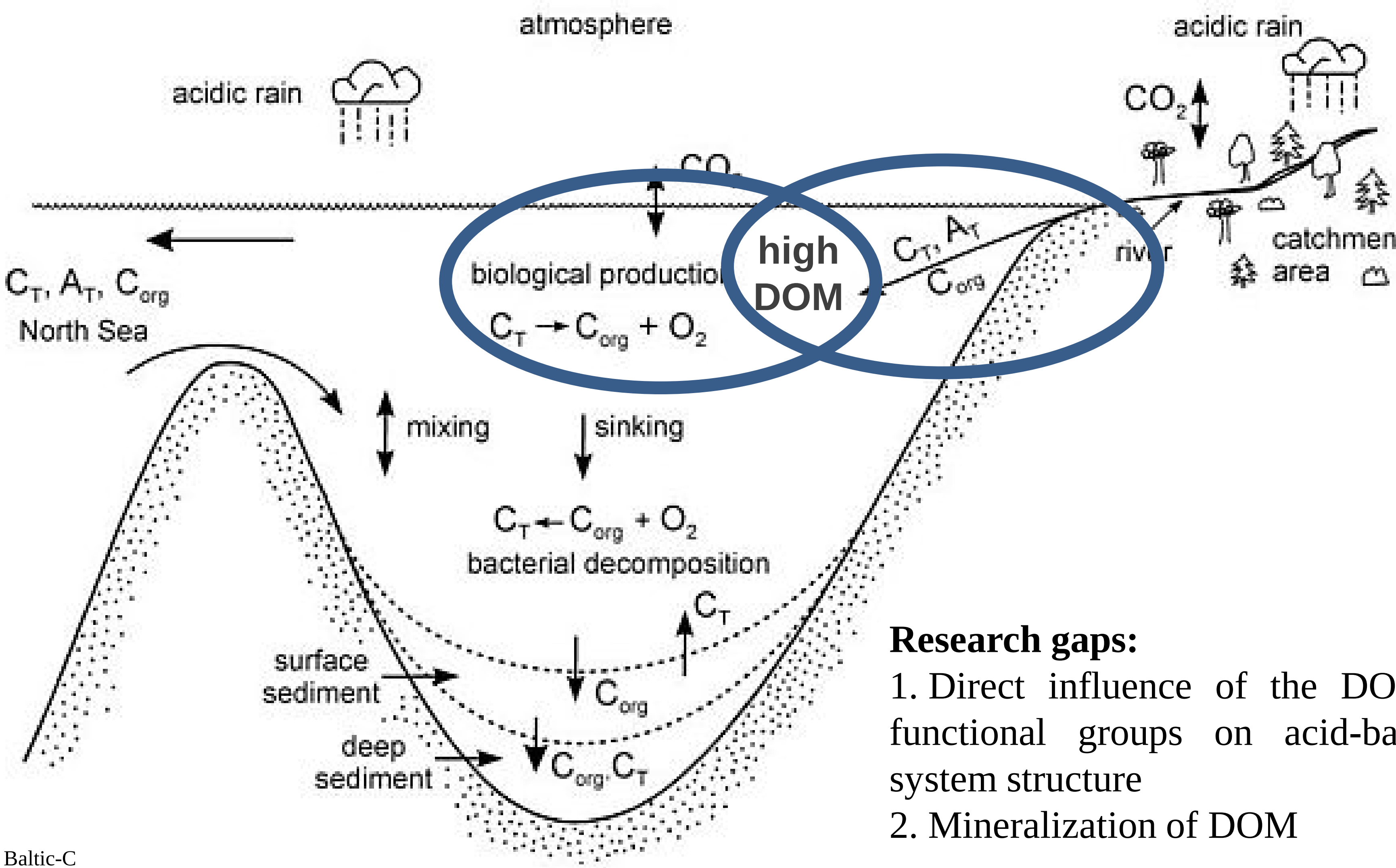
Organic matter in the Baltic Sea



Research gaps:

1. Direct influence of the DOM functional groups on acid-base system structure
2. Mineralization of DOM

source: Baltic-C

DOM as a weak acid

Seawater acid-base system

The measurable parameters are:

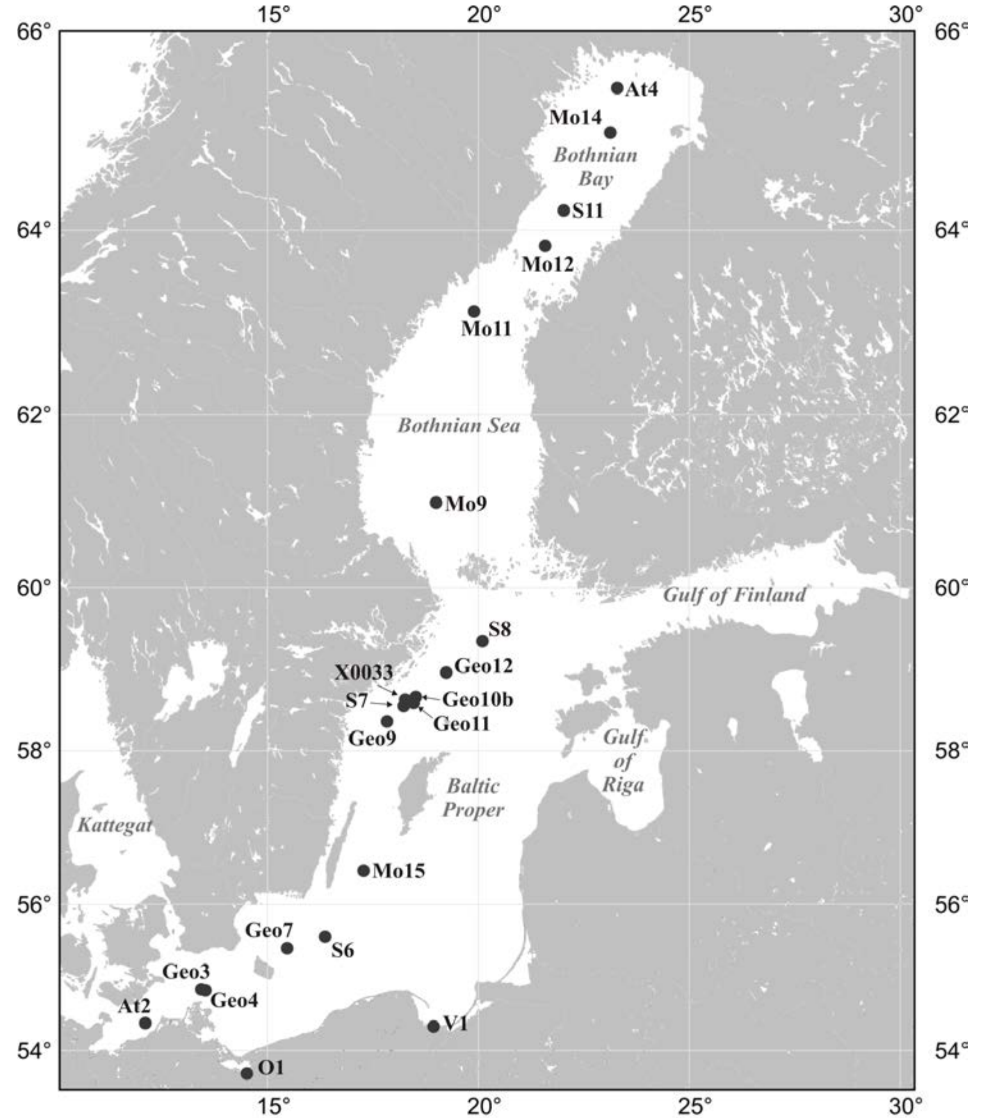
- C_T – total CO_2 concentration
- A_T – total alkalinity
- pCO_2 – partial pressure of CO_2
- pH

It is possible to calculate 2 parameters when other 2 are known

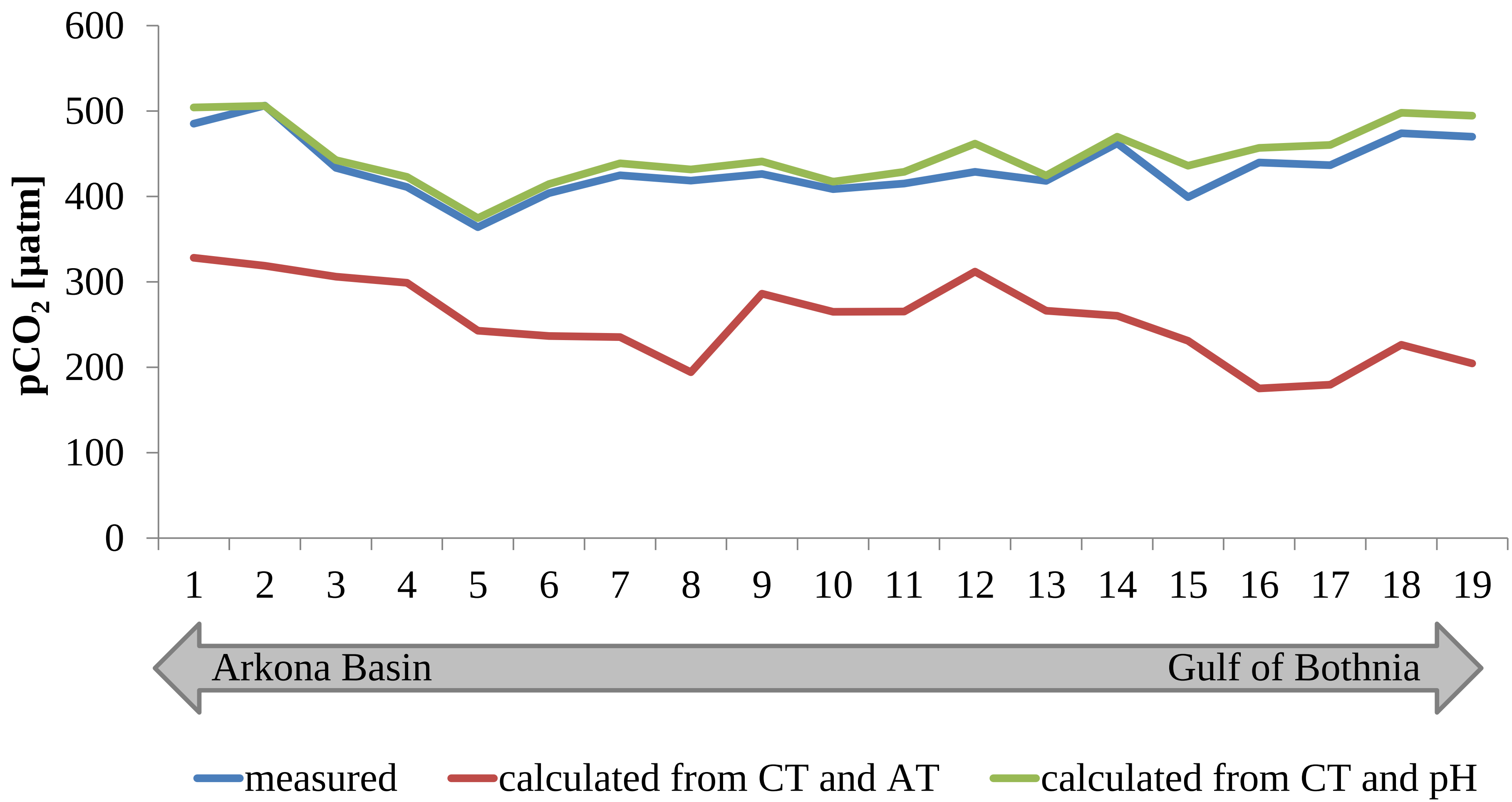
- C_T & A_T – used in biogeochemical modelling
- A_T & pH – measured within the monitoring programmes

r/v Meteor cruise, November 2011 Database

- C_T, A_T, pH, pCO_2



(In)consistency of the acid-base system parameters



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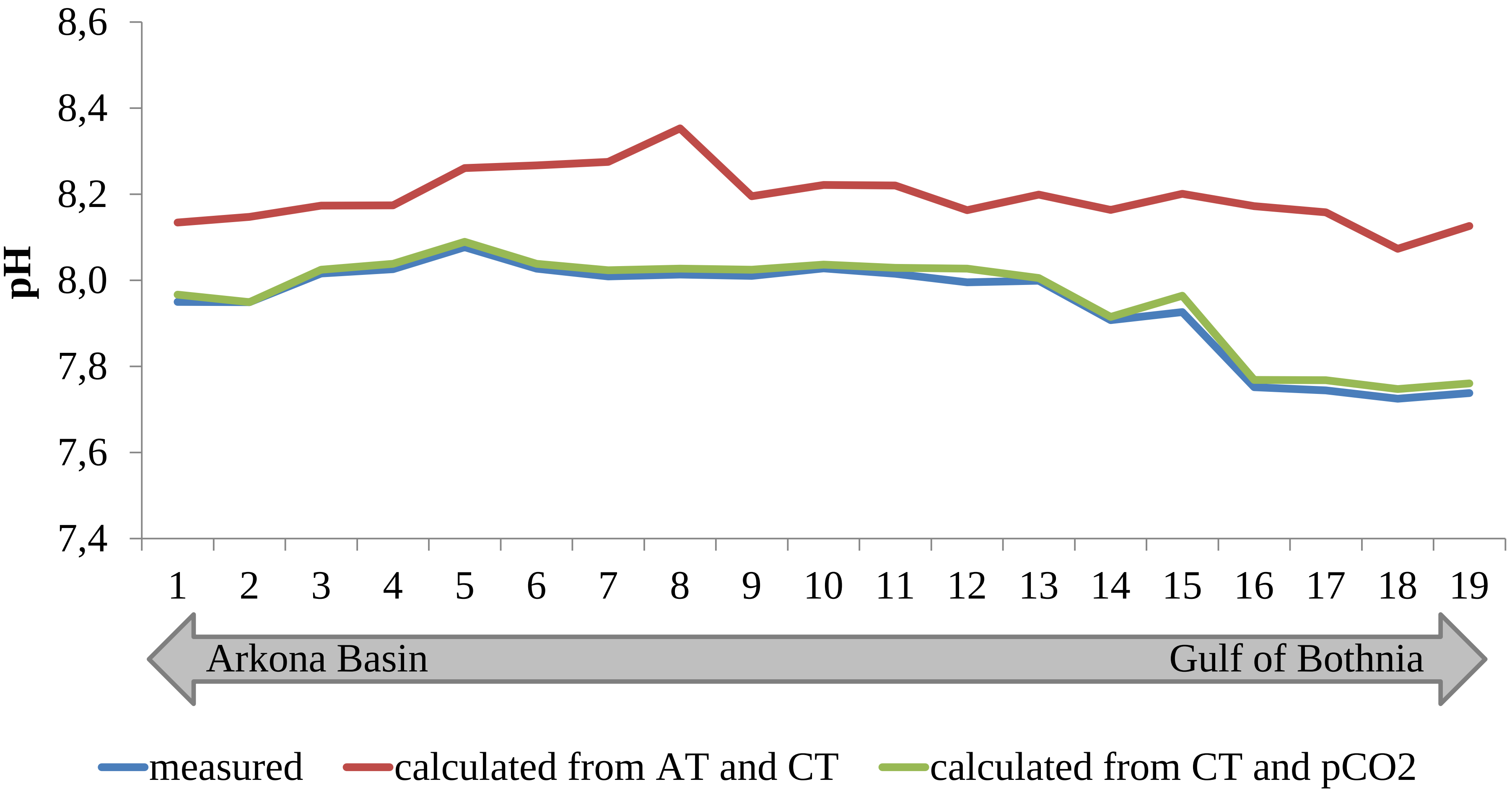

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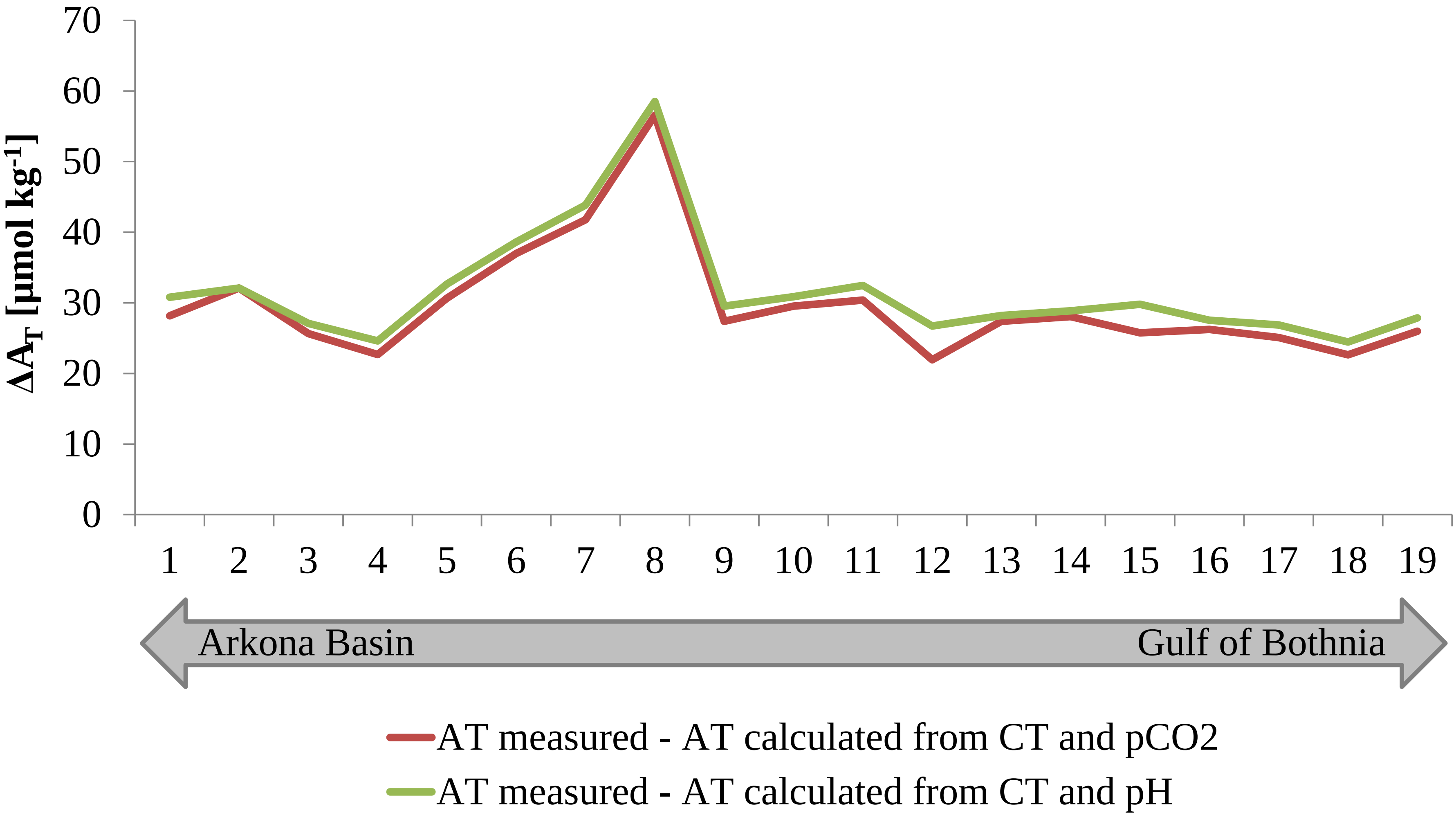
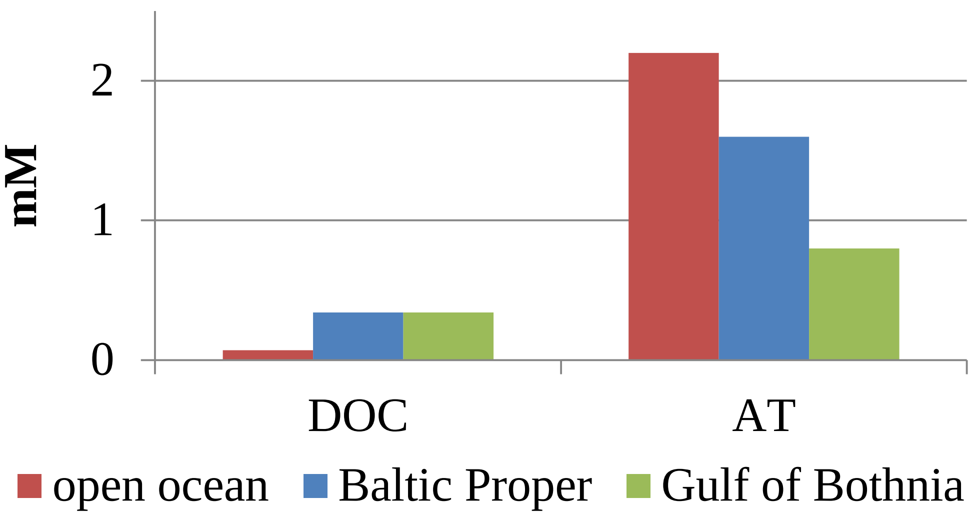
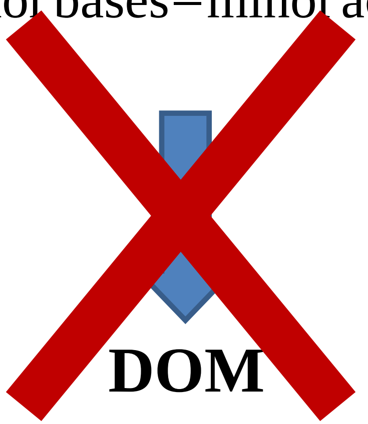


The total alkalinity of seawater is defined as the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25°C) over proton donors (acids with $K > 10^{-4.5}$) and expressed as a hydrogen ion equivalent in one kilogram of sample (Dickson, 1981):

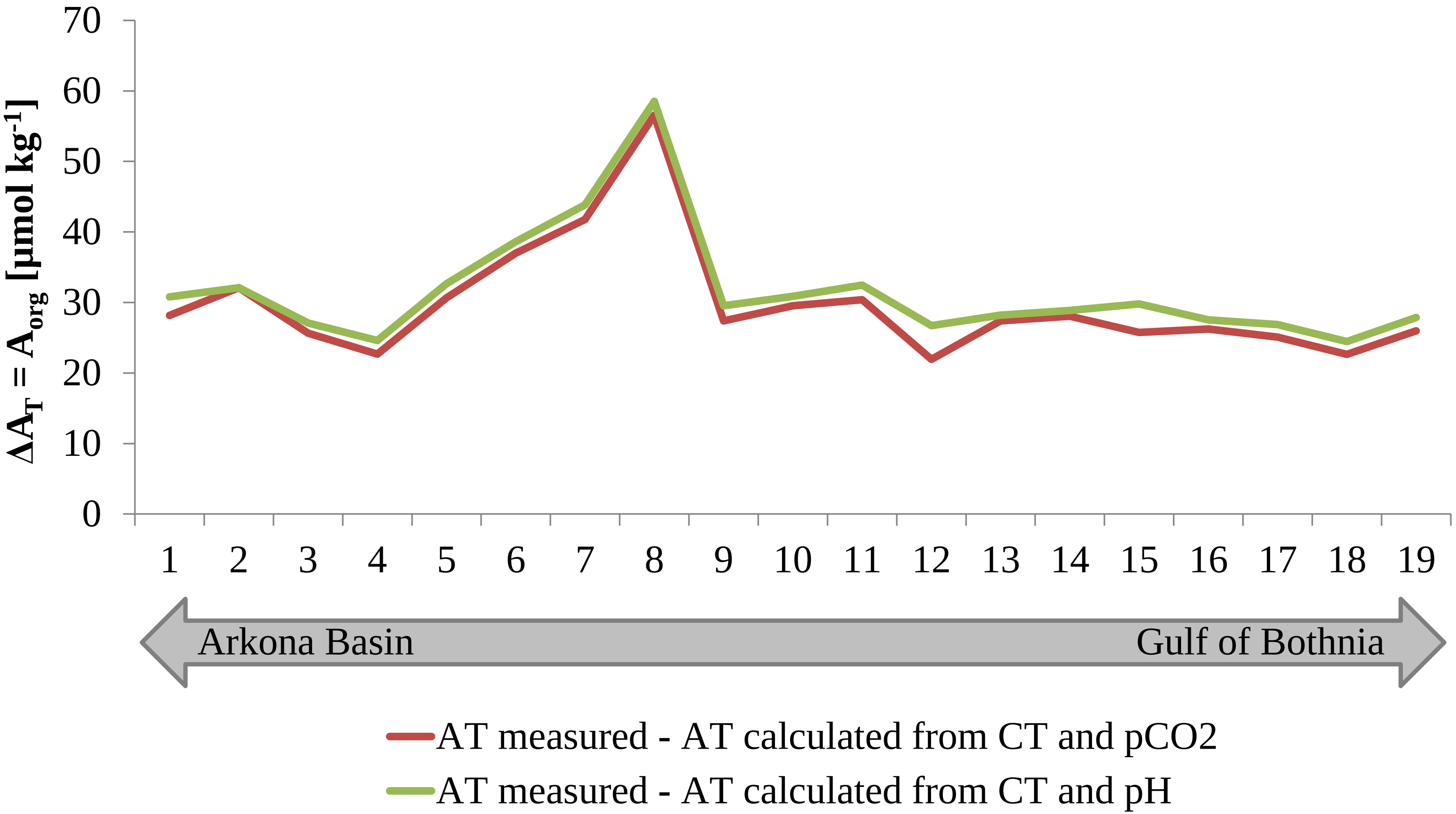
$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^-] + \ldots + [\text{minor bases} - \text{minor acids}]$$



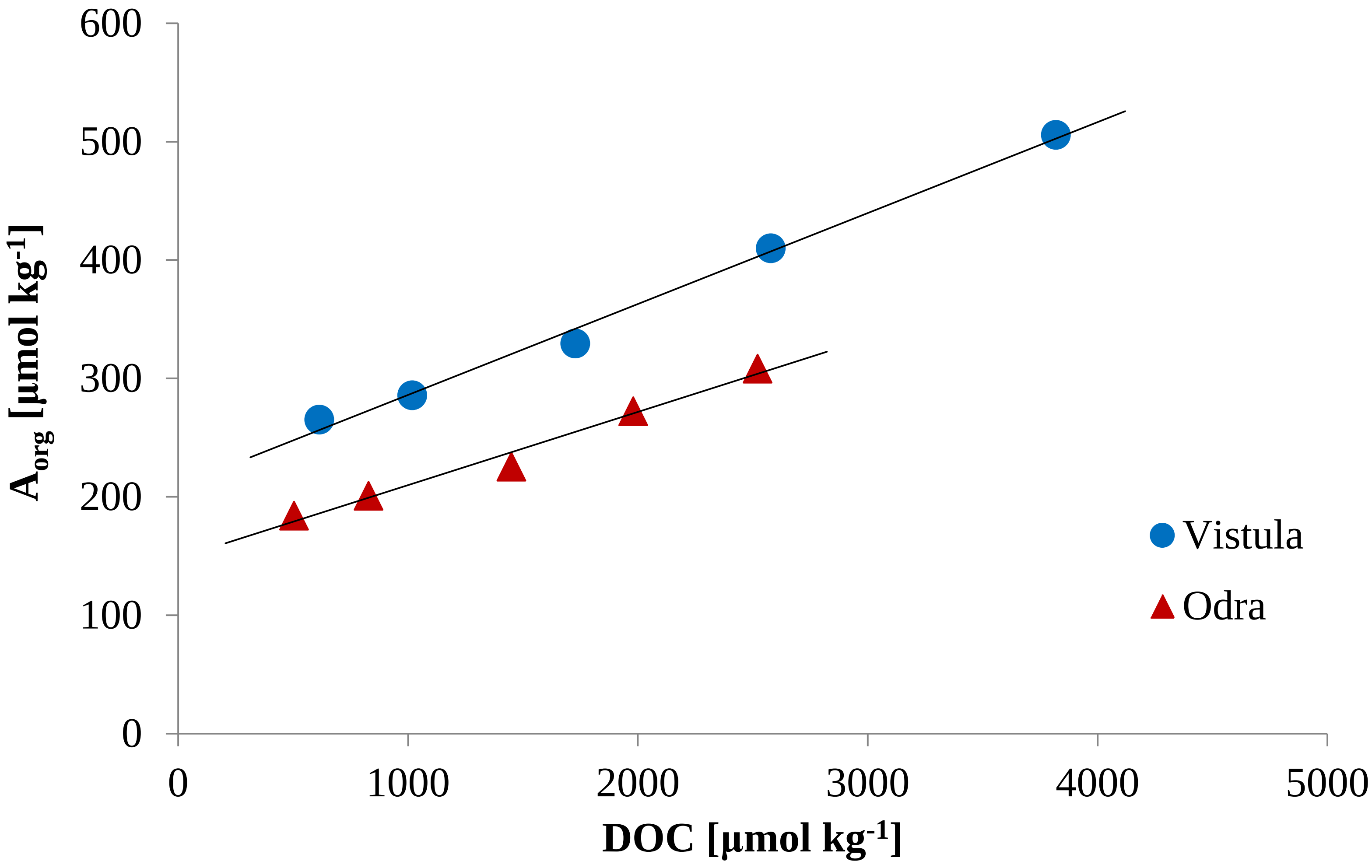


DOM effect on the acid-base system is not included in the thermodynamic model of a seawater

(In)consistency of the acid-base system parameters



$$A_{org} = A_{T(measured)} - A_{T(calculated)}$$



Monoprotic acid dissociation

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

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

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 = 0.2

pK_{DOM} = 7.85

Conclusions 1/2

- Significant inconsistency exists between the acid-base system parameters in the Baltic Sea

- 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. A_{org} in river water is significantly higher: 170 µmol kg^{-1} in Odra and 250 µmol kg^{-1} in Vistula.

- 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 20% of DOC carry the functional groups dissociating in seawater. The pK_{DOM} in the Baltic Sea water amounts to 7.85

- Further studies on geographical and temporal resolution of DOM acid-base properties are required.

DOM
mineralization

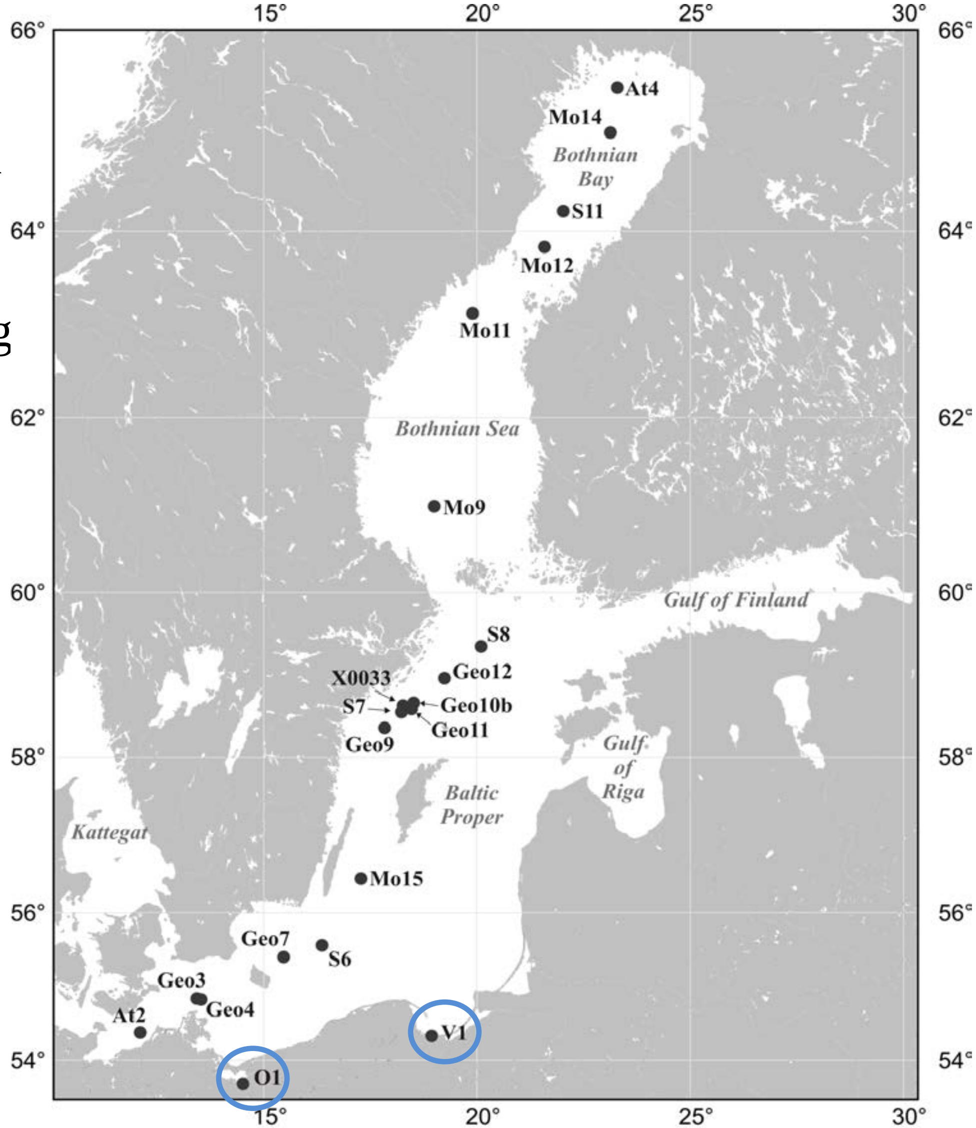
Terrestrial DOM mineralization in sea water

Incubation (dark, 20ºC) of sea water samples spiked with enriched tDOM from Vistula and Odra

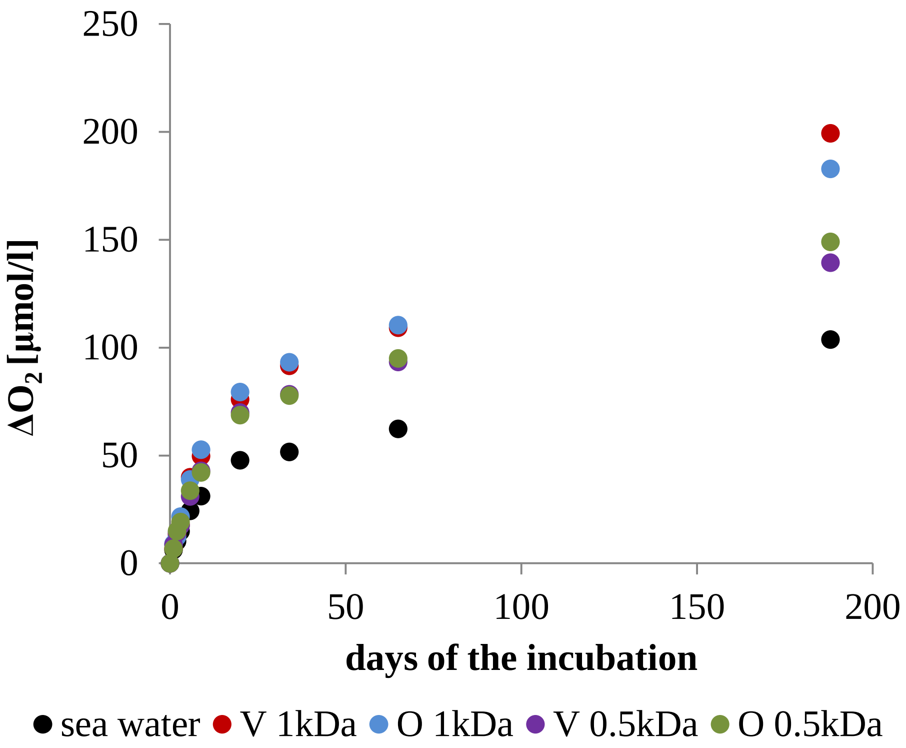
1. sea water (SW) from Bay of Mecklenburg
2. SW + Vistula tDOM > 1kDa
3. SW + Odra tDOM > 1kDa
4. SW + Vistula 0.5kDa > tDOM <1kDa
5. SW + Odra 0.5kDa > tDOM <1kDa

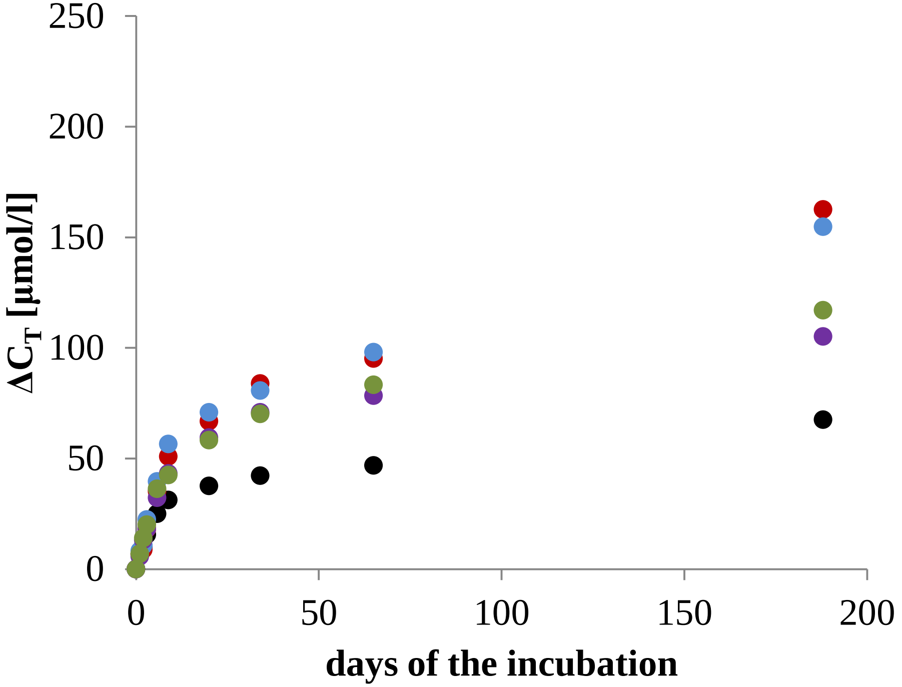
Initial DOC concentrations:

1. 341 µmol L^{-1}
2. 1198 µmol L^{-1}
3. 1129 µmol L^{-1}
4. 847 µmol L^{-1}
5. 891 µmol L^{-1}

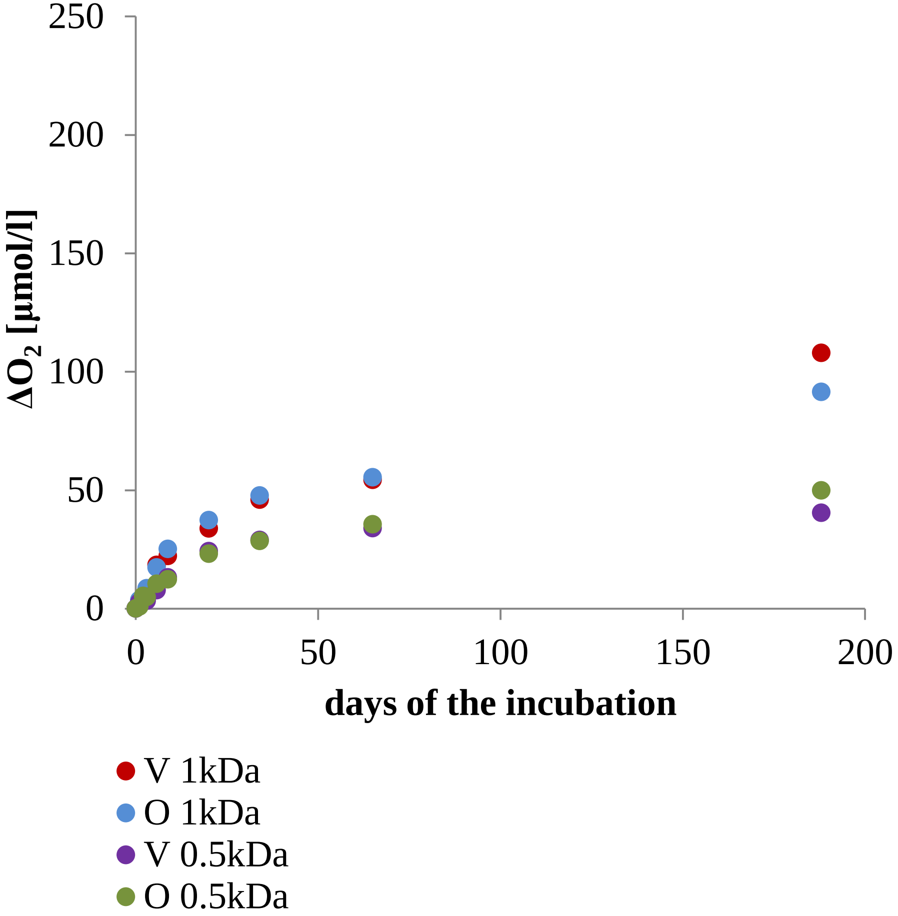


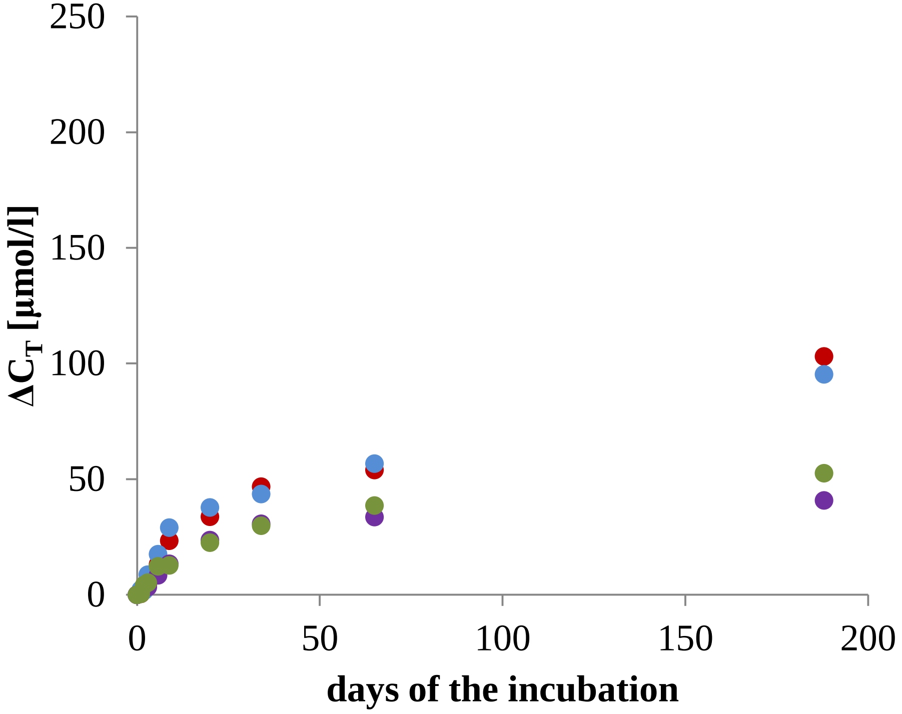
O_2 consumption and CO_2 production





O_2 consumption and CO_2 production due to the terrestrial DOM mineralization





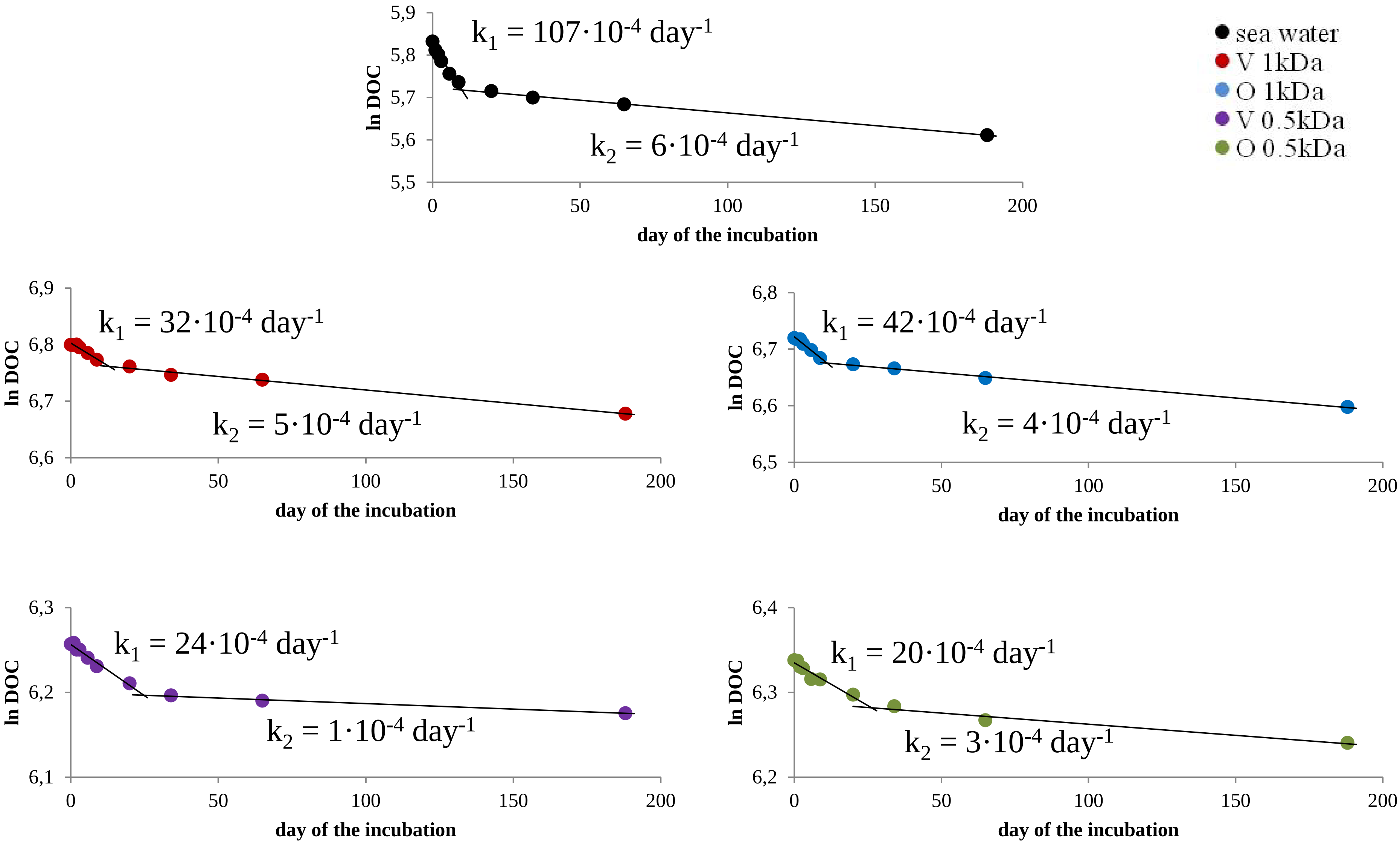
DOM mineralization rate constant (k)

$$DOC_t = DOC_0 \cdot e^{-kt}$$

$$\ln[DOC] = -kt + \ln[DOC_0]$$

$$\mathbf{y = -ax + b}$$

DOM mineralization rate constant (k)

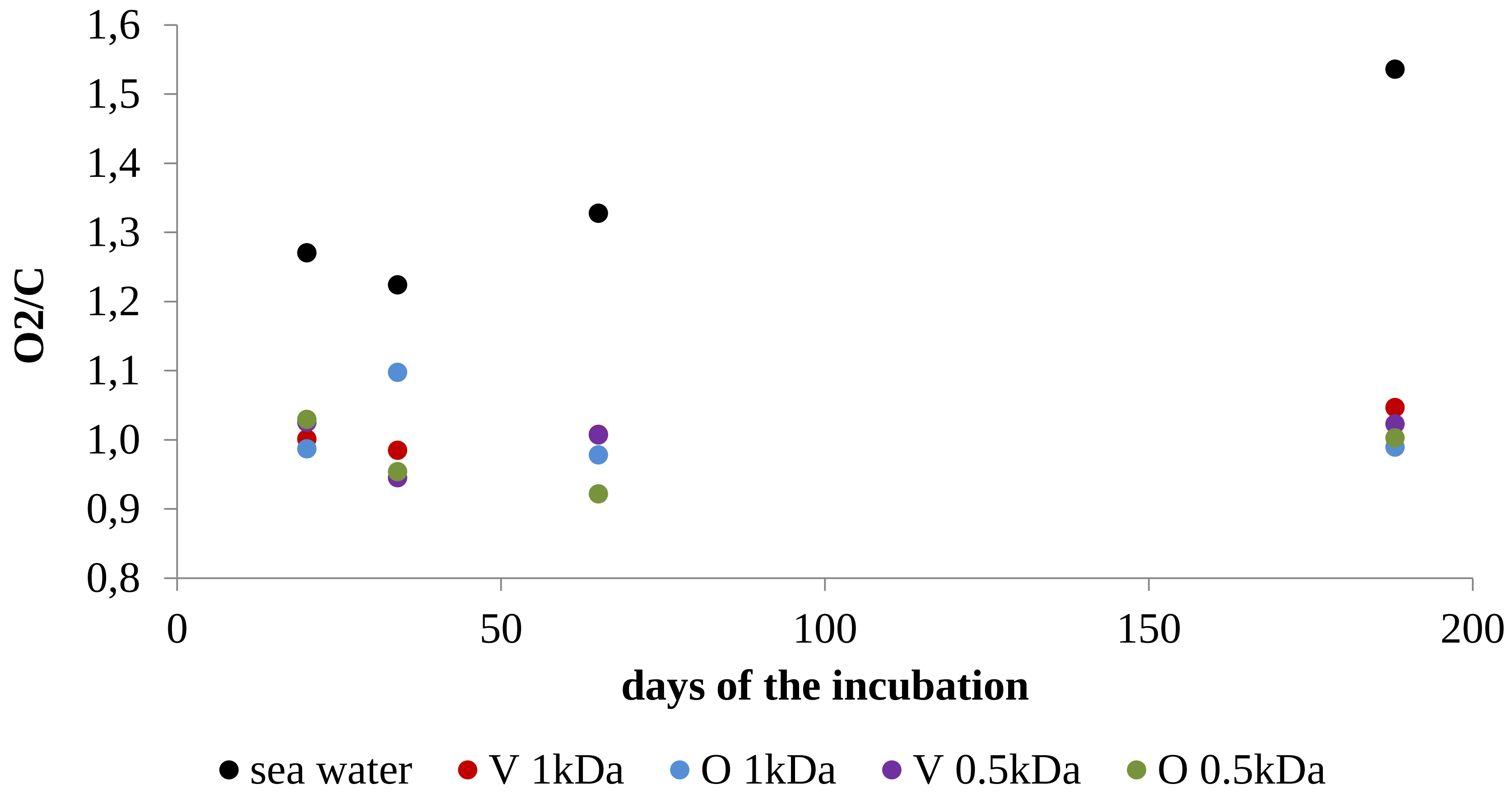


DOM mineralization rate constant (k) and DOM half-life time ($T_{1/2}$)

$$T_{1/2} = \frac{\ln(2)}{k}$$

DOM source	size fraction	labile fraction		semi-labile fraction	
		k_1 [10^{-4} day^{-1}]	$T_{1/2}$ [days]	k_2 [10^{-4} day^{-1}]	$T'_{1/2}$ [days]
seawater	bulk	107	65	6	1155 (3.2 years)
Vistula	DOM > 1kDa	32	217	5	1386 (3.8 years)
	0.5kDa < DOM < 1kDa	24	289	1	6931 (19.0 years)
Odra	DOM > 1kDa	42	165	4	1733 (4.7 years)
	0.5kDa < DOM < 1kDa	20	347	3	2310 (6.3 years)

O_2/C ratio



1,6
1,5
1,4
1,3
1,2
1,1
1,0
0,9
0,8
O2/C
0
50
100
150
200
days of the incubation
sea water
V 1kDa
O 1kDa
V 0.5kDa
O 0.5kDa

O_2/C ratio

Material	Formula	Example	H/C	O/C	N/C	S/C	[a]O_2/C
[b]Polysaccharide	$C_{100}H_{167}O_{83}$	Cellulose	1.67	0.83	0	0	1.00
[b]Protein	$C_{100}H_{158}O_{32}N_{26}S_{0.9}$	Net plankton	1.58	0.32	0.26	0.01	1.57
[b]Lipid	$C_{100}H_{189}O_{11}$	Oleic acid	1.89	0.11	0	0	1.42
[b]RNA	$C_{100}H_{100}O_{50}N_{10}$	Net plankton	0.92	0.32	0.400	0	1.57
[b]Chlorophyll	$C_{100}H_{140}O_{9.5}N_{7.5}$	Chlorophyll *a*	1.40	0.10	0.08	0	1.40
[b]Lignin	$C_{100}H_{108}O_{38}$	Gymnosperm	1.08	0.38	0	0	1.08
[b]Tannin	$C_{100}H_{66}O_{42}$	Angiosperm	0.66	0.42	0	0	0.96
[b]Marine plankton	$C_{100}H_{167}O_{35}N_{16}S_{0.4}$	Net plankton	1.67	0.35	0.16	0.004	1.45
Bacteria	$C_{100}H_{167}O_{35}N_{16}S_{0.4}$	Gram-negative	1.67	0.35	0.16	0.004	1.45
Wood	$C_{100}H_{100}O_{50}$	Gymnosperm	1.00	0.50	0	0	1.00
Tree leaf	$C_{100}H_{100}O_{50}N_{10}$	Angiosperm	1.00	0.50	0.10	0	1.13
Grass	$C_{100}H_{100}O_{50}N_{10}$	Tropical	1.00	0.50	0.10	0	1.13

[a] O_2 requirement for total respiration to CO_2, H_2O and HNO_3 was calculated by using the equation: $C_\alpha H_\beta O_\gamma N_\delta S_\sigma + \omega O_2 = \alpha CO_2 + \beta H_2O + \delta HNO_3 + \sigma SO_3$, where $\omega = 1.00\alpha + 0.25\beta + 1.25\,\delta + 1.5\sigma - 0.5\gamma$ (Hedges *et al.*, 2002).

[b] Calculated from representative structures (rather than directly measured).

Emerson & Hedges, 2008

Conclusions 2/2

- There are two significantly different fractions of DOM: labile and semi-labile (refractory)
- The half-life time of labile fraction of DOM varies from ~2 months for marine DOM to ~6-12 months for terrestrial DOM
- The half-life time of semi-labile (refractory) fraction of DOM amounts to ~3-6 years for marine and terrestrial
- The mass fraction of terrestrial DOM > 1kDa is mineralizaed faster than the DOM < 1kDa
- Mineralization of marine DOM consumes 20-50% more oxygen than mineralization of terrestrial DOM

Thank you