Organic matter mineralization in Baltic Sea deep waters:

Rates and stoichiometry

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Studies of the organic matter mineralization by total CO_2 (C_T, DIC) measurements:

Bulk composition of particulate organic matter (plankton) and standard (Redfield) mineralization stoichiometry (without nitrification and acid-base equilibria):

$$C(H_2O)_{106}(NH_3)_{16}H_3PO_4 + 106\ O_2 = 106\ CO_2 + 16NH_3 + H_3PO_4 + 106\ H_2O$$

O_2 may be replaced by:

NO_3^- (denitrification)

SO_4^{2-} (sulfate reduction)

redox sensitive metal oxides (MnO_2, Fe_2O_3)

Release of CO_2 results in a change of total CO_2:

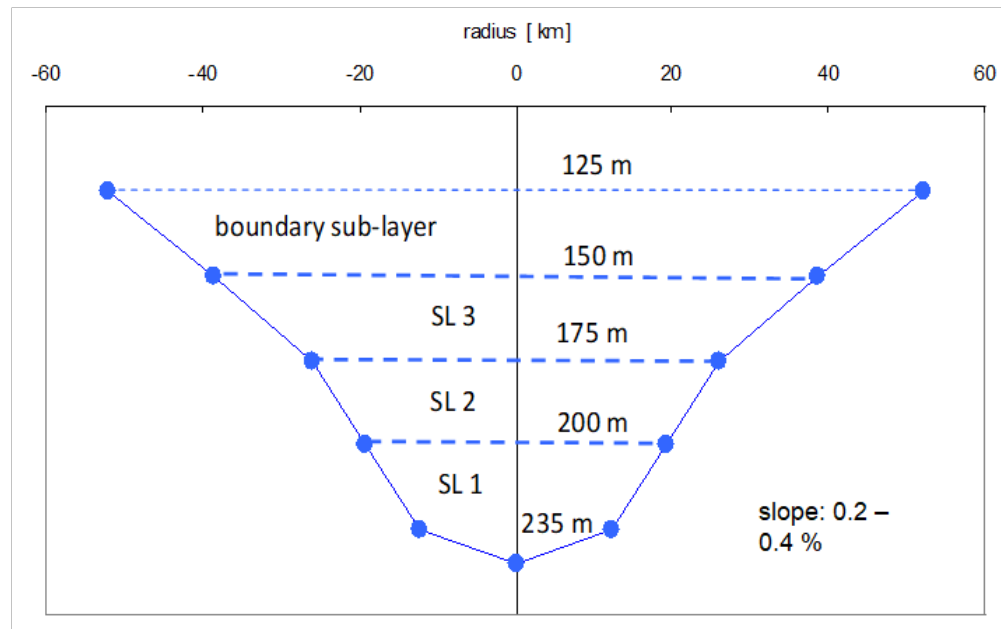$$C_T\ (DIC) = CO_2 + H_2CO_3 + HCO_3^- + CO_3^{2-}$$

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Measurements of total CO_2 in the eastern Gotland Sea at BY15:

- Since 2003, five times per year

- Depth resolution below 125 m: 25 m + bottom water;

- Additional variables: S,T, O_2/H_2S, DIN, PO_4, SiO_2;
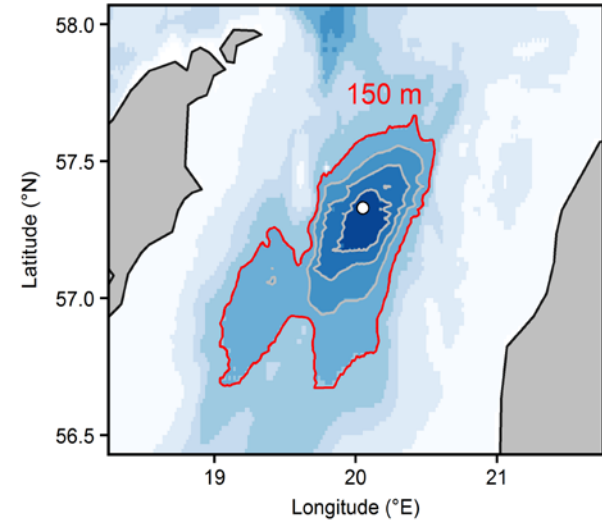
Calculation of mean values for 3 sub-layers (SL) + 1 upper boundary layer:
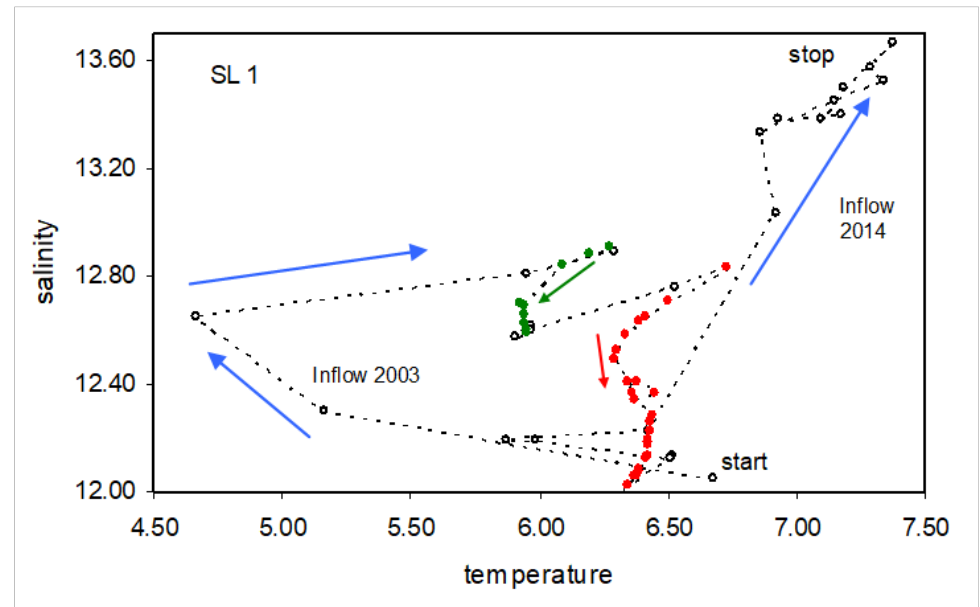
Identification of stagnation periods:

1. Continuous decrease of salinity

2. Continuity in the T-S diagram

Stagnation 1: May 2004 – July 2006
(Schneider et al., 2010)

Stagnation 2: July 2007 – February 2014

Mixing between sub-layers:

salinity flux: $F_S = k_{mix} \cdot \dfrac{\Delta S}{\Delta z}$

(salinity given as mass salt per volume seawater)

➡ salt mass balance for the individual SL ➡ $k_{mix} \cdot$

flux of any variable i: $F_i = k_{mix} \cdot \dfrac{\Delta c_i}{\Delta z}$

➡ $F_i = F_S \cdot \dfrac{\Delta c_i}{\Delta S}$

Mass balance for any variable i in SL n:

$\Delta c = [F_i^{in} \cdot A(n-1) - F_i^{out} \cdot A(n)] \cdot \Delta t / V(n) + \; \Delta q$
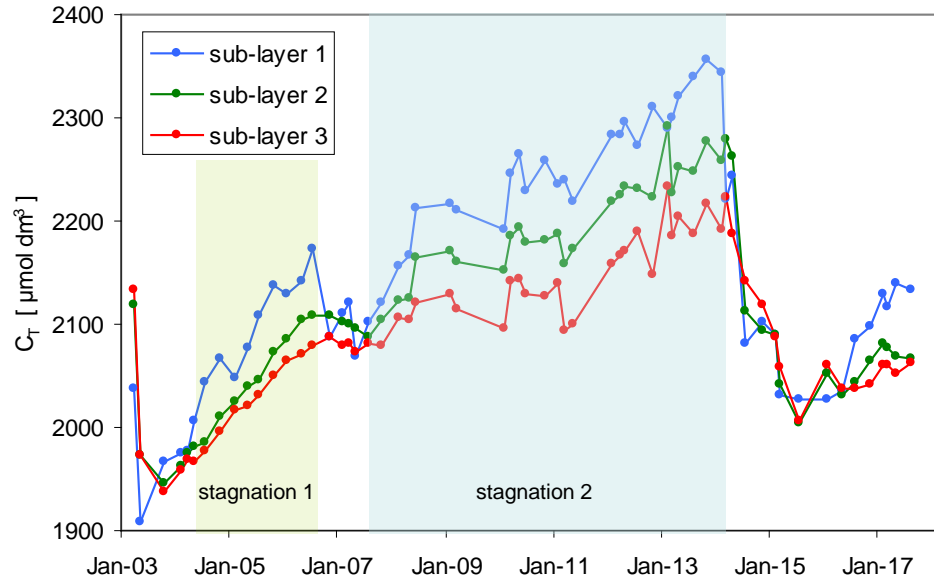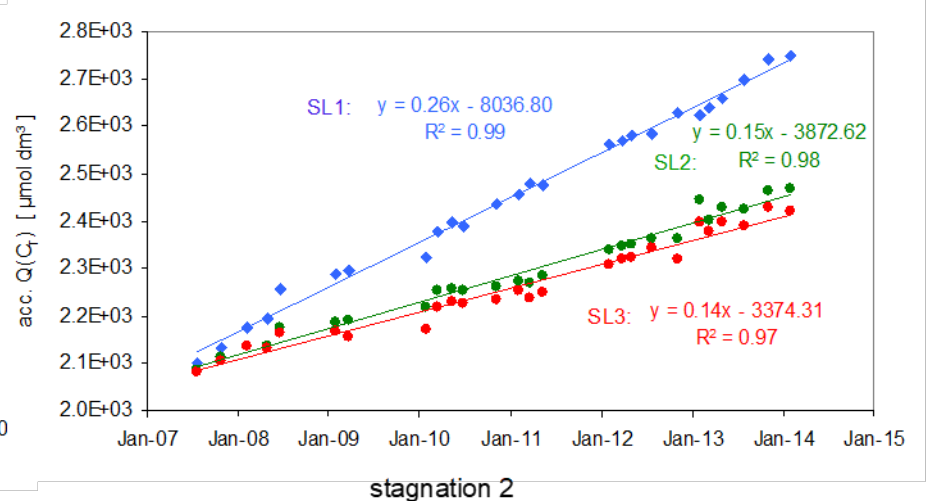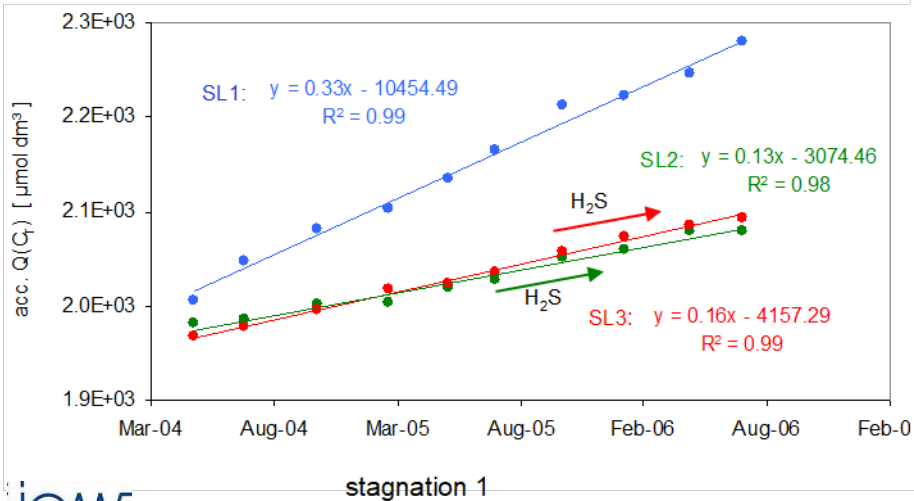
A – SL area;
V – SL volume;
Δq – source/sink term, given as concentration change per time interval;

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Accumulation of total CO_2:

Total CO_2 **concentrations**,

January 2003 – August 2017:

Accumulated total CO_2 **production, $Q(C_T)$,** by OM mineralization, slope corresponds to the mineralization rate:

stagnation 1

SL1: $y = 0.33x - 10454.49$ $R^2 = 0.99$

SL2: $y = 0.13x - 3074.46$ $R^2 = 0.98$

SL3: $y = 0.16x - 4157.29$ $R^2 = 0.99$

stagnation 2

SL1: $y = 0.26x - 8036.80$ $R^2 = 0.99$

SL2: $y = 0.15x - 3872.62$ $R^2 = 0.98$

SL3: $y = 0.14x - 3374.31$ $R^2 = 0.97$

Summary:

Mineralization rates presented as:

- total CO_2 concentration per day;
- total CO_2 per year and sediment
  area of the respective SL;

	stagnation 1[*]			stagnation 2	
	15.5.05 — 23.7.06			31.7.07 — 9.2.14	
	$\mu mol/dm^3$ d	mol/m^2 yr		$\mu mol/dm^3$ d	mol/m^2 yr
SL1	0.327	2.53	SL1	0.259	2.00
SL2	0.131	1.96	SL2	0.152	2.28
SL3	0.161	1.94	SL3	0.139	1.68
z > 150 m	0.180	2.09	z > 150 m	0.162	1.88

*Schneider et al., 2010

Budget for organic carbon???

Outputs:

2.0 mol m^{-2} yr^{-1}, mineralization;

1.5 – 3.0 mol m^{-2} yr^{-1}, accumulation in sediments;

Input:

0.5 mol m^{-2} yr^{-1}, sediment trap;

Imbalance:

3.0 – 4.5 mol m^{-2} yr^{-1}, lateral transport (> 80 %) ???

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Oxidant demand for organic matter mineralization:

Stagnation 1:

1. Oxygen

2. Nitrate (denitrification)

3. Sulphate (sulphate reduction, formation of H_2S)

4. Metal oxides (MnO_2 ?)
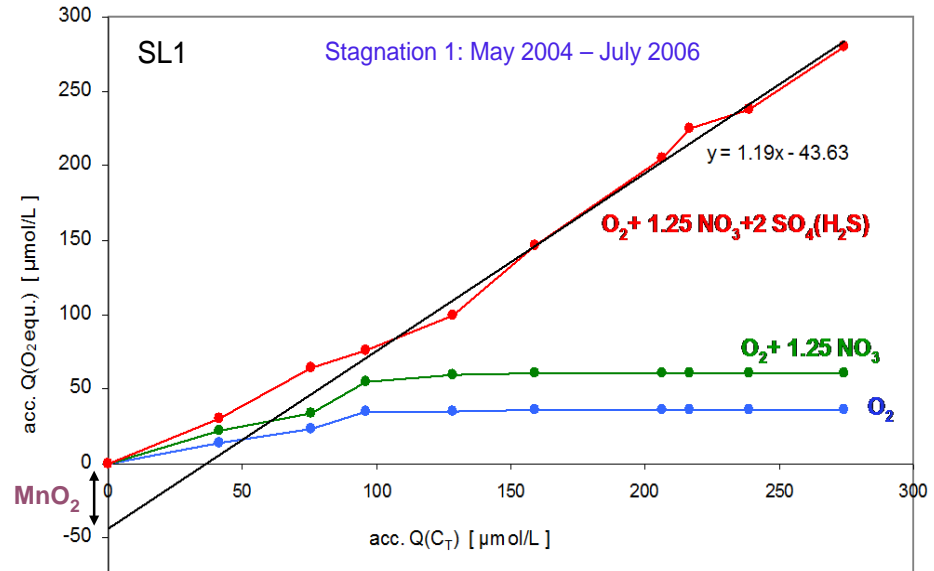
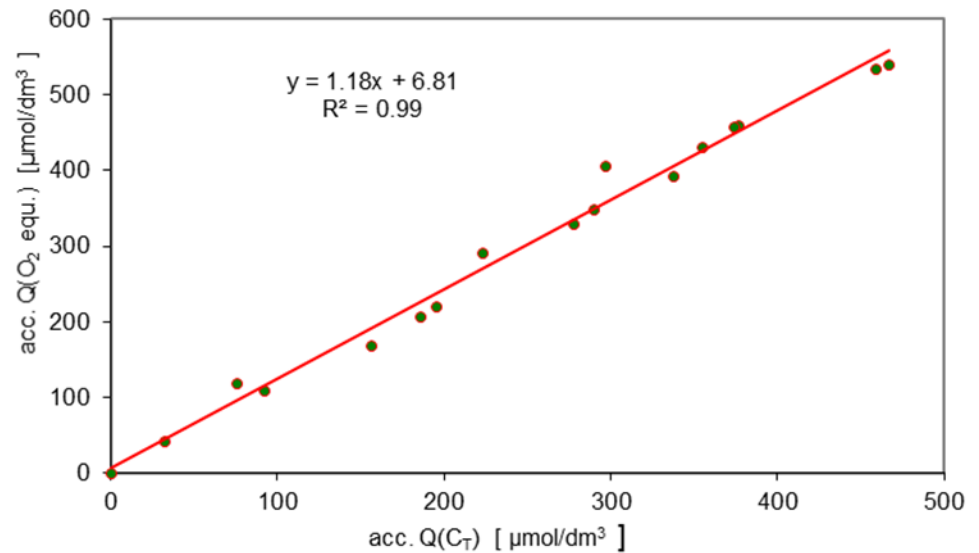**Stagnation 2:**

Only sulphate reduction, formation of H_2S

Mean:

$$\frac{\Delta O_2(equ.)}{\Delta OM} = 1.2$$

Redfield: 1.00 (carbohydrates)

Other studies:

1.11 (Anderson, 1995)

1.20 (Körtzinger et al., 2001)

SL1 — Stagnation 1: May 2004 – July 2006

$y = 1.19x - 43.63$

$O_2 + 1.25\ NO_3 + 2\ SO_4(H_2S)$

$O_2 + 1.25\ NO_3$

O_2

MnO_2

acc. $Q(O_2\ equ.)$ [µmol/L]

acc. $Q(C_T)$ [µmol/L]

$y = 1.18x + 6.81$
$R^2 = 0.99$

acc. $Q(O_2\ equ.)$ [µmol/dm^3]
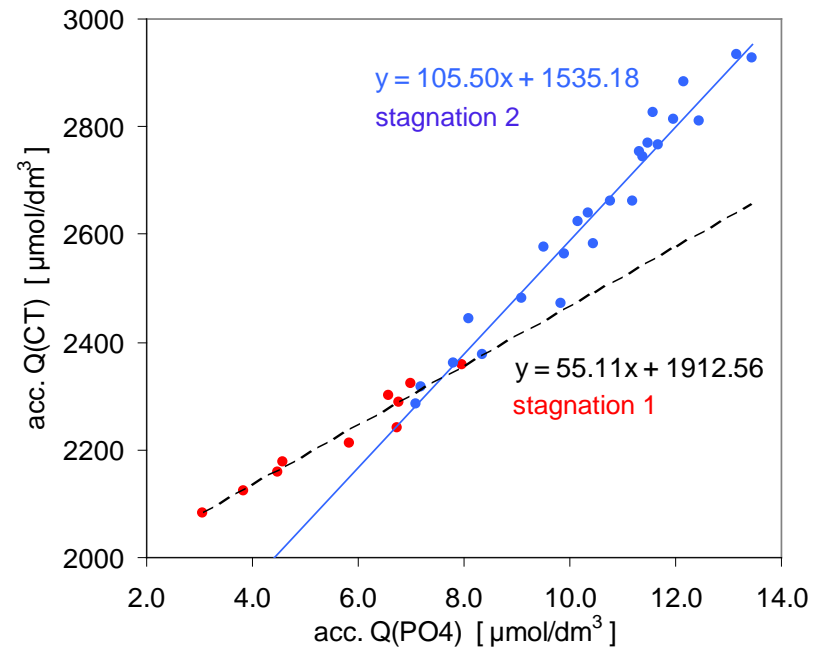
acc. $Q(C_T)$ [µmol/dm^3]

Phosphate release:

Stagnation 1:

OM mineralization and reduction of FeO(OH)-PO$_4$
and release of PO4;

Stagnation 2:

Only OM mineralization and release of PO4
according to the Redfield C/P ratio;

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The message:

- Periods of stagnation exist during which the Gotland Sea below 150 m can be considered as a natural laboratory for studying the kinetics and the stoichiometry of mineralization processes.

- T-S diagrams are useful to identify undisturbed periods of stagnation.

- Vertical mixing must be taken into account for the quantification of mineralization rates.

- Mineralization rates below 150 m amount to 2 mol-C/m^2 yr and indicate strong lateral input of POM.

- The mineralization rates do not change at the switch to sulfate reduction (H_2S formation).

- The oxygen demand for organic carbon mineralization exceeds the Redfield stoichiometry by about 20 %.

- During long-lasting anoxia of PO_4 is released according to the Redfield C/P ratio, excess PO_4 release from $FeO(OH)$-PO_4 is observed during the transition from oxic to anoxic conditions;
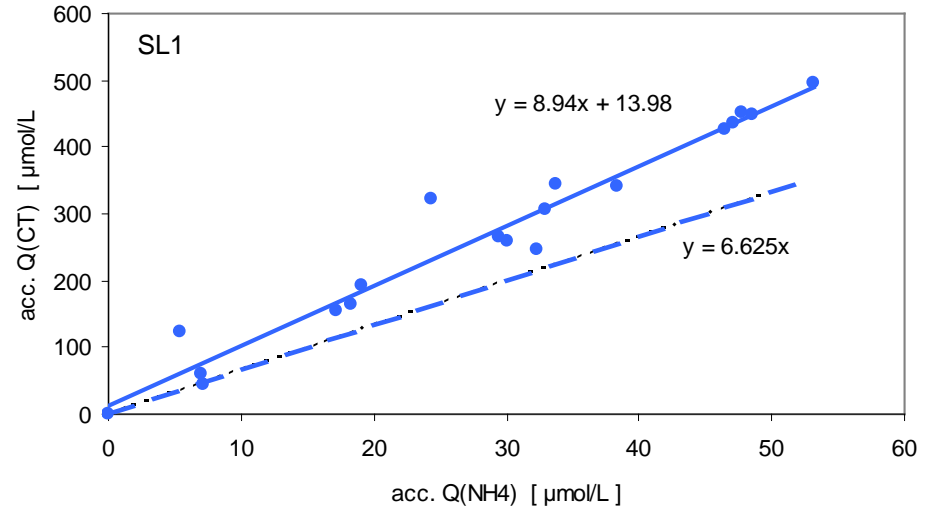
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Release of ammonia during anoxic mineralization:

$$\frac{\Delta Q(C_T)}{\Delta Q(NH_4)} = 8.9$$

C/N ratio of particulate organic material, POM:

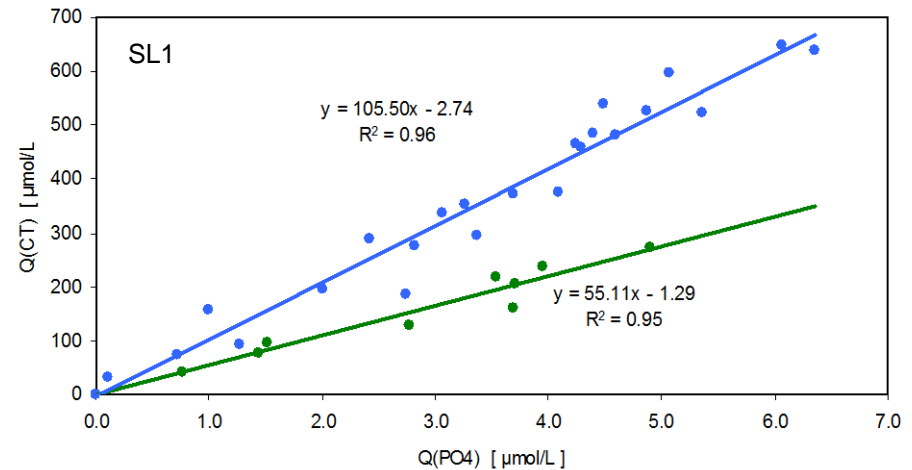Surface: 8.3 (May), 7.7 (July);

> 200 m: 7.5

Release of phosphate:

During transition oxic-anoxic, reduction of FeO(OH)*PO4:

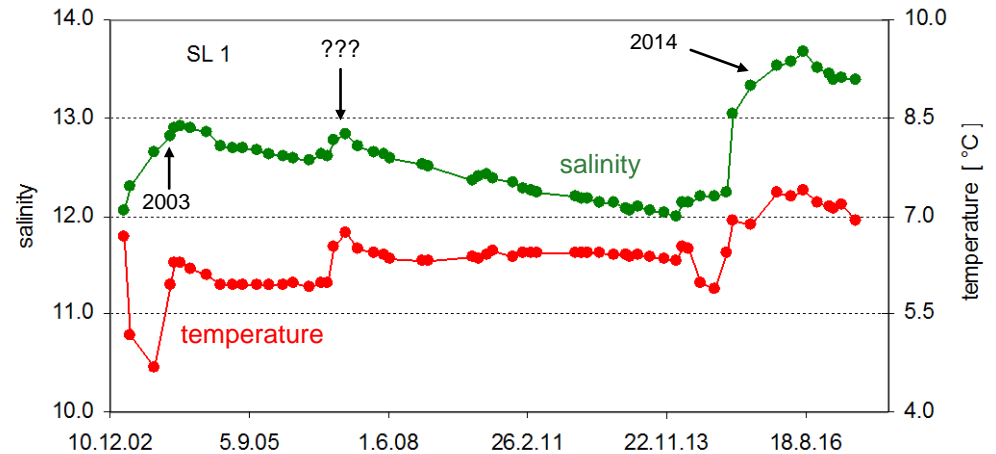$$\frac{\Delta Q(C_T)}{\Delta Q(PO_4)} = 55$$

During long-lasting anoxia:

$$\frac{\Delta Q(C_T)}{\Delta Q(PO_4)} = 106$$

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Identification of stagnation periods:
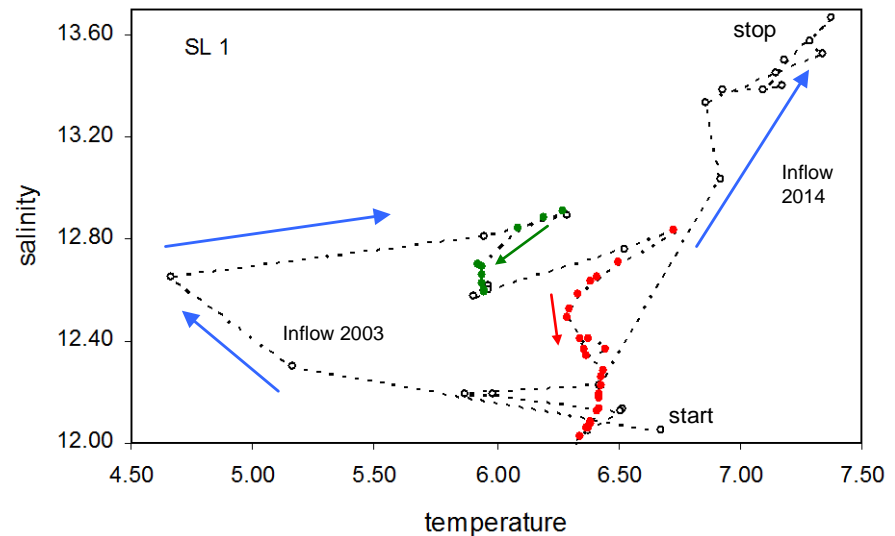
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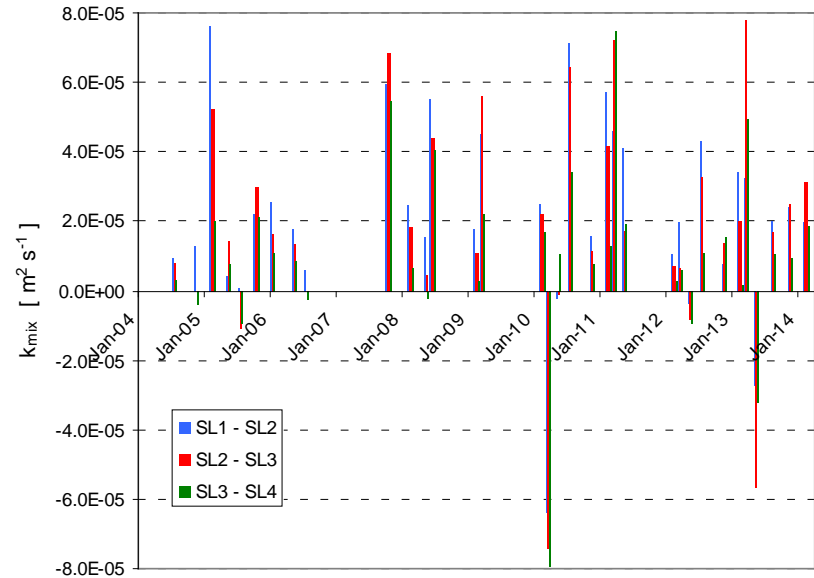
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