

Supplement of Biogeosciences, 16, 437–456, 2019
<https://doi.org/10.5194/bg-16-437-2019-supplement>
© Author(s) 2019. This work is distributed under
the Creative Commons Attribution 4.0 License.



Supplement of

Sedimentary alkalinity generation and long-term alkalinity development in the Baltic Sea

Erik Gustafsson et al.

Correspondence to: Erik Gustafsson (erik.gustafsson@su.se) and Mathilde Hagens (mathilde.hagens@wur.nl)

The copyright of individual parts of the supplement might differ from the CC BY 4.0 License.

Primary and secondary redox reactions

Here we present the redox reactions represented in the RTM (Table S1-S2) and BALTSEM (Table S3), respectively, that are important in terms of TA dynamics and buffering capacity. A more complete description of sediment reactions is available in the supplementary material by Reed et al. (2016). Organic material (OM) in the reactions below is defined as $(\text{CH}_2\text{O})_a(\text{NH}_3)_b(\text{H}_3\text{PO}_4)_c$, where a:b:c defines the molar C:N:P ratios for OM. $\lambda \approx 0.18$ is the P:Fe ratio for iron-bound phosphorus (Reed et al., 2016).

TA in the RTM is defined according to (see Section 2.2.1 of corresponding article):

$$TA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HPO}_4^-] + 2[\text{PO}_4^{3-}] + [\text{NH}_3] + [\text{HS}^-] - [\text{H}^+]$$

TA in BALTSEM is defined according to (see Section 2.2.2 of corresponding article):

$$TA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{HPO}_4^-] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] - [\text{H}^+] - [\text{HF}] - [\text{H}_3\text{PO}_4] + \textit{organic alkalinity}$$

Tables and figures

Table S1. Primary redox reactions implemented in the RTM and the related changes in TA (Δ TA).

Process	Δ TA
Aerobic mineralization $OM + aO_2 \rightarrow aCO_2 + aH_2O + bNH_3 + cH_3PO_4$	$b - c$
Denitrification $OM + \frac{4a}{5}NO_3^- \rightarrow \frac{a}{5}CO_2 + \frac{4a}{5}HCO_3^- + \frac{3a}{5}H_2O + \frac{2a}{5}N_2 + bNH_3 + cH_3PO_4$	$0.8a + b - c$
Manganese oxide (MnO ₂) reduction $OM + 2aMnO_2 + 3aCO_2 + aH_2O \rightarrow 4aHCO_3^- + 2aMn^{2+} + bNH_3 + cH_3PO_4$	$4a + b - c$
Iron oxyhydroxide (Fe(OH) ₃) reduction $OM + 4a\{Fe(OH)_3 - \lambda HPO_4^-\} + 7aCO_2 \rightarrow 8aHCO_3^- + 3aH_2O + 4aFe^{2+} + bNH_3 + cH_3PO_4 + 4a\lambda HPO_4^-$	$8a + b - c + 4a\lambda$
Sulfate (SO ₄ ²⁻) reduction $OM + \frac{a}{2}SO_4^{2-} \rightarrow aHCO_3^- + \frac{a}{2}H_2S + bNH_3 + cH_3PO_4$	$a + b - c$
Methanogenesis $OM \rightarrow \frac{a}{2}CO_2 + \frac{a}{2}CH_4 + bNH_3 + cH_3PO_4$	$b - c$

Table S2. Secondary redox reactions implemented in the RTM and the related changes in TA (ΔTA).

Process	ΔTA
Nitrification $2O_2 + NH_4^+ + 2HCO_3^- \rightarrow NO_3^- + 2CO_2 + 3H_2O$	-2
Manganese re-oxidation $O_2 + 2Mn^{2+} + 4HCO_3^- \rightarrow 2MnO_2 + 4CO_2 + 2H_2O$	-4
Iron re-oxidation $O_2 + 4Fe^{2+} + 8HCO_3^- + 2H_2O + 4\lambda HPO_4^- \rightarrow 4\{Fe(OH)_3 - \lambda HPO_4^-\} + 8CO_2$	-8 - 4 λ
Iron monosulfide (FeS) re-oxidation $2O_2 + FeS \rightarrow SO_4^- + Fe^{2+}$	0
Pyrite re-oxidation $7O_2 + FeS_2 + 2H_2O \rightarrow 4SO_4^- + 2Fe^{2+} + 4H^+$	-4
Dissolved sulfide (H ₂ S) re-oxidation $2O_2 + H_2S + 2HCO_3^- \rightarrow SO_4^- + 2CO_2 + 2H_2O$	-2
Aerobic methane oxidation $2O_2 + CH_4 \rightarrow CO_2 + 2H_2O$	0
Iron re-oxidation coupled to manganese oxide reduction $MnO_2 + 2Fe^{2+} + 2\lambda HPO_4^- + 2H_2O + 2HCO_3^- \rightarrow 2\{Fe(OH)_3 - \lambda HPO_4^-\} + Mn^{2+} + 2CO_2$	-2 - 2 λ
Manganese oxide reduction using dissolved sulfide $MnO_2 + H_2S + 2CO_2 \rightarrow Mn^{2+} + S_0 + 2HCO_3^-$	2
Iron oxyhydroxide reduction using dissolved sulfide $2\{Fe(OH)_3 - \lambda HPO_4^-\} + H_2S + 4CO_2 \rightarrow 2Fe^{2+} + 2\lambda HPO_4^- + S_0 + 4HCO_3^- + 2H_2O$	4 + 2 λ
Iron monosulfide (FeS) formation $Fe^{2+} + H_2S + 2HCO_3^- \rightarrow FeS + 2H_2O + 2CO_2$	-2
Anaerobic CH ₄ oxidation by SO ₄ ²⁻ reduction $SO_4^- + CH_4 + CO_2 \rightarrow 2HCO_3^- + H_2S$	2
Elemental sulfur disproportionation $4S_0 + 4H_2O \rightarrow 3H_2S + SO_4^- + 2H^+$	-2
Pyrite (FeS ₂) formation using dissolved sulfide $FeS + H_2S \rightarrow FeS_2 + H_2$	0
Pyrite (FeS ₂) formation using elemental sulfur $FeS + S_0 \rightarrow FeS_2$	0
Vivianite (Fe ₃ (PO ₄) ₂ ·8H ₂ O) formation $3Fe^{2+} + 2HPO_4^- + 8H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O + 2H^+$	-4
Transformation from amorphous (α) to well-crystalline (β) iron oxyhydroxide (Fe(OH) ₃) $Fe(OH)_3^\alpha \rightarrow Fe(OH)_3^\beta$	0
Transformation from amorphous (α) to well-crystalline (β) manganese oxide (MnO ₂) $MnO_2^\alpha \rightarrow MnO_2^\beta$	0

Table S3. Reactions included in BALTSEM and the related changes in TA (ΔTA).

Process	ΔTA
Primary production	
$aCO_2 + (a + b)H_2O + bHNO_3 + cH_3PO_4 \rightarrow OM + (a + 2b)O_2$	b + c
$aCO_2 + aH_2O + bNH_3 + cH_3PO_4 \rightarrow OM + aO_2$	-b + c
Aerobic mineralization	
$OM + aO_2 \rightarrow aCO_2 + aH_2O + bNH_3 + cH_3PO_4$	b - c
Denitrification	
$OM + \frac{4a}{5}NO_3^- \rightarrow \frac{a}{5}CO_2 + \frac{4a}{5}HCO_3^- + \frac{3a}{5}H_2O + \frac{2a}{5}N_2 + bNH_3 + cH_3PO_4$	0.8a + b - c
Sulfate ($SO_4^{=}$) reduction	
$OM + \frac{a}{2}SO_4^{=} \rightarrow aHCO_3^- + \frac{a}{2}H_2S + bNH_3 + cH_3PO_4$	a + b - c
Nitrification	
$2O_2 + NH_4^+ + 2HCO_3^- \rightarrow NO_3^- + 2CO_2 + 3H_2O$	-2
Dissolved sulfide (H_2S) re-oxidation	
$2O_2 + H_2S + 2HCO_3^- \rightarrow SO_4^{=} + 2CO_2 + 2H_2O$	-2

Table S4. Equilibrium constants and associated equations for pH-dependent species.

Parameter	Equation K-value	Reference K-value
K_{CO_2}	$\frac{[HCO_3^-][H^+]}{[CO_2(aq)]}$	Millero et al. (2006)
$K_{HCO_3^-}$	$\frac{[HCO_3^-]}{[CO_3^{2-}][H^+]}$	Millero et al. (2006)
$K_{NH_4^+}$	$\frac{[NH_3][H^+]}{[NH_4^+]}$	Millero et al. (1995)
$K_{H_2PO_4^-}$	$\frac{[H_2PO_4^-]}{[HPO_4^{2-}][H^+]}$	Millero et al. (1995)
$K_{HPO_4^{2-}}$	$\frac{[H_2PO_4^-]}{[PO_4^{3-}][H^+]}$	Millero et al. (1995)
K_{H_2S}	$\frac{[HS^-][H^+]}{[H_2S]}$	Löffler et al. (2011)

Table S5. Pore water DIC and TA data (both in mM) measured at site F80 in June 2016.

Depth (cm)	DIC (mM)	TA (mM)
0	1.8	2.2
0.25	2.2	2.3
0.75	2.3	2.8
1.25	3.0	3.3
1.75	3.5	3.9
2.5	4.3	4.7
3.4	4.7	5.2
4.5	5.5	5.8
5.5	6.0	6.3
6.5	6.5	6.8
7.5	7.2	7.4
8.5	8.0	8.3
9.5	8.5	8.6
11	9.3	9.3
13	10.2	10.0
15	11.2	11.2
17	12.0	11.7
19	12.7	12.2
22	13.4	13.3
26	14.4	13.7
30	15.8	15.8
34	16.8	16.8
38	17.4	17.9
42	17.5	17.6
45.5	18.3	17.9

Table S6. Depth-integrated reaction rates of all processes involved in the S solids cycle at F80, as well as total formation rates for each of the three S solid species (all in mmol S m⁻² y⁻¹). Negative numbers indicate a net loss of this species.

Rates (all in mmol S m ⁻² y ⁻¹)						
Period	FeS from $\Sigma\text{H}_2\text{S}$ and Fe^{2+}	FeS ₂ from FeS and S ⁰	FeS ₂ from FeS and $\Sigma\text{H}_2\text{S}$	S ⁰ from MnO ₂ and $\Sigma\text{H}_2\text{S}$	S ⁰ from Fe(OH) ₃ and $\Sigma\text{H}_2\text{S}$	FeS re-oxidation
1970-1973	19	7.1	12	6.5	8.0	0.01
1973-1978	65	24	37	5.5	25	0.02
1978-1981	283	73	182	0.82	76	0.06
1981-2009	73	36	39	0.49	42	0.00
Average	82	34	47	1.7	39	0.01

Period	FeS ₂ re-oxidation	S ⁰ disproportionation	Total FeS ₂ formation	Total FeS formation	Total S ⁰ formation	Total S solid formation
1970-1973	0.00	1.87	137	0.00	-0.06	37
1973-1978	0.12	1.82	120	5.2	-0.08	125
1978-1981	0.11	0.77	512	27	-0.14	539
1981-2009	0.00	1.63	151	-2.3	-0.05	148
Average	0.02	1.61	163	1.1	-0.06	164

Table S7. Observed linear TA-salinity relations for the mixing of Baltic Proper and Kattegat waters.

Year	Observed TA-salinity relation	Reference
1957	$TA = 48S + 1128$ ($\mu\text{mol kg}^{-1}$)	Gripenberg (1960) ¹
1986	$TA = 31S + 1270$ ($\mu\text{mol kg}^{-1}$)	Ohlson and Anderson (1990)
2000-2004	$TA = 29.2S + 1417$ ($\mu\text{mol l}^{-1}$)	Perttilä et al. (2006)
2008	$TA = 25.3S + 1470$ ($\mu\text{mol kg}^{-1}$)	Beldowski et al. (2010)

1. Calculated by Dyrssen (1993).

Table S8. Observed linear TA-salinity relations for the mixing of Baltic Proper and Gulf of Bothnia waters.

Year	Observed TA-salinity relation	Reference
1927-1935	$TA = 179S + 274$ ($\mu\text{mol l}^{-1}$)	Based on Buch (1945)
1957	$TA = 180S + 177$ ($\mu\text{mol kg}^{-1}$)	Gripenberg (1960) ¹
1986	$TA = 177S + 139$ ($\mu\text{mol kg}^{-1}$)	Ohlson and Anderson (1990)
2000-2004	$TA = 223S + 89.7$ ($\mu\text{mol l}^{-1}$)	Perttilä et al. (2006)
2008	$TA = 205S + 229$ ($\mu\text{mol kg}^{-1}$)	Beldowski et al. (2010)

1. Calculated by Dyrssen (1993).

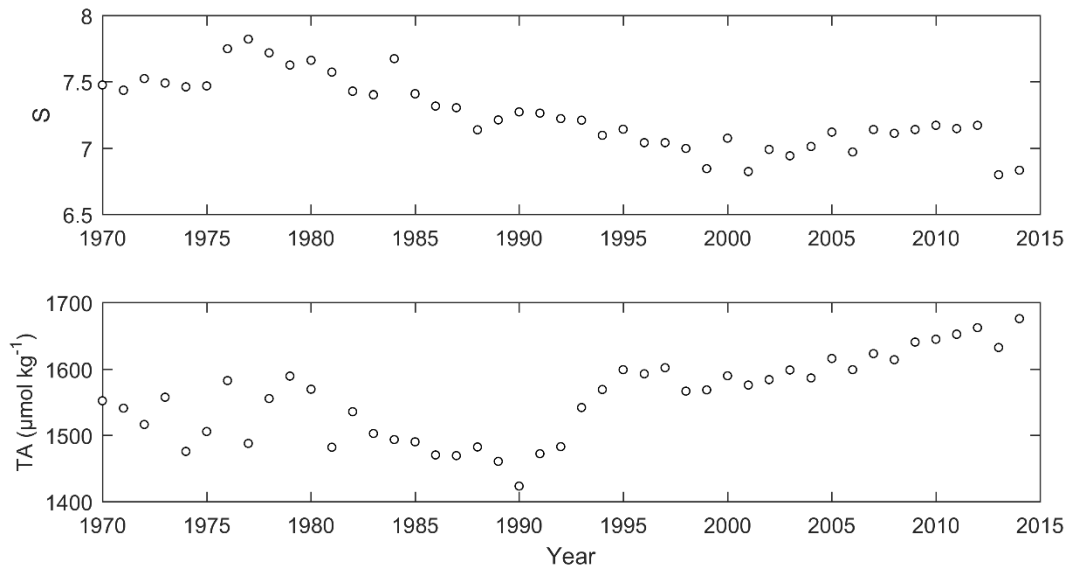


Figure S1. Annual mean observed surface water salinity and TA at station BY15 in the Gotland Sea.

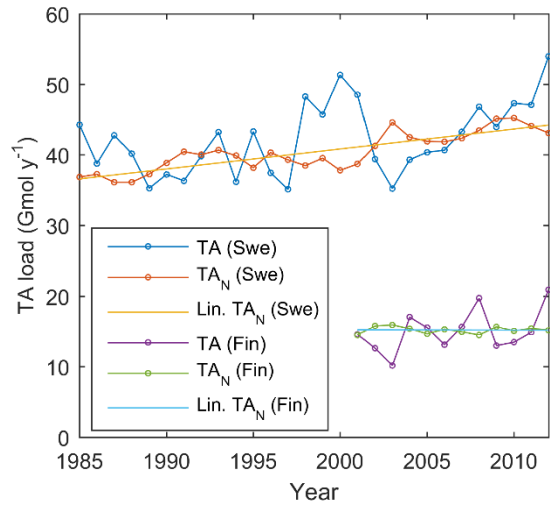


Figure S2. Observed riverine TA loads, flow normalized TA loads (TA_N) (Gmol y⁻¹), and linear trends (Lin. TA_N) in Swedish (Swe) and Finnish (Fin) rivers respectively.

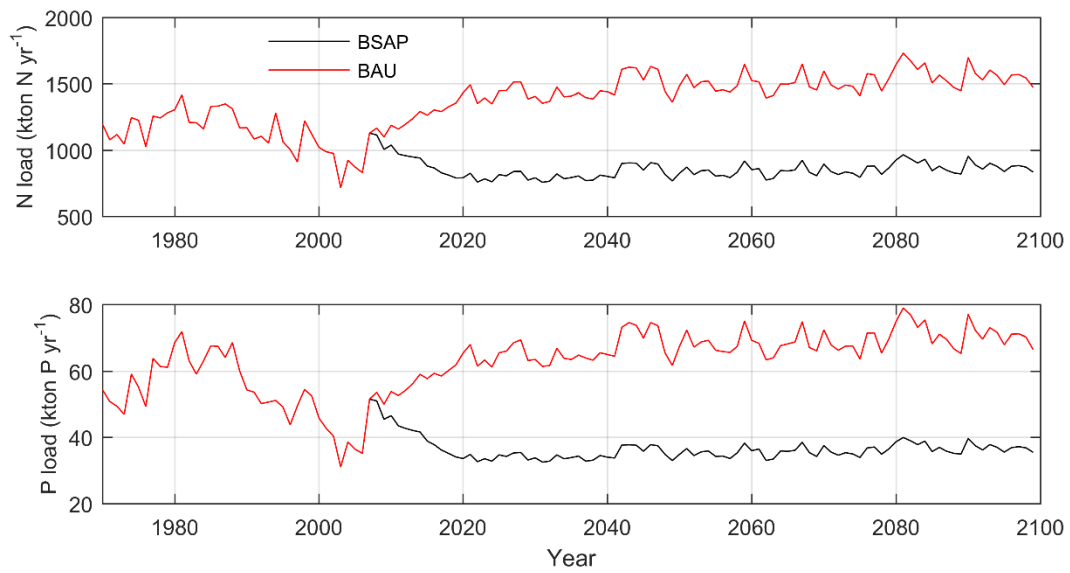


Figure S3. Nitrogen and phosphorus loads (land loads + atmospheric depositions) according to the BSAP and BAU scenarios respectively.

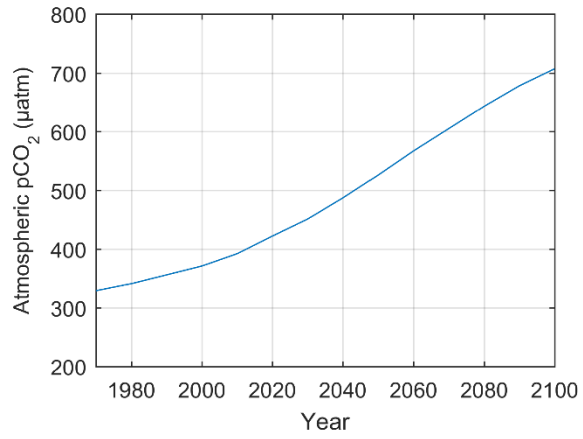


Figure S4. Annual mean atmospheric CO₂ partial pressure (pCO₂) according to the A1B emission scenario.

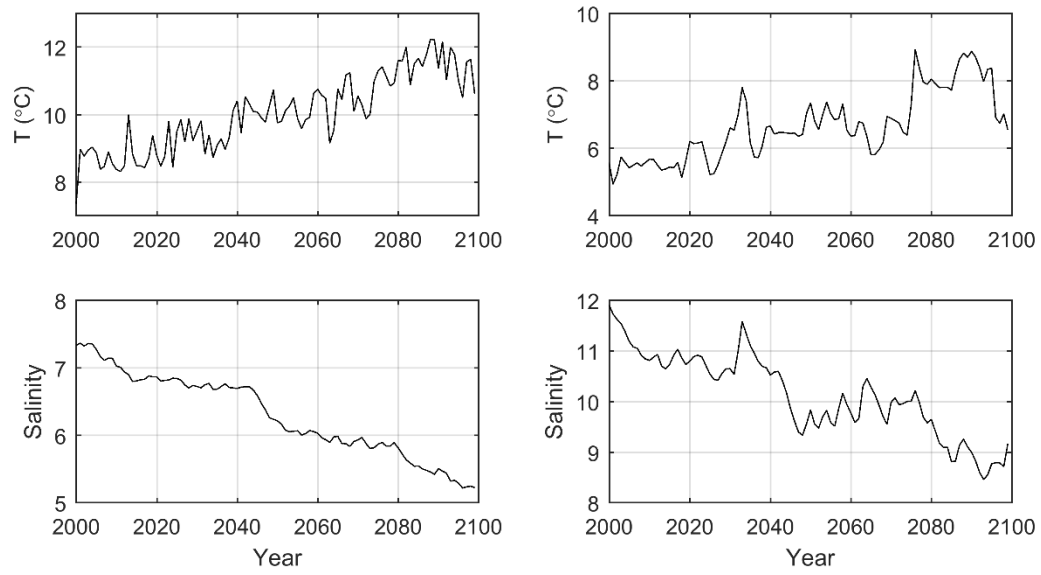


Figure S5. Simulated annual mean surface water (left) and deep water (right) temperature and salinity in the Gotland Sea.

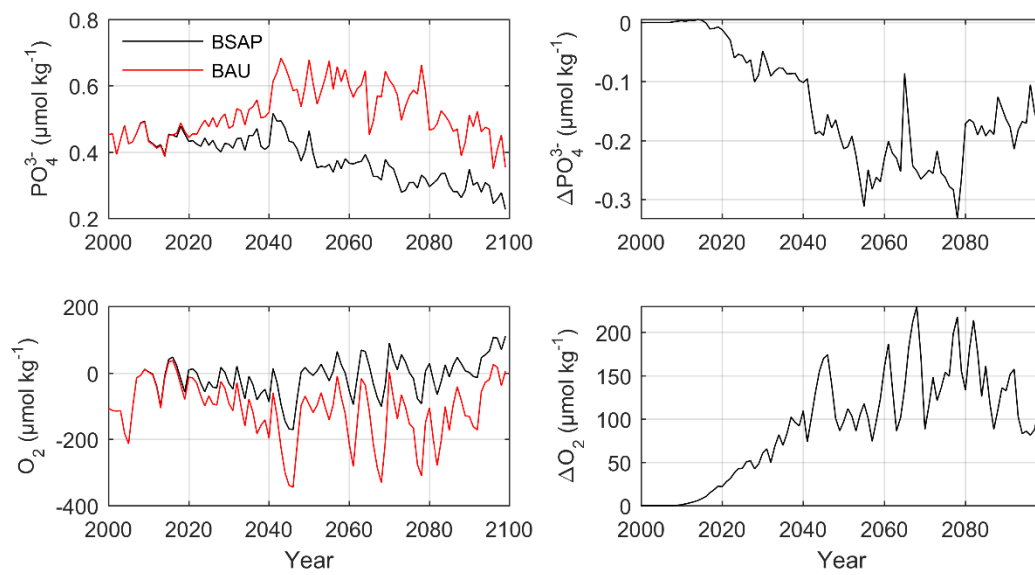


Figure S6. Left: simulated annual mean surface water phosphate and deep water oxygen concentrations in the Gotland Sea according to the BSAP (black lines) and BAU (red lines) nutrient load scenarios respectively. Right: differences between the BSAP and BAU scenarios.

References

- Beldowski, J., Löffler, A., Schneider, B. and Joensuu, L.: Distribution and biogeochemical control of total CO₂ and total alkalinity in the Baltic Sea, *Journal of Marine Systems*, 81(3), 252–259, doi:10.1016/j.jmarsys.2009.12.020, 2010.
- Buch, K.: Kolsyrejämvikten i Baltiska Havet. *Fennia*, 68, 29–81, 1945.
- Dyrssen, D.: The Baltic-Kattegat-Skagerrak Estuarine System, *Estuaries*, 16(3), 446, doi:10.2307/1352592, 1993.
- Gripenberg, S.: On the alkalinity of Baltic waters, *Journal du Conseil International pour l'Exploration de la Mer*, 26(1), 5–20, 1960.
- Löffler, A., Schneider, B., Schmidt, M. and Nausch, G.: Estimation of denitrification in Baltic Sea deep water from gas tension measurements, *Marine Chemistry*, 125(1–4), 91–100, doi:10.1016/j.marchem.2011.02.006, 2011.
- Millero, F. J.: Thermodynamics of the carbon dioxide system in the oceans, *Geochimica et Cosmochimica Acta*, 59(4), 661–677, doi:10.1016/0016-7037(94)00354-O, 1995.
- Millero, F. J., Graham, T. B., Huang, F., Bustos-Serrano, H. and Pierrot, D.: Dissociation constants of carbonic acid in seawater as a function of salinity and temperature, *Marine Chemistry*, 100(1–2), 80–94, doi:10.1016/j.marchem.2005.12.001, 2006.
- Ohlson, M. and Anderson, L.: Recent investigation of total carbonate in the Baltic Sea: changes from the past as a result of acid rain?, *Marine Chemistry*, 30, 259–267, doi:10.1016/0304-4203(90)90075-N, 1990.
- Perttilä, M., Terrihauta, S., Lemponen, P., Riikonen, J., Grau Garcia, M., Hernández Abós, E. and Rodríguez Moles, J.: Alkalinity - calcium - salinity relations in the Baltic Sea 1. Data description and general considerations, Meri: Report Series of the Finnish Institute of Marine Research, Finnish Institute of Marine Research., 2006.
- Reed, D. C., Gustafsson, B. G. and Slomp, C. P.: Shelf-to-basin iron shuttling enhances vivianite formation in deep Baltic Sea sediments, *Earth and Planetary Science Letters*, 434, 241–251, doi:10.1016/j.epsl.2015.11.033, 2016.