

### Primary and secondary redox reactions

Here we present redox reactions represented by 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 ( $\Delta$ TA).**

Process	$\Delta$ 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 <sub>2</sub> ) 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) <sub>3</sub> ) 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 <sub>4</sub> <sup>=</sup> ) reduction $OM + \frac{a}{2}SO_4^= \rightarrow aHCO_3^- + \frac{a}{2}H_2S + bNH_3 + cH_3PO_4$	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 ( $\Delta$ TA).**

Process	$\Delta$ TA
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 $\lambda$
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 <sub>2</sub> 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 $\lambda$
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 $\lambda$
Iron monosulfide (FeS) formation $Fe^{2+} + H_2S + 2HCO_3^- \rightarrow FeS + 2H_2O + 2CO_2$	-2
Anaerobic CH <sub>4</sub> oxidation by SO <sub>4</sub> <sup>2-</sup> 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 <sub>2</sub> ) formation using dissolved sulfide $FeS + H_2S \rightarrow FeS_2 + H_2$	0
Pyrite (FeS <sub>2</sub> ) formation using elemental sulfur $FeS + S_0 \rightarrow FeS_2$	0
Vivianite (Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O) formation $3Fe^{2+} + 2HPO_4^- + 8H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O + 2H^+$	-4
Transformation from amorphous ( $\alpha$ ) to well-crystalline ( $\beta$ ) iron oxyhydroxide (Fe(OH) <sub>3</sub> ) $Fe(OH)_3^\alpha \rightarrow Fe(OH)_3^\beta$	0
Transformation from amorphous ( $\alpha$ ) to well-crystalline ( $\beta$ ) manganese oxide (MnO <sub>2</sub> ) $MnO_2^\alpha \rightarrow MnO_2^\beta$	0

**Table S3. Reactions included in BALTSEM and the related changes in TA ( $\Delta$ TA).**

Process	$\Delta$ TA
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)
$K_{HPO_4^{2-}}$	$\frac{[HPO_4^{2-}]}{[PO_4^{3-}][H^+]}$	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<sup>-2</sup> y<sup>-1</sup>). Negative numbers indicate a net loss of this species.**

Rates (all in mmol S m <sup>-2</sup> y <sup>-1</sup> )						
Period	FeS from $\Sigma$ H <sub>2</sub> S and Fe <sup>2+</sup>	FeS <sub>2</sub> from FeS and S <sup>0</sup>	FeS <sub>2</sub> from FeS and $\Sigma$ H <sub>2</sub> S	S <sup>0</sup> from MnO <sub>2</sub> and $\Sigma$ H <sub>2</sub> S	S <sup>0</sup> from Fe(OH) <sub>3</sub> and $\Sigma$ H <sub>2</sub> 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 <sub>2</sub> re-oxidation	S <sup>0</sup> disporportionation	Total FeS <sub>2</sub> formation	Total FeS formation	Total S <sup>0</sup> 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) <sup>1</sup>
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)

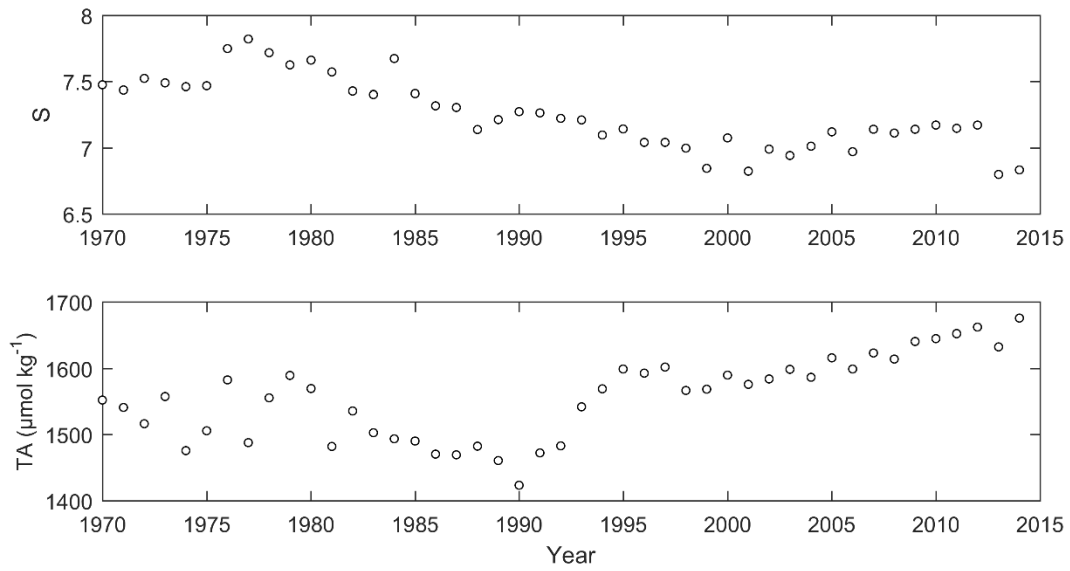
1. Calculated by Dyrssen (1993).

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

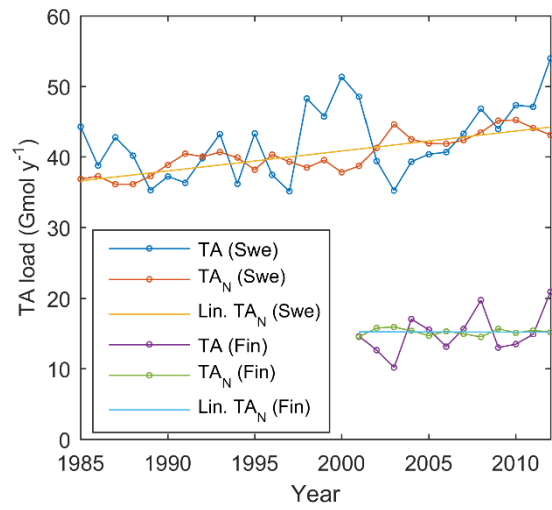
Year	Observed TA-salinity relation	Reference
1927-1935	$TA = 179S + 274$ ( $\mu\text{mol l}^{-1}$ )	Based on Buch (1945)
1957	$TA = 180S + 177$ ( $\mu\text{mol kg}^{-1}$ )	Gripenberg (1960) <sup>1</sup>
1986	$TA = 177S + 139$ ( $\mu\text{mol kg}^{-1}$ )	Ohlson and Anderson (1990)
2000-2004	$TA = 223S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

1. Calculated by Dyrssen (1993).

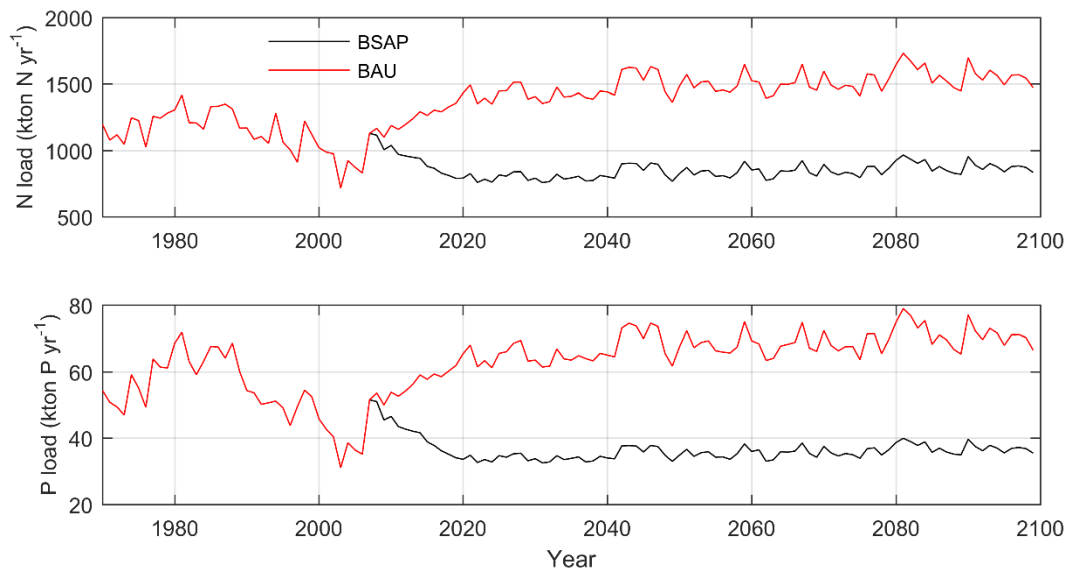




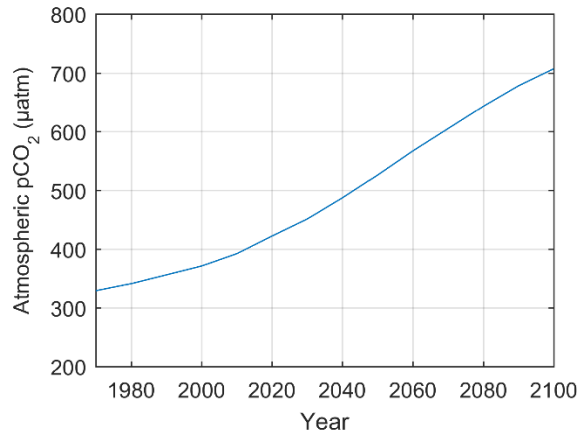
**Figure S1. Annual mean observed surface water salinity and TA at the BY15 station in the Gotland Sea.**



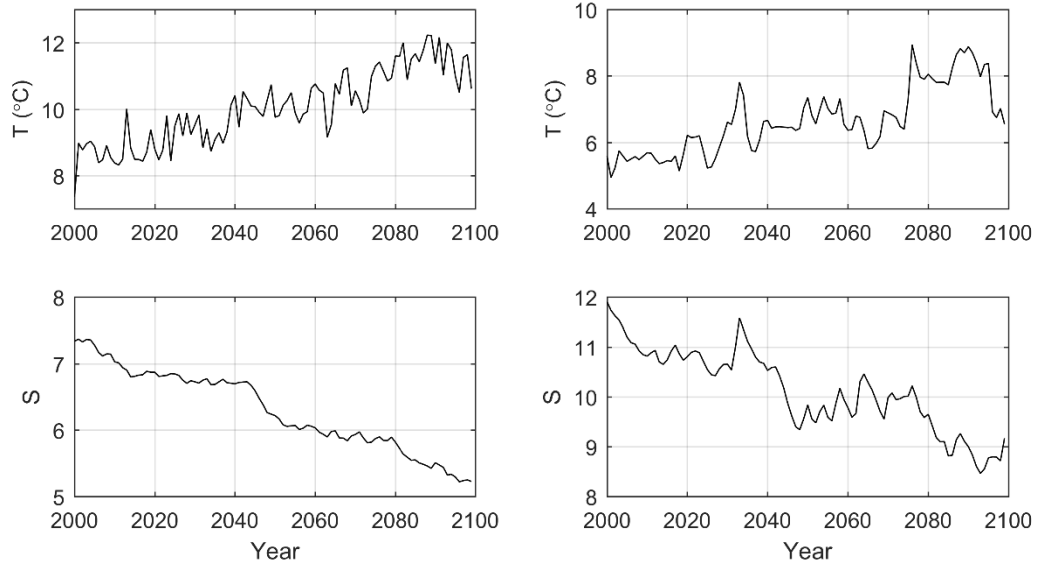
**Figure S2. Observed riverine TA loads, flow normalized TA loads (TA<sub>N</sub>) (Gmol y<sup>-1</sup>), and linear trends (Lin. TA<sub>N</sub>) in Swedish (Swe) and Finnish (Fin) rivers respectively.**



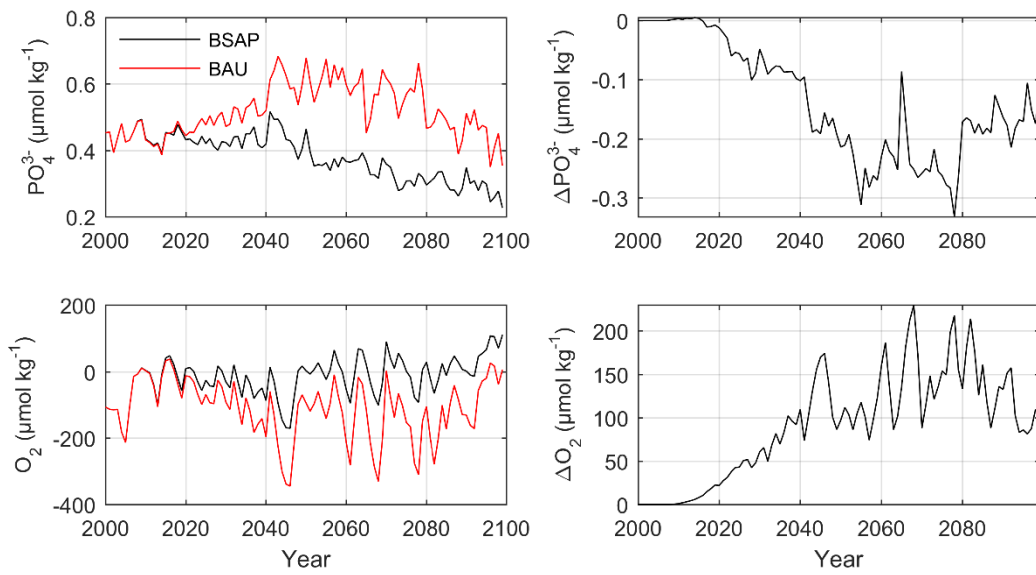
**Figure S3. Nitrogen and phosphorus loads (land loads + atmospheric depositions) according to the BSAP and BAU scenarios respectively.**



**Figure S4. Annual mean atmospheric CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) 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

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