PO_4 release at the sediment surface under anoxic conditions: a contribution to the eutrophication of the Baltic Sea?*

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Bernd Schneider

Leibniz Institute for Baltic Sea Research,
Seestrasse 15, Warnemünde 18119, Germany;

e-mail: bernd.schneider@io-warnemuende.de

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Abstract

The vertical profiles of phosphate, total CO_2 and oxygen/hydrogen sulphide were determined in the deep water of the Gotland Sea during March 2003 to July 2006 with a temporal resolution of 2–3 months. This time span included the shift from anoxic to oxic conditions resulting from a water renewal event, as well as the transition back to anoxic waters during the subsequent two-year stagnation period. The data from depths below 150 m were used to identify and quantify phosphate release and removal processes. The relationship between the total CO_2 generated by mineralization ($C_{T,\,min}$) and the PO_4 concentrations indicated that the initial decrease in the phosphate concentrations after the inflow of oxygen-rich water was mainly a dilution effect. Only about one third of the PO_4 removal was a consequence of the precipitation of insoluble iron-3-hydroxo-phosphates (Fe-P), which occurred slowly at the sediment surface under oxic conditions. From the $C_{T,\,min}/PO_4$ ratios it was also concluded that the formation of Fe-P was reversed during the later phase of the stagnation, when the redoxcline approached a depth of 150 m. A phosphate mass balance was performed for four deep water sub-layers in order to quantify the dissolution of Fe-P during the stagnation period and thus

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to estimate the amount of Fe-P deposited during the last inflow of oxygen-rich water. A value of about 50 mmol-P m^{-2} was found, which refers to the specific biogeochemical conditions during the change from anoxic to oxic conditions that preceded the stagnation period.

1. Introduction

The Baltic Sea is considered to be a eutrophic sea, although the seasonal maximum of the nutrient concentrations in the central Baltic are much lower than in high latitude oceanic regions. Current mean nitrate and phosphate concentrations in the Baltic Proper amount to about 3–4 μmol dm^{-3} and 0.4–0.6 μmol dm^{-3} respectively, and are lower by a factor of 2–3 than those in the North Atlantic. Nonetheless, the use of the term 'eutrophication' for the Baltic Sea nutrient conditions is adequate in the historical perspective, because nutrient loads and productivity increased by a factor of about 3 during the last century as a result of anthropogenic activities (Schneider & Kuss 2004, Savchuk et al. 2008). Moreover, the existence of a permanent halocline in the Baltic Sea together with the succession of sills and basins lead to frequently long-lasting stagnation of the deep water in the central basins. This favours the depletion of oxygen and ultimately the development of anoxic conditions in large areas of the central Baltic Sea despite the relatively low biomass production in the surface water.

The respective annual inputs of dissolved inorganic nitrogen (DIN =nitrate+ammonia) and PO_4 into the Baltic Sea in 1995 amounted to 990 000 t-N yr^{-1} (7.1×10^{10} mol-N yr^{-1}) and 40 000 t-P yr^{-1} (1.3×10^{9} mol-P yr^{-1}) (HELCOM 2001). Whereas PO_4 is mainly transported by river water, the DIN input includes about 20% atmospheric deposition. The input data correspond to a molar N/P ratio of 55, which is much higher than the ratio of the DIN and PO_4 inventories of the central Baltic Sea, which have values of less than 10 (Nausch et al. 2008). This shift in the N/P ratio can only be explained by intense denitrification, which probably occurs largely in coastal areas directly affected by riverine nutrient inputs. The low N/P ratios have far-reaching consequences for the plankton succession during the productive period. The molar NO_3/PO_4 ratios in the winter surface water of the Baltic Proper vary interannually between 6 and 9 (HELCOM, 2001) and are thus about 50% smaller than the Redfield N/P ratio of 16 (Redfield et al. 1963), which characterizes nutrient uptake during primary production. As a consequence, the spring plankton bloom is limited by the availability of NO_3 and further net production based on the PO_4 excess is sustained by nitrogen fixing cyanobacteria. The net biomass production fuelled by nitrogen fixation may be as large as or even exceed the spring bloom production (Schneider et al. 2009) and thus contributes substantially to oxygen depletion and hydrogen sulphide formation in the deep water of the central basins.

In a steady state PO_4 sources are balanced by burial of phosphorus in the sediments, which thus constitute a PO_4 sink. The PO_4 concentrations in the water column are governed by the efficiency with which P-containing particles are recycled. These particles consist mainly of organic carbon (POC) generated by biological production and thus contain organic phosphorus (POP). During mineralization of POP, PO_4 is released and again becomes available for production. Mineralization occurs to some degree already in the surface water and fuels the regenerated production. The POC fraction removed from the surface by particle sinking is mineralized mainly at the immediate sediment surface (Schneider et al. 2010) and after some delay in deeper sediment layers. Under anoxic conditions mineralization occurs as a result of sulphate reduction, the mineralization products being CO_2, NH_3 and PO_4. The release of PO_4 from the sediment surface is frequently regarded as a PO_4 source and compared with riverine PO_4 input. However, this is a misleading view since the released PO_4 originates from riverine input and does not constitute an independent term in the mass balance. It is therefore more appropriate to consider the POP mineralization at the sediment surface as part of the recycling process.

The cycling of phosphorus at the sediment surface changes if the overlying water and thus the upper sediment layers are oxic. In this case, a second class of P-containing particles consisting of iron-3-hydroxo-phosphates (Fe-P) are formed, which are dissolved again when Fe^{3+} is reduced to Fe^{2+} under anoxic conditions. These processes are considered to have an important impact on the PO_4 budget of the Baltic Sea and have been the subject of many studies (e.g. Conley et al. 2002, 2009, Gustafsson & Stigebrandt 2007, Mort et al. 2010). In this study we aim to elucidate the processes of PO_4 transformation and removal, and to quantify PO_4 release during the transition from oxic to anoxic conditions in the deep water of the Gotland Basin. For the evaluation of the PO_4 data we shall also use the data and results of a previous study that was related to the determination of carbon mineralization rates in the Gotland Basin on the basis of mass balances for total CO_2 (Schneider et al. 2010).

2. Methods

2.1. Sampling and chemical analysis

Samples for the determination of the concentrations of PO_4, total CO_2 (C_T), O_2, H_2S and other biogeochemical variables were taken at the international station BY15 in the central Gotland Sea in the Baltic Sea (Figure 1). The measurements were part of the monitoring programme of the Baltic Sea Research Institute (Warnemünde, Germany) that started more than three decades ago. Since March 2003 the determination of total CO_2, C_T, has been included in the measurement programme. As five cruises took place each year, the temporal resolution was approximately 2–3 months. The depth resolution of the sampling in the deep water below 125 m was 25 m. High-resolution temperature and salinity profiles were recorded in conjunction with the sampling.

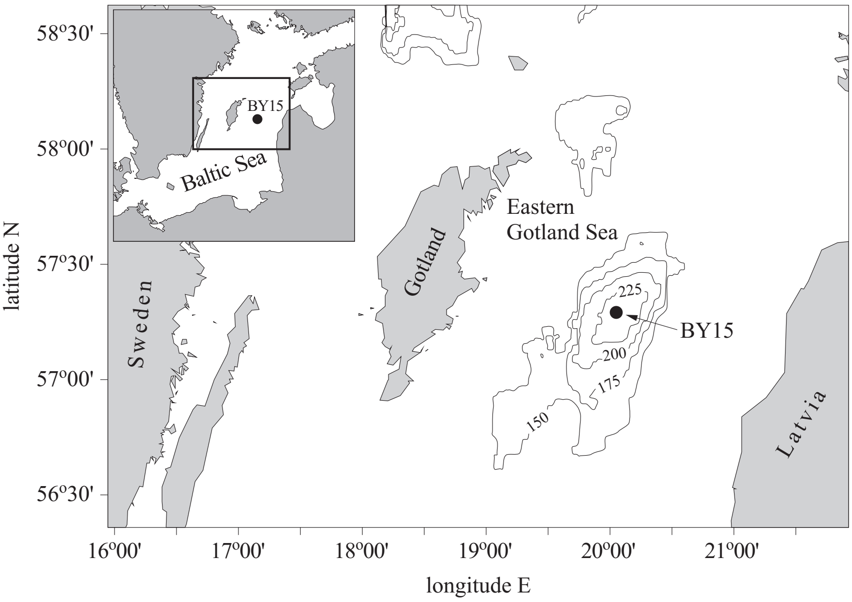

Figure 1. Location of the sampling station BY15 in the Gotland Sea (Baltic Sea)

The analysis of O_2 by the Winkler titration and of PO_4 and H_2S by the standard photometric methods were performed according to the recommendations given by the HELCOM monitoring working group MONAS (http://www.helcom.fi/groups/monas/CombineManual). The samples for the determination of C_T were preserved by the addition of mercury chloride and analysed in the home laboratory by the coulometric SOMMA system (Johnson et al. 1993). Interferences with hydrogen sulphide in samples from anoxic waters were avoided by the precipitation of HgS in the presence of $HgCl_2$. The system was calibrated with certified carbon reference material (CRM, provided by Dr. A. Dickson, University of California, San Diego) and yielded an accuracy of $+/-2$ μmol kg^{-1}.

2.2. Results from a previous study

In a previous study (Schneider et al. 2010) we used the C_T data from depths below 150 m to determine carbon mineralization rates during the period of stagnation that lasted from May 2004 to July 2006. The calculations were based on the C_T fraction generated by the mineralization of organic matter, $C_{T,\,min}$. The $C_{T,\,min}$ was estimated from the difference between the measured C_T and the C_T that the water mass had during its last contact with the atmosphere. The latter was calculated using CO_2 partial pressure and alkalinity data of the winter water in the transition area between the North Sea and the Baltic Proper, which was considered to represent the source area of the Gotland Sea deep water.

The deep water below 150 m was subdivided into four sublayers (SLs 1–4, Table 1) and the measurements were used to calculate the mean $C_{T,\,min}$ for each SL and for each measurement date. C_T mass balances were then applied to calculate the carbon mineralization Q_{CT} for each SL during

Table 1. Subdivision of the Gotland Basin into sublayers (SL). Areas, sediment areas and volumes of the sublayers are based on the topographic information given by Seifert et al. (2001)

Sublayer No.	Depth of SL [m]	Area of SL [km^2]	Sediment area of SL [km^2]	Volume of SL [km^3]
1	>225	464	464	3.8
2	200–225	1160	696	20.8
3	175–200	2120	960	39.7
4	150–175	4680	2560	84.9
total	> 150	4680	4680	149.2

Table 2. Mixing coefficients k_{mix} between neighbouring sublayers calculated from changes in the vertical salinity distributions during the stagnation period from May 2004 to July 2006 (Schneider et al. 2010). In cases where the calculations yielded negative values, k_{mix} was set to zero

Time interval	k_{mix}, SL1–SL2 $10^6 \times [m^2\ s^{-1}]$	k_{mix}, SL2–SL3 $10^6 \times [m^2\ s^{-1}]$	k_{mix}, SL3–SL4 $10^6 \times [m^2\ s^{-1}]$	k_{mix}, SL4-above $10^6 \times [m^2\ s^{-1}]$
May 04–July 04	2.1	8.6	7.9	2.4
July 04–Nov. 04	11.3	11.9	0.0	0.0
Nov. 04–Feb. 05	36.0	68.6	52.3	17.6
Feb. 05–May 05	3.2	3.8	14.4	6.7
May 05–July 05	2.3	0.6	0.0	0.0
July 05–Oct. 05	7.8	19.7	30.1	19.6
Oct. 05–Jan. 06	14.9	22.6	16.1	9.8
Jan. 06–May 06	8.8	16.0	13.4	7.9
May 06–July 06	7.4	5.4	0.0	0.0

Table 3. Accumulated carbon mineralization ${}^{acc}Q_{CT}$ in the individual sub-layers and the total ${}^{acc}Q_{CT}$ below 150 m. Annual mineralization rates are given in the last line

Time interval	${}^{acc}Q_{CT}$–SL1	${}^{acc}Q_{CT}$–SL2	${}^{acc}Q_{CT}$–SL3	${}^{acc}Q_{CT}$–SL4	${}^{acc}Q_{CT}$ z >150 m
	[μmol dm^{-3}]				
May 04–July 04	68	36	4	11	14
July 04–Nov. 04	121	66	22	27	34
Nov. 04–Feb. 05	165	82	23	50	50
Feb. 05–May 05	218	111	39	55	63
May 05–July 05	264	138	46	66	76
July 05–Oct. 05	319	183	72	88	102
Oct. 05–Jan. 06	331	191	80	104	115
Jan. 06–May 06	370	210	100	116	131
May 06–July 06	426	241	102	123	141
rates [μmol dm^{-3} yr^{-1}]	192	108	46	55	64

the time between two successive measurements. Since the mass balances must include C_T transport by mixing between the SLs, mixing coefficients were determined (Table 2) on the basis of the temporal changes of the SL salinities. The Q_{CT} values obtained for the individual sub-layers and for the entire depth below 150 m are presented in Table 3 as the concentrations accumulated since the start of the stagnation period in May 2004 (${}^{acc}Q_{CT}$) and as mean annual carbon mineralization rates. Further details of the calculations are given in Schneider et al. (2010).

3. Results and discussion

3.1. Mean PO_4 and total CO_2 in the deep water

Mean PO_4 and $C_{T,\,min}$ for depths below 150 m were calculated from the vertical concentration profiles by weighting the concentrations at the different depth intervals with the corresponding water volume (Table 1). The results are presented as a time series starting in March 2003 (Figure 2a), when C_T determinations were included in the measurements for the first time. PO_4 was high at the beginning of our observations, but concentrations dropped sharply from 4.9 μmol dm^{-3} to 3.0 μmol dm^{-3} during the following six weeks and continued to decrease to a minimum value of 2.0 μmol dm^{-3} in February 2004. This is attributed to a water renewal event that occurred during February/March 2003 and generated a fully oxic water column in the Gotland Sea deep water. The shift to an oxic regime favours the precipitation of Fe-P. However, the initial decrease in dissolved PO_4 from

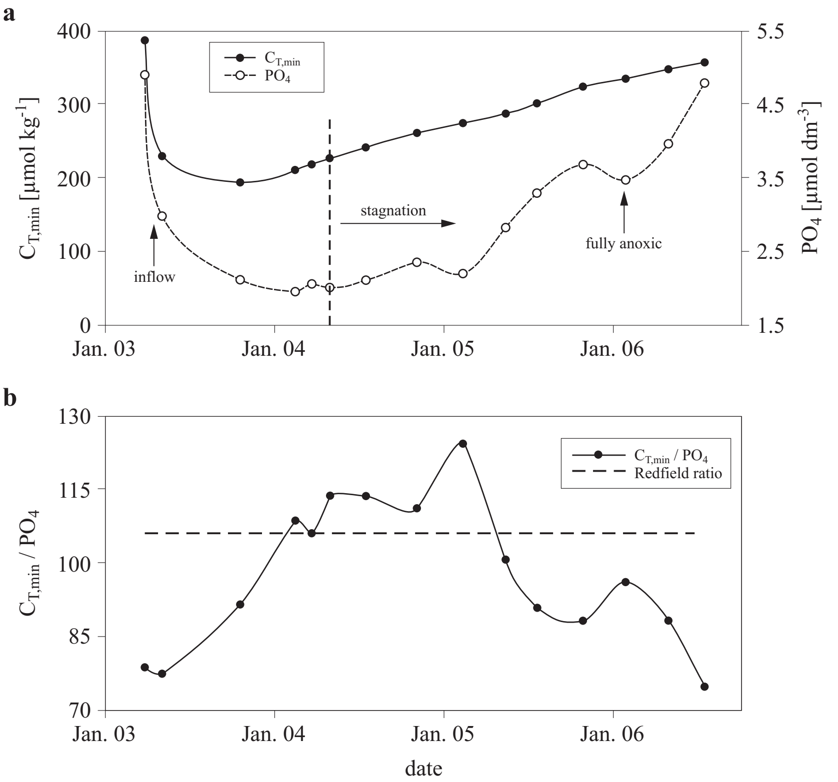

Figure 2. Temporal development of the fraction of total CO_2 generated by carbon mineralization $C_{T,\,min}$ and of the phosphate concentrations PO_4 during changing redox conditions in the deep water of the Gotland Sea (a), and the corresponding $C_{T,\,min}/PO_4$ ratios (b). The data are volume-weighted averages for depths below 150 m

March 2003 to May 2003 by a factor of 0.6 is caused by dilution due to the inflowing water masses. This is clearly indicated by the concurrent and almost identical $C_{T,\,min}$ decrease, which can only be caused by dilution since C_T is not redox-sensitive and cannot be removed from the deep water by any other process. Hence, the dilution effect (1.9 μmol dm^{-3}) contributed 66% to the total PO_4 decrease of 2.9 μmol dm^{-3} between March 2003 and February 2004 that was caused by the water renewal. After October 2003, $C_{T,\,min}$ started to increase steadily as a result of organic matter mineralization, while no further significant input of new water occurred. In contrast, the PO_4 level remained approximately constant for some time and increased only slightly until February 2005. This is attributed to the formation of Fe-P at the oxic sediment surface and occurs at the expense of either the existing PO_4 pool or the PO_4 released by the ongoing organic matter mineralization. PO_4 removal is also reflected in the $C_{T,\mathrm{min}}/PO_4$ ratios (Figure 2b), which were low (77) immediately after the water renewal because of the accumulation of PO_4 during the previous stagnation period. But because of the continual formation of Fe-P, it increased steadily until February 2005, when a value of 124 was found (Figure 2b). These observations are consistent with the fact that at the beginning of the stagnation period the redoxcline propagated only slowly from the bottom water to the upper water layers and was located at depths between 225 m and 200 m in February 2005. Hence, most of the sediment surface below 150 m was still covered with oxic water, which facilitated Fe-P formation. The gradual increase in the $C_{T,\mathrm{min}}/PO_4$ ratios also indicates that the formation of Fe-P is a slow process that takes place mainly at the sediment surface and is thus controlled by mixing. The possible spontaneous precipitation of Fe-P in the water column after the inflow of high-oxygen water masses is of minor importance. This conclusion can be drawn from the low Fe concentrations under anoxic conditions in the Gotland Sea deep water (1–2 μmol dm^{-3}) and the low molar P/Fe ratios (0.17) of P-containing FeO(OH) particles (Turnewitsch & Pohl 2010). Also, significant PO_4 removal by adsorption on manganese oxides, formed in the water column during the shift to oxic conditions, is unlikely. Indeed, the Mn concentrations are about one order of magnitude higher than those of Fe, however, this is approximately compensated for by the lower molar P/Mn ratios (0.03) of MnO_2/PO_4 associates (Turnewitsch & Pohl 2010).

After February 2005 a strong increase in PO_4 concentrations until the end of the stagnation period in July 2006 was observed, which coincided with a substantial decrease in $C_{T,\mathrm{min}}/PO_4$ ratios. During this phase the anoxic dissolution of previously deposited Fe-P prevailed over the oxic precipitation of Fe-P because the redoxcline moved further upwards and arrived at the 150 m depth level in February 2006. As a result, the system returned approximately to its state before the water renewal, with no net effect on the PO_4 concentrations having occurred.

3.2. Calculation of PO_4/Fe-P transformations

For the period from May 2004 to July 2006 the temporal development of the salinity indicated almost ideally stagnant conditions below 150 m. The slight decrease in the salinity distribution during this period (Figure 3a) can be explained by vertical mixing. No indication was found either in the salinity or the temperature distribution for a lateral water inflow. The basin was therefore considered to be like a closed biogeochemical reaction vessel that was affected only by the input of organic matter produced in the euphotic zone, by mineralization of organic matter in the water column and in the sediments, and by vertical mixing. Accordingly, the

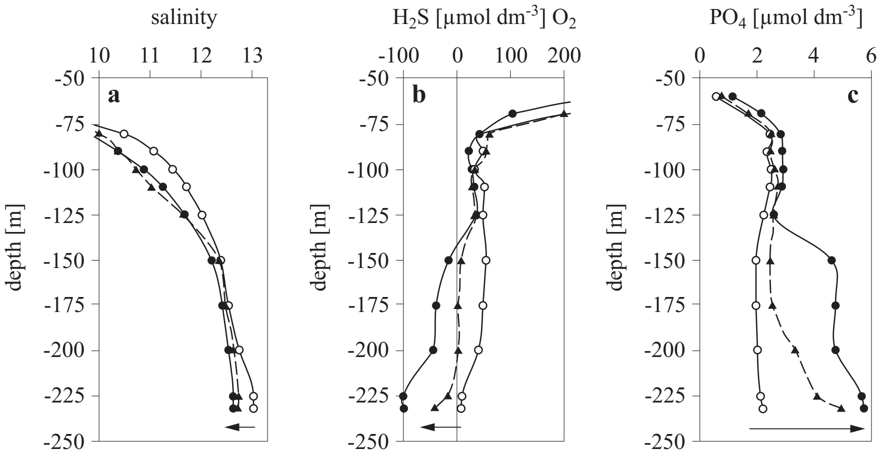

Figure 3. Measured depth profiles of salinity (a), H_2S (negative numbers) and O_2 (b) and phosphate (c) in May 2003 (open circles), May 2005 (filled triangles) and July 2006 (filled circles). The arrows indicate the passage of time

continual mineralization of POC caused O_2 depletion and after about two years resulted in fully anoxic conditions at depths below 150 m (Figure 3b). The vertical PO_4 profiles at the beginning, middle and end of the stagnation period (Figure 3c) show quite different distribution patterns, which are the result of a complex interplay between POP mineralization, Fe-P dissolution and formation, and vertical mixing. In order to quantify PO_4 production and removal in the individual sub-layers (Table 1), a mass balance was applied describing the temporal change in the PO_4 concentrations for each time interval and in each SL (Table 1) by vertical mixing with the neighbouring SL and by PO_4 production/removal, Q_{PO4} (eq. (1)). Q_{PO4} thus includes all PO_4 related processes in the water column and PO_4 exchange at the sediment surface of the individual SL.

$$\frac{\Delta PO_4}{\Delta t} = \frac{A_{n-1}\, F_{n-1} + A_n\, F_{n+1}}{V_n} + Q_{PO4}, \tag{1}$$

where

n – SL number;

A – SL area;

V – SL volume;

F – PO_4 exchange by turbulent diffusion between the lower (n − 1) and upper (n + 1) SL;

Q_{PO4} – phosphate production/removal term;

PO_4 concentration data measured at the lower and upper boundaries of the SLs were used to calculate mean PO_4 concentrations for each SL. Relating these to the time difference between the measurements yielded the temporal change in the PO_4 concentrations for each time interval, $\frac{\Delta PO_4}{\Delta t}$. The vertical exchange of PO_4 between the SLs were calculated according to eq. (2).

$$F = k_{\mathrm{mix}} \frac{\Delta PO_4}{\Delta z}, \tag{2}$$

where k_{mix} represents the turbulent diffusion coefficient. The values of k_{mix} were taken from Schneider et al. (2010) and are presented in Table 2.

The PO_4 gradients were obtained from the difference between the mean PO_4 concentrations in neighbouring SLs and division by the distance between the centres of the corresponding SLs. On the basis of these experimentally derived quantities, eq. (1) enables Q_{PO4} to be calculated, which represents the PO_4 release by organic matter mineralization and the Fe-P dissolution/precipitation for each time interval and each SL. The accumulation of Q_{PO4} over time ($^{acc}Q_{PO4}$) for each SL and for the entire basin below 150 m were determined by the successive addition of Q_{PO4} values (Table 4). A rapid increase in $^{acc}Q_{PO4}$ in SL1 occurred during the first year of the stagnation. This is a consequence of the fact that the bottom water had already become anoxic during the first time interval of the stagnation period (Figure 3b) and that previously deposited Fe-P was redissolved by reduction of Fe^{3+} to Fe^{2+}. In SL2 to SL3 the $^{acc}Q_{PO4}$ increase occurred during later stages of the stagnation, coinciding with the upward migration of the redoxcline.

Table 4. Accumulated phosphate release rates $^{acc}Q_{PO4}$ in the individual sub-layers and the total $^{acc}Q_{PO4}$ below 150 m

Time interval	$^{acc}Q_{PO4}$–SL1	$^{acc}Q_{PO4}$–SL2	$^{acc}Q_{PO4}$–SL3	$^{acc}Q_{PO4}$–SL4	$^{acc}Q_{PO4}$–SL1–4
			[μmol dm^{-3}]		
May 04–Jul. 04	1.43	0.65	–0.06	0.01	0.1
Jul. 04–Nov. 04	2.82	1.16	0.10	0.15	0.3
Nov. 04–Feb. 05	3.69	1.05	–0.32	0.05	0.2
Feb. 05–May 05	5.25	2.24	0.47	0.42	0.8
May 05–Jul. 05	6.63	3.08	0.88	0.78	1.3
Jul. 05–Oct. 05	6.32	3.11	1.20	1.38	1.7
Oct. 05–Jan. 06	6.17	2.91	0.94	1.27	1.5
Jan. 06–May 06	6.85	3.28	1.47	1.79	2.0
May 06–Jul. 06	7.92	4.20	2.17	2.64	2.9

The dependence of varying PO_4 release rates on the redox conditions in the different SL is also reflected in the relationship between the $^{acc}Q_{PO4}$ and the accumulated carbon mineralization, $^{acc}Q_{CT}$ (Figure 4). During the first phase of the stagnation, $^{acc}Q_{PO4}$ in SL1 and SL2 increased almost linearly with $^{acc}Q_{CT}$ (Figures 4a, 4b) . The slopes of the regression lines

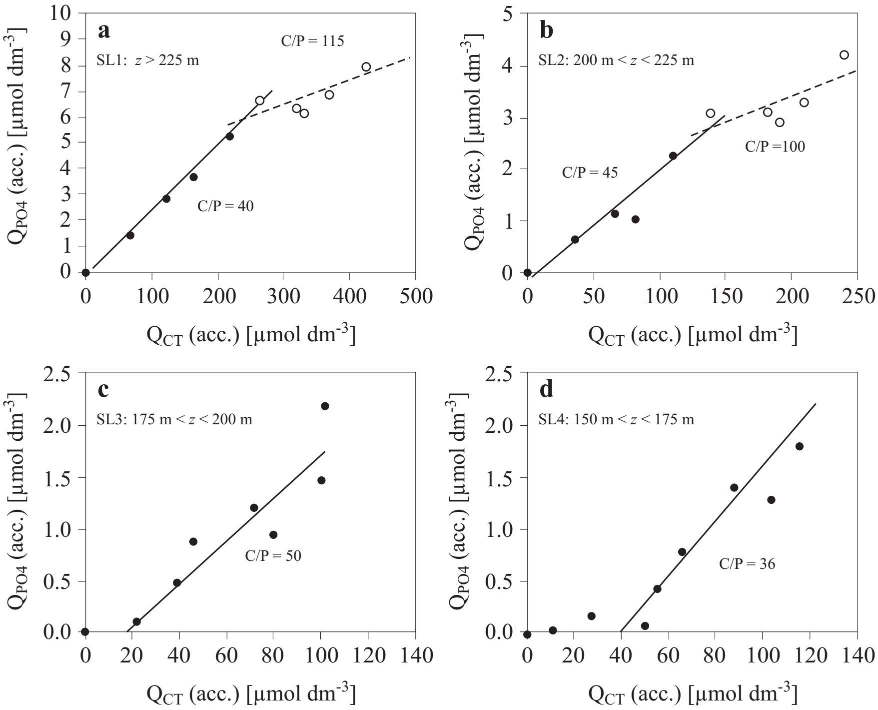

Figure 4. Relationships between the accumulated release of phosphate and total CO_2 ($^{acc}Q_{PO4}$ and $^{acc}Q_{CT}$ respectively) during a stagnation period at different depth levels (a–d) of the Gotland Sea deep water

correspond to a C/P ratio of 40 and 45 respectively, and are thus far below the Redfield ratio of 106, which is assumed to characterize the organic matter composition. The decrease in the C/P ratio of the mineralization products may be due to the fact that the microbial decomposition of organic matter does not occur synchronously for the different elements and that organic P is the first to be mineralized. However, our observations refer to a time span of more than two years, and in the long term the elemental ratios of the mineralization products will correspond to the composition of the organic matter. Therefore, the low C/P ratios derived from the relationship between $^{acc}Q_{PO4}$ and $^{acc}Q_{CT}$ during the early development of anoxic conditions in SL1 and SL2 are attributed to the dissolution of Fe-P. However, at higher $^{acc}Q_{CT}$ in the later stage of the stagnation the increases of $^{acc}Q_{PO4}$ in SL1 and SL2 are smaller (Figure 4a, 4b) and the relationships to $^{acc}Q_{CT}$ are characterized by C/P ratios (115 and 100 respectively) close to the Redfield ratio. This shift in the $^{acc}Q_{PO4}/^{acc}Q_{CT}$ relationship is explained by the complete exhaustion of the previously deposited Fe-P supply and the confinement of PO_4 release to organic matter mineralization. The Redfield-like composition of the organic matter contrasts with the C/P ratios of up to 400 that were observed during intense blooms of N_2-fixing cyanobacteria (Larsson et al. 2001). Possibly this does not affect the $^{acc}Q_{PO4}/^{acc}Q_{CT}$ ratio, because the excess carbon is mineralized before the corresponding particles have arrived in the deeper water layers. The opposite pattern for the relationship between $^{acc}Q_{PO4}$ and $^{acc}Q_{CT}$ is observed in SL4 (Figure 4d). Because of the oxic conditions during the initial stagnation, PO_4 generated by organic matter mineralization is precipitated as Fe-P and the $^{acc}Q_{PO4}$ values are close to zero. Only at higher $^{acc}Q_{CT}$, when a shift to anoxic conditions develops in SL4, is a drastic increase of $^{acc}Q_{PO4}$ observed due to Fe-P dissolution. The situation is less clear in SL3 (Figure 4c), where no clear distinction between PO_4 release by mineralization of organic matter and Fe-P dissolution can be made.

Based on $^{acc}Q_{PO4}$, we estimated the amount of Fe-P deposited at the sediment surface during the previous deep water renewal and redissolved during the subsequent stagnation period. Therefore, we used only the data from SL1 and SL2, because we were unable to judge whether the Fe-P supply in SL3 and SL4 was entirely dissolved at the end of the stagnation period. Multiplication of $^{acc}Q_{PO4}$ in SL1 and SL2 at the end of the 26-month stagnation period (Table 4, last line) by the corresponding SL volumes (Table 1) gives the total $^{acc}Q_{PO4}$ inventory below 200 m. Relating this value to the underlying sediment area (Table 1) yields a total PO_4 release of 100 mmol m^{-2}, which includes contributions by Fe-P dissolution and organic phosphorus mineralization. To estimate the latter we first calculated the total C_T release in SL1 and SL2 (Table 3) during the stagnation period following the same procedure as for the calculation of the total PO_4 release. A value of 5.7 mol-C m^{-2} was obtained which, based on the Redfield C/P ratio of 106, corresponds to an organic P mineralization of 54 mmol m^{-2}. Hence, the Fe-P dissolution and thus the Fe-P storage during the previous transition from anoxic to oxic conditions amounted to 46 mmol m^{-2}. This is roughly 50% less than the value given by Gustafsson & Stigebrandt (2007) for the average release of PO_4 by Fe-P dissolution at the sediment surface when the overlying waters are turning to anoxic conditions. The calculations by Gustafsson & Stigebrandt (2007) are based on the analysis of 14 stagnation periods that had occurred since 1965, but unfortunately covered only the first year of the stagnation period considered in our study. Their data reveal large differences between the individual stagnation events with regard to the Fe-P dissolution rates. This may explain the deviation of the long-term mean from our estimate, which refers to a specific period.

4. Conclusions and summary

A detailed analysis of the temporal variability in the phosphate and total CO_2 concentrations during the full cycle from anoxic to oxic and back to anoxic conditions provided insight into a number of processes that are important for the cycling of phosphorus in the deep water of the Baltic Sea. It was shown that the frequently documented abrupt decrease in PO_4 concentrations, occurring concurrently with the change from anoxic to oxic conditions caused by a water renewal event, is to a large extent due to dilution and only partly a consequence of the precipitation of iron-3-hydroxo-phosphates. Owing to the low concentrations of dissolved iron in the water column and the limited capacity of FeO(OH) to bind PO_4, the formation of Fe-P in the water column is low and takes place predominantly at the sediment surface where, depending on the redox conditions, Fe accumulates as either oxide or sulphide. The formation of Fe-P is thus a slow process since it requires the transport of PO_4 to the sediment surface by vertical and/or lateral mixing. The release of Fe-P previously deposited by a shift from anoxic to oxic conditions amounted to about 50 mmol m^{-2}. However, this value cannot be generalized because it depends on the PO_4 accumulation during the previous stagnation period. It was further shown that the dissolution and precipitation of Fe-P during changing redox conditions constitute a closed cycle and that in the long term, phosphate is added to the system only by mineralization of organic matter approximately according to the Redfield ratio. Hence, PO_4 is recycled in the same way as carbon and nitrogen, and anoxic conditions do not generate an extra source of PO_4.

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