



# A new approach to model oxygen dependent benthic phosphate fluxes in the Baltic Sea



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## ARTICLE INFO

### Article history:

Received 17 March 2014

Received in revised form 25 September 2014

Accepted 17 November 2014

Available online 26 November 2014

### Keywords:

Phosphorus release

Oxygen penetration depth

Eutrophication

Saltwater inflow

Biogeochemical modelling

Baltic Sea

## ABSTRACT

The new approach to model the oxygen dependent phosphate release by implementing formulations of the oxygen penetration depths (OPD) and mineral bound inorganic phosphorus pools to the Swedish Coastal and Ocean Biogeochemical model (SCOBI) is described. The phosphorus dynamics and the oxygen concentrations in the Baltic proper sediment are studied during the period 1980–2008 using SCOBI coupled to the 3D-Rosby Centre Ocean model. Model data are compared to observations from monitoring stations and experiments. The impact from oxygen consumption on the determination of the OPD is found to be largest in the coastal zones where also the largest OPD are found. In the deep water the low oxygen concentrations mainly determine the OPD. Highest modelled release rate of phosphate from the sediment is about  $59 \times 10^3 \text{ t P year}^{-1}$  and is found on anoxic sediment at depths between 60–150 m, corresponding to 17% of the Baltic proper total area. The deposition of organic and inorganic phosphorus on sediments with oxic bottom water is larger than the release of phosphorus, about  $43 \times 10^3 \text{ t P year}^{-1}$ . For anoxic bottoms the release of total phosphorus during the investigated period is larger than the deposition, about  $19 \times 10^3 \text{ t P year}^{-1}$ . In total the net Baltic proper sediment sink is about  $23.7 \times 10^3 \text{ t P year}^{-1}$ . The estimated phosphorus sink efficiency of the entire Baltic Sea is on average about 83% during the period.

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## 1. Introduction

Phosphorus has been discussed to be a key nutrient for the eutrophication of the Baltic Sea (Conley et al., 2009). Not only external supplies of nutrients (phosphorus and nitrogen) from land and atmosphere contribute to the increasing eutrophication, but also internal loads, i.e. the impact from an intensified recycling of nutrients in the sediment (Conley et al., 2002; Stigebrandt et al., 2014). Gustafsson et al. (2012) estimated that external phosphorus loads increased by a factor of 5 from 1850 to around 1980. After 1980 external phosphorus loads started to decrease, but the phosphorus efflux from the sediments and the phosphorus pool in the water continued to increase. A number of studies have shown that the sediments play an important role in controlling the phosphorus supply to the pelagic realm as they regionally act as an internal source or sink for dissolved phosphate (Emeis et al., 2000; Lukkari et al., 2009b; Viktorsson et al., 2012, 2013).

The deep water in the southern and central basins of the Baltic Sea is separated from the surface water by a permanent halocline at a depth of about 60 m (Stigebrandt, 2001; Väli et al., 2013), which prevents vertical circulation and ventilation of the bottom water. Only major water inflows of dense surface water from Kattegat with higher salinity and oxygen can oxygenate the deep waters in the basins. The inflowing water replaces the anoxic and phosphate rich bottom water in the deeper part of the basins, which is lifted up to more shallow water depths (Eilola et al., 2014; Fischer and Matthäus, 1996; Reissmann et al., 2009; Schneider, 2011). The vertical transport and mixing of the deep bottom water due to MBI have been discussed in earlier studies (e.g. Reissmann et al., 2009; Schneider, 2011). The destiny of the deep water due to MBI in the Baltic proper was investigated in a tracer study by Eilola et al. (2014), who concluded that regionally the direct impact on the uplift of nutrients from waters below the halocline to surface waters due to MBI could be quite large, but that the overall direct impact was small because comparably large vertical transports occur also in years without MBI. The impact from the East Gotland Deep water on eutrophication in the Baltic Sea is expected to be small because the volume of water below 150 m is small (Eilola et al., 2014). During the stagnant periods, between the major inflows, the oxygen concentrations in the deep water decrease

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with time, often until depletion (Lass and Matthäus, 2008, and references therein).

Phosphate has the ability to adsorb on hydrated metal oxides, e.g. iron(III) oxy hydroxides (oxides), which build up in the oxidized sediment layer. Large amounts of phosphate can thus build up in the sediment during oxic bottom water conditions. During anoxic periods the oxides reductively dissolve, which prevents further adsorption of phosphate to iron oxides and the previously adsorbed phosphorus is released to the pore water in the sediment and can thus diffuse to the water column (Froelich, 1988; Mortimer, 1941, 1942; Sundby et al., 1992). Thus, the low retention capacity of phosphorus in the sediment during anoxic conditions and the limited vertical circulation and ventilation of the bottom water leads to high phosphate concentrations in the anoxic bottom water. Further, Jilbert et al. (2011) suggested that preferential phosphorus mineralization with respect to carbon, may be a key player besides the mineral bound redox dependent phosphorus dynamics. However, with the present model setup this effect cannot be investigated. Sediment that has been anoxic for a longer period might get the accumulated pool of mineral bound inorganic phosphorus depleted. The release of phosphate will then depend on the supply and degradation of organic matter and the mineralization rate of organic phosphorus (Viktorsson et al., 2012). Today, about 40% of the total bottom area in the Baltic proper (including the Gulf of Riga and the Gulf of Finland) is estimated to be overlain by hypoxic (dissolved  $O_2$  concentrations less than  $2 \text{ ml l}^{-1}$  or  $91 \text{ } \mu\text{M}$ ) or anoxic bottom water (Hansson and Andersson, 2013). In contrast to soft water lakes marine waters also have a sink for iron. Saline water contains sulfate which is used during bacterial anaerobic decomposition of organic material. The produced hydrogen sulfide reacts with iron and precipitates as minerals, e.g.  $\text{FeS}$  or pyrite  $\text{FeS}_2$  (Blomqvist et al., 2004; Skoog et al., 1996). Iron(III)oxides and phosphate form aggregates with the molar (Fe:P) ratio of 2:1 (Gunnars and Blomqvist, 1997; Gunnars et al., 2002). If the molar ratio is less than two, the phosphate can escape from the sediment without binding to iron(III)oxides. The produced  $\text{FeS}$  and  $\text{FeS}_2$  acts as a sink of iron and may thus lead to a reduced retention capacity of phosphate in the sediment (Blomqvist et al., 2004; Lehtoranta et al., 2009). The salinity dependence of the phosphorus release capacity from the sediments in the Swedish Coastal and Ocean Biogeochemical model (SCOBI; Eilola et al., 2009; Marmefelt et al., 1999) was discussed by Eilola et al. (2009).

Field studies in the Gulf of Finland have shown that in spite of oxic/sub-oxic conditions in the water column there were high release rates of phosphate from the sediment (Conley et al., 1997; Lehtoranta and Heiskanen, 2003; Lehtoranta et al., 2009; Pitkanen et al., 2007). Lehtoranta and Heiskanen (2003) argued that a low availability of iron(III)oxides, due to limited vertical diffusion of iron(II) towards the oxidized surface layer of the sediment, limited the phosphorus adsorption and allowed for high release rates of phosphorus. According to Lehtoranta et al. (2009) the release of phosphate in spite of oxic bottom water was due to high deposition of organic material and that sulfate reduction and thus formation of  $\text{FeS}_2$  decreased the availability and recycling of iron in the sediment. Conley et al. (1997) concluded that the phosphorus content in the sediment was very high in the Gulf of Finland as compared to other Baltic Sea sediments. Also Hille (2005) discussed, based on measurements in the Baltic proper, that the high phosphorus flux rates correspond to sites with high accumulation rates of organic matter. Decomposition and oxidation rate of organic matter at these sites is therefore high. The depth of the oxidized sediment layer, and hence the amount of hydrated metal oxides available for phosphorus adsorption, depends on the oxygen concentrations in the bottom water and also on the oxygen consumption rate in the sediment (Cai and Sayles, 1996). Hence, if the oxygen penetration depth is large more iron can transform to iron(III)oxides and larger fractions of the mineralized phosphorus may be adsorbed. The importance of oxygen consumption rate on the oxygen diffusion and penetration into the sediment has not previously been accounted for in the state-

of-the-art model described by Eilola et al. (2011). Oxygen concentrations in the bottom water have usually been used to describe the status in the sediment.

The model system in the present study consists of the SCOBI model coupled to a three-dimensional high resolution ocean circulation model, the Rossby Centre Ocean model (RCO; Meier et al., 2003). The aim with this study was to further develop the description of the benthic phosphorus dynamics in SCOBI and to discuss the model results in comparison to available observations. A map of the horizontal variability of the oxygen penetration depth and the effects of major deep water inflows on the phosphate release in the Baltic proper will be described. The relative importance of oxygen consumption rate, compared to the importance of bottom water oxygen concentration, on the actual oxygen penetration depth as well as the sink efficiency of phosphorus in the Baltic Sea will be studied.

## 2. Material and methods

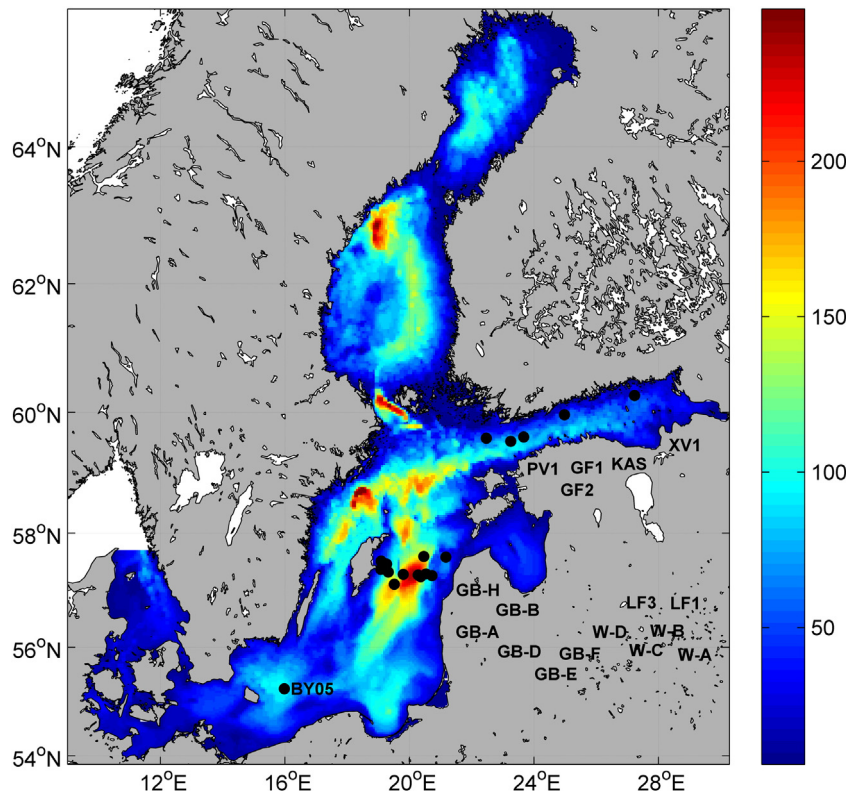
The Baltic Sea is a sensitive environment which is highly affected by the large amount of people living around its coast. Eutrophication with increased nutrient concentrations and, as a consequence, algae blooms and bottom anoxia has been observed during decades in the Baltic Sea. It is a landlocked sea that can be divided into several sub-basins connected by sills. The connection to the North Sea goes through the shallow Danish straits, Little Belt, Great Belt and Sound, and Kattegat. The model domain of the coupled RCO-SCOBI model system used in this study covers the entire Baltic Sea, including Kattegat (Fig. 1) and has been used in several applications for the Baltic Sea (e.g. Eilola et al., 2012, 2013; Meier et al., 2011, 2012a; Neumann et al., 2012; Skogen et al., 2014). The model system has shown good performance compared to other Baltic Sea models and observations (Eilola et al., 2011). In this study the main focus has been on the Baltic proper, including the Gotland, Bornholm and Arkona basins, and the Gulf of Riga and Gulf of Finland during the period 1980–2008.

### 2.1. The RCO-model

The RCO-model, Rossby Centre Ocean model (Meier et al., 2003), is a three-dimensional Bryan-Cox-Semtner primitive equation circulation model with a free surface (Killworth et al., 1991) and open boundary conditions (Stevens, 1991) in the northern Kattegat (Fig. 1). Subgrid-scale mixing is parameterized using a turbulence closure scheme of the  $k$ - $\epsilon$  type with flux boundary conditions to include the effect of a turbulence enhanced layer due to breaking surface gravity waves and a parameterization for breaking internal waves (Meier, 2001). The deep water mixing is assumed to be inversely proportional to the Brunt-Väisälä frequency with a proportionality factor  $\alpha = 1 \times 10^{-7} \text{ m}^2 \text{ s}^{-2}$  following Lass et al. (2003). As the layer thicknesses of the vertical grid are too large to resolve the bottom boundary layer (BBL) accurately, a BBL model is embedded to allow the direct communication between bottom boxes of the step-like topography (Beckmann and Döscher, 1997). The ocean model is coupled to a Hibler-type sea ice model (Hibler, 1979) with elastic-viscous-plastic rheology (Hunke and Dukowicz, 1997) and explicit representation of five undeformed and two deformed sea ice categories (Mårtensson et al., 2012). RCO is used with a horizontal resolution of 3.7 km (2 nautical miles) and with 83 vertical levels with layer thicknesses of 3 m. In the model the maximum depth amounts to 249 m. For further details of the RCO model and the performance of relevant model variables compared to observations the reader is referred to Meier (2001), Meier et al. (2003), Meier (2007) and Väli et al. (2013).

### 2.2. SCOBI

The Swedish Coastal and Ocean Biogeochemical model (SCOBI; Eilola et al., 2009) describe the dynamics of nitrate, ammonium,



**Fig. 1.** The model domain of the RCO-SCOBI model covers the Baltic Sea, including Kattegat. The color bar shows the depth in meter and the black filled circles shows positions of the stations used for validation. The names of the stations in the Gulf of Finland and central Baltic proper are displaced to the right and down for clarity. The SMHI monitoring station BY15 has approximately the same position as GB-F and is not separately shown.

phosphate, phytoplankton, zooplankton, detritus, and oxygen. Phytoplankton consists of three algal groups representing diatoms, flagellates and others, and cyanobacteria (corresponding to large, small and nitrogen fixing cells). The growth rates depend on nutrient concentrations, irradiance, and water temperature. The modelled cyanobacteria also have the ability to fix molecular nitrogen. Organic matter sinks and enters the sediment containing benthic nitrogen and phosphorus. The sediment processes include oxygen dependent nutrient regeneration and denitrification as well as permanent burial of nutrients. Resuspension of organic matter depends on the combined effects of waves and current induced shear stress (Almroth-Rosell et al., 2011). In this study detritus is separated into different nitrogen and phosphorus pools in accordance with the description given by Savchuk (2002). The nutrient loads for the present run are identical to the historical loads described by Gustafsson et al. (2012). The sediment part in the SCOBI model has been further developed compared to the model described by Eilola et al. (2009) and Almroth-Rosell et al. (2011). New pelagic and sediment pools of inorganic phosphorus have been implemented to simulate the adsorption behavior of phosphate on e.g. iron(III)oxides, which in the sediment is regulated by the oxygen penetration depth (OPD).

Soetaert et al. (2000) tested five different levels of coupled sediment-water nutrient flux model complexity for continental shelf areas. The most complex model version (level 4) couples the water column processes to a vertically resolved biogeochemical sediment model (e.g. Reed et al., 2011). The results by Soetaert et al. (2000) suggested, however, that the vertically integrated dynamic sediment model (level 3) approach represent the best balance between computational demand and attained accuracy. The level 3 type model has been used with good results in the coupled physical-biogeochemical RCO-SCOBI model and other Baltic Sea models as well (Eilola et al., 2011). The aim is therefore to keep the basic structures of the SCOBI model formulations, described in Eilola et al. (2009) and Almroth-Rosell et al. (2011), for the new formulations to account for the oxygen penetration depth

and dynamics of inorganic phosphorus, described in Sections 2.2.1 and 2.2.2, respectively.

### 2.2.1. Oxygen penetration depth

The depth to which oxygen penetrates into the sediment depends on the rate of oxygen consumption in the sediment and the diffusive transport of oxygen from the bottom water to the sediment (Cai and Sayles, 1996). The OPD is calculated using Eq. (1) from Cai and Sayles (1996), who showed that this estimation of OPD describes well the situation in continental marginal seas. This equation describes the OPD at steady state pore water oxygen profiles and a homogenous depth distribution of carbon decomposition in the OPD layer with no bioirrigation included. In frontal areas with highly variable oxygen concentrations in the bottom water the equation might therefore temporary give deviations from observations, but these occasions are believed to be of less importance for the long term study of the present paper.

$$OPD = 2\varnothing D_s \frac{[O_2]_{BW}}{F_{O_2}^0} \quad (1)$$

$$D_s = \frac{D}{1 - \ln(\varnothing^2)} \quad (2)$$

where OPD is the oxygen penetration depth in meter,  $\varnothing$  is the sediment porosity,  $[O_2]_{BW}$  is the bottom water oxygen concentration ( $\text{ml O}_2 \text{ l}^{-1}$ ),  $F_{O_2}^0$  is the oxygen flux to the sediment ( $\text{ml O}_2 \text{ m}^{-2} \text{ s}^{-1}$ ) and  $D_s$  is the diffusivity of oxygen in the sediment ( $\text{m}^2 \text{ s}^{-1}$ ).

Local sediment porosity is in the model grid described by three different values representing sediment types at accumulation bottoms (0.94), transport bottoms (0.85) and erosion bottoms (0.64). The bottom types were defined by the method described by Almroth-Rosell et al. (2011). The oxygen flux  $F_{O_2}^0$  is in the SCOBI model given by the

oxidation rate of organic matter and nitrification (of ammonia to nitrate) and the corresponding uptake of oxygen to the sediment. The oxygen penetration depth is properly described by this equation down to about 8 cm (Cai and Sayles, 1996). The porosity dependent diffusivity of oxygen in the sediment ( $D_s$ ) is described by Eq. (2) where  $D$  is the salinity ( $S$ ) and temperature ( $T$ ) dependent diffusivity for oxygen in water (Boudreau, 1996; Hall et al., 2007), which is calculated from Eq. (3). The Eqs. (3) and (4) were defined from the best polynomial fits to data from an oxygen diffusion table (Ramsing and Gundersen, 2014) based on calculations using more sophisticated equations (e.g. Broecker and Peng, 1974; Himmelblau, 1964; Li and Gregory, 1974).

$$D = A \cdot (1 - S \cdot B1 \cdot (B2 + B3 \cdot T)) \quad (3)$$

$$A = (C1 \cdot T^2 + C2 \cdot T + C3) \cdot C4 \quad (4)$$

where the salinity is in the range 0–35 and the water temperature in the range 0–30 °C. The values of the constants are shown in Table 1.

The relative impact of oxygen concentration and oxygen consumption on the magnitude of the OPDs was calculated from Eq. (5):

$$R = \frac{[O_2]^a / [O_2]^b}{F_{O_2}^b / F_{O_2}^a} \quad (5)$$

where  $[O_2]$  is the oxygen concentration and  $F_{O_2}^0$  is the oxygen consumption at yearly minimum OPD denoted by the superscripted letter  $a$  and at yearly maximum OPD denoted by the superscripted letter  $b$ . The equation was derived from Eq. (1) as  $OPD_{\min}/OPD_{\max}$  where the oxygen concentrations were clustered and compared to the oxygen fluxes. The ratio ( $R$ ) is higher than 1 when the oxygen consumption in the sediment controls the OPD and lower than 1 when it is the oxygen concentrations that determines the OPD. The temperature dependent sediment diffusivity is also a parameter that affects the OPD (Eq. (1)) and its relative contribution can be calculated in a similar way, using Eq. (5). Thus, instead of oxygen concentrations the modelled sediment diffusivity at the maximum OPD and minimum OPD, respectively, are used.

### 2.2.2. Benthic inorganic phosphorus

The new elements of the present SCOBI model are described below using formulations similar to the tables in the Appendix of Eilola et al. (2009). The source terms describing the change in time for each variable of the sediment model equations are described by changes in benthic organic phosphorus (PBT in Eq. (6)) and mineral bound inorganic phosphorus (BIP in Eq. (7)). The mineral bound inorganic phosphorus in the water (WIP) is followed in each discrete depth layer as a passive tracer without any biogeochemical sources or sinks in the water (WIP in Eq. (8)). The formulations of sediment resuspension of organic and mineral bound phosphorus are similar and follow in detail the formulations described by Almroth-Rosell et al. (2011) and Eilola et al. (2009), and will not be further discussed here. Also the sinking rate of WIP is similar

**Table 1**  
Constants of Eqs. (3) and (4).

Parameter	Value
B1	$35^{-1}$
B2	0.05
B3	0.00075
C1	0.000424
C2	0.042265
C3	1.105
C4	$10^{-9}$

**Table 2**  
List of biogeochemical state variables.

State variables	Description	Units
$O_2$	Oxygen	$ml O_2 l^{-1}$
OPD	Oxygen penetration depth	meter
PO4	Phosphate	$mmol P m^{-3}$
WIP	Mineral bound phosphate in the water	$mmol P m^{-3}$
PBT	Benthic organic phosphorus	$mmol P m^{-2}$
BIP	Benthic inorganic phosphorus	$mmol P m^{-2}$

to the sinking of detritus described by Eilola et al. (2009). The units of relevant variables of the present paper are listed in Table 2.

$$S_{PBT} = SINKI_{OP} - PBTOUT_{PO4} - PBTOUT_{BIP} - SEDPLOSS - BURIAL_{PBT} \quad (6)$$

$$S_{BIP} = SINKI_{IP} + PBTOUT_{BIP} + SCAV_{PO4} - LIBP_{PO4} - SEDILOSS - BURIAL_{BIP} \quad (7)$$

$$S_{WIP} = SINKI_{IP} - SINKOUT_{IP} + SEDILOSS \quad (8)$$

The basic model concept of the new sediment model is illustrated in Fig. 2, where sinking organic phosphorus is deposited on the sediment and a pool of benthic organic phosphorus builds up. Organic matter is mineralized (Eq. (9)) and an oxygen penetration depth (OPD) dependent fraction (PRC) of the mineralized phosphorus ( $DCOMP_{PBT}$ ) is released directly to the overlying water (Eq. (10)). The salinity ( $S$ ) dependence of the PRC (Eilola et al., 2009) is not used in the present model setup. The remaining fraction (Eq. (11)) is added into the pool of BIP. Under anoxic conditions ( $OPD = 0$ ) all the mineralized phosphorus is directly released to the overlying water ( $PRC = 1$ ). Burial of PBT and BIP are similar and described by Eq. (14) and (15), respectively, and the values of the constants are shown in Table 3.

$$DCOMP_{PBT} = \alpha_{PBT} \cdot EXP(\beta_{PBT} \cdot T) \cdot PBT \quad (9)$$

$$PBTOUT_{PO4} = PRC \cdot DCOMP_{PBT} \quad (10)$$

$$PBTOUT_{BIP} = (1 - PRC) \cdot DCOMP_{PBT} \quad (11)$$

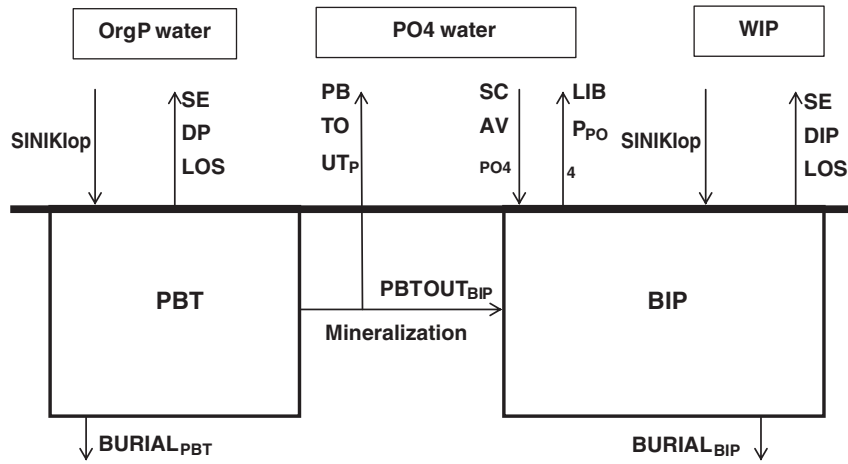
$$PRC = \alpha_{PRC} - \delta_{PRC} \quad (12)$$

$$\delta_{PRC} = 1 / \left( 1 + a_{\delta} \cdot EXP \left( -b_{\delta} \cdot \left( \frac{OPD}{d_{\delta}} - c_{\delta} \right) \right) \right) \quad (13)$$

$$BURIAL_{PBT} = \alpha_{BUR} \cdot PBT \quad (14)$$

$$BURIAL_{BIP} = \alpha_{BUR} \cdot BIP \quad (15)$$

The basic ideas of the modelled mineral bound inorganic phosphorus dynamics follow Neumann and Schernewski (2008) and Reed et al. (2011). In order to account for the dynamics of changing strength of vertical gradients of phosphorus and oxygen in the sediment regulations according to the first order reaction kinetics was introduced. Hence, the release rate ( $LIBP_{PO4}$ ) of PO4 from the sediment (Eq. (16)) decreases as the sediment concentration of BIP decreases below a half saturation value. Similarly the release rate increases when the oxygen penetration depth decreases and reaches its maximum at anoxic conditions. At small OPD values, the half saturation value limits the amount of hydrated metal oxides available for phosphate adsorption. The values of the half saturation constants were evaluated from theoretical considerations and tested and calibrated against realistic values of sediment concentrations in a spread data-sheet model before the implementation into the RCO-SCOBI model. These calibration constants might be further studied and tuned in future experiments using a level 4 type of diagenetic model.



**Fig. 2.** The new benthic model concept of organic and mineral bound inorganic pools of phosphorus in SCOB. Organic phosphorus from phytoplankton and detritus (including resuspended matter) are deposited on the sediment ( $SINKI_{OP}$ ) and builds up the pool of benthic organic phosphorus (PBT). A fraction of the mineralized PBT is released directly to the overlying water ( $PBTOUT_{PO4}$ ) and the remaining fraction ( $PBTOUT_{BIP}$ ) adds to the sediment pool of mineral bound inorganic phosphorus (BIP). Mineral bound inorganic phosphorus from the water (WIP, only resuspended particles) is deposited on the sediment ( $SINKI_{IP}$ ) and adds to the pool of BIP. Phosphorus can be released from the pool of BIP to the overlying water ( $LIBP_{PO4}$ ) as well as become scavenged/adsorbed ( $SCAV_{PO4}$ ) from the water into the sediment. Burial occur from both the organic ( $BURIAL_{PBT}$ ) and inorganic ( $BURIAL_{BIP}$ ) pools of phosphorus. Resuspension may occur from both sediment pools of phosphorus ( $SEDPLOSS$  and  $SEDILOSS$ ).

The uptake of phosphate from the bottom water to the sediment ( $SCAV_{PO4}$ ) is regulated by interfacial reactions and phosphate diffusion across the sediment interface. The diffusion is driven by the gradient between the bottom water and the sediment pore water concentration at the sediment-water interface (cf. Eq. (3) in Reed et al., 2011). The formulation (Eq. (17)) may transfer  $PO4$  from the water to the sediment if the sediment is under saturated with BIP with regard to the amount of hydrated metal oxides available for phosphate adsorption. This situation may occur e.g. after a period with anoxic conditions when most BIP have been released to the overlying water and BIP decreases below the half saturation value. The uptake requires, however, also that the oxygen penetration depth is deep enough to produce an active oxidized layer. This is regulated by the half saturation value of OPD. The values of the constants are shown in Table 4.

$$LIBP_{PO4} = \alpha_{LIBP} \cdot \frac{BIP}{BIP + \beta_{LIBP}} \cdot \left(1 - \frac{OPD}{OPD + \eta_{LIBP}}\right) \cdot BIP \quad (16)$$

$$SCAV_{PO4} = \alpha_{SCAV} \cdot \left(1 - \frac{BIP}{BIP + \beta_{LIBP}}\right) \cdot \frac{OPD}{OPD + \eta_{LIBP}} \cdot PO4_{water} \quad (17)$$

The transfer rate ( $\alpha_{SCAV}$ ) of phosphate from the water to the sediment ( $m s^{-1}$ ) is regulated by the sediment porosity and the temperature ( $^{\circ}C$ ) dependent phosphate diffusivity ( $m^2 s^{-1}$ ) formula ( $D'$ ) adopted from Krom and Berner (1980).

$$\alpha_{SCAV} = D_{PO4} \cdot \frac{\phi}{\Delta X} \quad (18)$$

$$D_{PO4} = \frac{D'}{1 - \ln(\phi^2)} \quad (19)$$

$$D' = C1_{SCAV} + C2_{SCAV} \cdot (T - C3_{SCAV}) \quad (20)$$

The length scale of the diffusion gradient  $\Delta X$  was set to 1 cm (0.01 m) and the values of the constants are shown in Table 5.

### 2.3. Model validation

The pelagic modelled oxygen and phosphate concentrations are validated qualitatively by comparison of long time series of the model results and data from the central Baltic proper. Observations from the database Svenskt HavsARKiv (SHARK, 2014) at SMHI are used for validation. Hydrogen sulfide concentrations are both in the models and in the observations represented by “negative oxygen” equivalents ( $1 \text{ ml H}_2\text{S l}^{-1} = -2 \text{ ml O}_2 \text{ l}^{-1}$ ) (Fonselius and Valderrama, 2003)

Modelled OPDs in SCOB have been validated through comparison with observed OPD found in the literature for the Eastern Gotland Basin (Steenbergh et al., 2011; Wenzhöfer et al., 2002), and to calculated OPD according to formulations from Cai and Sayles (1996) using observation data of bottom water oxygen concentrations and benthic oxygen fluxes together with known porosity (Viktorsson et al., 2013; Nilsson et al., unpublished results; M. Kononets, pers. comm.). Observation data for the OPD have preferentially been chosen because both P-fluxes and oxygen penetration depths from the same study site at the same occasion are included. Stations used for validation are shown in Fig. 1.

**Table 3**  
Constants and units of Eqs. (9)–(15).

Parameter	Unit	Value	Description
$\alpha_{PBT}$	$\text{day}^{-1}$	0.0005	Mineralization rate, of benthic organic phosphorus, at 0 °C
$\beta_{PBT}$	$^{\circ}C^{-1}$	0.15	PBT mineralization temperature dependence
$\alpha_{PRC}$	-	1.15	Constant in benthic redox dependence of phosphate
$a_6$	-	0.5	Constant in benthic redox dependence of phosphate
$b_6$	$\text{l ml}^{-1}$	1.5	Constant in benthic redox dependence of phosphate
$c_6$	$\text{ml l}^{-1}$	0.7	Constant in benthic redox dependence of phosphate
$d_6$	$\text{m}^{-1} (\text{ml l}^{-1})^{-1}$	$6.164 \times 10^{-4}$	Constant in benthic redox dependence of phosphate
$\alpha_{BUR}$	$\text{day}^{-1}$	$2.8/1.8/1.4/1.0 \times 10^{-4}$	Burial rate in the Bothnian Sea/Gulf of Finland/Bothnian Bay/Elsewhere

**Table 4**  
Constants of Eqs. (16) and (17).

Parameter	Unit	Value	Description
$\alpha_{\text{LIBP}}$	$\text{day}^{-1}$	0.01	Maximum release rate of benthic inorganic phosphorus
$\beta_{\text{LIBP}}$	$\text{mmol m}^{-2}$	484	Half saturation value of BIP
$\eta_{\text{LIBP}}$	meter	$10^{-4}$	Half saturation value of OPD

### 3. Results and discussion

#### 3.1. Validation of model results

Validation processes of large scale biogeochemical models are complicated and include many variables. It is not only the variability of the weather, but the statistics (mean, standard deviation, etc.) or the climate which needs to be simulated correctly. The nutrient and oxygen concentrations at certain times are much influenced by the characteristics of the hydrodynamic model, such as the timing of inflows or the vertical stratification. The chronology between observed and modelled concentrations may therefore differ. For the present study it is desirable that the model captures the characteristic dynamics of oxygen and phosphate concentrations in the deepest water layer.

##### 3.1.1. Variability of oxygen and phosphate concentrations

Modelled oxygen and phosphate concentrations have been compared to observations from monitoring stations (Eilola et al., 2009) and results from the present model version from the stations BY05 and BY15 (for locations see Fig. 1) in the bottom water are shown (Fig. 3). Generally the model captures the long-term variability of oxygen and phosphate concentrations in the Baltic proper.

In the bottom water (90 m depth) and ten meters above bottom at station BY05 the variability of phosphate concentrations is satisfactory reproduced (Fig. 3) during large parts of modelled period. However, during a few occasions e.g. at the end of the 1980s and from about 2006 and forward the concentrations are too low because the modelled oxygen concentrations were not low enough during these periods (Fig. 3). About ten meters above the bottom the oxygen mean value is too high compared to observations, which probably is due to the a weakness in the simulation of the stratification (Väli et al., 2013). These higher oxygen concentrations do, however, not seem to affect significantly the oxygen concentrations at the bottom most water layer at this station. Overall are the dynamics of oxygen and phosphate concentrations at station BY05 reasonably reproduced (Fig. 3).

At BY15 are the stagnation periods as well as the consequences from deep water inflows (1970, 1976, 1993 and 2003) captured by the model both at the bottom most layer (240 m) and at about 100 m depth (Fig. 3). During the stagnation periods the oxygen concentrations decrease while the phosphate concentrations in the deep water increase. However, the modelled phosphate concentrations in the bottom most layer are lower compared to observations, which is clearly seen during the stagnation period 1983–1993. The increase in phosphate concentrations levels off from the mid-1980s much because the modelled benthic inorganic phosphorus pool becomes depleted (not shown). The modelled oxygen concentrations follow the observations at both 240 m and 100 m depth, with the exception in the end of the period where the modeled oxygen does not capture the observed, fast depletion of oxygen.

**Table 5**  
Constants of Eq. (20).

Parameter	Value
$C1_{\text{SCAV}}$	$7.34 \times 10^{-10}$
$C2_{\text{SCAV}}$	$0.16 \times 10^{-10}$
$C3_{\text{SCAV}}$	25

The long-time average profiles (1980–2008) of the modelled and observed phosphate and oxygen concentrations at station BY15 (Fig. 4) confirm that the model manages to capture the oxygen and phosphate dynamics. However, below the halocline oxygen and phosphate concentrations are too high and too low, respectively, with largest differences closest to the bottom.

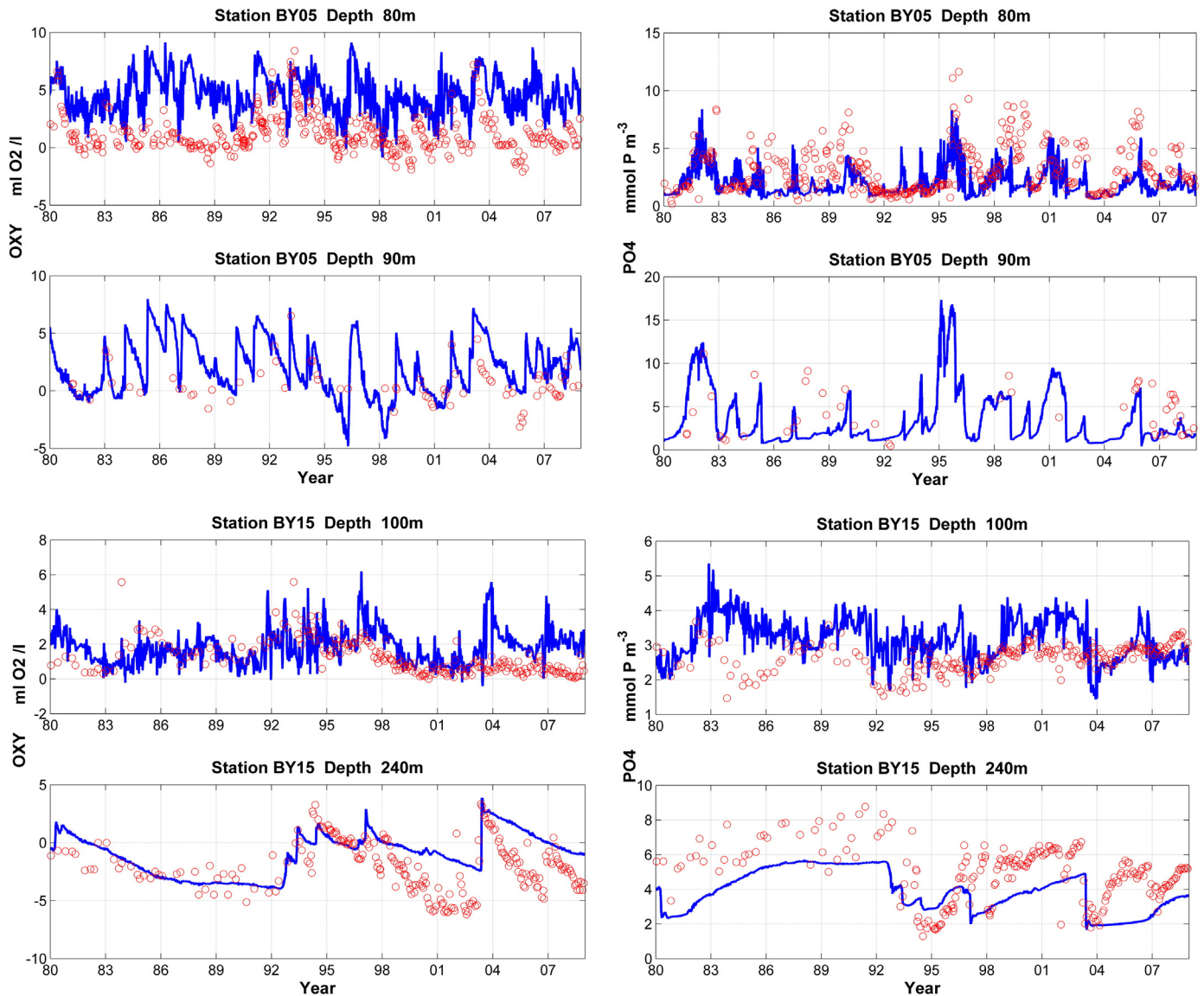
A comprehensive validation of the physics is presented by Väli et al. (2013).

##### 3.1.2. Oxygen penetration depth

The model seems to simulate oxygen penetration depth with reliable magnitude and variability. However, there are differences between model results and observations (Table 6) that will be discussed below. The OPD in a coastal zone is in general of the magnitude of millimeters (Glud, 2008) and fluctuates depending on the bottom water oxygen concentrations and the amount of organic material. E.g. Rasmussen and Jørgensen (1992) found seasonal variations of the OPD in Aarhus Bay in the range from  $-5.1$  mm during winter to  $-1.2$  mm during spring. During summer the OPD was between  $-1.3$  and  $-2.5$  mm. However, there are some general problems when model results are compared to observations, especially for measurements in the sediment. One important factor is the size of the horizontal grid and the lack of spatial variation in each grid cell of the model. Observations are made on a very limited spatial scale which is assumed to represent a larger area, while the horizontal resolution of the present model system is about 3.7 km. This causes the differences between the observed and modelled water depths at some of the stations (Table 6). It is also important to remember that the model results in Table 6 are monthly means while the observations are snapshots at specific dates, or at the most averages of snapshots from two or maximum three measurement occasions. The limited number of observations restricts the possibilities to perform a statistical evaluation. It would therefore be desirable to have more observations of OPD to be able to do a more comprehensive validation in the future.

Largest difference between modelled and observed OPD is found at station GB-A (Table 6) which is a station in the Eastern Gotland Basin at about 60 m depth with oxic bottom water (Viktorsson et al., 2013). The estimated observation of OPD at this station is  $-1.5$  mm while the modelled monthly mean value for the same month is as deep as  $-21$  mm. The limited numbers of measurements of the OPD make it hard to determine whether or not they are representative as well as the fact that the observed OPD is estimated from observations of oxygen concentrations and consumption instead of a direct measurement. The estimation is on the other hand calculated in the same way as the modelled OPD (Eq. (1)). Another important factor is that the bottom depth in the model at this station (45 m) is in the ventilated waters above the modelled halocline, why the oxygen concentrations and the OPD are higher.

At the stations GB-B and Kasuuni the difference between modelled and observed OPD was in the range from  $-2.4$  mm to  $-3.1$  mm, thus the modelled OPD was underestimated. The Kasuuni station is classified as transport/accumulation bottom at about 55 m water depth (Almroth et al., 2009; Viktorsson et al., 2012) but in the model the water depth is larger, 66 m. The modelled halocline in the Gulf of Finland is too strong and shallow, approximately at about 50 m depth (Meier, 2007; Väli et al., 2013). The water exchange, and hence, the supply of oxygen below the halocline is much less effective than in the surface layers above. This can be one of the reasons why the modelled OPD is zero at Kasuuni, while the observations show non-zero OPDs. At GB-B the modelled and observed depths are about 70 m, which approximately coincide with the depth of the fluctuating halocline in the Baltic proper (Väli et al., 2013). The bottom water at this station may therefore often shift between anoxic and oxic conditions. This is reflected in the variability of the modelled OPD (Fig. 5, left). It is not possible to simulate the exact timing and amplitude of observed OPD variations with a large-scale model although the variability of the model well captures



**Fig. 3.** Modelled (line) bottom water concentrations of oxygen ( $\text{ml l}^{-1}$ ) (left) and phosphate ( $\text{mmol m}^{-3}$ ) (right) are compared to observations (circles) at the stations BY05 in the Bornholm Basin (top), and BY15 (bottom) in the Eastern Gotland Basin, during the period 1980–2008.

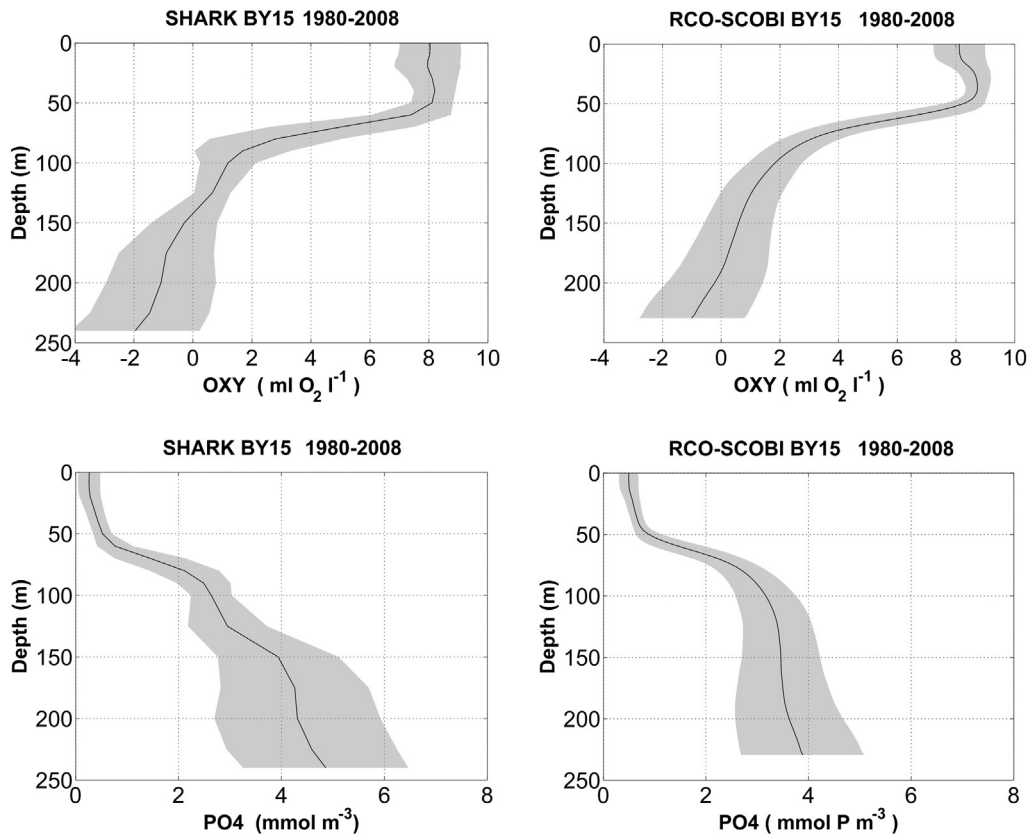
the magnitudes of the observed OPD. A similar fluctuating pattern can be observed for station W-B (Fig. 5, right). The observed and modelled water depth at W-B is about 120 m. Due to the restricted water exchange the bottom water has low oxygen concentrations with shallow OPD, at the most about 2 mm for the period 1980–2008. The bottom water often becomes anoxic during long periods with zero OPD as a result.

### 3.1.3. Phosphate release from sediment

The oxygen conditions in the sediment affect the release of phosphate from the sediment to the overlying water and the bottom water phosphate concentration. Most observations of phosphate concentrations in the bottom water fit within the variability of the modelled (1980–2008) phosphate concentrations depicted at different OPD (Fig. 6A). The mean phosphate release rates from the sediment to the water column is low with a small standard deviation at large oxygen penetration depths (Fig. 6B), which is in accordance with observations. There is also an uptake of phosphate by the sediment, which is seen by observations (Fig. 6B) for OPD > 1 mm depth in the sediment. These occasions are not captured by the variability of the model results as

seen from the modelled standard deviation, but the modelled minimum values shows that the model has the capability to a low uptake of phosphate from the water column. Some observations show high phosphate release rates also under oxic conditions in the sediment, which is not captured by the variability (standard deviation) of the model. However, the maximum release rates of phosphate at different OPD shows that the model has the capacity to also capture higher release rates both at oxic conditions and at zero OPD. It is difficult to judge whether these observations can be regarded as representative values for the monthly means or if the momentary measurements of sediment fluxes are influenced by temporary fluctuations in the bottom water oxygen concentrations. There are also challenges with measuring low phosphate fluxes (Almroth et al., 2009) that may affect the observations.

The long-term mean (1980–2008) of phosphate concentrations at different bottom water oxygen concentrations corresponds very well with the observations, that mainly are within the  $\pm 1$  standard deviation of the model results (Fig. 6C). The phosphate release from the sediment is very low at oxygen concentrations higher than about  $100 \text{ mmol m}^{-3}$  (Fig. 6D) and increases with oxygen depletion. The variability of modelled phosphate release at anoxic conditions captures



**Fig. 4.** The long-term (1980–2008) mean profiles of oxygen ( $\text{ml l}^{-1}$ ) and phosphate ( $\text{mmol m}^{-3}$ ) concentrations at station BY15 are shown by the black line in the top and low panels, respectively. The  $\pm 1$  standard deviation is shown by the grey shaded area. Observations are to the left and model results to the right.

well the variability of observed fluxes (Fig. 6D). The modelled maximum values of phosphate release rates show that the model capture also the high observed values. The results of the validation to *in situ* observations show that the model captures well the dynamics of oxygen and phosphate in the bottom water.

### 3.2. Spatial variation of the oxygen penetration depth

The spatial variability of the simulated OPD (Fig. 7) show highest values in shallow coastal zones, approximately at depth above the halocline. Lowest values are found in the deeper central basin,

**Table 6**

The mean observed oxygen penetration depth (OPD obs) and the standard deviation (STDV obs) for each field study at the different stations in the Gulf of Finland (GF) and Baltic proper (BP) with the observed (ObsDepth) and modelled (ModDepth) water depth during the given date (year; month). The model results are calculated as monthly mean (OPD mod) with the representative standard deviation (STDV mod). The difference between OPD obs and OPD mod is given as  $\Delta\text{OPD}$ . For location of the stations, see Fig. 1.

Basin	Station	Year	Month	Obs Depth (m)	Mod Depth (m)	OPD Obs (mm)	STDV Obs	OPD Mod (mm)	STDV Mod	$\Delta\text{OPD}$ (mm)
BP	GB-A <sup>2</sup>	2008	9	60	45	-2.9	0.3	-21.0	1.4	17.8
BP	GB-B <sup>2</sup>	2008	9	75	72	-5.3	0.2	-2.6	0.2	-2.7
BP	GB-D <sup>2</sup>	2008	9	128	123	0.0		0.0	0.00	0.0
BP	GB-E <sup>2</sup>	2008	9	180	165	0.0		0.0	0.02	0.0
BP	GB-F <sup>2</sup>	2008	9	210	216	0.0		0.0	0.00	0.0
BP	W-A <sup>3</sup>	1996	8	75	75	-1.5	0.0	-1.1	0.00	-0.4
BP	W-B <sup>3</sup>	1996	8	115	120	-1.5	0.0	0.0	0.00	-1.5
BP	W-C <sup>3</sup>	1996	8	155	165	-0.9	0.0	0.0	0.00	-0.9
BP	W-D <sup>3</sup>	1996	8	210	231	0.0	0.0	0.0	0.00	0.0
GF	GF1 <sup>2</sup>	2002	6	72	81	0.0		0.0	0.00	0.0
GF	GF2 <sup>2</sup>	2002	6	81	81	0.0		0.0	0.00	0.0
GF	PV1 <sup>1</sup>	2003	6	75	45	0.00	0.00	0.0	0.00	0.0
GF	PV1 <sup>1</sup>	2004	9	70	45	-1.9	0.2	0.0	0.00	-1.9
GF	PV1 <sup>1</sup>	2005	5	73	45	-0.6	0.2	0.0	0.00	-0.6
GF	XV1 <sup>1</sup>	2005	5	17	39	-1.8	0.4	-0.2	0.3	-1.6
GF	Kasuuni <sup>1</sup>	2003	7	53	66	-3.1	0.7	0.0	0.00	-3.1
GF	Kasuuni <sup>1</sup>	2004	9	54	66	-2.4	0.4	0.0	0.00	-2.4
GF	Kasuuni <sup>1</sup>	2005	5	54	66	-2.4	0.5	0.0	0.00	-2.4

<sup>1</sup> The observed OPD from these stations are calculated from oxygen data (Almroth et al., 2009).

<sup>2</sup> The observed OPD from these stations are calculated from unpublished data.

<sup>3</sup> The observed OPD from these stations are adopted from Wenzhöfer et al. (2002).



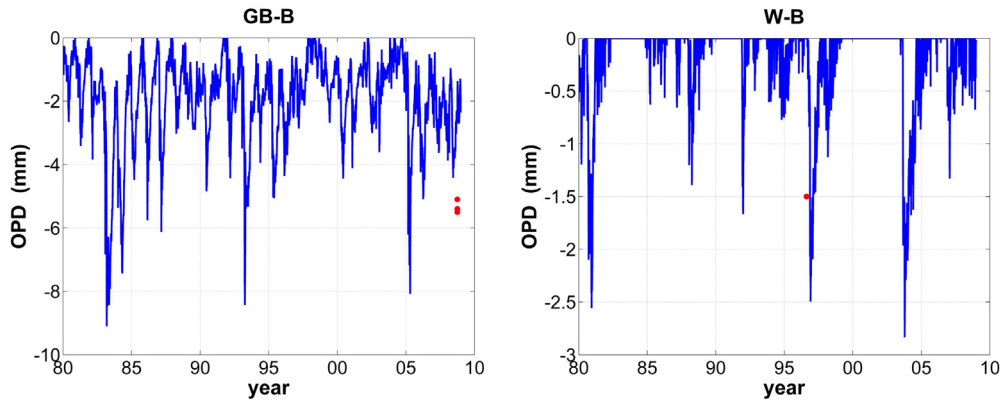


Fig. 5. The modelled (line) OPD (mm) at station GB-B (left) and at W-B (right) over time. Observations are shown as filled circles.

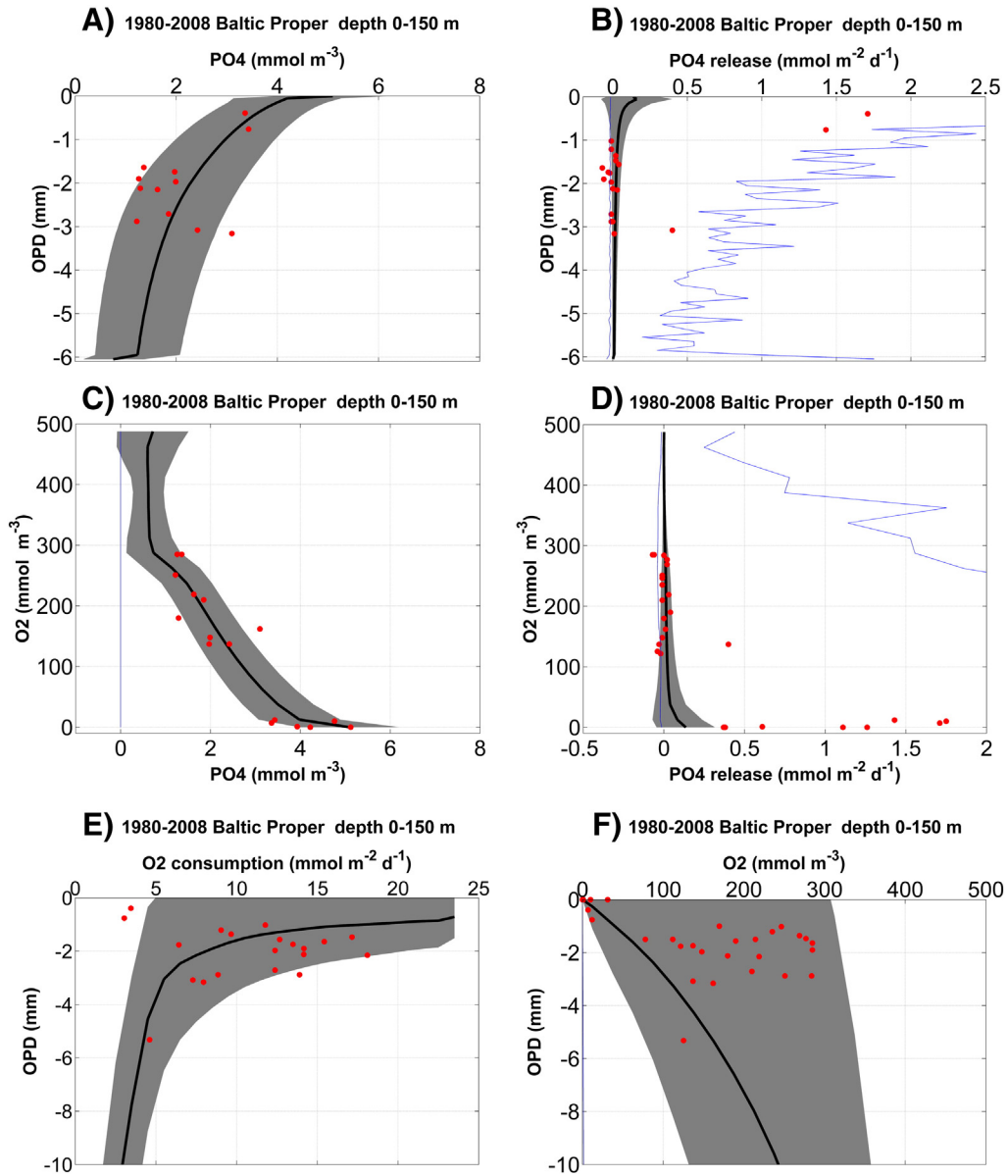
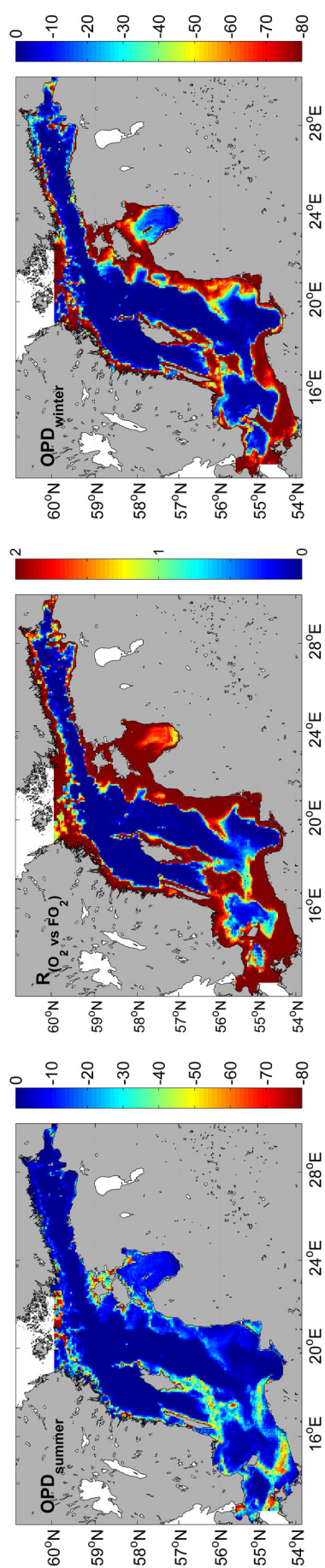


Fig. 6. The average values (black line) of the annual mean, during the period 1980–2008,  $\pm 1$  standard deviation (grey shaded area) of modelled; A) phosphate concentrations ( $\text{mmol m}^{-3}$ ) in the bottom water and B) phosphate release rates ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) from the sediment to the overlying water for different oxygen penetration depths (mm); C) the phosphate concentrations ( $\text{mmol m}^{-3}$ ) and D) phosphate release rates ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) from the sediment at different bottom water oxygen concentrations ( $\text{mmol m}^{-3}$ ); oxygen penetration depths (mm) for E) different oxygen consumptions ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) in the sediment and F) oxygen concentrations ( $\text{mmol m}^{-3}$ ) in the bottom water. The thin black lines are the maximum and minimum values of the phosphate release rates during the period and filled circles are observations from different stations during the year 1996, 2002–2005 and 2008–2010.



**Fig. 7.** The spatial variability in the Baltic Proper of the August–September (left) and January–February (right) long term (1980–2008) monthly mean of OPD (mm) and the long-term mean of OPD from oxygen consumption versus oxygen concentrations (middle). The impact from the consumption and concentrations of oxygen on the OPD is equal at areas shown by green color. In areas with yellow–red colors the oxygen flux have larger impacts on the OPD compared to oxygen concentrations, while the turquoise–blue color shows areas where the oxygen concentrations controls the OPD.

where the oxygen concentration often is low. The seasonal variations show lowest long-term (1980–2008) monthly mean values of OPD (Fig. 7, left) during late summer and early fall (August–September), while the sediment still is enriched by organic material from algal blooms. This area is approximately the same as where the minimum oxygen concentrations are found (not shown). Largest mean OPD values (Fig. 7, middle) are mainly found during winter (January–February), before the productive season, thus before high deposition of organic material on the sediment surface. The seasonal variation of OPD has been shown also in field studies, e.g. in the study by Rasmussen and Jorgensen (1992) in the Aarhus Bay, in Denmark. They also found that the OPD decreased during spring/summer and then increased again during next winter when the fresh organic material was depleted. The largest OPD in the Baltic Sea found in literature is  $-40$  mm in the northern Bothnian Bay (Slomp et al., 2013). OPD down to  $-3.2$  mm has been found in other studies for the Baltic proper (Hietanen and Kuparinen, 2008; Steenbergh et al., 2011; Wenzhöfer et al., 2002), while the maximum OPD calculated from the observation data used in the present study was  $-5.5$  mm.

During storm events increased water mixing (improved oxygen conditions) and resuspension cause increased OPD. The immediate response in the model for changes in the consumption and concentration of oxygen in the OPD calculations can during resuspension events momentary lead to large OPD. Thus, during a resuspension event lasting for a day or more the organic material in the sediment is removed and by that the oxygen consumption decrease to very small values causing a maximum OPD (see Eq. (1)). However, the mean release rate of mineral bound phosphate is decreased by 90 % already at OPD of about  $-1$  mm (Eq. (16)).

The modelled largest mean OPD is reached at oxygen consumptions between  $>0$  and  $\leq 0.5$   $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  and gets then rapidly shallower with increasing oxygen consumption (Fig. 6E). This is in accordance with the discussions from earlier studies (Conley et al., 1997; Lehtoranta and Heiskanen, 2003; Lehtoranta et al., 2009; Pitkanen et al., 2007) that high amounts of organic matter on the sediment surface can lead to decreased OPD and thus decreased phosphate retention capacity in the sediment, in spite of oxic bottom water. The OPDs at different bottom water oxygen concentrations are more variable (Fig. 6F), which also confirms that the OPD not necessary is large at high oxygen concentrations.

The mean (1980–2008) relative impact of oxygen concentration and oxygen flux on the magnitude of the OPDs in different areas (Fig. 7, right) showed that the oxygen consumption controlled the variability of OPD in the coastal zones. These are approximately at the same areas as where the large winter values of OPDs are found and where the seasonal variations seem to be large. The consumption of oxygen has generally a greater impact on the OPD than the temperature dependent sediment diffusivity (not shown).

### 3.3. Phosphate fluxes in the Baltic Proper

The net phosphate release rates from the sediment are calculated as long time means (1980–2008) for the whole Baltic Proper at four different depth levels (0–30, 30–60, 60–150 and  $>150$  m) during oxic and anoxic conditions. This categorization of depths is similar to what has been done in previous studies (Mort et al., 2010; Viktorsson et al., 2013).

The sum of deposition of organic and inorganic phosphorus on oxic sediments is at all depth levels larger than the release of phosphorus (Table 7). For anoxic bottoms the opposite is seen; the release of total phosphorus during this period is larger than the deposition of phosphorus. About  $43 \times 10^3$  t P year $^{-1}$  is taken up by the oxic sediments while about  $19 \times 10^3$  t P year $^{-1}$  is released from the anoxic sediments. In total the net Baltic proper sediment sink is then about  $23.7 \times 10^3$  t P year $^{-1}$ . The largest net loss (sources-sinks) of phosphate from

**Table 7**

The long term (1980–2008) mean of net phosphate release (PO4 Release) from the sediment to the overlying water, the net deposition of organic (OrgP Deposition) and inorganic (IorgP Deposition) phosphorus to the sediment and the burial of phosphorus is given for the different depth levels (Depth) during oxic and anoxic conditions in the Baltic Proper. The corresponding area to each depth level is given, as well as the fraction (%) of the total area which is 262,900 km<sup>2</sup>.

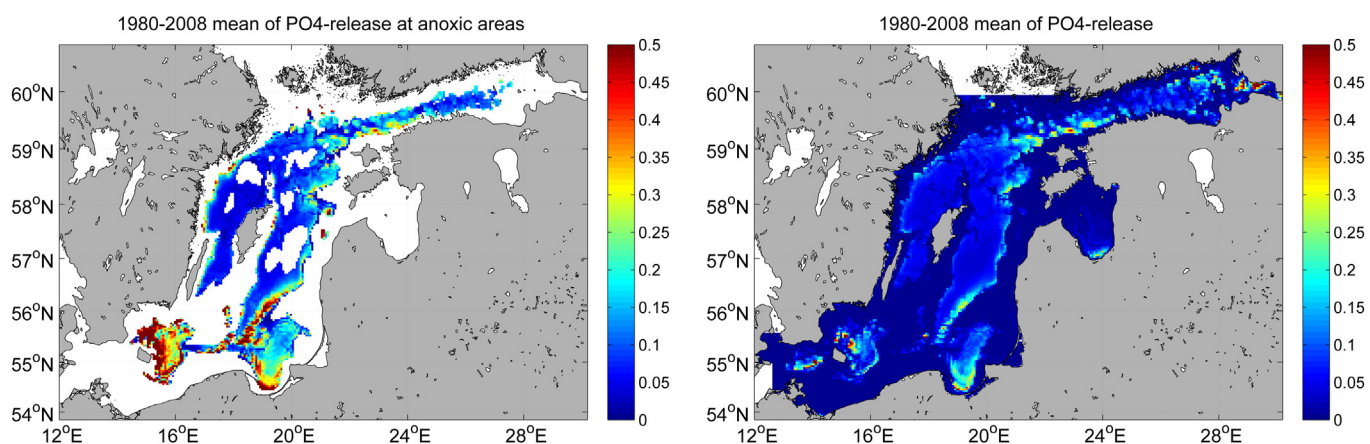
	Depth (m)	PO4 Release 10 <sup>3</sup> t P yr <sup>-1</sup>	OrgP Deposition 10 <sup>3</sup> t P yr <sup>-1</sup>	IorgP Deposition 10 <sup>3</sup> t P yr <sup>-1</sup>	Burial 10 <sup>3</sup> t P yr <sup>-1</sup>	Area km <sup>2</sup>	Area of tot %
OXIC	0–30	4.5	23.8	–15.2	4.1	85,400	32
	30–60	8.0	28.9	–10.5	8.2	70,800	27
	60–150	17.4	34.6	9.9	8.2	49,700	19
	>150	0.6	1.1	0.3	0.3	1970	0.8
ANOXIC	0–250	30.4	88.4	–15.5	20.7	208,000	79
	0–30	3.8	2.7	0.7	0.3	400	0.2
	30–60	8.5	3.7	2.6	1	2700	1
	60–150	59.4	30.7	12.8	5.3	43,800	17
	>150	5.5	4.0	1.1	0.6	8000	3
	0–250	77.0	41.0	17.1	7.2	54,900	21

the sediment to overlying water was about  $59 \times 10^3 \text{ t P year}^{-1}$  (Table 7) which corresponds to a phosphate release rate of  $0.12 \text{ mmol P m}^{-2} \text{ d}^{-1}$ . This flux was found on anoxic bottoms at depths between 60 and 150 m. On average these anoxic bottoms (Fig. 8, left) cover about 17% of the total area in the Baltic proper. During oxic conditions on this depth level the phosphate release was about  $17 \times 10^3 \text{ t P year}^{-1}$  (Table 7), which corresponds to a phosphate release rate of about  $0.03 \text{ mmol P m}^{-2} \text{ d}^{-1}$ . This release rate is in agreement with the observations found by Viktorsson et al. (2013) who measured a phosphate release rate of  $0.027 \text{ mmol P m}^{-2} \text{ d}^{-1}$  at the same depth level. In accordance with earlier studies (Jilbert et al., 2011; Koop et al., 1990; Mort et al., 2010) the highest phosphate fluxes are mainly found at periodically anoxic areas where the bottom water varies between oxic, hypoxic and anoxic oxygen conditions. Lowest release rates of phosphate,  $0.007 \text{ mmol P m}^{-2} \text{ d}^{-1}$ , were found at the oxic areas, of which 59% were found between surface and 60 m depth (Fig. 8, right) and 17% at the depth level 60–150 m (Table 7). Measurements at oxic sediments has shown a variability of phosphate fluxes that range from an uptake to the sediment of  $0.25 \text{ mmol P m}^{-2} \text{ d}^{-1}$  to a release up to  $0.36 \text{ mmol P m}^{-2} \text{ d}^{-1}$  (Conley et al., 1997; Koop et al., 1990; Laima et al., 2001; Lehtoranta and Heiskanen, 2003; Lukkari et al., 2009a; Pitkänen et al., 2001; Viktorsson et al., 2012, 2013). The spatial variability of the iron content in the Baltic Sea sediments is not well known and is therefore not included in the present model setup. The model therefore uses a spatially invariant half saturation constant (Table 4) that describes the limitation from hydrated metal oxides available for phosphate adsorption. A possible limitation in phosphate retention due to too low iron concentrations (relative to the need for phosphate binding) would under oxic conditions lead to higher effluxes of phosphate from the

model sediment. The model formulation may be further studied when more knowledge about the iron dynamics in the Baltic Sea becomes available.

At anoxic sediments below 150 m depth the model showed average phosphate release rates of about  $0.06 \text{ mmol P m}^{-2} \text{ d}^{-1}$ . The modelled release rates at anoxic sediments in the Baltic Proper ( $0.06$ – $0.12 \text{ mmol P m}^{-2} \text{ d}^{-1}$ ) are within the large range of measured fluxes of phosphate at anoxic bottoms,  $0.001$  to  $1.75 \text{ mmol P m}^{-2} \text{ d}^{-1}$  (Hille, 2005; Jilbert et al., 2011; Lukkari et al., 2009a; Mort et al., 2010, Fig. 7; Viktorsson et al., 2012; Viktorsson et al., 2013).

As mentioned in Section 3.1.1 the deep water phosphate concentrations became too low when compared to measurements especially during the latter part of the stagnation period in the 1980s. At other depth levels no depletion of the benthic pools of phosphorus occurred. This is explained by the buildup of the pools during oxic conditions when more phosphorus is deposited on the sediment surface than is released. During the long anoxic period, however, the benthic pools of inorganic and organic phosphorus declined substantially and caused low release rates of phosphate. This shortcoming occurs in the deepest part of the Baltic proper where the mean anoxic bottom area at depth below 150 m represents only about 3% of the total bottom area why the impact is of minor importance for the Baltic Sea on the long term. The degradation rate of benthic organic matter in the present model has a shorter time scale on which the benthic pools of nutrients can be depleted (Meier et al., 2012a), compared to the model setup described by Eilola et al. (2009). The slower degradation rate of organic material in the sediment used in the model study by Eilola et al. (2009) lead to a larger pool of phosphorus which could be released on longer time scales. Stigebrandt et al. (2014) discussed whether there is a source of phosphate in the sediment that



**Fig. 8.** The net long term mean (1980–2008) of phosphate release rate ( $\text{mmol m}^{-2} \text{ d}^{-1}$ ) at the depth 60–150 m during anoxic conditions (left) and on all depth levels and oxygen conditions (right).

was accumulated before the sediment became anoxic to be able to maintain the high phosphate release during longer anoxic periods. They mean that the phosphate source could consist of either organic phosphorus and/or a hydrous ferric phosphate mineral that undergoes very slow dissolution contributing to the long term phosphate release from the sediment in addition to the degradation of the deposited organic material from the water column. The importance of the degradation rate may be further studied from sensitivity experiments with the present model.

### 3.4. The Baltic Sea phosphorus sink

The balance between phosphorus loads to the Baltic Sea and the export of phosphorus to the Kattegat is determined by the sink efficiency in the Baltic Sea, i.e. how large fraction of the loads are permanently removed and stored within the Baltic Sea. The calculated phosphorus sink efficiency, was on average about 83 % during the period 1980 to 2008, i.e. about 17% of the average loads of phosphorus were exported from the Baltic Sea. The calculation of the net export to Kattegat ( $9.5 \times 10^3 \text{ t year}^{-1}$ ) is derived from the mass balance between the load from land, burial and change in the pools of phosphorus (cf. Meier et al., 2012b). The total annual supply of phosphorus to the Baltic Sea in the present simulation decreased from a maximum of  $74 \times 10^3 \text{ t year}^{-1}$  in 1980 to about  $35 \times 10^3 \text{ t year}^{-1}$  in 2008 and was on average  $54.4 \times 10^3 \text{ t year}^{-1}$  during the period. On average about  $50 \times 10^3 \text{ t year}^{-1}$  was permanently buried and removed from the sediment while the pools of active phosphorus in the water and sediment decreased by  $5.1 \times 10^3 \text{ t year}^{-1}$ . The decrease in phosphorus pools is caused by the imbalance between sources and sinks that was caused by the reduced phosphorus loads during the period.

Meier et al. (2012b) estimated for the period 1978–2007 from a model ensemble of three coupled physical–biogeochemical models the sink efficiency to 85 %. According to the numbers by Stigebrandt et al. (2014) the sink capacity was 88 % in year 1980 and decreased to 75 % in 2005. The calculation of the phosphorus sink efficiency is, however, somewhat delicate since it depends on the time period of consideration. There were drastic changes in the external loads of phosphorus after 1980 while the changes in total pools in the water and sediment are quite slow due to the large pools compared to the relatively slow burial and export to the Kattegat. The variability of the phosphorus pools in the water is large due to the varying oxygen conditions and exchanges with the sediment. However, the present results corresponds to the average sink capacity (82%) of the two years 1980 and 2005 estimated from the numbers presented by Stigebrandt et al. (2014). Hence, it is difficult to obtain accurate numbers just by judging from one single year and using information solely from the water column at a few stations in the Baltic proper. In order to obtain a representative figure of the sink efficiency, the calculation should preferably be performed during a period of equilibrium or cover a longer period accounting for the natural variability of inter-annual and decadal fluctuations caused by Baltic Inflows. Because of the long water residence time in the Baltic Sea also the pools in the Bothnian Sea and Bothnian Bay should be taken into consideration as the sediments here may act as sinks for phosphorus exported from the Baltic proper (e.g. Slomp et al., 2013).

The modelled sink efficiency for the periods 1980–1989 and 2000–2008 was 79% and 88%, respectively. Thus, the modelled sink efficiency increased from the 1980s to the 2000s in the present simulation. This result is in contradiction to the results by Stigebrandt et al. (2014) who saw decreased sink efficiency in 2005 compared to 1980. According to basin scale integrated observations (see Fig. 11 in Eilola et al., 2011) the phosphorus pool in the Baltic Proper increased from the late 1990s and accelerated rapidly after the Major Baltic Inflows (MBI) in 2003. The rapid increase after 2003 is not reproduced by the present simulation. The reason for the increased sink efficiency in the current simulation is much because phosphorus was retained on large areas with oxic sediments. These areas remained for the last part of the model run while observations indicated an increase of the hypoxic

and anoxic areas (Hansson and Andersson, 2013). Also the relatively high burial ( $50 \times 10^3 \text{ t year}^{-1}$ ), that causes decreasing sediment pools of phosphorus, partly describes the increased sink efficiency in the last part of the run. In the present model the burial rates of the inorganic and organic sediment pools are assumed equal (Eqs. (14), (15)), thus about two thirds of the buried phosphorus in sediment with oxic bottom water (Table 7) originates from the mineral bound pool. In sediment with anoxic condition about half of the buried phosphorus in the sediments originates from the mineral bound pool. It is possible that there should be differential burial rates of the different pools because of the quite different dynamic behavior of the inorganic and organic fractions of phosphorus in the sediment. Hence, a fraction of the buried inorganic phosphorus in the present run could for instance be transferred to the pool of mineral bound phosphorus and become available for release during anoxic conditions. The main conclusions of the present paper will however not be affected by this. More model experiments are needed to investigate further the details of this issue.

Studies in a fjord (Roskilde fjord), different estuaries (Humber and Ems) and river mouths (Ouse, Trent) show that the retention of phosphorus varies between 40 and 90% (Kamp-Nielsen, 1992; Sanders et al., 1997; Van Beusekom and De Jonge, 1998), while in the North sea a retention (burial) of the phosphorus load from land was calculated to only 2% (Brion et al., 2004). Thus, the estimated sink efficiency (80–85%) of the present Baltic Sea is in the higher range compared to other areas, which can be explained by the high residence time of the water in the Baltic Sea. The net export of phosphorus through estuaries was found to be inversely correlated with the mean residence time of the water system (Nixon et al., 1996).

In the future scenarios by Meier et al. (2012b) for the period 2069–2097, the estimated phosphorus sink efficiency becomes 67% in the reference scenario and 64% in the worst nutrient load case “the Business as Usual” scenario. According to the conclusions by Meier et al. (2012b) the reduced sink efficiency depends on the increased temperature. Higher water temperatures are projected to reduce oxygen concentrations due to lower solubility in warmer water and accelerate organic matter mineralization and oxygen consumption. Expanding anoxia increase the phosphate release rates from the sediments, and amplify the phosphorus recycling which will reduce the permanent removal of phosphorus from the ecosystem. Together with an accelerated pelagic recycling loop, this intensifies primary production and oxygen consumption and reinforces the phosphorus release from the sediments.

### 3.5. Phosphate dynamics during deep water inflows

The impact of major deep water inflows on oxygen conditions and release of phosphate from the sediment in the deep parts of the Baltic proper is studied using the present model setup. The decrease in deep water phosphate concentrations due to MBI (Fig. 3 and e.g. Conley

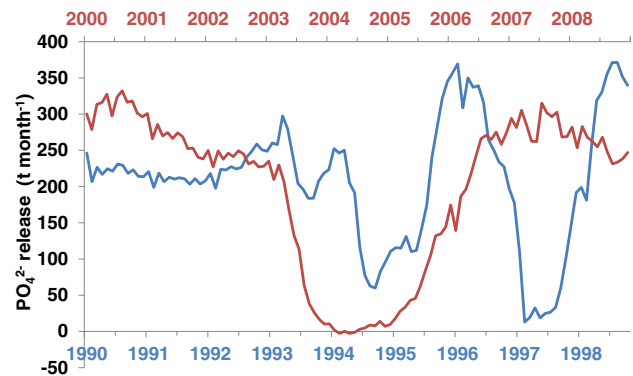


Fig. 9. Monthly mean of the phosphate release ( $\text{t P month}^{-1}$ ) from sediment to water column during two different time periods, 1990–1998 (blue) and 2000–2008 (red) in the Eastern Gotland Basin.

et al., 2002; Savchuk, 2013) is a result from a combination of dilution effects and decreased phosphate release from the sediment because of increased sediment retention capacity since the bottom water is oxygenated.

The modelled monthly mean of the net phosphate release from the sediment at depth below 150 m in the Eastern Gotland Basin was in the range of 200 and 350 t P month<sup>-1</sup> in the beginning of the periods 1990–1998 and 2000–2008, respectively (Fig. 9). In 1993, 1994, 1997 and 2003 large decreases in the phosphate release rates are observed, which coincidence with MBIs (Reissmann et al., 2009). Also in 2001 there was an inflow, which resulted in a decrease in the modelled phosphate release rate, which is observed in Fig. 9. Due to the MBI in 2003 the modeled net release even becomes negative during 2004, i.e. phosphate is taken up by the sediment. In the beginning of 2005 the net phosphate release rate increases again in agreement with the increased phosphate concentrations in the deep water shown in Fig. 3. Modelled net uptake of phosphate from the water to the sediment is only found in the period from May 2003 to June 2004 and to a very low extent, on average 2.9 t P month<sup>-1</sup>, which in total corresponds to about 40 t phosphorus. The total phosphorus pool in the water the month before the MBI was  $26 \times 10^3$  t P. Thus, the uptake of phosphate by the sediment corresponded to only 0.15 % of the total phosphorus content in the bottom water (>150 m depth), and can thus be concluded to play a minor role in the decreased bottom water phosphate concentrations. This uptake is much lower compared to the uptake calculated in the study by Schneider (2011), in which it was concluded that the immediately decrease in phosphate and dissolved inorganic carbon concentrations due to the MBI in the beginning of 2003 was caused to 66% by dilution of the incoming water and to 33% of adsorption to newly formed iron(III)oxides on the sediment surface. About seven month after the inflow Schneider (2011) stated that the C<sub>T</sub> started to increase again while the phosphate concentrations stayed on a low level. The phosphate concentrations started to increase in the beginning of 2005, which is in accordance with the increased phosphate release rate in 2005 seen in the present study. Eilola et al. (2014) found in their model experiment that about 85% of the tracer mass was removed due to dilution effects which also is a larger dilution effect compared to that obtained by Schneider (2011). Sediment uptake of phosphate from the water column at a normally anoxic station which became oxic for a period has been measured *in situ* by Viktorsson et al. (2012). The time-scale for how long this uptake of phosphate may take place was, however, not studied why this is a question for future investigations.

#### 4. Conclusions

The RCO-SCOBI model reproduces well the bottom water phosphate and oxygen concentrations in the Baltic proper during the studied period 1980–2008. In general the new approach to model benthic phosphorus captures much of the phosphate dynamics, and the oxygen penetration depths shows good results compared to observations.

Largest OPDs are found during winter time in the coastal zones, where also the impact from oxygen consumption on the determination of the OPD is found to be largest. During late summer the OPD decreases due to increased deposition of organic material on the sediment surface. Lowest OPD are found in the deeper parts of the basin where the oxygen concentrations often are low, which mainly determines the OPD at these areas. The temperature and salinity dependent sediment diffusivity had a relatively modest contribution to the determination of the OPD compared to the oxygen consumption and concentrations.

Highest modelled release rate of phosphate from the sediment to the overlying water is about  $59 \times 10^3$  t P year<sup>-1</sup>, which corresponds to a phosphate release rate of 0.12 mmol P m<sup>-2</sup> d<sup>-1</sup>. It is found on anoxic sediment in the depth layer between 60–150 m, which is an area that varies between presence of oxygen, hypoxia and anoxia. The sum of deposition of organic and inorganic phosphorus on oxic sediments is at all

depth levels larger than the release of phosphorus from the sediment. For anoxic bottoms the opposite is seen; the release of total phosphorus during the investigated period is larger than the deposition of phosphorus. In total the net Baltic proper sediment sink is about  $23.7 \times 10^3$  t P year<sup>-1</sup>. The estimated phosphorus sink efficiency of the entire Baltic Sea is on average about 83% during the period, i.e. about 17% of the average external loads are exported from the Baltic Sea.

The phosphate release rate from the sediment is shown to drastically decrease and even become negative as a result of Major Baltic Inflows, which transports oxygenated water to the previously anoxic bottoms in the Baltic proper. However, the decrease in the bottom water concentrations of phosphate due to the MBI is mainly explained by dilution. The uptake of phosphate by the sediment from the water column was in this study concluded to be negligible.

The number of available observations of Baltic Sea sediment oxygen penetration depth and sediment–water fluxes is limited, and more observations are needed to be able to do more comprehensive validations covering longer time periods and larger areas.

#### Acknowledgements

The research presented in this study is part of the Baltic Earth programme (Earth System Science for the Baltic Sea region, see <http://www.baltex-research.eu/balticearth>) and was funded by the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS) within the projects “Impact of accelerated future global mean sea level rise on the phosphorus cycle in the Baltic Sea” (grant no. 214-2009-577) and “Impact of changing climate on circulation and biogeochemical cycles of the integrated North Sea and Baltic Sea system” (grant no. 214-2010-1575). Additional support came from Stockholm University’s Strategic Marine Environmental Research Funds “Baltic Ecosystem Adaptive Management (BEAM)” and as part of the COCOA and BIO-C3 projects from the BONUS, the joint Baltic Sea research and development programme (Art 185), funded jointly from the European Union’s Seventh Programme for research, technological development and demonstration and from FORMAS.

The RCO model simulations were performed on the climate computing resources “Ekman” and “Vagn” jointly operated by the Centre for High Performance Computing (PDC) at the Royal Institute of Technology (KTH) in Stockholm and the National Supercomputer Centre (NSC) at Linköping University. “Ekman” and “Vagn” are funded by a grant from the Knut and Alice Wallenberg foundation.

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