

Benthic Phosphorus Dynamics in the Gulf of Finland, Baltic Sea

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Abstract Benthic fluxes of soluble reactive phosphorus (SRP) and dissolved inorganic carbon (DIC) were measured in situ using autonomous landers in the Gulf of Finland in the Baltic Sea, on four expeditions between 2002 and 2005. These measurements together with model estimates of bottom water oxygen conditions were used to compute the magnitude of the yearly integrated benthic SRP flux (also called internal phosphorus load). The yearly integrated benthic SRP flux was found to be almost 10 times larger than the external (river and land sources) phosphorus load. The average SRP flux was $1.25 \pm 0.56 \text{ mmol m}^{-2} \text{ d}^{-1}$ on anoxic bottoms, and $-0.01 \pm 0.08 \text{ mmol m}^{-2} \text{ d}^{-1}$ on oxic bottoms. The bottom water oxygen conditions determined whether the SRP flux was in a high or low regime, and degradation of organic matter (as estimated from benthic DIC fluxes) correlated positively with SRP fluxes on anoxic bottoms. From this correlation, we estimated a potential increase in phosphorus flux of $0.69 \pm 0.26 \text{ mmol m}^{-2} \text{ d}^{-1}$ from presently oxic bottoms, if they would turn anoxic. An almost full annual data set of in situ bottom water oxygen measurements showed high variability of oxygen concentration. Because of this, an estimate of the time which the sediments were exposed to oxygenated overlying bottom water was computed using a coupled thermohydrodynamic ocean–sea and ecosystem model. Total phosphorus burial rates were calculated from vertical profiles of total phosphorus in

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sediment and sediment accumulation rates. Recycling and burial efficiencies for phosphorus of 97 and 3%, respectively, were estimated for anoxic accumulation bottoms from a benthic mass balance, which was based on the measured effluxes and burial rates.

Keywords Sediment · Fluxes · Burial · Oxidic-anoxic · Gulf of Finland · Baltic Sea

1 Introduction

Phosphorus (P) is an essential nutrient in the ocean, and on geological timescales, the availability of phosphate limits primary production (Paytan and McLaughlin 2007; Van Cappellen and Ingall 1994 and references therein). The availability of P for primary production is influenced by the oxygen conditions, as P regeneration from sediments is enhanced during anoxic periods of the global ocean (Ingall and Jahnke 1994; Ingall et al. 1993). This results in a positive feedback between primary production, anoxia and sediment efflux of P. Efflux of P from sediments has been shown to strongly inversely correlate with bottom water oxygen concentration in many types of aquatic environments (e.g., Sundby et al. 1986; Skoog et al. 1996, marine water; Holm 1978; Balzer et al. 1983; Gunnars and Blomqvist 1997, brackish water; Mortimer 1942, fresh water). The above references all refer to the redox-sensitive adsorption of phosphate on iron oxides. This process has been known for many years and was first described in freshwaters (Mortimer 1942). In addition to the effect of iron adsorption on the benthic P cycling, microorganisms have also been suggested to affect P cycling by accumulating P under oxic conditions, and then consuming and releasing it as phosphate under anoxic conditions (Davelaar 1993; Gachter and Meyer 1993). These two processes result in enhanced P regeneration relative to carbon under anoxic conditions (Ingall and Jahnke 1997; Ingall et al. 1993). Enhanced P regeneration under anoxic conditions has also been observed in the Baltic Sea (Jilbert et al. 2011); however, it is still uncertain which mechanism or mechanisms control this process.

The influence of anoxic and oxic water conditions on the P cycle is evident in the Baltic Sea, a semi-enclosed sea connected to the North Sea through the Danish straits, the Kattegat and the Skagerrak. The periodically anoxic conditions are due to the limited water exchange with the Kattegat, the strong vertical stratification and the long residence time of Baltic Sea water (e.g., Kullenberg and Jacobsen 1981; Stigebrandt 2001). These physical characteristics of the Baltic Sea in combination with an increased nutrient supply have led to an increased frequency of cyanobacterial blooms since the 1960s (Finni et al. 2001). The frequent cyanobacterial blooms and high P concentrations in the basin water have been explained by a positive feedback between increased bottom hypoxia and release of P from iron oxides (e.g., Conley et al. 2002; Gustafsson and Stigebrandt 2007; Vahtera et al. 2007). Nitrogen-fixing cyanobacteria are limited by P, and the blooms are in part triggered by low N:P ratios in the nutrient pool (e.g., Larsson et al. 2001). The low N:P ratios are caused by denitrification and anammox together with enhanced P regeneration due to oxygen depletion in deep waters. The change in the bottom area covered by hypoxic water in the Baltic Sea, but not the external P load, has been found to correlate well with variations in the dissolved P pool size (Conley et al. 2002). This correlation indirectly indicates the importance of oxygen in regulating the capacity of sediments to release/retain P in the Baltic Sea. A recent study of Baltic Sea sediments also supports the importance of oxygen conditions for benthic P dynamics (Jilbert et al. 2011). In the Baltic Sea, the Gulf of Finland is the most eutrophied sub-basin relative to its area (Pitkanen and Tallberg 2007), and surface water winter levels of nitrogen (N) and P are higher in the Gulf of

Finland than anywhere else in the Baltic Sea. The main reason that the Gulf of Finland is more eutrophied than the other Baltic Sea basins is the large external input of nutrients to the eastern part of the Gulf of Finland from the Russian River Neva.

The Gulf of Finland (like the Baltic Proper) has different bottom types, which can be divided into accumulation, transport, and erosion bottoms (Jonsson et al. 1990; Carman and Cederwall 2001). Accumulation bottoms are mostly situated in deep parts of the Gulf of Finland or in depressions and are characterized by high organic matter content. P release from bottoms should be influenced by organic matter content of sediment, which is related to bottom type, and oxygen conditions in bottom water. Oxygen conditions in the bottom water vary in the Gulf of Finland, with more frequent occurrence of anoxia in deep than in shallow parts. Also, anoxic bottoms and accumulation bottoms often coincide in the Gulf of Finland. It is therefore difficult to distinguish between soluble reactive phosphorus (SRP) fluxes due to desorption of phosphate from Fe(III), release from bacteria and SRP fluxes due to rapid degradation of fresh organic matter containing P. Likewise, it is difficult to see how large the flux would be at an oxic bottom, if there were no adsorption to Fe(III) and/or accumulation by bacteria.

Previously, benthic P fluxes in the Gulf of Finland have been estimated from laboratory incubations or from calculations of pore water gradients (Conley et al. 1997; Lehtoranta 1998; Lehtoranta and Pitkanen 2003; Pitkanen et al. 2003; Lukkari et al. 2009a). These types of measurements have some limitations, compared to in situ measurements, and for P, one main difficulty is to maintain sediments and bottom water at in situ oxygen conditions. Especially low oxygen conditions are difficult to maintain when bringing cores up on deck and in the laboratory during handling and incubations. If low in situ oxygen conditions cannot be maintained, measured P fluxes from originally anoxic bottoms are likely to be underestimates. Also, the sediment surface area of a laboratory-incubated sediment core is small and thus less representative, this is especially important at oxic sites where fauna is present since fauna create horizontal heterogeneity. In addition, physical disturbances of sediment during sample collection and recovery can result in measured fluxes that do not represent the in situ flux. Flux calculations from pore water gradients also suffer from some difficulties. The gradient that controls the flux should ideally be measured over only a few millimeters, while in reality, sampling of pore water is performed with 0.5–1 cm vertical resolution, and the bottom water is easily disturbed when sampled just above the core itself. A bottom water sample taken from a rosette sampler on a CTD is usually collected a few meters above the sediment where the P concentration often is lower than closer to the bottom. These facts likely cause fluxes determined from pore water gradients to be underestimated compared to in situ measured fluxes, since too-coarse vertical resolution of the gradient across the sediment–water interface will underestimate the steepness of the gradient and thus the flux (e.g., Sundby et al. 1986). The advantages with in situ flux measurements using benthic chambers include the following: (1) chambers better reflect the ambient in situ conditions in the benthic boundary layer, (2) incubated volume versus sampling volume is greater, which largely avoids dilution problems that are difficult to correctly compensate for (Tengberg et al. 1995), and (3) keeping the sediment and bottom water anoxic during incubations is not a problem since ambient conditions are maintained during in situ work. Earlier studies of benthic P flux in the Gulf of Finland, based on laboratory incubations (Pitkanen et al. 2001, 2003; Conley et al. 1997) and diffusive flux calculations from pore water gradients (Lehtoranta 1998), reached the common conclusion that benthic P release is important to maintain a state of eutrophication. The present study is the first to report results from in situ measurements of benthic P fluxes and bottom water oxygen variations in the Gulf of Finland.

The aim of this study was to enhance the understanding of benthic P dynamics in the open Gulf of Finland by measuring P fluxes in situ, using autonomous landers, on different bottom types and under varying bottom water oxygen conditions. From these measurements and predicted frequency of bottom water anoxia as a function of bottom depth (from long-term oxygen measurements in bottom water and modeling), an improved quantification of the integrated benthic P flux in the Gulf of Finland was made. We also estimated P burial, constructed a benthic P mass balance for anoxic accumulation bottoms, calculated recycling and burial efficiencies for P, and described the relation between fluxes of SRP and dissolved inorganic carbon (DIC) to better understand the influence of sediment organic matter content and bottom water oxygen conditions, respectively, on SRP fluxes.

2 Materials and Methods

2.1 Study Site

The Gulf of Finland is situated in the eastern part of the Baltic Sea between Finland in the north, Estonia in the south and Russia in the east (Fig. 1). The surface area is 30,000 km², and only 6% of the bottoms are deeper than 70 m (Carman and Cederwall 2001). The water depth decreases from the west (60–80 m) to the east (20–40 m) (Perttala et al. 1995). The single largest source of freshwater is the River Neva, which is also the largest river in the catchment of the Baltic Sea. This large fresh water inflow in the east of the Gulf gives it characteristics of a mixed estuary with large horizontal gradients in salinity. The result of this is that the western part of the Gulf is more influenced by the Baltic Sea, with a halocline at around 60 m and higher salinity than the eastern part. Benthic oxygen conditions are largely determined by stratification and vary between the eastern and the western parts of the Gulf.

The data for this study were collected at seven different stations (Fig. 1) in the Gulf of Finland between the years 2002 and 2005. Four of the stations were only visited in June 2002 (GF1, GF2, GF5 and GF6), two stations (PV1 and Kasuuni) were visited in June 2003, September 2004 and May 2005 and one station (XV1) was only visited in May 2005. The stations represent different bottom types in the Gulf of Finland and are spread from the

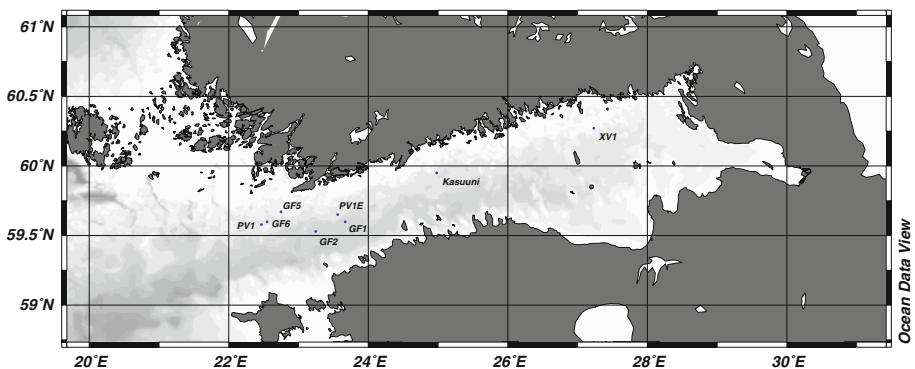


Fig. 1 Map showing the Gulf of Finland and stations from west to east. In situ flux measurements 2002–2005: PV1, GF6, GF5, GF1, GF2, Kasuuni, XV1. Mooring stations July 2003–May 2004: PV1E, Kasuuni, XV1

very east of the Gulf to the western parts near the Baltic Proper. The spatial variability in the Gulf of Finland is relatively high, and although each station was situated in an area dominated by one bottom type, some stations exhibit different bottom types depending on the exact location where the sample was taken. In general, the following classification of bottom types at the stations can be made; the three stations PV1, GF1 and GF2 represent deep (70–80 m) accumulation bottoms and are all situated in the western half of the Gulf. The station Kasuuni is a shallower (50 m) transport bottom, although showing signs of being an accumulation bottom in 2004. The three stations GF5, GF6 and XV1 are all transport or erosion bottoms. For an overview of station characteristics each year, see Table 1.

2.2 Sampling and Analysis

On each cruise, the Göteborg benthic lander was used to measure in situ fluxes of nutrients and DIC. The DIC fluxes are described in Andersson et al. (2011). A thorough description of the flux measurements is presented in Almroth et al. (2009). In addition to fluxes, the following variables were also measured: bottom water nutrient and oxygen concentrations; P in sediment; and sediment accumulation rates at all sites. Sediment accumulation rate was determined using the ^{210}Pb technique. Oxygen inside and outside incubation chambers was measured at 1- or 2-min intervals with single-point oxygen optodes (Tengberg et al. 2006) with an approximate absolute accuracy of $\pm 3\%$ (see Almroth et al. 2009). Water samples for nutrients were taken from a Niskin bottle on the lander 1.5 m above the bottom. Nitrogen data and sediment accumulation rate results are presented in Brunnegård et al. (2011).

The content of total phosphorus (TP) in sediments was determined using a “yellow complex” formation method. The method consists of colorimetric analysis of yellow phosphorus–molybdenum–vanadium heteropoly-acid (Jeffery 1973). The samples of bottom sediments were homogenized and dried at 105°C to constant weight. To prepare samples for analysis, they were dissolved in aqua-regia and sulfuric acid under heating, which resulted in acidic decomposition of the samples. The procedure was repeated with hydrochloric and nitric acids until humid salts were formed as a result of evaporation and heating. The nitric acid was then heated to 60–80°C and added into a tube. The samples were then filtered and elutriated in cold water. After adding 10 mL Meike reagent (ammonium molybdate and ammonium vanadate in nitric acid medium) to the tube, the product was diluted twice by distilled water. When the solution turned into an intensive yellow color, it was analyzed spectrophotometrically using violet (or blue) FS-1 filters. A blank sample was used as zero solution in the course of analysis. The detection limit of the method was 0.01% (w/w) and the standard deviation less than 4%. Use of Russian governmental standard samples (GSS) of bottom sediments and sedimentary rocks (SBS-1, 2; BM-1 and others) as reference material confirmed adequate accuracy.

2.3 Oxygen Mooring Measurements

One mooring at each of the three stations PV1E (56 m), Kasuuni (56 m) and XV1 (43 m) was deployed in July 2003 and recovered in May 2004. The instrument used on each mooring was a Recording Current Meter #9 (RCM 9, www.aadi.no) on which was mounted sensors to measure current speed and direction, oxygen concentration (Tengberg et al. 2006), salinity, temperature and turbidity in two levels (Almroth et al. 2009). Recordings were made every hour, and most sensors including the oxygen optodes were located about

Table 1 Station description

| Station | Year | Lander position (Lat/Long) | Depth (m) | O ₂ BW (μ M) | S BW | T BW ($^{\circ}$ C) | SAR ($\text{g cm}^{-2} \text{ year}^{-1}$) | Corg avg when \pm (% d.w.) | Porosity (vol%) | Bottom type |
|---------|------|-------------------------------|-----------|---------------------------------|------|-------------------------|---|---------------------------------|--------------------|----------------|
| GF1 | 2002 | 59.60N 23.67E | 72 | 0 | 9.9 | 4.9 | 0.049 | 6.0 \pm 0.3 | 87 | Accu |
| GF2 | 2002 | 59.53N 23.25E | 81 | 0 | 9.9 | 5.0 | 0.063 | 4.6 \pm 0.4 | 86 | Accu |
| GF5 | 2002 | 59.67N 22.75E | 52 | 330 | 6.9 | 3.2 | 0.043 | 1.2 | 56 | Transp |
| GF6.1 | 2002 | 59.60N 22.55E | 48 | 347 | 6.8 | 3.5 | – | 1.0 | 25 | Erosion |
| GF6.2 | 2002 | 59.60N 22.55E | 56 | 308 | 7.4 | 3.5 | – | 1.0 | 25 | Erosion |
| PV1.1 | 2003 | 59.58N 22.47E | 75 | 10 | 9.2 | 4.1 | – | 8.4 \pm 1.7 | 90 | Accu |
| PV1.2 | 2003 | 59.58N 22.47E | 75 | 1 | 9.2 | 4.0 | – | 8.4 \pm 1.7 | 90 | Accu |
| PV1.1 | 2004 | 59.58N 22.47E | 70 | 137 | 7.8 | 3.6 | 0.09 | 4.7 | 88 \pm 2 | Accu |
| PV1.2 | 2004 | 59.58N 22.47E | 70 | 148 | 7.7 | 2.8 | 0.09 | 4.7 | 88 \pm 2 | Accu |
| PV1.1 | 2005 | 59.58N 22.47E | 73 | 7 | 10.4 | 5.0 | 0.07 | 3.1 | – | Accu |
| PV1.2 | 2005 | 59.58N 22.47E | 73 | 12 | 10.4 | 5.2 | 0.07 | 3.1 | – | Accu |
| Kas1 | 2003 | 59.59N 24.98E | 53 | 162 | 7.5 | 2.4 | – | 3.4 \pm 0.8 | 70 | Transp |
| Kas2 | 2003 | 59.59N 24.98E | 53 | 137 | 7.6 | 2.5 | – | 3.4 \pm 0.8 | 70 | Transp |
| Kas1 | 2004 | 59.59N 24.98E | 54 | 210 | 7.1 | 2.9 | – | 4.5 | 87 \pm 3 | Accu |
| Kas2 | 2004 | 59.59N 24.98E | 54 | 219 | 6.5 | 4.7 | – | 4.5 | 87 \pm 3 | Accu |
| Kas1 | 2005 | 59.59N 24.98E | 54 | 180 | 8.1 | 3.4 | 0.048 | 2.2 | – | Transp |
| Kas2 | 2005 | 59.59N 24.98E | 54 | 251 | 7.8 | 2.9 | 0.048 | 2.2 | – | Transp |
| XV1.1 | 2005 | 60.27N 27.23E | 37 | 285 | 6.8 | 2.0 | 0.028 | 0.75 | – | Tran/Eros |
| XV1.2 | 2005 | 60.27N 27.23E | 37 | 285 | 6.5 | 2.0 | 0.028 | 0.75 | – | Tran/Eros |

Oxygen, temperature and salinity were measured outside chambers close to the sediment. Organic carbon (Corg) 2003 is given in % of dry weight (d.w.) as a mean of the top slice (0–5 mm) of 3–4 cores with standard deviation. Porosity is from the top slice (0–5 mm), as average when 2 cores \pm SD and is given as volume percentages. Corg from (Andersson et al. 2011), sediment accumulation rate (SAR in Table) from (Brunnegard et al. 2011). Positions are given in decimal degrees

1.1 m above the seafloor. This set of in situ data, covering almost a complete annual cycle, was used to estimate the temporal and spatial variability of bottom water oxygen conditions in the Gulf of Finland and to validate model results (see below). Before and after deployments, the optodes (a total of 3) were checked against Winkler titrations and found to be without drift and with an absolute accuracy within $\pm 3\%$ or $\pm 3 \mu\text{mol L}^{-1}$ at lower oxygen concentrations (below $100 \mu\text{mol L}^{-1}$).

2.4 Model Description

SPBEM is a coupled thermohydrodynamic ocean–sea and ecosystem model developed by Neelov et al. (2003) in St. Petersburg Branch, P.P. Shirshov Institute of Oceanology, Russian Academy of Sciences, and recently used by a consortium of St. Petersburg institutes. The hydrodynamic component of the model was validated within the EMAPS inter-comparison project (Myrberg et al. 2010).

The biogeochemical cycling (BGC) module in the SPBEM is based on the BGC model developed by Savchuk and Wulff (2001). The BGC module describes nutrient cycling in the coupled pelagic and sediment sub-systems and contains 12 pelagic (zooplankton, diatoms, cyanobacteria, flagellates, nitrogen, phosphorus and silica detritus, ammonium, nitrite + nitrate, phosphate, silicate and dissolved oxygen) and three sediment (benthic nitrogen, phosphorus and silica) state variables.

3 Results

3.1 SRP Fluxes

On bottoms with anoxic water, SRP fluxes were positive (effluxes) while they were low or negative (uptake) at oxic bottoms (Table 2; Fig. 6). Out of 20 chamber measurements on accumulation bottoms with anoxic bottom water conditions, 19 showed effluxes of SRP (Table 2). In contrast, five of six chamber fluxes measured on oxic accumulation bottoms (PV1 2004) were negative or zero. Fluxes measured at oxic water conditions at transport and erosion bottoms (GF5, GF6, Kasuuni and XV1) varied around zero, and on average there was a small uptake. Fluxes differing more than two standard deviations from the average flux at oxic and anoxic stations, respectively, were not used to generate the average values given in Table 4. These values are still, however, included in Table 2 and Figures.

Examples of typical in situ chamber incubations on an anoxic and an oxic bottom are shown in Fig. 2 with linear regressions showing which points were used in this particular case for calculating the flux. The anoxic bottoms had higher starting SRP concentration and a faster increase in concentration with time as compared to the oxic bottoms.

3.2 Total Phosphorus (TP) in Sediment and TP Burial

At accumulation bottoms, the vertical profiles of TP concentration were relatively uniform from the sediment surface to 10 cm sediment depth and varied between 16 and $32 \mu\text{mol g}^{-1}$ at GF1, GF2 and PV1 (Table 3). On oxic bottoms, the TP concentration in the surface sediment was in general higher than on anoxic bottoms and then decreased to a constant concentration that here will be referred to as the TP burial concentration (i.e., the concentration at 9–10 cm depth in the sediment cores). At the oxic stations Kasuuni (2004

Table 2 Measured in situ SRP fluxes presented for each chamber on every deployment on the four cruises 2002–2005

| Year | Station | Chamber | SRP Flux (mmol m ⁻² d ⁻¹) | Uncertainty (mmol m ⁻² d ⁻¹) |
|------|---------|---------|---|--|
| 2002 | GF1 | 1 | 0.76 | – |
| 2002 | GF1 | 2 | – | – |
| 2002 | GF1 | 3 | 0.52 | – |
| 2002 | GF1 | 4 | 2.06 | – |
| 2002 | GF2 | 1 | 1.08 | – |
| 2002 | GF2 | 2 | – | – |
| 2002 | GF2 | 3 | 1.11 | – |
| 2002 | GF2 | 4 | 1.6 | – |
| 2002 | GF5 | 1 | –0.23 | – |
| 2002 | GF5 | 2 | – | – |
| 2002 | GF5 | 3 | – | – |
| 2002 | GF5 | 4 | –0.03 | – |
| 2002 | GF6.1 | 1 | –0.02 | – |
| 2002 | GF6.1 | 2 | – | – |
| 2002 | GF6.1 | 3 | 0.14 | – |
| 2002 | GF6.1 | 4 | – | – |
| 2002 | GF6.2 | 1 | –0.09 | – |
| 2002 | GF6.2 | 2 | 0.04 | – |
| 2002 | GF6.2 | 3 | 0.03 | – |
| 2002 | GF6.2 | 4 | – | – |
| 2003 | PV1.1 | 1 | 0.83 | 0.07 |
| 2003 | PV1.1 | 2 | 2.34 | 0.58 |
| 2003 | PV1.1 | 3 | 3.39 | 0.74 |
| 2003 | PV1.1 | 4 | 0.44 | 0.42 |
| 2003 | PV1.2 | 1 | –0.48 | 0.42 |
| 2003 | PV1.2 | 2 | 0.98 | 0.19 |
| 2003 | PV1.2 | 3 | 1.15 | 0.46 |
| 2003 | PV1.2 | 4 | 0.53 | 0.17 |
| 2003 | Kas.1 | 1 | – | – |
| 2003 | Kas.1 | 2 | 0.01 | 0 |
| 2003 | Kas.1 | 3 | – | – |
| 2003 | Kas.1 | 4 | – | – |
| 2003 | Kas.2 | 1 | – | – |
| 2003 | Kas.2 | 2 | 0.67 | 0.31 |
| 2003 | Kas.2 | 3 | 0.13 | 0.12 |
| 2003 | Kas.2 | 4 | – | – |
| 2004 | PV1.1 | 1 | – | – |
| 2004 | PV1.1 | 2 | –0.12 | 0.04 |
| 2004 | PV1.1 | 3 | –0.26 | 0.09 |
| 2004 | PV1.1 | 4 | 0 | 0.08 |
| 2004 | PV1.2 | 1 | –0.11 | 0.05 |
| 2004 | PV1.2 | 2 | –0.04 | 0.03 |

Table 2 continued

| Year | Station | Chamber | SRP Flux (mmol m ⁻² d ⁻¹) | Uncertainty (mmol m ⁻² d ⁻¹) |
|------|--------------|----------|---|--|
| 2004 | PV1.2 | 3 | – | – |
| 2004 | PV1.2 | 4 | 0.05 | 0.04 |
| 2004 | Kas.1 | 1 | – | – |
| 2004 | Kas.1 | 2 | – | – |
| 2004 | Kas.1 | 3 | 0 | 0.02 |
| 2004 | Kas.1 | 4 | –0.03 | 0.01 |
| 2004 | Kas.2 | 1 | –0.03 | 0.01 |
| 2004 | Kas.2 | 2 | 0.09 | 0.03 |
| 2004 | Kas.2 | 3 | 0.05 | 0.02 |
| 2004 | Kas.2 | 4 | 0 | 0.03 |
| 2005 | <i>PV1.1</i> | <i>1</i> | – | – |
| 2005 | <i>PV1.1</i> | <i>2</i> | – | – |
| 2005 | <i>PV1.1</i> | <i>3</i> | <i>1.77</i> | <i>0.07</i> |
| 2005 | <i>PV1.1</i> | <i>4</i> | <i>1.65</i> | <i>0.17</i> |
| 2005 | <i>PV1.2</i> | <i>1</i> | <i>1.91</i> | <i>0.13</i> |
| 2005 | <i>PV1.2</i> | <i>2</i> | <i>1.53</i> | <i>0.19</i> |
| 2005 | <i>PV1.2</i> | <i>3</i> | <i>1.29</i> | <i>0.09</i> |
| 2005 | <i>PV1.2</i> | <i>4</i> | <i>0.97</i> | <i>0.04</i> |
| 2005 | Kas.1 | 1 | –0.13 | 0.06 |
| 2005 | Kas.1 | 2 | 0.06 | 0.02 |
| 2005 | Kas.1 | 3 | 0.04 | 0.03 |
| 2005 | Kas.1 | 4 | 0.02 | 0.02 |
| 2005 | Kas.2 | 1 | – | – |
| 2005 | Kas.2 | 2 | 0.01 | 0 |
| 2005 | Kas.2 | 3 | 0 | 0.02 |
| 2005 | Kas.2 | 4 | –0.05 | 0.01 |
| 2005 | XV1.1 | 1 | –0.06 | 0.01 |
| 2005 | XV1.1 | 2 | –0.05 | 0.03 |
| 2005 | XV1.1 | 3 | –0.1 | 0.05 |
| 2005 | XV1.1 | 4 | – | – |
| 2005 | XV1.2 | 1 | – | – |
| 2005 | XV1.2 | 2 | – | – |
| 2005 | XV1.2 | 3 | –0.06 | 0.02 |
| 2005 | XV1.2 | 4 | –0.05 | 0.01 |

The uncertainty of the linear regression of the concentration change versus time in each incubation gives the uncertainty of the flux; see Almroth et al. (2009) for further details on flux calculations. Flux measurements where bottom water oxygen concentration was below 20 $\mu\text{mol L}^{-1}$ are in italic

and 2005) and XV1 (2005), TP decreased sharply from values of around 120 $\mu\text{mol g}^{-1}$ in the upper half centimeter to a burial concentration similar to that at GF1, GF2 and PV1 (Table 3). At the oxic station Kasuuni (2003), the profile was more similar to profiles from the anoxic stations. Kasuuni (2003) also had lower bottom water oxygen concentration and higher bottom water SRP concentration than Kasuuni 2004 and 2005 (Table 3).

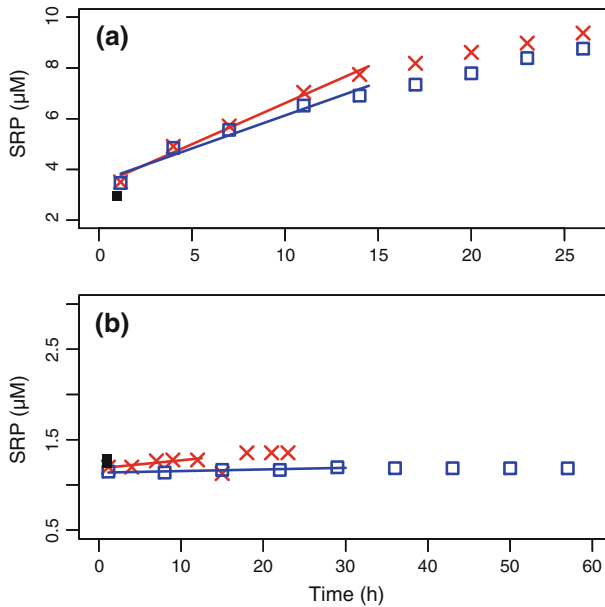


Fig. 2 Examples of measured SRP concentrations in chambers during two lander deployments in the Gulf of Finland. **a** top panel PV1 2005 during anoxic conditions, **b** bottom panel Kasuuni 2005 during oxic conditions. Open squares and crosses show samples taken during incubation in two different chambers, and the lines represent the points used for flux calculations. Black square is SRP concentration in bottom water outside the chamber

Table 3 TP in sediments given in $\mu\text{mol g}^{-1}$ at all measured depths

| Station Year | GF1 2002 | GF2 2002 | PV1 2003 | PV1 2004 | PV1 2005 | KAS 2003 | KAS 2004 | KAS 2005 | XV1 2005 |
|---|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| <i>Sediment depth (cm)</i> | | | | | | | | | |
| 0.5 | 32.3 | 22.6 | 29.0 | 29.0 | 25.8 | 41.9 | 122.6 | 112.9 | 119.4 |
| 1.5 | 32.3 | 16.1 | 22.6 | 22.6 | 22.6 | 41.9 | 158.1 | 116.1 | 29.0 |
| 2.5 | 29.0 | 19.4 | 19.4 | 25.8 | 22.6 | 29.0 | 180.6 | 87.1 | 22.6 |
| 3.5 | 19.4 | 22.6 | 32.3 | 22.6 | 16.1 | 35.5 | 151.6 | 38.7 | 19.4 |
| 4.5 | 25.8 | 22.6 | 29.0 | 22.6 | 22.6 | 32.3 | 71.0 | 25.8 | 22.6 |
| 5.5 | 25.8 | 16.1 | 25.8 | 22.6 | 22.6 | 32.3 | 22.6 | 25.8 | 19.4 |
| 6.5 | 22.6 | 29.0 | 22.6 | 22.6 | 22.6 | 29.0 | 22.6 | 29.0 | 16.1 |
| 7.5 | 22.6 | 19.4 | 25.8 | 22.6 | 22.6 | 22.6 | 22.6 | 29.0 | 19.4 |
| 8.5 | 22.6 | 25.8 | 22.6 | 16.1 | 22.6 | 22.6 | 22.6 | 25.8 | 19.4 |
| 9.5 | 25.8 | 22.6 | 22.6 | 19.4 | 19.4 | 19.4 | 19.4 | 25.8 | 19.4 |
| TP Burial (ton $\text{km}^{-2} \text{year}^{-1}$) | 0.36 | 0.47 | 0.58* | 0.56 | 0.47 | 0.35* | 0.32* | 0.41 | 0.16 |

TP surface concentrations are highest at Kasuuni (2004, 2005) and XV1 (2005), whereas concentrations below 5 cm were relatively similar at all stations. TP burial rates were calculated from TP burial concentration and sediment accumulation rate. As is seen, the TP burial concentration was relatively similar at all stations, and burial rates were thus largely determined by sediment accumulation rate

* Sediment accumulation rates from 2004 and/or 2005 were used for calculating TP burial in 2003, 2004 and 2005. For sediment accumulation rate values, see Table 1

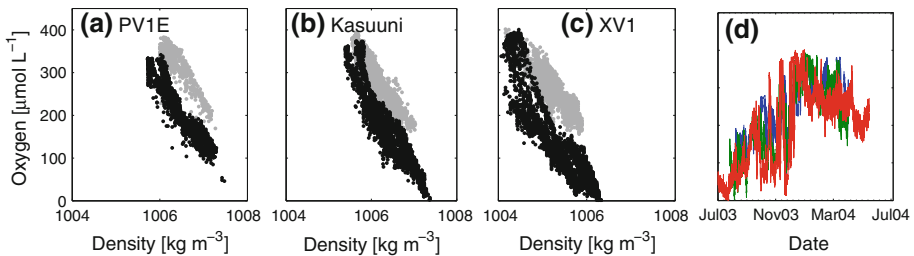


Fig. 3 Panel a–c shows oxygen concentration versus density from the three mooring stations, PV1E, Kasuuni and XV1. Gray dots are measurements from January 1, 2004, to April (XV1 July) 2004 and black dots are from July 2003 until January 1, 2004. Panel d shows the same oxygen data as a time series for the three stations, PV1E (blue), Kasuuni (green) and XV1 (red)

3.3 Bottom Water Oxygen: Measured

The in situ data from the three mooring stations showed that the bottom water oxygen concentration was highly variable (Fig. 3). Variations from a few $\mu\text{mol L}^{-1}$ to around $400 \mu\text{mol L}^{-1}$ were observed on very short timescales, that is, hours–weeks. Apart from the high frequency variations (hours–weeks), the data showed a clear seasonal variation with generally lower concentrations during the last part of the year and higher concentrations from midwinter until spring bloom (approximately May). Oxygen concentration correlated with water density, but with lower concentrations and a larger concentration range for the second half of the year (Fig. 3).

3.4 Bottom Water Oxygen: Modeled

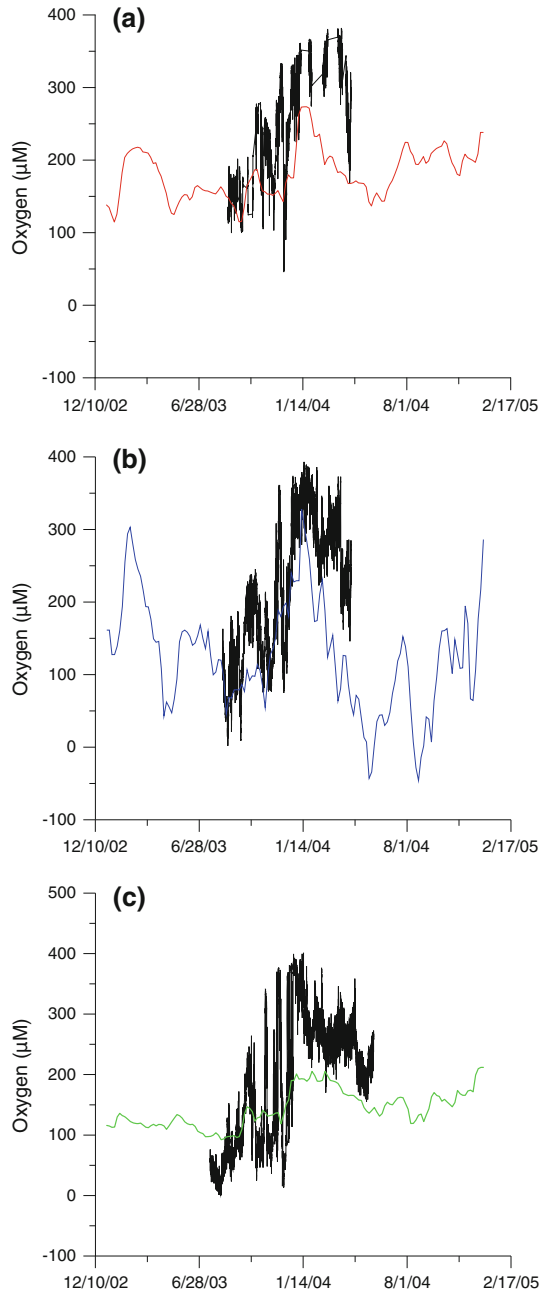
Evolution of near-bottom oxygen concentrations during the years 2003–2004 was reproduced by the SPBEM model. The model setup includes atmospheric forcing, climate data for river runoff and nutrient loads from rivers and the atmosphere. The modeling domain includes the entire Baltic Sea with 2 miles horizontal and 5 m vertical resolution. A comparison between modeled near-bottom (5-m layer) and measured bottom water oxygen concentration (Fig. 4) validated the model and showed that it adequately represented seasonal dynamics of oxygen. At the same time, the model was unable to reproduce some anoxic recordings at the XV1 and PV1 stations. This is mainly explained by a spatial averaging of the actual bathymetry. As a result, the model grid at this point was dramatically shallower than the measured depth (15 m difference). Taking into account the outcome of the comparison of measured and modeled results, the calculations presented in Table 5 can be considered as conservative estimates (minimum level) of spatial/temporal distributions of anoxic zones. Finally, the number of anoxic days was computed and averaged using the depth intervals 0–40, 40–60 and 60–120 m (see Table 5). These intervals were based on depths of the lander deployments on stations PV1, Kasuuni and XV1.

4 Discussion

4.1 Comparison with Previous Studies

The in situ measured averaged SRP flux on anoxic bottoms presented in this study was significantly higher than the previously measured ex situ average P flux on anoxic or reducing

Fig. 4 **a** Top panel PV1, **b** middle panel Kasuuni, **c** bottom panel XV1. Comparison of modeled near-bottom (5-m layer) and measured bottom water oxygen concentrations. *Black lines* represent measurements, and *colored lines* represent model results



bottoms (Table 4). In situ fluxes on oxic bottoms were on the other hand close to previously reported laboratory incubation fluxes on such bottoms (Lehtoranta 2003; Lehtoranta and Heiskanen 2003). SRP fluxes on oxic bottoms in the Gulf of Finland were also similar to fluxes reported from adjacent seas, such as the Skagerrak [-0.015 – $0.08 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Hall et al. 1996)] and Aarhus Bay [uptake up to $0.054 \text{ mmol m}^{-2} \text{ d}^{-1}$; (Jensen et al. 1995)].

Table 4 Average SRP fluxes for anoxic accumulation bottoms, oxic accumulation bottoms and permanently oxic transport and erosion bottoms in the Gulf of Finland

| Source | Stations (year) | Sediment surface | BW O ₂ (μM) | SRP flux (mmol m ⁻² d ⁻¹) |
|---------------------------------|--|------------------|------------------------------|--|
| This study | XV1(05) | | Oxic (aver 285) | -0.06 ± 0.01 |
| This study | GF5(02), GF6(02), Kas(03-05), XV1(05) | | Oxic (137–347) | -0.01 ± 0.08 |
| This study | PV1(04) | | Oxic (137–148) | -0.08 ± 0.07 |
| Lehtoranta (2003) | | Oxidizing | Oxic | <0 |
| Lehtoranta and Heiskanen (2003) | | – | Varying (30–343) | <0–1 |
| Conley et al. (1997) | | Oxidizing | Oxic (186–266) | 0.04–0.7 |
| Pitkanen et al. (2001) | | Reducing | Oxic | 0.24–0.68, aver 0.4 |
| Lehtoranta (2003) | | Reducing | – | 0.42 |
| Lehtoranta (1998) | | Reducing | – | -0.01–0.21 |
| Lukkari et al. (2009a) | | – | Varying (0–112) aver <100 | -0.25–1.77, aver 0.38 |
| This study | GF1(02), GF2(02), PV1(03, 05) | Reducing | Anoxic (0–11.6) | 1.25 ± 0.56 |

Values given in parenthesis in the bottom water (BW) O₂ column are intervals or average of measured oxygen concentrations

This mismatch and match on anoxic and oxic bottoms, respectively, strongly suggests that it is very difficult to keep laboratory incubations anoxic, which indicates that ex situ measurements under anoxic conditions are underestimates, as described in Introduction. High SRP fluxes on oxic (mostly coastal) bottoms in the Gulf of Finland have been reported (Pitkanen et al. 2001; Conley et al. 1997; Lehtoranta and Heiskanen 2003) and could be due to high sediment accumulation rates as discussed by Conley et al. (1997), Hille et al. (2005) and Eilola et al. (2009). High sediment accumulation rate may lead to more sulfate reduction in the sediment and a consequent loss of iron into FeS and FeS₂ pools. This would result in low ratios of available Fe/P in sediment and consequently high SRP fluxes, even though bottom waters are oxic. Published data on sediment accumulation rates in the open Gulf of Finland (Lukkari et al. 2009a) and the northern coastal Gulf of Finland (Lukkari et al. 2009b) also show that sediment accumulation rates are higher in the coastal Gulf of Finland than in the open Gulf. This would mean that more iron is available for SRP sorption in the open Gulf than in the coastal areas. Lukkari et al. (2009a) reported measurable but low amounts of iron-bound P in the open Gulf even at low oxygen concentrations. All this supports the hypothesis that relatively high benthic SRP effluxes in oxic bottom water, which have been found during laboratory experiments and most often in the coastal part of the Gulf of Finland, may be due to low Fe:P ratios in those sediments. We did not, with one exception, find high oxic SRP fluxes during our in situ studies. This is most likely because most stations in this study were from the open Gulf of Finland with lower sediment accumulation rates than in the coastal parts of the Gulf.

4.2 Influence of Fresh Organic Matter Input and Bottom Water Oxygen Conditions on the Benthic SRP Flux

The highest SRP fluxes were measured at very low or zero bottom water oxygen concentrations and the low SRP fluxes at high oxygen concentrations (Fig. 6). Since all the

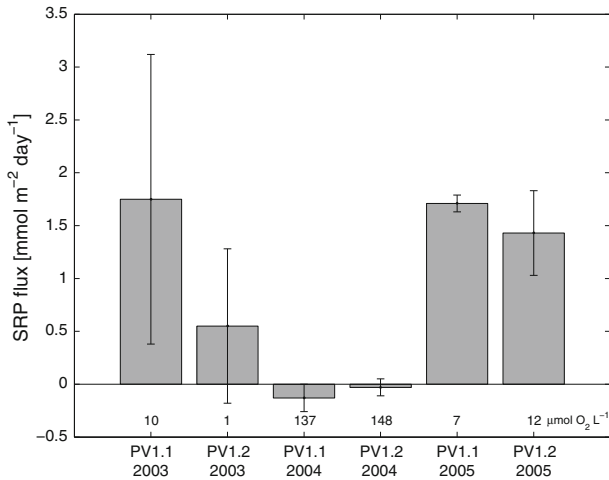


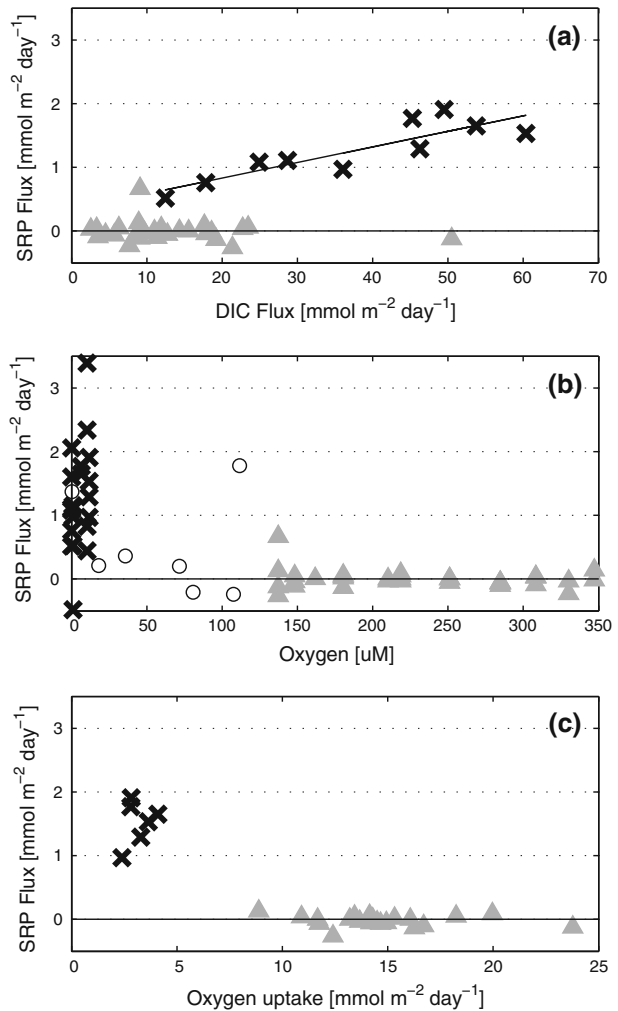
Fig. 5 High average SRP fluxes ($0.55\text{--}1.75\text{ mmol m}^{-2}\text{ day}^{-1}$) during anoxic condition (2003 and 2005) and a small uptake during oxic (2004) bottom water conditions at accumulation bottom PV1. Error bars indicate standard deviation of the average of 3–4 chambers

measurements of high SRP fluxes were made on anoxic organic-rich accumulation bottoms, it is not certain that the reason for the high SRP fluxes is enhanced P regeneration under anoxia and not the higher input of fresh organic matter on these bottoms. We here argue that the two redox-dependent mechanisms (Fe(III) sorption and microbial assimilation) have an effect on the SRP flux on oxic bottoms and that the P regeneration on anoxic bottoms is enhanced, as described in Jilbert et al. (2011) and Ingall and Jahnke (1997). However, we also argue that the degradation rate of organic matter largely determines the SRP flux on anoxic bottoms. The argumentation above is consistent with the observed difference between SRP fluxes on an accumulation bottom (PV1) at oxic and anoxic conditions (Fig. 5), and with the observed relation between SRP fluxes and DIC fluxes on different bottom types and oxygen conditions (Fig. 6). Taken together, we were in this study able to separate the influence of oxygen condition and organic matter degradation rate on SRP fluxes.

The effect of different bottom water oxygen conditions on the SRP flux (Fig. 5) indicates that oxygenation of bottom water can affect the SRP flux despite a high content of organic matter and likely sulfidic sediments. Also, this constitutes the first in situ observation clearly showing that oxygenation of deep anoxic accumulation bottoms will stimulate SRP retention in the sediment. The correlation between Baltic hypoxic bottom area and SRP pool size presented by Conley et al. (2002) can thus, with our direct experimental results, be mechanistically substantiated.

Oxic bottoms with low SRP fluxes had higher oxygen uptake than anoxic bottoms with high SRP and DIC fluxes (Fig. 6c). This is at first somewhat contradictory as high oxygen uptake would be expected on bottoms with high SRP and DIC fluxes, since this indicates high degradation rates of organic matter. The reasons for low oxygen uptake rates on bottoms with high SRP and DIC fluxes likely include the low bottom water oxygen concentration, which in itself causes lower oxygen uptake rate (Hall et al. 1989), and the dominance of suboxic/anoxic organic matter degradation pathways, for example Mn(IV), Fe(III) and, probably most importantly, SO_4 reduction, together with a delayed oxidation

Fig. 6 **a** SRP flux versus DIC flux, **b** SRP flux versus bottom water oxygen concentration, **c** SRP flux versus oxygen uptake (at stations with bottom water oxygen $<20 \mu\text{mol L}^{-1}$, this could only be measured in 2005) in the Gulf of Finland. Each chamber measurement plotted individually. *Crosses* represent accumulation bottoms with bottom water oxygen $<20 \mu\text{mol L}^{-1}$, and *triangles* represent all bottom types with oxitic bottom water in this study; *open circles* are SRP fluxes from Lukkari et al. (2009a) water in this study; SRP fluxes that do not appear in panel (a) but can be found in panel (b) are from PV1 2003 where no DIC fluxes are available



by oxygen of the reduced inorganic compounds formed by these pathways. This again suggests that the use of DIC flux as a measure of organic matter oxidation, rather than oxygen flux, is superior in this type of sediments (Anderson et al. 1986; Stahl et al. 2004).

In marine and brackish waters, the formation of FeS and FeS₂ in anoxic sediments should undermine the sediments capacity to hold SRP in the sediment, in comparison with fresh waters [as described by, e.g., Gunnars and Blomqvist (1997), Blomqvist et al. (2004) and Lehtoranta et al. (2009)]. On more or less permanently anoxic accumulation bottoms, there should be a high efflux of SRP due to high concentrations of fresh organic matter and the mineralization of it, but no release from iron oxides since they are not present and the iron is trapped as iron sulfides. Thus, there should be different controls of the SRP flux in different types of bottom “climate,” which to a large extent is dependent on which type of organic matter oxidation pathway that prevails, iron reduction or sulfate reduction (Lehtoranta et al. 2009). The effect of adsorption/release should be most pronounced on permanently oxitic bottoms and those with shifting oxygen conditions, whereas the SRP flux

on permanently anoxic bottoms should be controlled only by the abundance and degradation rate of organic matter. On permanently oxic bottoms, the flux of SRP should be less than what can be estimated from the DIC flux, because SRP is adsorbed on iron oxides at the sediment surface and/or accumulated by bacteria. On bottoms with shifting oxygen conditions, SRP fluxes are affected by iron adsorption/desorption both when oxic and when they recently have turned anoxic, as SRP is then released from iron oxides being reduced as the sediment surface becomes increasingly reducing.

To investigate the effect of oxygen/iron oxides compared to the input of P with organic matter, the benthic SRP flux was compared to the DIC flux, which is considered a good measure of oxidation and input of fresh organic matter (Anderson et al. 1986). This is consistent with the modeling of SRP fluxes made by Kiiirikki et al. (2006) where a critical value of the DIC flux ($240 \text{ mg C m}^{-2} \text{ d}^{-1}$ or $20 \text{ mmol C m}^{-2} \text{ d}^{-1}$) was used to determine whether aerobic or anaerobic processes prevailed in the sediment. This study includes more data than what was available to Kiiirikki et al. (2006) (we also included data from 2004 to 2005), and we suggest that a critical value of the DIC flux might not be the best way to describe the control of SRP fluxes in the Gulf of Finland. Our results showed that anoxic sediments can in fact have as low DIC fluxes as oxic sediments, but with higher SRP fluxes than oxic sediments with the corresponding DIC flux (Fig. 6a). Rather than the DIC flux, it seems to be bottom water oxygen conditions (Fig. 6b) that determined if the SRP flux is in a high or low regime. It is clear that a redox-dependent mechanism, possibly microorganism accumulation or iron oxide adsorption, greatly reduced the SRP flux during oxic conditions. The linear correlation between SRP fluxes and DIC fluxes for anoxic bottoms was good ($R^2 = 0.76$) and strongly suggests that the DIC flux is a good predictor of SRP fluxes on anoxic bottoms (Fig. 6a). The C:P (DIC:SRP) ratio of fluxes under anoxic conditions was relatively constant with a flux almost four times more P rich relative to the Redfield ratio (the C:P mol ratio being 29 ± 6), while fluxes on oxic bottoms had very variable and very high absolute C:P ratios (-1249 – 1431). High P regeneration compared to C regeneration from anoxic sediments has previously been reported from both geological records (Ingall et al. 1993) and present-day flux measurements with autonomous benthic landers (Ingall and Jahnke 1994, 1997). The correlation, and lack of correlation, between SRP and DIC fluxes on anoxic and oxic bottoms, respectively, in this study strengthens the view that P regeneration is redox dependent in the Baltic Sea, as discussed in Jilbert et al. (2011), even though the mechanism is still not completely understood. Iron reduction and thus release from iron oxides should be low on bottoms that have been anoxic for months or longer since reducible iron concentrations should be low. Jilbert et al. (2011) proposed that the redox sensitivity of P regeneration might be associated with accumulation and release by microorganisms (as discussed in Ingall and Jahnke 1997), but how much, if any, of the P regeneration that can be attributed to this process remains uncertain. Ingall et al. (1993) also discussed the possibility of enhanced C preservation in anoxic sediments (in that case laminated shales), which would also result in a low C:P flux ratio.

From the linear regression in Fig. 6a, an estimate of the potential release of SRP from oxic bottoms, if they would turn anoxic, was made. Hence, DIC fluxes on oxic stations were used to calculate theoretical SRP fluxes under anoxic conditions using the linear regression of SRP flux and DIC flux on anoxic stations (slope 0.025, intercept 0.34). Station PV1 was oxic in 2004, and the resulting theoretical anoxic SRP flux calculated for this station ($0.8 \pm 0.4 \text{ mmol m}^{-2} \text{ d}^{-1}$) was not statistically significantly different from the measured anoxic fluxes on PV1 in 2003 and 2005 ($1.3 \pm 0.9 \text{ mmol m}^{-2} \text{ d}^{-1}$). Using all oxic stations to calculate the theoretical anoxic SRP flux and then subtracting the measured

oxic SRP flux gave an average SRP flux increase on oxic bottoms of $0.69 \pm 0.26 \text{ mmol P m}^{-2} \text{ d}^{-1}$ or $21 \pm 8 \text{ kg km}^{-2} \text{ d}^{-1}$. This means that if the whole Gulf of Finland below 40 m would become anoxic, there would be an additional flux of almost 35,000 tons P year⁻¹ from the bottoms in addition to the integrated benthic P flux for the year 2003–2004 given below.

4.3 Integrated Benthic Phosphorus Flux

The estimated total integrated benthic P flux for the year 2003 in the Gulf of Finland was around 66,000 ton SRP. It was calculated using the number of days with bottom water oxygen lower than $20 \mu\text{mol L}^{-1}$ (called anoxic days), the estimated areas for the different depth intervals from the model (Table 5) and the mean SRP fluxes given in Table 4. For all oxic days in the shallowest depth interval, the mean flux at transport/erosion bottoms ($-0.01 \text{ mmol P m}^{-2} \text{ year}^{-1}$) was used, and for oxic days in the deepest interval, the mean flux from PV1 2004 ($-0.08 \text{ mmol P m}^{-2} \text{ year}^{-1}$) was used. In the middle depth interval, the mean flux for accumulation bottoms and that for transport/erosion bottoms were used on 50% of the area, respectively. This assumes that bottoms below 60 m are mostly accumulation bottoms, that bottoms shallower than 40 m are not, and that there are 50% accumulation and transport bottoms, respectively, between 40 and 60 m. Since we do not have a reliable estimate of the percentage of different bottom types in each depth interval, this assumption is the best available. For all anoxic days, the average flux at anoxic accumulation bottoms ($1.25 \text{ mmol P m}^{-2} \text{ d}^{-1}$) was used for all bottom types.

The total integrated benthic P flux of 66,000 tons P year⁻¹ is almost 10 times larger than the external load of approximately 7,000 tons P year⁻¹ (Pitkanen and Tallberg 2007). Previous estimates of the integrated benthic P flux are lower than our estimate, 4,000–18,000 tons P year⁻¹ using an average SRP flux of $0.06 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Lehtoranta 2003), and 10,000 tons P using a SRP efflux of $0.42 \text{ mmol m}^{-2} \text{ d}^{-1}$ and assuming anoxic conditions for 120 days (50 m depth) and an area with accumulation bottoms in reducing/anoxic state of $9,000 \text{ km}^2$ (Pitkanen et al. 2003). The model-calculated area of bottoms with oxygen concentration $<20 \mu\text{mol L}^{-1}$ in this study was around $9,500 \text{ km}^2$, which is very similar to the estimate of Pitkanen et al. (2003). For the depth interval 40–60 m, the average number of anoxic days was 125 compared to 120 used by Pitkanen et al. (2003). However, including the deepest interval (60–120 m) with an area of $3,000 \text{ km}^2$ and 319 model-calculated days with oxygen concentration $<20 \mu\text{mol L}^{-1}$, the estimated integrated benthic P flux became 6.6 times larger than that estimated by Pitkanen

Table 5 Estimation of integrated benthic P flux for the year 2003 in the Gulf of Finland

| Oxygen limit | Depth interval (m) | Bottom area (km^2) | Anoxic/suboxic (days) | Oxic (days) | Anoxic, load (ton P year ⁻¹) | Oxic, load (ton P year ⁻¹) | Total (ton P year ⁻¹) |
|-------------------|--------------------|-------------------------------|-----------------------|-------------|--|--|-----------------------------------|
| $<20 \mu\text{M}$ | 0–40 | 22,328 | 0 | 365 | 0 | -2,526 | -2,526 |
| | 40–60 | 6,174 | 125 | 240 | 29,906 | -2,067 | 27,839 |
| | 60–120 | 3,354 | 319 | 46 | 41,460 | -383 | 41,078 |
| | | | | | | | 66,390 |

The number of days with oxygen $<20 \mu\text{mol L}^{-1}$ (anoxic/suboxic days) was based on model calculations of bottom water oxygen conditions

The bold value is the sum of the total P load in ton year⁻¹

et al. (2003). This shows that even though the deepest accumulation bottoms constitute a small part of the total area, they can have a large effect on the integrated benthic P flux as they suffer from anoxic conditions for almost the entire year. Another major reason why our calculated integrated benthic P flux was significantly larger than previous estimates is that the in situ measured anoxic SRP fluxes reported here were on average about three times higher than previous laboratory measurements of anoxic fluxes.

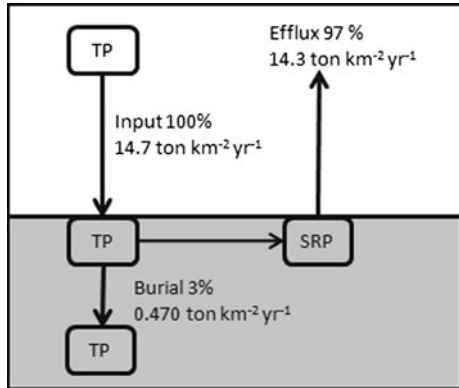
Our estimate of the integrated benthic P flux is 4–17 times higher than previous estimates, based on laboratory core incubations and change in winter water column P pool. The large disagreement is mainly due to higher fluxes measured in situ in this study compared to previous ex situ measurements. A comparison between model results and mooring data showed that oxygen concentrations were likely somewhat overestimated in the model and the estimation should thus give a minimum of the number of anoxic days in the Gulf of Finland during 2003–2004. All fluxes were measured between May and September, which is the season with highest SRP fluxes (Lehtoranta and Heiskanen 2003). This might have caused some overestimation of the integrated benthic P flux. However, we believe this potential overestimation is minor, both because we have measured fluxes during both oxic and anoxic conditions, and because we have used the model estimation of oxygen conditions in the extrapolation of fluxes over time. We did not intend to make a complete P budget for the Gulf of Finland and want to emphasize that 66,000 ton P year⁻¹ is the area-integrated benthic SRP flux in the Gulf. Previous estimates have been compared to yearly variations in winter P concentration in the open water, and they have been found to compare relatively well (Pitkanen et al. 2003). This means that the estimated release from sediments presented here is not reflected in Gulf of Finland water winter P concentration. We do not propose a final answer to where the 66,000 tons P will end up, but considering the open mouth between the Gulf of Finland and the Baltic Proper, and the variability of water exchange between these two basins, we propose that a part (possibly significant) of the 66,000 tons could be exported to the Baltic Proper.

4.4 Benthic Phosphorus Mass Balance

To improve the understanding of the efficiency with which the Gulf of Finland sediments recycle and bury P, a mass balance for anoxic sediments was constructed from measurements of TP burial rate and benthic SRP efflux (Fig. 7). TP burial rate was calculated using TP burial concentration and sediment accumulation rate (see Table 3), and input to sediment (deposition) was computed as the sum of TP burial rate and SRP efflux, assuming steady state and constant benthic biomass. We also assumed that the benthic flux of dissolved organic P was insignificant. The assumption that the sum of the burial flux and the SRP flux equals the total input of P to sediment (the deposition flux) does not hold for oxic bottoms where some of the TP input is retained on iron oxides or assimilated by bacteria, and thus not released to the bottom water. Therefore, we have only made a mass balance for anoxic accumulation bottoms [i.e., GF1 and GF2 (2002) and PV1 (2003, 2005)] where SRP adsorption to Fe(III) is not important. Although SRP release and TP burial are processes occurring on different timescales, we still find it trustworthy to assume that our SRP fluxes measured during about 24 h are representative for an average flux on a longer timescale.

Our average benthic P mass balance suggests that a dominant fraction (97%) of the P deposited on anoxic Gulf of Finland bottoms is mineralized and recycled back to the water column, and only a small fraction (3%) is undergoing long-term burial (Fig. 7). Reasons for this high recycling efficiency may be explained by the anoxic conditions including

Fig. 7 Benthic P mass balance for anoxic bottoms of the Gulf of Finland. Burial rate was calculated from sediment accumulation rate and TP burial concentration (see *text*), SRP efflux is the measured in situ flux, and input to sediment is the sum of the two. The percentages given are % of input



preferential release of P by bacteria (Ingall et al. 1993; Jilbert et al. 2011) and not only lack of adsorption of SRP on metal oxides (as discussed above).

We did not investigate which P fractions dominated in the burial flux, but 60–80% of the P burial in the Baltic Proper was found to be organic P, and apatite-P was not found to be important (Mort et al. 2010). P undergoing burial in the Gulf of Finland plausibly has a similar chemical composition as in the Baltic Proper.

The sediment accumulation rates of this study were on the same order of magnitude as sediment accumulation rates in the Gulf of Finland reported by Mattila et al. (2006) and Lukkari et al. (2009a). A comparison of station JML of Mattila et al. (2006) and our station GF1, which are situated very close to each other, showed that our sediment accumulation rates are similar to those measured by Mattila et al. (2006). They made nine measurements at station JML with a sediment accumulation rate of 0.0170–0.0490 (average $0.0349 \pm 0.0105 \text{ g cm}^{-2} \text{ year}^{-1}$), and GF1 in this study had a sediment accumulation rate of $0.049 \text{ g cm}^{-2} \text{ year}^{-1}$. Lukkari et al. (2009a) reported a sediment accumulation rate at site 7 of $0.033 \text{ g cm}^{-2} \text{ year}^{-1}$. Station XV1, which is situated close to site 7, had a sediment accumulation rate of $0.028 \text{ g cm}^{-2} \text{ year}^{-1}$. In other words, our estimated sediment accumulation rates are similar to previous estimates in the Gulf of Finland.

The measured TP in sediment of anoxic stations in this study was similar to TP concentrations in the Gulf of Finland sediments presented in Lukkari et al. (2009a). Our TP data were somewhat lower on the oxic station XV1 ($119 \mu\text{mol g}^{-1}$) compared to site 7 ($>250 \mu\text{mol g}^{-1}$) adjacent to XV1 (Lukkari et al. 2009a). TP burial rates and sediment accumulation rates are also comparable between this study and the study of Lukkari et al. (2009a). Since the TP burial concentration did not vary much between stations, the TP burial rate was largely determined by the sediment accumulation rate, and we thus found higher burial rates on accumulation bottoms than on transport/erosion bottoms as would be expected (Table 3).

5 Conclusions

This study of benthic P dynamics in the Gulf of Finland showed that SRP fluxes measured in situ at oxic bottoms were comparable to those previously measured ex situ, whereas in situ measurements on anoxic bottoms gave around 3 times higher fluxes than previous ex situ measurements in the Gulf of Finland. Using the in situ measured fluxes and model

calculations of bottom water oxygen concentration (validated with long-term in situ bottom water oxygen measurements) as well as calculations of bottom areas within different depth intervals, we found the total integrated benthic P flux for the year 2003–2004 to be about 66,000 tons P or almost 10 times larger than the external load, and 4–17 times larger than previous estimates of the total integrated benthic P flux. Like previous studies, we found that the benthic SRP flux was inversely correlated with bottom water oxygen concentration with high SRP fluxes at low oxygen concentrations. In particular, we showed that even deep accumulation bottoms in the open Gulf of Finland, normally anoxic with high SRP effluxes, with a high content of organic matter and high rates of organic matter degradation retained SRP when bottom water became oxic. In addition to the negative correlation between SRP flux and oxygen concentration, the SRP flux from reducing sediments was positively correlated with degradation rate and thus input of organic matter as measured by benthic DIC fluxes. This implies that the benthic SRP flux from anoxic bottoms can be predicted from the DIC flux. It also implies that it is possible to estimate the increase in the benthic SRP flux as an effect of increased anoxia as the difference between the flux calculated from the positive correlation between anoxic SRP and DIC fluxes, and the measured oxic SRP flux. The minimum average theoretical flux increase on oxic bottoms, would they turn anoxic, was estimated to be $21 \pm 8 \text{ kg P km}^{-2} \text{ d}^{-1}$. This equals an additional 35,000 tons year⁻¹ compared to the total integrated benthic P flux of 66,000 tons year⁻¹.

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