

Impact of the 2014 Major Baltic Inflow on benthic fluxes of ferrous iron and phosphate below the permanent halocline in the southern Baltic Sea

by

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Abstract

The impact of 2014 Major Baltic Inflow (MBI) on ferrous iron ($F_{\text{Fe(II)}}$) and phosphate (F_{PO_4}) benthic fluxes was investigated. Sampling took place few months after the MBI, in August 2015, and over one year after the inflow, in February 2016. Materials were collected from three sites (depth of 106–108 m) located in the Gdańsk Deep. Total dissolved iron, Fe(II), phosphate, H_2S and sulfate were analyzed in bottom and pore water. Benthic fluxes were estimated using Fick's first law. All fluxes were directed from sediment. $F_{\text{Fe(II)}}$ ranged from 0.31×10^{-2} to $1.25 \times 10^{-2} \mu\text{mol m}^{-2} \text{hr}^{-1}$ and F_{PO_4} from 1.53 to $2.70 \mu\text{mol m}^{-2} \text{hr}^{-1}$. At the deepest site, $F_{\text{Fe(II)}}$ was similar in both seasons, while at two other sites fluxes in August 2015 were 40–50% smaller than in February 2016. The increase in bottom water oxygen after the MBI enhanced Fe(oxyhydr)oxides formation. As a consequence, bottom and pore water concentrations of Fe(II) and $F_{\text{Fe(II)}}$ decreased. Adsorption of phosphate onto Fe(oxyhydr)oxides resulted in binding of P in surface sediment and lower F_{PO_4} in August 2015. This was particularly evident at the shallowest site. The reductive dissolution of Fe(oxyhydr)oxides and desorption of P during the subsequent months resulted in higher F_{PO_4} in February 2016.

Key words: iron, phosphate, benthic fluxes, Baltic inflows, pore water, Baltic Sea

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Introduction

The cycles of P and Fe in the marine environment are closely related (Sundby et al. 1992; Jensen et al. 1995; Lehtoranta, Heiskanen 2003; Raiswell, Canfield 2012). In aerobic conditions in the surface layer of sediment, phosphates undergo strong adsorption onto Fe(oxyhydr)oxides, which is an important mechanism preventing the release of P into the water (Ruttenberg, Berner 1993; Slomp et al. 1996). In hypoxic and anoxic conditions, Fe(oxyhydr)oxide phases are reduced and undergo dissolution (Mortimer 1941). As a result, benthic P release is much higher than it would be in aerobic conditions (e.g. Jensen et al. 1995; Rozan et al. 2002; Lehtoranta, Heiskanen 2003).

Fe(oxyhydr)oxides are formed as a result of the oxidation of Fe(II), which diffuses from the anoxic sediment layer into surface sediment and bottom water. Oxidation can be both chemical (inorganic oxidation of aqueous Fe(II) with oxygen) and microbiological (Raiswell, Canfield, 2012). Fe(oxyhydr)oxides can be used by microorganisms during anoxic decomposition of organic matter (Canfield et al. 1993; Thamdrup, Canfield 1996). However, owing to high availability, it is sulfates that are the main oxidant used for organic matter mineralization in anoxic conditions

(Jørgensen 1982; Reeburgh 1983; Canfield 1993). Hydrogen sulfide, a product of the bacterial reduction of sulfates, reacts with Fe(II), causing the formation of insoluble sulfides, which are accumulated in anoxic sediments (Rickard, Luther 1997; Raiswell, Canfield 2012). Pyrite formation reduces the availability of iron for phosphate binding (Lehtoranta et al. 2009). In reducing, organic and iron rich sediment, iron can be bound to P (when no free HS⁻ is available), resulting in the formation of an authigenic mineral – vivianite (Fe₃(PO₄)₂ × 8H₂O) (Rothe et al. 2016).

The research discussed in the present paper was conducted in the Gdańsk Deep (max depth of 118 m), located in the southern part of the Baltic Sea. A halocline (60–80 m) present in the water column in the study area separates the surface waters from more saline and denser deepwater, resulting in reduced mixing of these two strata (Andrulewicz, Witek 2002). Infrequent and irregular inflows of water from the North Sea are the main source of oxygen in the deepwater of the Gdańsk Deep area (Kruk-Dowgiałło, Szaniawska 2008). Owing to the considerable depth and permanent stratification, the bottom of the Gdańsk Deep is covered with silty clay and clayey silt (Szczepańska, Uścińowicz 1994). The large amount of organic matter reaching the sediments, together with

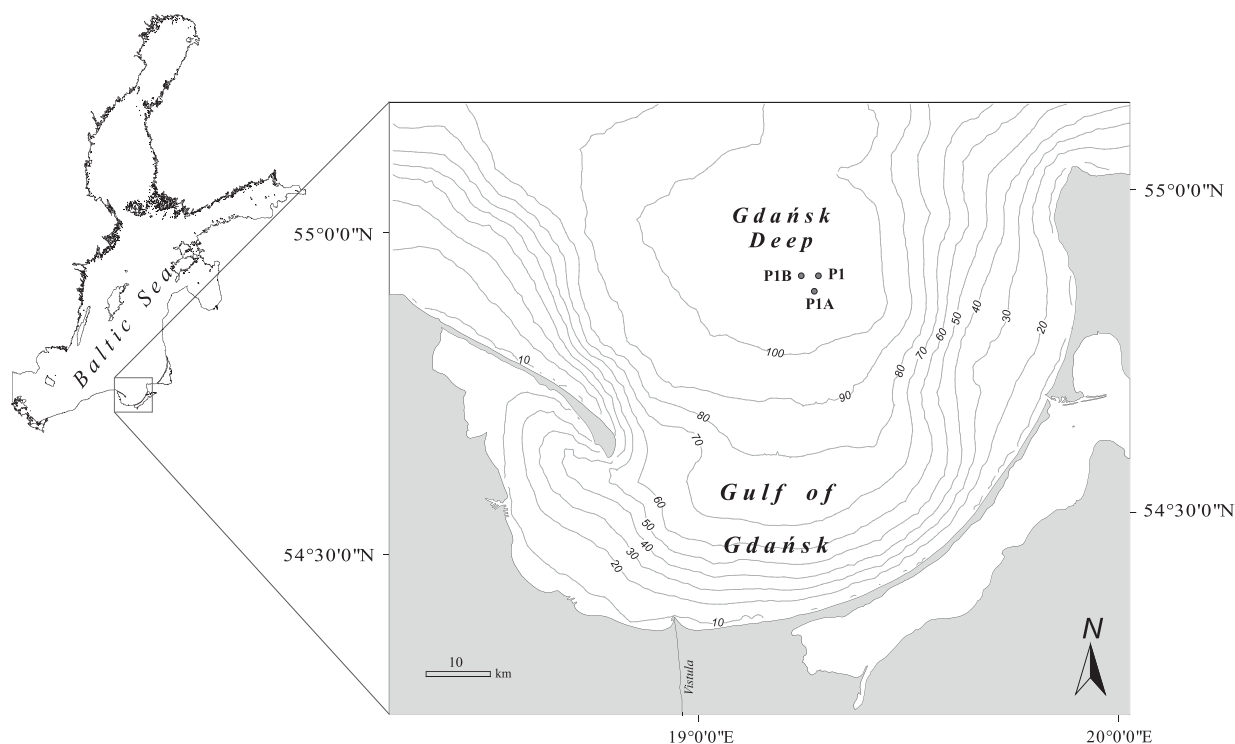


Figure 1

Map of the Gdańsk Basin with the location of sampling sites (contour lines are depth in meters)

the limited oxygen resources in the deepwater, results in a deficiency or complete lack of oxygen which persists for most of the year.

The studies were carried out twice at three sampling sites. The first voyage took place in August 2015, a few months after a very strong inflow from the North Sea. The inflow occurred in December 2014, reaching the Gdańsk Deep in January/February 2015 (Rak 2016; Mohrholz et al. 2015), and interrupted a stagnation in the Baltic Sea that had lasted for over ten years. It was one of the largest inflows observed since 1880 (Mohrholz et al. 2015). The second voyage took place over one year after the inflow, i.e. in February 2016. The main objective of the study was to estimate the fluxes of Fe(II) and phosphates at the water-sediment interface in the Gdańsk Deep area. Apart from Fe(II) and phosphates, we also analyzed the concentration of total iron (Fe_{tot}), hydrogen sulfide and sulfate in near-bottom and pore waters in the studied region.

Materials and methods

Sampling

Sampling was conducted during two voyages (8–10 August 2015 and 7–8 February 2016) aboard the R/V Baltica. In the course of each voyage, samples of seawater, sediments and pore water were collected at three sites located in the Gdańsk Deep (Fig. 1). The sites were located at a depth ranging from 106 m (P1B) to 108 m (P1). Seawater was collected using a rosette of Niskin bottles integrated with a CTD probe (Falmouth Scientific Inc.). The following parameters were measured in the water column: temperature (T), salinity (S) and the concentration of dissolved oxygen (DO; potentiometric titration with automatic titrator SM-Titrino 702, Metrohm and combined Pt-ring electrode; analytical precision $\leq 1.6\%$).

Sediment cores of up to 60 cm in length and 7.5 cm in diameter were collected using a Rhumor Lot corer equipped with plexiglass core liners. Pore water was extracted from the intact and tightly capped sediment cores, avoiding contact with the air, using Rhizon® samplers. The samplers were placed in holes drilled into the plexi tube. The holes were located at 2 cm intervals between 0 cm and 10 cm of the sediment depth, and at 4 cm intervals in the deeper sediment layers, down to a depth of 50 cm. The first sampler was placed a few centimeters above the sediment, in order to collect bottom water samples. The concentrations of total dissolved iron (Fe_{tot}), ferrous iron (Fe(II)), phosphate (PO_4^{3-}), hydrogen sulfide

(H_2S) and sulfate (SO_4^{2-}) in bottom and pore water were measured in the on-board laboratory directly after collection of the samples.

Analytical procedures

The concentrations of Fe_{tot} , Fe(II), phosphate and hydrogen sulfide were measured applying standard spectrophotometric methods (Grasshoff et al. 1999) and using Cadas 200 UV/VIS-Spectrophotometer (HACH LANGE DR6000), while the concentration of sulfate was determined using High Performance Ion Chromatography (Methrom 850 Professional IC). The precision (RSD) of hydrogen sulfide, phosphate, iron and sulfate assays in individual samples was 2%, 1%, 2.5% and 3%, respectively. The sediment samples for the determination of water content (WC) and loss on ignition (LOI) were divided into layers (at 1 cm intervals), placed in polyethylene bags and frozen at $-20^\circ C$ until analysis. WC in sediments was determined by drying samples at $105^\circ C$, while LOI was obtained by igniting sediment samples at $550^\circ C$. In addition, the oxidation reduction potential (Eh) was measured in the sediment directly after the sediment core collection.

Iron and phosphate benthic fluxes

The fluxes of phosphate ($F_{PO_4^{3-}}$) and ferrous iron ($F_{Fe(II)}$) at the sediment-water interface were estimated based on Fick's First Law in accordance with the following equation (Li, Gregory 1974; Boudreau 1996; Lavery et al. 2001):

$$J = -\Phi D_s \delta C / \delta z \quad (1)$$

where: J – benthic flux ($\mu mol m^{-2} hr^{-1}$); $\delta C / \delta z$ – concentration gradient at the sediment-water interface ($\mu mol dm^{-3} cm^{-1}$); Φ – sediment porosity; D_s – diffusion coefficient ($10^{-6} cm^2 s^{-1}$) expressed as $D_s = D_{sw} / \theta^2$, where θ is tortuosity and D_{sw} is the molecular diffusion coefficient of phosphate and ferrous iron in seawater, adjusted to temperature and salinity in accordance with the equations of Li & Gregory (1974).

The concentration gradients of PO_4^{3-} and Fe(II) at the sediment-water interface were calculated as the first derivative of the function describing changes in the concentrations of these substances in bottom and pore water for $z = 0$ as described by Łukawska-Matuszewska, Kiełczewska (2016). Functions were fitted to the data, and the function parameters were calculated by means of the Statistica v.12 non-linear estimation module, employing the Gauss-Newton approach. All of the obtained function coefficients were statistically significant at a confidence level of 95%.

Results

Water column

During both voyages, water salinity (S) increased with depth (Fig. 2). Salinity in the surface layer varied from 7.30 to 7.70 and was similar in both seasons. Below 70 m, S increased to 13.39 in August 2015 and to 12.31 in February 2016. The temperature profile (T) showed a strong variability between the seasons (Fig. 2). In August 2015, the highest surface temperature was 19.8°C, while in February 2016 – 4.9°C. The thermocline was present in August 2015 at a depth of 30–50 m. In both seasons, the concentration of dissolved oxygen (DO) decreased with depth (Fig. 2). In layers down to 70 m, DO ranged between 8.30 and 7.00 $\text{cm}^3 \text{dm}^{-3}$ in August 2015 and between 10.00 and 10.40 $\text{cm}^3 \text{dm}^{-3}$ in February 2016. In deeper layers, the concentration of oxygen decreased below 2 $\text{cm}^3 \text{dm}^{-3}$.

Temperature and salinity in the bottom water were higher in summer than in winter (Table 1). Higher salinity values measured in the summer were a consequence of the inflow of waters from the North Sea, which occurred in December 2014, and reached the Gdańsk Deep in January 2015 (Mohrholz et al. 2015; Rak 2016). In summer, about 6 months after the inflow, hypoxia was observed in the bottom water of the Gdańsk Deep, and oxygen saturation was

between 11 and 19%. Further oxygen consumption in subsequent months resulted in oxygen concentration and saturation decreasing to 7–17% (Table 1). The change in oxygen concentration was accompanied by a change in Eh in the water above the sediment (Table 1). In summer, Eh was in the range of 162–247 mV. In winter, Eh was smaller and values were from 92 to 217 mV (Table 1).

The pH in the water above the sediment was in the range of 7.78–7.90 at all the sites in both seasons. At P1B, the pH level was slightly lower than at the other sites (Table 1).

The concentration of phosphate in the water above the sediment was 8.21–27.27 $\mu\text{mol dm}^{-3}$ and in February 2016 was more than two times higher than in August 2015 (Table 1). The Fe(II) concentration in the winter season (0.42–0.53 $\mu\text{mol dm}^{-3}$) was also higher than in summer (0.13–0.23 $\mu\text{mol dm}^{-3}$). Sulfate concentration ranged from 4.99 to 16.19 mmol dm^{-3} . The summer period was characterized by markedly higher sulfate concentration and lower concentration of hydrogen sulfide than the winter period (Table 1). In summer, hydrogen sulfide was present only at the deepest site (P1) and its concentration was 1.10 $\mu\text{mol dm}^{-3}$. In winter, hydrogen sulfide was present at all sites. Concentration of H_2S in February 2016 varied from 17.80 to 27.22 $\mu\text{mol dm}^{-3}$.

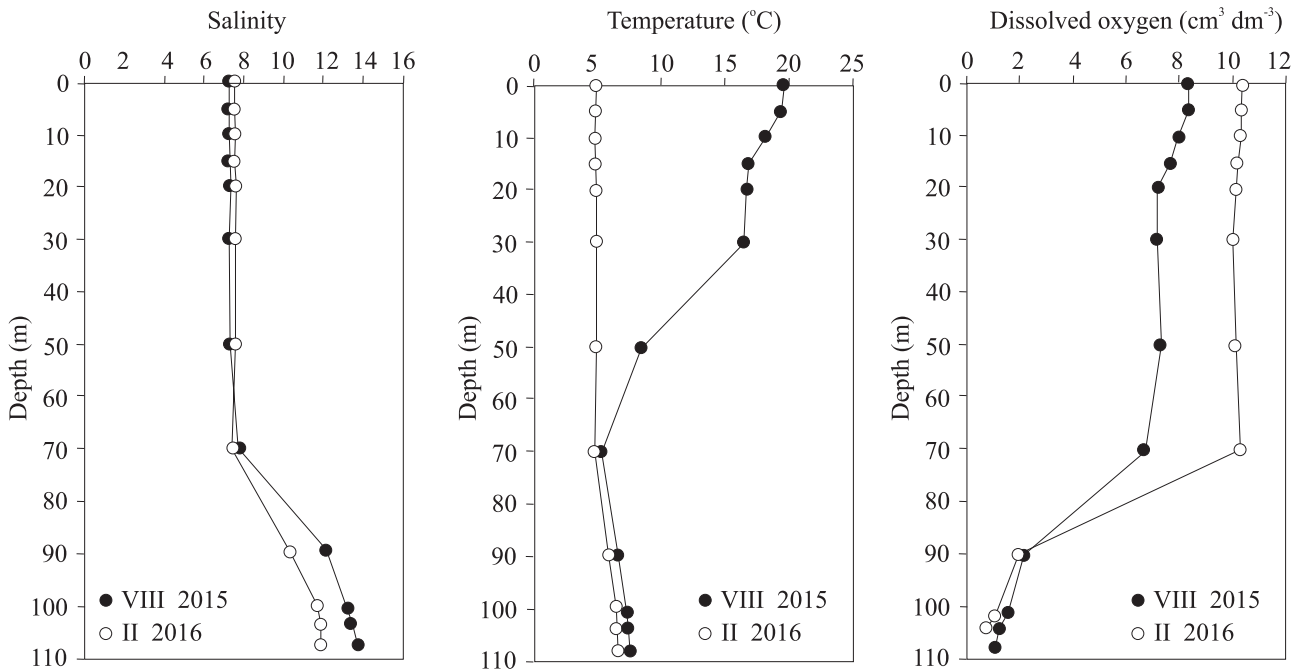


Figure 2

Variability profile of salinity, temperature and concentration of dissolved oxygen along with depth in the water column in the area of the Gdańsk Deep in August 2015 and February 2016

Table 1

Temperature (T), salinity (S), dissolved oxygen (DO) concentration, oxygen saturation (DO_{sat}), oxidation reduction potential (Eh), pH and the concentrations of sulfate (SO₄²⁻), hydrogen sulfide (H₂S), phosphate (PO₄³⁻) and ferrous iron (Fe(II)) in water above the sediment measured in the Gdańsk Deep during the summer and winter voyages (T, S and DO was measured 1 m and other parameters several cm above the sediment surface)

Voyage	Site	T (°C)	S	DO (cm ³ dm ⁻³)	DO _{sat} (%)	Eh (mV)	pH	SO ₄ ²⁻ (mmol dm ⁻³)	H ₂ S (μmol dm ⁻³)	PO ₄ ³⁻ (μmol dm ⁻³)	Fe(II) (μmol dm ⁻³)
VIII 2015	P1	7.27	13.37	0.86	11	162	7.81	16.19	1.10	12.56	0.13
	P1A	7.32	13.21	1.43	18	224	7.80	14.90	0.00	8.21	0.18
	P1B	7.22	13.39	1.51	19	247	7.78	15.59	0.00	12.66	0.23
II 2016	P1	6.32	12.31	0.58	7	92	7.90	4.99	27.22	27.27	0.42
	P1A	6.63	11.44	1.17	15	194	7.90	11.04	17.80	24.66	0.51
	P1B	6.35	11.45	1.37	17	217	7.88	10.63	20.85	25.68	0.53

Sediment

WC and LOI at each site decreased with sediment depth (Fig. 3). Both WC and LOI reached the highest values in the surface layers of sediment. WC ranged from 82.6 to 95.6%, and LOI ranged from 12.3 to 19.2% (Fig. 3). In August 2015, Eh was measured only at the deepest site and decreased with sediment depth from 139 mV in the surface layer to a level of -251 mV. In February 2016, Eh dropped from 156 to -277 mV at all sites. In the surface layer of sediment in February 2016, Eh was positive at P1A and P1B. At P1, Eh was < 0 throughout the sediment column (Fig. 4).

Pore water

The concentration of substances in pore waters varied considerably, both seasonally and depending

on the site. The Fe_{tot} in both seasons ranged from 0.64 μmol dm⁻³ to 1.49 μmol dm⁻³. Slightly higher values were observed in August 2015 in the surface layers of the sediments at sites P1 and P1B and in the whole sediment profile at P1A (Fig. 5). The concentration of Fe(II) ranged from 0.01 μmol dm⁻³ to 1.31 μmol dm⁻³. In general, the Fe(II) values measured in deeper layers of sediment were higher than in the surface layer at all study sites (Fig. 5).

Phosphate concentration increased with sediment depth (Fig. 5) at all sampling sites. Higher concentration values were measured in the winter season, ranging from 38.70 μmol dm⁻³ to 379.55 μmol dm⁻³. In the summer season, however, they ranged from 15.72 μmol dm⁻³ to 327.71 μmol dm⁻³ (Fig. 5).

The concentration of hydrogen sulfide (H₂S) in pore waters ranged from 2.21 μmol dm⁻³ to 2858.2 μmol dm⁻³ in both seasons. Generally, H₂S concentration

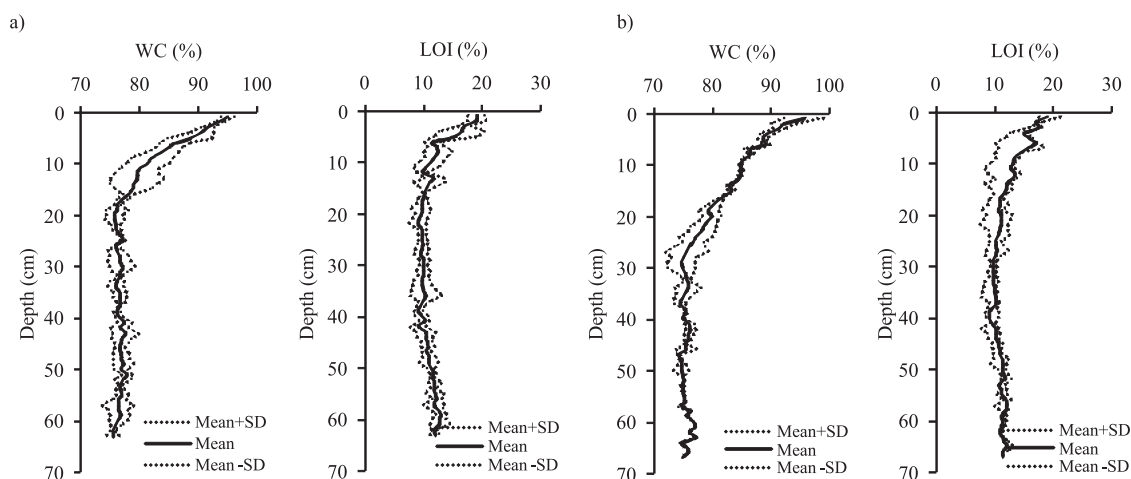


Figure 3

Changes in water content (WC) and loss on ignition (LOI) along with sediment depth in the Gdańsk Deep in August 2015 (a) and February 2016 (b)

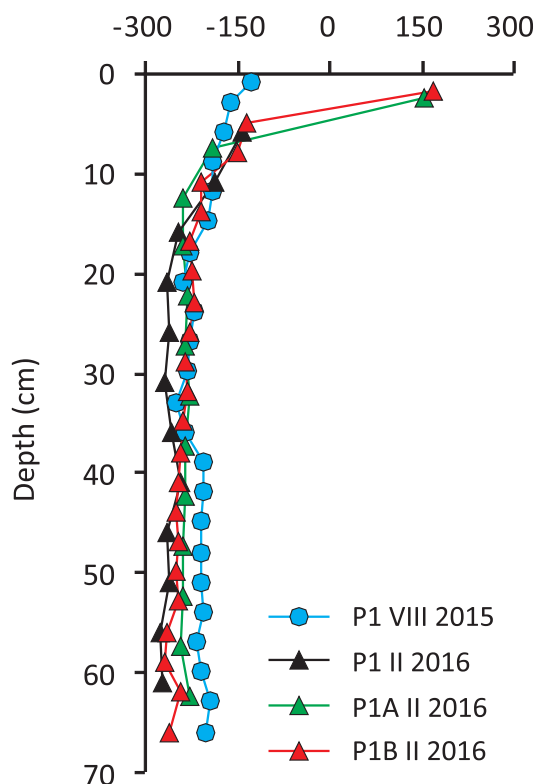


Figure 4

Changes of the oxidation reduction potential (Eh) with sediment depth in the Gdańsk Deep in August 2015 and February 2016

increased with increasing sediment depth. This corresponded to a decrease in sulfate content in the pore water (Fig. 5). Concentration of H_2S in the top 10–15 cm of sediment in summer was lower than in winter (Fig. 5). Sulfate concentration (SO_4^{2-}) in all analyzed samples ranged from $0.10 \text{ mmol dm}^{-3}$ to $27.12 \text{ mmol dm}^{-3}$. In August 2015, significantly higher concentrations were observed in the upper layers of sediment than in February 2016 (Fig. 5).

Benthic fluxes of phosphate and ferrous iron

The estimated fluxes of phosphate ($F_{PO_4^{3-}}$) and ferrous iron ($F_{Fe(II)}$) at the water-sediment interface are presented in Table 2. The values of $F_{PO_4^{3-}}$ ranged from $1.53 \text{ } \mu\text{mol m}^{-2} \text{ hr}^{-1}$ to $2.70 \text{ } \mu\text{mol m}^{-2} \text{ hr}^{-1}$. At sites P1 and P1A, the $F_{PO_4^{3-}}$ values were similar in both seasons. Only at the shallowest site (P1B), the flux measured in August 2015 was significantly smaller than in February 2016. The $F_{Fe(II)}$ values ranged from $0.31 \times 10^{-2} \text{ } \mu\text{mol m}^{-2} \text{ hr}^{-1}$ to $1.25 \times 10^{-2} \text{ } \mu\text{mol m}^{-2} \text{ hr}^{-1}$ (Table 2). Fluxes measured at sites P1A and P1B in August 2015 were about 2 times larger than in February 2016.

Discussion

The exchange of P and Fe between water and sediment depends on many factors, both biotic and abiotic (Canfield et al. 1993; Hartnett et al. 1998; Jäntti, Hietanen 2012; Graca et al. 2006). Dissolved Fe and phosphate are released from the sediment as a result of bioturbation and bioirrigation, as well as wave and current-driven resuspension and diffusion into the water column (Krom, Berner 1980; Santschi et al. 1990; Mortimer et al. 1999; Graca et al. 2006). Benthic release of P and Fe into the water also depends on the concentration of oxygen and Eh in sediment and bottom water. These factors affect sorption of phosphate on Fe(oxyhydr)oxides and thus the ability of sediment to bind P (Ku et al. 1978; Krom, Berner 1980; Boląlek 1992; Lehtoranta et al. 2009; Reed et al. 2011). Fe(III) reduction in anaerobic conditions results in the release of Fe(II) and adsorbed phosphate into the pore water (Mortimer 1941).

The bottom water oxygenation in the Gdańsk Deep depends mainly on the inflows of more saline and oxygenated water from the North Sea. It can therefore be expected that such inflows will be reflected in the porewater chemical composition and the benthic fluxes of phosphate and iron. In the present study, salinity in the water above the sediment was higher in summer 2015 than in winter 2016, the result of 2014/2015 MBI. The MBI ended a stagnation period in the Baltic that had lasted over ten years, renewing oxygen in the near-bottom water layer (Mohrholz et al. 2015). However, in August 2015, about 6 months after the inflow, hypoxia occurred in the bottom water of the study area, while the oxygen saturation was $< 19\%$. Oxygen consumption in the subsequent months resulted in further deterioration of bottom water oxygenation (Table 1). The effect of the MBI was particularly evident in the concentrations of sulfate and hydrogen sulfide (Fig. 5). It was manifested by lower concentration of H_2S and higher concentration of sulfate (Table 1, Fig. 5) in bottom water and upper layers of sediment in August 2015 compared to February 2016.

Phosphate benthic fluxes ($F_{PO_4^{3-}}$) in the Gdańsk Deep ranged from $1.53 \text{ } \mu\text{mol m}^{-2} \text{ hr}^{-1}$ to $2.70 \text{ } \mu\text{mol m}^{-2} \text{ hr}^{-1}$ and were similar to those recorded in other Baltic regions (Table 3). At sites P1 and P1A, the influence of the MBI on $F_{PO_4^{3-}}$ was less pronounced – regardless of the season, the flux was similar for each of the sites. Only at the shallowest site (P1B), the flux measured 6 months after the inflow (August 2015) was found to be significantly smaller than a year after the inflow (February 2016).

While fluxes of $F_{PO_4^{3-}}$ at the sediment-water interface

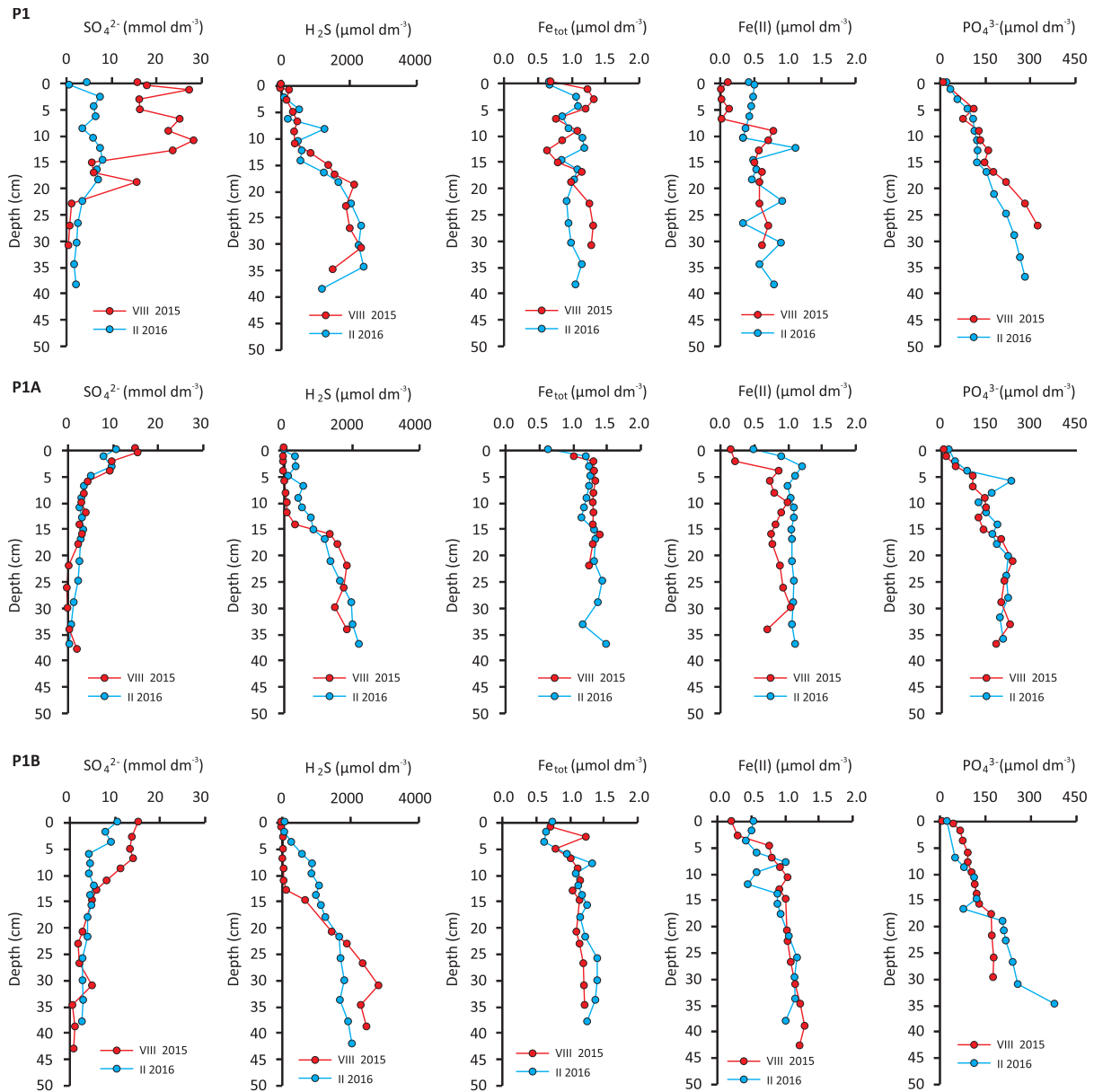


Figure 5

Changes in the concentration of sulfates (SO_4^{2-}), hydrogen sulfide (H_2S), total iron (Fe_{tot}), ferrous iron (Fe(II)) and phosphates (PO_4^{3-}) with sediment depth in the Gdańsk Deep in August 2015 and February 2016

Table 2

Benthic fluxes of phosphate ($F_{\text{PO}_4^{3-}}$) and ferrous iron ($F_{\text{Fe(II)}}$) and parameters used for calculations

Voyage	Site	Porosity	Diffusion coefficient in sediment ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$)		Concentration gradient in surface sediment ($\delta C \delta z^{-1}$) ($\mu\text{mol dm}^{-3} \text{ cm}^{-1}$)		Benthic flux ($\mu\text{mol m}^{-2} \text{ hr}^{-1}$)	
			PO_4^{3-}	Fe(II)	PO_4^{3-}	Fe(II)	$F_{\text{PO}_4^{3-}}$	$F_{\text{Fe(II)}}$
VIII 2015	P1	0.975	5.034	4.932	9.468	0.018	1.67	0.31×10^{-2}
	P1A	0.975	4.145	4.060	18.57	0.046	2.70	0.62×10^{-2}
	P1B	0.975	5.040	4.937	8.618	0.029	1.53	0.50×10^{-2}
II 2016	P1	0.983	4.321	4.233	10.645	0.021	1.63	0.31×10^{-2}
	P1A	0.983	4.322	4.234	16.888	0.078	2.58	1.17×10^{-2}
	P1B	0.983	4.323	4.233	16.580	0.084	2.54	1.25×10^{-2}

Table 3

Benthic fluxes of phosphate ($F_{PO_4^{3-}}$) and iron ($F_{Fe(II)}$) in different regions of the Baltic Sea

Region	Estimation method	$F_{PO_4^{3-}}$ ($\mu\text{mol m}^{-2} \text{hr}^{-1}$)	References
Gullmarsfjorden	Porewater gradient calculations	5.42	Sundby et al. 1986
Gulf of Finland		0.002–0.07	Ignatieva 1999
Gulf of Gdansk		–0.1–7.9	Graca 2009
Gdansk Deep		5.3–5.7	Graca et al. 2006
Puck Bay		2.12–2.56	Łukawska-Matuszewska & Burska 2011
Gotland Basin	Chamber incubations	0.04–3.17	Bolałek 1992
		–0.13–15.67	Viktorsson et al. 2013
		8.33–9.58	Noffke et al. 2015
Region	Estimation method	$F_{Fe(II)}$ ($\mu\text{mol m}^{-2} \text{hr}^{-1}$)	References
Gullmarsfjorden	Porewater gradient calculations	0.83	Sundby et al. 1986
Gulf of Finland	Sediment core incubation	3.93	Lehtoranta & Heiskanen 2003
Gulf of Finland	Chamber incubations	5.84 ^{a)}	Almorth et al. 2009
		0.21 ^{a)}	Pakhomova et al. 2007
Vistula Lagoon		4.16 ^{a)}	Pakhomova et al. 2007

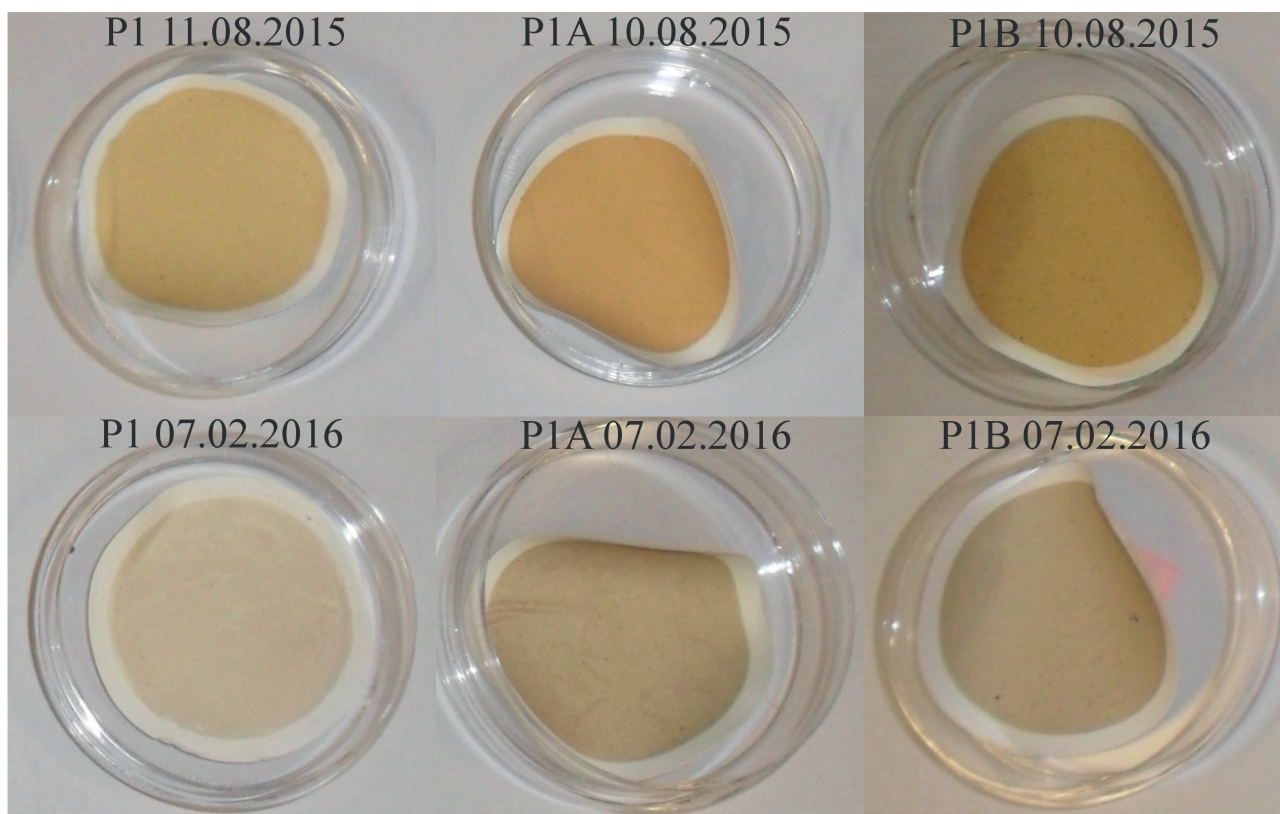
^{a)} fluxes of dissolved total iron

in the Gdańsk Basin have been studied frequently (e.g. Graca et al. 2006; Graca 2009; Łukawska-Matuszewska, Burska 2011), there is no published information on $F_{Fe(II)}$ in this area. Compared to dissolved Fe fluxes in other regions of the Baltic Sea (Table 3), the fluxes recorded in the present study ($0.31 \times 10^{-2} \mu\text{mol m}^{-2} \text{hr}^{-1}$ to $1.25 \times 10^{-2} \mu\text{mol m}^{-2} \text{hr}^{-1}$) are small. It should be noted, however, that the values of dissolved iron fluxes presented in Table 3 were mostly estimated in situ using benthic chambers. Fluxes measured with benthic chamber incubations tend to be significantly higher than those calculated based on the porewater concentration (e.g. Glud et al. 1994; Pakhomova et al. 2007). This is caused by the fact that fluxes calculated from the concentration gradient reflect only diffusion processes, while benthic chamber incubation allows the total flux to be measured (Tengberg et al. 2004). The discrepancy between fluxes measured with the two methods is particularly large in shallow areas where macrofauna is present and water is mixed in the whole column (Berner 1977; Klump, Martens 1981; Santschi et al. 1990). In the present study, the fluxes were estimated for a deepwater area (> 100 m) with permanent water stratification, where effects of bioturbation and turbulent diffusion are limited (Warzocha, 1995; Jankowski, 1996). Therefore, it can be assumed that molecular diffusion is the main way of phosphate and iron exchange at the sediment-water interface. Diffusive fluxes of redox sensitive components calculated from the concentration gradient can be overestimated due to adsorption in the oxic surface layer of sediment (Lavery et al. 2001). The use of a function describing the concentration

profile in bottom and pore water allowed to minimize the risk of overestimation. This method has been commonly applied in other studies (e.g. Urban et al. 1997; Srithongouthai et al. 2003; Denis & Grenz 2003).

Although $F_{Fe(II)}$ was the same in both seasons at the deepest site (P1) (Table 2), the flux measured at the two other sites in August 2015 was 40–50% smaller compared to February 2016. The lower rate of Fe(II) exchange in August 2015 compared to February 2016 was most likely the effect of 2014/2015 MBI. Fe(II) released into pore water in the anoxic sediment layer diffused upward to the sediment surface and bottom water. In oxygenated seawater, Fe(II) was rapidly oxidized, which has led to the formation of Fe(oxyhydr)oxides (Millero et al. 1987). The increase in dissolved oxygen in bottom water after the MBI enhanced the precipitation of particulate forms of Fe. The presence of Fe(oxyhydr)oxides in bottom water in August 2015 gave the suspended particulate matter a yellow-orange color (Fig. 6). As a consequence of the formation of Fe(oxyhydr)oxides, decrease in Fe(II) concentration was observed in the bottom water and the top sediment layers (Table 1, Fig. 5). At the same time, lower fluxes were also recorded (Table 2).

In the subsequent months, limited mixing due to the halocline and the input of organic matter from the water column resulted in further depletion of oxygen in bottom water of the study area. Microbiological reduction and dissolution of Fe(oxyhydr)oxides during anoxic decomposition of organic matter have led to an increase in Fe(II) concentration in the bottom and pore water (Table 1, Fig. 5). In February 2016, Fe(II) fluxes from sediment to water were significantly

**Figure 6**

Filters with suspended particulate matter collected from bottom water (about 1 m above sediment surface) in the Gdańsk Deep in August 2015 and February 2016

higher (Table 2). Interestingly, a simultaneous increase in $F_{\text{PO}_4^{3-}}$ from the sediment was observed only at the shallowest ($h = 106$ m) and most westward site (P1B) (Table 2). This may have been related to the reductive dissolution of Fe(oxyhydr)oxides and the desorption of P. This was not observed at other sites and may be explained by different composition of sediment at sites P1 and P1A, compared to site P1B. At P1 and P1A, the sediment contains more organic matter than at P1B (LOI = 8.0–21.0% vs. 7.6–17.8% at P1B), and it is therefore possible that P in the sediment at these first two sites is present mainly in the form of organic compounds. Eutrophication and consequent increase in primary production, the high sediment accumulation rate (about 2 mm yr^{-1} ; Suplińska 2002) and predominantly hypoxic/anoxic conditions close to the seabed, all enhance organic matter burial in sediment (Balzer 1986; Ingall et al. 1993). P is buried mainly in its organic form and not in the Fe-bound form. Previous studies show that in the fine-grained sediment of the deepest part of the Gdańsk Deep, organic P accounts for more than 50% of the total P in sediment (Łukawska-Matuszewska, Bolałek 2008). Most organic P is present in the refractory form, consisting

mainly of compounds highly resistant to degradation. Therefore, there is no correlation between $F_{\text{PO}_4^{3-}}$ and $F_{\text{Fe(II)}}$, and increased phosphate concentrations mainly reflect the degradation of organic compounds containing P.

Sediments in the coastal seas constitute an important source of P and Fe in the water column (Johnson et al. 1999; Almroth et al. 2009; Nausch et al. 2009; Rydin et al. 2011), and release of nutrients from sediment may affect the phytoplankton production. The elemental ratio of P to Fe in marine phytoplankton ($\text{C}_{106}\text{N}_{16}\text{P}_1\text{S}_{0.7}\text{Fe}_{0.05}$) is approx. 20 (Stumm, Morgan 1981). However, the ratio of benthic fluxes of PO_4^{3-} to Fe(II) obtained in the present study was 203–539 (372 on average). Fe(II) deficiency in relation to P was evident in both seasons. In the case of sites P1A and P1B, $F_{\text{PO}_4^{3-}}:F_{\text{Fe(II)}}$ in August 2015 was about twice as high as in February 2016 when the fluxes of Fe(II) increased as a result of the reductive dissolution of Fe(oxyhydr)oxides. However, despite the enhanced release, the flux of Fe(II) was very small in February 2016. That was probably due to the accumulation of reduced iron in the form of sulfides (i.e. pyrite, iron monosulfides or metastable minerals like greigite) in the sediment. In

anoxic sediment, the concentration of other electron acceptors (i.e. oxygen, Mn, nitrate, Fe) is low compared to sulfate and therefore reduction of sulfate becomes the main pathway of organic matter mineralization (Jørgensen et al. 1990). In addition, sulfate can be used during anaerobic oxidation of methane (Brodecka et al. 2013). The resulting hydrogen sulfide reacts with Fe(II), and Fe can be almost completely precipitated from pore water (Raiswell, Canfield 2012). The concentration of Fe(II) in the pore water of the study area was relatively low compared to other parts of the Baltic Sea (e.g. Carman, Rahm 1997; Pakhamova et al. 2007), suggesting formation of iron sulfides. The accumulation of iron sulfides, in particular pyrite, in anaerobic sediment results in Fe removal from pore water and reduces the ability of the sediment to bind P in the Fe-bound form (Lehtoranta et al. 2009). This concerns both the sorption of P on Fe(oxyhydr)oxides in aerobic conditions and the formation of Fe(II) and P minerals, such as vivianite, the presence of which was documented in the deepest part of the Baltic – the Landsort Deep (Dijkstra et al. 2016).

Conclusions

Benthic fluxes of ferrous iron ($F_{\text{Fe(II)}}$) and phosphate ($F_{\text{PO}_4^{3-}}$) measured below the permanent halocline in the Gdańsk Deep depend mainly on the concentration of oxygen in bottom water. The 2014 Major Baltic Inflow (MBI), which reached the Gdańsk Deep in January 2015, renewed oxygen in bottom water. Benthic fluxes of Fe(II) measured several months after the MBI, in August 2015, were significantly lower than fluxes measured over one year after the inflow, i.e. in February 2016.

The increased concentration of dissolved oxygen in water above sediment after the MBI enhanced the formation of Fe(oxyhydr)oxides and reduced benthic fluxes of Fe(II). Oxygen consumption in bottom water during the subsequent months have led to reductive dissolution of Fe(oxyhydr)oxides and release of Fe(II). In February 2016, $F_{\text{Fe(II)}}$ was about 40–50% higher than in August 2015. Precipitation of Fe(oxyhydr)oxides after the MBI also had an impact on $F_{\text{PO}_4^{3-}}$. Adsorption of phosphates onto oxidized particulate forms of Fe resulted in P binding in the surface sediment layer and lower $F_{\text{PO}_4^{3-}}$ in August 2015. This was particularly evident at the shallowest site.

The ratio of $F_{\text{PO}_4^{3-}}:F_{\text{Fe(II)}}$ in the Gdańsk Deep is very high. This is probably due to the accumulation of Fe(II) in anoxic sediments in the form of sulfides. The accumulation of reduced Fe and S minerals reduces the ability of sediment to bind P in the Fe-bound form. This affects both the adsorption of P onto Fe(oxyhydr)

oxides as well as the formation of vivianite.

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