Phosphate at the water-sediment interface in Puck Bay

JERZY BOLAŁEK
Institute of Oceanography,
University of Gdańsk,
Gdynia

Abstract

The quantity of phosphate transferred from sediments to near-bottom water was determined from phosphate concentration gradients across the near-bottom water-interstitial water interface. In Puck Bay, phosphate was found to be released from sediments into the overlying water. The mean flux is slightly over 20 μmol m^{-2} day $^{-1}$, and the total annual load of phosphate from sediments is ca 100 t. Phosphate concentrations in near-bottom water, interstitial water and in the sediments of Puck Bay are also analysed in this paper. Phosphate concentrations increase eastwards from the western end of the Bay. Concentration changes depended on diagenetic processes related to the oxidation of organic matter, freshwater inflow from the proglacial valleys of the Reda and Płutnica rivers and sorption processes in sediments.

1. Introduction

An element indispensable to life in all organisms, phosphorus is also an element limiting primary production in aquatic ecosystems. In the Baltic Sea, the only basin where phosphorus limits phytoplankton production is the Gulf of Bothnia, while in the Sea of Bothnia phosphorus or nitrogen act as limiting factors. In the Baltic Proper, the Danish Straits and Kattegat, the factor limiting primary production is nitrogen (Rosenberg et $al.,$ 1990). Rivers, the major source of phosphorus input, and the atmosphere together introduce about 50 000 t of phosphorus into the Baltic Sea per year (Rosenberg et $al.,$ 1990). In seawater phosphorus most commonly occurs as orthophosphate, the exact form of which depends on the pH and salinity of the seawater (Carman, 1990). At pH 8 and S = 7 psu the main ions are HPO_4^{2-} – (34.6%), $H_2PO_4^-$ – 25.5%, $Na_2HPO_4^-$ – 17.6% and $MgHPO_4$

(13.4%). At pH $= 7$ the proportions change: HPO_4^{2-} – 41.3%, $NaHPO_4^-$ – 20.9%, $MgHPO_4$ – 15.9% and $MgPO_4^-$ – 11.5%. Sediments play a significant role in the marine phosphorus cycle (Carman and Jonsson, 1991; Gunnars, 1990; Holm, 1978), acting as they do as a centre of phosphorus deposition and possible release.

Phosphorus fluxes across the water-sediment interface can be estimated by:

- *in situ* analysis of chemical exchange with the use of a set of cells isolating the near-bottom water from its surroundings (Holm, 1978; Bolałek *et al.*, 1991),

- modelling the diffusion processes on the basis of the chemical composition of interstitial waters or interstitial and near-bottom waters (Ishikawa and Nishimura, 1989; Yoshida, 1981),

- investigating phosphorus sorption and desorption by sediments (Carman and Wulff, 1989; Krom and Berner, 1980),

- studying the changes in concentration of phosphorus compounds in an incubated sediment – near-bottom water system (Koop *et al.*, 1990).

No permanent studies on phosphorus exchange between the near-bottom water and sediment have yet been carried out in Puck Bay. Experiments conducted at two measurement stations in Puck Bay (Bolałek *et al.*, 1991) yielded sediment – water phosphate fluxes of 24.2 and 6.5 mg m^{-2} day^{-1}, approximately the values for the Baltic Sea as a whole (Holm, 1978). These data were insufficient to determine the annual phosphorus flux from sediments to near-bottom water. Furthermore, these data refer to the change in phosphate concentration after 14 days and, besides the exchange across the water-sediment interface, include the quantity of phosphates transferred from sediments to water as a result of oxygen depletion in isolated seawater. For this reason, the results obtained are probably overestimated.

The phosphorus cycle in the marine environment is not fully balanced because phosphate is deposited in sediments at a faster rate than it is released back to the cycle. This paper aims to estimate the quantity of phosphate released from sediments to near-bottom water in Puck Bay and reintroduced to the cycle. The estimation was based on the magnitude of phosphorus adsorption by sediments, the phosphate concentration gradients across the interstitial water – near-bottom water interface, the diffusion coefficient and the sediment porosity. Phosphate concentrations in interstitial and near-bottom waters, and total phosphorus concentrations in Puck Bay sediments are also given. An attempt has been made to elucidate the causes of the broad range of phosphate concentrations in interstitial water.

2. Material and methods

2.1. Sampling methods and analysis of samples

Sediment cores were collected at 26 stations in Puck Bay (Fig. 1) in 1987 from r/v 'Oceanograf 2' with a 5 cm diameter GOIN sediment corer or directly from the shore with a 7 cm diameter Kajak sampler. The cores were from several to 110 cm long. They were cut up into 5 cm segments immediately after sampling and stored at 4°C for further analysis in the on-shore laboratory (about 6 h).

Interstitial water was expressed by a low pressure gas-mechanical method (Bolałek, 1988) in an apparatus similar to that described by Robbins and Gustinis (1967). The interstitial water phosphate concentration was determined by reaction with ammonium molybdate and subsequent reduction of the ensuing complex (Grasshoff, 1976). 183 interstitial water samples were analysed.

In the period 1986–1990 near-bottom water was sampled using a hydrographic bottle about 0.5 m over the sea floor or directly from the shore at 22 measuring stations (Fig. 1). Phosphates were determined by the molybdate method (Grasshoff, 1976). For the analysis, the results were split into two seasons: April-September was the warm season, October-March the cold one. Exceptionally, the results from the end of March and the end of October 1988 were included in the warm season because of the significantly prolonged growing season.

The moisture content of the sediment was determined by the loss of weight during drying to constant mass at 110°C. Organic matter was determined by weight loss by roasting to constant weight at 550°C.

The sorptive properties of the sediment towards phosphate were determined by the Carman and Wulff (1989) method. The sediments collected at four stations (Fig. 1) were analysed. The surface sediments (0–5 cm) from these stations differed with respect to lithology, organic matter content and degree of diagenesis. The sediments from station 7 were silty, from station they were 18 sandy with admixed mud, from station 19 muddy with fine-grain sand and from station 20 muddy. After roasting, the sandy sediments were grey, the others were various shades of red. The orthophosphate standard was prepared from KH_2PO_4 p. a. by dissolution in artificial seawater. 50 cm^3 each of the following concentrations of standard solution was poured over 1 g samples of roasted sediment: 0.004, 0.01, 0.017, 0.023, 0.035, 0.10, 0.15, 0.5, 1.0, 5.0, 10.0, 20.0 and 25.0 mmol dm^{-3}. The pH in all standards was brought up to that the near-bottom water in Puck Bay. Changes in sediment sorption capacity due to high temperature were disregarded.
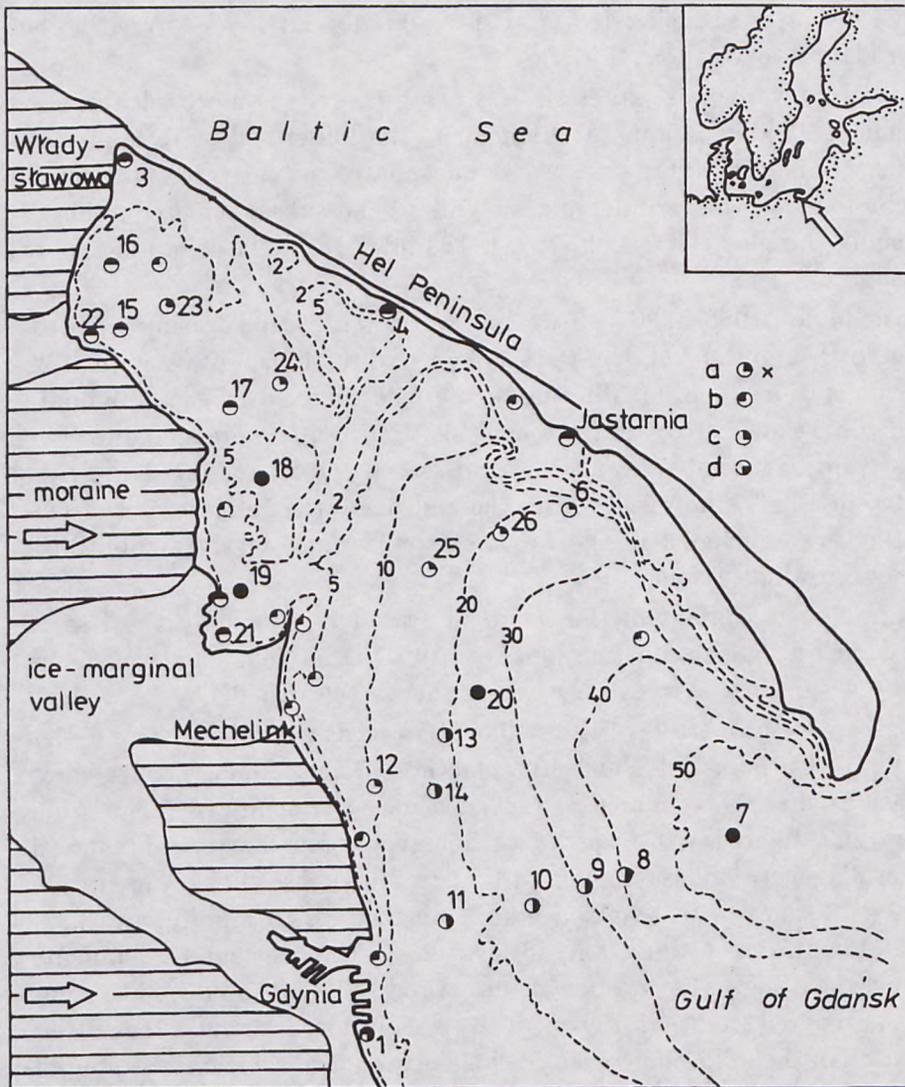
Fig. 1. Location of measurement stations in Puck Bay: sediment sampling stations (a), near-bottom water sampling stations (b), total phosphorus determination in sediments (c), determination of adsorption capacity of sediments (d)

Sediment samples were kept in a thermostat for three weeks, after which the phosphate concentration was determined by the molybdate method.

Total phosphorus was extracted from sediments (77 samples) with 5 M HNO_3 using the method described by Love (1967) and Hallberg (1974).

3. Calculations

The phosphate flux across the sediment – near-bottom water interface was calculated from an equation based on Fick's first law (Berner, 1971; Holm, 1978)

$$J_x = -D_s \Phi (C_{x\prime} - C_0) x\prime^{-1}, \tag{1}$$

where

J_x – flux from depth x [μmol cm^{-2} s^{-1}],
D_s – diffusion coefficient [cm^2 s^{-1}],
C – concentration [μmol cm^{-3}],
$C_{x\prime}$ – concentration at $x = x\prime$,
C_0 – concentration at $x = 0$,
x – sediment depth, cm; with the negative sense towards sediments,
Φ – sediment porosity.

Sediment porosity was determined from the relationship (Engvall, 1978)

$$\Phi = W\left[(100-W)\phi + W\right]^{-1}. \tag{2}$$

The volumetric density (Φ) of the sediment was calculated from an equation in Carman and Jonsson (1991)

$$\phi = 260\left[100 + 1.6(W + IG^\circ)\right]^{-1}, \tag{3}$$

where

ϕ – sediment density (g cm^{-3} w. w.),
W – percentage moisture content of the sediment,
IG° – weight loss on roasting expressed as a percentage of wet weight.

The phosphate flux from sediment to near-bottom water was additionally calculated from adsorption measurements using the Carman and Wulff (1989) approach.

4. Results and discussion

4.1. Phosphate concentration in the near-bottom water of Puck Bay

In 1986–1990, the phosphate concentration in the near-bottom water of Puck Bay, including coastal water of 0.5 m depth, ranged from 0.01 to 36.90 μmol dm^{-3} (Tab. 1). 43.3% of the results lay within the 0–1.00 μmol dm^{-3} concentration range (Fig. 2). Concentrations exceeding   5 μmol dm^{-3}

Table 1. Phosphate concentrations [μmol dm^{-3}] in near-bottom and interstitial water and total phosphorus concentrations in sediments [μmol g^{-1} d. w.] of Puck Bay

Period		n	max		min	x	σ
				Estimator			
Near-bottom water							
	May^w	14	1.13	(5.84)*	0.03	0.32	0.31
1986	July^w	17	4.10		0.67	1.62	0.99
	Sept^c	16	4.50		0.47	1.95	0.96
	Mar^c	13	4.92	(35.52)	0.41	1.46	1.16
1987	Aug^w	18	1.50	(21.50)	0.01	0.39	0.38
	Sept^w	20	2.15	(9.02)	0.50	1.09	0.47
	Nov^c	18	5.00		0.45	1.70	1.17
	Mar^w	19	5.75	(21.50)	0.76	1.65	1.15
1988	May^w	19	1.35	(36.90)	0.08	0.45	0.35
	Aug^w	21	3.91		0.27	1.70	0.99
	Oct^w	18	2.52	(11.44; 14.4)	0.23	1.23	0.65
	Mar^c	20	3.61	(17.10)	1.06	1.71	0.57
1989	May^w	22	2.12		0.13	0.63	0.65
	Sept^w	19	3.88	(11.79)	0.22	1.25	0.98
	Nov^w	22	4.32		0.30	1.52	0.82
1990	Apr^w	17	3.79		0.37	1.12	0.82
	Dec^c	17	2.22	(12.51; 12.88)	0.61	1.45	0.55
Season							
warm		163	4.10		0.01	0.96	0.87
cold		144	5.75		0.23	1.59	0.91
Interstitial waters							
		169	90.82		0.28	18.28	20.29
Sediment		77	29.71		0.97	12.34	5.49

n   – number of data,
max – maximum concentration,
min – minimum concentration,
x   – mean,
σ – standard deviation,
*   – maximum phosphate concentrations in near-bottom water rejected from calculations are given in brackets,
w   – warm season,
c   – cold season,
d. w. – dry weight.
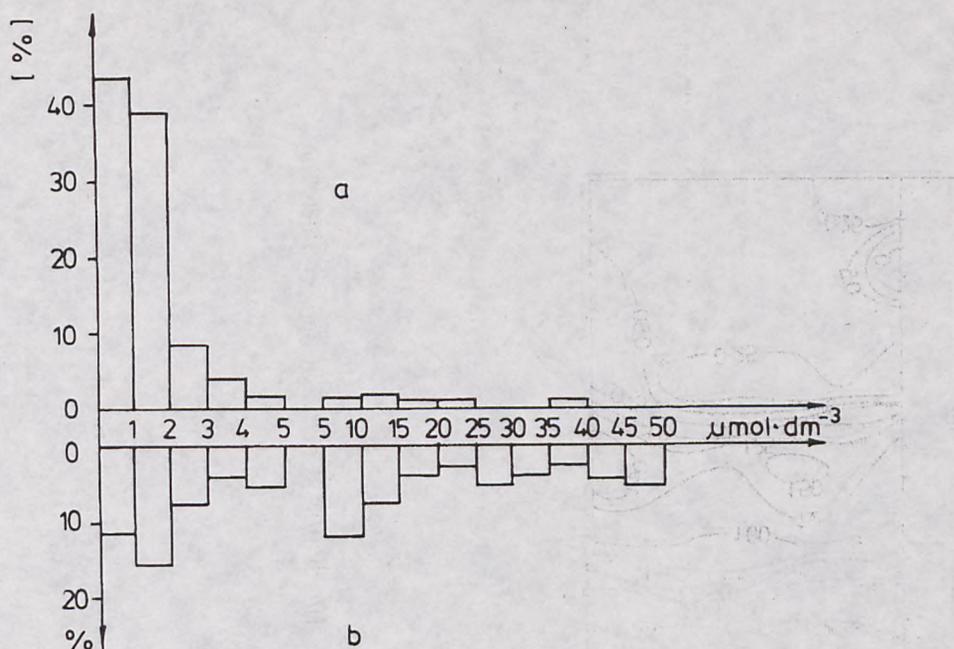
Fig. 2. Histograms of phosphate concentrations in near-bottom water (a) and in interstitial water (b) of Puck Bay

comprised 3.3% of the data set, and concentrations over 30 μmol dm^{-3} were recorded twice in the region of the Zagórska Struga channel outfall.

Phosphate concentrations in Puck Bay exhibited considerable seasonal fluctuations (Fig. 3, Tab. 1) related to the primary production cycle and the inflow of phosphorus compounds from watercourses. In Puck Bay, as in the entire Gulf of Gdańsk, phosphate fluctuates seasonally in a two-phase cycle (Trzosińska *et al.,* 1989). The growing season usually lasted from April to the end of September and was characterized by low concentrations of nutrients. However, in some years it included March or October. In the warm season, the mean phosphate concentration in near-bottom water was 0.96 μmol dm^{-3} (maximum values disregarded) (Tab. 1). In 1986–1990 phosphate consumption was incomplete, both in the shallow part of the Bay and in the deeper region. In the cold season, phosphate concentrations were higher, and the mean concentration in near-bottom water, excluding values over 5.0 μmol dm^{-3}, was 1.59 μmol dm^{-3} (Tab. 1). Figure 4 shows the effect of land run-off on the distribution of the mean phosphate concentrations in the warm and cold seasons. Particularly elevated concentrations were characteristic for the outfall of the Zagórska Struga channel near Mechelinki, the mouth of the Płutnica river, and in the vicinities of Jastarnia
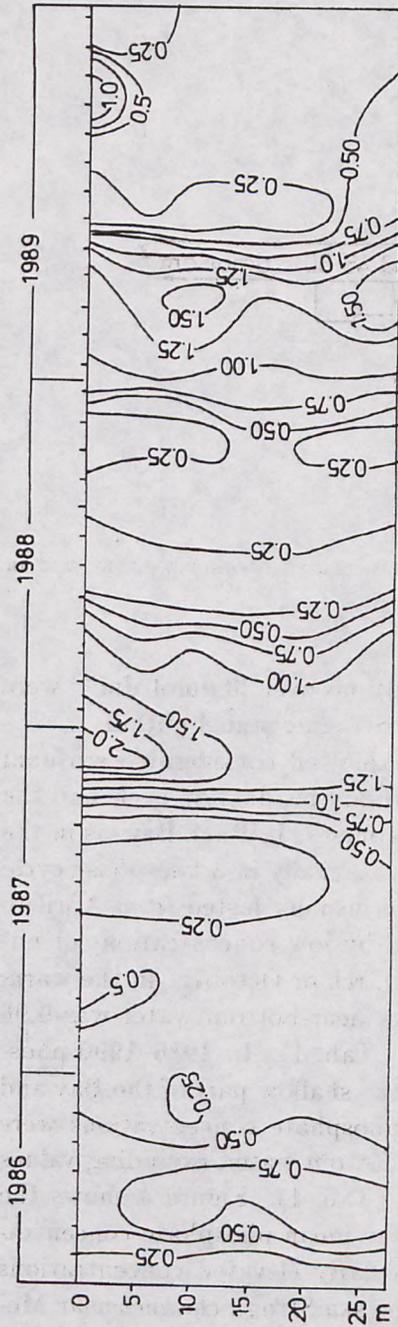
Fig. 3. Examples of seasonal fluctuations of phosphate concentration [μmol dm^{-3}] in the waters of Puck Bay (station 20)
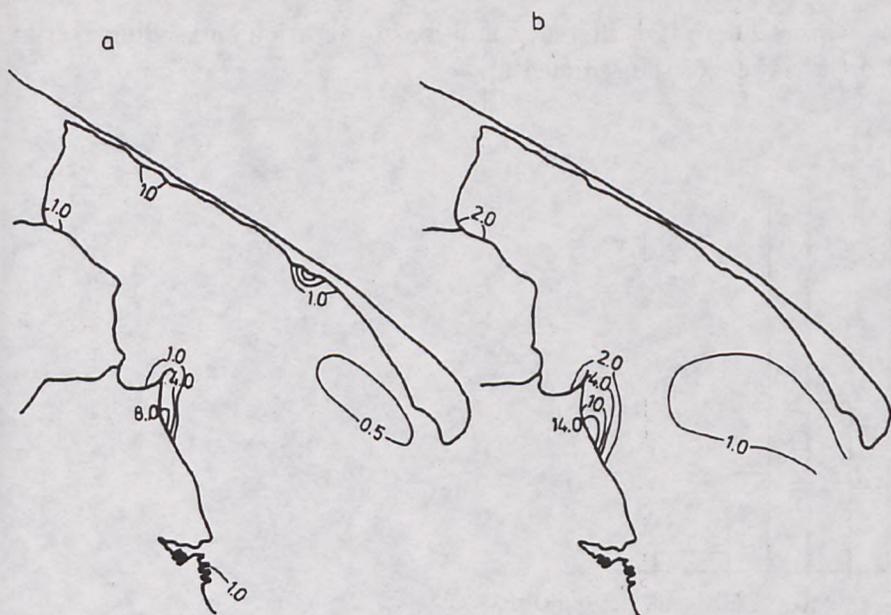
Fig. 4. Distribution of mean phosphate concentration [μmol dm^{-3}] in near-bottom water of Puck Bay in the warm (a) and cold seasons (b)

and Chałupy. However, local sources were of limited range. In general, lower phosphate concentrations were recorded in Outer Puck Bay; higher concentrations were found in the inner part of the Bay, in both the warm and cold seasons.

4.2. Phosphate concentrations in interstitial water and total phosphorus content in the sediments of Puck Bay

Phosphate concentrations in interstitial water varied very widely – from 0.28 to 90.82 μmol dm^{-3}. The mean concentration was over ten times greater than that in the near-bottom water (Tab. 1). The most common range was 1.0–2.0 μmol dm^{-3} (Fig. 2). In comparison with near-bottom water, the proportion of low concentrations decreased, and that of higher concentrations increased. More than 55% of concentrations were < 10 μmol dm^{-3} and nearly 10% were > 50 μmol dm^{-3}.

The total phosphorus concentration in sediments ranged from 0.97 to 29.71 μmol g^{-1} d. w. (Tab. 1), the usual range (Fig. 5) being from 10.0 to 15.0 μmol g^{-1} d. w. (49.4%). The mean phosphorus concentration in the Puck Bay sediments was lower than that in the Baltic Sea sediments

(Tab. 2); this is due to the different conditions of aeration and sedimentation and also the nature of the sediments.
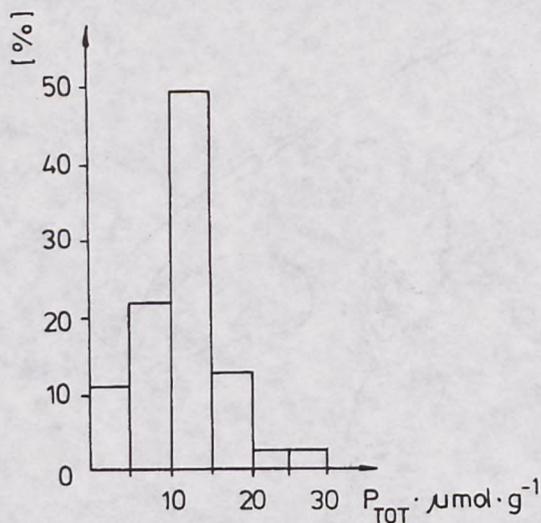
Fig. 5.   Histogram of total phosphorus concentrations in dry sediments of Puck Bay

Table 2. Mean concentration of total phosphorus in Baltic Sea sediments [μmol g^{-1} d. w.]

Region	Mean	Range	Number of data	Source
Baltic Proper	31.3	28.7–33.5	2	Carman and Jonsson, 1991
Baltic Proper	31.6	18.1–56.1	14	Jonnson et al., 1990
Baltic Proper	36.2	32.2–40.3	9	Holm, 1978
Baltic Sea	25.8		163	Emelyanov, 1988
Bothnian Sea	54.9		372	Niemistö et al., 1978
Bornholm Basin	38.7		52	Kogler and Larsen, 1979
Puck Bay		<16.1		Emelyanov, 1988
Puck Bay	12.3	1.0–29.7	77	Bolałek (Tab. 1)

d. w. – dry weight.

In the vertical sediment profiles (Fig. 6), no evident trends in depth-related concentration changes were observed either as regards phosphates in interstitial waters, or in the total phosphorus in sediments. In interstitial waters the maximum phosphate concentrations were found within the sediment, on average at the depth where sulphates were completely utilized
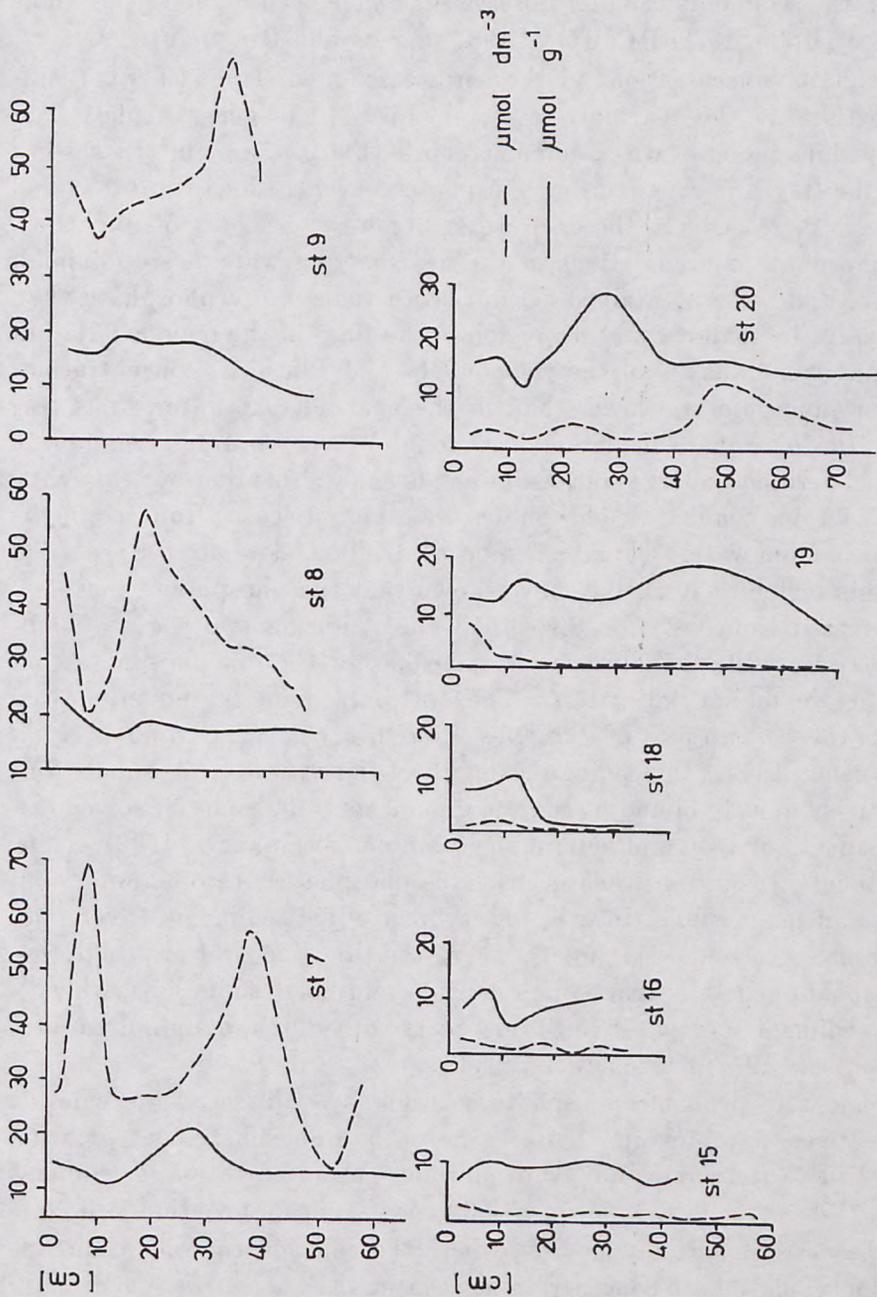
Fig. 6. Vertical profiles of phosphate concentrations [μmol dm^{-3}] in interstitial water (broken line) and total phosphorus in sediments [μmol g^{-1} d. w.] (continuous line)

(25–45 cm). This observation leads to the hypothesis that the elevated phosphate concentrations resulted from the decomposition of organic matter by disproportionation. As no distinct enrichment zone was found, the increased phosphorus content in Puck Bay is presumably not yet reflected to any extent in the sediments. Similar observations have been made in the whole Baltic Sea (Holm, 1978; HELCOM, 1987; Larsen and Brügman, 1991).

Phosphate concentrations in the surface sediment layer (0–5 cm) differ from those in the near-bottom water (Fig. 7). In general, phosphate concentrations increase with sediment depth (Fig. 6, 7a,b) in the eastern part of the Bay; the range of low phosphate concentrations (up to 5 μmol dm^{-3}) also increased. In the deep-water north-eastern part of Puck Bay, where phosphate concentrations in the near-bottom water were minimal, the interstitial water contained several score times more phosphate than the water of the shallow, western region of the Bay. In the regions adjacent to the proglacial valleys of the rivers Reda and Płutnica, concentrations were < 1 μmol dm^{-3} – lower than in the near-bottom water. The reasons for the phosphate depletion here could be the continuous inflow of fresh, well-aerated underground water or phosphate sorption by sediments. Under anaerobic conditions, phosphates are rapidly released from sediments into near-bottom water. Chamber experiments (Bolałek et al., 1991) carried out in this region of Puck Bay have shown that the phosphate concentration increased from 0.25 to 28.96 μmol dm^{-3} during two weeks. Thus, sorption could well be the process responsible for the low phosphate concentrations in interstitial waters. The bottom sediments and interstitial waters of the western part of Puck Bay are rich in calcium (Trimonis et al., 1987; Bolałek, 1992). Depending on the pH of the seawater, phosphate ions are relatively quickly bound by marine organisms and also by dissolved calcium, magnesium, iron and aluminium compounds (Gunnars, 1990). Thus, the sediments become enriched in insoluble phosphates of iron, aluminium, calcium and magnesium. In calcium carbonate-rich sediments (Syers and Curtin, 1988; Korzeniewski, 1990), where the pH is neutral or weakly basic, phosphate generally reacts with calcium and magnesium ions, while in mineral sediments of low pH (5.5) they react with iron and aluminium ions (Ryden et al., 1977; Korzeniewski, 1990).

In regions of probable phosphate sorption by sediments, the chloride concentration was < 3 g dm^{-3}. Here, the ratio of phosphate concentration in interstitial water (μmol dm^{-3}) to phosphorus concentration in sediment (μmol g^{-1} d. w.) was < 1 (mean = 0.29 and standard deviation = 0.25).

In the eastern part of the Bay, where the chloride concentration was > 3 g dm^{-3}, phosphate concentrations in interstitial water were very high. The ratios of phosphate concentration in interstitial water (μmol dm^{-3}) to
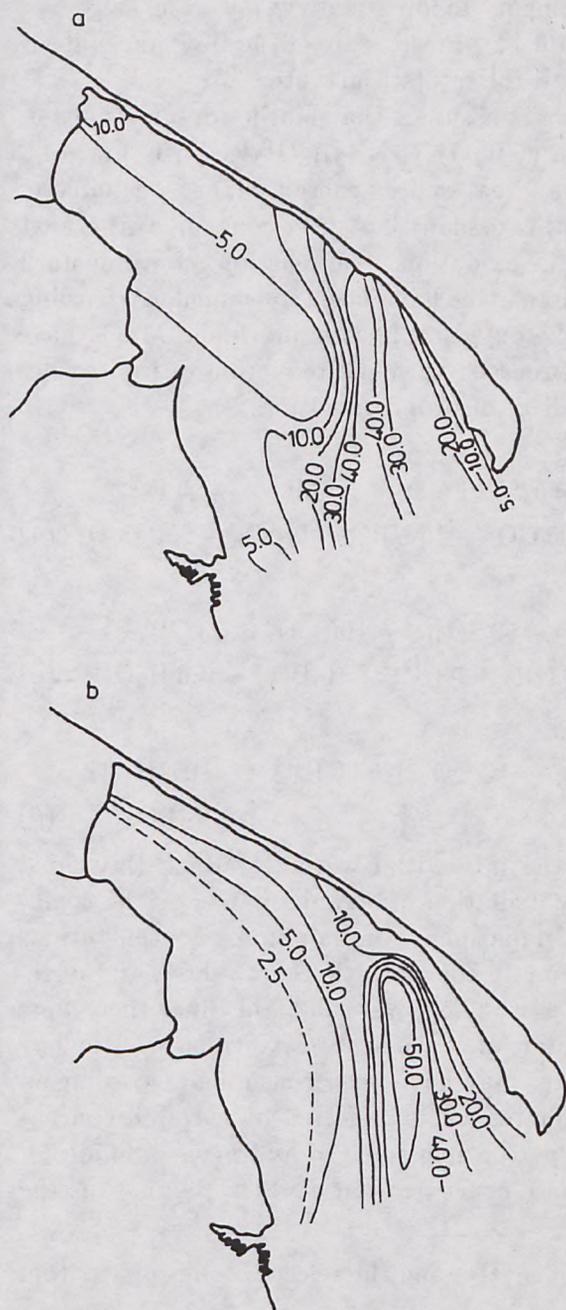
Fig. 7.   Phosphate distribution in interstitial water of Puck Bay sediments at depths of 0–5 cm (a) and 0–25 cm (b)

phosphorus concentration in sediment (μmol g^{-1} d. w.) were usually > 1 (mean $= 1.44$, standard deviation 0.14). In this part of the Bay, phosphorus was released from the sediments to the interstitial water.

The simplest model of diagenesis assumes that marine organic matter, described by the general formula $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$, is first oxidized by that oxidant yielding the greatest free energy change per mole of oxidized organic carbon. When this oxidant has been consumed, the next most effective oxidant continues the oxidation. The reactions continue until all the oxidants or all the organic matter have been consumed. According to Froelich et $al.,$ (1979) when the oxygen, nitrates and labile MnO_2 have been utilized, further oxidation proceeds with the reduction of iron oxides and sulphates, and also as a result of disproportionation

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212\,Fe_2O_3 + 848\,H^+ \rightarrow 424\,Fe^{2+} + $$
$$+106\,CO_2 + 16\,NH_3 + H_3PO_4 + 530\,H_2O, \quad (4)$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\,SO_4^{2-} \rightarrow 106\,CO_2 + 53\,CH_4 + $$
$$+16\,NH_3 + 53\,S^{2-} + H_3PO_4 + 106\,H_2O, \quad (5)$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53\,CO_2 + 53\,CH_4 \quad + \quad 16\,NH_3 + $$
$$+ \quad H_3PO_4. \quad (6)$$
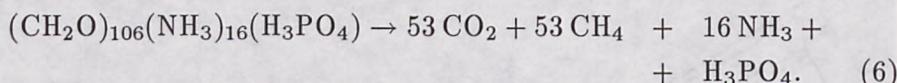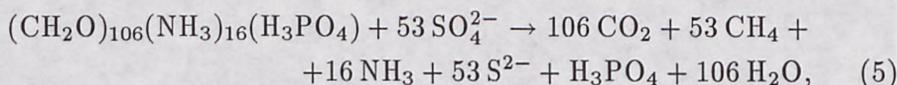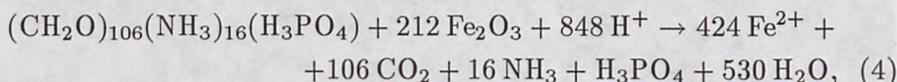
Phosphate concentration in the interstitial waters of Puck Bay must have resulted from the diagenetic oxidation of organic matter as the coefficients of linear correlation between phosphate and ammonia concentrations ($r = 0.71$), phosphate and bicarbonate concentrations ($r = 0.64$) and phosphate and sulphate concentrations ($r = 0.50$) were all high. Since there were no sulphates in the interstitial waters of of the north-eastern part of the bay (Bolałek, 1992), the organic matter may have been consumed according to reaction (6). The absence of sulphates was manifested by elevated concentrations of bicarbonates and the perceptible smell of hydrogen sulphide.

The interstitial-water phosphate concentration in Puck Bay is thus the resultant of two opposing processes:

- the mineralization of organic matter and the release of phosphate from sediments into water,

- the formation of insoluble phosphates of calcium, iron and aluminium and their deposition in sediments.

The domination of one of these processes at some stage of diagenesis gives rise to local phosphate concentration gradients, which in turn leads to

phosphate diffusion and thus, to a change in its distribution. The diversity of the sediments and the two opposing processes occurring in them are responsible for the fact that the organic matter concentration had no effect on the phosphate concentration in the interstitial water of Puck Bay (linear correlation coefficient $r = -0.34$).

4.3. Phosphorus adsorption by sediments from Puck Bay

Phosphate adsorption on four different sediments is shown in Figure 8. To make the figure clearer, the results of phosphate adsorption below 100 μmol dm^{-3} have been excluded. These sediments became saturated at phosphate concentrations of ca 20 μmol dm^{-3} (stations 7, 18 and 20) and 25 μmol dm^{-3} (station 19). Sediment from station 7 registered the highest sorptive capacity – about 600 μmol^{-1} d. w. – whereas sandy-slimy sediment from station 18 the lowest – about 40 μmol g^{-1} d. w.

The slopes of phosphate adsorption curves (coefficient k) varied significantly for four sediment samples containing from 0 to 40 μmol dm^{-3} phosphate (Fig. 9). The equations of linear regression were as follows ($y = kx + a$):
station 7

$$y = 41.5253\,x - 0.8107, \tag{7}$$

station 18

$$y = 22.2849\,x - 0.4415, \tag{8}$$

station 19

$$y = 63.1999\,x - 2.6338, \tag{9}$$

station 20

$$y = 143.077\,x - 7.1332, \tag{10}$$

where y denotes phosphate adsorption by sediments (μmol per g of dry weight) at various concentrations in water (μmol dm^{-3}).

Sorptive properties are affected by various factors – the pH (Jits, 1959; Hingston et al., 1967; Ku et al., 1978), Eh (Ku et al., 1978; Krom and Berner, 1980), temperature (Ku et al., 1978) and chemical composition of the sediment (Berner, 1973). During the experiment pH and temperature were kept constant, hence the diversity in sorptive properties was due solely to the chemical composition of the sediments.

At low phosphate concentrations (up to 40 μmol dm^{-3}) adsorption curves ran below the OX axis. This meant that, for a given range of concentrations, desorption from sediments to water had begun. All four analysed sediments desorbed at phosphate concentrations below 20 μmol dm^{-3} (Fig. 9). In slimy sediments (stations 19 and 20), desorption persisted up
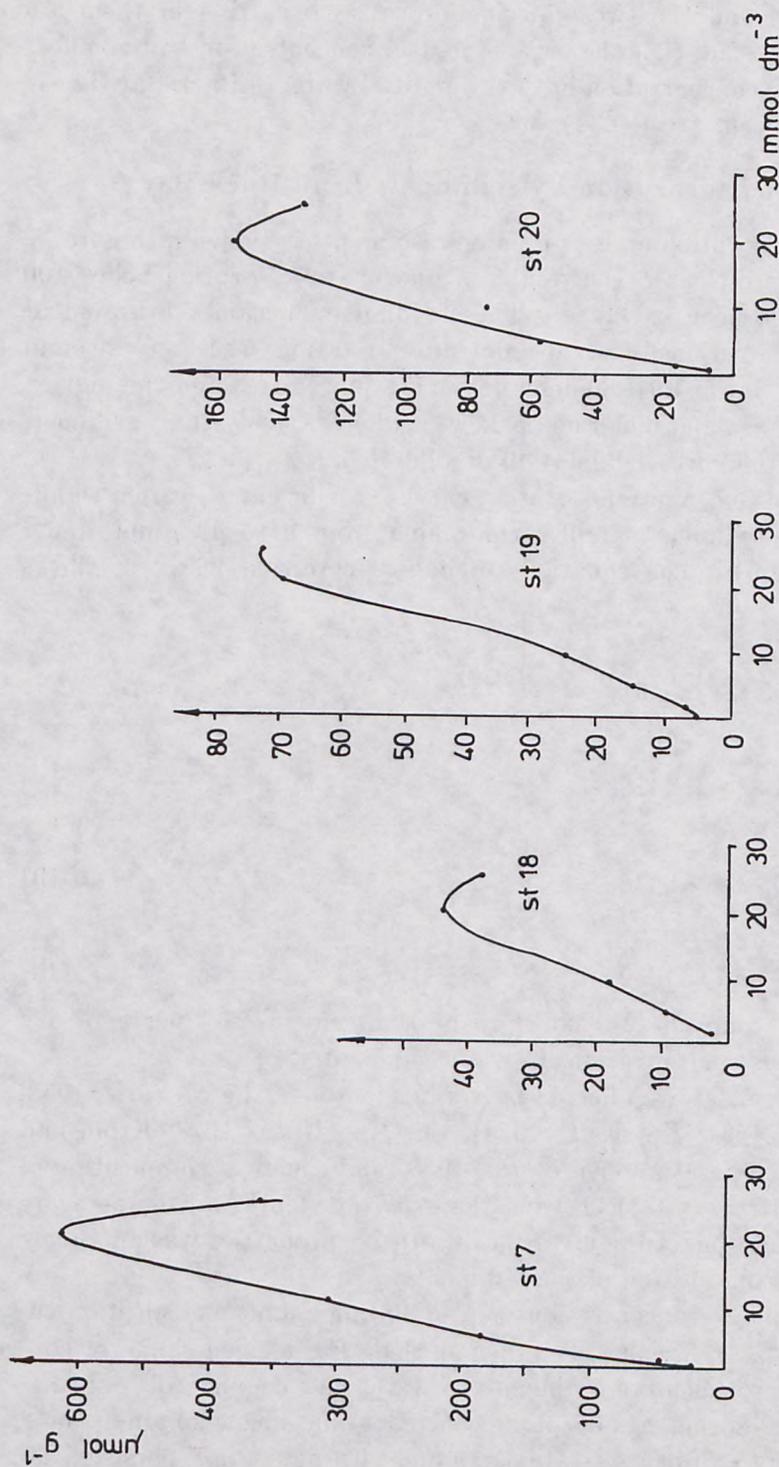
Fig. 8. Phosphate adsorption variations in four different sediments [μmol g^{-1} d. w.] at phosphate concentrations from 0.1 to 25 mmol dm^{-3} (the scale of the y axis is not identical in all cases). Temperature 19°–21°C, pH = 8–8.2.
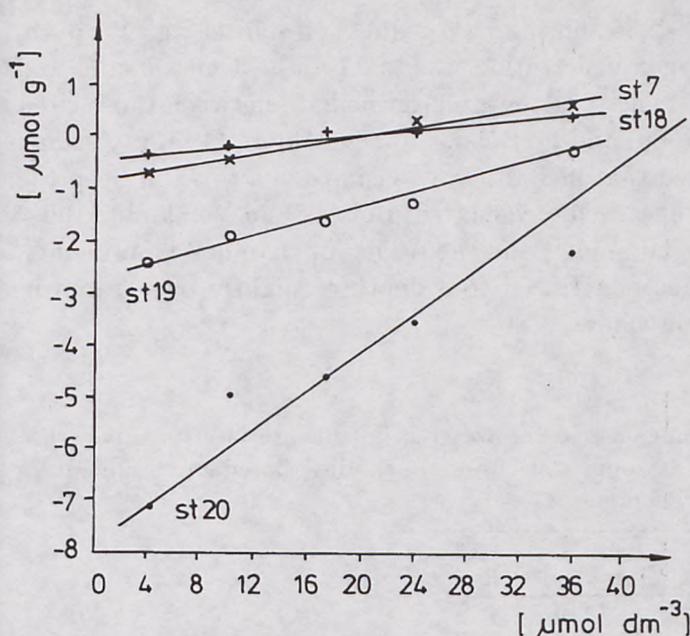
Fig. 9. Differences in phosphate adsorption by sediment at phosphate concentrations from 4 to 40 μmol dm^{-3}. The coefficients of linear correlation (r) determined for stations 7 (x), 18 (+), 19 (o) and 20 ($\bullet$) are 0.99, 0.92, 0.99 and 0.97 respectively. (Temperature 19°–21°C, pH = 8–8.2)

to phosphate concentrations of 45 μmol dm^{-3}. The conclusion can then be drawn that surface sediments in Puck Bay do not adsorb phosphates dissolved in the near-bottom water. Desorption was at a minimum in sandy sediments with the lowest phosphorus (0.23 mg P g^{-1} d. w.) and iron (8.1 mg Fe g^{-1} d. w.) contents, and was at a maximum in slimy sediments with the highest phosphorus (0.48 mg g^{-1} d. w.) and iron (43.3 mg Fe g^{-1} d. w.) contents.

4.4. Release of phosphorus from sediments to water

Equations 7–10 were applied to estimate the phosphorus flux between the sediment and near-bottom water in Puck Bay. In order to perform the calculations, the phosphate concentration in near-bottom water, sediment density and depth of oxygen penetration had to be known. The phosphate concentration in near-bottom water was taken to be the mean value in the warm and cold seasons from 1986 to 1990 at any station. To calculate the maximum fluxes it was assumed that the phosphate concentration in near-bottom water was equal to that in interstitial water. The adsorption was calculated per 1 g of wet weight of sediment. The mean densities assumed

were: sand – 2.65, slime – 2.55 and silt – 2.5 g dm^{-3} (Kępińska and Wypych, 1990). The depth of oxygen penetration was taken to be 1 cm in sand and 0.5 cm in slime and silt. These values are intermediate between those cited by Carman and Wulff (1989) and by Bolałek and Vershinin (1991). Carman and Wulff (1989) assumed that in Baltic Sea basins down to 75 m deep the top 2 cm layer of sediment is well oxygenated; Bolałek and Vershinin (1991) on the other hand, analysed models and the results of chamber experiments, demonstrated that oxygen penetrated to a depth of slightly over 5 mm in sands and nearly 3 mm in slimes.

Table 3. Phosphate exchange across the water-sediment interface (positive sense from sediment to water) at some stations in Puck Bay, based on results from sediment adsorption experiments

Station	ρ	h	F_s	F_w	F_i
	[g cm^{-3}]	[cm]	[μmol m^{-2} day^{-1}]
7	2.50	0.5	11	10	5
18	2.60	1.0	17	16	17
19	2.55	0.5	51	50	42
20	2.55	0.5	69	68	65

F_s – phosphate flux calculated from the mean phosphate concentration in near-bottom water in the warm season,

F_w – phosphate flux calculated from the mean phosphate concentration in near-bottom water in the cold season,

F_i – phosphate flux calculated from the mean phosphate concentration in interstitial water,

h – depth of oxygen penetration in sediment,

ρ – sediment density.

Phosphate fluxes from sediment to near-bottom water at four stations are presented in Table 3. The calculations showed that no significant differences existed between the warm season and cold season fluxes. The results based on phosphate concentrations in interstitial water were slightly lower. This applies in particular to stations 7 and 19, where the phosphate concentration in interstitial water was high.

The characteristic parameters of surface sediments in Puck Bay and the parameters necessary to calculate phosphate exchange across the water-sediment interface according to Fick's first law (equation 1) are presented in Table 4. The interstitial water phosphate concentration in the 0–5 cm layer was assumed to be that at the centre of the layer, i.e. $x = 2.5$ cm; the coefficient of diffusion D_s was taken from literature on Baltic Sea sediments. From chamber experiments Holm (1978) calculated $D_s = 5.8 \times 10^{-5}$ cm^2 s^{-1} and

this value was adopted in calculations of the phosphate flux across the water-sediment interface in Puck Bay.

Table 4. Phosphate fluxes across the water-sediment interface in Puck Bay calculated from Fick's first law

Station	C_i	C_s	C_w	W	S_{org}	Φ	F_s	F_w	F_a	F_{al}
	[μmol dm^{-3}]				%		[μmol m^{-2} day^{-1}]			
1	6.85	1.80	2.40	19.38	0.51	32	32	29	30	
2	7.28	1.00	1.40	16.01	0.50	28	38	33	36	
3	12.71	11.42	11.40	22.21	1.74	35	16	16	16	
4	6.28	0.61	1.30	17.80	0.21	32	36	32	34	
5	40.00	14.85	14.85	15.97	0.23	28	141	141	141	
6	4.86	1.00	1.40	62.12	6.02	56	39	43	41	
7	27.75	0.51	1.72	58.13	5.88	65	355	339	347	17
8	46.06	0.51	1.72	45.41	3.39	55	502	489	495	25
9	44.06	0.51	1.72	61.79	4.63	68	621	604	612	31
10	19.25	0.78	1.51	43.61	2.82	54	201	192	196	10
11	2.55	0.78	1.51	39.31	4.55	50	18	10	14	
15	2.28	1.06	1.43	77.07	20.11	79	19	13	16	
16	2.86	1.06	1.43	64.26	12.05	69	23	20	21	
17	1.83	0.60	1.30	24.16	0.80	37	9	4	6	
18	1.37	0.60	1.30	42.11	2.42	53	8	1	4	
19	8.05	0.77	1.28	41.54	4.03	52	76	71	74	
20	2.91	0.59	0.77	70.17	6.74	77	36	33	34	
21	1.14	0.77	1.28	28.42	4.51	41	8	-1	4	
22	2.97	0.77	1.28	27.36	1.33	33	15	11	13	
23	2.32	1.06	1.43	20.09	0.75	33	8	6	7	
24	3.88	0.65	1.31	30.41	1.85	43	28	22	25	
25	2.06	0.59	0.77	56.54	8.65	63	18	16	17	
26	1.83	0.59	0.77	63.23	7.94	68	17	14	16	

C_i – phosphate concentration in interstitial water from the 0–5 cm sediment layer,

C_s – mean phosphate concentration in near-bottom water in the warm season,

C_w – mean phosphate concentration in near-bottom water in the cold season,

W – water content in sediment,

S_{org} – organic matter content in sediment,

Φ – sediment porosity,

F_s – phosphate flux in the warm season,

F_w – phosphate flux in the cold season,

F_a – mean flux,

F_{al} – mean phosphate flux calculated for $xl = 50$ cm.

Phosphate fluxes across the water-bottom interface were calculated for both warm and cold seasons. Of 48 values, only one was directed from the water to the sediment (Tab. 4). This observation was in agreement with laboratory experiments on phosphate desorption from sediments (Fig. 9). Maximum fluxes were found in the eastern part of the bay, although phosphate concentrations in near-bottom water did not corroborate this finding. One possible reason for this was the movement of water masses in this region, removing phosphates released from sediment to water. Another reason could have been the method of sampling the near-bottom water from about 0.5 m over the sea floor. This problem applies especially to deep-water stations, because at shallow stations, wind-generated wave-action makes for good mixing conditions, and there is no difference between phosphate concentrations a few cm over the bottom and several score cm higher up. If it was assumed that $xl = 50$ cm at deep stations (7, 8, 9 and 10), the resulting phosphate fluxes would be of the same order as in other regions of Puck Bay. The exceptionally large phosphate flux at station 5 resulted from the elevated concentration of phosphates in interstitial water, the effect of large quantities of nutrients flowing in from the adjacent sewage outflow.

Table 5 compares phosphate fluxes from sediments to near-bottom water in Puck Bay estimated from data yielded by

- chamber experiments (Bolałek *et al.,* 1991),
- the phosphate concentration gradient across the water-sediment interface and Fick's first law,
- adsorption curves.

The chamber experiment results in Table 5 (Bolałek *et al.,* 1991) were calculated for several consecutive measurements. Calculations were done only for measurements made when the oxygen concentration exceeded 1 cm^3 dm^{-3}. Without the extreme results, the mean phosphate fluxes were 223 μmol m^{-2} day^{-1} and 0.088 mmol m^{-2} day^{-1} from slimy and sandy sediments respectively.

The flux values obtained from chamber experiments were the highest. This was because they take into account not only simple diffusion due to the phosphate gradient across the water-sediment interface, but also processes connected with the presence of living organisms in the sediments.

Since the fluxes obtained by these three calculation methods were hardly comparable, the annual phosphate fluxes were calculated from Fick's equation, because the largest number of data were available in this case. In Inner Puck Bay the mean phosphate exchange flux across the water-sediment interface was 21 μmol m^{-2} day^{-1} (237 kg PO$_4$-P km^{-2} year^{-1}), in Outer Puck Bay – 25 μmol m^{-2} day^{-1} (283 kg PO$_4$-P km^{-2} year^{-1}). Assuming the area

Table 5. Comparison of phosphate fluxes across the water-sediment interface of the Puck Bay calculated by various methods

Method	Number of data	Flux [μmol m^{-2} day^{-1}] max	min	mean
Chamber experiments	14*	276	26	155
Fick's I law				
warm season	19	76	8	23
cold season	19	71	-1	20
Description				
warm season	4	69	11	37
cold season	4	68	10	36

* based on results from two testing grounds at different times.

of Inner Puck Bay to be 104.7 km^2 and that of Outer Puck Bay to be 254.5 km^2 (Nowacki, 1980) *ca* 97 tons of phosphorus as phosphate are released from the sediments into the water per year.

5. Recapitulation and conclusions

- Concentrations of phosphate dissolved in the near-bottom water of Puck Bay display strong seasonal variation related to the primary production cycles and the inflow of phosphorus compound from watercourses.

- Those parts of Puck Bay where land run-off has the greatest impact on phosphate concentration are the outfall of the Zagórska Struga channel, the mouth of the river Płutnica and the vicinity of Jastarnia and Chałupy. However, local sources are of little importance.

- The phosphate concentration in interstitial water varied over a wide range from 0.28 to 90.82 μmol dm^{-3}. The mean phosphate concentration in interstitial water was 10 times greater than that in near-bottom water.

- The sediment cores revealed no clear trends in the changes either in phosphate concentration in interstitial waters or in total phosphorus content in solid sediment. This suggests that the increase in phosphate concentration in Puck Bay water is not clearly reflected by the sediments. Maximum phosphate concentrations in interstitial waters were found within the sediment, on average at depths where sulphates were exhausted.

- Interstitial water phosphate concentration increases eastwards from the western end of the Bay.

- Diagenetic processes, oxidation of organic matter, fresh-water inflow from the proglacial valleys of the Płutnica and Reda rivers and sorption on sediments all affect the interstitial water phosphate concentration.

- Puck Bay sediments are capable of adsorbing large quantities of phosphates: from 40 to 600 μmol g^{-1} d. w. of sediment. At phosphate concentrations < 20 μmol dm^{-3}, phosphates are desorbed.

- Analysis of phosphate concentrations in near-bottom water and in interstitial water of surface sediments, as well as of experiments on surface sediment adsorption indicates that surface sediments in Puck Bay do not adsorb phosphates from near-bottom water; however, phosphates are released from the sediments to the near-bottom water. The mean phosphate fluxes, in Inner and Outer Puck Bay were 237 kg PO$_4$-P km^{-2} year^{-1} and 283 kg PO$_4$-P km^{-2} year^{-1} respectively, which means that annually around 100 tons of phosphorus as phosphate enters the Bay's near-bottom waters from the sediments.

References

Berner R. A., 1971, *Principles of chemical sedimentology*, McGraw-Hill, New York, 340 pp.

Berner R. A., 1973, *Phosphate adsorption from sea water by adsorption on volcanogenic ferric oxides*, Earth and Planetary Letters, 18, 77–86.

Bolałek J., 1988, *Interstitial water obtained from marine sediments by a low pressure gas-mechanical method*, Stud. Mater. Oceanol., 54, 131–142, (in Polish).

Bolałek J., 1992, *Ionic macrocomponents of interstitial water of Puck Bay sediments*, Oceanologia, 33, 131–158.

Bolałek J., Falkowska L., Jankowska H., Vershinin A., 1991, *Investigation on the transfer of chemical substances at the water-sediment interface in the Puck Bay*, Oceanologia, 30, 105–123.

Bolałek J., Vershinin A., 1991, *Oxygen uptake kinetics at the sediment – sea water interface in the Puck Bay*, Oceanologia, 30, 57–75.

Carman R., 1990, *A thermodynamic approach to the occurrence of discrete phosphorus minerals in sediments and the speciation of some inorganic elements of the Baltic Sea*, [In:] *Biogeochemical constraints on phosphorus exchange and related diagenetic processes in Baltic Sea sediments*, R. Carman (ed.), Ph. D. Thesis, Dep. of Geology and Geochemistry, Stockholm University, Paper I, 1–38.

Carman R., Jonsson P., 1991, *Distribution patterns of different forms of phosphorus in some surficial sediments of the Baltic Sea,* Chem. Geol., 90, 91–106.

Carman R., Wulff F., 1989, *Adsorption capacity of phosphorus in Baltic Sea sediments,* Estuarine Coastal Shelf Sci., 29, 447–456.

Emelyanov E. M., 1988, *Biogenic sedimentation in the Baltic Sea and its consequences,* [In:] *The Baltic,* B. Winterhalter (ed.), Geological Survey of Finland, Special Paper 6, 127–135.

Engvall A. G., 1978, *The fate of nitrogen in early diagenesis of Baltic Sediments,* Ph. D. thesis, Dept. of Geology, Univ. of Stockholm, 103 pp.

Froelich P. N., Klinkhammer G. P., Bender M. L., Luedtke N. A., Heath G. R., Cullen D., Dauphun P., Hammond D., Hartman B., Maynard V., 1979, *Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis,* Geochim. Cosmochim. Acta, 43, 1075–1090.

Grasshoff K., 1976, *Methods of seawater analysis,* Verlag Chemie, Weinheim – New York, 103 pp.

Gunnars A., 1990, *Exchange of phosphorus and silicon over the sediment-water interface during positive redox-turnover – the role of iron and manganese,* Chemical Communication Univ. of Stockholm, 4, 51.

Hallberg R. O., 1974, *Metal distribution along a profile of an inter-tidal area,* Estuarine, Coastal and Marine Science 2, 153–170.

HELCOM, 1987, *First periodic assessment of the state of the marine environment of the Baltic Sea, 1980–1985,* Baltic Sea Env. Proc., 17B.

Hingston F. J., Atkinson R. J., Posner A. M., Quirk J. P., 1967, *Specific adsorption of anions,* Nature, 215, 1459–1461.

Holm N. G., 1978, *Phosphorus exchange through the sediment-water interface. Mechanism studies of the dynamic processes in the Baltic Sea,* Ph. D. Thesis, Dept. of Geology, Univ. of Stockholm, 149 pp.

Ishikawa M., Nishimura H., 1989, *Mathematical model of phosphate release rate from sediments considering the effect of dissolved oxygen in overlaying water,* Water Res., 23, 351–359.

Jits H. R., 1959, *The adsorption of phosphate by estuarine bottom deposits,* Australian Journal of Marine and Freshwater Research, 10, 7–21.

Jonsson P., Carman R., Wulff F., 1990, *Laminated sediments in the Baltic – A tool for evaluating nutrient mass balances,* Ambio, 19, 152–158.

Kępińska U., Wypych K., 1990, *Sediments,* [In:] *The Gulf of Gdańsk,* A. Majewski (ed.), Wyd. Geolog., Warszawa, 55–66, (in Polish).

Kogler F. C., Larsen B., 1979, *The West Bornholm basin in the Baltic Sea: Geological structure and quaternary sediments,* Boreas 8, 1–22.

Koop K., Boynton W. R., Wulff F., Carman R., 1990, *Sediment-water oxygen and nutrient exchanges along a depth in the Baltic Sea,* Mar. Ecol. Prog., 63, 65–77.

Korzeniewski K., 1990, *Principles of chemical oceanography,* Univ. of Gdańsk Press, 198 pp., (in Polish).

Krom M. D., Berner R. A., 1980, *Adsorption of phosphate in anoxic marine sediments,* Limnol. Oceanogr., 25, 797, 797–806.

Ku W. C., DiGiano F. A., Feng T. H., 1978, *Factors affecting phosphate adsorption equilibria in lake sediments,* Water Research Oxford, 12, 1069–1074.

Larsen B., Brügman L., 1991, *Phosphorus accumulation in the sediments of the Baltic Sea,* [In:] *Pollution studies in the Baltic Sea sediments,* M. Perttila and L. Brügman (eds.), ACMP 15, 111–123.

Love L. G., 1967, *Early diagenetic iron sulphide in recent sediments of the Wash (England),* Sedimentology, 9, 327–352.

Niemistö L., Tervo V., Voipio A., 1978, *Storage of iron and phosphorus in the sediments of the Bothnian Sea,* Finnish Mar. Res., 244, 36–41.

Nowacki J., 1980, *The importance of the sunken strait in the water exchange in Puck Bay,* Ph. D. Thesis, Univ. of Gdańsk, (in Polish).

Robbins J. A., Gustinis J., 1967, *A squeezer for efficient extraction of pore water from small volumes of anoxic sediment,* Limnol. Oceanogr., 21, 905–909.

Rosenberg R., Elmgren R., Fleicher S., Jonsson P., Persson G., Dahlin H., 1990, *Marine eutrophication case studies in Sweden,* Ambio, 3, 102–108.

Ryden J. C., McLaughlin J. R., Syers J. K., 1977, *Mechanism of phosphate sorption by soils and hydrous ferric oxide gel,* J. Soil Sci., 21, 353–358.

Syers J. K., Curtin D., 1988, *Inorganic reactions controlling phosphorus cycling,* [In:] *Phosphorus cycles in terrestial and aquantic ecosystem. Regional workshop 1: Europe,* E. Tissen (ed.), Univ. of Saskatchewan, Saskatoon Canada, 17–29.

Trimonis E. S., Wypych K., Kępińska U., 1987, *Razpredeleniye i sostav sovremennykh osadkov,* [In:] *Protsesy osadkonakopleniya v Gdanskom Basseyne (Baltiyskoye more),* E. M. Emelyanov and K. Wypych (eds.), Akademiya Nauk SSSR, Moskva, 99–149.

Trzosińska A., Pliński M., Rybiński J., 1989, *Hydrochemical and biological characteristics of the Polish coastal zone of the Baltic Sea,* Stud. Mater. Oceanol., 54, 5–70, (in Polish).

Yoshida T., 1981, *Mathematical model of phosphorus release from lake sediment,* Verb. int. Ver. Limnol., 21, 268–274.