

**Transformations
and release of
phosphorus forms at the
sediment–water interface
in the Pomeranian Bay
(southern Baltic)***

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Abstract

A laboratory chamber experiment was carried out to estimate the release of phosphate from sediments to water. The phosphate thus released originated almost exclusively from the mineralisation of organic matter. Since the release took place between the fifth and the tenth day of the experiment, the compounds undergoing mineralisation were most probably proteins, aminoacids or lipids, whose decomposition times are of the order of several days to several weeks.

Principal component analysis (PCA) was applied to determine the similarities and differences in the chemical composition of the surface sediments of the Pomeranian Bay. The study area can be divided into three subregions based on PCA. The first is the estuarine region A with a distinct station located next to the Świna River estuary; the second is the central Pomeranian Bay (region B),

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and the third is the deep region C, with a distinct subregion in the vicinity of the Sassnitz Deep.

The phosphorus flux from sediments to water was estimated at 14×10^3 t per year, but was balanced by the deposition flux of organic matter. Phosphorus deposition and release at the sediment-water interface in the Pomeranian Bay therefore play a crucial role in qualitative transformations of the phosphorus compounds, although Pomeranian Bay sediments may not be important as a source or sink of phosphorus compounds.

1. Introduction

The sediment–water interface is a boundary layer between two different environments, where all physical, chemical and biological processes become more intensive. This is also the site where gradients in physical and chemical properties are the greatest and where many chemical compounds cease their cycling in the environment (Santschi *et al.* 1990).

The cycling of chemical substances (*e.g.* phosphorus compounds) between the sediments and near-bottom water is a very complicated process, and its complexity arises mainly from the impact of a number of physical, chemical and biological factors. To a high degree these factors are decisive with respect to either phosphorus release or to phosphorus accumulation in sediments. Among the most important factors affecting phosphorus exchange at the water–sediment interface are the salinity of near-bottom water (Balls 1992, Bolalek 1992, Lebo *et al.* 1994), oxidation-reduction potential (Engvall 1973, Holm 1978), and pH (Boström *et al.* 1988, Seitzinger 1991). The content of Ca, Fe and Al in the sediments is also of importance as these elements bind with phosphates and increase sorption (Kajak 1994). The organic matter content affects phosphorus cycling quite differently; its mineralisation leads to a decrease in the redox potential and in consequence increases phosphate release from sediments (Holm 1978).

The main aim of the study was to estimate the release of phosphorus from the sediments of the Pomeranian Bay and to investigate the mechanisms by which phosphorus forms are transformed in the sediments.

2. Region of study

The Pomeranian Bay is located at the western end of the Polish coast. It stretches from the Słowiński Littoral in the east to the shores of the islands of Wolin, Uznam and Rügen in the west (Fig. 1). In the north-west, the Bay is open and its waters can flow freely to the Arkona Deep region. In the north and east, the Bay is partly separated from the Bornholm Deep by the Odra Bank and a long underwater sandbar linking the Odra Bank and with the Mrzeżyno region. The Pomeranian Bay covers an area of nearly 6000 km², and contains 73 km³ of water. Its mean depth is 13 m (Majewski 1972).

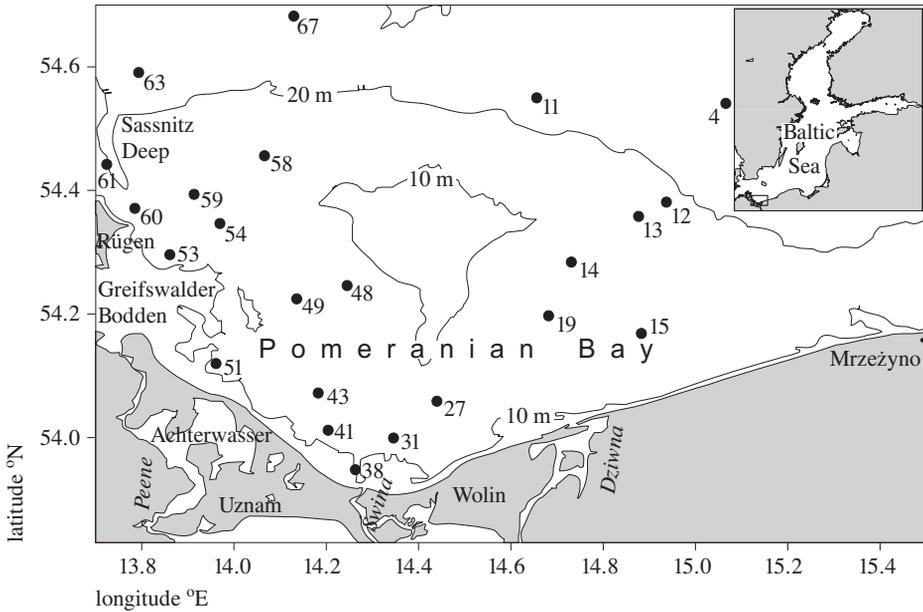


Fig. 1. Study area and location of sampling stations

The bottom of the Bay is mostly covered with fine grey sand. There is white sand, as well as streaked and red sand on the northern slopes of the Odra Bank. The sediments at the mouth of Świna river are also poorly diversified. Fine sands with admixtures of coarser fractions and a certain amount of organic matter can be found there. The finest fractions with admixtures of silts occur in the vicinity of the Świna estuary and off the coast of the Bay east of the estuary. The north-western part of the Bay, the Sassnitz Deep, also includes areas covered with fine fractions (Majewski 1974).

Phosphorus in the Odra (Oder) is dominated by particulate and dissolved organic forms (Grelowski & Pastuszak, 1996). Between 1988 and 1994, the annual loads of phosphates ranged from 1648 to 3259 t year⁻¹, while total phosphorus loads ranged from 4500 to 8383 t year⁻¹.

3. Materials and methods

Samples were collected from on board the r/v 'Baltica' in March and July 1996 and in May and October 1997 using a Reineck box sampler. All sediment cores were divided into 2.5 cm segments, placed in plastic containers and frozen at -20°C until analysis. Both the pH and the redox potential (Eh) of the sediments were measured immediately after sampling using an Eijkelkamp pH-meter. The salinity and temperature of near-bottom

water were measured with a CTD Neil Brown Mark III probe. Sediment cores and water samples were taken at 23 stations in the Pomeranian Bay (Fig. 1).

The organic matter content was estimated from losses on ignition to constant mass (about 6 hours) at 550°C. Grain size was analysed using a sieving machine (sieve mesh sizes: 2.000, 1.000, 0.500, 0.250, 0.125 and 0.063 mm).

Total phosphorus in the sediments was determined using a method developed by Gericke & Kurmies (1952), and modified by Golachowska (1977a). In this method, the sediment sample is dissolved in a mixture of perchloric and sulphuric acids. Following filtration total phosphorus is determined by the molybdenum yellow method. The reproducibility of results for total phosphorus in sediments among the replicated sediment samples was satisfactory (the relative standard deviation for 10 samples was < 8%).

Total inorganic phosphorus was determined using a method developed for soils by Mehta *et al.* (1955), modified by Golachowska (1977b). The organic phosphorus content was calculated as the difference between total phosphorus and total inorganic phosphorus. Speciation of inorganic phosphorus was carried out using a method developed for soils by Chang & Jackson (1957), adapted for bottom sediments by Golachowska (1977c). The method is based on sequential extractions of the sediment to produce four forms of inorganic phosphorus: loosely sorbed phosphorus ($\text{NH}_4\text{Cl-P}$), phosphorus bound to aluminium ($\text{NH}_4\text{F-P}$), phosphorus bound to iron (NaOH-P) and phosphorus bound to calcium ($\text{H}_2\text{SO}_4\text{-P}$).

The contents of organic carbon and organic nitrogen in the sediments were determined by means of a CHN autoanalyser (PERKIN ELMER 2400 series). The samples for analysis were dried to constant mass and homogenised, after which calcium carbonate was removed (Hedges & Stern 1984).

The interstitial water samples were obtained from the sediments by centrifuging them at 4000 rpm in test tubes containing gaseous nitrogen. The samples thus obtained were then analysed for sulphate (Hermanowicz *et al.* 1976).

An attempt was made to estimate the release of phosphate from sediments to water by using the modified method elaborated by Schippel *et al.* (1973). Each 0–2 cm sediment segment was placed in a separate container with a bottom area of 0.012 m². Afterwards the container was filled with near-bottom seawater (1.6 dm³). The seawater was taken from the same station as the sediment sample. The incubation temperature was about 18°C and the boxes were kept in a dark place. Once every two or

three days the phosphate concentration and redox potential in water were determined. The experiment was continued for over three weeks because, according to Carman & Wulff (1989), that period of time is necessary for the phosphates absorbed by the sediments and those dissolved in water to reach a state of equilibrium.

4. Results and discussion

Spatial differentiation of surface sediments (0–2.5 cm)

The surface sediments in the Pomeranian Bay are mainly fine sands. Silty sands occur only in the region of the Świna estuary and in a small area in the western part of the Bay. There are clay and silty sediments solely north of Rügen, in the Sassnitz Deep area.

Owing to the sandy nature of the Pomeranian Bay sediments, their humidity and loss on ignition (LOI) are low. The highest humidity and LOI were reported in the surface sediments of the north-west part of the Bay close to Rügen (humidity > 60%, LOI > 7.5%) and in the Świna estuary. These two parameters were the lowest for the sediments from the central part of the Bay.

Total phosphorus content (P_{tot}) of the surface layer of Pomeranian Bay sediments ranged from $0.050 \text{ mg g}^{-1} \text{ d.w.}$ to $0.700 \text{ mg g}^{-1} \text{ d.w.}$ P_{tot} levels were highest in sediments from the western part of the Bay off Rügen ($0.700 \text{ mg g}^{-1} \text{ d.w.}$) and from the Świna estuary (*ca* $0.400 \text{ mg g}^{-1} \text{ d.w.}$). Relatively high values were also recorded in the north-eastern part of the basin ($> 0.300 \text{ mg g}^{-1} \text{ d.w.}$). Phosphorus levels were lowest in the central part of the Bay ($< 0.150 \text{ mg g}^{-1} \text{ d.w.}$ – Frankowski *et al.* in press).

Principal Components Analysis (PCA) was applied to determine the similarities and differences in the chemical composition of the sediments from different regions of the Pomeranian Bay. The *Factor Analysis* module of the STATISTICA software package by Statsoft was used for this purpose.

PCA is a statistical procedure facilitating the understanding of complex multiparameter processes. It enables the number of variables describing the processes examined to be reduced, usually to two or three. A smaller number of variables gives a better insight into the nature of the process (Dolédec & Chessel 1990, Jajuga 1993, Maksymowska 1998). The following ten parameters (Fig. 2) describing the composition of the sediments and the interstitial waters were used for the PCA: calcium-bound phosphorus ($\text{H}_2\text{SO}_4\text{-P}$), iron-bound phosphorus (NaOH-P), aluminium-bound phosphorus ($\text{NH}_4\text{F-P}$), loosely bound phosphorus ($\text{NH}_4\text{Cl-P}$), organic carbon (C_{org}), the molar ratio of organic carbon to organic nitrogen (C/N), losses on ignition (LOI), redox potential of the sediments (Eh), pH of the sediments, and sulphate concentration in the interstitial waters (SO_4^{2-}).

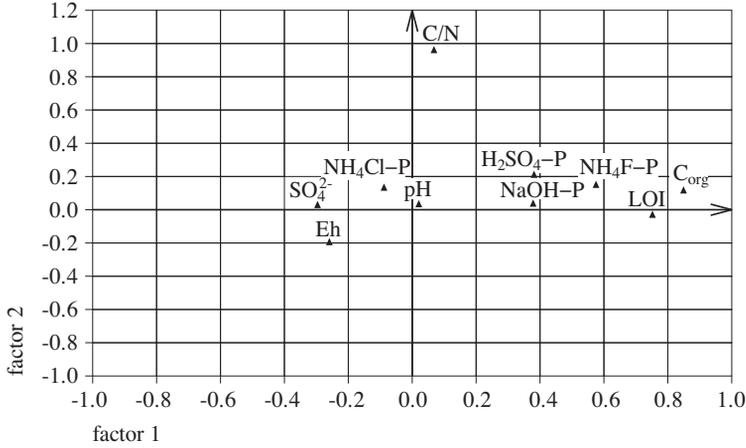


Fig. 2. Location of variables on the map of principal factors

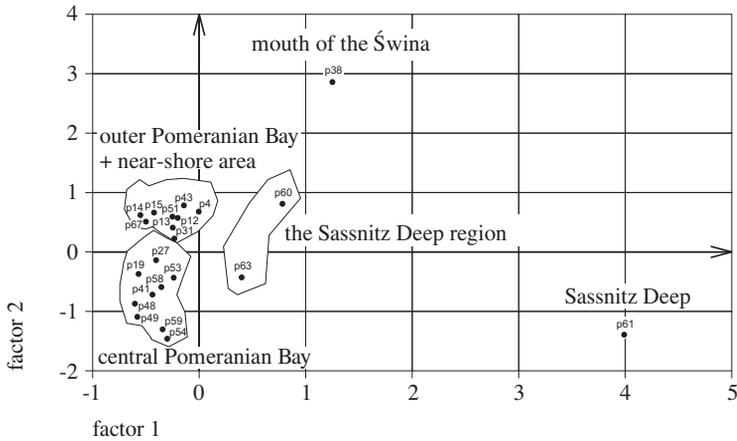


Fig. 3. Location of stations on the map of principal factors

The location of stations on the map of principal factors (Fig. 3) demonstrates that the Pomeranian Bay surface sediments are quite uniform with respect to their chemical composition and origin of organic matter. Only the sediments from the Sassnitz Deep area (stations 60, 61 and 63) and the Świna estuary (station 38) are significantly different. The remaining stations are grouped along the principal factor axis in two areas. The first one includes the stations located in the central Pomeranian Bay (stations 19, 27, 41, 48, 49, 53, 54, 58 and 59), the second covers the estuarine stations (31, 43 and 51) and those located on the edges of the Bay (4, 12, 13, 14, 15 and 67). These areas differ mainly with respect to the value of the second

principal component. This means that sediments from the stations in the two areas differ mainly with respect to the origin and degree of mineralisation of the organic matter, although there are also differences in the chemical composition.

On the basis of PCA of the chemical composition of the surface sediments, the Pomeranian Bay can be divided into three characteristic regions (Fig. 4):

- the estuarine region A with a distinct station located next to the Świna estuary;
- the central Pomeranian Bay (region B) characterised by the lowest values of all phosphorus forms analysed;
- the deep region C, with a distinct subregion in the vicinity of the Sassnitz Deep.

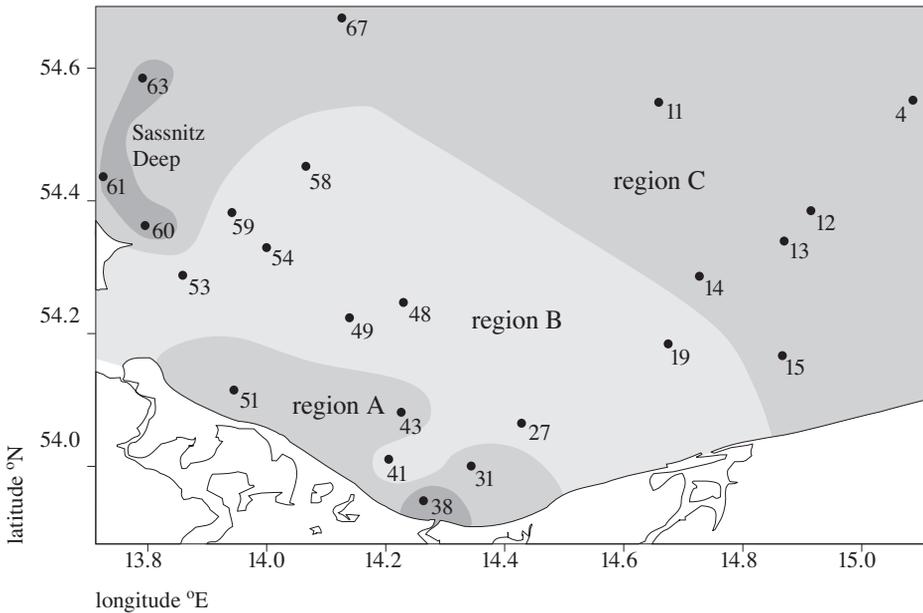


Fig. 4. Zonation of the Pomeranian Bay on the basis of PCA analysis

Phosphate release from sediments to water

Example results obtained in a laboratory chamber experiment for sediments collected in May 1997 are presented in Fig. 5. The largest increase in phosphate concentration in water coincided with a short-term decrease in the redox potential. Several days afterwards the Eh increased significantly

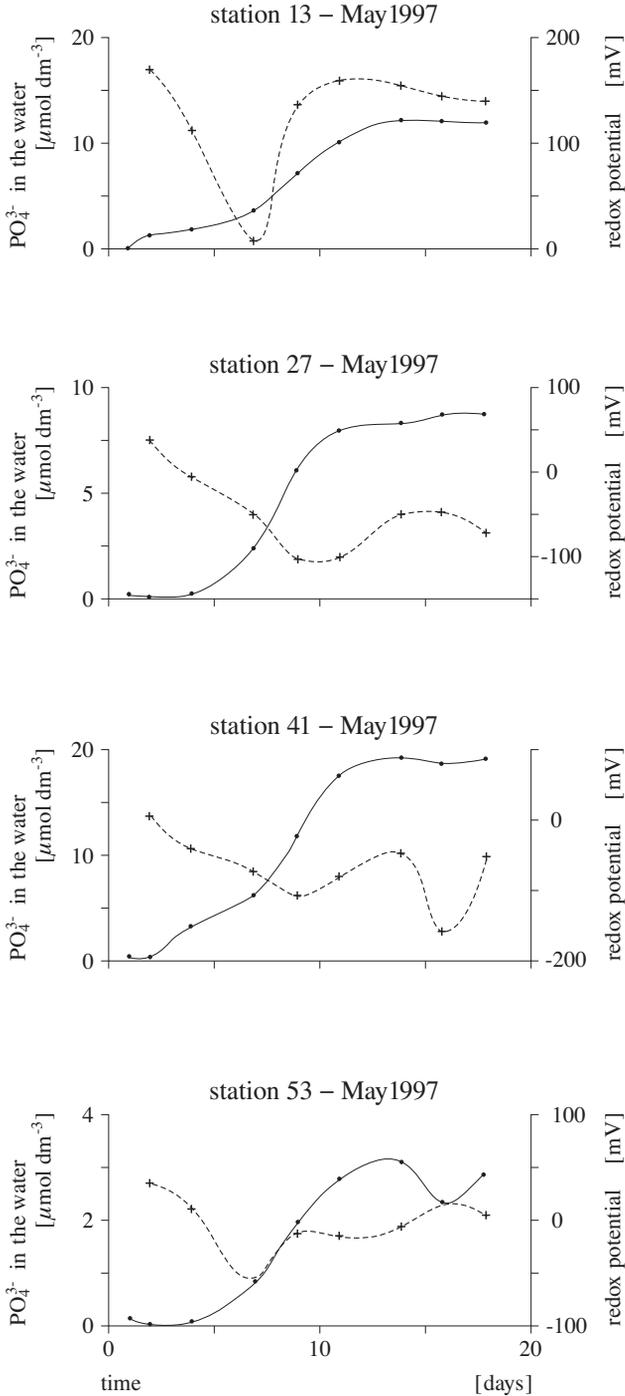


Fig. 5. Changes in phosphate concentrations PO_4^{3-} (continuous lines) and redox potential Eh (dashed lines) during the laboratory chamber experiment

and equilibrium was established between the phosphate ions dissolved in water and sorbed by the sediment. This seems to indicate that mineralisation of organic matter in the sediments took place during the experiment. The fastest phosphate release and the greatest changes in the redox potential occurred most probably when the rate of mineralisation of the sediment organic matter was the highest. As these processes took place between the fifth and tenth day of the experiment, the compounds undergoing mineralisation were most probably proteins, aminoacids or lipids, whose decomposition rates are of the order of several days to several weeks (Deming & Baross 1993, Macko *et al.* 1993, Wakeham & Lee 1993). Mineralisation of lignin, cellulose or chitin takes much longer – from several months to several years (Henrichs 1993, Macko *et al.* 1993, Summons 1993), so could not be observed during the experiment.

In addition, the changes in the content of phosphorus forms in the sediment samples collected in May and October 1997 were investigated during the chamber experiment. Total phosphorus and inorganic phosphorus forms were determined in the sediment samples collected prior to the beginning and after the completion of the chamber experiment. Fig. 6 shows the mean relative changes in the content of phosphorus forms in the samples examined.

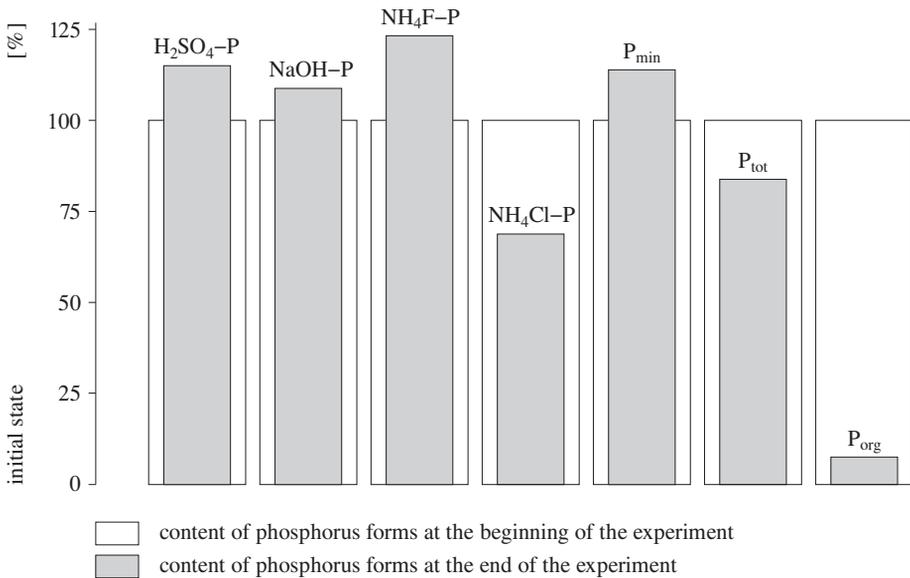


Fig. 6. Relative changes in the content of the phosphorus forms in the sediments during the experiment

Total phosphorus decreased during the experiment by an average of 16%. It follows from the chart that the phosphates released from the sediment to water during the experiment were derived almost exclusively from the mineralisation of the organic matter. Organic phosphorus was reduced to 8% of its initial value, and in eight cases out of ten it was completely exhausted. On the other hand, concentrations of inorganic phosphorus forms in the sediments altered very little (except for the loosely bound phosphorus). Calcium-, iron- and aluminium-bound phosphorus, as well as total inorganic phosphorus, increased slightly compared to the initial state.

Holm & Linstrom (1980) also noted the importance of organic matter in the processes leading to phosphorus transfer from the sediment to water. They found a linear relationship between the rate of phosphates liberated from the sediment to water and the amount of fresh organic matter added to the sediments. In closed chamber systems, equilibrium was reached after 3 weeks at the most, when all the organic matter in the sediments was exhausted.

The results obtained were used to estimate the fluxes of phosphates at the water-sediment interface in the Pomeranian Bay. The fluxes were estimated, taking into account the surface area of the bottom of the chamber used in the experiments, the differences between the initial and final phosphate concentrations, and the number of days required to

Table 1. Mean values of phosphate fluxes from sediments to water [$\mu\text{mol m}^{-2} \text{day}^{-1}$] and total release of phosphorus [tonnes of P] in the four periods analysed on the basis of a laboratory chamber experiment (incubation temperature 18°C)

Phosphate fluxes from sediments to water [$\mu\text{mol m}^{-2} \text{day}^{-1}$]							
March 1996		July 1996		May 1997		October 1997	
<i>n</i>	$\frac{\text{min-max}}{\text{mean}}$	<i>n</i>	$\frac{\text{min-max}}{\text{mean}}$	<i>n</i>	$\frac{\text{min-max}}{\text{mean}}$	<i>n</i>	$\frac{\text{min-max}}{\text{mean}}$
12	$\frac{20-531}{220}$	12	$\frac{18-566}{207}$	11	$\frac{19-555}{204}$	6	$\frac{28-488}{192}$
Phosphate release [tonnes of phosphorus] from sediments to water							
winter		summer		spring		autumn	
3.7×10^3		3.5×10^3		3.5×10^3		3.3×10^3	

min – minimum value, max – maximum value, *n* – number of samples

reach equilibrium between the phosphate ions sorbed by the sediment and dissolved in water. The fluxes differed very significantly depending on the sampling site and the season, their values ranging from a few to over $500 \mu\text{mol m}^{-2} \text{ day}^{-1}$ (Table 1). The largest values were recorded for sediments from the north-west part of the Bay, the estuarine region, as well as the east and south-east peripheries of the basin. Sediment-water phosphate transfer was less efficient in the central part of the Pomeranian Bay (Fig. 7).

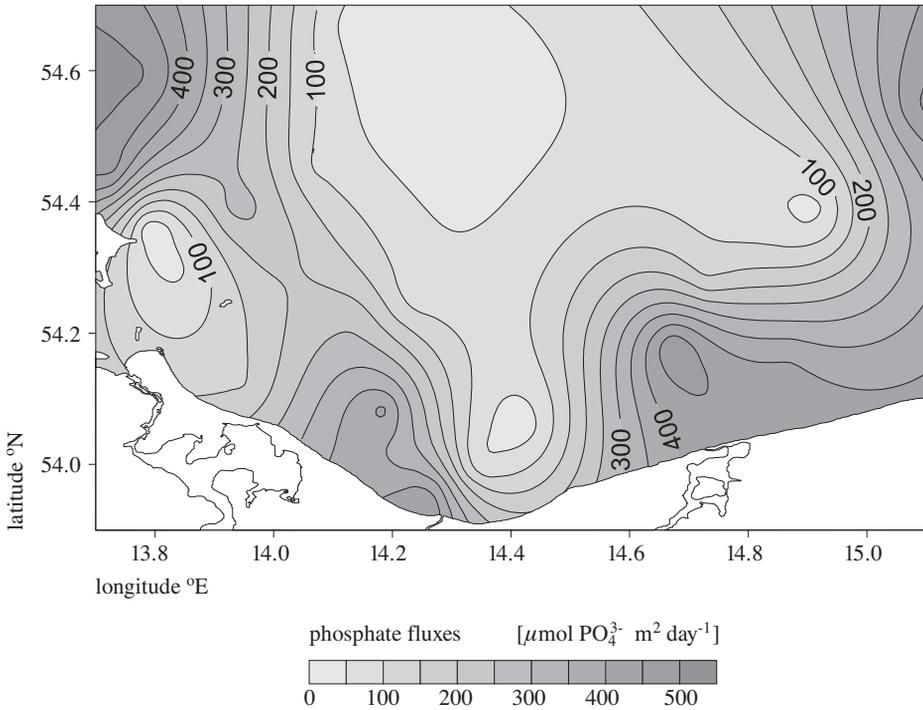


Fig. 7. Phosphate fluxes from sediment to water calculated on the basis of the laboratory chamber experiment

It is therefore evident that transfer of phosphate from the sediment to water in the Pomeranian Bay is continuous. The results of the chamber experiment were used to estimate the total amount of phosphorus liberated from the sediment to water (Table 1). The estimations were based on the assumption that the results obtained were representative of a given season (March 1996 – winter, July 1996 – summer, May 1997 – spring, October 1997 – autumn). Each season was assumed to last for 91 days and that the surface area of Pomeranian Bay is $6\,000 \text{ km}^2$. All the experiments were carried out at a temperature of 18°C .

It follows from the calculations (Table 1) that the total phosphorus transfer from the sediment to water is *ca* 14×10^3 tonnes per year. Such high fluxes from the sediment to water would have to result in a rapid depletion of phosphorus compounds in the sediments. However, nothing of the kind has been observed (Table 2). This can only be explained by a continuous influx of organic matter to the sediment. It follows from the data obtained that the highest total phosphorus levels in the sediments were generally observed in July 1996. Processes leading to phosphorus accumulation in the sediment must have prevailed in this period.

Table 2. Mean concentrations of total phosphorus in the surface sediments of the Pomeranian Bay in the four periods analysed [mg g^{-1} d.w.]

Mean concentrations of P_{tot} in the surface sediments [mg g^{-1} d.w.]							
March 1996		July 1996		May 1997		October 1997	
<i>n</i>	$\frac{\text{min-max}}{\text{mean}}$	<i>n</i>	$\frac{\text{min-max}}{\text{mean}}$	<i>n</i>	$\frac{\text{min-max}}{\text{mean}}$	<i>n</i>	$\frac{\text{min-max}}{\text{mean}}$
12	$\frac{0.124-0.426}{0.228}$	12	$\frac{0.094-0.754}{0.259}$	11	$\frac{0.079-0.650}{0.171}$	6	$\frac{0.087-0.296}{0.201}$

min – minimum value, max – maximum value, *n* – number of samples

The annual flux of phosphates from the sediment to water in the Pomeranian Bay is very large (14×10^3 t P per year). This is over twice as high as the phosphorus discharge to the Szczecin Lagoon with the waters of the Odra. In 1988–1994 the total phosphorus discharge from the Odra ranged from *ca* 5000 to 8383 t year⁻¹ (6000 t year⁻¹ on average). In the same period, the mean discharge of inorganic phosphorus was *ca* 2000 t year⁻¹, hence organic phosphorus was dominant in the Odra, its discharge being approximately 4000 t year⁻¹ (Grelowski & Pastuszak 1996). It can be assumed that most of this amount is transferred to the Bay. Compared to these loads, the amount of phosphorus that reaches the Pomeranian Bay with wet and dry precipitation is relatively small – 88 t year⁻¹ (Forsberg 1991).

However, the cycling of phosphorus compounds at the sediment-water interface does not significantly affect the abundance of this element in the basin or the sediment. It can therefore be stated that phosphorus exchange at the water-sediment interface plays a crucial role in qualitative transformations of the phosphorus compounds in the Pomeranian Bay. Phosphorus reaching the sediments from the aqueous phase is mainly

organic phosphorus, originating from terrigenous or autochthonous organic matter. Organic phosphorus compounds undergo microbial mineralisation in the sediments, followed by a slow release in the form of phosphate to the interstitial waters, and later to the near-bottom waters of the Bay.

This large amount of inorganic phosphorus originating from the sediments (about $14 \times 10^3 \text{ t year}^{-1}$), together with the inorganic phosphorus reaching the Bay with the Odra waters via the Szczecin Lagoon (*ca* $2 \times 10^3 \text{ t year}^{-1}$), replenishes the supply of phosphate gradually consumed in the water as a result of primary production. The mean annual potential primary production in the Pomeranian Bay was estimated on the basis of the papers by Ochocki *et al.* (1999) and Witek *et al.* (1997) to be 70–75% of the Gulf of Gdańsk primary production, *i.e.* $168 \text{ gC m}^{-2} \text{ year}^{-1}$. On the basis of the Redfield formula (1958) and assuming the total surface area of the Pomeranian Bay to be 6000 km^2 , it was calculated that 25 000 t of organic phosphorus per year is formed in the Bay as a result of primary production.

The results obtained indicate that phosphorus deposition and release at the sediment – water interface in the Pomeranian Bay is extremely important in terms of qualitative transformations of phosphorus compounds. Vast amounts of organic phosphorus settle at the bottom of the Pomeranian Bay, where they undergo mineralisation, after which vast amounts of phosphate phosphorus are released. On the other hand, Pomeranian Bay sediments may not be important as a source or sink of phosphorus compounds. In other words, the Pomeranian Bay is a region where phosphorus compounds are transformed rather than accumulated.

5. Conclusions

- The Pomeranian Bay can be divided into three characteristic regions based on the principal component analysis of the chemical composition of the sediments. The first is the estuarine region A with a distinct station located next to the Świna estuary; the second is the central Pomeranian Bay (region B), and the third is the deep region C, with a distinct subregion in the vicinity of the Sassnitz Deep.
- The phosphate released from sediments to water during the experiment originates almost exclusively from the mineralisation of organic matter. As this release takes place between the fifth and the tenth day of the experiment, the compounds undergoing mineralisation are most probably proteins, aminoacids or lipids, whose decomposition times are of the order of several days to several weeks.

- The phosphorus flux from sediments to water was estimated at 14×10^3 t per year, but it was balanced by the deposition flux of organic matter. It can be stated that phosphorus deposition and release at the sediment–water interface in the Pomeranian Bay plays a crucial role in the qualitative transformation of the phosphorus compounds, but the Pomeranian Bay sediments may not be important as a source or sink of phosphorus compounds

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