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Original Research Paper

Interdependence between phosphorus forms in sediments and iron in interstitial waters in the Gulf of Gdańsk

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Abstract

The content of various phosphorus forms in sediments and the content of iron in interstitial waters were measured in sediment samples collected in the Gulf of Gdańsk in March 2001. The studies showed that the greatest amounts of the total phosphorus and total dissolved iron were present in the uppermost sediment layer, and their respective concentrations ranged from 203.99 μmol g^{-1} d.w. to 1894.02 μmol g^{-1} d.w., and from 0.02 μmol dm^{-3} to 4.68 μmol dm^{-3}. The contents of these parameters were directly connected with the type of sediment – the greatest concentrations were measured in fine sediments. The analysis of multiple correlation coefficients demonstrated that in over 90% of cases the concentration of phosphorus bound with iron depended on: the sediment type and its humidity, the content of organic matter, and the concentration of the total iron dissolved in the interstitial waters.

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INTRODUCTION

Both phosphorus and iron play a very important role in the environment (Graca and Bolałek 2000, Hay 1990), because these elements are essential as electron acceptors in oxidation/reduction processes taking place during organic matter degradation in sediments and in near-bottom waters (Lovley et al. 1991). Iron plays an essential role in photosynthesis and it has been suggested to be a potential factor limiting phytoplankton production in high-nutrient, low-chlorophyll areas of the oceans (Liu and Millero 2002, Santana-Casiano et al. 2000). In phytoplankton, Fe is required more than any other trace element as it plays a role in nitrogen acquisition, chlorophyll synthesis, oxygen cycling, and sulphate reduction (Gobler et al. 2002). Phosphate concentrations, as well as their seasonal patterns in the photic zone of coastal seas and open oceans, are greatly affected by processes taking place in sediments; therefore, there is an obvious need for better understanding of phosphorus transformations in sediments (Graca and Bolałek 2000, Jensen et al. 1995, Koch et al. 2001, Williams et al. 1976). Phosphorus transformations in sediments encompass its numerous forms because this element may form complexes with calcium, iron, aluminium, may be adsorbed on mineral particles, or may occur in various organic forms (living and dead) (Andrieux-Loyer and Aminot 2001, Koch 2001). Under certain conditions, phosphorus liberated from sediments may stimulate eutrophication (Andrieux-Loyer and Aminot 2001, Jansson 1987). Phosphorus and iron cycling in marine environment are strongly connected (Anshutz et al. 1998, Yao and Millero 1995). There are two main processes in which these elements are involved: sedimentation of iron phosphate (III) under oxic conditions, and iron reduction under anoxic conditions (Białkowska and Bolałek 2000, Golterman 1995, Slomp et al. 1995). The particular importance of the latter process consists in phosphate liberation from sediments (Fleisher et al. 1998), and in the prevention of hydrogen sulfide formation (Chapelle and Lovley 1992).

The main goal of this work was to investigate a connection between phosphorus and iron cycling in the Gulf of Gdańsk, and to find out the impact of sediment type and concentration of major constituents of interstitial water on the cycling of these two elements.

MATERIAL AND METHODS

Surface sediment samples were collected at 14 stations in the Gulf of Gdańsk in March 2001 (Fig. 1). The Nemisto corer was used for the sample collection and it was lowered from the deck of *r/v BALTICA*.

The following analyses were performed:

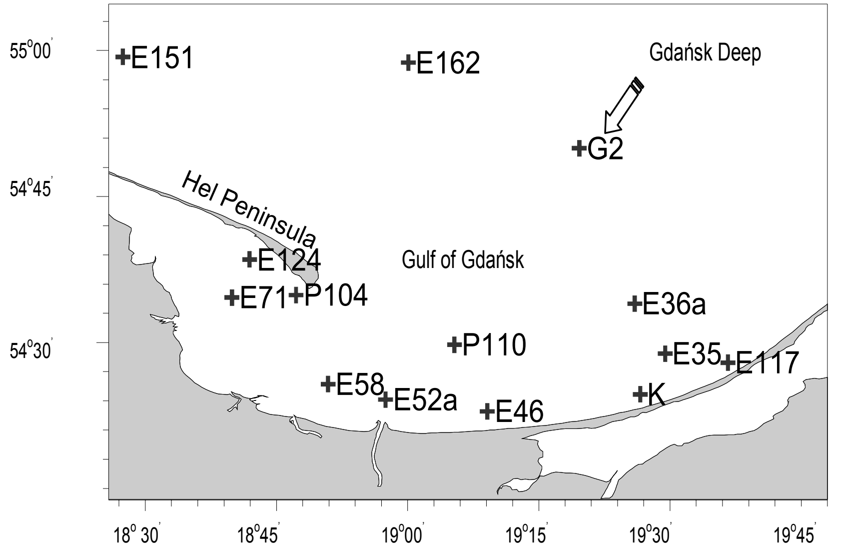

Fig. 1. Distribution of sampling sites in the Gulf of Gdańsk in March 2001.

- humidity - W (drying at 105°C to constant mass),
- sediment granulometry (sieve analysis), to separate the following fractions: fine sand, sandy mud, and mud (containing over 80% of grains, below the size of 0.063 mm),
- the loss on ignition (LOI) giving an approximate content of organic matter (ashing at 550°C to constant mass),
- iron species dissolved in interstitial waters (total, Fe^{2+}, Fe^{3+}) (Falkowska et al. 1999).
- content of hydrogen sulfide, sulfates, silicates, ammonium and phosphates in interstitial waters (Falkowska et al. 1999, Koroleff 1976).

In order to determine phosphorus in the sediments the sequential extraction was applied to 14 wet sediment samples. The following five phosphorus (P) fractions were determined:

- P loosely bound (extraction with 0.4M NaCl);
- P bound with iron (P-Fe) (extraction with bicarbonate buffered dithionite solution (pH=7.0);
- mineral forms of P adsorbed onto silt minerals or aluminium oxides (extraction with 0.1M NaOH), thus on surfaces other than those which can be provided by reducible metal oxides;
- apatite P (extraction with 0.5M HCl);
- organic P (combustion and extraction with 1M HCl);

RESULTS

Several factors affect phosphorus content in sediments including: the sediment type, the oxygen conditions in sediment and near-bottom water, organic matter content and its type, the intensity of mineralization processes, the amount of iron, calcium and aluminium in sediments and in the near-bottom water. The studies demonstrated that the highest concentrations of the total phosphorus (P_{tot}) was observed in the uppermost sediment layer (Table 1), in agreement with findings in other regions (Jensen et al. 1995, Jensen and Thamdrup 1993, Sundby et al. 1992). The highest content of various phosphorus forms, as well as the highest content of the total dissolved iron and organic matter were detected in mud-silt sediments, while the lowest contents of these parameters were measured in sandy sediments (Figs. 2 and 3). Concentrations of P_{tot} and P bound with Fe (P-Fe), determined in the surface sediment layer, ranged from 83.14 μmol g^{-1} d.w. to 1894.01 μmol g^{-1} d.w., and from 8.36 μmol g^{-1} d.w. to 169.08 μmol g^{-1} d.w., respectively (Table 1). The lowest P_{tot} concentrations in the uppermost sediment layer were observed in fine sand samples from the coastal stations (Fig. 2). The samples collected from these zones were characterized by a low content of organic matter (0.01%), their humidity reaching max. 34%.

Table 1

Average concentrations (and their ranges) of various forms of phosphorus in the sediments and of dissolved iron in the interstitial waters

Sediment layer [cm]	N	Loosely bounded P	Fe-bound P	Mineral P	Apatite P	Organic P	Total P	Total dissolved iron
		μmolP g^{-1}d.w.						μmol dm^{-3}
0-1	14	1.08-105.07	8.36-169.08	14.59-580.39	36.61-442.06	22.51-1016.36	203.99-1894.01	0.02-4.68
		26.46	50.62	230.874	168.82	348	875.72	1.16
1-2	14	0.91-12.35	1.11-73.09	12.08-391.53	22.98-188.72	12.04-525.05	66.02-1016.13	0.00-4.30
		5.03	29.02	138	92.58	208.54	451.18	0.93

N – number of samples analyzed

The highest P_{tot} concentrations were noted in silt and mud sediments of the Gulf of Gdańsk (Fig. 2). Those sediments were characterized by high humidity (93%) and a high organic matter content (0.22%). The highest concentrations of phosphorus bound with iron were found in the sediments in the eastern part of

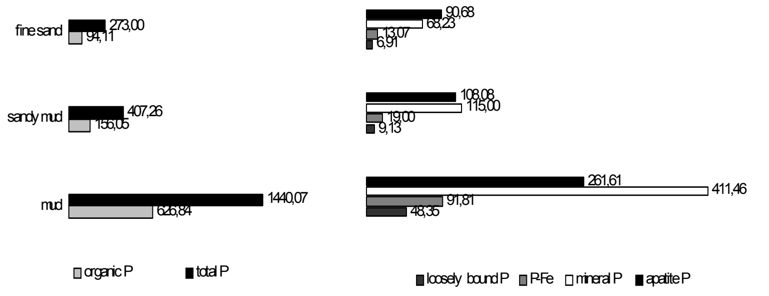

Fig. 2. Content of various phosphorus forms [µmolP g^{-1} d.w.] in different types of sediments collected in the Gulf of Gdańsk.

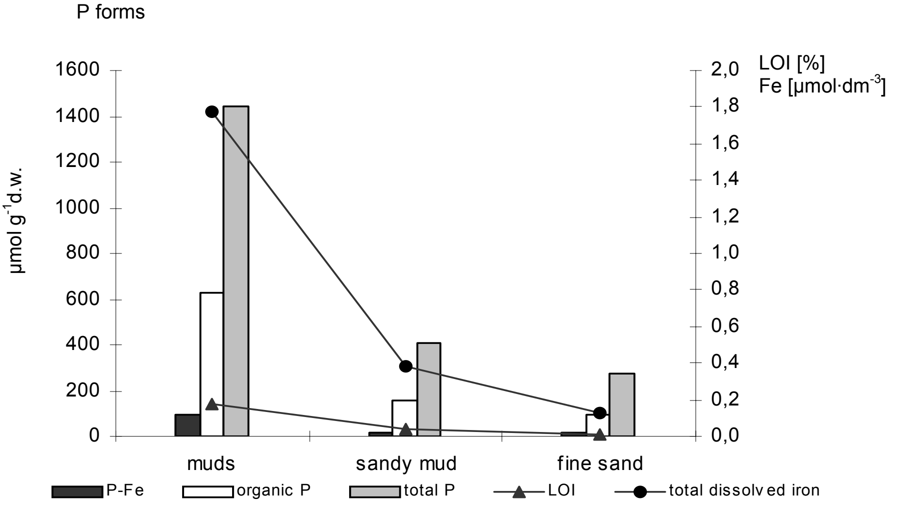

Fig. 3. Content of parameters analyzed in various types of the sediment.

the Gulf of Gdańsk and at two stations located close to the tip of the Hel Peninsula (Fig. 1). The humidity of mud and silt sediments ranged from 66% to 86%, while the organic matter content varied from 0.11% to 0.19%. The maximum concentrations of P bound with Fe in these regions were accompanied by high concentrations of the total dissolved iron (up to 4.68 µmol dm^{-3}), organic phosphorus (up to 603.65 µmol g^{-1} d.w.), sulfates (on average 232.63 µmol dm^{-3}), phosphates (on average 18.43 µmol dm^{-3}), and ammonium (on average 139.72 µmol dm^{-3}). Hydrogen sulfide was not found in these regions. The lowest content of P-Fe was measured in sandy sediments from the coastal stations.

DISCUSSION

The obtained average P_{tot} concentrations (varying from 451.18 μmol g^{-1} d.w. to 875.72 μmol g^{-1} d.w.) are nearly two orders of magnitude higher than those reported for other regions. Maximum P_{tot} concentrations measured in the Aarhus Bay amounted to 60 μmol g^{-1} d.w. (Jensen et al. 1995), in the Kattegat and Skagerrak – 25 μmol g^{-1} d.w. and 34 μmol g^{-1} d.w., respectively (Jensen and Thamdrup 1993), and in the St. Lawrence Bay - 55 μmol g^{-1} d.w. (Sundby et al. 1992).

Similarly, concentrations of phosphorus bound with iron, measured in the surface layer of the Gulf of Gdańsk, and amounting to (50-60) μmol g^{-1} d.w., were also higher compared with the results from other regions [in the St. Lawrence Bay – 22.4 μmol g^{-1} d.w., (Sundby et al. 1992), in the Kattegat and the Skagerrak – from 9.5 to 16 μmol g^{-1} d.w., (Jensen and Thamdrup 1993), in the Aarhus Bay – 30 μmol g^{-1} d.w., (Jensen et al. 1995)].

The Gulf of Gdańsk is a water-body that is under strong anthropogenic influence. The most pronounced pressure is due to nutrient loads coming mainly from the Vistula River. The input of the total phosphorus (7000 t y^{-1}, on average for the 1993-1998 period) consists of 19% of the total riverine discharge into the Baltic Sea (Andrulewicz and Witek 2002). The Gdansk Deep, with a maximum depth of 118 m, acts as a sink for locally-produced, suspended matter as well as particles carried in by the Vistula and other land sources. Due to its significant depth and permanent water stratification, the Gdansk Deep can be classified as an accumulation bottom (Andrulewicz and Witek 2000). Therefore, the highest concentration of P was observed at the station located in the Gdansk Deep. Concentrations of the total iron in the surface sediment layer ranged from 0.02 μmol dm^{-3} to 4.68 μmol dm^{-3} (Table 1), with the minimum values found in the sandy sediments, while the maximum ones in the mud and silt sediments (Fig. 3). Concentrations of iron (II) fluctuated from 0.01 μmol dm^{-3} to 4.67 μmol dm^{-3}, while concentrations of iron (III) in the uppermost sediment layer ranged from 0.01 μmol dm^{-3} to 0.20 μmol dm^{-3} (Table 2). An increase in the sediment depth was followed by a decrease in sediment humidity and an ignition loss (the latter being an approximate measure of organic matter content), and by an increase in nearly all concentrations of chemical compounds measured (sulfates were an exception) (Table 2). An application of multiple correlation showed several interdependencies among the parameters analyzed. It was possible to state that:

- in 92.5% of the samples, the concentration of P bound with Fe depended on: the sediment type and its humidity, organic matter content expressed as LOI; in 90.3% of the samples, the concentration of P bound with Fe depended on the total Fe dissolved in interstitial waters,
- in 88.4% of the samples, concentrations of the total Fe depended on: P_{tot} concentrations, organic matter content, and the content of P bound with Fe, while in 66% of the samples, it depended on: the sediment humidity, phosphate and ammonium concentrations in interstitial waters.

The percentage of nearly all forms of phosphorus was the highest in silt and mud sediments (Table 3); only apatite phosphorus showed the highest content in fine sands. The results obtained indicate that concentrations of phosphorus and

Table 2

Outcome of statistical analyses of the chemical results

Sediment layer	N	LOI	W	Fe(II)	Fe(III)	Hydrogen sulfide	sulfates	phosphates	ammonium	silicates
[cm]		%		μmol dm^{-3}						
0-1	14	0,00-0,23	0,22-0,94	0,01-4,67	0,01-0,20	0,00-4,44	41,66-385,31	1,05-45,71	7,45-286,27	25,41-334,74
		0,12	0,58	1,20	0,04	0,52	175,45	14,54	96,84	137,34
1-2	14	0,00-0,19	0,22-0,90	0,00-3,81	0,00-0,49	0,00-11,23	46,90-374,82	1,74-100,85	16,54-481,68	23,78-507,77
		0,11	0,53	0,86	0,07	9,59	158,09	32	158,15	213,36

N – number of samples analyzed

Table 3

Percentage contribution of various phosphorus forms in different types of sediments in the Gulf of Gdańsk

Sediment type	N	Loosely bounded P	Fe-bound P	Mineral P	Apatite P	Organic P
mud	14	3,36	6,38	28,57	18,17	43,53
sandy mud	14	2,24	4,67	28,24	26,54	38,32
fine sand	14	2,53	4,79	24,99	33,22	34,47

N – number of samples analyzed

its various fractions were related to the sediment type, which in turn changes with the depth of the region studied. The sediment spatial variability follows the general sedimentation law for big water reservoirs, and according to this law the diameter of grains declines with the depth. The content of P-Fe was higher in silt and mud than in other sediments, and it is probably connected with the fact that fine-grain sediments have a greater sorption capacity caused by the presence of silt minerals and by a greater content of organic matter (Sundareshwar and Morris 1999). It is known that organic matter forms complex compounds with silt minerals and that these are very resistant to degradation and therefore they accumulate in fine-grain sediments. That is the main reason why the content of organic phosphorus, an integral component of organic matter, remains in close connection with the lithological type of sediment (Table 1 and 3, Fig. 2).

CONCLUSIONS

The results obtained indicate that phosphorus and iron concentrations are closely connected with each other. Concentrations of these elements also depend on numerous physical and chemical parameters of sediment, and that proves strong interdependence in cycling of these elements in marine environment. Concentrations of various forms of phosphorus and iron were the highest in the uppermost sediment layer. The content of the analyzed parameters was closely connected with the sediment type, and the highest P and Fe concentrations were found in the finest sediments.

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