

# Transformation of Phosphorus in the Wadden Sea: Apatite Formation

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## Summary

Between February 1992 and June 1993 the distribution of particulate and dissolved phosphorus in the Ems estuary was investigated in approximately monthly intervals. Furthermore, the phosphorus content of sediments was assessed. These data as well as literature data were used to construct a phosphorus budget of the Ems estuary. Fluxes were dominated by the particulate fraction representing 77% of the total phosphorus input. 40% of the phosphorus input is lost to the sediment. In suspended matter from the coastal zone and from rivers, organic and iron-bound phosphorus dominate (>75%). Within the sediments phosphorus is mainly associated with calcium minerals like apatites (65%). The presence of authigenic apatites was confirmed with a sequential extraction method. Combination of the phosphorus budget with the data on the composition of particulate phosphorus shows that the organic and iron bound phosphorus is not stable on longer time scales: about 80% is either transformed into dissolved phosphorus and exported from the estuary or transformed to apatites and buried. It is suggested that formation and retention of authigenic apatites is the major process withdrawing phosphorus from the coastal biogeochemical cycle.

## Phosphorumwandlung im Wattenmeer: Apatitbildung (Zusammenfassung)

Von Februar 1992 bis Juni 1993 wurde die Verteilung von partikulärem und gelöstem Phosphor in der Emsmündung in ca. monatlichen Abständen untersucht. Der Phosphorgehalt der Sedimente wurde ebenfalls bestimmt. Aufgrund der Meßwerte und Literaturangaben wurde ein Phosphorhaushalt der Emsmündung erstellt. Bestimmend für die Umsätze war der partikuläre Anteil von 77% des Gesamtposphoreintrags. 40% des Phosphoreintrags lagert sich im Sediment ab. In Schwebstoffen aus den Küsten- und Flußbereichen dominiert der organische und eisengebundene Phosphor (>75%), während Phosphor im Sediment hauptsächlich an Calciummineralien wie Apatit gebunden ist. Das Vorhandensein authigener Apatite wurde mit Hilfe einer sequentiellen Extraktionsmethode bestätigt. Eine Gegenüberstellung des Phosphorhaushalts und der Daten über die Zusammensetzung des partikulär gebundenen Phosphors zeigt, daß der organische und eisengebundene Phosphor längerfristig nicht stabil ist: ca. 80% werden entweder in gelösten Phosphor umgewandelt und aus dem Ästuar ausgetragen oder in Apatite umgewandelt und abgelagert. Es wird angenommen, daß der Hauptmechanismus, durch den Phosphor dem biogeochemischen Kreislauf der Küstengewässer entzogen wird, die Bildung und Ablagerung authigener Apatite ist.

## Introduction

The North Sea coastal zone along the Netherlands and Germany is characterized by high nutrient concentrations during winter (e. g. BROCKMANN et al. [1990]) and a high primary production during spring and summer (COLIJN [1983]; PEETERS et al. [1991]; CADÉE AND HEGEMAN [1993]; JOINT AND POMROY [1993]). There is some evidence that the phytoplankton standing stock and primary production of the coastal zone is directly related to the nutrient load into the coastal zone (DE JONGE [1990];

SCHAUB AND GIESKES [1991]; CADÉE [1992]). Part of the organic matter produced in the North Sea accumulates in the Wadden Sea and in the estuaries intersecting this area. Accumulation mechanisms are described by POSTMA [1954] and VAN STRAATEN AND KUENEN [1958]. Due to the accumulation and subsequent remineralisation of organic matter, the Wadden Sea may act as a source of nutrients in summer (DE JONGE AND POSTMA [1974]), thus fueling primary production in the Wadden Sea and the adjacent coastal zone. Which part of the imported particulate nutrients can be released as dissolved

nutrients depends on the extent of transformation processes that remove nutrients from the biogeochemical cycle. These processes include burial of particulate nutrients, removal of nitrogen nutrients through denitrification and the formation and retention of phosphorus minerals.

Iron hydroxides have a high capacity to adsorb phosphates (e. g. FROELICH [1988]). The adsorption of inorganic phosphorus onto iron hydroxides in Wadden Sea sediments is one potential mechanism to retain phosphorus within the Wadden Sea. However, under reducing conditions iron hydroxides dissolve and the adsorbed phosphorus is released. Therefore, the efficiency of iron hydroxides to retain phosphorus within the Wadden Sea on long time scales is questionable. Recently, attention has been drawn to the *in situ* formation of apatites as permanent phosphorus sinks. RUTTENBERG [1992] developed a sequential extraction technique that allowed the identification of authigenic apatites. RUTTENBERG AND BERNER [1993] presented evidence to support that authigenic apatite formation presently occurs in continental margin sediments. Model calculations by VAN CAPPELLEN AND BERNER [1988] demonstrated the feasibility of authigenic apatite formation.

This paper presents the first results of a study on the different forms of phosphorus in Wadden Sea sediments and suspended matter. Based on a phosphorus budget for a part of the Wadden Sea – the Ems estuary – the possibility of authigenic apatite formation as a permanent phosphorus sink is discussed. Details of the phosphorus budget will be discussed elsewhere (VAN BEUSEKOM AND DE JONGE, accepted).

## Material and Methods

### *Dissolved and particulate nutrients in the Ems estuary*

During the period February 1992–June 1993 water samples from 1.5 m depth were taken in approximately monthly intervals at 17 stations from aboard the R.V. van Veen using a pumping device. In addition, water samples were taken by hand from the river Ems upstream of the weir near Herbrum

(St. 22). For better coverage of the fresh water part of the Ems, two additional stations (St. 23, 24) were sampled by hand between Leer and Herbrum from July '92 onward. All surveys started at the seaward station just before high water. During the first day, stations 1–11 and during the second day stations 12–16 and 22–24 were sampled. Because of adverse weather conditions the first four stations could not always be sampled. The location of the sampling stations is shown in Figure 1.

Water samples were filtered on board using GF/C filters. The filtrate and filters were frozen immediately and stored at  $-20\text{ }^{\circ}\text{C}$  until analysis of dissolved and particulate nutrients. Details on the analytical procedures are given by VAN BEUSEKOM AND DE JONGE [accepted].

Nutrient import via the rivers Ems and Westerdoldse Aa has been quantified by multiplying the particulate and dissolved nutrient concentrations by river discharge. No nutrient concentrations available for the river Leda which enters the river Ems near the city of Leer (Fig. 1). Nutrient input was quantified by applying the Ems river concentrations. The resulting river load was assumed to represent the period ranging from halfway between the previous and present sampling until halfway between the present and next sampling. Export of dissolved nutrients from the estuary was quantified for each cruise by extrapolating the linear part of the nutrient-salinity plot for the outer part of the estuary to zero salinity and multiplying this nutrient concentration by the river discharge. The resultant nutrient export from the estuary was assumed to represent the period ranging from halfway between the previous and present sampling until halfway between the present and next sampling. Details on the evaluations of the nutrient salinity plots will be given elsewhere (VAN BEUSEKOM AND DE JONGE [accepted]).

### *Sediment analysis*

At four locations in the Ems estuary, sediment cores of approximately 1 meter length were taken during October 1992 (Fig. 1). The cores were stored at  $-20\text{ }^{\circ}\text{C}$ . The sediment cores were divided into

## EMS ESTUARY

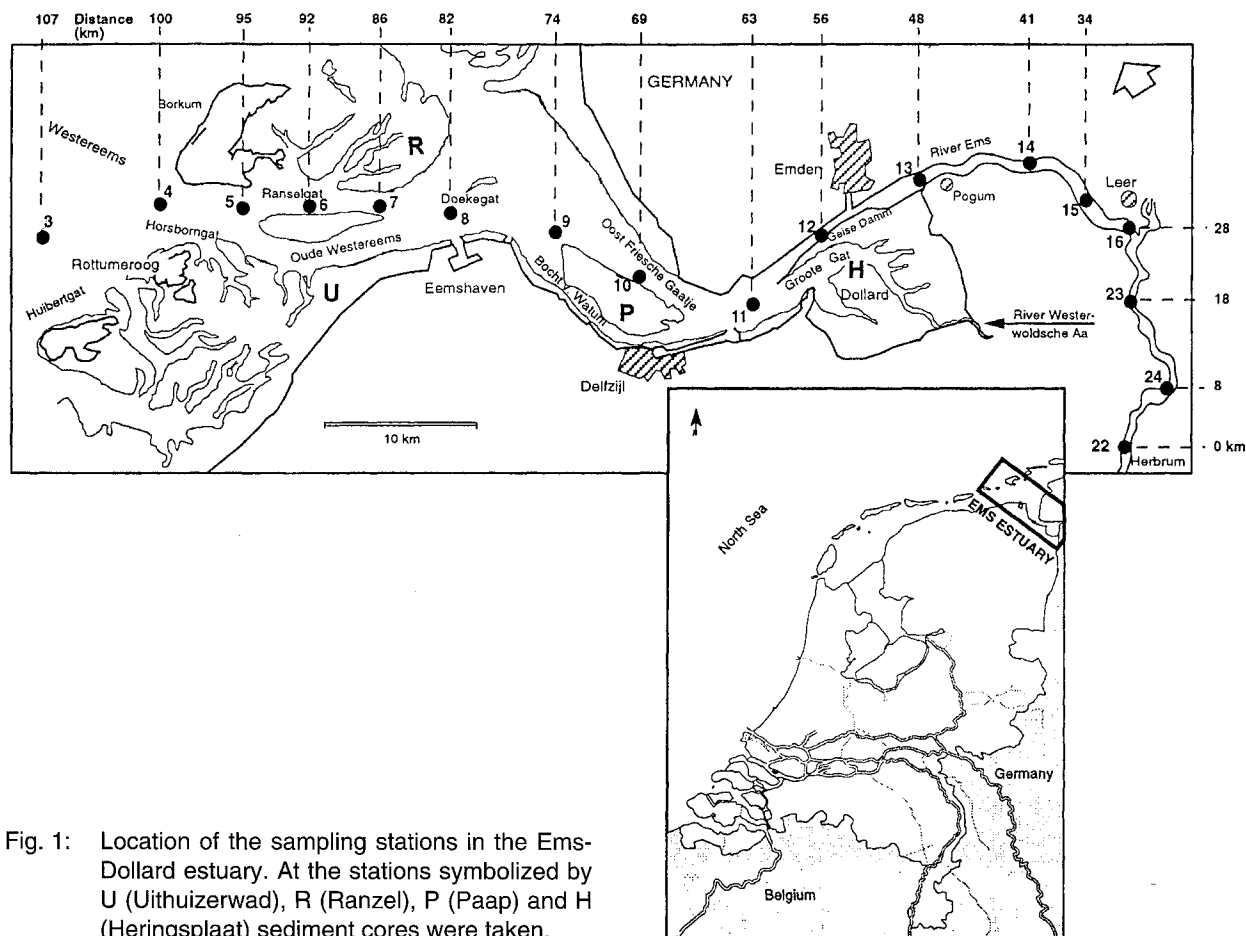


Fig. 1: Location of the sampling stations in the Ems-Dollard estuary. At the stations symbolized by U (Uithuizerwad), R (Ranzel), P (Paap) and H (Heringsplaat) sediment cores were taken.

2 cm slices. The upper 2 cm were subdivided into a lower 1 cm slice and two upper 5 mm slices. The subsamples were again stored at  $-20\text{ }^{\circ}\text{C}$  until further processing.

Shortly before further processing, the samples were quickly thawed within their polythene bags at  $75\text{ }^{\circ}\text{C}$ . After cooling, one third of the available sample was homogenized and from this 0.5 g was filled into polystyrene tubes for sequential extraction. This sample was processed immediately. About 3 g was filled into glass vials for the determination of water content.

A sequential extraction was carried out after PSENNER et al. [1988] and DE JONGE et al. [1993]. This scheme differentiates between adsorbed phos-

phorus, iron(oxy)hydroxide-bound phosphorus released by reduction with dithionite, non-reducible metal-bound phosphorus and  $\text{CaCO}_3$ -bound phosphorus. In addition, the amount of reducible iron was also determined in the dithionite fraction. The extraction scheme, extractants and extraction times used are presented in Table 1.

An alternative sequential extraction scheme which differentiates between authigenic apatite and  $\text{CaCO}_3$ -bound phosphorus on the one hand and detrital apatite on the other (RUTTENBERG [1992]) was used for deep samples (69–85 cm) from the Uithuizerwad core. We simplified the extraction scheme by skipping the first step, in which adsorbed phosphorus was extracted. Furthermore we used a diffe-

Table 1

**Sequential extraction of particulate phosphorus from sediments modified after DE JONGE et al. [1993]**

	Extractant	ml Extractant used	Extraction time	Phase extracted
0.5 g fresh sediment	1 M NH <sub>4</sub> Cl, pH 7	25 ml	2 hours	Adsorbed P
residue	1 M NH <sub>4</sub> Cl, pH 7	25 ml	2 hours	Adsorbed P
residue	0.1 M NaHCO <sub>3</sub> /Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> , pH 7	10 ml	1 hour	Fe-bound P and Fe
residue	0.1 M NaHCO <sub>3</sub> /Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> , pH 7	10 ml	1 hour	Fe-bound P and Fe
residue	0.1 M NaOH	25 ml	18 hours	Fe/Al-bound P
residue	0.5 M HCL	25 ml	18 hours	Ca-bound P

Table 2

**Sequential extraction of particulate phosphorus from sediments modified after RUTTENBERG [1992]**

amount of sediment used	Extractant	ml Extractant used	Extraction time	Phase extracted
0.5 g fresh sediment	0.1 M NaHCO <sub>3</sub> /Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> , pH 7	10 ml	1 hour	Fe-bound P and Fe
residue	0.1 M NaHCO <sub>3</sub> /Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> , pH 7	10 ml	1 hour	Fe-bound P and Fe
residue	0.1 M NaOH	25 ml	18 hours	Fe/Al-bound P
residue	1 M Na-acetate, pH 4	15 ml	6 hours	Authigenic Apatite plus Carbonate-bound P plus biogenic Apatite
residue	1 M MgCl <sub>2</sub> , pH 8	25 ml	2 hours	Authigenic Apatite plus Carbonate-bound P plus biogenic Apatite
residue	1 M MgCl <sub>2</sub> , pH 8	25 ml	2 hours	Authigenic Apatite plus Carbonate-bound P plus biogenic Apatite
residue	0.5 M HCL	25 ml	18 hours	Carbonate-bound P detrital Apatite

rent dithionite solution by leaving out the citrate (cf. DE JONGE et al. [1993]; JENSEN AND THAMDRUP [1993]). This scheme is summarized in Table 2.

Total inorganic and organic phosphorus were analyzed after ASPILA et al. [1976]. Of two subsamples one was first ashed for 2 hours at 520 °C. Both were subsequently extracted with 1 N HCl for 18 hours. The difference between both samples is the amount of organic phosphorus.

Dissolved reactive phosphorus was determined spectrophotometrically after GRASSHOFF et al. [1983]. The extraction solutions were diluted with nanopure water and, if necessary, neutralized with NaOH or HCl. All extractions were carried out at ambient temperatures (20 °C). All analyses were carried out with the supernatant after centrifugation for 10 minutes at 2000 rpm.

*Phosphorus speciation in suspended matter*

Suspended matter samples were collected on precombusted GF/C and Nuclepore filters using a pressure filtration system. All filters were stored at -20 °C until further analysis. GF/C filters were used to differentiate between particulate organic phosphorus and particulate inorganic phosphorus after ASPILA et al. [1976].

The suspended matter on Nuclepore filters was used to investigate the speciation of particulate inorganic phosphorus with a sequential extraction similar to the one used for sediment samples. Details of this extraction method are given by VAN BEUSEKOM AND BROCKMANN [accepted]. The inorganic phosphorus fractions from sequential extraction were normalized to total inorganic phosphorus by multiplying the relative contribution of each fraction with the particulate inorganic phosphorus content measured with the combustion method.

**Results**

*Phosphorus budget of the Ems Estuary*

For the construction of the Ems estuary phosphorus budget we followed a simple black box

model consisting of fluxes along the interfaces river, sediment, atmosphere and sea (Fig. 2). The nutrient import and export estimates from March 1992 to March 1993 were used for the annual budget. The fluxes are summarized in Table 3.

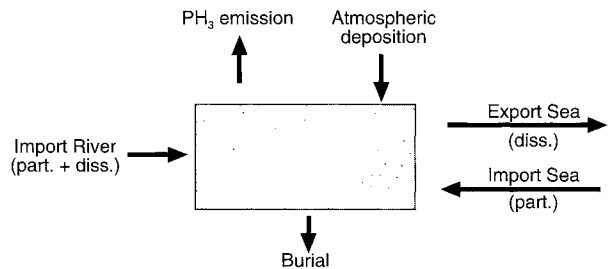


Fig. 2: A simple box model representing the phosphorus fluxes in the Ems estuary.

Table 3  
**A phosphorus budget of the Ems estuary**

	Import (10 <sup>6</sup> mol y <sup>-1</sup> )	Export (10 <sup>6</sup> mol y <sup>-1</sup> )
River (dissolved)	9.8	
River (particulate)	22.1	
Atmosphere	0.6	0.2
Sea (dissolved)		26.5
Sea (particulate)	12.2	
Sediment		18
<b>Total</b>	<b>44.7</b>	<b>44.7</b>

River import was based on own measurements and amounted to 31.9 10<sup>6</sup> mol P y<sup>-1</sup>.

Atmospheric deposition was taken from SCHLÜNZEN [1994]. She estimated an atmospheric deposition in the Wadden Sea of 0.04 tonnes P km<sup>-2</sup> y<sup>-1</sup>.

Atmospheric loss: A small part of the phosphorus import is lost to the atmosphere by reduction to phosphine (PH<sub>3</sub>). Based on an estimate by GASSMANN et al. [1996] for the North Frisian Wadden Sea we estimated an annual phosphine emission of 0.6 10<sup>6</sup> mol P y<sup>-1</sup>.

Sedimentation: REINDERS AND VAN DER MEULEN [1972] reported an annual accretion rate of 8 mm y<sup>-1</sup>

in the Dollard. Since the Dollard is relatively protected against erosive forces like wind and waves, we have not extrapolated this accretion rate to the entire estuary, for which we used a more conservative value of  $2 \text{ mm y}^{-1}$  (EISMA [1993]). This value is based on the assumption that accretion in the more exposed parts of the estuary keeps pace with the long-term water rise. Since the Dollard occupies about 20% of the Ems estuary a mean accretion rate of  $3.2 \text{ mm y}^{-1}$  was used. Loss of phosphorus through sedimentation is based on the sediment composition at depth ( $>10 \text{ cm}$ ) to eliminate the influence of temporal deposits like iron-bound phosphorus. We found a mean sediment content of  $5.5 \mu\text{mol P g}^{-1}$ . Given a mean water content of 20%, an annual accretion rate of  $18 \cdot 10^6 \text{ mol P y}^{-1}$  is calculated.

Export to sea was estimated from the monthly cruises and amounted to  $26.5 \cdot 10^6 \text{ mol P y}^{-1}$ .

Import from sea was estimated by assuming a balanced budget. The annual amount of phosphorus retained within the estuary when neglecting particulate matter import from sea is  $5.8 \cdot 10^6 \text{ mol P y}^{-1}$  (river import river:  $31.9 \cdot 10^6 \text{ mol P y}^{-1}$ , atmospheric import:  $0.6 \cdot 10^6 \text{ mol P y}^{-1}$ , atmospheric loss:  $0.2 \cdot 10^6 \text{ mol P y}^{-1}$ , export to sea:  $26.5 \cdot 10^6 \text{ mol P y}^{-1}$ ). Compared to a sedimentation rate of  $18 \cdot 10^6 \text{ mol P y}^{-1}$ ,  $12.2 \cdot 10^6 \text{ mol P y}^{-1}$  has to be imported additionally from sea.

#### *Forms of phosphorus in sediments of the Ems estuary*

The phosphorus content of the upper 2 cm of the Ems estuary sediment contained on average  $8.6 \mu\text{mol P g}^{-1}$ . The main fractions were organic phosphorus (about 14%), iron-bound phosphorus (29%) and calcium-bound phosphorus (49%). The deeper sediment layers ( $>10 \text{ cm}$ ) contained less ( $5.5 \mu\text{mol P g}^{-1}$ ). Organic phosphorus contributed 14%, Fe-bound phosphorus 15% and calcium-bound phosphorus 65%. Figure 3 compares the relative contributions of the various phosphorus fractions.

The above results demonstrate that in Ems estuary sediments the calcium-bound phosphorus

fraction dominates. To test whether this fraction also contained authigenic apatites we performed a sequential extraction scheme after RUTTENBERG [1992] with deep sediment samples (69–85 cm) from the Uithuizerwad-core. The extraction showed that on average 28% of the calcium-bound phosphorus was present as authigenic apatites.

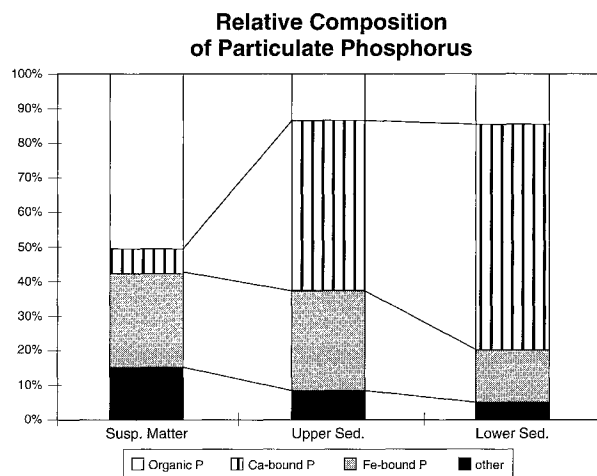


Fig. 3: A comparison between the phosphorus speciation in suspended matter from the coastal zone and in sediments from the Ems estuary.

## Discussion

### *Phosphorus transformation in the Ems estuary: Evidence for the formation of authigenic apatites*

Phosphorus fluxes in the estuary are dominated by the interaction between particles and sediment: 77% of the phosphorus is imported in particulate form, and 40% of the imported phosphorus is retained in the sediment. A comparison between the particulate phosphorus fractions imported into the Ems estuary and the particulate phosphorus fractions in the sediment could provide information about phosphorus transformation in the estuary. A prerequisite for such a comparison is that comparable extraction schemes are applied. For suspended matter such data presently are only available for the Elbe estuary during March 1995 (VAN BEUSEKOM AND BROCKMANN [accepted]). In the

outer reaches of the estuary, organic phosphorus prevailed (51%), 27% was adsorbed to iron(oxy)hydroxides and only 7% of the particulate phosphorus was present in the calcium fraction. We will assume this value to be representative of coastal zone suspended matter. Figure 3 compares the relative composition of particulate phosphorus in suspended matter from the outer reaches of the Elbe estuary and from Ems estuary sediments. The most conspicuous difference is the that suspended matter is dominated by the organic and iron-bound fraction whereas in sediments the calcium-bound phosphorus fraction dominates.

To identify the transformations of particulate phosphorus that are taking place, we calculated for each fraction the annual amount imported into the estuary and compared this to the annual amount lost to the sediment (Table 4). For particulate phosphorus imported from the sea and lost to the sediment we used the relative composition given in

Fig. 3. Since no data are available yet on the composition of particulate phosphorus in the Ems river, we used data from the Elbe river (Org. P = 33%, Fe-bound P = 48%, Ca-bound P = 4%; Rest: 15%; cf. VAN BEUSEKOM AND BROCKMANN [accepted]). The applicability of these values is supported by studies from other rivers which also show dominance of the organic and Fe-bound fractions and a low amount of calcium-bound phosphorus (FROELICH [1988]; LEBO [1991]; CONLEY et al. [1993]; RAO AND BERNER [1993]). Table 4 shows that about one third of imported particulate phosphorus is released and exported as dissolved phosphorus (see also VAN BEUSEKOM AND DE JONGE [accepted]). This is in accordance with earlier studies (DE JONGE AND POSTMA [1974]). While only  $1.8 \cdot 10^6$  mol P  $y^{-1}$  is imported as calcium-bound phosphorus,  $11.7 \cdot 10^6$  mol P  $y^{-1}$  is buried as Ca-bound phosphorus, indicating that practically all is locally formed. With the extraction scheme after RUTTENBERG [1992] only 28% of

Table 4

**Annual import and burial of the major particulate phosphorus species in the Ems estuary**

P-Fraction	Import River ( $10^6$ mol P $y^{-1}$ )	Import Sea ( $10^6$ mol P $y^{-1}$ )	Total ( $10^6$ mol P $y^{-1}$ )	Loss to sediment ( $10^6$ mol P $y^{-1}$ )
Organic P	7.3	6.2	13.5	2.7
Fe-bound P	10.6	3.3	13.9	2.7
Ca-bound P	0.9	0.9	1.8	11.7
Rest	3.3	1.8	5.1	0.9
Total	22.1	12.2	34.3	18.0

the calcium-bound phosphorus was identified as authigenic apatites. Possibly not all apatite bound phosphorus was extracted with the method applied.

*Phosphorus loss to the sediments: Implications for the ratio of dissolved nitrogen and phosphorus exported to sea*

Table 5 summarizes relevant aspects of a nitrogen budget from the Ems estuary (VAN BEUSEKOM AND DE JONGE [accepted]). Internal loss within the estuary makes up a quarter of the nitrogen budget.

Denitrification is the major loss factor (19%) whereas sedimentation of particle-bound nitrogen is of minor importance. This contrasts sharply with the phosphorus budget which shows that sedimentation of particle-bound phosphorus removes 50% of the imported phosphorus and underlines the particle-reactive nature of phosphorus.

The N to P ratio of riverine imported nutrients amounts to 68 (Table 5) and is considerably higher than the Redfield ratio of 16. The N to P ratio of all imported nutrients (riverine + atmosphere + marine particulate matter) amounts to 53. The lower ratio is

mainly due to the import of marine particulate matter which has an N to P ratio of 12 (VAN BEUSEKOM AND DE JONGE [accepted]). The N to P ratio of exported dissolved nutrients is 66, i. e. higher than the import ratio. Apparently the removal rates of phosphorus within the Ems estuary are so high that the disba-

lance of nutrients – as compared to the Redfield ratio – is increased. Whether the strong removal of phosphorus is typical of the entire Wadden Sea or is a characteristic of the Ems estuary is an issue for future research.

Table 5

**Ratios of annual N and P import, export and loss (sedimentation, denitrification) in the Ems estuary**

	P ( $10^6$ mol P $y^{-1}$ )	N ( $10^6$ mol P $y^{-1}$ )	N/P
Import (river)	31.9	2180	68
Import (river + sea + atm.)	44.7	2362	53
Loss (sedimentation + denitrif.)	18.0	522	29
Loss (denitrification only)		460	
Export to sea	26.7	1756	66

**Conclusions**

- Organically bound and Fe-bound phosphorus are not stable in the long term. About 80% is transformed either into dissolved phosphorus and exported from the estuary or transformed into apatites.
- The formation and retention of apatites is the major process withdrawing phosphorus from the coastal biogeochemical cycle.

**Acknowledgements**

The authors gratefully acknowledge the excellent technical support by Gertrud Delfs and Bernhard Seemann. The manuscript benefited from comments by E. Andrulowicz and an anonymous reviewer. The first author was supported by a grant of the German Ministry of Education, Science, Research and Technology (grant no. O3F0130-C).

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Submitted: 03. 02. 1997

Accepted: 30. 08. 1997

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