

Copyright ©

Es gilt deutsches Urheberrecht.

Die Schrift darf zum eigenen Gebrauch kostenfrei heruntergeladen, konsumiert, gespeichert oder ausgedruckt, aber nicht im Internet bereitgestellt oder an Außenstehende weitergegeben werden ohne die schriftliche Einwilligung des Urheberrechtlichsinhabers. Es ist nicht gestattet, Kopien oder gedruckte Fassungen der freien Onlineversion zu veräußern.

German copyright law applies.

The work or content may be downloaded, consumed, stored or printed for your own use but it may not be distributed via the internet or passed on to external parties without the formal permission of the copyright holders. It is prohibited to take money for copies or printed versions of the free online version.

Nutrient turnover at the sediment/water interface in shallow eutrophic coastal waters

G. Schlungbaum and G. Nausch

Wilhelm-Pieck-Universität Rostock, Sektion Biologie,
Rostock, German Democratic Republic

Abstract

The nutrient situation in eutrophic shallow coastal water systems is characterized by particular features. In addition to water exchange with the open sea, interactions at the sediment/water interface play a significant role. With the help of investigation on phosphate sorption/desorption balances and on the denitrification capacity of shallow coastal waters, the following general conclusions can be made: The phosphate concentrations in the water are primarily determined by physico-chemical reactions with the sediment, and less by the rhythm of the phytoplankton primary production. Through intensive interactions between sediment and water, a phosphate "equilibrium" concentration which fluctuates very little is maintained over the whole year. High primary production rates are possible at these low equilibrium concentrations of phosphate. The phosphate sorption capacity of sediments is a characteristic parameter of shallow systems. Sediments with a high organic matter content exhibit the highest phosphate sorption capacities. With the development of nearly anearobic conditions, nitrate reduction can occur at a rate, when the appropriate amount of nitrate is made available to the reaction. Under optimal conditions for nitrate reduction, nitrate concentration is also not a parameter characterizing the nature of the water body.

Introduction

Eutrophication of surface waters is currently a worldwide problem that is rapidly spreading to include coastal waters. The increased primary production and biomass typical of eutrophic waters are caused mainly by excessive nutrient load in the form of nitrogenous and phosphorus compounds.

Coastal waters of estuarine character, which represent regions where fresh water and brackish water mix, are naturally also affected in terms of quality, as shown for instance by increased turbidity.

In addition, in shallow coastal waters interactions between the water body and the surface layer of the sediment play an important role in this respect. Following up THIENEMANN's (1927) fundamental statement that "Sedimente sind Regulator des Nahrungskreislaufes im Wasser" (sediments regulate nutrient cycles in water), NAGUIB (1982) described the significance of the sediment for water quality adequately as follows: "... sowohl aerobe als auch anaerobe mikrobielle Umsetzungen verleihen diesem dominanten Standort (Gewässerboden) die Eigenschaft einer zentralen Schaltstelle für fast alle funktionellen Kreisläufe ..." ("... both aerobic and anaerobic microbial turnover gives this dominant location (the

bottom of the water) the property of a central switch point for almost all functional cycles in the water ...”).

In other words, nutrient cycles in shallow waters where the influence of the sediment is strong, will be greatly affected by sediment quality. Some of these control mechanisms are explained in this article.

Nutrient cycles in shallow waters

Nutrient cycles in the water column can be regarded as a complex network of inputs and outputs of matter, reactions taking place in the water and interactions between the water and the sediment, all of which depend on more or less specific internal and external conditions, including

- geomorphological factors,
- hydrological factors,
- hydrographical factors,
- meteorological factors,
- physical factors and structures,
- chemical factors and structures, and
- biological factors, structures or functions.

Special features of the phosphate cycle

It is often found in shallow coastal waters that orthophosphate concentrations of the water remain at an almost constant, relatively low level throughout the year regardless of external inputs and independently of seasonal variations in the primary production level. This is probably a result of the equilibrium established between phosphate sorption and desorption processes through intensive interactions between water and sediment. A comprehensive description of the corresponding theoretical and experimental background is presented together with a detailed discussion of the relevant literature in SCHLUNGBAUM (1979, 1982a, b).

Normally, the orthophosphate concentration determined by the molybdenum blue method is equalized with the reactive phosphate. But as proved by gelchromatic separations, for coastal waters also this reactive phosphate consists of orthophosphate, lower organic phosphates and polyphosphates (BACHER and SCHLUNGBAUM, 1987). Thus the determined phosphate is not in all cases biologically available. The concentration at which equilibrium is reached in a water/sediment system is determined to different degrees by the following factors:

- a) Factors acting in the water columns
- phosphate concentration
 - dissolved organic matter
 - particulate matter
 - ionic composition (salinity in brackish waters)
 - free Ca and Fe ions
 - temperature
 - oxygen concentration
 - pH value
 - biological activity

b) Factors acting in the sediment

- organic matter (quality and quantity)
- mineral matter (quality and quantity)
- grain size composition
- composition of interstitial water
- Ca/Fe ratio
- reaction time
- sediment structure
- redox status
- abiotically and biotically induced turbulence
- biological metabolic activity

The establishment of the phosphate sorption equilibrium can be described by a Langmuir adsorption isotherm (JACOBSEN 1977, SCHLUNGBAUM 1979, 1982a, b) (Fig. 1).

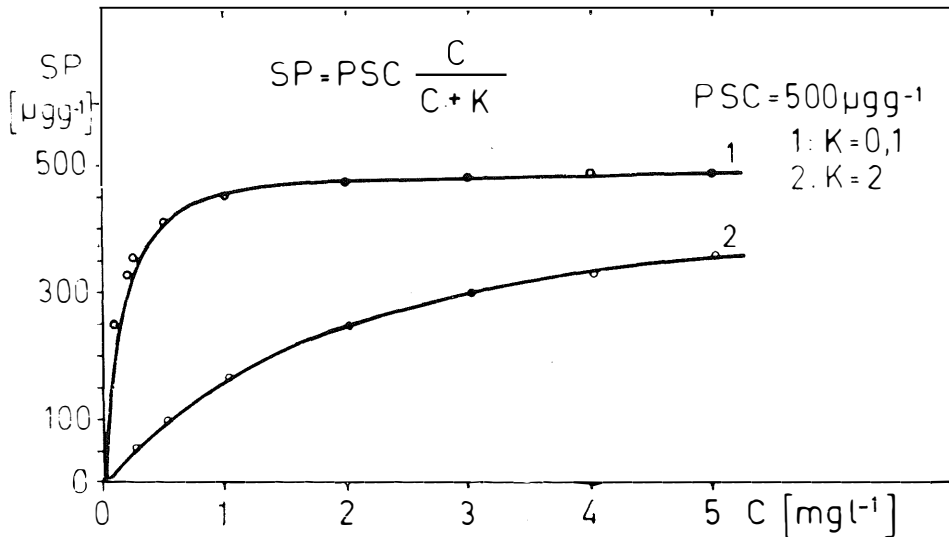


Figure 1

Langmuir-Adsorption-Isotherm

PSC phosphorus adsorbance capacity	[P $\mu\text{g g}^{-1}$]
SP adsorbed phosphorus	[P $\mu\text{g g}^{-1}$]
C equilibrium concentration in solution	[P mg dm^{-3}]
K half saturation constant	[P mg dm^{-3}]

The curvature of the isotherm can be used to calculate the maximum phosphate sorption capacity (PSC) for a sediment under given reaction conditions. The value of this parameter (PSC) can be regarded as a useful criterion for the classification of different sediments. The following PSC values have been calculated for a variety of water bodies in contact with different sediment structures (all sediments collected from shallow waters or regions of shallow water).

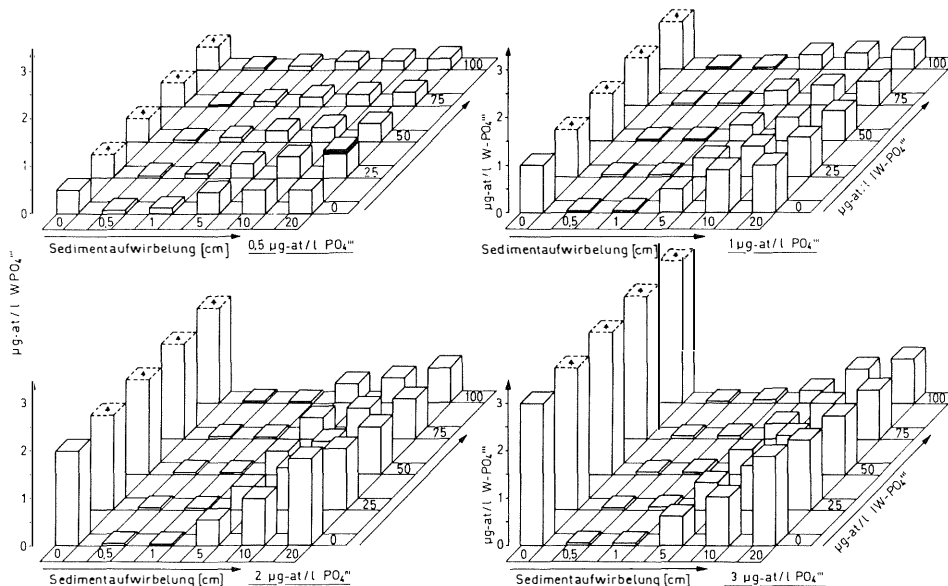
Table 1

Maximum phosphate sorption capacity (PSC in mg P g DW⁻¹) of sediments from different waters in relation to organic matter content of the sediments (results obtained by author and taken from literature)

organic content (sediment)*)	< 5 % DW	> 5 % DW	Source
Brackish waters			
Bodden waters in GDR	0.03...1.0	0.5...6.7	(1)
Baltic Sea	0.05	1.8...2.7	(1)
Black Sea	0.06...0.10	-	(1)
Natural and artificial lakes			
Natural lakes in GDR	-	1.3...2.0	(2)
Artificial lakes in GDR	-	1.0...6.2	(3)
Lakes in USA	-	1.1...1.2	(4)
Danish lakes	-	0.9...6.0	(5)
Australian lakes	-	1.7...5.2	(6)
Streams			
River Warnow (GDR)	0.10	3.6...7.2	(1)

*) as determined by weight difference after combustion at 550° C

Sources: (1) SCHLUNGBAUM and BAADER (1983), (2) KLAPPER et al. (1977) in SCHLUNGBAUM (1982a), (3) RÜHLE (1971) in SCHLUNGBAUM (1982a), (4) KU et al. (1978) in SCHLUNGBAUM (1982a), (5) JACOBSEN (1977) in SCHLUNGBAUM (1982a), (6) SLATER et al. (1978) in SCHLUNGBAUM (1982a)

**Figure 2**

Simulations based on model experiments using different sediment characteristics of the Barther Bodden. Further details in the text

The main factors affecting PCS are the organic content of the sediment, the mean grain size composition, the iron content and the amount of phosphate already present in the sediment. Multiple regression analysis showed that in different sediments these factors can be arranged in the following order of decreasing importance:

- Bodden sediments (organic content below 5 % DW)

$$\text{PSC} = f(\text{org. cont.} > \text{grain size} > \text{Fe}_i > \text{P}_i)$$

The relation between PSC and the organic content as the most significant variable is $r = 0.84$.

$$\text{PSC (mg P} \cdot \text{g}^{-1}) = -0.15 + 0.18 \cdot \text{organic content (\% DW)}$$

- Bodden sediments (organic content above 5 % DW)

$$\text{PSC} = f(\text{org. cont.} > \text{P}_i > \text{Fe}_i > \text{grain size})$$

The relation between PSC and the organic content as the most significant variable is $r = 0.81$.

$$\text{PSC (mg P} \cdot \text{g}^{-1}) = -0.40 + 0.20 \cdot \text{organic content (\% DW)}$$

- Sediments from Baltic and Black Sea, Boddens and river Warnow

$$\text{PSC} = f(\text{org. cont.} > \text{Fe}_i > \text{P}_i > \text{grain size})$$

The relation between PSC and the organic content as the most significant variable is $r = 0.87$.

$$\text{PSC (mg P} \cdot \text{g}^{-1}) = -0.07 + 0.18 \cdot \text{organic content (\% DW)}$$

These results show that organic matter is the main factor influencing phosphate immobilization in eutrophic waters. Since about 1979 new knowledge has stimulated the discussion concerning the complex relationships linking the role of phosphate, iron, organic matter and possibly calcium. The attention formerly paid to iron, which is regarded as the main pathway in classical limnology (e.g. TESSENOW 1979, SCHLUNGBAUM 1979, 1985, SCHWOERBEL 1984), has diminished considerably.

In addition, correlation analysis revealed that the degree to which the total sorption capacity is saturated (expressed in terms of total phosphorus content P_i) owing to sea-water loads plays an increasingly important role in sediments with a high organic content.

Apart from the maximum sorption capacity of the sediment, which mostly is far from being exhausted, the equilibrium concentration in the water is a factor of great importance in relation to nutrient cycles and bioproductivity.

Model experiments based on the example of the sediment characteristics (organic content, grain size distribution) of the Barther Bodden (bodden chain south of Darß-Zingst) have been used to simulate various situations (Fig. 2). The model inputs consisted of

- four different phosphate concentrations in the water before interaction with the sediment (0.5, 1, 2 and 3 $\mu\text{mol dm}^{-3}$)
- five different concentrations in the interstitial water (0, 25, 50, 75 and 100 $\mu\text{mol dm}^{-3}$)
- and six different degrees of sediment perturbation (0, 0.5, 1, 5, 10 and 20 cm). The results can be summarized as follows:
- During calm weather (nearly zero turbulence) the phosphate concentration of the water can rise and the concentrations in the interstitial water increase simultaneously as a result of diffusion.

- Slight turbulence (0.5 cm of sediment whirled up for no more than three hours) is sufficient to reduce the phosphate concentration of the water body to a minimal equilibrium level of 0.05 to 0.1 $\mu\text{mol dm}^{-3}$. Increasing concentrations in the interstitial water also contribute to decreasing the equilibrium concentration.
- Considerable turbulence (5 cm sediment layer or more perturbed) is needed to maintain the equilibrium concentration at a higher level: considerable amounts of suspended sediment relative to a given phosphate concentration reduce the sorption capacity. The action of the increasing concentrations in the interstitial water, however, restores the equilibrium at lower levels again.

The results of our model experiments are consistent with those obtained in the field.

Summarizing, it can be said that phosphate concentrations measured in shallow waters are mainly a consequence of sorption equilibrium and reflect neither the actual phosphate load nor the level of primary production. The sediment water interaction keeps the phosphate concentration almost constant. Phosphate concentrations in this state of equilibrium, however, are sufficient to render extreme differences in primary production levels.

In other words, biological production in such waters is not limited by phosphate concentration (see also LUND 1970, GOLTERMAN 1977, SCHLUNGBAUM 1979).

Primary production levels in shallow coastal waters can be reduced only by reducing phosphate inputs from outside (material import) or from inside the system (mobilization from the sediment). In shallow eutrophic waters phosphorus inputs from within the system are often three to four times higher than those from outside. In restoring waters it is therefore necessary to take both sources into account to achieve lasting results.

Special features of the nitrogen cycle

Contrary to phosphate, nitrate concentrations in bodden waters show a pronounced seasonality, the maximum levels from February to March depending mainly on hydrological factors. The high nitrate concentrations sink rapidly to very low summer levels as the water temperature increases.

It has been known for some time that this annual drop in nitrate concentration is caused by both assimilation and various reduction processes. Among the reduction reactions denitrification seems to predominate over nitrate ammonification. Various authors report that these mechanisms can eliminate up to 50 to 60 % of the nitrate load (PETZOLDT 1987).

Denitrification can take place in waters only during oxygen deficiency (below 0.24 ml dm^{-3}). In highly eutrophicated deep water these conditions occur mainly in the hypolimnion. In shallow waters with a continuous interaction between water and sediment these conditions are encountered in so-called microhabitats where the ready availability of reduced substances (needed for oxygen consumption) can also lead to optimal conditions for denitrification within a very short time.

By evaluation of the very extensive literature and based on own experiments we were able to show that:

- up to 2000 $\mu\text{mol dm}^{-3}$ of nitrate can be rapidly consumed by reduction. The value was obtained during in situ investigations with plexiglass enclosures (50 l content, bottom area 0.16 m^2 , duration two days, water temperature 21–22°C).
- when the sediment surface is stationary, more nitrate is reduced by mineral than organic sediments (mineral sediments were defined as sediments containing less than

5 % organic matter on dry weight basis) owing to the combination of optimal reaction space and rapid replenishment of nitrate from the water body. The process soon ceases, however, when the labile organic matter serving as a carbon source is depleted. The total organic content is only slightly influenced.

- when sediment is stirred up by turbulence, muddy sediments are superior as a denitrification agent because both the reaction space and the supply of nitrate are optimal for the available carbon source.

In other words, bodden waters where the interactions at the water/sediment interface are intensive are able to absorb shock loads of up to $120 \text{ mg NO}_3 \text{ dm}^{-3}$ in a very short time.

Actual nitrate concentrations found in the water are therefore not a reliable indicator of the nitrate load of a water body, particularly if it is shallow, because the concentrations measured are always those left over by various turnovers.

References

- GOLTERMAN, H. L., 1977. Sediments as a source of phosphate for algal growth. In: H. L. GOLTERMAN (ed.), SIL-UNESCO-Symp.: Interactions between sediments and fresh water. Junk and Pudoc, The Hague, 289–293.
- JACOBSEN, O. S., 1977. Sorption of phosphate by Danish Lake Sediments. *Vatten* **3**, 290–298.
- LUND, J. W. G., 1970. Primary production. *Water Treat. Exam.* **19**, 332–358.
- NAGUIB, M., 1982. Methanogenese im Sediment der Binnengewässer. 1. Methanol als dominanter Methan-Precursor im Sediment eines eutrophen Sees. *Arch. Hydrobiol.* **95**, 317–329.
- PETZOLDT, H., 1987. Stickstofftransformation an der Sediment/Wasser-Kontaktzone eutropher Flachgewässer unter besonderer Berücksichtigung der Denitrifikation. Dissertation, Wilhelm-Pieck-Univ. Rostock.
- SCHLUNGBAUM, G., 1979. Untersuchungen über die Sedimentqualität in den Gewässern der Darß-Zingster Boddenkette unter besonderer Berücksichtigung der Stoffaustauschprozesse zwischen Wasser und Sediment. Dissertation B, Wilhelm-Pieck-Univ. Rostock.
- SCHLUNGBAUM, G., 1982a. Sedimentchemische Untersuchungen in Küstengewässern der DDR. – Teil 10: Die Rolle der Stoffaustauschprozesse an der Sediment/Wasser-Kontaktzone eutropher Flachgewässer und Möglichkeiten zur Untersuchung am Beispiel des Phosphatkreislaufes – ein Überblick am Beispiel der Darß-Zingster Boddenkette. *Acta hydrochim. hydrobiol.* **10**, 2, 119–134.
- SCHLUNGBAUM, G., 1982b. Sedimentchemische Untersuchungen in Küstengewässern der DDR. – Teil 11: Phosphatsorptionsgleichgewichte zwischen Sediment und Wasser in flachen eutrophen Küstengewässern. *Acta hydrochim. hydrobiol.* **10**, 135–152.
- SCHLUNGBAUM, G. and G. BAADER, 1983. Sediment-chemical investigations in GDR coastal waters. – XVIII. Phosphate exchange at the sediment-water interface in Baltic coastal region of the GDR. *Proc. XIII. Conf. of the Baltic Oceanographers*, **1**, 126–134.
- SCHWOERBEL, J., 1984. Einführung in die Limnologie, 5th edition Gustav-Fischer-Verlag Jena.
- TESSENOW, U., 1979. Die Wechselwirkung zwischen Sediment und Wasser in ihrer Bedeutung für den Nährstoffhaushalt von Seen. *Z.f. Wasser-Abwasser-Forsch.* **12**, 29–36.