

Appendix 1

Sources, sinks and pathways of contaminants in estuaries

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1 Introduction

Temperate marine ecosystems are some of the most productive and diverse of all ecosystems. Over the past century the resources contained within these communities have been subjected to gross mismanagement. They are continually subjected to threats from multiple stresses imposed mostly by human activities, predominantly as a result of increased population growth. The most significant categories of threats derive from:

- ◆ habitat loss and degradation,
- ◆ pollution from numerous sources including sewage, pesticides, polychlorinated biphenyls, heavy metals, oil and radionuclides,
- ◆ over-exploitation,
- ◆ species introductions,
- ◆ global climate change and
- ◆ misguided human perceptions (Suchanek, 1994).

Observations on marine communities were made on short term levels so that changes are mostly unnoticed. Impacts from stresses on coastal marine communities are manifested at the individual species level, but magnify in effect throughout the entire ecosystem. The reasons are complex inter-connected relationships between species at different trophic levels, including interactions such as predation, competition and mutualism. Therefore, one missing species or group of species that may be affected by some particular local pollutant, e.g., may have unpredictable direct or indirect consequences through secondary effects on the ecosystem, possibly leading to the loss of a few to many species. Rather than striving to maintain some specific level of diversity, we should endeavour to understand the basic ecological processes that control populations, communities and ecosystems so we can best predict what kinds of stresses will cause the most serious alterations to the system and avoid them (Suchanek, 1994). The aim of this review is to analyse pathways and effects of nutrients and pollutants in the Wadden Sea, including possible transformations, storage or even degradation processes. To give an insight into the subject of pollution in the Wadden Sea, a summary of the different sources of nutrients (mainly nitrogen and phosphorus) and contaminants (heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls) is given. Then the fate of these compound classes in the marine environment and their impact and toxicity on the biota will be described. Finally the influence of different biotopes within the Wadden Sea, primarily mussel beds and salt-marshes, on cycling, deposition or breakdown of nutrients and contaminants is summarised.

Because of their different fate in the marine environment, the above mentioned pollutants and nutrients will be discussed separately. Some heavy metals, e.g. copper, cobalt, molybdenum or zinc, are necessary elements for the metabolism of organisms. Therefore they are essential in trace amounts, but above a threshold level they become toxic. On the other hand some polycyclic aromatic hydrocarbons (PAH) are known to be synthesised in low amounts by organisms. Nutrients are important for primary production, but also cause eutrophication.

2 Sources

Nutrients and pollutants reach the Wadden Sea on several pathways. Main sources are rivers, diffuse inputs (sewage plants, sluices) and atmospheric input. Next to these sources there is a permanent exchange with the sediment and the coastal North Sea (Fig. 1). A distinction between gaseous, dissolved, solid and adsorbed state of the components is important, because the chemical and physical state of a compound decides about the transport mechanism. The major exchange processes between Wadden Sea and the surrounding environment are shown in Fig. 1.

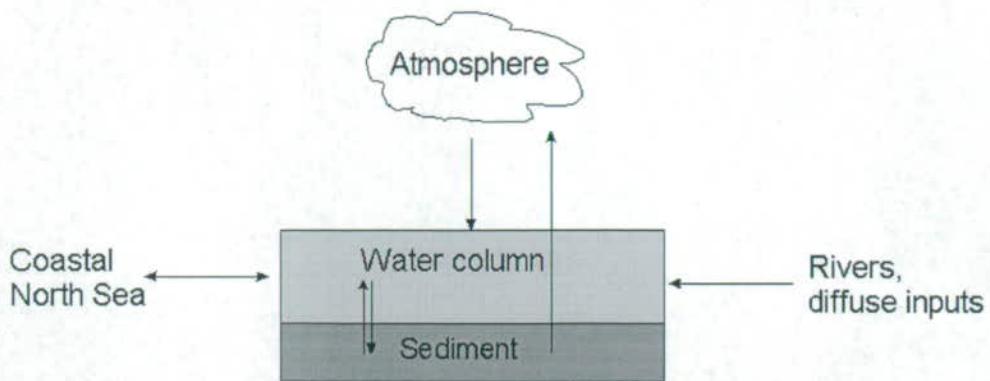


Fig. 1: Major exchange processes between the Wadden Sea and the surrounding environment.

2.1 Nutrients

Both, inorganic and organic nutrients have to be regarded as nutrients. Inorganic nutrients are the major controlling components for primary production in aquatic systems. Except of the HNLC-areas (high nutrient-low chlorophyll) in the open ocean, in which production obviously depends on bioavailable iron (e.g. Martin & Fitzwater, 1988; Behrenfeld et al., 1996; Frost, 1996), especially in coastal regions the primary production is limited by reactive phosphate and nitrate.

Because of the currents, the nutrients and pollutants, introduced by rivers, stay in form of a thin belt along the continental coastline. This is the area where first eutrophication effects were observed. Long term measurements of nutrients on Helgoland since 1962 gave the first hints on the correlation of increasing nutrients and eutrophication (Radach et al., 1986; Hickel & Eickhoff, 1997).

As a consequence of eutrophication, increasing phytoplanktonblooms (*Phaeocystis* sp. or *Chrysochromulina polylepsis*) have been observed (PARCOM, 1992). The introduction of phosphate precipitation in sewage plants and the reduction of phosphates in washing powders lead to a decrease of phosphate. The resulting shift in the N/P-relation is made responsible for an increasing toxicity of the *Chrysochromulina* blooms. In addition the extended growth of macroalgae (mainly *Enteromorpha* sp. and *Ulva* sp.) is related to eutrophication (Siebert et al., 1997).

An additional effect of eutrophication is oxygen deficiency at bottom sediments, since oxygen is necessary for the degradation of deposited organic material. The lowest tolerable oxygen concentration for fishes is $<2 \text{ mg L}^{-1}$. Oxygen concentration fell below this level in the summers 1981-1983 in some areas in the German Bight (Niermann & Bauerfeind, 1990). After the breakdown of phytoplanktonblooms, the oxic layer of the sediment decreases to a minimum. Under extreme conditions (after a strong winter with ice rafting, high organic input, calm weather, heat etc.) like in 1996, the oxygen deficiency lead to anoxic spots in the Wadden Sea ([1] e.g. Günther & Niesel, 1998). The appearance of anoxic spots is caused by anoxic sediment (pyrite) at the surface after total loss of the oxic layer.

The main terrestrial sources for nutrients in the Wadden Sea are rivers and the atmosphere.

Rivers

For a comparison the average annual import of nutrients via rivers into the Wadden Sea is shown in Tab. 1.

Tab. 1: Supply of nitrogen and phosphorus to the whole Wadden Sea via rivers and bays.

Rivers/bays	Q ($10^9 \text{ m}^3 \text{ a}^{-1}$)	N (t a^{-1})	P (t a^{-1})	Comments
IJsselmeer	16,3 ¹	23 000 ²	3 000 ²	average 1980 - 90
Ems-Dollart Ästuar	3,4 ¹	11 000 (Ems) ²	1 000 (Ems) ²	Ems/Westerwoldse = 9/1
Jade ³	0,39	1 648	242	
Weser	11,3 ¹	53 000 ²	4 600 ²	
Elbe	24,5 ¹	71 000 ²	6 000 ²	
Eider ⁴	0,83	4 333	208	
Ribe Å ⁴	1,32	7 758	223	
Sonderjylllland ⁴	0,84	3 373	125	
Sum	58,88	175 112	15398	

¹ = QSR, 1998; ² = Wulfrath et al. 1993; ³ = StAWA Brake 1989-96; ⁴ = QSR, 1993

The Rhine enters the coastal North Sea direct (80 %) and indirect via IJsselmeer (20 %) (Zimmermann & Rommets, 1974). In the Dutch Wadden Sea a significant positive correlation between nutrient load of the IJsselmeer and nutrient concentrations in the Wadden Sea was found (QSR, 1998). In comparison with the other rivers, the Elbe has sometimes a direct influence on the Wadden Sea. Under calm weather conditions the water of the Elbe remains in the coastal North Sea water. The Elbe accounts for 42 % to total freshwater input into the whole Wadden Sea from the Netherlands up to Denmark (QSR, 1998). The nutrient load of the rivers is directly dependent on drainage from the main land and therefore from wet precipitation.

But nitrate and phosphate behave contrary. With high water flows the nitrate concentrations increase and the phosphate concentrations decrease. This is a direct consequence of the different behaviour of these nutrients in soils. Nitrogen containing nutrients are less particle bound than phosphates and therefore easily eluted from soils by rainfall. In the case of phosphates longer time spans have to be taken into account.

Rivers additionally discharge large amounts of organic nitrogen into the Wadden Sea, which also has to be taken into account. Fig. 2 shows the contribution of organic nitrogen to total nitrogen in the Ems from 1982/83 - 1993/94. The sampling station at Herbrum is not affected by the tide. Organic nitrogen contributes between 37 % (1982/83) and 28 % (1993/94) to the total nitrogen load.

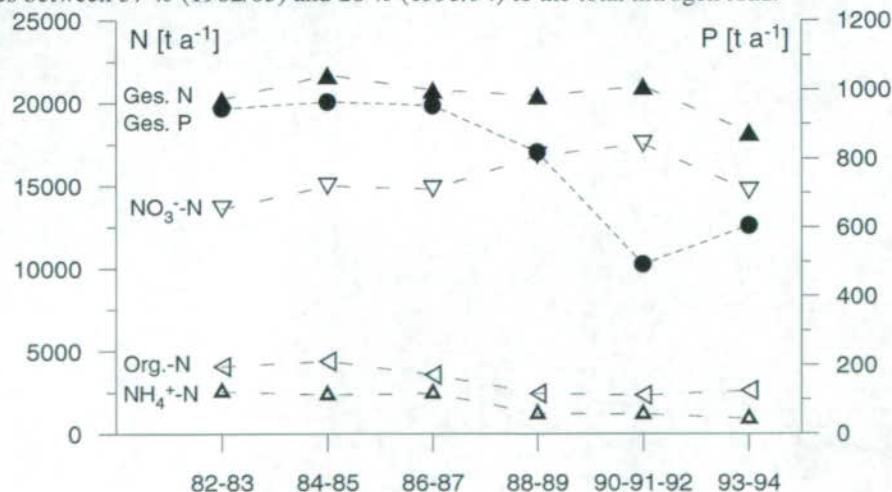


Fig. 2: Organic and inorganic nutrient loads of the Ems at Herbrum 1982/83 - 1993/94.
Data: Bezirksregierung Weser Ems Dez. 502, Meppen.

Atmosphere

The emissions by industry, power plants, traffic, households and agriculture contribute to pollution of the atmosphere and therefore to the nutrient load of the Wadden Sea. On the one hand the nutrients reach the Wadden Sea directly from the atmosphere near the ground and on the other hand they are deposited by dry and wet precipitation. A large amount of atmospheric nutrients is transported by aerosols

(Schatzmann et al. 1994). The input of nutrients from the atmosphere is directly dependent on the concentrations in the air (Fig. 3).

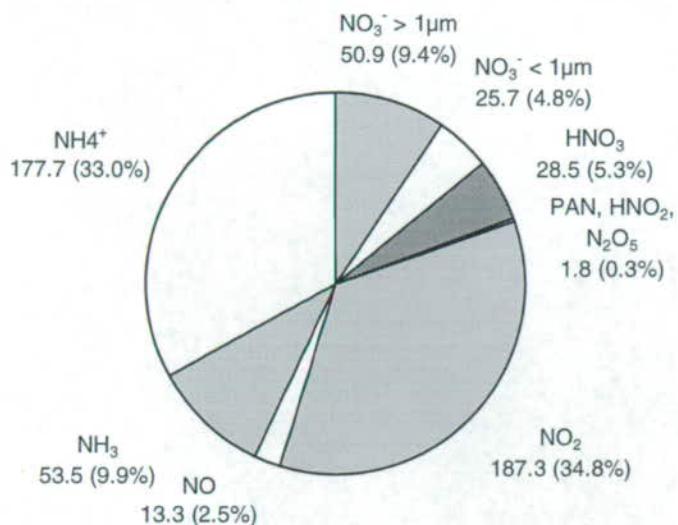


Fig. 3 : Mean composition of atmospheric nitrogen compounds (nmol m^{-3}) in the German Bight (Schulz et al., 1998), PAN: peroxyacetyl nitrate.

Atmospheric nitrogen compounds are transported over long distances (Schulz et al. 1998). During transport they undergo specific physical-chemical changes. NO_x -compounds are typical anthropogenic precursors of oxidised nutrients like Nitrate. The extremely complicated reactions within the atmosphere are described in detail by Holland (1978). For example a dramatic change in the composition of aerosols concerning sea-salt in the coastal area has been observed by Schulz et al. (1998). This change is caused by the reaction of sodium chloride with the (anthropogenic) nitric acid. The chloride of the sea-salt is exchanged by nitrate and hydrochloric acid is formed:



By this reaction up to 55 % of the original sodium chloride in aerosols may be replaced by sodium nitrate during winds from the main land. The extremely hygroscopic aerosols are easily deposited because of their high masses. This causes a remarkable amount of nitrogen deposition in the coastal area. Schulz et al. (1998) regard this reaction as one of the most important sink for oxidised nitrogen compounds in the coastal marine atmosphere.

Deposition of nutrients by wet precipitation is more important than dry deposition, but of stochastic nature. There are large variations by time and space. Atmospheric nitrogen input may account for >26 % of total terrestrial sources (Rendell et al., 1993). These amounts may support phytoplankton blooms during nitrogen limitation.

As an example for balance calculations, the relative contributions of the sources for nutrients for the complete Wadden Sea is shown in Tab. 2. The rivers contribute for about 93 % of phosphorus and nitrogen inputs into the Wadden Sea. The exchange with the coastal North sea is not quantified for a complete year yet. During phosphate maximum in summer, an export of 0.7t per tide was estimated by Dick et al. (1998), but the amount is extremely dependent on primary production and therefore on season.

Tab. 2: Sources of nutrients for the Wadden Sea on an average annual basis.

Sources	Phosphorus		Nitrogen	
	t a ⁻¹	%	t a ⁻¹	%
Rivers	15400	93.8	175112	92.4
Diffuse inputs	716	4.4	6401	3.4
Atmosphere	300	1.8	7950	4.2
Sum	16416		189463	

2.2 Heavy metals

Main sources of heavy metals are like for nutrients rivers and atmospheric precipitation. The origins of atmospheric heavy metals are metal processing industry and combustion processes in power plants, industry, households and traffic. Deposition of particle adsorbed heavy metals occurs by dry and wet precipitation and is dependent on rainfall and wind direction. As the wet precipitation in coastal areas is about 55 % higher than over open North Sea, the deposition is correspondingly higher.

Other important sources for heavy metals are the dumping of harbour sediments or sewage sludge in coastal areas or the remobilisation from the sediment by dredging actions. These are point sources for many pollutants, which are distributed by physical forces like currents or wave action. Since 1989 all nations around the North Sea, except of Great Britain, have stopped the dumping of polluted sludges or sediments in the North Sea. Also the combustion of waste on sea has been stopped since 1991.

The major part of heavy metals is imported by the rivers, most of them bound to inorganic and organic suspended matter. This is not true for cadmium and nickel. Their main appearance in seawater is in dissolved form and sometimes this also the case for copper (Haarich, 1994).

During summer time the sediment of the Wadden Sea itself can be regarded as a source for heavy metals. Hild (1997) found higher copper and manganese contents in the suspended matter (SPM) from May to August, whereas in winter time these metals plus iron correlated well with the aluminium oxide content of the SPM (Al_2O_3 is mainly incorporated in clay minerals). The correlation in winter time can be explained by resuspension of clay, but in summer biological processes must play an important role. This appearance is explained by an elevated microbial activity, leading to a remobilisation of the metals in the sediment, followed by precipitation on SPM-surfaces.

2.3 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons are formed by a variety of processes:

1. Direct and indirect biosynthesis
2. Diagenesis of organic material resulting in fossil fuels
3. Incomplete combustion of organic material

Direct and indirect biosynthesis

Direct biosynthesis of PAH by aerobic and anaerobic bacteria, fungi and plants is discussed controversial in literature. It is unclear if PAH have been synthesised in the organisms or have their origin in external sources. There is evidence for both processes. PAH biosynthesis may occur under conditions when certain bacterial growth substrates are present. The resulting PAH assemblages would have a relatively simple composition.

Indirect biosynthesis occurs when extended quinones and related polycyclic materials (mostly plant and animal pigments) are exposed to reduced conditions in anoxic sediments. The formed PAH accumulate in the anoxic sediments and are of simple composition.

Both, direct and indirect biosynthesised PAH, represent the natural background concentration of PAH in ecosystems.

Diagenesis of organic material resulting in fossil fuels

Fossil fuels including peat, coal and petroleum are relatively rich in PAH. PAH assemblages in crude and refined petroleum are extremely complex. There are many homologous series of PAH with a higher concentration of the alkylated homologues than that of the unalkylated parent compound.

One of the actual oil spills is that of the tanker "Pallas" (30.10.1998). The tanker stranded on a sandflat close to Amrum (Schleswig Holstein) and lost 540 L crude oil. Finally, at the 7.11.1998 the tanker lost

an unknown amount (ca. 12 t) of crude oil and diesel, which produced a 10 seamiles wide oil film. The oil drifted in direction of the open North Sea, but also reached beaches of Amrum and Föhr. The oil film did not affect the Wadden Sea yet, where it would have had much more dramatic consequences. Under certain circumstances like permanent strong winds from north-west, the Wadden Sea in that area will be heavily polluted.

Incomplete combustion of organic material

Pyrolysis of organic matter at temperatures between 400 and 2000 °C results in generation of a wide variety of PAH. Reducing conditions in the pyrolytic environment favour PAH production. The resulting PAH assemblages are also of extremely complex composition. In comparison to the PAH of diagenetic origin, the composition is dominated by the unalkylated forms in the homologous series.

Pathways into aquatic environment

Naturally formed PAH are quite static and remain in the ecosystem where they are formed. PAH biosynthesised by soil microorganisms may be leached out of the soil and may enter fresh and marine water by surface runoff from land. PAH from fossil fuels may enter the aquatic environment in coal dust, in leachate of peat bogs, or in petroleum spillage into water bodies. The petroleum spillage is quantitatively the most important. PAH with their origin in pyrolysis are released into atmosphere adsorbed to soot (Ruß).

Occurrence of PAH in marine environments is directly related to their solubility in water. Solubility of PAH is quite low, reflecting the nonpolar, hydrophobic nature. As expected, solubility tends to decrease as the number of aromatic rings or the molecular weight increases. Naphthalene has a solubility of about 30 ppm while five-ring PAH have solubilities in 0.5 - 5.0 ppb range (factor ca. 10000). PAH concentrations in the dissolved phase in the Seine estuary are by an order of magnitude lower than in the particulate phase (Fernandes et al., 1997).

The alkylated PAH have a lower solubility than unalkylated parent compounds. Exceptions: benz[a]anthracene is less soluble than methyl- or ethylbenz[a]anthracene and same with chrysene and methy- and dimethylchrysene. PAH are slightly less soluble in seawater than in freshwater owing to salting out. Linear PAH are less soluble than angular or pericon sidered PAH isomers.

Solubility is enhanced in presence of dissolved or colloidal organic matter. Another mechanism for solubilisation of PAH is hydrotropy, the enhancement of the solubility of organic compounds as a result of the introduction of other organic compounds not associated with colloid or micelle formation. Most important organics increasing solubility of PAH are nitrogen containing organics like amino acids (Eisenbrand, 1971).

Because of their low aqueous solubility, PAH readily adsorb to particulate materials and solid surfaces in water. Adsorption to particulate organic material is much more important than adsorption to particulate mineral material (Herbes, 1977; Meyers & Quinn, 1973). Total PAH concentrations in the Seine estuary correlate positively with the load of suspended matter (Fernandes et al., 1997). Further the authors describe a decrease of PAH levels from ebb to flood tide, which could be cause by simple dilution processes.

2.4 Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are synthetic chlorinated organic compounds. Theoretically 210 different PCBs (congeners) with one up to ten chlorines per biphenyl are possible. PCBs achieved technical importance, because of their physical and chemical properties like persistence against acids and bases, thermal resistance and low solubility in water. PCBs have been produced commercially for use as coolant /dielectric fluids for transformers and capacitors, heat transfer fluids, flame retardants, additives in paints, PVC, inks, self copying paper and pesticides. Combustion of PCBs can lead to dioxin production.

PCBs enter the Wadden Sea via rivers and the atmosphere. Like the PAH of high molecular weight, they are hydrophobic and preferentially associated with the particulate material. PCBs belong to the class of micropollutants, because already low amounts have toxic effects.

The annual input of PCBs into the German Bight via the rivers Ems, Weser and Elbe accounts for 0.03, 0.1 and 0.17 t PCB a⁻¹, respectively (Hühnerfuss et al., 1997). The authors also estimated an atmospheric input of 0.074 t PCB a⁻¹ by analysis of rainwater samples, which is comparable with the riverine inputs. Because of the low water solubility of PCBs, the rainwater only contains about 20 % of the PCBs in the atmosphere. Therefore Hühnerfuss et al. (1997) conclude that the measured values only represent the lower limit of PCB input by the atmosphere. Although atmospheric inputs might be higher in the Wadden Sea, it is assumed that the inputs are of same order.

3 Sinks

Sinks are regarded as a loss of a contaminant/nutrient from the ecosystem Wadden Sea, as there are degradation, metabolism, mineralisation and loss to the atmosphere. The storage of contaminants/nutrients in the sediment is no real loss, but components can be stored in a non-bioavailable form over long time periods.

3.1 Nutrients

As already mentioned, both, the organic and the inorganic nutrients, have to be taken into account, when discussing sources and sinks for nutrients. Inorganic Nutrients (DIN) support primary production and consequently formation of organic nitrogen (PON and DON). Major nitrogen containing compounds are amino acids, nucleic acids and urea, but also Chlorophyll contains nitrogen. Important organic phosphorus components are phospholipids (cell membranes) and ATP (adenosine triphosphate), which serves as energy carrier. Silicate is used by diatoms for the formation of cell walls (biogen opal). Pelagic and benthic phytoplankton are the most important consumers of nutrients.

Nitrogen

Deposition of organic material (plankton and detritus) into surface sediments supports benthic mineralisation. Mineralisation of organic nitrogen compounds occurs in several enzymatic steps (proteins - peptides - amino acids). Finally ammonia is liberated from amino acids by a variety of deamination processes. Degradation of organic material by heterotrophs leads to DIN again (Schlegel, 1981). Ammonia production is highest under anoxic conditions (Fig. 4). The concentration of ammonia in the porewater is governed by production, adsorption to particles, diffusion and reaction processes.

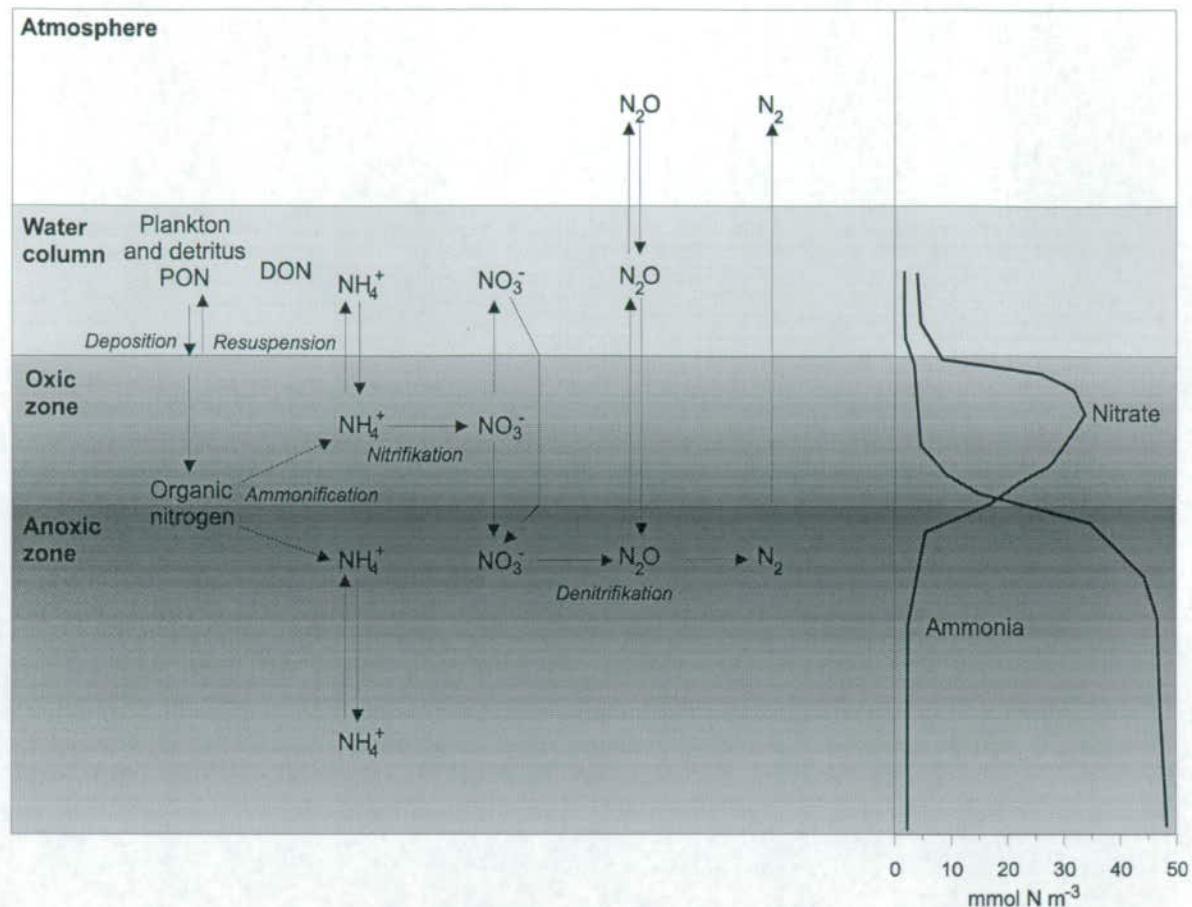


Fig. 4: Major reactions and pathways in the marine benthic nitrogen cycle (Lohse, 1996)

In the presence of oxygen ammonia is oxidised in two steps via nitrite to nitrate. This process is called nitrification and is performed by the bacteria *Nitrosomonas* sp. and *Nitrobacter* sp. These bacteria are restricted to the aerobic part of the sediment. Nitrate as endproduct of nitrification can diffuse via porewater into the water column or deeper into the sediment where it undergoes further reactions. The nitrification rate correlates positively with temperature and is enhanced by a factor of seven in muddy sediments compared with sandy sediments (Bruns et al., 1996). During summer months - high input of organic material and high remineralisation rates - the nitrification can be inhibited by oxygen deficiency. The oxic sediment layer decreases to a minimum (ca. 1 mm) and a return of the nitrification occurs, that means ammonification becomes the dominant process.

Another sink for ammonia is adsorption, which increases in presence of large surfaces and with high organic contents of the sediment. The amount of adsorbed ammonia is higher than the ammonia in solution (Bruns et al., 1996). Consequently the sediment can be regarded as a temporary sink for ammonia.

Denitrifying bacteria (facultative anaerobic) use nitrate instead of oxygen as terminal electron acceptor. Endproduct of this reaction is molecular nitrogen via the intermediates nitrous oxide and nitric oxide. The resulting gases diffuse into the water column and finally into atmosphere. Denitrification is the only real sink for nitrogen containing nutrients, because the elemental nitrogen is no nutrient anymore (air contains 78 % nitrogen), but nitrous oxide is known to be a greenhouse gas. Nitrate can also be reduced to ammonia again (ammonification). This reaction becomes important under oxygen deficiency.

Mathieu (1994) estimated nitrous oxide release rates by sediments in the tidal area of the Elbe (Mühlenberger Loch) of about $4,4 \text{ mmol N}_2\text{O m}^{-2} \text{ a}^{-1}$, whereas in the area at Sylt lower amounts were released. During summer and autumn, when nitrate is limited, even an uptake of $N_2\text{O}$ is possible. Bodenbender & Papen (1996) estimated an average uptake of $-0,63 \pm 0,24 \mu\text{g N m}^{-2} \text{ h}^{-1}$ in sandy sediments but an average release of $1,96 \pm 0,65 \mu\text{g N m}^{-2} \text{ h}^{-1}$ from muddy sediments in August 1992. The release rate of nitrous oxide is enhanced by coverage with macroalgae and in presence of sea-grass, probably because of a higher input of organic material. This hypothesis is supported by the fact that

denitrification rate of muddy sediments is by a factor of six higher than in sandy sediments (Bodenbender & Papen, 1996).

The denitrification rate of Wadden Sea sediments correlate positively with nitrate concentrations in the overlying water, that means high denitrification rates are found in Winter and early spring, whereas rates in summer are low (Kieskamp et al., 1991; Bruns et al., 1996). Measurements of denitrification rates Wadden Sea of Schleswig Holstein vary between $45 \text{ mMol N m}^{-2} \text{ a}^{-1}$ in sand and $60 \text{ mMol N m}^{-2} \text{ a}^{-1}$ in mud (Bruns et al., 1996). In the Marsdiep an annual average of $110 \text{ mMol N m}^{-2} \text{ a}^{-1}$ was estimated by Kieskamp et al. (1991). But Lohse et al. (1996) point at the fact of underestimation by the acetylene inhibitions method by a factor up to ten.

A comparison of denitrification rates in the German Bight and the adjacent Wadden Sea result in an average loss of nitrogen to the atmosphere between 8 - 16 % of the complete imported nitrogen.

Between 8 - 16 % of the complete imported nitrogen in the German Bight and the adjacent Wadden Sea are lost to the atmosphere by denitrification (Beusekom et al., 1998).

Phosphorus

Iron(II) from deeper anoxic sediment is oxidised to iron(III)hydroxide in the oxic sediment. Phosphate is adsorbed by iron(III)hydroxide and stored temporarily. Long term storage of phosphate is possible by precipitation of apatite ($\text{CaCO}_3\text{-PO}_4$ -minerals), which takes place under high concentrations ($>80 \mu\text{mol L}^{-1}$) like sometimes in the porewater (Kölling, 1991). Balance calculations for the Ems estuary show that 65 % of the sedimenting phosphate is apatite and therefore of low solubility Beusekom et al. (1998).

Export to the coastal North Sea water

The tide causes a permanent exchange between Wadden Sea water and coastal North Sea water. During each tide about 50 % of the water volume in the Wadden Sea is exchanged. In case of excess nutrients in the Wadden Sea like in winter, nutrients are exported and during nutrient limitation (phytoplanktonblooms), the coastal North Sea water serves as source for nutrients. The models developed in the projects KUSTOS and TRANSWATT to calculate exchange processes between the Wadden Sea and the North Sea support this hypothesis (Dick et al., 1998).

The general seasonal development of nutrients is characterised by a decrease of during spring time (phytoplanktonblooms; Fig. 5). In summer the nutrients reach a minimum leading sometimes to limitation of certain nutrients. For example spring boom starts with the growth of diatoms until silicate is depleted, then dinoflagellates start to grow. Remineralisation processes in the sediment may support a second phytoplanktonbloom in late summer. In autumn nutrients increase because of low primary production to maximum concentrations in winter.

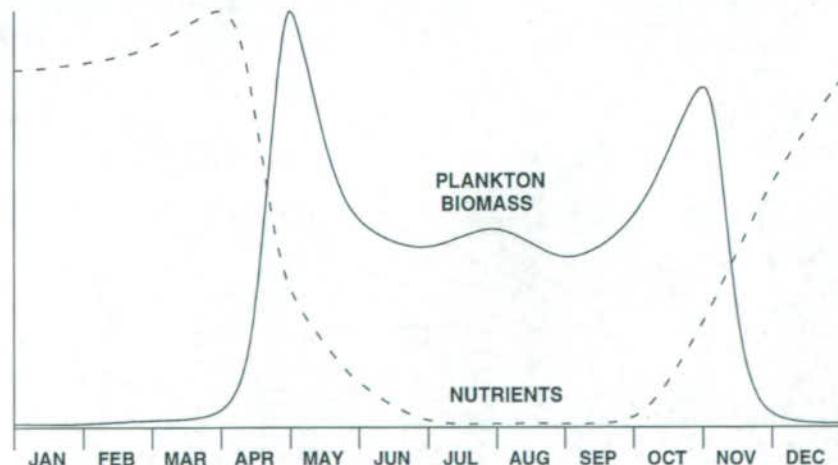


Fig. 5: Schematic seasonal variation of nutrients and phytoplankton biomass in temperate areas.

In comparison with the general seasonal trend of nutrient concentrations, phosphate behaves different. Compared with the other nutrients, phosphate concentrations already increase in summer (Fig. 6). The release of phosphate is caused by a reduced thickness of the oxic layer of the sediment in summer. Under these conditions the remineralised phosphate can diffuse into the water column without adsorption to iron(III)hydroxide. The summer maximum even exceeds the winter concentrations (Hesse et al.,

1995). Recurrent high phosphate concentrations in summer are responsible for a pronounced net export of phosphate from the Schleswig Holstein area into the German Bight (0.7 t per tide; Dick et al., 1998), which is about 8 times higher than the phosphate input deriving from the Elbe (Pohlmann et al., 1998).

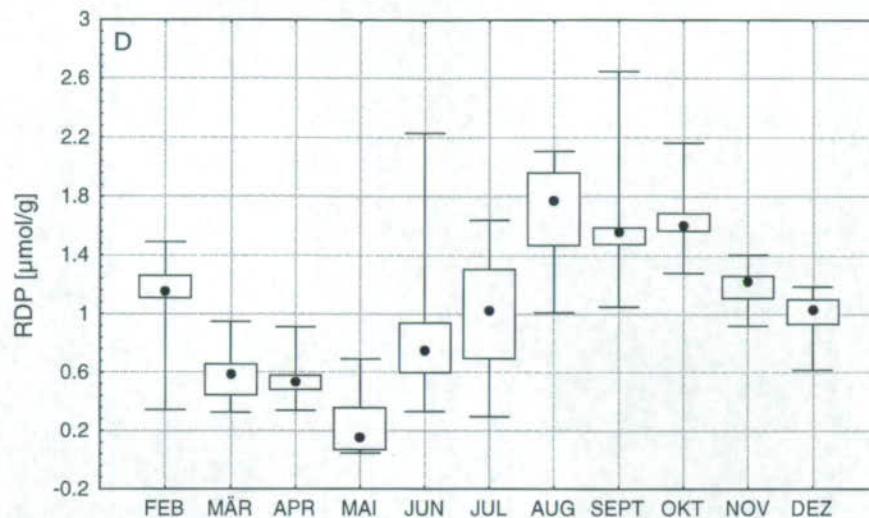


Fig. 6: Box & Whisker plots of phosphate concentrations in the Otzumer Balje (Lower Saxonian Wadden Sea) in 1995. (n = 21-25 respectively)

Already Postma (1954) concluded an export of dissolved phosphate, because of a gradient in phosphate concentrations between the Wadden Sea and the coastal North Sea. Next to the export phosphate as a result of high remineralisation capacities in the Wadden Sea, the remineralisation of organic carbon exceeds the primary production (Beusekom et al. 1998). In the Wadden Sea an excess of about 80 - 160 $\text{g C m}^{-2} \text{ a}^{-1}$ is remineralised, which must be imported into the Wadden Sea. As a conclusion, organic material is imported into the Wadden Sea, so the remineralisation processes are dominant in comparison to primary production and finally nutrients are exported into the coastal North Sea water.

3.2 Heavy metals

The difference between heavy metals and other pollutants is that they can only be changed in their chemical state but they can never be mineralised like organic pollutants. A loss of heavy metals by an ecosystem occurs by conservation of insoluble metals in the sediment and the export of contaminated organisms. For example plants may leave the ecosystem as detritus or indirect via consumption by heterotrophs.

3.2.1 Heavy metals in the sediment

During mixing of riverine freshwater sea water heavy metals undergo chemical changes. In the transition zone of fluvial freshwater and marine seawater agglomeration and sedimentation of suspended material occurs, because of pH and salinity changes. Hence, estuaries are important sinks for particle adsorbed and bound pollutants. Salomons & Eysing (1981) estimate that effectively only of 15 % of total pollutants in the Rhine enter the North Sea via the Rhine-Scheldt estuary.

Not only the SPM plays a significant role during transport of contaminants in the water column. Anikiev, et al. (1986) describe the importance of natural dissolved organic matter in complexing of heavy metals (Fe, Mn and Cu) in estuaries of Japan and China. At salinities over 4 ppt the main migration forms for Fe and Mn in solution are as complexes with humic and fulvic acids. The dissolved zinc in the riverine parts of the estuaries migrates mainly as inorganic complexes and ions. It has been found that the suspended matter is enriched in copper in the latter case at pH greater than or equal to 7.6 and salinity 18-20 ppt, an inorganic labile form of copper begins to predominate at salinities over 20 ppt.

The composition of SPM is strongly variable with seasonally changing contributions of mainly living and dead plankton, bacteria and inorganic clay minerals (kaolinit, illit, montmorillonit, chlorit). Nutrients and pollutants easily adsorb on the surface of the particles because of the large surface. Heavy metals may have a 6 orders of magnitude higher concentration in the SPM than in the surrounding water column (Kersten et al., 1992).

The transport of SPM is extremely dependent on physical parameters like currents and wave action. Sedimentation of the SPM occurs in areas with low currents (physical sedimentation) or by the filtration activity of benthic suspension feeders, which deposit faeces or pseudofaeces on the sediment surface in the vicinity (biodeposition).

Grain size effect

The chemical composition of Wadden Sea sediments is strongly dependent on the grain size distribution. Each grain size class (clay, silt, sand) of Wadden Sea sediments generally has its typical element composition (Hild, 1997). For example, the clay fraction (<2 µm) of a sandy sediment has the same element composition like the clay fraction of a muddy sediment. The reason is a permanent mixing process caused by tidal currents, which produces a well sorted grain size gradient from the tidal inlets (coarse sediments) towards the mainland (fine sediment) (Flemming & Ziegler, 1995).

As a consequence, the distribution of heavy metals in the sediment is dependent on the grain size. Most of the heavy metals accumulate in the fine fraction (Fig. 7). Because of the different compositions of the sediments in the Wadden Sea, data have to be normalised, preferentially to the finer, heavy metal containing fraction <20 µm (Koopmann et al., 1993).

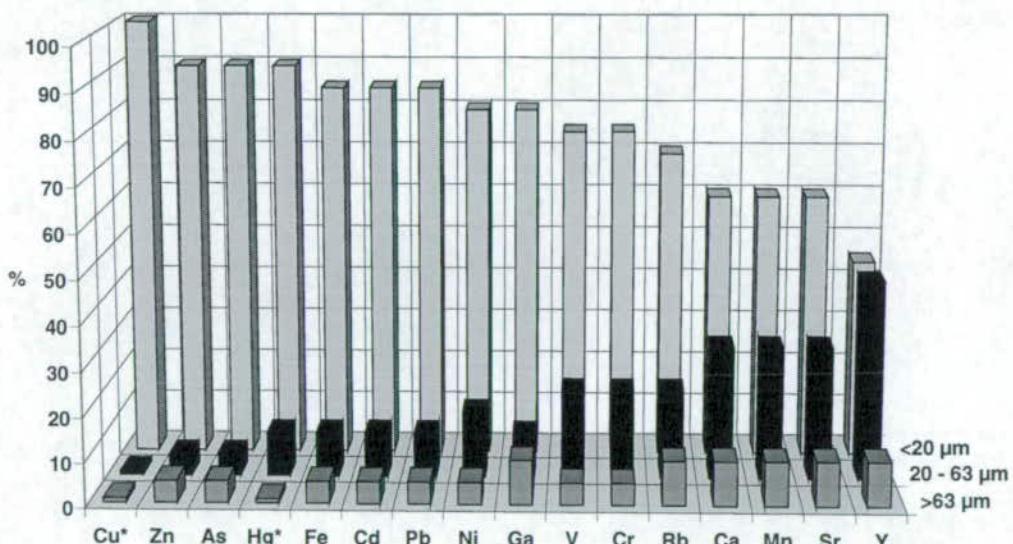


Fig. 7: Relative distribution of metals in the grain size classes >63 µm, 20 - 63 µm and <20 µm (Data: Koopmann et al., 1993).

As the contents of micropollutants are closely related to grain sizes of sediments, first of all definitions of the terms concentration and content have to be explained. Concentration is a term for the mass (or number of moles) of a substance in a certain volume, e.g. g L⁻¹, or M L⁻¹. In the case of sediments authors mostly relate the mass or mol of a substance to a mass of sediment (µg g⁻¹ or M g⁻¹) but not to a volume. In this case the term content has to be used, because this is no concentration. For example the bulk density changes from 1,42 g cm⁻³ to 0,62 cm⁻³ from a pure sandy sediment to a sediment with 50 % mud (<63 µm) (Delafontaine et al., 1996).

Some authors use a grain size correction, some relate their results to a certain grain size or to the POC content of the sediment. But many use the wrong term concentration although they didn't relate the results to a volume. This causes an error when comparing the content of a substance in sediments with different grain size distributions. Others undergo this problem by using concentration terms for the sediment like ppm or ppb (parts per million or parts per billion), which is also a content. Another con-

venient method to present heavy metal data is to calculate a factor of enrichment compared to background levels.

Geochemical mechanisms

The chemical behaviour of heavy metals varies significantly between the elements. This is caused by their different atomic structure and therefore different chemical properties like redox sensitivity.

Tab. 3: Occurrence of iron and manganese in oxic, suboxic and anoxic sediments.

	Fe	Mn
Oxic	Fe(III)oxides and oxihydrates	Mn(IV)oxides and oxihydrates
suboxic	mixed Fe(II)- and Fe(III)-silicates, Siderit ($FeCO_3$), Vivianit ($Fe_3(PO_4)_2$)	Rhodochrosit ($MnCO_3$)
Anoxic, sulphuric	Fe(II) like Pyrite (FeS_2), Mackinawit (FeS)	$Mn(II)$ MnS_x

Under anoxic conditions precipitation of metal sulphides. Oxidation of sulphide minerals and organic substances is a sensitive mechanism regarding mobilisation of heavy metals from reduced sludges (Calmano & Foerstner, 1985).

Maximum concentrations of manganese are found in the oxic layer. The mobility of Cu, Cd, Ni, Pb, Zn, Fe and Mn in marine sediment increases by aerobic degradation of organic matter (Gerringa, 1990). Dissolved Cu and Ni concentrations show a strong relationship with the content of dissolved organic carbon (DOC), indicating their complexed state in solution. Cd and Cu are released by degradation of particulate organic carbon (POC). Per mol POC degraded, 1.8×10^{-5} mol Cu and 2×10^{-6} mol Cd are released into solution.

Investigations on samples from estuarine, coastal and shallow marine areas of the Southern North Sea indicate, that cadmium is particularly labile-bound, whereas lead and copper are associated with more stable chemical forms (Calmano & Foerstner, 1985).

3.2.2 Uptake of heavy metals by marine organisms

Heavy metals are toxic to marine organisms above a threshold availability yet many are essential to metabolism at lower concentrations. Heavy metal concentrations are raised locally in coastal waters but levels in open oceans have stabilised during the earth's history. Oceanic dissolved concentrations are typically controlled not by the rate of entry of metals from land but by the rate of their removal from solution by way of geochemical and more usually biological processes.

Uptake of heavy metals from solution by marine organisms depends on the availability of free metal ions. Hydrophobic metal compounds are taken up relatively quickly and metal uptake may involve the binding of the hydrophilic free metal ion with a ligand for passage across the cell membrane. Metals accumulated by marine organisms may either be maintained in a metabolically available form with the concurrent possibility of toxic effects or may be detoxified (Rainbow, 1985).

Dissolved organic matter (DOM) in aquatic systems is known to reduce the bioavailability of heavy metals. Polychaetes were used as indicators of heavy-metal availability in marine deposits (Bryan & Gibbs, 1987, Pocklington & Welles, 1992). Some polychaetes incorporate heavy metals into particular body structures (Tab. 4). But even closely related species have different capacities to accumulate metals or metalloids in the genus *Tharyx*, at least two species exhibit arsenic levels differing by one order of magnitude. Most polychaetes show some ability to regulate certain metals, especially Zn; for example in *Glycera convoluta*. Of the species studied to date, the most promising indicators appear to be the members of the family Nephtyidae, a group found world-wide in estuaries and coastal waters (Bryan & Gibbs, 1987).

Tab. 4: Anthropogenic compounds accumulated by polychaetes (Pocklington & Welles, 1992)

Species	Contaminants
<i>Neanthes areneceodentata</i>	Cu
<i>Nephtys incisa</i>	PCB, HCBP
<i>Nephtys hombergii</i>	Ag, Co, Cu, Fe, Pb, Zn, Cd
<i>Nephtys caeca</i>	Ag, Co, Cu, Fe, Pb, Zn, Cd
<i>Nephtys cirrosa</i>	Ag, Co, Cu, Fe, Pb, Zn, Cd

<i>Nereis diversicolor</i>	Pb, As, Cd
<i>Nereis succinea</i>	Pb, As, Cd
<i>Nereis virens</i>	PAH
<i>Pectinaria belgica</i>	heavy metals
<i>Glycera convoluta</i>	heavy metals
<i>Melinna palmata</i>	Cu

Uptake of heavy metals by marine organisms from solution, food or sediment is clearly dependent on their feeding strategies. Obviously herbivores, suspension and filter feeders, carnivores and sediment feeders will obtain different body loads through various routes. In most molluscs the body load of metals appears to reflect that of the environment (Simkiss & Mason, 1983). The uptake of heavy metals in solution by *Mytilus edulis*, for example, is minimal compared to the uptake by food or particulate sources (Pentreath, 1973).

The tissues of bivalve molluscs generally show the largest accumulations of metals in the kidneys, by storage in the granules (Simkiss & Mason, 1983). The metal-containing granules of *Mytilus edulis* contain an inorganic component (10% of their dry weight). This inorganic component contains principally iron, zinc and calcium, associated with sulphur and phosphorus together with a pigmented organic component, probably lipofuscin (George et al., 1982). For more information about uptake, transport, storage, detoxification fluxes of heavy metals in molluscs, see Simkiss & Mason (1983).

Bioaccumulation of copper in *Littorina littorea* occurs in the excretory cells (Martoja et al. 1980). Copper is precipitated as clusters of copper sulphide needles inside the lysosomes. Maxima concentrations have been found in animals coming from polluted zones, but an excess of copper ions in the environment has no effect on them. Intoxication by copper sulphate causes branchial lesions. Progressive accumulation of copper sulphide, independent of the environment, makes *L. littorea* an unreliable biological indicator of pollution by copper.

3.2.3 Uptake of heavy metals by vegetation

Next to geochemical mechanisms, a reduction of heavy metal concentrations in the surface sediments by the salt marsh vegetation is possible. An export will take place by consumption of the plants by birds and later deposition outside the Wadden Sea or by the transport of plant detritus by the tides into the coastal North Sea water.

Macrophytes were used as indicators for heavy metal contamination in the Baltic (Kruk-Dowgiallo & Pempkowiak, 1995). Heavy metal concentrations in different taxa vary considerably. *Ruppia rastellata* is the plant cumulating heavy metals most intensively. Brown algae of the genera *Ectocarpus* and *Pilayella* exhibited very high lead concentrations. In the stems of the vascular plants, the highest metal concentrations were observed in the summer -- in the middle of the vegetation season.

3.2.4 Background levels for heavy metals in the different compartments

Background values for several parameters according to different publications are listed in Tab. 5. Only values presented by Kramer & van der Vlies (1983) specifically apply to the Wadden Sea. With regard to the metal concentrations in mussels also the 50 % quartiles of the 1985 ICES baseline study and 1990 supplementary baseline study (OSPAR, 1992) have been included. For comparison the results of the NSTF workshop on background concentrations of natural compounds (Laane, 1992) have been included in the table (QSR, 1993).

Tab. 5: Background levels for heavy metals in the different compartments (<63 µm), in: QSR, 1993.

		Hg	Cd	Cu	Pb	Zn
Water (µg l⁻¹)						
Freshwater	van Eck, 1985	0.01-0.03	0.03-0.08	1.0-3.0	0.2-0.5	2-10
	ARGE Elbe, 1990	0.004-0.008	0.004-0.008	0.4-0.6	0.5-0.6	1.8-2.2
	Laane, 1992	0.002	0.01	2.0	0.05	0.5
Seawater (35 ppt)	van Eck, 1985	0.0025	0.02-0.03	0.2-0.3	0.02	0.3-0.4
Sediment (mg kg⁻¹ DW)						
	van Eck, 1985	0.1-0.2	0.2-0.4	15-40	20-40	50-100
	BLMP, 1984	0.2	0.3	20	25	100
	ARGE Elbe, 1990	0.2-0.4	0.2-0.4	20-30	25-30	90-110
	Kramer, 1983		0.125	20	45	105
	Laane, 1992	0.067	0.5	22	37	103
Mussel (mg kg⁻¹ DW)						
	van Eck, 1985	0.0-0.15	0.75	6.0-9.0	0.5-2.0	50-125
	ICES, 1988	0.1	1.03	7.9	1.7	95.7
	OSPAR, 1992	0.13	0.91	7.3	2.2	108
	Laane, 1992	<0.2	<2	<10	<5	<200

3.3 Polycyclic aromatic hydrocarbons

3.3.1 PAH in sediments

The study of Wilcock et al. (1996) has shown that anthropogenic PAHs have persistences comparable with organochlorine pesticides in aerobic sediments of intertidal sandflats. They applied 13 different PAHs to the surface of a sandflat and then monitored concentrations over time. After initial losses, the total masses of PAHs declined slowly, so that after 256 d 12% of the applied material remained. Vertical concentration profiles indicated that little downward movement occurred and that most of the mass was concentrated in the top 2 cm, where most losses also occurred.

3.3.2 PAH in aquatic organisms

Aquatic organisms are able to accumulate PAH from water, food, and sediment. In most cases, accumulation from water is more efficient than from food or sediment. Sediment-adsorbed PAH have only a very limited bioavailability to aquatic organisms. Benthic infaunal animals rarely contain higher concentrations than the sediment in which they live (Neff, 1979).

McLeese & Burridge (1987) examined the mean concentrations of five PAH (phenanthrene, fluoranthene, pyrene, triphenylene, and perylene) in the clam *Mya arenaria*, the mussel *Mytilus edulis*, the shrimp *Crangon septemspinosa*, and the polychaete worm *Nereis virens*. After a 4-d exposure to the PAHs in water, the mean concentrations showed the following pattern: mussel > clam > shrimp ≥ polychaete.

After exposure of the animals to contaminated sediment for 4 d, the general pattern changed to:
polychaete ≥ mussel > clam ≥ shrimp.

Unlike mussels and clams, relative uptake of PAH by polychaetes was enhanced in the presence of sediment. The reason might be the feeding mechanism.

Contamination of aquatic organisms is generally found to be directly dependent on the distance to a point source. Dunn & Stich (1976) describe a seasonal variability of benzo[a]pyrene levels in mussels (*Mytilus edulis*) collected at the harbour of Vancouver, British Columbia. Highest concentrations were found in winter and lowest in Summer. Dunn & Stich (1976) attribute these seasonal variations to enlarged surface runoff from land during winter months.

PAH background concentration in mussels is about 0.45 mg kg⁻¹ DW (van Eck, 1985).

3.3.3 Degradation and mineralisation of PAH

PAH are nearly ubiquitous trace contaminants of marine and freshwater ecosystems.

Routes of removal of PAH from aquatic environments include volatilisation of PAH from the water surface (mainly PAH of low molecular weight), photooxidation, chemical oxidation, microbial metabolism, and metabolism by higher metazoans.

Photooxidation

Photo-induced oxidation of PAH occurs by singlet oxygen, ozone, HO. Radicals and other oxidising agents in solution. Most common products are endoperoxides. The reactions will not be discussed in detail, because of the great variety. For further information see Neff (1979), but the following general rules were found:

- The reactivity of particle adsorbed PAH seems to be substantially greater than that of PAH in solution.
- The rate of photooxidation is dependent on oxygen concentration and light penetration in water.
- Photooxidation follows the kinetics of the Arrhenius equation and therefore increases exponentially with increasing temperature.
- The conclusion is that photooxidation in natural waters is dependent on season, depth, turbidity, oxygen concentration and temperature.

Chemical oxidation

Chemical oxidation of PAH is dependent on chlorine concentration and pH. Chlorine (Cl₂) is used for drinking water treatment, but is not an important chemical in natural waters. The pH of natural waters do not vary significantly and is also of less importance.

Degradation of PAH by aquatic bacteria and fungi

Both rates and total amounts of PAH mineralization are strongly controlled by oxygen content and temperature (Bauer & Capone, 1985). PAHs have usually been found to persist under strict anaerobic conditions. In a previous study an unusual site was found in San Diego Bay in which two PAHs, naphthalene and phenanthrene, were oxidised to carbon dioxide under sulfate-reducing conditions (Coates, et al., 1997). The PAH degrading populations are supposed to be specialised on certain PAHs.

As PAHs are abundant in nature in trace amounts, for this reason some organisms are able to metabolise PAH. Some organisms have developed the ability to use PAH as sole hydrocarbon source. For example a mycobacterium species, strain BG1, is able to use phenanthrene as sole carbon and energy source (Guerin, 1986). Complete oxidation leads to CO₂ and H₂O. PAH degrading activities correlate positively with the degree of previous exposure to PAH (Guerin, 1986). The rates and total amounts of PAH mineralised are directly related to compound concentration, pre-exposure time, and concentration (Bauer & Capone, 1985). Particularly active are sediments close to contaminant sources (e.g. oil refineries).

Tab. 6: Microbial degradation of 14C-PAH in water from a controlled ecosystem enclosure three days after addition of fuel (No. 2) had been added (Lee & Takahashi, 1977).

PAH (initial concentration in $\mu\text{g L}^{-1}$)	Collection depth (m)	Degradation rate ($\mu\text{g L}^{-1} \text{d}^{-1} \pm \text{SD}$)	Turnover time (days)
Benzo[a]pyrene (16)	5 - 10	1 \pm 0.7	1400
Fluorene (30)	5 - 10	0	-
Methylnaphthalene (50)	0 - 5	26 \pm 4	200
Naphthalene (50)	0 - 5	250 \pm 7	22
Naphthalene (50)	5 - 10	500 \pm 11	10

Heitkamp & Cerniglia (1987) used microcosms to analyse the microbial mineralization of six polycyclic aromatic hydrocarbons (PAHs), containing two to five fused benzene rings. A ranking of the PAHs by order of mineralization rates along with calculated half-lives (weeks) are as follows: naphthalene (2.4-4.4) \geq phenanthrene (4-18) $>$ 2-methylnaphthalene (14-20) \geq pyrene (34- >90) \geq 3-methylcholanthrene (87- >200) \geq benzo(a)pyrene (200- >300). PAH residues persisted from two to over four times longer in a pristine ecosystem than in an ecosystem chronically exposed to low levels of petroleum hydrocarbons.

Biotransformation of PAH by aquatic animals

Mammals have an enzyme system (cytochrome P-450-mixed function oxidase; MFO), that is responsible for initiating the metabolism of various lipophilic (hydrophobic) organic compounds, including xenobiotics (foreign organic compounds like alkanes, PAH, pesticides, and drugs). The primary function of this enzyme system appears to enhance the water solubility of these compounds and therefore make them more available for excretion. Although this system effectively detoxifies some xenobiotics, others, such as certain PAH and alkenes, are transformed to intermediates which are highly toxic, mutagenic, or carcinogenic to the host (Neff, 1979).

Oxidative metabolism of PAH in this system proceeds via highly electrophilic arene oxides, some of which bind covalently to cellular macromolecules such as DNA, RNA and protein. It is now generally agreed that metabolic activation of the MFO-system is a necessary prerequisite for PAH-induced carcinogenesis and mutagenesis (Jerina & Daly, 1974; Hubermann et al., 1976).

PAH metabolites produced by marine and freshwater animals are analogues to those produced by mammals. Metabolites include e.g. PAH diols, phenols, and quinones. For example the major metabolite of benzo[a]pyrene in the oyster *Crassostrea virginica* is the 1,6- or 3,6-quinone (Anderson, 1978).

3.3.4 PAH in Foodwebs

Carman et al. (1997) analysed the response of a benthic food web to hydrocarbon contamination in a microcosm. Sediments with hydrocarbon contamination (diesel) show reduced grazing of copepods on microalgae. Concurrent with reduced grazing by copepods, nematode grazing rates increased significantly, indicating possible competition for microalgae between copepods and nematodes. A large (10x) increase in microalgal biomass was observed and was likely a consequence of reduced meiobenthic grazing. The general responses observed in microcosms were also observed in a field study of polycyclic aromatic hydrocarbon contamination. The results demonstrate the complicated links in food webs.

Indicator organisms?

The bioaccumulation of PAHs by marine organisms depends on feeding mode. The deposit-feeder *Macomona liliana* has significantly higher accumulation factor (the lipid normalised concentration in organisms divided by the organic carbon normalised sediment concentration) for PAHs than the filter-feeder *Austrovenus stutchburyi* (Hickey et al., 1995). Further Hickey et al. (1995) describe that the abundance and condition of *M. liliana* is reduced at more contaminated sites. These results suggest that *M. liliana* are sensitive indicators of contaminant stress and may be usefully incorporated into chemical contaminant and biological effects monitoring programs.

3.4 Polychlorinated biphenyls

Like PAH and heavy metals, most PCBs are particle adsorbed and accumulate in the sediment. For example 80 - 100 % of PCB 138 in the water occurs particle adsorbed (Sturm & Gandrass, 1988).

Polychlorinated biphenyls (PCBs) are a class of man-made halogenated aromatic hydrocarbons that are distributed throughout the environment. Because PCBs are hydrophobic and resistant to environmental degradation, aquatic plants and animals tend to accumulate them from the surrounding water environment. Results of several investigators indicated that aquatic organisms accumulate total body concentrations of PCBs thousands of times greater than that of the surrounding water.

3.4.1 PCB in sediments

The PCB content of the sediments (top 2 cm) shows a clear seasonal variation with low contents in winter and sometimes twice as much PCBs in spring. Hühnerfuss et al. (1997) relate this appearance to the higher frequency of storm events in spring and a resulting resuspension of particle adsorbed PCBs. During summer the calm weather periods allow sedimentation of the particles including adsorbed PCBs.

3.4.2 PCB in aquatic organisms

Polychlorinated biphenyls (PCBs) are a class of man-made halogenated aromatic hydrocarbons that are distributed throughout the environment. Because PCBs are hydrophobic and resistant to environmental degradation, aquatic plants and animals tend to accumulate them from the surrounding water environment. Results of several investigators indicated that aquatic organisms accumulate total body concen-

trations of PCBs thousands of times greater than that of the surrounding water (e.g. Gooch & Hamby, 1982). PCBs are accumulated in the lipid tissues of organisms and may bioaccumulate PCBs by a factor of 1 Mill from the surrounding water (biomagnification; Bester & Faller, 1994).

Degradation and mineralisation of PCB

Degradation of different monochlorinated biphenyls may occur already in the water column by microbial communities less (Reichardt, et al. 1981). The turnover time of monochlorobiphenyls in an Alaskan estuary is estimated to be on the order of one year at a concentration of 0.1 g L^{-1} or less (Reichardt, et al. 1981). The authors also report a significant build-up of partially degraded products. Sayler et al. (1978) describe degradation of polychlorinated biphenyls in surface water and in the sediment of the Chesapeake Bay and the south-eastern Atlantic Coast (USA). Both PCB-degrading bacteria and PCB were found in higher concentrations in estuarine waters and sediment, compared with marine samples. Ernst et al. (1977) give evidence for the degradation of di-, tri- and pentachlorobiphenyl by the marine annelid *Nereis virens* with the method of ^{14}C -labelling. The PCBs are transformed to medium and high polar metabolites in the polychaete *N. virens*. Faecal excretion is a major route of elimination. Only weak degradation of atropisomeric PCBs occurs in *Mytilus edulis* (Hühnerfuss et al., 1995). PCBs in Foodwebs

A model to propose the PCB accumulation in a food web with the dab (*Limanda limanda*) as endmember is presented by Loizeau & Menesguen (1993). A five-compartment steady-state food web model is proposed for the benthic food web leading to the dab (*L. limanda*) by three exposure pathways are considered in the description of accumulation by benthic animals: ingestion of particulate contaminants associated with either sediment or phytoplankton, and respiratory uptake of free dissolved contaminant in overlaying water. Application of the model to a simple food web in the Bay of Seine (Eastern Channel) indicates that: a) feeding is the principal route of contamination, especially for PCB which have more than four chlorine atoms in the molecule; b) excretion and growth rates, phytoplankton lipid fraction and organic carbon content of sediment are the parameters which mostly determine the chemical bioaccumulation in the food web.

4 BIOTOXICITY

4.1 Heavy metals

Lopez et al. (1995) studied the effect of heavy metals on exoenzymatic activities (alpha -glucosidase and exoproteolytic) in sediments off the coast of Catalonia (NE of Spain). Covariance analyses showed that the expected relationship between organic matter content and the enzymatic activities of coastal benthic bacterial communities was altered due to the effect of heavy metals. Laboratory experiments showed the inhibitory effect of heavy metals on exoenzymatic bacterial activities. Thus, although more substrate was potentially available to heterotrophs, enzymatic degradation of organic matter was negatively affected because of the inhibitory effect of the heavy metals. A direct result of this perturbation is that the turnover of polymeric compounds is much slower in polluted areas.

4.2 Polycyclic aromatic hydrocarbons

PAH can interact with cells in two ways to cause toxic responses. They may bind reversibly to lipophilic sites in the cell and thereby interfere with several cellular processes. Alternatively, their metabolites, being more hydrophilic, reactive, and electrophilic may bind covalently to many cellular structures causing long term damages (Neff, 1979). The most toxic aromatics are those with a carbon number up to 14. Above a carbon number of 14 toxicity decreases (Van Overbeek & Blondeau, 1954). But these PAH of higher molecular weight cause chronic toxicity.

Phototoxicity resulting from photoactivated polycyclic aromatic hydrocarbons (PAHs) has been reported in the literature for a variety of freshwater organisms. The magnitude of increase in PAH toxicity often exceeds a factor of 100. Larvae and juveniles of the bivalve *Mulinia lateralis*, and juveniles of the mysid shrimp *Mysidopsis bahia*, were exposed by Pelletier et al. (1997) to individual known phototoxic PAHs (anthracene, fluoranthene, pyrene). Phototoxicity of individual PAHs was 12 to $>50,000$ times

that of conventional toxicity. The non-ortho coplanar congener PCB 126 has the highest toxic potential in blue mussels (Hühnerfuss et al., 1995).

Previous studies indicated that PAH toxicity increased with increasing molecular weight up to phenanthrene; heavier compounds were less toxic than phenanthrene, possibly due to their limited solubility.

4.3 Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) and halogenated pesticides comprise a group of compounds which have considerable environmental interest because of their ubiquity, stability, and potential for bioaccumulation. Since PCBs were first reported in fish and sea bird extracts in the 1960s, many subsequent analytical studies have demonstrated the presence of PCBs in almost every part of the global ecosystem, including polar regions.

The degree of toxicity of PCBs depends on the chlorine substitution pattern of the congeners (Safe & Phil, 1990). Due to their persistency to metabolism, PCBs accumulate in aquatic organisms such bivalves (Pruell et al., 1986; Bromann et al., 1992; Hektoen et al., 1994; Gilek et al., 1996) and fish (Gobas et al. 1989; Loonen et al., 1994) and especially so in organisms of higher trophic level (Bromann et al., 1992).

5 Biotopes

5.1 Mussel beds (*Mytilus edulis*)

Mussels (*Mytilus edulis*) may occur in high densities on tidal flats, in estuaries or as reef communities. They structure tidal flats by depositing fine grained material in an energetically unfavourable environment (Flemming and Delafontaine, 1994; Flemming and Ziegler, 1995). By offering secondary hard substrates they create unique sub-ecosystems not otherwise found on soft substrates (Dittmann, 1990).

With their high filtration capacity of up to 20 l d^{-1} (Asmus, 1994), mussels efficiently remove suspended particles from the water column and deposit these as faeces or pseudofaeces onto the sediment. Above a threshold concentration of about 5 mg l^{-1} mussels produce pseudofaeces (Widdows et al., 1979). In estuarine waters most of the sediment filtered (90 - 100 %) is transformed into pseudofaeces (Widdows et al., 1979). Faeces and pseudofaeces occurring as significant constituents of the sediment are designated as biodeposits.

From the ingested food between 38 and 52 % of total organic carbon and 43 % total nitrogen is digested (Hawkins and Bayne, 1985). According to Smaal and Prins (1993) Phytoplankton-carbon constitutes about 50 % to the total net POC flux. Hence, a significant amount of organic material is removed from the water column and made available via faeces to other hererotrophs associated with the mussel bed. The remineralisation activity of the mussels and other organisms allows mussel beds to play a significant role in nutrient cycling (Dame and Dankers, 1988; Asmus et al. 1992; Smaal and Prins, 1993) and limitation of phytoplankton blooms. Filtration and remineralisation processes therefore closely link pelagic and benthic processes in intertidal environments. Normally only mussels are investigated although other consumers and decomposers play an important role in degradation processes (Dankers et al., 1989).

Benthic filter feeders are reported to contribute substantially to settling flux of cohesive sediment (Haven & Morales-Alamo, 1972). Sedimentation rates of $5 - 20 \text{ cm a}^{-1}$ in an intact mussel bed are possible (Ten Brinke, 1995), but this is dependent on season. Mean accretion rates are high during summer season ($>0.5 \text{ mm d}^{-1}$), whereas in the winter season deposition rates decrease to zero or show erosional trends (Flemming & Delafontaine, 1994). In general, fine-grained sediments are stored beneath the mussel beds on the intertidal flats in summer, and they are - partly - resuspended in winter. The re-suspended sediments are partly deposited on the tidal marshes and/or exported towards the North Sea (Oost, 1995). Remobilisation of faeces takes place above currents of about $3 - 4 \text{ cm s}^{-1}$ (Rhoads & Young, 1970), but the threshold value for consolidated material is ca. 60 cm s^{-1} (Friedmann & Sanders, 1978). Not only consolidation stabilises the surface sediment, but also benthic diatoms.

Another appearance of mussel beds with has an influence on the benthic/pelagic exchange of dissolved and particulate matter, is the growth of macroalgae during summer months. Intense growth of macroal-

gae on mussel beds near Mellum has already been described by Linke (1939). The mussels entangle the macroalgae (preferably *Fucus vesiculosus*) by their byssus threads. The macroalgae utilise the nutrients released from the mussel bed, so that after a short time period the whole mussel bed may be covered by the algae. The secondary effect of macroalgae growth is to intensify the physical current reduction by the mussels. The result is an increase of the sedimentation rate, so that the mussels are covered by the fine material (Reise et al., 1994). This material is of less nutritional quality, because of low relative amino acid content Behrends (1997). The year after coverage the density of the mussel population can be reduced by about 50 % (Reise et al., 1994).

5.1.1 The impact of mussel beds on nutrient cycling

As already mentioned, mussels utilise 38 - 52 % of the organic carbon and 43 % of the total nitrogen ingested (Hawkins & Bayne, 1985). Kreeger et al. (1996) radiolabelled proteins and hydrocarbons to analyse the assimilation of organic carbon and nitrogen by *M. edulis*. The sequence of assimilation is as follows: 26,6 % protein-N > 16,3 % hydrocarbon -C > 8,6 % protein-C. The uptake of amino acids, deriving from proteins, is important to maintain the nitrogen demand of the mussels.

Fig. 8 shows the nitrogen fluxes in a mussel bed of *Geukensia demissa*. About 50 % of the ingested nitrogen are excreted with the faeces and 27 % are released in dissolved form. The rest is used for the metabolism and gametogenesis of the mussel. These results coincide with those of Kreeger et al. (1996).

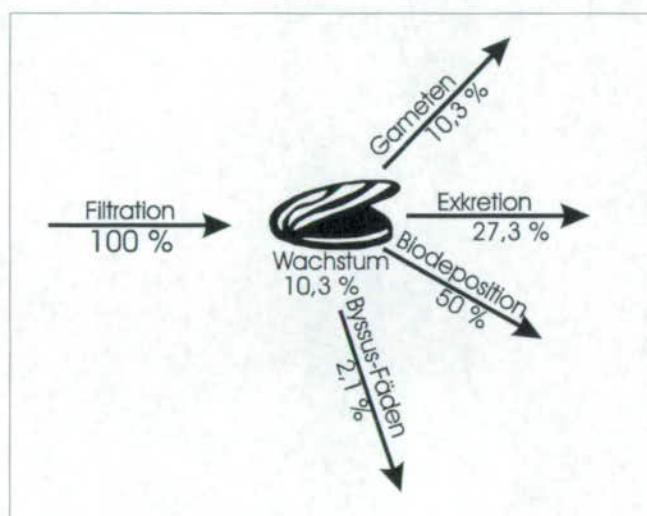


Fig. 8: Relative nitrogen flux in a mussel population (*Geukensia demissa*) in a salt-marsh in New England (Jordan & Valiela, 1982).

The biodeposition of about half of the ingested nitrogen leads to an increase of organic nitrogen in the sediment below a mussel bed. The remineralisation steps of organic nitrogen, which is mainly represented by amino acids, have already been described in chapter 3.1.

The importance of mussel beds in nutrient cycling is not only the enhanced sedimentation of organic nitrogen, but also the fact that denitrification rate of muddy sediments is by a factor of six higher than in sandy sediments (Bodenbender & Papen, 1996). By this mussel beds indirectly support the release of gaseous nitrogen compounds (N_2O , N_2) into the atmosphere and reduce the turnover time of nutrients in the Wadden Sea.

5.1.2 The importance of *M. edulis* in transfer of contaminants from the water column to the sediment

Heavy metals

Major pathway for the assimilation of contaminants by *M. edulis* is that of feeding. Mainly particulate, but also, to a lower extent, dissolved contaminants are taken up by the filtration activity of the mussels. Metal and organic contaminant assimilation is related to carbon assimilation, to distribution in the phy-

toplankton and gut passage time (Wang & Fisher, 1996). The dependence of contaminant and organic carbon uptake by *M. edulis* was also found for PAHs and PCBs (Gilek et al., 1997). Unassimilated particle adsorbed metals are removed from suspension in the overlying water and enriched in biodeposits in the sediments, whereas assimilated metals are enriched in the mussels. In case of lead and cadmium, only a minor part of the heavy metals in the particulate material is incorporated into the tissue of the mussels, the most are excreted with the faeces and pseudofaeces (Karbe, 1987). These results are dependent on season, temperature, contamination in the environment etc., and therefore extremely variable.

The biodeposition of metals may have pronounced impact on SPM loads and the cycling of elements in coastal waters (Dame, 1993). Metals that are not efficiently assimilated are packed into faeces and pseudofaeces and thereby lead to an enrichment in the surface sediments below a mussel bed (Brown, 1986). The biodeposition of metals has an influence on their cycling in the environment. The sedimentation rate and retention time of these elements is enhanced by the mussels. The fate of the biodeposits is (1) resuspension or desorption, (2) burial in the sediment, (3) reingestion by *M. edulis* itself or other benthic heterotrophs or (4) degradation by microorganisms.

Mussel beds on elevated central platforms of tidal flats are exposed to several physical forces (high energy), like storms, extreme wave action or ice rafting. In addition dredging by fishermen or bioturbation lead to resuspension the particulate heavy metals and therefore to a new distribution of contaminants and availability for other organisms.

As long as the mussel bed remains undisturbed, the major part of the particulate heavy metals will be stored within the mud layer. Biosedimentary mud layers can be preserved after several years with low storm intensity and frequency or in marginal parts of tidal flats near the low-water level. The abundance of old shell and mud layers in deeper parts of the sediment has been proved by Hertweck & Liebezeit (1995). The authors related the conservation of organic material with the depth of burial.

Resuspension of sediment by currents and wave action makes the biodeposits reavailable for the mussels. Especially during autumn and winter, detritus makes up the major part of the SPM.

Microbial biomass, bacterial cell numbers, and enzymatic activities (protease, glucosidase and phosphatase) are higher in the sediments of a mussel bed compared to the surrounding sandy sediments (Leu et al. 1997).

The heavy metal content of sediments is not only dependent on the grain size and the POC content, but also on the molecular composition of POC. A significant correlation ($p < 0.01$) between metal content and total amino acid content in limnic sediments has been described by Prosi & Müller (1987). The total content of amino acids in the sediment is able to complex all heavy metals (Pb, Cd, Zn, Cu and Fe) in the interstitial water. As a consequence, the organo-metal complexes are available for resorption or uptake by organisms. Amino acids are necessary for protein synthesis and therefore taken up in large amounts.

Organic contaminants (PCBs and PAHs)

Dense blue mussel beds modify the cycling of hydrophobic organic pollutants. On the basis of an estimated carbon budget Gilek et al. (1997) constructed an annual mass budget for the flux of hydrophobic organic contaminants (HOCs) for *Mytilus edulis* in the Baltic proper (

Tab. 7). Estimated hydrophobic organic contaminants are PAHs, PCBs, and PCDD/F (polychlorinated dibenzo-*p*-dioxins and dibenzofurans). The results show that not all of the consumed contaminants are assimilated by the mussels (assimilation efficiencies between 77 and 84 %). This leads to an increase of the annual net sedimentation of HOCs by at least 13 - 19 %. Contaminant biodeposition by blue mussels thus significantly increases the supply of organic contaminants to deposit-feeding benthic organisms, as there are bivalves (*Macoma balthica*), polychaetes, gastropods, amphipods, and benthic meiofauna.

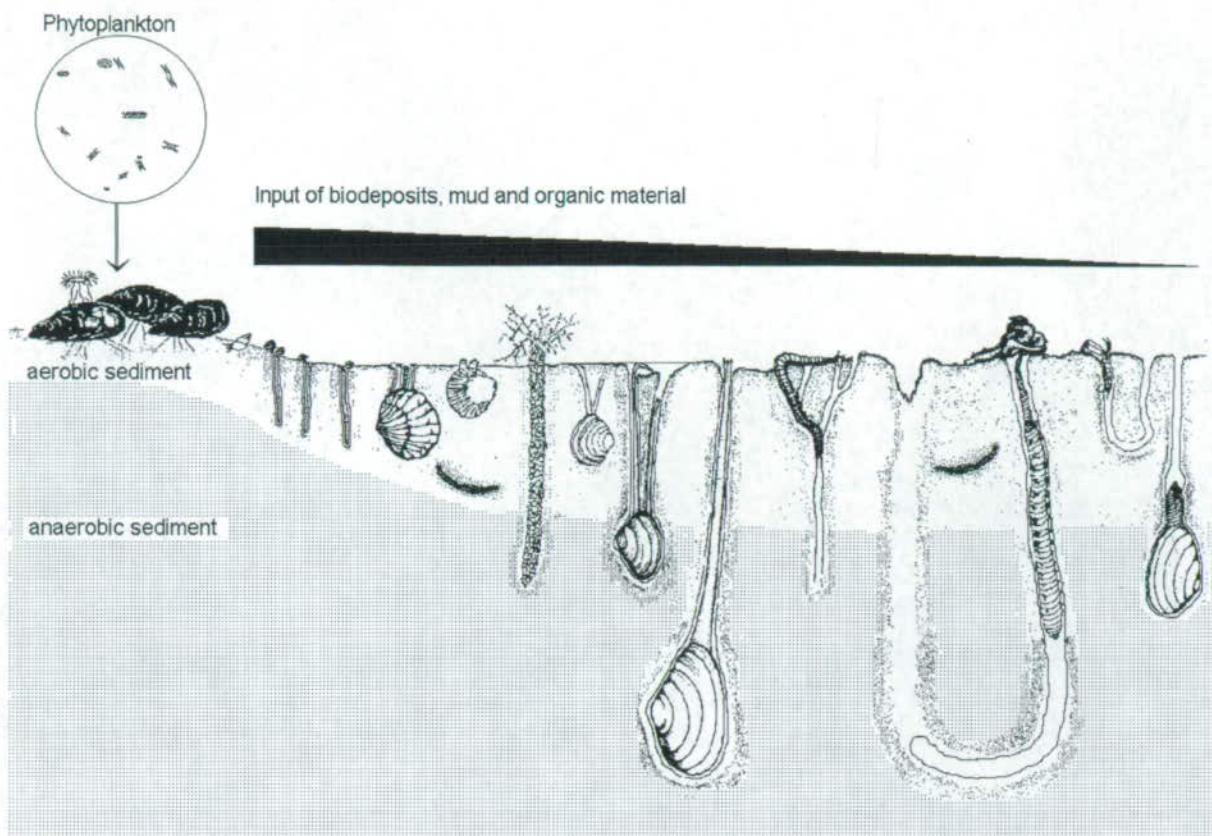
Tab. 7: Some parameters and processes estimated using calculated annual HOC flows through Baltic blue mussels. Since the HOC budgets were established by multiplying the annual carbon flows with the observed or, in the case of spawning, assumed HOC concentrations, the estimated parameters and processes are highly affected by the assumptions made when establishing the annual carbon budget (Gilek et al., 1997). AE = assimilation efficiency of consumed particle associated contaminant.

	Food AE (%)	Food uptake (%)	Faeces/net sedimentation (%)	Half-life (days)	Spawn./Elim. (%)
sum PAH	77	75	19	1.6	0.32
sum PCB	79	62	17	38	8
sum PCDD/F	84	98	13	1.1	0.22

5.1.3 Effect of mussel beds on benthic fauna

The faunal assemblages of a mussel bed (*Mytilus edulis*) and ambient sandflat were compared by (Karbe et al., 1996) to study how a bioherm of suspension feeding organisms affects benthic communities in a tidal flat. During a survey of mussel beds in the Wadden Sea at the island of Sylt (North Sea), a total of 52 macrofaunal species and 44 meiobenthic platelmint species were detected. They occupied different microhabitats in the mussel bed. 56% of the macrofauna species were dwelling in the sediment beneath the mussels and 42% were epibenthic or epiphytic. The latter were restricted in their occurrence to the mussel bed. Along a transect from the sandflat to the mussel bed the mean species densities of macrofauna did not differ significantly, while abundances were significantly lower in the mussel bed than in the sandflat. The composition of the assemblages shifted from a dominance of Poly-chaeta in the sandflat to Oligochaeta in the mussel bed.

The dominance of oligochaetes and small subsurface-feeding polychaetes in the macrofaunal community of a mussel bed is also reported by Kröncke (1996). With increasing distance from the mussel bed deep-burrowing species, surface-feeding and predatory polychaetes become more dominant.



5.1.4 Disturbance, Storms, fishery, long term development, abundance

A decrease of the area covered by mussel beds has been observed in the recent decades. In the Dutch Wadden sea the musselbeds decreased from 41.2 km² in the seventies over 6.5 km² in 1987 to less than 2 km² today. In the Lower Saxonian Wadden Sea a decrease of almost 95 % between 1989/91 and 1996 was found (Herleyn & Millat, 1998).

5.2 Salt-marshes

Salt-marshes are transition zones between the Wadden Sea and the mainland. Dependent on their exposition, they flooded periodically or only sometimes e.g. during spring-tides with seawater. Due to the decreasing physical energy towards the mainland, fine material can settle along the mainland coast (FLEMMING & ZIEGLER, 1995). The enrichment of mud in this area was originally explained by the well-known settling lag model of Van Straaten & Kuenen (1957).

Intertidal sediments receive organic matter from the water column, while organic matter of the salt-marsh sediments results mainly from the decomposition of litter material. The roots of the plants may deliver oxygen and other oxidants below the surface of the sediment, creating certain zones, where high decomposition of organic matter takes place. Salt-marshes also receive resuspended faeces/pseudofaeces from mussel beds and other communities. Deposition of fluid mud layers up to several dm thick occurs in the marshes, especially in the second half of autumn, a period formerly called the "mud-months" by owners of coastal salt-marshes (In: Oost, 1995).

The salt-marsh plants take up nutrients and contaminants. Different sink capacities for heavy metals in salt-marsh sediments in Portugal were observed by Caçador et al. (1997): Pb >> Zn > Cu > Cd. The vegetated sediments contain more metals (mainly sulphur species) than the non-vegetated sediments. This appearance seems to be related to the presence and activity of roots. Since metals become immobilised in vegetated sediments, the salt-marshes are efficient retaining systems for heavy metals. Protection of these areas enhance the ecosystem health by storing contaminants over long time periods or even geological time scales.

Saltmarsh sediments contain more solid phase reactive Fe than other marine sediments studied so far. The majority of solid Fe in these sediments is cycled rapidly and completely between oxidised reactive Fe and reduced Fe as pyrite. Vegetated porewaters have a lower pH and much higher Fe(II) concentrations on average than unvegetated porewaters in the top 10 cm, whereas sulfate, alkalinity, and sulphide concentrations are similar in the two environments. Solid phase and porewater chemistry support the dominant role of the biota (*Spartina alterniflora* and bacteria) in controlling the reactivity of Fe and suggest that the current definition of solid phase, reactive Fe should be expanded to include crystalline Fe(III) minerals which are available for pyrite formation in saltmarsh sediments (Kostka et al., 1995).

6 Recent developments in biodiversity

The benthos is a good integrator and indicator when evaluating environmental changes in marine ecosystems, owing to the sedentary and long live span of macrozoobenthic species (Daunin, 1993). Environmental changes are mainly caused by climatic changes and anthropogenic inputs. The classic paper dealing with the influence of anthropogenic input of organic material on the benthos is published by Pearson & Rosenberg (1978).

7 Literature

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