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Biogeochemistry of the MAximum TURbidity Zone of Estuaries (MATURE): some conclusions

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Abstract

In this paper, we give a short overview of the activities and main results of the MAximum TURbidity Zone of Estuaries (MATURE) project. Three estuaries (Elbe, Schelde and Gironde) have been sampled intensively during a joint 1-week campaign in both 1993 and 1994. We introduce the publicly available database, and compare trends and patterns in suspended matter, nutrients and organic matter in the three estuaries. Despite the large differences in suspended particulate matter concentrations between the estuaries, some general relationships can be deduced. Organic matter dynamics is shown to be determined by sorption onto the particulate matter. This in turn induces a predictable change in bacterial degradability. Floc size, determined by an in situ camera, is a function of organic content, suspended matter concentration and (in a highly non-linear way) salinity. Higher trophic levels in the biological system are negatively affected by the dilution of their food with indigestible particles.

1. Introduction

Temperate, well-mixed, tidal estuaries are generally characterised by the presence of a maximum turbidity zone (MTZ) in the region of low salinity. These zones, where suspended particulate matter concentrations may be as high as several grams per liter, result from a complex interplay of several factors. The particulate matter in suspension, mostly derived from riverine sources, accumulates in the MTZ where it has a longer residence time than in the river upstream. The typical position of the MTZ in the low salinity zone has suggested both physical and chemical mechanisms for its generation. From a chemical point of view, it has classically been suggested that the increasing salinity of the water influences the double layer dynamics at the particle surface and, hence, increases the probability of flocculation and the settling velocity of the particles (e.g., Krone, 1962). Others have opposed to the concept of salt flocculation and stressed the importance of organic coating (e.g., Eisma et al., 1991). From a physical point of view, the important mechanism is the generation in this zone of a residual circulation pattern with bottom currents directed upstream, thus increasing the residence time of the suspended particles. The two mechanisms are not necessarily mutually exclusive, but whatever the dominant mechanism, the resulting zone of maximum turbidity has a profound influence on the biogeochemistry and biology of the estuary.

The increased turbidity changes the light climate in the water. Primary production is likely to be light-limited in the MTZ. Even if nutrient concentrations are high, they are of little use to the phyto-

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plankton, which furthermore has to cope with the changes in salinity (resulting in faster species turnover) at the freshwater–brackish interface. As a result, one expects to find lower primary production and much lower biomass of phytoplankton in the MTZ than in the upstream and downstream stretches of the estuary. The increased mortality of phytoplankton may furthermore inject fresh organic matter in the MTZ, which is likely to enhance bacterial productivity. Goosen et al. (1999) (this issue) and Muylaert and Sabbe (1999) (this issue) approach the problem from the point of view of primary production, phytoplankton species composition and bacterial production.

The existence of a MTZ affects the fate of the organic matter load from the freshwater. Land and freshwater derived organic matter is transported by the river into the MTZ, where the longer residence time of particulate matter leads to enhanced breakdown. At the same time, the high concentration of suspended particulate matter provides potential adsorption sites for organic matter, which may influence the fate of the dissolved organic matter brought with the river. It is known from sediments that the availability of organic matter to bacteria is largely determined by its adsorption to inorganic particles (Mayer, 1994; Hedges and Keil, 1995). Recently, Keil et al. (1997) showed that organic matter adsorbed onto suspended particles in rivers is dynamically exchanging with dissolved fractions during the transition from the river to the delta. The data in that study apply to river-dominated deltaic systems, but there is little reason to suspect that the processes are fundamentally different in inner estuaries.

Flocs of suspended material provide a habitat for specific microbial populations. In ocean waters and sediments, a remarkable discrepancy between rates of nitrification in the sediment and in the water column has been described. Soetaert et al. (in press) conclude from a coupled pelagic–benthic model that the first-order rate constant of nitrification on ammonium is two orders of magnitude higher in the top layer of the sediment than in the water column. This phenomenon is ascribed to the low growth rates of nitrifying bacteria and possibly to their need to attach to a surface. The availability of suspended particulate substrate with a long residence time in the MTZ, could therefore enhance bacterial processes such as nitrification. This would make the MTZ into an enhanced reactor site.

Although, in principle, metazoan animals are producers of particles and could therefore influence the flocculation and particle concentration in a MTZ, in practice it is the concentration of suspended particles that affects the animals. Suspended particulate matter dilutes their potential food sources. Ingestion of valuable food items (e.g., phytoplankton cells) is very difficult in an environment where low-food value particles abound. Non-selective filter-feeding is expected to be a disadvantageous strategy in such an environment, because it requires handling of large amounts of indigestible material. However, the existence of selective feeding mechanisms remains an area of active research. Billones et al. (1999) (this issue) explore new methodologies to study the selection processes. Fockedey and Mees (1999) (this issue) concentrate on the potential food source of hyperbenthic animals.

In the EU-Environment and Climate programme MATURE (Biogeochemistry of the MAximum TURbidity Zone in Estuaries) a multidisciplinary group of scientists collaborated in a joint study of three European estuaries, the Elbe, Schelde and Gironde. In 2 consecutive years, 1993 and 1994, a joint 1-week campaign was organised in each of the estuaries. These campaigns consisted of a sampling transect through the estuary, a 24-h anchor station, followed by another transect. During the campaigns, basic hydrographic measurements were made with frequent CTD casts, and water was sampled for nutrients, organic matter, plankton, primary production and bacterial activity. The flocs of suspended material were analysed by in situ cameras. Experiments were conducted with zooplankton and hyperbenthos collected during the campaign. Beside this field work, hydrodynamic and sediment transport numerical models were developed. The present issue represents part of the results obtained in the programme.

In this introductory paper, we set the scene by presenting some of the basic descriptions of the MTZ in the estuaries during the sampling campaigns. We then summarise some results of the programme in the light of the original questions asked (see above). Many of the subjects are extensively treated in the papers in this volume and will only be briefly dealt with. Others have been reported (Herman and Heip, 1996) and the data have been stored in a publicly available database (FTP://ftp.nioo.knaw.nl/cemo/mature). We drew on this database to present some relationships between the various measured variables.

2. The MTZ in the estuaries during the campaigns

Table 1 summarises the activities during the six MATURE campaigns in the three estuaries. Although, for logistic reasons, the dates in the 2 years did not exactly coincide, the major difference between the 2 years was the very rainy winter and early spring of 1994, which caused maximum freshwater discharges in all three estuaries during the 1994 campaign. As a consequence, the oligohaline zone of the estuaries was considerably shifted seaward, as was the MTZ. It is difficult to specify a precise geographical location for the MTZ during any campaign, because it shifts with the tidal excursion, as was clearly visible in all 24-h station data. A quasi-synoptic transect, made from a vessel sailing up- or downstream, also necessarily gives a distorted image, as there is inevitably aliasing between the tidal shift and the movement of the ship. Moreover, due to sedimentation–resuspension processes, the actual concentration of suspended solids in the water is dependent on the actual current velocity; it will peak during peak ebb and flood current velocity phases. However, when expressed against salinity, the turbidity maximum was very clearly visible by lower transmission values in five out of the six campaigns (Fig. 1). In Fig. 1, vertically averaged (relative) turbidity values for all CTD casts made during the transect are plotted vs. salinity.

In Gironde and Elbe, peak turbidity values are found at salinities between 0.1 and 4 psu. Turbidity in the Gironde is so high that transmissometry cannot differentiate gradients at the highest turbidity values. Vertically averaged suspended matter concentration can easily reach 1 g l^{-1}, and actual values near the bottom may even be much higher. The situation in the Schelde seems to differ from the other two estuaries. In 1993, no clear MTZ could be detected; in 1994 a peak value was found at a

Table 1
Overview of the sampling points in the MATURE campaigns[a]

Estuary	Date	Type	km points in estuary
Elbe	21–22/4/93	Transect	630, 650, 670, 695, 720, 745, 770, 695, 705, 720, 730, 670, 680
Elbe	22–25/4/93	Anchor station	695
Elbe	25/4/93	Transect	770, 745, 720, 705, 695, 670, 650, 630
Elbe	6/4/94	Transect	630, 650, 670, 695, 705, 720, 745, 770
Elbe	7–9/4/94	Anchor station	695
Elbe	9–10/4/94	Transect	770, 745, 720, 695, 705, 695, 670, 650, 630
Gironde	19/5/93	Transect	90, 70, 60, 50, 40, 30
Gironde	20–21/5/93	Anchor station	50
Gironde	22/5/93	Transect	30, 40, 50, 60, 80, 90
Gironde	15/4/94	Transect	30, 40, 50, 60, 70, 80, 100, 110
Gironde	16–17/4/94	Anchor station	100
Gironde	17/4/94	Transect	100, 80, 70, 60
Schelde	4/5/93	Transect	40, 45, 60, 58, 64, 70, 79, 86, 94, 100, 105
Schelde	4–5/5/93	Anchor station	79
Schelde	6–7/5/93	Transect	40, 45, 49, 60, 70, 79, 86, 94, 100, 105
Schelde	27/4/94	Transect	40, 45, 49, 58, 64, 70, 79, 86, 94, 96
Schelde	27–28/4/94	Anchor station	79
Schelde	29/4/94	Transect	105, 100, 94, 86, 79, 70, 64, 58, 49, 45, 40

[a]At the Anchor stations, sampling was done every 1 to 2 h (depending on the variable) during at least 24 h. For most biogeochemical variables, sampling was at three depths (surface, mid-depth and bottom). CTD casts had a higher vertical resolution.

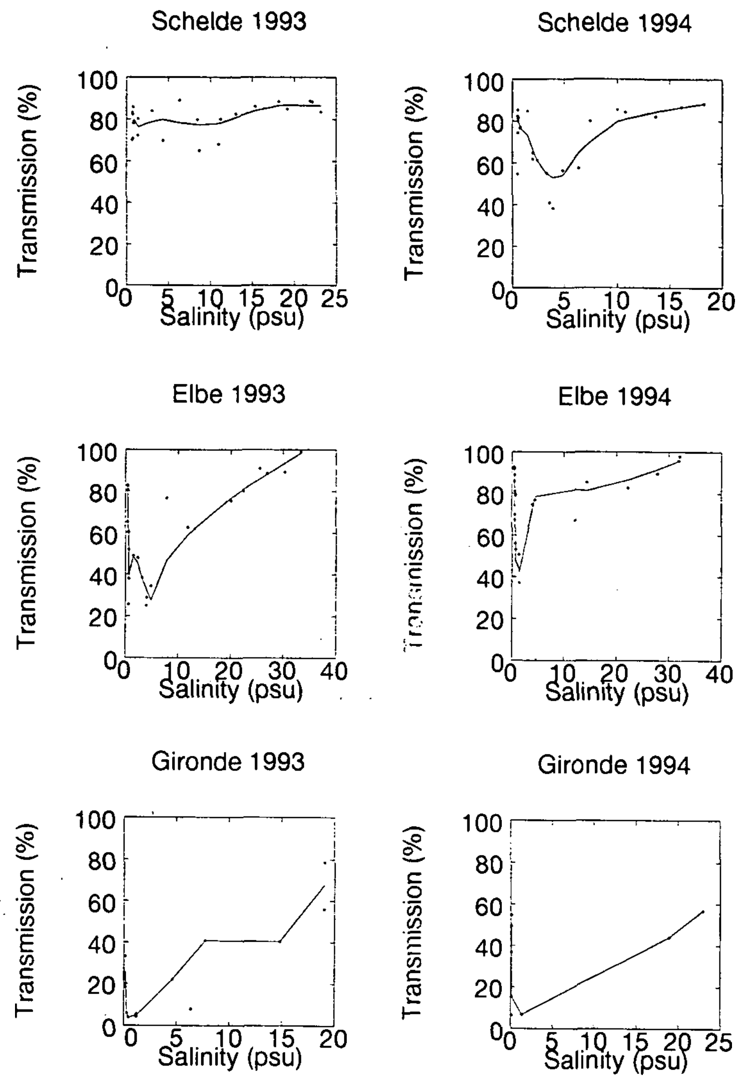
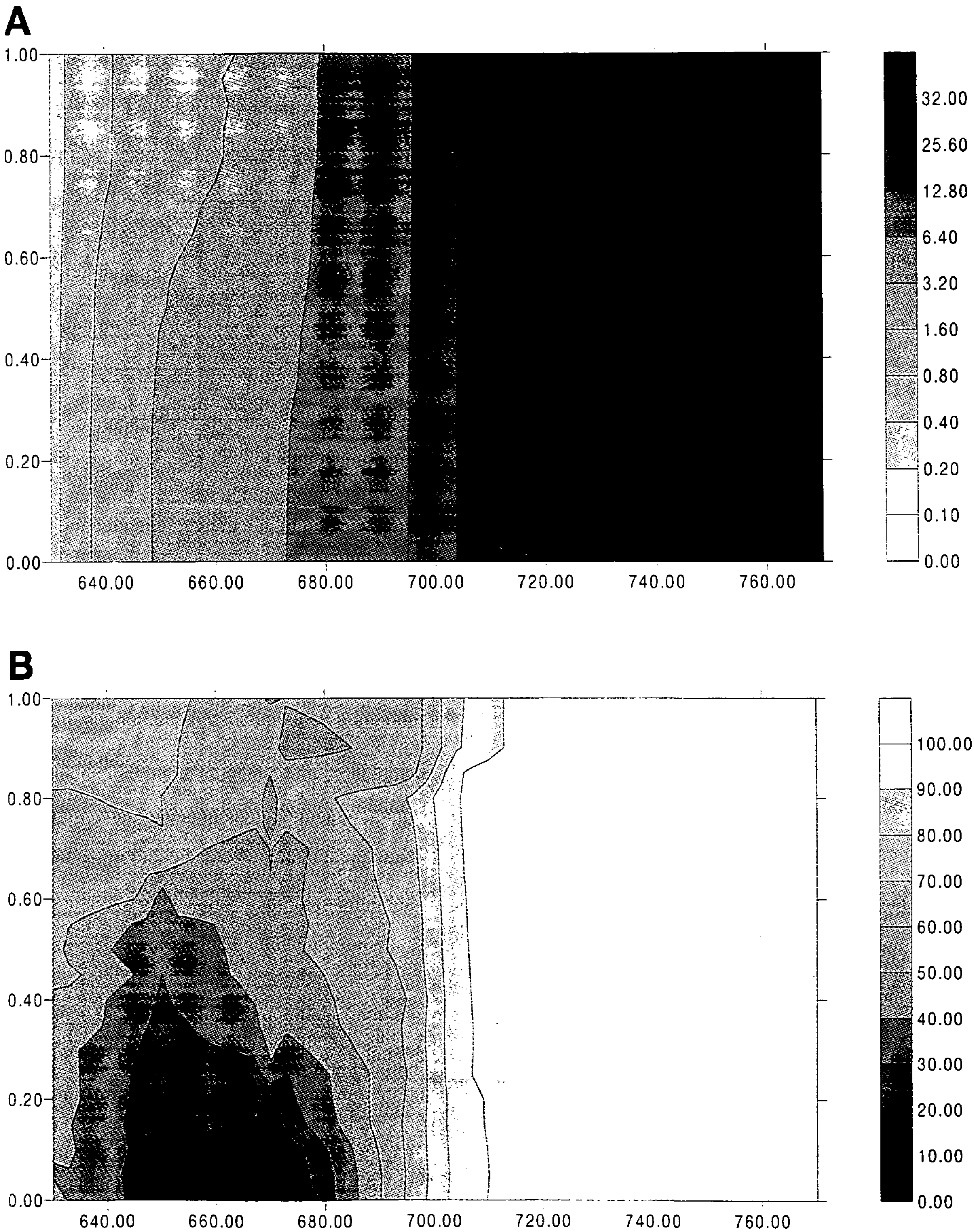


Fig. 1. Depth-averaged light transmission in the water column, as a function of depth-averaged salinity. Measurements were obtained from a vessel sailing a transect through the MTZ of the estuaries, and are not corrected for the phase of the tide. Dots represent replicate observations, lines are a distance-weighted linear smoother.

slightly higher salinity than in the other estuaries (peak at 4 psu, distinctly lower turbidity in the range 0.1–3 psu). Due to the difference in river discharge rates between 1993 and 1994, the resolution with respect to salinity was restricted in the Elbe and Gironde in 1994 (the same 10 km spacing between sampling stations was used in both years, but the horizontal salinity gradients were sharper in 1994).

Fig. 2. Isoline plots of salinity (psu, A) and light transmission (%, B) in the Elbe (second transect, 1993). Horizontal axis is the kilometre scale of the estuary, vertical axis is relative height in the water column (0: sediment; 1: top of water column). Two transects of this type are available per estuary and per year in the MATURE database.


A
1.00
0.80
0.60
0.40
0.20
0.00
640.00
660.00
680.00
700.00
720.00
740.00
760.00
32.00
25.60
12.80
6.40
3.20
1.60
0.80
0.40
0.20
0.10
0.00
B
1.00
0.80
0.60
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740.00
760.00
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90.00
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70.00
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50.00
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30.00
20.00
10.00
0.00

The available data do not indicate large differences in the relation of transmission with salinity between the 2 years in these estuaries.

Vertically resolved, on a (slightly distorted—due to tidal effects) kilometre scale along the axis of the estuary, the same trend along the axis of the estuary can be seen. In addition, vertical gradients in light transmission were clearly visible and most pronounced where the average transmission was lower than approximately 60% (e.g., Fig. 2). This vertical

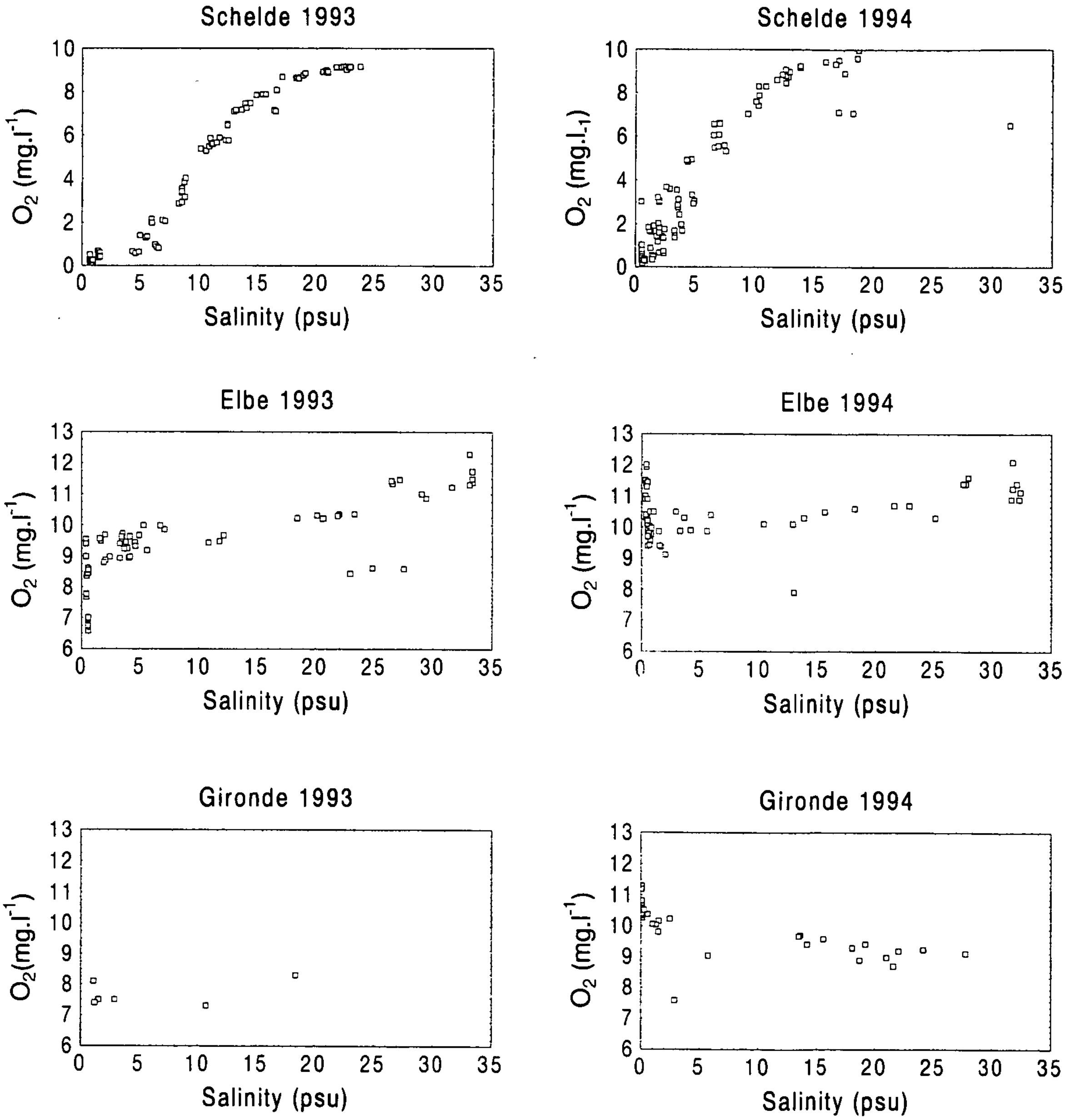

Fig. 3. Oxygen concentration vs. salinity in the different estuaries. The plots contain all data available in the database.

gradient in the suspended matter is obviously related to gravity. With respect to salinity, the Schelde and Elbe were usually well-mixed vertically, although the Elbe sometimes showed deep salt intrusion in the profiles. In the Gironde, persistent salt stratification (with vertical differences of 10 psu) was not uncommon. This stratification was pronounced even at high current velocities. Occasionally, extremely high suspended matter concentrations near the bottom increased the density of the water to a degree where water of lower salinity resided stably under higher salinity water with less suspended matter.

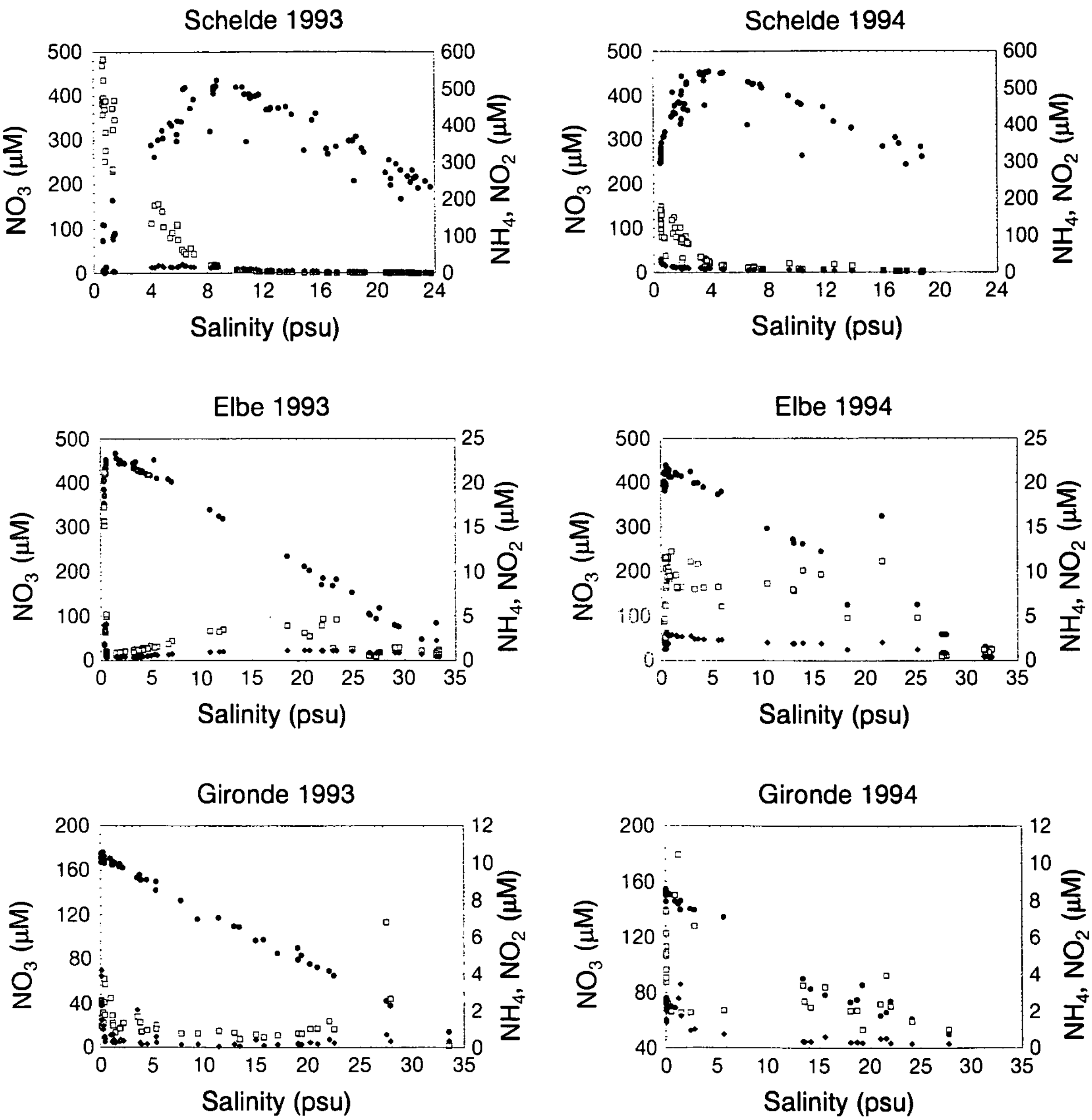

Fig. 4. Nitrate (filled circles; left axis), ammonium (empty squares; right axis) and nitrite (filled diamonds; right axis) vs. salinity in the different estuaries. Remark the differences in scale, especially of the right axes.

3. Nutrients

Fig. 3–6 summarise the longitudinal concentration gradients of dissolved inorganic nutrients and oxygen in the three estuaries. Compared to the Gironde, the Schelde and Elbe had much higher nutrient levels and (particularly in the Schelde) lower oxygen concentrations (Fig. 3). Oxygen concentrations in the freshwater part of the Schelde are generally very low, but in 1994, when discharge was high, the suboxic zone occurred at lower salinity than in 1993. Spatially, however, this was almost the same area, as the salinity gradient was shifted downstream in 1994.

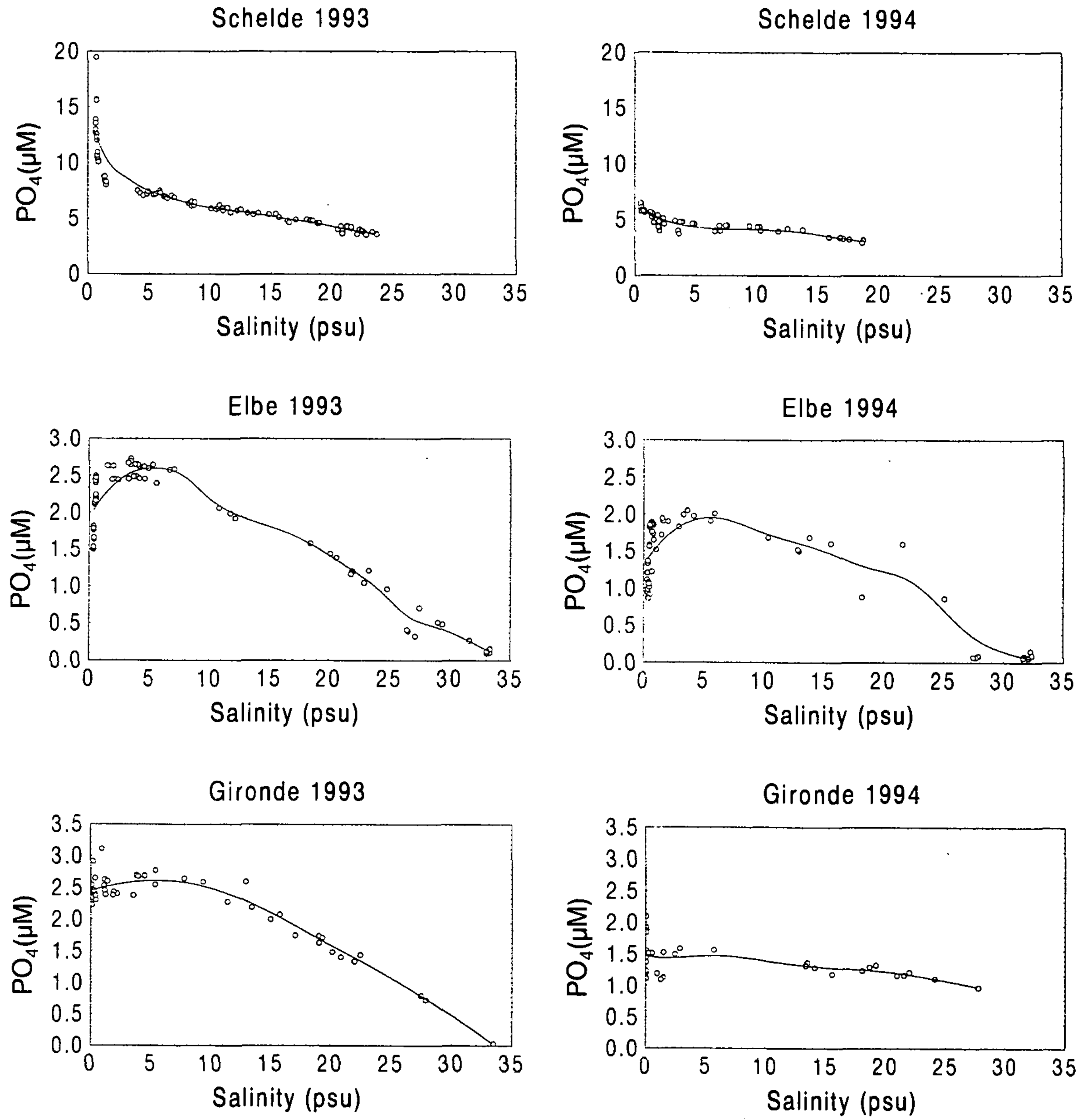

Fig. 5. Dissolved phosphate concentrations as a function of salinity in the different estuaries. Lines are distance-weighted linear smoothers.

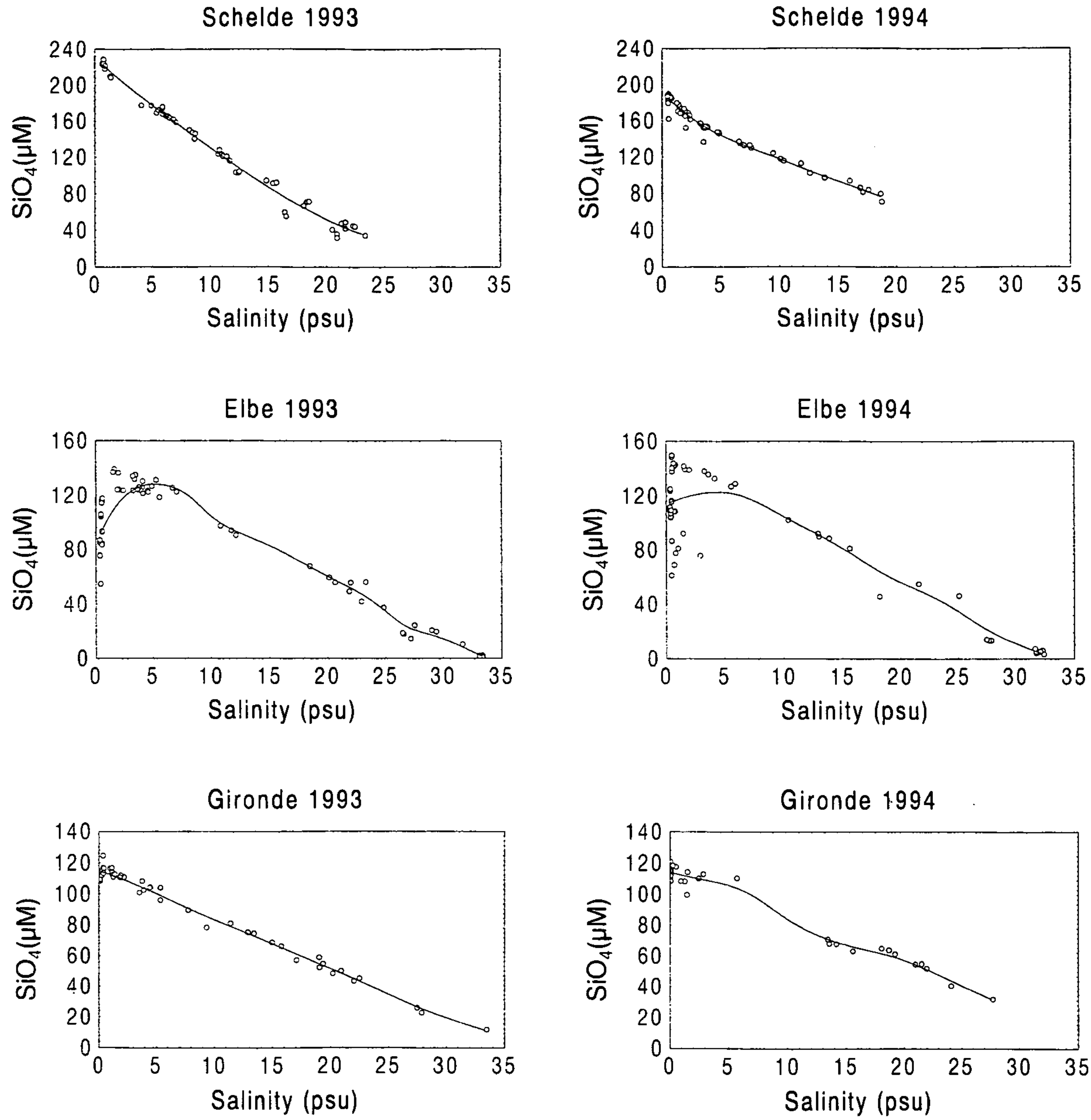

Fig. 6. Dissolved silicate concentrations as a function of salinity in the different estuaries. Lines are distance-weighted linear smoothers.

Schelde and Elbe have comparable nitrogen loading, but this load arrives mostly in reduced form in the Schelde, whereas in the low salinity zone of the Elbe, only about 5% of the DIN is in the form of ammonium (Fig. 4). Although the ammonium loads in the freshwater end member differ by an order of magnitude between the two estuaries, the years 1993 and 1994 differ in a consistent way. In the latter year, characterised by high runoff, peak ammonium concentrations in the freshwater are substantially lower than in 1993. Most probably, this is caused by a dilution effect of point sources of ammonium.

Nitrification, as evidenced by a drop in ammonium concentration and a simultaneous rise in nitrite and/or nitrate concentration, occurs in all three estuaries, but it is quantitatively much more important in the Schelde than in the other two estuaries. In fact, model calculations have shown that nitrification is the most important oxygen consuming process in the MTZ of the Schelde (Soetaert and Herman, 1995a). The zone of nitrification corresponds with the MTZ in all three estuaries. It is narrower and restricted to lower salinity zones in Elbe and Gironde than in the Schelde. The hypothesis of dependence of nitrification on suspended substrate for the bacterial populations is confirmed by these data.

With respect to dissolved orthophosphate, there is a very clear difference between its dynamics in the three estuaries (Fig. 5). In the Schelde, phosphate concentration in the freshwater was much higher than in the other two estuaries. It was also much higher in 1993 than in 1994, consistent with the hypothesis that phosphorus is mainly released by point sources. The difference between the 2 years is approximately a factor three, similar to the factor of 2–3 difference for ammonium concentrations in the freshwater end member. Phosphorus concentration in the low salinity part of the Schelde seems to be determined largely by the interaction with the suspended solids. A considerable fraction of the phosphate disappears from the dissolved phase in the MTZ. Most probably this is due to adsorption onto iron oxides, which are formed as a result of changing redox conditions in the transition from the anoxic to oxic parts of the estuary.

In the Elbe in both years, a substantial source of dissolved phosphate was present in the MTZ and downstream of it, up to around 8 psu. The source of dissolved phosphate corresponded to a clear source of dissolved silicate in 1993, although this was less clear in 1994 (Fig. 6; the trendlines are fairly similar in form, but the raw data present more variability in the low-salinity reaches in 1994). The general pattern suggests that the MTZ in the Elbe was a site of remineralisation of freshwater material of algal origin. In the Gironde, the 1993 profile of orthophosphate also showed a source located in and just downstream of the MTZ. However, the silicate profile (although with concentrations in the same order of magnitude as in the Elbe) was nearly linear, suggesting that the mineralised material was of terrestrial, rather than freshwater (algal) origin (at least of non-diatom origin; however, it can be assumed that freshwater algal material will be rich in silicon at this time of the year, when freshwater silicate concentrations are very high).

In all three estuaries, total particulate phosphorus correlated well with suspended matter concentrations. The relation between the two variables, however, was not the same for the estuaries. The total particulate phosphorus had similar concentrations (range 5–20 μM, with some exceptions) in all three estuaries. Consequently, the ratio of total particulate phosphorus to total suspended matter was considerably lower in the Gironde (where SPM was higher) than in the other estuaries.

In conclusion, nutrient concentrations were influenced by redox conditions (through interaction with the solid phase, mainly in the Schelde), by microbiological activity (nitrification and mineralisation) that was enhanced by the higher suspended solids concentrations in the MTZ, and by advective transport (dilution). Uptake of nutrients for primary production was presumably too small to leave any clear trace in the dilution curves.

4. Organic matter

Organic matter in estuaries can have different sources, and consequently widely different chemical characteristics. Apart from local production, both in the pelagos and benthos, the river is a source of organic matter to the estuary. As shown for the Westerschelde (Soetaert and Herman, 1994, 1995b; Soetaert et al., 1994) the sea can also be a source of high quality organic matter in the seaward part of the estuary.

In the three estuaries studied during the MATURE cruises, local primary production in the water column was primarily light limited (Goosen et al., 1999, this issue). Primary production can be predicted very well from biomass and euphotic depth in the estuary. Goosen et al. (1999) (this issue) noted that the primary production characteristics of the phytoplankton in the Gironde were much less adapted to high turbidity than in the Elbe and Schelde. Although this result is surprising at first sight, it was most probably caused by the complete lack of a genuine estuarine phytoplankton community (as judged from the species composition) in the MTZ of the Gironde (Muylaert and Sabbe, 1999, this issue). Apparently, the minimal conditions for the development of such a community (sufficiently long residence time with sufficient growth conditions) was not present in the Gironde. The low amounts of chlorophyll found in the estuarine waters were transported into the MTZ from the end member communities. In the Schelde, with the highest residence time of the water in the MTZ, such an estuarine community was best developed. Biomass remains relatively low, though, as a consequence of the shifts from a freshwater to a brackish water phytoplankton community. This also entails a local minimum in species diversity around the MTZ (Muylaert and Sabbe, 1999, this issue). The local primary production is relatively low compared to the bacterial production in the MTZ of all three estuaries, and these turbid zones of the estuaries are therefore highly heterotrophic.

An MTZ in an estuary can only be present if the residence time of particulate substances differs from the residence time of water and dissolved substances. This relates to the sinking, sedimentation and resuspension of the particulate matter; these processes have been worked out in a model for sediment transport for the estuaries concerned (Cancino and Neves, 1999a,b, this issue). For the transport dynamics of organic matter, this poses particular problems. The data clearly showed a correlation between particulate organic matter and total suspended matter concentrations in all three estuaries (although the predictive regression parameters differed between the estuaries), indicating that the particulate matter always contains a certain amount of organic matter.

In marine sediments, adsorption onto the surface of inorganic particles has been shown to be the major factor determining the degradability and preservation of organic material (Mayer, 1994). It is a reasonable hypothesis that adsorption onto inorganic particles determines the degradation rate and general biological availability of the organic material also in the MTZ of estuaries. This hypothesis provides two testable predictions: the ratio POC/DOC is dependent on the concentration of suspended inorganic material, and the degradation rate constant of organic material in the water column of the MTZ is of the same order of magnitude as that in marine sediments (i.e., much lower than typical marine water column values). The adsorption process (assuming equilibrium) may be represented by the following model:

$$\frac{\mathrm{dPOC}}{\mathrm{d}t} = k_1^* \mathrm{SPM}^* \mathrm{DOC} - k_2^* \mathrm{POC} = 0 \quad (1)$$

which can be rewritten as (writing TOC = POC + DOC and $K = k_2/k_1$):

$$\frac{\mathrm{POC}}{\mathrm{TOC}} = \frac{\mathrm{SPM}}{\mathrm{SPM} + K} \quad (2)$$

This relation was fitted to all data available in the MATURE database from the three estuaries. The relationship is shown in Fig. 7. Considering that these data come from three different estuaries in two different years, the fit is good. $K = 89.97$, r^2 (nonlinear least-squares fit) = 0.524. The estuaries do not separate themselves on the graph. This is remarkable, since in the Gironde both DOC concentrations and the ratio POC/SPM are considerably lower than in the other estuaries.

The reasonable fit of the data to Eq. 2 is, in itself, insufficient to accept the validity of the model (Eq. 1). Several other assumptions could lead to expressions similar to Eq. 2. For example, if the concentra-

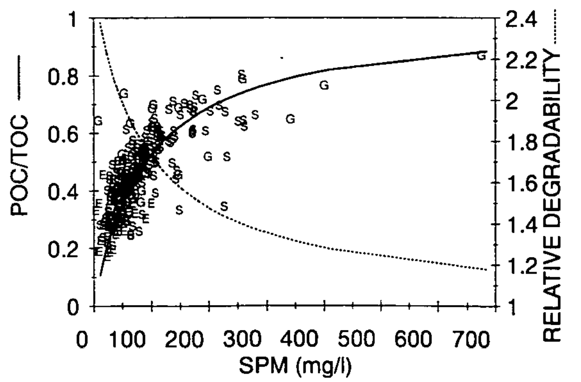

Fig. 7. Ratio of particulate organic carbon to total (particulate + dissolved) organic carbon as a function of suspended particulate matter. Data of the three estuaries and 2 years are pooled. Letters indicate the estuary sampled. Solid line: fitted equilibrium adsorption model according to Eq. (2). Dashed line: relative degradability of the organic carbon, calculated based on Eq. (3), where the degradability of pure particulate organic carbon is taken as 1.

tion of DOC and the ratio POC/SPM were constant everywhere, exactly the same solution would be found. However, the data clearly show variability in DOC and POC/SPM, and moreover the two are correlated (which would not be the case if they were equal to a constant + a random noise term). Similarly, if both DOC and POC/SPM were linearly related to a common factor, expressions such as Eq. 2 can be expected. Salinity is an obvious candidate as a common factor. Within each of the estuaries, DOC concentrations decrease linearly with increasing salinity. For POC/SPM, the linear decrease is less obvious but still suggested by the data. By taking a different upstream concentration for each estuary (especially for the Gironde, where concentrations of both variables are much lower), a good explanation of the ratio POC/TOC by using salinity as an explaining variable can be obtained. However, the problem is then transferred to an explanation of the upstream concentrations, and in particular to an explanation of the apparent correlation between DOC and POC/SPM in the upstream conditions of the different estuaries. This correlation is most probably generally valid. Meybeck (1982) shows that over more than three orders of magnitude variation in SPM in the world's rivers, the ratio POC/SPM varies over less than two orders of magnitude, and the ratio DOC/TOC is generally between 0.1 and 0.9. This pattern can only be explained if DOC covaries with the ratio POC/SPM. Decisive evidence on this problem, however, should come from kinetic studies on the relation between organic and suspended matter in estuaries.

Keil et al. (1997) provide strong direct evidence that in rivers, as in marine sediments, organic matter is adsorbed to mineral surfaces. For suspended matter in rivers, they show a strong correlation between organic content and mineral surface area. This correlation is similar for most rivers studied. Per unit area, the organic content in the riverine suspended matter is significantly higher than for sediments in the river deltas. Additional data on stable isotope ratios show a high turnover of the organic matter coating of the mineral particles between the time they are suspended in the river and the time they are deposited in the deltaic sediments. Less than 30% of the organic matter adsorbed to the suspended particles in the rivers is eventually buried in the delta. The direct evidence for adsorption, and the demonstration that the adsorbed organic matter is dynamic in the river-delta transition, supports the view of an equilibrium between adsorbed and dissolved organic matter in estuaries. In many respects (e.g., the salinity gradient, sedimentation, flocculation) the tidal inner estuaries studied here are comparable to the deltas of river-dominated systems.

A second prediction of the adsorption hypothesis is the relatively low bacterial degradation rate of the organic material adsorbed onto inorganic particles. Degradation rate of the organic matter has not been determined directly in the present research project. However, from measurements of bacterial production by thymidine uptake (Goosen et al., 1997) one can estimate roughly the relative rate of breakdown of the dissolved and particulate organic matter. We regressed bacterial production rate on POC and DOC in the following multiple regression model:

$$BAPR = -0.66 + 0.35^{*} DOC + 0.14^{*} POC \quad (3)$$

Bacterial production rate ($\mu g\ C\ l^{-1}\ h^{-1}$) was temperature-corrected using a Q_{10} of 2.5. Due to the error structure of bacterial production data (multiplicative error), fitting was performed after log-transforming both sides of the equation. r^2 of this non-linear estimation was 0.77. Fig. 8 shows the correspondence between predicted and observed temperature-corrected bacterial production in the three estuaries.

With an r^2 of 0.77 most of the variation in bacterial production rates is described as a simple

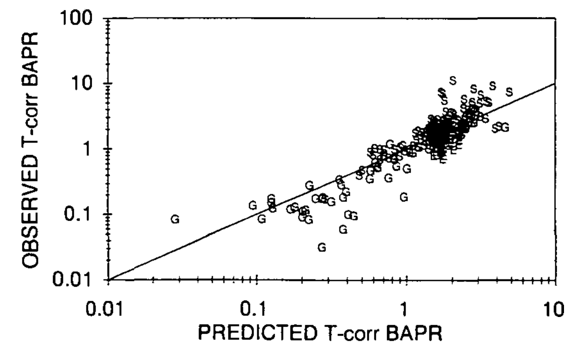

Fig. 8. Comparison between observed (temperature-corrected) bacterial production rate ($\mu g\ C\ l^{-1}\ h^{-1}$) and predictions based on a linear function of POC and DOC concentrations. Data are labelled by the first letter of the estuary sampled. For comparison, the 1:1 line is also given.

function of substrates available. It was not possible to relate any of the remaining variance to a measured environmental variable, such as SPM or salinity, nor to the estuary sampled. Strikingly, the largest deviation between observation and model occurred in a few samples from the Hoboken–Rupelmonde region in the Schelde, both in 1993 and in 1994. This is a zone of intense biological and biogeochemical activity and gradients in the Schelde. It is at the confluence of the Rupel and Schelde, where the Rupel brings in heavy loads of ammonium and organic matter. It is also at the oxygen front in the river, where maximal nitrification activity takes place. It is, finally, the zone with a pronounced sink of dissolved phosphate. Whether the bacterial production relates to a higher quality of the substrate, a transient higher degradability due to salinity increases, enhanced activity due to the nitrification front or other factors is a question that remains open for further research. However, the comparison with the Elbe and Gironde data, where this localised deviation does not occur, suggests that it is not related to salinity in itself. Also nitrification, although more intense in the Schelde, is a factor common to the three estuaries. The oxygen front therefore seems to be involved in the explanation of the phenomenon.

Goosen et al. (1997) studied bacterial production rates, together with algal primary production in the Schelde over the whole year 1991. They describe a strong relation between bacterial production and both DOC and POC concentration. In contrast to the present data, these relations are based on a sampling of the whole estuary, including the lower parts. The slope of the regression on organic matter concentration changes significantly during the season. During phytoplankton blooms the regression slope is much lower than during non-bloom periods. This is explained by the relatively large contribution of algal products to the substrates used by the bacteria in the lower estuary during blooming periods. The slope derived from the present data on the three estuaries is intermediate between blooming and non-blooming periods, but most data are derived from the upper estuary where the influence of primary production on bacterial production is small year-round (Goosen et al., 1997).

The bacterial production rates are not very high, considering the important amount of organic matter present in most samples. By assuming that organic matter decay rate equals two times the bacterial production rate, and recalculating units, we conclude that the first order decay rates of DOC are in the order of 6 $year^{-1}$, and for POC in the order of 2.4 $year^{-1}$. The difference in decay rates of POC and DOC in Eq. 3 leads to the predicted overall decay rate of the organic matter added to Fig. 7. The dependence of degradability on SPM is most pronounced in the range of SPM between 0 and 100 mg l^{-1}. Heip et al. (1995) review degradability constants of organic matter in sediments of tidal estuaries. They found typical values in the order of magnitude of 1–10 $year^{-1}$. Middelburg et al. (1996) derived degradability constants of organic matter between 0.5 and 7 $year^{-1}$ for surface (top 10 cm) sediments in the same part of the Schelde as studied here. There appears to be no substantial difference in degradability of organic matter in suspended material and in surface sediments. Similar values (0.3–5 $year^{-1}$) have been found in suspended material in the upper Bay of Fundy (Hargrave and Philips, 1989). This observation is again consistent with the hypothesis that organic matter degradation in the MTZ of estuaries is determined by the association with mineral particles.

5. Floc size

The dynamics of flocs in the MTZ were studied in the first place by in situ camera systems (Eisma et al., 1990; Eisma and Kalf, unpublished report). Two different camera systems were deployed: a camera with a 1:1 image, and one with a 1:10 magnification. The volume of water photographed by the latter camera is approximately 100 times smaller than that covered by the 1:1 camera.

Although detailed analysis of the particle spectra resolved by both cameras indicates consistency between the spectra, the (volume-based) mean particle sizes calculated from both cameras have a relatively low correlation coefficient of 0.32. The data show considerable scatter, especially in the larger diameter classes which have a large weight in the calculation of the volume-based mean size. To filter out as much of the random variability as possible, we calculated the geometric mean of the volume-based particle size

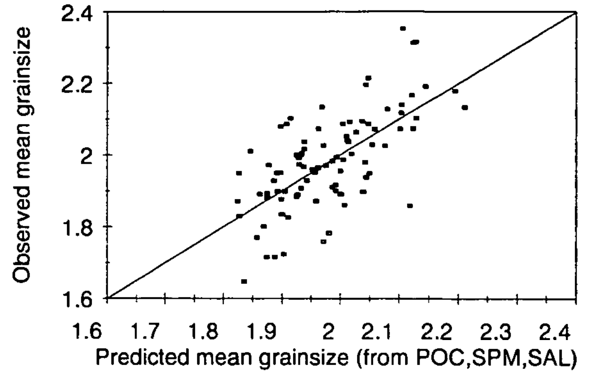

Fig. 9. Relation between predicted and observed mean particle size. Mean particle sizes are the log-transformed geometric means (μm) of both camera systems used. The linear predictor used is explained in the text.

of both cameras as a relative measure of particle size that can be related to other measured variables.

In Fig. 9, the geometric mean particle size is plotted against the best predictor we could calculate from the environmental data available from the joint field campaigns. This predictor is expressed as:

$$\log_{10}(\text{Particle size}) = 1.714 + 0.105^* \log_{10}(\text{SPM}) + 0.145^* \log_{10}(\text{POC}) - 0.103^* \log_{10}(\text{SAL}) \quad (4)$$

where: SPM = suspended particulate matter concentration (mg l^{-1}); POC = particulate organic carbon concentration (mg C l^{-1}); SAL = salinity of the water (psu).

This regression had an r^2 of 0.44 ($n = 97$) and was highly significant. In view of the rather low correlation between particle sizes determined by the two camera systems, its value may actually indicate that most of the non-random variation in the particle size is effectively explained by the three environmental variables.

Among the single environmental factors, POC explains most of the variation in particle sizes. The (log–log) regression of particle size on POC has an r^2 of 0.31. This value is 0.21 for SAL, and 0.15 for SPM. The result of this regression analysis using the average of the 1:1 and 1:10 camera systems is qualitatively in accordance with regressions of the particle sizes obtained by the 1:1 camera or the 1:10 camera systems on environmental variables separately. We consistently find that POC is the single most important variable in the environment explaining the size of the flocs as observed in the field.

Two main factors are thought to be important for the formation of a floc upon collision between two particles (van Leussen, 1994): the organic coating of the particles and the salinity of the surrounding water influencing the double layer dynamics. The regression equation qualitatively indicates the importance of this coating with the positive exponents for POC and SPM. The influence of salinity is more complex. In the regression equation particle size decreases with increasing salinity, contrary to what is expected from theory. However, a closer inspection of the data suggests that the influence of salinity is non-linear. Fig. 10 plots, as a function of salinity, the residuals of a regression of particle size on POC and SPM. It can clearly be seen that particle sizes are larger than expected at salinity up to 1 psu, but decrease again at higher salinity. Salinity change (from freshwater to slightly brackish) has a more profound effect than salinity per se, possibly because a new equilibrium between organic coating and salinity is established at higher salinity than appr. 1 psu. It should be noted that, although most observations in this salinity range

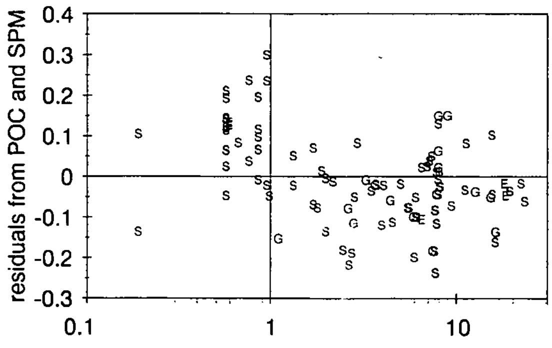

Fig. 10. Dependence of floc size on salinity. The ordinate gives the residuals of (log-transformed) geometric mean floc size (μm) from the linear predictor terms for POC and SPM only. The abscissa is salinity on a logarithmic scale. Highest residuals are found in the 0.1–1 psu salinity range. Letters indicate the estuary sampled.

come from the Schelde estuary, the Elbe observations are fully in line with the Schelde data.

6. SPM, organic matter and higher trophic levels

Goosen et al. (1999) (this issue) estimated that in the Schelde MTZ 5–20% of net bacterial production was grazed by the dominant protists (small heterotrophic flagellates). Assuming quasi-steady state in the system, this leaves a considerable fraction of the bacterial production (which itself is largely based on allochtonous organic matter) for grazing by other components in the system. The organic matter in the MTZ can be considered as the basis of a detrital small food chain in a quite complicated way: it can be consumed by mesozooplankton and hyperbenthos either directly, through the bacterial production or through consumption of the microplankton. Fockedey and Mees (1999) (this issue) showed that, although mesozooplankton forms a dominant component of the food of the hyperbenthic mysid *Neomysis*, large quantities of unidentifiable detritus are present in the stomachs. The energetic value of this detritus, which in composition reflects the flocs in the suspended matter, remains unclear. For the dominant estuarine copepod species *Eurytemora* sp., Gasparini et al. (1999) (this issue) showed that high SPM concentrations negatively affect egg production. Phytoplanktonic food seems to enhance productivity of the copepod, which most probably actively selects phytoplankton from a mixture of particles. However, its survival in estuaries with very high SPM and very low chlorophyll concentrations indicates its capacity to survive and even reproduce when detrital particles form the bulk of its prey. The precise role of bacteria and microfauna in the diet of the copepod remains an interesting area of research.

Overall, these studies indicate that even for the few species specifically adapted to the MTZ in estuaries, the high concentrations of SPM present specific physiological difficulties. Their feeding and reproduction seems to be hampered by the suspended material, but does not drop to zero even in extreme conditions. This characteristic may constitute an important competitive advantage over other species that would not be able to cope with the high SPM concentrations. The precise processes by which land- or river-derived organic matter is converted into food for higher trophic levels are, however, not fully described.

7. Conclusions

The field observations during the MATURE campaigns have confirmed the importance of the MTZ processes for the biogeochemistry of the three estuaries studied. The MTZ is a zone of enhanced mineralisation and nitrification. Both processes can be related to the longer residence time of particles in this zone, giving rise to a concentration of organic substrate (important for mineralisation) and of a physical substratum for the nitrifying bacteria. The association between particles and organic matter can be explained by a single sorption equilibrium for the three estuaries considered, irrespective of the large differences between the systems. It can also be related to the rate of bacterial breakdown of the organic matter. Finally, the high concentrations of suspended solids in the MTZ constitute a physiological difficulty for higher trophic levels, which suffer dilution of their food by indigestible material. However, specialised species find a unique niche in this zone, which is poor in competitors. They may also profit from the high concentrations of organic matter, either directly or through the microbial food chain.

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