Biogeochemical Processes in Estuaries

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Abstract: The hydrodynamic properties of estuaries are extremely variable and depend on the relative ratio of tidal mixing of freshwater and seawater. This ratio influences essential properties of the estuarine system such as the degree of vertical stratification of the water column, the residence time of freshwater, and the existence and intensity of a turbidity maximum. The estuaries, which are the obligated pathways for the transfer of freshwater to the ocean, act often as a filter for many constituents, whose efficiency increases with the residence time of freshwater in the system. This is especially the case for suspended particulate matter, which is often removed to a large extent from the water column by flocculation and sedimentation, generally occurring in the area of the turbidity maximum. Particulate organic matter and trace metals are therefore largely trapped in the estuarine sediments and never reach the sea. The turbidity maximum may, furthermore, generate anoxic conditions, which affect the behaviour of numerous components such as nutrients and redox-sensitive metals like iron and manganese. Finally, the intense biological activity, characteristic of the estuarine environment, is responsible for emissions of various biogases (CO_2, CH_4, N_2O) to the atmosphere. Due to the complexity of the hydrodynamic properties, the existence of strong gradients of chemical and biological parameters as well as the numerous processes occurring in estuaries, the evaluation of elemental fluxes requires the development of elaborated coupled hydrodynamic-biogeochemical models. Large errors could be generated by the use of simplified hypothesis (such as in the AZE method). In addition, estuaries are usually far from steady-state conditions and the estimation of fluxes requires intensive measurements at the boundaries of the systems.

Introduction

Being obligatory pathways between fresh water and marine systems, estuaries play an essential role in the transfer of material from the continents to the oceans. Both the hydrodynamics and the biogeochemical processes characteristic of this environment are however very complex and render the evaluation of the transfer fluxes of dissolved and solid components difficult. Most of the present-day evaluations of the river input to the coastal zone are still based on the concentration of the component of interest at the estuarine mouth multiplied by the fresh water discharge, neglecting the process which may occur within the estuary. In a region heavily populated like Western Europe (see Table 1), the fresh water entering the estuaries is strongly disturbed by human activities and transports excess concentrations of organic matter, nutrients and a large spectrum of organic or inorganic contaminants. In addition, European estuaries are usually areas of intense harbor activities linked to a large variety of industries. Navigation of increasingly large ships implies continuous dredging and other hydraulic works. For these reasons, estuaries are very disturbed ecosystems whose assimilative capacity of pollutants has often been overestimated.

Definition, classification and physical parameters

The most widely accepted definition of estuaries is that given by Pritchard (1967): "An estuary is a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage".

However, this definition does not take into account the area of the river subjected to the oscillations of the tide but where only fresh water flows.

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River	Mean water discharge ($m^3 sec^{-1}$)	Surface area (10^3 km^2)	Residence time (days)	Inhabitants per km^2	Inhabitants per m^3 sec^{-1}
Elbe	715	146	15-30	230	47000
Rhine	2200	224	2.5	190	19000
Scheldt	120	21.6	30-90	209	37600
Thames	350	14	30	775	31000
Seine	435	78.6	30	211	38000
Loire	830	115	30	135	18700
Gironde	1000	71	30-90	68	4800
Douro	1700	115	3 - 7	101	6800
Rhone	1670	97	2	103	6000
Po	1540	65	2	167	7000

Table 1. Characteristics of some important European estuaries including the surface area of the hydrographic basin, the mean residence time of freshwater in the estuarine zone and the density of inhabitants in the basin.

This represents often a large stretch of the river which cannot be ignored in estuarine studies, especially if sediment transport is considered. The limit of tidal influence on surface elevation can be traced as the point where the river bed rises above the sea level, in the absence of dams and sluices. This is the most commonly used limit of the hydrodynamic models. From a geomorphological standpoint, various types of subdivisions can be considered besides the classical coastal plain estuary (or drowned river valley), fjord type estuaries, bar-build estuaries and some lagoons are also included in the definition of Pritchard.

From a biogeochemical point of view, the characteristics of the water circulation induced by the mixing of fresh water and salt water are however more important. In a salt-wedge estuary, fresh water tends to spread out over the denser salt water, which flow landwards along the bottom. Under these stratified conditions, which mainly occur when the river discharge is large and the tidal amplitude low, vertical mixing is limited and the residence time of fresh water in the estuarine zone is very short. In European estuaries, this is typically the case for the Rhine, the Rhone and the Po where relatively little salt water mixes with fresh water. Nearly all fresh water is discharged into the adjacent coastal ocean within the surface water layer giving rise to a well-established river plume and an "external" estuarine circulation induced by density gradients.

The tidal effect becomes more important when the fresh water discharge diminishes and the salt intrusion increases. Friction with the bottom and at the pycnocline interface tend to mix vertically the water masses giving rise to a well-mixed estuary. Under these conditions, the volume of salt water entering the estuary per tide is much larger than the volume of fresh water discharged by the river during the same period of time. The ratio of these volumes is a convenient way to characterize the type of estuarine circulation. Except for the three stratified rivers mentioned above, many of the European estuaries may be considered as moderately to well-mixed estuaries. Due to its large dilution by seawater, the residence time of fresh water and river born material in the estuarine zone may reach several months (see Table 1) and this enables potential changes of its composition and properties.

The circulation pattern in fjords is more complicated because of their greater depth (typically 300-400 m) and often the existence of a sill at the entrance which isolates deeper water from the ocean. Fresh water entering fjords forms a low salinity surface water with little vertical mixing. In the Norwegian fjords, the sill depth is often so shallow that the deeper basin waters remain stagnant for prolonged periods.

In the bar-build estuaries and lagoons, the width of the sea-water inlet is small compared to the horizontal dimensions of the estuary. This inlet does not always allow free passage of sea-water flow at all stages of the tide. In these systems with reduced circulation, the influence of wind may become important. There are many lagoons bordering the coast of Italy, Spain and France in the Mediterranean Sea and those of Spain and Portugal along the North Atlantic. Due to the reduced circulation, lagoons are often highly polluted but they do not contribute significantly to the continental input.

Behaviour and transfer of material through estuaries

We will mainly discuss in this section the processes affecting the transfer of material through moderately to well-mixed estuaries where the residence time of fresh water is long enough to affect the transfer of many dissolved or particulate species from land to sea. In the framework of this book, emphasis will be put on european estuaries.

Particulate matter

The behaviour of particulate matter in estuaries is particularly complex. Most of the particulate matter, organic and inorganic, transported by rivers exhibits a negative surface charge. The increase of ionic strength during the mixing of fresh water and sea-water leads to the compression of the charged double layer. As a consequence, the river borne particles, often colloidal, are flocculated and more able to settle. This process occurs at relatively low salinities (1 - 5 ‰) and favours sedimentation in this area. Furthermore the hydrodynamic properties of the estuarine circulation also favour the flocculated material to settle and accumulate within this zone (Fig. 1). The net effect of the density current induced by the horizontal salinity gradient, is that the residual bottom flow, integrated over a tidal period, is predominantly oriented landwards. These strong currents are responsible for an intense bottom transport and the river borne solid is trapped to a certain extent by this net non tidal current. In addition these currents are also able to carry upstream, by bedload transport, large amounts of coarse marine sediments. The conjunction of these currents and the flocculation process are favouring the occurrence of a turbidity maximum often located at the upper part of the estuary. This zone is also characterized by intensive shoaling where sediments of continental or marine origin tend to accumulate. This phenomenon is particularly spectacular in the Gironde estuary where the turbidity maximum may extend over more than 100 km and the concentration of suspended matter in the water column may exceed there 100 gl^{-1} (Jouanneau et Latouche 1981).

The bottom currents generated by the tides are also responsible for a deposition-resuspension cycle of sediments. If the sediments are organic rich, the resuspension generates anoxic events in the

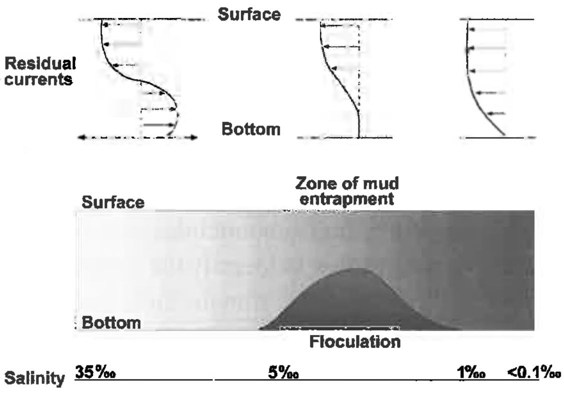

Fig. 1. Influence of density currents on the residual transport of suspended matter and on sediment accumulation in a partially well mixed estuary.

water column which may have deleterious effects on aquatic life. This fact has been well established in the Gironde (Abril et al. 1999), Loire (Thouvenin 1994) and in the Humber estuaries (Uncles et al. 1998). Besides this short term fluctuation, there are also large fluctuations of the concentration of suspended matter influenced by the river discharge. In coastal plain estuaries most of the sediment transport to the sea occurs during flood events, due to the resuspension of the material accumulated in the river and estuarine system during periods of normal discharge.

The evaluation of a budget for suspended material is therefore complex and requires more than discontinuous measurements of turbidity and water velocities at discrete stations. In addition to the longitudinal gradient of suspended matter, there is also a strong vertical gradient due to resuspension by bottom flow. The bed load transport, which is particularly difficult to measure directly, is of major importance in the sedimentary dynamics of an estuary. Finally, dredging complicates further attempts to evaluate budgets for the particulate material. On geological time scales, it is obvious that estuaries and deltas are very active systems characterized by intensive accumulation of sediment and particularly of organic rich muds (Berner 1982). Therefore physical models have been used in the past, to understand the behaviour of cohesive sediments in estuaries and to predict the effects of dredging activities. Today, several mathematical models of the sediment transport in estuaries have been developed and represent probably the best approach to quantify the fluxes of solids in these environments (Burchard and Baumert 1998; Guan et al. 1998; Brenon and Le Hir 1999). Some of these models are able to predict the occurrence and properties of the turbidity maximum.

Natural and artificial radionuclides are very useful markers which allow to identify the origin of the suspended matter and to estimate their residence time within the estuarine zone. For example, some specific radionuclides discharged by reprocessing plants such as those of La Hague and Sellafield, are good tracers for particles of marine origin which can be identified in the European estuarine sediments (Martin et al. 1993). The utilisation of short half-live radionuclides such as ^{234}Th and ^{7}Be looks as another promising tool in order to gain a better understanding of the particle dynamics, especially in the turbidity maximum (Feng et al. 1999).

Dissolved and particulate carbon

Recent estimation of the amount of dissolved (DOC) and particulate organic carbon (POC) transported by rivers on a global basis are in rather good agreement and amount to about 0.4 - 0.5 GtC yr^{-1} (Meybeck 1993; Ludwig et al. 1996) of which 0.1 GtC yr^{-1} is of anthropogenic origin. The organic load is roughly equally distributed between the dissolved and the particulate phase. There are however still large uncertainties concerning the fate of the dissolved and particulate organic matter in estuaries and in the adjacent coastal zone.

It is generally considered that the organic matter entering the estuarine zone is relatively refractory and that only a small fraction can be respired before to be transferred to the shelf. Spitzy and Ittekkot (1991) have evaluated the speciation of the river borne organic matter and concluded that only 15% of both DOC and POC is degradable in the estuarine environment. This agrees well with the observation that DOC behaves quite conservatively in estuaries (Laane 1980; Mantoura and Woodwards 1983) or in other words that the concentration of DOC is simply proportional to salinity in these environments (Fig. 2). This is even true in heavily polluted estuaries such as the Scheldt and the Elbe which receive high loads of anthropogenic organic matter.

The behaviour of particulate organic carbon (POC) is more complex and diverse (Fig. 3). Planktonic and benthic primary production within the estuary may constitute a significant source of organic matter. The primary production is most often limited by the light penetration which is reduced due to the high concentration of suspended matter. The decrease of turbidity in the upper part of the estuary favours the development of phyto-plankton in the brackish water part or in the adjacent coastal zone. The classical pattern often found in estuaries is the production of large amounts of phytoplankton as soon as the turbidity has been reduced due to flocculation and sedimentation of suspended matter of continental origin. In this

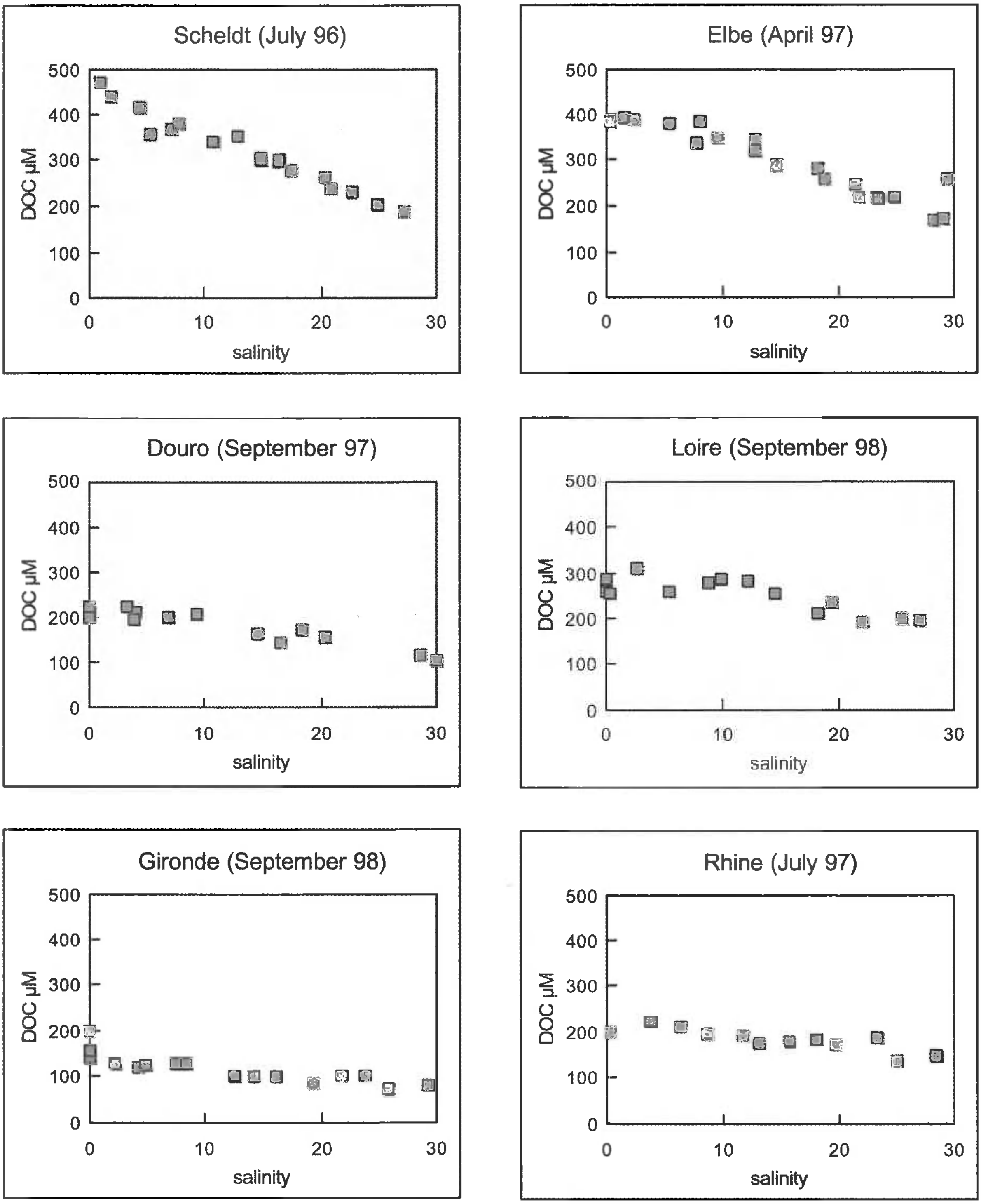

Fig. 2. Evolution of the concentration of dissolved organic carbon as a function of salinity in various european estuaries (BIOGEST Project, database: web site: http://www.ulg.ac.be/oceanbio/biogest/biogest.htm).

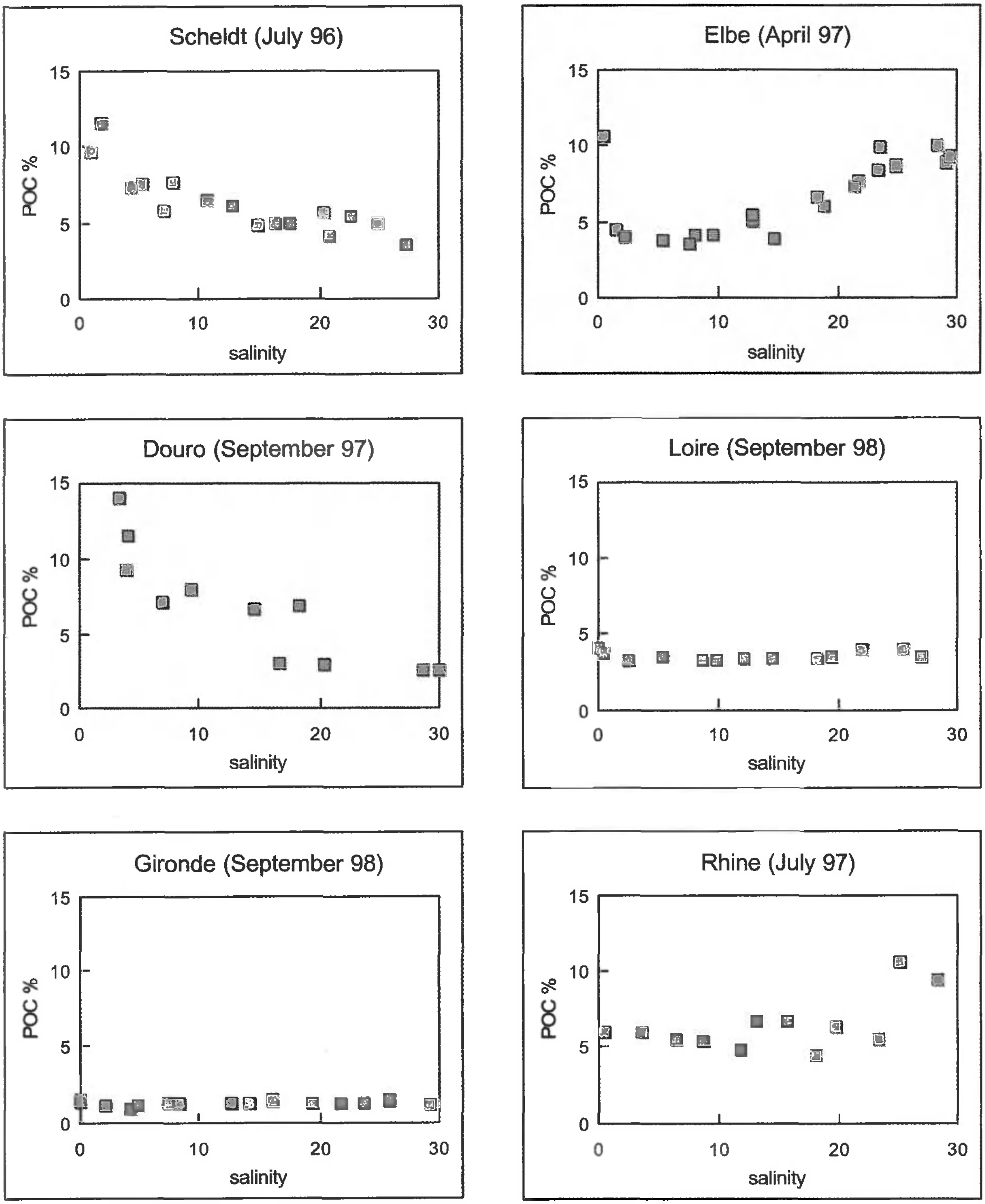

Fig. 3. Evolution of the organic carbon content (weight %) in the suspended matter of as a function of salinity in various european estuaries (BIOGEST Project, database: web site: http://www.ulg.ac.be/oceanbio/biogest/biogest.htm).

case,the percentage of POC in the suspended matter exhibits an increase with salinity. This situation can be seen in the Rhine and Elbe during spring and summer. In highly eutrophicated systems, the maximum of primary production is observed in the fresh water part and the suspended matter is characterized by a high POC content upstream with a progressive decrease with salinity.This is typically the case of the Scheldt and Douro. Note that both processes may coexist in the same estuary. Very high concentrations of chlorophyll-a (often exceeding 100 µg/l) can be observed in the fresh water part of estuaries (Meybeck et al. 1988; Rendel et al. 1997), but this biomass decays very rapidly when the salinity increases (Fig. 4). The decrease of chlorophyll-a is partly due to the mortality of fresh water phytoplankton when salinity increases but also to the flocculation and deposition of the particulate matter.In strong tidal estuaries, the contribution of benthic organisms living on the sand banks is often predominant, which complicates the evaluation of the primary production.

By comparing organic carbon distribution in sediments from the deltas of major world rivers with published data on riverine transport of organic carbon, Berner (1982) demonstrated that a major part of the riverine POC is deposited in estuaries and deltas. The amount of organic carbon trapped in these areas is intimately related to the rate of deposition and accumulation of suspended matter in the estuaries, which is known to be high but remains poorly quantified. It is however well established that the organic rich sediments deposited in estuaries are strongly anoxic and that their resuspension may generate deleterious effects in the water column. Due to the resuspension - deposition cycles of the sediments, turbulent mixing dominates in the benthic boundary layer and enhances the exchange of dissolved constituents across the water-sediment interface.

Respiration measurements as well as investigation of the composition of the pore water indicate that the organic matter is intensively degraded after deposition in the muddy sediments. Anaerobic conditions prevail and one can identify the successive use of nitrate, manganese, iron and sulfate as oxidants. Methanogenesis is also observed mostly in the low salinity zone of estuaries where the amount of sulfate available is limited. The products of the respiration are partially transferred to the water column and dissolved Mn^{++}, Fe^{++} and H_2S can be detected in the water column of the muddy areas, even if this water column remains well oxygenated.

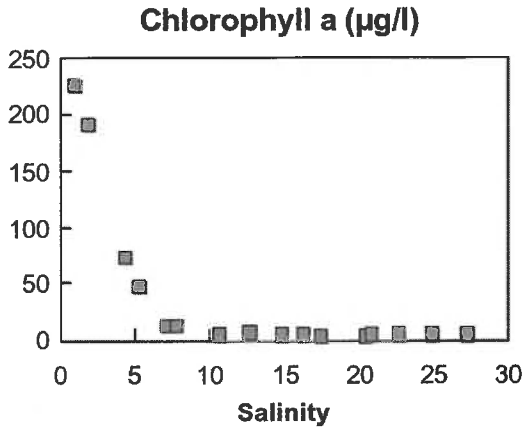

Fig. 4. Evolution of the concentration of chlorophyll-a with salinity in the Scheldt estuary in July 1996 (BIOGEST Project, database: web site: http://www.ulg.ac.be/oceanbio/biogest/biogest.htm)

The balance between autotrophy and heterotrophy has been significantly modified by human activity but in an antagonistic way. The increase of nutrient load has lead to enhancement of net ecosystem production but on the other hand increased respiration of the organic carbon load has shifted the system to heterotrophy. A compilation of the data published in the literature (Gattuso et al. 1998) indicates that estuaries are most often net heterotrophic with a mean ratio of gross primary production to respiration equal to 0.8 (Fig. 5).

There are still considerable efforts required to understand the factors controlling the primary production, the behaviour and fate of phytoplankton in eutrophicated estuaries.The relative importance of production and consumption of biological particles has been reviewed thoroughly by Heip et al. (1995). It is likely that light is not the only controlling factor of photosynthesis in these systems. Furthermore, the intensive vertical mixing imposes to the phytoplankton short term fluctuation

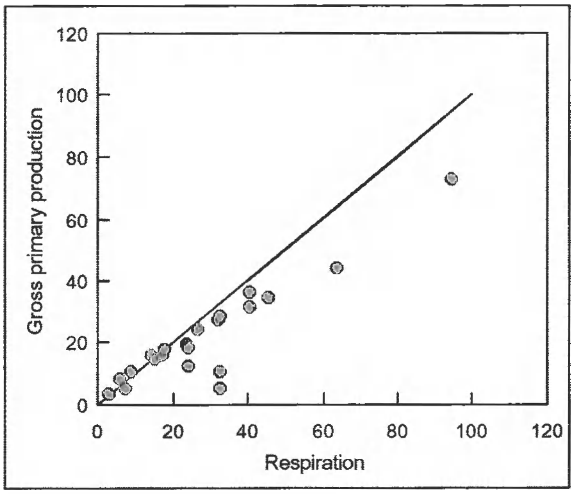

Fig. 5. Gross primary production (Pg) versus respiration (R) in world estuaries according to Gattuso et al. (1998). The straight line corresponds to a 1:1 relationship. The regression equation obtained gives $P_g = 1 + 0.76\,R$; r = 0.92 ; N = 21.

of the light intensity, but it is not clear how this modifies the photosynthetic efficiency of the cells. More specifically, the influence of changing salinity on the photosynthetic activity and mortality needs to be better documented. Finally, the importance of benthic productivity on tidal flats has not been studied carefully until now. According to Heip et al. (1995), it may be in the range of 25 to 50% of the total primary production. Long term respiration experiments of suspended matter or deposited sediments are also necessary in order to quantify the fate of organic matter. The stable isotopes ^{13}C and ^{15}N have been used with success to identify the origin and fate of organic matter in estuaries (Thornton and McManus 1994). Their use should be intensified in order to gain a better understanding of the carbon and nitrogen cycle in these complex environments.

Nutrients

Agriculture, industry and domestic activities, all contribute to the enhancement of the concentration of nutrients in estuaries. In developed and heavily populated countries as in Europe, the concentration of N and P nutrients have been increased almost by one order of magnitude with respect to the pristine levels. The only exception is the concentration of silica which did not increase or has even decreased in several rivers, most often where dams have been constructed, retaining the opal of fresh water diatoms in the sediments of the artificial lakes (Humborg et al. 2000). This is of considerable importance for the coastal zone where the reduced Si flux may contribute to the shift in species dominance from diatoms to flagellates (Billen et al. 1991; Rendel et al. 1997).

Due to the long residence time of fresh water in estuaries and to the intense biological activity, the nutrients exhibit a strong non conservative behaviour. First, because of their multiple source, there are strong seasonal fluctuations of the river input of dissolved N, P and Si species. Furthermore because of the changing physico-chemical conditions and of the strong biological activity, modifications of the nutrient species distribution may occur in the estuarine zone and modify their transport to the sea.

Ammonium originates mainly from domestic waste water, intensive stock farming and *in situ* degradation of organic matter. It is unstable in well oxygenated water and is transformed by nitrifying bacteria into nitrate and nitrate. This process has strong effects on the water quality of the estuary. It has been shown by model calculations (Vanderborght et al. 2002) that nitrification is predominantly responsible for the oxygen minimum observed in the Scheldt estuary (Fig. 6). Abril et al. (2000) came to the same conclusion in the Gironde estuary. Furthermore, the nitrification reaction produces protons, according to the reaction:

$$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$$

This reaction is also mainly responsible for the pH minimum often observed in estuaries, which in turn decreases the alkalinity, increases pCO_2 and may led to the dissolution of calcium carbonate.

Nitrate in turn may undergo denitrification, mainly in the area of the turbidity maximum where anoxia is favourable to the bacterial use of NO_3^- as an oxidant. Deposited sediments are also active denitrifying environments inducing the consumption of nitrate, which diffuses from the water column to the benthic boundary layer (Middelburg

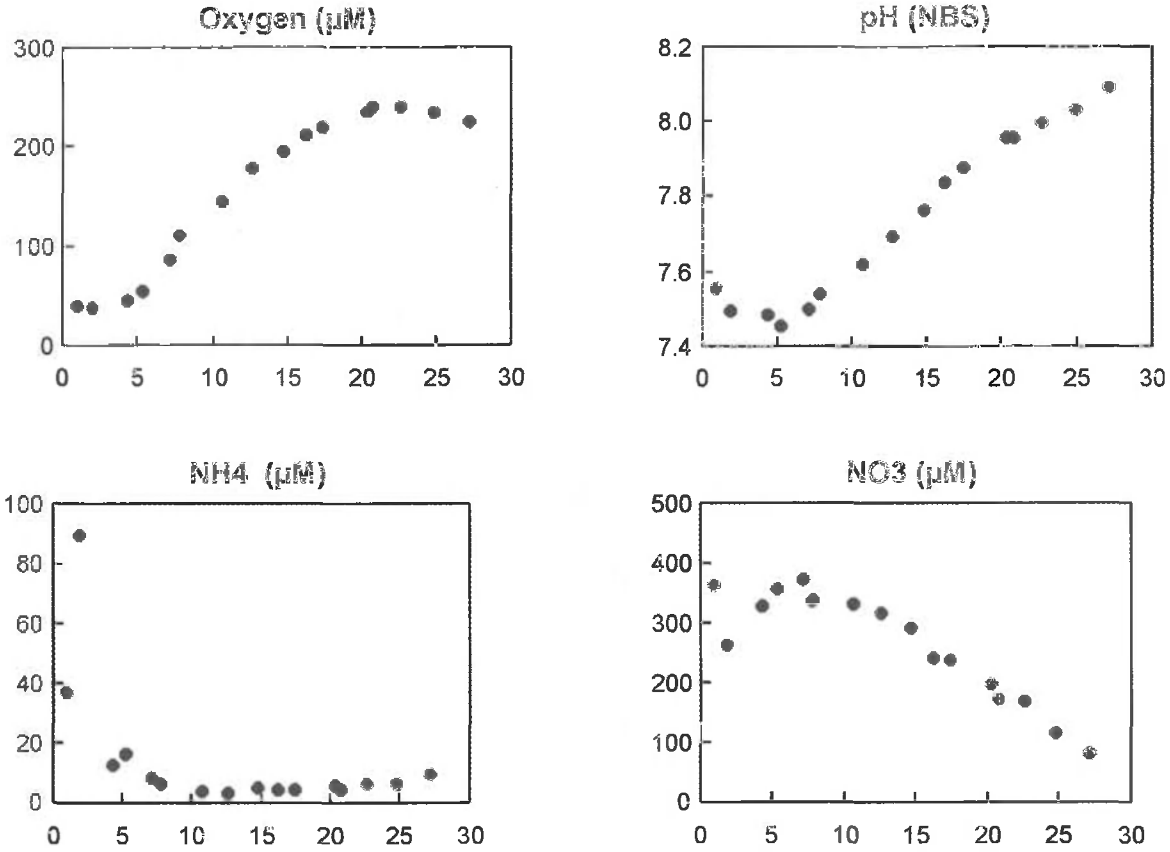

Fig. 6. Evolution of the concentration of oxygen, NH_4^+, NO_3^- and pH with salinity in the Scheldt estuary (July 1996) (after Vanderborght et al. 2002).

et al. 1995). N_2 and N_2O produced during this process are transferred to the atmosphere and lost for the aquatic system. Finally, both nitrate and ammonia are consumed during photosynthesis. The seasonal evolution of N-nutrients is often characterized by a marked decrease of their concentration during the summer, mainly du to the photosynthetic activity of phytoplankton and macrophytes.

All these processes have a strong influence on the transfer of nitrogen species from the continents to the oceans. They occur in all estuaries but to a variable extent, depending on the residence time of fresh water in the system, as shown in Figure 7 resulting from an overview of North Atlantic estuaries by Nixon et al. (1996). According to this study, estuarine process remove 30-65% of the total river born nitrogen and thus a significant fraction of the continental input does not reach the marine system.

The behaviour of phosphorus is not simpler. The freshwater discharge of this element has been essentially affected by the use of polyphosphates in washing powders, degradation of detrital organic matter and to a smaller extent by discharge of industrial waste water. In the estuarine zone it may be further released by sediments under anoxic conditions, in relation to the dissolution of iron oxyhydroxides which have a high affinity for phosphate. Conversely, precipitation of Fe^{2+} in the water column is sequestering phosphate ions which are removed from the water column by sedimentation. Dissolved phosphorus is also significantly consumed during photosynthesis when light is sufficient. The net effect of these processes is a removal of phosphorus from the water column. According to Nixon et al. (1996) 10-15% of the total phosphorus transported by rivers of the North

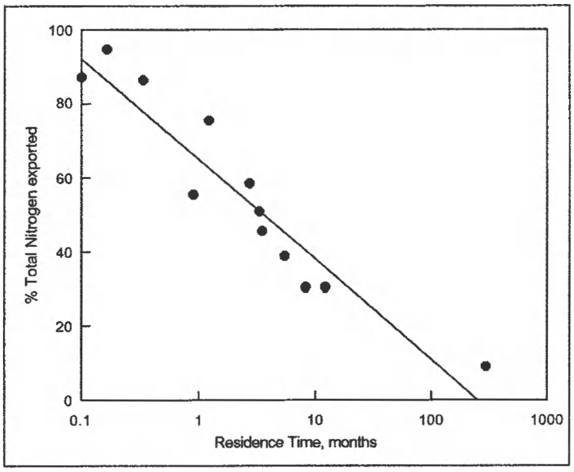

Fig. 7. Percent of total nitrogen input from land exported by estuaries as a function of mean water residence time in the system (after Nixon et al. 1996).

Atlantic area is entrapped in the delta and estuarine sediments and never reach the coastal ocean. This conclusion is however based on a restricted number of estuaries and requires more experimental data.

The behaviour of silica looks less complicated. Since the N:Si and P:Si ratio have been strongly decreased, Si is almost completely removed during the summer when the phytoplankton activity is at the highest. One question however remains : why is the diatom bloom occurring so late in the year compared to what happens in the marine system where the diatom bloom in our latitudes are typically observed in early spring. Light availability may be one explanation. There is a lack of recent studies on the transfer of silica in estuaries and especially on the possible role of eutrophication in the scavenging of this element in estuarine sediments.

The transfer of nutrients through estuaries is often influenced by processes occurring in the sediments. Furthermore, bottom turbulence enhances exchanges with the water column. The early diagenetic processes occurring in the upper sediment may thus significantly affect the composition of the water column in these shallow environments. There is at present a lack of studies of the early diagenesis in estuarine sediments and of the resulting coupling of benthic and pelagic processes.

Trace metals

The distribution of trace elements between the dissolved and the particulate phase is strongly dependent on the physico-chemical processes occurring in the aquatic system. Many trace elements are also involved in biological processes either actively, due to their metabolic role, or passively due to the adsorption capacity of organic particles. Their speciation may also be influenced by the changes of physico-chemical properties related to the biological activity. For these reasons, trace elements exhibit often a non conservative behaviour in estuarine system, where strong gradients of physico-chemical parameters (ionic strength, redox potential, pH, turbidity,...) are observed and where the biological activity is intense. Furthermore, in these shallow areas, the fluxes generated at the sediment-water interface related to early diagenesis may also affect significantly the concentration of trace metals in the water column. We will discuss below, a few examples of the well established behaviour of trace elements in estuaries. Evolution of the concentration of dissolved metals as a function of salinity observed in the Scheldt estuary will be given as a typical example to illustrate the processes which may affect their transfer to the sea.

The non-conservative behaviour of dissolved iron and manganese is a well established fact in many estuaries. The concentration of these elements exhibit high values in the fresh water part (Fig. 8) with frequently the occurrence of a peak corresponding to the turbidity maximum, where anoxic condition may be encountered. Iron and manganese are highly involved as electron acceptor in the bacterial respiration of organic matter in muddy sediments, inducing high concentrations of Fe^{2+} and Mn^{2+} in pore waters. The sediments act thus as a potential source of these metals for the water column. However, dissolved iron and manganese are rapidly precipitated in the overlying water column as oxy-hydroxides when oxic conditions are prevailing or restored. Removal of iron during estuarine mixing is always reported as being high. Martin and Windom (1991) have estimated that on the average 90% of dissolved Fe present in the river water is removed by various estuarine processes on a global scale. It is also

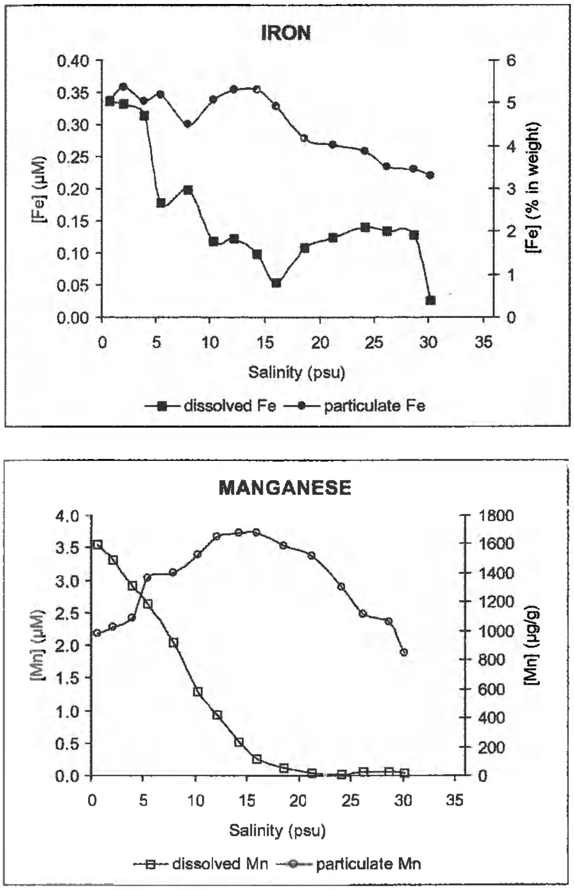

Fig. 8. Evolution with salinity of dissolved and particulate iron and manganese in the Scheldt estuary (November 1995; after Herzl 2000).

observed that the fresh water entering the estuary transport colloidal iron (often analysed as dissolved iron passing through a 0.45 µm porosity filter) which is flocculated and removed from the water column by sedimentation (Sholkovitz 1978). Experiments performed on natural water samples after addition of the radionuclides ^{54}Mn and ^{59}Fe (Herzl 2000) indicate that the transfer of iron is mainly due to the activity of bacterial and phytoplanktonic micro-organisms. For manganese, abiotic transfer due to adsorption or precipitation of Mn^{++} appears to be dominant. In addition, photoreduction of newly formed amorphous Mn oxyhydroxides occurs also in the lower Scheldt estuary, when turbidity becomes low enough to allow high light intensities. The removal of dissolved Mn in estuaries is less efficient that that of iron due to its rapid remobilization from reduced sediments (Paucot and Wollast 1997; Martin and Windom 1991). Cobalt behaves very similarly to manganese.

Cadmium is also known for its strong non-conservative behaviour in estuaries (Fig. 9). The concentration of dissolved Cd exhibits first a marked minimum of concentration in the fresh water part of the estuaries and increases rapidly with increasing salinity. Like other heavy metals (e.a. Hg, Pb), Cd has a tendency to produce very stable complexes with the chloride ion. As the salinity increases, the solubility of particulate Cd is enhanced by the formation of the chloride complexes leading to the dissolution of the reactive solid Cd compound. This reaction is very rapid and has been identified even in estuaries with a very short residence time such as the Rhone (Elbaz-Poulichet et al. 1996). The concentration of dissolved Cd then decreases by dilution with seawater. Elbaz-Poulichet et al. (1987) have estimated that this mobilization process might increase the riverine flux of dissolved Cd by a factor of 2 to 30. The behaviour of zinc and copper in estuaries is more complex. Both release and uptake have been reported during mixing of fresh water and sea water (Martin and Windom 1991). Physico-chemical as well as biological processes have been evoked to explain their non-conservative properties. Considering their metablic role, one may expect a rapid uptake of these elements in the area of high productivity and a release when intensive respiration of the detrital organic matter occurs (e.g. Windom et al. 1999).

Furthermore, the solubility of many elements is decreased in the fresh water zone where muddy sediments prevail. This is due to the release of H_2S from anaerobic sediments to the water column. The distribution of dissolved copper and zinc are two examples which have been identified to be affected by the presence of H_2S in the Scheldt estuary (Paucot and Wollast 1997). Nickel and chromium exhibit generally a more conservative behaviour in estuaries.

A large fraction of the particulate metals are trapped in the fine sediments which are accumulating in the estuaries. These metals are either coprecipitated with or adsorbed onto Fe and Mn oxihydroxides and clay minerals. They are preferen-

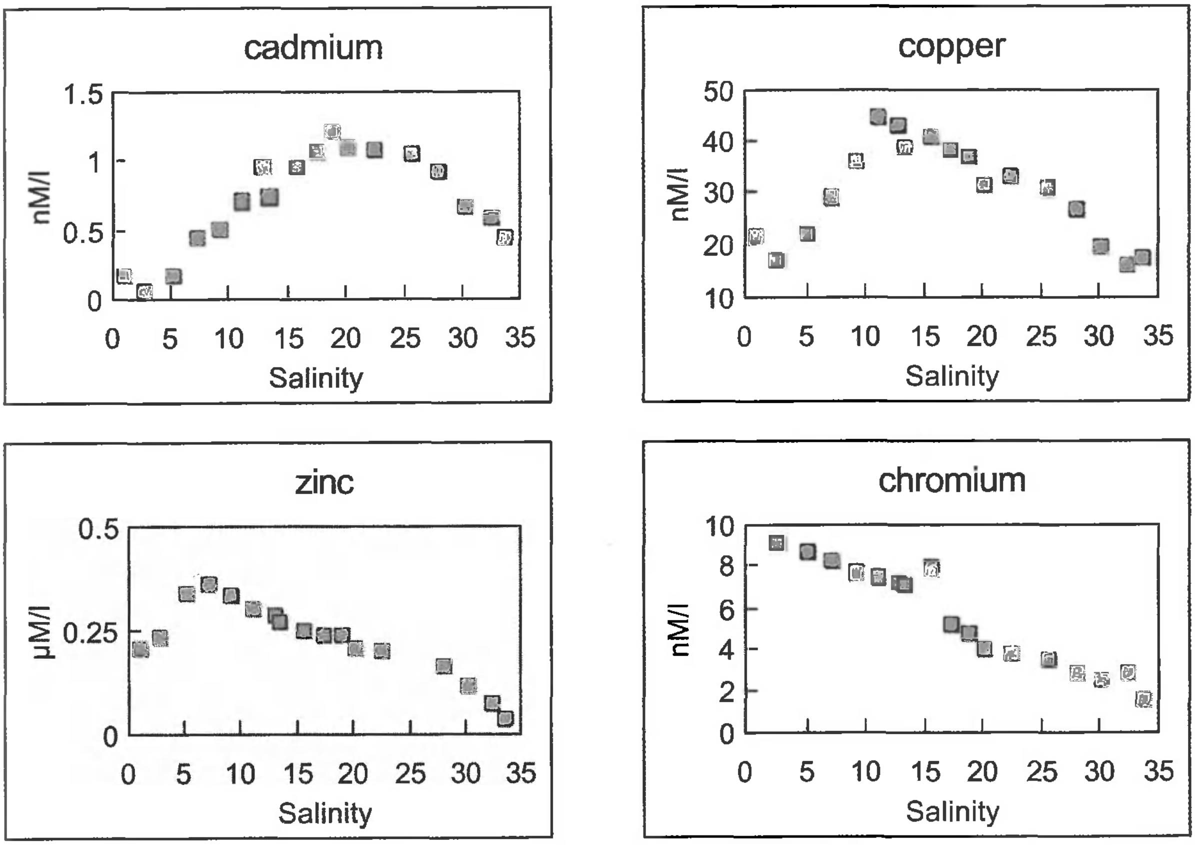

Fig. 9. Evolution of the concentration of dissolved Cd, Zn, Cu and Cr as a function of salinity in the Scheldt estuary in March 1993 (after Paucot and Wollast 1997)

tially deposited in the area of the turbidity maximum where they are often present as sulfides (Fig. 10). Organic contaminants are also associated preferentially to the fine fraction of the sediments (<20μm) but there is a considerable lack of data for these chemicals. The handling and disposal of contaminated muds dredged in estuaries is often a critical management problem. There is only a very few data on the speciation of the trace metals in these sediments and it is thus difficults to predict their behaviour during dredging and after disposal. The behaviour of trace elements and organic contaminants during estuarine mixing needs still large research efforts before an input-output budget can be established for most of the estuaries. Their transfer to the coastal zone remains often a critical, unknown flux.

Biogases

The production and exchange with the atmosphere of several biogases were investigated in various estuaries during the European project BIOGEST. Because of the respiration of detrital organic carbon in the upper stretch of the hydrographic basins, fresh waters entering the estuarine zone are often spectacularly oversaturated in CO_2 with respect to the atmosphere (Frankignoulle et al. 1998). In heavily polluted estuaries such as the Scheldt, the oversaturation exceeds by one to two orders of magnitude the equilibrium concentration, inducing intensive fluxes of CO_2 to the atmosphere (see Fig. 11). The exchange coefficients of the gases with the atmosphere are particularly high in estuaries due to the strong tidal currents. According to

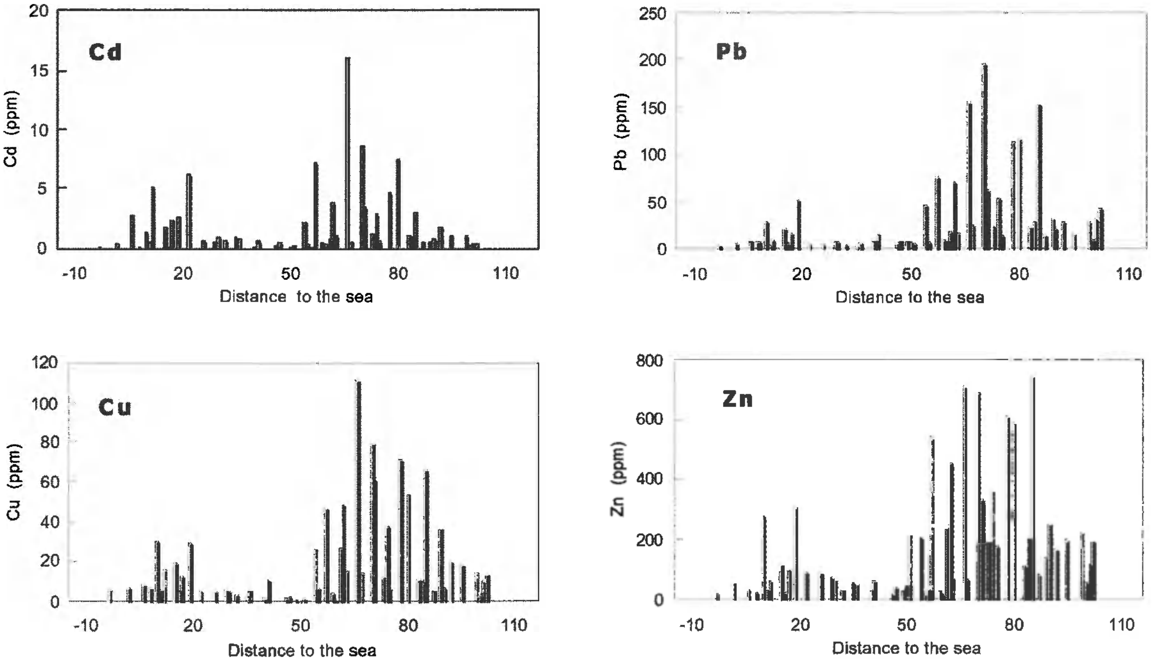

Fig. 10. Longitudinal distribution of trace elements in the sediments of the Scheldt showing their preferential accumulation in the area of the turbidity maximum (km 50-100) (Bouezmarni pers. com.).

Frankignoulle et al. (1998), the atmospheric flux of CO_2 generated by estuaries may represent a significant contribution to the global carbon cycle.

Nitrous oxide is also strongly oversaturated in most estuaries due to the nitrification and to a smaller extent to denitrification, in all the European estuaries investigated in the BIOGEST project (Fig. 11). This gas is not only known for its greenhouse effect but also for its involvement in photochemical reactions in the stratosphere where it destroys ozone. Here again the estuaries may be considered as a significant source of N_2O for the atmosphere and the fluxes are a hundred time those observed in oceanic systems.

In the upper estuary, the concentration of sulfate in fresh water is low compared to that in sea water and SO_4 does not contribute significantly to the respiration of organic carbon in the sediments. A large fraction of reactive organic matter is therefore available for methanogenesis. The methane produced in the sediments is only partially reoxidized in the overlying water column and most of it is transferred to the atmosphere. High methane concentrations correspond usually to the occurrence of organic rich sediments, mainly in the fresh water part of the estuary Salt marshes associated with estuaries are also well known sources of methane for the atmosphere.

The biogas fluxes estimated for the European estuaries during the BIOGEST project are based on a limited amount of data which should be enlarged in the future. There are also uncertainties concerning the exchange coefficient with the atmosphere either measured with a Lagrangian bell jar or calculated from biogeochemical models (Vanderborght et al. 2002).

Modelling the estuarine processes

Many biogeochemical processes occuring in estuaries have been identified and often studied in detail. It remains nevertheless very difficult to obtain estimates of the overall effect of these processes on the fluxes of components through the mixing

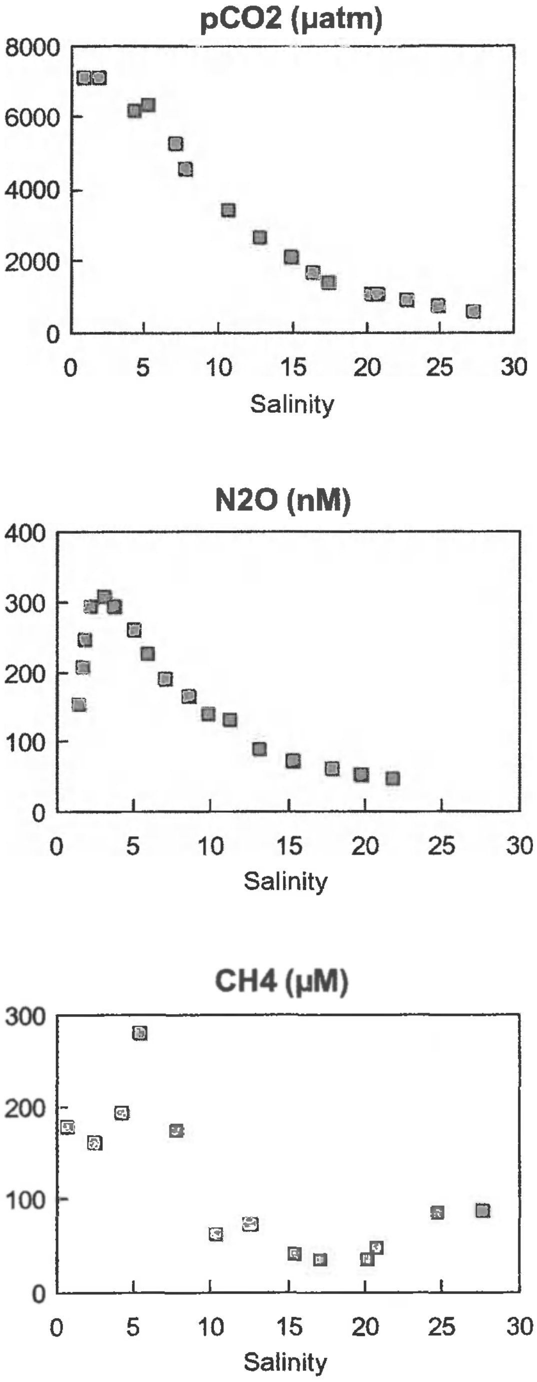

Fig. 11. Evolution of pCO_2 (Frankignoulle et al. 1998), of the concentration of N_2O (de Wilde and de Bie 2000), and of CH_4 (Iversen, BIOGEST database: web site: http://www.ulg.ac.be/oceanbio/biogest/biogest.htm) as a function of salinity in the Scheldt estuary.

zone and on their input to the coastal zone. In the best cases, long time series of measurements of the concentration of dissolved or particulate species in the river water allows to evaluate the fresh water input into the estuarine zone, if the river discharge is known. In most case, however, the frequency of sampling is too low with respect to the fluctuations of the concentration of a large variety of components. There is thus a need for long term, high frequency measurements of the composition of fresh water entering the estuaries.

As demonstrated here above, there are in addition a number of biogeochemical processes which may affect significantly the fluxes of riverborne material in the estuarine zone. The understanding and quantification of these processes is especially complicated in estuaries because of the changing physical, chemical and biological properties along the mixing zone of fresh water with salt water. The hydrodynamics is driven by external forces such as fresh water discharge and tidal amplitude at the mouth of the estuary. The balance among external forcing determines the water residence time, which in turn influences the degree of chemical or biological transformation of terrigenous material. The problem is further complicated by the fact that both river discharge and tidal amplitude are strongly variable at various time scales.They are however usually short with respect to the residence time of fresh water in the estuary and the system is therefore far from reaching steady state conditions. Unfortunately, many attempts to evaluate the transfer of components from the estuary to the coastal zone are based on the hypothesis of stationarity of the estuarine system.

It is the case for the widely used "apparent zero end-member" (AZE) method, (GESAMP 1987), where the concentrations observed in the high salinity range (> 30‰) are linearly extrapolated to zero salinity. The apparent zero end-member concentration is assumed to represent the concentration that would have been observed upstream if only conservative mixing was occurring. This approach assumes also that the distribution of any conservative dissolved element is completely determined by the dilution curve of river water with seawater. Time dependent transport models, which include tidal and river discharge fluctuations, indicate that the residual water flow to the coastal zone differs markedly from the fresh water discharge (Regnier et al. 1998) and that non linear property-salinity plots can be obtained for a conservative element under time varying conditions (tide, river discharge, fresh water composition). The results of the transport model indicate that the fluxes estimated by AZE method are meaningless.

Another method which has also been frequently applied is to use a simple one-dimensional model where it is assumed that the estuarine system is at quasi steady state. It is then easy to compute the longitudinal diffusion coefficient from the distribution of salinity, which is considered to be conservative, and the instantaneous river discharge. Here again the time dependant model shows that this approach introduces large errors especially for estuaries with long residence times, where steady-state conditions are almost never attained. Thus, long term contaminant flux estimates need to take into account the fluctuations of tidal amplitude, river discharge composition of river water.

A one-dimensional full transient model provides usually a satisfactory description of the residual estuarine circulation (Regnier et al. 1998). Implementation of the various physico-chemical and biological transformations allows to resolve the complex, non-linear behaviour of estuarine systems and evaluate much more carefully the fluxes to the adjacent coastal zone (Regnier et al. 1997; Vanderborght et al. 2002). The use of such models becomes an obligated path both to help in the quantification of biological processes occurring in the estuaries and for the evaluation of fluxes to the marine system.

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