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North Sea Estuaries as Filters for Contaminants

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delft hydraulics

North Sea Estuaries as Filters for Contaminants

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Abstract

This report deals with the filtering capacity of North Sea estuaries for contaminants. The filtering capacity (retention factor) of an estuary is a measure for the removal of contaminants during their transport through the estuary to the sea. A simple generic method is developed in order to quantify the filtering capacity of twelve estuaries for 37 contaminants (chiefly trace metals, PCB's, PAH's, and pesticides). The assessment is based on the (assumed) retention of fluvial suspended matter within the estuaries, estuarine residence time, and characteristic physico-chemical properties of the studied compounds (sorption, degradation, and volatilization). The filtering capacities given in this study can be used to correct the river load of contaminants to the North Sea.

The report consists of two sections. Section I deals with the retention of fluvial suspended matter and fresh water residence times in six U.K. estuaries (Forth, Tyne, Tees, Humber, Wash, Thames), three Dutch estuaries (Scheldt, Rhine-Meuse, Wadden Sea), and three German estuaries (Ems, Weser, Elbe). General physical and hydrodynamical aspects of each estuary are briefly mentioned, and water quality problems are discussed briefly in an historical perspective. Section II deals with the development of the method to estimate the filtering capacity of estuaries and its application. Special attention is given to coefficients and rate constants for physico-chemical processes, because they are key variables in the estimation of filtering capacity.

In spite of the inevitable shortcomings of the approach followed, there appears to be reasonable agreement between the filtering capacities estimated in this study with those derived from model and field studies (in the Scheldt and Rhine estuaries). If the filtering capacity of North Sea estuaries is taken into accocunt, the river load of contaminants to the sea is probably more realistically estimated.

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SECTION I

Suspended matter retention in North Sea Estuaries

1 Introduction

1.1 Scope and aim of the report

Fine-grained particles are major carriers for contaminants such as trace metals, organic micropollutants, radionuclides, and phosphorus. Therefore, the river input of contaminants to the sea depends strongly on the fate of the fine particles transported by them. Estuaries are important ecosystems in this context, because many estuaries act as a sink for suspended matter. Hence, sedimentation in estuaries can account for a substantial reduction of the contaminant load to the sea (Salomons and Eysink, 1981; Schubel and Carter, 1984; Nichols, 1986; Dronkers and Van Leussen, 1988). Other removal processes in estuaries, applicable to organic micropollutants only, are (bio-)degradation and volatilization (e.g. Readman et al., 1982; Rogers et al., 1992). These and other removal processes (e.g. primary production) make an estuary act as a 'filter' for the transport of contaminants to the sea (Kennedy, 1984). The removal of contaminants in estuaries may be substantial and should therefore be included in geochemical mass balances. However, there have been very few serious attempts to quantify contaminant fluxes through estuaries (Bewers and Yeats, 1978; Jouanneau and Latouche, 1982; Walling and Webb, 1985; Church et al., 1986), which is due to the difficulty of the research involved. Contaminant fluxes in estuaries can only be assessed through long-term sampling programs, paying attention to natural variability in river flow, temperature, etc.. Moreover, since most of the material may be transported during storm surges and extreme river flows, these episodic events need to be included in the sampling program too.

The North Sea is one of the best studied coastal seas in the world. Routine monitoring surveys have yielded large data sets for the water quality of its major rivers (reviewed by Wulffraat et al., 1993). However, even if sufficient and reliable data on river composition are available (which is not always the case), it is doubtful if these data can be used to calculate the contaminant input from rivers to the North Sea. The reason for this is that estuarine filtering processes are not taken into account in the calculation of the river inputs (e.g. Critchley, 1984; Grogan, 1985). For more accurate input assessments it is essential to quantify the role of the North Sea estuaries as filters for contaminants. However, there is a remarkable lack of knowledge of the filtering capacity of the North Sea estuaries. The aim of this report is to fill in this gap by estimating, in a semi-quantitative way, the removal of a selected group of contaminants in twelve major North Sea estuaries. The first step in such an evaluation should be to assess the fate of fine suspended matter supplied by the rivers (*fluvial suspended matter*), because of its important role as a carrier for contaminants. This is the topic of first section of the report. In the second section, the filtering capacity of North Sea estuaries for 37 contaminants is estimated.

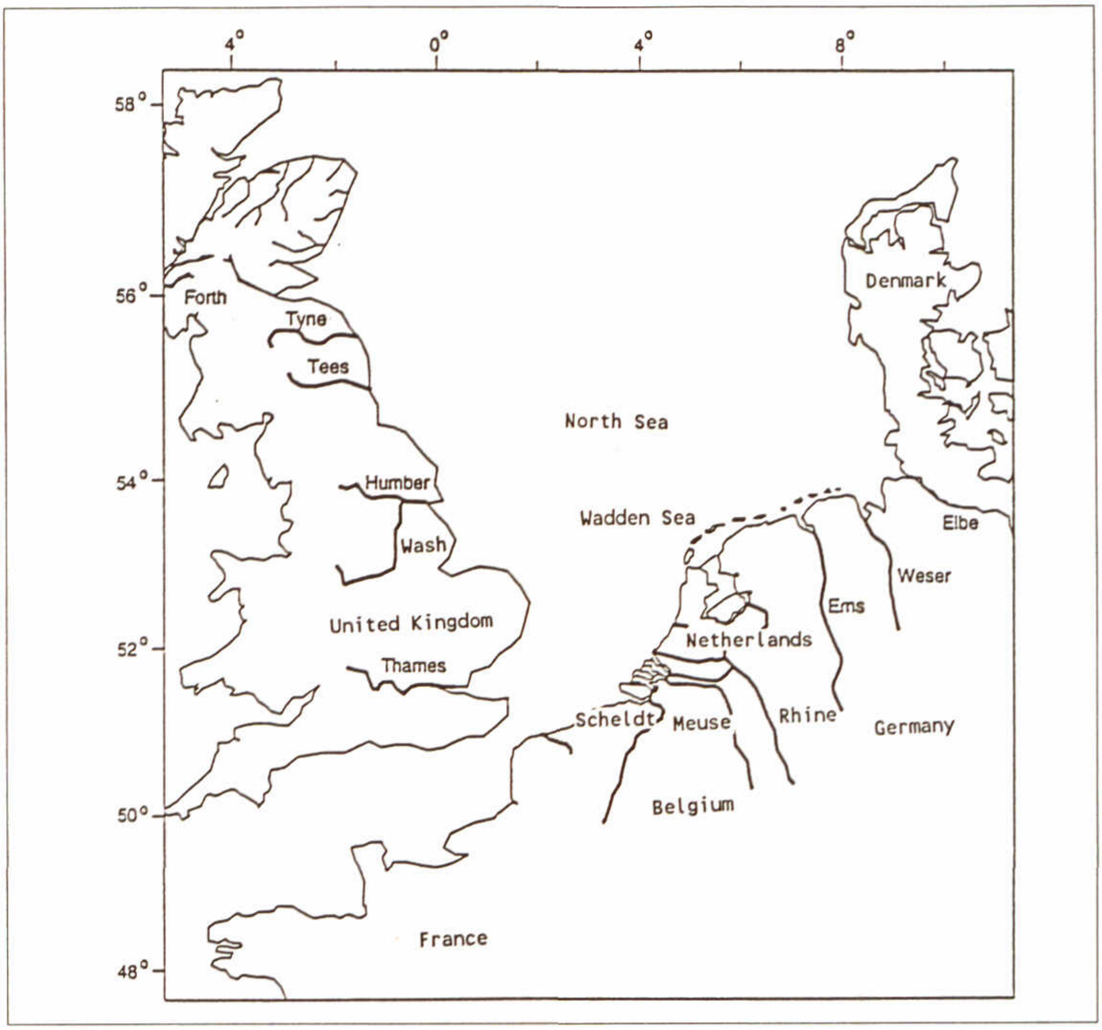

Figure 1.1 The North Sea and its major estuaries. From Wulffraat et al. (1993)

1.2 Structure of the report

This report is composed of two sections. The first section reviews the available literature on the retention of fluvial suspended matter in twelve North Sea estuaries. In other words, it is investigated which part of the fluvial suspended matter load does not reach the North Sea. The location of the estuaries is indicated in Figure 1.1. Six estuaries are situated in the United Kingdom (Forth, Tyne, Tees, Humber, Wash, Thames), three in the Netherlands (Scheldt, Rhine/Meuse, Wadden Sea), and three in Germany (Ems, Weser, Elbe). Before dealing with these estuaries, a general introduction is given on the dynamics of suspended matter in estuaries (chapter 1) and on the suspended matter (or mud) balance of the North Sea (chapter 2). The retention of suspended matter in the North Sea estuaries is discussed in the chapters 3 (United Kingdom), 4 (the Netherlands), and 5 (Germany).

In the second section of this report, the removal of a selected number of contaminants in North Sea estuaries, due to sedimentation and physico-chemical processes, is estimated semi-quantitatively. This assessment is based on the retention of fluvial suspended matter in each estuary and the sorption characteristics of the contaminants considered. Removal of organic contaminants due to (bio-)degradation and volatilization is estimated from the rates of these processes in relation to the residence time of the river water in the estuaries. This approach yields a net 'filtering capacity' for a given contaminant in a given estuary, defined as the fractional loss in the contaminant flux during transport through the estuary. This filtering capacity has to be taken into account in assessments of the river input of contaminants to the North Sea.

1.3 Sources of information

The literature that is reviewed in this report was gathered from various sources. Firstly, literature on the behaviour of contaminants in estuaries has been collected by the author on a regular basis during the years 1986-1992. The second source of information were articles and reports collected at DELFT HYDRAULICS over the years in the framework of various North Sea projects (MANS, RISMARE, etc.). Thirdly, three computerized searches have been carried out in literature databases, using the names of the estuaries as keywords. The databases consulted at DELFT HYDRAULICS were the internal library index and Current Contents-ABES (period 1990-1993). In addition, the GEOREF database, specialized in geology, geophysics, and geochemistry, was consulted at the Institute of Earth Sciences, University of Utrecht (period 1978-1993). The fourth major source of information was the annual bibliography 'Estuaries and Coastal Waters of the British Isles', which was screened for the period 1985-1993. In addition, some 25 books relevant to estuarine processes and the North Sea have been screened, including (ECSA) conference proceedings, monographs, textbooks and theses. Finally, various specialists have been consulted during the ECSA conference 'Particles in Estuaries and Coastal Waters', held at the University of Groningen (NL) in August 1993.

1.4 Suspended matter transport in estuaries

1.4.1 Estuaries as dynamical systems

The coastline of the North Sea as we know it today was created some 6000 years ago after the sea level rise during the Flandrian Transgression (the period of rising sea level after the last Ice Age). During this geological period, wide and deep estuaries were created in the lower reaches of the rivers, forming traps for both fluvial and marine sediments. Deposition of fluvial and marine suspended matter in the North Sea estuaries started in middle to late Holocene time. In fact, the origin of most modern estuaries dates back to the rise of sea level after the last Ice Age. For instance, a similar history of creation and infilling is described by Nichols (1986) for the U.S.A. east coast estuaries. In geological time, an estuary must be regarded as a dynamical system, going through a life cycle from valley creation, followed by the drowning phase, and ending with the progressive infilling with sediments. The North Sea estuaries are in a permanent stage of infilling, however, as reflected by their dredging needs and accretion of intertidal areas (Kirby, 1987). Maintenance of a deep river channel for shipping purposes has resulted in a continuous fine sediment demand, reinforcing the 'normal' trend of long-term infilling.

1.4.2 Estuarine circulation and suspended matter transport

The transport and fluxes of suspended matter in estuaries have been studied widely in the past. Only some general features will be discussed here; more comprehensive reviews can be found in the literature (e.g. Dronkers and Van Leussen, 1988; Eisma, 1993). The estuarine circulation type, which depends on the ratio of the freshwater input to the flood volume (also called tidal prism) and the estuarine geometry, is a major controlling factor in suspended matter retention (Schubel and Carter, 1984; Nichols, 1986; Geyer, 1993). Most North Sea estuaries have a well-mixed to partially mixed circulation pattern, except for the Rhine, Tees and Tyne estuaries, which are partially stratified during most of the time. Regardless of their mixing type, the North Sea estuaries display a similar circulation pattern of the water masses (though differing in intensity). Typically, the net current at the surface is directed towards the sea, whereas the net current along the bottom is landwards oriented. Due to the circulation of the water masses, suspended matter can be trapped in estuaries, at least temporarily (Figure 1.2).

Small-sized particles, moving seaward in the surface layer, tend to sink slowly to the bottom layer during transport to the sea. Through the net landward current in the bottom layer the particles are transported to the upper estuary. In the low salinity, high turbidity zone, the upward tidal bottom current is balanced by the net seaward river current, making this zone ideal for sedimentation. After resuspension, e.g. due to an increase in current velocities, the particles may reach the surface layer again, resume their way to the sea, sink to the bottom layer, to be transported in upstream direction and deposited in the low salinity zone, etc.. This so-called 'gravitational circulation' pattern creates a sediment trap in the upper estuary. Other mechanisms which contribute to suspended matter retention in estuaries are the 'ebb-flood asymmetry' and 'tidal pumping'. The ebb-flood asymmetry relates to the fact that flood currents are stronger than ebb currents and, consequently, have a greater sediment transport competency. Tidal pumping involves asymmetry in the tides interacting with lags in sediment response (Dyer, 1988; 1994) and is especially important in macrotidal (North Sea) estuaries (tidal range >3 m). These mechanisms not only cause entrapment of fluvial suspended matter, but also of marine suspended matter in estuaries (Allen et al., 1980; Nichols, 1986). In most estuaries, the suspended matter supply from the sea dominates over the river supply.

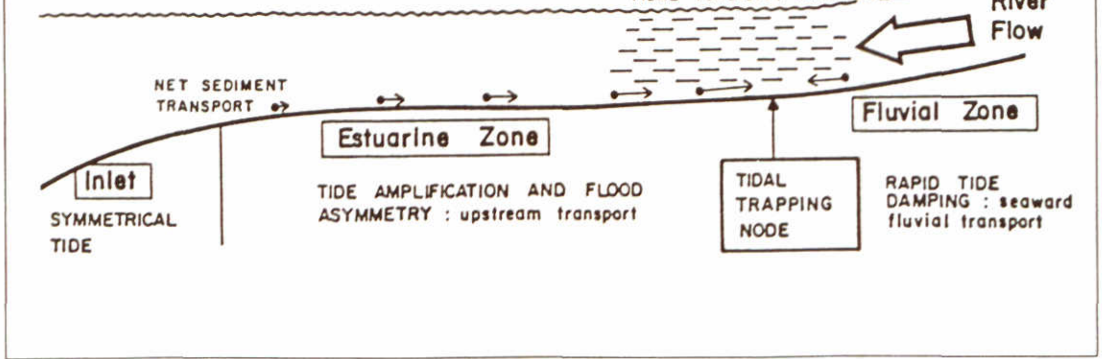

Figure 1.2 Schematic representation of net tidal bottom transport and trapping of suspended matter in a well-mixed or partially mixed estuary. From Allen et al. (1980)

1.4.3 Sedimentation in estuaries

In the previous paragraph it was argued that the estuarine circulation pattern causes suspended matter deposition in the low salinity zone. This trapping may only be temporal, however, because during spring tides and storms large-scale erosion and resuspension may occur, greatly enhancing the seaward escape of the resuspended sediments (Allen et al., 1980; Van Leussen, 1991). More permanent deposition of suspended matter takes place in low-energy environments such as deep navigation channels, harbour basins and intertidal areas (mudflats and salt marshes). Many harbours and navigation channels need to be dredged regularly in order to keep even with sedimentation. In this case, the retention of fluvial suspended matter is eventually determined by the fate of the dredge spoils (Nichols, 1986). For instance, sea dumping results in 'escape' of suspended matter from estuaries which would otherwise have been retained. On the other hand, storage of dredged sediments on land effectively reduces the fluvial suspended matter load to the sea.

As mentioned before, mud accumulation in estuaries is caused by the input of both fluvial and marine suspended matter. Discrimination between fluvial and marine sources is necessary if the retention of fluvial suspended matter in estuaries is to be assessed. Various geochemical tracers are adopted for this purpose, based on differences in chemical, mineralogical or isotopic composition of the fluvial and marine end-members (Salomons and Mook, 1987; Laane et al., 1990). If the fluvial component of each relevant mud deposit has been determined and the mud accumulation rates are known (e.g. through radiodating), the retention of fluvial suspended matter in the estuary can, in theory, be quantified. Obviously, this method needs a large set of data which is usually not available. Mathematical modelling of suspended matter fluxes provides an alternative method for quantifying the retention of fluvial suspended matter in estuaries (Owen, 1977; Schubel and Carter, 1984). The uncertainty in suspended matter balances is high, however, due to the fact that the net suspended matter fluxes are made up by the difference of two large opposite fluxes (ebb and flood) which are of comparable magnitude.

In conclusion, the physical and geological processes which regulate the retention of suspended matter in estuaries are understood qualitatively at best. Truly quantitative estimations of suspended matter retention in estuaries are still difficult due to the uncertainty in the key assumptions inherent in the calculation of estuarine fluxes. Moreover, discrimination between fluvial and marine suspended matter fluxes in estuarine mass balances is the exception rather than the rule. Therefore, the fluvial suspended matter budgets presented in this study should be considered as first approximations which may need to be refined considerably in the future as more reliable data become available. Or, in the words of P. Balls (pers. comm.):

'The report's main achievement will be in highlighting what we do not know rather than what we do.'

1.5 Acknowledgements

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2 The North Sea

2.1 Introduction

2.1.1 Policy and research

The North Sea is one of the most intensively used shelf seas in the world. Bordered by seven highly industrialized and densely populated countries, the North Sea is the scene of an extensive oil and gas industry, shipping, dumping of sewage, industrial wastes and dredge spoils, and chemical waste incineration (Wulffraat et al., 1993). In addition, the North Sea also supports a highly productive fishery, with a regular yield of 2.5 million tonnes per year or 3.5% of the world total catch of fish (Portman, 1989). These various functions have to be matched within an international policy framework which protects the North Sea from contamination beyond an extent it can sustain. Concern over the health of the North Sea was expressed at the Oslo and Paris Conventions in the early seventies. The Sandoz incident in the Rhine was another turning point in the contaminant history of the North Sea. Shortly after this incident, the North Sea states agreed upon a 50% reduction of the contaminant loads via the rivers, to be implemented between 1985 and 1995 (Second International Conference on the Protection of the North Sea, 1987).

Apart from legislation, the growing concern about the North Sea ecosystem has initiated large-scale research programs, such as the NERC North Sea Program in the UK, the Management Analysis of the North Sea (MANS) in the Netherlands, and the ZISCH and TOSCH programs in Germany (Sündermann and Degens, 1989). The ultimate goal of these research programs is to derive a prognostic model of the water quality of the North Sea, in relation to the inputs of contaminants (and reductions thereof). Such models are valuable tools for policy makers involved in the integral management of the North Sea. For instance, local areas which are under stress, such as the Wadden Sea and the German Bight, can be identified in model calculations. Examples of North Sea models can be found in the literature (Taylor, 1987; Postma et al., 1989; Klomp, 1990; Krohn et al., 1991; Huthnance et al., 1993).

2.1.2 Contamination of the North Sea

The actual pollution status of the North Sea is still subject of discussion (Salomons et al., 1988; Portman, 1989). One group of contaminants which has received considerable attention are the trace metals (reviewed by Kersten et al., 1988). Organic microcontaminants which have been studied include polychlorinated biphenyls (PCB) (Klamer et al., 1991; Schulz-Bull et al., 1991), polychlorinated dioxins and furans (PCDD and PCDF) (Evers et al., 1993), polyaromatic hydrocarbons (PAH) and mineral oil (Massie et al., 1985), and pesticides such as lindane and DDT (Knickmeyer and Steinhart, 1989). Nutrients (nitrogen and phosphorus) have been studied for decades because of eutrophication problems in coastal areas (reviewed by Brockmann et al., 1990). Radionuclides, especially those discharged by reprocessing plants (137Cs, 134Cs, 90Sr, 106Ru, 125Sb and Tr), are reason for concern too (Kautsky, 1988).

There are several anthropogenic sources for contaminants to the North Sea, the most important being atmospheric deposition and river inputs (Kersten et al., 1988; Portman, 1989; Wulffraat et al., 1993). Smaller inputs arise from direct discharges (land-based sources and ships) and dumping, but for specific contaminants these may be important sources too (e.g. oil spills). It should be realized, however, that natural inputs from the Atlantic Ocean represent the largest source to the North Sea for contaminants which occur naturally in sea water (at trace levels), i.e. trace metals and nutrients. This is so because the inflow of Atlantic water into the North Sea exceeds the combined river inputs by two orders of magnitude, thus compensating for the low contaminant concentrations in oceanic water. For instance, Kühn et al. (1992) state that inflow from the North Atlantic accounts for 59% of the total cadmium input to the North Sea, whereas all anthropogenic inputs together (atmosphere, rivers, direct discharges and dumping) account for only 27%. On the other hand, organic microcontaminants such as PCB's and pesticides are exclusively derived from anthropogenic sources (Wulffraat et al., 1993). Moreover, since the rivers do not mix with the entire volume of the North Sea, it is obvious that river inputs have a major impact on the coastal zone for all the contaminants considered (e.g. Dethlefsen, 1988; Wolff, 1988).

2.2 Hydrography of the North Sea

A basic knowledge of the hydrodynamics of the North Sea is essential if we are to understand the fate of contaminants introduced in the system, e.g. by using mathematical models. Only a general outline of the hydrodynamics is given here; for a comprehensive review of the physical oceanography of the North Sea the reader is referred to Otto (1983) and Reid et al. (1988). The hydrographic balance of the North Sea (see Figure 2.1) is dominated by the inflow of North Atlantic water (51000 km3/yr). Smaller seawater inputs come from the Channel (4900 km3/yr) and the Baltic (500 km3/yr). Compared to the seawater input, the fresh water input supplied by the rivers is very small (290 km3/yr). The high rates of inflow across its marine boundaries lead to a short residence time for the North Sea as a whole which is in the order of six months (Portman, 1989). In other words, the average North Sea water is replaced efficiently by 'clean' water from the North Atlantic, the Channel and the Baltic, at least in the central part of the North Sea. In recirculation areas the residence time may be considerably longer, however.

An overview of the residual circulation in the North Sea is shown in Figure 2.1. This figure represents the average situation which, of course, does not always apply. The hydrodynamics are different for summer and winter conditions, due to seasonal fluctuations in river discharge, changes in meteorological conditions, the frequency of storm surges, etc.. Concerning the contaminant input by rivers, it is of particular importance to know the behaviour of the river plumes which carry the fluvial suspended matter into the North Sea (Lewis, 1990; Turner, 1990). The dispersal of river plumes in the North Sea is highly dynamic due to short and long-term variation in the hydrographic and meteorological conditions. However, the general behaviour of the plumes can be described as follows (Eisma and Kalf, 1987; Portman, 1989; Dronkers et al., 1990). The plumes of the Rhine and Scheldt rivers move northwards along the Dutch coast, join the Ems, Weser and Elbe plumes, circulate around the German Bight, move north up the Danish coast, through the Skagerrak and eventually out of the North Sea via the Norwegian coastal current. The plumes of the UK rivers initially stay close to the UK coast, moving southwards, until being caught by inflow water from the Channel upon which they change direction towards the continental coast.

They do not have a great impact on the continental coast itself, because the low-salinity water from the Rhine and other rivers forms an effective physical barrier along the coastline. The UK river plumes are more likely to affect central North Sea areas such as the Dogger Bank.

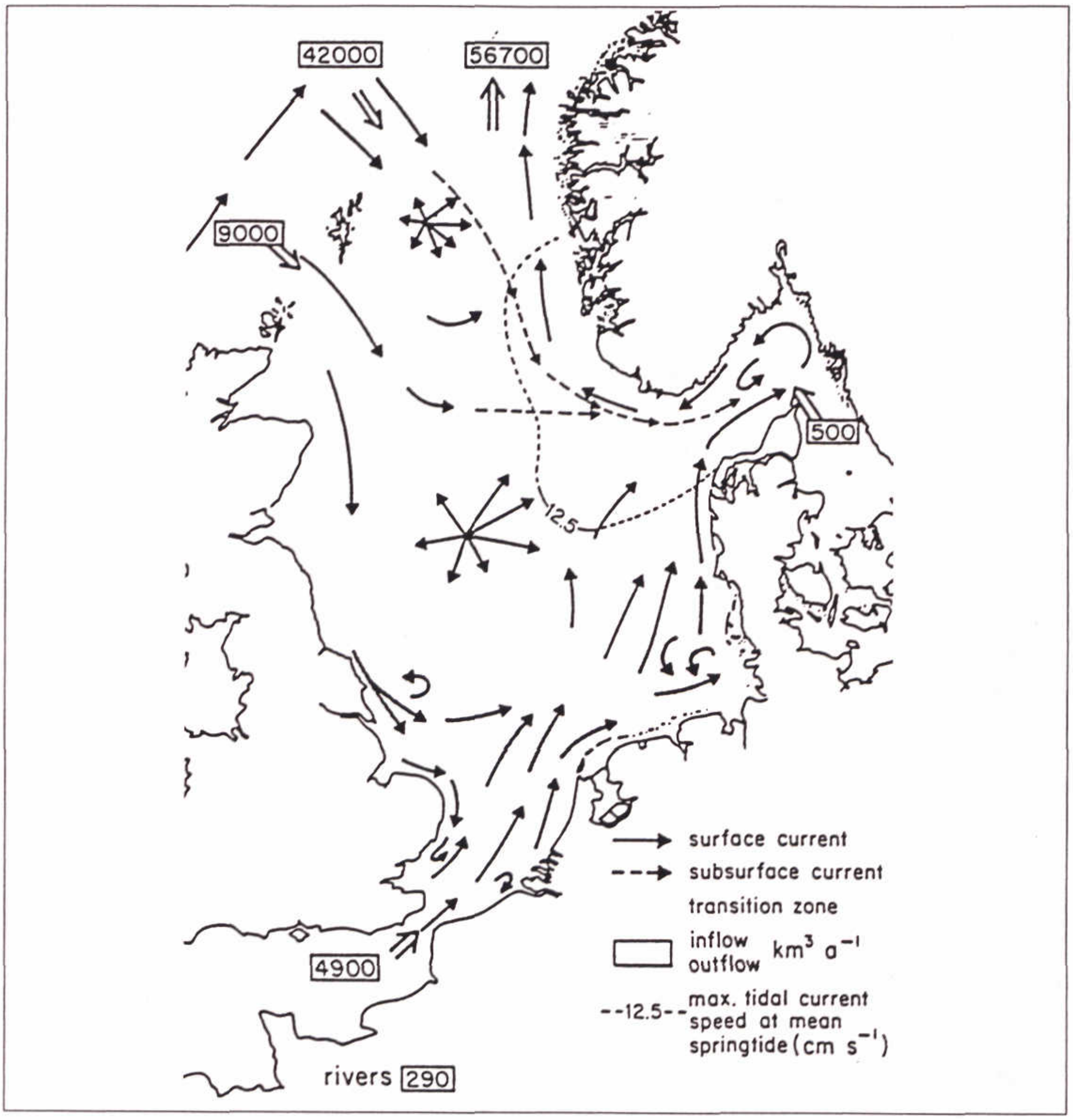


Figure 2.1 General hydrographic balance and residual circulation of the North Sea. From Eisma and Kalf (1987)

2.3 Suspended matter in the North Sea

2.3.1 Introduction

Numerous field studies in the North Sea have provided information on the composition, concentration, origin and budgets of the suspended matter (summarized by Eisma and Kalf, 1987). In general, the suspended matter in the North Sea is transported through the same anticlockwise circulation as described before for the river plumes. Suspended matter transport and suspended matter balances are usually calculated by multiplication of suspended matter concentrations and residual water transport rates averaged over the entire water column. The results are likely to underestimate the true suspended matter transport fluxes, however, because the suspended matter measurements are mostly carried out at the sea surface during calm weather (Van Alphen, 1990). Moreover, the budgets are sensitive to time-dependent fluctuations in the magnitude and direction of the residual current velocities, the effects of which are not included. Therefore it is extremely difficult to construct a comprehensive suspended matter budget for the North Sea. In fact, the suspended matter budget for the North Sea has been adjusted several times during the eighties (Tables 2.1 and 2.2), reflecting the gradual scientific progress due to collection of more data. It should also be realized that every budget bears the personal views of its author(s) and is therefore to a certain extent speculative. It is not surprising, therefore, that there are differences between suspended matter budgets constructed by different authors. For instance, the budget of Eisma and Irion (1988) differs considerably from that of Dronkers et al. (1990) or that quoted in Dyer and Moffat (1994).

Information on the dispersion of suspended matter in the North Sea may also come from numerical models which have been designed at various institutes. In these models, transport of suspended matter is determined mainly by wind and density driven currents and by residual tidal currents. Erosion and deposition of solids depends on the bed shear stress which is calculated from near-bed current velocities and from surface waves. For instance, the model computations of Puls and Sündermann (1990) rightly predict long-term deposition of suspended matter in the Norwegian Trough, the Outer Silver Pit and the Fladen Ground. Their model however fails to predict deposition in the German Bight. Moreover, the scale of their model is too large for a correct simulation of suspended matter deposition in the North Sea estuaries, including the Wadden Sea. Insufficient resolution in the coastal zone (including the estuaries) is a common problem of models designed to simulate the entire North Sea. Regional North Sea models are more successful in predicting suspended matter transport processes in the coastal zone. For example, a coastal zone model for the southern North Sea shows that suspended matter transport along the Dutch coast is mainly confined to a relatively narrow cross section with a width of 20 to 70 km (Dronkers et al., 1990; Van Alphen, 1990).

2.3.2 Sources of suspended matter

The total supply of suspended matter to the North Sea, estimated by Eisma and co-workers, is summarized in Table 2.1. The major sources of suspended matter are the Atlantic Ocean, the Channel, seafloor erosion and rivers. According to the most recent estimate, inflow through the Straits of Dover accounts for a much higher suspended matter supply than previously assumed and in fact dominates the total budget (Table 2.1).

Also, the contribution of seafloor erosion (e.g. Flemish Banks) is considerably higher than previously assumed and is perhaps still underestimated. Smaller inputs are due to inflow from the Baltic, atmospheric deposition, and primary production. Though primary production yields an enormous load of organic matter in the North Sea (150 Mton of organic carbon per year; Brockmann et al., 1990), its net impact on the suspended matter budget is small because most of the phytoplankton is consumed or decomposed and mineralized (Eisma and Kalf, 1987). However, on short time scales primary production represents a very important source of suspended matter in the North Sea, especially during spring and summer.

Coastal erosion probably accounts for a larger suspended matter source to the North Sea than the 2.2 Mton per year listed in Table 2.1. Recent data suggest that erosion of the Suffolk, Norfolk and Holderness cliffs contributes 3.32, 2.95 and 2.61 Mton of mud per year, respectively (Dyer and Moffat, 1994). The cliffs of Norfolk and Holderness are retreating at a rate of 0.90 and 1.34 meter per year, respectively (Clayton, 1989; Mason and Hansom, 1988). The mud content of the cliffs varies from 33% at Norfolk (Clayton, 1989) to 67% for the Holderness cliffs (McCave, 1987), the remainder being sand and gravel which is not included in the suspended matter budget. Due to these high erosion rates, the suspended matter budget of the UK east coast from Flamborough Head (north of the Humber) to the mouth of the Thames estuary is dominated by supply from cliff material, the contribution of the rivers being of minor importance (10%) only (McCave, 1987; Dyer and Moffat, 1994).

Compared to the total suspended matter input to the North Sea, the rivers account for a modest contribution which is in the order of 10%. In spite of this low contribution, this report focuses on the fluvial suspended matter input to the North Sea because fluvial suspended matter is a major carrier for contaminants, whereas marine suspended matter can be considered to be relatively clean (Salomons and Eysink, 1981; Turner et al., 1991; Zwolsman and Van Eck, 1993). Thus, the contribution of fluvial suspended matter to the contamination of the North Sea is far more important than 10% as based on suspended matter input only.

Table 2.1 Sources of suspended matter to the North Sea (Mton/year)

origin/reference	ref. 1	ref. 2	ref. 3
Channel	10	10	22-30
Atlantic Ocean	10	10	10.4
seafloor erosion	5	6-7.5	9-13.5
rivers	4.5	4.8	4.8
coastal erosion	0.7	0.7	2.2
atmosphere	1.6	1.6	1.6
primary production	1	1	1
Baltic	0.5	0.5	0.5
total	33	35-36	52-64

References: 1. Eisma (1981); 2. Eisma and Kalf (1987); 3. Eisma and Irion (1988)

2.3.3 Sinks of suspended matter

When turbulence generated by currents or waves falls below a critical level the suspended matter particles settle out of the water column. The processes involved in suspended matter deposition are very complex and known only qualitatively at present. Quantitative relationships between suspended matter deposition on the one hand and tidal flow, wave effects, water depth, suspended matter concentration, particle characteristics and bottom conditions on the other are still poorly known. However, low wave activity appears to be critical for the deposition of suspended matter from suspension. Areas with low wave activity are rivermouths and bays, tidal flats and the deeper parts of the water column. Deposition of suspended matter in these sheltered areas accounts for removal of most of the suspended matter supplied to the North Sea; only 20-25% escapes to the Norwegian Sea (11-14 Mton per year according to Eisma and Irion, 1988). A characteristic feature of all depositional areas is the presence of muddy sediments, reflecting the grain-size composition of the deposited material. A map of muddy sediments in the North Sea is given in Figure 2.2. It must be emphasized that not all the muddy sediments in the North Sea are the result of recent suspended matter deposition. The mud deposits in the northern and central North Sea are Holocene deposits which are somewhat reworked at the surface, except for the Oyster Grounds deposits (Eisma and Kalf, 1987).

The major areas of active suspended matter deposition in the North Sea are summarized in Table 2.2. These areas have been identified by Eisma and co-workers using field data (e.g. radiodated sediment cores). Most of the suspended matter is deposited in the Skagerrak-Kattegat-Norwegian Channel. The German Bight is also a major depositional area, as are the Wadden Sea and the Wash, and rivermouths in general. The underlying mechanisms for suspended matter deposition in these areas are discussed extensively in the literature (e.g. Eisma and Kalf, 1987; Dyer and Moffat, 1994; and references cited therein). Unfortunately, in these studies no explicit discrimination is made between fluvial suspended matter and suspended matter derived from other sources (marine suspended matter or cliff material). The sum of suspended matter deposition in the estuaries and dumping on land is about equal to the supply of fluvial suspended matter delivered by the rivers (cf. Tables 2.1 and 2.2). This does not imply, however, that fluvial suspended matter does not reach the sea to a considerable extent, because part of the deposition in estuaries is caused by marine suspended matter (see chapter 1).

Table 2.2 Deposition of suspended matter in the North Sea (Mton/year)

area	ref. 1	ref. 2	ref. 3
Kattegat	8	8	8
Skagerrak	4-7	4-7	17*
German Bight	3-7.5	3-7	3-7.5
Wadden Sea + Wash	3	3.5	5
Outer Silver Pit	1-4	1-4	1-4
Oyster Grounds	-	-	2
dumped on land	2	-	2.7
estuaries	1.8	2.5	1.8
total	23-33	22-32	41-48

1. Eisma (1981); 2. Eisma and Kalf (1987); 3. Eisma and Irion (1988). * Skagerrak and Norwegian Channel

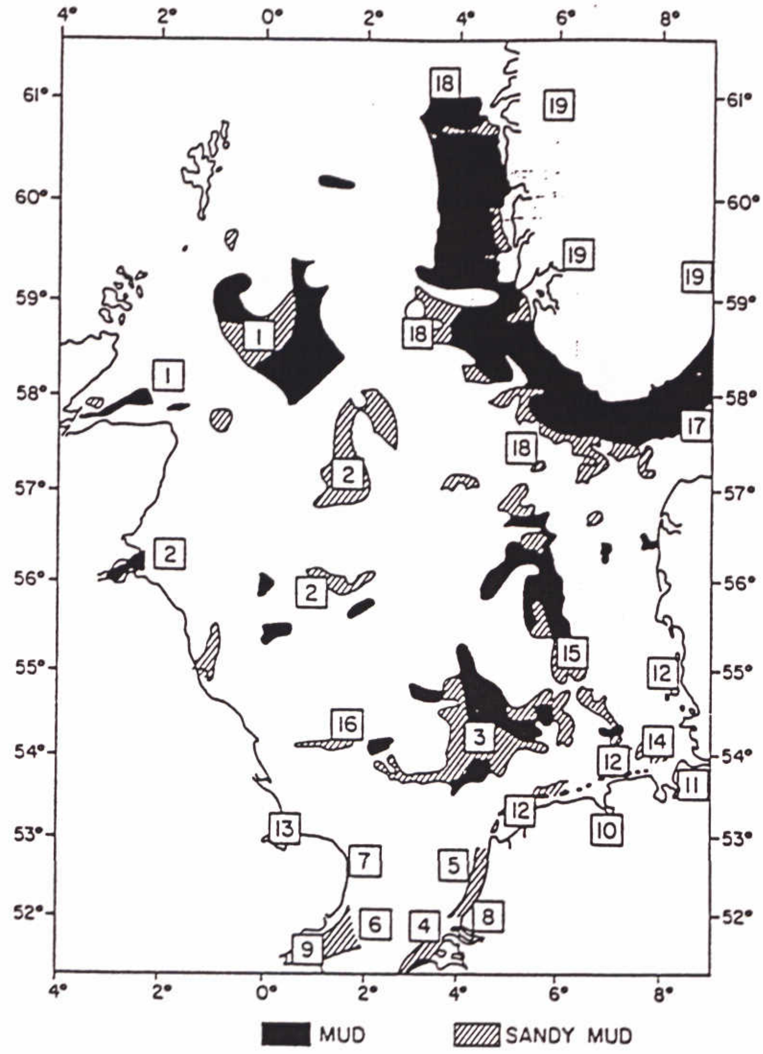


Figure 2.2 Distribution of mud and sandy mud in the North Sea. From Eisma and Kalf (1987). Legend: 1. Northern North Sea; 2. Central North Sea; 3. Oyster Grounds; 4. Flemish Banks; 5. Dutch coast; 6. East Anglia coast; 7. Yarmouth-Lowestoft; 8. Rhine-Meuse-Scheldt Delta; 9. Thames estuary; 10. Ems estuary; 11. Elbe-Weser estuary; 12. The Wadden Sea; 13. The Wash; 14. German Bight; 15. Elbe Rinne; 16. Outer Silver Pit; 17. Skagerrak; 18. Norwegian Channel; 19. Norwegian and some Swedish fjords

3 SPM retention in U.K. North Sea estuaries

3.1 The Forth estuary

3.1.1 Description of the area

The catchment area of the Forth estuary and the connecting Firth of Forth contains approximately a quarter of the population of Scotland (ca. 1,3 million people) and a significant proportion of its industry. Fresh water is supplied at the head of the estuary by the rivers Teith (23.4 m^3/s), Forth (14.8 m^3/s), and Allan (6.3 m^3/s), accounting for 71% of the total river flow which on the average amounts 63 m^3/s (Leatherland, 1987). The actual river flow depends highly on the season, with values less than 10 m^3/s during summer, exceeding over 300 m^3/s during winter (Balls, 1992). Smaller fresh water inputs, discharged into the estuary itself, come from the rivers Devon (4.4 m^3/s), Carron (4.7 m^3/s), Avon (3.6 m^3/s) and a few other tributaries (5.5 m^3/s). Sewage and industrial discharges contribute a further 7.5 m^3/s of 'fresh' water to the estuary (Leatherland, 1987). The physical aspects of the Forth estuary, mainly based on the review of Webb and Metcalfe (1987), are briefly described here. A summary of the data is given in Table 3.1.

The Forth estuary is a macrotidal coastal plain estuary. Hydrographically, the estuary comprises two distinct regions (Figure 3.1). The upper estuary stretches from the tidal limit, 4-6 km upstream of Stirling, to Kincardine, 28 km downstream of Stirling. From Stirling to Alloa, a distance of 22 km, the upper estuary is a meandering channel, less than 200 m wide. Between Alloa and Kincardine the channel widens and becomes flanked by intertidal areas up to 100 m wide. The water depth increases gradually from 2-4 m at Stirling to 8 m at Kincardine. The lower estuary stretches over 24 km from the Kincardine Bridge to the Forth Rail and Road Bridges near Queensferry. Contrary to the upper estuary, the lower estuary is straight, deep, wide, and flanked by large intertidal flats. The water depth in the lower estuary exceeds 15 m, with maxima up to 70 m (Pomfret et al., 1991). Downstream of the Forth Bridges the estuary widens rapidly into the Firth of Forth, which is described in paragraph 3.2.

Vertical salinity profiles show that the Forth estuary is in a well-mixed to partially mixed state, depending on the river flow and tidal range. The salinity at Kincardine, marking the transition from the upper to the lower estuary, varies from 18-31 ppt at the surface to 26-32 ppt at the bottom. Salinity intrusion into the Forth estuary is highly dependent on the river flow and tidal range (Webb and Metcalfe, 1987), which in turn depend on the season and the lunar cycle. The river flow ranges from 10-300 m^3/s (Balls, 1992), whilst the tidal range at the mouth varies from 2.5 to 5.0 m during neap and spring tides, respectively (Webb and Metcalfe, 1987). Therefore, the freshwater-seawater interface and the associated turbidity maximum are dynamic in space and time, migrating within a zone 2-16 km downstream of Stirling (Webb and Metcalfe, 1987). Within the turbidity maximum, suspended matter concentrations up to 500 mg/l may occur during summer, whilst the winter concentrations are 5-10 times lower (Balls, 1992). The high summer values are caused by penetration of seawater into the upper reaches of the estuary, causing resuspension of the fine-grained bottom sediments rich in organic carbon (recent POC contents vary from 3 to 8% according to McLusky et al., 1993). The resuspended solids account for a large fraction of the oxygen demand in the water column.

In consequence, an oxygen dip occurs in the low-salinity waters during the summer, with a minimum dissolved oxygen concentration of 3 mg/l upstream of Alloa (Griffiths, 1987; Pomfret et al., 1991).

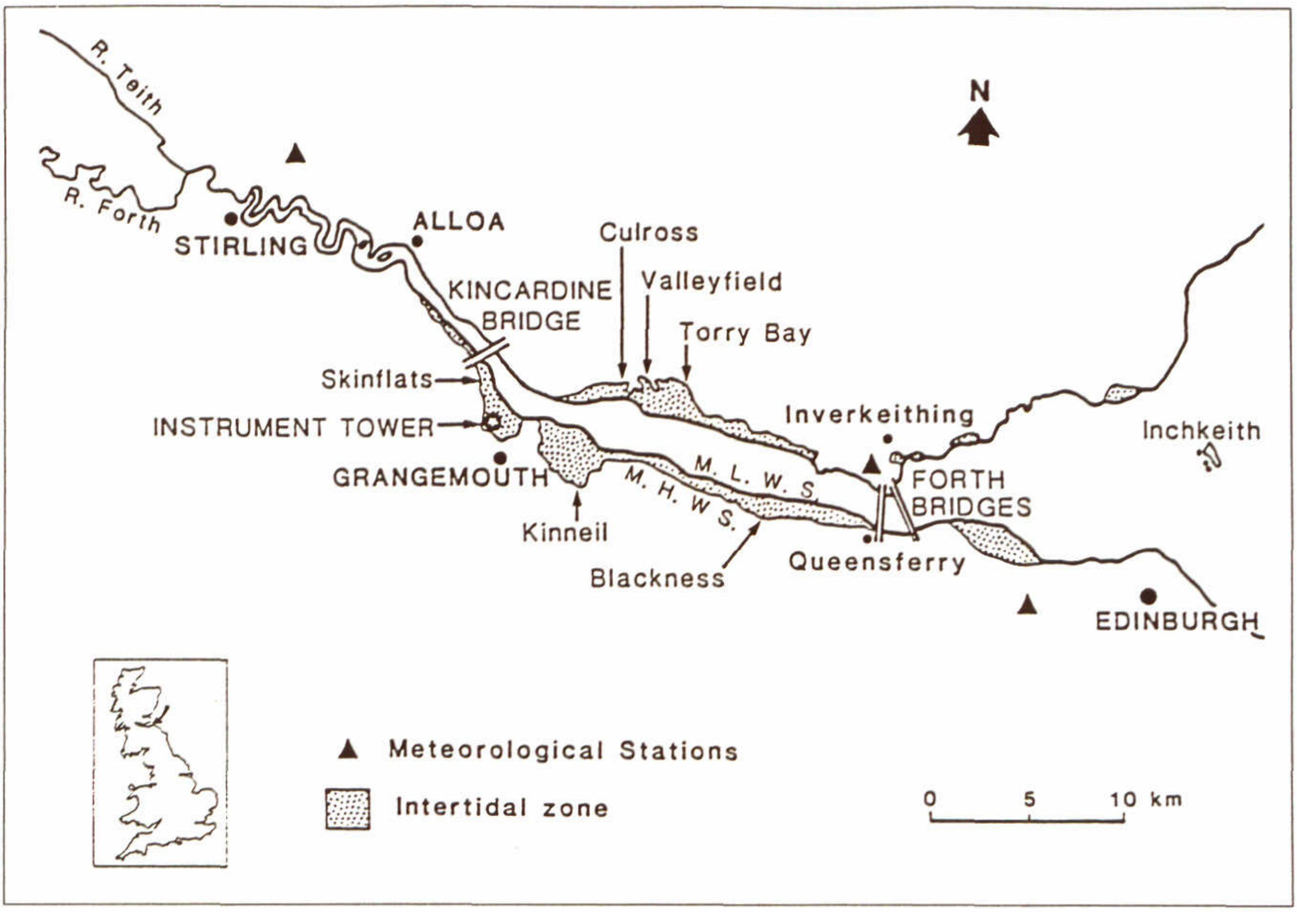


Figure 3.1 The Forth estuary. The dotted areas between M.L.W.S. and M.H.W.S. (mean low/high water stage) are intertidal zones. From Harrison and Phizacklea (1987)

Table 3.1 Physical properties of the Forth estuary

property	unit	value	reference
catchment area	km^2	4655	Griffiths (1987)
river flow	m^3/s	63 (10-300)	Balls (1992)
length mixing zone	km	36-50	Webb and Metcalfe (1987)
depth upper estuary	m	2-8	Webb and Metcalfe (1987)
depth lower estuary	m	15-70	Pomfret et al. (1991)
tidal range mouth	m	2.5-5.0	Webb and Metcalfe (1987)
salinity at mouth	ppt	30-33	Balls and Topping (1987)
circulation type	-	w.m./p.m.*	Webb and Metcalfe (1987)
residence time	d	25 (7-48)	Balls (1992)
SPM (tidal river)	mg/l	50	Lindsay et al. (1993)
SPM (turb. max.)	mg/l	50-500	Balls (1992)
SPM (mouth)	mg/l	< 10	Balls (1992)
input fluvial SPM	kton/yr	95-99	see paragraph 3.1.2

* well-mixed/partially mixed, depending on river flow and tidal range

An overview of the historical and present-day contamination of the Forth estuary is given by Davies (1987), Griffiths (1987) and Leatherland (1987). The dissolved oxygen 'sag' in the low-salinity waters is the most serious water quality problem in the Forth estuary. Though a transient dip in dissolved oxygen is a natural feature of the turbidity maximum zone, the problem has been aggravated in the Forth estuary due to excessive organic matter inputs in the form of treated and untreated sewage and industrial wastes (Griffiths, 1987; Pomfret et al., 1991; Balls, 1992). Pollution by mercury, petroleum hydrocarbons, tributyltin, and chlorobenzenes used to be a serious problem in the Forth, but the present-day situation has improved. There are about 270 consented discharges to the estuary, and this number is slowly growing (Leatherland, 1987). Direct discharges to the Forth estuary are more important than the river inputs at the head (Davies, 1987). This is in fact a common feature of many U.K. estuaries, in which the population centres and industrial activities are concentrated near the mouth (Hupkes, 1990; Wulffraat et al., 1993). Hence, the filtering capacity of the Forth and most other U.K. estuaries cannot be solely based on the fate of fluvial suspended matter, because the latter is not the only important carrier of contaminants. However, in view of the strong landward transport of suspended matter in its bottom waters (Lindsay et al., 1993), a first approximation might be that the filtering capacity of the Forth estuary for direct discharges is similar to that for fluvial inputs.

3.1.2 Suspended matter retention

An extensive study on sediment and solute transport in the Forth river basin has been published by McManus (1986). The loads are based on field measurements at six stations in the rivers Forth, Teith, and Allan during a near average water year. The results indicate an annual erosion of the catchment area of about 192 kton, of which 77 kton is in dissolved and 115 kton is in particulate form. It is worth mentioning that the organic fraction of the suspended matter was very high in the period considered (1978-1982), averaging 29% in the Forth, 41% in the Teith, and 44% in the Allan river. Assuming an average organic matter content of 35%, the organic load follows as 40 kton/yr, and the inorganic load as 75 kton/yr. However, a considerable reduction of the anthropogenic input has occurred in the eighties, reflected by a 50% decrease of organic carbon in the sediments (McLusky et al., 1993). Assuming a similar decrease in the organic matter load carried by the rivers, the present-day fluvial suspended matter load is estimated at 95 kton per year (75 kton inorganic + 20 kton organic matter). The suspended matter load can also be estimated from the mean river flow (63 m^3/s) and suspended matter concentration (50 mg/l; Lindsay et al., 1993). The resulting load is 99 kton/yr, in close agreement with the aforementioned estimate.

The extent to which the fluvial suspended matter load is retained within the Forth estuary is unknown. It is unlikely that a significant part of the fluvial suspended matter load is deposited in the upper estuary, due to its shallow nature and virtual lack of intertidal areas. In the lower estuary, however, this is not the case. Within the lower estuary there are about 28 km^2 of intertidal areas (Figure 3.1), composed of sediments with a range of particle sizes, from coarse sands to fine clays (Harrison and Phizacklea, 1987). The most extensive mudflats are found at Torry Bay, Skinflats, and Kinneil Flats. The upper 1 m of these flats is composed of approximately 4% organic matter, 16% sand and coarse material, and 80% silt and clay (on a dry weight basis). Based on the contamination of the surface sediments by e.g. trace metals and oil, it follows that the mudflats are sites of recent sedimentation (Davies, 1987).

In the absence of data on sediment accretion rates and without knowing the ratio of fluvial to marine sediment in the flats, it is impossible to estimate their contribution to the retention of fluvial suspended matter in the estuary, unfortunately. However, the high degree of trace metal retention in the Forth estuary found by Leatherland and Halcrow (cited by McLusky, 1990) appears to indicate that export of (contaminated) suspended matter from the Forth to the North Sea is not important. It was found that 75, 73, 66 and 52% of the respective total inputs (riverine plus direct discharges) of copper, nickel, zinc, and cadmium was retained within the estuary. Considering that some 20-30% of the trace metal transport to the sea is in dissolved form (excluding Cd), which is not unlikely, these data suggest that retention of contaminated suspended matter in the Forth estuary is virtually complete. Recent field and modelling results support the conclusion that very little sediment escapes from the estuary; most of the suspended matter is simply recycled internally (Lindsay et al., 1993; P. Balls, pers. comm.). For calculations of filtering capacity, the retention of fluvial suspended matter in the Forth estuary is, therefore, assumed to be 80-90%.

The input of marine suspended matter into the Forth estuary has not been studied, but dredging data suggest this to be important. The dredging requirements of the Forth estuary are summarized in Table 3.2. The spoils are dredged mainly from the harbours within the estuary, in particular at Grangemouth Docks which is dredged at a rate of 600-700 kton/yr (Leatherland, 1987). Even if only a small fraction of the dredged sediments consists of mud (say 30-40%), it is obvious that the input of fluvial suspended matter alone (order 100 kton/yr) cannot be responsible for the siltation of the harbours. Additional sources of sediment have to be involved, such as recirculation of the disposed sediments to the harbours and input of marine sediments, as demonstrated by Lindsay et al. (1993). Since the dredged spoils are exclusively disposed of in the estuary itself or the inner Firth of Forth (i.e. **internal waters**), dredging activities are unlikely to cause significant escape of fluvial suspended matter from the Forth estuary to the North Sea.

Table 3.2 **Amount of sediments dumped in internal waters of the estuary and Firth of Forth in the period 1987-1990 (wet kilotonnes per year). No spoils are dumped seaward of the Firth of Forth. Source: Oslo Commission (1992)**

dumping site	1987	1988	1989	1990	average
FO40	6	11	18	0	9
FO41	358	322	205	263	287
FO44	1647	1747	1489	704	1397
FO46	80	83	90	60	78
FO47	0	10	0	3	3
FO48	113	19	60	34	57
FO43/45/49	0	16	0	0	4
TOTAL (WET)	2204	2208	1862	1064	1835

3.1.3 The Firth of Forth

The Firth of Forth can be regarded as an extension of the Forth estuary, but it is actually an embayment of the North Sea. The Firth has its western boundary at the Forth Bridges and its eastern boundary is a line from Fife Ness to Dunbar (Figure 3.2). Typical surface salinities at the bridges range from 30-33 ppt, whilst in the outer Firth values are ca. 34 ppt (Balls and Topping, 1987). Freshwater is discharged to the Firth by the Forth estuary and by a number of small tributaries, adding up to a long-year average of 87 m^3/s (Leatherland, 1987). The Firth has a length of 55 km and a width of 2.5 km at the bridges, expanding to 30 km at the seaward limit; its volume is about 30 km^3 (Balls and Topping, 1987). Based on an estimated average width of 20 km (Figure 3.2), the mean depth of the Firth is about 27 m. The inner Firth is relatively shallow due to the presence of many sand banks. The outer Firth is much deeper, sometimes over 60 m (Dyke, 1987). The general circulation pattern in the Firth is of sea water inflow along the north coast and outflow along the southern shore (Balls and Topping, 1987), though this is regarded as highly speculative by Dyke (1987). The residence time in the Firth may be as long as eight months (Craig, 1972), but under stormy conditions the Firth can be flushed out in a few days (Dyke, 1987).

There is some controversy as to the fate of fluvial particles in the Firth of Forth. Based on elevated copper and lead contents in the suspended matter leaving the Firth (with respect to the sediments), Balls and Topping (1987) suggest that the Firth acts as a source of suspended matter to the North Sea. Grain-size differences between the suspended matter and the sediments (which were not considered) might provide an alternative explanation, however. The long residence time of the water in the Firth of Forth and the presence of deep channels would favour deposition of suspended matter. Moreover, upstream transport of suspended matter has been reported for the bottom waters of the inner Firth (Webb and Metcalfe, 1987), though seaward transport was also found to occur. According to a study of the Forth River Purification Board (cited by Griffiths, 1987), escape of particulate matter from the Firth to the North Sea appears to be negligible. Expert opinion is in agreement with this statement (K. Dyer, pers. comm.).

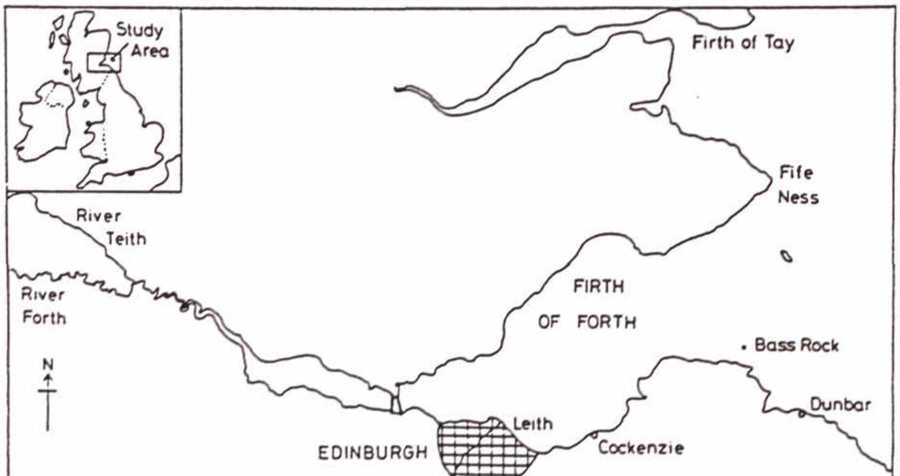


Figure 3.2 The Forth estuary and Firth of Forth. From Balls and Topping (1987)

3.2 The Tyne estuary

3.2.1 Description of the area

The Tyne river basin contains part of the Northern Pennine orefield, which was mined extensively for lead and zinc since medieval times. The historic mining activity in the Tyne basin has resulted in a significant input of metal-contaminated fine-grained sediment in the river system (Macklin and Lewin, 1989; Passmore et al., 1992). The major rivers are the North Tyne and South Tyne, draining the northern Pennines and the southern part of the Cheviot Hills, respectively. The North and South Tyne join at Warden, some 25 km upstream of Wylam, to become the Tyne river. The Tyne river flow is gauged at Bywell, 10 km upstream of Wylam (Cassie et al., 1962), whilst the water quality from which the river input to the North Sea is calculated is monitored at Wylam (Wulffraat et al., 1993). The estuarine zone of the Tyne river stretches over 32 km from Wylam to the piers at Tynemouth (Figure 3.3). Fresh water is supplied at the head by the Tyne river (45 m^3/s), and 10 km downstream of Wylam by the highly polluted river Derwent which adds another 4.5 m^3/s (Cassie et al., 1962). Several other tributaries discharge into the estuary (Figure 3.3), but they make an insignificant contribution to the river flow. Being dependent on rainfall, the Tyne river flow varies from 7 m^3/s (10 percentile) to 120 m^3/s (95 percentile). The probability of a flood exceeding 650 m^3/s is once every year, whilst a flood of 1000 m^3/s may occur once every seven years (Cassie et al., 1962).

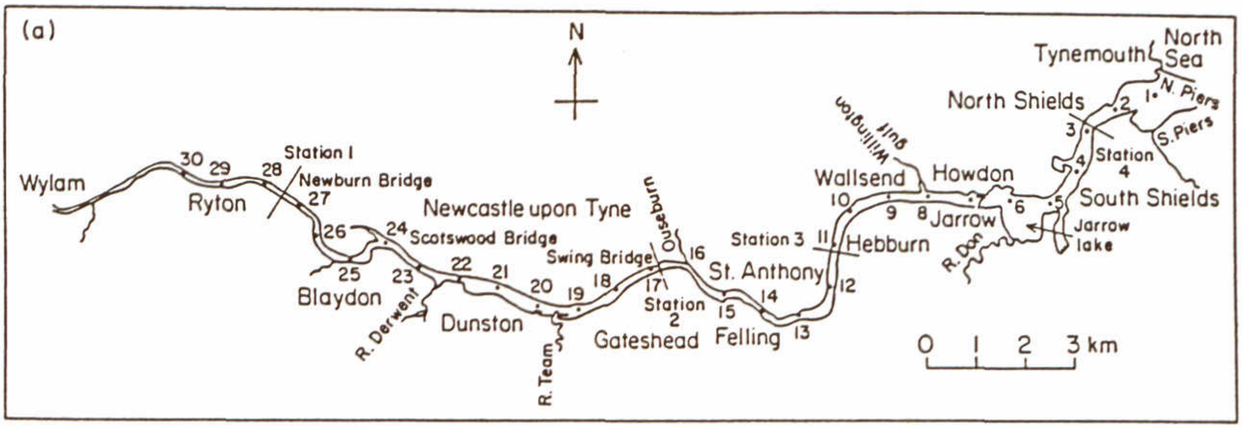


Figure 3.3 The Tyne estuary. From Park and James (1988)

The physical characteristics of the Tyne estuary are summarized in Table 3.3. The estuary can be divided in three zones (Pomfret et al., 1991). The upper estuary is a tidal freshwater river, stretching from Wylam to Ryton (3.5 km). The middle estuary stretches over 25 km from Ryton to Shields and comprises the entire salinity gradient (0-34 ppt). The lower estuary is the final 3.5 km between Shields and the North Sea. The water depth increases continuously from 3-4 m in the upper estuary to 12 m at the mouth (Park and James, 1989). The estuary is relatively narrow, the maximum width being 150 m in the upper zone, 500 m in the middle zone, and 1000 m in the lower zone (Pomfret et al., 1991). The estuary has been subject to extensive channel embanking, while channel straightening has also occurred on a major scale.

In fact, the middle estuary is flanked by rigid banks formed by quays and docks for most of its length. Due to this major canalization, the (natural) intertidal areas have almost completely disappeared in the Tyne; some small remains are left above Newcastle and in the Jarrow area (Pomfret et al., 1991). The absence of intertidal areas is one of the factors contributing to the strong stratification observed in the estuary (Cassie et al., 1962; Park and James, 1988). Salinity stratification is most important near the head of the estuary and decreases towards the mouth (Park and James, 1988). Due to this stratification, the river water is carried rapidly to the sea, reflected by a residence time of about 6 days for a river flow of 26 m^3/s (Cassie et al., 1962). Assuming an inverse relation between residence time and river flow, the residence time under average discharge conditions (45 m^3/s) is estimated to be 4 days.

Table 3.3 Physical properties of the Tyne estuary

property	unit	value	reference
catchment area	km^2	2927	Passmore et al.(1992)
river flow	m^3/s	45 (7-120)	Park and James (1989)
length mixing zone	km	28	Pomfret et al. (1991)
water depth	m	4-12	Park and James (1989)
tidal range mouth	m	2.1-4.3	Park and James (1989)
salinity at mouth	ppt	< 33	Lewis (1990)
circulation type	-	stratified	Park and James (1988)
residence time	d	4 (average)	Cassie et al. (1962)
SPM (tidal river)	mg/l	21	see note (*)
SPM (turb. max.)	mg/l	(?)	
SPM (mouth)	mg/l	16 (11-27)	Fileman (1987)
input fluvial SPM	kton/yr	15-98	see paragraph 3.2.2

* based on a fluvial suspended matter input of 30.3 kton/year (Wilmot and Collins equation)

Direct inputs of trace metals in the Tyne estuary do not play an important role. There are not sufficient data to evaluate the impact of direct inputs of organic microcontaminants in the estuary (Hupkes, 1990). The main water quality problem in the Tyne estuary is oxygen depletion due to its high organic load. Until recently, raw sewage from 700.000 people was discharged into the estuary between Ryton and the mouth, together with a major load from industry which was discharged mainly via the public sewerage system. In consequence, anoxic conditions developed during the warm summers of 1975 and 1976. The situation has improved because the sewage sludge is disposed of directly in the North Sea since 1986 (after primary treatment); only the effluent is discharged into the estuary (Ord, 1988). However, the present-day oxygen status of the Tyne estuary still poses a problem. For instance, oxygen depletion occurred upstream of Newcastle in the summers of 1988 and 1989, with dissolved oxygen concentrations falling to 1-3 mg/l (Pomfret et al., 1991). Resuspension of organic-rich sediments in the turbidity maximum zone, combined with the input of organic effluents, is responsible for this (Pomfret et al., 1991). Downstream of Newcastle, dissolved oxygen increases again due to mixing with seawater, in spite of the high organic loading of the lower estuary (Park and James, 1989).

3.2.2 Suspended matter retention

A comprehensive study of the suspended matter load to the Tyne estuary was made by Cassie et al. (1962). Based on measurements of river discharge and suspended matter concentrations, a fluvial suspended matter load of 96 kton/yr has been estimated, derived from the rivers Tyne (71 kton/yr) and Derwent (25 kton/yr). In addition, the bed loads of the Tyne and Derwent rivers were estimated as 20 and 8 kton/yr, respectively, while floating debris was estimated to account for another 2 kton/yr. If the bed load is excluded, because this is mainly coarse material, the total fluvial suspended matter input into the Tyne estuary follows as 98 kton/yr. Two other sources of solid material were identified by Cassie et al. (1962), namely domestic and industrial discharges (50 kton/yr), and marine sediments carried into the estuary from the sea (420 kton/yr, of which 145 kton/yr is deposited near the mouth and 275 kton/yr is carried into the estuary). Alternative estimates of the fluvial suspended matter input to the Tyne estuary are lower than the 98 kton/yr mentioned before. According to a study of the Durham Department of Civil Engineering (cited by Cassie et al., 1962), the fluvial suspended matter input is only 15 kton/yr. A load of 30 kton/yr is calculated using an empirical equation which relates the fluvial suspended matter load (y, kton/yr) to the size of the catchment area (x, km^2):

$$y = 0.060\ x^{0.78}$$

This equation is applicable to (U.K.) estuaries with small catchment areas (Wilmot and Collins, 1981). Whatever estimate is used, the fluvial suspended matter load discharged at the head (15-98 kton/yr) is small compared to the 420 kton/yr of marine sediment coming in through the mouth (the latter includes also sandy material, however).

The retention of fluvial suspended matter in the Tyne estuary has not been quantified in the past. However, it is unlikely that significant retention occurs within the estuary, because of the short residence time of the river water, the major canalization and the lack of intertidal areas. According to expert judgement (K. Dyer, pers. comm.), about 80-90% of the fluvial suspended matter load is carried directly to the sea; the remaining 10-20% will accumulate in the turbidity maximum zone. However, this storage is only temporal because the area is heavily dredged in order to ensure the navigability of the channel (Cassie et al., 1962). Off the Tyne mouth there are two major dumping sites which are used for dredged spoil disposal (Table 3.4). The spoils dumped in the period 1987-1990 consist, on the average, of 90% estuarine sediment (probably the Tyne) and 10% harbour sediment (Oslo Commission, 1992). Thus, any suspended matter deposited in the Tyne estuary soon finds its way to the North Sea due to dredging and off-shore dumping.

Table 3.4 Amount of sediments dumped in coastal waters off the Tyne in the period 1987-1990 (wet kilotonnes per year). Source: Oslo Commission (1992)

dumping site	1987	1988	1989	1990	average
TY70	117	66	9	122	79
TY81	580	294	358	321	388
TOTAL (WET)	697	360	367	443	467

3.3 The Tees estuary

3.3.1 Description of the area

The river Tees rises in the hills of North Yorkshire and flows eastwards between the industrial cities of Stockton and Middlesbrough, eventually entering the North Sea to the north of Redcar. The Tees estuary comprises the final 44 km of the river from Middleton St. George up to the mouth (Figure 3.4). The estuary can be divided in two zones, namely a tidal fresh water section with a length of 18 km, and an estuarine mixing zone with a length of 26 km, comprising a complete salinity gradient (Lewis and Lewis, 1983). Within the tidal reach, the only major tributary of fresh water is the river Leven, which flows into the Tees 14 km downstream of Middleton St. George. The mean freshwater inflow at the head of the estuary is only 20 m^3/s, of which 17 m^3/s is supplied by the Tees and 3 m^3/s by the river Leven. The instantaneous river flow varies commonly from 2-70 m^3/s but may increase at times to a few hundred m^3/s after heavy rainfall (Whitton and Crisp, 1984; Hupkes, 1990). The contaminant load from the Tees to the North Sea is calculated from the river flow and the water quality as measured at Worsall, located in the tidal freshwater section (Wulffraat et al., 1993).

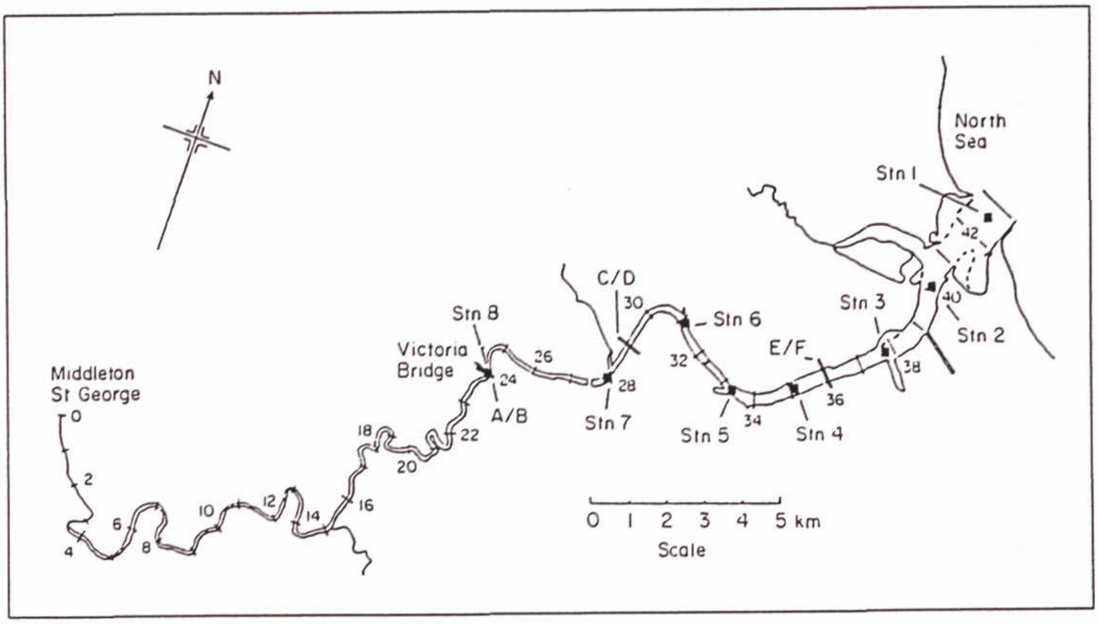


Figure 3.4 The Tees estuary. From Lewis and Lewis (1987)

The physical characteristics of the Tees estuary are summarized in Table 3.5. Human perturbations have changed the geometry of the estuary to a significant extent, especially near the seaward end. Reclamation activities have reduced 2500 ha of intertidal land present in 1860 to 200 ha by 1974 (McLusky, 1990). Construction of tide-training walls along both sides of the Tees was completed in 1929, so that since that time the main channel was clearly defined. Extensive reclamation of the sandflats at the seaward end, combined with deepening of the estuary, took place over the period 1970 to 1975 (Lewis and Lewis, 1987). As a result, the estuary is narrow, with a maximum width of 700 m occurring at the mouth.

The final 20 km of the estuary in fact consists of a dredged channel bounded on both sides by port areas and industrial installations. The depth increases rapidly from 4-5 m at Victoria Bridge (km 24) up to 18 m at the mouth, permitting the passage of ships of deep draught to Teesport. The tidal range at the mouth varies between 2.3 m and 4.6 m during neap and spring tides, respectively. In spite of the small river discharge, the Tees has a partially stratified circulation pattern (Lewis and Lewis, 1983). Due to the partial mixing of the water masses, the residence time of river water in the estuary is only five days or less.

Table 3.5 Physical properties of the Tees estuary

property	unit	value	reference
catchment area	km^2	2210	Turner (1989)
river flow	m^3/s	20 (2-70)	Lewis and Lewis (1983)
length mixing zone	km	26	Lewis and Lewis (1983)
depth upper estuary	m	4-5	Lewis and Lewis (1983)
depth lower estuary	m	4-18	Lewis and Lewis (1983)
tidal range mouth	m	2.3-4.6	Lewis and Lewis (1983)
salinity at mouth	ppt	32.5-33.5	Lewis (1990)
circulation type	-	stratified	Lewis and Lewis (1983)
residence time	d	≤ 5	Turner (1989)
SPM (tidal river)	mg/l	39	see note (*)
SPM (turb. max.)	mg/l	≤ 450	HRS (1966)
SPM (mouth)	mg/l	7 (6-10)	Fileman (1987)
input fluvial SPM	kton/yr	20-24	see paragraph 3.3.2

* based on a fluvial suspended matter input of 24.4 kton/year (Wilmot and Collins equation)

Similar to many other U.K. rivers, the Tees river is of good quality for most of its length, but becomes highly contaminated towards its estuary, where most of the population and industry is located. Darlington is the only major town (population 100000) whose effluent reaches the Tees above the tidal limit. The Tees estuary has received waste discharges since the middle of the 19th century when an iron and steel industry was established in the area. Serious pollution problems developed in the early twenties of this century, and by 1930 the salmon and trout had disappeared completely from the estuary (Whitton and Crisp, 1984). There are indications that the Tees is slowly recovering after 1970, but the estuary still receives many discharges from industry, as well as domestic sewage from adjacent towns. The total volume of effluents discharged into the estuary is 5.8 m^3/s, or 30% of the river input at the head (Johnston et al., 1991). The effect of the wastes is reflected by a five to ten-fold increase of the BOD load at the mouth of the estuary (Shillabeer and Tapp, 1990). In the central part of the estuary, Victoria Bridge to Cargo Fleet (km 24-34), dissolved oxygen could be severely depleted and at times even be absent in the water column. This situation persisted in 1985, despite the progressive reduction of the pollution load (Ord, 1988). Other recognized pollutants in the Tees estuary are phenols, cyanide (both related to cokes industry), ammonia, and trace metals, in particular chromium (Ord, 1988; Davies et al., 1991; Johnston et al., 1991).

3.3.2 Suspended matter retention

The load of fluvial suspended matter to the Tees estuary can be estimated in two ways. Multiplication of the average annual river flow and suspended matter concentration yields a suspended matter load of 20 kton/yr (HRS, 1966). This is probably an underestimation because during high river flows the suspended matter concentration is higher than the mean. The fluvial suspended matter load can also be estimated from the catchment area of the Tees (2210 km^2), using the empirical equation of Wilmot and Collins (1981) described before. This estimation yields a suspended matter load of 24 kton per year. Direct discharges into the estuary are a significant source of suspended matter too. In the years 1985-1987, the suspended matter load resulting from direct inputs was estimated at 8-24 kton/yr (Hupkes, 1990), i.e. of similar magnitude as the riverine input.

The dredging requirements of the Tees estuary suggest that the major source of sediments to the estuary is the North Sea. In the sixties, the volume of sediments dredged for maintenance purposes was in the order of one million cubic yards per year (HRS, 1966). Assuming a water content of 50% (porosity 0.714), it follows that 550 ktonnes of dry material were dredged annually. At present, the amount of sediments dredged from the Tees estuary and its harbours is about 2200 kton/yr wet material (Table 3.6), or about 1100 kton of dry material (sand and silt). Since dredging balances the siltation in the estuary (HRS, 1966) and because riverine and direct inputs account for a maximum supply of 50 kton/yr, it is clear that the bulk of the sediments dredged from the Tees estuary is of marine origin.

The retention of fluvial suspended matter in the Tees estuary is unlikely to be important, for similar reasons as discussed for the Tyne estuary. Due to the virtual complete loss of intertidal area, the major canalization of the channel and the short residence time, the fluvial suspended matter is transported rapidly to the North Sea. The outflow of suspended matter from the Tees estuary is e.g. reflected by elevated copper and lead contents in suspended matter sampled off the Tees mouth (Balls, 1985). Similar to the Tyne, direct export of fluvial suspended matter from the Tees to the North Sea is estimated to account for 80-90% of the total load; the remaining 10-20% will accumulate in the turbidity maximum zone (K. Dyer, pers. comm.). Again, storage of suspended matter in the estuary is only temporal because sedimentation is balanced by dredging. Despite the serious contamination of the dredged sediments by trace metals, the spoils are dumped in the North Sea off the Tees mouth (Davies et al., 1991; Table 3.6).

Table 3.6 **Amount of sediments dumped in coastal waters off the Tees in the period 1987-1990 (wet kilotonnes per year). Source: Oslo Commission (1992)**

dumping site	1987	1988	1989	1990	average
TY150	0	17	99	134	63
TY160	2362	1720	2050	2368	2125
TOTAL (WET)	2362	1737	2149	2502	2188

3.4 The Humber estuary

3.4.1 Description of the area

The catchment of the Humber estuary is the largest of the U.K. estuaries. It covers about 20% of the area of England and drains, amongst other areas, the heavily industrialized areas of the West Midlands and the old West Riding of Yorkshire. Several rivers flow into the Humber 'river', which in fact is entirely estuarine. Freshwater is supplied by the Trent (101 m^3/s) and the Ouse (130 m^3/s), the latter being composed of five tributaries: Yorkshire Ouse (45 m^3/s), Wharfe (17 m^3/s), Derwent (16 m^3/s), Aire (36 m^3/s), and Don (16 m^3/s). The river Hull (3 m^3/s) is the only major river which discharges directly into the estuary (Wulffraat et al., 1993). The water quality is monitored for each river separately, usually in the tidal fresh water section. The largest tributary of fresh water, the river Trent, is of good quality and reasonably well oxygenated. The Yorkshire Ouse and its tributaries are more polluted and frequently low in dissolved oxygen. As a result the water quality in the upper reaches of the Humber estuary can be poor (Morris, 1988). The tidal Trent and tidal Ouse flow together at Trent Falls where the Humber estuary begins (Figure 3.5). The Humber estuary runs for 62 km in easterly to southeasterly direction until it reaches the North Sea at Spurn Point. The marine limit of the Humber estuary is defined here as a line extrapolated from the Spurn peninsula to the southern shore. The width of the estuary increases from 1 km at Trent Falls to 8 km at the mouth.

The physical parameters of the Humber estuary are summarized in Table 3.7. The river flow is highly variable but ranges for 90% of the time between 60 and 450 m^3/s. During floods, the river flow may exceed 1500 m^3/s, however. Consequently, the estuarine mixing zone may only be 40 km long during river floods, increasing to 100 km during drought conditions (Morris, 1988). More commonly, the interface of fresh and saline water is located at Trent Falls during low water, and a few km upstream of Trent Falls during high water. Seaward from Trent Falls, the water quality of the Humber improves due to dilution by sea water. Nearer to the mouth, however, direct inputs are manyfold due to the presence of major industrial complexes. An historic review on the development of industrial activity in the Humber estuary is given by Bellamy (1988) and Jones (1988). There are about 1600 factories of all sizes in Humberside, 40 of which are very large. These large factories (more than 500 employers) were established during the 1950's and 1960's and encompass industries such as pharmaceuticals, fertilizer manufacture, dyes and pigments (e.g. titanium dioxide), man-made fibres and oil-refining. For many contaminants, direct discharges into the estuary may be more important than the load contributed by the rivers themselves. For instance, the trace metal distribution in sediments from the Humber estuary clearly indicates the presence of 'hot spots' near the mouth (Barr et al., 1990), probably associated with the effluents of titanium dioxide manufacturing plants.

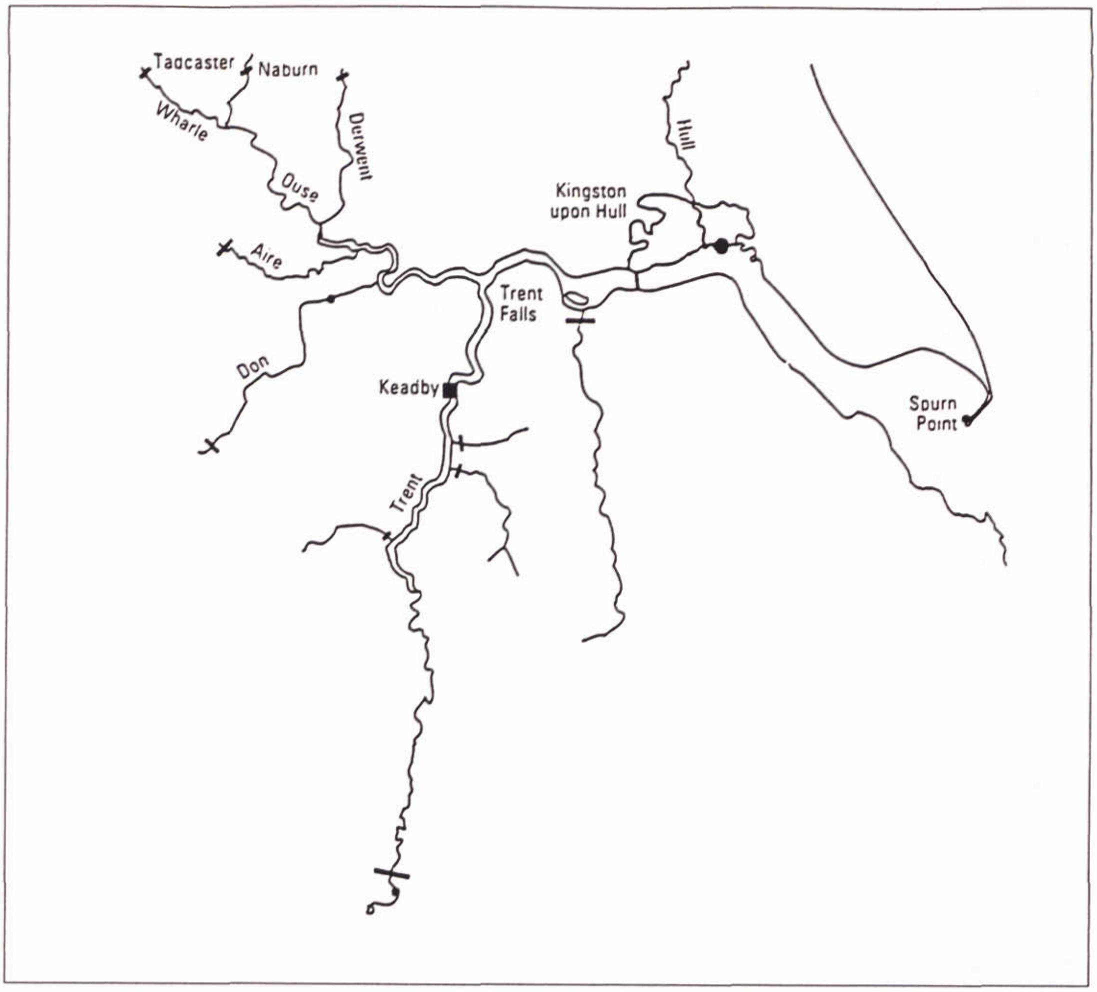


Figure 3.5 The Humber estuary. From Hupkes (1990)

Table 3.7 Physical properties of the Humber estuary

property	unit	value	reference
catchment area	km^2	27000	Woodward (1984)
river flow	m^3/s	246 (60-450)	Gameson (1976)
length mixing zone	km	62 (40-100)	Morris (1988)
water depth	m	8-30	Denman (1979)
tidal range mouth	m	3.5-6.2	Gameson (1976)
salinity at mouth	ppt	27-30	Morris (1988)
circulation type	-	well-mixed	Morris (1988)
residence time	d	40	Turner et al. (1991)
SPM (tidal river)	mg/l	26	see note (*)
SPM (turb. max.)	mg/l	400 (50-5000)	Morris (1988)
SPM (mouth)	mg/l	65 (30-108)	Fileman (1987)
input fluvial SPM	kton/yr	172-225	see paragraph 3.4.2

* based on a fluvial suspended matter input of 200 kton/year (Pethick, 1988)

3.4.2 Suspended matter retention

Various estimations have been made of the fluvial suspended matter discharge to the Humber. Based on the size of the catchment area, the load is estimated at 172 kton/yr. According to Pethick (1988), the load is slightly higher, namely 200 kton/yr. The most recent estimate for the suspended matter load of the Humber is 225 kton/yr, as quoted in Dyer and Moffat (1994). A second source of fine suspended matter to the Humber estuary is erosion of the Holderness cliffs, located north of the estuary. The latter process yields 1.4 Mton (McCave, 1987) or 2.6 Mton (Dyer and Moffat, 1994) of fine suspended matter per year. Though most of the eroded cliff material is transported directly southwards along the coast, some moves into the Humber estuary via the tides (Pethick, 1988). Experiments with seabed drifters, released at the mouth of the estuary, appear to indicate that only 7% of the eroded cliff material contributes to siltation within the estuary (O'Connor, 1987). Hence, the import of fine cliff material into the Humber estuary can be estimated at 98 to 182 kton/yr. The third source of suspended matter to the Humber is the North Sea, with a contribution twice as high as the fluvial import (O'Connor, 1987).

In the Humber estuary, physical mixing of fluvial suspended matter, eroded cliff material, and marine suspended matter takes place. Some 63 kton of this mixed material is deposited annually on the mudflats and salt marshes adjacent to the Humber estuary (McCave, 1987; Pethick, 1988). Unfortunately, it is not known just how much of this material is derived from river or sea and cliff sources. Assuming that all of the deposited material is of fluvial origin (which obviously is not true), the retention of fluvial suspended matter in the Humber estuary is calculated to be maximal 32%, based on a fluvial suspended matter load of 200 kton/yr. If it is assumed that fluvial suspended matter, cliff material, and marine suspended matter are deposited proportional to their respective inputs (200, 140, and 400 kton/yr, respectively), the retention of fluvial suspended matter is only 17 kton/yr, or 8.5% of the river input. Thus, by far the largest part of the suspended matter delivered to the Humber seems to escape from the estuary (say 70-90%). This is in agreement with Pethick's opinion (1988) that most of the suspended matter supplied to the Humber by rivers is merely on its way to the sea, and with that of Turner (1989) who states that most of the suspended matter is kept in suspension and will eventually be swept out of the Humber estuary.

In view of the large mudflat areas present in the Humber estuary (Pethick, 1988), one may wonder why the retention of fluvial suspended matter is only 10 to 30%. Of course, it can be doubted if the (surprisingly low) sedimentation rate of 63 kton/yr is correct. Otherwise, the explanation may be that sedimentation of suspended matter in the Humber is efficiently reduced by strong tidal currents (Morris, 1988) and the intensity of the dredging activities, which is enormous (Table 3.8). Though the dredged spoils are all disposed of in internal waters of the Humber, dredging favours outflow of suspended matter through continuous resuspension of the bottom sediments (similar to tidal action). Dredging activities may, therefore, contribute to the outflow of suspended matter from the Humber estuary.

The fate of the material escaping from the Humber estuary illustrates that the concept of 'retention' or 'filtering' in estuaries should take into account the entire coastal zone. Suspended matter discharged by the Humber is transported in a distinct and poorly dispersing plume which stays close to the coast, moving southwards to the Wash, a major depositional area (see next paragraph).

Based on sediment composition, there is evidence that Humber suspended matter is deposited in the Wash to a very great extent (Turner, 1989; K. Dyer, pers. comm.). According to the balance of McCave (1987), some 80% of the mud supplied to the U.K. east coast is deposited in the Wash and some smaller depositional areas. Thus, though the retention of suspended matter appears to be quite small in the Humber estuary itself, most of the suspended matter which escapes from the Humber is deposited in the Wash and does not reach the open North Sea.

Table 3.8 Amount of sediments dumped in internal waters of the Humber estuary in the period 1987-1990 (wet kilotonnes per year). No spoils are dumped seaward of the Humber estuary. Source: Oslo Commission (1992)

dumping site	1987	1988	1989	1990	average
Hu020	2003	1984	2673	2888	2387
Hu030	1536	205	197	250	547
Hu040	63	54	79	52	62
Hu041	-	-	-	19	5
Hu055	425	42	10	0	119
Hu060	3433	2047	1798	1407	2171
Hu080	2995	5294	6592	0	3720
Hu090	864	632	612	670	695
Hu110	0	0	0	7114	1779
TOTAL (WET)	11319	10258	11961	12400	11485

3.5 The Wash

3.5.1 Description of the area

The Wash is a macrotidal embayment bordering the Lincolnshire and Norfolk coastlines (Figure 3.6). The seaward boundary of the Wash is defined here as a line from Gibraltar point in the North to Hunstanton in the south. The Wash is approximately 20 km wide at the mouth and 30 km in length and has an area of 615 km^2, of which 325 km^2 are exposed during extreme low tide. During the low-tide periods, a broad intertidal zone with a width between 2.6 and 10 km emerges around the margin of the bay, grading from sandflats, mudflats and salt marshes going from seawards to landwards (Collins et al., 1981). The salt marshes have developed naturally in front of man-made sea walls and form a virtually continuous fringe over 75 km from Gibraltar Point in Lincolnshire to Snettisham in Norfolk, covering an area of just over 40 km^2 (Schofield et al., 1992). The Wash is not really an estuary with a full salinity gradient but should be considered as a coastal lagoon, similar to the Dutch Wadden Sea (Eisma and Irion, 1988). The major difference between both systems is that there are no barrier islands protecting the Wash from the North Sea today. These were probably present in the past but have moved inland during Roman times (Evans and Collins, 1987). The physical characteristics of the Wash are summarized in Table 3.9. Fresh water is supplied by four rivers in the interior part of the embayment (see Figure 3.6). These rivers and their mean annual discharges are the Great Ouse (18.5 m^3/s), the Nene (6.9 m^3/s), the Welland (1.5 m^3/s) and the Witham (presumably 20 m^3/s; Wilmot and Collins, 1981; Table 3.9).

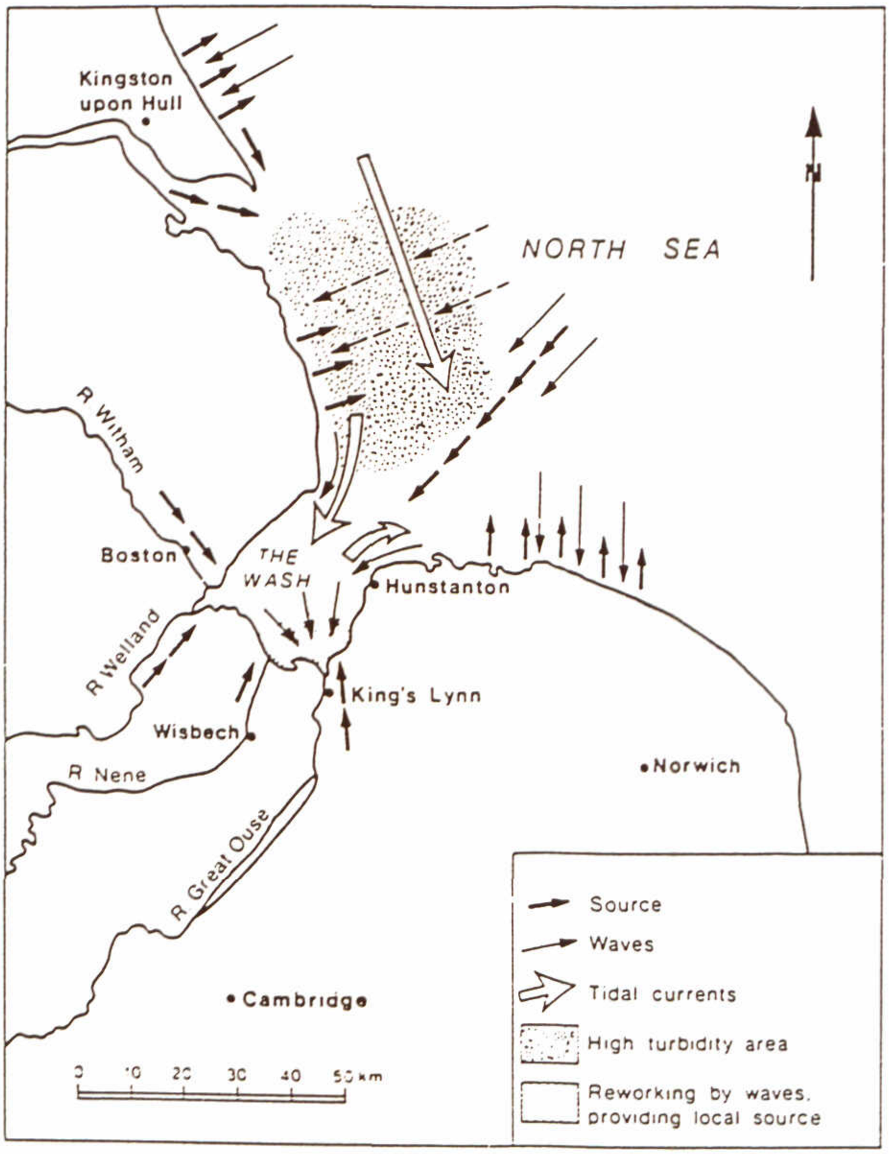


Figure 3.6 Map of the Wash and its neighbouring areas, showing the ambient sediment sources and transport paths. From Evans and Collins (1987)

Table 3.9 Physical properties of the Wash

property	unit	value	reference
catchment area	km^2	12500	Evans and Collins (1987)
river flow	m^3/s	48	
water depth	m	10 (max. 40)	Evans and Collins (1975)
tidal range mouth	m	3.6-6.5	Collins et al. (1981)
salinity at mouth	ppt	33-34	Evans and Collins (1987)
circulation type	-	well-mixed	K. Dyer (pers. comm.)
residence time	d	100	K. Dyer (pers. comm.)
SPM (tidal rivers)	mg/l	60	Wilmot and Collins (1981)
SPM (mouth)	mg/l	10-100	Collins et al. (1981)
input fluvial SPM	kton/yr	100 (43-173)	Wilmot and Collins (1981)

These rivers all have entrained estuarine channels with sluice-controlled outlets which only allow freshwater discharge at low tide. Salinity levels in the Wash range from 18-26 ppt near the river outfalls to 34 ppt at the mouth (Evans and Collins, 1987). The maximum depth is 40 m at the mouth but, over most of its area, depths are generally less than 10 m (Evans and Collins, 1975). The Wash is relatively turbid, with suspended matter concentrations ranging from 100 to 200 mg/l. Part of this is sandy material, however, and the silt and clay concentration in suspension ranges between 10 and 100 mg/l, except during stormy weather when the silt and clay concentration may increase by an order of magnitude (100-1000 mg/l). Tidal current speeds typically range from 20 to 60 cm/s (Collins et al., 1981). The residence time of the water in the Wash is in the order of 100 d (K. Dyer, pers. com.). The Wash is different from the other U.K. estuaries discussed here in that its drainage basin is neither densely populated nor heavily industrialised (Balls, 1985; Schofield et al., 1992). The main function of the hinterland is agricultural, for which large areas of salt marsh have been reclaimed. However, recognizing the major importance of the Wash as a coastal wetland, no reclamation proposals have been successful since 1979. Another threat which is recently emerging is the increasingly industrial development in the hinterland, which may lead to water quality problems (Schofield et al., 1992). The actual pollution status of the Wash is relatively low, however. The high organic matter content of the suspended matter in the Ouse, Nene and Welland rivers (about 30%) would seem to contradict this statement. However, most of this organic matter has a natural origin, namely erosion of the seaward region of the catchment area (known as the Fenland) which is partly underlain by freshwater peats (Wilmot and Collins, 1981).

3.5.2 Suspended matter retention

It is widely acknowledged that the Wash is an area of recent sand and mud deposition. The mechanisms involved in suspended matter deposition in the Wash are similar to those occurring in the Dutch Wadden Sea (e.g. Evans and Collins, 1987; Eisma and Irion, 1988). The origin of the sediment supply to the Wash has been studied intensively by Collins and his co-workers (Evans and Collins, 1975; Collins et al., 1981; Wilmot and Collins, 1981; Evans and Collins, 1987). Depending on the method of calculation, the suspended matter input from the Wash rivers together has been estimated at 43, 129, 146 and 173 kton/yr, including a bed load of 20% (Wilmot and Collins, 1981). Based on these data, the fluvial suspended matter load to the Wash is often assumed to be in the order of 100 kton/yr (Wilmot and Collins, 1981; McCave, 1987; Dyer and Moffat, 1994). This fluvial load is an order of magnitude lower than the annual deposition of fine suspended matter in the Wash, which varies from 790-1600 kton/yr, depending on the rate at which progradation is assumed to be taking place (Dyer and Moffat, 1994). Other sources of suspended matter to the Wash are 1) the Humber estuary, 2) erosion of the coastline of Lincolnshire and Yorkshire, and 3) erosion of the North Sea floor (Evans and Collins, 1987; McCave, 1987; Dyer and Moffat, 1994).

Based on a mud deposition rate of 1.6 Mton/yr in the Wash, McCave (1987) concludes that the total mud demand for the Eastern England coast is in the order of 2.0 Mton/yr, slightly less than the total supply of 2.5 Mton/yr from cliff erosion and the Wash and Humber rivers. According to this balance, 64% of the total suspended matter supply to the Eastern England coast is deposited in the Wash, and 16% in other areas (small estuaries and salt marshes).

According to the budget quoted in Dyer and Moffat (1994), the suspended matter supply to Eastern England is four times as high, however, primarily because of higher cliff erosion rates (9.9 Mton of fine suspended matter per year, of which 8.9 Mton/yr comes from cliff erosion). The latter balance would indicate that only 16% of the total mud supply to the eastern England coast is retained in the Wash.

As far as the suspended matter of the Wash rivers themselves is concerned, it seems very unlikely that this material is discharged to the sea because the mud deposition rate in the Wash is an order of magnitude higher than the rate of fluvial suspended matter supply. Moreover, the fluvial suspended matter is discharged in the interior part of the basin, i.e. in the most sheltered area. Dredging activities are unlikely to cause escape of fluvial suspended matter from the Wash to the North Sea because their intensity is quite small and the spoils are disposed of in internal waters (Table 3.10). According to expert judgement (K. Dyer, pers. comm.), the fluvial suspended matter supplied by the Wash rivers is likely to be retained almost quantitatively. Hence, the retention of fluvial suspended matter in the Wash can be estimated at 80-90 %, similar to the figure for the Dutch Wadden Sea. In view of the similar geomorphology of the Wash and the Wadden Sea, it is reasonable to expect a similar retention of fluvial suspended matter in both systems.

Table 3.10 Amount of sediments dumped in internal waters of the Wash in the period 1987-1990 (wet kilotonnes per year). No spoils are dumped in coastal waters off the Wash (site Hu120). Source: Oslo Commission (1992)

dumping site	1987	1988	1989	1990	average
Hu130	12	0	47	39	25
Hu135	0	46	-	-	11
Hu140	125	121	85	74	101
TOTAL (WET)	137	167	132	113	137

3.6 The Thames estuary

3.6.1 Description of the area

The Thames estuary (Figure 3.7) extends almost 100 km from its mouth at Southend to Teddington Weir, which marks the limit of tidal range; the main river extends a further 236 km landwards. The estuary has a funnel-like shape with a cross-sectional area increasing almost exponentially towards the North Sea. The load of contaminants carried by the Thames is calculated from the river flow and water quality measured at Teddington (Wulffraat et al., 1993). Note that inputs from the agglomeration of London are not included in the monitoring of river water quality (these can be considered as direct discharges). The physical properties of the Thames estuary are summarized in Table 3.11. The river flow is relatively high during winter but may drop to very low values during summer (almost zero). With normal winter river flow, freshwater prevails roughly as far as London Bridge, situated 32 km seaward of Teddington. In late summer, salt water penetrates a further 10-20 km into the estuary (DSIR, 1964). The mean tidal range at Southend varies from 3.3 m at neap tides to 5.1 m at spring tides, so that the estuary can be considered as macrotidal.

Near London Bridge, the tidal range maximises to about 5.8 m. Though minor vertical stratification has been recorded in the middle reaches of the estuary, the estuary can be regarded as a well-mixed system for most purposes. The Thames has a well-developed turbidity maximum with suspended matter concentrations of several g/l.

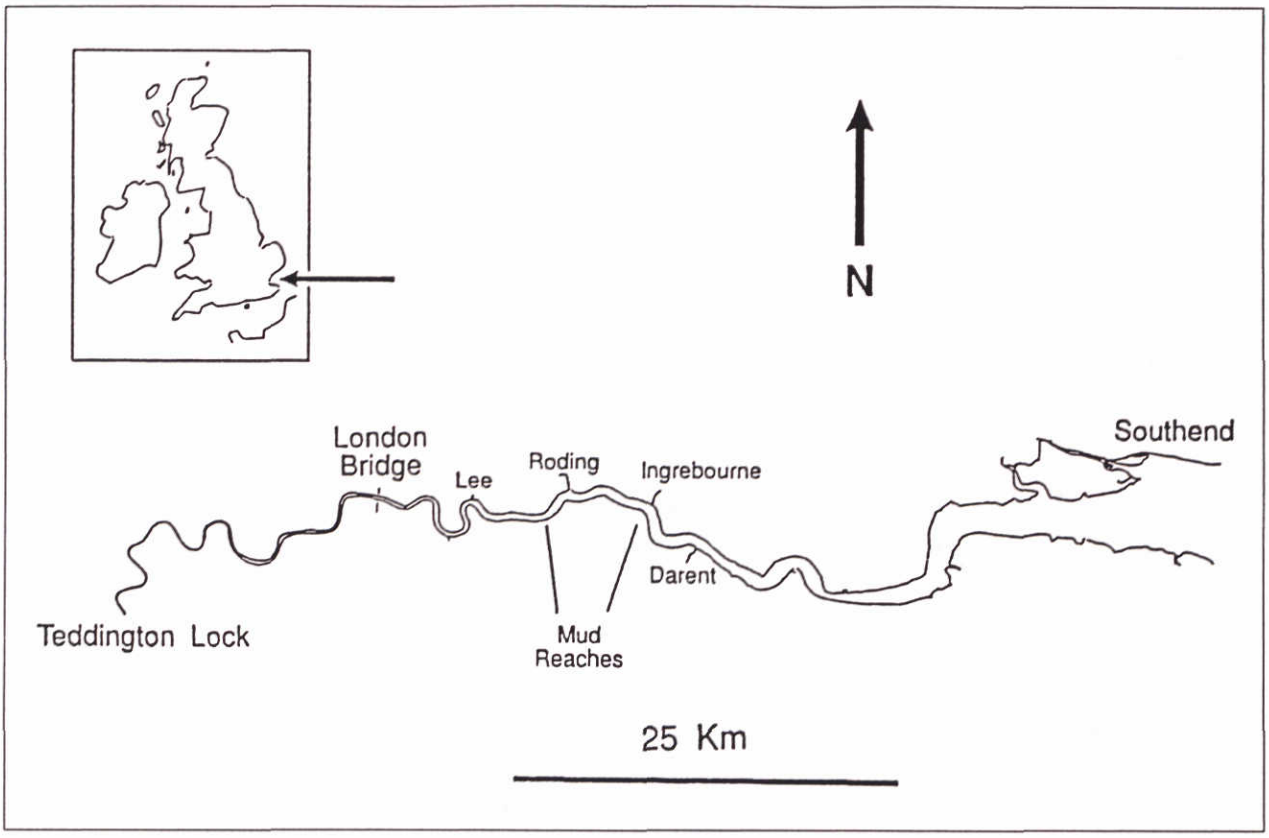


Figure 3.7 The Thames estuary (Harris et al., 1993)

Table 3.11 Physical properties of the Thames estuary

property	unit	value	reference
catchment area	km^2	9900	DSIR (1964)
river flow	m^3/s	82 (9-210)	DSIR (1964)
length mixing zone	km	100	Morris (1988)
water depth	m	7.6	Odd and Owen (1972)
tidal range mouth	m	3.3-5.1	Inglis and Allen (1957)
salinity at mouth	ppt	21-34	Turner (1989)
circulation type	-	well-mixed	Morris (1988)
residence time	d	40 (20-75)	Turner et al. (1991)
SPM (tidal river)	mg/l	30	see note (*)
SPM (turb. max.)	mg/l	50-5000	Burt (1986)
SPM (mouth)	mg/l	16-325	Turner (1989)
input fluvial SPM	kton/yr	78	see paragraph 3.6.2

* based on a fluvial suspended matter input of 78.5 kton/year (Wilmot and Collins equation)

Pollution of the Thames accompanied by oxygen depletion has long been a major environmental problem. The oxygen demand resulted mainly from local discharges (e.g. the London agglomeration) rather than from the riverine input. One of the first measures being taken was the dumping of vast amounts of sewage sludge outside the estuary, which started at the beginning of this century. However, the increasing population has led to deterioration of the estuary, despite the building of new sewage works and development of improved treatment methods. Severe deoxygenation in the Thames developed through the first half of the present century; around 1950 there were stretches in the estuary (seaward of London Bridge) which were at times totally devoid of oxygen. However, remedial actions have resulted in a major improvement in the oxygenation and ecological status of the Thames since the late 1950's. Today, the estuary is well oxygenated, and salmon has returned in the estuary since the late 1970's. More details on the history of pollution and recovery of the Thames can be found in Wood (1982), Andrews (1984), and Lloyd and Whiteland (1990). Much less attention has been paid to contaminants other than oxygen consumers (BOD, ammonia). Concentrations of trace metals and organic contaminants generally increase from Teddinton towards London Bridge, where broad maxima are centred in the low salinity, high turbidity region, then decrease towards the mouth of the estuary (Morris, 1988). Mercury distributions differ in showing a number of distinct peaks along the waterway (Nelson, 1981). Mercury in sewage effluents is thought to be responsible for this distribution pattern. Elevated trace metal concentrations are also found off the Thames mouth; these are associated with dumping of sewage sludge in the Barrow Deep and dredged spoils at South Falls (Harper, 1988). In view of the enormous amounts of sewage sludge dumped annually in the Barrow Deep (about 5 Mton wet material per year; Heap et al., 1991), this practice constitutes a major (local) source of contaminants to the North Sea. Investigations on the biological effects of the dumping activities showed no clear evidence of detrimental effects on the macrobenthic community, though sub-lethal physiological stress in mussels was detected (Whitelaw and Andrews, 1988).

3.6.2 Suspended matter retention

Based on the size of the catchment area, the suspended matter load of the Thames is estimated at 78 kton/yr (Wilmot and Collins, 1981). More recently, the suspended matter discharge by the Thames has been estimated at 690 kton/yr, an order of magnitude higher (quoted in Dyer and Moffat, 1994). However, the latter estimate includes erosion of the intertidal mudflats, particularly in the small estuaries surrounding the Thames (Medway, Blackwater), which is clearly beyond the scope of this study. The transport of suspended matter in the Thames estuary has been the subject of considerable study (Kendrick, 1972; Odd and Owen, 1972; Dyer, 1978; Burt, 1986; Odd, 1988; Partheniades, 1988), the early research being prompted by the construction of a storm-surge barrier in the estuary. As a result, the siltation regime of the Thames is well-known, at least qualitatively. Deposition of suspended matter is confined to the 'mud reaches', 45-53 km upstream of Southend. The remaining part of the estuary has a hard bed made up of gravel, clay and chalk, and features current velocities which are sufficiently high to prevent permanent deposition of suspended matter. This mud distribution pattern was successfully reproduced by early model simulations (Odd and Owen, 1972). According to more recent model simulations, suspended matter, deposited in the mud reaches, can be re-eroded and deposited again in the wide intertidal zones near the mouth. In turn, mud deposited on intertidal banks near the mouth can be partly re-eroded by local wave action and storm water run-off (Odd, 1988).

Despite the concentrated research efforts described before, truly quantitative estimates of suspended matter retention in the Thames estuary are not available. Expert judgements of the retention of fluvial suspended matter in the Thames range from 25-30% (K. Dyer, pers. comm.) to nearly 100% (J. Winterwerp, pers. comm.). A very crude estimate of suspended matter retention is presented below, based on maintenance dredging data. In the year 1985, a total volume of 332000 m^3 was dredged from the port of London (Donze, 1990). The dredged spoils are dumped on land, because of the costy transport over long distances to the sea. Hence, the sediments are permanently withdrawn from the estuary, leading to artificial (man-made) retention of fluvial suspended matter. Given the muddy nature of the sediments, it is assumed that dredged spoils from the port of London have similar characteristics to muddy sediments from Rotterdam Harbour, i.e. a water content of 55% (porosity 0.753) and 57% silt in the solid phase (J. Boon, pers. comm.). Thus, the volume of sediments dredged from the port of London in 1985 (332000 m^3) is equivalent to approximately 205 kton solid material (dry density 2.5 ton/m^3), of which 117 kton is silty sediments. This amount is comparable in magnitude to the annual amount of suspended matter supplied by the Thames river (78 kton). However, an important (though unknown) fraction of the dredged sediment will be of marine origin. Assuming the contribution of marine sediments to be at most 50% (because of the low salinity of the port waters), the retention of fluvial suspended matter follows as 75-100%. In view of the much lower estimate by Keith Dyer (25-30%), a retention in the range of 50-70% is proposed. Clearly, this is a very uncertain guess, but the available data allow no better than this.

Sediments dredged from areas less remote from the sea are dumped in coastal waters off the Thames mouth. An overview of dredged spoil dumping off the Thames mouth is given in Table 3.12. According to the quantities involved, the origin of the dumped sediments will be mostly marine.

Table 3.12 Amount of sediments dumped in coastal waters off the Thames in the period 1987-1990 (wet kilotonnes per year). Source: Oslo Commission (1992)

dumping site	1987	1988	1989	1990	average
TH010	-	114	60	26	50
TH040	2293	1634	1369	222	1380
TH043	-	-	1270	470	435
TH045	54	824	2389	25	823
TH070	9	177	165	222	143
TH140	31	90	123	105	87
TOTAL (WET)	2387	2839	5376	1070	2918

4 SPM retention in Dutch North Sea estuaries

4.1 The Scheldt estuary

4.1.1 Description of the area

The drainage basin of the Scheldt river covers 21600 km^2 in northwestern France, western Belgium and the southwestern Netherlands. The Scheldt and Rupel rivers are the major tributaries of fresh water. Under average river discharges, seawater intrudes into the estuary up to the Rupel confluent. The tidal wave propagates into the Scheldt river up to the city of Gent, located 180 km from the mouth. The fluvial boundary of the Scheldt estuary is chosen at the confluence of the Scheldt and Rupel rivers (Rupelmonde), and the marine boundary is set at the axis Vlissingen-Breskens (Figure 4.1). Typical salinity ranges encountered at these boundaries are 0.3-1.0 and 25-30 ppt, respectively. At the Dutch-Belgian border, where the water quality is monitored, the salinity varies from 2 to 15 ppt, depending on the river flow and the state of the tide. Between the city of Antwerp and the Dutch-Belgian border, a high turbidity zone (HTZ) is located, its exact location depending on the river discharge and state of the tide.

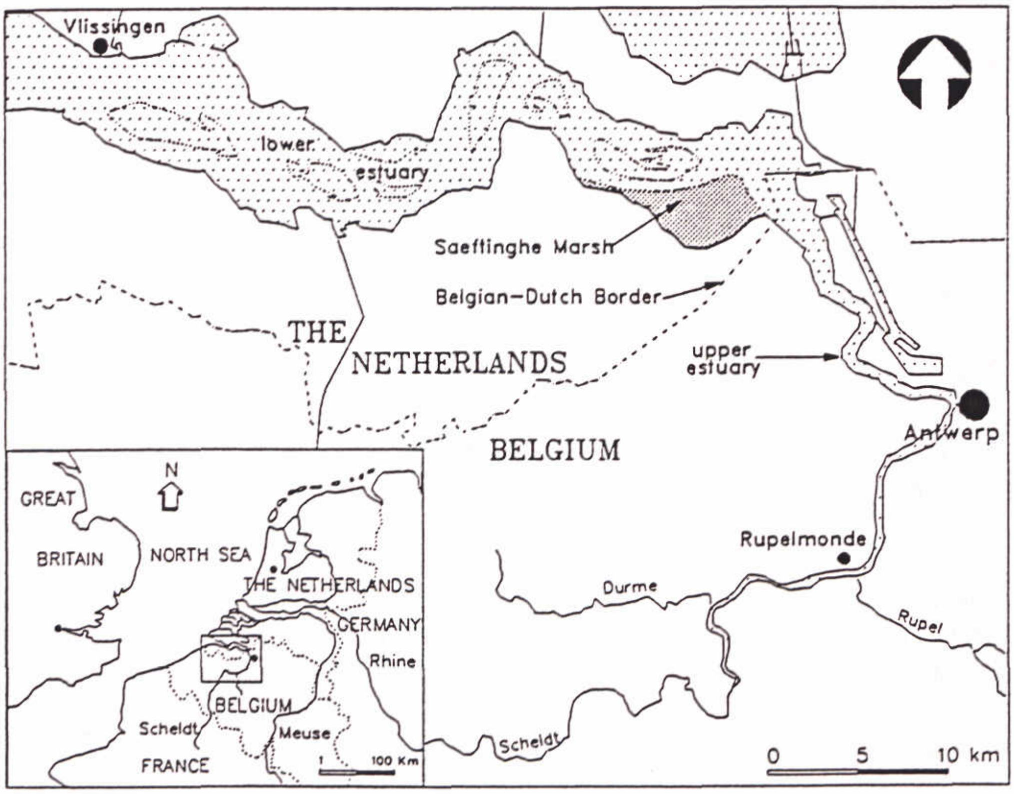


Figure 4.1 The Scheldt estuary. From Zwolsman and Van Eck (1993)

The Scheldt estuary is a typical macrotidal coastal plain estuary with a tidal range of 4-5 m and a mean water depth of 10 m (maximum 50 m). The length of the estuarine mixing zone and the residence time of the fresh water depend on the river discharge, which in turn depends on the season. The river flow is measured at Schelle, just downstream of Rupelmonde. The fresh water discharge at the mouth is estimated to be 30% higher than the river flow measured at Schelle. Though there is a small vertical salinity gradient in the upper estuary, the water column can be regarded to be well-mixed, except during extreme river flows. This explains the long residence time of fresh water in the estuary which may vary from one to three months. The physical parameters of the Scheldt estuary are summarized in Table 4.1.

Table 4.1 Physical properties of the Scheldt estuary

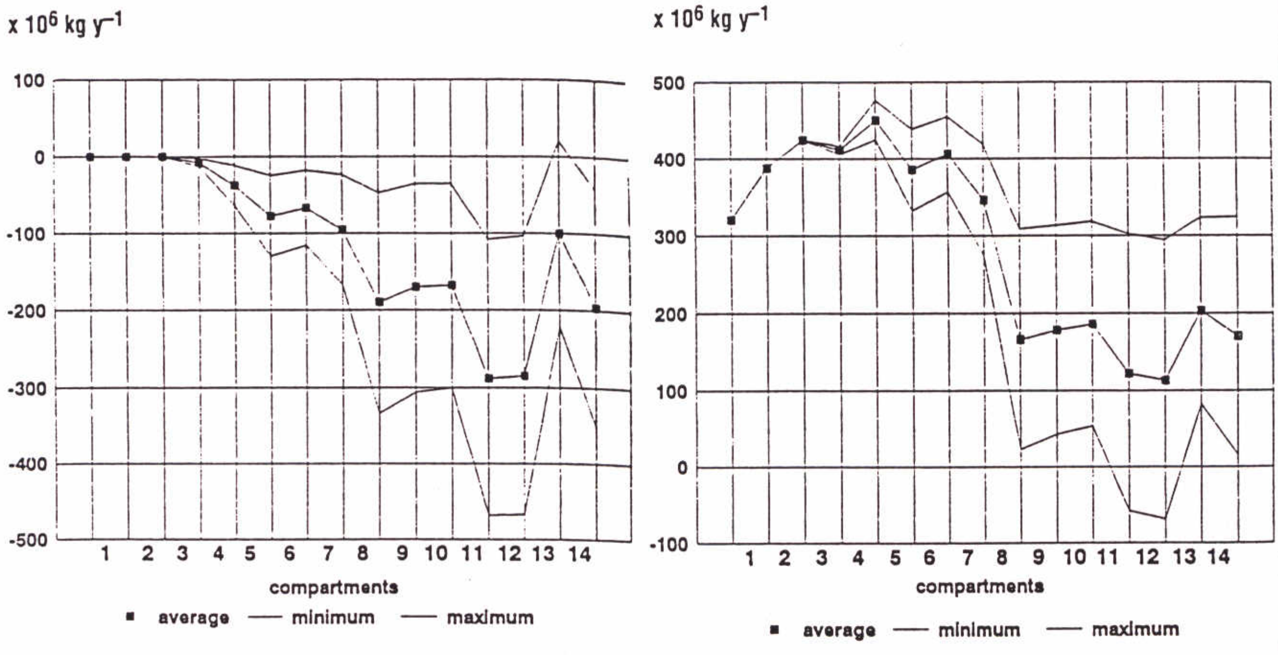
property	unit	value	reference
catchment area	km^2	21580	Nihoul et al. (1978)
river flow (Schelle)	m^3/s	100 (40-350)	Nihoul et al. (1978)
length mixing zone	km	70-100	Wollast (1988)
water depth	m	10 (max. 50)	SAWES project*
tidal range mouth	m	4	Nihoul et al. (1978)
salinity at mouth	ppt	25-30	SAWES project*
circulation type	-	well-mixed	Nihoul et al. (1978)
residence time	d	30-90	Wollast (1988)
SPM (tidal river)	mg/l	100	SAWES project*
SPM (turb. max.)	mg/l	100-250	SAWES project*
SPM (mouth)	mg/l	25	SAWES project*
input fluvial SPM	kton/yr	315-970	see Table 4.2

* SAWES project: field data from eight cruises carried out between February 1987 and February 1988 (Zwolsman and Van Eck, 1993)

The upper Scheldt estuary (situated in Belgium) is heavily polluted due to a variety of industrial and domestic waste water inputs in the Scheldt and its tributaries (Wollast, 1988; Wulffraat, 1989; Van Eck et al., 1991). In addition, numerous sources of pollution are located in the industrial zone around Antwerp. Due to the high organic load, the water column in the low salinity zone is frequently devoid of oxygen, especially during the summer. There are only a few point sources in the lower estuary, the major ones being located around the cities Terneuzen and Vlissingen (Wulffraat, 1989). The contaminant load of the Scheldt to the North Sea is calculated from the river flow at the mouth (averaging 139 m3/s) and the water quality recorded at the Dutch-Belgian border (Wulffraat et al., 1993). Since the border station (Schaar van Ouden Doel or simply Doel) is situated in the brackish part of the estuary, the contaminant load should be corrected for dilution by sea water. If this correction is omitted, the contaminant load that crosses the border and hence also the load that reaches the North Sea will be underestimated.

4.1.2 Suspended matter retention

The suspended matter load of the Scheldt river has increased significantly as a result of human influences. It has been estimated that industrial and domestic sources accounted for two thirds of the suspended matter load of the Scheldt river in the seventies (Wollast, 1988). However, man-made loads have decreased significantly in the eighties due to waste water treatment. Today, the suspended matter concentration in the Scheldt river at the onset of estuarine mixing averages about 100 mg/l (SAWES data 1987-1988). Using this value and a mean river discharge of 100 m^3/s, the input of fluvial suspended matter is calculated at 315 kton/yr. This figure forms the basis of a mud balance for the Scheldt estuary, constructed by Van Maldegem et al. (1993). A more comprehensive description of the balance is given in Van Maldegem (1993). Based on field data (sedimentation, erosion, dredging, etc.), the balance describes the fate of cohesive sediments, defined as inorganic particles with a particle size smaller than 63 μm. The results of the balance, which holds for the situation around 1985, are presented in Figure 4.2. The balance makes an explicit distinction between fluvial and marine suspended matter transport.



Net annual natural transport of marine mud.

Net annual natural transport of fluvial mud.

Figure 4.2 Net annual transport of fluvial and marine suspended matter in the Scheldt estuary. Boundary compartments: 1 = Scheldt river, 6 = Dutch-Belgian border, 14 = North Sea. From Van Maldegem et al. (1993)

The highlights of the suspended matter balance can be summarized as follows:

1. The seaward transport of fluvial suspended matter is about 315 kton/yr at the start of the salinity gradient, increasing to 400 kton/yr at the Dutch-Belgian border (due to numerous waste water inputs, mainly from industry), and decreasing to 100-200 kton/yr in the lower estuary. A sudden decrease of the fluvial suspended matter transport occurs in the eastern part of the lower estuary (compartments 7 and 8), which is due to sedimentation in salt marsh areas located there (e.g. Land van Saeftinge). The increase of the fluvial suspended matter transport near the mouth (compartment 13) is caused by erosion of old mud deposits. On the average, 160 kton of fluvial suspended matter reaches the North Sea every year. This is probably an overestimation as will be shown later.

2. The import of marine suspended matter into the estuary amounts on the average 200 kton/yr at the mouth, of which about 100 kton/yr passes the Dutch-Belgian border. This 100 kton of marine suspended matter is deposited in the upper estuary and is assumed not to penetrate in the tidal river. Experimental evidence from 'marine' radio-isotopes, released from reprocessing plants at La Hague and Sellafield, confirm that marine suspended matter intrudes the estuary as far as 100 km from the mouth, i.e. up to Rupelmonde (Martin et al., 1994).

3. The results of the balance depend dramatically on assumptions as to the true end-member composition of fluvial and marine suspended matter (Van Maldegem, 1993). Small variations in the end-member composition lead to large uncertainties in the balance, as reflected by the minimum and maximum lines in Figure 4.2. In this respect it should be noted that the average fluvial suspended matter transport shown in Figure 4.2 is based on a fluvial suspended matter percentage at the mouth of 20%. However, based on the suspended matter composition at the mouth, a fluvial suspended matter contribution of at most 10% can be estimated (Zwolsman, in prep.). The net escape of fluvial suspended matter to the sea should therefore be less than given by the 'average' line in Figure 4.2. A more realistic prediction on fluvial suspended matter export would fall between the minimum and average line, yielding an export of 20 to 160 kton/yr. Compared to the 400 kton/yr that crosses the border, the net retention of fluvial suspended matter in the lower Scheldt estuary (downstream of the monitoring station at Doel) follows as 60 to 95%. This range can be considered as the best estimate of fluvial suspended matter retention in the Scheldt estuary to date. Alternative estimates are discussed in the next paragraph.

4.1.3 Alternative estimations

Various estimations of suspended matter transport in the Scheldt estuary have been made in the past. Contrary to the cohesive sediment balance discussed before, these estimations are based on total suspended matter composition (organic and inorganic), except for the budget of Mulder (1990). A summary of these suspended matter balances is given in Table 4.2; for comparison the suspended matter balance of Van Maldegem et al. (1993) is also indicated.

Table 4.2 Previous estimations of suspended matter transport through the boundaries of the Scheldt estuary (in kton/yr). From Van Maldegem (1993)

	fluvial SPM			marine SPM	
Reference	river	border	sea	sea	border
Wollast and Peters (1980)	970	320	120		
Salomons et al. (1981)	800	340	100	930	200
Steyaert and Van Maldegem (1987)	800	350	10	570	220
Bijlsma and Steyaert (1988)	800	350	220	380	80
Mulder (1990)	540	550	-60	1600	110
Van Maldegem et al. (1993)	315	400	160	200	100
average SPM transport fluxes	700	385	90	740	140

The fluvial suspended matter input estimated by Van Maldegem et al. (1993) is much lower than that estimated in the other studies, which is partly explained by the fact that the other studies include organic matter. There is good agreement between all estimates of the fluvial suspended matter transport across the Dutch-Belgian border, however. On the other hand, the estimates of the fluvial suspended matter export to the sea and the import of marine suspended matter into the estuary vary strongly among the different studies. It should be realized that the import of marine suspended matter into the estuary is highly uncertain because it is frequently used as a closing-term in mass balance calculations. Based on the average transport fluxes shown in Table 4.2, the retention of fluvial suspended matter in the Scheldt estuary is estimated as 87% for the estuary as a whole. With respect to the border-crossing load, the fluvial suspended matter retention is 77%. It is obvious that these retention percentages have a high degree of uncertainty. For instance, the retention of fluvial suspended matter with respect to the border-crossing load varies from 37% to 100%, according to the data in Table 4.2. These figures illustrate clearly that estimations of the fluvial suspended matter export to the sea remain uncertain as long as there is no direct method of measuring these fluxes. The balance of Van Maldegem et al. (1993) is considered to be the most reliable one, because this balance is based on a more comprehensive data set than the others.

Since 1992, a further increase of the retention of fluvial suspended matter in the Scheldt estuary has occurred, due to withdrawal of contaminated sediments in the Antwerp region. In the last three years, a total of 1.3 Mton (dry weight) of fine sediment has been removed from the system (G. van Eck, pers. comm.), roughly equal to the fluvial suspended matter input of four years. Though the origin of the sediments withdrawn is not entirely fluvial (about 25% is marine sediment), it is obvious that the withdrawal of such large amounts of sediments (which are stored on land) increases the retention of fluvial suspended matter to nearly 100% (or more, if suspended matter deposited in previous years is included in the calculation of retention in a specific year). Of course, this increase in retention will only be temporal, since withdrawal of sediments on such a major scale will not continue for a long time.

4.2 The Rhine/Meuse estuary

4.2.1 Description of the area

The Rhine/Meuse estuary forms part of the Northern Delta basin, which is a complex hydrological system in the southwestern Netherlands (Figure 4.3). Fresh water is supplied to the basin by three rivers, namely the Lek, Waal, and Meuse, the first two rivers being branches of the Rhine. With a yearly averaged flow of about 1500 m^3/s, the river Waal represents the largest source of fresh water to the basin. The yearly averaged flows of the rivers Lek and Meuse are 400 m^3/s and 300 m^3/s, respectively. Thus, some 86% of the fresh water input to the basin is supplied by the Rhine. The usual directions of flow within the Northern Delta basin are shown in Figure 4.3. A reversed flow can occur in the Dordtsche Kil canal during high river discharges, and under extremely high river flows also in the Spui canal. The shipping canal 'Nieuwe Waterweg' and the sluices in the Haringvliet Basin connect the Rhine with the North Sea. The Haringvliet is a fresh water system since the closure of the Haringvliet dam on 2 November 1970. Therefore, the Haringvliet is not considered here, though the sedimentation in this basin (including the Hollands Diep) is important. The truly estuarine part of the Northern Delta basin is formed by the river branches Nieuwe Maas (New Meuse), Oude Maas (Old Meuse) and Nieuwe Waterweg (New Waterway). Together, these branches are referred to either as Rotterdam Harbour (Salomons and Eysink, 1981), Rotterdam Waterway (Abraham et al., 1986), or Rhine/Meuse estuary (Kramer and Duinker, 1988). It is this system for which the suspended matter balance will be derived (Figure 4.4).

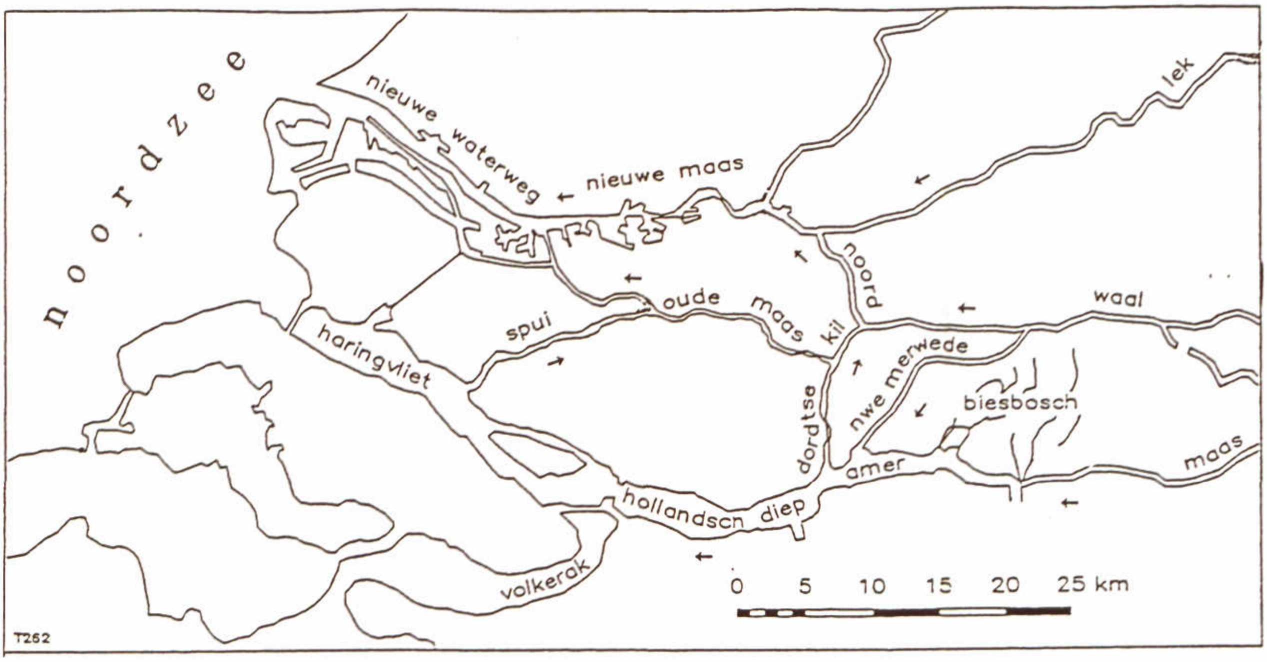


Figure 4.3 The Northern Delta basin

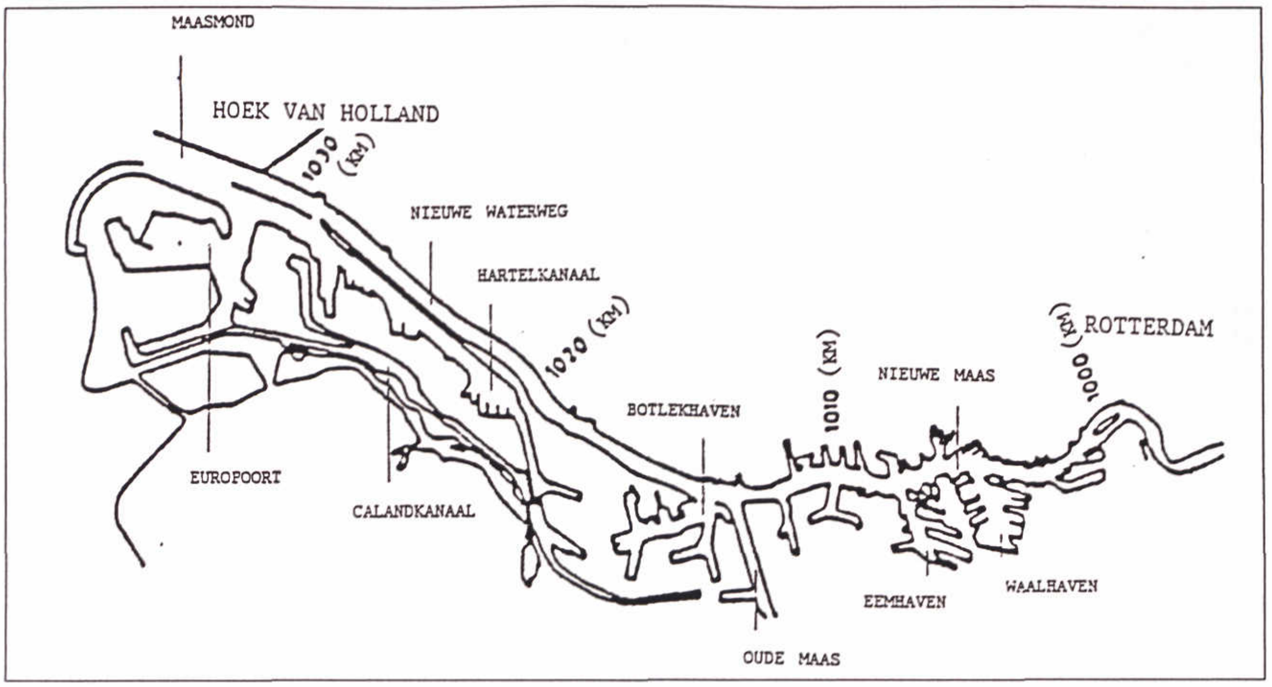


Figure 4.4 The Rhine/Meuse estuary

The Nieuwe Waterweg constitutes the major part of the Rhine/Meuse estuary. Salinity intrusion into the side branches Nieuwe Maas and Oude Maas is not important, except during high tide. An approximate net flow of 1500 m^3/s is maintained in the Nieuwe Waterweg through regulation of the river discharge in the Haringvliet basin. Due to this high river flow and the complete canalization of the waterway, the Nieuwe Waterweg has a partially mixed to stratified circulation pattern (Abraham et al., 1986; Van Gils et al., 1993; Figure 4.5). The high river flow results in a very short fresh water residence time in the estuary, which is in the order of a few days. Another consequence of the high river flow is the occurrence of low salinity waters near the mouth of the estuary, especially in the surface layer of the water column (Figure 4.5). Usually, the suspended matter concentration shows an exponential decrease with increasing salinity; a turbidity maximum is only occasionally found. The physical properties of the Rhine/Meuse estuary are summarized in Table 4.3.

Table 4.3 Physical properties of the Rhine/Meuse estuary (see Figure 4.4)

property	unit	value	reference
catchment area	km^2	220000	Eisma et al. (1982)
river flow	m^3/s	1476	Wulffraat et al. (1993)
length mixing zone	km	25-30	Duinker (1985)
water depth	m	15	Abraham et al. (1986)
tidal range mouth	m	1.5-1.9	Van Alphen et al. (1988)
salin. mouth-upper	ppt	13 (4-28)	Figure 4.5
salin. mouth-lower	ppt	28 (20-33)	Figure 4.5
circulation type	-	stratified	Van Gils et al. (1993)
residence time	d	3-6	Duinker (1985)
SPM (tidal river)	mg/l	30	Kramer and Duinker (1988)
SPM (turb. max.)	mg/l	no T.M.	Kramer and Duinker (1988)
SPM (mouth)	mg/l	10	Kramer and Duinker (1988)
input fluvial SPM	kton/yr	1420-1500	see paragraph 4.2.2

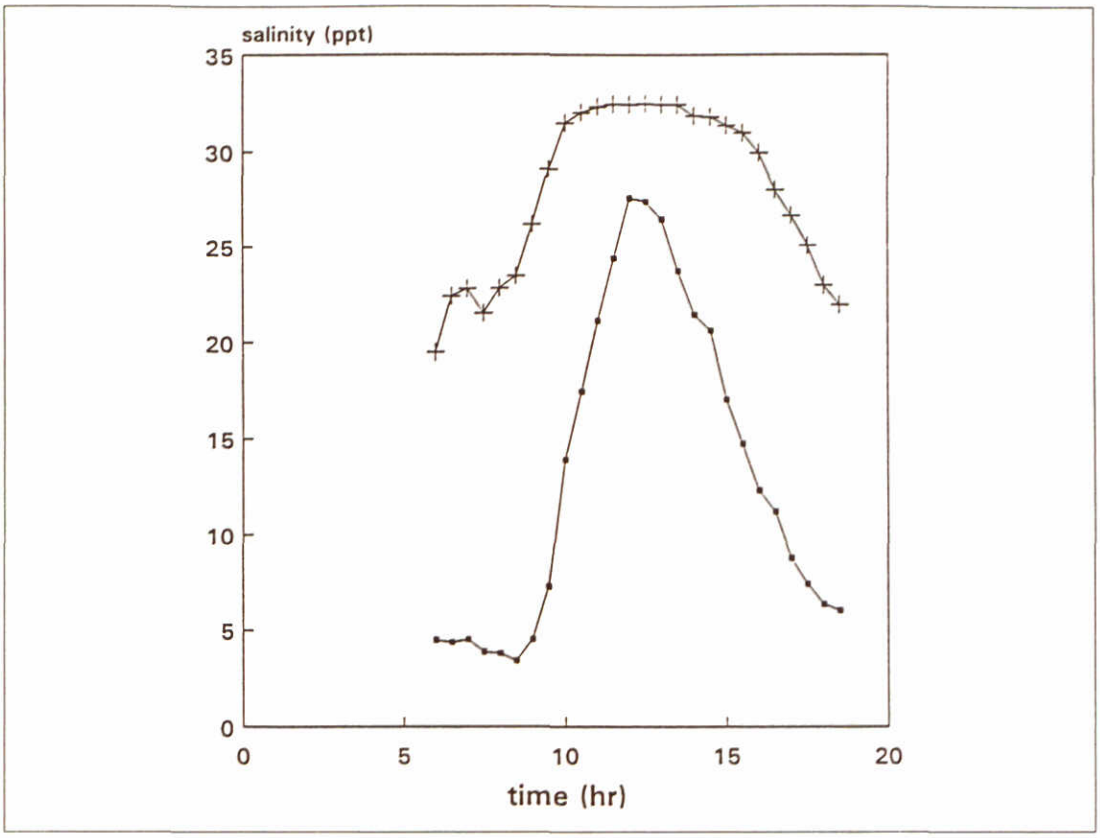


Figure 4.5 Evolution of salinity during a tidal cycle in the surface (■) and bottom layer (+) near the mouth of the Rhine/Meuse estuary (Rhine km 1029)

The contaminant load discharged by the Rhine/Meuse estuary to the North Sea is calculated from the water quality measured at Maassluis (station NW 37). This station is located 18 km upstream of the mouth (km 1017.5) in the brackish water zone. Water samples are taken from the surface layer during low water slack, corresponding with typical salinities of 0.3 to 6 ppt. The reason that the water quality is monitored at the Maassluis station and not at the interface of fresh and saline water (located 10-15 km upstream) is that there are many contaminant discharges in the estuary which have to be included in the water quality monitoring program (Bons and Bleeker, 1993).

4.2.2 Suspended matter retention

Introduction

Suspended matter balances for the Rhine/Meuse estuary have been constructed by Eisma et al. (1982), De Kok et al. (1992), and Van Gils et al. (1993). Unfortunately, the suspended matter balance of Eisma et al. (1982) does not explicitly discriminate between (sedimentation of) fluvial and marine suspended matter. Therefore, this balance is not considered in detail here. The suspended matter balance of Van Gils et al. (1993) has been derived for the year 1985.

The mass balance for fluvial material is partly based on model simulations for the entire Northern Delta Basin. The mass balance for marine suspended matter is based on the net sedimentation rates in the estuary (e.g. inferred from dredging works). The suspended matter balance of De Kok et al. (1992) is also based on computer simulations (TRISULA) and field data but holds for the year 1990.

Fluvial suspended matter balance

In 1985, a total quantity of 2.1 Mton of suspended matter was delivered to the Northern Delta Basin via the Rhine and Meuse rivers (Van Gils et al., 1993). In the southern part of the basin (Hollands Diep-Haringvliet), 42% of this load was retained through settling (880 kton), whereas an additional 5% was exported to the North Sea via the Haringvliet sluices (105 kton). The remaining load was discharged to the Rhine/Meuse estuary (53% or 1.1 Mton). Due to the fact that 1985 was a relatively dry year, the loads in 1985 are not representative of loads in other years. According to Eisma et al. (1982), the annual suspended matter supply by the Rhine and Meuse rivers is 3.5 to 4.0 Mton, 1.5 Mton of which goes to the Rhine/Meuse estuary. The same suspended matter load has been used recently in mass balance studies for the Dutch coastal zone (Van Alphen, 1990; De Kok et al., 1992). Based on a typical suspended matter concentration of 30 mg/l and a river flow of 1500 m3/s, the fluvial suspended matter load to the estuary follows as 1.42 Mton per year, similar to the long-year average of 1.45 Mton/yr estimated by the Rotterdam Municipality Engineering Department (1988).

Model simulations for the year 1985 show that 56% of the fluvial suspended matter load of the Rhine/Meuse estuary reaches the sea directly. Dredging not accounted for, 44% settles (Van Gils et al., 1993). Simulations for the year 1990, combined with field data, suggest that 53% is deposited in the estuary while 47% is flushed to the sea (De Kok et al., 1992).
Thus, **in the absence of dredging**, the retention of fluvial suspended matter in the Rhine/Meuse estuary would be 44-53%. Including dredging in the balance, the retention of fluvial suspended matter is less, because the least contaminated sediments (class I) are disposed of at sea ('Loswal Noord' dumping location). Some 75% of the deposited fluvial suspended matter settles in class II and III areas, from which the sediments are dredged and stored on land (in the 'Slufter' deposit). The remaining 25% settles in class I areas from which the sediments are dredged and dumped at sea (Figure 4.6). About one third (35%) of the suspended matter dumped at sea is recirculated to the estuary, however. Of the recirculated suspended matter, 85% settles again in class I areas, to be dredged and dumped at sea, etc. (Figure 4.6). The other 15% settles in class II and III areas and becomes stored on land. Thus, only 5% of the fluvial suspended matter dumped at sea ends up in the class II and III areas and is permanently withdrawn from the system. In other words, the contribution of the recirculation flux to the retention of fluvial suspended matter in the estuary is negligible (less than 1% of the fluvial suspended matter input to the estuary). Therefore, the contribution of the sea dumping to the output of fluvial suspended matter equals the amount that settles in the class I areas, namely 11% to 13% of the total fluvial suspended matter input. Summarizing, the overall retention of fluvial suspended matter in the estuary, **including the dumping at sea**, varies from 33% to 40%. To visualize these figures, the absolute fluxes of fluvial suspended matter through the Rhine/Meuse estuary, based on a load of 1.5 Mton per year, are shown in Table 4.4.

Table 4.4 Fluxes of fluvial suspended matter through the Rhine/Meuse estuary (in kton per year), including sea disposal of dredged sediments. The recirculation flux is neglected

river input	direct output	dumping at sea	total output	storage (on land)	retention (%)	ref.
1500	840	160	1000	500	33	1
1500	700	200	900	600	40	2
1500	-	-	800	700	47	3

references: 1. Van Gils et al. (1993); 2. De Kok et al. (1992); 3. Van Alphen (1990)

As mentioned before, the contaminant load discharged by the Rhine/Meuse estuary to the North Sea is calculated from the water quality monitored at Maassluis, which is an estuarine station. Therefore, the important question remains which part of the fluvial suspended matter is deposited upstream of Maassluis. Based on the location of the harbours in the estuary, it follows that most of the fluvial suspended matter is deposited upstream of Maassluis. For instance, the Botlek Harbour, situated four km upstream of Maassluis (river km 1014), accounts for almost half of the total fluvial suspended matter retention (Van Gils et al., 1993). Most of the remaining suspended matter deposition occurs in the harbours of the Nieuwe Maas, situated 5 to 15 km upstream of Maassluis (Eisma et al., 1982). This might suggest that the retention of the fluvial suspended matter load that passes Maassluis is insignificant. This is not the case, however, because the water quality at Maassluis is measured during low water slack. When the flood comes in, the suspended matter that is present at Maassluis is pushed back in upstream direction to the harbours. Moreover, the mud deposits in the harbours are very likely to originate from the upstream transport of suspended matter along the bottom. Thus, an important (though unknown) fraction of the fluvial suspended matter that is eventually deposited in the harbours upstream of Maasluis has probably passed Maasluis first in the surface layer and has returned afterwards via bottom transport.

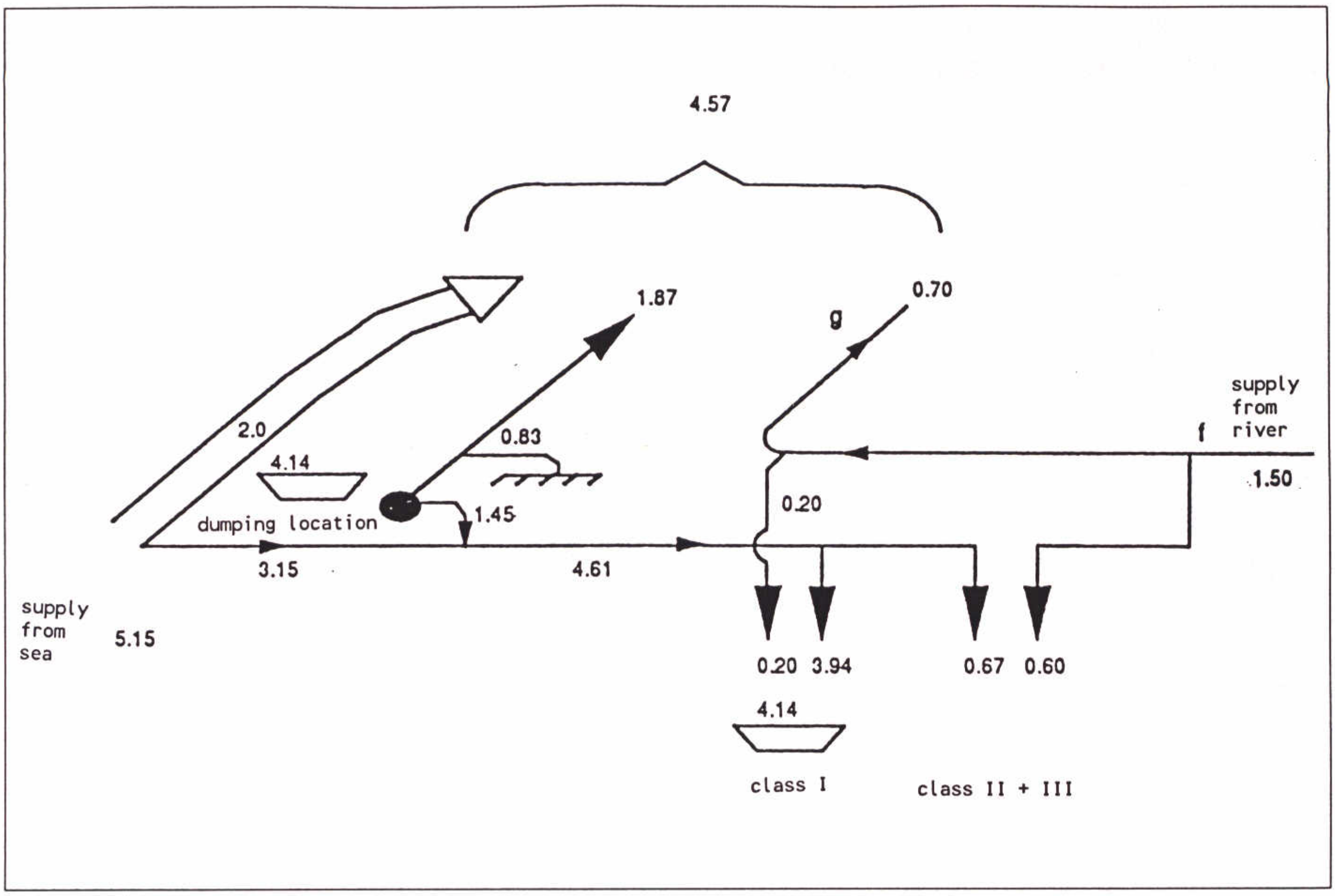


Figure 4.6 Schematic picture of the suspended matter balance for the Rhine/Meuse estuary for the year 1990, including the dumping at 'Loswal Noord' (De Kok et al., 1992). All figures in Mton per year. The main features of the budget are:

Fluvial suspended matter: supply = 1.5 Mton/yr; direct outflow to the sea = 0.7 Mton/yr (47% of annual supply); sedimentation in class II and III areas = 0.6 Mton/yr (40% of annual supply, stored on land); sedimentation in class I areas = 0.2 Mton/yr (13% of annual supply, dumped at sea).

Marine suspended matter: 'new' supply = 3.15 Mton/yr; sedimentation in class I areas = 2.70 Mton/yr (3.15/4.60 * 3.94); sedimentation in class II and III areas = 0.46 Mton/yr (3.15/4.60 * 0.67).

Dumping: Amount of mud dredged from class I areas = 4.14 Mton/yr of which 7% is fluvial and 93% is marine mud (based on sedimentation rates of 0.20 and 2.70 Mton per year, respectively). Recirculation flux = 1.45 Mton/yr (35% of dumped amount), of which 1.24 Mton/yr settles in class I areas (1.45/4.60 * 3.94) and 0.21 Mton/yr in class II and III areas (1.45/4.60 * 0.67).

Marine suspended matter balance

It is well known that a large amount of marine suspended matter is transported from the North Sea into the Rhine/Meuse estuary. Gravitational circulation and tidal pumping (and to a lesser extent tidal asymmetry) cause a net landward sediment transport along the bottom. The annual supply of marine suspended matter to the class I areas of the Rhine/Meuse estuary, including the Maasgeul, Maasmond, and Caland-Beer canal, has been estimated at 3.94 Mton in 1990, 2.70 Mton of which is 'new' marine suspended matter (De Kok et al., 1992; Figure 4.6). The remaining 1.24 Mton is suspended matter recirculating from the dumpsite Loswal Noord, which is predominantly of marine origin too (93%). This material is continuously dredged and dumped at sea, together with the 0.2 Mton of fluvial suspended matter which is also deposited in this area. A much smaller quantity of marine suspended matter is deposited in the class II and III areas, namely 670 kton in 1990, 460 kton of which is 'new' marine suspended matter and 210 kton of which is recirculated suspended matter (Figure 4.6). Alternative estimates of the sedimentation of marine suspended matter in the class II and III areas are 450 kton (Van Gils et al., 1993), 580 kton (Rotterdam Municipality Engineering Department, 1988) and 700 kton (Van Alphen, 1990). These deposition rates are of comparable magnitude as the fluvial suspended matter deposition rate in the class II and III areas of the estuary (500-700 kton/yr, see Table 4.4). The mass balance of marine suspended matter in the class II and III areas is shown in Table 4.5. According to Van Leussen and Van Velzen (1989), the majority of the marine suspended matter is deposited in the Botlek harbour, which is confirmed by the data in Table 4.5 (74-81%). Smaller sedimentation areas are the other harbours, and the bottom sediments of the Nieuwe Waterweg and the Nieuwe Maas.

Table 4.5 Input and sedimentation of marine suspended matter in the class II and III areas of the Rhine/Meuse estuary (all fluxes in kton per year)

total input	Nieuwe Waterweg	Botlek harbour	Nieuwe Maas	other harbours	ref.
446	1	361	26	58	1
580	80	430	20	50	2

references: 1. Van Gils et al. (1993); 2. Rotterdam Municipality Engineering Department (1988)

4.3 The Dutch Wadden Sea

4.3.1 Description of the area

The Dutch Wadden Sea is a shallow coastal area off the northern Dutch coast, extending from the city of Den Helder to the Ems-Dollart estuary (Figure 4.7). The total surface area is approximately 2500 km². The area is enclosed by a chain of wadden islands, separated by tidal inlets. The exchange of water and suspended matter between the North Sea and Wadden Sea occurs via these inlet channels (Postma, 1981). The Wadden Sea is a very dynamic system. The hydrodynamic forcing by tidal currents and waves leads to formation and erosion of channels, gullies and tidal flats in the entire area. Muddy sediments occur primarily in the eastern part of the Dutch Wadden Sea, where salt marshes and extensive mudflats are present. The surface area of the mudflats and salt marshes accounts for 16% and 3% of the total intertidal area of the Wadden Sea, respectively (Eisma, 1993).

Wadden Sea water is a mixture of saline North Sea water and fresh water supplied directly through two sluices from the adjacent lake IJssel (Den Oever and Kornwerderzand). The contaminant load imported from Lake IJssel is calculated from the fresh water discharge of the sluices (543 m3/s) and the quality of the lake water which is monitored 50 km upstream in the lake (Wulfffraat et al., 1993). Another 'fresh' water input comes from the plumes of the Scheldt and Rhine/Meuse estuaries (including the Haringvliet) which are transported to the north-east along the Dutch coast (Figure 4.7). The water masses in the Wadden Sea are rapidly renewed by North Sea water (Ridderinkhof, 1990), reflected by a short residence time which is in the order of eight days for the western part of the Wadden Sea (the Marsdiep Basin) and maximal 13 days for the most eastern part (the mouth of the Ems estuary). The water column is well-mixed throughout the entire system. The salinity range in the Wadden Sea varies from 18 to 31 ppt (Nienhuis, 1992), indicating that the area is dominated by seawater inputs. Thus, the Wadden Sea is not a real estuary with a full salinity gradient but should be considered as a coastal lagoon, similar to the Wash.

The ecosystem of the Dutch Wadden Sea has been studied intensively over the last three decades. Useful reviews are given by Dijkema et al. (1980), NIOZ (1988) and Anonymous (1991). Due to the influence of the Rhine river, the Wadden Sea is subject to inputs of a large number of contaminants such as trace metals, organochlorines, and nutrients (Jagtman, 1984, Kramer et al., 1985; de Jonge, 1990). The impact of pollution on the biology of the Wadden Sea is reviewed by Wolff (1988).

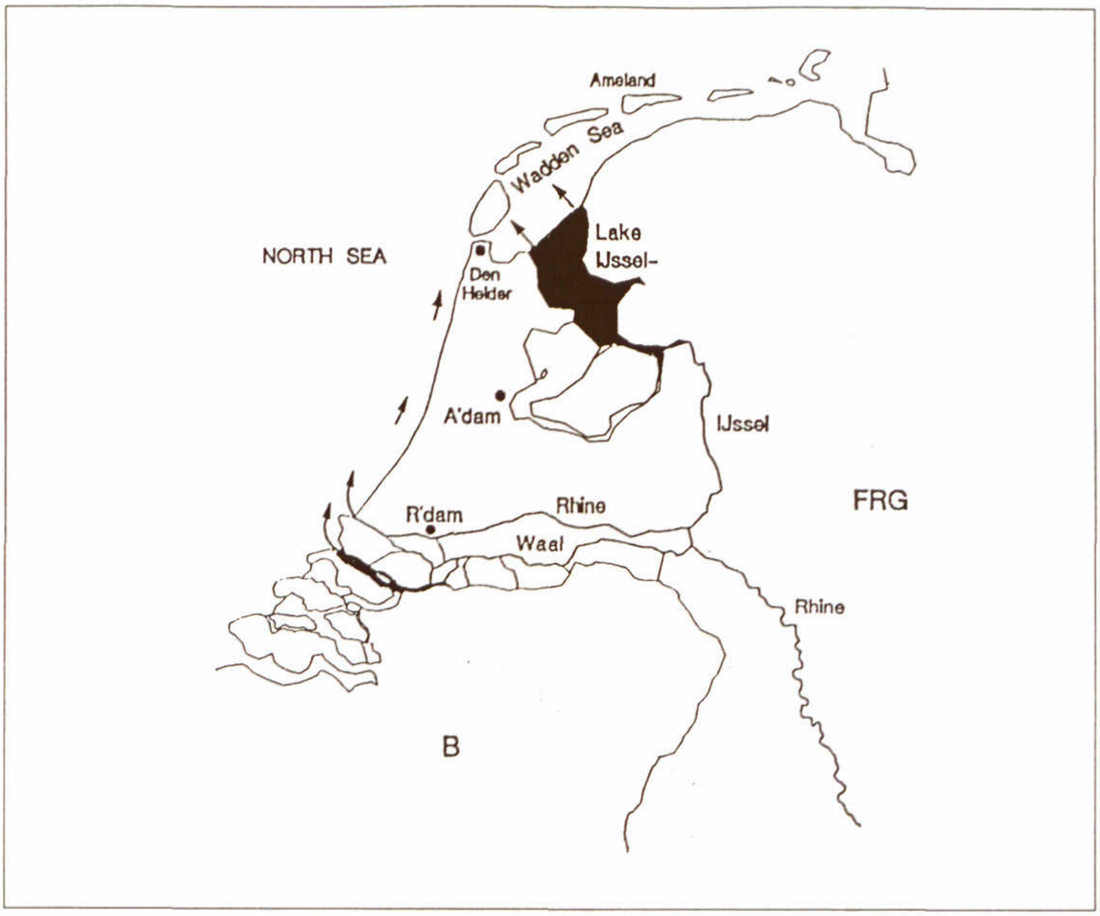


Figure 4.7 The Dutch Wadden Sea. Fresh water is imported via the coastal zone (Rhine-Meuse estuary and Haringvliet) and via two inlet points from Lake IJssel (the latter indicated by arrows). From De Jonge (1990)

4.3.2 Suspended matter retention

Import of water from the North Sea and Lake IJssel results in an input of suspended matter into the Wadden Sea. Generally, the suspended matter concentration increases from the North Sea towards the Wadden Sea's interior. The average suspended matter concentration in coastal sea water is 10 mg/l, whereas in the inner part of the Wadden Sea several hundred milligrams per litre may occur, showing large fluctuations in space and time due to variability in the hydrodynamical and meteorological conditions. Though it is known for a long time that the Wadden Sea is a mud deposition area (Van Straaten and Kuenen, 1957; Postma, 1961), the net flux of suspended matter may be seaward during winter storms (Eisma, 1993). In fact, the deposition of suspended matter in the Wadden Sea is the result of a delicate balance between slow net inward transport, erosion, and net rapid outward transport during storms. In turn, these processes are influenced by the degree of consolidation of the sediments, which depends on factors such as the presence of mussel banks (biodeposition) and benthic diatoms, and the degree of protection offered by the intertidal flats and salt marshes (reviewed by Eisma, 1993).

A comprehensive mass balance of suspended matter in the Wadden Sea is still not available at the present time. However, some individual literature data are available which allow to estimate the order of magnitude of the fluxes. The values given here refer to suspended matter with particle sizes up to 63 μm. The import of suspended matter into the Wadden Sea has been estimated by De Kok et al. (1992) at 138 kg/s or 4.35 Mton per year. This material is derived from 1) the North Sea (55 kg/s or 1.73 Mton/yr), 2) dumping of dredged material at Loswal Noord (60 kg/s or 1.89 Mton/yr), 3) the Rhine-Haringvliet system (10 kg/s or 0.32 Mton/yr), 4) Lake IJssel (13 kg/s or 0.41 Mton/yr). Considering that the fluvial suspended matter content of the dredged material dumped at 'Loswal Noord' is about 7% (see Figure 4.6), the total fluvial suspended matter input into the Dutch Wadden Sea follows as 27 kg/s or 0.85 Mton per year. Given the total import of 138 kg/s, the import of marine suspended matter amounts 111 kg/s or 3.50 Mton/yr. Thus, the origin of the suspended matter imported into the Wadden Sea is about 80% marine and 20% fluvial, about half of the latter coming from Lake IJssel and half from the Rhine-Meuse-Haringvliet. Since the suspended matter from lake IJssel is primarily derived from the Rhine river too (via the river IJssel), it is concluded that 20% of the suspended matter imported in the Wadden Sea comes from the Rhine (including a minor contribution from the Meuse) and 80% from the North Sea.

Molegraaf (1987) has reviewed estimations of suspended matter sedimentation rates in the Wadden Sea in the period 1973-1983. Viewed in historical perspective, the 'best' estimates tend to be in the order of 3.0-3.5 Mton/yr. Given the total suspended matter import of 4.35 Mton/year (De Kok et al., 1992), the overall retention of suspended material in the Wadden Sea follows as 70 to 80%. Suspended matter supplied by Lake IJssel is likely to be retained to a slightly higher extent, due to the fact that this material is discharged nearshore in a low current velocity area. Therefore, it is assumed that the retention of Lake IJssel suspended matter is in the order of 80 to 90%. A tentative mass balance of suspended matter in the Wadden Sea, based on the figures given above, is given in Table 4.6. This balance is rather premature and needs to be confirmed by more field data, especially with respect to the recent sedimentation rates.

Table 4.6 Tentative mass balance for suspended matter in the Dutch Wadden sea (fluxes in Mton per year)

origin	supply	deposition	export	retention
North Sea	1.73	1.30	0.43	75 %
dumping	1.89	1.42	0.47	75 %
Rhine-Meuse*	0.32	0.24	0.08	75 %
Lake IJssel	0.41	0.35	0.06	85 %
total	4.35	3.31	1.04	76 %

* including the Haringvliet basin

5 SPM retention in German North Sea estuaries

5.1 The Ems estuary

5.1.1 Description of the area

The Ems estuary, which forms the border between the Netherlands and Germany, discharges into the Wadden Sea (Figure 5.1). The estuary is characterized by extensive tidal flats, which make up 40 to 50% of the total surface area (Helder and Ruardij, 1982). The Ems estuary has been studied intensively in the past within the framework of the BOEDE project. The aim of the BOEDE project was to analyze the functioning of the ecosystem and predict the impact of management options on the estuary. Among the pertinent publications are the BOEDE report (1983), the theses of De Jonge (1992a) and Van Leussen (1994), and the mathematical model that has been developed (Baretta and Ruardij, 1988). A summary of the data extracted from the literature is given in Table 5.1.

The Ems estuary can be divided in four sections, including its extension into the Wadden Sea (De Jonge, 1992b). Under average discharge conditions, the tidal freshwater part of the Ems extends from the weir at Herbrum up to the city of Leer. The upper Ems estuary is situated between Leer and the mouth of the Dollart, which is a shallow embayment covered for 80% by tidal flats. The Dollart is a major sedimentation area (e.g. Dankers et al., 1984). The middle estuary extends downstream of the Dollart to Eemshaven, where the estuary joins the Wadden Sea. The lower estuary stretches from Eemshaven up to the tidal inlet at the wadden island Borkum. With a mean annual discharge of 125 m^3/s, the major supplier of fresh water is the Ems river. A second river, supplying water directly to the estuary via the Dollart area, is the Westerwoldsche Aa. The discharge of this canalized river is roughly 10% of the Ems river discharge. Vertical salinity differences are present in the Ems estuary, especially near the interface of fresh and brackish water. Maximum differences between surface and bottom salinities, observed around high water slack, range from 2.5 ppt in the Ems to 6 ppt in the southern part of the Dollard. Stratification in the rest of the estuary is relatively unimportant, however (Helder and Ruardij, 1982). Thus, the Ems estuary can be classified as intermediate between partially mixed and well-mixed. There are three important harbours in the estuary, one in Germany (Emden) and two in the Netherlands (Eemshaven and Delfzijl). Dredging takes place primarily in the harbour of Emden and to a lesser extent in the river stretch between Emden and Knock (a length of 10 km). The volume of dredged sediments (which are stored on land) has been reduced recently because the harbour of Emden is not so intensively dredged any more. For instance, the amount of sediments dredged from Emden harbour in 1993 was only 15% of that dredged in 1990 (Puls, 1994).

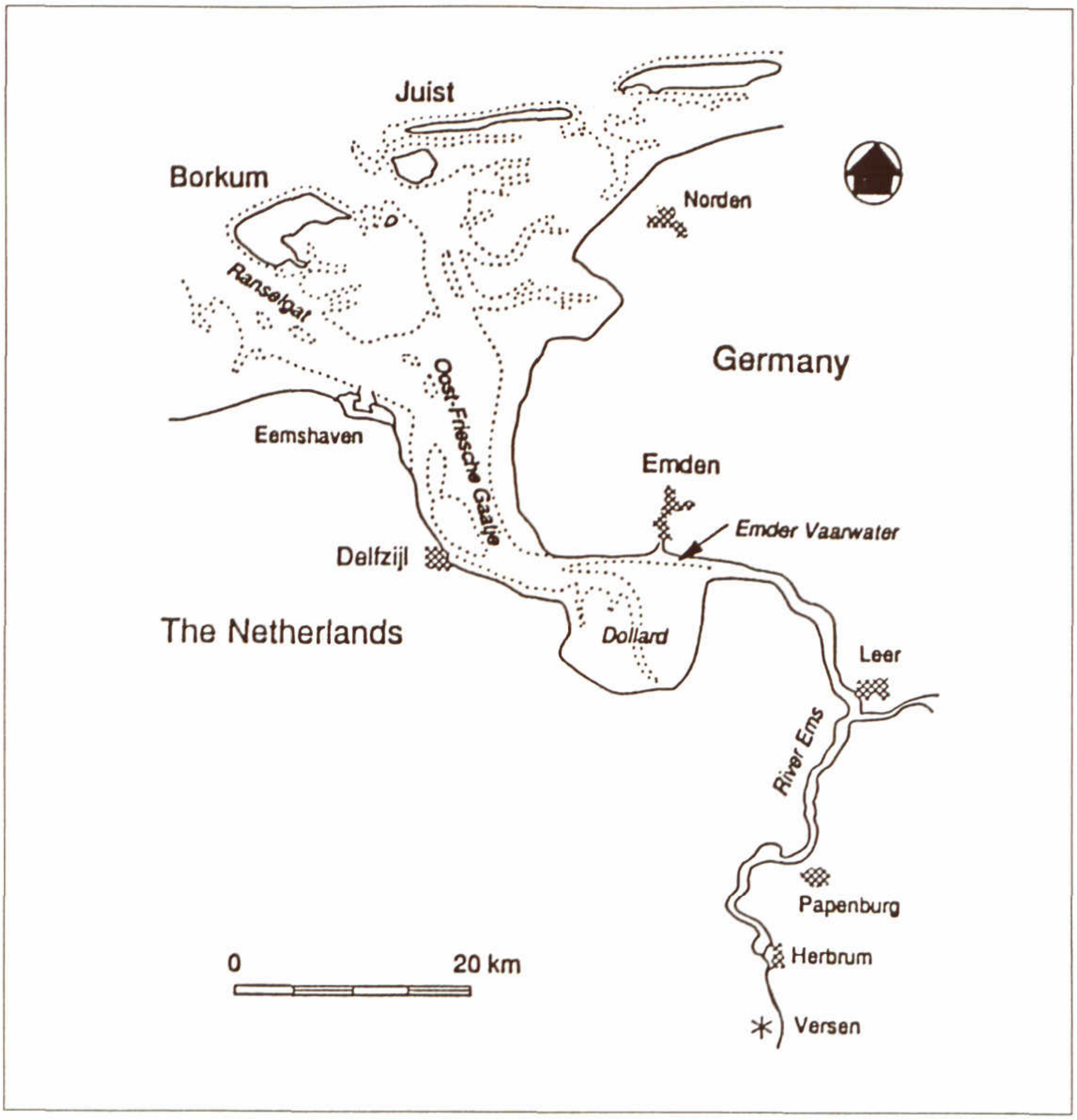


Figure 5.1 The Ems estuary. From Van Leussen (1991)

Table 5.1 Physical properties of the Ems estuary (mouth = Borkum)

property	unit	value	reference
catchment area	km^2	12650	De Jonge and Essink (1992)
river flow	m^3/s	125 (25-390)	De Jonge and Essink (1992)
length mixing zone	km	75	De Jonge (1992b)
water depth	m	5-13	Van Leussen (1994)
tidal range mouth	m	2.3	De Jonge (1992b)
salinity at mouth	ppt	30	De Jonge (1992b)
circulation type	-	w.m./p.m.*	Helder and Ruardij (1982)
residence time	d	40 (12-72)	Helder and Ruardij (1982)
SPM (tidal river)	mg/l	20	Wulffraat et al. (1993)
SPM (turb. max.)	mg/l	400	De Jonge (1983)
SPM (mouth)	mg/l	20	De Jonge (1983)
input fluvial SPM	kton/yr	70-100	see paragraph 5.1.3

* well-mixed/partially mixed

The load of contaminants from the Ems to the North Sea is based on the river flow measured at Versen and the water quality monitored at Herbrum (Wulffraat et al., 1993). Both stations are located in the fresh water zone of the Ems (Figure 5.1). The hinterland of the Ems estuary is mainly used for agricultural purposes with only minor industrial activity. Therefore, water quality problems in the Ems estuary are mainly related to eutrophication and oxygen consumption. The Ems estuary has received large amounts of organic wastes since the end of the 19th century. Anoxic waters, originating from strawboard producing and potato processing industries, entered the Ems estuary via the Dollart (river Westerwoldse Aa), causing an extensive anoxic zone in the estuary. The present-day situation has improved dramatically, however, because of a strong reduction of the number of factories and implementation of waste water purification techniques in those remaining active today (Hoogweg and Colijn, 1992). Pesticides may also pose a problem in the Ems, in view of their common usage in agriculture (Duinker et al., 1985; Ernst, 1985).

5.1.2 Sediment mixing

The sediments of the Ems river are, in contrast to those of the North Sea, rich in the clay mineral smectite. Therefore, it is easy to establish the origin of the sediments in the Ems estuary. Using the smectite/kaolinite ratio as a tracer of sediment mixing, Irion et al. (1987) give convincing evidence that the sediments of the Ems estuary are primarily of marine origin. In fact, fine-grained marine particles were found to dominate the sediment composition up to 15 km upstream of the limit of salt intrusion, i.e. in the tidal freshwater part of the Ems. Mixing of marine and fluvial sediments was found to occur primarily in a restricted area 15 km south of the city of Leer (Figure 5.2). Downstream of the city of Papenburg, the sediments were of fluvial origin. Based on these and similar observations, it is generally assumed that fluvial sediment, supplied by the Ems river, hardly reaches the North Sea (Favejee, 1960; Van Straaten, 1960; Eisma, 1981). On the other hand, the zinc content of the sediments at the most marine station investigated (Emden) is higher than that of uncontaminated marine sediment (marine background value is about 100 μg/g; Irion et al., 1987), suggesting that fluvial sediment penetrates at least to the city of Emden. This is still 40 km remote from the mouth of the Ems estuary at Borkum, however (Figure 5.1).

5.1.3 Suspended matter retention

The annual suspended matter load carried by the Ems river is quite small. Estimations are in the order of 70 kton/yr (Hinrich, 1974) to 100 kton/yr (Ruardij, 1988). In dry years, the suspended matter load may be as low as 30 kton/yr (Table 5.2). The input of fluvial suspended matter is overwhelmed by the input of marine suspended matter, which is in the order of 900 kton/yr (Ruardij, 1988; Table 5.2). According to the silt transport model described by Ruardij (1988), suspended matter is imported into the estuary throughout the year, except for a short period in the winter when suspended matter is flushed out of the system. On an annual basis, suspended matter deposition equals the total supply of (marine and fluvial) suspended matter to the estuary. However, this does not completely exclude the possibility that fluvial suspended matter escapes to the North Sea, because this can be compensated for by a small extra inflow of marine suspended matter.

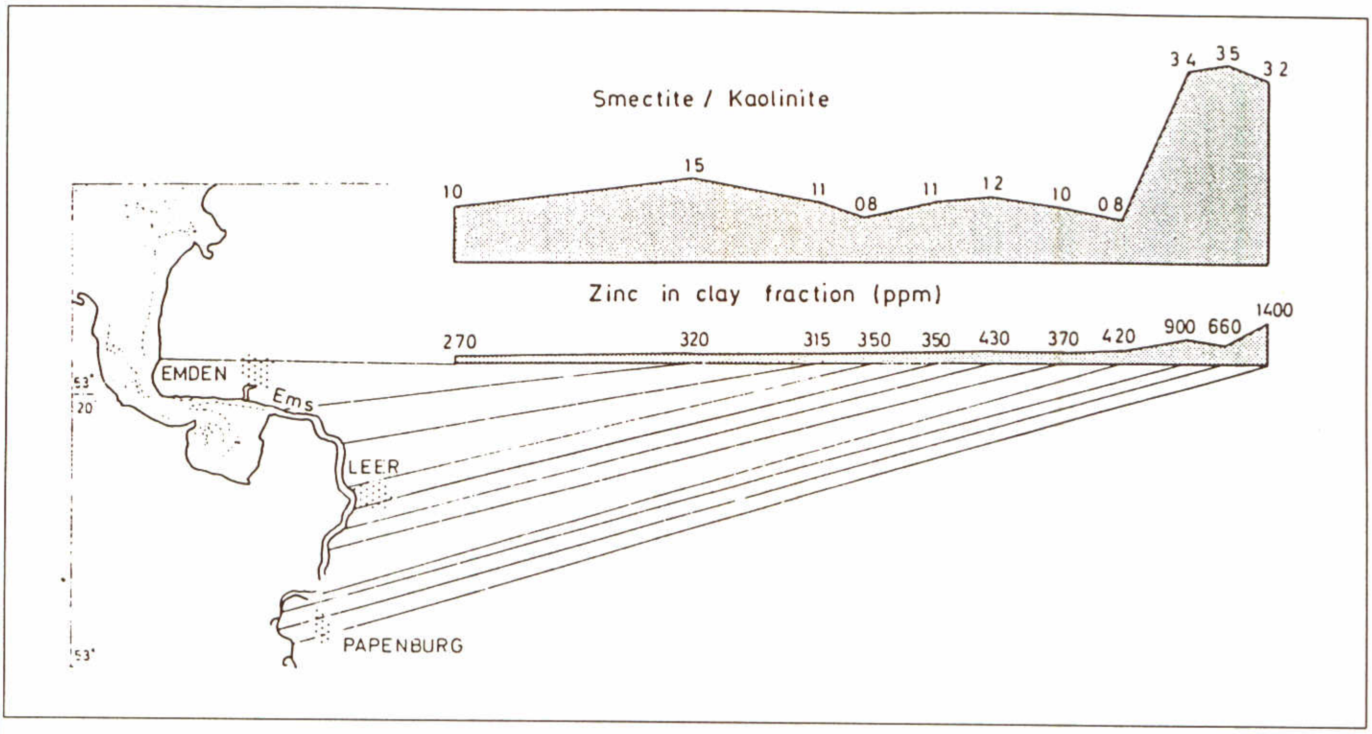


Figure 5.2 Zinc content and smectite/kaolinite ratio in the clay fraction of sediments from the Ems estuary. Based on smectite content, the fluvial suspended matter cannot be traced downstream of the city of Papenburg. The zinc content of the sediments suggests a somewhat further penetration of fluvial suspended matter up to the city of Emden, however. From Irion et al. (1987)

A fine sediment budget (particles <20 μm) for the Ems estuary has recently been constructed by Puls (1994). The budget applies to the years 1990 and 1991, which were quite dry and as such not truly representative of average conditions. However, these are the most recent figures published to date. The results (Table 5.2) show that the supply of suspended matter by the river Ems is negligible compared to the input of marine suspended matter, in agreement with previous observations. In view of the very small supply of fluvial suspended matter in comparison to the total retention within the estuary, it is tempting to assume that the fluvial suspended matter is retained almost completely. This assumption is supported by expert judgement as well (V. De Jonge, pers. comm.). Hence, the retention of fluvial suspended matter in the Ems estuary is estimated at 80-90%. This figure is open to criticism, but it is not unlikely that the retention of fluvial suspended matter in the Ems estuary is similar to that in the Wadden Sea, because the outer part of the Ems estuary (Eemshaven-Borkum) forms part of the Wadden Sea itself.

Table 5.2 Fine sediment budget for the Ems estuary (in kton/yr). Figures refer to particles <20 μm, unless otherwise noted. From Puls (1994)

year	fluvial SPM input*		marine	sediment.	storage
	total	<20 μm	SPM inp.	Dollart	on land
1990	40	30	900	100	800
1991	30	20	600	100	500

* fluvial suspended matter loads were measured at Versen

5.2 The Weser estuary

5.2.1 Description of the area

The Weser estuary (Figure 5.3) is a coastal plain estuary discharging into the German Bight. Morphologically it can be divided into a channel-like inner part (Unterweser), situated between a tidal weir at Bremen and Bremerhaven, and an outer part (Auszenweser), seaward of Bremerhaven. The river flow is measured at Intschede, 25 km upstream of Bremen. The tidal Weser river, which forms part of the Unterweser, stretches from the weir at Bremen up to the limit of salt intrusion. The position of the latter and, therefore, the length of the tidal fresh water zone, ranges from 40 to 70 km downstream of Bremen, depending on the river discharge. At station Brake (km 38), where the contaminant load to the North Sea is monitored, the water is 'fresh' throughout the year. Under normal flow conditions, the freshwater limit of the Weser is situated near Nordenham, 12 km upstream of Bremerhaven. Typical salinity values at Bremerhaven are 4 ppt at the end of the ebb and up to 20 ppt at the end of the flood. The outer Weser estuary forms part of the German Wadden Sea and has no clearly defined seaward limit (Mart and Nürnberg, 1986). The physical characteristics of the Unterweser are summarized in Table 5.3 (stretch Brake-Bremerhaven).

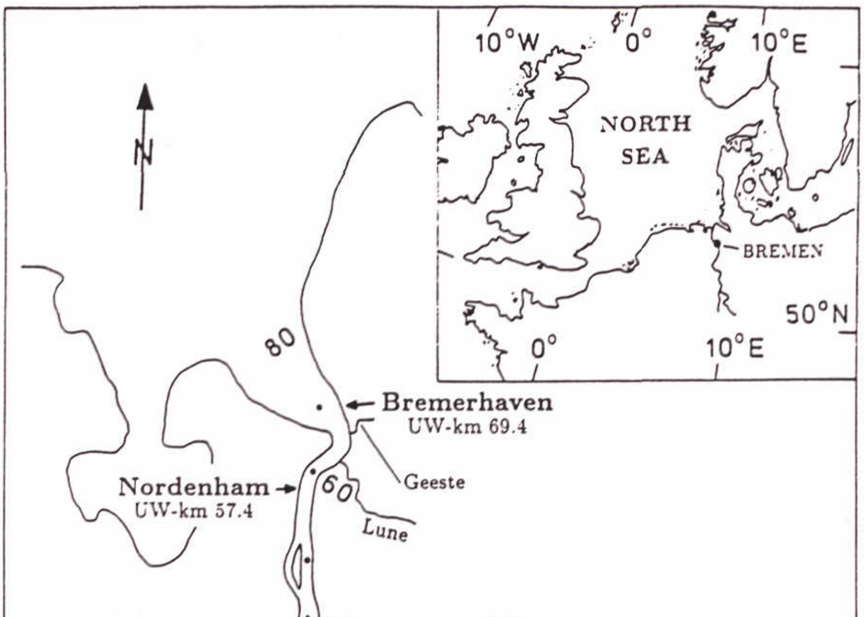


Figure 5.3 The inner Weser estuary. From Müller et al. (1993)

Table 5.3 Physical properties of the inner Weser estuary (mouth = Bremerhaven)

property	unit	value	reference
catchment area	km^2	46000	Schuchardt et al. (1993)
river flow	m^3/s	326 (120-1180)	Müller et al. (1990)
length mixing zone	km	12 (0-30)	Schuchardt et al. (1993)
water depth	m	9-13	Müller et al. (1990)
tidal range mouth	m	3.6	Müller et al. (1990)
salinity at mouth	ppt	4-20	Müller et al. (1990)
circulation type	-	well-mixed	Müller et al. (1990)
residence time	d	8 (2-20)*	Grabemann et al. (1990)
SPM (tidal river)	mg/l	30-40	Müller et al. (1990)
SPM (turb. max.)	mg/l	up to 1500	Müller et al. (1990)
SPM (mouth)	mg/l	30-1500	Müller et al. (1990)
input fluvial SPM	kton/yr	310-500	see paragraph 5.2.3

* applies to section Brake-Bremerhaven; average residence time for the section Bremen-Bremerhaven is 18 days (Schuchardt et al., 1993)

The river Weser is seriously polluted by trace metals, especially cadmium (Calmano et al., 1985; Müller et al., 1993). A number of pesticides have been found in the water as well (Ernst, 1985). In addition, the Weser carries a major salt burden due to potash mining in its upstream drainage basin. The salinity of the 'fresh' water ranges from 0.6 to 2.0 ppt, as opposed to 0.3 ppt for 'normal' rivers (Müller et al., 1990). Dissolved oxygen values are generally above 50% saturation (Schuchardt et al., 1993).

5.2.2 Sediment mixing

The sediments of the Weser river do not contain smectite, contrary to those of the North Sea. Thus, the smectite content of the sediments (normalized on kaolinite) permits recognition of mixing of fluvial and marine material in the Weser estuary. The zinc content of the sediments can also be used for this purpose, because of the high zinc content of the fluvial sediments (other trace metals might do as well, provided that mobilization from the sediments during estuarine mixing is small). Based on zinc content and clay mineral composition, mixing of fluvial and marine sediments appears to start 10-20 km north of Bremen (Figure 5.4). The high zinc content observed off Bremerhaven (500 μg/g), which is five times as high as the natural zinc content of marine clay (100 μg/g; Irion et al., 1987), indicates that river Weser sediments reach the German Bight. This distribution pattern is, at least partly, caused by large-scale dumping of metal-contaminated dredged spoils downstream of Bremerhaven (Calmano et al., 1982).

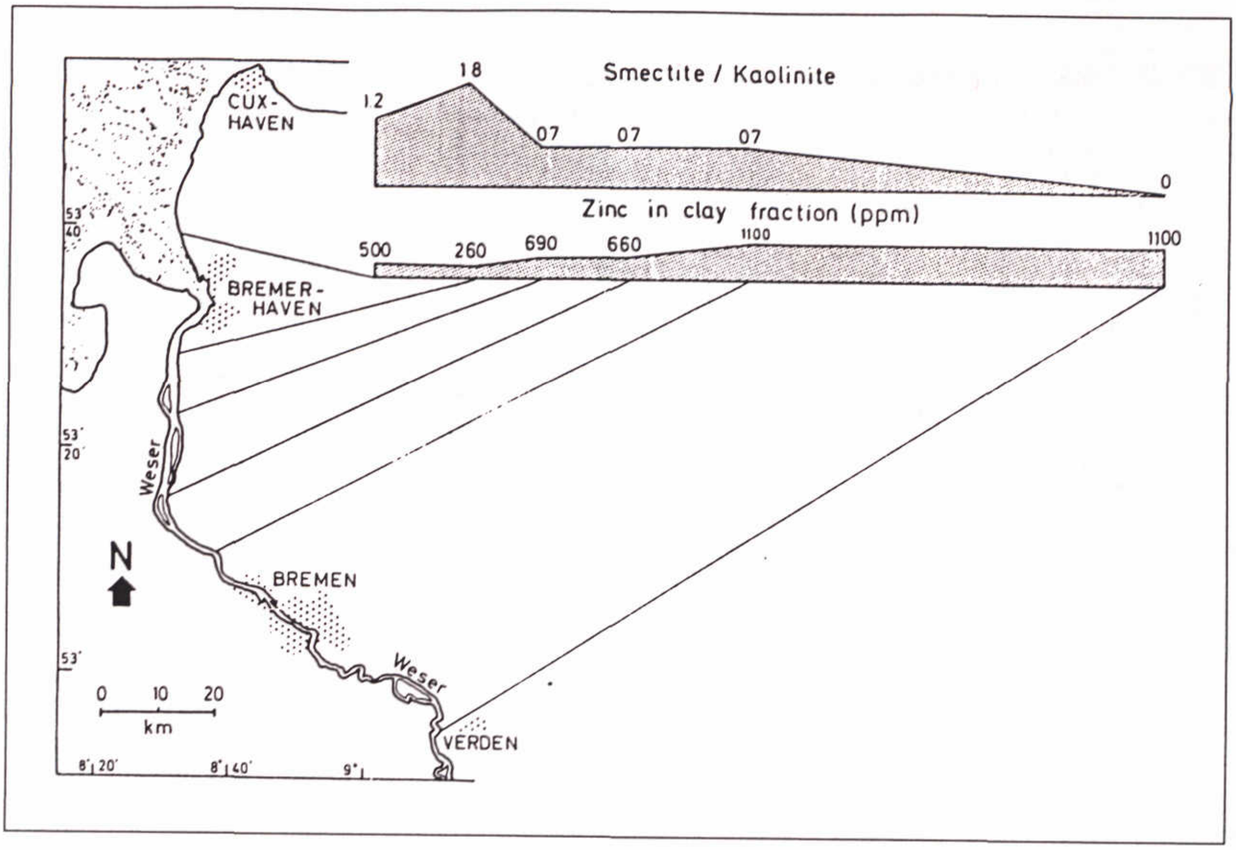


Figure 5.4 Zinc content and smectite/kaolinite ratio in the clay fraction of sediments from the Weser estuary. From Irion et al. (1987)

5.2.3 Suspended matter retention

The suspended matter load carried by the Weser river has been estimated in various studies. Based on the data of Müller et al. (1990), i.e. a mean river flow of 326 m^3/s and a mean suspended matter concentration of 30-40 mg/l, the fluvial suspended matter load is calculated at 308 to 411 kton/yr. Similar estimates of the suspended matter load are given by Hinrich (1975) and Irion et al. (1987), namely 350 and 480 kton/yr, respectively. The 'official' suspended matter load of the Weser river at Intschede, averaged over the period 1970-1987, is 500 kton/yr (Deutsches Gewässerkundliches Jahrbuch, Weser-Emsgebiet, 1987).

The suspended matter dynamics of the Weser estuary, especially of its high turbidity zone, have been studied widely in the past (e.g. Riethmüller et al., 1988; Grabemann and Krause, 1989; Lang et al., 1989). In spite of the concentrated effort, a cohesive sediment balance for the Weser estuary has not been constructed yet. Recently, however, a first attempt was made by Puls (1994). The budget, which applies to particles $< 20\ \mu m$, is based on suspended matter loads measured at Intschede and dredging figures provided by the Bremen harbour authorities (Table 5.4). The main assumption of the budget is that there is no accumulation of mud in the Unterweser, because of the lack of intertidal areas due to the artificial embankments along the shore. Moreover, sediments dredged from the shipping channel are disposed of downstream of Bremerhaven, as mentioned before.

The only contribution to the retention of fluvial suspended matter in the Unterweser is made by dredging of the harbour of Bremen, because these spoils are stored on land. According to Figure 5.4, the sediments at Bremen are entirely fluvial.

Table 5.4 Budget for fluvial suspended matter in the Unterweser (kton/yr). From Puls (1994)

year	input total	input <20 μm	stored* <20 μm	export <20 μm	export %
1990	350	240	50	190	79
1991	330	230	60	170	74

* sediments dredged from Bremen harbour which are stored on land

According to Table 5.4, some 20 to 25% of the fluvial suspended matter load of the tidal Weser is retained around Bremen. Since this retention occurs 40 km upstream from the monitoring station Brake, it is unlikely that this will affect the recorded pollution load. Within the estuarine mixing zone, Brake to Bremerhaven, retention of the fluvial suspended matter load is negligible. This implies that the water quality measured at Brake is a fair measure of the contaminant load that reaches the coastal zone. In the outer Weser estuary, downstream of Bremerhaven, major retention is to be expected, due to the presence of extensive depositional (wadden) areas. According to W. Puls (pers. comm.), there are no sedimentation figures for fluvial suspended matter in the outer Weser estuary. In view of its location in the German part of the Wadden Sea, it might be reasonable to assume a retention similar to that of the Ems estuary and the Dutch Wadden Sea (i.e. 80-90%). This high degree of retention in the outer Weser estuary is supported by measurements of lead concentrations in the water column (Mart and Nürnberg, 1986). Particulate lead levels were found to decrease from 4650 ng/l in the Unterweser to 1000 ng/l in the outer Weser estuary (in 1977). Assuming this decrease to be caused by sedimentation, as indicated by Mart and Nürnberg (1986), the retention of contaminated (fluvial) suspended matter in the outer Weser estuary would be 78%, only slightly lower than the aforementioned estimate of 80-90%.

5.3 The Elbe estuary

5.3.1 Description of the area

The Elbe river rises in eastern Europe where it flows for 415 km before entering Germany. In Germany, the river flows for another 728 km before entering the German Bight. Almost all of its total length has been made navigable for shipping. The port of Hamburg is situated in the fresh water (limnic) zone of the Elbe estuary, some 100 km upstream of the mouth (Figure 5.5). The city of Hamburg is a major economic and commercial centre. Important industries are oil refining, production of chemicals and metals, and shipbuilding. Due to the increasing size of vessels on the Elbe, the shipping channel has been deepened from about 5.5 m at the end of the last century to its current depth of 13.5 m. Large areas of Hamburg harbour are dredged even deeper (Tent, 1987). The estuarine mixing zone begins some 50 km downstream of Hamburg. The mouth of the inner (tidal Elbe) estuary is situated near Cuxhaven. The outer estuary stretches 30-40 km into the German Bight without a clearly defined seaward limit (Mart and Nürnberg, 1986). Although dredged and channelled over its main course, some shallow side-arms and mudflats are still present in the Elbe estuary (e.g. Mühlenberger Loch). The physical characteristics of the inner estuary are summarized in Table 5.5.

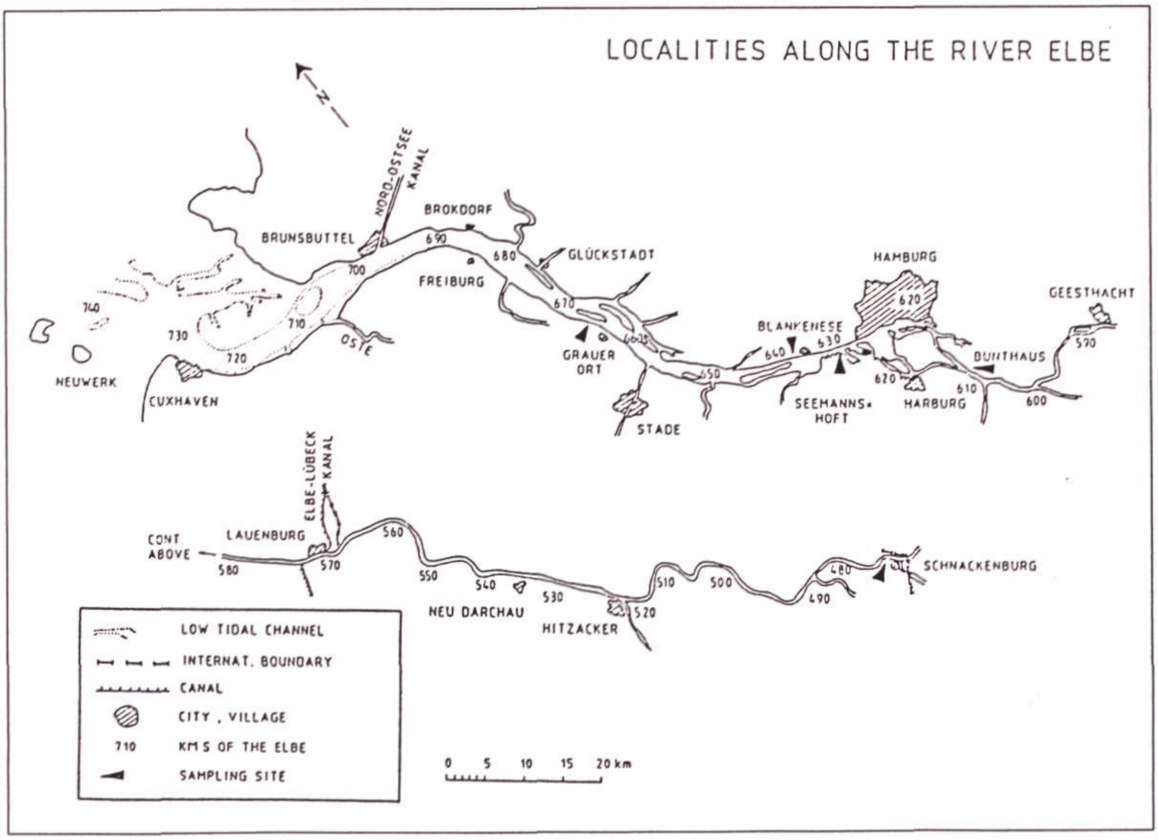


Figure 5.5 The tidal Elbe estuary (Wassergütestelle Elbe)

Table 5.5 Physical properties of the tidal Elbe estuary (mouth = Cuxhaven)

property	unit	value	reference
catchment area	km^2	148500	Tent (1987)
river flow	m^3/s	726 (145-3620)	Tent (1987)
length mixing zone	km	50	Tent (1987)
water depth	m	13.5	Tent (1987)
tidal range mouth	m	2.5-3.3	Duinker et al. (1982)
salinity at mouth	ppt	10-24	Lucht (1964)
circulation type	-	w.m./p.m.*	ARGE Elbe (1984)
residence time	d	17 (8-36)#	ARGE Elbe (1984)
SPM (tidal river)	mg/l	63	Wulffraat et al.(1993)
SPM (turb. max.)	mg/l	up to 600	Grabemann et al. (1994)
SPM (mouth)	mg/l	up to 200	W. Puls (pers. comm.)
input fluvial SPM	kton/yr	800-860	see paragraph 5.3.3

* well mixed/partially mixed

transect Geesthacht-Brunsbüttel (discharge 300-2000 m^3/s)

The calculated load of contaminants from the Elbe to the North Sea is based on the river flow measured at Neu Darchau and the water quality monitored either at Glückstadt or at Grauerort (Wulffraat et al., 1993). These water quality monitoring stations are situated at the beginning of the salinity gradient. The Elbe river receives large amounts of sewage and waste water along its course, and is already severely polluted upstream of Hamburg (where the water quality deteriorates further). Consequently, the Elbe suffers from severe oxygen depletion during the summer (Tent, 1987). In addition, the pollution by trace metals and organic contaminants is substantial (e.g. Knauth et al., 1993). Due to the closure of factories in the former DDR, the water quality is gradually improving, however.

5.3.2 Sediment mixing

The zinc content of the sediments in the Elbe estuary shows a similar trend as that observed in the Ems and Weser estuaries (Figure 5.6). The decrease of zinc starts downstream of Hamburg, marking the onset of (fluvial and marine) sediment mixing. At the mouth of the tidal Elbe estuary (Cuxhaven), the zinc content is still 400 $\mu g/g$, four times the natural background of 100 $\mu g/g$ (Irion et al., 1987). This indicates that fluvial sediment escapes to the German Bight, as concluded before for the Weser estuary. Most of this material appears to be deposited in the outer Elbe estuary, however (Mart et al., 1985; Mart and Nürnberg, 1986).

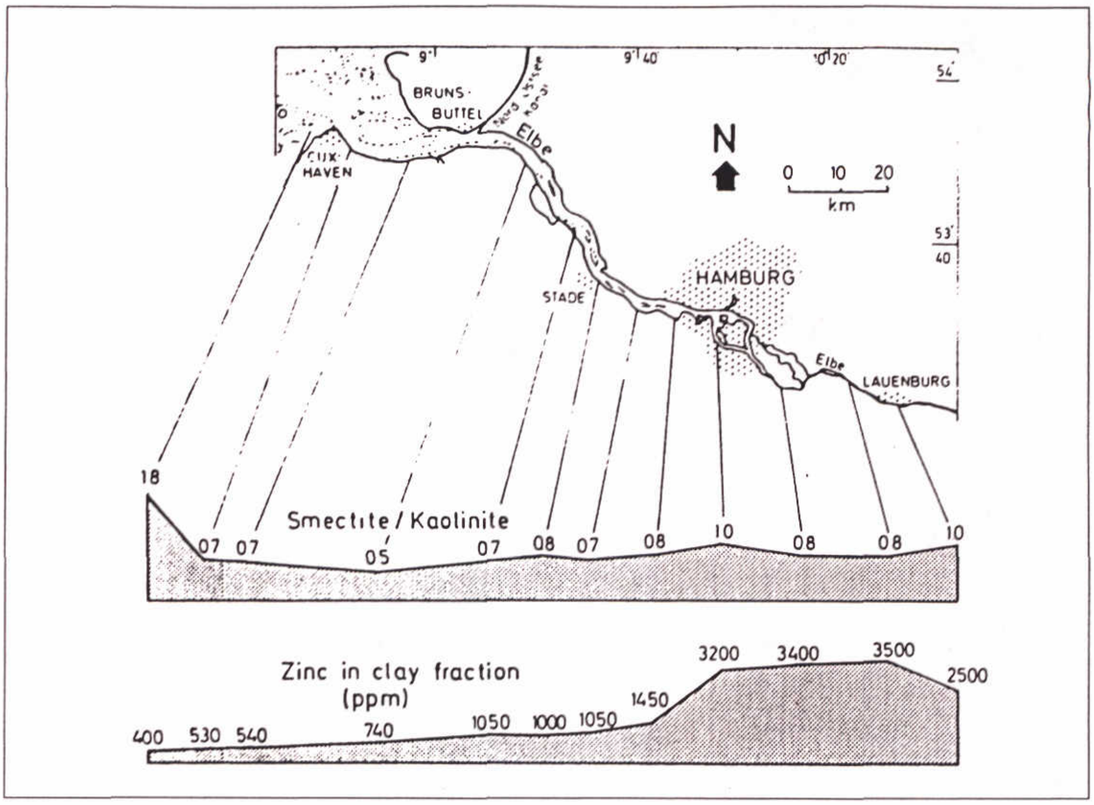


Figure 5.6 Zinc content in the clay fraction of sediments from the Elbe estuary. From Irion et al. (1987)

5.3.3 Suspended matter retention

The load of suspended matter carried by the Elbe river was estimated by Hinrich (1975) to be 860 kton/yr. The 'official' suspended matter load at Hitzacker (100 km upstream of Hamburg) in the period 1964-1992 is slightly lower, namely 800 kton/yr (Bundesanstalt für Gewässerkunde, 1993). Based on a river flow of 726 m^3/s, the latter load corresponds with a suspended matter concentration of 35 mg/l. The suspended matter concentration at station Grauerort is higher (63 mg/l; Wulffraat et al., 1993), probably because of its proximity to the turbidity maximum zone. The suspended matter dynamics of the Elbe estuary have been studied widely in the past by the GKSS research institute at Geesthacht (near Hamburg); examples are Fanger et al. (1989), Lobmeyr and Puls (1991), Müller et al. (1991) and Wilken et al. (1991). A first attempt to construct a cohesive sediment balance for the Elbe estuary was made recently by Puls (1994). The budget, which applies to particles $<20\ \mu m$, is based on suspended matter loads measured at Hitzacker and dredging figures provided by the Hamburg harbour authorities (Table 5.6). Storage of suspended matter within the tidal Elbe estuary was estimated from accretion rates of intertidal flats, discriminating between the contribution of fluvial and marine sources.

Table 5.6 Budget for fluvial suspended matter in the inner Elbe estuary (kton/yr). From Puls (1994)

year	input total	input <20 μm	stored* <20 μm	deposited# <20 μm	export <20 μ
1990	500	350	230	50	70
1991	460	320	170	50	100

* Dredged from Hamburg harbour and stored on land

Deposited in the intertidal flats of the inner Elbe estuary

Due to the presence of deep harbour basins, the port of Hamburg is a major sedimentation zone. According to Table 5.6, dredging activities in Hamburg harbour lead to a reduction of the fluvial suspended matter load by 53% (1992) to 66% (1991). This high degree of retention is probably not representative of the average situation, because of the relatively small suspended matter loads in 1990 and 1991 (the long-year average is 800 kton/yr). According to previous estimates, about one third of the fluvial suspended matter load is retained in the Hamburg harbour area (Fanger et al., 1989; Wilken et al., 1991). Marine suspended matter is also retained at Hamburg (50 km upstream of the mixing zone!), in much smaller quantities, however (30-40 kton/yr according to Puls, 1994). Additional deposition of fluvial and especially marine suspended matter takes place in the intertidal flats of the inner Elbe estuary (50 and 250 kton/yr, respectively).

Based on the data in Table 5.6, the total retention of fluvial suspended matter in the tidal Elbe estuary, including the land disposal of dredged sediments at Hamburg, is 70-80%. In the estuarine mixing zone (Grauerort-Cuxhaven) itself, the retention with respect to the fluvial suspended matter load seaward of Hamburg (120-150 kton/yr; see Table 5.6) is only 33-42%, however. Similar to the Weser and Ems estuaries, most of the fluvial suspended matter that escapes from the mouth of the tidal Elbe estuary (at Cuxhaven) is deposited in the outer estuary. This can be inferred from particulate trace metal levels in the water column, which decrease dramatically downstream of Cuxhaven, where the outer estuary begins (Mart and Nürnberg, 1986). Based on dissolved and total lead measurements in the years 1977-1983, Mart et al. (1985) estimated the particulate lead load of the Elbe estuary to be 58 ton/yr, of which 9 ton/yr reaches the German Bight. Hence, 85% of particulate lead would be removed in the Elbe estuary (due to sedimentation). Similar calculations, based on the reduction of particulate copper and cadmium loads, indicate a sedimentation of 80-82% of the suspended matter load (Mart et al., 1985). Therefore, the retention of fluvial suspended matter in the Elbe estuary, including its extension (30-40 km) into the German Bight, is estimated to be 80-85%. This high degree of retention seems reasonable in view of the similar estimates given before for the Ems and Weser estuaries (80-90%), which form part of the same morphological system (the Wadden Sea-German Bight).

6 Synopsis

The general findings of this study can be summarized as follows. Retention of suspended matter is to be expected in estuaries as long as the intertidal areas (salt marshes and mud flats) are actively accreting. If an estuary is deprived of its natural intertidal areas, due to canalization and land reclamation, the retention of fluvial (and marine) suspended matter will decline. Deposition of suspended matter in the subtidal sediments is, at most, a temporal feature if the estuary is dredged for maintenance purposes (as is the case for almost every urbanized estuary). The same holds for suspended matter deposition in harbour basins, which can be very important. In the latter case, the retention of fluvial suspended matter depends merely on the fate of the dredge spoils. Significant (man-made) retention will occur if the sediments are stored on land, but if they are disposed of at sea (e.g. Tyne and Tees estuaries), there will be no retention whatsoever.

The major conclusions from this study with respect to retention of fluvial suspended matter in North Sea estuaries and fresh water residence times are summarized in Table 6.1. Before using this information, it is recommended to consult the individual paragraphs on each estuary because it is not possible here to comment on every individual figure. The retention percentages for the U.K. estuaries are mostly based on expert judgement, those for the Dutch estuaries are based on field data and modelling studies, and those for the German estuaries on expert judgement, modelling studies, and field research.

Table 6.1 Major physical characteristics of the North Sea estuaries. In the estimation of suspended matter retention, dredging effects are not included

estuary	length km	river flow m^3/s	residence time (d)	fluvial SPM load kton/yr	fluvial SPM ret.%
1 Forth	52	63 (10-300)	25 (7-48)	95-99	80-90
2 Tyne	28	45 (7-120)	4	15-98	10-20
3 Tees	26	20 (2-70)	5	20-24	10-20
4 Humber	62	246 (60-450)	40	172-225	10-30
5 Wash	-	48	100	43-173	80-90
6 Thames	100	82 (9-210)	40 (20-75)	78	50-70
7 Scheldt	100	100 (40-350)	60 (30-90)	315-970	60-95*
8 Rhine-Meuse	25	1476	4 (3-6)	1420-1500	44-53
9 Wadden Sea	-	543 (IJssel)	10 (8-13)	410 (IJs.)	80-90
10 Ems	75	125 (25-390)	40 (12-72)	70-100	80-90
11 Weser	60	326 (120-1180)	15 (10-25)**	310-500	75-85
12 Elbe	90	726 (145-3620)	25 (15-40)**	800-860	80-90

river stretches considered:
1. Stirling-Forth Bridges; 2. Wylam-Tynemouth; 3. Worsall-Teesmouth; 4. Trent Falls-Spurn Point; 5. Gibraltar Point-Hunstanton; 6. Teddington-Southend; 7. Rupelmonde-Vlissingen (* Doel-Vlissingen); 8. Rotterdam-Hoek van Holland (Rhine km 1005-1030); 9. Den Helder-Borkum; 10. Herbrum-Borkum; 11. Brake-outer Weser estuary (up to salinity 30 ppt); 12. Grauerort-outer Elbe estuary (up to salinity 30 ppt).

** including residence time in the outer estuary which is estimated to be in the order of one week.

According to Table 6.1, retention of fluvial suspended matter is relatively small in the Tyne, Tees, and Humber estuaries, moderate in the Rhine and Thames estuaries, and very important in the Forth, Wash, Scheldt, Wadden Sea, Ems, Weser, and Elbe estuaries. It should be noted that these figures do not provide the final answer to the problem. For instance, the role of extreme river flows in suspended matter transport (which seems to be quite important) is completely neglected. Therefore, the retention percentages given in Table 6.1 should be regarded as first tentative estimations which are open for discussion. Nevertheless, these figures do represent the present-day state of knowledge about the retention of fluvial suspended matter in North Sea estuaries.

7 References

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SECTION II

Filtering capacity of North Sea Estuaries

1 Introduction

In this section, the contaminant filtering capacity of the twelve North Sea estuaries is estimated. The filtering capacity of an estuary for a given contaminant is defined as the fractional 'loss' of the river load of that contaminant within the estuary. Three types of processes are responsible for the filtering of contaminants in estuaries, namely sedimentation, degradation (biological, chemical, photolytical), and volatilization. Degradation and volatilization are true loss processes in the sense that the contaminant is lost from the system. On the other hand, sedimentation leads to a build-up of contaminants within the sediments and is, thus, only an apparent loss process. In view of budget constraints, a very simple method has been developed to estimate the filtering capacity of North Sea estuaries for contaminants. The contaminants include 5 trace metals, 6 polycyclic aromatic hydrocarbons (PAH's), 7 polychlorinated biphenyls (PCB's), 2 dioxins, and 19 other organic contaminants, chiefly pesticides (see Table 1.1). An outline of the method is given in chapter 2.

Table 1.1 **Full names and classification of the selected contaminants**

compound	classification
Cd = cadmium	trace metal
Cu = copper	trace metal
Hg = mercury	trace metal
Pb = lead	trace metal
Zn = zinc	trace metal
FLA = fluoranthene	Polycyclic aromatic hydrocarbon
BbF = benzo[b]fluoranthene	Polycyclic aromatic hydrocarbon
BkF = benzo[k]fluoranthene	Polycyclic aromatic hydrocarbon
BaP = benzo[a]pyrene	Polycyclic aromatic hydrocarbon
BgP = benzo[ghi]perylene	Polycyclic aromatic hydrocarbon
IP = indeno[1,2,3-cd]pyrene	Polycyclic aromatic hydrocarbon
PCB-28 = 2,4,4'-trichlorobiphenyl	Polychlorinated biphenyl
PCB-52 = 2,2',5,5'-tetrachlorobiphenyl	Polychlorinated biphenyl
PCB-101 = 2,2,'4,5,5'-pentachlorobiphenyl	Polychlorinated biphenyl
PCB-118 = 2,3',4,4',5-pentachlorobiphenyl	Polychlorinated biphenyl
PCB-138 = 2,2',3,4,4'5'-hexachlorobiphenyl	Polychlorinated biphenyl
PCB-153 = 2,2'4,4',5,5'-hexachlorobiphenyl	Polychlorinated biphenyl
PCB-180 = 2,2'3,4,4'5,5'-heptachlorobiphenyl	Polychlorinated biphenyl
TCDD = 2,3,7,8-tetrachlorodibenzo-p-dioxin	Polychlorinated dioxin
OCDD = octachlorodibenzo-p-dioxin	Polychlorinated dioxin
bentazon	acid
chloridazon	acid (?)
2,4-D = 2,4-dichlorophenoxyacetic acid	acid
DNOC = 4,6-dinitro-o-cresol	acid
aldicarb	carbamate
azinphosmethyl	organophosphate
dichlorvos	organophosphate
dimethoate	organophosphate
mevinphos	organophosphate
parathion-ethyl (= parathion)	organophosphate
TBT = tributyltin (cation)	organotin
TPTH = triphenyltin-hydroxide	organotin
atrazine	triazin
simazine	triazin
diuron	urea
endosulfan	-
lindane	-

2 Method and assumptions

2.1 Definition of filtering capacity

As stated before, the filtering capacity of an estuary is defined as the fractional 'loss' of the **river load** of a contaminant within the estuary. Hence, the filtering capacity for a given contaminant is expressed as:

$$\text{filtering capacity} = (\text{import-export})/\text{import} \qquad (2.1)$$

So if the export from the estuary equals the import into the estuary the filtering capacity is zero, whereas the other extreme, no export from the estuary, is reflected by a filtering capacity of 1. Note that the filtering capacity applies exclusively to the river load of a contaminant (measured at the start of the salinity gradient); direct discharges into the estuary or sediment-water interactions (mobilization, e.g. Booij et al., 1992) are not included. The filtering capacity defined above should be used to 'correct' the river load of contaminants to the North Sea.

2.2 Filtering capacity for organic contaminants

2.2.1 Partitioning of the total load

Consider a monitoring station in a river where the contaminant load to the North Sea is determined. Usually, this monitoring station is located at the transition from fresh to brackish water, though there are exceptions to this rule (e.g. the Scheldt estuary). The river load of a contaminant may be chosen arbitrarily because the export from the estuary is proportional to the import (as will be shown later). For practical purposes, the river load of each contaminant is taken as 100 units. This total load is divided over three sub-loads:

$$\text{dissolved load} = f_{dis} * 100 \qquad (2.2a)$$

$$\text{complexed load} = f_{doc} * 100 \qquad (2.2b)$$

$$\text{adsorbed load} = f_{ads} * 100 \qquad (2.2c)$$

The fractions f_{dis}, f_{doc} and f_{ads} can be calculated from the following equations (Gschwend and Wu, 1985; Baker et al., 1986):

$$f_{dis} = 1 / (1 + DOC * X_{DOC} * K_{oc} + POC * K_{oc}) \qquad (2.3a)$$

$$f_{doc} = DOC * X_{DOC} * K_{oc} / (1 + DOC * X_{DOC} * K_{oc} + POC * K_{oc}) \qquad (2.3b)$$

$$f_{ads} = POC * K_{oc} / (1 + DOC * X_{DOC} * K_{oc} + POC * K_{oc}) \qquad (2.3c)$$

where:

DOC = concentration of dissolved organic carbon (kg C/l)
POC = concentration of particulate organic carbon (kg C/l)
K_{oc} = the organic-carbon based partition coefficient (l/kg C)
X_{doc} = the sorption efficiency of DOC relative to POC (-)

Division of the total load over three sub-loads is essential because each sub-load has its own removal processes. Sedimentation is the only 'loss' process for the adsorbed load, whereas the dissolved and complexed loads (at least indirectly) are subject to degradation and volatilization. The partition coefficients used in the calculations are given in chapter 3.

2.2.2 Removal of adsorbed organic contaminants

In quantifying the sedimentation flux of adsorbed (organic) contaminants, **it is assumed that there is no interaction between adsorbed and dissolved forms during transport through the estuary.** This assumption is supported by a number of field studies. In the Rhine and Exe estuaries, where possible interactions of PCB's and PAH's between solution and particulates have been investigated, no evidence for such interactions has been found (Herrmann and Hübner, 1982; Duinker, 1988, Klamer and Laane, 1990). Similarly, in the Tamar estuary, adsorbed PAH's were not in equilibrium with the dissolved phase because occlusion into the organic matrix of particles rendered them unavailable for exchange (Readman et al., 1984). In the Scheldt estuary, which has a residence time up to three months, conservative behaviour of particulate PCB's and high-molecular weight PAH's was reported (Van Zoest and Van Eck, 1990). Thus, field studies provide no evidence that adsorbed organic contaminants are involved in exchange processes within the estuary. However, standard modelling techniques, based on equilibrium chemistry, predict desorption of adsorbed contaminants if the dissolved contaminant concentration decreases (e.g. due to degradation or volatilization). This discrepancy between model predictions and field experience reflects that equilibrium chemistry fails to predict the fate of organics in estuaries. The degree of chemical equilibrium in estuaries depends on the timescale of desorption in relation to the residence time of the contaminant within the estuary (Morris, 1990). Desorption kinetics of organic contaminants can be very slow (half-lives of several months; Oliver, 1985; Coates and Elzerman, 1986), because the contaminant is captured in the interior of the organic matrix (Wu and Gschwend, 1986; Brusseau et al., 1991).

If adsorbed and dissolved organic contaminants do behave independently, the only 'loss' process for the adsorbed contaminant load is sedimentation. The filtering capacity for the adsorbed contaminant load is proportional to the retention of fluvial suspended matter (which carries the adsorbed load) in the estuary. Vice versa, the export of adsorbed contaminants to the sea is proportional to the fluvial suspended matter load which escapes to the sea:

$$\text{export (adsorbed load)} = 100 * f_{ads} * (1 - RF) \qquad (2.4)$$

where RF represents the retention factor for fluvial suspended matter (as discussed in section I of this report). So if there is no sedimentation of fluvial suspended matter, the export of adsorbed contaminants equals their import ($100 * f_{ads}$). On the other hand, if the fluvial suspended matter is retained completely within the estuary (retention factor 1), the export of the adsorbed load is zero.

2.2.3 Removal of dissolved organic contaminants

The loss processes affecting the dissolved contaminant load are degradation and volatilization. Degradation includes hydrolysis, photolysis, (chemical) oxidation and biodegradation. These removal processes are usually described by first-order kinetics:

$$dC/dt = -k_d\,C - k_v\,C \qquad (2.5)$$

where

C = dissolved contaminant concentration (e.g. nmole/l)
t = time (d)
k_d = rate constant for degradation (d^{-1})
k_v = rate constant for volatilization (d^{-1})

By defining an overall rate constant $k = k_d + k_v$, equation (2.5) simplifies to:

$$dC/dt = -k\,C \qquad (2.6)$$

Integration of equation (2.6) and conversion yields:

$$C_m/C_0 = e^{-kt} \qquad (2.7)$$

where C_0 is the concentration at the beginning of the salinity gradient, C_m is the concentration at the mouth of the estuary, and t is the residence time of the river water in the estuary. Since C_m/C_0 represents the fraction of the dissolved load that remains unaffected during transport through the estuary, the dissolved contaminant load leaving the estuary is given as:

$$\text{export (dissolved load)} = 100 * f_{dis} * e^{-kt} \qquad (2.8)$$

Thus, the export of dissolved contaminants from the estuary depends on the residence time of river water in the estuary (t, d) and the sum of the rate constants for degradation and volatilization (k, d^{-1}). The impact of loss processes within an estuary can be assessed rapidly by comparing its fresh water residence time to the chemical half-life ($t_{½}$) for each contaminant (Morris, 1990). The half-life is related to the overall rate constant as:

$$t_{½} = (\ln 2)/k \qquad (2.9)$$

If the residence time of river water in an estuary equals the half-life for a given contaminant, half of the **dissolved** contaminant load will be lost in the estuary, and half will be transported to the sea. If the residence time is twice the half-life, only one quarter of the dissolved load will reach the sea, etc. An overview of rate constants and chemical half-lives used in the calculations is presented in chapter 3.

2.2.4 Removal of complexed organic contaminants

The availability of complexed contaminants (with DOC) for degradation and volatilization is different from that of dissolved contaminants (Carter and Suffet, 1983). It appears that complexation with DOC may lower the rates of hydrolysis and volatilization, but on the other hand the rate of photolysis can be increased (probably as a result of indirect photolysis). Contrary to adsorbed contaminants, desorption of complexed contaminants is likely to occur rapidly because the contaminant is readily available at the surface of the DOC molecules. For instance, McCarthy and Jimenez (1985) found that complexation of organic contaminants with DOC is a truly reversible process. In view of the rapid desorption of DOC-bound contaminants, it is assumed here that the complexed contaminant load is readily available for physico-chemical loss processes. Hence, the physico-chemical behaviour of complexed contaminants is assumed to be identical to that of dissolved contaminants. On the analogy of equation (2.8), the export of complexed contaminants to the sea is given as:

$$\text{export (complexed load)} = 100 * f_{doc} * e^{-kt} \qquad (2.10)$$

Equation (2.10) may lead to overestimation of the loss rates for organic contaminants which are complexed to a significant extent, i.e. for PAH's, PCB's and, dioxins. However, since the complexed load is, generally, lower than 20% of the total load (see chapter 4), the overestimation of the loss rate is relatively small and acceptable within the purpose of this study.

2.2.5 Total removal of organic contaminants

The total export of a contaminant from an estuary is given as the sum of the export of the dissolved, complexed and adsorbed loads. Combination of equations (2.4), (2.8), and (2.10) yields:

$$\text{export (total load)} = 100\ (f_{dis} + f_{doc})\ e^{-kt} + 100\ f_{ads}\ (1 - RF) \qquad (2.11)$$

Recalling that the contaminant load imported by the estuary was taken as 100 units, and combining equations (2.1) and (2.11), the filtering capacity of the estuary is given as:

$$\text{Filtering capacity} = 1 - (f_{dis} + f_{doc}) * e^{-kt} - f_{ads} * (1 - RF) \qquad (2.12)$$

Thus, the filtering capacity is independent of the river load (100 units).

2.3 Filtering capacity for trace metals

The filtering capacity of an estuary for trace metals is exclusively due to sedimentation. In order to quantify the sedimentation flux of trace metals, the total metal load carried by the river (100 units) is partitioned into a dissolved and a particulate (adsorbed) load, according to the equations:

$$\text{dissolved load} = f_{dis} * 100 \qquad (2.13a)$$

$$\text{adsorbed load} = f_{ads} * 100 \qquad (2.13b)$$

The dissolved metal load includes both truly dissolved and colloidal forms (e.g. complexed with DOC). According to the equilibrium partitioning theory (Balls, 1988; Van Der Kooij et al., 1991), the fractions f_{dis} and f_{ads} are calculated as follows:

$$f_{dis} = 1 / (1 + K_d * SPM) \qquad (2.14a)$$

$$f_{ads} = K_d * SPM / (1 + K_d * SPM) \qquad (2.14b)$$

where

K_d = the distribution (partitioning) coefficient (l/g)
SPM = the suspended matter concentration (g/l)

Assuming that exchange processes between the adsorbed and dissolved metal fractions are insignificant, the filtering capacity of an estuary for trace metals is given as:

$$\text{Filtering capacity} = 1 - f_{dis} - f_{ads} * (1 - RF) \qquad (2.15)$$

Equation (2.15) is valid as long as desorption of trace metals, which has been demonstrated for Cd, Cu, and Zn in estuaries (e.g. Ackroyd et al., 1986; Elbaz-Poulichet et al., 1987; Zwolsman and Van Eck, 1993), does not affect the trace metal content of the suspended matter to a significant extent. This appears to be the case for all the trace metals considered here, except for Cd. Apparent conservative behaviour of particulate trace metals, i.e. no measurable influence of exchange processes on the adsorbed trace metal content, was found for the Humber, Thames, Scheldt, Rhine, Weser, and Elbe estuaries (Turner et al., 1991, Paalman and Van Der Weijden, 1992; Zwolsman and Van Eck, 1993). On the other hand, desorption of Cd may have a distinct impact on the adsorbed Cd content, and should therefore be taken into account. In quantifying the filtering capacity for Cd, desorption was considered implicitly by choosing a distribution coefficient between fresh water and marine values (see next chapter).

3 Processes, coefficients and rate constants

3.1 Sorption of organic contaminants

3.1.1 Partition coefficients

The partition coefficients (log K_{oc}) for organic contaminants are listed in Table 3.1. The effect of salinity on the K_{oc} is small, typically a 20% increase when going from fresh to sea water (Karickhoff, 1984). Since this 'salting-out' effect is very small compared to the uncertainty in the K_{oc} values, the K_{oc}'s used in this work have not been corrected for salinity. Complexation with DOC is only important for very hydrophobic contaminants (e.g. PAH's, PCB's, dioxins), but not for less hydrophobic contaminants (many pesticides). The choice of X_{doc} is dubious because few measurements have been published in the literature, which are often conflicting. Measurements with natural DOC, extracted from surface water, indicate that the efficiency of DOC for sorption is up to an order of magnitude less than that of POC (reviewed by Zwolsman, 1992). Thus, X_{doc} should be chosen as, say, 0.1-0.5, but with the present-day knowledge it is neither possible to select the 'right' value for each contaminant, nor to use a contaminant-specific X_{doc}. The value of X_{doc} used in thus study is 0.17 for each contaminant, which is the average X_{DOC}-value for PCB's measured by Brannon et al. (1991).

Table 3.1 Log K_{oc} values of the organic contaminants. Numbers between brackets (n) refer to number of determinations

compound	ref. 1 avg. ± s.d. (n)	ref. 2 avg. (n)	ref. 3	selected log K_{oc}
FLA		5.10 (6)		5.10
BbF		5.72 (2)		5.72
BkF		5.73 (5)		5.73
BaP	5.29 ± 0.56 (2)	6.24 (6)		6.24
BgP		6.23 (2)		6.23
IP		6.23*		6.23
PCB-28	4.62 ± 0.88 (3)	4.45 (14)		4.45
PCB-52	4.73 ± 1.20 (5)	5.07 (22)		5.07
PCB-101	5.87 ± 0.50 (9)	5.31 (27)		5.31
PCB-118		5.81# (1)		5.81
PCB-138		6.22 (7)		6.22
PCB-153	5.65 ± 0.71 (40)	6.11 (26)		6.11
PCB-180		6.36 (9)		6.36
TCDD		6.44 (19)		6.44
OCDD		6.97 (3)		6.97
2,4-D	1.66 ± 0.56 (58)		1.67	1.66
aldicarb	1.22 ± 0.33 (27)			1.22
atrazine	2.19 ± 0.34 (217)		2.19	2.19
azinphosmethyl	3.10 ± 0.52 (7)		3.18	3.10
bentazon	1.52 ± 0.37 (6)			1.52
chloridazon	2.04 ± 0.23 (30)			2.04
dichlorvos	1.83 ± 0.34 (5)			1.83
dimethoate	1.51 ± 0.47 (12)			1.51
diuron	2.47 ± 0.33 (156)			2.47
DNOC	2.34 ± 0.26 (12)			2.34
endosulfan	4.13 (1)		3.67	3.67
lindane	2.98 ± 0.28 (94)		2.98	2.98
mevinphos	2.80 ± 0.73 (21)			2.80
parathion	3.17 ± 0.46 (89)		3.17	3.17
simazine	2.04 ± 0.36 (265)		2.02	2.04
TBT	4.10 ± 0.48 (30)			4.10
TPTH	4.34 (1)		3.64	3.64

ref. 1. Bockting et al. (1993); ref. 2. Mackay et al. (1992 a,b); ref. 3. De Voogt and Lourens (1992); * estimated value; # Paya-Perez et al. (1991)

3.1.2 Binding forms of organic contaminants

The effect of K_{oc} on the partitioning of organic contaminants in the water column is shown in Table 3.2. This table indicates that, for realistic DOC and POC concentrations, the adsorbed (and complexed) fraction makes up a significant part of the total fraction for PAH's, PCB's, and dioxins. This implies that the fate of these contaminants is, to a major extent, governed by transport and sedimentation of suspended matter. On the other hand, the adsorbed fraction appears to be completely unimportant for the pesticides, which occur nearly completely (usually >99 %) as truly dissolved species. Hence, these contaminants are unaffected by the transport and sedimentation of suspended matter within estuaries. The filtering capacity of estuaries for pesticides (if any) is solely due to degradation and volatilization.

Table 3.2 Binding forms of organic contaminants in surface water, based on equations 2.3a-c (selected K_{oc}-values from Table 3.1, X_{doc} = 0.17, DOC = 4 mg/l, and POC varying from 1-6 mg/l)

	(POC = 1 mg/l)			(POC = 3 mg/l)			(POC = 6 mg/l)		
compound	% dis	% doc	% ads	% dis	% doc	% ads	% dis	% doc	% ads
FLA	82.5	7.1	10.4	68.3	5.9	25.8	54.3	4.7	41.0
BbF	53.1	19.0	27.9	34.1	12.2	53.7	22.2	7.9	69.9
BkF	52.6	19.2	28.2	33.6	12.3	54.1	21.8	8.0	70.2
BaP	25.5	30.1	44.3	13.5	16.0	70.5	7.9	9.4	82.7
BgP	26.0	30.0	44.1	13.8	15.9	70.3	8.1	9.4	82.5
IP	26.0	30.0	44.1	13.8	15.9	70.3	8.1	9.4	82.5
PCB-28	95.5	1.8	2.7	90.6	1.7	7.7	84.2	1.6	14.2
PCB-52	83.5	6.7	9.8	69.8	5.6	24.6	56.0	4.5	39.5
PCB-101	74.5	10.3	15.2	57.1	7.9	35.0	42.3	5.9	51.8
PCB-118	48.0	21.1	31.0	29.6	13.0	57.4	18.8	8.3	72.9
PCB-138	26.4	29.8	43.8	14.1	15.9	70.1	8.3	9.3	82.4
PCB-153	31.6	27.7	40.7	17.4	15.3	67.3	10.4	9.1	80.5
PCB-180	20.6	32.1	47.2	10.6	16.5	72.9	6.1	9.6	84.3
TCDD	17.8	33.3	48.9	9.0	16.8	74.2	5.2	9.7	85.2
OCDD	6.0	38.0	56.0	2.8	18.0	79.2	1.6	10.0	88.4
2,4-D	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0
aldicarb	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0
atrazine	100.0	0.0	0.0	99.9	0.0	0.0	99.9	0.0	0.1
azinphosm.	99.8	0.1	0.1	99.5	0.1	0.4	99.2	0.1	0.7
bentazon	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0
chloridazon	100.0	0.0	0.0	100.0	0.0	0.0	99.9	0.0	0.1
dichlorvos	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0
dimethoate	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0
diuron	100.0	0.0	0.0	99.9	0.0	0.1	99.8	0.0	0.2
DNOC	100.0	0.0	0.0	99.9	0.0	0.1	99.9	0.0	0.1
endosulfan	99.2	0.3	0.5	98.3	0.3	1.4	97.0	0.3	2.7
lindane	99.8	0.1	0.1	99.6	0.1	0.3	99.4	0.1	0.6
mevinphos	99.9	0.0	0.1	99.8	0.0	0.2	99.6	0.0	0.4
parathion	99.8	0.1	0.1	99.5	0.1	0.4	99.0	0.1	0.9
simazine	100.0	0.0	0.0	100.0	0.0	0.0	99.9	0.0	0.1
TBT	97.9	0.8	1.2	95.6	0.8	3.6	92.2	0.8	7.0
TPTH	99.3	0.3	0.4	98.4	0.3	1.3	97.2	0.3	2.5

3.2 Sorption of trace metals

3.2.1 Distribution coefficients

The distribution coefficient K_d is the ratio of the adsorbed trace metal content and the dissolved trace metal concentration. Contrary to the partition coefficient for organic contaminants (K_{oc}), the value of the K_d depends on environmental factors such as salinity, pH, redox status, and composition (e.g. mineralogy) of the suspended matter. Therefore, the K_d may vary among different estuaries. It is, however, not feasible to use different K_d's for each North Sea estuary, because this would require a time-consuming analysis of specific trace metal data for each estuary. The fresh water K_d's used here are typical for river water in the Netherlands, and the marine K_d's for the Dutch coastal zone (0-20 km, see Table 3.3).

Table 3.3 Distribution coefficients for trace metals in river water and coastal seawater (Appelzak and Walcheren transects) of the Netherlands

metal	Cd	Cu	Hg	Pb	Zn	ref.
fresh water K_d (l/g)	130	50	170	640	110	1
coastal sea K_d (l/g)	10	30	120*	420	120	2, *3
estuarine K_d (l/g)	35	40	145	530	115	see text

1. Van der Kooij et al. (1991); 2. Coastal zone monitoring data, 'Appelzak' and 'Walcheren' transect (quarterly reports Rijkswaterstaat 1984-1989); 3. Baeyens et al. (1987)

According to Table 3.3, the marine K_d's are lower than their fresh water analogues, except for Zn. The most striking difference is observed for Cd, reflecting its rapid mobilization in sea water (e.g. Comans and Van Dijk, 1988: Paalman et al., 1994). The difficult question which K_d should be used in the filter calculations (this depends on the location of the sedimentation zones) was dealt with provisionally by choosing the average fresh water and marine K_d for all trace metals, except Cd. The K_d for Cd was based on field observations of exponential decrease with increasing salinity (Förstner et al., 1982). These 'average' estuarine K_d's were used for all the estuaries, except for the Wash, the Wadden Sea, and the Weser estuary. In the latter three systems, the sedimentation takes place in the outer estuary (coastal marine waters), and therefore the marine K_d's have been used.

3.2.2 Binding forms of trace metals

The effect of the distribution coefficient on the binding forms of trace metals in fresh and sea water is shown in Table 3.4. In fresh water, the dissolved metal concentration is generally low, except at low suspended matter concentrations (< 20 mg/l). Thus, sedimentation of fluvial suspended matter in estuaries can lead to a major reduction of the trace metal load to the North Sea. In coastal sea water, on the other hand, the dissolved metal concentration predominates for Cd and sometimes for Cu, considering a suspended matter concentration between 20 and 50 mg/l. This is due to trace metal mobilization (K_d effect) and the lower suspended matter concentration in the coastal zone compared to that in the rivers.

Table 3.4 Calculated binding forms of trace metals in river water and sea water at different suspended matter concentrations (based on equations 2.14a-b)

		SPM = 20 mg/l		SPM = 50 mg/l		SPM = 100 mg/l	
metal	K_d (l/g)	% dis	% ads	% dis	% ads	% dis	% ads
river water							
Cd	130	27.8	72.2	13.3	86.7	7.1	92.9
Cu	50	50.0	50.0	28.6	71.4	16.7	83.3
Hg	170	22.7	77.3	10.5	89.5	5.6	94.4
Pb	640	7.2	92.8	3.0	97.0	1.5	98.5
Zn	110	31.3	68.8	15.4	84.6	8.3	91.7
sea water							
Cd	10	83.3	16.7	66.7	33.3	50.0	50.0
Cu	30	62.5	37.5	40.0	60.0	25.0	75.0
Hg	120	29.4	70.6	14.3	85.7	7.7	92.3
Pb	420	10.6	89.4	4.5	95.5	2.3	97.7
Zn	120	29.4	70.6	14.3	85.7	7.7	92.3

3.3 Volatilization of organic contaminants

3.3.1 Process formulations

Volatilization is described, according to the double-film theory (Liss and Slater, 1974), by the following equations (Southworth, 1979). The first-order volatilization rate constant (k_v, d^{-1}) depends on the overall mass transfer coefficient for the water phase (K_L, m/d) and the depth of the water column (Z, m):

$$k_v = K_L/Z \tag{3.1}$$

The overall mass transfer coefficient for the water phase is calculated from Henry's law constant (He, Pa m^3/mol), the temperature (T, K), the gas constant (R = 8.3145 J/mol/K), and the exchange coefficients for the water phase (k_l, m/d) and the gas phase (k_g, m/d):

$$1/K_L = 1/k_l + 1/(k_g\ He/RT) \tag{3.2}$$

Combining equations (3.1) and (3.2) yields:

$$k_v = k_g\ k_l\ He/(He\ k_g + RT\ k_l)/Z \tag{3.3}$$

The exchange coefficient for the water phase (k_l) is estimated from the wind and current speed (v_w and v_c, both in m/s), the molecular weight of the contaminant (M, g/mol) and the depth of the water column (Z, m). For (common) wind speeds between 1.9 and 5 m/s, the equation reads:

$$k_l\ (m/d) = 5.6424\ v_c^{0.969}/Z^{0.673}\ \surd(32/M)\ \exp(0.526\ (v_w\text{-}1.9)) \tag{3.4}$$

The exchange coefficient for the gas phase is estimated according to:

$$k_g\ (m/d) = 273\ (v_w+v_c)\surd(18/M) \tag{3.5}$$

According to equations (3.1) to (3.5), the rate constant for volatilization depends on parameters specific for the contaminant (Henry's law constant, molecular weight), the season (temperature, wind speed), and the estuary (depth, current speed). Though volatilization is a seasonal process, its impact is described on a yearly basis, using the following environmental characteristics: wind speed = 5 m/s, current speed = 0.5 m/s, water depth = 10 m, temperature = 10 °C. Hence, the volatilization rate constant used here applies to the average situation and does not differ among different estuaries. This generalization is crude but essential in view of the lack of specific data for each estuary.

3.3.2 Henry's law constants and volatilization rates

The selected Henry's law constants and molecular weights for the organic contaminants are listed in Table 3.5. Based on these data and the annual environmental conditions given in the previous paragraph, the coefficients k_g and k_l, and the volatilization rate constant k_v and half-life $t_{½}$ were calculated for each contaminant, irrespective of the estuary. The results are summarized in Table 3.6.

Table 3.5 Molecular weight (M) and Henry's law constants (He) for organic contaminants. Values at 10 °C were estimated as 0.5 * He (20 °C) or 0.35 * He (25 °C), according to Ten Hulscher et al. (1992)

compound	M g/mol	T °C	He Pa.m^3/mol	estimated from	ref.
FLA	202.26	10	0.26	direct measurement	1
BbF	252.31	10	0.025	direct measurement	1
BkF	252.31	10	0.022	direct measurement	1
BaP	252.31	10	0.022	direct measurement	1
BgP	276.34	10	0.019	direct measurement	1
IP	276.34	10	0.018	direct measurement	1
PCB-28	257.55	10	13.37	26.75 at 20 °C	2
PCB-52	291.99	10	12.06	24.12 at 20 °C	2
PCB-101	326.44	10	9.07	18.14 at 20 °C	2
PCB-118	326.44	10	4.31	8.61 at 20 °C	2
PCB-138	360.88	10	3.80	7.60 at 20 °C	2
PCB-153	360.88	10	5.02	10.03 at 20 °C	2
PCB-180	395.33	10	1.62	3.24 at 20 °C	2
TCDD	321.97	10	1.17	3.337 at 25 °C	3
OCDD	459.75	10	0.24	0.683 at 25 °C	3
2,4-D	221.04	10	0.275	0.55 at 20 °C	5
aldicarb	190.25	10	1.6 E-4	3.2 E-4 at 20 °C	5
atrazine	214.68	10	1.45 E-4	2.9 E-4 at 20 °C	5
azinphosmethyl	317.34	10	1.6 E-3	3.2 E-3 at 20 °C	5
bentazon	240.28	10	2.4 E-6	<4.81 E-6 at 20 °C	4
chloridazon	221.65	10	2.8 E-6	<5.54 E-6 at 20 °C	4
dichlorvos	220.98	10	0.095	0.19 at 20 °C	5
dimethoate	229.28	10	5.5 E-5	1.1 E-4 at 20 °C	5
diuron	233.10	10	6.0 E-4	1.2 E-3 at 20 °C	5
DNOC	148.10	10	5.5 E-3	0.011 at 20 °C	5
endosulfan	406.95	10	1.49	2.98 at 20 °C	5
lindane	290.85	10	0.065	0.13 at 20 °C	5
mevinphos	224.1	10	3.2 E-5	6.4 E-5 at 20 °C	6
parathion	291.27	10	6.0 E-3	0.012 at 20 °C	5
simazine	201.67	10	1.7 E-4	3.4 E-4 at 20 °C	5
TBT (cation)	290.04	10	0.01	0.02 at 20 °C	7
TPTH	367.02	10	6.2 E-4	1.24 E-3 at 20 °C	8

1. Ten Hulscher et al. (1992); 2. Murphy et al. (1987); 3. Shiu et al. (1988); 4. Bol et al. (1992); 5. Suntio et al. (1988); 6. Ordelman et al. (1994); 7. Evers et al. (1993); 8. Crijns et al. (1992)

Table 3.6 Calculated rate constants and half-lives for volatilization of organic contaminants in estuaries under average annual conditions (see text)

compound	M g/mol	He Pa.m^3/mol	k_l m/d	k_g m/d	k_v d^{-1}	$t_{½}$ d
FLA	202.26	0.26	1.243	447.9	4.76 E-3	150
BbF	252.31	0.025	1.113	401.0	4.2 E-4	1630
BkF	252.31	0.022	1.113	401.0	3.7 E-4	1860
BaP	252.31	0.022	1.113	401.0	3.7 E-4	1860
BgP	276.34	0.019	1.064	383.2	3.1 E-4	2250
IP	276.34	0.018	1.064	383.2	2.9 E-4	2370
PCB-28	257.55	13.37	1.102	396.9	7.40 E-2	9
PCB-52	291.99	12.06	1.035	372.8	6.71 E-2	10
PCB-101	326.44	9.07	0.979	352.6	5.69 E-2	12
PCB-118	326.44	4.31	0.979	352.6	3.89 E-2	18
PCB-138	360.88	3.80	0.931	335.3	3.42 E-2	20
PCB-153	360.88	5.02	0.931	335.3	4.04 E-2	17
PCB-180	395.33	1.62	0.889	320.4	1.77 E-2	39
TCDD	321.97	1.17	0.985	355.0	1.50 E-2	46
OCDD	459.75	0.24	0.825	297.1	2.92 E-3	240
2,4-D	221.04	0.275	1.189	428.5	4.80 E-3	140
aldicarb	190.25	1.6 E-4	1.282	461.8	3.1 E-6	2.2 E5
atrazine	214.68	1.45 E-4	1.207	434.8	2.7 E-6	2.6 E5
azinphosm.	317.34	1.6 E-3	0.993	357.6	2.4 E-5	2.9 E4
bentazon	240.28	2.4 E-6	1.141	410.9	4.2 E-8	1.7 E7
chloridazon	221.65	2.8 E-6	1.188	427.9	5.1 E-8	1.4 E7
dichlorvos	220.98	0.095	1.189	428.5	1.70 E-3	410
dimethoate	229.28	5.5 E-5	1.168	420.7	9.8 E-7	7.1 E5
diuron	233.10	6.0 E-4	1.158	417.2	1.1 E-5	6.5 E4
DNOC	148.10	5.5 E-3	1.453	523.4	1.2 E-4	5.7 E3
endosulfan	406.95	1.49	0.876	315.8	1.63 E-2	43
lindane	290.85	0.065	1.037	373.5	1.02 E-3	680
mevinphos	225.90	3.2 E-5	1.176	423.8	5.8 E-7	1.2 E6
parathion	291.27	6.0 E-3	1.036	373.2	9.5 E-5	7.3 E3
simazine	201.67	1.7 E-4	1.245	448.6	3.2 E-6	2.1 E5
TBT	290.04	0.01	1.038	374.0	1.6 E-4	4.4 E3
TPTH	367.02	6.2 E-4	0.923	332.5	8.8 E-6	7.9 E4

From the half-lives in Table 3.6, it can be concluded that volatilization is an extremely important removal process for (dissolved) PCB's. In view of the residence time in the estuaries (up to 60 days), volatilization is also a significant removal process for dissolved TCDD, OCDD, 2,4-D, endosulfan, and FLA (but not for the other PAH's). Slight removal of dichlorvos and lindane may also occur (5-10%), but the other organic contaminants are not affected by volatilization within the estuaries.

3.4 Degradation of organic contaminants

3.4.1 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons can be degraded by sunlight and bacteria. Hydrolysis of PAH's is unimportant. For the high-molecular weight PAH's considered here, photolysis is far more important than biodegradation (Zepp and Schlotzhauer, 1979; Readman et al., 1982; Lee and Ryan, 1983; Payne and Philips, 1985). Photolysis affects both dissolved and complexed PAH's (also indirectly), but probably not adsorbed PAH's. The reason for this is that adsorbed PAH's are far less accessible for sunlight than dissolved PAH's. Rate constants for photolysis of PAH's in clear water for summer and winter conditions are shown in Table 3.7. The average near-surface rate constants vary from 0.0042/d for IP to 30/d for BaP. The very high rate constant for photolysis of BaP is confirmed by two other studies (using sunlight radiation), yielding rate constants of 16-34/d (Payne and Philips, 1985) and 49-119/d (Literathy et al., 1991).

Rate constants for direct photolysis are usually measured in clear solution and are, therefore, only applicable to the near-surface layer of the water column. The rate constant (k_p) has to be corrected for light extinction if the whole water column is considered. According to Schwarzenbach et al. (1993), the rate constant for photolysis in the entire wate column can be estimated from the near-surface rate constant as follows:

$$k_p \text{ (water column)} = k_p \text{ (near-surface)} * (1 - 10^{-\alpha DZ})/2.303\alpha DZ \qquad (3.6)$$

where

α = the diffuse attenuation coefficient (m^{-1})
D = a water system constant (-)
Z = the depth of the water column (m)

In turbid waters (e.g. estuaries), D should be chosen as 2.0 (Schwarzenbach et al., 1993). The value of α depends on the suspended matter concentration in the water column. In the Chesapeake Bay (USA), α varied from 4.0 to 8.5 m^{-1}. At a suspended matter concentration of 55 mg/l, typical of most North Sea estuaries, α was found to be 6 m^{-1} (Campbell and Spinrad, 1987). This value is adopted for all the North Sea estuaries.

Using a mean water depth of 10 m, $D = 2.0$, and $\alpha = 6\ m^{-1}$, photolysis rate constants for the whole water column were calculated from the near-surface rate constants (Table 3.7). In terms of chemical half-lives (equation 2.9), photolysis appears to be a very important loss process for BaP ($t_{1/2}$ = 6 d), and moderately important for BkF ($t_{1/2}$ = 90 d), BbF ($t_{1/2}$ = 200 d), and FLA ($t_{1/2}$ = 360 d). The prominent role of photolysis as loss process of BaP was also stressed in a model study of the Tamar estuary, yielding BaP half-lives of 0.9 days during summer and 6.6 days during winter (Harris et al., 1984). However, significant export of BaP to the North Sea may still be possible, because the adsorbed load, which is very important for BaP (Table 3.2), is unlikely to be affected by photolysis.

Table 3.7 Rate constants for photolysis of PAH's at 40°N in near-surface water (winter-summer) and annual rate constants for the whole water column

PAH	k_p (d^{-1})* surface	k_p (d^{-1})# water column	$t_{½}$ (d) water column
FLA	0.26-0.79	0.0019	360
BbF	0.02-1.91	0.0035	200
BkF	0.03-4.38	0.0080	90
BaP	15-45	0.11	6
BgP	no data	0	-
IP	0.0028-0.0056	0.000015	46000

* Howard et al. (1991); # based on average k_p (surface), see text

3.4.2 Polychlorinated biphenyls

Field studies on the aerobic degradation of polychlorinated biphenyls in aquatic systems are very scarce. However, it is known that biodegradation may be important for PCB's with up to four chlorine atoms, but not for higher-substituted PCB congeners (Furukawa et al., 1978; Fries and Marrow, 1984). Half-lives for dichloro- and trichlorobiphenyls range from 0.2 to 3 years under aerobic conditions (Rapaport and Eisenreich, 1988), indicating that biodegradation is a slow process even for low-substituted PCB's. This may also be true for photolysis, though data are almost absent here (Mackay et al., 1992a). Hydrolysis of PCB's is insignificant. The absence of reliable data on PCB degradation is no major problem, however, since volatilization is the most important loss process for PCB's in aquatic systems (e.g. Eisenreich, 1987; Achman et al., 1993).

3.4.3 Polychlorinated dioxins

Photolysis is considered to be the most important degradation process for 2,3,7,8-TCDD in the water column. Photolysis half-lives for 2,3,7,8-TCDD at 40°N latitude were estimated at 4.9, 1.1, 0.9 and 2.1 days for winter, spring, summer and fall, respectively (Podoll et al., 1986). Based on the average annual half-life (2.25 days), the near-surface rate constant for photolysis of TCDD is calculated at 0.31/d, and the depth-corrected rate constant (see paragraph 3.4.1) is estimated at 0.0011/d. The (depth-corrected) rate constant adopted for OCDD is 0.038/d, as calculated by Servos et al. (1992) for simulated lake enclosures.

3.4.4 Acids

Detailed information on the degradation of bentazon and chloridazon is not available. According to a review report (Bol et al., 1992), bentazon seems to be stable in surface water, whereas chloridazon is somewhat susceptible for photolysis ($t_{½}$ = 30 d for near-surface water) and hydrolysis ($t_{½}$ = 72 d). Based on these data, the rate constant for degradation of chloridazon is taken as 0.010/d ($t_{½}$ = 69 d), and that of bentazon as 0/d.

Biodegradation of 2,4-D in water is a relatively rapid process, with half-lives in the order of 10-25 days in muddy river water (Howard, 1991). Based on a half-life of 20 days, the first-order rate constant for degradation of 2,4-D is chosen as 0.035/d, as previously used for North Sea modelling (De Voogt and Lourens, 1992).

Degradation of DNOC is due to (direct and indirect) photolysis. The half-life for photo-oxidation via peroxy radicals has been estimated at 58 days (Howard, 1991). The significance of biodegradation is uncertain, whereas hydrolysis is not expected to be important (Howard, 1991). Using a depth correction for photolysis (see before), the rate constant for degradation of DNOC is taken as $4.3*10^{-5}$/d ($t_{½}$ = 44 year). Due to its low reactivity, DNOC will pass the estuarine mixing zone without significant losses.

3.4.5 Organophosphates

Hydrolysis is the best studied degradation process for organophosphates. Photolysis may also be important, but has been studied to a lesser extent. In general, the degradation rate constants for organophosphates are high.

The half-life for azinphosmethyl has been estimated at 1.5-2 days in fresh water (Ordelman et al., 1994) and at 2.4 days in seawater (De Voogt and Lourens, 1992). Studies with water/sediment microcosms indicate a half-life of 3.3 days, as opposed to 2.7 days in field studies (Howard, 1991). The degradation rate constant used in this study is chosen as 0.28/d, based on a half-life of 2.5 days.

The half-life for dichlorvos has been estimated at 1-1.4 days in fresh water (Ordelman et al., 1994). Half-lives in lakes and rivers are about 4 days (Howard, 1991). Based on the latter value, the degradation rate constant for dichlorvos used in this study is chosen as 0.17/d.

Dimethoate is transformed, mainly through hydrolysis, with a half-life of 34 days in fresh water (Ordelman et al., 1994). In another study, the half-life for degradation in river water was found to be 56 days (Howard, 1991). Based on the average half-life (40 days), the rate constant for degradation of dimethoate follows as 0.017/d.

Mevinphos is hydrolysed in fresh water (pH 8) with a half-life of 18 days (Ordelman et al., 1994). In natural river water, the half-life of mevinphos was found to be 14 days (Sharom et al., 1980). Based on the latter value, the rate constant for mevinphos degradation is chosen as 0.050/d.

In natural river water, parathion was transformed into aminoparathion with a half-life of 7 days (Sharom et al., 1980). This experiment was apparently carried out under anaerobic conditions, as suggested by the high organic matter concentration in the river water (TOC = 40 mg/l) and the exclusion of air. Moreover, aminoparathion is known to be formed under reducing conditions (Howard, 1991). Under aerobic conditions, the half-life for degradation is much longer. Degradation of parathion in surface water from the Mississippi estuary was reported to occur with a half-life of 45 days at 30 °C (Howard, 1991).

Assuming a doubling of the reaction rate for every 10 °C temperature increase, this is equivalent to a half-life of 180 days at 10 °C. A very similar half-life (178 days) has been proposed for North Sea modelling at 10 °C (De Voogt and Lourens, 1992), yielding a rate constant of 0.0039/d.

3.4.6 Organotin compounds

The most important degradation pathway for TBT is microbial dealkylation, yielding dibytyltin (DBT), monobutyltin (MBT), and finally inorganic tin as metabolites. In turbid waters, such as estuaries, typical half-lives range from 6-12 days during the summer to 12-18 days during the winter (Evers et al., 1993). Taking the average half-life as 12 days, the degradation rate constant follows as 0.058/d.

Sequential loss of the phenylgroups can occur with TPTH in the aquatic environment. Half-lives for near-surface photolysis vary from 7.5-18 days in fresh water, whereas biodegradation takes place with a half-life of 140-240 days in fresh water and over 200 days in sea water (Crijns et al., 1992). The depth-corrected photolysis half-life (see before) will be much longer (2100-5000 days), indicating that biodegradation is more important in estuaries. Under annual average conditions, the rate constant for TPTH in the North Sea (10 °C) has been proposed as 0.0026/d, equivalent to a half-life of 270 days (De Voogt and Lourens, 1992). The latter value is adopted here.

3.4.7 Triazins

In general, chemical degradation of atrazine seems to be more important than biodegradation. Atrazine is hydrolysed, in the presence of natural fulvic acid (5 mg/l), with a half-life of 742 days at pH 7 (Howard, 1991). The half-life of sunlight-exposed atrazine in aerobic estuarine water is only 3-12 days (Howard, 1991). The half-life for atrazine in fresh water has been proposed as 60 days (Ordelman et al., 1993), and that for the North Sea as 2 days (De Voogt and Lourens, 1992). The difference between these estimates is striking and cannot be explained. The rate constant used in this work is 0.058/d, corresponding with a half-life of 12 days. The choice of the rate constant determines the filtering capacity of North Sea estuaries for atrazine to a major extent. This is discussed in more detail in chapter 5.

The half-life for simazine in fresh water has been proposed as 30 days (Ordelman et al., 1993), and that for the North Sea as 5 days (De Voogt and Lourens, 1992). Again, there is a large difference between these estimates. The rate constant used in this work is 0.035/d, corresponding with a half-life of 20 days.

3.4.8 Other organic contaminants

Aldicarb is subject to hydrolysis, with a half-life of 266-324 days at pH 8 and 25 °C (Howard, 1991). Photolysis is important in clear water, but not in turbid waters. The half-life used in this study is 300 days, yielding a rate constant of 0.0023/d.

Diuron is stable in dark aqueous solution under laboratory conditions. In surface waters, diuron should photolyze within a few days (Howard, 1991). Assuming a near-surface half-life of three days, the depth-corrected half-life is estimated at 830 days (see paragraph 3.4.1), corresponding with a rate constant of 0.00083/d.

First-order rate constants for degradation of endosulfan in estuarine water were found to range from 0.084/d to 0.12/d, with an average of 0.099/d at 25 °C (Walker et al., 1988). Assuming a doubling of the rate constant with 10 °C temperature increase, a rate constant of 0.035/d is estimated at 10 °C. This agrees well with the value of 0.030/d used previously in North Sea modelling (De Voogt and Lourens, 1992).

Lindane is slowly hydrolysed, photolyzed, and biodegraded in surface waters. The combined rate constant for these processes in Lake Ontario has been estimated at 0.0023/d (Halfon, 1986). In natural river water, lindane was transformed with a half-life of 40 days (Sharom et al., 1980). However, this experiment was probably carried out under anaerobic conditions, as mentioned before. It is well known that lindane is degraded much faster in anaerobic environments (Howard, 1991). In surface water samples with a pH of 7.8, the rate constant for hydrolysis was found to be 0.026/d at 25 °C (Howard, 1991), from which a rate constant of 0.0091/d can be estimated at 10 °C (doubling of the rate constant for each 10 °C temperature increase). Based on the latter value and that for Lake Ontario, the rate constant for lindane is chosen as 0.0057/d, equivalent to a half-life of 120 days.

3.5 Overall rate constants

The rate constants for volatilization (k_v) and degradation (k_d) as discussed before are summarized in Table 3.8. The overall chemical loss rate constant ($k_v + k_d$) and the corresponding half-lives **for dissolved contaminants** in the water column are indicated as well. According to this compilation, PAH's (except FLA) and pesticides (except DNOC) are mainly removed by degradation processes, whereas PCB's are removed by volatilization. Dioxins are removed both by degradation and volatilization, depending on their chlorination pattern.

Table 3.8 Summary of (estimated) rate constants and half-lives for chemical loss processes in North Sea estuaries

compound	volatilization		degradation		total removal	
	k_v (d^{-1})	$t_{\frac{1}{2}}$ (d)	k_d (d^{-1})	$t_{\frac{1}{2}}$ (d)	k (d^{-1})	$t_{\frac{1}{2}}$ (d)
FLA	0.00476	150	0.0019	360	0.0067	100
BbF	0.00042	1630	0.0035	200	0.0039	180
BkF	0.00037	1860	0.0080	90	0.0084	83
BaP	0.00037	1860	0.11	6	0.11	6
BgP	0.00031	2250	0	-	0.00031	2250
IP	0.00029	2370	0.000015	4.6 E4	0.00031	2270
PCB-28	0.07400	9	-	-	0.074	9
PCB-52	0.06711	10	-	-	0.067	10
PCB-101	0.05688	12	-	-	0.057	12
PCB-118	0.03889	18	-	-	0.039	18
PCB-138	0.03422	20	-	-	0.034	20
PCB-153	0.04044	17	-	-	0.040	17
PCB-180	0.01767	39	-	-	0.018	39
TCDD	0.01496	46	0.0011	630	0.016	43
OCDD	0.00292	240	0.038	18	0.041	17
2,4-D	0.00480	140	0.035	20	0.040	17
aldicarb	<0.00001	2.2 E5	0.0023	300	0.0023	300
atrazin	<0.00001	2.6 E5	0.058	12	0.058	12
azinphosm.	0.00002	2.9 E4	0.28	2.5	0.28	2.5
bentazon	<0.00001	1.7 E7	0	-	0	-
chloridazon	<0.00001	1.4 E7	0.010	69	0.010	69
dichlorvos	0.00170	410	0.17	4.0	0.17	4.0
dimethoate	<0.00001	7.1 E5	0.017	40	0.017	40
diuron	0.00001	6.5 E4	0.00083	830	0.00084	830
DNOC	0.00012	5.7 E3	0.000043	1.6 E4	0.00016	4250
endosulfan	0.01627	43	0.035	20	0.051	14
lindane	0.00102	680	0.0057	120	0.0067	100
mevinphos	<0.00001	1.2 E6	0.050	14	0.050	14
parathion	0.00010	7.3 E3	0.0039	180	0.0040	170
simazin	<0.00001	2.1 E5	0.035	20	0.035	20
TBT	0.00016	4.4 E3	0.058	12	0.058	12
TPTH	0.00001	7.9 E4	0.0026	270	0.0026	270

4 Results

4.1 SPM, POC, and DOC data

When calculating the partitioning of organic contaminants it is essential to know the DOC and POC concentrations at the relevant monitoring stations in the estuaries. However, DOC and POC data were not available for the U.K. estuaries, whereas for the German estuaries only TOC (total organic carbon) data were available. For the Dutch estuaries, TOC and DOC data were available; POC concentrations were calculated by difference: POC = TOC - DOC. The results for relevant monitoring stations in the Netherlands are shown in Table 4.1. Regression analysis on the Dutch dataset revealed the following linear relations between TOC and POC and (less significant) TOC and DOC:

$$\text{POC (mg/l)} = -1.67 + 0.643 * \text{TOC (mg/l)};\ r^2 = 0.758,\ n = 160 \quad (4.1)$$

$$\text{DOC (mg/l)} = 1.67 + 0.357 * \text{TOC (mg/l)};\ r^2 = 0.490,\ n = 160 \quad (4.2)$$

Combining these equations gives the following relation between DOC and POC:

$$\text{DOC (mg/l)} = 2.60 + 0.555 * \text{POC (mg/l)} \quad (4.3)$$

Equations (4.1) and (4.2) were used to estimate DOC and POC concentrations in the Ems and Elbe estuaries for which only TOC data were available. Comparison with field data for the Elbe shows a satisfactory agreement with the estimated DOC and POC concentrations. DOC and POC concentrations of 7.0 and 7.5 mg/l have been measured at the beginning of the salinity gradient in the Elbe (Michaelis et al., 1986), whereas the estimated concentrations (based on TOC = 14.6 mg/l) are 6.9 and 7.7 mg/l, respectively (Table 4.2).

With respect to the U.K. estuaries, POC concentrations were estimated by multiplying the POC content of the suspended matter with the suspended matter concentration at the beginning of the salinity gradient. Suspended matter concentrations were based on the suspended matter load predicted by the Wilmot and Collins equation (see section I), divided by the mean river discharge (except for the Humber and the Forth). DOC concentrations were estimated from POC concentrations using equation (4.3). The estimated SPM, POC and DOC concentrations are listed in Table 4.3.

Table 4.1 SPM, POC, and DOC concentrations at relevant monitoring stations in the Netherlands (data 1990-1993)

estuary/station	SPM (mg/l)			POC (mg/l)			DOC (mg/l)		
	min	max	avg	min	max	avg	min	max	avg
Scheldt/Doel	11	230	62	0.1	8.6	3.4	1.8	7.4	5.1
Rhine/Maassluis	2	140	23	0.1	9.0	1.7	0.9	4.8	2.8
Wadden Sea/IJ2*	2	55	16	0.1	10.2	4.7	2.0	7.7	5.4

* data for 1990-1992

Table 4.2 Estimated SPM, POC, and DOC concentrations in German North Sea estuaries at the beginning of the salinity gradient

estuary	SPM mg/l	TOC mg/l	POC mg/l	DOC mg/l
Ems	20 (1)	9.3 (2)	4.3 (3)	5.0 (4)
Weser	49 (5)		2.9 (6)	4.2 (7)
Elbe	63 (1)	14.6 (8)	7.7 (3)	6.9 (4)

Notes: 1. Wulffraat et al. (1993); 2. monitoring results at Herbrum (1987-1992); 3. equation (4.1); 4. equation (4.2); 5. Based on an annual SPM load of 500 kton and a river flow of 326 m^3/s; 6. based on a POC content of 6% at Brake (Turner et al., 1992); 7. Michaelis et al. (1986); 8. monitoring results at Grauerort (1990-1992)

Table 4.3 Estimated SPM, POC, and DOC concentrations in U.K. North Sea estuaries at the beginning of the salinity gradient

estuary	SPM mg/l	POC %	POC mg/l	DOC mg/l
Forth	50	7 (1)	3.5	4.5 (2)
Tyne	21	6 (3)	1.3	3.3 (2)
Tees	39	10 (3)	3.9	4.8 (2)
Humber	26	5 (4)	1.3	3.3 (2)
Wash	60	15 (5)	9.0	7.6 (2)
Thames	30	9 (4)	2.7	4.1 (2)

Notes: 1. average POC content of the six most fine-grained intertidal muds in the Forth estuary (McLusky et al., 1993); 2. equation (4.3); 3. author's estimate; high POC content in the Tees due to peat erosion in the catchment area; 4. Turner (1990); 5. based on an organic matter content of 30% (Wilmot and Collins, 1981)

4.2 Filtering capacity of North Sea estuaries

Based on the DOC and POC concentrations at the beginning of the salinity gradient (Tables 4.1-3) and the compound-specific K_{oc}, the partitioning of organic contaminants within each estuary was calculated according to equations (2.3a-c). The partitioning of trace metals was calculated from the suspended matter concentration at the beginning of the salinity gradient and the average estuarine K_d values (equations 2.14a-b). The (arbitrarily chosen) total input of each contaminant (100 units) was, according to its partitioning, divided over a dissolved, complexed, and adsorbed load (equations 2.2a-c). The export of these sub-loads out of the estuary was calculated according to equations 2.4, 2.8, and 2.10. Finally, the estuary's filtering capacity for each contaminant was calculated according to equations (2.12) or (2.15), using the fluvial suspended matter retention and fresh water residence times discussed in section I of this report. The results of these calculations are presented in Tables 4.4 to 4.15.

Table 4.4 Filtering capacity of the Forth estuary (fluvial SPM retention = 85%, residence time = 25 d, SPM = 50 mg/l, POC = 3.5 mg/l, DOC = 4.5 mg/l)

compound	log K_{oc} (or K_d)	$k_{(d+v)}$ (d^{-1})	INPUT (total = 100)			OUTPUT			F.C.
			dis	doc	ads	dis	doc	ads	%
Cd	35	-	36.4	-	63.6	36.4	-	9.5	54.1
Cu	40	-	33.3	-	66.7	33.3	-	10.0	56.7
Hg	145	-	12.1	-	87.9	12.1	-	13.2	74.7
Pb	530	-	3.6	-	96.4	3.6	-	14.5	81.9
Zn	115	-	14.8	-	85.2	14.8	-	12.8	72.4
FLA	5.10	0.0067	65.1	6.3	28.7	55.0	5.3	4.3	35.4
BbF	5.72	0.0039	30.9	12.4	56.7	28.0	11.2	8.5	52.2
BkF	5.73	0.0084	30.4	12.5	57.1	24.6	10.1	8.6	56.7
BaP	6.24	0.11	11.9	15.8	72.3	0.8	1.0	10.8	87.4
BgP	6.23	0.00031	12.1	15.8	72.1	12.0	15.6	10.8	61.5
IP	6.23	0.00031	12.1	15.8	72.1	12.0	15.6	10.8	61.5
PCB-28	4.45	0.074	89.3	1.9	8.8	14.0	0.3	1.3	84.3
PCB-52	5.07	0.067	66.6	6.0	27.4	12.5	1.1	4.1	82.3
PCB-101	5.31	0.057	53.5	8.3	38.2	12.9	2.0	5.7	79.4
PCB-118	5.81	0.039	26.6	13.2	60.2	10.0	5.0	9.0	76.0
PCB-138	6.22	0.034	12.4	15.7	71.9	5.3	6.7	10.8	77.2
PCB-153	6.11	0.040	15.4	15.2	69.4	5.7	5.6	10.4	78.3
PCB-180	6.36	0.018	9.3	16.3	74.4	5.9	10.4	11.2	72.5
TCDD	6.44	0.016	7.8	16.5	75.6	5.3	11.1	11.3	72.3
OCDD	6.97	0.041	2.5	17.5	80.1	0.9	6.3	12.0	80.8
2,4-D	1.66	0.040	100.0	0.0	0.0	36.8	0.0	0.0	63.2
aldicarb	1.22	0.0023	100.0	0.0	0.0	94.4	0.0	0.0	5.6
atrazine	2.19	0.058	99.9	0.0	0.1	23.4	0.0	0.0	76.5
azinphosm.	3.10	0.28	99.5	0.1	0.4	0.1	0.0	0.1	99.8
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	100.0	0.0	0.0	77.8	0.0	0.0	22.1
dichlorvos	1.83	0.17	100.0	0.0	0.0	1.4	0.0	0.0	98.6
dimethoate	1.51	0.017	100.0	0.0	0.0	65.4	0.0	0.0	34.6
diuron	2.47	0.00084	99.9	0.0	0.1	97.8	0.0	0.0	2.2
DNOC	2.34	0.00016	99.9	0.0	0.1	99.5	0.0	0.0	0.5
endosulfan	3.67	0.051	98.0	0.4	1.6	27.4	0.1	0.2	72.3
lindane	2.98	0.0067	99.6	0.1	0.3	84.2	0.1	0.0	15.7
mevinphos	2.80	0.050	99.7	0.0	0.2	28.6	0.0	0.0	71.4
parathion	3.17	0.0040	99.4	0.1	0.5	89.9	0.1	0.1	9.9
simazine	2.04	0.035	100.0	0.0	0.0	41.7	0.0	0.0	58.3
TBT	4.10	0.058	94.9	0.9	4.2	22.3	0.2	0.6	76.9
TPTH	3.64	0.0026	98.2	0.3	1.5	92.0	0.3	0.2	7.5

Table 4.5 Filtering capacity of the Tyne estuary (fluvial SPM retention = 15%, residence time = 4 d, SPM = 21 mg/l, POC = 1.3 mg/l, DOC = 3.3 mg/l)

compound	log Koc	k(d+v)	INPUT (total = 100)			OUTPUT			F.C.
	(or Kd)	(d^{-1})	dis	doc	ads	dis	doc	ads	%
Cd	35	-	57.6	-	42.4	57.6	-	36.0	6.4
Cu	40	-	54.3	-	45.7	54.3	-	38.8	6.8
Hg	145	-	24.7	-	75.3	24.7	-	64.0	11.3
Pb	530	-	8.2	-	91.8	8.2	-	78.0	13.8
Zn	115	-	29.3	-	70.7	29.3	-	60.1	10.6
FLA	5.10	0.0067	81.0	5.7	13.3	78.9	5.6	11.3	4.3
BbF	5.72	0.0039	50.6	14.9	34.5	49.8	14.7	29.3	6.2
BkF	5.73	0.0084	50.0	15.1	34.9	48.4	14.6	29.7	7.4
BaP	6.24	0.11	23.6	23.0	53.4	15.2	14.8	45.4	24.6
BgP	6.23	0.00031	24.0	22.9	53.1	24.0	22.9	45.1	8.0
IP	6.23	0.00031	24.0	22.9	53.1	24.0	22.9	45.1	8.0
PCB-28	4.45	0.074	95.0	1.5	3.5	70.7	1.1	3.0	25.3
PCB-52	5.07	0.067	82.1	5.4	12.5	62.8	4.1	10.7	22.4
PCB-101	5.31	0.057	72.5	8.3	19.2	57.7	6.6	16.3	19.4
PCB-118	5.81	0.039	45.4	16.5	38.1	38.9	14.1	32.4	14.7
PCB-138	6.22	0.034	24.5	22.8	52.8	21.3	19.9	44.9	13.9
PCB-153	6.11	0.040	29.4	21.3	49.3	25.1	18.1	41.9	14.9
PCB-180	6.36	0.018	19.0	24.4	56.6	17.7	22.7	48.1	11.5
TCDD	6.44	0.016	16.3	25.2	58.5	15.3	23.7	49.7	11.3
OCDD	6.97	0.041	5.4	28.5	66.1	4.6	24.2	56.1	15.0
2,4-D	1.66	0.040	100.0	0.0	0.0	85.2	0.0	0.0	14.8
aldicarb	1.22	0.0023	100.0	0.0	0.0	99.1	0.0	0.0	0.9
atrazine	2.19	0.058	100.0	0.0	0.0	79.3	0.0	0.0	20.7
azinphosm.	3.10	0.28	99.8	0.1	0.2	32.6	0.0	0.1	67.3
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	100.0	0.0	0.0	96.1	0.0	0.0	3.9
dichlorvos	1.83	0.17	100.0	0.0	0.0	50.7	0.0	0.0	49.3
dimethoate	1.51	0.017	100.0	0.0	0.0	93.4	0.0	0.0	6.6
diuron	2.47	0.00084	99.9	0.0	0.0	99.6	0.0	0.0	0.3
DNOC	2.34	0.00016	100.0	0.0	0.0	99.9	0.0	0.0	0.1
endosulfan	3.67	0.051	99.1	0.3	0.6	80.8	0.2	0.5	18.4
lindane	2.98	0.0067	99.8	0.1	0.1	97.2	0.1	0.1	2.7
mevinphos	2.80	0.050	99.9	0.0	0.1	81.8	0.0	0.1	18.1
parathion	3.17	0.0040	99.7	0.1	0.2	98.1	0.1	0.2	1.6
simazine	2.04	0.035	100.0	0.0	0.0	86.9	0.0	0.0	13.1
TBT	4.10	0.058	97.7	0.7	1.6	77.5	0.5	1.4	20.6
TPTH	3.64	0.0026	99.2	0.2	0.6	98.2	0.2	0.5	1.1

Table 4.6 Filtering capacity of the Tees estuary (fluvial SPM retention = 15%, residence time = 5 d, SPM = 39 mg/l, POC = 3.9 mg/l, DOC = 4.8 mg/l)

compound	log K_{oc} (or K_d)	$k_{(d+v)}$ (d^{-1})	INPUT (total = 100)			OUTPUT			F.C.
			dis	doc	ads	dis	doc	ads	%
Cd	35	-	42.3	-	57.7	42.3	-	49.1	8.7
Cu	40	-	39.1	-	60.9	39.1	-	51.8	9.1
Hg	145	-	15.0	-	85.0	15.0	-	72.2	12.7
Pb	530	-	4.6	-	95.4	4.6	-	81.1	14.3
Zn	115	-	18.2	-	81.8	18.2	-	69.5	12.3
FLA	5.10	0.0067	62.7	6.4	30.8	60.7	6.2	26.2	6.9
BbF	5.72	0.0039	28.8	12.3	58.9	28.2	12.1	50.1	9.6
BkF	5.73	0.0084	28.3	12.4	59.3	27.1	11.9	50.4	10.6
BaP	6.24	0.11	10.9	15.4	73.7	6.3	8.9	62.6	22.2
BgP	6.23	0.00031	11.1	15.4	73.5	11.1	15.4	62.5	11.1
IP	6.23	0.00031	11.1	15.4	73.5	11.1	15.4	62.5	11.1
PCB-28	4.45	0.074	88.3	2.0	9.7	61.0	1.4	8.2	29.4
PCB-52	5.07	0.067	64.3	6.2	29.5	46.0	4.4	25.1	24.5
PCB-101	5.31	0.057	50.9	8.5	40.6	38.3	6.4	34.5	20.8
PCB-118	5.81	0.039	24.7	13.0	62.3	20.3	10.7	52.9	16.0
PCB-138	6.22	0.034	11.3	15.3	73.3	9.6	12.9	62.3	15.2
PCB-153	6.11	0.040	14.1	14.9	71.0	11.6	12.2	60.4	15.9
PCB-180	6.36	0.018	8.5	15.8	75.7	7.7	14.5	64.3	13.4
TCDD	6.44	0.016	7.1	16.1	76.8	6.6	14.8	65.3	13.3
OCDD	6.97	0.041	2.2	16.9	80.9	1.8	13.8	68.7	15.7
2,4-D	1.66	0.040	100.0	0.0	0.0	81.9	0.0	0.0	18.1
aldicarb	1.22	0.0023	100.0	0.0	0.0	98.8	0.0	0.0	1.1
atrazine	2.19	0.058	99.9	0.0	0.1	74.8	0.0	0.1	25.2
azinphosm.	3.10	0.28	99.4	0.1	0.5	24.5	0.0	0.4	75.0
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	99.9	0.0	0.0	95.1	0.0	0.0	4.9
dichlorvos	1.83	0.17	100.0	0.0	0.0	42.7	0.0	0.0	57.2
dimethoate	1.51	0.017	100.0	0.0	0.0	91.8	0.0	0.0	8.1
diuron	2.47	0.00084	99.9	0.0	0.1	99.4	0.0	0.1	0.4
DNOC	2.34	0.00016	99.9	0.0	0.1	99.8	0.0	0.1	0.1
endosulfan	3.67	0.051	97.8	0.4	1.8	75.8	0.3	1.5	22.4
lindane	2.98	0.0067	99.6	0.1	0.4	96.3	0.1	0.3	3.3
mevinphos	2.80	0.050	99.7	0.1	0.2	77.6	0.0	0.2	22.1
parathion	3.17	0.0040	99.3	0.1	0.6	97.3	0.1	0.5	2.1
simazine	2.04	0.035	99.9	0.0	0.0	83.9	0.0	0.0	16.1
TBT	4.10	0.058	94.4	1.0	4.6	70.6	0.7	3.9	24.7
TPTH	3.64	0.0026	98.0	0.3	1.7	96.7	0.3	1.4	1.5

Table 4.7 Filtering capacity of the Humber estuary (fluvial SPM retention = 20%, residence time = 40 d, SPM = 26 mg/l, POC = 1.3 mg/l, DOC = 3.3 mg/l)1

compound	log K_{oc} (or K_d)	$k_{(d+v)}$ (d^{-1})	INPUT (total = 100)			OUTPUT			F.C.
			dis	doc	ads	dis	doc	ads	%
Cd	35	-	52.4	-	47.6	52.4	-	38.1	9.5
Cu	40	-	49.0	-	51.0	49.0	-	40.8	10.2
Hg	145	-	21.0	-	79.0	21.0	-	63.2	15.8
Pb	530	-	6.8	-	93.2	6.8	-	74.6	18.6
Zn	115	-	25.1	-	74.9	25.1	-	59.9	15.0
FLA	5.10	0.0067	81.0	5.7	13.3	62.0	4.4	10.6	23.0
BbF	5.72	0.0039	50.6	14.9	34.5	43.3	12.7	27.6	16.4
BkF	5.73	0.0084	50.0	15.1	34.9	35.7	10.8	27.9	25.6
BaP	6.24	0.11	23.6	23.0	53.4	0.3	0.3	42.7	56.7
BgP	6.23	0.00031	24.0	22.9	53.1	23.7	22.6	42.5	11.2
IP	6.23	0.00031	24.0	22.9	53.1	23.7	22.6	42.5	11.2
PCB-28	4.45	0.074	95.0	1.5	3.5	4.9	0.1	2.8	92.2
PCB-52	5.07	0.067	82.1	5.4	12.5	5.6	0.4	10.0	84.0
PCB-101	5.31	0.057	72.5	8.3	19.2	7.4	0.8	15.4	76.4
PCB-118	5.81	0.039	45.4	16.5	38.1	9.5	3.5	30.5	56.5
PCB-138	6.22	0.034	24.5	22.8	52.8	6.3	5.8	42.2	45.7
PCB-153	6.11	0.040	29.4	21.3	49.3	5.9	4.3	39.4	50.3
PCB-180	6.36	0.018	19.0	24.4	56.6	9.2	11.9	45.3	33.6
TCDD	6.44	0.016	16.3	25.2	58.5	8.6	13.3	46.8	31.3
OCDD	6.97	0.041	5.4	28.5	66.1	1.1	5.5	52.8	40.6
2,4-D	1.66	0.040	100.0	0.0	0.0	20.2	0.0	0.0	79.8
aldicarb	1.22	0.0023	100.0	0.0	0.0	91.2	0.0	0.0	8.8
atrazine	2.19	0.058	100.0	0.0	0.0	9.8	0.0	0.0	90.2
azinphosm.	3.10	0.28	99.8	0.1	0.2	0.0	0.0	0.1	99.9
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	100.0	0.0	0.0	67.0	0.0	0.0	33.0
dichlorvos	1.83	0.17	100.0	0.0	0.0	0.1	0.0	0.0	99.9
dimethoate	1.51	0.017	100.0	0.0	0.0	50.7	0.0	0.0	49.3
diuron	2.47	0.00084	99.9	0.0	0.0	96.6	0.0	0.0	3.3
DNOC	2.34	0.00016	100.0	0.0	0.0	99.3	0.0	0.0	0.6
endosulfan	3.67	0.051	99.1	0.3	0.6	12.9	0.0	0.5	86.6
lindane	2.98	0.0067	99.8	0.1	0.1	76.4	0.0	0.1	23.5
mevinphos	2.80	0.050	99.9	0.0	0.1	13.5	0.0	0.1	86.4
parathion	3.17	0.0040	99.7	0.1	0.2	85.0	0.1	0.2	14.8
simazine	2.04	0.035	100.0	0.0	0.0	24.7	0.0	0.0	75.3
TBT	4.10	0.058	97.7	0.7	1.6	9.6	0.1	1.3	89.1
TPTH	3.64	0.0026	99.2	0.2	0.6	89.4	0.2	0.5	9.9

Table 4.8 Filtering capacity of the Wash (fluvial SPM retention = 85 %, residence time = 100 d, SPM = 60 mg/l, POC = 9.0 mg/l, DOC = 7.6 mg/l)

compound	log K_{oc} (or K_d)	$k_{(d+v)}$ (d^{-1})	INPUT (total = 100)			OUTPUT			F.C.
			dis	doc	ads	dis	doc	ads	%
Cd	10	-	62.5	-	37.5	62.5	-	5.6	31.9
Cu	30	-	35.7	-	64.3	35.7	-	9.6	54.6
Hg	120	-	12.2	-	87.8	12.2	-	13.2	74.6
Pb	420	-	3.8	-	96.2	3.8	-	14.4	81.8
Zn	120	-	12.2	-	87.8	12.2	-	13.2	74.6
FLA	5.10	0.0067	43.6	7.1	49.4	22.3	3.6	7.4	66.7
BbF	5.72	0.0039	15.6	10.6	73.8	10.6	7.2	11.1	71.2
BkF	5.73	0.0084	15.3	10.6	74.0	6.6	4.6	11.1	77.7
BaP	6.24	0.11	5.3	11.9	82.8	0.0	0.0	12.4	87.6
BgP	6.23	0.00031	5.4	11.9	82.7	5.2	11.5	12.4	70.8
IP	6.23	0.00031	5.4	11.9	82.7	5.2	11.5	12.4	70.8
PCB-28	4.45	0.074	77.5	2.8	19.7	0.0	0.0	2.9	97.0
PCB-52	5.07	0.067	45.3	6.9	47.9	0.1	0.0	7.2	92.8
PCB-101	5.31	0.057	32.2	8.5	59.3	0.1	0.0	8.9	91.0
PCB-118	5.81	0.039	13.1	10.9	76.0	0.3	0.2	11.4	88.1
PCB-138	6.22	0.034	5.5	11.9	82.6	0.2	0.4	12.4	87.0
PCB-153	6.11	0.040	7.0	11.7	81.3	0.1	0.2	12.2	87.5
PCB-180	6.36	0.018	4.1	12.0	83.9	0.7	2.0	12.6	84.8
TCDD	6.44	0.016	3.4	12.1	84.5	0.7	2.4	12.7	84.2
OCDD	6.97	0.041	1.0	12.4	86.5	0.0	0.2	13.0	86.8
2,4-D	1.66	0.040	100.0	0.0	0.0	1.8	0.0	0.0	98.2
aldicarb	1.22	0.0023	100.0	0.0	0.0	79.4	0.0	0.0	20.6
atrazine	2.19	0.058	99.8	0.0	0.1	0.3	0.0	0.0	99.7
azinphosm.	3.10	0.28	98.7	0.2	1.1	0.0	0.0	0.2	99.8
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	99.9	0.0	0.1	36.7	0.0	0.0	63.2
dichlorvos	1.83	0.17	99.9	0.0	0.1	0.0	0.0	0.0	100.0
dimethoate	1.51	0.017	100.0	0.0	0.0	18.3	0.0	0.0	81.7
diuron	2.47	0.00084	99.7	0.0	0.3	91.7	0.0	0.0	8.3
DNOC	2.34	0.00016	99.8	0.0	0.2	98.2	0.0	0.0	1.8
endosulfan	3.67	0.051	95.4	0.6	4.0	0.6	0.0	0.6	98.8
lindane	2.98	0.0067	99.0	0.1	0.9	50.7	0.1	0.1	49.1
mevinphos	2.80	0.050	99.4	0.1	0.6	0.7	0.0	0.1	99.2
parathion	3.17	0.0040	98.5	0.2	1.3	66.0	0.1	0.2	33.7
simazine	2.04	0.035	99.9	0.0	0.1	3.0	0.0	0.0	97.0
TBT	4.10	0.058	88.5	1.4	10.0	0.3	0.0	1.5	98.2
TPTH	3.64	0.0026	95.7	0.5	3.8	73.8	0.4	0.6	25.2

Table 4.9 Filtering capacity of the Thames estuary (fluvial SPM retention = 60%, residence time = 40 d, SPM = 30 mg/l, POC = 2.7 mg/l, DOC = 4.1 mg/l)

compound	log K_{oc} (or K_d)	$k_{(d+v)}$ (d^{-1})	INPUT (total = 100)			OUTPUT			F.C.
			dis	doc	ads	dis	doc	ads	%
Cd	35	-	48.8	-	51.2	48.8	-	20.5	30.7
Cu	40	-	45.5	-	54.5	45.5	-	21.8	32.7
Hg	145	-	18.7	-	81.3	18.7	-	32.5	48.8
Pb	530	-	5.9	-	94.1	5.9	-	37.6	56.4
Zn	115	-	22.5	-	77.5	22.5	-	31.0	46.5
FLA	5.10	0.0067	70.0	6.1	23.8	53.6	4.7	9.5	32.2
BbF	5.72	0.0039	35.9	13.1	50.9	30.7	11.2	20.4	37.6
BkF	5.73	0.0084	35.4	13.3	51.3	25.3	9.5	20.5	44.7
BaP	6.24	0.11	14.5	17.5	68.0	0.2	0.2	27.2	72.4
BgP	6.23	0.00031	14.8	17.5	67.7	14.6	17.3	27.1	41.0
IP	6.23	0.00031	14.8	17.5	67.7	14.6	17.3	27.1	41.0
PCB-28	4.45	0.074	91.3	1.8	6.9	4.7	0.1	2.8	92.4
PCB-52	5.07	0.067	71.5	5.9	22.7	4.9	0.4	9.1	85.6
PCB-101	5.31	0.057	59.0	8.4	32.6	6.0	0.9	13.0	80.1
PCB-118	5.81	0.039	31.3	14.1	54.6	6.6	3.0	21.8	68.6
PCB-138	6.22	0.034	15.1	17.4	67.5	3.9	4.5	27.0	64.7
PCB-153	6.11	0.040	18.6	16.7	64.7	3.8	3.4	25.9	67.0
PCB-180	6.36	0.018	11.4	18.2	70.4	5.5	8.9	28.2	57.4
TCDD	6.44	0.016	9.7	18.5	71.8	5.1	9.8	28.7	56.4
OCDD	6.97	0.041	3.1	19.9	77.1	0.6	3.9	30.8	64.7
2,4-D	1.66	0.040	100.0	0.0	0.0	20.2	0.0	0.0	79.8
aldicarb	1.22	0.0023	100.0	0.0	0.0	91.2	0.0	0.0	8.8
atrazine	2.19	0.058	99.9	0.0	0.0	9.8	0.0	0.0	90.2
azinphosm.	3.10	0.28	99.6	0.1	0.3	0.0	0.0	0.1	99.9
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	100.0	0.0	0.0	67.0	0.0	0.0	33.0
dichlorvos	1.83	0.17	100.0	0.0	0.0	0.1	0.0	0.0	99.9
dimethoate	1.51	0.017	100.0	0.0	0.0	50.7	0.0	0.0	49.3
diuron	2.47	0.00084	99.9	0.0	0.1	96.6	0.0	0.0	3.3
DNOC	2.34	0.00016	99.9	0.0	0.1	99.3	0.0	0.0	0.7
endosulfan	3.67	0.051	98.4	0.3	1.2	12.8	0.0	0.5	86.7
lindane	2.98	0.0067	99.7	0.1	0.3	76.2	0.1	0.1	23.6
mevinphos	2.80	0.050	99.8	0.0	0.2	13.5	0.0	0.1	86.4
parathion	3.17	0.0040	99.5	0.1	0.4	84.8	0.1	0.2	15.0
simazine	2.04	0.035	100.0	0.0	0.0	24.7	0.0	0.0	75.3
TBT	4.10	0.058	95.9	0.8	3.3	9.4	0.1	1.3	89.2
TPTH	3.64	0.0026	98.5	0.3	1.2	88.8	0.3	0.5	10.5

Table 4.10 Filtering capacity of the Scheldt estuary (fluvial SPM retention = 80%, residence time = 60 d, SPM = 62 mg/l, POC = 3.4 mg/l, DOC = 5.1 mg/l)

compound	log K_{oc} (or K_d)	$k_{(d+v)}$ (d^{-1})	INPUT (total = 100)			OUTPUT			F.C.
			dis	doc	ads	dis	doc	ads	%
Cd	35	-	31.5	-	68.5	31.5	-	13.7	54.8
Cu	40	-	28.7	-	71.3	28.7	-	14.3	57.0
Hg	145	-	10.0	-	90.0	10.0	-	18.0	72.0
Pb	530	-	3.0	-	97.0	3.0	-	19.4	77.6
Zn	115	-	12.3	-	87.7	12.3	-	17.5	70.2
FLA	5.10	0.0067	65.1	7.1	27.8	43.5	4.8	5.6	46.2
BbF	5.72	0.0039	30.9	14.0	55.1	24.4	11.1	11.0	53.4
BkF	5.73	0.0084	30.4	14.1	55.5	18.4	8.5	11.1	62.0
BaP	6.24	0.11	11.9	17.9	70.2	0.0	0.0	14.0	85.9
BgP	6.23	0.00031	12.1	17.9	70.0	11.9	17.5	14.0	56.6
IP	6.23	0.00031	12.1	17.9	70.0	11.9	17.5	14.0	56.6
PCB-28	4.45	0.074	89.3	2.2	8.6	1.1	0.0	1.7	97.2
PCB-52	5.07	0.067	66.6	6.8	26.6	1.2	0.1	5.3	93.4
PCB-101	5.31	0.057	53.4	9.5	37.1	1.7	0.3	7.4	90.5
PCB-118	5.81	0.039	26.6	14.9	58.5	2.6	1.4	11.7	84.3
PCB-138	6.22	0.034	12.4	17.8	69.8	1.6	2.3	14.0	82.1
PCB-153	6.11	0.040	15.4	17.2	67.4	1.4	1.6	13.5	83.6
PCB-180	6.36	0.018	9.3	18.4	72.3	3.2	6.3	14.5	76.1
TCDD	6.44	0.016	7.8	18.7	73.4	3.0	7.2	14.7	75.1
OCDD	6.97	0.041	2.4	19.8	77.7	0.2	1.7	15.5	82.6
2,4-D	1.66	0.040	100.0	0.0	0.0	9.1	0.0	0.0	90.9
aldicarb	1.22	0.0023	100.0	0.0	0.0	87.1	0.0	0.0	12.9
atrazine	2.19	0.058	99.9	0.0	0.1	3.1	0.0	0.0	96.9
azinphosm.	3.10	0.28	99.5	0.1	0.4	0.0	0.0	0.1	99.9
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	100.0	0.0	0.0	54.9	0.0	0.0	45.1
dichlorvos	1.83	0.17	100.0	0.0	0.0	0.0	0.0	0.0	100.0
dimethoate	1.51	0.017	100.0	0.0	0.0	36.1	0.0	0.0	63.9
diuron	2.47	0.00084	99.9	0.0	0.1	95.0	0.0	0.0	5.0
DNOC	2.34	0.00016	99.9	0.0	0.1	99.0	0.0	0.0	1.0
endosulfan	3.67	0.051	98.0	0.4	1.6	4.6	0.0	0.3	95.1
lindane	2.98	0.0067	99.6	0.1	0.3	66.6	0.1	0.1	33.3
mevinphos	2.80	0.050	99.7	0.1	0.2	5.0	0.0	0.0	95.0
parathion	3.17	0.0040	99.4	0.1	0.5	78.2	0.1	0.1	21.6
simazine	2.04	0.035	100.0	0.0	0.0	12.2	0.0	0.0	87.8
TBT	4.10	0.058	94.9	1.0	4.1	2.9	0.0	0.8	96.2
TPTH	3.64	0.0026	98.2	0.4	1.5	84.0	0.3	0.3	15.4

Table 4.11 Filtering capacity of the Rhine-Meuse estuary (fluvial SPM retention = 45%, residence time = 4 d, SPM = 23 mg/l, POC = 1.7 mg/l, DOC = 2.8 mg/l)

compound	log K_{oc}	$k_{(d+v)}$	INPUT (total = 100)			OUTPUT			F.C.
	(or K_d)	(d^{-1})	dis	doc	ads	dis	doc	ads	%
Cd	35	-	55.4	-	44.6	55.4	-	24.5	20.1
Cu	40	-	52.1	-	47.9	52.1	-	26.4	21.6
Hg	145	-	23.1	-	76.9	23.1	-	42.3	34.6
Pb	530	-	7.6	-	92.4	7.6	-	50.8	41.6
Zn	115	-	27.4	-	72.6	27.4	-	39.9	32.7
FLA	5.10	0.0067	78.5	4.7	16.8	76.4	4.6	9.2	9.8
BbF	5.72	0.0039	46.7	11.7	41.7	46.0	11.5	22.9	19.6
BkF	5.73	0.0084	46.1	11.8	42.1	44.6	11.4	23.2	20.9
BaP	6.24	0.11	20.9	17.3	61.8	13.5	11.1	34.0	41.4
BgP	6.23	0.00031	21.3	17.2	61.5	21.3	17.2	33.8	27.7
IP	6.23	0.00031	21.3	17.2	61.5	21.3	17.2	33.8	27.7
PCB-28	4.45	0.074	94.2	1.3	4.5	70.1	0.9	2.5	26.5
PCB-52	5.07	0.067	79.6	4.5	15.9	60.9	3.4	8.7	26.9
PCB-101	5.31	0.057	69.2	6.7	24.0	55.1	5.4	13.2	26.3
PCB-118	5.81	0.039	41.6	12.8	45.6	35.6	10.9	25.1	28.4
PCB-138	6.22	0.034	21.7	17.1	61.2	18.9	15.0	33.7	32.5
PCB-153	6.11	0.040	26.3	16.1	57.6	22.4	13.7	31.7	32.2
PCB-180	6.36	0.018	16.7	18.2	65.1	15.5	17.0	35.8	31.7
TCDD	6.44	0.016	14.3	18.7	67.0	13.4	17.6	36.8	32.2
OCDD	6.97	0.041	4.7	20.8	74.5	4.0	17.7	41.0	37.4
2,4-D	1.66	0.040	100.0	0.0	0.0	85.2	0.0	0.0	14.8
aldicarb	1.22	0.0023	100.0	0.0	0.0	99.1	0.0	0.0	0.9
atrazine	2.19	0.058	100.0	0.0	0.0	79.3	0.0	0.0	20.7
azinphosm.	3.10	0.28	99.7	0.1	0.2	32.5	0.0	0.1	67.3
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	100.0	0.0	0.0	96.1	0.0	0.0	3.9
dichlorvos	1.83	0.17	100.0	0.0	0.0	50.7	0.0	0.0	49.3
dimethoate	1.51	0.017	100.0	0.0	0.0	93.4	0.0	0.0	6.6
diuron	2.47	0.00084	99.9	0.0	0.1	99.6	0.0	0.0	0.4
DNOC	2.34	0.00016	100.0	0.0	0.0	99.9	0.0	0.0	0.1
endosulfan	3.67	0.051	99.0	0.2	0.8	80.7	0.2	0.4	18.7
lindane	2.98	0.0067	99.8	0.0	0.2	97.2	0.0	0.1	2.7
mevinphos	2.80	0.050	99.9	0.0	0.1	81.8	0.0	0.1	18.2
parathion	3.17	0.0040	99.7	0.1	0.3	98.1	0.1	0.1	1.7
simazine	2.04	0.035	100.0	0.0	0.0	86.9	0.0	0.0	13.1
TBT	4.10	0.058	97.3	0.6	2.1	77.2	0.5	1.1	21.2
TPTH	3.64	0.0026	99.1	0.2	0.7	98.0	0.2	0.4	1.4

Table 4.12 Filtering capacity of the Dutch Wadden Sea (fluvial SPM retention = 85%, residence time = 10 d, SPM = 16 mg/l, POC = 4.7 mg/l, DOC = 5.4 mg/l)

compound	log K_{oc}	$k_{(d+v)}$	INPUT (total = 100)			OUTPUT			F.C.
	(or K_d)	(d^{-1})	dis	doc	ads	dis	doc	ads	%
Cd	10	-	86.2	-	13.8	86.2	-	2.1	11.7
Cu	30	-	67.6	-	32.4	67.6	-	4.9	27.6
Hg	120	-	34.2	-	65.8	34.2	-	9.9	55.9
Pb	420	-	13.0	-	87.0	13.0	-	13.1	74.0
Zn	120	-	34.2	-	65.8	34.2	-	9.9	55.9
FLA	5.10	0.0067	58.6	6.8	34.7	54.8	6.3	5.2	33.7
BbF	5.72	0.0039	25.3	12.2	62.5	24.4	11.7	9.4	54.5
BkF	5.73	0.0084	24.9	12.3	62.8	22.9	11.3	9.4	56.4
BaP	6.24	0.11	9.3	14.8	75.9	3.1	4.9	11.4	80.6
BgP	6.23	0.00031	9.5	14.8	75.7	9.5	14.7	11.4	64.4
IP	6.23	0.00031	9.5	14.8	75.7	9.5	14.7	11.4	64.4
PCB-28	4.45	0.074	86.3	2.2	11.4	41.2	1.1	1.7	56.0
PCB-52	5.07	0.067	60.2	6.5	33.3	30.8	3.3	5.0	60.9
PCB-101	5.31	0.057	46.6	8.7	44.7	26.3	4.9	6.7	62.0
PCB-118	5.81	0.039	21.6	12.8	65.6	14.6	8.7	9.8	66.9
PCB-138	6.22	0.034	9.7	14.8	75.6	6.9	10.5	11.3	71.3
PCB-153	6.11	0.040	12.1	14.4	73.5	8.1	9.6	11.0	71.2
PCB-180	6.36	0.018	7.2	15.2	77.6	6.0	12.7	11.6	69.7
TCDD	6.44	0.016	6.1	15.3	78.6	5.2	13.1	11.8	70.0
OCDD	6.97	0.041	1.9	16.0	82.1	1.2	10.6	12.3	75.8
2,4-D	1.66	0.040	100.0	0.0	0.0	67.0	0.0	0.0	33.0
aldicarb	1.22	0.0023	100.0	0.0	0.0	97.7	0.0	0.0	2.3
atrazine	2.19	0.058	99.9	0.0	0.1	55.9	0.0	0.0	44.0
azinphosm.	3.10	0.28	99.3	0.1	0.6	6.0	0.0	0.1	93.9
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	99.9	0.0	0.1	90.4	0.0	0.0	9.6
dichlorvos	1.83	0.17	100.0	0.0	0.0	18.3	0.0	0.0	81.7
dimethoate	1.51	0.017	100.0	0.0	0.0	84.4	0.0	0.0	15.6
diuron	2.47	0.00084	99.8	0.0	0.1	99.0	0.0	0.0	1.0
DNOC	2.34	0.00016	99.9	0.0	0.1	99.7	0.0	0.0	0.2
endosulfan	3.67	0.051	97.4	0.4	2.1	58.5	0.3	0.3	40.9
lindane	2.98	0.0067	99.5	0.1	0.4	93.0	0.1	0.1	6.8
mevinphos	2.80	0.050	99.6	0.1	0.3	60.4	0.0	0.0	39.5
parathion	3.17	0.0040	99.2	0.1	0.7	95.3	0.1	0.1	4.5
simazine	2.04	0.035	99.9	0.0	0.1	70.4	0.0	0.0	29.6
TBT	4.10	0.058	93.4	1.1	5.5	52.3	0.6	0.8	46.3
TPTH	3.64	0.0026	97.6	0.4	2.0	95.1	0.4	0.3	4.2

Table 4.13 Filtering capacity of the Ems estuary (fluvial SPM retention = 85 %, residence time = 40 d, SPM = 20 mg/l, POC = 4.3 mg/l, DOC = 5.0 mg/l)

compound	log K_{oc} (or K_d)	$k_{(d+v)}$ (d^{-1})	INPUT (total = 100)			OUTPUT			F.C.
			dis	doc	ads	dis	doc	ads	%
Cd	35	-	58.8	-	41.2	58.8	-	6.2	35.0
Cu	40	-	55.6	-	44.4	55.6	-	6.7	37.8
Hg	145	-	25.6	-	74.4	25.6	-	11.2	63.2
Pb	530	-	8.6	-	91.4	8.6	-	13.7	77.7
Zn	115	-	30.3	-	69.7	30.3	-	10.5	59.2
FLA	5.10	0.0067	60.7	6.5	32.8	46.4	5.0	4.9	43.7
BbF	5.72	0.0039	27.0	12.0	60.9	23.1	10.3	9.1	57.4
BkF	5.73	0.0084	26.6	12.1	61.3	19.0	8.7	9.2	63.2
BaP	6.24	0.11	10.1	14.8	75.1	0.1	0.2	11.3	88.4
BgP	6.23	0.00031	10.3	14.8	74.9	10.1	14.6	11.2	64.0
IP	6.23	0.00031	10.3	14.8	74.9	10.1	14.6	11.2	64.0
PCB-28	4.45	0.074	87.3	2.1	10.6	4.5	0.1	1.6	93.8
PCB-52	5.07	0.067	62.3	6.2	31.5	4.3	0.4	4.7	90.6
PCB-101	5.31	0.057	48.7	8.5	42.8	5.0	0.9	6.4	87.7
PCB-118	5.81	0.039	23.1	12.7	64.2	4.9	2.7	9.6	82.8
PCB-138	6.22	0.034	10.5	14.8	74.7	2.7	3.8	11.2	82.3
PCB-153	6.11	0.040	13.1	14.3	72.6	2.6	2.9	10.9	83.6
PCB-180	6.36	0.018	7.8	15.2	77.0	3.8	7.4	11.5	77.2
TCDD	6.44	0.016	6.6	15.4	78.0	3.5	8.1	11.7	76.7
OCDD	6.97	0.041	2.0	16.2	81.8	0.4	3.1	12.3	84.2
2,4-D	1.66	0.040	100.0	0.0	0.0	20.2	0.0	0.0	79.8
aldicarb	1.22	0.0023	100.0	0.0	0.0	91.2	0.0	0.0	8.8
atrazine	2.19	0.058	99.9	0.0	0.1	9.8	0.0	0.0	90.2
azinphosm.	3.10	0.28	99.4	0.1	0.5	0.0	0.0	0.1	99.9
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	99.9	0.0	0.0	67.0	0.0	0.0	33.0
dichlorvos	1.83	0.17	100.0	0.0	0.0	0.1	0.0	0.0	99.9
dimethoate	1.51	0.017	100.0	0.0	0.0	50.7	0.0	0.0	49.3
diuron	2.47	0.00084	99.8	0.0	0.1	96.5	0.0	0.0	3.4
DNOC	2.34	0.00016	99.9	0.0	0.1	99.3	0.0	0.0	0.7
endosulfan	3.67	0.051	97.6	0.4	2.0	12.7	0.1	0.3	87.0
lindane	2.98	0.0067	99.5	0.1	0.4	76.1	0.1	0.1	23.8
mevinphos	2.80	0.050	99.7	0.1	0.3	13.5	0.0	0.0	86.5
parathion	3.17	0.0040	99.2	0.1	0.6	84.6	0.1	0.1	15.2
simazine	2.04	0.035	99.9	0.0	0.0	24.6	0.0	0.0	75.3
TBT	4.10	0.058	93.9	1.0	5.1	9.2	0.1	0.8	89.9
TPTH	3.64	0.0026	97.8	0.4	1.8	88.1	0.3	0.3	11.3

Table 4.14 Filtering capacity of the Weser estuary (fluvial SPM retention = 80%, residence time = 15 d, SPM = 49 mg/l, POC = 2.9 mg/l, DOC = 4.2 mg/l)

compound	log K_{oc}	$k_{(d+v)}$	INPUT (total = 100)			OUTPUT			F.C.
	(or K_d)	(d^{-1})	dis	doc	ads	dis	doc	ads	%
Cd	10	-	67.1	-	32.9	67.1	-	6.6	26.3
Cu	30	-	40.5	-	59.5	40.5	-	11.9	47.6
Hg	120	-	14.5	-	85.5	14.5	-	17.1	68.4
Pb	420	-	4.6	-	95.4	4.6	-	19.1	76.3
Zn	120	-	14.5	-	85.5	14.5	-	17.1	68.4
FLA	5.10	0.0067	68.7	6.2	25.1	62.2	5.6	5.0	27.2
BbF	5.72	0.0039	34.5	12.9	52.5	32.6	12.2	10.5	44.7
BkF	5.73	0.0084	34.0	13.0	53.0	30.0	11.5	10.6	47.9
BaP	6.24	0.11	13.7	17.0	69.2	2.6	3.3	13.8	80.2
BgP	6.23	0.00031	14.0	17.0	69.0	13.9	16.9	13.8	55.3
IP	6.23	0.00031	14.0	17.0	69.0	13.9	16.9	13.8	55.3
PCB-28	4.45	0.074	90.8	1.8	7.4	29.9	0.6	1.5	68.0
PCB-52	5.07	0.067	70.2	5.9	23.9	25.7	2.2	4.8	67.4
PCB-101	5.31	0.057	57.5	8.4	34.1	24.5	3.6	6.8	65.1
PCB-118	5.81	0.039	30.0	13.8	56.2	16.7	7.7	11.2	64.3
PCB-138	6.22	0.034	14.3	16.9	68.8	8.6	10.2	13.8	67.5
PCB-153	6.11	0.040	17.7	16.3	66.1	9.7	8.9	13.2	68.2
PCB-180	6.36	0.018	10.8	17.6	71.6	8.2	13.5	14.3	64.0
TCDD	6.44	0.016	9.1	18.0	72.9	7.2	14.1	14.6	64.1
OCDD	6.97	0.041	2.9	19.2	77.9	1.6	10.4	15.6	72.5
2,4-D	1.66	0.040	100.0	0.0	0.0	54.9	0.0	0.0	45.1
aldicarb	1.22	0.0023	100.0	0.0	0.0	96.6	0.0	0.0	3.4
atrazine	2.19	0.058	99.9	0.0	0.0	41.9	0.0	0.0	58.1
azinphosm.	3.10	0.28	99.5	0.1	0.4	1.5	0.0	0.1	98.4
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	100.0	0.0	0.0	86.0	0.0	0.0	14.0
dichlorvos	1.83	0.17	100.0	0.0	0.0	7.8	0.0	0.0	92.2
dimethoate	1.51	0.017	100.0	0.0	0.0	77.5	0.0	0.0	22.5
diuron	2.47	0.00084	99.9	0.0	0.1	98.6	0.0	0.0	1.3
DNOC	2.34	0.00016	99.9	0.0	0.1	99.7	0.0	0.0	0.3
endosulfan	3.67	0.051	98.3	0.3	1.3	45.8	0.2	0.3	53.8
lindane	2.98	0.0067	99.7	0.1	0.3	90.1	0.1	0.1	9.8
mevinphos	2.80	0.050	99.8	0.0	0.2	47.1	0.0	0.0	52.8
parathion	3.17	0.0040	99.5	0.1	0.4	93.7	0.1	0.1	6.1
simazine	2.04	0.035	100.0	0.0	0.0	59.1	0.0	0.0	40.9
TBT	4.10	0.058	95.6	0.9	3.5	40.1	0.4	0.7	58.9
TPTH	3.64	0.0026	98.4	0.3	1.2	94.7	0.3	0.2	4.8

Table 4.15 Filtering capacity of the Elbe estuary (fluvial SPM retention = 85 %, residence time = 25 d, SPM = 63 mg/l, POC = 7.7 mg/l, DOC = 6.9 mg/l)

compound	log K_{oc} (or K_d)	$k_{(d+v)}$ (d^{-1})	INPUT (total = 100)			OUTPUT			F.C.
			dis	doc	ads	dis	doc	ads	%
Cd	35	-	31.2	-	68.8	31.2	-	10.3	58.5
Cu	40	-	28.4	-	71.6	28.4	-	10.7	60.9
Hg	145	-	9.9	-	90.1	9.9	-	13.5	76.6
Pb	530	-	2.9	-	97.1	2.9	-	14.6	82.5
Zn	115	-	12.1	-	87.9	12.1	-	13.2	74.7
FLA	5.10	0.0067	47.2	7.0	45.8	40.0	5.9	6.9	47.3
BbF	5.72	0.0039	17.7	10.9	71.4	16.0	9.9	10.7	63.4
BkF	5.73	0.0084	17.3	10.9	71.7	14.1	8.9	10.8	66.3
BaP	6.24	0.11	6.1	12.4	81.5	0.4	0.8	12.2	86.6
BgP	6.23	0.00031	6.2	12.4	81.4	6.2	12.3	12.2	69.3
IP	6.23	0.00031	6.2	12.4	81.4	6.2	12.3	12.2	69.3
PCB-28	4.45	0.074	80.0	2.6	17.4	12.6	0.4	2.6	84.4
PCB-52	5.07	0.067	49.0	6.7	44.3	9.2	1.3	6.6	82.9
PCB-101	5.31	0.057	35.6	8.5	55.9	8.6	2.0	8.4	81.0
PCB-118	5.81	0.039	14.9	11.3	73.9	5.6	4.2	11.1	79.1
PCB-138	6.22	0.034	6.4	12.4	81.3	2.7	5.3	12.2	79.8
PCB-153	6.11	0.040	8.0	12.2	79.8	3.0	4.5	12.0	80.6
PCB-180	6.36	0.018	4.7	12.6	82.7	3.0	8.0	12.4	76.6
TCDD	6.44	0.016	3.9	12.7	83.4	2.6	8.5	12.5	76.3
OCDD	6.97	0.041	1.2	13.1	85.7	0.4	4.7	12.9	82.0
2,4-D	1.66	0.040	100.0	0.0	0.0	36.8	0.0	0.0	63.2
aldicarb	1.22	0.0023	100.0	0.0	0.0	94.4	0.0	0.0	5.6
atrazine	2.19	0.058	99.9	0.0	0.1	23.4	0.0	0.0	76.6
azinphosm.	3.10	0.28	98.9	0.1	1.0	0.1	0.0	0.1	99.8
bentazon	1.52	0	100.0	0.0	0.0	100.0	0.0	0.0	0.0
chloridaz.	2.04	0.010	99.9	0.0	0.1	77.8	0.0	0.0	22.2
dichlorvos	1.83	0.17	99.9	0.0	0.1	1.4	0.0	0.0	98.6
dimethoate	1.51	0.017	100.0	0.0	0.0	65.4	0.0	0.0	34.6
diuron	2.47	0.00084	99.7	0.0	0.2	97.7	0.0	0.0	2.3
DNOC	2.34	0.00016	99.8	0.0	0.2	99.4	0.0	0.0	0.5
endosulfan	3.67	0.051	96.0	0.5	3.5	26.8	0.1	0.5	72.5
lindane	2.98	0.0067	99.2	0.1	0.7	83.9	0.1	0.1	15.9
mevinphos	2.80	0.050	99.4	0.1	0.5	28.5	0.0	0.1	71.4
parathion	3.17	0.0040	98.7	0.2	1.1	89.3	0.2	0.2	10.4
simazine	2.04	0.035	99.9	0.0	0.1	41.6	0.0	0.0	58.3
TBT	4.10	0.058	90.0	1.3	8.7	21.1	0.3	1.3	77.3
TPTH	3.64	0.0026	96.3	0.5	3.2	90.2	0.5	0.5	8.8

5 Discussion and conclusions

5.1 General comment and comparison with previous estimates

This study is the first serious attempt to estimate the filtering capacity of North Sea estuaries for contaminants. The results should be regarded as indicative, because of the assumptions and simplifications that had to be made in the calculations. The major causes of uncertainty arise from the choice of the environmental characteristics (suspended matter retention, residence time, SPM, DOC and POC concentrations) and process parameters (K_d, K_{oc}, degradation rate constant; see paragraph 5.4). Besides, the method used to calculate filtering capacities is very simple, compared to complex estuarine models which are available for some of the estuaries considered here. Also, the role of adsorption onto marine suspended matter is completely negelected, though the input of 'uncontaminated' marine suspended matter into the estuaries is, generally, higher than that of fluvial suspended matter. However, in spite of the (inevitable) shortcomings, the results (Tables 4.4-15) can be used in a first attempt to correct the river load of contaminants to the North Sea. These corrected figures are more representative of the actual river load to the North Sea than the uncorrected river loads, based on contaminant concentration times river discharge.

Instead of discussing the results in great detail, it is more interesting to compare them with previous estimates of filtering capacity in North Sea estuaries. A preliminary estimate of filtering capacities in the estuaries of the Scheldt, Rhine-Meuse, and Wadden Sea, was made by Wulffraat et al. (1993). This estimate was based on a fluvial suspended matter retention of 70%, 50%, and 90%, respectively, sorption characteristics (K_d or K_{ow}), and expert judgement (degradation and volatilization). The results are listed in Table 5.1, together with the findings of this study. To ensure a fair comparison, the filtering capacities were recalculated at the same fluvial suspended matter retention as adopted by Wulffraat et al. (1993).

Table 5.1 **Contaminant filtering capacity (%) of Dutch estuaries, estimated by Wulffraat et al. (1993, first column) and this study (second column)**

compound	Rhine		Scheldt		Wadden Sea	
Cd	35	22	60	48	60	12
Cu	35	24	50	50	60	29
Hg	40	38	60	63	70	59
Pb	50	46	70	68	80	78
Zn	35	36	50	61	60	59
FLA	35	11	50	43	75	35
BaP	35	44	50	79	75	84
PCB-153	50	35	70	77	80	75
endosulfan	10	19	20	95	20	41
lindane	10	3	20	33	20	7

The filtering capacities for Hg, Pb, and Zn calculated here are similar to those estimated previously (Wulffraat et al., 1993), but those for Cu and especially Cd are lower. This is a reflection of the higher (fresh water) K_d's used in the previous study (50 l/g for Cu and even 130 l/g for Cd). The K_d's used here are representative for the estuarine (Scheldt and Rhine) or marine (Wadden Sea) environment. Considering the filtering capacity for organic contaminants, there is a reasonable match for PCB-153 and lindane. This study predicts a relatively low filtering capacity for FLA, because of its predominant presence in the dissolved phase (60-80%, see Tables 4.10-12). Hence, sedimentation is less effective in removing FLA from the water column. The filtering capacity for BaP and especially that of endosulfan is higher than previously estimated, because of the high rate constants chosen for photochemical (BaP) and microbial (endosulfan) degradation.

5.2 Comparison with the SAWES model (Scheldt estuary)

The SAWES model is a one-dimensional model which predicts the water and sediment quality of the Scheldt estuary and the fate of contaminants within the system (Van Gils et al., 1993). In the model, the estuary is divided in 14 compartments. The fate of organic contaminants is predicted according to equilibrium chemistry. Thus, exchanges between dissolved and particulate phases are included in the model. The SAWES model can be used, among other things, to predict the flux of contaminants to the North Sea. A comparison between the results of the SAWES model (with respect to filtering capacity) and the simple one-box 'model' used in this study is shown in Table 5.2. To ensure a fair comparison, the critical process parameters (see Table 5.2) and environmental data were chosen identical in both models, i.e. retention fluvial SPM = 80%, residence time 60 d, POC = 3.38 mg/l, DOC = 5.37 mg/l, wind speed = 6 m/s, current speed = 0.5 m/s, depth = 10 m, T = 10 °C. There appears to be a very good match between the outcome of the two models, with differences in filtering capacity being limited to 5-10%. In view of the different concepts in the models (e.g. sorption kinetics), this is a spectacular (and encouraging) result.

Table 5.2 Filtering capacity of the Scheldt estuary for five organic contaminants, as predicted by this study and by the SAWES model

compound	log K_{oc}	X_{doc}	He*	k_g (m/d)	k_l (m/d)	k_v (d^{-1})	k_d (d^{-1})
lindane	3.48	0.60	0.18	441	1.75	0.0017	0.0046
FLA	4.98	0.20	0.586	529	2.10	0.0064	0.0010
BaP	6.5	0.20	0.045	474	1.88	0.0005	0.0175
PCB-52	5.6	0.17	23.2	441	1.75	0.097	0
PCB-153	5.8	0.17	11.0	396	1.57	0.058	0

	INPUT			OUTPUT			filtering capacity	
	dis	doc	ads	dis	doc	ads	this work	SAWES model
lindane	98.0	1.0	1.0	67.3	0.7	0.2	31.8	41.6
FLA	70.2	7.2	22.6	45.0	4.6	4.5	45.8	46.7
BaP	6.6	22.5	70.9	2.3	7.7	14.2	75.9	71.6
PCB-52	36.9	13.4	49.7	0.1	0.0	9.9	89.9	100
PCB-153	27.0	15.5	57.5	0.8	0.5	11.5	87.2	94.9

* Henry constant at 20 °C (Pa.m^3/mol)

5.3 Comparison with field studies (Scheldt and Rhine)

The filtering capacity of the Rhine and Scheldt estuaries for PCB's and PAH's has been estimated recently by H. Klamer (pers. comm.). The filtering capacity was estimated from (total) concentration versus salinity plots, recorded between 1987-1988 in the Scheldt estuary (5 surveys) and 1988-1990 in the Rhine estuary (3 cruises). The estimation method is based on the concept of the 'effective river water concentration', which is obtained by extrapolating the regression line at the seaward end of the mixing curve to zero salinity (Officer, 1979; Klamer et al., 1992). It is important to note that this method integrates the effects of all sources and sinks within the estuary, including direct discharges. The theoretical method presented in this report does not cover the effects of direct discharges to the estuary.

As could be expected, the field data show that the filtering capacity depends on the season. In fact, the Rhine estuary may be a source of PCB's during summer (i.e. filtering capacity <0), and a sink during the rest of the year. On an annual basis, the Scheldt estuary was estimated to remove 68% of the PAH (Borneff) load and 53% of the PCB load. According to this study, and assuming an equal contribution of each individual PAH or PCB, the removal would be 60% for the PAH load and 87% for the PCB load. There is a good match between both estimates of PAH removal, but the PCB removal may be overestimated here. Otherwise, the difference between both estimates may be due to direct discharges within the estuary, which are not included in the theoretical calculation of filtering capacity. Moreover, the extrapolation (to zero salinity) method is only applicable to dissolved substances. In the Rhine estuary, the annual filtering capacity was estimated to be -16% for PAH's (suggesting direct discharges) and 19% for PCB's (Klamer, pers. comm.), compared to 25% (PAH) and 29% (PCB) in this study. Again, lower filtering capacities are obtained in the field situation, probably due to direct discharges. Considering the order of magnitude, there is a reasonable match between the theoretical filtering capacity and that determined from field data, however.

5.4 Variation of process parameters (BaP and atrazine)

The effect of the choice of the process parameters on the calculated filtering capacity is illustrated briefly with BaP and atrazine as examples. These contaminants were selected because of the doubt that was expressed about their high extent of removal within most of the estuaries, despite their widespread occurrence in coastal North Sea waters. This would suggest that the filtering capacity for BaP and atrazine is overestimated. Therefore, it was decided to recalculate the filtering capacities of the North Sea estuaries for BaP and atrazine, with modified process parameters. The parameters to be changed are the partition coefficient for BaP ($\log K_{oc} = 8.37$ instead of 6.24; Evers and Smedes, 1993) and the degradation rate constant for atrazine ($k_d = 0.012/d$ instead of 0.058/d; Ordelman et al., 1993). The results of the 'old' and 'new' calculations are compared in Tables 5.3 (BaP) and 5.4 (atrazine).

Table 5.3 Influence of the partition coefficient (K_{oc}) on the calculated filtering capacity of North Sea estuaries for BaP

estuary	log K_{oc}	$k_{(d+v)}$ (d^{-1})	INPUT (total = 100)			OUTPUT			F.C.
			dis	doc	ads	dis	doc	ads	%
Forth	6.24	0.11	11.9	15.8	72.3	0.8	1.0	10.8	87.4
Forth	8.37	0.11	0.1	17.9	82.0	0.0	1.1	12.3	86.6
Tyne	6.24	0.11	23.6	23.0	53.4	15.2	14.8	45.4	24.6
Tyne	8.37	0.11	0.2	30.1	69.7	0.1	19.4	59.2	21.2
Tees	6.24	0.11	10.9	15.4	73.7	6.3	8.9	62.6	22.2
Tees	8.37	0.11	0.1	17.3	82.6	0.1	10.0	70.2	19.7
Humber	6.24	0.11	23.6	23.0	53.4	0.3	0.3	42.7	56.7
Humber	8.37	0.11	0.2	30.1	69.7	0.0	0.4	55.8	43.9
Wash	6.24	0.11	5.3	11.9	82.8	0.0	0.0	12.4	87.6
Wash	8.37	0.11	0.0	12.5	87.4	0.0	0.0	13.1	86.9
Thames	6.24	0.11	14.5	17.5	68.0	0.2	0.2	27.2	72.4
Thames	8.37	0.11	0.1	20.5	79.4	0.0	0.3	31.8	68.0
Scheldt	6.24	0.11	11.9	17.9	70.2	0.0	0.0	14.0	85.9
Scheldt	8.37	0.11	0.1	20.3	79.6	0.0	0.0	15.9	84.1
Rhine	6.24	0.11	20.9	17.3	61.8	13.5	11.1	34.0	41.4
Rhine	8.37	0.11	0.2	21.8	78.0	0.1	14.1	42.9	42.9
Wadden	6.24	0.11	9.3	14.8	75.9	3.1	4.9	11.4	80.6
Wadden	8.37	0.11	0.1	16.3	83.6	0.0	5.4	12.5	82.0
Ems	6.24	0.11	10.1	14.8	75.1	0.1	0.2	11.3	88.4
Ems	8.37	0.11	0.1	16.5	83.4	0.0	0.2	12.5	87.3
Weser	6.24	0.11	13.7	17.0	69.2	2.6	3.3	13.8	80.2
Weser	8.37	0.11	0.1	19.7	80.1	0.0	3.8	16.0	80.2
Elbe	6.24	0.11	6.1	12.4	81.5	0.4	0.8	12.2	86.6
Elbe	8.37	0.11	0.0	13.2	86.7	0.0	0.8	13.0	86.1

The impact of the selected K_{oc} on the calculated filtering capacity appears to be negligible for all the estuaries (less than 5% difference), except for the Humber (13% difference). This is so because of the 'compensation mechanism' included in the filtering capacity calculations. If the dissolved BaP fraction becomes very small (higher K_{oc}), there will be less degradation, but the removal due to sedimentation will increase. These opposite effects appear to cancel out each other (at least for BaP).

Table 5.4 Influence of the degradation rate constant (k_d) on the filtering capacity of North Sea estuaries for atrazine

estuary	log K_{oc}	$k_{(d+v)}$	INPUT (total = 100)			OUTPUT			F.C.
		(d^{-1})	dis	doc	ads	dis	doc	ads	%
Forth	2.19	0.058	99.9	0.0	0.1	23.4	0.0	0.0	76.5
Forth	2.19	0.012	99.9	0.0	0.1	74.0	0.0	0.0	26.0
Tyne	2.19	0.058	100.0	0.0	0.0	79.3	0.0	0.0	20.7
Tyne	2.19	0.012	100.0	0.0	0.0	95.3	0.0	0.0	4.7
Tees	2.19	0.058	99.9	0.0	0.1	74.8	0.0	0.1	25.2
Tees	2.19	0.012	99.9	0.0	0.1	94.1	0.0	0.1	5.8
Humber	2.19	0.058	100.0	0.0	0.0	9.8	0.0	0.0	90.2
Humber	2.19	0.012	100.0	0.0	0.0	61.9	0.0	0.0	38.1
Wash	2.19	0.058	99.8	0.0	0.1	0.3	0.0	0.0	99.7
Wash	2.19	0.012	99.8	0.0	0.1	30.1	0.0	0.0	69.9
Thames	2.19	0.058	99.9	0.0	0.0	9.8	0.0	0.0	90.2
Thames	2.19	0.012	99.9	0.0	0.0	61.8	0.0	0.0	38.1
Scheldt	2.19	0.058	99.9	0.0	0.1	3.1	0.0	0.0	96.9
Scheldt	2.19	0.012	99.9	0.0	0.1	48.6	0.0	0.0	51.3
Rhine	2.19	0.058	100.0	0.0	0.0	79.3	0.0	0.0	20.7
Rhine	2.19	0.012	100.0	0.0	0.0	95.3	0.0	0.0	4.7
Wadden	2.19	0.058	99.9	0.0	0.1	55.9	0.0	0.0	44.0
Wadden	2.19	0.012	99.9	0.0	0.1	88.6	0.0	0.0	11.4
Ems	2.19	0.058	99.9	0.0	0.1	9.8	0.0	0.0	90.2
Ems	2.19	0.012	99.9	0.0	0.1	61.8	0.0	0.0	38.2
Weser	2.19	0.058	99.9	0.0	0.0	41.9	0.0	0.0	58.1
Weser	2.19	0.012	99.9	0.0	0.0	83.5	0.0	0.0	16.5
Elbe	2.19	0.058	99.9	0.0	0.1	23.4	0.0	0.0	76.6
Elbe	2.19	0.012	99.9	0.0	0.1	74.0	0.0	0.0	26.0

The results for atrazine show that the calculated filtering capacity is extremely sensitive to the choice of the degradation rate constant. This effect may be limited in estuaries with short residence times (Rhine, Tees, Tyne; 16-19% difference). In the other estuaries, with longer residence times, the effect of the degradation rate constant on the filtering capacity is very important (30-52% difference).

5.5 Recommendations for future research

As mentioned before, the filtering capacity calculated here bears a certain degree of uncertainty, which is hard to quantify yet. In a follow-up study, the following aspects need to be addressed in more detail:

1) The retention of fluvial suspended matter, used in the calculation of filtering capacity, is mostly based on expert judgement or incidental field data. Further support of the fluvial suspended matter balances is needed, e.g. from long-term field monitoring, analysis of dredging activities, and mathematical modelling.

2) The import of marine suspended matter into an estuary would lead to additional sorption and, hence, enhance the filtering capacity for adsorbed contaminants. This effect has not been regarded in this study.

3) Instead of estimations of DOC and POC (U.K. and two German estuaries), it is preferred to use measured concentrations in the calculation of filtering capacities.

4) The K_{oc}'s used in the partitioning calculations were usually determined in the laboratory, under conditions not entirely representative of those in the field. Evidence is growing that field K_{oc}'s are one to two orders of magnitude higher than lab K_{oc}'s (e.g. Evers and Smedes, 1993). Hence, the adsorbed (and complexed) fraction of organic contaminants may be higher than that calculated here, and the dissolved fraction will be lower (see Table 5.3). This may lead both to an increase or a decrease of the filtering capacity of a given contaminant in a given estuary, depending on the relative importance of sedimentation and chemical removal mechanisms (degradation and volatilization).

5) The filtering capacity depends strongly on the choice of the degradation rate constant, which is to some extent disputable. It is probably justified to conclude that the choice of the process parameters is the most critical step in the calculation of filtering capacities (see Table 5.4), more important than e.g. the model set-up. A critical evaluation of the degradation rate constants adopted in this study is therefore recommended.

6) Seasonal variability is not taken into account in the calculations. The relatively long residence times during spring and summer (because of low river flows) will lead to increased removal of organic contaminants. This has important implications for contaminants which are not randomly introduced in the water throughout the year. For instance, pesticides are mostly applied during spring and early summer. The combination of high concentrations in river water, combined with long residence times in the estuaries, will lead to increased removal on an annual basis.

6 References

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