LAND DEGRADATION & REHABILITATION, VOL. 4, 317–332 (1993)

# POTENTIAL CHEMICAL TIME BOMBS IN THE SCHELDE ESTUARY

G. T. M. VAN ECK* AND N. M. DE ROOIJ†

**Ministry of Transport, Public Works and Water Management, PO Box 8039, 4330 EA Middelburg, The Netherlands*
*†Delft Hydraulics Laboratory, PO Box 177, 2600 MH Delft, The Netherlands*

## ABSTRACT

The Schelde estuary is heavily polluted with many different (micro)pollutants. This results in high concentrations in the abiotic and biotic compartments of the Schelde estuary and in various effects. The present day suboxic and anoxic conditions in the upper estuary are probably responsible for the high distribution coefficients for some trace metals in the lower Schelde estuary (Western Schelde). A future reduction in discharges with a high biological oxygen demand will therefore not only result in higher oxygen concentrations, but probably also in lower distribution coefficients for trace metals in the Western Schelde. Simulations show that lower trace metal distribution coefficients will probably result in higher concentrations of dissolved (bioavailable) trace metals, even with substantially reduced discharge rates, due to the desorption of trace metals from resuspended bottom sediments.

KEY WORDS Schelde estuary Sediment pollution modelling Trace metals Organic pollutants

## SCHELDE ESTUARY: THE NEED FOR POLLUTION MODELLING

The Schelde estuary, which drains a densely populated and industrialized area in northern France, west Belgium and the southwest Netherlands, is faced with two major problems: (1) extensive dredging and dumping of (contaminated) sediments to keep the port of Antwerp accessible; and (2) large domestic and industrial waste water discharges, a significant proportion of which is discharged without treatment.

The Schelde estuary (Figure 1; Wollast, 1988; Zwolsman and Van Eck, 1993) is a macrotidal coastal plain estuary with a tidal range of 4–5 m and an average water depth of 10 m. The river Schelde and its tributaries drain about 21 600 km$^2$ and the river discharge ranges from 20 m$^3$ s$^{-1}$ in summer to 400 m$^3$ s$^{-1}$ during winter, averaging 104 m$^3$ s$^{-1}$ over the period 1949–86. The length of the estuarine mixing zone is 60–120 km and the residence time of the water in the estuary ranges from one to three months. The water column generally shows a well mixed circulation pattern, except during extreme river discharges in winter. The estuary can be divided into two zones with different hydrographical characteristics.

The upper estuary or Zeeschelde, located in northwest Belgium, is heavily polluted by organic wastes, trace metals and organic contaminants. One of the most striking features of this area is the presence of an anoxic water column during most of the year (Zwolsman and Van Eck, 1993). Previous studies in the Schelde estuary have suggested that this anoxic zone plays an important part in the behaviour of trace metals (Salomons and Eysink, 1981; Duinker, *et al.*, 1982). The bottom sediments consist of sands, sandy muds and clayey muds. The origin of the sediments is predominantly fluvial, but the marine component of the sediments increases in a seaward direction. The finest sediments are found in the so-called high turbidity zone (HTZ) between the city of Antwerp and the Dutch–Belgian border (Wartel, 1977). The HTZ is an important sedimentation zone.

The lower estuary or Western Schelde, situated between the Dutch–Belgian border and the North Sea, has a complex morphology with well defined flood and ebb channels surrounding intertidal sandflats and mudflats. The water column is well oxygenated, with oxygen saturation values increasing from 20–60 per

*Received 4 May 1993*

0898–5812/93/040317–16$13.00

cent at the border to 90–100 per cent at the mouth. The bottom sediments consist mainly of medium to coarse sands; mud deposits are exceptional here (Wartel, 1977). Sand ripples with a height of about 0·5 m and lengths of 10–20 m are common in the lower estuary. These ripples appear to be very mobile (Boderie, *et al.*, 1993). Finer sediments can be found in the intertidal areas of the lower estuary (Zwolsman and Van Eck, 1993), especially in the salt marshes (e.g. Saeftinghe; see Figure 1).

The input of fluvial suspended matter into the upper estuary is calculated at 10 kg $s^{-1}$ or 520 × $10^6$ kg $y^{-1}$ (Van Maldegem, *et al.*, 1993). A second source of suspended matter is marine mud, which accounts for an input of 320 × $10^6$ kg $y^{-1}$. A third source of suspended matter is primary production, which is not very important. Most of the suspended matter is deposited between Antwerp and the Dutch–Belgian border (Figure 1), and in the large intertidal areas such as Saeftinghe adjacent to the estuary. The most recent estimate is that 40 per cent of the fluvial suspended matter reaches the coastal zone (Van Maldegem, *et al.*, 1993).

The sediments in the channels downstream of Antwerp are continuously dredged to keep the port accessible. Most of the dredged sediments are dumped on the intertidal flats near the dredging sites.

In 1988 it was decided to develop a management-oriented combined transport, (biogeo)chemical and bioaccumulation model for the Schelde estuary to help to understand the influence of the large discharges of (micro)pollutants on the Schelde estuary ecosystem. The model attempts to relate the (micro)pollutants discharged into the estuary with the concentrations found in the abiotic components and in some organisms.

Calibration of the model gave a much higher distribution coefficient ($K_d$) for some trace metals (e.g. Cd) between the suspended matter and water in the presence of oxygen than that found in other estuaries (e.g. the Rhine estuary). This means that, at the same total and suspended matter concentrations, the dissolved trace metal concentration, and therefore the bioavailable fraction, is lower in the Schelde estuary than elsewhere. The higher $K_d$ value in the oxygenated lower Schelde estuary may be explained

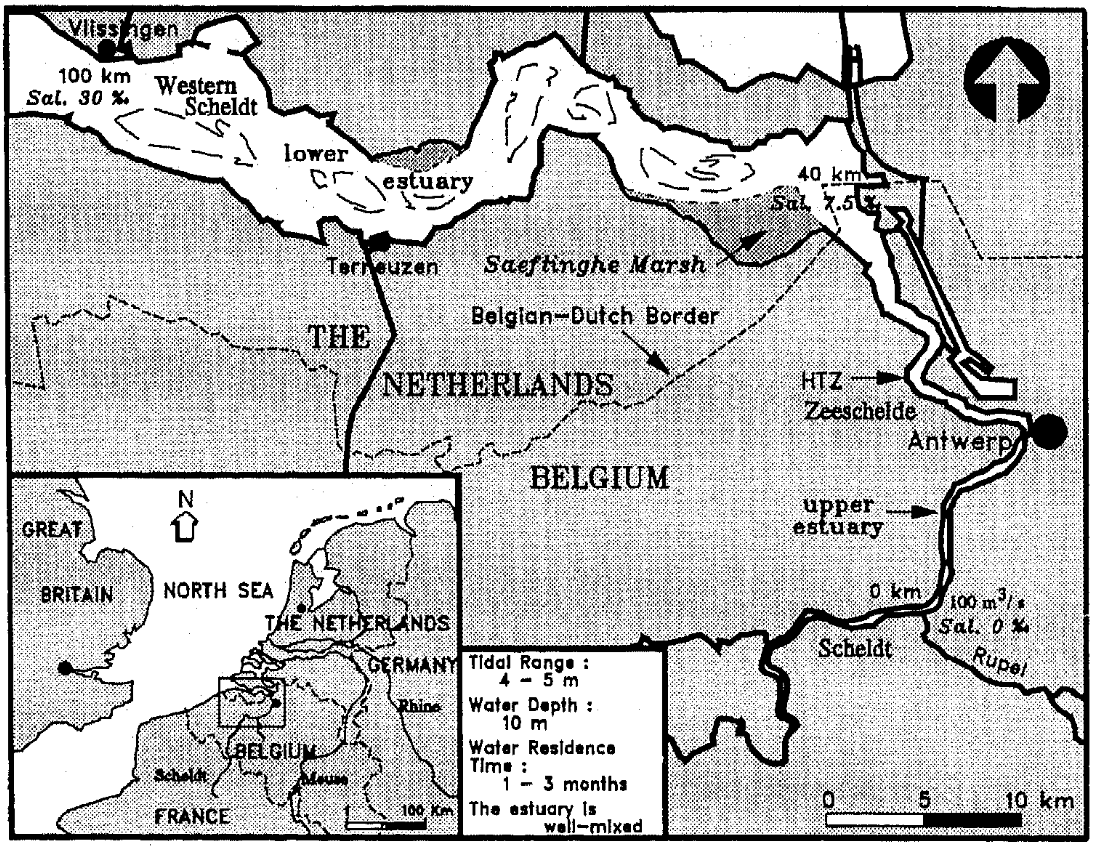


Figure 1. Map of the Schelde estuary

by the high biological oxygen demand (BOD) loads and therefore the high and specific carbon content of suspended matter, or by the strong adsorption of trace metals to newly formed FeOOH, which precipitates in the HTZ between the anoxic upper and (sub)oxic lower estuary. If these explanations are correct, the disappearance of the anoxic conditions in the future as the result of a reduction in the organic waste water loads will result in a lower $K_d$ value. This will result in higher concentrations of dissolved, and therefore more bioavailable, trace metals, perhaps even at lower trace metal discharges. Model simulations were used to test this hypothesis and verify if the sediments of the Schelde estuary are a potential chemical time bomb (CTB). Before the model results are given, the present day pollution status of the Schelde estuary is presented.

## POLLUTION STATUS

The input of water, suspended sediment, nitrogen, phosphorus and some trace metals and organic micropollutants by the rivers Rhine, Maas and Schelde across the German–Dutch and Belgian–Dutch borders, together with discharges into the surface waters of The Netherlands, are given in Table I.

Table I shows that the loads into the Western Schelde are much lower than the loads from the Rhine into the Netherlands and that they are comparable with the loads from the Maas. The loads are relatively much higher because the ratios of the Rhine or Maas loads to the Schelde load are lower than the water or sediment ratios of 25 and 7·5 for the Rhine/Schelde and 3 and 1·25 for the Maas/Schelde, respectively. This also implies that, in general, the concentrations in the Schelde are much higher than in the Rhine and Maas.

Table I also shows that around 1990 The Netherlands loads were comparable with the loads from the three rivers for some compounds (e.g. phosphorus, cadmium, lindane). It indicates that, especially in the Rhine drainage area, the discharges between 1980 and 1990 have decreased, as the loads from the rivers into the Netherlands around 1980 were higher than the loads in The Netherlands.

Table I also shows that around 1990 point sources represented only a small percentage of the total Netherlands' load. It indicates that for most compounds, except cadmium, the important point source

Table I. Estimated input of various pollutants from the rivers Rhine, Maas and Schelde across the Dutch–German and Dutch–Belgian borders in 1990 and comparisons with discharges within The Netherlands

| | Rhine[*] | Maas[†] | Schelde[‡] | Netherlands[§] (% from diffuse sources) |
|---|---|---|---|---|
| River discharge ($m^3 s^{-1}$) | 2500 | 300 | 100 | |
| Suspended matter ($10^3$ t) | 3000 | 500 | 400 | |
| N ($10^3$ t) | 400 | 30 | 35 | 250 (95) |
| P ($10^3$ t) | 25 | 3 | 4 | 30 (60) |
| Cd (t) | 5 | 3 | 3 | 7 (30) |
| Cu (t) | 300 | 30 | 50 | 150 (80) |
| Pb (t) | 300 | 50 | 50 | 100 (75) |
| Zn (t) | 1500 | 500 | 200 | 300 (80) |
| Fluoranthene (kg) | 1000 | 500 | 400 | 1000 (95) |
| Benzo(a)pyrene (kg) | 500 | 400 | 250 | 500 (100) |
| Lindane (kg) | 500 | 100 | 150 | 750 (100) |
| PCB52 (kg) | 15 | 5 | 5 | 6 (100) |
| PCB153 (kg) | 25 | 7·5 | 7·5 | 20 (100) |

*Note*:
[*] Ministerie van Verkeer en Waterstaat (1990a).
[†] Ministerie van Verkeer en Waterstaat (1990b).
[‡] Ministerie van Verkeer en Waterstaat (1991).
[§] Ministerie van Verkeer en Waterstaat (1990c); Tweede Kamer der Staten-Generaal (1989).

discharges have cleaned up and that the remaining discharges are diffuse and therefore more difficult to control.

### *Basic parameters: oxygen, nitrogen, pH, suspended matter and chlorophyll*

The general estuarine chemistry is illustrated in Figure 2 (Zwolsman and Van Eck, 1993). Winter conditions (February 1987 in Figure 2) are characterized by low water temperatures and a high river discharge. Under these favourable circumstances a complete anoxic zone does not develop in the upper estuary. A rapid increase in pH and dissolved oxygen conditions with increasing salinity is observed. Increased suspended matter concentrations are found in the HTZ zone. Phytoplankton activity is negligible throughout the estuary.

During spring and summer (May and August 1987 in Figure 2) the water of the river entering the upper

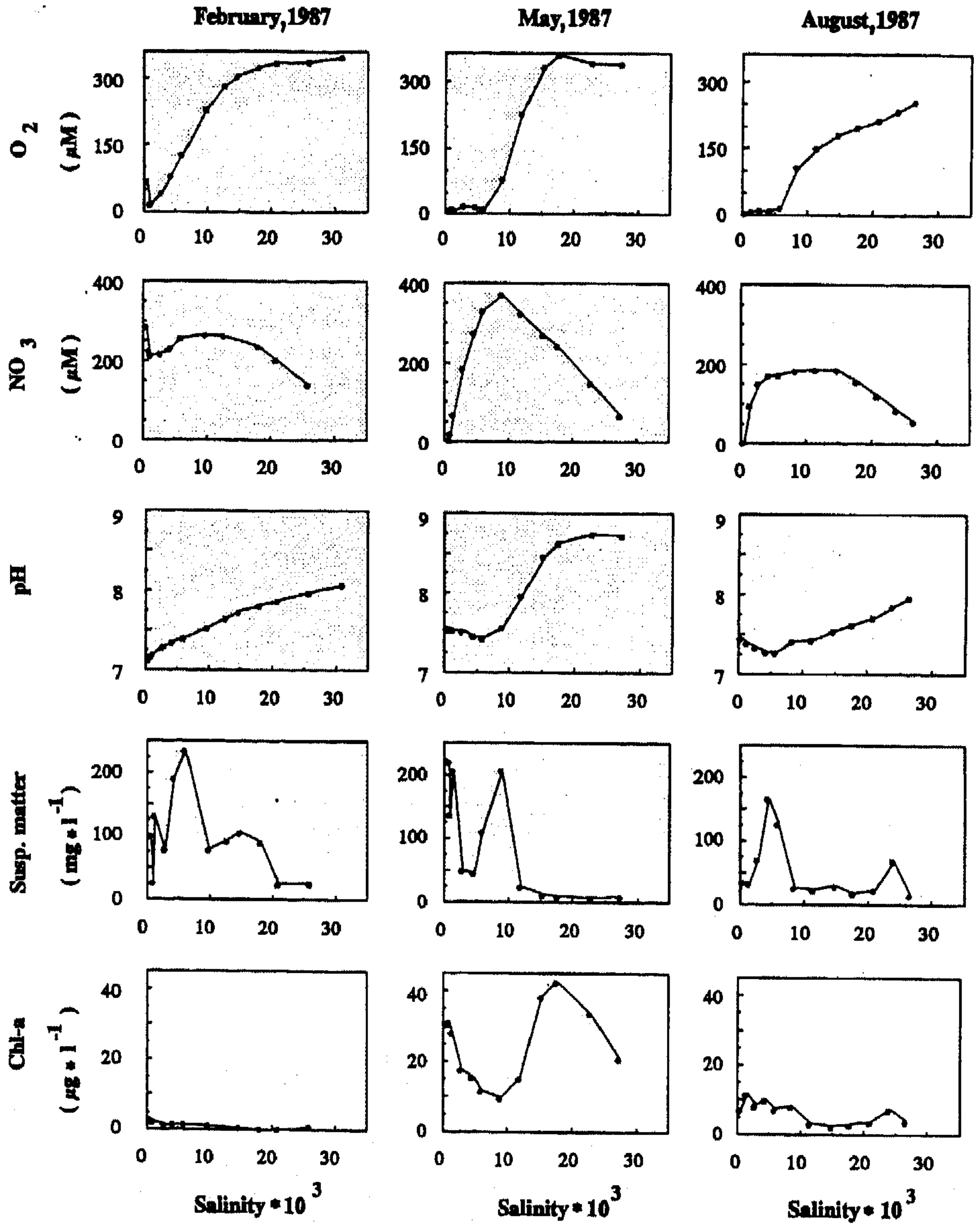


Figure 2. Seasonal distribution of dissolved oxygen, nitrate, pH, suspended matter and chlorophyll *a* in the Schelde estuary in the winter, spring and summer of 1987

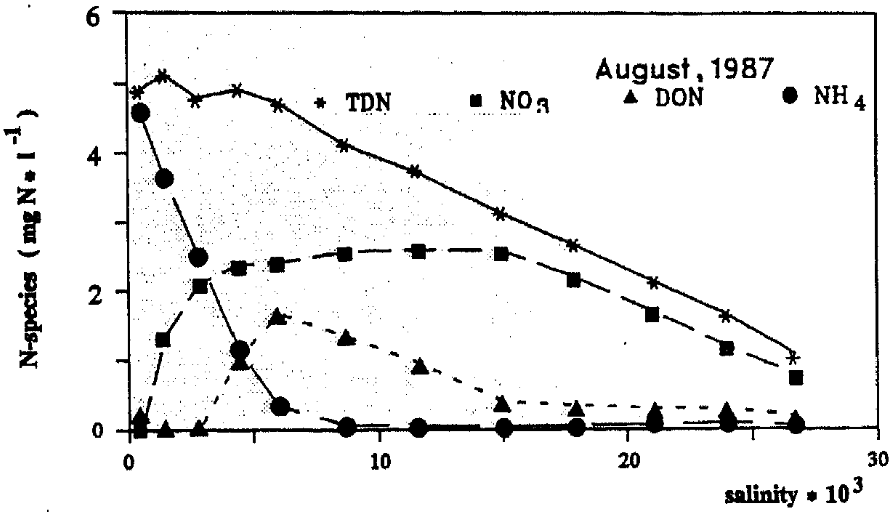


Figure 3. Dissolved nitrogen species as a function of salinity in the Schelde estuary in August 1987. (*) Total dissolved nitrogen; (■) nitrate; (▲)DON (dissolved organic nitrogen) and (●) $NH_4^+$

estuary is anoxic and enriched in ammonium and depleted in nitrate (Figure 3), indicating highly reducing conditions. Dissolved nitrate is rapidly regenerated in the upper estuary due to nitrification (Figure 3), but the anoxic water column persists for a distance of approximately 30 km (Somville and De Pauw, 1982). The so-called conservative behaviour of total dissolved nitrogen (TND) in Figure 3 indicates that the extent of denitrification is similar to the nitrogen input along the estuary. Further downstream dissolved oxygen reappears in the water, and dissolved oxygen concentrations are restored in the lower estuary. The recorded pH profiles typically show a transient minimum in the upper estuary, caused by the high nitrification rates. The suspended matter concentrations in the lower estuary are much lower during spring–summer than during winter. Phytoplankton blooms are recorded during spring, causing supersaturation of dissolved oxygen and high pH values in the lower estuary.

### *Phosphorus and oxygen saturation*

The seasonally strongly varying reducing conditions and high phosphorus loads are also illustrated by the orthophosphate concentrations at the Dutch–Belgian border (Figure 4). Figure 4 shows high orthophoshate concentrations up to 1 mg P l$^{-1}$ and phosphorus pronounced seasonal behaviour related to

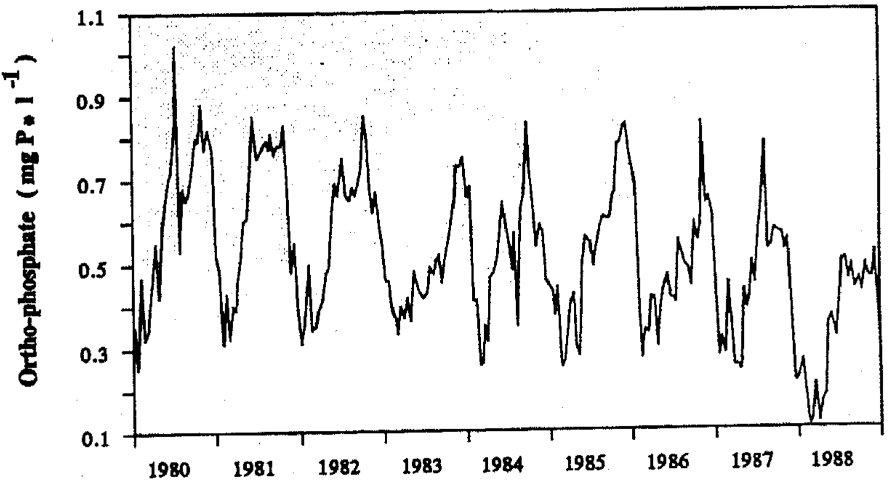


Figure 4. Orthophosphate concentrations in the Schelde estuary at the Dutch–Belgian border (average salinity 7·5 × $10^{-3}$) from 1980 to 1988

the oxygen concentrations and to the coprecipitation of iron with phosphate during the suboxic conditions in winter and the dissolution of iron phosphates during the anoxic summer conditions. The pollution history of the Schelde estuary is illustrated in Figure 5, which shows the average annual oxygen concentrations at the Dutch–Belgian border from 1964 to 1991. The average oxygen concentration at Lillo in 1950, which is about 1 mg $l^{-1}$ lower than at the border, indicates that the oxygen status was satisfactory at the border around 1950 (about 75 per cent saturation). The situation deteriorated in the 1960s and early 1970s and remained poor for the rest of the 1970s. The situation then improved in the early 1980s. The low concentrations in 1988 and 1989 are related to the high water temperatures and therefore low oxygen solubility in the warm winters of these years and show that the present day oxygen status of the estuary is unstable.

*Trace elements*

The pollution status of the Schelde estuary with respect to trace metals is illustrated in Tables II, III and IV (see Zwolsman and Van Eck, 1993); the dissolved, suspended and bottom sediment trace metal

Table II. Concentrations of dissolved metal in the rivers Elbe, Ems, Rhine, Maas and Schelde

| | | Concentration (nmol $l^{-1}$) | | | |
|---|---|---|---|---|---|
| River | Year | Cd | Cu | Zn | Reference |
| Elbe | 1983 | 1.15 | 50 | 332 | Ahlf (1983); Ahlf and Wellershaus (1984) |
| Ems | 1989 | 0·09 | 8 | 61 | Gemeinsames Bund-Länder mess programm (1990) |
| Rhine | 1989 | 0·51 | 36 | 215 | Paalman (personal communication) |
| Maas | 1989 | 1·00 | 30 | 150 | Ministerie Verkeer en Waterstaat (1990b) |
| Schelde | 1987 | 0·18 | 29 | 291 | Zwolsman and Van Eck (winter) (1993) |
| Schelde | 1987 | <0·09 | 10 | 45 | Zolsman and Van Eck (spring/summer) (1993) |

Table III. Concentrations of trace metals in the suspended sediments of the rivers Elbe, Weser, Ems, Rhine, Maas and Schelde. Ranges indicate the concentrations measured in river water and at the mouth of the estuary

| | Concentrations (μg $g^{-1}$) | | | |
|---|---|---|---|---|
| River | Cd | Cu | Zn | Reference |
| Elbe | 12–0·5 | 343–55 | 700–210 | Ahlf (1983); Ahlf and Wellershaus (1984) |
| Weser | 18–2·5 | 190–15 | 1030–130 | Calmano, *et al.* (1985) |
| Ems | 1 | 20 | 200 | Gemeinsames Bund-Länder mess programm (1990) |
| Rhine | 12–2·6 | 115–25 | 960–200 | Paalman (personal communication) |
| Maas | 25 | 175 | 1750 | Ministerie van Verkeer en Waterstaat (1990b) |
| Schelde | 12–0·8 | 218–23 | 1090–190 | Zwolsman and Van Eck (1993) |

Table IV. Concentrations of trace metals in the bottom sediments of the Elbe, Weser, Ems, Rhine and Schelde estuaries

| | | Concentrations (mg $kg^{-1}$) | | | |
|---|---|---|---|---|---|
| River | Year | Cd | Cu | Zn | Reference |
| Elbe | 1983 | 0·1–7·7 | 8–248 | 42–570 | Ahlf (1983); Ahlf and Wellershaus (1984) |
| Weser | 1980–1 | 0·1–12·4 | 9–162 | 43–1432 | Calmano, *et al.* (1982) |
| Ems | 1986–8 | 0·6±0·5 | 20±5 | 150±25 | Kramer, *et al.* (1989) |
| Rhine | 1986 | 2·0–10 | 36–195 | 240–760 | Steneker, *et al.* (1988) |
| Schelde | 1980–90 | 0·1–45 | 1–207 | 3–1325 | Zwolsman and Van Eck (1993) |

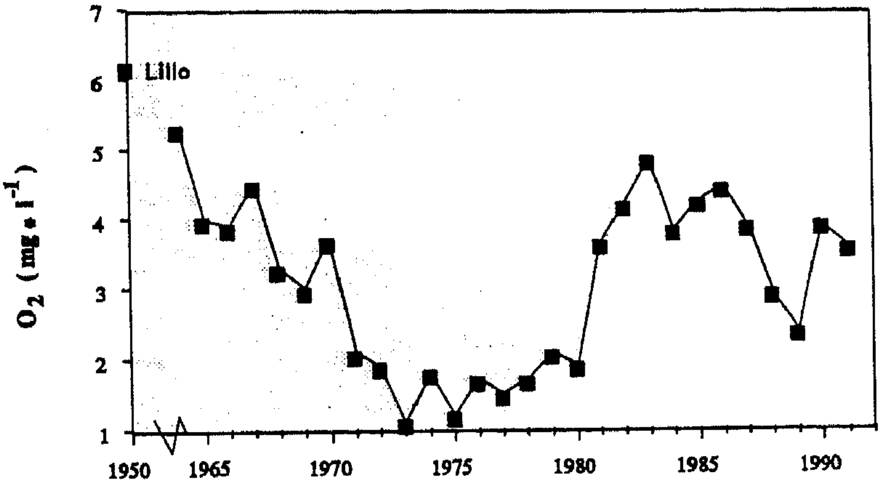


Figure 5. Average annual oxygen concentrations in the Schelde estuary at the Dutch–Belgian border (average salinity 7.5 × $10^{-3}$) from 1964 to 1991

concentrations in the Schelde river and estuary are compared with data for the other rivers and estuaries of the so-called EWERMS (*E*lbe, *W*eser, *E*ms, *R*hine, *M*aas and *S*chelde) region of Europe. Table II shows that the dissolved trace metal concentrations in the Schelde estuary in winter are comparable with the trace metal concentrations in the other estuaries, but that the concentrations in summer are much lower due to the precipitation of metal sulphides in the anoxic upper estuary. Table III shows that of the EWERMS estuaries the Schelde has the highest particulate Zn and Cr contents, whereas the Cd, Cu and Pb contents are comparable with the contents in the other estuaries. Table IV shows that the Schelde estuary has the highest bottom sediment concentrations for almost all trace metals.

The trace metal pollution history is illustrated in Figure 6, in which the annual average calculated trace metal contents of fluviatile suspended matter from 1980 to 1989 are given. The contents were calculated

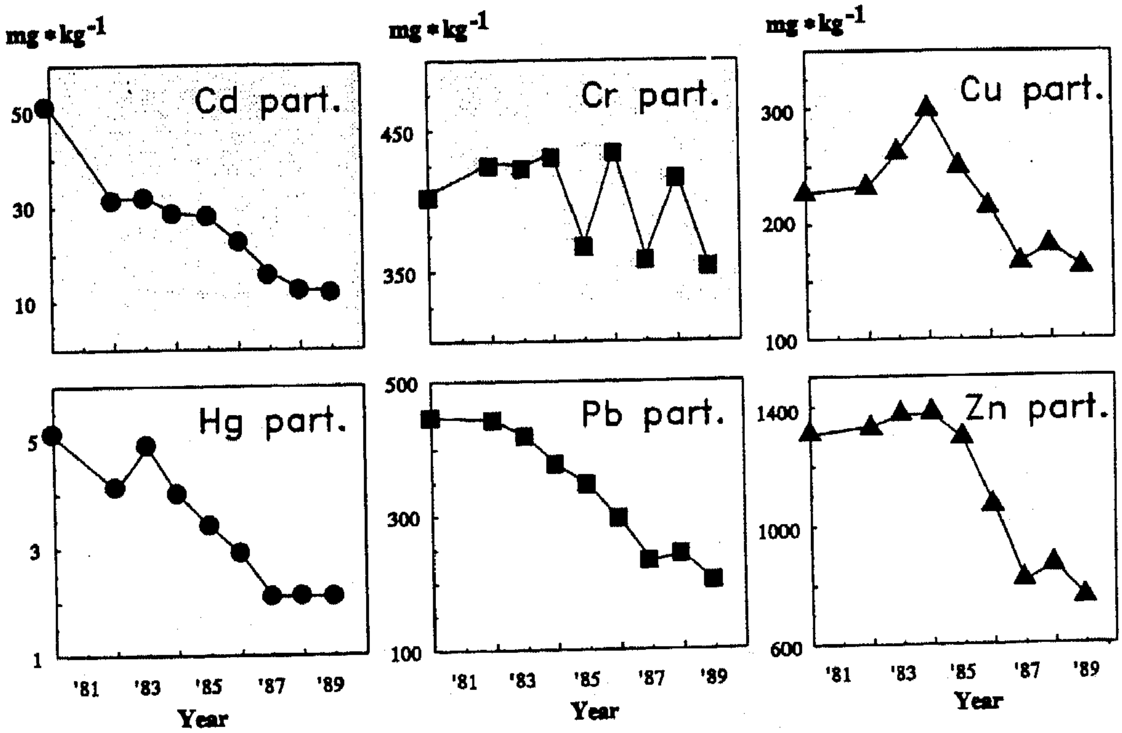


Figure 6. Average annual calculated trace metal concentrations in fluviatile suspended matter of the Schelde estuary from 1980 to 1989

Table V. Average concentrations of some PCBs in suspended sediments of the Elbe, Weser, Ems, Rhine, Maas and Schelde estuaries

| | Concentrations (ng $g^{-1}$) | | | | |
|---|---|---|---|---|---|
| River | PCB 52 | PCB 101 | PCB 153 | PCB 180 | Reference |
| Elbe | 21 | 25 | 28 | 12 | Sturm, *et al.* (1986) |
| Weser | 4·8 | 5·9 | — | 97·6 | Duinker (1986) |
| Ems | 4·2 | 1·8 | — | 29·0 | Duinker (1986) |
| Rhine | 27·3 | 31·1 | 36·9 | 15·4 | Klamer (personal communication) |
| Maas | 7·5 | 15 | 20 | 15 | Ministerie van Verkeer en Waterstaat (1990b) |
| Schelde | 35·9 | 70.5 | 101·9 | 73·6 | Van Zoest and Van Eck (1990) |

from monitoring data for suspended matter at the Dutch–Belgian border; this is a mixture of fluviatile suspended matter with a high trace metal content and marine suspended matter with a low trace metal content. Figure 6 shows that the trace metal concentrations of suspended matter have decreased considerably in the 1980s. These conclusions are supported by a study on trace metal distributions in radiodated sediment cores (Zwolsman and Van Eck, 1993a) and the trace metal contents in bottom sediments in 1959, 1971–9 and 1984–7 in the area around the Dutch–Belgian border (Zwolsman and Van Eck, 1993). The studies show that: (1) the Schelde estuary was already severely polluted with trace metals in 1959; (2) there was a pollution maximum in the mid 1960s; (3) decreasing contents of especially As, Cr, Pb and Zn were present in the 1970s; (4) a second maximum was seen at the end of the 1970s; and, finally (5) decreasing contents of Cd, Cu and Hg were seen in the 1980s.

### *Organic micropollutants*

The pollution status of the Schelde estuary with respect to organic micropollutants is illustrated in Table V and Figure 7 (Van Zoest and Van Eck, 1990; 1993). Table V gives the contents of some organic micropollutants in suspended matter for the EWERMS estuaries. Table V shows that the concentrations in suspended matter from the Schelde estuary are the highest.

Figure 7 gives the average and locally highest concentrations of polychlorinated biphenyl (PCB) 153 and benzo(*a*)pyrene in different segments of the Schelde estuary. The contents of organic micropollutants and trace metals in the bottom sediments gradually decrease from east to west as a result of the mixing of fluvial silt with high micropollutant concentrations and marine silt with low micropollutant concentrations. Discharges into the estuary itself result in locally high concentrations.

The pollution history of Schelde estuary with respect to organic micropollutants is shown in Figure 8 (Van Zoest and Van Eck, 1993); the concentrations of PCBs 52 and 138, fluoranthene and benzo(*a*)-pyrene in the $<63$ μm fraction of a dated sediment core from the Emanuelpolder salt marsh in the eastern part of Western Schelde are given. Figure 8 shows that the sharp increase in the use of PCBs since 1940 resulted in maximum concentrations of PCBs around 1965. After 1965 the PCB content decreased two to three fold. Maximum concentrations of polycyclic aromatic hydrocarbons (PAHs) are also found around 1965. In contrast with PCBs, the PAH concentrations have now decreased to below the 1940 level.

## EFFECTS OF POLLUTION

The high concentrations of contaminants have several different effects on the biota of the Schelde estuary. A summary is given by Stronkhorst (1993). In the fluvial and upper estuary the oxygen status, an important biological indicator, is poor and the water quality standard of 5 mg $l^{-1}$ $O_2$ is not met. Biological investigations show that the fluvial estuary in particular is nearly lifeless (De Pauw and Vannevel, 1991). The concentrations of micropollutants almost always exceed the official Dutch standards, which are based on the relevant ecotoxicological data for freshwater organisms (Van der Gaag, *et al.*, 1991).

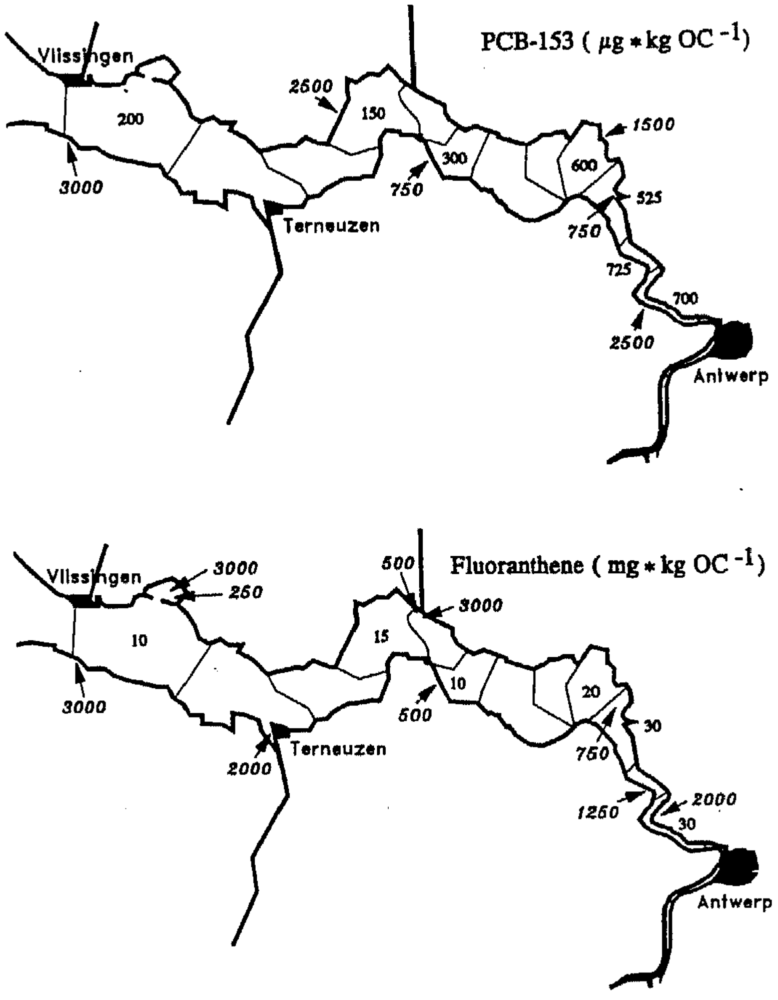


Figure 7. Average and locally highest PCB 153 and fluoranthene concentrations in the bottom sediments of the 14 compartments (see Figure 9) of the Schelde estuary water quality model. OC = organic carbon

In the lower estuary or Western Schelde several different effects are seen. Tributyltin concentrations are high, especially near discharge points and in harbours and marinas (Laane, *et al.*, 1989). The concentrations in these areas are higher than 1 ng $l^{-1}$, the concentration which causes sterility in the dog whelk (*Nucella lapillus*) and leads to reproduction failure and finally to local extinction. A field survey in 1988 indeed showed no live dog whelks along the Western Schelde coastline. A feeding study conducted by Reijnders (1986) on common seals (*Phoca vitulina*) has shown that a population fed with contaminated flounders (*Platichthys flesus*) from the Dutch Waddenzee had a decrease in reproduction success of 60 per cent compared with the group fed with fish from the Atlantic Ocean. PCBs were thought to be responsible for the decrease in reproduction success. The PCB concentrations in flounders from the Western Schelde are at least as high as those in the flounders used to feed the seals, suggesting a possible impairment of seal reproduction in the Western Schelde estuary.

Kubiak, *et al.* (1989) found a strong relationship between reproduction impairment and the PCB concentrations in eggs from Forster's tern (*Sterna forsteri*) in Lake Michigan. Reproduction in the polluted colony was 85 per cent lower than in the control colony. The PCB concentration in eggs from sandwich tern (*Sterna sandvicensis*) in the mouth of the Schelde estuary suggests that the reproduction success of this colony is probably not affected, in contrast with the success of the colony of the common tern (*Sterna hirundo*) in the Saeftinghe salt marsh. Den Besten (1991) suggested that the local extinction of the sea star (*Asterias rubens*) in the Western Schelde is probably related to reproduction failure caused

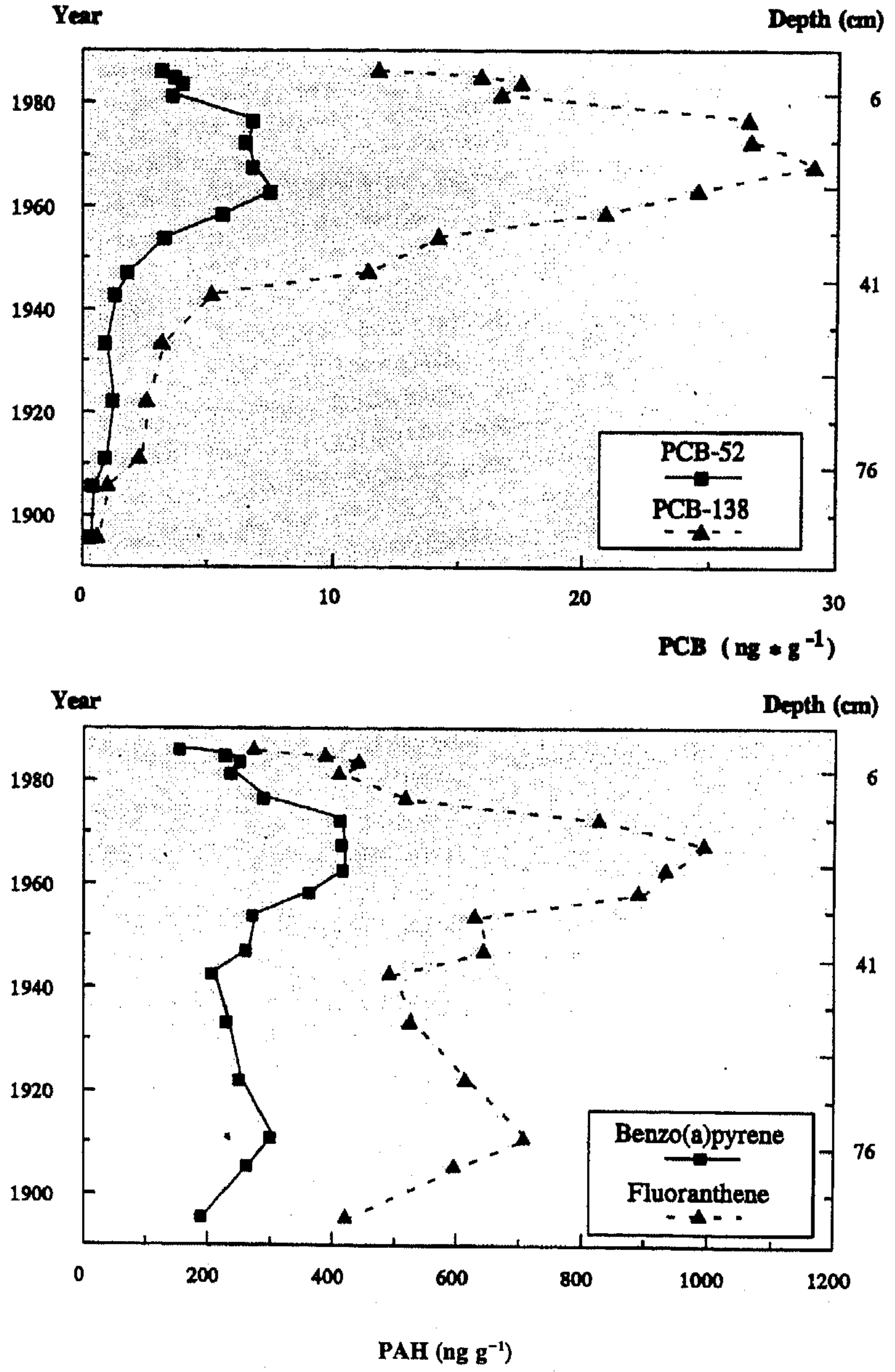


Figure 8. PCB 52, PCB 138, benzo(*a*)pyrene and fluoranthene concentrations as a function of sediment depth and age in the <63 μm fraction of a radiodated sediment core from the Saeftinghe salt marsh of the Schelde estuary

by the high PCB and cadmium concentrations. Veldhuizen-Tsoerkan (1991) concluded that high concentrations of micropollutants such as cadmium in mussels from the Western Schelde result in an increased vulnerability to natural stresses such as temperature changes. Stronkhorst and Van den Hurk (1990) showed that the general gradient in sediment pollution status from the upper to lower estuary coincides with the percentage mortality of oyster larvae.

## SCHELDE ESTUARY WATER QUALITY MODEL

An outline of the Schelde estuary water quality model is given in Van Eck and De Rooij (1990). The water quality model used here is described in Van Gils, *et al.*, (1993) and the bioaccumulation model is

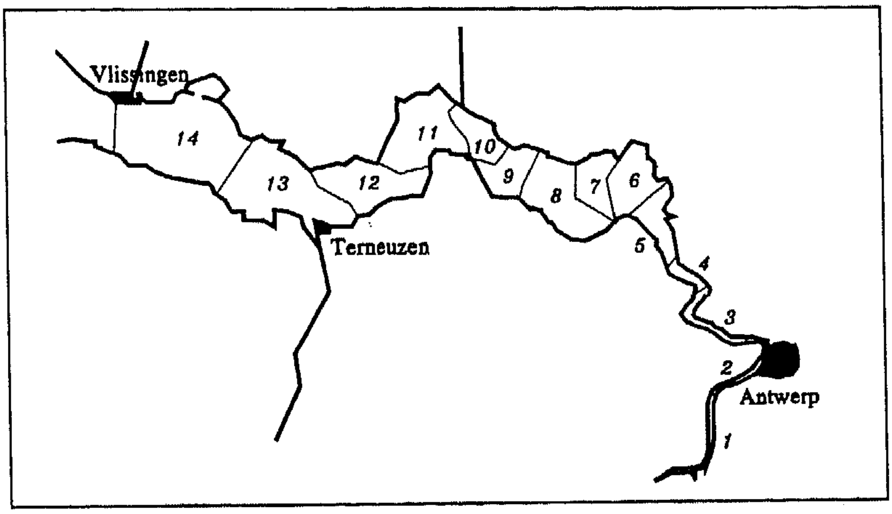


Figure 9. The 14 compartments of the Schelde estuary water quality model

described in Kooijman and Van Haren (1990). Briefly, the water quality model developed is a one-dimensional dynamic tidal-average box model (14 compartments; see Figure 9) for the Schelde estuary (salinity 0–30 $\times 10^{-3}$) for personal computers. It has been calibrated for 1987 and validated for 1980–9. A one-dimensional approach was chosen because the Schelde estuary is vertically well mixed and the lateral gradients are small compared with the longitudinal gradients. The parameters modelled are chloride, suspended matter, dissolved oxygen, pH, BOD, dissolved organic carbon (DOC), dissolved nitrogen species, dissolved reactive silicate, chlorophyll *a*, and dissolved, particulate and bottom sediment Cd, Cu, Cr, Zn, benzo(*a*)pyrene, fluoranthene, PCB 52, PCB 153 and lindane. Suspended matter concentrations and the basic water quality (Cl, $O_2$, DOC, pH) were calculated first because they largely determine the behaviour of micropollutants. Advective and dispersive water transport were taken into account. The sediment transport in the model is based on a one-dimensional sediment balance and a resuspension/sedimentation of the upper 0·5 m of sediment twice a year. The model calculates processes that attain equilibrium instantaneously, such as the pH–$CO_2$–alkalinity system, and kinetically controlled processes such as the decay of organic matter, nitrification/denitrification and reaeration. The inputs for the model are the discharges at the boundaries of the model and along the estuary from (un)treated industrial and domestic waste waters, canals and polders, and in parts from deposition.

Special attention has been given to modelling trace metals (see Figure 10) because metal sulphides are present in the anoxic or suboxic upper estuary (Zwolsman, *et al.*, 1993). The total metal concentration is divided into two parts, suspended metal sulphides and equilbrated metals, using the $K_d$ value for the oxygenated lower estuary and the measured dissolved metal concentrations. The oxidation of suspended metal sulphides is described as a function of temperature and oxygen in the kinetic part of the model. The partition of equilibrium metals over dissolved species and suspended metals depends on the pH, salinity, DOC and alkalinity, and is described by the equilibrium part of the model.

## MODEL SIMULATIONS

The background to the hypothesis is that in the oxygenated Western Schelde estuary the distribution coefficients ($K_d$) for trace metals are higher than in comparable estuaries such as the Rhine (Comans and Van Dijk, 1988) (Figure 11) (see Ouboter and De Rooij, 1990). Figure 11 shows significantly higher distribution coefficients for Cd in the Western Schelde than in the Rhine estuary. Higher pH values in the Western Schelde, which result in higher $K_d$ values, are not responsible for the difference. The pH in the Western Schelde is even lower than in the Rhine estuary. The high adsorption capacity of the Schelde estuary suspended matter probably results from the precipitation of FeOOH in the (high turbidity) transition zone between the anoxic upper and (sub)oxic lower estuary, from the high organic matter

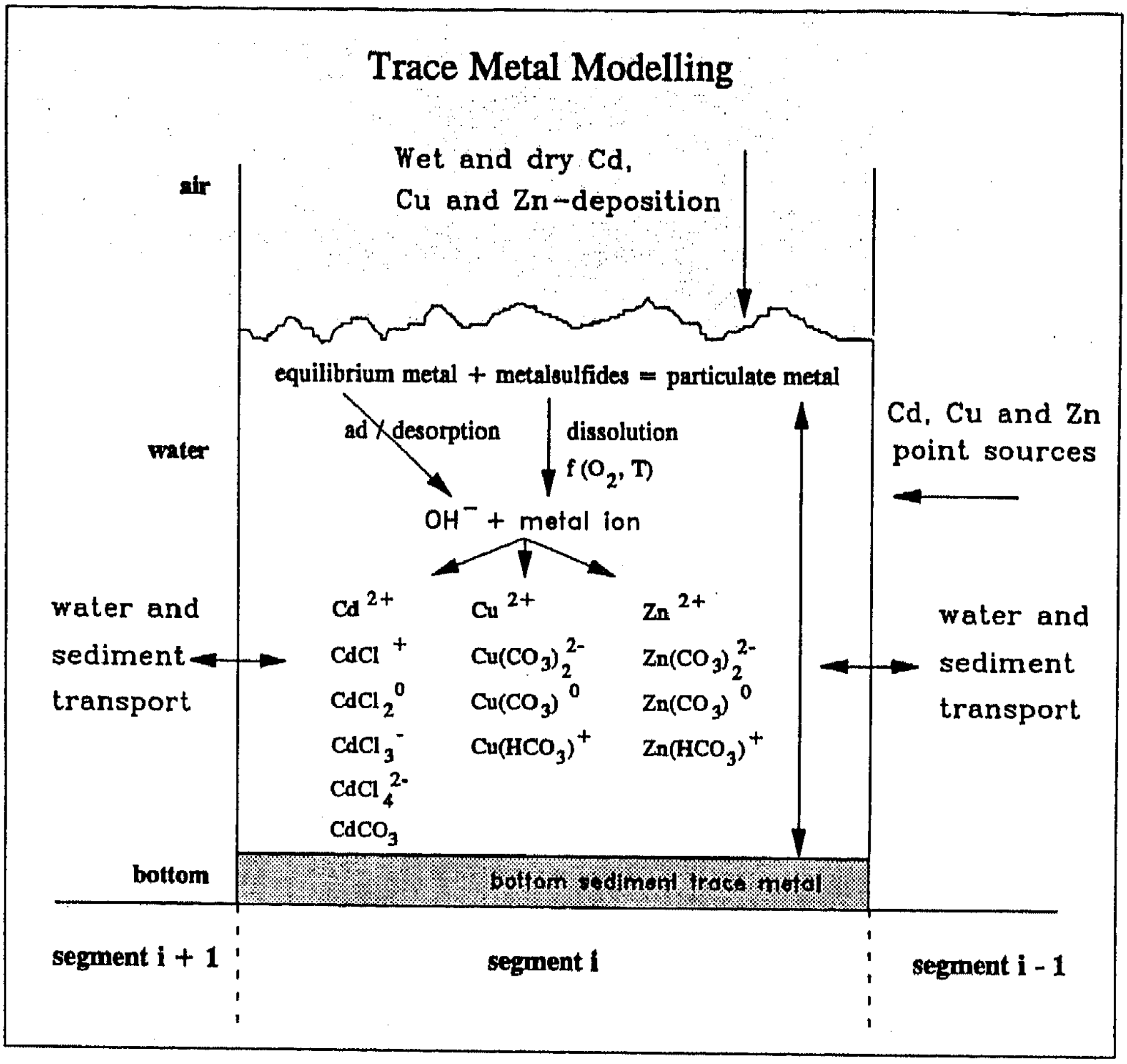


Figure 10. Trace metal modelling in the Schelde estuary water quality model

content, or from the organic matter composition in the upper estuary. Figure 11 suggests that $K_d$ values in the Western Schelde will become lower in the future and therefore higher dissolved (bioavailable) trace metal concentrations, perhaps even at lower trace metal discharges, will result. The following four model simulations were performed to test this hypothesis and to determine if the sediments of the Schelde estuary are a potential CTB (Stigliani, 1991): (1) a 10 year model nominal run with no reduction in trace metal discharges and the calibrated $K_d$ values: (2) a 10 year model run with a 50 per cent reduction in all discharges (trace metals and all other compounds) and the calibrated $K_d$ values: (3) a 10 year model run with 50 per cent reduction in all discharges and instantaneously new $K_d$ values; and (4) a nine year model run with a 50 per cent reduction in all discharges and the calibrated $K_d$ values, followed by a one year model run with new $K_d$ values.

The results of the model simulations are given in Figure 12. This figure shows the dissolved and bottom sediment Cd concentrations in the first and tenth years in compartment 5, just across the Dutch–Belgian border, and in compartment 14 adjacent to the North Sea (see Figure 9) for the four simulations.

Figure 12 shows that the dissolved concentrations in the nominal run remain the same during the 10 years. The dissolved concentrations in winter for the first year in compartment 5 at 50 per cent reduction (run 2) are slightly higher than in the nominal run because the higher oxygen concentrations in winter in the preceding compartments 3 and 4 cause a higher oxidation of metal sulphides. After 10 years the dissolved concentrations in compartment 5 in run 2 are always lower than in the nominal run. In

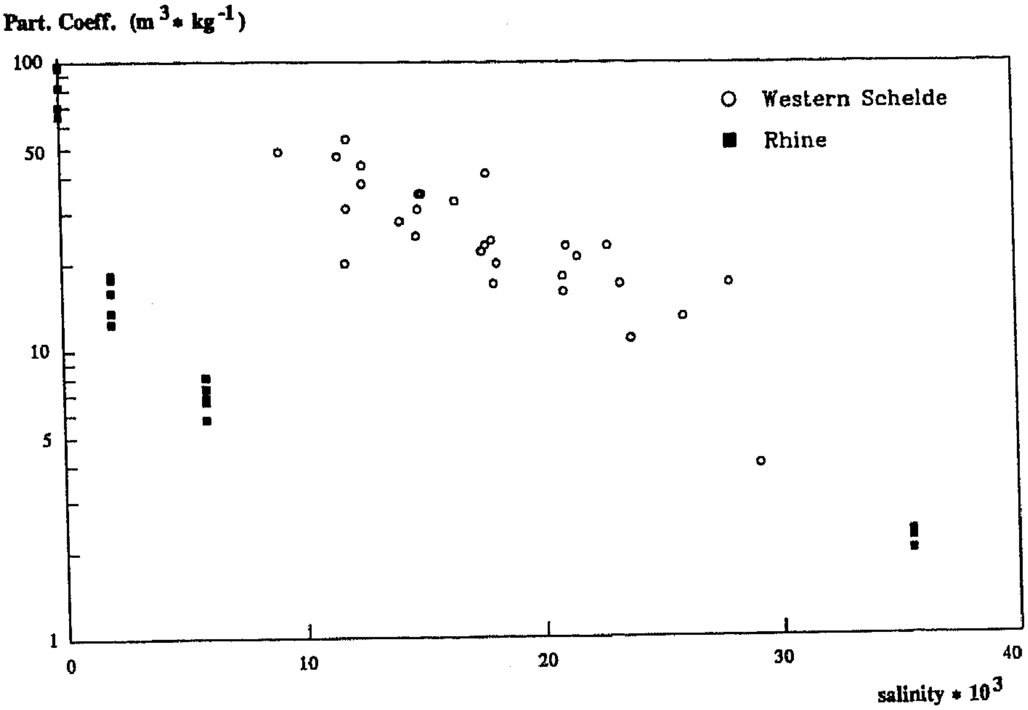


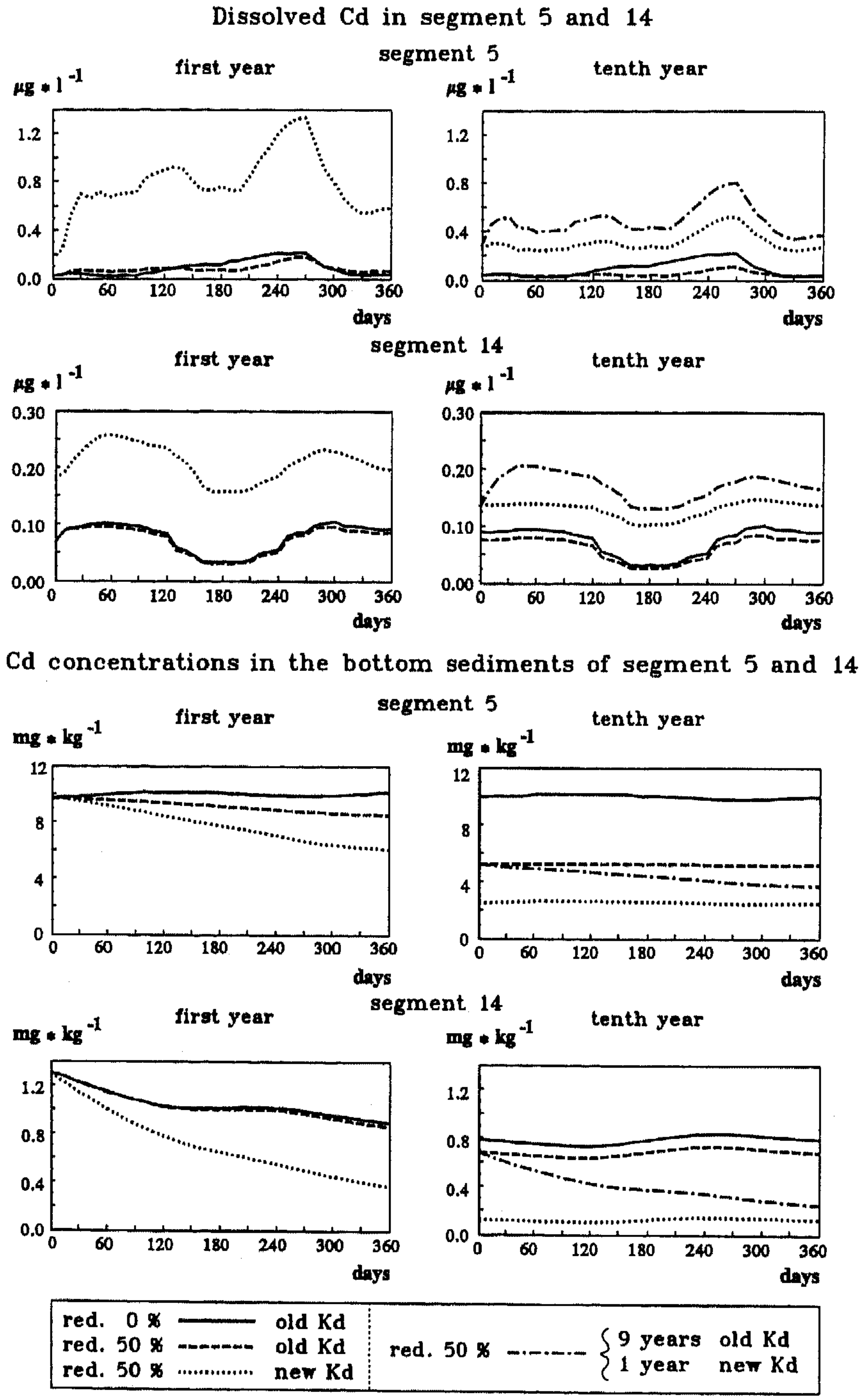
Figure 11. Relationship between the distribution coefficient $K_d$ of cadmium and salinity for the Western Schelde and Rhine estuaries. Data from Zwolsman and Van Eck (1993) and Comans and Van Dijk (1988)

compartment 14 the dissolved concentrations in run 2 are always lower than in the nominal run, as expected. A 50 per cent reduction and instantaneously new (lower) $K_d$ values (run 3) result, in compartments 5 and 14, in an immediate and strong increase in dissolved Cd concentrations because of the desorption of Cd from resuspended sediments. After 10 years the concentrations have decreased, but are still higher than in the nominal run because the desorption of resuspended sediments still supplies enough Cd to keep the dissolved concentrations high. The dissolved concentrations in compartments 5 and 14 in run 4 in the tenth year are higher than in run 3 because the old $K_d$ values have decreased during the first nine years in run 4 the bottom sediment concentrations less than in run 3. Finally, Figure 12 shows that after 10 years the real dissolved Cd concentrations at 50 per cent reduction for all discharges will probably lie between the concentrations predicted by runs 3 and 4.

The data in Figure 12 show that the bottom sediment concentrations in the nominal run remain the same during the 10 years, as expected. The initial decrease in compartment 14 is due to a slightly too high assumed initial bottom concentration. A reduction of 50 per cent in all discharges and the old $K_d$ values (run 2) also reduces the bottom concentration in compartment 5 by about 50 per cent in 10 years. The reduction is much less in compartment 14 because the time required to reduce the concentration in compartment 14 is much higher than 10 years. It also illustrates that a long time is needed to restore the Schelde estuary. The reduction is much stronger (75 per cent) in compartments 5 and 14 if lower $K_d$ values are assumed due to the release of Cd from the resuspended bottom sediments. We must, however, also realize that the price to be paid for a rapid improvement in the Schelde estuary is much higher pollutant loads to the North Sea. In run 4 the contents in the tenth year decrease, as expected, because of the lower $K_d$ values. The decrease in compartment 14 is higher than in compartment 5 because the concentrations in compartment 5 were reduced to a considerable extent during the first nine years with 50 per cent reduction in discharge and using the old $K_d$ values. The real bottom sediment Cd concentrations after 10 years will again probably lie between the concentrations predicted by runs 3 and 4.

## ACKNOWLEDGEMENTS

The help of B. J. Kater in carrying out the model simulations is gratefully acknowledged. J. P. F. Pieters and G. Burger processed the data and drew the figures.



Dissolved Cd in segment 5 and 14

Cd concentrations in the bottom sediments of segment 5 and 14

Figure 12. Dissolved cadmium concentrations and bottom sediment cadmium concentrations in compartments 5 and 14 of the Schelde estuary in the first and tenth years in four different 10 year model simulations

## REFERENCES

Ahlf, W. 1983. 'The river Elbe: behaviour of Cd and Zn during estuarine mixing', *Environmental Technology Letters*, **4**, 405–410.

Ahlf, W. and Wellershaus, S. 1984. 'Trace metals in the Elbe river estuary', pp. 257–260 *in* J. P. Vernet (ed.) *Interactions Between Sediments and Water*, CEP Consultants, Edinburgh.

Boderie, P. M. A., Zwolsman, J. J. G., Van Eck, G. T. M. and Van der Weyden, C. H. 1993. 'Nutrient biogeochemistry in the water column (N, P, Si) and pore-water (N) of sandy sediment of the Scheldt estuary, S.W. Netherlands', *Netherlands Journal of Aquatic Ecology*, **27**, 309–318.

Calmano, W. and Wellershaus, S. 1982. 'Dredging of contaminated sediments in the Weser Estuary: Chemical Forms of some Heavy Metals.' *Environmental Technology Letters*, **3**, 199–208.

Calmano, W., Wellershaus, S. and Liebsch, H. 1985. 'The Weser estuary: a study on heavy metal behaviour under hydrographic and water quality conditions', *Veröffentlichungen Institut Meeresforschung Bremerhafen*, **20**, 151–182.

Comans, R. N. J. and Van Dijk, C. P. J. 1988. 'Role of complexation processes in cadmium mobilization during estuarine mixing', *Nature*, **336**, 151–154.

Den Besten, P. J. 1991. 'Effects of cadmium and PCBs on reproduction of the sea star *Asterias rubens*', *Thesis*, Rijksuniversiteit Utrecht.

De Pauw, N. and Vannevel, R. 1991. 'Macro-invertebrates and water quality', *Dossier No. 11*, Stichting Leefmilieu, Antwerp.

Duinker, J. C. 1986. 'The role of small, low density particles on the partition of selected PCB congeners between water and suspended matter (North Sea area)', *Netherlands Journal of Sea Research*, **20**, 229–238.

Duinker, J. C., Nolting, R F. and Michel, D. 1982. 'Effects of salinity, pH and redox conditions on the behaviour of Cd, Zn, Ni and Mn in the Scheldt estuary', *Thalassia Jugoslavia*, **18**, 191–201.

Gemeinsames Bund-Länder mess programm für die Nordsee, 1990. *Gewässergütemessungen im Küstenbereich der Bundesrepublik Deutschland 1988/1989.*

Kooijman, S. A. L. M. and Van Haren, R. J. F. 1990. 'Animal energy budgets affect the kinetics of xenobiotics', *Chemosphere*, **21**, 681–694.

Kramer, C. J. M., Misdorp, R. and Duijts, R. 1989. *Contaminants in Sediments of North Sea and Wadden Sea*, Rijkswaterstaat Dienst Getijdewateren, Den Haag and MT-TNO, Den Helder.

Kubiak, T. J., Harris, H. J., Smirh, L. M., Schwartz, T. R., Stalling, D. L., Trick, J. A., Sileo, L., Docherty, D. E. and Erdman, T. C. 1989. 'Microcontaminants and reproductive impairment of the Foster's Tern on Green Bay, Lake Michigan—1983', *Archives of Environmental Contamination and Toxicology*, **18**, 706–727.

Laane, R. W. P. M., Marquenie, J., Ritsema, R., Van Den Ende, K. C. J., Donard, O. F. X. and Quevauviller, Ph. 1989. 'Impact of tributyltin in Dutch coastal waters: an environmental problem', *Report No. 89.024*, Rijkswaterstaat Dienst Getijdewateren, Den Haag.

Ministerie van Verkeer en Waterstaat 1990a. 'Resultaten van het waterkwaliteitsonderzoek in de Rijn in Nederland in 1970–1989', *Notanr. 90,048, Rijkswaterstaat Dienst Binnenwateren/RIZA, Lelystad.*

Ministerie van Verkeer en Waterstaat 1990b. 'Resultaten van het waterkwaliteitsonderzoek in de Maas in Nederland in 1970–1989', *Notanr. 90.047, Rijkswaterstaat Dienst Binnenwateren/RIZA, Lelystad.*

Ministerie van Verkeer en Waterstaat 1990c. 'Diffuse verontreiniging. Basisrapport t.b.v. Derde Nota Water huishouding', *Notanr. 90.016, Rijkswaterstaat Dienst Binnenwateren/RIZA, Lelystad.*

Ministerie van Verkeer en Waterstaat 1991. 'Grensoverschrijdende vrachten bij Schaar van Ouden Doel in de periode 1980 t/m 1990', *Notitie GWWS-91.13091, Rijkswaterstaat Dienst Getijdewateren, Middelburg.*

Ouboter, M. R. L. and De Rooij, N. M. 1990. 'Use of an autocalibration procedure to evaluate the consistency of a data set in relation to geochemical model formulations', pp. 195–202 *in* K. Kovar (ed.) *Calibrations and Reliability in Ground Water Modelling*, IAHS Press, Wallingford.

Reijnders, P. J. H. 1986. 'Reproduction failure in common seals feeding on fish from polluted coastal waters', *Nature*, **324**, 456–457.

Salomons, W. and Eysink, W. D. 1981. 'Pathways of mud and suspended trace metals from rivers to the southern North Sea', pp. 429–450 *in* Nio, S. D. Shüttenhelm, R. T. E. and Van Weering, T. C. E. (eds.), *Holocene Marine Sedimentation in the North Sea Basin. Special Publication of the International Association of Sedimentologists No. 5*, Blackwell Scientific, Oxford.

Somville, M. and De Pauw, N. 1982. 'Influence of temperature and river discharge on water quality of the Western Schelde estuary', *Water Research*, **16**, 1349–1356.

Steneker, R. C. H., Van Der Sloot, H. A. and Das, H. A. 1988. 'Leaching studies on dredged material in oxidized and reduced state', *The Science of the Total Environment*, **68**, 11–23.

Stigliani, W. M. 1991. 'Chemical time bombs: definition, concepts, and examples', *Executive Report 16*, International Institute for Applied Systems Analysis, Laxenburg.

Stronkhorst, J. 1993. 'The environmental risks of pollution in the Scheldt estuary', *Netherlands Journal of Aquatic Ecology*, **27**, 383–393.

Stronkhorst, J. and Van den Hurk, P. 1990. 'Toxicity of sediments from the Scheldt estuary; results of bio-assays with oyster larvae', *Report GWWS-90.087*, Ministry of Transport, Public Works and Water Management, Tidal Waters Division, Middelburg.

Strum, R., Knauth, H.D., Reinhardt, K. H. and Gandrass, J. 1986. 'Chlorkohlenwasserstoff-Verteilung in Sedimenten und Schwebstoffen der Elbe', *Vom Wasser*, **67**, 23–38.

Tweede Kamer der Staten-Generaal 1989. 'Water voor nu en later, Derde Nota Waterhuishouding', *Tweede Kamer Vergaderjaar*, 1988–1989, **21 250**, nrs 1–2, SDU Uitgeverij, 's Gravenhage.

Van der Gaag, M. A., Stortelder, P. B. M., Van der Kooij, L. A. and Bruggeman, W. A. 1991. 'Setting environmental quality criteria for water and sediment in The Netherlands: a pragmatic ecotoxicological approach', *European Water Pollution Control*, **1**, 1–8.

Van Eck, G. T. M. and De Rooij, N. M. 1990. 'Development of a water quality and bio-accumulation model for the Scheldt estuary', pp. 95–104 *in* W. Michaelis (ed.) *Estuarine Water Quality Management*, Springer Verlag, Berlin.

Van Gils, J. A. G., Ouboter, M. R. L. and De Rooij, N. M. 1993. 'Modelling of water and sediment quality in the Scheldt estuary', *Netherlands Journal of Aquatic Ecology*, **27**, 257–265.

Van Maldegem, D. C., Mulder, H. P. J. and Langerak, A. 1993. 'A cohesive sediment balance for the Scheldt estuary', *Netherlands Journal of Aquatic Ecology*, **27**, 247–256.

Van Zoest, R. and Van Eck, G. T. M. 1990. 'Behaviour of particulate polychlorinated biphenyls and polycyclic aromatic hydrocarbons in the Scheldt estuary', *Netherlands Journal of Sea Research*, **26**, 89–96.

Van Zoest, R. and Van Eck, G. T. M. 1993. 'Behaviour of selected PCBs, PAHs and HCH in the Scheldt estuary, S.W. Netherlands', *Netherlands Journal of Aquatic Ecology*, **27**, 301–308.

Veldhuizen-Tsoerkan, M. 1991. 'Effects of cadmium in the sea mussel *Mytilus edulis L.', Thesis*, Rijksuniversiteit, Utrecht.

Wartel, S. 1977. 'Composition, transport and origin of sediments in the Schelde estuary', *Geologie en Mijnbouw*, **56**, 219–233.

Wollast, R. 1988. 'The Scheldt estuary', pp. 183–193 *in* Salomons, W., Bayne, B. L., Duursma, E. K. and Förstner, U. (eds.) *Pollution of the North Sea: an Assessment*, Springer Verlag, Berlin.

Zwolsman, J. J. G. and Van Eck, G. T. M. 1993. 'Behaviour of trace metals in the Scheldt estuary, S.W. Netherlands', *Netherlands Journal of Aquatic Ecology*, **27**, 287–300.

Zwolsman, J. J. G., Berger, G. W. and Van Eck, G. T. M. 1993a. 'Sediment accumulation rates, historical input, postdepositional mobility and retention of major and trace elements in two salt marsh sediment cores from the Scheldt estuary, S.W. Netherlands', *Marine Chemistry*, **44**, 79–94.