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**The chemistry of the Scheldt estuary with emphasis on
the behaviour of organic micropollutants**

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PREFACE

In the last few years, the interest in pollution problems of the Scheldt estuary has increased. A great variety of pollutants is present in this watersystem. The heavy metal load is high. Despite sanitation programs in Belgium, the oxygen-balance improves only slightly and the upper estuary is still temporarily anoxic. Numerous organic micropollutants are present, some of them in very high concentrations, compared to other Dutch watersystems.

In 1985 the DDMI-DGW project "Chemistry of the eastern part of the Western Scheldt" was started. The purpose of the project was to summarize all the existing data firstly and to describe all geochemical processes that affect the occurrence and behaviour of the pollutants in the estuary, and secondly, to record the lack in necessary knowledge to achieve this.

In chapter one of this report, general characteristics of estuarine water and sediment circulation patterns, as well as aspects of estuarine chemistry are presented. Some general data of the Scheldt estuary are given in the second section of chapter one.

Organic micropollutants are dealt with in chapter two. Before studying estuarine behaviour, some attention is paid to nomenclature and physio-chemical characteristics. A field study has been taken place in winter-spring 1986. During four cruises, the behaviour of PCBs was studied in the Scheldt estuary. The results are to be published elsewhere (van Zoest & van Eck, Behaviour of PCBs in the Scheldt estuary, in prep.).

The chapter concerning nutrients in the Scheldt estuary is presented separately (Zwolsman, 1986: Nutrient biogeochemistry in estuaries, with an emphasis on the Scheldt estuary). The chapter on heavy metal behaviour is in preparation.

The results of this report will be used in the DGW project SAWES (System Analysis Western Scheldt). The purpose of SAWES is to formulate a mathematical model that describes the nutrient and micropollutant behaviour in the Scheldt estuary, which facilitates management decisions.

This report has been composed under the supervision of dr. G.Th.M. van Eck, while the author carried out his duty in substitution of the military service at the DGW of Rijkswaterstaat from April 1985 - October 1986. The gathering of literature for this report has been finished in the summer of 1986.

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1. ESTUARIES; THE SCHELOT ESTUARY

1.1. Characteristics of estuaries, with emphasis on chemical processes

1.1.1. Introduction

The term estuary comes from the Latin adjective aestuarium, which means tidal. An estuary (Fairbridge, 1980) is: "an inlet to the sea reaching into a river valley as far as the upper limit of the tidal rise".

An estuary can be divided into three sectors. Firstly the lower or marine estuary, in free connection with the open sea, secondly the middle estuary subject to strong salt and freshwater mixing, and thirdly the upper or fluvial estuary, characterized by freshwater, but subject to daily tidal action.

The importance of estuaries is manifold. They provide navigational access to a broad hinterland, have sheltered anchorages and most times fertile waters. Man has changed the natural balance within a lot of estuaries by altering the topography and by large-scale pollution. Deforestation of the land leads to increased runoff and, consequently an increased sediment load, while building and paving of large areas produces a quick response of runoff to rainfall.

Estuaries are studied for several reasons. Some are purely scientific, whereas others are related to specific engineering or pollution problems. When considering the chemical and biological aspects of water quality, and related to this, sediment transport and distribution, knowledge of the estuarine water circulation and mixing is essential.

1.1.2. Water and sediment circulation patterns

Bowden (1980) described the main phenomena of water circulation and mixing in estuaries. He distinguished two basic features involving the distribution of the salinity and the dynamics of the flow within an estuary:

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1. There is a horizontal density gradient, from the point(s) of river water inflow to the sea, and

2. The presence of tidal currents.

The density gradient acting alone would cause the river water to flow out as a surface layer over an intruding saltwater wedge. The action of tidal currents introduces a considerable amount of kinetic energy, some of which is used to mix the river and seawater and so modify the circulation. This interaction, in addition to the topography of the estuary, gives rise to a range of circulation types.

Three main types of estuarine circulation can be distinguished:

1. Highly stratified estuaries, in salt wedge estuaries and in many fjords;
2. Partially mixed estuaries, with a significant vertical density gradient which inhibits vertical mixing to some extent;
3. Well mixed estuaries, with a very small vertical salinity gradient.

A rough indication of the characteristics of an estuary is given by the ratio of the freshwater discharge during a tidal cycle and the tidal prism, the volume of water entering the estuary from the sea during flood tide. If this ratio is about 1, salt wedge conditions normally exists. Partially and well mixed conditions are most likely when the ratio is about 0.1, respectively 0.01. It is doubtful, however, whether a single parameter can indicate adequately the overall characteristics of the flow.

In Figure 1, three types (salt wedge and partially mixed estuaries and a transition form) are diagrammatically presented. In a salt wedge estuary (Figure 1a), the river flow dominates the circulation completely. The salt water extends as a wedge into the river and, in the absence of friction, the interface would remain horizontal and extend up the river to where the bed approaches sea level. In practice, due to the small amount of friction between the layers, the interface slopes slightly downwards in the upstream direction. If the velocity

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of the seaward moving layer of river water exceeds a certain value, internal waves, formed at the interface, tend to break and cause entrainment of saltwater into the freshwater.

As a result, the salinity of the water in the upper layer increases, as well as its volume. This usually results in a higher velocity of flow rather than an increase in depth of the layer. A slow movement of water in an upstream direction compensates for the loss by entrainment.

Disturbances at the interface may cause a broad mixing zone, the halocline, in which turbulent processes allow a transfer of the fresher water downwards, as well as saltwater upwards. The halocline is thus an intermediate stage between the salt wedge and partially mixed types (Figure 1b).

In the partially mixed estuary, vertical mixing caused by tidal currents extends over the entire depth and the halocline becomes replaced by a gradual increase in salinity from surface to bottom (Figure 1c). There is still a two layer flow, with a surface of no motion, usually occurring a little above mid-depth. The volume of flow in each layer is typically an order of magnitude greater ($10R$) than the river discharge (R), but an order of magnitude lower than the oscillatory tidal currents ($100R$).

When the influence of tidal mixing relative to that of river flow is very strong, the estuary becomes well-mixed, with very little variation in salinity or mean current with depth. The mean velocity is seaward at all depths. The upstream transport of salt by the mean flow is caused by diffuse processes rather than by advection.

- The circulation pattern governs an important parameter: the residence time. The residence time has influence on the equilibration of certain processes in an estuary. For highly stratified estuaries, residence times may be typically of the order of several days. Residence times

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increase with rising vertical mixing owing to the dilution of freshwater in a large body of seawater (Wollast & Duinker, 1982).

In this classification, it is assumed that circulation occurs entirely in the longitudinal direction and that there are no differences in velocity or density across the estuary. However, the flows involved in these patterns will not be homogeneously distributed (Dyer, 1977). The transverse and vertical component of the spiral flow create secondary flows in the plane of the cross-section. In addition, temperature and wind stress may alter the circulation pattern considerably, with different intensity in time and place (e.g. sheltering).

Dyer (1977) reports the results of a year-long study of the Pontomac estuary, where fluctuations in the circulation pattern were attributable to the wind. The expected pattern of seaward flow and landward bottom flow occurred for only 43% of the time. The reverse was present for 21%, total inflow (storage) occurred for 22% of the time. The remainder was accounted for by total outflow and three layer circulations.

The water movements in the three types of estuaries result in a different behaviour of the sediment load (Dyer, 1979; Figure 2). In a salt wedge estuary the river discharge is large and fluctuates often seasonally. Both suspended and bed load are important. The bed load will be deposited at the tip of the salt wedge, which position is dependend on the river discharge. The sediments may thus be spread over a long distance. The fine grained particles are transported to the sea as a plume.

In a partially mixed estuary, the landward bottom flow is sufficiently strong to move sediment up the estuary as far as the head of the salt intrusion. Around the head of the salt intrusion concentrations become much higher then either in the river or seawater endmembers. Thus, this net non-tidal water movement acts as a sediment trap and forms a

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turbidity maximum. The magnitude and location of the turbidity maximum depends on particle size, the amount of suspended matter available and the strength of the estuarine circulation. In a well mixed estuary a similar situation may prevail, although, the large tidal range may cause more active exchange of the sediment with the offshore waters.

In addition two other sediment transport mechanisms act in estuaries:

1) the net onshore movement of especially sand size material caused by wave action and 2) an unidirectional transport of sediment resulting from the tidal movement: there is a time lag between the tidal current rythm and the changes in suspended matter concentration. An increasing current needs time to stir up sediment from the bottom and carry it upwards, whereas in a decreasing current the suspended sediment needs time to settle.

In some estuaries fluid mud is associated with the turbidity maximum. Mud concentrations exceed 20 g.L^{-1} (Postma, 1980) and are generally around 100 g.L^{-1} or more (McCave, 1979). The fluid mud is mainly built up by settling of material from the overlying turbidity maximum at slack tide.

1.1.3. Quantitative treatment of solute dynamics

One way to describe quantitatively the mixing of sea and freshwater is to treat the solute dispersal according to a one-dimensional advection-diffusion model (Harris et al., 1984; Daamen & Lefèvre, 1983). In such a model secondary flows are ruled out for simplicity, while inhomogenities are assumed to be absent in cross-sections. The formulation of the basis equation used by Daamen and Lefèvre (1983) is:

$$A \frac{dc}{dt} = - \frac{d}{dx} (Qc - AD \frac{dc}{dx}) + \text{local sources} \quad (1.1)$$

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A = the cross-sectional area at mean sea level, at a certain point in the estuary (m^2)

c = the mean tidal, cross-section averaged concentration, ($g.L^{-1}$) at x (m) and time t (s)

Q = the discharge at A ($m^3.s^{-1}$)

D = the dispersion coefficient ($m^2.s^{-1}$)

An estuary is subdivided into sections of some kilometers. The dispersion coefficients are calibrated for each section using salinity and discharge observations, commonly measured during periods of several years. The coefficients do not only representate molecular and turbulent diffusion, but also the large scale mixing due to tidal action.

When calibrating the model, a conservative parameter is used, i.e. the salinity. Conservative behaviour means that the aqueous concentration of a solute is fully dependent on the physical mixing of two (or more) water bodies and not susceptible to chemical or biological reactions (removal or enrichment processes). Although not all, especially minor constituents, that form part of the salinity, behave conservatively, the salinity is treated as a conservative parameter within the precision of the measurement.

For convenience, salinity is commonly used as an indicator for the freshwater - seawater ratio. However, because of the high correlations, also the conductivity, the density or the chlorinity may be used. Millero (1984) determined these relationships in estuarine waters. The true salinity (S_{true}) can be coupled to the chlorinity (Cl, as g halide per kg of solution) by:

$$S_{true} = 0.092 + 1.80271 Cl \quad (1.2)$$

The relations between the salinity and the conductivity and density yielded respectively S_{cond} and S_{dens} , which were expressed as a function of Cl. It appeared that S_{dens} showed good agreement with S_{true} ,

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while the discrepancy of S_{cond} with S_{true} increases with smaller chloride concentration. This is due to the different specific conductivities of major components in seawater and riverwater. Millero (1984) concluded that if errors of ± 0.04 ‰ in salinity can be tolerated, no knowledge of the detailed ionic composition is necessary in estuarine waters.

Officer (1979) discussed non-conservative behaviour in estuaries. His relations are valuable at steady state conditions. In determining the behaviour of a dissolved constituent, S-c diagrams are constructed. The concentrations of the solute under consideration is plotted as a function of the salinity. The observed S-c relation is compared to the theoretical (conservative) dilution line. In Figure 3 the various possibilities are considered: the concentration of the solute may be lower in the river endmember relative to the seawater or may be higher (the most prevailing situation). In both cases, addition and removal processes may occur.

For one-dimensional, tidally averaged conditions, the net flux F of a solute, as measured in a downstream direction, x , will be:

$$F = Qc - DA \frac{dc}{dx} \quad (1.3)$$

At steady state, the one-dimensional continuity equation may be formulated for the conservative salinity distribution:

$$Qs - DA \frac{ds}{dx} = 0 \quad (1.4)$$

Combining 1.3 and 1.4, it gives:

$$F = Q \left(c - s \frac{dc}{ds} \right) \quad (1.5)$$

The removal or loss, L , during estuarine mixing is simply the difference in the flux at the river and ocean end. Thus (see Fig. 4):

$$L = Q \left(c - s \frac{dc}{ds} \right)_{s_0} - Q \left(c - s \frac{dc}{ds} \right)_{s_1} \quad (1.6)$$

For $S_0 = 0$, the fractional loss, G , within the estuary, referred to F , is:

$$G = \frac{L}{Q \cdot c_0} = \frac{c_0 - c_0^*}{c_0} \quad (1.7)$$

where c_0^* is the regression line intercept at $S = 0$ for the tangent to the c - S curve in the vicinity of s_1 . Curve B in Figure 4a obeys equation 1.7, where the fractional loss can be determined. For curve C, no net flux out of the estuary is present.

Equation 1.5 defines a linear relation between c and S for conservative behaviour, anywhere in the estuary. In Figure 5 the diagram is redrawn in a way, that the loss is entirely associated with a transition region between two linear regions.

The applicability of the model is wholly dependent on the assumption that steady state is a reasonable approximation. Steady state may not be achieved within the relevant time constant within an estuary, the residence time, due to river runoff and/or source variations.

1.1.4. The water phase

The major constituents in water behave conservatively. No evidence is present in literature for non-conservative behaviour of Na^+ , K^+ , Ca^{2+} , Cl^- , SO_4^{2-} during the mixing of freshwater and seawater (Liss, 1976). Mg^{2+} may have a conservative distribution, but may also be removed as a result of ion exchange on clay mineral sites.

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The pH distribution in estuaries was studied by Mook & Koene (1975). They found that the pH as a function of the salinity shows a minimum value, going in seaward direction from 7.0-7.5 in the river to pH 8.3 in the seawater. This is the result of the rapid increase of the apparent dissociation constants of carbonic acid with salinity. The pH distribution is therefore simply a consequence of the physical mixing process. Besides, there will be a variation in pH due to biological processes with a marked seasonal dependence. During an algal bloom (which in itself is salinity dependent), nutrients and CO₂ will be assimilated. Thus, small temporal and spatial variations in the pH distribution may be expected.

In general, oxygen concentrations decrease with increasing temperature and salinity. McKay & Gilligan (1972) investigated the factors influencing the dissolved oxygen level in the Clyde estuary. The most important factor appeared to be the Biochemical Oxygen Demand (BOD). Dependencies on tidal range (negatively) and river discharges (positively correlated) were also established.

Morris et al. (1982) found a dissolved oxygen minimum in the Tamar estuary, related to the turbidity maximum. It was suggested that more or less permanently suspended trapped particles are the predominant oxygen consumers. In a prior publication, Morris et al. (1978) investigated the very low salinity region (0.1-1.0 ‰) in the Tamar estuary. According to this study, oxygen was also consumed in the water column. The decomposition of riverine plankton was probably responsible for this observation.

Some conflicting evidence is presented in literature concerning the behaviour of dissolved organic matter (DOM). It seems that the distribution of DOM (often also denoted as dissolved organic carbon, DOC) may be different in various estuaries. Sholkovitz (1976) mixed filtered river water with seawater and observed flocculation (his appellation for coagulation, flocculation and precipitation, i.e. transforma-

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tion from the dissolved to the solid phase) of dissolved organic matter. Removal of DOM and humic material (which accounts for 4-20% of DOM in 4 Scottish rivers) increases as the salinity increases from zero to 15-20 ‰, above which no additional removal occurred. In all cases removal was rapid. The percentage of DOM which was removed upon mixing varies between 3 and 11%. Non-conservative behaviour was also found by Höpner and Orliczek (1978), who performed mixing experiments with filtered bog water.

Hunter & Liss (1982), Laane (1982) and Mantoura & Woodward (1983) found conservative behaviour of DOC in respectively four English estuaries, the Ems-Dollard estuary and the Severn estuary. In the Severn, where the water remains 100-200 days, neither microbial degradation, nor flocculation or adsorption processes affected the DOC distribution. Half lives of DOM exceeded five years. The DOM of this estuary consisted approximately for 80% of fulvic/humic acids. In general, fulvic acids ($M < 1000$) do not flocculate. These substances are hydrophilic polyanions and are stabilized in a saltwater regime. It is suggested by these authors that DOM consisted mainly of fulvic acid and that estuarine flocculation was restricted to higher molecular weight constituents.

Carlson et al. (1985) concluded from ultrafiltration experiments that their data do not clearly indicate loss of high molecular weight DOM during estuarine mixing. In the Beaulieu estuary, Moore et al. (1979) found that the DOC behaved essentially conservatively. The dissolved organic material existed mainly in the molecular weight range of 10^3 - 10^5 .

So far, the distribution of DOM due to inorganic processes (flocculation) has been discussed. Some organic processes, often seasonally dependent, are present when primary productivity is not strongly inhibited (e.g. by high turbidities). Dissolved organic material may be the carbon source for bacteria (Head, 1976 and references therein). Further, DOC may be (partly) released from the pore water after decomposition processes and DOC is produced by algae.

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Owens (1985) and Sholkovitz & Price (1980) showed in respectively the Tamar and Amazon estuaries that biological transformations can significantly alter the chemical composition of the suspended material. From $\delta^{15}\text{N}$ (Owens, 1985), and element/Al ratios (Sholkovitz & Price, 1980) it is concluded that estuarine material of biological origin (phytoplankton) is mixed with material of riverine and marine sources.

Sigleo & Helz (1981) determined seasonal variations in the composition of the colloidal material in the Patuxent estuary. In summer, the colloidal fraction (in the study under consideration: $< 0.40 \mu\text{m}$) is composed of mineral particles and planktonic organisms. In winter, both fractions are mainly composed of mineral components. Thus, especially for summer samples, the operationally defined distinction between particulate and dissolved-colloidal has also a more fundamental character.

The aggregation of colloids in estuarine systems is dependent on hydrodynamic factors that determine the rate of collisions and by interfacial effects that (de)stabilize aggregates (Hunter & Liss, 1982). Concerning the second point, it is generally stated, that colloidal stability is decreased at increasing electrolyte concentration due to the decreasing extent of the electric double layer. In the estuarine mixing zone, during initial mixing, ion adsorption undergoes large changes which results in flocculation of riverine colloids. This may lead to differential settling of different clay minerals (e.g. Edzwald et al., 1974).

However, surface charge measurements do not confirm this (Hunter & Liss, 1982; Hunter, 1983; Loder & Liss, 1985). The results of these studies indicate that the surface charge distribution of estuarine colloids is highly uniform and always negative, in spite of the mixed nature of colloids and particulates in estuaries. It is therefore probable that surface charge is controlled by organic coatings (treatment of particulates with UV radiation resulted in positive surface charges

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(Loder & Liss, 1985)). It is concluded from these studies that flocculation occurs independently on the colloidal particulate matrix and that colloid destabilization probably results from compression of the electrical double layer.

1.2. The Scheldt estuary

1.2.1. Introduction

The Scheldt is a small river on a world scale. This can be evaluated in terms of some important parameters: drainage area, length of the major stream and freshwater discharge. To visualize the above statement, one can compare these figures for the Scheldt with the world largest river, the Amazon, and some other rivers (Table 1).

Table 1. Some important parameters for the Scheldt, compared with other fluvial systems. Data from Fairbridge (1980)

	length km	discharge area km ² * 1000	mean discharge m ³ .s ⁻¹
Scheldt	280*	22**	100**
Thames	340	16	80
Seine	780	79	500
Rhine	1360	224	2500
Brahmaputra-Ganges	2980	935	17700
Yangtze-Kiang	5000	1770	30000
Niger	4070	1500	14300
Mississippi-Missouri	6400	3250	18000
Amazon	6300	7050	200000

* v.d. Kooy (1982)

** Hendriksma (1981)

The Scheldt will thus not be of major importance in flux calculations of riverine dissolved constituents and solid material to the oceans. The importance of an investigation of the estuarine chemistry of the Scheldt lies within its regional functions and its acute pollution problems. Besides temporarily anoxic conditions in the brackish water region of the estuary, there is a considerable load of heavy metals and organochlorines.

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1.2.2. Description of the Scheldt estuary

The drainage area is shown in Figure 6. The Scheldt which is exclusively provided with rainwater, drains a small region in northern France, western Belgium and a small part of southwestern Netherlands. The largest freshwater mass is contributed by the Rupel, with an average fraction of 58% (Baeyens & Jacques, 1979).

The estuary may be divided into three sections:

1. Genthbrugge-Rupelmouth, where only freshwater is present. At Genthbrugge there is still a tidal rise of approximately 2 meters. This is at the same time the tidal limit, because of the presence of a dam;
2. A single channel and transitional sector from Rupel to Walsoorden;
3. A multiple channel section, with typical ebb and flood channels.

The average discharge of the Scheldt as determined at Schelle, is approximately $100 \text{ m}^3 \cdot \text{s}^{-1}$. In Figure 7 the river discharge is shown in the period 1959-1978. There is a strong seasonal dependency. The tidal volume, entering the estuary at Vlissingen during flood is one billion cubic meters. Combining these data, one would expect a well mixed circulation pattern (see section 1.1.2.).

The Scheldt estuary belongs indeed to the category of well mixed estuaries. Vertical salinity gradients are generally lower than $1^{\circ}/\infty$, although differences of $2^{\circ}/\infty$ have been observed between surface and bottom water at the Belgian-Dutch border. Some differences in the estuarine mixing pattern exist between summer and winter. In the wet period, the winter, the estuary has a partially mixed circulation pattern (Hendriksma, 1981).

Besides longitudinal and vertical salinity gradients, lateral gradients are present. Van der Kooij (1985) studied lateral and vertical gradients in the Western Scheldt. At the Belgian-Dutch border the water at the left bank has a somewhat higher chlorinity than the water

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at the right bank, during the entire tidal cycle. This situation is consistent with the local circulation pattern: during flood, inflow takes place along the left bank, while the ebb moves along the right bank.

Theoretically, a three-dimensional advection and diffusion model, describing the circulation pattern, may be drawn. Solution of these equations requires a huge amount of field data and cannot be solved without drastic simplifications. For the Scheldt estuary, one- (Daamen & Lefèvre, 1983) and two- (Dekker, 1983) dimensional models have been constructed.

A limited number of parameters is required in these models:

- freshwater discharges (often represented as monthly or 10-days averages);
- tidal characteristics (range and propagation);
- morphological characteristics (especially cross-sections).

The one-dimensional model is calibrated with salinity measurements. For each estuary section of 5 km, a dispersion coefficient can be computed (Figure 8). These values need to be re-evaluated continuously due to changes in the morphology of the estuary (e.g. dredging, sedimentation-erosion processes).

The output of the one-dimensional model may be the tidally averaged or low-tide concentrations of a conservative constituent. Besides, it is possible to study the effects of changes in freshwater discharge on the circulation. In Figure 9 longitudinal profiles of the chlorinity are compared at high and low tide conditions and at the lowest and highest discharges. The evaluations of the salinity at a given point, at low tide, as a function of the discharge, is shown in Figure 10. At one discharge-value, large differences in salinity can be observed, indicating a strong memory effect of the estuary. This memory effect is proportional to the residence time (Wollast & Duinker, 1982). If

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the establishment of a steady state is very fast, the phenomenon of Figure 10 would not be observed. In the simplified one-dimensional model for the salinity, the departure from the steady-state is included in the dispersion coefficients.

It is expected that wind influences are of minor importance in estuaries with long residence times like the Scheldt estuary. The duration of wind events is at most a few days, which is short compared to the time needed for an estuary to reach a new steady state (Wollast & Duinker, 1982).

As seen in section 1.1.2. in partially and well mixed estuaries a net nontidal bottomflow may move upstream. This also occurs in the Scheldt estuary at the downstream zone of the salt intrusion, whereas upstream the net nontidal flow is downstream in the entire water column. At the intermediate zone, where no net residual currents are present near the bottom, a turbidity maximum has formed (Figure 11). The location of this zone of mud entrapment is dependent on the river discharge. It varies between the Rupel at low discharges (approximately $25 \text{ m}^3 \cdot \text{s}^{-1}$) to the Belgian-Dutch border (at $Q > 200 \text{ m}^3 \cdot \text{s}^{-1}$). This specific circulation pattern gives also rise to a considerable longer residence time for particles, compared to the water.

Besides, the mechanisms of mud entrapment by the circulation pattern, flocculation contributes to the particle enrichment in the turbidity maximum. This flocculation process starts at 1‰ salinity and has its upper limit at 2.5‰ (Wollast, 1982) or 5‰ (Peters & Wollast, 1978). A further increase of salinity produces larger flocs with generally lower densities. The zone of sediment accumulation and flocculation is associated with intense shoaling in a restricted area (Figure 11). A net erosion of such areas may occur during spring tides, while a net sedimentation predominates at neap tides. The zone underlying the turbidity maximum, consisting mainly of mud and fine silt, is bordered by areas, upstream as well as downstream, with coarser deposits, e.g. sand.

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In the Scheldt estuary, a net sedimentation probably takes place. A small amount of the sediment load of the river can escape to the sea. In addition, a residual transport into the estuary of marine sediments occurs. These particulates may enter the estuary as far as the Rupel.

Figure 12a shows the ratio fluvial/marine suspended particles in the Scheldt estuary. It appears that the ratio is not a simple function of salinity. From Figure 12b, it is concluded that the ratio fluvial/marine suspended particles is not conform to this ratio in the sediment of the Scheldt estuary. Whereas the isotopic composition of the suspended matter indicates a continuous change in a seaward direction, the sediment exhibits an erratic behaviour. The exceptional high $\delta^{13}\text{C}$ values at two locations, indicating anomalous high marine mud levels may reflect old marine particles, deposited during low runoff or storms (Salomons & Förstner, 1984).

Besides marine and riverine sources for sedimentary material a third component can be distinguished. Mariotti et al. (1984) used the isotopic composition of nitrogen in studying the origin of the suspended particulate organic matter in the Scheldt estuary. In winter, terrestrial organic matter is mixed with a marine component (which possesses marked differences in $\delta^{15}\text{N}$). In summer phytoplankton growth is another $\delta^{15}\text{N}$ source. In chapter 3 (Zwolsman, 1986), attention will be paid to the nutrient cycling in more detail. Here, it will be referred to NH_4^+ uptake by organisms throughout the estuary. The autochthonous phytoplankton reflects the $\delta^{15}\text{N}$ of ammonia, which is the result of a continuous fractionation during the nitrification (transformation of NH_4^+ to NO_3^- by bacteria, resulting in an enrichment of $\delta^{15}\text{N}$ of the residual ammonia).

In Figure 13, April and October conditions are diagrammatically compared. In the first case (Figure 13a) the $\delta^{15}\text{N}$ distribution reflects a simple mixing of two end members, while in October a phytoplankton growth influences the $\delta^{15}\text{N}$ distribution. From the diagram it appears that the isotopic composition of the end members is seasonally dependent.

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Van der Kooij (1985) determined also the distribution of suspended particles along cross-sections in the estuary. The variability of the suspended particles (and associated components) appeared to be much larger than for the salinity (see above). In the watercolumn, suspended matter concentrations varied over 100 mg.L^{-1} . These maximum differences occurred short after low-water slack, probably as a result of dredging activities.

1.2.3. Behaviour of major components and organic carbon

No evidence has been found in literature for the non-conservative behaviour of the major elements (Cl^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} , Mg^{2+}) in the Scheldt estuary. Although it is expected, that Ca^{2+} and $\text{Mg}^{2+}/\text{Na}^+$ will join in exchange reactions, these quantities will hardly be measurable in the aqueous phase.

The distribution of the pH along the axis is well-established. The pH can be predicted with good accuracy and is solely the result of the mixing of two water masses (see above, result of Mook & Koene (1975); Figure 14)). Obviously changes due to biological processes (e.g. production of CO_2) are of minor importance.

The dissolved oxygen concentration does reflect biological processes. The Scheldt river contains an enormous load of organic substances (Biochemical Oxygen Demand, BOD) as a consequence of the insufficient sewage purification in Belgium. O_2 uptake by the water cannot compensate for the loss by degradation reactions. Temporarily, the Scheldt is anoxic or has oxygen levels for below standard values (freshwater standard in The Netherlands is $5.0 \text{ mg O}_2.\text{L}^{-1}$). In the winter season, oxygen levels are generally higher than in summer; the organic matter is diluted more effectively during the "wet" season, while bacteriological degradation is slowed down due to the lower temperature. On the other hand, during algal blooms in summer, O_2 is produced. During mixing of the freshwater with the oxygen-rich seawater, the dissolved oxygen level increases rapidly (Figure 14).

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The study of Van der Kooij (1985) proved O_2 -inhomogeneties in the cross-section. These variations were just as for chlorinity: concentrations were highest near the bottom and at the left bank.

The DOC and POC (particulate organic carbon) concentrations in the Scheldt are high, respectively 7 and 15 $mg.L^{-1}$ (Wollast, 1982), while the average in unpolluted rivers in temperate climates amounts respectively 3 and 2 $mg.L^{-1}$ (Meybeck, 1980). Two important processes affecting the organic matter transport through the estuary are registered by Wollast (1982). The deposition of the particulate matter in the low salinity range (1-10 ‰) leads to an almost complete mineralization of the POC by heterotrophic bacteria. Secondly, the decrease in turbidity with increasing salinity leads to plankton blooms during spring and early autumn. Most of this organic matter is transported to the coastal zone. No conclusions were drawn concerning the DOC.

The Scheldt estuary is a highly polluted system. In the seventies, dissolved oxygen levels in the Belgian part of the Scheldt were extremely low. Only recently, an improvement has started, due to a continuously decreasing load of waste water. According to Wollast (1982), approximately an 80% reduction of the maximum organic load of 1974 would be required to eliminate anoxic conditions all over the year.

Van der Kooy (1982) estimated the BOD, nutrient and heavy metal load, introduced into the Dutch part of the estuary in 1981. He distinguished several sources of these, in majority, pollutants (Table 2). The river Scheldt appears to be the main source, whereas the canal Genth-Terneuzen, which is partly fed by Scheldt water, is also highly polluted.

Considering the BOD, the Scheldt is improving slowly, although in 1981 still anoxic conditions were present near the Belgian-Dutch border. Other quality improvements have been established with Hg, Cr, fenol and 3H . On the contrary, Ni, drins and PAH concentrations were increasing. Decreasing concentrations will not always coincide with decreasing load of pollutants, dependently on the river discharge (which

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Table 2. Estimation of the pollution load in the Western Scheldt in 1981 (tons per year). Data from v.d. Kooij (1982).

	N	P	BOD	Cu	Ni	Zn	Cr	Cd	Hg	Pb
Scheldt	40000	4500	15000	66	166	450	100	13	12	105
Direct discharges	3350	1185-1260	15555	56-18	20-40	249-413	20-31	051-056	002-004	22-79
Dumping (e.g. dredging sludge, gypsum waste)		675		112		19 -23	7	14 -18		52-64
Canals	7800	1300	1700	2	10	70	2	03	002	4
Polder discharges	4250	25	4250							
Rain water	580	35		32	04	13	01	02		42
Total	55980	8320-8395	36505	88-100	178-182	565-582	111-112	154-159	124-126	120-128

showed an increasing trend in the seventies). Lower concentrations, but approximately equal loads were observed for K_j -N, NH_4^+ and Zn.

1.2.4. Future changes

Three major man-made changes are actual in the Scheldt estuary:

1. A decreasing load of organic substances due to increasing purification of French and especially Belgian waste waters.
2. The deepening of the main channel by dredging for shipping reasons. The purpose is to improve the accessibility of the Antwerp harbour.
3. The discharge of water excess of the Zoommeer from 1987 via a canal at Bath.

Another plan, the construction of a canal at Baalhoek, is still in its initial stage. Because of the uncertainty of the realization, no attention will be paid to eventual consequences.

Some aspects dealing with 1 have already been discussed in the preceding section. The deepening of the main channel has been studied (Technische Scheldecommissie, 1984) and will have minor consequences

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in the vertical tide, e.g. at Bath approximately 15 cm. Due to the smoothening of the channel (changing dispersion coefficients), the salt water will intrude somewhat further, resulting in higher average salinities (at most 400 mg.L^{-1} at the Belgian-Dutch border). The turbidity is expected to increase permanently with 15-30% due to continuous dredging activities with a consequent decrease in the primary productivity.

The increase of BOD (and decrease of O_2) can be neglected relative to the Scheldt load.

The discharge of the Bath sluice will partly counteract the above mentioned effects of the deepening. The water from the Zoommeer is a mixture of Rhine-Meuse water and will be discharged with a maximum of $100 \text{ m}^3.\text{s}^{-1}$. Besides, a continuous freshwater loss by way of the Zandvliet sluices amounts $20 \text{ m}^3.\text{s}^{-1}$. This water is well-oxygenated ($10 \text{ mg O}_2.\text{L}^{-1}$), has a considerable BOD load ($5-7 \text{ mg.L}^{-1}$) and a low salinity (the Rhine chlorinity is $100-150 \text{ mg.L}^{-1}$). The expected effects are calculated with the one-dimensional advection-diffusion model (Daamen & Lefèvre, 1983).

The results (Bitter & Lefèvre, 1983) indicate a slight decrease in the dissolved oxygen concentration (0.4 mg.L^{-1} at most at the section Hansweert-Terneuzen). The O_2 -level near Bath will be higher due to the discharge (at most 0.7 mg.L^{-1}).

Abbreviations

A Cross-sectional area (m^2)	L Loss (g.s^{-1})
c Concentration (g.L^{-1})	Q Discharge ($\text{m}^3.\text{s}^{-1}$)
Cl Chlorinity (g halide.kg^{-1} solution)	S Salinity ($^{\circ}/\text{oo}$)
D Dispersion coefficient ($\text{m}^2.\text{s}^{-1}$)	t Time (s)
F Flux (g.s^{-1})	x Longitudinal distance (m)
G Fractional loss	

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LITERATURE

- Baeyens, W. & T.G. Jacques, 1979. Environmental management in the Scheldt estuary, Belgium. A review of past and present trends. NATO/CCMS: Pilot study on estuarine management.
- Bale, A.J., A.W. Morris & R.J.M. Howland, 1984. Size distributions of suspended material in the surface waters of an estuary as measured by Laser Fraunhofer Diffraction. In: Transfer processes in cohesive sediments, W.R. Parker & D.J.J. Kinsman (eds.) Plenum Press, New York p. 75-85.
- Bitter, G. & F.O.B. Lefèvre, 1983. Effect zoommeerlozing op zuurstof-en chlorideconcentratie Westerschelde. Notitie WWKZ-83.V313, 9 pp (in Dutch).
- Bowden, K.F., 1980. Physical factors: salinity, temperature, circulation and mixture processes. In E. Olausson and I. Cato (eds.). Chemistry and biogeochemistry of estuaries. John Wiley & Sons, New York, p. 37-70.
- Carlson, D.J., L.M. Brann, T.H. Mague & L.M. Mayer, 1985. Molecular weight distribution of dissolved organic materials in seawater determined by ultrafiltration: a re-examination. Mar. Chem. 16: p. 155-171.
- Daamen, J.W. & F.O.B. Lefèvre, 1983. Beschouwingen omtrent de chloridegehalten op de Westerschelde in de periode 1971-1980. Notitie WWKZ-83.V286, 18 pp. (in Dutch).
- Dekker, L., 1983. Tweedimensionaal model Westerschelde - Presentatie-model. Nota WWKZ-83.V010, 9 pp. (in Dutch).
- Dyer, K.R., 1977. Lateral circulation effects in estuaries. Estuaries, geophysics and the environment, p. 22-29.
- Dyer, K.R., 1979. Estuaries and estuarine circulation. In: Estuarine hydrography and sedimentation. K.R. Dyer (ed.) Cambridge University Press, London, p. 1-18.
- Edzwald, J.K., J.B. Upchurch & C.R. O'Melia, 1974. Coagulation in estuaries. Environ. Sci. Technol. 8, p. 58-63.

behoort bij: NOTA
datum: 31 oktober 1986
bladnr: 25

GWAO-86.111

- Duinker, J.C., R.F. Nolting & D. Michel, 1982. Effects of salinity, pH and redox conditions on the behaviour of Cd, Zn, Ni and Mn in the Scheldt estuary. *Thalassia Jugosl.* 18, p. 191-202.
- Fairbridge, R.W., 1980. The estuary: its definition and geodynamic cycle. In: E. Olausson & I. Cato (eds.). *Chemistry and biogeochemistry of estuaries*. John Wiley & Sons, New York, p. 1-36.
- Harris, J.R.W., A.J. Bale, B.L. Bayne, R.F.C. Mantoura, A.W. Morris, L.A. Nelson, P.J. Radford, R.J. Uncles, S.A. Weston & J. Widdows, 1984. A preliminary model of the dispersal and biological effect of toxins in the Tamar estuary, England. *Ecological Modelling*, 22, p. 253-284.
- Head, P.C., 1976. Organic processes in estuaries. In: *Estuarine Chemistry*, J.D. Burton & P.S. Liss (eds.). Academic Press, London. p. 53-91.
- Hendriksma, J., 1981. Waterkwaliteitsaspecten van de Westerschelde. RIZA nota-81.049, 45 pp (in Dutch).
- Höpner, T. & C. Orliczek, 1978. Humic matters as a component in sediments and estuaries. In: *Biogeochemistry of estuarine sediments*. UNESCO-SCOR Workshop, p. 70-74.
- Hunter, K.A., 1983. On the estuarine mixing of dissolved substances in relation to colloid stability and surface properties. *Geochim. Cosmochim. Acta* 47, p. 467-473.
- Hunter, K.A. & P.S. Liss, 1982. Organic matter and the surface charge of suspended particles in estuarine waters. *Limnol. Oceanogr.* 27, p. 322-335.
- Johnson, B.D. & P.J. Wangersky, 1985. Seawater filtration: Particle flow and impaction considerations. *Limnol. Oceanogr.* 30, p. 966-971.
- Kooy, L.A. v.d., 1982. De waterkwaliteit van de Westerschelde in de periode 1964-1981. RIZA nota 82.063 (in Dutch).
- Kooy, L.A. v.d., 1985. Dwarsraaionderzoek Westerschelde, 1982. RIZA nota 85-06 (in Dutch).
- Laane, R.W.P.M., 1982. Chemical characteristics of the organic matter in the waterphase of the Ems-Dollard estuary. Thesis Groningen, 134 pp.

behoort bij: NOTA
datum: 31 oktober 1986
bladnr: 26

GWA0-86.111

- Liss, P.S., 1976. Behaviour of dissolved constituents. In: Estuarine Chemistry. J.D. Burton & P.S. Liss (eds.). Academic Press, London, p. 93-130.
- Loder, T.C. & P.S. Liss, 1985. Control by organic coatings of the surface charge of estuarine suspended particles. Limnol. Oceanogr. 30, p. 418-421.
- Loring, D.H. R.T.T. Rantala, A.W. Morris, A.J. Bale & R.J.M. Howland, 1983. Chemical composition of suspended particles in an estuarine turbidity maximum zone. Can. J. of Fish. and Aq. Sci. 40 (supplement), p. 201-206.
- Mantoura, R.F.C. & E.M.S. Woodward, 1983. Conservative behaviour of riverine dissolved organic carbon in the Severn Estuary: chemical and geochemical implications. Geochim. Cosmochim. Acta 47, p. 1293-1309.
- Mariotti, A., C. Lancelot & G. Billen, 1984. Natural isotopic composition of nitrogen as a tracer of origin for suspended organic matter in the Scheldt estuary. Geochim. Cosmochim. Acta 48, p. 549-555.
- McCave, I.N., 1979. Suspended sediment. In: K.R. Dyer (ed.), Estuarine hydrography and sedimentation. Cambridge University Press, London, p. 131-185.
- McKay, D.W. & J. Gilligan, 1972. The relative importance of freshwater input, temperature and tidal range in determining levels of dissolved oxygen in a polluted estuary. Water Res. 6, p. 183-190.
- McManus, J. R.W. Duck, A.H.A. Alrasoul & J.D. Thomas, 1985. Effects of storage before analyzing suspended sediment samples from lakes, rivers and estuaries. J. of Sed. Petrol. 55, p. 613-616.
- Meybeck, M., 1980. Pathways of major elements from land to ocean through rivers. In: J.M. Martin, J.D. Burton & D. Eisma (eds.) River inputs to ocean systems. Unesco, Paris.
- Millero, F.J., 1984. The conductivity-, density-, salinity-, chlorinity relationships for estuarine waters. Limnol. Oceanogr. 29, p. 1317-1321.
- Mook, W.G. & B.K.S. Koene, 1975. Chemistry of dissolved inorganic carbon in estuarine and coastal brackish waters. Est. Coast. Mar. Sci. 3, p. 325-336.

behoort bij: NOTA

GWA0-86.111

datum: 31 oktober 1986

bladnr: 27

- Moore, R.M., J.D. Burton, P.J. LeB Williams & M.L. Young, 1979. The behaviour of dissolved organic material, iron and manganese in estuarine mixing. *Geochim. Cosmochim. Acta* 43, p. 919-926.
- Morris, A.W., R.F.C. Mantoura, A.J. Bale & R.J.M. Howland, 1978. Very low salinity regions of estuaries: important sites for chemical and biological reactions. *Nature* 274, p. 678-680.
- Morris, A.W., D.H. Loring, A.J. Bale, R.J.M. Howland, R.F.C. Mantoura & E.M.S. Woodward, 1982. Particle dynamics, particulate carbon and the oxygen minimum in an estuary. *Oceanol. Acta* 5, p. 349-353.
- Officer, C.B., 1979. Discussion of the behaviour of nonconservative dissolved constituents in estuaries. *Est. Coast. Mar. Sci.* 9, p. 91-94.
- Owens, N.J.P., 1985. Variations in the natural abundance of ^{15}N in estuarine suspended particulate matter: A specific indicator of biological processing. *Est. Coast. Shelf Sci.* 20, p. 505-510.
- Peters, J.J. and R. Wollast, 1978. Role of sedimentation in the self-purification of the Scheldt Estuary. Hydraulic Research Laboratory, Borgerhout.
- Postma, H., 1980. Sediment transport and sedimentation. In: E. Olausson, & I. Cato (eds.). *Chemistry and biogeochemistry of estuaries*. John Wiley & Sons, New York, p. 153-186.
- Salomons, W. & U. Förstner, 1984. Trace metals in the hydrocycle Springer Verlag, Berlin, pp.
- Sholkovitz, E.R., 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochim. Cosmochim. Acta*, 40, p. 831-845.
- Sholkovitz, E.R. & N.B. Price, 1980. The major element chemistry of suspended matter in the Amazon Estuary. *Geochim. Cosmochim. Acta* 44, p. 163-171.
- Sigleo, A.C. & G.R. Helz, 1981. Composition of estuarine colloidal material: major and trace elements. *Geochim. Cosmochim. Acta* 45, p. 2501-2509.

behoort bij: NOTA GWA0-86.111
datum: 31 oktober 1986
bladnr: 28

Technische Scheldecommissie, 1984. Verdieping Westerschelde. Programma 48'/43', Studierapport STSC 6/84, Technische Scheldecommissie, Antwerpen (in Dutch).

Wollast, R., 1982. Behaviour of organic carbon, nitrogen and phosphorous in the Scheldt Estuary. *Thalassia Jugosl.* 18, p. 11-34.

Wollast, R. & J.C. Duinker, 1982. General methodology and sampling strategy for studies on the behaviour of chemicals in estuaries. *Thalassia Jugosl.* 18, p. 471-491.

Zwolsman, G.J., 1986. Nutrient biogeochemistry in estuaries, with an emphasis on the Scheldt estuary. DGW report, 85 pp.

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2. ORGANIC MICROPOLLUTANTS

2.1. Introduction

The use of synthetic organic chemicals has increased enormously the last two decades. Fertilizers and herbicides were introduced into the agriculture and the chemical industry developed new products. Besides, the large scale use of fossile fuels has increased enormously after World War II.

Awareness of the risks and dangers of the presence of these, in majority, xenobiotics in the environment came only later. After some more or less hazardous incidents in several parts of the world, man began to realize the problems of the growing pollution. This was enhanced by the fact that some man-made chemicals were shown to be extremely persistent in the environment and accumulated in the fatty tissues of animals.

Once discharged in the environment, a pollutant is subject to a great variety of psysical, chemical and biological processes. As a result, a distribution between the various compartments of the ecosystem occurs. The distribution of a micropollutant is determined by its chemical nature as well as by environmental factors. Both determine ultimately the accumulation in the fatty tissues of animals and therefore the intrinsic danger of a micropollutant in the food chain.

A pollutant becomes an environmental problem, when it meets the three following requirements:

1. Presence of a source
2. A pathway
3. A target

In the system under consideration, the Scheldt estuary, the three conditions are fulfilled. The target, the food chain, with human life on top, is quite sensitive at every level for pollutants. Sources are present in an overwhelming quantity: the river Scheldt, polder discharges, dry and wet deposition, harbour discharges and, from 1987 the

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sluice at Bath, which will supply a mixture Rhine and Meuse water to the Western Scheldt.

The objective of this chapter is to evaluate, from a geochemist point of view, the processes that determine the pathways and fates of organic micropollutants in estuaries in general and particularly in the Scheldt Estuary. The knowledge of concentrations in, and distributions between the various abiotic compartments is necessary for biologists to determine its bioaccumulation. Processes discussed in this chapter are e.g. sorption, volatilization, biological degradation, and photochemical degradation. Knowledge of these processes is necessary in order to predict the effects of future changes in the Scheldt Estuary, such as the extra discharge of freshwater at the Bath sluice, the recovery of oxygen in the lower Scheldt as a result of the reduction of the BOD load and the permanent and incidental dredging activities which takes place for shipping reasons.

Only recently the investigation of organic micropollutants was accelerated. One factor responsible for this development is the improvement of analytical techniques. Especially the transition from packed column chromatography, which has been used almost exclusively until 1980, to capillary column (plus electron capture detector) has increased both quality and accuracy of analytical results (Duinker et al., 1984).

In the following, firstly some general characteristics of the micropollutants under consideration will be discussed. A subdivision into groups, dependant on use and molecule structure will be made. Furthermore, aspects of the chemical behaviour and properties (such as water solubility, sorption, microbial degradation) will be dealt with.

Secondly, the knowledge of the behaviour of the organic micropollutants in estuaries is evaluated. A considerable amount of papers is present in literature on this subject, but the majority is of a monitoring or descriptive nature, rather than that they unravel the processes. Finally, the situation of the Scheldt estuary will be described.

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2.2. Physico-chemical characteristics of organic micropollutants

2.2.1. Nomenclature

The namegiving of organic micropollutants can be based on several criteria. One criterium is to subdivide them to their use. So insecticides, herbicides and fungicides can be distinguished. The chemicals belonging to these groups are all chlorinated hydrocarbons. Some subdivisions are based on their biological effects (e.g. carcinogenic substances) or on their physico-chemical properties (e.g. surfactants or chelate forming substances).

Another subdivision is based on the structure (and thus behaviour). So, polycyclic aromatic hydrocarbons (PAHs), polychloribiphenyls (PCBs), phenol and its derivates, drins, etc. can be distinguished.

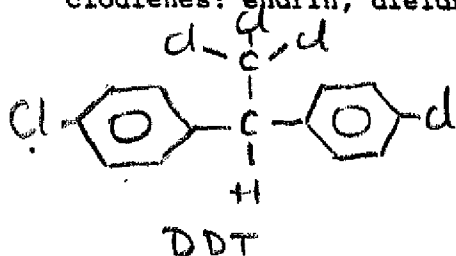
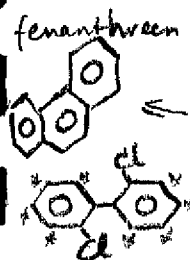
The nomenclature is according to standard rules in organic chemistry, although many of them are known under their trivial names (e.g. γ -hexachlorocyclohexane is lindane).

Without going into detail (for systematic treatment of the nomenclature, see any organic chemistry handbook) some remarks concerning the molecule structure will be made. The basic constituent of an aromatic compound is the benzene ring, which contains three double bonds. The PAHs contain two or more fused rings, while no chlorine atoms are bound (Figure 1a). The PCBs are compounds with linked rings (biphenyl) with one to ten chlorine atoms (Figure 1b). The production of technical mixtures of PCB leads to about 80 congeners among the 209 theoretically possible components (Abarnou et al, 1986).

Some PAHs are naturally occurring compounds. They are identified in oil and smoke, while PCBs are merely industrially produced.

DDT (trichloro,2,2-bis(4-chlorophenyl)ethane (Figure 1c), and its derivates are among the first insecticides used in the environment. The benzene rings are connected via a carbon atom.

Substances containing saturated hydrocarbon rings are the drins (cyclodienes: endrin, dieldrin, aldrin) and hexachlorocyclohexane (HCH).



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The three-dimensional structure of the molecules gives rise to the existence of stereo isomers, in contrast with the aromates (the benzene ring acts as a plate).

2.2.2. Solubility and octanol-water partition coefficient

Many pollutants have hydrophobic properties in common. Hydrophobicity is the driving force for in general low aqueous solubilities and lipophilicity. Due to strong attraction between water molecules, the hydrophobic molecules are pulled out of the molecular water structure. Benzene rings and unsaturated bonds do not affect the polarity to a great extent. Hence, their water solubility is not very different from parafins.

Solubility

In general, a relationship exists between molecule structure and solubility. Within a homologous series the solubility decreases with increasing molecular weight (e.g. Figure 2, for PAHs).

Eganhouse and Calder (1976) for example, determined the solubilities of some aromatic hydrocarbons. The solubility proved to be dependent on molar volume. The alkyl naphtalenes exhibited solubilities which were a function of substituent size and position of the alkyl group. Due to solute-solute interactions and/or solid solutions, solubilities decreased in a multicomponent system, e.g. the addition of phenanthrene reduced the water solubility of anthracene. More relevant to estuarine studies is the role of ionic strength (I). As a function of the salinity, solubilities decreased considerably. This relationship between salt concentration and solubility, the Setchenow-equation, generally holds for solution up to 1 or 2 M.

In a symplified form the expression is given as

$$\log (S^0_i/S_i) = K_S C_S \quad (2.1)$$

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in which S^0_i and S_i are respectively the solubilities of compound i in distilled water and saltwater; K_s is the empirical salting parameter (the Setchenow constant) and C_s is the molar salt concentration. Thus, when the constant, K_s , is known, the "salting out" effect of increasing ionic strength in an estuary can be predicted.

Whitehouse (1985b) investigated this relation for six PAHs. Four compounds (anthracene, phenanthrene, 2-methylanthracene and 2-ethylanthracene) yielded a constant slope K_s and a zero intercept at different temperatures, when plotting $\log (S^0_i/S_i)$ against C_s .

Benzo(a)anthracene and benzo(a)pyrene on the other hand did not obey the Setchenow equation. The first compound lacked to response significantly to increasing salt concentrations (at salinities $> 8\text{‰}$). This phenomenon is called "salting-in". Benzo(a)pyrene appeared to be insensitive to changes in salinity. No satisfactory explanation was given for these observations.

Whereas it has previously been thought that K_s was dependent on molar volumes (e.g. McDevit & Long, 1952 and Rossi & Thomas, 1981), Whitehouse (1985b) relates the surface area A (\AA^2) of the solute to the observed K_s :

$$K_s^{\text{obs}} = \lambda^{\text{obs}} A \quad (2.2)$$

in which λ^{obs} is a constant ($1.41 \cdot 10^{-3}$) derived from the plots. With this result, it is possible to predict the salting-out from pure component parameters.

Octanol-Water Partition Coefficient

Closely related to the aqueous solubility is the octanol-water partition coefficient, K_{ow} . Its definition is: the ratio of the equilibrium concentration C of a dissolved substance in a two-phase system consisting of two immiscible solvents, n -octanol and water

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$$Kow = \frac{C_{octanol}}{C_{water}} \quad (2.3.)$$

Kow is pressure and temperature dependent and is usually given as a logarithm.

Similar to solubilities, the partition coefficients change linearly as a function of molecule structure within a homologous series. The additive effect on log Kow of functional groups is most times also known (Figure 3) and may be formulated as:

$$\pi_x = \log K_x - \log K_H \quad (2.4)$$

where K_x is the partition coefficient of the derivate of the parent molecule with partition coefficient K_H , and π_x is the logarithm of the partition coefficient of the functional group X; equation 2.4 is only valid when no spherical effects are present.

Relation S-Kow

In literature numerous attempts can be found to link the aqueous solubility and the octanol-water partition coefficient.

One would expect a correlation between the two properties: a higher solubility will coincide with a lower octanol-water partition coefficient. Based on experimentally values of Kow and S, for various types of substances, a regression can be obtained. This line (Figure 4) spans the majority of chemicals, with different polarities and molecular states (liquid vs solid). If S is expressed in mg.L^{-1} , the regression line becomes (Verschuere, 1983):

$$\log Kow = 4.5 - 0.75 \log S \quad (2.5)$$

There are, however, some important deviations. An example is pentachlorophenol. The predicted log Kow differs from the true value almost two orders of magnitude.

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Chiou et al. (1982) also derived a relation between the aqueous solubility and octanol-water partition coefficient. The regression line obtained by these authors for selected aromatics is somewhat different from 2.5.

$$\log Kow = 0.710 - 0.862 \log S \quad (2.6)$$

The correlation extends over six orders of magnitude (of S) and the slope is significantly different from -1. The authors concluded that, especially for liquids, a good predictability exists for the partition coefficient from solubility data.

Ideally, calculated with the assumption that Raoult's law is obeyed, the slope of the relationship must be -1. Two phenomena explain the deviation. Firstly, the effect of dissolved octanol (in water) on aqueous solubility of the chemicals and secondly, liquid solute incompatibility in the (water-saturated) octanol phase.

Besides, a correction must be made for solids. The effect of melting on solubility will always cause a downward deviation from the ideal line: it reduces water solubility, but not the partition coefficient, since it affects both solvents equally (Chiou et al., 1982). This correction includes heat of fusion for the solids.

More recently, Millar et al. (1985) discussed the relationship from a thermodynamical point of view. They found that the activity coefficients of hydrophobic chemicals in aqueous solution and in octanol solution both increase with increasing molar volume, V.

This implicates good correlations between Kow and S with V (Figure 5). Their thermodynamical considerations provide a basis for the experimental lines as found by Chiou et al. (1982). The slope will tend to have values in the range 0.79 - 0.86.

2.2.3. Interactions with Dissolved Organic Matter (DOM)

Before the influence of DOM on aqueous solubilities of micropollutants is discussed, DOM must be defined. Whitehouse (1985a) defines DOM as

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organic matter which passes through a Whatman GF/C glass fibre filter. Because this is rather unsatisfying, he distinguishes "quality" and "quantity" in describing the DOM in the environment. Quality refers to its origin: terrestrial or marine organic matter, whereas quantity stands for the concentration of dissolved organic carbon (DOC).

It appears that the partitioning of PAHs in the dissolved phase is significantly influenced by the presence of naturally occurring DOM. This is in agreement with the investigations of Hassett & Anderson (1979) for cholesterol. The dissolved concentration of an organic micropollutant is considerably smaller after pretreatment of the water with UV-radiation. This indicates that the binding to DOM causes the "thermodynamical" solubility to be exceeded. Especially the interaction of PAHs with terrestrial humic material has great consequences for their solubilities. From ultrafiltration data it can be concluded that PAH-DOM association mainly occurs with high molecular weight material (Molecular weight, $M > 500$). Hassett & Anderson (1982) found that adsorption of cholesterol and a tetrachlorobiphenyl onto particles was less efficient in the presence of high DOM concentrations. Whether this was due to formation of associations between DOM and the two hydrophobic compounds or to competition between DOM and the two compounds for adsorption sites was not clear.

These authors do not specify what they mean by "association": it may be adsorption to or dissolution in the colloidal humic phase. Carter & Suffet (1982), who determined DDT-binding to DOM, and McCarthy & Jimenez (1985) who studied PAH sorption on dissolved humic material found the same as Hassett & Anderson (1982).

Carter & Suffet (1982) also concluded that this binding greatly affects the fate of organic pollutant in natural systems. The differences between bound and unbound pollutant are marked by a higher hydrolysis rate, a lower volatilization rate and changes (in what direction is not indicated) in rate of photolysis and extent of bioaccumulation. They constructed "association curves" which may be interpreted as adsorption isotherms. They found that a substantial part of total dissolved DDT is bound to DOM. These curves appeared to be linear over

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great concentration ranges of DDT. The slope of the curve is humic acid dependent. All curves went through the origin.

Dependencies of the association with DOM on pH, ionic strength I and Ca^{2+} have also been observed. Both the presence of Ca^{2+} and the increase of I cause an increase of the association constant. The same applies for a decreasing pH. These effects are, according to the authors, consistent with the known effects of solution parameters on the aqueous behaviour of humic materials. As hydrogen and metal ion concentrations are enhanced, or as ionic strength is increased some changes in the physico-chemical characteristics occur: the humic polymers may enlarge molecular size and may coil, while their charge will decrease. The result is that the humic material is more prone to sorption because the polymers become less hydrophilic and may bound hydrophobic chemicals more effectively.

The specific ionic strength effect is probably due to salting-out of the hydrophobic organic compound, because the chemical potential of a dissolved nonionic compound in water increases with enhanced I.

A rather puzzling phenomenon is the negative correlation between the association constant and humic acid concentration. No mechanism for this observation is suggested by the authors, except that it could have been caused by an experimental problem (leakage through dialysis bags). McCarthy & Jimenez (1985) also observed a slightly negative but significant correlation between the association constant and dissolved humic material (DHM). The association constant did not change by more than a factor of 2 over a range of 0-40 mg C-DHM.L⁻¹. Hassett & Milićic (1985), however, found no significant dependence of the binding constants on the DOC concentration. By utilizing a gas purging technique, they found a binding constant of $7.4 \cdot 10^4$ for 2,2',5,5'-tetrachlorobiphenyl.

In another publication, Carter & Suffet (1983) reported the different binding properties of several humic and fulvic acids. In all cases the binding constants are greater for humic acids, relative to fulvic acids. They found no correlation between binding constants and humic-fulvic characteristics (e.g. %C, %Fe, molecular size estimates). They

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concluded that, at this moment, no predictions can be made how strongly a pollutant will be bound to DOM in a particular sample, without actually measuring the binding constant.

The dependence of the binding constant on the temperature is consistent: the binding constant increases with decreasing temperature.

2.2.4. Sorption on to sediments

Karickhoff et al. (1979) and Karickhoff (1981) stated that sorption isotherms for hydrophobic compounds are linear over a broad range of pollutant concentrations. The partition coefficients are relatively independent on sediment characteristics but directly related to its organic carbon content.

The adsorption data fitted well to linear isotherms:

$$C_S = K_p C_L \quad (2.7)$$

where C_S is the concentration of sorbate in the sediment ($\mu\text{g.g}^{-1}$), C_L is the equilibrium sorbate concentration in the aqueous phase ($\mu\text{g.L}^{-1}$) and K_p is the partition coefficient (L.g^{-1}). This is in fact the equation of the Freundlich isotherm:

$$C_S = K C_L^{1/n} \quad (2.8)$$

with $n=1$ (Figure 6). Because K_p correlates strongly with organic carbon content and is more or less independent of other substrate properties such as cation exchange capacity and elemental composition (Means et al., 1980), it is convenient to normalize partition coefficients to organic carbon:

$$K_{OC} = K_p / f_{OC} \quad (2.9)$$

where f_{OC} denotes the fractional mass of organic carbon in the sediment.

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60% contact
Furthermore, the authors showed that sorption behaviour was dependent on the grain size distribution. Greatest affinity occurred for medium-fine silt fractions, whereas affinity was lower at larger and smaller grain sizes. Especially coarse silt and sand acted as diluting agents. Karickhoff et al. (1979) plotted normalized partition coefficients against other sorbate properties. They found a perfect correlation ($r^2=1.0$) between Koc and Kow:

$$\log Koc = 1.00 \log Kow - 0.21 \quad (2.10)$$

for some PAHs, benzene and a hexachlorobiphenyl. (Karickhoff (1981), however, found a slightly different equation, based on 4 PAHs and benzene:

$$\log Koc = 0.989 \log Kow - 0.346 \quad (2.11)$$

The aqueous solubility - Koc correlation was only slightly smaller ($r^2=0.94$)

$$\log Koc = - 0.54 \log S + 0.44 \quad (2.12)$$

The author suggested that Kow provides a much better estimator for sediment-water partitioning than solubility, because crystal energy contributions affect solubilities (and no other properties, such as Kow and Koc).

It is concluded from both studies that, although sorption is most times described using Langmuir or Freundlich isotherms, at low concentrations the behaviour can adequately be characterized by simple linear adsorption coefficients, normalized to organic carbon (this is confirmed by O'Connors & Connolly, 1980).

Sorption-kinetics

The sorption behaviour of individual organic chemicals appears to be

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more complicated than the generalized model above indicates. Two observations illustrate this. Firstly, besides reversible adsorption behaviour, it is thought that some compounds adsorb non-reversibly (i.e. a certain fraction is resistant to desorption). In that case the adsorption isotherm does not match the desorption isotherm (hysteretic isotherms) under equilibrium conditions (e.g. Di Toro & Horzempa, 1982; Horzempa & Di Toro, 1983).

Di Toro & Horzempa (1982) demonstrated resistant desorption behaviour for a PCB congener (a hexachlorobiphenyl) and for various natural adsorbents at environmental significant conditions (i.e. low concentration levels). They performed desorption, after adsorption, by subsequent multiple desorptions (Figure 7). From diagrams of this kind, they concluded that a considerable amount of the hydrophobic chemicals adsorbed irreversibly. It appeared that this resistant amount was dependent on the aqueous concentration. The ultimate shape of the consecutive desorption isotherm has not yet been determined. This is important since it is related to the question of desorbability when aqueous concentration approaches zero.

Secondly, a dependence of K_p on particle concentration has been observed (e.g. O'Connor & Connolly, 1980). This effect is clearly demonstrated in Figure 8. For compounds with relative high K_p the influence is highest. Recently, two reports have dealt with hydrophobic adsorption on particles.

Gschwend & Wu (1985) proposed that the role of non-settling (non-filterable) microparticles or organic macromolecules (= NSP) has been overlooked in sorption tests. These microparticles or macromolecules have sorption capacities. During experiments, they remain in the aqueous phase and disappear with the supernatant. This leads to the higher observed partition coefficients during desorption experiments. When precautions are taken to eliminate or account for this effect, the observed partition coefficients for hydrophobic chemicals are constant over a wide range of solid/solution ratios.

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It appeared that this "third phase" had equal affinities for hydrophobic compounds as those exhibited by the larger mass of solids (i.e. $K_{NSP} = K_p$, Gschwend & Wu, 1985). It can, however, not be excluded that this colloidal matter has greater affinities because of its larger surface area.

The importance of non-settling particles is twofold. To evaluate this, one can compare true and observed partition coefficients. By definition, the true partition coefficient is given by:

$$K_p^{\text{true}} = \frac{P/\text{mass of settleable particles}}{D/\text{volume of water}} \quad (2.13)$$

Because of the sorption of molecules to non-settling particles one measures another K_p , the observed partition coefficient

$$K_p^{\text{obs}} = \frac{P/\text{mass of settleable particles}}{(D+N)/\text{volume of water}} \quad (2.14)$$

where P is the mass of compound sorbed to settleable particles, D is the mass of compound dissolved and N is the mass of compound sorbed to NSP.

According to Gschwend & Wu (1985), the amount of NSP increases proportionally with suspended matter concentration (for two sediments about 5%). This is not surprising, considering that particle distributions are continuous and abundancies do not coincide with arbitrarily chosen phase separation values. At sufficient low suspended solid loadings D greatly exceeds N and K_p^{obs} approaches K_p^{true} . At higher particle loadings, D no longer greatly exceeds N and the observed partition coefficient is substantially lower than the true partition coefficient.

After combining 2.13 and 2.14, and defining

$$K_{nsp}^{\text{true}} = \frac{N/\text{mass of NSP}}{D/\text{volume of water}} \quad (2.15)$$

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$$\text{then } K_p^{\text{obs}} = K_p^{\text{true}} \left(1 + K_{\text{NSP}}^{\text{true}} \frac{\text{mass of NSP}_s}{\text{volume of water}} \right)^{-1} \quad (2.16)$$

Since $K_p = f_{\text{oc}} K_{\text{oc}}$ and correspondingly $K_{\text{wsp}} = f_{\text{oc,NSP}} K_{\text{oc,NSP}}$, then

$$K_{\text{oc}}^{\text{obs}} = K_{\text{oc}}^{\text{true}} \left(1 + K_{\text{oc,NSP}}^{\text{true}} \frac{f_{\text{oc,NSP}} (\text{mass of NSP}_s)}{\text{volume of water}} \right)^{-1} \quad (2.17)$$

Thus, since $f_{\text{oc,NSP}}$ may be expressed as DOC

$$K_{\text{oc}}^{\text{obs}} = K_{\text{oc}}^{\text{true}} (1 + K_{\text{oc,NSP}}^{\text{true}} \cdot \text{DOC})^{-1} \quad (2.18)$$

Using this equation, one can predict the change of K_p as a function of suspended particle concentration. Gschwend & Wu (1985) successfully predicted this dependence with the assumption that $K_{\text{oc,NSP}} = K_{\text{oc}}$. The authors concluded that in predicting the behaviour of hydrophobic constituents in the environment (transport processes, chemical activity), a third compartment, the non-settling particles must be included. It is likely that NSP partly consists of humic and fulvic acids with colloidal properties. Since much of the DOC in natural waters is polymeric humic substance, measurements of DOC may be suitable to quantify non-settling microparticles and/or organic macromolecules.

Voice & Weber (1985) presented an alternative model attempting to explain the particulate matter concentration effect in the liquid/solid partitioning. Partitioning can be regarded as the thermodynamically favoured distribution of a chemical between two readily separable homogeneous phases. In their "solute complexation model", Figure 9, it is proposed that the liquid phase is comprised of at least two, non-separable fractions. Whereas the subphases cannot be distinguished by common analytical procedures, the solute molecules are present in two states: free (C_{01}) and bound solute (C_{02}). Both free and bound solute can be adsorbed onto organic matter of the solid phase. These independent reactions are described by linear partition coefficients.

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It leads too far to evaluate the mathematical framework of the model (for this, we refer to the original literature). Here, the result of the model, an expression for the overall distribution coefficient is presented.

$$K_p = \frac{1/(S+1/K_1) + K_1AS^B/(S+1/K_2)}{1/(K_1S+1) + K_1AS^B/(K_2S+1)} \quad (2.19)$$

See for parameterdefinition Figure 9. A and B are experimentally defined coefficients. One of the assumptions is that a significant part of the organic matter in solution originates from the solid phase, but cannot be separated by the usual techniques.

The model predicts well the observed dependence of the partition coefficient on the solid matter concentration (Figure 10). From uncertainty analyses, it is concluded that the influence of the coefficients A and B (which are determined inaccurately, due to scatter in the data) is not very large.

From their experiments and model calibration, Voice & Weber (1985) concluded that their results have far-reaching consequences. Because of the non-linearity of K_p , partitioning of a contaminant in the water column is very different from the one in the sediments. Another implication is that the variability of DOC, caused by factors as trophic state, temperature, season and watershed characteristics, will influence the partitioning of a pollutant.

2.2.5. Volatilization

The complexity of the volatilization processes is enormous. The prediction of volatilization rates under any meteorological or hydrological condition is probably impossible. Besides, other processes, such as sorption, influence these rates. The occurrence of surface films, usually believed to consist of surface active materials, impede transfer processes at the air-seawater interface (MacKay, 1980). It may diminish turbulence and, more actively, bind compounds.

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Some modelling efforts have been made. Three parameters are included for each compound: Henry's law constant and two empirical parameters: the gas phase mass transfer coefficient and the liquid phase mass transfer coefficient. These coefficients can be regarded as resistances against the transfer across the interface. Practically no measurements are available for quantifying volatilization of the organic substances under consideration.

2.2.6. Microbial degradation

The majority of studies has been conducted in the context of waste water treatment; whereas more recently more attention has been paid to microbial kinetics at low, environmental relevant, concentration levels. Little is known about relative contributions of different genera. Besides, results from laboratory investigations are often poorly correlated with field measurements (Baughman & Burns, 1980).

Carlberg (1980) gives some general trends in microbial degradation rates. Rates increase in the sequence n-alkanes, iso-alkanes, cyclo-alkanes, aromates. Degradation is generally slower in sediments compared with the water phase, whereas in anaerobic sediments no degradation may occur at all.

Verschueren (1983) summarizes the environmental factors, which can affect biodegradability:

1. temperature,
2. pH
3. salinity
4. dissolved oxygen
5. compound concentration
6. concentration of micro-organisms
7. availability of nutrients
8. time, and
9. microbial species

In general, it is stated that microbial activity (as well as chemical oxidation) yield more polar compounds (with higher solubilities).

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2.2.7. Photolysis

Sunlight may transform chemicals. The rate of reaction is influenced by the wavelength, the turbidity and sometimes the dissolved oxygen concentration (Baughman & Burns, 1980). Photolysis may be affected by sorption processes. It may be concluded from Mill (1980) that the rate of photo-oxidation of organic pollutants in aquatic systems is generally small compared to the water residence time in an estuary. So, photochemical conversions may be relatively unimportant in determining the fate of pollutants in natural waters.

Some examples, however, indicate, opposite to Mill (1980), that photo-oxidation can have great consequences (Carlberg, 1980). With photo-oxidation of e.g. naphthalene, the solubility of the metabolite increases from 32 to 740 mg.L⁻¹ (as α -naphthol).

Baxter & Sutherland (1984) showed degradation of 2,4'-dichlorobiphenyl by a pseudomonad and subsequent conversions as a result of photochemical processes. Transformations occurred rapidly. Translation to the natural environment is hard because of two laboratorial artefacts: the PCB concentration used in the experiment was unrealistic high and the PCB acted as the only carbon source in the medium.

In a review article Payne & Philips (1985) showed that near surface half lives for direct photochemical transformations were in the range of minutes to several days for some PAHs. These half lives were negatively correlated with molecular weight, and were determined at 40°N latitude in the summer season. These rates are probably decreased by the presence of suspended material.

2.2.8. Sedimentation

Santschi et al. (1984) concluded from the studies in the MERL mesocosm tanks that any chemical species which has a partition coefficient in the order of 5-10.10⁴ (e.g. Th, Pb, Pu, isotopes, stable Pb and Cu, and many hydrocarbons) has a 2-14 days residence time in the water column with respect to transfer to the sediment. This residence time

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is seasonally dependent. These investigations were carried out in the Narragansett Bay, where the water residence time is approximately 30 days. It was estimated that 23-58% of total hydrocarbon input in the estuary accumulated in the sediment (total input: 400-1000 tons.yr⁻¹). Complicating factors in this kind of analysis are the quantitative contribution on the process of dredging activities and bioturbation (resuspension, transfer of particles from anoxic to oxic layers).

Jagtman (1984) correlated the micropollutant concentrations with sedimentological parameters in the Wadden Sea and Dollard estuary. Both organic carbon and the fraction smaller than 16 µm correlated well with the micropollutants under consideration. It is realistic to normalize pollutant content with respect to organic carbon, because of the physico-chemical binding characteristics (see 2.2.4). A great deal of the concentration scatter in sediments may be explained by organic carbon variations. Besides, processes such as bioturbation, resuspension and point discharges play important roles in determining the distribution of these hydrophobic substances.

Mesocosm experiments

Quite suitable for comparing the extend of these various processes influencing the fate of organic chemicals, is the use of mesocosms (MERL). Santschi (1982) stated that mesocosms lie between the complex and highly variable natural world and the tightly controlled but less natural laboratory experiment. Some difficulties arose in the MERL studies: wall effects, leaks, nonrepresentative sampling and lack of turbulence.

Wakeman et al. (1982) suggest that volatilization rates of compounds may be lower in MERL tanks compared to the natural system. Due to hydrodynamics of the water body within the tank, a stagnant boundary layer (400-600 µm) will form, which inhibits evaporation. Another phenomenon is the retardation of microbial activity (lag-phase) after introduction of pollutants in the MERL tank. This will most certainly lengthen the residence time.

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Lee et al. (1982) studied the fate of three radiolabeled chemicals benzo(a)anthracene, 7,12-dimethylbenzo(a)anthracene, pentachlorophenol (Figure 11). Large differences appear in the behaviour of the two, strongly related PAH. Whereas 7,12-dimethylbenzo(a)anthracene is largely removed by photochemical processes, the most important removal mechanism for benzo(a)anthracene is sedimentation. After a rapid adsorption the compound is taken up by the sediment, where a slow CO₂ production indicates degradation processes. As a result of the rapid photo-oxidation, 7,12-dimethylbenzo(a)anthracene does not accumulate to a great extent in the sediment. Besides, it appears that the metabolites of the latter do not adsorb as well as those of benzo(a)anthracene. The fate of pentachlorophenol shows resemblance with 7,12-dimethylbenzo(a)anthracene, although the time scale is very different. This indicates that adsorption of PCP is less important compared to 7,12-dimethylbenzo(a)anthracene.

2.3. Behaviour in estuaries

Duinker & Hillebrand (1979) were among the first, who studied the behaviour of organic pollutants in estuaries. From not very convincing evidence, they concluded that the behaviour of some organochlorines (HCH, PCB, HCB) in the Rhine estuary was conservative, whereas dieldrin and endrin showed marked maxima in the low salinity range. Local pollution could not be excluded.

Duinker & coworkers (1980, 1982a, 1982b, 1985) attempted to obtain an estimate of the levels of metals and organochlorines in water and seston in the Wadden Sea and of the relative influence of rivers entering this area directly. Physical mixing and physiochemical processes were studied in four rivers: Varde A, Elbe, Weser and Ems. From the studies the authors concluded that no conclusions concerning physiochemical processes affecting organochlorines could be drawn because, firstly, the concentrations were near detection limits and secondly, concentration gradients between the investigated rivers and Wadden Sea are small (opposite to the Rhine-Meuse estuary).

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To gather maximum information, they extracted water and seston of 120 (or 180)L freshwater samples. It appeared that in the four estuaries the same organic pollutants were present (although a considerable amount of peaks in the chromatograms have not yet been identified).

For the Elbe, Ems and Weser estuaries, the partition coefficients are computed and can be compared (Table I). Especially for PCB congeners, good agreement is found. In general it is established that particle affinity increases with increasing number of chlorine atoms. Other organochlorines, especially HCHs are more present in the waterphase. No dependence on O₂ saturation could be detected: whereas the Weserend-member contained more O₂ than the Elbe, no differences in the partition coefficients could be detected.

Recently, Duinker et al. (1984) presented the results of an investigation in the Dutch Wadden Sea. For comparison reasons, and because of the very similar composition of PCBs in solution they determined PCB, besides pentachlorobenzene and hexachlorobenzene. According to the authors there is no evidence for non-conservative behaviour for these organochlorines in the 0.5-23.3‰ salinity range.

The amount of particulate organochlorines is strongly dependent on the grain size distribution of the seston. Two fractions are distinguished: firstly a permanently suspended fraction with high contents of organochlorines (and heavy metals) and secondly, a temporarily resuspended fraction (acting as a diluting factor). This distinction is consistent with variations in size and/or density of the particles. Because of the large seston content in the Wadden Sea during the sampling, the effects of permanently suspended particles on the PCB content of the total suspended matter was not observed. The influence can only be observed at low particulate matter concentrations (e.g. $\leq 5 \text{ mg.L}^{-1}$).

Pavlou & Dexter (1979) studied the distribution of tri- and pentachlorobiphenyls in Puget Sound (U.S.A.). They found conservative behaviour in a very narrow salinity range (27-29‰). No extrapolation

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may be made for initial mixing of fresh- and seawater. Ernst & Weber (1978) studied the behaviour of pentachlorophenol in the Weser estuary. They found a seasonal variation, with highest concentration in spring. From tidal measurements it appeared that PCP levels were highest at low tide.

Weber & Ernst (1983) investigated a number of organic chemicals in three German estuaries. Concentrations were negatively correlated with salinity. The same relation between salinity and concentration levels were found within a tidal cycle.

A clear example of non-conservative behaviour is given by Helz & Hsu (1978). In the Back River, the C_1 and C_2 halocarbons are removed by a number of processes. Volatilization is probably the most effective, although winter ice cover minimized it. In this case chemical and biological degradation are responsible for the removal process. Half-lives are in the order of a few days in coastal waters.

Wakeham et al. (1982) studied the behaviour of volatile compounds in the Narragansett Bay and divided them into three groups depending on their origin: substances supplied by river input, substances of natural origin (e.g. alkylsulfides) and from dispersed sources with probably a significant atmospheric contribution.

Wakeham et al. (1982) concluded that the amount of total volatiles is not simply diluted in this estuarine environment. Where salinity predicts a certain organic compound concentration, it appeared that the volatiles concentration was one-tenth of that value. Degradation, volatilization, adsorption/sedimentation were proposed as the removal mechanisms but were not individually specified.

Some important papers have been dedicated to the Tamar estuary. Readman et al. (1982) divided PAHs, based on their environmental behaviour, into two groups. The first group consisted of low molecular PAHs (e.g. naphthalene, phenanthrene, anthracene) and showed no significant correlation with either salinity or suspended particles. The second group, with larger molecular weight homologues (e.g. fluoranthene, pyrene), was strongly correlated with suspended particles.

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Microbial degradation was slow and occurred in association with particles.

A considerable difference in residence times between group I and II is acknowledged. Whereas members of group I have short residence times in the estuary due to relatively high volatilization and degradation rates, the high particulate affinity causes sedimentation as the principal fate for members of group II.

In another study, Readman et al. (1984) determined the distribution of PAHs in the Tamar sediments. In the catchment area individual PAH levels were low (1-50 ng(g dry sediment)⁻¹. In the low salinity range, however, levels increased rapidly to 30-1500 ng.g⁻¹. This enormous elevation is due to the settlement and flocculation of particles, that are rich in pollutants and susceptible to an estuarine circulation pattern which leads to the occurrence of a turbidity maximum and a fluid mud layer.

In seaward direction these levels progressively decreased as a result of the physical mixing with marine sediments with possible degradation processes. Besides the decrease of total PAHs in seaward direction, the relative abundance of the PAHs changed systematically too. Compounds with a low molecular weight decreased at a greater rate than the higher molecular weight homologues. The authors described this to a preferential degradation and/or solubilization.

Readman et al. (1984) found that the PAH sorption on particulates was not in equilibrium. The in-situ determined partition coefficients were about two orders of magnitude higher than the empirically derived ones and as determined by a sorption experiment. The PAHs were enriched in the suspended particle phase, probably because, as suggested by the authors, occlusion of PAH in particulates originating from combustion processes or erosion of asphalt surfaces.

Harris et al. (1984) developed a one-dimensional model, which described the dispersion of toxins in the Tamar estuary. Solute dynamics were treated as an advection-diffusion process. Concerning particle dynamics, sedimentation, resuspension as well as effects of run-off and the tides on suspended load were included. For the hydrocarbon be-

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haviour, several mechanisms were included: volatilization, photo-oxidation and microbial degradation. It was assumed that sorption processes were reversible and in-equilibrium. Hydrocarbons with rather contrasting properties were used in the model: benzene with a rather high solubility, and benzo(a)pyrene with a relatively low solubility. Longitudinal dispersion coefficients were determined from salt budgets. For particle dynamics tentative results obtained by field measurements were needed.

Harris (1983) reported in an earlier publication an empirical relation for the salinity-dependence of K_{ow} :

$$K_{ow}(s) = K_{ow}(s=0) \cdot \exp(3.8 \cdot 10^{-2} K_s \cdot s) \quad (2.20)$$

where s is the salinity (‰). For example, the K_{ow} of benzo(a)pyrene at $s=35\%$ is 1.5 times the value of the freshwater endmember.

Summer and winter situations were distinguished in the Harris et al. (1984) model. Due to variations in river discharge, the flushing time varied (highest in summer) as well as the position of the turbidity maximum and the steepness of the salinity gradient. The volatilization was described with an experimental equation (e.g. dependent on current speed, wind speed, Henry's law constant) as the rate of volatilization per day. The photolysis is treated the same way, taking annual variations in light intensity into account. Due to the lack of reliable data, the authors did not consider microbial degradation.

In Table II the results of the model are presented. The two extremes, benzene and benzo(a)anthracene, show a marked different behaviour due to relative importance of volatilization and photolysis. The authors noted, however, that no temperature effects were taken into account; this may alter the diagram.

Hermann & Thomas (1984) discussed the behaviour of some PAHs, PCBs and organochlorine pesticides in the Exe, an English estuary. They performed a statistical analysis of micropollutant concentration in the estuary. No clear conclusions were made. It was stated that all PAHs behaved similar, just like the PCBs and a third group was formed by

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the pesticides HCH, γ -HCH (lindane) and HCB. Mechanisms for the regional distribution were sedimentation, resuspension and mixing of fluvial with marine sediments. The distribution patterns were dominated by multiple local inputs.

In the Narragansett Bay, Pruell & Quinn (1985) estimated PAH half-distances in sediments, i.e. the distances at which the concentration of a compound is decreased to one-half of its initial value in a downbay direction. The half-distances were similar for all investigated PAHs (2-5 rings), in spite of essential differences in physicochemical properties (e.g. Kow). The half-distance for TOC was almost twice as high. One explanation is, according to the authors, a local input of organic material or in-situ production. This material must obviously have other binding properties.

2.4. The Scheldt Estuary

Little work has been done on organic micropollutants in the Scheldt estuary. So far, some separate sampling has taken place, while as a result of the Dutch monitoring program, organic micropollutants are analyzed on a monthly basis at the Dutch/Belgian border (Schaar van Ouden Doel).

Van de Kooy (1984) compared the concentrations in surface waters of the SW-Netherlands. No specifications for analytical procedures were presented, as sample size and whether the samples were filtered or not.

One of the conclusions is that the Scheldt estuary is among the more seriously polluted water systems, together with the canal Ghent-Terneuzen, which discharges in the higher salinity range of the Western Scheldt.

Table III shows some results. For organic constituents other than PAHs and PCBs, only the number of significant observations in the samples in stead of concentrations are given. At Schaar van Ouden Doel, DDT and its derivatives, dieldrin, HCH-isomers and HCB were detected in 1982-83.

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Table III. Average PAH and PCB concentrations in the Western Scheldt at the Dutch/Belgian border.

PAH (n=6)	170 ngL ⁻¹
PCB (n=6)	11 ngL ⁻¹

source: Van de Kooy (1984)

Only very recently, Salomons & Kerdijk (1985) presented an outline of processes, involved with pollutants uptake by sediments. Because of the dependence of the partition coefficient on the organic matter concentration of the sediment, they normalized PAH and PCB concentrations to organic carbon.

From Figure 12 it can be concluded that PAH and PCB concentrations decrease in seaward direction. The physical mixing between terrestrial and marine sediment particles is mainly responsible for this observation. No stable isotope measurements are presented, thus it is impossible to indicate whether conservative behaviour occurs.

Duinker & Boon (1985) presented a compilation of distribution coefficients (K_p) for some Dutch and German rivers (see section 2.3) and the North Sea.

PCB congeners were treated individually. Results are presented in Table IV. It appears that K_p increases with increased chlorination. In spite of major differences in concentration and nature of suspended material, K_p values are very similar for the different rivers.

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Abbreviations

A	surface area (A^2) (eq. 2.2)
A	experimental coefficient (eq. 2.19)
B	experimental coefficient (eq. 2.19)
C	concentration (mg.L^{-1})
C _{octanol}	concentration of compound in Octanol (mg.L^{-1})
C _{water}	concentration of compound in water (mg.L^{-1})
C _O , C _L	dissolved concentration ($\mu\text{g.L}^{-1}$)
C _{O1}	free dissolved concentration ($\mu\text{g.L}^{-1}$) (Fig. 9)
C _{O2}	bound dissolved concentration ($\mu\text{g.L}^{-1}$) (Fig. 9)
C _S	particulate concentration ($\mu\text{g.g}^{-1}$)
C _S	molar salt concentration (mole.L^{-1}) (eq. 2.1)
D	mass of dissolved compound (μg) (eq. 2.14)
f _{OC}	fractional mass of particulate organic carbon
I	ionic strength (mole.L^{-1})
K	constant (L.g^{-1}) (eq. 2.8)
K _H	partition coefficient of the parent molecule (eq. 2.4)
K _P	partition coefficient (L.g^{-1})
K _{NSP}	partition coefficient concerning the non-settleable particles (L.g^{-1})
K _{OC}	normalized partition coefficient (L.gC^{-1})
K _{OW}	octanol-water partition coefficient
K _S	Setchenow constant (L.mole^{-1}) (eq. 2.1)
K _X	partition coefficient of the derative of the parent molecule (eq. 2.4)
K _X	binding coefficient (eq. 2.19)
K ₁	partition coefficient of free compound (L.g^{-1}) (eq. 2.19)
K ₂	partition coefficient of bound compound (L.g^{-1}) (eq. 2.19)
M	molecular weight
N	mass of compound sorbed to non-settleable particles (μg) (eq. 2.14)
n	constant (eq. 2.8)

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P mass of compound sorbed to settleable particles (μg)(eq. 2.14)
S solubility (mg.L^{-1})
S solids concentration (mg.L^{-1})(eq. 2.19)
s salinity ($^{\circ}/\text{oo}$)
S_i solubility of compound in distilled water (mg.L^{-1})(eq. 2.1)
S₁ solubility of compound in salt water (mg.L^{-1})(eq. 2.1)
 λ constant ($\text{L.mole}^{-1}.\text{\AA}^{-2}$)(eq. 2.2)
 π_x logarithm of partition coefficient of functional group x

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Literature

- . Abarnou, A., J. Avoine, J.P. Dupont, R. Lafite & S. Simon, 1986. Role of suspended sediments on the distribution of PCB in the Seine estuary (France), 16th EBSA Symposium. Dynamics of turbid coastal environment, Plymouth 1986.
- Baughman, G.L. & L.A. Burns, 1980. Transport and transportation of chemicals: a perspective. In: The handbook of environmental chemistry 2A. O. Hutzinger (ed.), Springer Verlag Berlin, p. 1-17.
- Baxter, R.M. & D.A. Sutherland, 1984. Biochemical and photochemical processes in the degradation of chlorinated biphenyls. Environ. Sci. Technol. 18, p. 608-610.
- Carlberg, S.R., 1980. Oil pollution of the marine environment - with an emphasis on estuarine studies. In: E. Olausson & I. Cato (eds.). Chemistry and biogeochemistry of estuaries. John Wiley & Sons, New York, p. 367-402.
- Carter, C.W. & I.H. Suffet, 1982. Binding of DDT to dissolved humic materials. Environ. Sci. Technol. 16, p. 735-740.
- Carter, C.W. & I.H. Suffet, 1983. Interactions between dissolved humic and fulvic acids and pollutants in aquatic environments. In: Fate of chemicals in the environment. R.L. Swann & A. Esschenroeder (eds.), American Chemical Society Symposium Series 225, American Chemical Society, Washington, p. 215-229.
- Chiou, C.T., D.W. Schmedding & M. Manes, 1982. Partitioning of organic compounds in octanol-water systems. Environ. Sci. Technol. 16, p. 4-10.
- Di Toro, D.M. & L.M. Horzempa, 1982. Reversible and resistant components of PCB adsorption-desorption: isotherms. Environ. Sci. Technol. 16, p. 594-602.
- Duinker, J.C. & J.P. Boon, 1985. PCB congeners in the marine environment - a review. In: Bjørseth, A. & G. Angeletti (eds.). Organic micropollutants in the aquatic environment. Proc. of the fourth european symp. Vienna, October 22-24, 1985. D. Reidel publ. company Dordrecht, p. 187-205.

behoort bij: NOTA

GWAO-86.111

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bladnr: 57

- Duinker, J.C., J.P. Boon & M.T.J. Hillebrand, 1984. Organochlorines in the Dutch Wadden Sea. In: Proc. 4th Int. Wadden Sea Symp. "The role of organic matter in the Wadden Sea" Texel, The Netherlands, p. 211-228.
- Duinker, J.C. & M.T.J. Hillebrand, 1979. Behaviour of PCB, pentachlorobenzene, hexachlorobenzene, -HCH, α -HCH, dieldrin, endrin and p,p'-DDD in the Rhine-Meuse estuary and the adjacent coastal area. *Neth. J. Sea Res.* 13, p. 256-281.
- Duinker, J.C., M.T.J. Hillebrand, R.F. Nolting & S. Wellershaus, 1982a. The river Elbe: processes affecting the behaviour of metals and organochlorines during estuarine mixing. *Neth. J. Sea Res.* 15, p. 141-169.
- Duinker, J.C., M.T.J. Hillebrand, R.F. Nolting & S. Wellershaus, 1982b. The river Weser: processes affecting the behaviour of metals and organochlorines during estuarine mixing. *Neth. J. Sea Res.* 15, p. 170-195.
- Duinker, J.C., M.T.J. Hillebrand, R.F. Nolting & S. Wellershaus, 1985. The river Ems: processes affecting the behaviour of metals and organochlorines during estuarine mixing. *Neth. J. Sea Res.* 19, p. 19-29.
- Duinker, J.C., M.T.J. Hillebrand, R.F. Nolting, S. Wellershaus & N. Kingo Jacobson, 1980. The river Varde A: processes affecting the behaviour of metals and organochlorines during estuarine mixing. *Neth. J. Sea Res.* 14, p. 237-267.
- Duursma, E.K. & J.M. Bowers, 1985. Application of K_ds in the marine geochemistry and environmental assessment. Scientific seminar on the application of distribution coefficients to radiological assessment models, Louvain-la-neuve, Belgium.
- Eganhouse, R.P. & J.A. Calder, 1976. The solubility of medium molecular weight aromatic hydrocarbons and the effects of hydrocarbon co-solutes and salinity. *Geochim. Cosmochim. Acta* 40, p. 555-561.
- Ernst, W. & K. Weber, 1978. The fate of pentachlorophenol in the Weser estuary and the German Bight. *Veröff. Inst. Meeresforsch. Bremerh.* 17, p. 45-53.

behoort bij: NOTA

GWA0-86.111

datum: 31 oktober 1986

bladnr: 58

- Gschwend, P.M. & S.C. Wu, 1985. On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. *Environ. Sci. Technol.* 19, p. 90-96.
- Harris, J.R.W., 1983. Modelling the fate and effects of toxins discharged into an estuary. Institute for marine environmental research, Plymouth, p. 21-27.
- Harris, J.R.W., A.J. Bale, B.L. Bayne, R.F.C. Mantoura, A.W. Morris, L.A. Nelson, P.J. Radford, R.J. Uncles, S.A. Weston & J. Widdows, 1984. A preliminary model of the dispersal and biological effect of toxins in the Tamar estuary, England. *Ecol. Modelling* 22, p. 253-284.
- Hassett, J.P. & M.A. Anderson, 1979. Association of hydrophobic organic compounds with dissolved organic matter in aquatic systems. *Environ. Sci. Technol.* 13, p. 1526-1529.
- Hassett, J.P. & M.A. Anderson, 1982. Effects of dissolved organic matter on adsorption of hydrophobic organic compounds by river- and sewage-borne particles. *Water Res.* 16, p. 681-686.
- Hassett, J.P. & E. Milicic, 1985. Determination of equilibrium and rate constants for binding of a polychlorinated biphenyl congener by dissolved humic substances. *Environ. Sci. Technol.* 19, p. 638-643.
- Helz, G.R. & R.Y. Hsu, 1978. Volatile chloro- and bromocarbons in coastal waters. *Limnol. Oceanogr.* 23, p. 858-869.
- Herrmann, R. & W. Thomas, 1984. Behaviour of some PAH, PCB and organochlorine pesticides in an estuary, a comparison - Exe, Devon. *Fres. Z. Anal. Chem.* 319, p. 152-159.
- Horzempa, L.M. & D.M. Di Toro, 1983. The extent of reversibility of polychlorinated biphenyl adsorption. *Water Res.* 17, p. 851-859.
- Jagtman, E., 1984. Het voorkomen van organische micro verontreinigingen in sediment van Waddenzee en Eems-Dollard estuarium, 1982. RIZA nota-84.098, 44 pp. (in Dutch).
- Karickhoff, S.W., D.S. Brown & T.A. Scott, 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* 13, p. 241-248.

behoort bij: NOTA

GWAO-86.111

datum: 31 oktober 1986

bladnr: 59

- Karickhoff, S.W., 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* 10, p. 833-846.
- Kooy, L.A. van de, 1984. Organische microverontreinigingen in de Zeeuwse wateren, 1982-1983. RIZA nota-84.102, 24 pp. (in Dutch).
- Lee, R.F., K. Hinga & G. Almquist, 1982. Fate of radiolabeled polycyclic aromatic hydrocarbons and pentachlorophenol in enclosed marine ecosystems. In: G.D. Grice & M.D. Reeve (eds.). *Marine mesocosms*. Springer Verlag, New York, p. 123-135.
- MacKay, D., 1980. Solubility, partition coefficients, volatility and evaporation rates. In: *The handbook of environmental chemistry*, 2A. O. Hutzinger (ed.) Springer Verlag, Berlin p. 31-45.
- McCarthy, J.F. & B.D. Jimenez, 1985. Interactions between polycyclic aromatic hydrocarbons and dissolved humic material: binding and dissociation. *Environ. Sci. Technol.* 19, p. 1072-1076.
- McDevit, W.F. & F.A. Long, 1952. The activity coefficient of benzene in aqueous salt solutions. *J. Am. Chem. Soc.* 74, p. 1773-1777.
- Means, J.C., S.G. Wood, J.J. Hassett & W.L. Banwart, 1980. Sorption of polynuclear aromatic hydrocarbons by sediment and soils. *Environ. Sci. Technol.* 14, p. 1524-1528.
- Mill, T., 1980. Chemical and photo-oxidation. In: *The handbook of environmental chemistry*. O. Hutzinger (ed.), Springer Verlag, Berlin, p. 77-105.
- Millar, M.M. & S.P. Wasik, 1985. Relationships between octanol-water partition coefficients and aqueous solubility. *Environ. Sci. Technol.* 19, p. 522-529.
- O'Connors, D.J. & J.P. Connolly, 1980. The effect of concentration of adsorbing solids on the partition coefficients. *Water Res.* 14, p. 1517-1523.
- Pavlou, S.P. & R.W. Dexter, 1979. Distribution of polychlorinated biphenyls (PCB) in estuarine ecosystems. Testing the concept of equilibrium partitioning in the marine environment. *Environ. Sci. Technol.* 13, p. 65-71.

behoort bij: NOTA
datum: 31 oktober 1986
bladnr: 60

GWAO-86.111

- Payne, J.R. & C.R. Philips, 1985. Photochemistry of petroleum in water. *Environ. Sci. Technol.* 19, 569-579.
- Pruell, R.J. & J.G. Quinn, 1985. Geochemistry of organic contaminants in Narragansett Bay Sediments. *Est. Coast. Shelf Sci.* 21, p. 295-312.
- Readman, J.W., R.F.C. Mantoura, M.M. Rhead & L. Brown, 1982. Aquatic distribution and heterotrophic degradation of polycyclic aromatic hydrocarbons (PAH) in the Tamar estuary. *Est. Coast. Shelf Sci.* 14, p. 369-389.
- Readman, J.W., R.F.C. Mantoura & M.M. Rhead, 1984. The physico-chemical speciation of polycyclic aromatic hydrocarbons (PAH) in aquatic systems. *Fres. Z. Anal. Chem.* 319, p. 126-131.
- Rossi, S.S. & W.H. Thomas, 1981. Solubility behaviour of three aromatic hydrocarbons in distilled water and natural seawater. *Environ. Sci. Technol.* 15, p. 715-716.
- Salomons, W. & H. Kerdijk, 1985. Contaminanten in sedimenten: uit het oog, uit het hart? Congresverslag KNCV symposium "Onderwaterbodems, rol en lot." Rotterdam, 28-29 mei.
- Santschi, P.H., 1982. Application of enclosures to the study of ocean chemistry. In: G.D. Grice & M.R. Reeve (eds.). *Marine mesocosms*. Springer Verlag, New York, p. 63-80.
- Santschi, P.H., S. Nixon, M. Pilson & C. Hunt, 1984. Accumulation of sediments, trace metals (Pb, Cu) and total hydrocarbons in Narragansett Bay, Rhode Island. *Est. Coast. Shelf Sci.* 19, p. 427-449.
- Verschueren, K., 1983. *Handbook of environmental data on organic chemicals*. 2nd ed. Van Nostrand Reinhold, New York, 1310 pp.
- Voice, T.C. & W.J. Weber jr., 1985. Sorbent concentration effects in liquid/solid partitioning. *Environ. Sci. Technol.* 19, p. 789-796.
- Wakeham, S.G., A.C. Davis & J.T. Goodwin, 1982. Biogeochemistry of volatile organic compounds in marine experimental ecosystems and the estuarine environment - initial results. In: G.D. Grice & M.D. Reeve (eds.). *Marine mesocosms*. Springer Verlag, New York, p. 137-151.
- Weber, K. & W. Ernst, 1983. Vorkommen und Fluktuation von organischer Umweltchemikalien in deutschen Estuarien. *Von Wasser* 61, p. 111-123.

behoort bij: NOTA

GWA0-86.111

datum: 31 oktober 1986

bladnr: 61

Whitehouse, B., 1985a. The effects of dissolved organic matter on the aqueous partitioning of polynuclear aromatic hydrocarbons. Est. Coast. Shelf Sci. 20, p. 393-402.

Whitehouse, B., 1985b. Observation of abnormal solubility behaviour of aromatic hydrocarbons in seawater. Mar. Chem. 17, p. 277-284.