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CE*T*EM

Are Tropical Estuaries Environmental Sinks or Sources?

Série Tecnologia Ambiental

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A **Série Tecnologia Ambiental** divulga trabalhos relacionados ao setor mínero-metalúrgico, nas áreas de tratamento e recuperação ambiental, que tenham sido desenvolvidos, ao menos em parte, no CETEM.

PRESENTATION

The articles and studies of Prof. Duursma are all very known of those that devote their attentions on the investigations of the fate of the heavy metals into the environment.

This present monography was written by Prof. Duursma and presented as a lecture at the "Workshop of Heavy Metals in Tropical Environments", coordinated by CETEM in conjunction with the "International Symposium on Perspectives for Environmental Chemistry in Tropical Countries", held in Niteroi, (Brazil), in December of 1993, at UFF - Fluminense Federal University.

Editing difficulties are responsible for the publication of this very intrigating work just, a year later.

Rio de Janeiro, May, 1995

Roberto C. Villas Bôas
Director

C O N T E N T S

1. INTRODUCTION

The major terrestrial freshwater and fluvial sediment runoff to the world oceans takes place between 30 ºN and 30 ºS (Milliman, 1991; Al-Gharib, 1992). These two discharges occur at different velocities, which has its consequence for contaminant transport. Since most contaminants are 'strongly' adsorbed to particular matter, the conclusion is often drawn that estuaries and coastal regions, where fluvial sediments are deposited, are sinks of contaminants.

Though this conclusion seems in first instance correct, it requires however a thorough investigation of the involved sorption and transport processes in order to be fully acceptable. Even when an estuary is at steady state, it shows the typical features of a sink for contaminants, although input from rivers into the estuary may equal output from the estuary to the sea, thus sinks are practically insignificant. A basic elaboration of this phenomena has to be made in order to distinguish between 'natural' and man-made sources of contaminants (Mee, 1978; Mee & Osuna-Lopez, 1991).

2. PRINCIPLES

In order to understand changes of concentrations between compartments and transfer of molecules from one compartment to another, it is necessary to define properly those compartments and the processes involved.

a) Compartment or Phase: Unit of space in which molecules have a defined state of freedom (or non-freedom) of movement and reaction.

b) Processes: Reactions between molecules and transfer of molecules inside and between compartments.

c) Equilibria: Reactions and transfer processes being counterbalanced by feedback processes.

2.1 Particulate Matter and Sediments

In marine and fresh-water systems there is practically always some suspended material present, either settling or floating due to turbulence or having a similar density as sea water. The amount (concentration) of particulate matter in the oceans, coastal seas and estuaries is ranging from a few μg PM (particulate matter)/l in open oceans to tenths of mg/l in estuaries. Some rivers may even have loads of a few g's/l. Characteristic is that the PM concentrations can be locally and temporarily different, which means that it is very essential, for purposes of studying processes in which PM is involved, to determine the PM concentrations as function of time and space. In the next paragraphs we will focus on the essential properties which determine the processes and transfer of contaminants between different compartments.

2.1.1 Specific surface of particulate matter

Particulate matter, suspended in sea or freshwater is generally low grain-sized and has, due to these low grain sizes, a relative large specific surface (Sp.S.).

The grain size - specific surface relation is given by formula (1), valid for spheres:

$$Sp.S. = \frac{(4\pi r^2)}{\frac{4}{3}\pi r^3 \sigma} = \frac{3}{r\sigma} \, cm^2 g^{-1} \qquad [1]$$

where r = radius of grain in cm and σ = specific weight in g/cm^3. Using grain sizes (d = 2r) in μm, the specific surface is:

$$Sp.S. = \frac{6 \times 10^4}{d \times \sigma} \, cm^2 g^{-1} \qquad [2]$$

For example, grains with d = 1μm (r = ½.10^{-4} cm) and a σ of 2.0 gcm^{-3}, the Sp.S. = 6x10^4 cm^{2}g^{-1}.

2.1.2 Composition

In principle the composition of the surface and crystal structures of PM can differ extensively, but there are a number of common features which can be taken into regard with respect to the sorptive and desorptive properties. Deviation from spheres, which is the case for aggregates, the Sp.S. is usually larger than given in formula's (1) or (2). Through adsorption of water molecules (intermediate layer) on PM a similarity of charge conditions is created, which depends solely on the polarity-charge distribution. Organic matter, with surface-active properties (depending again on polarity), is or can be adsorbed onto the PM surfaces, thus producing sites for specific reactions between dissolved substances and these organic molecules.

Hence, in spite of PM having different origins like biotic debris of living matter, including faeces, organic aggregates (from dissolved organic compounds), atmospheric dust (fine desert materials), minerals (from terrestrial sources), a number of similarities may be expected, at least with respect to surface properties.

2.1.3 Determination of surface-active properties

There is no complete theory to define the surface-active properties of PM that determines its sorption capacity. The best empirical methods are taken over from soil science, which encounters the same problems. In fact three methods are applied, determining either:

a) The Sp.S. (Specific Surface) by adsorption of ethyleneglycol (Dyal & Hendricks, 1950; Duursma & Eisma, 1973).

b) The Base Exchange Capacity (B.E.C.), with as a principle a first saturation of all exchange sites with Na^+, and subsequent replacement of these with NH_{4^+}. The determination of Na^+ in the NH_4Cl-percolate gives the Base Exchange Capacity in meq/100g (Duursma & Eisma, 1973).

c) The Specific Exchange Capacity based on the properties of the clay minerals themselves. Each clay mineral has a specific exchange capacity, and by multiplying this value with its relative content in a sediment, the specific exchange capacity Q' can be calculated by:

$$Q\mathreferenced = \mathring{a}(\frac{n}{100}) \times (\frac{P}{100}) \times k \qquad [3]$$

where k is 10, 25, 25 and 100 meq/100g for kaolinite, illite, chlorite and montmorillonite, respectively, n = size fraction and P is % of mineral in this size fraction (Grim, 1953).

As is demonstrated for 45 ocean and coastal-sea sediments (Figure 1), the correlation between the Sp.S., Q' and the B.E.C. is not too bad (from original data of Duursma & Eisma, 1973), although for the Sp.S. this is not a linear one.

Correlation BEC, Sp.S. and Q'
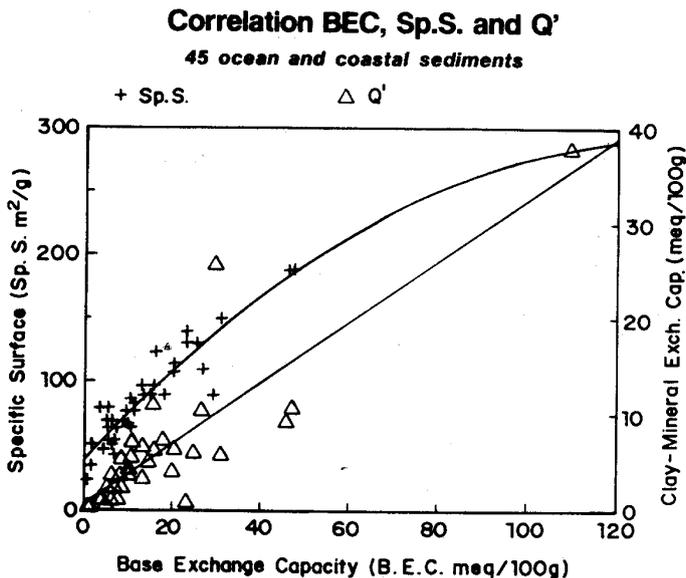
45 ocean and coastal sediments

Figure 1 - Correlation of the Base-Exchange Capacity (B.E.C.) with the Specific Surface (Sp.S.) and the calculated clay-mineral exchange capacity (Q') of 45 different ocean and coastal sediments. Graph prepared from the original dat of Duursma & Eisma (1973).

2.1.4 Strength of sorption

The term sorption covers two processes, (i) the rapid (matter of hours) sorption of substances to the surface of particulate matter, and (ii) that of absorption which is the binding of substances inter-layerly in clay minerals and inside crystal lattices. The latter process is considered slow (matter of days-weeks-months). The reverse reaction of desorption involves both surface desorption, inter-layer and crystal lattice releases, each having different speeds.

In agriculture the availability of soil-attached trace metals is of essence for plant growth and the B.E.C. is an indicative factor for the availability of soil trace metals to the roots of plants. The actual amounts available can be determined by weak leaching techniques. These can also be applied for aquatic soils and particulate matter as is shown in Table 1.

Table 1 - Leaching of metals from marine sediments was carried out by applying two media (in excess) of Acetic Acid/Ammonia Acetate and Acetic Acid, creating pH's of 5.4 and 2.3, respectively. Radiotracers of metals had been previously sorbed by Mediterranean fine-grained clay sediment for 7 months (Duursma *et al.*, 1975).

% Metal leached after 7 months sorption										
Elements	Mn	Fe	Co	Zn	Sr	Ru	Ag	Cd	Cs	Ce	Pb
pH = 5.4	50	0	33	4-33	100	10	0	100	2	50	50
pH = 2.3	100	75	100	10-80	100	25	0	100	30	90	50

Supposed is that the treatment at pH 5.4 is leaching the adsorbed part, and leaching at pH 2.3 removes part of the exchangeable absorbed fraction.

Most peculiar is that Cd and Sr seem to be only adsorbed, while the alkaline metal Cs is rather firmly bound. This is due to the fact that Cs is inter-layerly bound in a clay mineral like illite, its ionic radius matching the interlayer space.

2.1.5 Conclusion

It is very essential to understand the **complete** picture on how compounds are sorbed to PM, and not only part of it. It is, i.e., common practice to correlate adsorption of some metals (and also organochlorines) to the amount of clay, aluminum or organic matter of PM, and to correlate metal adsorption to only the clay or Aluminum content. However, the causality of these correlations needs to be proven, since also organic matter (POM, Particulate Organic Matter) can itself be proportional to the clay content. This was determined for sediments of three estuaries together with a correlation coefficient R being 0.88 (Duursma *et al.*, 1989).

3. EXCHANGE PROCESSES AND EQUILIBRIA

For the determination of the distribution of natural and anthropogenic substances between the compartments water, PM, sediments and organisms, many errors are made by either approaching the involved processes too theoretically or by neglecting major competitive reactions that do occur. A number of essential points will be treated.

Sea water contains a variety of cations, anions and uncharged molecules, and any reaction between two of them in the dissolved phase will have to compete with identical reactions of other (competitive) molecules. This has to be understood from the start, and should never be neglected.

3.1 Basic Exchange Reactions

The basic exchange reaction of for example a metal is given by the following reaction, from which the distribution coefficient K_d can be defined from:

$$Me^{n+}Cl_n \ + \ nNaMP \ \underset{K_2}{\overset{K_1}{\Leftrightarrow}} \ MeMP \ + \ nNaCl \qquad\qquad [4]$$
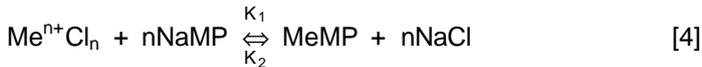
in which Me = a metal or a radionuclide in concentrations <<< than Na; k_1 et k_2 are the two reaction speed constants, defined as:

$$\begin{aligned} k_1 &= f_1[Me^{n+}Cl_n][NaMP]^n \\ k_2 &= f_2[MeMP][NaCl]^n \end{aligned} \qquad\qquad [5]$$

in which f_1 and f_2 are constant factors.

At equilibrium $k_1 = k_2$ and we obtain from (5) the following equation:

$$f_1 / f_2 = \frac{[MeMP][Me^{n+}Cl_n]}{[Me^{n+}Cl_n]} \times \frac{[NaCl]^n [NaMP]^n}{[NaMP]^n} \qquad [6]$$

The second term is quasi constant because the dissolved Na and particulate Na are in excess to the dissolved Me and particulate Me, respectively. In consequence changes in dissolved Me to particulate Me will not significantly change the ratio dissolved Na to particulate Na. Hence the second ratio remains constant. Since f_1/f_2 is a constant, the first ratio $[MePM]/[Me^{n+}Cl^n]$ will be also a constant factor. This is called the distribution coefficient K_d.

Hence:

$$K_d = \frac{\mu gMe / g\ PM}{mgMe / g\ water} \ (dimensionless\ g / g) \qquad [7]$$

Since, however, reaction (4) is only of a semi-thermodynamical nature, the K_d's have to be understood as **apparent** distribution or partitioning constants. But as long as their values are known in space and time, processes of transfer and equilibrium can be studied with help of this factor.

So far the K_d was defined as a dimensionless factor[1], which was dimensionless on the basis of g/g. K_d values thus obtained can be used in determining the % distribution of metals between water and particulate matter. Knowing the K_d (as g/g), the suspended load, the water transport and the PM transport (sometimes because of settling and resuspension slower than the water), the effective transport can be calculated. It is only

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[1]. K_d can also be expressed (dimensionless) in ml/ml, which is required for diffusion calculations, see formula (14).

necessary to know on each spot and time which % of the metal is in solution and which % is particulate.

Suppose for the metal cadmium (Cd) there is P µg Cd/l (total Cd in solution particulate) and S mg PM/l. We take 1 litre water as 1000 g and neglect the S mg PM in suspension. When the percentage Cd in solution is given as X % Cd), X can be found using the definition of K_d (7):

$$K_d = \frac{(\frac{100 - X0}{100}P)/(\frac{S}{1000})}{(\frac{X}{100}P)/1000} \qquad [8]$$

From this equation the percentage X can be derived:

$$X = \frac{10^8}{SK_d + 10^6}\% \text{ dissolved cadmium} \qquad [9]$$

This formula (9) can be graphically plotted, with as result that for rapidly exchanging metals on PM, the % dissolved can easily be read (Fig. 2) of Duursma & Bewers (1986). For a K_d of 10^4 and S of 1 mg/l, X is 99.0 %. For the same K_d but with an S of respectively 10 and 100 mg/l, X is 90 and 50 %. This can have consequences on a long distance, as is demonstrated by an example of plutonium. This nuclide, originating from the effluents of Sellafield at the Irish Sea was detected in sediments close to Spitsbergen (Svalbard, 78 °N and 20 °W) at 2800 km distance. Plutonium is 'strongly' adsorbed to particulate matter (PM) and bottom sediments, with a K_d between 10^4 and 10^5. Surely the Irish Sea sediments have not been transported so far, but the transport must have occurred in dissolved form by the Gulf Stream, since S in the oceans is << 1 mg/l.
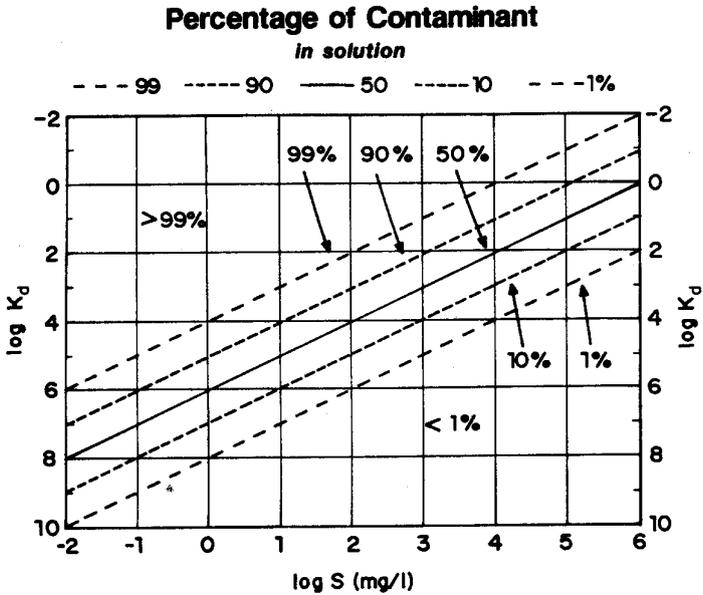
Figure 2 - Percentage of contaminant in solution as dependent on K_d and particulate matter (PM = S) load, according to formula (9).

3.2 Competition Between Complexation and Sorption

Most natural waters, and in particular fresh waters contain additional to suspended matter dissolved organic (or inorganic) matter that is capable of complexing trace metals, thus favouring them to be in dissolved form. For this three-compartment system a theoretical approach is possible. The reactions involved are the following:

$$Me^{++} + L^- \Leftrightarrow MeL^+ \quad K_{st} = \frac{MeL}{[Me^{++}][L^-]}$$

$$Me^{++} + MP^- \Leftrightarrow MeMP \quad Kd = \frac{[MePM}{[Me^{++}]}$$

[10]
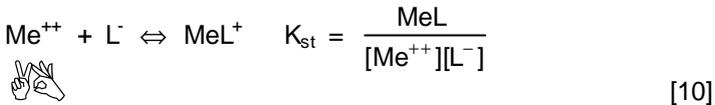
in which K_{st} is the stability constant of the above complexing reaction. This competition effect between complexation and sorption can be made clear with the following example. To a sea water suspension of PM and containing radioactive ^{60}Co, leucine is added. Sampling of 5 ml suspension is carried out after equilibrium is attaint. Subsequent filtration produces a filtrate and PM on a filter. These are analyzed for radioactivity/ml filtrate and radioactivity/g PM.

The apparent distribution coefficient K_{da} becomes, according to (7) the ration of total particulate metal concentration to total dissolved metal concentration, which is:

$$K_{da} = \frac{[MeMP]}{[Me^{++}] + [MeL^+]}$$

[11]

from which, according to (10):

$$[MeL^+] = [Me^{++}][L^-] \times K_{st}$$

[12]

From (10, (11) and (12) we can derive at:

$$\frac{1}{K_{da}} = \frac{1}{K_d} (1 + K_{st}[L^-]) \qquad\qquad [13]$$

Since K_d is the distribution coefficient without addition of ligand and K_{da} with addition of ligand, this latter formula can serve for determining stability constants (K_{st}) of complexing organic matter with metals. Just a simple experiment is required, such as adding progressing amounts of particulate matter to a solution containing metal and organic matter, or by adding progressing amounts of organic matter to a suspension containing metal(s). But for natural waters the situation is more complicated, since the results are affected by competing reactions of other metals and H^+ ions with the same ligand. This illustrated in Fig. 3 (Duursma, 1970). This figure shows that the calculated $1/K_{da}$ values for ^{60}Co and [65]Zn seem to match the determined $1/K_{da}$ only when the competition of the major sea water ions H^+, Ca^{++} and Mg^{++} is taken into account. For these calculations the formulas (10) to (13) have to be extended for these cations.

Conclusion: Any reaction in natural systems between compartments is multi-competitive.
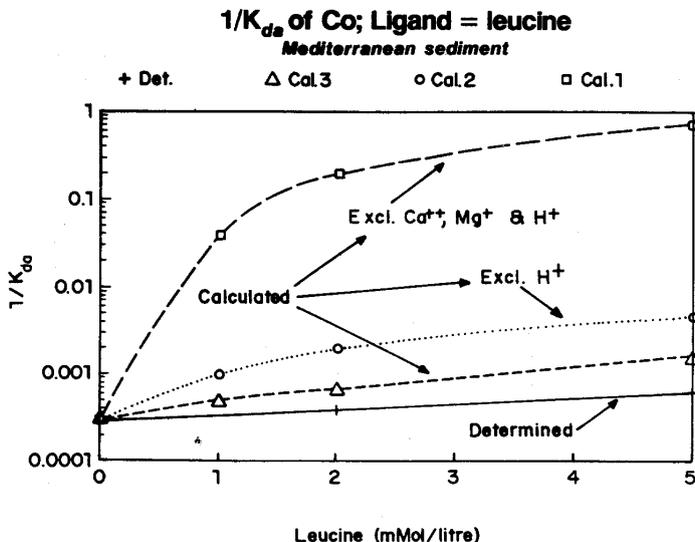
Figure 3 - Determined and calculated reciprocals of the apparent distribution coefficient K_{da} of ^{60}Co in relation with leucine additions to sea water. From Duursma (1970).

3.3 Correlations of K_d's with Sediment and Metal Properties

There have been always intensive discussions on how exchange reactions occurs between metals in solution and available sites on PM. Usually people believe that only the ionic metal species take part in the adsorption-desorption reactions.

Particulate matter has all kind of possibilities for adsorption reactions, like ion exchange, chemical binding and precipitation-dissolution (the latter are more or less independent of the surface properties). Taking this into account, many scientists believe that also **threshold** phenomena may play a role, so that exchange sites may become saturated. For **ion exchange**, however, this <u>t</u>hreshold approach does not seem to hold, since the principle of ion exchange is equilibrium, and concentrations in the water compartment should be extremely high to have 100 % exchange sites occupied (in exchange to something else, which will then also become high in concentration in the water). For **precipitation** this holds **neither**, since precipitation may continue in many layers on the surface. For **binding** the threshold model might **hold**, however, also binding has exchange reactions up to a certain equilibrium.

3.3.1 Results of K_d's with sediment and radionuclide properties

During 1965 and 1973 intensive studies have been carried out to understand the major reactions of fallout radionuclides with various ocean sediments. The studies comprised the cooperative efforts of 20 national laboratories together with the marine laboratory of the International Atomic Energy Agency (IAEA), in Monaco. In fact with 35 characteristic ocean and coastal sediments which were sent to Monaco, radionuclide sorption experiments were carried out. Table 2, made after Duursma & Eisma (1973) demonstrates clearly that for these 35 ocean sediments the range of K_d's/B.E.C. and that of the half-time of sorption (t½) is large, but the order of magnitude is characteristic for each radionuclide.

Table 2 - Average K_d's/B.E.C [1/(meq/100g)] ratios and their range for 35 marine sediments and 14 radionuclides (Duursma & Eisma, 1973). The half-time of sorption (t½) is indicative for the kind or sorption, where ion exchange is the fastest and precipitation on surfaces the slowest.

Radionuclide	K_d/B.E.C.	K_d/B.E.C.	t½ of sorption
	Average	Range	days
^{45}Ca	45	?	<1
^{54}Mn	1000	200-2000	6.1 $\pm$ 4.6
^{59}Fe	1250	400 - 2500	18.0 $\pm$ 6.5
^{60}Co	?	100 - 4000	8.2 $\pm$ 5.1
^{65}Zn	150	100 - 400	1.9 $\pm$ 1.3
^{86}Rb	620	?	<0.5
^{90}Sr/Y	1	0.5 -1.5	2.3 $\pm$ 1.7
^{95}Zr/Nb	1000	200-1600	5.7 $\pm$ 2.3
^{106}Ru	2850	1400 -5000	8.9 $\pm$ 3.3
^{137}Cs	50	25-90	0.7 $\pm$ 0.4
^{144}Ce	4000	2000- 8000	10.5 $\pm$ 4.4
^{147}Pm	3300	2800-6700	11.4 $\pm$ 3.5
^{210}Pb	2700	?	?
^{239}Pu	52		?

Conclusion: Although correlations may be found, extrapolation to other sediments is speculative.

3.4 Determined and Calculated Diffusion Coefficients of 10 Radionuclides

Since diffusion of radionuclides in sediments is a very slow process, the determination of diffusion coefficients is a tedious process. Therefore it has been made possible by calculation, using the K_d and applying formula (14) developed by Duursma & Hoede (1976):

$$D_{metal} = \frac{D_{molecular}}{1 + K_d} \qquad [14]$$

In order to confirm the validity of this calculation, this calculation was compared with the direct method of determining the diffusion coefficient (Table 3).

Table 3 - The diffusion technique with instantaneous source (Duursma & Bosch, 1970) was applied for the direct determination of D_{metal}, having as sources ten radioisotopes. The time of the experiment for allowing diffusion was 1 yr. The sediment was Mediterranean clay sediment. With the same sediment and radionuclides Kd's were determined. By applying formula 14 the 'calculated' D_{metal}'s were determined.

Radionuclide	Diffusion coefficient (D_{metal}), x10^{-10} cm^2/sec (average values)	
	Calculed	Determined
^{90}Sr	17,500	9,000
^{137}Cs	60	?
^{136}Ru	22	95
^{59}Fe	4.5	82
^{65}Zn	12.2	10
^{60}Co	25	15
^{147}Pm	2	7
^{54}Mn	4	4
^{95}Zr	2.8	33
^{144}Ce	2	13

The results, given in Table 3 demonstrate that a fairly rough agreement exists, at least in the order of magnitude. This is rather astonishing, taking into regard that the K_d's were determined during a four weeks experiment, and K_d's may be higher when sorption occurs over a year period, as shown by Duursma & Bewers (1970) for ^{65}Zn.

Conclusion: Although it is determined that K_d's are only empirical factors which can depend on many circumstances, at least in one sediment it was demonstrated that the order of magnitude of experimentally determined diffusion matched that of the calculated ones.

3.5 Residence Times of Metals in an Estuary

In many estuaries of the world, bottom sediments are contaminated with heavy metals. Dissolved metals are both sorbed to PM, settled to the bottom and migrating by diffusion into the bottom.

A case study on processes, comparable to what actually happens at Sepetiba Bay west of Rio de Janeiro (Lacerda & Barcellos, 1993) has been made in a Dutch estuary the Haringvliet, where during a number of years the dissolved and sediment-attached metals were analyzed. From these analyses Van de Vrie and Duursma (1986) have calculated the turn-over time (residence time) and 50% adaptation time of three metals Zn, Cd and Pb with 2-box model (Table 4).

Table 4 - Turnover and 50% adaptation times for Zn, Cd and Pb for water and a 10 cm top layer of the sediment of the Haringvliet (Netherlands).

	Turner-over time (yr)				50% adaptation time (yr)			
	Water		Sediment		Water		Sediment	
	Box 1	Box 2	Box 1	Box 2	Box 1	Box 2	Box 1	Box 2
Zn	42	86	975	1230	18	37	24	45
Cd	42	86	975	1230	34	68	35	69
Pb	39	86	975	1230	28	59	36	70

From these data it can be concluded that it will take at most 1230 yr to contaminate a bottom layer of 10 cm (Box 2) or to have it completely decontaminated, supposing the water over the estuary becomes clean. For 50% of the contamination level this

will happen in 45 yr for Zn, 69 yr for Cd and 70 yr for Pb, respectively, again for Box 2.

4. ESTUARIES, SINKS OR SOURCES

For estuaries with a long freshwater-seawater mixing section and a turbidity maximum, the question can be posed whether the distribution of the dissolved and particulate contaminants along the estuary is conservative, meaning that the total inflow of contaminants (particulate and dissolved) from the river equals the discharge from the estuary into the sea, while there is no loss to or gain from the bottom. Model calculations have been made to solve this problem for different adsorption and complexing processes (Duursma & Ruardij, 1989).

In Figure 4, results from such a model calculation are presented with as boundary conditions $K_d = 10^5$ (K_d = (µg contaminant/g part. matter)/µg contaminant/ml water) and $K_{st} = 10^2$ (K_{st} = [Mecompl.]/[Me]x[Org.m.]), called stability coefficient of a metal with organic matter. For a given particulate matter distribution with turbidity maximum, the amount of total metal (TMET = total dissolved + total particulate metal, expressed in µ g/l water) shows also a maximum at the point of the turbidity maximum. Nevertheless at each cross-section of the estuary, the total amount transported to the sea is constant. The explanation has to be found in the difference of the residence times of water (which are constant) and particulate matter (which is dependent on the PM concentration).

Once these boundary conditions for the processes involved have been established, it is possible to investigate whether real sources or sinks exist in the system. These have to be found from the difference of the actually determined concentrations as compared to the 'mixing' concentrations.

With this calculation in mind it is possible to determine the contamination from effluents into the estuary. The total transport per cross-section should differ along the estuary. In that case the

exchange between water and bottom sediments plays a buffering role with turnover times as mentioned in Table 4.
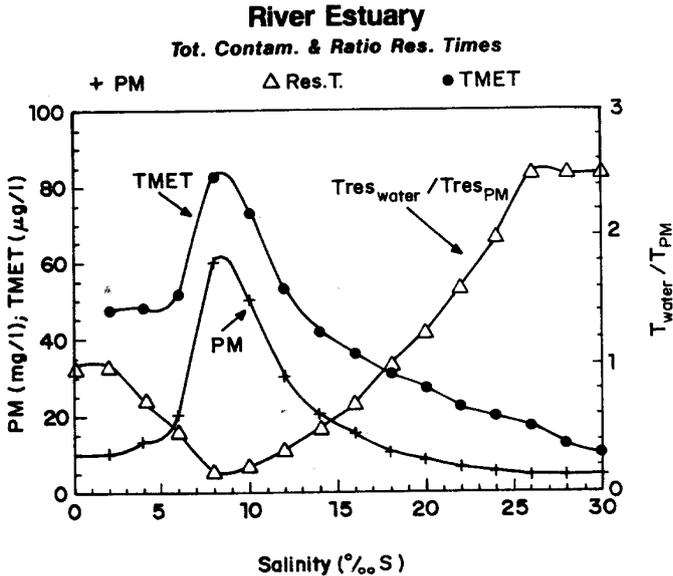
Figure 4 - Calculation of the total amount of contaminant in solution + in particulate matter for a model estuary with steady state contaminant input (from the river) and output (to the sea), where the distance is a linear function of the salinity. There is no loss to or gain from the bottom, which means a full conservative situation. RUN 3 of the model given by Duursma & Ruardij (1989). The residence time of particulate matter is the largest at the turbidity maximum.

5. ORGANOCHLORINES

For organochlorine pesticides similar calculations can be made, although time-dependent transformation processes are involved. In particular in the tropics such processes of transformation are more rapid than in temperate water (Duursma, 1976), and are additionally accelerated in estuaries by the presence of microbiota attached to particulate matter. This counts also for the new generation of organophosphorus pesticides (Readman *et al.*, 1992) which have their impact in tropical estuarine and lagoon systems.

In 1962 the first edition o0f the book `Silent Spring' of Rachel Carson (1987) was published, which brought a large change in public and scientific opinion on the use a persistent pesticides. DDT and its metabolites were found as residues in the lipids of very remote living animals and birds, while the decrease of top predators of the food chain in number was very clear with birds. The idea of accumulation through the food chain was launched and is still quoted today as a major environmental principle.

Since DDT has been banned from the early 1970's, although for anti-malaria programmes production may still be going on, the DDT concentrations have decreased largely in environmental samples. Attention is now focused on PCB's, which product was worldwide produced and applied during the last 40 years, in particular as a useful nonflammable grease or oil. It was beside other applications used as isolation liquid in electrical transformers and grease in mines.

However, PCB's, are even more persistent than DDT and have similar and for some of its congeners higher toxicity values such as in vivo ED-50 inhibition body weight gain of 750 and 1120 μ mol/kg (234 and 350 mg/kg) for the PCB congeners 105 and 118 respectively (Goldstein & Safe, 1989). Since about one decennia, there is a ban on PCB production and use. However, the world is

left with an amount of about 1.2 million tons of PCB (Tanabe, 1988), from which 65% is in stock or in use, 31% in the environment (and for 3/5 in the marine environment), while only <3.2 % is degraded or burned. The option to burn PCB's has not yet been applied extensively, due to the very high temperatures being required, and the possible production of toxic Oxines.

5.1 PCB Behaviour in Estuarine Compartments of Water, PM, Sediments

$$K_{ow} = \frac{[PCB]_{octanol}}{[PCB]_{water}} \qquad [15]$$

PCB congeners are non-polar compounds and have therefore a low solubility in water. They adsorb to solid surfaces (being less-polar than water) and `dissolve' easily in lipids and fats. Their degree of non-polarity is defined by the partition ratio between water and octanol, giving a partition coefficient K_{ow} which is defined as:

Each PCB congener has a specific K_{ow} value, which almost corresponds proportionally with its IUPAC Nr. (Brownawell & Farrington, 1985, and Duursma *et al.*, 1986).

The principle of a partition coefficient K_d, as defined by (7), is adopted for studying the partition of PCB congeners between the dissolved and particulate compartment:

$$K_d = \frac{\mu g\ PCB\ /\ g(dry)\ PM}{\mu g\ PCB\ /\ g\ water} \qquad [16]$$

A study was made to determine these K_d's in an estuarine system where a large variety of salinities, PM concentrations and PCB concentrations occurred. As given in Fig. 5 of Duursma *et al.* (1986), $logK_d$ (which is the left bar) is at the level of about 5

(K_d about 10^5), independent of the salinity (right bar) of the concentration of PCB's in solution (middle bar).
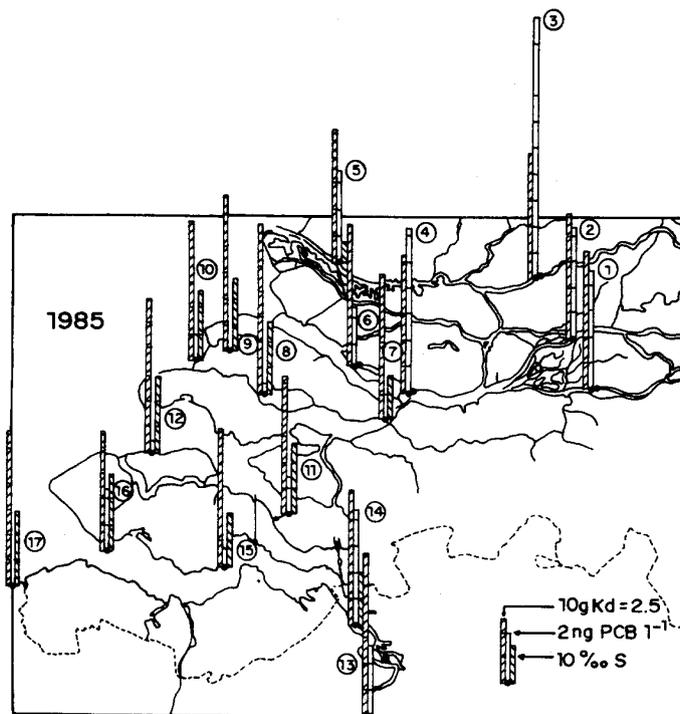
**Figure 5 - Concentrations of dissolved PCB's (middle columns),
logK$_d$'s (left columns) of PCB partitioning between water and
particulate matter and salinities (right columns).
From Duursma *et al.* (1989).**

5.2 PCB Accumulation in Organisms

5.2.1 K_d's

The thesis whether accumulation through the food chain is correct or incorrect is of essence to understand the impact of this pollutant on ecosystems and man. In 1982 a German scientists (Schneider, 1982) posed the thesis that organochlorines in marine organisms were in apparent equilibrium with the environmental concentrations of these compounds in the water compartment. This thesis implies that although there is uptake of organochlorines through the food chain, the eventual level of contamination is **independent** of this food chain. Calculated on (lipid) fat basis, the level of DDT and PCB should be equal for those organisms occurring in the same region. Fig. 6 of Duursma *et al.* (1986) presents K_d values for ΣPCBs (on lipid basis) of a number of benthic organisms, which individually have different body lipid contents. The log K_d's are, even for eggs of shrimp, all of the level of 6.5 **+** 0.2. The findings by Duursma *et al.* (1989) for mussels confirm this for individual PCB congeners, since the standard error for K_d is very low for Kd's determined over a period of 1.5 year. There is even for some congeners little difference between the stations.
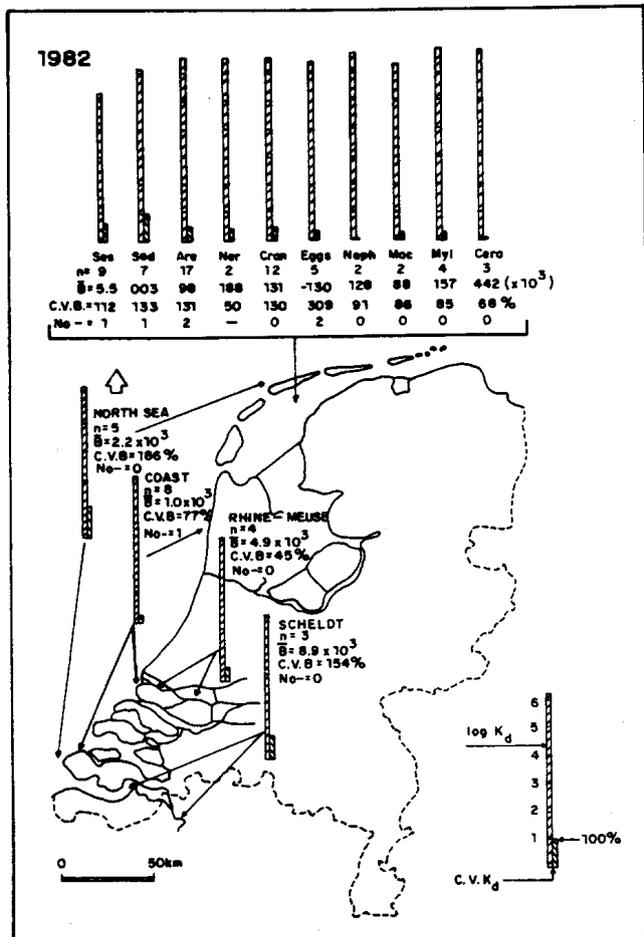
Figure 6 - LogK$_d$'s of partitioning of PCB's between lipids in various organisms and sea water (upper bars) and of PCB's between particulate matter and sea water (lower four bars). From Duursma *et al.* (1989). Ses. = seston or PM, Sed = sediment, Ara = *Arenicola marina*, Ner = *Nereis virens*, Cran = *Crangon crangon*, Eggs = eggs from shrimp, Neph = *Nephtys hombergii*, Mac = *Macoma balthica*, Myt = *Mytilus edulis* and Cer = *Cerastoderma edule*.

5.2.2 The eel-case

For the European eel **Anguilla anguilla**, which reproduces in the open sea, the question was posed to what extent contamination by polychlorinated biphenyls (PCBs), accumulated in the lipid fraction of these organisms during their stay in contaminated freshwater systems, continues to be present during migration into the open sea. Although such specific partitioning of PCB congeners has not yet been demonstrated for eel, the principle of constant partitioning between water and lipids in living organisms suggests that loss of PCB congeners should occur when eel migrates from freshwater systems to the sea, where lower dissolved PCB concentrations occur. It is known that during migration to their ocean reproduction regions eels fast and have to live on their reserve of lipids and organs such as their alimentary track. This may have a particular effect on their metabolism and as such also on the PCB congener loss processes from the lipid to the water compartments. Shifts may also occur in the spectra of the PCB congeners, indicating specific metabolic activity on the PCB congeners.

A simulation experiment was set where a number of female and male migrating adult silver eels, captured in the river Rhine-branch the Waal (Duursma *et al.* 1991). The eels were kept under starvation conditions for 91 days in running seawater. Eels were periodically sampled for PCB analysis, in order to obtain an answer to the above-mentioned questions and, in particular to how starvation affects PCB congener spectra and partitioning between the lipid (in eel) and water compartment.

The results of this study showed that a constant partitioning coefficient Kd (defined as the ratio of PCB in lipid, given in $\mu g.g^{-1}$ and dissolved PCB in $pg.g^{-1}$ with time was **not** found for selected PCB congeners in eel. There was **no** loss of PCB's from the eel to the water compartment, such as should be expected on the basis of the equal partitioning hypothesis.

The explanation is given that for aquatic organisms equal partitioning of PCB's between water and lipids in organisms is only possible when the organisms have an **active** metabolism. This would match the results that for various marine organisms under normal *in situ* feeding conditions such an equilibrium is attained, while for starving eels, with no metabolic activity the exchange between PCB's in lipids and the water compartment outside these eels has been blocked.

For other reasons, the exchange of PCB's with the environment is also 'blocked' for terrestrial organisms, such as birds and mammals which feed on marine organisms. Therefore they can accumulate PCB's in their lipids to a much higher level than was found for aquatic organisms. This counts also for man.

The principle of accumulation in the food chain has therefore to be understood in another sense. Within the aquatic environment there is **no** accumulation through the food chain, at least when there is active feeding and involved metabolism. But outside the aquatic system, birds, mammals and other organisms can accumulate PCB's to high levels in their lipids. Obviously these PCB's must have arrived there through food and drinking water. What does not to be true that there should be a gradual increase towards the top predator, since all of the organisms have the same chance of accumulation PCB's into their lipids. In that sense it will rather depend on the food consumed than the place in the food chain.

The principle of accumulation in the food chain has also often been used for metals and radionuclides. Here there is even less reason for a general principle, since accumulation is different for each metal, and specific with respect to many processes involved. Known is that for example for mercury accumulation is time-dependent, thus showing an increase of mercury level with age in for example Mediterranean tuna (Bernhard, 1985, 1988).

5.2.3 Conclusion

The behaviour of contaminants in aquatic and terrestrial organisms, including man that feed on aquatic organisms is both specific and complex and cannot be approached by a too simplistic principle. Nevertheless exchange equilibria may exist between the contamination of the water system and the aquatic organisms only, from which use can be made to test water quality by analyzing for example shellfish.

Equilibria will certainly be faster established at elevated temperatures, such as in the tropics, which also indicates that findings obtained in temperate waters cannot be extrapolated without knowledge on the temperature effects.

6. CONCLUSIONS

1. Contaminants may be partitioned between water, sediment, particulate matter and organisms compartments, for which partition coefficients (K_d's) can be determined. These K_d's are useful empirical factors to calculate the percentage distribution between dissolved and particulate matter, the diffusion of contaminants into the bottom and the accumulation in organisms. Thus analyzing either sedimentary materials and organisms may give useful indications of the concentrations of the contaminants in the water compartment.

2. Are tropical estuaries sinks or sources has to be answered in a time context. A tropical estuary, newly contaminated will be a sink for a very long period, although equilibrium between input and output may be sooner obtained than in temperate climates. It may afterwards become a source, where the bottom sediments act as a buffer with very long turnover times up to 1000 years.

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