Spatial and Temporal Heavy Metal Distribution Model under Estuarine Mixing

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ABSTRACT:

In modelling the fate and transport of heavy metals often the distribution coefficient, K_d, concept is applied to determine the amount of sorbed and dissolved fractions. Usually, these distribution coefficients are assumed to depend only on suspended sediment concentrations. In estuaries however, observations indicate that dissolved concentrations increase with salinity. It is hypothesised that salt competes for the binding sites leading to lower distribution coefficients. To study the fate and transport of heavy metals in an estuarine environment, a 2-D finite volume depth averaged toxic transport model has been developed. The distribution coefficients are approximated as a function of sodium activity or salt concentration. Other model parameters are obtained from a recently developed hydrodymanic model, salt transport and cohesive sediment transport modules. The model has been applied to the Scheldt estuary and the results for both sorbed and dissolved heavy metal concentrations agree quite well with measured data, indicating that under estuarine mixing, salt concentration is an important factor affecting the fate and transport of heavy metals.

1 Introduction

In the transport of heavy metal through an estuarine salinity gradient, various physical and chemical processes occur such as, dissolution, precipitation, binding to and release from suspended particulate matter, complexing with organic and inorganic ligands, and removal from the water column by sedimentation of the heavy metal loaded suspended particulates to the estuarine bottom.

Because metals do not degrade, volatilize or decay, their fate in natural waters is mainly controlled by transport processes (Novotny, 1995). It has been shown by many rearchers that the behaviour of heavy metal in estuarine environment is strongly influenced by sorption on suspended solids (Duinker et al., 1982; Valenta et al., 1986; Va Alsenoy et al., 1990). A spatially lumped distribution or partition coefficient K_d is used to describe the two phases (Figure 1).

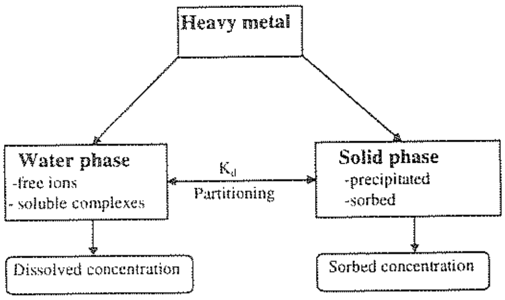

Figure.1 Phase transfer of heavy metals by sorption.

Settling and deposition of sediment sorbed solutes are the major removal mechanism for contaminants in the overlaying waters, while resuspension of contaminated sediment together with desorption processes serve as major sources of contaminants.

In order to provide a better insight into the complicated transfers of metals in estuaries the distribution of trace metals between water and particulate needs to be known and how it is affected by salinity. Usually distribution coefficients are approximated based on suspended sediment concentrations (Delos et al., 1984), though they are a bit higher than the normal values (Ambrose et al., 1991). In estuaries, observed data indicates that dissolved concentrations increase with salinity, a phenomenon which cannot be unequivocally interpreted (Valenta et al., 1986). Mixing of metal-loaded fluvial sediments with unpolluted marine sediments, or precipitation and dissolution are the possible causes of this phenomenon. More likely salt increases competition for binding sites leading to lower distribution coefficients but at present no specific relationship has been formulated to relate the salinity and distribution coefficients.

Spatial resolution of many developed heavy metal models is limited by the numerical approach. In order to represent the complex estuarine geometry a finite volume numerical technique is used in this study. The mesh is composed of arbitrary triangular and quadrilateral elements. The model is linked to the hydrodynamic module, the salt transport module and the sediment transport modules which were developed earlier (Mwanuzi et al., 1997; Mwanuzi and De Smedt,1997a,b). Then the model is applied to the Scheldt estuary and simulated sorbed and dissolved heavy metal concentrations will be compared with measured data such that the salt concentration affecting the fate and transport of heavy metals can be investigated.

2 Estimation of the distribution/partition coefficient K_d

In field and laboratory sorption studies the distribution coefficient, K_d, $[L^3/M]$, is defined as (Li et al., 1984; Bale, 1987; Turner et al., 1992a)

$$K_d = C_s / C_a \qquad (1)$$

where C_s is the sorbed constituent concentration $[MM^{-1}]$, C_a is the aqueous dissolved constituent concentration $[ML^{-3}]$. Both variables are highly sensitive to methods of determination (Bourg, 1987; Turner et al., 1992a,b), and their interpretation has often implicitly relied on the assumption of equilibrium and fully reversible sorption (Li et al., 1984; Morris, 1986)

A wide range of distribution coefficients for various heavy metals is given by Delos et al. (1984) as cited by Ambrose et al. (1991). These values are given as a function of suspended sediment concentration. Incorporating these values into the model requires an interpolation. Reyns (1995) applied a piece wise linear interpolation. For a wider range of suspended sediment concentration Novotny (1995) proposed a non-linear interpolation

$$K_d = K_{po} SS^{\alpha} . 10^3 \qquad (2)$$

where K_{po} and α, are constants and SS is the suspended sediment concentration.

However, the parameters cited by Novotny (1995) seem to be wrong.. Writing the equation in logarithmic form

$$\mathrm{Log} K_d = b \mathrm{Log} SS + c \qquad (3)$$

and performing a linear regression on the data as cited by Ambrose et al. (1991), gives optimal values for parameters b and c as shown in Table 1. Table 2 shows an example for copper.

Table 1 (Optimum parameters)

Metal	This study		Novotny (1995)	
	b	c	Kpo	alfa
Aresnic	-0.732	5.706	4.80E+05	0.27
Cadmium	-1.108	6.582	4.00E+06	0.87
Chrom.	-0.924	6.505	3.36E+06	0.07
Copper	-0.749	6.013	1.04E+06	0.26
Lead	-0.187	5.464	3.10E+05	0.81
Nickel	-0.563	5.659	4.90E+05	0.43
Zinc	-0.66	5.99	1.25E+06	0.3

In general there is no consistency in reported K_d values for any particular metal mainly due to high experimental variability (Van Alsenoy et al., 1989). Partition coefficients depend upon the characteristics of the sorbents, including mineralogy, chemical structure, composition and electrical properties, presence of coatings, etc. Hence, site specific values should be used when possible.

Table 2 Distribution coefficient at variable susupended sediment (*Ambrose et al., 1991, **This study, ***Novotny (1995)

Metal	SS	*Kd	b and c	Kd**	Kpo, alfa	Kd***
	(mg/l)	(l/kg)		(l/kg)		(l/kg)
Copper	1	1.E+06	-0.749	1.E+06	1.04E+06	1.E+06
	10	2.E+05	6.013	2.E+05	0.26	2.E+06
	100	3.E+04		3.E+04		3.E+06
	1000	6.E+03		6.E+03		6.E+06

3 Model development

3.1 Salinity dependent distribution coefficient

Research findings show that the distribution coefficient increases with decreasing suspended sediment. The smaller the suspended sediment, the higher the distribution coefficient and vice versa (Delos et al., 1984, Ambrose et al., 1991) Because usually sea end has low suspended sediment then the K_d is larger at the sea end than the fluvial end. However, in a saline environment, the elevated salt concentration create an increased competition between cations and metal ions, leading to less sorbed heavy metal concentrations, such that K_d decreases with increasing salinity.

If we assume that the cations present in salt water compete with metal for binding sites, we can represent the reaction equilibrium equation as;

$$C_{me} + A_{sa} \Leftrightarrow A_{me} + C_{sa} \qquad (4)$$

$$K = \frac{A_{me} C_{sa}}{C_{me} A_{sa}} \qquad (5)$$

where K is the equilibrium constant, C_{me} and C_{sa} are the dissolved metal and salinity expressed in activities, A_{sa} is the sorbed salt cations concentration $[MM^{-1}]$ and A_{me} is the sorbed metal concentration $[MM^{-1}]$. From the above equation we can write the distribution coefficient equation as

$$K_d = \frac{K A_{sa}}{C_{sa}} = \frac{K'}{C_{sa}} \qquad (6)$$

Suppose for river water we have $C_{sa} = C_{sa}^u$ and $K_d = K_d^u$, such that

$$K' = K_d^u C_{sa}^u \qquad (7)$$

where C_{sa}^u is the salt ion activity in riverine and K_d^u the corresponding distribution coefficient.

The general equation for the distribution coefficient becomes

$$K_d = K_d^0\left(\frac{C_{sa}^0}{C_{sa}}\right) \tag{8}$$

In a very dilute aqueous systems such as fresh natural water we can use concentrations in terms of moles/liter directly. In more concentrated solutions it is necessary to use the activity coefficient, because as the concentration of ions in solution increases, electrostatic interactions between the ions also increase and the activity of ions become somewhat less than their measured or analytical concentration (Soyenik, 1980)

The salinity of sea water is about 35g/l, with an ionic strength of 0.7M. The major cation in the sea water is sodium which contributes to 31% of the total salinity. If sodium is taken to represent the cations of salt water then its activity at various salinities can be computed. The salinity ratios in equation (8) can then be computed and the distribution coefficient as a function of salinity determined.

The plot of the reciprocal ratios of salt concentration and activity versus salinity is given in Figure 2. If the ratio of activities is replaced by the ratio of salt concentration, then the distribution coefficient can be calculated approximately as.

$$K_d = K_d^0 / \frac{C_s}{C_0}\left(1 - a\frac{C_s}{C_0}\right) \tag{9}$$

where the symbol C on the right hand of equation (9) now represent salt concentration and a, is a coefficient equal to 0.01368

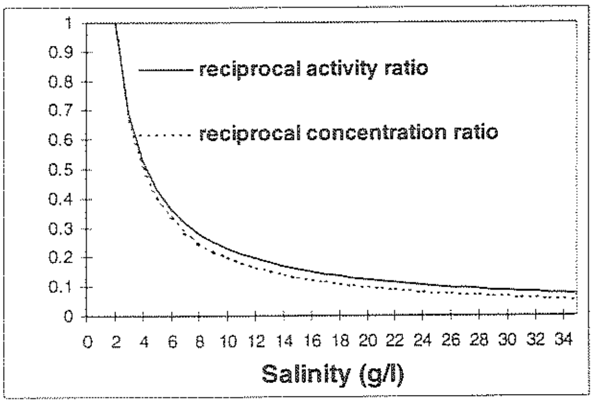

Figure 2. Plot of reciprocal activity and concentration versus salinities

3.2 Transport Model

A two dimensional, depth averaged, toxic pollutant transport model can be written as

$$\frac{\partial(hC_t)}{\partial t} = \nabla\cdot(h\mathbb{D}\cdot\nabla C_t) - \nabla\cdot(h\mathbf{V}C_t) - W_d C_s + W_e C_{sb} \tag{10}$$

where C_t is the total heavy metal concentration $[ML^{-3}]$, h is the water depth [L], $\mathbb{D}$ is the dispersion tensor $[L^2T^{-1}]$, C_s is the concentration of sorbed heavy metal on suspended solids $[MM^{-1}]$, C_{sb} is the concentration of sorbed heavy metal on bottom solids $[MM^{-1}]$, W_d is the rate of sedimentation $[ML^{-2}T^{-1}]$, and W_e is the rate of sediment resuspension $[ML^{-2}T^{-1}]$. The first and second terms on the right hand side of equation (10) represent transport fluxes while the third and fourth terms are reaction rates (rate of removal of sorbed chemical by settling and rate of resuspension). The sedimentation and erosion rates are obtained from the sediment transport model.

The total solute concentration (sorbed and dissolved) is given by

$$C_t = C_a + C_p = C_a + SC_S \tag{11}$$

where C_p is the particulate concentration of heavy metal sorbed on the sediment $[ML^{-3}]$.

The sediment sorbed concentration of heavy metal in the bottom layer changes according to its mass balance equation

$$H\frac{\partial C_b}{\partial t} = C_s W_d - \frac{C_b}{S_b} W_e \tag{12}$$

Where C_b is the bottom sediment heavy metal concentration $[ML^{-3}]$, given by $C_b = C_{sb}S_b$ and S_b is the concentration of sediment at the bottom $[ML^{-3}]$, while H is the depth of the active bottom layer [L].

Sorption of heavy metal on suspended sediment is modelled by a linear adsorption isotherm with a partitioning coefficient K_d $[L^3M^{-1}]$, such that the concentration of sorbed solute is gives as

$$C_p = K_d S C_a \tag{13}$$

3.3 Solution procedure

The solution of equation (10) is determined in the same way as for previous developed modules (Mwanuzi et al., 1997) and the same finite volume spatial discretization of the study domain is applied. The hydrodynamic module computes discharges, velocities and water heads, the salt transport module provide mixing parameters, while the sediment transport module computes suspended sediment concentrations and erosion and sedimentation rates. These parameters are then used as input to the heavy metal transport model.

$$A_e\frac{\partial h_e C_e}{\partial t} = -\sum_b\left(Q_b C_b + D_L w_b h_b \frac{\partial C_b}{\partial n}\right) - W_d C_s A_e + W_e C_{sb} A_e \tag{14}$$

The numerical solution of equation (14) becomes;

$$(h_e C_e)^{t+\Delta t} = (h_e C_e)^t - W_d C_s + W_e C_{sb} + \frac{\Delta t}{A_e}\left[\left(\sum_{j=1}^{4\,\mathrm{or}\,3} \underline{D} w_{b_j}^{t+\frac{\Delta t}{2}} h_{b_j}^{t+\frac{\Delta t}{2}} \left(\frac{C_r^t - C_l^t}{d}\right)\right) - \sum_{j=1}^{4\,\mathrm{or}\,3}\left(Q_{b_j}^{t+\frac{\Delta t}{2}} C_{b_j}^t\right)\right] \quad (15)$$

Where the symbol C_e now represents the total metal concentration in an element e.

4 Application to the Scheldt estuary

The heavy metal transport model is applied to the Scheldt estuary and Belgian coast area (Figure 3). To be able to apply the model, all input data and parameters have to be estimated and necessary boundary conditions have to be set.

There is a very limited data about the distribution of heavy metal in the Scheldt estuary. The most recent reliable data found are those of a series of measurement campaigns conducted in the period of December 1987 to July 1988 (Van Alsenoy et al., 1989; 1990; 1993), where the amounts of heavy metals (Cu, Cr, Zn, Pb, and Ni) sorbed on the suspended sediment fraction less than 63μm were measured at 20 stations in the North sea and the Scheldt estuary. Measurements in the sea have been conducted by Everaarts and Fischer (1992) and are used as marine end boundary conditions. For the upstream boundary at Rupel, data measured south of Antwerpen were extrapolated (Reyn, 1995). Fluvial sediment concentrations of 130mg/l were used while 65mg/l were applied at the sea boundary condition.

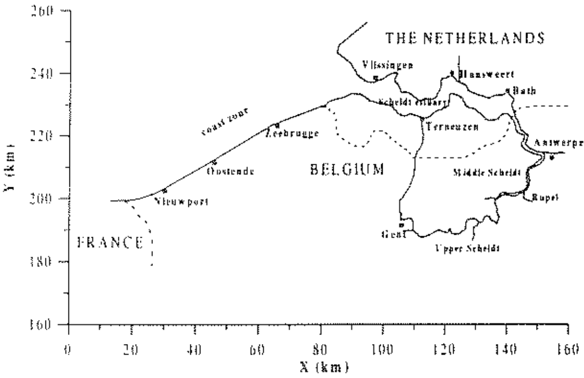

Figure 3. Map of the Scheldt estuary and coastal areas.

To determine the distribution coefficient, different approaches are used and later compared. Literature laboratory and field values, literature empirically approximated value and the formulation discussed earlier are also applied (Table 3) and their results compared. Experimental K_d values are obtained from Monteny et al. (1993).

From Table 3 it can be observed that the dissolved metal fractions at both boundaries, river end member (REM) and sea end member (SEM) are not well represented if the distribution coefficients are interpolated as a function of suspended solids when compared with measurement. For instance experimental results of copper (Cu), indicate that the dissolved fraction is much higher at the SEM as compared to REM (Monteny et. al., 1993). By using the salinity dependent distribution coefficients we obtained dissolved fraction percentages close to the measurement.

Table 3 Boundaries copper concentrations (River End Member-REM and Sea End Member- SEM)

Metal	Sorbed Solids REM	Sorbed Solids SEM	Distr. Coef. REM	Distr. Coef. SEM	Total Solute REM	Total Solute SEM	Dissol. Solute REM	Dissol. Solute SEM
Function of sed. conc. (linear interpolation)								
	Cs (μg/g)	Cs (μg/g)	Kd (l/kg)	Kd (l/kg)	Ct (μg/l)	Ct (μg/l)	Cw %Ct	Cw %Ct
Cu	170.00	12.00	23000	90000	29.49	0.91	25.1	14.6
Function of sed conc. (loglinear interpolation)								
Cu	170.00	12.00	31336	43697	27.53	1.09	19.7	25.2
Function of salinity								
Cu	170.00	12.00	220000	16863	22.87	1.49	3.4	47.7
Experimental results								
Cu	170.00	17.00	233880	23014	22.83	1.89	3.2	39.0
Constant (fluvial end characteristics)								
Cu	170.00	12.00	233880	233880	22.83	0.87	3.2	5.9
Constant (marine end characteristics)								
Cu	170.00	12.00	23014	23014	29.49	1.34	25.1	39.0

The salinity dependent distribution coefficients were determined using the salinities obtained from the salt transport module. The only unknown is the river end distribution coefficient. Matching the observed data with simulations results proper values of distributions coefficients were determined, (K^o_d of 220001/kg for Cu)

Initially concentrations in each computation element were set to zero. Other parameters are obtained from the flow hydrodynamic module, sediment transport and salt transport models. Equilibrium condition for heavy metals are readily established after a period of 60 tides in the Scheldt estuary (Reyns , 1995). In this study simulations were carried out for about 9 neap-spring tidal cycle (243 tidal cycles). The last two neap spring cycles (54 tides) were used to report the average concentrations. The resulting profiles of total, sorbed and dissolved metal concentration for Copper are given in Figure 4 a,b and c.

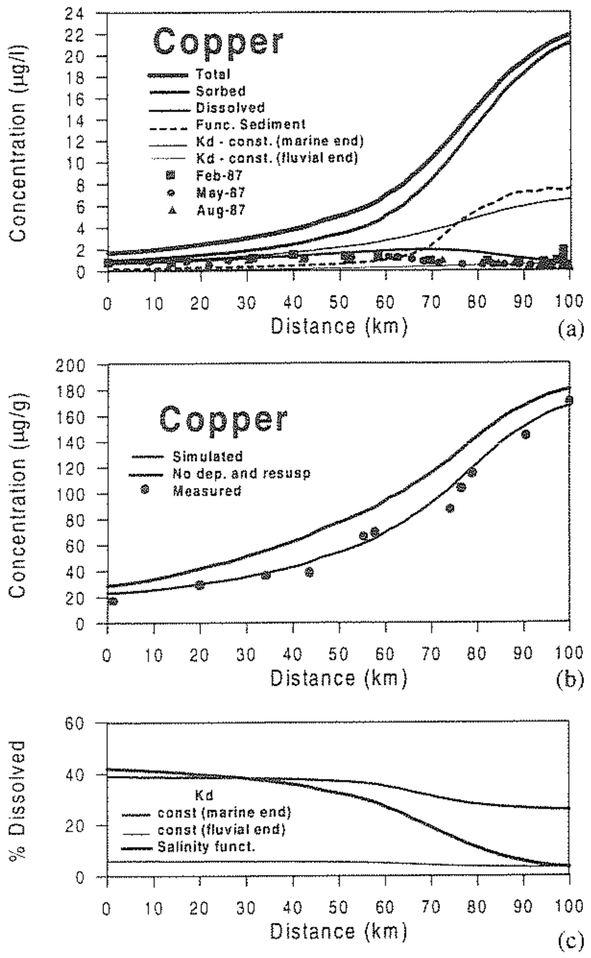

Figure 4 (a,b,c). Profiles of total, sorbed and dissolved copper concentrations

From the figure it can be observed that, if a constant distribution coefficient equal to that of REM (fluvial end) is applied then the percentage of dissolved fraction remain quite low throughout the estuary (Figure 4a,c). If a smaller distribution coefficient applicable to the SEM is applied then the dissolved fraction percentages are quite higher throughout the estuary. These observations, indicate that a distribution coefficient which is a function of the mixing indicator is the only compromise solution.

When the distribution coefficient is varied as a function of salinity, reasonable results close to measured data are obtained for both sorbed and dissolved metal. In the scenario where sedimentation and resuspension were not considered, sorbed metal concentrations are relatively higher (Figure 4b). Clearly it can be seen that there is a net sedimentation of the metals in the estuary. The coefficient is obtained as explained earlier above. This is based on an analogy of the mass action law (Freeze and Cherry, 1979). In the saline environment, the presence of other ions compete with the dissolved metal for the same binding sites leading to less amount of sorbed metal. For Humber estuary, Betty et.al., (1996) applied an emperical relationship (Millward and Turner, 1995) between salinity and distribution coefficient to study the geochemistry of cadmium and zink in the estuary.

$$\ln K_d = b \ln(C+1) + \ln K_d^o \qquad (16)$$

With this distribution coefficient, they were able to reproduce only the dissolved metal fraction while the particulate metal concentration differed substantially with the measured data. This major disprepancy of the results was attributed to the non-representativeness of the measured data, mainly due to the problem is the isolation of particulate metal fraction during laboratory analysis.

The resulting distributions of total heavy metal concentrations captured during ebb tide are shown in Figure 5. The highest concentrations are situated in the main flow channels. This is in agreement with the velocity fields. Higher velocities in the main channel are responsible for resuspension of bottom sorbed solute leading to higher concentrations in the main channel, while low velocities in the shallow areas cause sedimentation, thus a sink or loss of sorbed metal.

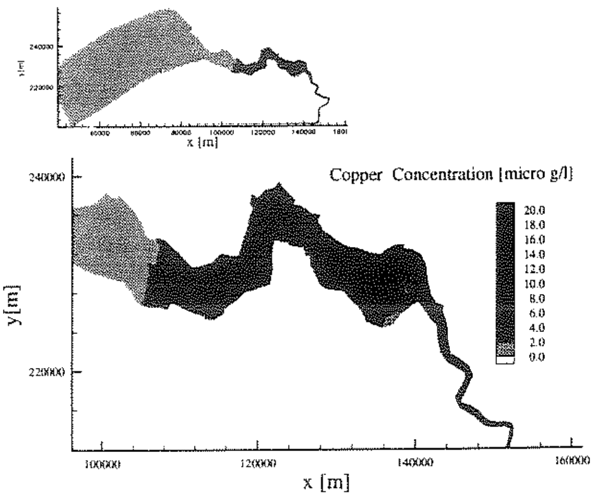

Figure 5. Distribution of copper concentrations

5 Conclusions

In the modelling transport of heavy metals, often the distribution coefficient, K_d, concept is applied to determine the amount of sorbed and dissolved fractions. Usually, these distribution coefficients are approximated based on suspended sediment concentrations. However, in estuaries, the observed data indicate that dissolved concentrations increase with salinity. It is hypothesised that salt creates an increased competition for binding sites, leading to lower distribution coefficients. In this study, the distribution coefficient is approximated as a function of sodium (Na^+) activity and eventually salt concentration. A comparison is made with the distribution coefficients obtained as a function of suspended sediment concentrations as given in the literature. The model was also applied to the Scheldt estuary, and the results for both sorbed and dissolved heavy metal concentrations agree quite well with measured data, indicating that under estuarine mixing salt concentration is an important factor affecting the fate and transport of heavy metals

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