Simulation of transport of toxic pollutants in surface waters

F. De Smedt, F. Mwanuzi

Laboratory of Hydrology, Free University Brussels, Pleinlaan 2, B-1050 Brussels, Belgium

Abstract

A model is presented for simulating the transport of toxic pollutants in rivers, estuaries and seas. Such transport strongly depends on the presence of suspended sediment, which is known to be an important carrier of sorbed chemicals. Hence, the movement of these contaminants can only be predicted if the movements of sediments is well understood, which also necessitates a detailed understanding of the hydrodynamic processes. Consequently, the developed model consists of different submodels for simulation of water movement, salt transport, suspended sediment transport, and transport of sorbing toxic pollutants. The model is applied to the river Scheldt (Belgium), the Scheldt estuary (The Netherlands), and the sea along the Belgian coast. Simulation results are presented for several heavy metals and organic micropollutants, as PCB, proving the importance of particulate matter. In particular, it is shown that sorbing chemicals tend to accumulate in the estuarine sediments, while only small amounts are reaching the sea. In addition, it is found that the mobility of heavy metals is strongly influenced by salinity, and that the mobility of organic pollutants depends upon complexation with dissolved organic matter.

1 Introduction

In this paper a model is presented for the simulation of transport of toxic pollutants in the Scheldt estuary, which is known to be severely polluted by chemical compounds as heavy metals and organic micropollutants

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(van Zoest and van Eck [1]). It appears that the behaviour of many toxic pollutants in the Scheldt estuary is strongly governed by water flow dynamics and especially by sediment transport. Vuksanovic et al. [2] used the WASP model (Ambrose et al. [3]) to predict the fate of PCB and showed that hydrophobic sorption was the most important physicochemical reaction to determine the fate of such pollutants. The modelling results indicate that PCB accumulates in the bottom sediments of the estuary and that there is little transport to the sea. In the present study the application is extended, by developing a general model that is capable to simulate the transport of any sorbing pollutant in an estuarine environment. Emphasis is taken on the role of dissolved matter on transport of organic micropollutants and the effect of salinity on heavy metal transport.

2 Model equations

The model is based on the following physical relationships:

1) Continuity equation for water

$$\frac{\partial z}{\partial t} + \nabla \cdot (h\underline{v}) = 0 \tag{1}$$

with z the water level elevation [L], ∇ the del-operator [L^{-1}], h the water depth [L], $\underline{v}$ the water flow velocity vector [LT^{-1}], and t the time [T].

2) Momentum equation for water flow

$$\rho h \left[\frac{\partial \underline{v}}{\partial t} + (\underline{v} \cdot \nabla)\underline{v} \right] = -\nabla(\rho g \frac{h^2}{2}) - \rho g h \nabla z_b - f\rho h\underline{v} - \underline{\tau} \tag{2}$$

with ρ the fluid density [ML^{-3}], g the acceleration due to gravity [LT^{-2}], z_b the bottom elevation [L], f the coriolis factor [T^{-1}], and $\underline{\tau}$ the shear stress [FL^{-2}] at the bottom, which is calculated with the Manning equation.

3)   Transport equation for salt

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$$\frac{\partial hC}{\partial t} = \nabla \cdot (h\underline{\underline{D}} \cdot \nabla C) - \nabla \cdot (h\underline{v}C) \tag{3}$$

with C the salt concentration $[ML^{-3}]$, and $\underline{\underline{D}}$ the dispersion tensor $[L^2T^{-1}]$, which represents the effects of depth averaging and turbulent mixing processes.

4) Transport equation for suspended sediment

$$\frac{\partial hS}{\partial t} = \nabla \cdot (h\underline{\underline{D}} \cdot \nabla S) - \nabla \cdot (h\underline{v}S) - W_d + W_e \tag{4}$$

with W_d and W_e the rates of deposition and erosion $[ML^{-2}T^{-1}]$ and S the suspended sediment concentration $[ML^{-3}]$. The rate of deposition is related to the bed shear stress and a critical shear stress, and may be computed as a function of the fall velocity, v_s, and the sediment concentration. The erosion rate is related to a critical shear stress below which erosion does not occur (Mwanuzi and De Smedt [4])

$$W_d = \max\left[v_S S(1 - \tau/\tau_d)\,,\,0\right] \qquad W_e = \max\left[E(\tau/\tau_e - 1)\,,\,0\right] \tag{5}$$

with τ_d and τ_e critical shear stresses for sedimentation and erosion, and E the erodability $[ML^{-2}T^{-1}]$.

5) Transport equation for sorbing chemicals

$$\frac{\partial hC_t}{\partial t} = \nabla \cdot (h\underline{\underline{D}} \cdot \nabla C_t) - \nabla \cdot (h\underline{v}C_t) - W_d C_s + W_e C_{sb} \tag{6}$$

with C_t the total concentration $[ML^{-3}]$, C_s the sorbed concentration per mass of suspended solids $[MM^{-1}]$, and C_{sb} the concentration of sorbed chemical on the bottom solids $[MM^{-1}]$. For heavy metals the total concentration (sorbed and dissolved) is given by

$$C_t = C_a + SC_s \tag{7}$$

with C_a the aqueous concentration of dissolved heavy metal $[ML^{-3}]$. Sorption on suspended sediment is modelled by a linear adsorption isotherm with a partitioning coefficient, $K_d [L^3M^{-1}]$, i.e

$$K_d = C_s / C_a \qquad (8)$$

In the literature, K_d is often approximated as a function of the suspended sediment concentration (Ambrose et. al. [3]) resulting in higher K_d values near the sea. However, in a saline environment, the elevated salt concentration induces competition between cations and metal ions (Dzombak and Morel [5]) for the sorption sites, resulting in less sorption of heavy metals such that K_d decreases with increasing salinity. Assuming that the salt cations compete with metal ions for the binding sites, it can be shown that K_d decreases linearly with the salt activity (Mwanuzi and De Smedt [6]), which using the salt concentration can be stated as

$$K_d = \frac{K_d^o}{C/C_o \, (1 - a\, C/C_o)} \qquad (9)$$

with K_d^o the distribution coefficient in river water, C_o the salinity in river water, and a an activity coefficient.

For organic pollutants the total concentration is given by

$$C_t = C_a + S C_s + C_{om} C_c \qquad (10)$$

with C_c the concentration of organic solute complexed to dissolved organic matter [MM^{-1}], and C_{om} the dissolved organic matter concentration [ML^{-3}].

Sorption of organic micropollutants depends upon the fraction of organic matter, f_{om}, in the suspended sediment, such that K_d can be written in terms of a partitioning coefficient for particulate organic matter, K_{om}, as $K_d = f_{om} K_{om}$. In addition to sorption, the dissolved organic chemical can also bind to dissolved organic matter. This process can likewise be described by a partitioning coefficient, such that the complexed concentration of the solute is given as $C_c = K_c C_a$, in which K_c is the binding coefficient [$L^3 M^{-1}$]. Hence, the total concentration can be calculated as

$$C_t = \left(1 + f_{om} K_{om} S + K_c C_{om}\right) C_a \qquad (11)$$

In some studies (Ambrose et al. [3], van Meerbeeck [7]), K_c in equation (11) was considered to be equal to K_{om}, which is not true as

shown by Rav-Acha and Rebhun [8], and Rebhun et al. [9]. Other studies, like Vuksanovic et al. [2], did not differentiate between the free dissolved chemical and the complexed dissolved chemical, which introduces considerable error because complexed chemicals are not available for sorption on sediments or for biodegradation.

The partitioning coefficient for particulate organic carbon, K_{om}, can be calculated from the octanol-water partitioning coefficient, K_{ow}, which is easily obtained in laboratories even for low concentrations. Similarly, the binding coefficient, K_c, can also be calculated from the octanol-water partitioning coefficient (Rebhun et. al. [9]).

3 Model application

The model is applied to the Scheldt estuary and the sea near the Belgian coast (Figure 1). The Scheldt estuary is situated in the coastal plain border region between The Netherlands and Belgium. The estuary is well mixed. Freshwater inflows to the estuary vary between 20 to 600m³/s, with a mean value of 110m³/s, such that the residence time of the freshwater in the estuary is about 2 to 3 months. The tides are semi-diurnal with a period of approximately 12.4hrs and an amplitude of 2 to 3m. The average water depth is about 10m .
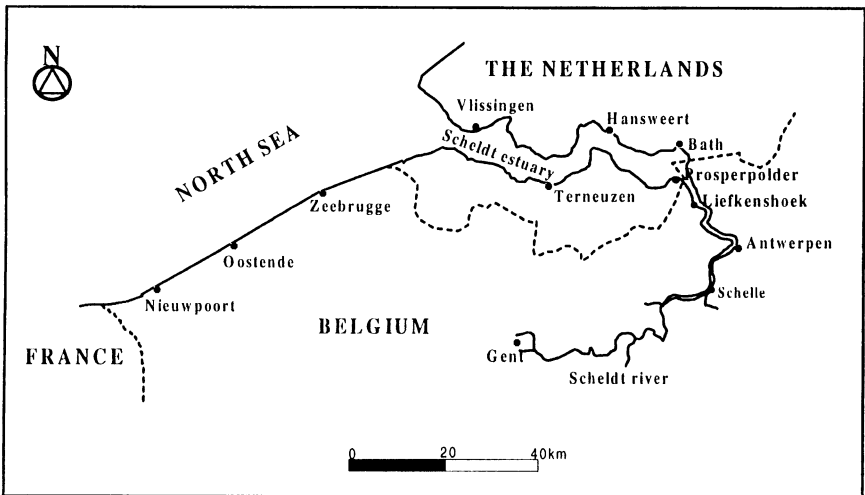

Figure 1.   Map of the Scheldt estuary and coastal area.

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There is 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. [10]). Measurements in the sea have been conducted by Everaarts and Fischer [11] and are used as marine end boundary conditions. For the upstream boundary at Schelle, data measured south of Antwerpen were extrapolated (Reyns [12]). Fluvial sediment concentrations of 130mg/l were used while 65mg/l was applied at the sea boundary. For the organic micropollutants data from 5 sampling campaigns in the estuary, undertaken between August 1987 to June 1988 (van Zoest and van Eck [1]) was used.

The simulation results for suspended sediment transport are represented in Figure 2, showing measured and calculated tidal averaged suspended sediments concentrations in the estuary. The ordinate is the longitudinal distance along the estuary, measured from the mouth at Vlissingen along the main navigation channel. In addition, also simulated results are given for suspended sediments of marine or of fluviatile origin. These calculations are necessary because the sediments have distinct compositions, in particular with respect to organic matter content. Measurements indicate that the organic matter fraction ranges from 0.16 upstream to only 0.03 in the sea. Hence, the fraction of organic matter is a function of the fluvial and marine sediment mixture, and can be approximated as

$$f_{om} = \frac{0.16 S_f + 0.03 S_m}{S_f + S_m} \qquad (12)$$

with S_f the fluvial suspended sediment concentration and S_m the marine suspended sediment concentration.

Once the suspended sediment transport is known, the heavy metal transport can be simulated using a fluviatile adsorption distribution coefficient deduced from measurements near Antwerpen. The resulting profiles of total, sorbed and dissolved metal concentration for copper and zinc are given in Fig. 3. From the simulations it was observed that, in case a constant distribution coefficient is used, the measurements could not be reproduced adequately. Also, when the distribution coefficient is determined as a function of the suspended sediment concentration as suggested in the literature, too high dissolved metal concentrations are obtained upstreams. When salinity dependent distribution coefficient are used the simulated values agree closely to the measured data for both sorbed and dissolved concentrations. This proves that the transport of

heavy metals is affected by salt, because of the competition for the absorbing sites on suspended sediment. From the figure it can be clearly seen that there is a net sedimentation of the metals in the estuary.

For the simulation of organic micropollutants the amount of organic matter is important. The mean concentration of dissolved organic matter in the fresh water over the whole estuary is about 5.5mg/l (Mwanuzi and De Smedt [13]).
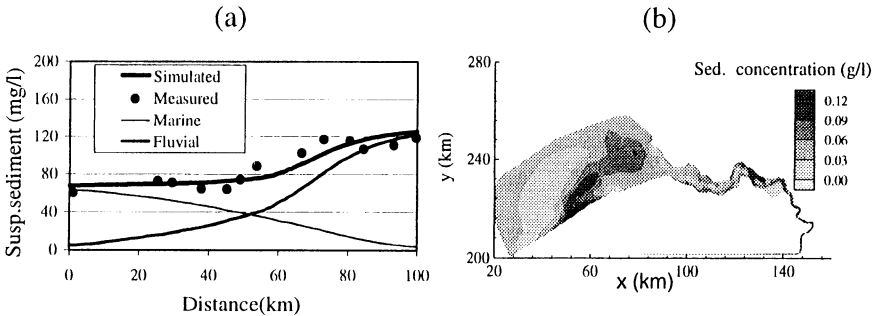
(a)   (b)

Figure 2. Average profiles of simulated (solid lines) and measured (symbols) suspended sediment in the estuary (a), and snap shot of sediment distribution in total study domain(b).
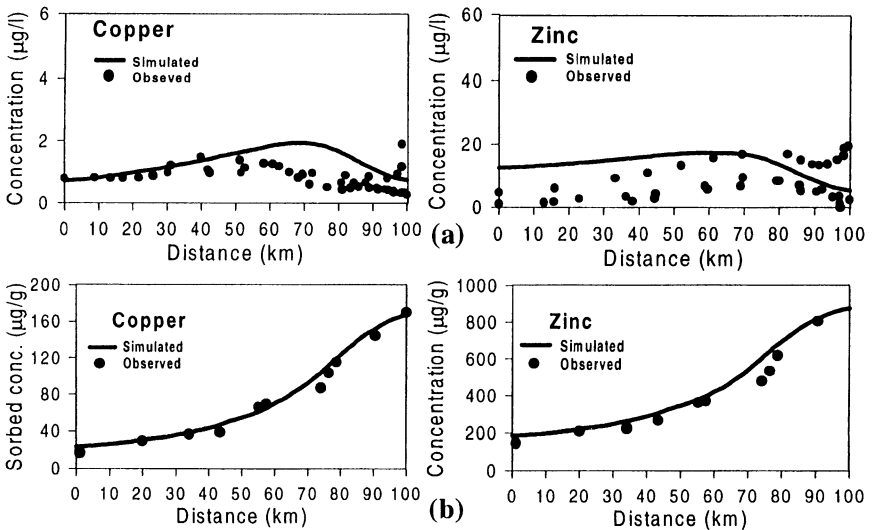

Figure 3.   Average profiles of dissolved concentrations (a), and sediment sorbed concentrations (b) of copper and zinc.

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For the simulation of PCB, the adsorption partitioning coefficients were calculated from the octanol-water partition coefficients (Mwanuzi and De Smedt [13]). To approximate the binding coefficient from the octanol-water partitioning coefficient the relationship suggested by Rav-acha and Rebhun [8] was used

Figure 4a shows the simulated and observed concentrations of PCB congeners 118 and 101, versus salinity, because no records were taken of the position of the samplings. Hence, salinity is used as a surrogate position indication. As can be seen from the figure the fit is reasonable. Results of van Meerbeeck [7] are not as good because he did not differentiate between free dissolved solute and complexed dissolved solute. Also, results of Vuksanovic et. al. [2] are not as good, because binding to dissolved organic matter was not considered at all.

Figure 4b gives the calculated average profiles of dissolved concentration, complexed solute concentration, sorbed concentration and total concentration in the estuary along the thalweg from the mouth of the estuary at Vlissingen (0km) to Schelle (100km). It can clearly be seen that the free dissolved fraction is the least important. Most important is the sorbed fraction, but the binded fraction is almost of the same order of magnitude. Hence, binding and complexing of PCB with dissolved organic matter is an important feature of the PCB transport mechanism. The obtained results indicate that also organic micro pollutants tend to accumulate in the estuary bottom sediments.
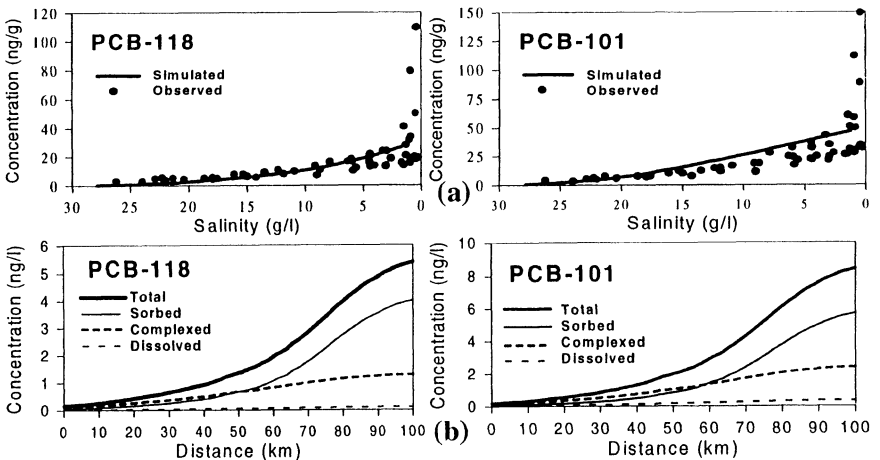

Figure 4. Simulated sorbed PCB-118 and PCB-101 concentrations versus salinity compared with data (a) and profiles of simulated total, sorbed, dissolved and complexed concentrations (b).

4 Conclusion

A model is presented for simulating pollutant transport in estuaries, when sorption is a dominant process. In such a case the model should take into consideration suspended sediment transport, because the fate of sorbing chemicals is strongly linked to it. The model was applied to the Scheldt estuary and it was shown that:

- the transport of heavy metals is affected by salt, because of competition for the absorption sites on suspended matter;
- the transport of micro organic pollutants is affected by dissolved organic matter because of complexing, which diminishes the free dissolved concentrations;
- all absorbing pollutants tend to accumulate in sedimentation areas within the estuary, while only small amounts are actually reaching the sea.

References

[1]   Van Zoest, R., and. van Eck, G.T.M,.Content, behaviour and modelling of organic micropullutants in water bottom of the Scheldt estuary. *Internal Report*. Rijkswatateren, Gravenhage and Rijksuniversiteit Utrecht: 23pp, 1989.

[2]   Vuksanovic, V., De Smedt, F. and Van Meerbeeck, S. Transport of polychlorinated biphenyls (PCB) in the Scheldt estuary simulated with the water quality model WASP. *Jour. Hydrol.*, Vol. 174, pp. 1-18, 1996

[3]   Ambrose, Jr. R.B., Martrin, J.L and Wool, T.A., WASP5, A Hydrodynamic and Water quality model: Model theory, *User's Manual and Programmer's guide,*. EPA,. Athens, GA: 76pp, 1991.

[4]   Mwanuzi, F., and De Smedt, F., A sediment transport model applied to the Scheldt estuary. *Proc. 9th Int. Conf. Transport and Sed. of solid particles,* Cracow, Poland, pp. 285-296, 1997.

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[5]   Dzombak, D.D., and Morel, F.M.M., Adsorption of inorganic pollutants in aquatic systems. *Jour. Hydr. Eng. ASCE*: Vol. 113(4) pp. 430-475, 1987.

[6]   Mwanuzi, F., and De Smedt, F., Spatial and temporal heavy metal distribution model under estuarine mixing. *Proc. The Int. Cong. On Modelling and Simulation,* Tasmania, Australia, pp. 373-378, 1997.

[7]   Van Meerbeeck, S., Simulatie van het sedimenttransport in de Scheldt met het waterkwaliteitsmodel WASP5. *Thesis,* Fac. Applied Sciences, Universiteit Brussel, 108pp, 1994.

[8]   Rav-Acha, C., and Rebhun, M., Binding of organic solutes to dissolved humic substances and its effects on adsorption and transport in the aquatic environment. *Jour. Water. Res.,* Vol. 26, pp. 1645-1660, 1992.

[9]   Rebhun, M., De Smedt, F. and Rwetabula, J., Dissolved humic substances for remediation of sites contaminated by organic pollutants: Binding-desorption model prediction. *Jour. Water Res.,* Vol. 30(9), pp. 2027-2038, 1996.

[10]   Van Alsenoy, V., Bernanard P., and Van Grieken, R., Elemental concentration and heavy metal pollution in sediments and suspended matter from the Belgian Nort Sea and Scheldt estuary. *Jour. Sci of Total environ,* Vol. 133, pp. 153-181, 1993.

[11]   Everaarts, J.M., and Fischer, C.V., The distribution of heavy metals (Cu, Zn, Cd, Pb) in the fine sediment fraction of surface sediment of the north sea. *Nether. jour. Sea. Res.* Vol. 29(4), pp. 323-331, 1992.

[12]   Reyns, D., Simulatie van het transport van zware metalen in het Schelde-estuarium met het waterkwaliteitsmodel WASP5. *Thesis, VUBussel,*: 120pp, 1995.

[13]   Mwanuzi, F., and De Smedt, F., Fate and transport of organic micropollutants (PCB) in an estuarine tidal environment: Application to the Scheldt estuary. *Proc, 6th BHS National Hydr. Sympo.* Manchester, UK, pp. 3.17-3.22, 1997.

SECTION 7

Waste Minimisation