A MODEL FOR THE BEHAVIOUR OF SOME TRACE METALS IN THE SCHELDT ESTUARY, S.W. NETHERLANDS.

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ABSTRACT

A management-oriented, one dimensional, dynamical, tidal average box model for personal computers for the behaviour of Cd, Cu and Zn in the Scheldt estuary was developed. The model calculates dissolved concentrations and particulate and sediment trace metal contents as well as their mass balance, containing transport and process fluxes. The calculations are based on emissions into the estuary, the transport of water and silt, and the processes observed in the estuary.

INTRODUCTION

The Scheldt estuary drains a densely populated and industrialized area in west Belgium and the south-west Netherlands. Since an important part of the industrial and domestic waste waters is discharged without prior treatment, both the river and its estuary are heavily polluted. During spring and summer, the low salinity zone is anoxic; during winter the oxygen saturation is 20-30%. A gradual restoration of the dissolved oxygen concentration occurs during estuarine mixing. Thus, the Scheldt estuary provides a unique opportunity to study the behaviour of trace metals along a combined longitudinal salinity and redox gradient. This study was done in 1987-1990.

Based on the results of this study a management-oriented water quality model was built. The model attempts to relate the trace metals discharged into the estuary to the concentrations and contents found in the water column and sediments. The behaviour of trace metals, the water quality model and model calibration are described below.

BEHAVIOUR OF TRACE METALS IN THE SCHELDT ESTUARY

The geochemistry of dissolved and particulate trace metals in the water column and sediments of the Scheldt estuary has been studied between 1987 and 1990. The results found are described in ref 1 and ref 2.

The geochemistry of dissolved Cd, Cu and Zn appears to be related to the redox conditions in the upper estuary and phytoplankton activity in the lower estuary. Both of these are seasonally dependent parameters. The Cd, Cu and Zn concentrations are controlled by sulphide precipitation in the (anoxic tidal) river and by metal sulphide oxidation in the estuary itself. Readsorption of Cd and Zn occurs in the lower estuary during the spring phytoplankton bloom.
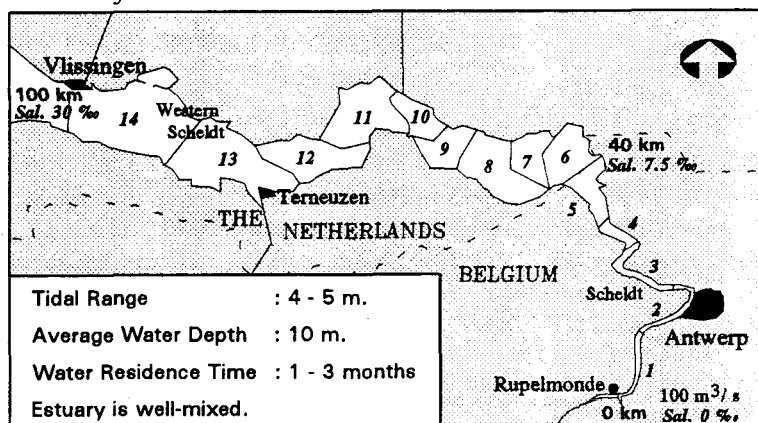
The Cd, Cu and Zn levels in the suspended matter decrease with increasing salinity, due to mixing of contaminated fluvial and relatively unpolluted marine particulates. Desorption of Cd, Cu and Zn can be identified but is of minor importance compared to the conservative mixing process. The Cd, Cu and Zn content of the bottom sediments is also mainly determined by the mixing of fluvial and marine silt.

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THE SCHELDT ESTUARY WATER QUALITY MODEL

A full description of the Scheldt estuary water quality model is given in ref 3 and ref 4. The developed model is an one dimensional, dynamical, tidal average box model for personal computers. An one dimensional approach has been chosen because the Scheldt estuary is well-mixed and the lateral gradients are small compared to the longitudinal gradients. The model is a dynamical model because, from a water management point of view, it is important to know when the result of a measure can be noticed. The model is a tidal average model because the time period of interest is always much greater than one tidal period. The 14 homogeneous segments of the box model between Rupelmonde and Vlissingen and some general characteristics of the Scheldt estuary are shown in Fig. 1. The 14 segments are sufficient to describe the longitudinal gradient of the estuary.

Tidal Range	: 4 - 5 m.
Average Water Depth	: 10 m.
Water Residence Time	: 1 - 3 months
Estuary is well-mixed.	

Fig. 1 Some characteristics and the 14 model segments of the Scheldt estuary.

Because the dissolved Cd, Cu and Zn concentrations are largely determined by the redox conditions and phytoplankton activity, the basic water quality (salinity, O_2, pH, alkalinity, chlorophyll-a and dissolved N-species) is calculated first by the model. This approach assumes that the trace metal concentrations do not affect the basic water quality. Salinity is calculated based on advective and dispersive water transport. The oxygen concentration is calculated by taking degradation of organic matter, primary production, reaeration, chemical oxidation and nitrification into account. The pH and alkalinity are calculated by incorporating the pH-CO_2-alkalinity system into the model. Chlorophyll-a is calculated by a separate simple plankton model. Nitrogen was added to the model because the oxygen concentration can not be modeled properly without processes such as nitrification.

A distinction is made within the model between processes that attain equilibrium instantaneously, like the pH-CO_2-alkalinity system, and kinetically controlled processes, like the decay of organic matter, nitrification/denitrification and reaeration. The equilibrium processes are described assuming thermodynamic equilibrium. The kinetically controlled processes are described as first or second order differential equations.

The transport of fluvial and marine particulates, important for calculating the trace metal contents of suspended and bottom sediments, is based in the model on an one dimensional sediment balance of the estuary and a resuspension/sedimentation of the upper 0.5 m of sediment twice a year.

The method for modelling Cd, Cu and Zn is shown in Fig. 2. The trace metal concentration in the inflowing water from the (anoxic tidal) river is divided over three fractions: dissolved metal species, particle bound metal (in equilibrium with each other) and particulate metal sulphides. The particle bound metal fraction is calculated from the pH, alkalinity and salinity dependant distribution coefficient K_d (see Fig. 2) for the oxygenated lower estuary and the measured dissolved concentration. The calculation is done in the equilibrium part of the model. The oxida-

tion of the suspended metal sulphides is described as a function of temperature and oxygen in the kinetic part of the model. The amount of metal released is incorporated in the equilibrium part of the model.
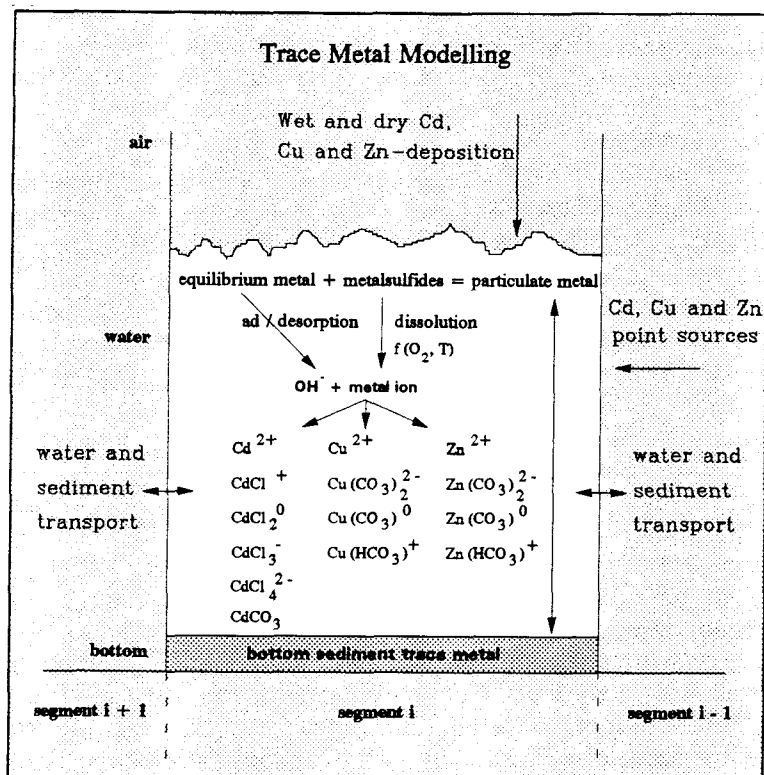

Fig. 2 Trace metal modelling in the Scheldt estuary water quality model.

CALIBRATION OF THE MODEL

Input for the model are the emissions at the model boundaries and along the estuary from (un)treated industrial and domestic waste waters, discharges from canals and polders, and atmospheric deposition. The number of input data required is quite large due to the large number of discharge points along the estuary. In addition the model requires quite a few other input data.

The model was calibrated, partly by hand and partly automatically on 1987 data. The year 1987 was chosen because in this year 7 cruises were specially carried out to obtain data for the calibration of the model (ref 2). The model calibration took place in three steps. First the dispersion coefficients were calibrated on measured salinity. Next, oxygen and nitrogen and the separate plankton model were calibrated. Finally, the trace metals were calibrated. The samples without particulate metal sulphides were used to calibrate the partition coefficients of the chemical equilibrium model. An automatic calibration procedure was used for this purpose (ref 5). The samples with sulphides were used to calibrate the kinetics of sulphide oxidation.

The model reproduces the measured trace metal levels to a large extent, as shown for Cd in Fig. 3. This figure shows the calculated and measured dissolved Cd concentrations and particulate Cd contents for the cruises in 1987. The model calculates trace metal retentions for the estuary between 50 and 90%.

The trace metals in the Scheldt estuary including the oxygenated lower estuary turn to be stronger bound to particles than in other estuaries (ref 6). This means that the dissolved trace metal concentration,

and therefore the bio-available fraction, is relatively low in the Scheldt estuary. The high partition coefficient K_d in the whole estuary is probably explained by the continuous precipitation and dissolution of iron hydroxides in the (partly) anoxic Scheldt river and upper estuary.

Model simulations (ref 6) show that the dissolved trace metal concentrations might increase in the future if the metal sulphides disappear because of the increase in oxygen concentrations due to the decrease in loads of BOD and ammonium.
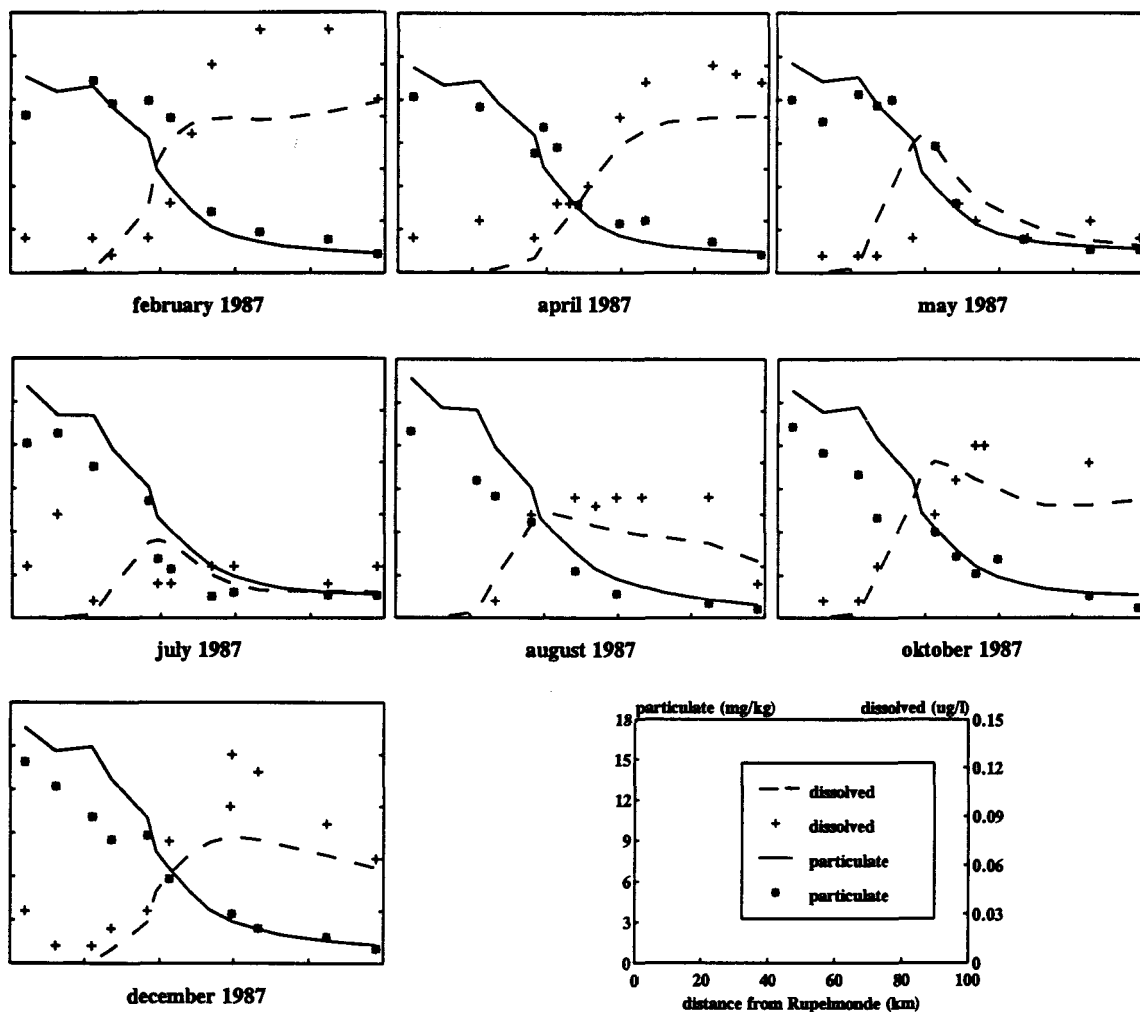
Fig. 3 Measured (*,+) and calculated dissolved and particulate Cd for the 7 cruises in 1987.

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