

Hydrochemical modeling of a seawater diffusion profile, Lake Yssel, The Netherlands

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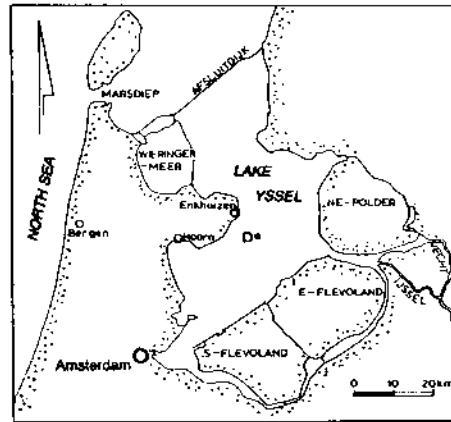
ABSTRACT: A diffusion profile in a former brackish water lagoon (the Zuiderzee, The Netherlands) has been analyzed and was modeled with the hydrogeochemical transport model PHREEQM. Seawater diffusion in fresh water sediments started in the early Middle Ages, and continued until a closure dam created a fresh water lake in 1932. Chemical reactions comprise the exchange of Na^+ and Mg^{2+} from seawater against Ca^{2+} from the fresh water cation exchange complex, and the pattern is further influenced by NH_4^+ released from organic matter. A peat layer creates sulfate reducing conditions at 6 m below the lake bottom.

1 INTRODUCTION

Lake Yssel in the central Netherlands (Fig.1) has distinct Cl^- diffusion profiles in its bottom sediments (Volker, 1961; Beekman, 1991; Beekman et al., this volume). The diffusion of salt water started in the early Middle Ages as a result of salinization of a lake, known to be fresh in Roman Times. Research attention so far was focused on the diffusion of Cl^- as a sign of harmful conditions for agricultural activity after possible poldering. Here, we present profiles for the other ions from a new core, discuss cation exchange, and include a modeling exercise with the multicomponent transport model PHREEQM (Appelo et al., this volume).

2 GEOLOGY AND PORE WATER CHEMISTRY

A new core was taken in 1987 on board of the Dutch Water Authority's "Heffesant". The core segments were immediately frozen by liquid nitrogen upon recovery, and stored at -20°C during and after transportation to the laboratory. Peat, clay and sand layers alternate in the core, as shown in fig. 2. The upper 10m has been deposited since about 10,000 BC and illustrates the alternation of fresh- and brackish- or seawater



• D = DIFFUSION PROFILE BORING D

Fig. 1. Location of sediment sampling (D).

ter conditions in the area. The Holland Peat (HP in fig. 2) has an age of ca. 3,400 - 2,000 BC. The area freshened in this period and solute salts of the previous Calais transgression (OM clay) were flushed. From about AD 0 onwards, sedimentation of Almere deposits (Al) occurred in more brackish conditions of the Zuiderzee. Historical sources (cf. Beekman, 1991) state that salinization of the Almere Lagoon reached its maximum at ca. AD 1570. High salinities prevailed after this date, although seawater concen-

trations were probably only attained during storm surges. In 1932 a dam was constructed ('Afsluitdijk' in fig. 1). One year after closure, the resulting lake was completely fresh.

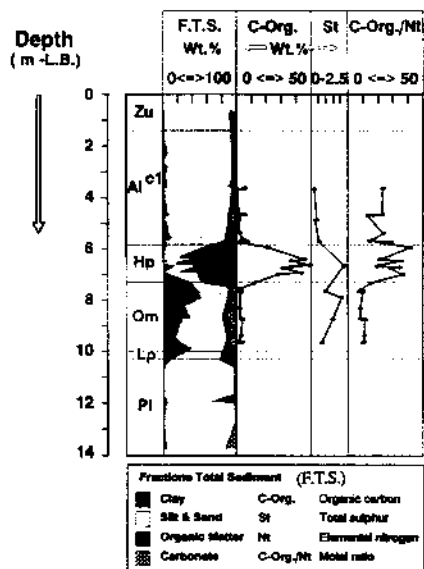


Fig. 2. Sediment characteristics and C-org, total Sulfur, and C-org/(total_N) ratios.

Samples from the core were pressure filtrated and analyzed according to the procedures of De Lange (1984). The pore water chemistry is a result of diffusion of (diluted) seawater into reducing fresh water sediments, and reactions between pore water and sediment.

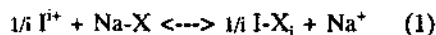
Cation exchange by Na^+ and Mg^{2+} removed Ca^{2+} from the exchange complex, and in addition, minor amounts of K^+ were exchanged for Ca^{2+} as well. Decomposition of organic matter increased alkalinity and NH_4^+ , and was accompanied by reduction of SO_4^{2-} which diffused downward together with Cl^- . Precipitates of FeS , FeS_2 (pyrite) were observed with SEM-EDAX. The release of Ca^{2+} by cation exchange, together with the alkalinity increase, induced the precipitation of calcite.

2.1 Cation exchange characteristics of the sediments

Nine samples at different depths from the core have been eluted with 0.05 or 0.25 N SrCl_2 to obtain the exchangeable cations as well as the

Cation Exchange Capacity (CEC, in meq/100g). The highest CEC values (up to 100 meq/100g) were found in the peaty layers, whereas the lowest value (6.8 meq/100g) was found in sediment with a low clay and organic matter content (fig. 3). The variations are less pronounced when CEC was expressed in meq/kg pore water as illustrated in fig. 5. This figure also shows extrapolated CEC's using a relation between clay and organic carbon content and measured CEC.

Exchange coefficients with respect to Na^+ were calculated for the reaction of a cation I^{i+}



with

$$K_{\text{Na}^+} = \frac{[I\text{-X}_i]^{1/i} [\text{Na}^+]}{[\text{Na-X}] [I^{i+}]^{1/i}} \quad (2)$$

where K_{Na^+} is the exchange coefficient, with subscripts indicating the reaction for the *solute* ions, $[I^{i+}]$ is the aqueous activity of I^{i+} , and $[I\text{-X}_i]$ is the activity of exchangeable I^{i+} , here taken equal to the equivalent fraction of CEC. Average values for these exchange coefficients are given in Table 1.

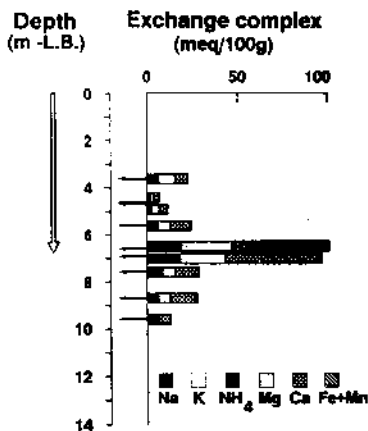


Fig. 3. CEC and exchange composition of the sediments.

3 MULTICOMPONENT TRANSPORT MODEL

The pore water chemistry was simulated with PHREEQM. It was assumed that seawater diffusion started at AD 1570, and continued until 1932. The sedimentary column was discretized in five layers with different chemical characteristics,

i.e. CEC's, mineral equilibria and reaction inputs (fig. 4).

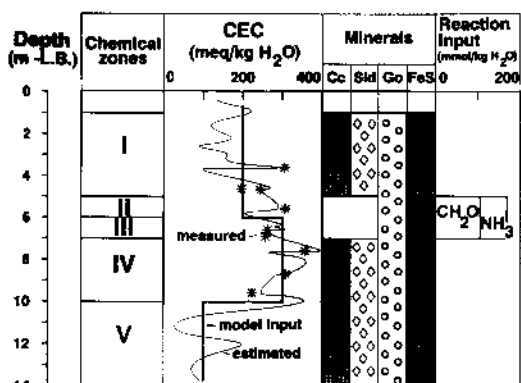


Fig. 4. Scheme of the model parameters used for PHREEQM modeling of the Lake Yssel diffusion profile.

A reaction input consisted of the addition of organic carbon (CH_2O) and NH_4^+ to the pore waters in the peat layers at 5 to 7 m-LB. The amounts of reaction of NH_4^+ were defined by matching the mass balance of observed NH_4^+ in solution in pore water and exchangeable on the sediment in pore water and exchangeable on the sediment in 1987. The amount of organic carbon reaction was similarly defined by the amount of SO_4^{2-} reduction that was necessary to match the observed SO_4 profile. Reaction input to match spread evenly over the simulation period. Exchange coefficients were assumed constant over the col-

umn, and calculated according to reaction (3) in the multicomponent model that includes all cations listed in Table 1. Table 1 also gives the aqueous compositions in Table 1. Table 1 also gives the simulation, viz. the initial pore water, the seawater, and the exchangeable cations.

TABLE 1. Solution compositions (mmol/kg H_2O) and exchange coefficients (% of CEC).

	Porew. Exch.		Seaw. Exch.		$K_{f/wa}$
pH	8.0		8.0		
Na^+	47.4	7.8	485.0	40.8	1.0
K^+	1.1	1.8	10.6	8.8	10.0
Mg^{2+}	5.5	24.0	55.1	39.6	5.0
Ca^{2+}	6.0	64.0	10.6	10.9	8.0
Fe^{2+}	0.0	-	0.0	-	3.2
NH_4^+	3.0	2.4	0.0	-	5.0
Cl^-	65.0		566.0		
Alk.	1.7		2.4		
SO_4^{2-}	3.9		29.3		

The importance of the different reactions can be illustrated with PHREEQM model results. Fig. 5 shows computed solute profiles at the end of the seawater diffusion period in 1932. A dashed line with empty rectangles at the layer transitions (cf. fig. 4) gives the initial concentrations in 1570, at the start of the simulation period.

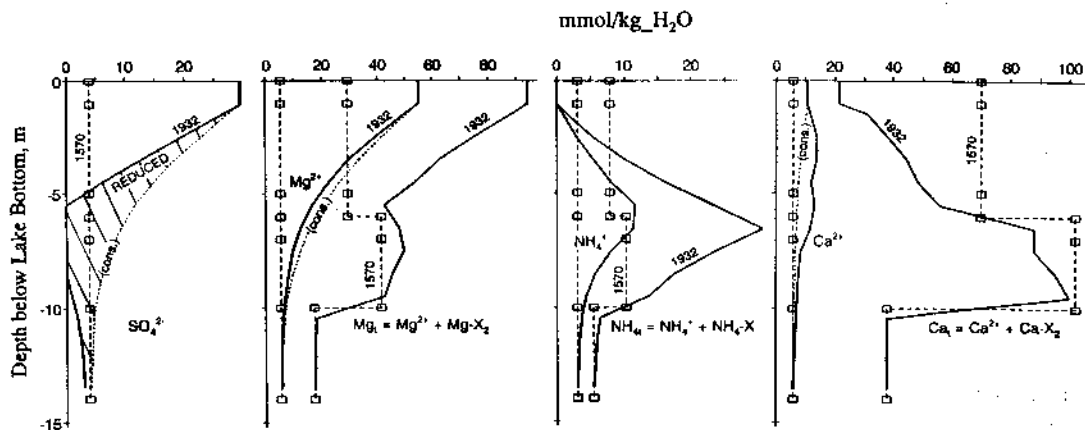


Fig. 5. Calculated profiles of solutes and sum of solute and exchangeable cations in 1932. Dashed lines, with empty rectangles at the layer transitions, represent starting conditions in 1570.

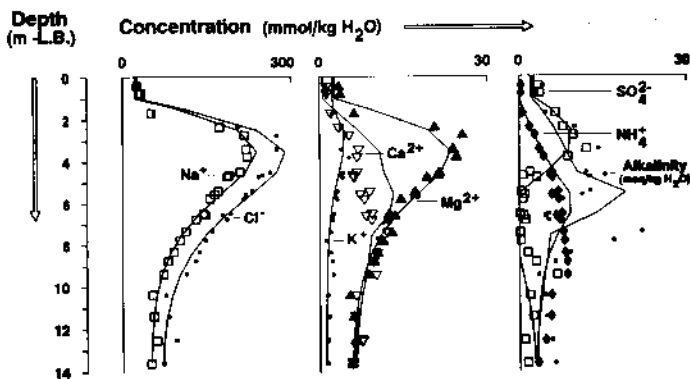


Fig. 6. Observed pore water chemistry in 1987 (indicated by single points) and modeled chemistry with PHREEQM (drawn lines).

A dotted line for SO_4^{2-} gives the conservative diffusion profile, while the full line shows modeled concentrations which are reduced by release of CH_2O from the peat between 5 and 7 m-LB.

A dotted line for Mg^{2+} similarly represents the conservative diffusion profile. The difference between conservative and non-conservative Mg^{2+} is small. However, the increase of Mg^{2+} in the exchange complex is notable, as the curve $\text{Mg}_{\text{tot}} = \text{Mg}_{\text{aq}} + \text{Mg-X}_2$ illustrates. The transitions at 5 to 7 m-LB are due to combined effects of CEC-variations and multicomponent effects.

The NH_4^+ profiles show the effect of decomposition of the peat. A peak in NH_4^+ coincides with an increase in CEC in the 6 - 7 m-LB layer.

The Ca^{2+} profiles are the most complicated as this ion is affected by three reactions, viz. cation exchange, HCO_3^- increase through SO_4^{2-} reduction, and CaCO_3 precipitation. The decrease of Ca_{tot} is mainly caused by CaCO_3 precipitation directly above and below the peat layers.

The final step in the modeling effort included the diffusion of fresh lake water from 1932 until 1987. Fig. 6 compares the model results with observed pore water chemistry and shows that the observed data are fitted well, given the sediment heterogeneities and the complex reaction scheme. The sharp alkalinity drop at 7m-LB is accompanied by a relatively low pH, but the reaction mechanism to explain this fluctuations is at present not known.

4 CONCLUSIONS

Pore water chemistry of a sedimentary sequence with clay, sand and peat layers shows seawater diffusion and back diffusion after freshening of the overlying water body. The hydrogeochemical reactions are diverse and comprise multicomponent exchange, reduction of SO_4^{2-} , release of CH_2O and NH_4^+ , and precipitation/dissolution of a.o. FeS and CaCO_3 . The complexity and interdependency of the processes prohibit a too simple approach, but the geochemical transport model PHREEQM can satisfactorily simulate the observed water qualities. For such successful modeling it is necessary to be able to include all the chemical processes. PHREEQM offers that capability.

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