

^{37}Cl - ^{35}Cl transport modeling in accumulating sediments of a former brackish lagoonal environment

H.E. Beekman & C.A.J. Appelo

Institute of Earth Sciences, Free University, Amsterdam, Netherlands

H.G.M. Eggenkamp & R. Kreulen

Department of Geochemistry, University of Utrecht, Netherlands

ABSTRACT: Pore water chemistry from cored sediments in a former brackish lagoon in The Netherlands was found to be controlled mainly by diffusion. Seawater diffusion into the sediments started at least 400 years ago, with dilution (freshening) of the upper few metres taking place since isolation of the lagoon from the sea by a dam in 1932. A one-dimensional numerical model was developed to describe historical transport of both Cl and $\delta^{37}\text{Cl}$. The model synthesizes present knowledge of geology and historical information on storm surges in the area and includes the following processes: erosion of sediments, mixing of pore water, sedimentation and diffusion (EMSD). The use of ^{37}Cl as a second conservative tracer greatly improved insight into the evolution of pore water salinity in this former brackish lagoon.

1 INTRODUCTION

Volker and van der Molen (1991) examined chloride profiles in sediments of Lake Yssel in The Netherlands (fig. 1). They explained present pore water salinity by downward diffusion of saltwater from a brackish lagoon since Medieval Times from 1238 to 1932 AD. Back-diffusion into overlying fresh surface water occurred after isolation from the sea by a dam in 1932. Here we present a reconstruction of historical transport in Lake Yssel sediments and include effects of sedimentation and storm surges based on chloride isotopes from a new boring (D).

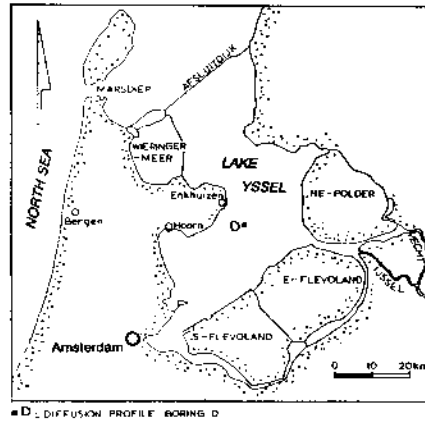


Fig. 1. Location of sediment sampling (D).

2 SALT- AND FRESHWATER PERIODS

Coring of sediments was carried out from a ship in 1987 at site D. Immediately after recovery the cores were frozen in liquid nitrogen and stored at $-20\text{ }^{\circ}\text{C}$. Pore water extraction for Cl and $\delta^{37}\text{Cl}$ analysis was carried out in a Reeburgh-type squeezer. Fig. 2 shows lithostratigraphic and sediment characteristics of upper Pleistocene and Holocene deposits at site D. Deposition of the

Al^{Cl} Member (sand) and subsequent salinization of underlying sediments took place from ~1250 to ~1600 AD in a brackish lagoon, called Almere. Enlargement of the lagoon was particularly enhanced by storm surges since the 13th century (cf. Beekman, 1991). The Al^{Cl} Member is characterized by abundant small-scale sediment structures. Diatoms, counted and summed in a

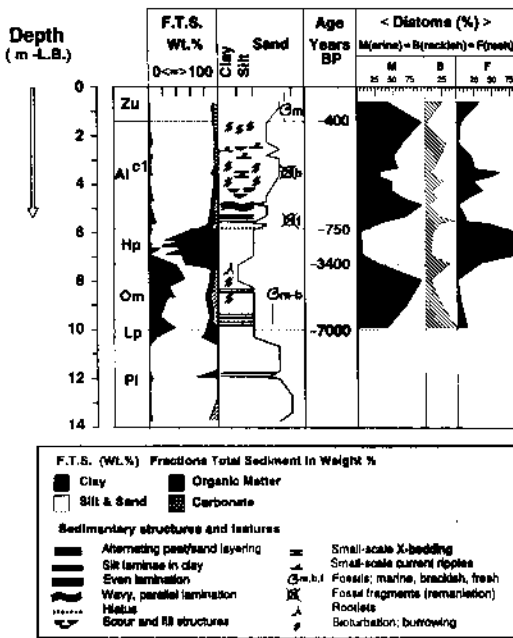


Fig. 2. Sediment characteristics and Diatoms.

M(arine), B(rackish) and F(resh) class, indicated variable surface water salinity in this member. The lagoon rapidly salinized following a severe storm surge in 1570, then called Zuiderzee. After isolation of the lagoon from the sea by a dam in 1932 the enclosed water then called Lake Yssel, became fresh within a few years and remained so until present.

3 HISTORICAL TRANSPORT MECHANISM

A one-dimensional transport model (explicit finite difference: forward in time and central in space) was constructed to predict the concentration distribution of both Cl ($= {}^{35}\text{Cl} + {}^{37}\text{Cl}$ (mM)) and $\delta^{37}\text{Cl}$ (in ‰) under a variety of hydrogeologically controlled initial and boundary conditions. $\delta^{37}\text{Cl}$ is defined as:

$$\delta^{37}\text{Cl} = ({}^{37}\text{R}_s / {}^{37}\text{R}_r - 1) \times 1000 \quad (1)$$

where ${}^{37}\text{R}_s$ is the isotopic abundance ratio ${}^{37}\text{Cl}/{}^{35}\text{Cl}$ of a water sample and subscript r denotes a reference sample.

Discrimination between different modes of transport, i.e. diffusion versus dispersive flow,

may be derived from ${}^{37}\text{Cl}/{}^{35}\text{Cl}$ ratios due to lower mobility of ${}^{37}\text{Cl}$ compared with ${}^{35}\text{Cl}$ in the diffusive domain (Desaulniers et al., 1986). Fractionation as a result of the mobility difference is given by:

$$\alpha^{37}\text{Cl} = {}^{37}\text{D} / {}^{35}\text{D} \quad (2)$$

where D_0 is the liquid phase diffusion coefficient [L^2T^{-1}]. Calculation of Cl concentrations and $\delta^{37}\text{Cl}$ was carried out simultaneously. $\delta^{37}\text{Cl}$ is obtained by substituting in equation (1) the ratio ${}^{37}\text{R}_s / {}^{37}\text{R}_r$ for the ratio ${}^{37}\text{Cl}/{}^{35}\text{Cl}$.

Two scenarios were developed:

- the first in which diffusion into the sediments proceeds from a fixed boundary plane: diffusion *without* sedimentation (A: Volker's scenario) and
- the second in which diffusion proceeds from a moving boundary plane: diffusion *combined with* sedimentation (B).

Advective mixing of surface and pore water, as a result of storm events, was also included in scenario B.

The sediment sequence (D) was divided into cells, each representing a depth interval of uniform length $\Delta z = 0.5\text{m}$. All cells of the sequence below the diffusion boundary plane (DBP) at depth z_d (in m below present lake bottom: -L.B.) were filled initially with the same chloride content (65 mM) and $\delta^{37}\text{Cl}$ (0 ‰). The initial Cl concentrations are within the range of minimum pore water chloride contents directly below the Holocene deposits where pore water salinity is influenced by groundwater flow.

For scenario A, z_d was fixed at 1m -L.B. The duration of saltwater transport in the bottom sediments was 362 years. The concentration of chloride and $\delta^{37}\text{Cl}$ at the lower boundary of the sediment sequence was fixed at its initial level for $t \geq 0$. For scenario B the DBP shifted with time from 5.5 m to 1 m below present lake bottom. The duration of the brackish water transport before closure of the Zuiderzee in 1932 was set at $\sim 700 \pm 50$ years. The depths for DBP's during the Al^{C1} period were chosen to be the sediment-bottom water interface; it is as-

sumed that advective mixing in Al^{37}Cl sediments below these interfaces only occurred during storm surges. During the Zuiderzee phase z_d was chosen at 1m -L.B. It is assumed that pore water during the more saline Zuiderzee phase is mixed completely above the DBP (upper metre) by storms and bioturbation. Because observed Cl concentrations are relatively low in the upper metre of the sequence and cannot be explained by either diffusive transport alone, or by vertical groundwater movement, the depth of the DBP for the Lake Yssel phase was also set at 1m. During the relatively fresh Lake Yssel phase (55 years) an average chloride value of 25 mM was used as input concentration at the DBP.

Core inspection did not reveal any compaction of sediments above the Hp layer; the porous medium diffusion coefficients (D_m) were therefore assumed to be time-invariant. D_m which is expected to vary with depth as a result of changing lithology and porosity is derived from:

$$D_m = D_0 \times \tau \quad (3)$$

where τ is a correction factor accounting for tortuosity effects. $\alpha^{37}\text{Cl}$ factors ranging from 0.9978 to 0.9988 (Desaulniers et al., 1986) were used to obtain $^{37}\text{D}_m$ values.

Sedimentation was simulated by adding a new layer (Δz) on top of existing layers during a storm event. The following cycle of events was designed for each sedimentation step during the

Al^{37}Cl period and is illustrated in fig. 3:

1. Saltwater diffuses from an initial DBL into underlying sediments.
2. During a storm event (higher surface water salinity) erosion of sediments and mixing of pore water with bottom water takes place to a certain depth (interval m_d); Cl concentration in the mixing zone becomes identical to the concentration for bottom water during the storm; $\delta^{37}\text{Cl}=0$.
3. After this erosion/mixing event current activity and salinity decline gradually while sediment is deposited; the DBP shifts upwards and $\delta^{37}\text{Cl}=0$.

There was no difficulty in obtaining a good fit between calculated and observed Cl concentrations for both scenarios. Table 1 shows the parameter values from which the best fit for both Cl and $\delta^{37}\text{Cl}$ was obtained. Fig. 4 illustrates their goodness of fit. The figure shows that sedimentation during the Al^{37}Cl period and mixing and/or displacement of pore water by storms must be included in the model in order to properly describe observed $\delta^{37}\text{Cl}$. However, $\delta^{37}\text{Cl}$ values in the upper zone are not yet explained and require further investigation.

Scenario B accurately predicts observed Cl concentrations and explains the general trend of observed $\delta^{37}\text{Cl}$ values reasonably well without contradicting present knowledge concerning geology of the sediment sequence and past environmental conditions.

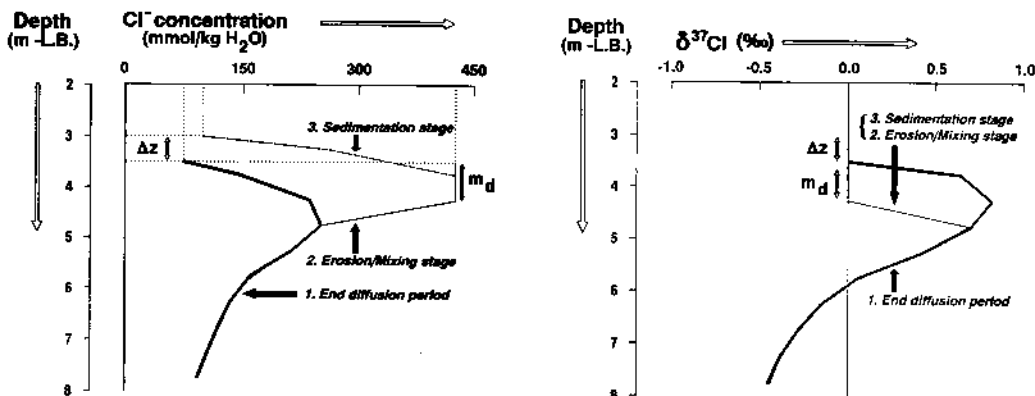


Fig. 3. Sedimentation cycles for Cl and $\delta^{37}\text{Cl}$.

TABLE 1. Model parameters for scenarios A and B.¹

	A		B ²	
τ	0.60		0.30	
$^{37}\alpha$	0.9988		0.99835	
$C(z,0)$	65		65	

	AI ^{CI} PERIOD (1250 - 1570 AD)		ZUIDERZEE PHASE (1570 - 1932 AD)		LAKE YSSEL PHASE (1932 - 1987 AD)
	B	A	B	A = B	
z_d^1	5.5 \Rightarrow 1.5	1.0	1.5 \Rightarrow 1.0	1.0	
Δt^1	320	362	362	55	
$C(z_d,t)$	100	566	350	25	

¹ $D_o=1.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ ($T=10^\circ\text{C}$); z_d in m -L.B.; Δt in years. ² $C(\text{AI}^{\text{CI}}\text{-storm})=425 \text{ mM Cl}$: one storm every 40 years; $m_o=4.5 \text{ m -L.B.}$ (first depth level of mixing); $m_d=1 \text{ m}$.

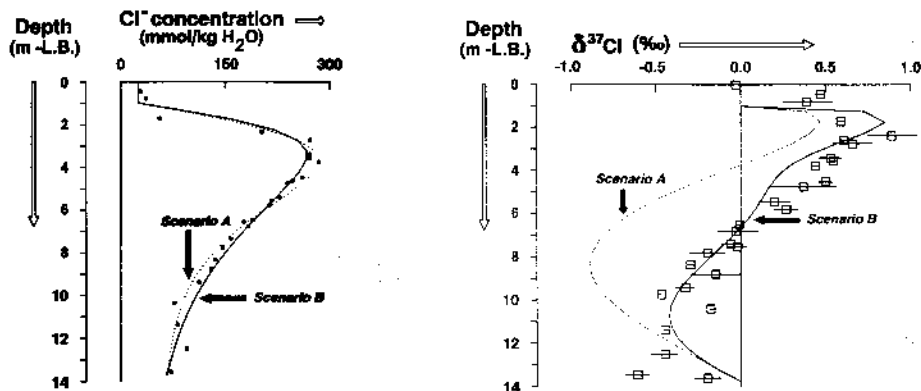


Fig. 4. Best fits between calculated and observed Cl^- and $\delta^{37}\text{Cl}$ for scenarios A and B.

4 CONCLUSIONS

Simulation of historical transport in sediments of a former brackish lagoon revealed good agreement between predicted and observed pore water Cl^- and $\delta^{37}\text{Cl}$ only when erosion of sediments, pore water mixing and sedimentation were taken into account. The EMSD model developed to include these processes, as well as diffusion, synthesizes present knowledge of geology and historical information on storm surges in the area. This study clearly demonstrates the use of ^{37}Cl for reconstruction of complex historical transport mechanisms in environments where fresh/seawater interaction dominates.

REFERENCES

- Beckman, H.E. 1991. Ion chromatography of fresh- and seawater intrusion: multicomponent dispersive and diffusive transport in groundwater. *Ph.D. thesis*, Free University Amsterdam: 198 pp.
- Desaulniers, D.E., Kaufmann, R.S., Cherry, J.A. & H.W. Bentley 1986. ^{37}Cl - ^{35}Cl variations in a diffusion-controlled groundwater system. *Geochim. Cosmochim. Acta* 50: 1757-1764.
- Volker, A. & W.H. Van der Molen 1991. The influence of groundwater currents on diffusion processes in a lake bottom: an old report reviewed. *J. Hydrol.* 126: 159-169.