

# PORE WATER CHEMISTRY OF CLAY LAYERS IN THE SOUTHERN NORTH SEA: CLUES TO THE HYDROGEOLOGICAL EVOLUTION OF COASTAL AREAS

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## ABSTRACT

Measurements of the pore water chemistry of a 5-meter thick clay layer in the southern North Sea reveal that the salinity at the bottom of the layer is less than 50% of seawater salinity. Modelling shows that the decrease of Cl<sup>-</sup> with depth is too fast to be explained by diffusion alone. There are a number of possible explanations for this discrepancy: (1) upward seepage of water with a lower salinity, (2) (continuous) erosion and (3) retardation due to anion exclusion. This latter possibility seems very likely since the distribution of (uncharged) <sup>18</sup>O does not show the same retardation as Cl<sup>-</sup>.

Hydrogeochemical investigations at other locations (i.e. Suriname, Poland and Indonesia) show that similar diffusive transition zones beneath the seafloor exist around the world. These salinity patterns demonstrate that the offshore plays an important part in the dynamics of fresh- and salt groundwater in coastal zones.

## INTRODUCTION

Clay layers exert an important control on groundwater quality. Their resistance to groundwater flow makes them an effective barrier against dissolved substances and because of their geochemical properties they have a significant effect on groundwater qualities. For example, their often-high organic carbon content leads to reducing conditions through the oxidation of organic matter and their ability to sorb cations can affect the groundwater composition. Especially in areas where fresh and saline waters meet, the effect of clay layers becomes very pronounced.

In the absence of flow, dissolved ions can only pass the clay through diffusion, which is a very slow process. Numerous examples can be

found in coastal areas. Volker (1961) studied the distribution of chloride with depth in the IJsselmeer area in the Netherlands, which is a former tidal basin. He found that the chloride concentrations could be explained by diffusion of salts from brackish water into the underlying sediments containing fresh water. Beekman (1991) refined Volker's theory by also studying the chlorine isotope <sup>37</sup>Cl and concluded that erosion, sedimentation and bioturbation have also to be taken into account. Eggenkamp et al. (1994) studied the diffusion of chloride into the sediment pore water of Kau Bay, Indonesia. The distribution of chloride in the pore waters of Puck bay (Poland) was reported by Piekarek-Jankowska (1996). Groen et al. (2000a) carried out a study of the

diffusion of chloride in clay layers in the coastal plain of Suriname.

Clay layers can thus protect fresh water bodies that underlie them from rapid salinization. Gieske (1991) showed the presence of fresh water bodies under thick and laterally extensive clay layers in otherwise brackish to saline groundwater in the IJsselmeer area. Groen et al. (2000a) observed that fresh to moderately brackish (250 to 1000 mg/l) groundwater extends several tens of kilometres offshore into the continental shelf deposits and that these waters are slowly salinized by diffusion. Groundwater dating, head measurements and modelling exercises indicate that these offshore groundwater bodies are relics of former groundwater flow systems that existed during the Weichselian glacial (110,000 – 10,000 BP) when the sea level was much lower and the continental shelves were exposed (Groen et al., 2000b). In a generic, numerical modelling study, Kooi et al. (2000) recently demonstrated that salinization of these fresh-water bodies during (Holocene) sea-level rise can indeed significantly lag behind coastline migration when clay-rich layers are present near the seafloor.

The purpose of the present study was to investigate if similar moderately brackish pore waters occur in the Southern North Sea, which was also subaerially exposed during the last ice age. To this aim, cores were taken from shallow clay layers and their pore water chemistry was analysed.

## PHYSICAL SETTING

The southern North Sea has experienced alternating periods of marine and continental conditions during the Pleistocene. During the last glacial period (Weichselian) that lasted

from 110,000 to 10,000 BP, the seafloor was exposed. The earliest brackish water incursion as a result of the Holocene transgression may have occurred as early as 10,000 BP but fully marine conditions only became established widely after 7,000 BP (Cameron et al., 1993).

Three clayey formations were sampled (see fig. 1): (1) the Dogger Bank Formation (glaciolacustrine clay and silt), (2) the Bolders Bank Formation (till) and (3) the Brown Bank Formation (marine to lacustrine clay). Here only the latter core will be discussed in detail.



Figure 1. Sample locations and coastline configuration at 8,300 <sup>14</sup>C years BP, after Zagwijn (1986).

The Brown Bank Formation is of Eemian to Early Weichselian age. It consists predominantly of stiff, greyish-brown laminated clays that are locally bioturbated and contain cracks filled with Holocene sands. The stiffness of the clay can be attributed to dehydration during permafrost conditions that prevailed during the Weichselian glacial (Laban, 1995). At the sampled location, the clay was encountered below a one-meter thick layer of Holocene sands. The clay has

a thickness of 5 meters, the upper two meters being very stiff. In the upper 20-cm, small cracks filled with sand and shell fragments are present. Fine marine sands containing shell fragments underlie the clay, at least to a depth of 12 meters below the seafloor.

## METHODS

In co-operation with the Netherlands Institute of Applied Geoscience (NITG-TNO), two drilling campaigns were carried out to obtain the clay cores. During the first campaign, in July 1998, three undisturbed sediment cores were taken with a vibrocorer at three different locations in the North Sea, see fig. 1. The cores were cut in sections of 1 meter length and the ends were sealed with a layer of paraffin at least 25 mm thick, a plastic cover and taped airtight. At the laboratory of the Vrije Universiteit in Amsterdam, pore water samples from these cores were obtained by squeezing in a glovebox filled with gaseous nitrogen and were analysed for  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Si}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}(\text{tot})$  and  $\text{Mn}^{2+}$ .

The method described above is the preferred one for accurate determination of pore water chemistry. However, owing to the stiffness of the clay, only the upper 2 to 3 meters could be penetrated by the vibrocorer. For this reason, it was decided to try and obtain clay samples using the Geodoff drilling method (developed by NITG-TNO), which is a counterflush technique. This method is not ideal for the analysis of the pore water composition due to the deformation of the samples (elongation due to different diameters of tubes in the drilling system) and the inevitable contact with seawater and the atmosphere.

During the second campaign, in February 1999, clay cores were obtained from the Brown Bank Formation at the same location as the first campaign. This time, the Geodoff sampling method made it possible to sample the entire clay layer. The samples were wrapped in cellophane foil and sealed in plastic to prevent evaporation from the clay. Clay samples were squeezed at intervals of 25 cm and their pore waters were analysed for  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at the laboratory of IWACO Rotterdam. Selected samples were analysed at the Centre for Isotope Research in Groningen for  $^2\text{H}$  and  $^{18}\text{O}$  and at Utrecht University for  $^{37}\text{Cl}$ .

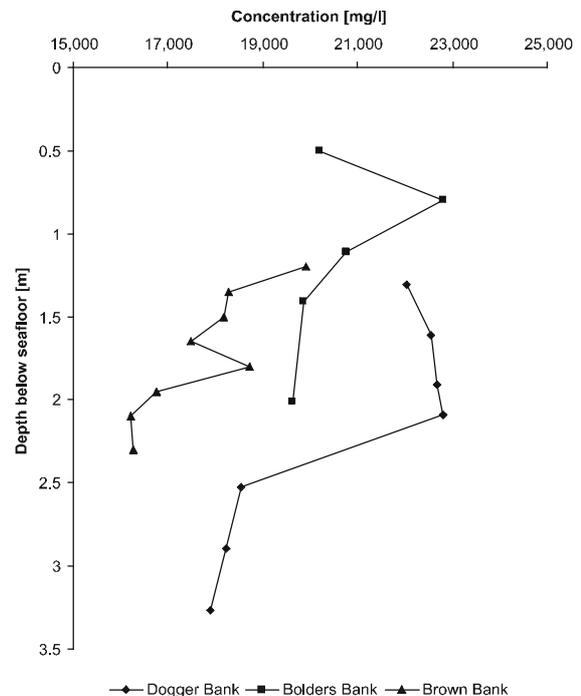


Figure 2. Chloride concentration vs. depth at the three sampled locations.

## RESULTS

In fig. 2 chloride concentration vs. depth is plotted for the three locations that were sampled during the first campaign (undisturbed cores). The chloride concentrations in the upper part of the clay of the Dogger Bank Formation are higher than that of seawater (20,000 mg/l) and show a

jump in the interval 2-2.5 m, which is difficult to interpret. With the exception of one outlier, the chloride concentrations in the till of the Bolders Bank Formation show a slight decrease with depth, but the sampled depth interval is too small to show any significant change. The most obvious decrease in chloride concentration is found in the clay of the Brown Bank Formation and the remainder of this article will be dedicated to this location.

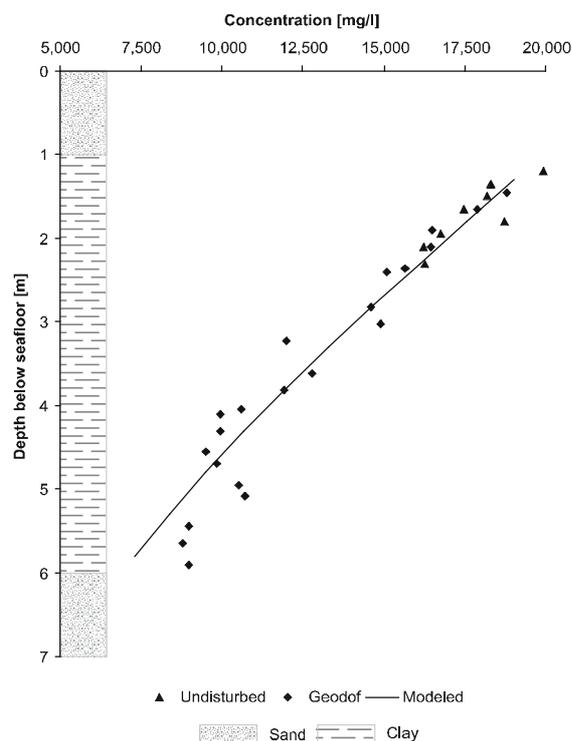


Figure 3. Chloride concentration vs. depth in the Brown Bank Formation.

Fig. 3 shows the chloride concentrations vs. depth in the clay of the Brown Bank Formation and includes both the points from the first campaign (undisturbed core) and the second campaign (core obtained with the Geodoff method). The chloride concentrations show a decrease from 19,000 mg/l (almost the seawater concentration) at the top of the clay layer to 8,900 mg/l at the bottom of the clay layer. The data from the undisturbed core show excellent agreement with the data from the core obtained with the Geodoff method.

This also holds for the other ions (not shown here), and it is therefore believed that the use of the Geodoff method has not negatively influenced the results.

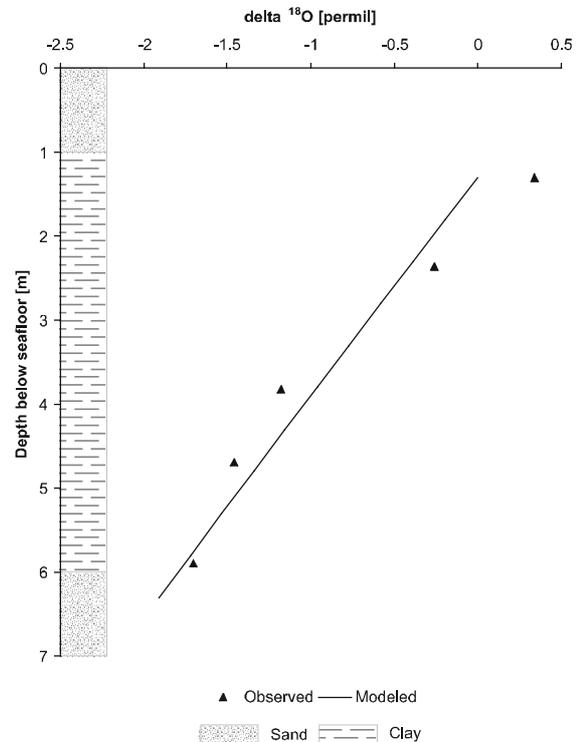


Figure 4.  $\delta^{18}\text{O}$  vs. depth in the Brown Bank Formation.

Fig. 4 shows the observed change of  $\delta^{18}\text{O}$  with depth. The positive value for  $\delta^{18}\text{O}$  in the sample at 1.3-m is not easily explained and may be due to some analytical error.  $\delta^2\text{H}$  and  $\delta^{37}\text{Cl}$  are not shown here but follow the same trend, namely a progressive depletion with depth.

## DISCUSSION

The decrease of the chloride concentration and  $\delta^{37}\text{Cl}$  with depth indicates that very slow salinization of fresh water takes place. The decrease of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  towards more negative values points to the presence of meteoric water.

In order to evaluate the salinization processes that are responsible for the observed pore water chemistry pattern, a simple

diffusion model was applied. The partial differential equation that describes the transport due to diffusion can be derived from Fick's law and the conservation of mass:

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial z^2}$$

where  $C$  denotes concentration (mg/l),  $t$  is time (s),  $D_{eff}$  the effective diffusion coefficient ( $m^2/s$ ) and  $z$  the depth below the top of the clay layer (m). The solution of this equation subject to:

$$\begin{aligned} t = 0: & C = C_i \text{ for } z \geq 0 \\ t > 0: & C = C_s \text{ for } z = 0 \\ & C = C_i \text{ for } z = \infty \end{aligned}$$

is:

$$C_{z,t} = C_i + (C_s - C_i) \cdot \operatorname{erfc}\left(\frac{z}{\sqrt{4D_{eff}t}}\right)$$

This formula was used to calculate the distribution of  $Cl^-$  and  $^{18}O$  in the sediment. Note that  $\delta^{18}O$  must first be recalculated to a concentration.

The assumptions contained in this model require some further attention. In the first place, it is assumed that the initial concentration distribution was uniform with depth. For  $Cl^-$  ( $C_i = 0$  mg/l) this is likely to have been the case up to great depth, because freshening occurred for many tens of thousands of years during the Weichselian. However,  $\delta^{18}O$  may not necessarily have been constant since it is affected by temperature variations. No information is available on the distribution of  $^{18}O$  prior to inundation and it is simply assumed that the initial  $\delta^{18}O = -10\text{‰}$  (Rozanski, 1985).

Secondly, it is assumed that the boundary condition at the top of the clay layer changed in a stepwise fashion upon inundation. So the concentrations instantly changed from fresh water values to seawater values.

For  $Cl^-$ ,  $C_s$  was set to 19,000 mg/l, corresponding to the chloride concentration of the uppermost sample in the clay layer. For  $\delta^{18}O$  the seawater value is 0‰.

$t$  was set to 8,500 years, since flooding of this location during the Holocene transgression occurred approximately 8,500 years BP (Zagwijn, 1986, figs. 25 and 26). The effective diffusion coefficients of  $Cl^-$  and  $^{18}O$  were optimised to match the observed data. The optimised values are listed in table 1, together with diffusion coefficients in free solution from literature. A direct comparison between these values is not possible since the optimised effective diffusion coefficients include the effects of tortuosity and other effects and processes that are not included in the diffusion model. From figs. 3 and 4 it can be seen that the model results match the observed concentrations reasonably well.

	$Cl^-$	$^{18}O$
$D_{eff}$	$5.0 \cdot 10^{-11}$	$8.0 \cdot 10^{-10}$
$D_{sea}$	$1.32 \cdot 10^{-9} \text{ (1)}$	$1.8 - 2.4 \cdot 10^{-9} \text{ (2)}$
$D_{sea}/D_{eff}$	26.4	2.25 - 3

Table 1. Effective diffusion coefficients (optimised) and diffusion coefficients from literature. <sup>(1)</sup> Value in seawater at 10 °C (Schulz and Zabel, 2000). <sup>(2)</sup> Reported range for distilled water to Dead Sea brine at 22 °C (Yecheili and Ronen, 1996).

If tortuosity ( $\theta$ ) were the sole cause for the difference between  $D_{eff}$  and  $D_{sea}$  then its value would follow from the ratio:

$$\theta^2 = \frac{D_{sea}}{D_{eff}}$$

and it would have to yield the same value for both  $Cl^-$  and  $^{18}O$ . The ratio for  $^{18}O$  (see table 1) is well within the range of tortuosity values reported in literature (Boudreau, 1997) and thus the difference between  $D_{eff}$  and  $D_{sea}$

can be attributed to the effect of tortuosity. The ratio for  $\text{Cl}^-$ , however, is much higher. Evidently, this ion moves at a much slower rate than would be expected from diffusion alone.

Deviations from the diffusion profile can be attributed to vertical flow components (Volker and Van der Molen, 1991; Piekarek-Jankowska, 1996) or to erosion. However, if one of these processes would occur, then the effective diffusion coefficients of  $^{18}\text{O}$  and  $\text{Cl}^-$  would both be affected to the same degree. Obviously, this is not the case here.

Another possible explanation for the relative immobility of  $\text{Cl}^-$  is the following. The charged surface of clay particles is surrounded by the so-called Gouy-Chapman diffuse double layer (Appelo and Postma, 1993). A negative potential extends into the adjacent pore water over a distance equal to the thickness of the double layer. If the pores are so small that the double layers overlap, anions are unable to pass the pores. This process is termed *anion exclusion*.  $\text{Cl}^-$  will therefore have a lower mobility, whereas the uncharged  $^{18}\text{O}$  (which is transported as  $^1\text{H}_2^{18}\text{O}$ ) is not affected by the negative potential. Since the double layer-thickness is a function of the normality of the solution (the double layer being thicker at lower normality) the “effective” diffusion coefficient is also a function of normality. Diffusion may initially be slower when the concentrations are still low, but may be faster when concentrations increase.

It is interesting to compare the effective diffusion coefficient of  $\text{Cl}^-$  found here to the values found by Volker (1961) and Beekman (1991) who studied the chloride distribution in the IJsselmeer area in the Netherlands. They found  $D_{\text{eff}} = 4.63 \cdot 10^{-10} \text{ m}^2/\text{s}$  and  $D_{\text{eff}} = 4.2 \cdot 10^{-10} \text{ m}^2/\text{s}$  respectively. These values are

significantly higher than the value found during the present study, which may be attributed to differences in lithology. The sediments in the IJsselmeer area consist of Holocene clay, peat and silt whereas the North Sea sediments studied here consist of Eemian clay that has been strongly weathered owing to the permafrost conditions during the Weichselian glacial. This strong weathering, that gave the clay its stiffness, may be the reason for the low diffusion coefficient of  $\text{Cl}^-$ .

## CONCLUSIONS

A detailed analysis of the distribution of  $\text{Cl}^-$  and  $^{18}\text{O}$  with depth at the Brown Bank Formation in the Southern North Sea shows that downward transport can be attributed to diffusion of these components from seawater into relic fresh water from the Pleistocene following the Holocene transgression of the area about 8,500 years BP. A simple diffusion model was fitted to the observed data by optimising the diffusion coefficients.  $\text{Cl}^-$  is moving much slower than  $^{18}\text{O}$ , which may be explained here by anion exclusion.

Two implications for the interpretation of fresh-salt water relationships in coastal areas arise from this study. In the first place, the occurrence of relatively fresh water offshore complicates the choice of boundary conditions in numerical models of saltwater intrusion. Secondly, the very low diffusion coefficient of  $\text{Cl}^-$  shows that it is not always possible to obtain a reliable effective diffusion coefficient from the reported relationships with tortuosity.

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