RECOGNITION, DATING AND GENESIS OF FRESH AND BRACKISH GROUNDWATERS IN THE HOLLANDSCH DIEP ESTUARY IN THE COMPOUND RHINE-MEUSE DELTA

P. J. STUYFZAND1,2,*, W. J. DE LANGE3 and J.A. ZINDLER3

1 Free University, Dept. Hydrology & Geo-Environmental Sciences, FALW, Boelelaan 1085, 1081 HV Amsterdam, Netherlands; Tel: +31.20.5987.968 or +31.6.10945021; Email: pieter.stuyfzand@falw.vu.nl.
2 Kiwa Water Research, PO Box 1072, 3430 BB Nieuwegein, Netherlands. Tel: +31.30.6069.552 or +31.6.10945021; Email: pieter.stuyfzand@kiwa.nl.
3 Institute for Inland Water Management and Waste Water Treatment, PO Box 17, 8200 AA Lelystad, Netherlands

Abstract

The groundwater flow and chemistry were studied in a system recharged by an infiltrating main distributary of the compound Rhine-Meuse delta with a salt water wedge: the Hollandsch Diep. All discerned groundwater types are composed of a mixture of Rhine River (72-82%), Meuse River (16-28%) and North Sea water (0.001-2%), as evidenced by chloride, oxygen-18 and tritium. The reconstructed input functions of these tracers were used for age determination of all 300 groundwater samples (1-200 years old). The spatial distribution of groundwater types is largely determined by: (I) the areal extent of a polluted sludge layer that formed in the Hollandsch Diep after 1971, (II) the areal extent of aquitards of Quarternary age and local short-cuts through these aquitards especially in the upper 20 m of the aquifer system, (III) the vertical salinity stratification in the estuary, and (IV) time dependent changes in boundary conditions (especially the damming of the Haringvliet outlet in 1971). The complex flow patterns could be visualized by integration of the spatial distribution of the recent sludge layer, older aquitards, chemical watertypes and tracers of age and origin.

Keywords: Estuarine groundwater, origin detection, groundwater dating, intrusion of freshwater; intrusion of brackish water, hydrochemical visualization of flow

Introduction

In the SW-Netherlands, 15 km south of Rotterdam, large amounts of contaminated silt accumulated in the Hollandsch Diep, a main distributary in the compound Rhine-Meuse delta with estuarine characteristics. This happened after 1971, when a dam with sluices in the Haringvliet outlet was completed as part of the famous 'Delta Works' (Figure 1). This closure strongly reduced river flows, tidal currents and salt water...
Recognition, dating and genesis of fresh and brackish groundwaters in the Hollandsch Diep estuary in the compound Rhine-Meuse delta

Intrusion in the Hollandsch Diep distributary. The water infiltrating through the polluted bottom deposits of this broad river was feared to contaminate the receiving aquifer system and adversely affect water quality in the low-lying polders bordering the river. On the other hand it was expected that salt water intrusion into the aquifer system was significantly reduced.

A representative site of 600 m by 1200 m (figures 1, 2 and 3) was investigated in great detail, in order to (a) quantify the contribution of North Sea, Rhine River and Meuse River waters to the estuarine groundwaters, and (b) determine the actual groundwater flow, the extent of salt and polluted groundwater intrusion, and the contaminant levels in this polluted 'estuarine groundwater'.

Figure 1. Location map of the study area, in the SW-Netherlands. Details in Figure 3.

Material and methods

About 300 groundwater samples were taken from the upper 35 m of the aquifer system, using the “sondage” technique with sampling through the conus at various depths, both on the water and at land (Figure3). This technique is described in more detail by Zindler (1998).

All samples were analysed on EC, pH, temperature, major ions (O\textsubscript{2}, CH\textsubscript{4}, Cl, SO\textsubscript{4}, HCO\textsubscript{3}, NO\textsubscript{3}, PO\textsubscript{4}-total, Na, K, Ca, Mg, NH\textsubscript{4}, Fe-total, Mn-total, SiO\textsubscript{2}, DOC), trace elements (As, B, Br, Cu, F, Ni, Pb, Zn), organic micro contaminants (EPA-PAHs, organochlorine pesticides, PCBs and chlorinated benzenes), and the natural isotopes \textsuperscript{18}O and \textsuperscript{3}H.
The samples were obtained by suction lift after purging the water content of riser plus well screen 3 times. Temperature, EC, pH and O₂ were measured on site. Alkalinity, pH and EC were measured in the laboratory, on the day of sampling. The portion to be analyzed for most trace elements, Ca, Mg, Fe-total, Mn-total, SiO₂ and PO₄-total was filtrated in situ over 0.45 µm, directly acidified to pH=1.5 using HNO₃-suprapure and was stored in the dark at 4 °C in polyethylene vessels rinsed out with HNO₃ and the water to be sampled. Main constituents were analysed with conventional, well-standardized analytical methods, most trace elements were analyzed using Atomic Absorption Spectrophotometry (AAS) with graphite furnace. The ¹⁸O isotope was measured by isotope ratio mass spectrometry after equilibration of water with CO₂ gas, with an accuracy, in δ¹⁸O relative to Vienna Standard Mean Ocean Water, of ±0.1 ‰. Tritium was measured by scintillation technique with an accuracy of about 1 TU (1 TU = 0.119 Bq/L).

The hydrogeological structure of the aquifer system was deduced from (a) depth logs of conus resistance, conus friction and water pressure in 95 soundings (Figure 3), following conventional interpretation protocols, and (b) available logs of 10 bailer drillings.

**Hydrogeology**

The studied aquifer system is composed of a complex sequence of peat, clay, loam, silty sand and medium grained sand layers of Quaternary age (Figure 2).

On top, at the bottom of the Hollandsch Diep, a 0.1-4 metres thick sludge layer formed since the closure of the Haringvliet dam in 1971. Apart from this layer, the upper 15 metres are composed of Holocene tidal flat and estuarine deposits, with a sandy aquifer roughly in between 7 and 15 m-MSL (Mean Sea Level). This aquifer is separated from the second aquifer by a 5 metres thick fluviatile loam layer of the Kedichem Formation (Middle Pleistocene). Below 20 m-MSL medium grained, fluviatile sands prevail, which were deposited during the Middle and Early Pleistocene.

![Figure 2. Hydrogeological cross-section AA’ of the study area, with the spatial distribution of the chloride concentration in 1997-1998. See position of cross-section in Figure 3.](image-url)
Important hydrological gaps in the sludge layer exist along the estuary banks, where sludge hardly deposits by wave action, and in the main fairway, which is periodically dredged (Figure 3). Two gaps occur in the loam layer at 15-20 m-MSL: in the main fairway (by dredging) and in a former channel that choked during the Holocene with sands at its base and with clays and very fine sands at its top (Figure 3).

Figure 3. Position of the hydrological gaps (short-cuts) in the recent sludge layer at the bottom of the Hollandsch Diep estuary (where sludge < 0.5 m thick, incl. fairway), and in the Kedichem loam layer at 15-20 m-MSL (Holocene channel and fairway).

Tracer composition of the influent Hollandsch Diep distributary

The surface water in the Hollandsch Diep estuary is composed of a mixture of local rainwater (negligible), Rhine River, Meuse River and North Sea water. The variation of the mean annual tracer composition of these 4 end-members in the period 1980-1997 is shown in Table 1. The data presented are largely based on selected monitoring points of the National Water Authority (RWS). Also shown is the composition of the Hollandsch Diep water, as measured in the close vicinity of the study area.

Table 1. Survey of the observed variations of annual means for the tracer concentrations of the 4 end-members mixing in the Hollandsch Diep estuary and the mixed water as well (1 m below water level), in the period 1980-1997.

<table>
<thead>
<tr>
<th>Water</th>
<th>$^\text{H}$</th>
<th>$^\text{18}$O</th>
<th>Cl$^-$</th>
<th>Cl/Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>TU @</td>
<td>% V-SMOW</td>
<td>mg/L</td>
<td>#</td>
</tr>
<tr>
<td>Rain water</td>
<td>10-15</td>
<td>-7.2 a -8.0</td>
<td>3-5</td>
<td>290</td>
</tr>
<tr>
<td>Meuse River</td>
<td>35-99</td>
<td>-7.2 a -7.6</td>
<td>45-76</td>
<td>409-564</td>
</tr>
<tr>
<td>Rhine River</td>
<td>29-55</td>
<td>-9.5 a -10.0</td>
<td>120-208</td>
<td>617-651</td>
</tr>
<tr>
<td>North Sea</td>
<td>0-20</td>
<td>0</td>
<td>19805</td>
<td>290</td>
</tr>
<tr>
<td>Hollandsch Diep</td>
<td>42-58</td>
<td>-8.8a -9.3</td>
<td>94-225</td>
<td>396-673</td>
</tr>
</tbody>
</table>

@ = corrected for radioactive decay till 1997.5; # = mg/L basis
Measurements at different depths and locations in the Hollandsch Diep indicate the presence of a diluted salt water wedge in the deeper parts of the fairway, close to the study area with a chlorinity about double as high as the water on top (Stuyfzand & Zindler, 1998).

The mixing ratio of 3 end-members

The mean mixing ratios in the infiltrating Hollandsch Diep water can be calculated by solving the 3 equations given in Table 2, for the period 1972-1996 (that is after closure of the Haringvliet Dam in 1971, when quality data abound). The contribution of local rainwater is thus neglected.

Table 2. The 3 equations to be solved for obtaining the mean mixing ratios in the Hollandsch Diep water for the period 1972-1996.

<table>
<thead>
<tr>
<th>Equation:</th>
<th>A*Rhine +</th>
<th>b*Meuse +</th>
<th>c*North Sea</th>
<th>Mix</th>
</tr>
</thead>
<tbody>
<tr>
<td>for Cl:</td>
<td>a*164 +</td>
<td>b*60 +</td>
<td>c*19,805</td>
<td>155 mg/L</td>
</tr>
<tr>
<td>for δ¹⁸O:</td>
<td>a*-9.8 +</td>
<td>b*-7.6+</td>
<td>c*0</td>
<td>-9.1 %</td>
</tr>
<tr>
<td>for a,b,c</td>
<td>a +</td>
<td>b +</td>
<td>c</td>
<td>1</td>
</tr>
</tbody>
</table>

Solution: a = 0.717, b = 0.282, c = 0.001

It follows from Table 2 that water that infiltrated in the Hollandsch Diep, in the study area, in the period 1972-1996, consisted of Rhine River water (72%), Meuse River water (28%) and North Sea water (0.1%). Similar calculations for the period before the closure of the Haringvliet dam, based on less complete data regarding surface water, result in the following mixture: 76-86% Rhine River water, 12-22% Meuse River water and 1.6-2.0% North Sea water (Stuyfzand & Zindler, 1998). The lower contribution of Rhine water after closure of the dam is explained by artificially enhanced discharges of Rhine River water through the other distributaries (Yssel and Nieuwe Waterweg).

The general solution for 3 end-members in a mixture with seawater reads:

\[
\begin{align*}
    c &= \frac{(\delta^{18}O_R - \delta^{18}O_M)(Cl_{HD} - Cl_M) + (Cl_R - Cl_M)(\delta^{18}O_M - \delta^{18}O_{HD})}{(\delta^{18}O_R - \delta^{18}O_M)(19805 - Cl_M) + \delta^{18}O_M(Cl_R - Cl_M)} \\
    a &= \frac{\delta^{18}O_{HD} - \delta^{18}O_M(1 - c)}{\delta^{18}O_R - \delta^{18}O_M} \\
    b &= 1 - a - c
\end{align*}
\]

The subscripts R, M and HD in Equations 1-2 indicate water from respectively the Rhine, Meuse and Hollandsch Diep.
Age determination

Tracer input signals

The groundwaters could be dated by spatial history matching of a combination of the tracers chloride, bromide, tritium and oxygen-18. This technique implies that in the hydrochemical snapshot of 1997-1998 either the hydrochemical consequences of dated events or anomalies in the recharging Hollandsch Diep water are searched for in the groundwater survey, or a copy of the whole input signal for a certain period is traced back in the groundwater along specific flow paths.

The success of this dating technique depends on the availability of the chemical input record and the presence of enough easily detectable anomalies in this record. The combination of several tracers yields (i) more anomalies and thus more possibilities of dating, and (ii) stronger evidence.

In this case the input signal was reconstructed on the basis of: (a) all available data on chloride (after 1880), bromide (after 1980), tritium (after 1960) and $^{18}$O (after 1966) in relevant surface waters; (b) ditto in relevant, well studied, dated river bank filtrates along the Rhine River; (c) correlation with tritium data on old wine samples, rain and surface waters elsewhere, and the knowledge that tritium levels in water that infiltrated before 1953 now are below detection by radioactive decay; (d) all available groundwater data in this study; (e) dated changes in surface water management; and (f) assumptions regarding the pollution record.

The resulting input functions are shown in Fig.4 (isotopes) and Fig.5 (halides), and the identifiable, anomalous recharge periods are characterized in Table 3. Further details are given by Stuyfzand and Zindler (1998) and Stuyfzand et al. (1999).

Table 3. Subdivision of the period 1800-2000 into diagnostic chemical episodes for dating groundwater deriving from the Hollandsch Diep (based on figures 4 and 5). Mean values are within brackets.
Results of groundwater dating
Spatial patterns of tracer analysis are shown in cross-section AA' for chloride in Figure 2, and for Cl/Br-ratio, $^{18}$O and $^3$H in Figure 6. The deduced groundwater ages are depicted in Figure 7. Ages vary between 1 and 200 years. It can be deduced that relatively young waters are found close to gaps in the aquitards: in the shallow aquifer along the estuary banks and in the fairway (in right hand corner); and in the deep aquifer in the fairway and down gradient of the Holocene channel fill.
Figure 6. Spatial patterns of selected tracers along the cross-section AA’ in 1997-1998.
Curious is the isolation of the latter low age groundwater body from this Holocene channel fill in drilling 64, which should be connected to low age groundwater in the upper aquifer. This is caused by 3-dimensional flow and perforation of the Kedichem aquitard by the Holocene channel fill not in the drillings used in this cross-section, but in between drillings 64 and 1, somewhere perpendicular to this cross-section.

Relatively old waters are observed in the upper aquifer just below the recent sludge layer near drilling 3, and just above the high flow zone at drillings 69-72; and in the deep aquifer in between both leakage zones in the loamy aquitard.

**Spatial distribution of groundwater types**

*Methods*

Groundwater types have been determined in both a generic and chemical way.

The generic classification is based on the following parameters: intensity of contact with the recent, polluted sludge layer in the Hollandsch Diep, intensity of contact with the Kedichem aquitard at 15-20 m-MSL, salinity (fresh or brackish) and groundwater age.

The chemical classification is based on the method described by Stuyfzand (1989, 1993).

*Results*

The spatial distribution of both generic and chemical groundwater types is shown in Figure 8. A short description of the generic watertypes is presented in Table 4.
Nearly all watertypes are fresh to brackish (85-740 mg/L), (deep) anoxic mainly by reaction with abundant labile organic material in sludge and aquitards, calcite saturated and with a positive Base EXchange index (BEX). This positive BEX, indicated by the ‘+’ at the final position of the chemical watertype code, means that the meq/L-sum of Na+K+Mg significantly exceeds the normal contribution of these cations by sea salt (Stuyfzand, 1993).

This is caused here by 3 factors: (a) freshening of the aquifer system (which salinized during the Holocene transgression), leading to exchange of Na, K and Mg for Ca; (b) discharge of K salts and dissolution of dolomite in the drainage basins of the Rhine and Meuse rivers; and possibly (c) dissolution of struvite (NH₄MgPO₄·6H₂O) in the contaminated sludge layer. Contact with this recent sludge at the bottom of the estuary yields extremely high concentrations, not only of NH₄ and Mg, but also of Ca, HCO₃, Br, NH₄, Mg, K, Fe, CH₄, As and B. The high Br concentrations, which probably derive from organic material, result in anomalously low Cl/Br ratios in watertype C.

Passage of the thick aquitard at 15-20 m depth strongly reduces the concentrations of NH₄, Fe, Mn and As, those of Fe and Mn probably by siderite precipitation, and those of NH₄ and As probably by sorption. For a further discussion of the hydrochemistry, including all geochemical reactions and a discussion of the potential effects of pressure filtration in compacting sludge layers, reference is made to Stuyfzand and Zindler (1998) and Stuyfzand et al. (1999).

In the next section the current spatial distribution of the generic watertypes is used for palaeohydrochemical reconstruction.

Table 4. Main characteristics of the generic groundwater types A-M discerned in Figure 8.

<table>
<thead>
<tr>
<th>Water type</th>
<th>Aquifer</th>
<th>Sludge contact</th>
<th>Aquitard at 15-20m</th>
<th>Recharge period</th>
<th>Dominant Chemical watertype</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>No</td>
<td>No</td>
<td>1960-1998</td>
<td>f₂CaHCO₃, f₂CaHCO₃⁺</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>Strong</td>
<td>No</td>
<td>1972-1992</td>
<td>f₂CaHCO₃⁺</td>
<td>Moderately polluted</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>Very strong</td>
<td>No</td>
<td>1972-1998</td>
<td>f₂NH₄H₂CO₃⁺, f₂CaHCO₃⁺</td>
<td>Most polluted #</td>
</tr>
<tr>
<td>D1</td>
<td>2</td>
<td>No</td>
<td>Little</td>
<td>1972-1985</td>
<td>f₂CaHCO₃⁺</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>2</td>
<td>Moderate</td>
<td>Little</td>
<td>1960-1976</td>
<td>f₂CaHCO₃⁺</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>No</td>
<td>Strong</td>
<td>1954-1972</td>
<td>B₂NaHCO₃⁺</td>
<td>$$</td>
</tr>
<tr>
<td>F</td>
<td>2</td>
<td>No</td>
<td>Strong</td>
<td>1920-1952</td>
<td>B₂NaHCO₃⁺, B₂NaHCO₃⁺</td>
<td>$$</td>
</tr>
<tr>
<td>G1</td>
<td>1</td>
<td>No</td>
<td>No</td>
<td>1980-1952</td>
<td>f₂MgHCO₃⁺, f₂NaHCO₃⁺</td>
<td>$$</td>
</tr>
<tr>
<td>G2</td>
<td>2</td>
<td>No</td>
<td>Strong</td>
<td>1800-1920</td>
<td>f₂NaHCO₃⁺</td>
<td>$$</td>
</tr>
<tr>
<td>M1</td>
<td>1</td>
<td>No</td>
<td>No</td>
<td>1954-1972</td>
<td>f₂CaHCO₃⁺, f₂CaHCO₃⁺</td>
<td>Mix of A + G1</td>
</tr>
<tr>
<td>M2</td>
<td>2</td>
<td>No</td>
<td>Strong</td>
<td>1954-1972</td>
<td>f₂NaHCO₃⁺, f₂NaHCO₃⁺</td>
<td>Mix of D2 + G2, $$</td>
</tr>
</tbody>
</table>

# = extremely high concentrations of Ca⁺⁺, HCO₃⁻, Br⁻, NH₄⁺, Mg⁺⁺, K⁺, Fe⁺⁺, CH₄, As and B.
$\$ = relatively very low concentrations of Fe⁺⁺, Mn⁺⁺, NH₄⁻ and As.
Encircled characters indicate main recharge zones: a = estuary banks; b = fairway, no sludge; c = fairway, disturbed Kedichem aquitard at 15-20 m-MSL; d = Holocene channel through Kedichem aquitard perpendicular to this cross-section.
Figure 8. Spatial distribution of generic watertypes A-M (above) and chemical watertypes (below) along the cross-section AA' in 1997-1998.

Palaeohydrochemical reconstruction

All information has been combined to tentatively reconstruct the palaeohydrochemical developments in the study area along cross-section AA'. The results are shown in Figure 9. Three periods have been discerned:
Recognition, dating and genesis of fresh and brackish groundwaters in the Hollandsch Diep estuary in the compound Rhine-Meuse delta

(1) 1850-1880: representative for an undisturbed, unpolluted estuary, without dam in the Haringvliet outlet, with relatively fresh unpolluted river water, high flow rates and little sea water intrusion, and with relatively high recharge rates of the upper aquifer thanks to the absence of thick bottom sludges in the estuary;

(2) 1950-1970: representative for a polluted estuary, still without the dam in the Haringvliet outlet, with polluted river water, lower flow rates and increased sea water intrusion, and still with relatively high recharge rates of the upper aquifer thanks to the absence of thick bottom sludges in the estuary; and

(3) 1990-1999: representative for a disturbed estuary with reduced sea water intrusion thanks to the dam in the Haringvliet outlet, less polluted surface water thanks to sanitation measures in the drainage basins of the Rhine and Meuse Rivers, with a reduced recharge rate of the upper aquifer by the formation of thick bottom sludges, and with increased recharge rates of the deep aquifer by injury to the aquitard at 15-20 m-MSL caused by the dredging of the fairway.

Concluding remarks

The hydrochemical situation in aquifers recharged by estuarine waters is complicated by pollution-related changes in river water quality, variations in the contribution of intruding sea water, and an intricate hydrogeological structure, with many discontinuous aquitards.

In the compound Rhine and Meuse delta there are additional complications due to changes in the mixing ratio of Rhine and Meuse River water and due to man-made changes by the construction of weirs, dams, storm surge barriers and fairways.

Nevertheless, a clear picture of the hydrochemistry, origin and ages of the groundwaters in the Hollandsch Diep estuary could be made. This required a dense monitoring network consisting of 95 monitoring points, with on average 3 samples at different depths in an area of 1200 by 600 m, with analysis on, at least, main constituents, Br and the natural isotopes $^3$H and $^{18}$O.

The study area shows a large scale fresh water intrusion of a mixture of mainly Rhine and Meuse river waters into an aquifer system that salinized probably during the Holocene transgression and during and after the so called St. Elisabeth’s storm surge in 1421 AD. The fresh water intrusion probably started after 1600 AD when many dikes were completed in the area, and drainage of the endiked land intensified. Remnants of the old saline groundwaters were not observed, because maximum age of the groundwaters studied is about 200 years.

Prior to the construction of the dam in the Haringvliet outlet, there was a period of about 50 years (1920-1970) with reduced river flows and a somewhat increased sea water intrusion. This is evidenced by the limited occurrence of brackish groundwater, dated 30-80 years old by various tracers, in the deep aquifer.
The dam in the Haringvliet outlet, completed in 1971, strongly reduced the sea water intrusion in the study area. The resulting deposition of a 0.1-4 metres thick sludge layer generated, however, a strongly polluted groundwater plume (watertypes B and C in Figure 8). Urgent problems with exfiltrating water from this plume are not expected. The first argument is that this plume does not flow, in the study area, in an upward direction but in a subhorizontal direction towards a remote deep polder 4-5 km to the north-west. The second argument is that accretion and compaction of this layer with time result in an ever increasing hydraulic resistance and thus in a shrinking recharge of the plume.
Future research should focus on the relevance and effects of pressure filtration in compacting sludge layers. The expelled pressure filtrate may have higher ion concentrations than the original pore water (Appelo and Postma, 1993, p.189), and may thus generate a limited volume of more saline water than the surface water.

References