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THE HYDROGEOLOGY AND HYDROCHEMISTRY OF THE LOWER RHINE FLUVIAL PLAIN

BY

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ABSTRACT

The water-bearing strata in the area under study consist mainly of fluviatile Pleistocene. The base is formed by the marine Plio-Pleistocene, the top by the Holocene clay and peat deposits.

The chemical composition of the ground-water in this aquifer depends on processes related to the geological history, not on the type of sediment. The most important of these processes is cation exchange, which occurs in two ways. When fresh water replaces salt water in the aquifer, an exchange takes place between the Ca^{2+} ions from the ground-water and the exchangeable Na^+ ions from the sediments. The reverse process takes place when sea-water infiltrates a sediment with fresh ground-water: the Na^+ ions from the sea-water are exchanged for Ca^{2+} ions from the sediments.

A classification of ground-water according to 8 types was made. These types are indicated on a map and on sections.

In the western part of the area, intrusion of salt water originating from the Eemian transgression can be recognized. During the Calais transgression salt water infiltrated the aquifer; this salt water has gradually been replaced by fresh water. In part of the area salt water also infiltrated during the Duinkerke transgression.

In an east-west zone, where the ground-water flows from the high-lying areas in the north and the Pleistocene outcrops in the south converge, the fresh/salt water boundary rises. In this zone high Cl^--concentrations occur at the surface locally, due to increased upward seepage through the Holocene clay and peat layers at places where the vertical resistance is low.

In some bore-holes the concentration of the minor constituents I^- and Br^- and of the isotopes of oxygen and carbon was measured. The $Cl^-:Br^-$ concentration ratio proved to be indicative of polluted ground-water. High ^{13}C concentrations are an indication for an upward flow of ground-water.

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CHAPTER I

INTRODUCTION

The area to be discussed is formed by the low-lying fluvial plain of the Rhine and Maas rivers and the adjoining coastal plain. The hydrogeology and hydrochemistry will be described on the basis of the results of chemical ground-water analyses recorded by the Government Institute for Drinking-Water Supply and of the ground-water level records deriving from observation wells maintained by the Ground-Water Survey TNO.

The geology is based on stratigraphic sections and other unpublished data of the Geological Survey of The Netherlands and on the geological description of bore-holes available in the archives of this organization. Various reports of geo-electrical surveys carried out by the Ground-Water Survey TNO and 'Rijkswaterstaat' were also available.

A computer program was developed for the statistical analysis of water-quality data. A total of 1,800 water analyses pertaining to the area were used in this study.

Additional information was obtained from measurements of isotope concentration ratios and of minor constituents concentrations in ground-water samples.

DESCRIPTION OF THE AREA

The area under study is formed by the fluvial plain along the lower courses of the Rhine and Maas rivers and the adjoining coastal plain extending westward from the German border in the east to the North Sea. This area is often referred to as the 'delta' of the Rhine and Maas, although whether it is a true delta is a matter of dispute (Kruit, 1963).

The eastern part of the plain is relatively narrow and bordered on both sides by steep hills. These hills are the ice-pushed ridges of Pleistocene sediments formed during the Saalian glaciation. The northern hills are part of the Utrecht Hills and southern Veluwe, while the southern hills are those of Groesbeek and Nijmegen. West of these barriers formed by the ice-pushed ridges the plain widens and merges with the coastal plain along the North Sea. In the south the plain is bordered by the high-lying Pleistocene deposits of Brabant.

Within the northern part of the valley several abandoned branches of the Rhine system, including the 'Old Rhine' and the Vecht, are found. Along the North Sea coast, the coastal plain is bordered by a narrow band of sand dunes. The area between the sand dunes and the Utrecht Hills and also the narrow eastern part of the valley, are covered by Holocene clay and peat deposits. These areas form the flat, low-lying 'polder' lands, which means that the water table is artificially controlled.

ACKNOWLEDGEMENTS

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Others who have been of assistance to me are mentioned in the text.

CHAPTER II

GEOLOGY

GEOLOGICAL SETTING

The present Rhine-Maas fluvial plain is situated in an area which has been a complex sedimentary basin since the beginning of the Mesozoic. Parts of it have at times subsided so as to form local sedimentary basins, whereas other parts were uplifted; the subsiding areas have repeatedly shifted their positions in the course of time. At the end of the Miocene the area with the greatest sediment thickness was situated southeast of the area under consideration, whereas in the Pliocene it shifted to the north; at these times the western part of the area under study, i. e. the area around the later mouth of the Rhine, was a region of non-deposition (Keizer and Letsch, 1963).

During the Upper Tertiary the basin was filled with marine deposits consisting of clays with intercalated silts rich in shells. These deposits generally still contain salt water.

Starting in the Early Pliocene, the sea began to retreat from this area and fresh-water sediments of the 'Kieseloolith' Formation were deposited in the southeastern part. The base of this formation contains coarse sands, the top consists of clay (Reuver clays). In the remaining area the marine sedimentation continued into the Pleistocene. It was not until the early Pleistocene that the area of greatest subsidence shifted to the northwest, near the present North Sea coast.

THE PLEISTOCENE

The Lower Pleistocene marine deposits belong to the Amstelian and the Icenian; they consist mainly of very fine silty sands, in the west having a thickness of several hundred metres. The Icenian is difficult to correlate with the fluvial sediments in the SE. The lower part of the Icenian is probably synchronous with the uppermost part of the Kieseloolith Formation.

In the early Pleistocene the sea retreated in a northwesterly direction (Fig. 1) and subsequently fluviatile sediments were deposited by the Rhine and the Maas. The first of these sediments, supplied by the Rhine, belong to the Tegelen Formation, the basal part of

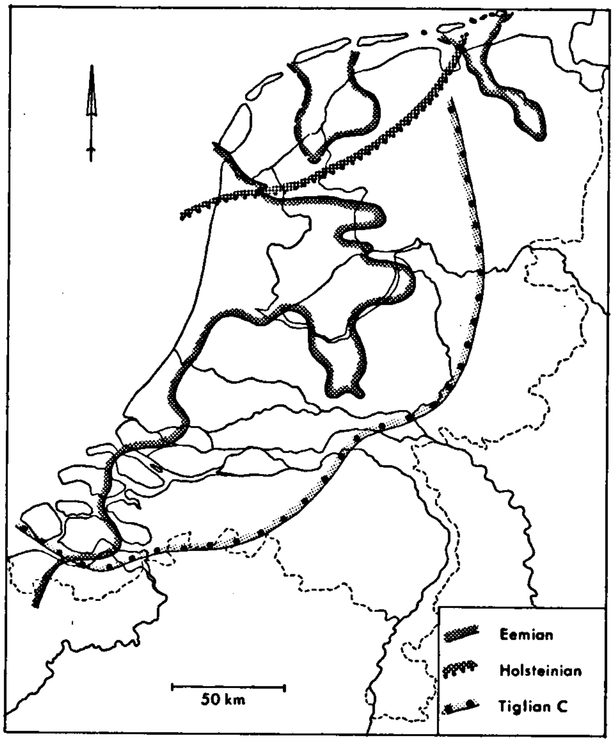

Fig. 1. Land-sea distribution in the Pleistocene of The Netherlands (after Zonneveld, 1958 and Zagwijn, 1963).

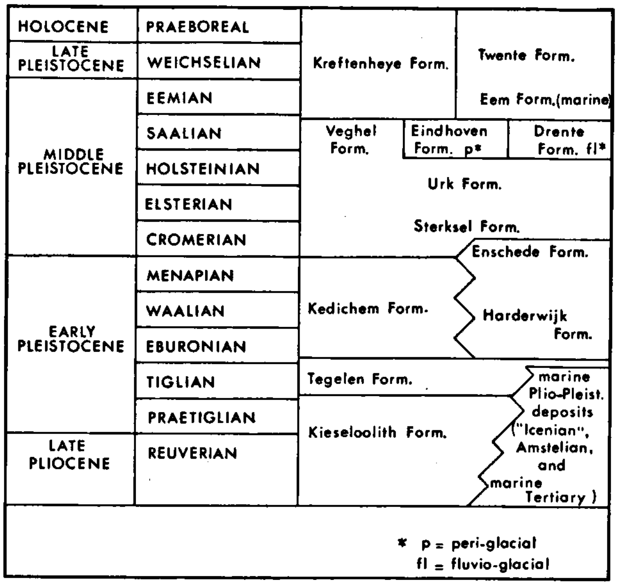

Fig. 2. Correlation chart of the Pleistocene in the central Netherlands (after Zagwijn, 1963).

which consists of coarse sands, the upper part of clay.

On top of the Tegelen Formation, the Kedichem Formation was deposited, in this area supplied by the Maas. The Kedichem Formation consists mainly of clays intercalated with fine-grained sands. The deposition of the Kedichem Formation occurred for the most part synchronously with that of the Harderwijk Formation. The latter is of northeastern origin and is found mainly in the central and northern parts of The Netherlands. This formation consists of coarse-grained sands with gravel. In the area under investigation, tongues of the Harderwijk Formation reach into the Kedichem Formation.

The Middle Pleistocene started with the deposition of the Sterksel Formation, which consists of coarse sands supplied by the Rhine. Along the outer limits of the Sterksel Formation area, clays and fine-grained sands are found.

More or less synchronous with the Sterksel Formation, part of which belongs to the so-called Cromerian Interglacial Complex, is the Enschede Formation in the north, supplied by rivers of eastern origin. The latter too consists mainly of coarse sands. On top of the Sterksel Formation is the Urk Formation dating approximately from the Elster Glacial and the Holstein Interglacial. The Urk sediments, also supplied by the Rhine, consist of coarse sands intercalated with clay lenses. More to the south, the Maas deposited the sands of the Veghel Formation. After the deposition of the Urk and Veghel Formations the sheet ice of the Saale Glaciation reached The Netherlands. The influence of the ice lobes and the morphological consequences are discussed in the next section.

The youngest Pleistocene sediments in the area belong to the Kreftenheye Formation, deposited by the Rhine and Maas. This formation consists of coarse sand and gravel deposits. The stratigraphy of the Pleistocene is given schematically in Fig. 2.

During the Middle and Late Pleistocene, marine ingressions occured only in the Holsteinian and Eemian Interglacials. These marine deposits are synchronous with parts of the Urk and Kreftenheye Formations, respectively. Only the Eemian transgression reached the area discussed in this paper. The extent of these transgressions is indicated in Fig. 1.

In the southern part of the area the upper Pleistocene deposits consist of coarse and fine sands alternating with loam layers, taken together as the 'Sand Diluvium'.

THE GLACIATION

Among the various glaciations in the Pleistocene, only the Saalian ice sheet reached the area under consideration. Before the coming of the ice, the Rhine and Maas rivers followed a northerly course to the Holstein Sea. The Rhine presumably flowed through the IJssel valley, the Maas through the 'Gelderse Vallei'. The ice first blocked the North-German rivers and later the Rhine and Maas, which were forced to bend to the west and follow the present Rhine fluvial plain.

The ice arriving from the north invaded the river valleys (Fig. 3). The soil was in a permafrost condition, but in the river valleys the underground was relatively warm. Here, the ice eroded the bottom of the valleys, so

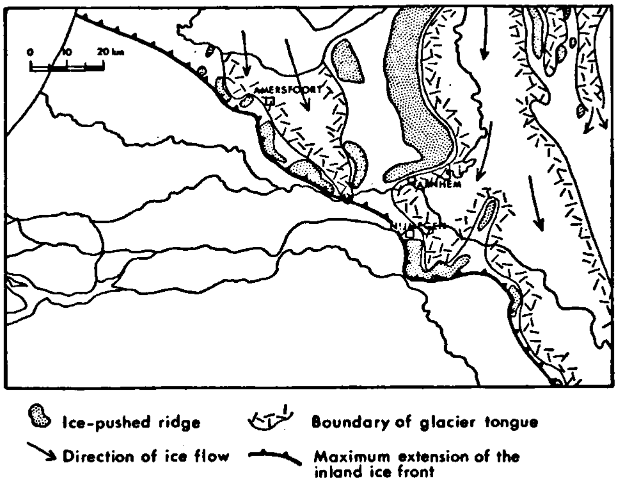

Fig. 3. Maximum extension of the Saalian ice-sheet (after Ter Wee, 1962).

that glacial basins were formed. The greatest depth of these basins was about 100 m –NAP (Netherlands datum plane), which was reached in the IJssel Valley near Deventer. The glacier tongue of the 'Gelderse Vallei' attained its maximum depth under the present IJsselmeer.

The eroded material was pushed in front of the advancing ice, and the frozen fluvial sediments on both sides of the ice lobes were simultaneously deformed into ice-pushed hills. According to Ter Wee (1962), the first stage of the advancing ice formed the Utrecht Hills, the Gooi area, and the eastern Veluwe. According to A. Brouwer (1950, 1963), in its first stage the ice sheet reached southern Drente and only in a later stage advanced as far as the Utrecht Hills. In a later stage the direction of the ice flow shifted more to the east and a glacier tongue entered the Rhine Valley between Arnhem and Nijmegen (Thomé, 1959). At this stage the hills of Nijmegen and Arnhem were formed. The ice flow in the 'Gelderse Vallei' did not show this change of direction because it was shielded on the east by the eastern Veluwe.

The ice-pushed hills consist of Middle and Lower Pleistocene fluvial deposits and show steep dips and imbrications due to the pushing of the ice. When the ice melted, the IJssel branch of the Rhine resumed its northerly course and its glacial basin filled with sand and clay deposits (Drente Formation). In the eastern part of this area, near Pannerden, basin clays of the Drente Formation are found to a depth of 70 to 80 m below NAP. The Maas did not return to its previous course, and in the Eemian interglacial the sea invaded part of the glacial basin in the 'Gelderse Vallei'.

THE HOLOCENE

At the end of the Pleistocene the lower part of The Netherlands was a plain sloping gently in the direction of the sea. The contours of the top of the Pleistocene sands are drawn in Fig. 4. The fluvial fan of the Rhine and Maas rivers roughly coincided at that time with that of the present fluvial plain. On this fan coarse sands and clays were deposited; outside the fan, the deposition of aeolian coversands of the Twente Formation continued.

The Holocene transgression reached western Holland at the end of the Boreal. Up to that time, fluvial sedimentation took place. The relative rise of the sea level in the Atlantic time was about 20 cm per century (Jelgersma, 1961). The rising sea level caused a rise of the ground-water level below the inclined Pleistocene surface, so that peat layers (called the Lower Peat) could be formed. Due to the continuous rise of the sea level, the peat was drowned and then covered by lagoonal and tidal deposits formed during Atlantic and early Sub-Boreal times. These deposits are called the Calais deposits.

During the early Sub-Boreal the rise in sea level slowed down to 10–12 cm per century, and this led to the formation of a series of coastal barriers which can be regarded as spits around the mouths of the branches of the Rhine and Maas rivers. This is especially clear around Hoek van Holland and Katwijk. Behind the protection of these coastal barriers, peat could again be formed on top of the Calais deposits (the so-called 'Holland Peat'). During the Sub-Atlantic the influence of the sea again became important and large parts of the Holland Peat in western Holland were eroded or covered by the marine Duinkerke deposits. The stratigraphy and lithology of the coastal Holocene deposits are summarized in Fig. 5. The Holocene section thus consists of alternating layers of peat, clay, and sand constituting evidence of various periods of regression and transgression (Pons et al., 1963).

In the Holocene, three different environments can be distinguished within the area under discussion. In the west a predominantly marine environment prevailed, with marine clay deposition of the Calais and Duinkerke transgressions, interrupted by peat formation at times when the influence of the sea diminished. East of the marine environment we find an area with fluvial deposition influenced by the level of the nearby sea. Still farther to the east, pure fluvial deposition by meandering rivers took place (Fig. 6). In the second of these three areas the lower reaches of the rivers were blocked by the rising sea level. The beds of these rivers shifted frequently. Abandoned river courses show up as sand gullies in the clay and peat sequence. Some of these old river courses were eroded into the Pleistocene Kreftenheye Formation. Upstream, river-clay and peat deposits occur that can be correlated with the marine Calais and Duinkerke Formations; these are called the Gorkum and Tiel Formations, respectively. Near the sea coast, on top of the coastal barriers, aeolian deposits were formed: the so-called older dunes. In historical times (since A.D. 1250), due to the retrograding coastline, younger dunes were formed, partly on top of the older ones. The outlet of the Rhine branch near Katwijk was blocked by this dune formation.

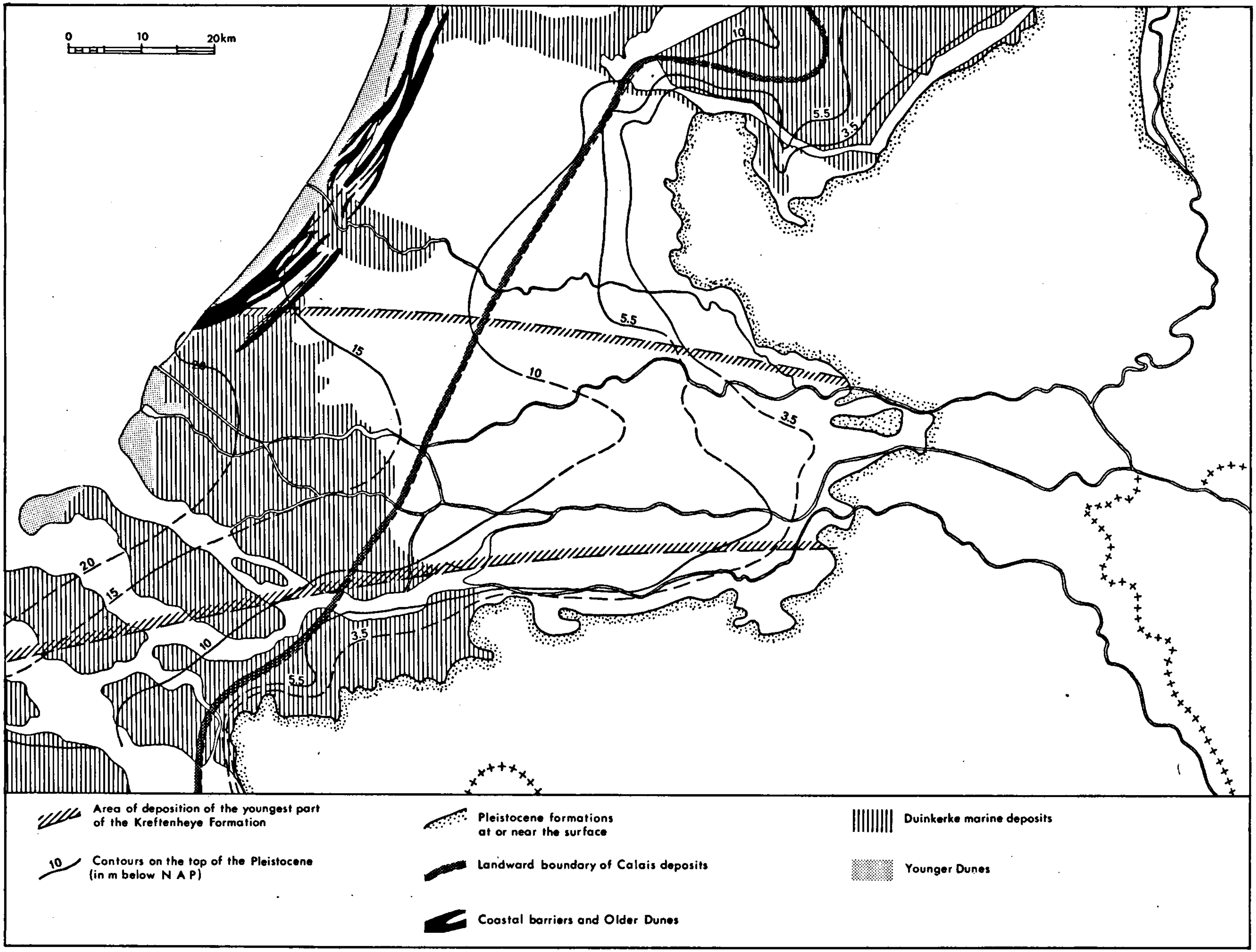

Fig. 4. Generalized geological map of the area (after Jelgersma et al., 1970 and Pons et al., 1963).

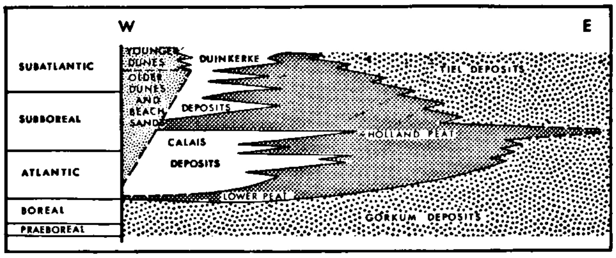

Fig. 5. Schematic cross-section of the Holocene in the western part of The Netherlands (after van der Heide and Zagwijn, 1967).

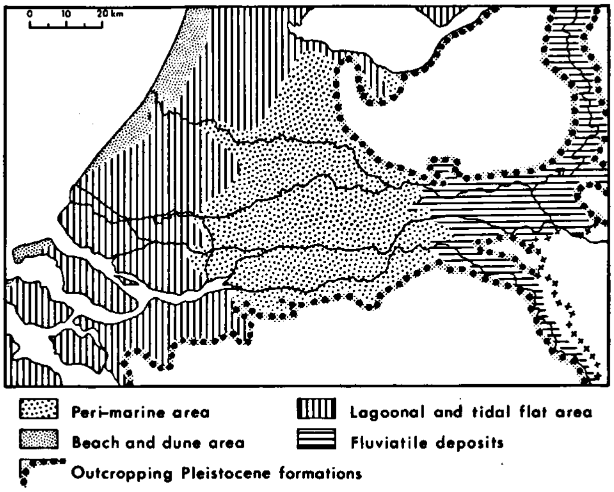

Fig. 6. Depositional environments during the younger Holocene (after Hageman, 1969).

Around A.D. 1200 dike building along the rivers, which had started around 1000, was completed. Since this embankment the riverbeds and flood plains have silted up to a level higher than the surrounding country. The compaction in the Holocene peat deposits, intensified by the reclamation and draining of land, also contributed to the difference in height between the rivers and the adjacent polder land (Bennema et al., 1954).

In the Middle Ages peat was the most important fuel, and the digging of peat led to the formation of lakes with depths to –5 m NAP. Later, most of these lakes were drained.

STRUCTURAL GEOLOGY

The most important structural features in the Pleistocene of The Netherlands are the ramifications of the Lower Rhine fault system, which run in a SE-NW direction and are mainly located in the SE part of the country. The activity of this system, which was accompanied by epirogenic movement of the Ardennes and the Rhenish Massif, was important and already apparent in the Paleozoic and Mesozoic; faulting also occurred in the Tertiary and Quarternary. The sedimentation in the Tertiary and Quarternary was strongly affected by this tectonic activity. In the Central Graben, Zagwijn (1963) recognized various sedimentary cycles in these periods, the beginning of a new cycle being attributed to renewed tectonic activity.

In the area under consideration the Lower Rhine fault system consists of the following units. The centre of the

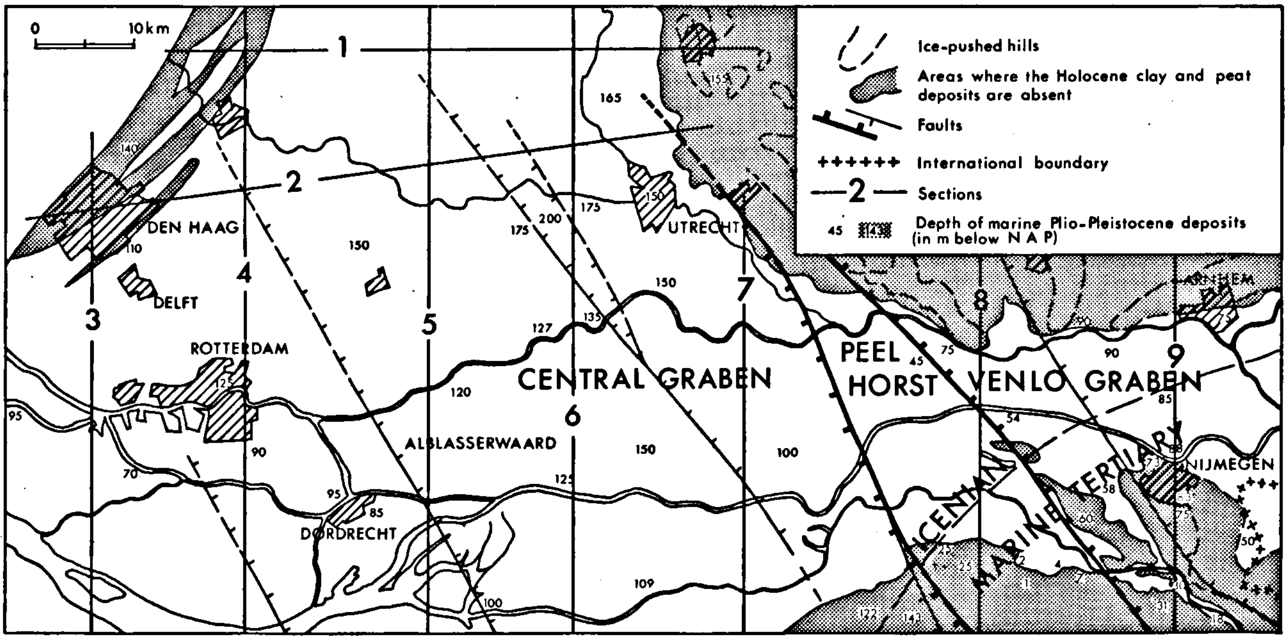

Fig. 7. Main tectonic features and depth of the marine Plio-Pleistocene deposits (based on the geological descriptions of bore-holes and on unpublished data of the Geological Survey).

eastern part is formed by the Peel Horst, which is separated from the Central Graben in the west by the Peel Boundary Fault. In the east the Venlo Graben is located. In the Central Graben the blocks become structurally higher in a westerly direction. All of the faults connected with the system decrease in importance to the north. The throw of the Peel Boundary Fault diminishes from about 115 m in the south of the area under study to about 30 m near Utrecht.

Because the fault activity in the Pleistocene was greatest during the sedimentation of the oldest deposits, the throw also diminishes in stratigraphically younger deposits. Since few of the bore-holes reached the older Pleistocene deposits, the faults are often difficult to trace and to recognize. Only the most important faults are indicated in Fig. 7.

CHAPTER III

HYDROGEOLOGY

HYDROGEOLOGICAL SUBDIVISION

The marine Plio-Pleistocene sediments have, in accordance with their lithological composition, a low to very low permeability. For a hydrogeological subdivision they can be considered as the impervious basement of the water-bearing strata. In the low-lying areas the upper boundary of the water-bearing strata is formed by the semi-pervious Holocene clay and peat deposits. The aquifer thus comprises the complete fluviatile and fluvio-glacial Pleistocene, and in the SE also includes the 'Kieseloolith' Formation. Although the aquifer shows various clay horizons, the most continuous being those in the Kedichem Formation, only part of the Central Graben (Alblasserwaard) can be subdivided into an upper and a lower aquifer (Geirnaert, 1970). The upper aquifer is formed by the Formations of Kreftenheye, Urk, and Sterksel. The lower aquifer comprises the lower parts of the Kedichem Formation and the Tegelen Formation. These two aquifers are divided by the clays of the Kedichem Formation. The occurrence of clay layers in the other formations locally reduces the importance of these formations as water-bearing strata.

HYDRAULIC PROPERTIES

Among the important properties of an aquifer is the transmissibility and the resistance to vertical flow of the confining layers. The transmissibility (T in m^2/day) is defined as the product of the horizontal hydraulic conductivity in m/day and the thickness of the aquifer in metres. The transmissibility varies considerably in this area, mainly because of variations in the thickness of the aquifer, which in turn depends on the depth of the impervious basement.

Faulting led to great differences in the depth of the impervious basement.

Pumping tests in the upper aquifer in the Alblasserwaard gave an average horizontal hydraulic conductivity of approximately 60 m/day (R.I.D., 1967). No results of pumping tests were available for the lower aquifer, but the hydraulic conductivity is probably lower there than in the upper aquifer, in view of the smaller grain-size of the sediments. In the Central Graben north of the Alblasserwaard, hydraulic conductivity values similar to those obtained for the first aquifer of the Alblasserwaard region were found. For the Peel Horst area and the Venlo Graben, few pumping-test data were available. The average value of the hydraulic conductivity here is approximately 30–40 m/day.

The resistance to vertical flow of the semi-pervious confining layers is defined as:

$c = d_1/k_1$ (expressed in days), where d_1 is the thickness of the covering layers in metres and k_1 the vertical hydraulic conductivity in m/day.

Laboratory tests on Holocene clays gave c values of 10,000 days and more, but pumping tests in the same region generally gave much lower values, varying from 200 to 600 days (Tielerwaard Report). The wide divergence in the results of laboratory and pumping tests is explained by the fact that in the laboratory the vertical hydraulic resistance was measured in clay samples, whereas the pumping tests measured the average hydraulic resistance of the Holocene clay and peat sequence. This sequence contains sand-filled abandoned river channels which lower the average hydraulic resistance.

MOVEMENT OF GROUND-WATER

Recharge

In the topographically high areas the principal source of recharge of the ground-water is precipitation. The piezometric surface in these areas is generally lower than the phreatic water level, and as a consequence downward movement of ground-water takes place. In the ice-pushed hills the imbricated structures with clay layers can locally obstruct the infiltration and the horizontal flow of the ground-water.

In the high-lying Pleistocene outcrops of Noord-Brabant the upper layers consist of fine sand. The piezometric surface of the underlying confined water is slightly lower than the phreatic water level, and recharge takes place (Visscher, 1967).

In the coastal dunes there is a natural recharge of the aquifer by precipitation and an artificial recharge by

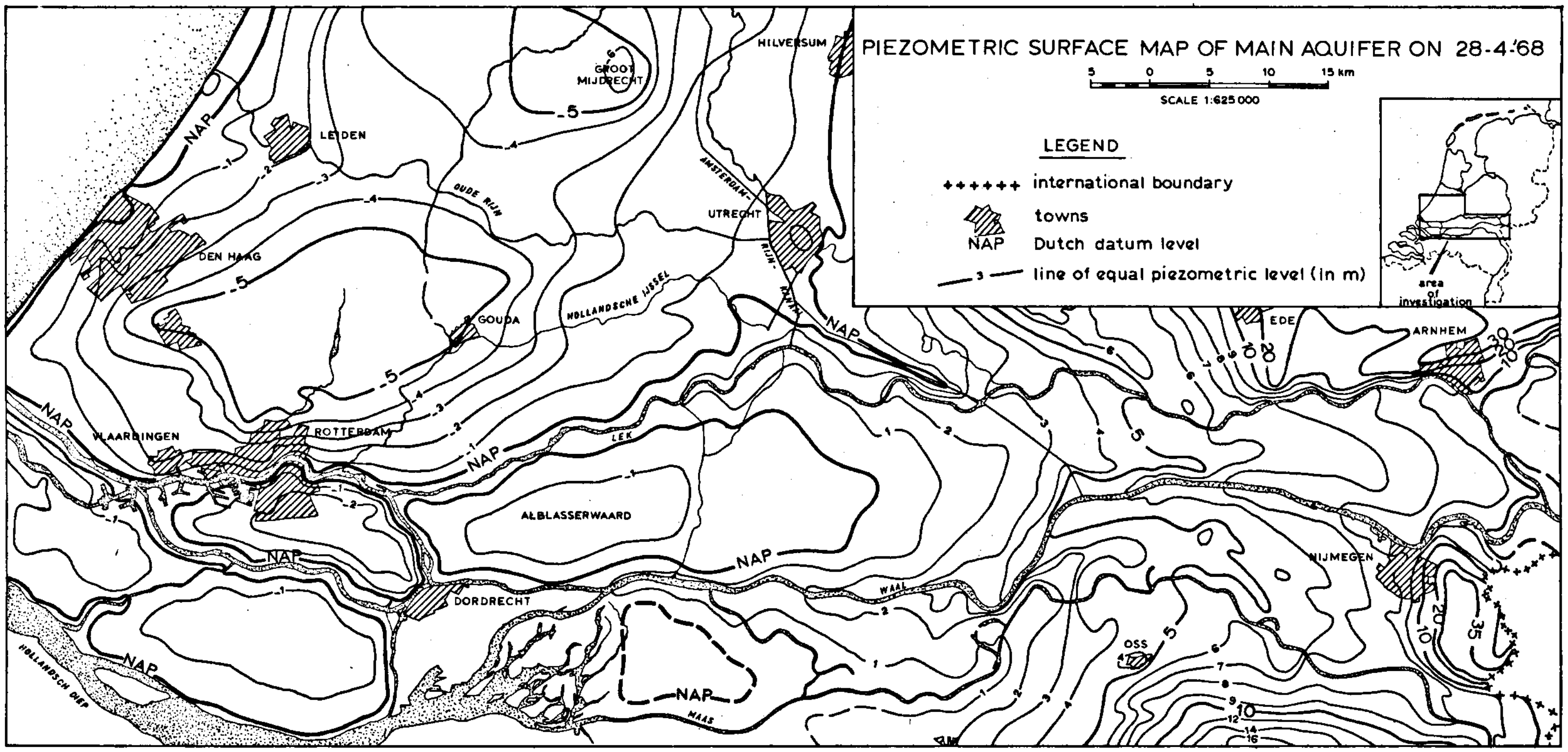

Fig. 8. Piezometric surface map of the upper part of the aquifer in the area under study.

man-made infiltration works. In the low-lying areas (the polders) recharge takes place by infiltration of river water, precipitation, and horizontal flow from the high to the low areas.

Infiltration of river water occurs because the levels of the Rhine and Maas are higher than the piezometric surface of the aquifer. At places where the rivers are partially incised in the Pleistocene sands or where a good hydraulic connection with the aquifer exists through the sand gullies which cross the rivers, the rate of infiltration is high.

Discharge

The precipitation infiltrating the high areas is discharged by sub-surface flow to adjacent low-lying areas. In the transition zone from high to low areas, seepage may occur locally. This seepage is discharged by ditches and brooks.

In the areas covered by the Holocene deposits water is discharged from the aquifer by upward seepage through the peat and clay layers (Dutch: 'kwel'). This upward seepage is concentrated at places where the hydraulic resistance of the confining layers is low and where there is a large difference in pressure between the phreatic water table and the piezometric surface of the deep ground-water. This generally occurs in the polders, because there the phreatic water table (i.e. the level in the canals) is controlled by man. An example of the latter is the Groot Mijdrecht polder, where the difference between the polder level and the piezometric surface is about 1 m. The hydraulic resistance is lowest where sand gullies in hydraulic connection with the aquifer are exposed or cut by polder canals. The upward seepage through such sand gullies can only be calculated roughly by water-balance studies. In four polders in the Alblasserwaard an average 'kwel' of 82 mm/year was found (R.I.D., 1967). Further to the east, in the Tielerwaard region, maximum values of 3–9 mm/day were found (Tielerwaard Report). Because of the irregular occurrence of the sand gullies, the amount of upward seepage varies widely from place to place. The difference in pressure between the polder level and the river level is often high.

Direction of ground-water movement

From the isopiezometric surface map of the aquifer (Fig. 8), the direction of ground-water movement can be deduced. The map is based on data from 800 observation wells, and gives the situation on the 28th of April, 1968. This date represents the transitional stage from the winter to summer piezometric levels. According to the C.O.L.N. Report (1958), the spring level is the most consistent through the years. Most of the piezometric surface readings on the map derive from observation wells with depths varying between 15 and 50 m below NAP. In places where a subdivision into two different aquifers can be made, the reading of the upper aquifer is given. In the high-lying areas most of the readings stem from the phreatic water table.

In the western part of the area the ground-water movement is directed toward the centre of the deep polders north of Rotterdam and the Groot Mijdrecht polder. The horizontal ground-water gradient is small in these areas, and upward ground-water movement predominates. In a small zone along the rivers there is a steep gradient, but between the two main rivers the gradient is again much smaller, with upward movement of ground-water predominating.

In the schematic section shown in Fig. 9 the direction of the ground-water movement is indicated.

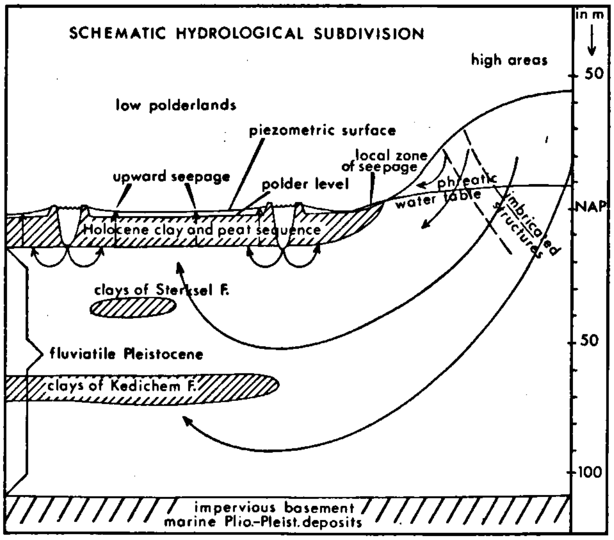

Fig. 9. Schematic hydrogeological subdivision.

CHAPTER IV

CHEMISTRY OF THE GROUND-WATER

INTRODUCTION

In The Netherlands ground-water is still the most important source of water for public water supply. The amount of fresh water (defined for the purpose of this study as water having a Cl^- content of less than 150 mg/litre) is limited, since the country is underlain by marine deposits which still contain salt water, and because salt water intruded into the aquifer in large parts of western Holland during the Holocene transgressions.

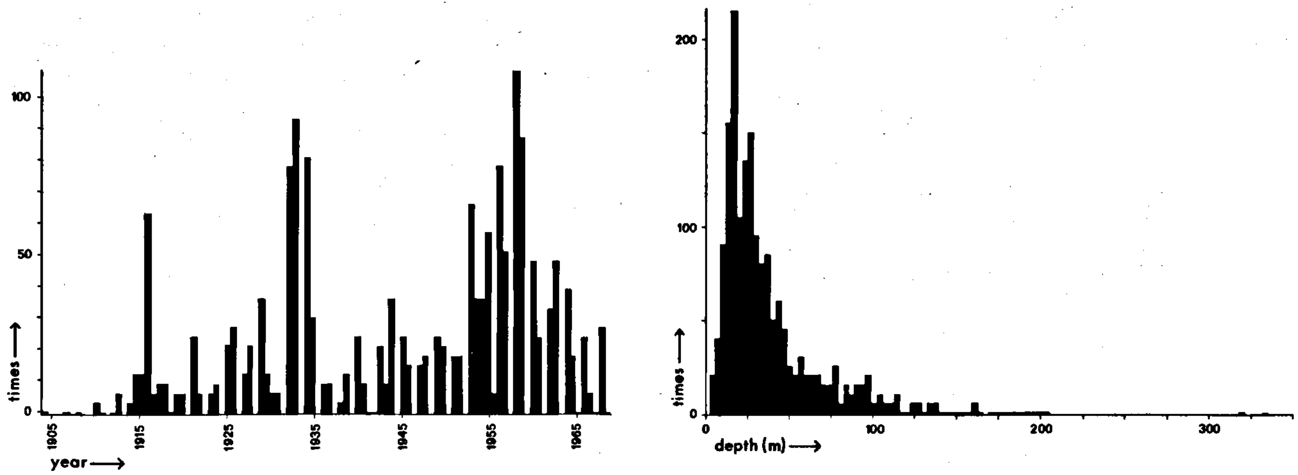

Fig. 10. Frequency of bore-hole sampling per year since 1900 and distribution of the depth at which the samples were taken.

In addition, the present salt encroachment of the sea through the river outlets and the upward movement of salt water under the deep polders also threaten the fresh-water reserves. Because of these problems, extensive drilling has been carried out in The Netherlands since about 1900.

For the area under consideration, the results of about 2,000 chemical analyses of ground-water were available. Fig. 10 gives the sampling frequency per year since 1900 and the distribution of the depths at which the samples were taken. Most of the analyses concern the fresh-water zone. About 46 % of the analyses were complete, which means that at least the concentrations of the main anions (Cl^-, SO_4^{2-}, HCO_3^-) and main cations (Ca^{2+}, Mg^{2+}, Na^+) were determined. In 29 % of the partial analyses, at least the concentration of the main anions and the hardness were determined. For the cations, often only the Ca^{2+} concentration was measured. These analyses could be completed by using the following relationships:

$$\text{Anions}^* = \text{Cations}^* \qquad (1)$$

$$\frac{\text{Hardness}^{**}}{2.8} = Ca^{2+\,*} + Mg^{2+\,*} \qquad (2)$$

$$Na^{+\,*} = (1) - (2)$$

The computed Na^+ concentrations thus contain the sum of the errors of the other values. In most of the remaining partial analyses only the hardness and the concentrations of chlorine and iron were determined. Measurements of the conductivity were carried out in 93 % of all analyses.

For the presentation of the results of chemical groundwater analyses, a modified version of the Piper diagram (Piper, 1944) will be used. This diagram gives relative concentrations of the main cations and anions measured in meq/litre. Therefore, for cases where concentrations are given in mg/litre, the original data had to be converted, and relative concentrations had to be computed according to:

mg/litre	meq/litre	% Anions
Cl^- ... /35,5	...	...
SO_4^{2-} ... /48	...	...
HCO_3^- ... /61	...	...
	Anions/litre	
		% Cations
Ca^{2+} ... /20	...	...
Mg^{2+} ... /12	...	...
Na^+ ... /23	...	...
	Cations/litre	

To process the large amount of data, a computer program was developed (Creusot and Geirnaert, 1971). The data of 1,840 analyses pertaining to the area in question were transferred to tape, and relative concentrations were computed. The program can execute the following operations:

a. Listing of the basic data.
b. Printing of a frequency distribution of one variable.
c. Plotting of a scatter diagram for two variables.
d. Plotting of the values of a variable on a map (e. g. Piper diagram).

The accuracy of the data is irregular, since the analyses were performed by several laboratories. Moreover, laboratory methods have changed, especially since 1940 when the flame spectrophotometer became available. For complete analyses the difference between the sum of cation and anion concentration may give a good indication of the reliability.

According to Hem (1959), for the best results this

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* Measured in meq/litre.
**Measured in °D.

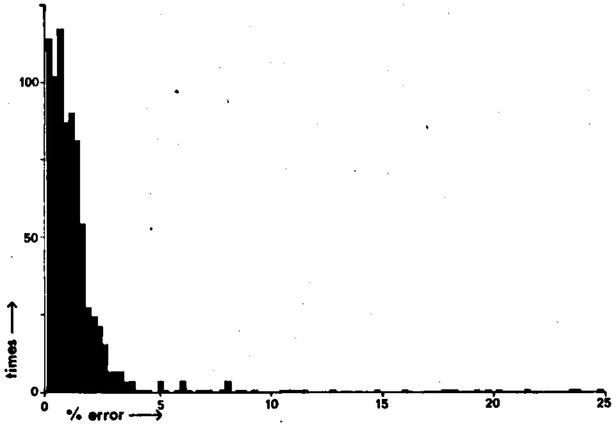

Fig. 11. Distribution of the percentage of error in the complete analyses.

difference should be less than 1 % of the total anion or cation concentration. Fig. 11 shows the distribution of the error for the complete analyses. Because high values of NO_3^-, NH_4^+, or Fe^{2+} may occur in some areas, these values were added to the sum of anions or cations. For analyses of samples with a low total ion concentration, the difference is generally more than 1 %. We found that for most of the analyses (88 % of total number) the error was less than 2.5 %. This value was arbitrarily chosen as the maximum permissible error.

PROCESSES AFFECTING THE COMPOSITION OF THE GROUND-WATER

Infiltrating rain-water

In the elevated areas precipitation is the main source of ground-water. The concentration of the various ions, which is low in rain-water, increases rapidly during infiltration. When $CaCO_3$ is available the CO_2 from the rain-water will form HCO_3^- ions according to the equilibrium reaction:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2HCO_3^-.$$

Due to plant respiration and decay of organic material, the partial pressure of the CO_2 is higher in the soil zone than in the atmosphere. This added CO_2 will shift the equilibrium to the right. Furthermore, the SO_4^{2-} and NO_3^- concentrations will increase in the soil zone due to bacterial activity.

In the areas with a thick soil zone and abundant vegetation the increase in CO_2, NO_3^-, and SO_4^{2-} will be greater than in the sand dunes and the highest parts of the ice-pushed hills, where the vegetation is relatively poor. The concentration of SO_4^{2-} and NO_3^- is reduced by anaerobic bacterial activity in the aquifer, especially when organic matter is present, whereas CO_2, H_2S and NH_4^+ are formed. In the presence of iron, H_2S formation will lead to the deposition of FeS_2, and CO_2 formation will free more HCO_3^- from $CaCO_3$. The Na^+ concentration of the infiltration water may change due to cation exchange processes in the soil zone. Of the original rain-water composition, only the Cl^- content will remain constant with depth, because no natural sources of Cl^- are present, unless mixing with ground-water having a higher Cl^- concentration occurs. From the concentration of Cl^- in the rain-water we can calculate the concentration in the ground-water according to:

$$C = C_N \frac{N}{N-E}$$

in which:

C = concentration of Cl^- in the ground-water
C_N = concentration of Cl^- in the rain-water
N = precipitation
E = evaporation.

In the eastern part of the area the average Cl^- concentration in rain-water is about 4 mg/litre (Leeflang, 1938). Since evaporation may amount to 50 % of the precipitation, a Cl^- concentration of about 8 mg/litre may be expected. This is in agreement with the values found in this area and in the ice-pushed hills of the Veluwe (R.I.D., 1971) (10 mg/litre). In the coastal dunes, however, the Cl^- concentration is much higher and can be explained only in part by a higher concentration of Cl^- in the rain-water. According to Erickson (1960), the Cl^- concentration in the precipitation of the coastal areas is about 10 mg/litre. With a net precipitation of about 50 %, we would expect about 20 mg/litre Cl^- in the ground-water. Near Katwijk, at a distance of less than 2,000 m from the coast, the average Cl^- concentration is 35 mg/litre. Part of this chloride probably originates from airborne salt particles. High Cl^- values (average 50 mg/litre) were also encountered on the island of Schiermonnikoog.

In general, the aquifer is depleted of $CaCO_3$ and of organic material in the high areas. Sulphate reduction will not take place, and the water still contains oxygen down to depths of 100 m and more. The hardness of this under-saturated water is generally less than 6 °D, the Fe content less than 1 mg/litre. In the direction of the ground-water flow, the ground-water outside the infiltration areas rapidly reaches the CO_2–$CaCO_3$ equilibrium and even becomes supersaturated. The hardness of these waters is often greater than 12 °D. The Fe content also increases when equilibrium is reached.

In the sand dunes, due to the presence of $CaCO_3$ (shell debris) and of organic material, saturation is already reached at a depth of about 30 m. The average hardness of this water is 12 °D.

In Fig. 12 the CO_2 concentration of the ground-water in the eastern part of the area is plotted against the HCO_3^- concentration. Since the CO_2 content was usually determined in the laboratory and in general no pH measurements were made in the field, the error in the CO_2 values may be large.

The equilibrium line between undersaturated and

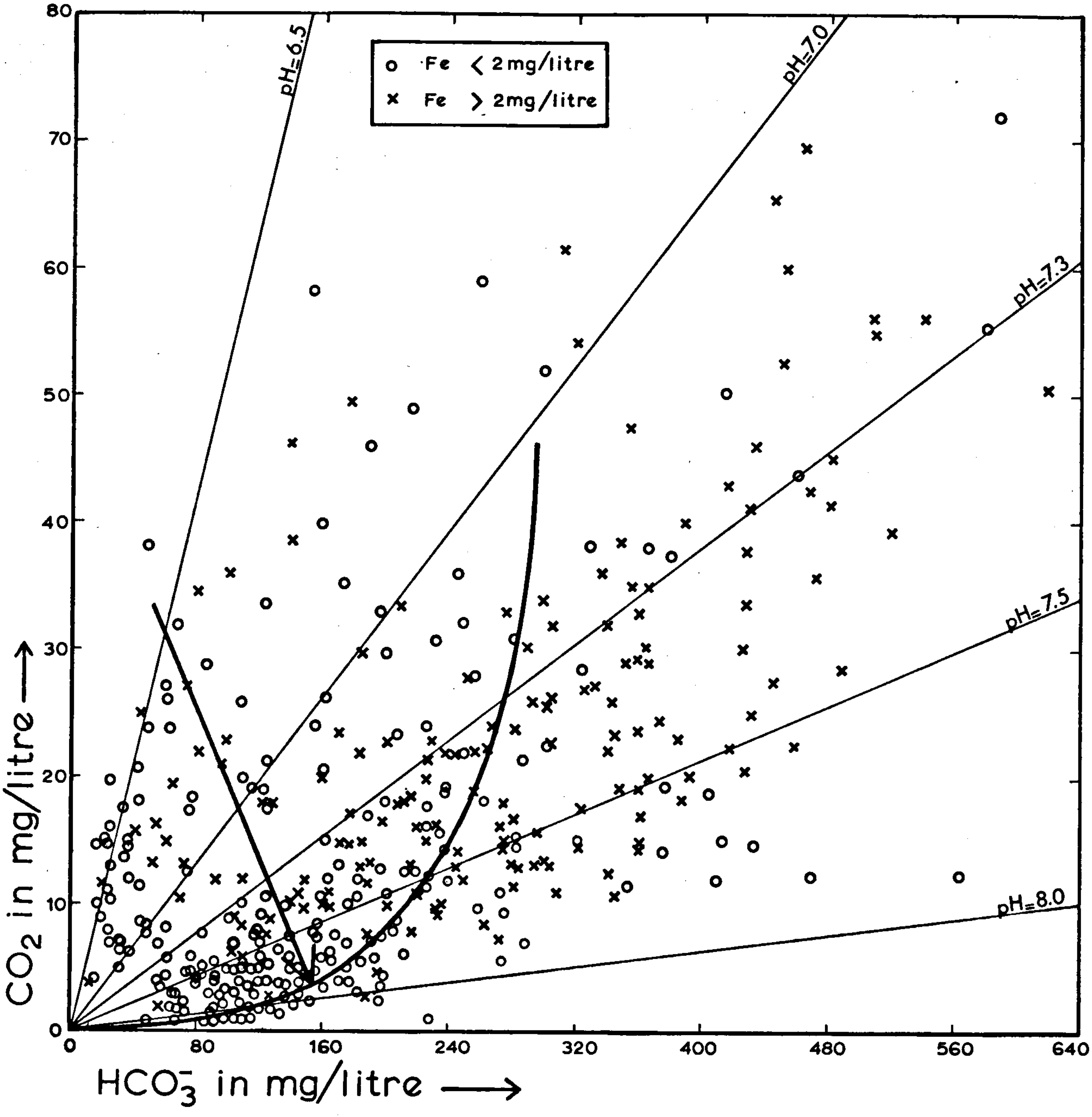

Fig. 12. CO_2-HCO_3-values for the eastern part of the area.

supersaturated water at various pH values is drawn according to Hem (1959). The arrow in the diagram shows the direction in which the composition of the undersaturated water will change when $CaCO_3$ is being dissolved. The supersaturated waters are found outside the infiltration areas. In general they have a high Fe content, probably due to the formation of $Fe(HCO_3)_2$.

In the Piper diagram in Fig. 13 the analyses deriving from the eastern part of the area are plotted. The large majority of the analyses with a hardness of less than 6 °D concern unpolluted infiltration waters. The lowest hardness values are found in the top part of the diagram. These points represent the unsaturated water from the upper part of the aquifer. The total ion concentration of these samples is low, and the points show a wide spread in the diagram. The Ca^{2+} : Mg^{2+} ratio is generally less than 3.

In the direction of the arrow (see Fig. 22B) the HCO_3^- content and also the hardness increase, due to the dissolving of $CaCO_3$, and the Ca^{2+} : Mg^{2+} ratio increases to about 10. Parallel to this process runs the reduction of the sulphates. When the proportion of HCO_3^- ions increases to more than 80 % of the total anions, we will call the water calcium bicarbonate water ($Ca(HCO_3)_2$).

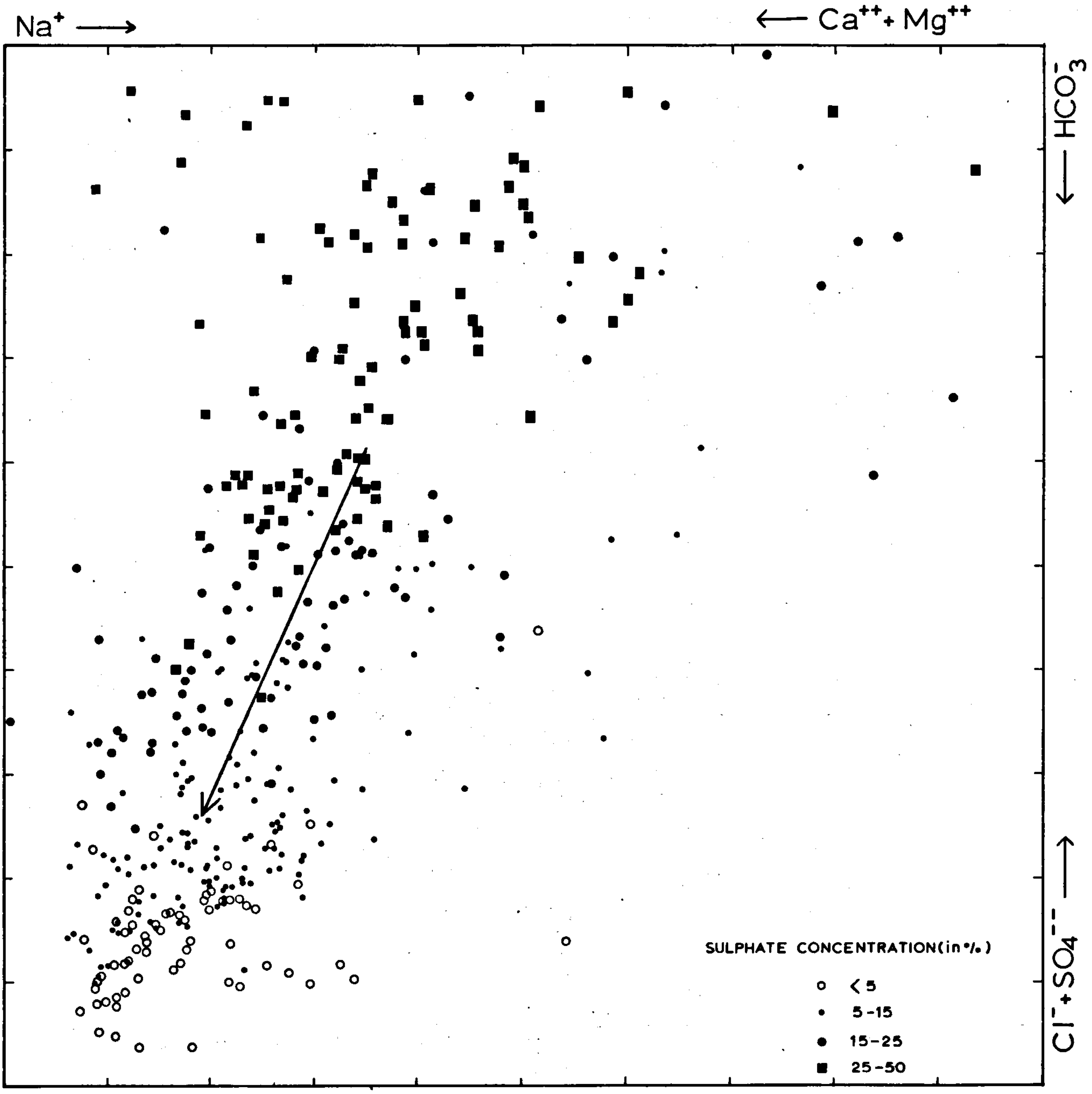

Fig. 13. Piper diagram of the results of analyses for the eastern part of the area.

This type of water can be regarded as the normal end-product of infiltrated rain-water. In the $Ca(HCO_3)_2$ water, the SO_4^{2-} content amounts to less than 5 % of total anion concentration. As the water moves out of the infiltration areas to the polders, the hardness increases to more than 12 °D (Figs. 13 and 18).

In the high-lying areas polluted ground-water occurs frequently, especially near towns and in agricultural areas. These polluted waters are characterized by a hardness greater than 6 °D and high Cl^- and/or SO_4^{2-} values. Because the relative concentrations of the main ions in polluted water is more or less the same as in normal infiltration water, the Piper diagram cannot be used to differentiate between them. In Fig. 14 the hardness values found in the eastern part of the area are plotted against the % $Cl^- + SO_4^{2-}$ (i. e. on the abscissa of the Piper diagram). In the direction of the arrow the infiltration water changes to $Ca(HCO_3)_2$ water.

Cation exchange

Important changes in the chemical composition of the ground-water are effected by cation exchange. Some minerals present in the water-bearing strata have the capacity to exchange certain cations in their structure

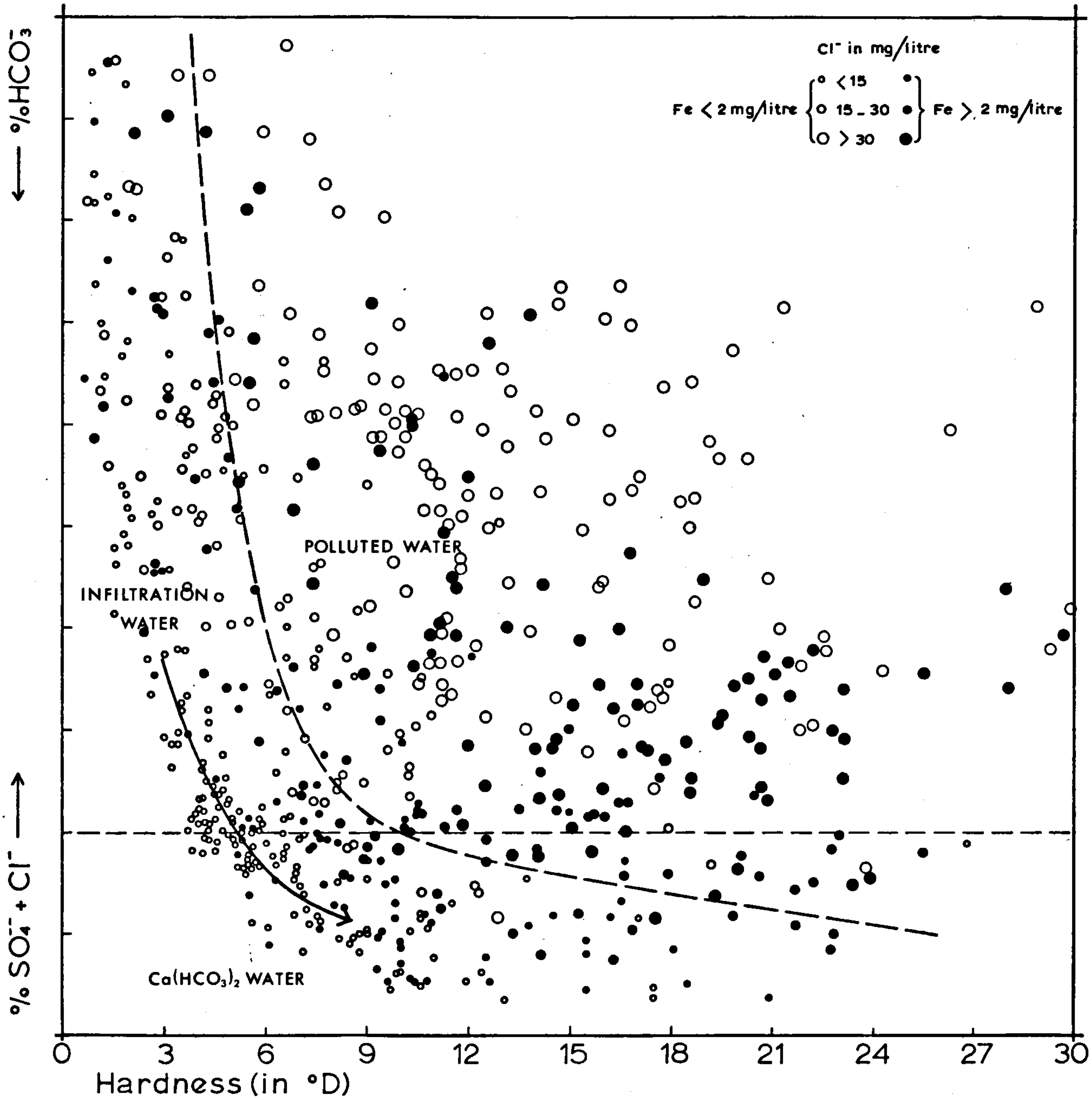

Fig. 14. Diagram showing the $Cl^- + SO_4^{2-}$ percentages and the hardness of the samples taken in the eastern part of the area.

against cations present in the surrounding water.

In the literature the exchange capacity of clays (especially montmorillonite but also glauconite) and of organic material is mentioned, among others by Foster, 1951; Schwille, 1953; van der Molen, 1958; Hecht, 1964; and Gillot, 1968.

The water-bearing strata of this area contain exchange material: clay occurs as irregular clay lenses, clayey sands, and also disseminated in the sands. This disseminated clay, which even in coarse sands can amount to more than 1 %, is probably responsible for the occurrence of cation exchange. Due to the fluvial origin of the sediments, wood and plant remains are also found in most sands. Besides their clay content, the marine Pliocene sediments are also rich in glauconite (Pannekoek et al., 1956).

The main exchangeable cations in sediments deposited in sea-water or in sediments which have been in contact with sea-water are Na^+ and Mg^{2+}. When the sea-water is replaced by fresh $Ca(HCO_3)_2$ water, cation exchange occurs. The Na^+ of the exchange material is exchanged for Ca^{2+} ions from the $Ca(HCO_3)_2$ water according to:

$$Na_2\,\text{'A'} + Ca(HCO_3)_2 \longrightarrow Ca\,\text{'A'} + 2NaHCO_3,$$

in which 'A' denotes acceptor sizes in the exchange material.

In the ground-water we see an enrichment of Na^+ and a decrease in Ca^{2+} concentration and consequently a decrease in hardness.

Although the cation exchange process mainly affects the Ca^{2+} and Na^+ concentrations, the HCO_3^- concentration can increase as a side-effect of this process. According to Foster (1950), less CO_2 is needed for Na^+–HCO_3^- equilibrium than for Ca^{2+}–HCO_3^- equilibrium. Thus, the CO_2 which becomes available when cation exchange occurs, will bring more HCO_3^- ions into solution. Moreover, in some bore-holes it was observed that for increasing $NaHCO_3$ concentration with depth (but with the same Cl^- concentration), the Mg^{2+} concentration also increased.

The exchangeable cations in sediments deposited in fresh water or in marine sediments once in contact with fresh water, are mainly Ca^{2+} (van der Molen, 1958). Therefore, we may conclude from the occurrence of $NaHCO_3$ water in fluviatile sediments that these sediments have been in contact with sea-water. This sea-water was gradually replaced by fresh water and cation exchange enriched the water with Na^+.

When sea-water enters a fresh-water sediment or a marine sediment containing fresh water, the reverse process takes place. The Na^+ and Mg^{2+} ions from the sea-water will now be exchanged for the exchangeable Ca^{2+} ions of the exchange material, according to:

$$2NaCl + Ca\,\text{'A'} \longrightarrow CaCl_2 + Na_2\,\text{'A'}.$$

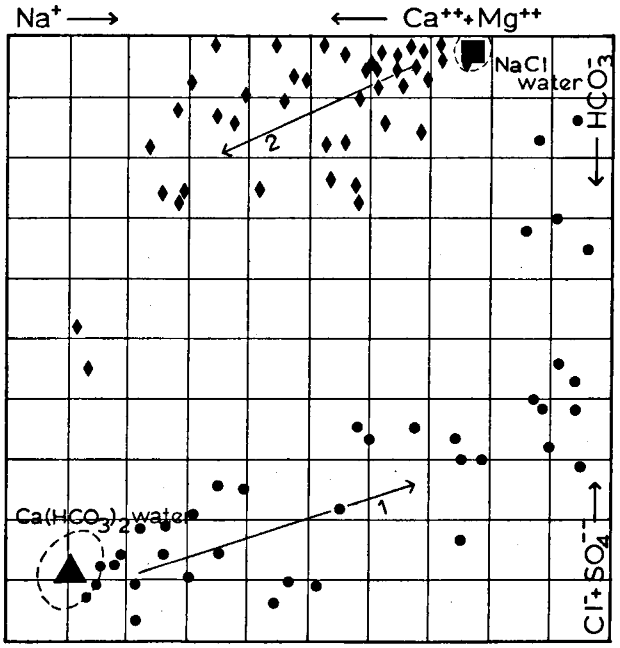

Fig. 15. Piper diagram for $NaHCO_3$ and $CaCl_2$ waters in the provinces of Friesland and Zeeland. Arrow 1: formation of $NaHCO_3$, Arrow 2: formation of $CaCl_2$.

In the water we see an enrichment of Ca^{2+} over Na^+ and consequently an increase in hardness. If the Ca^{2+} concentration is greater than the sum of the SO_4^{2-} and HCO_3^- concentration, we will call the solution $CaCl_2$ water.

The most important conclusion to be drawn from the occurrence of $CaCl_2$ water is that the sediments contained fresh water before the sea-water intrusion.

In the investigated area $CaCl_2$ water occurs only in a few places. But in the provinces of Friesland and Zeeland the occurrence is more general (Geirnaert, 1971). The results of the analyses of the $CaCl_2$ and $NaHCO_3$ types of water from Friesland and Zeeland are plotted on the modified Piper diagram in Fig. 15. In the direction of arrow 1 in this diagram the $NaHCO_3$ waters are progressively enriched with Na^+ until the Na^+ content amounts to about 80–90 % of the total anion concentration. Additional changes in the composition of the water are caused by mixing with salt water, and on the Piper diagram the points move toward the sea-water points.

Arrow 2 gives the direction in which sea-water changes when Na^+ is exchanged for Ca^{2+}. When the Na^+ ion concentration has diminished to about 20 % of the total cation concentration, further changes take place due to mixing with $Ca(HCO_3)_2$ water. Mixing of the different types of water with $Ca(HCO_3)_2$ water or with NaCl water can take place at any time in the exchange process. Such mixtures will be found closer to the centre of the Piper diagram.

In $Ca(HCO_3)_2$ water the Ca^{2+} : Mg^{2+} ratio is about 10, and in sea-water this ratio is 0.25. Due to the cation exchange process the ratio in $NaHCO_3$ water can diminish to less than 1, whereas in $CaCl_2$ water the Ca^{2+} : Mg^{2+} ratio increases to more than 1. In CaCl2 water the ratio is inversely proportional to the Cl^- concentration.

Mixing

Mixing of NaCl water with fresh water. – On the Piper diagram the results of the chemical analyses of sea-water all lie in a well-defined area. The Na^+ content varies from 75 to 80 % of the total cations, the HCO_3^- content is less than 4 % of the total anions. The type of water plotting in the same area but differing from sea-water by a lower Cl^- concentration, will be called NaCl water. The Cl^- content of such waters is generally more than 10,000 mg/litre.

If mixing of two water types takes place, the mixture will plot on the Piper diagram on a straight line through the two components and must be in accordance with the formula (Piper, 1944):

$$E_m = \frac{E_a \cdot E_b\,(a+b)}{aE_a + bE_b},$$

in which:

E_m = total ion concentration of the mixture
E_a and E_b = total ion concentration of the components
a and b = distances in length units between the plottings of the mixture and both components.

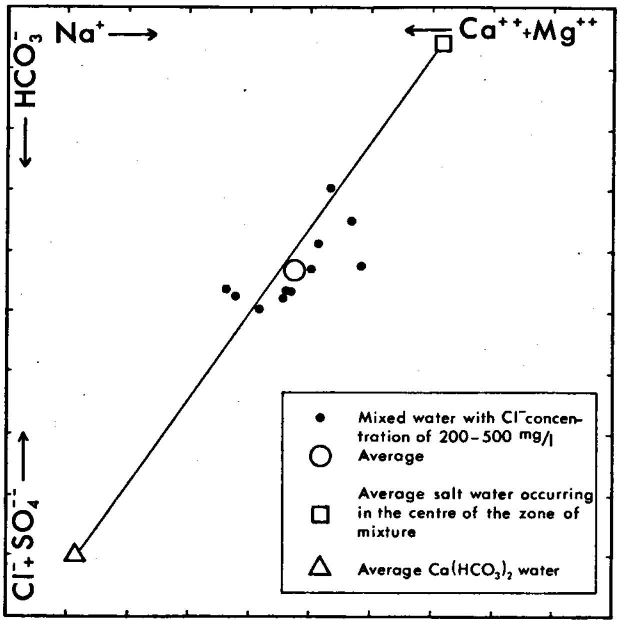

Fig. 16. Piper diagram based on analyses of samples collected near the Groot Mijdrecht polder.

The proportionate volume of each component in the mixture can be found with two equations:

$$V_a = \frac{bE_b}{aE_a+bE_b} \quad \text{and} \quad V_b = \frac{aE_a}{aE_a+bE_b}$$

It is difficult to apply these equations in most cases, since the total ion concentrations of the components of the mixture are unknown.

In the Groot Mijdrecht polder the contribution of each component of the mixture was calculated by assuming it to be composed of the $Ca(HCO_3)_2$ water occurring farther to the east, and the salt water found in the centre of the zone of mixture. Fig. 16 shows the Piper diagram of the three water types.

The average total ion concentrations found for the $Ca(HCO_3)_2$, NaCl, and mixed waters, were 15, 334, and 32 meq/litre, respectively. The concentration in the mixture calculated on the basis of the average composition of the three water types, would be 33 meq/litre, which is in good agreement with the determined average. The proportionate volume of the two components of the mixture would in this case be: 6 % NaCl water and 94 % $Ca(HCO_3)_2$ water.

In general, the mixed waters occupy the centre of the Piper diagram. The Cl^-content is more than 200 mg/litre and the SO_4^{2-} content is generally less than 5 % of the total anion concentration. The Ca^{2+} : Mg^{2+} ratio in these waters is normally less than 1. No appreciable excess occurs (in percentages) of Ca^{2+} over HCO_3^- + SO_4^{2-}or of Na^+over Cl^-+ SO_4^{2-}. The percentage of Na^+ is about equal to the percentage of Cl^-, and together they constitute more than 50 % of the total ion concentration.

Mixing of $Ca(HCO_3)_2$ water with polluted river-water. – In the low-lying areas the normal type of ground-water in which no cation exchange has occurred is $Ca(HCO_3)_2$ water with a hardness lying between 12 and 15 °D. The Cl^- content is less than 20 mg/litre, and SO_4^{2-} constitutes less than 5 % of total anions: in absolute values the SO_4^{2-}concentration is generally less than 20 mg/litre.

Polluted river-water is characterized by high $Cl^-$and SO_4^{2-}concentrations. Fig. 17 shows the increase in the concentrations of the various ions in the water of the Rhine River during the last century. Only the HCO_3^- and Mg^{2+} concentrations have not changed much in this time. The natural concentrations of $Cl^-$and SO_4^{2-}were calculated by Molt (1961) to be 14 and 35 mg/litre, respectively.

In Chapter III the infiltration of river-water into the aquifer was described. The mixing of the ground-water with river-water is evident from the sharp increase of the SO_4^{2-} and Cl^- contents. These waters differ from $Ca(HCO_3)_2$– NaCl water mixtures by their high SO_4^{2-} concentration. On the Piper diagram in Fig. 18 the results of all the analyses for the western part of the area are plotted and the percentage SO_4^{2-} of total anions is

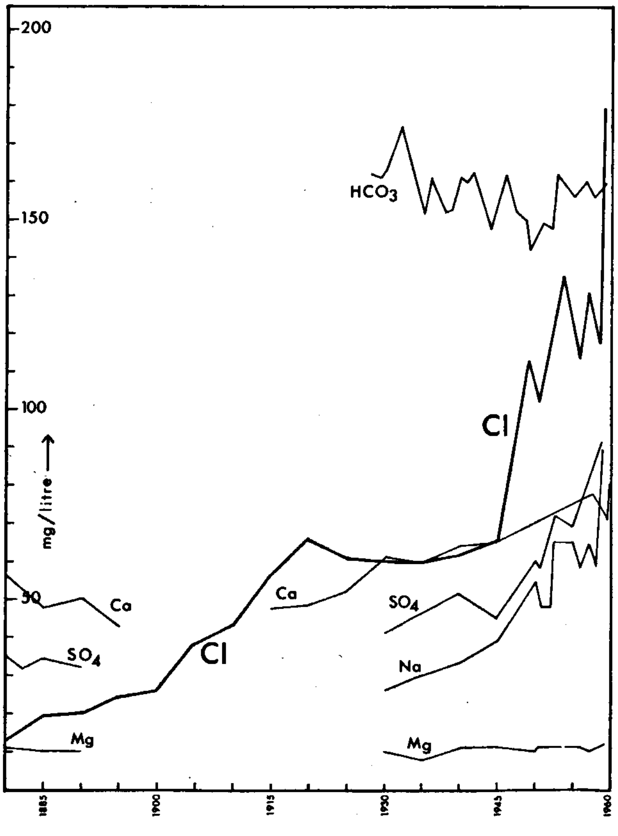

Fig. 17. Chemical composition of the Rhine between 1880 and 1960 (after Molt, 1961).

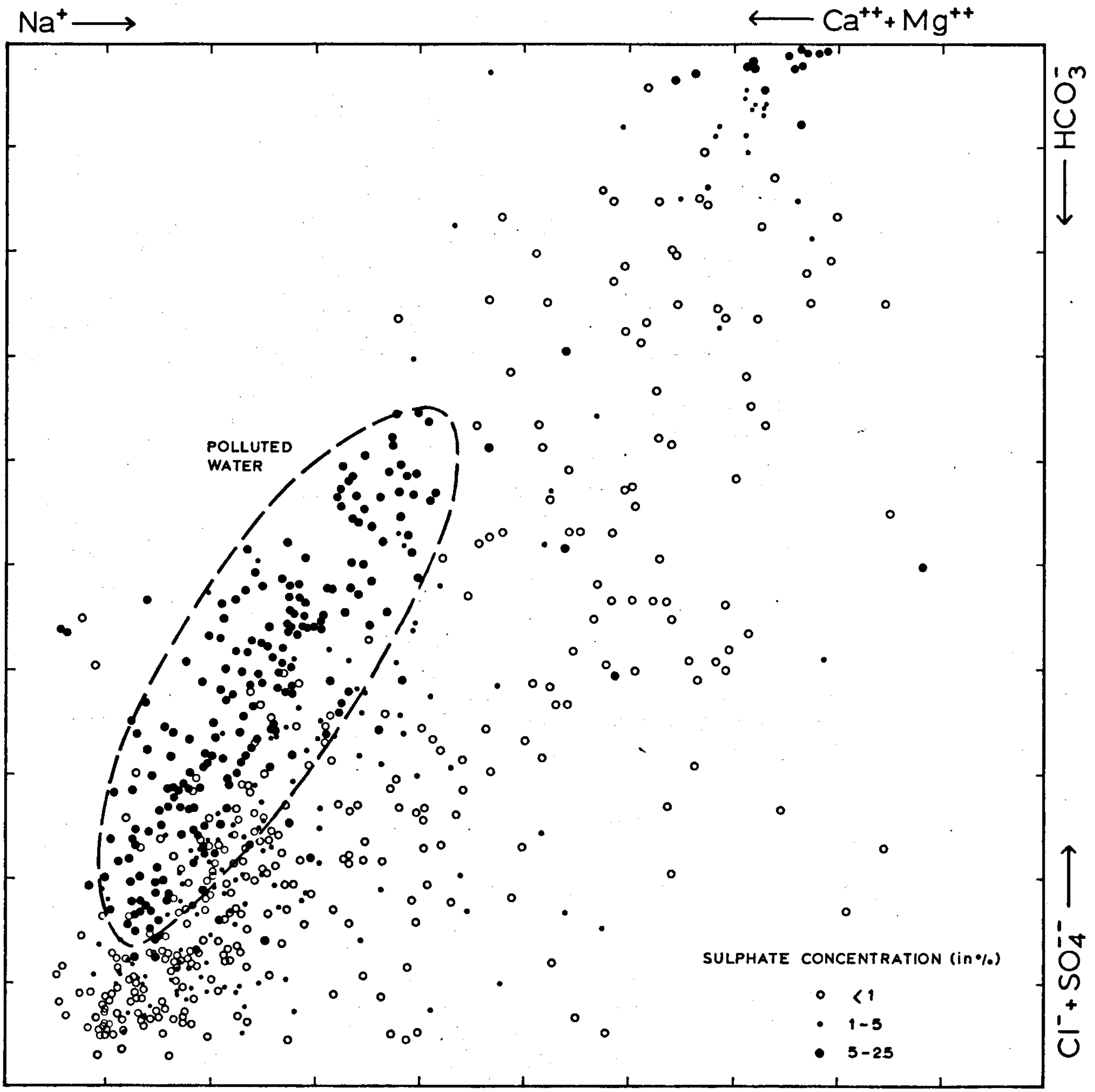

Fig. 18. Piper diagram of the results of analyses of samples taken in the western part of the investigated area.

indicated. The polluted waters are characterized by a SO_4^{2-} percentage lying between 5 and 25 %. The Cl^- concentration of these waters varies between 20 and 150 mg/litre. West of Dordrecht, the Cl^- concentration of the river-water can be much higher due to encroachment of sea-water via the estuaries. When this water infiltrates the aquifer, the composition of the ground-water changes in the direction of arrow 3 in Fig. 22.

DETERMINATION OF SOME MINOR CONSTITUENTS AND ISOTOPE MEASUREMENTS

The concentration of minor constituents in ground-water may serve as an indication for the geologic history of the water. We measured only Br^- and I^- concentrations, the former to obtain the Cl^- : Br^- ratio because we found this ratio to be constant in unpolluted water,

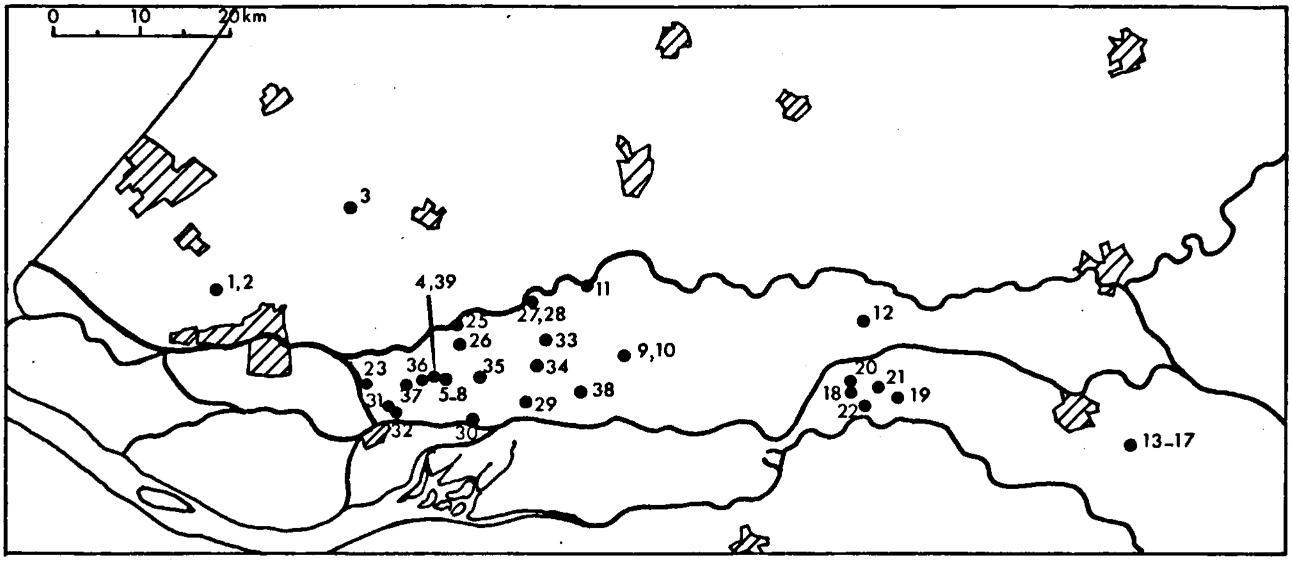

Fig. 19. Locations of the bore-holes sampled for the determination of minor constituents and/or isotopes (see also Tables 1 and 2).

whereas in polluted river-waters Cl^- concentrations are relatively increased. The I^- concentration was measured because a high concentration indicates contact of the water with I–rich plant remains, concentrations in both river- and sea-water being low (5 and 50 μgr/litre, respectively).

Determinations of ^{18}O and ^{13}C isotopes were also carried out. ^{18}O concentrations in rain-water vary with temperature; in cold areas low δ^{18} values occur. Due to the 'continental effect' the δ^{18} value decreases with increasing distance from the coast. Therefore, these values can serve as an indicator for the origin of the ground-water. ^{13}C concentrations reflect the interaction of dissolved CO_2 and $CaCO_3$ in the soil zone and in the aquifer. A low ^{13}C concentration usually indicates a preponderance of dissolved CO_2, the ^{13}C concentration in rain-water and in the CO_2 deriving from plant material being low. According to Mook (1968), a high ^{13}C concentration in ground-water results from the release of CO_2 from $CaCO_3$ in the aquifer by the action of humic acids.

Number on map (Fig. 19)	Sample location	Well nr.	Filter depth (m)	Cl^- mg/litre	I^- μg/litre	Br^- μg/litre	Ratio $Cl^-: Br^-$	^{18}O SMOW* 0/00	^{13}C PDB* 0/00	Conv.age (yr)	Water type
1	Delft	37E304	14.5	1840	330	4900	375	− 6.52	+ 7.1	6660±70	mixed
2	Delft	37E304	29	1310	540	6500	202	− 7.01	+ 5.1	6400±70	mixed
3	Waddinxveen	31C158	29.5	820	250	2900	283	− 6.74	+ 3.78	5560±65	mixed
4	Bleskensgraaf	P 14	30	512				− 7.76	− 0.56	7800±105	$CaCl_2$
5	Bleskensgraaf	380262	16	634	370	2200	288	− 7.4	− 9.48		$CaCl_2$
6	Bleskensgraaf	380262	32	870	460	3300	264	− 7.9	− 10.25		$CaCl_2$
7	Bleskensgraaf	380262	52.5	990	370	3700	267	− 7.8	− 10.58		$CaCl_2$
8	Bleskensgraaf	380262	68.5	1150	610	4700	245	− 8.1	− 3.48		$CaCl_2$
9	Leerdam	P 1	50	37	11	50	740				$Ca(HCO_3)_2$
10	Leerdam	P 11	98	16	12	70	229	− 9.27	− 11.10	13250±155	$NaHCO_3$
11	Lexmond	P 14	90	8				− 9.30	− 12.8	3640±80	$NaHCO_3$
12	Lienden	P VI	83	528	270	1900	278	− 8.82	− 11.5	31950±880	mixed
13	Groesbeek	XIII	7	31	5	80	388	− 7.16	− 20.42		polluted
14	Groesbeek	XIII	17	43	4	70	614	− 7.47	− 24.49		polluted
15	Groesbeek	XIII	27	35	3	90	389	− 6.51	− 23.14		polluted
16	Groesbeek	XIII	59	12	4	70	171	− 7.60	− 11.77		$Ca(HCO_3)_2$
17	Groesbeek	XIII	70	11	6	60	183	− 7.89	− 11.38		$Ca(HCO_3)_2$
18	Altforst	I	7.6	36	22	17	2118	− 8.69	− 13.43		polluted
19	Altforst	II	5.8	30	14	10	3000	− 5.9	− 12.50		polluted
20	Altforst	III	6.2	20	7	60	333	− 8.63	− 15.27		polluted
21	Altforst	IV	8.2	236	133	880	268	− 7.77	− 13.36		$CaCl_2$
22	Altforst	V	7.3	41	43	150	273	− 7.17	− 17.79		polluted

* Per mille deviations from the SMOW (Standard mean ocean water) and PDB Standard (Pedee Belemnite)

Table 1. Minor constituents and isotope concentrations.

In a few cases ^{14}C age determinations were performed. These measurements give independent information about the age of the samples.

The results of the determinations are given in Table 1, the locations of the sampled bore-holes in Fig. 19. I^- and Br^- concentrations were measured on the basis of an activation analysis. These measurements were carried out in the 'Reactorcentrum Nederland' at Petten *). Concentrations of the stable isotopes of carbon and oxygen were measured with a mass spectrometer. These measurements and the ^{14}C age determinations were performed at the Physics Research Laboratory of the University of Groningen *).

Discussion

Minor constituents. – In the samples representing mixing of fresh water and sea-water, the Cl^- : Br^-ratio is in the range of 200–400, with an average value of 267. This value corresponds with the Cl^- : Br^-ratio of 292 given for sea-water (Hem, 1959). In the high-lying Groesbeek area the ground-water originates from rain-water. The Cl^- : Br^-ratios of 171 and 183 found here in the $Ca(HCO_3)_2$ water are comparable to the ratios in the mixed waters. According to Erickson (1955), the Cl^-in rain-water derives from oceanic salts that occur in the air as very small hygroscopic particles (condensation nuclei). It is therefore supposed that the Br^-enters the water-bearing formations attached to the NaCl particles.

In the ground-water polluted by infiltrated river water and also in the upper samples from Groesbeek, the Br^- content is relatively low, the average Cl^- : Br^-ratio being 930.

About half the chloride charge of the Rhine comes from rock-salt waste of the Alsace potassium mines (Venhuizen, 1968). In the German potassium mines, according to Braitsch (1962), the weight percentage of Br^-in halite varies from 0.01 to 0.04 and in carnallite is higher by a factor of about 7. However, halite occurs relatively more often in rock-salt waste, which explains the low Br^-concentration in the river water.

The relatively low Br^- concentrations in the polluted ground-waters might offer a good criterion for the differentiation between diluted sea-water and polluted river water with Cl^- concentrations between 50 and 300 mg/litre. For instance in the dune areas, where artificial infiltration with river water is carried out, it is sometimes difficult to decide from the chemical analysis whether river-water was being pumped up or diluted sea-water had moved upward because of pumping.

In Fig. 20 the Cl^- concentrations are plotted against the Br^- concentrations with inclusion of the samples from Engelen (1969; Table 2). The I^-concentration of the mixed waters is generally high, but the relationship between the Cl^- and I^- concentrations is not constant. The Groesbeek samples are very low in I^- (7 μg/litre), whereas the samples taken from the polluted waters generally have a higher I^- concentration than the river-water.

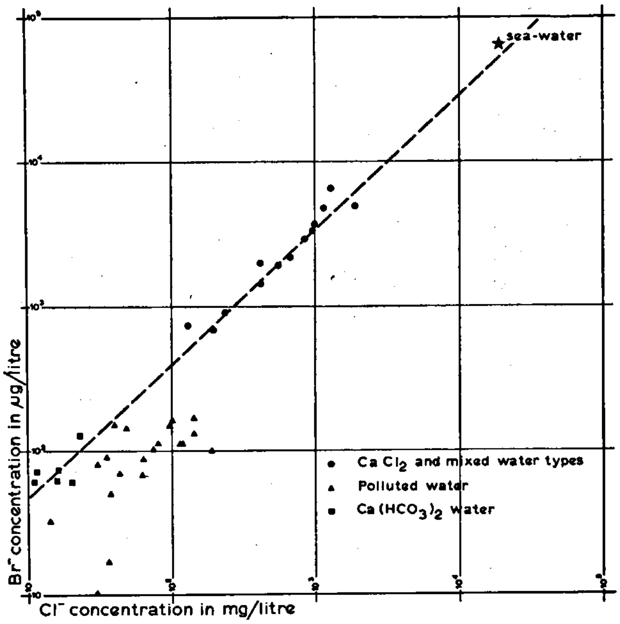

Fig. 20. Correlation of $Cl^-$with Br^-in polluted and mixed waters (see also Tables 1 and 2).

Number on map (Fig. 19)	Well nr.	Cl^- mg/litre	I^- μg/litre	Br^- μg/litre	Cl^-: Br^- ratio	Water type
23	22 DGV	140	24	165	848	polluted
24	24 DGV	144	60	130	1108	polluted
25	7 DGV	96	13	152	632	polluted
26	9 DGV	80	23	112	714	polluted
27	13 DGV upper	190	6	100	1900	polluted
28	13 DGV lower	74	37	106	698	polluted
29	21 DGV	62	21	88	704	polluted
30	13 DGV	98	28	159	616	polluted
31	23 DGV upper	49	16	142	345	polluted
32	23 DGV lower	61	9	67	910	polluted
33	18 DGV	16	25	63	254	$Ca(HCO_3)_2$
34	16 DGV	23	47	126	182	$Ca(HCO_3)_2$
35	11 DGV	130	195	730	178	$Ca(HCO_3)_2$
36	10 DGV	415	480	1400	296	mixed
37	21 DGV	193	205	680	283	mixed
38	14 DGV	14	4	32	437	$Ca(HCO_3)_2$
39	P 14	415	530	1970	211	$CaCl_2$
northern	Rhine branch	113	8	110	1027	
southern	Rhine branch	116	6	112	1035	

Table 2. Minor constituents in ground-water of the Alblasserwaard region (Engelen, 1969).

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*) Thanks are extended to Dr. A. H. Das and Dr. W. G. Mook.

The occurrence of endemic goitre due to iodine deficiency in certain areas of The Netherlands was investigated in detail in 1927 (Anonymous, 1927). About 170 iodine determinations in ground-water were dealt with in this report. Krul (1933) discussed these results and concluded that the low I^- values found in the high-lying areas result from leaching. According to him, the higher values in the ground-water of the low lying areas arise from a low rate of flow and are related to marine transgressions. The sea-water would be enriched in I^- by solution of I^- from the marine sediments, which are rich in plant remains.

The low I^- concentrations in Groesbeek can thus be explained by leaching. This is probably also the case in Leerdam, where the deepest sample shows $NaHCO_3$ water, indicating that salt water was originally present. During the replacement of salt water by fresh water here, the I^- was probably leached out.

The samples from Delft, Waddinxveen, and Bleskensgraaf containing very high levels of I^- derive from areas with a strong upward movement of ground-water. Since these waters are the result of mixing of fresh water with NaCl water, the I^- content can be expected to be high. The concentration is probably increased even more by the vertical movement of ground-water through Pleistocene peat layers from which I^- is dissolved. Engelen (1969) interpreted the updoming salt water in the Alblasserwaard as resulting from warm mineral water ascending through deep faults. His conclusion is partially based on the view that the chemical character of the water in the Alblasserwaard is analogous to thermo-mineral water in the coal district of South Limburg described by Kimpe (1963). According to Engelen, the analogies lie in the relatively high amounts of Br^-, I^-, Sr^{2+}; the high NaCl, CO_2, and NH_4^+ content; and the high degree of hardness. The solubility of Sr^{2+} depends, however, on the presence of sulphates in the water (Puchelt, 1964). If no SO_4^{2-} is present , the solubility of Sr^{2+} is defined by the solubility product of $SrCO_3$, which is much higher than that of $SrSO_4$. The samples from the updoming salt water in which Engelen found Sr^{2+} are completely reduced with respect to SO_4^{2-}. The process by which the Sr^{2+} is dissolved from the sediment probably runs parallel with the sulphate reduction.

Furthermore, the samples with a high Br^- concentration have a Cl^- : Br^- ratio comparable to the values found in diluted sea-water, and the high I^- concentration of these waters is in accordance with the I^- concentration found in the samples from Delft, Waddinxveen, and Lienden. This high level is sufficiently explained by enrichment from plant materials. Therefore the thermo-mineral origin of the water in the Alblasserwaard is questioned.

Isotopes. – The Groesbeek samples with $\delta^{18}O$ values between –7 and –8 ‰ can be considered as normal infiltrated rain-water. In Groningen the average δ^{18} of the precipitation measured by Mook (1968), is –7.6 ‰. According to him, the oxygen isotope concentrations of the Maas and Rhine rivers are determined by the origin of the water of these two rivers. The Rhine is a melt-water river with a δ^{18} content varying between –9 and –10.5 ‰, due to seasonal influences. The Maas is a rain-fed river with values varying between –7 and –8 ‰.

The samples from Altforst II and V were taken close to the Maas, numbers I, III, and IV between the two rivers. Although not corresponding with the δ^{18} ranges given for the rivers, samples II and V have higher δ^{18} values than the others. The high δ^{18} value found for Altforst II is probably due to admixture of water from the clay and peat sequence. The samples from Leerdam, Lexmond, and Lienden have δ^{18} values lying in the same range as those of the Rhine. The isotopic composition of the Rhine at the time when this water infiltrated is, however, unknown. In the samples from Bleskensgraaf the δ^{18} values diminish with depth, that is, with an increasing contribution of sea-water.

The samples from Groesbeek have $\delta^{13}C$ values of –20 to –24 ‰ down to a depth of 27 m. In the samples from deeper strata the δ^{13} increased to –10 to –11 ‰.

According to Mook, the δ^{13} value of the ground-water in The Netherlands normally varies between –10 and –12 ‰. This value is reached when rain-water which has dissolved CO_2 with a δ^{13} of –25 ‰ in the soil zone, reacts with $CaCO_3$ from the water-bearing strata having a δ^{13} of about +1½ ‰. Because of the absence of $CaCO_3$ due to leaching in the upper strata in the Groesbeek area, $HCO_3^- - CO_2$ equilibrium is not reached there and low δ^{13} values occur. The deeper samples have reached equilibrium and the δ^{13} has increased to normal values. The Altforst III and V samples have low δ^{13} values, although the $HCO_3^- - CO_2$ equilibrium has been reached. Since these samples were taken from filters placed just under the Holocene clay and peat sequence, some light carbon from the peat layers may have entered the formation.

In Bleskensgraaf (p14), Delft, and Waddinxveen, δ^{13} values ranging from –0.56 to +7.1 ‰ occur. Similarly high values were also found in Groningen and Friesland (Vogel, 1967). Mook (1968) explains the $\delta^{13}C$ enrichment on the basis of the action of humic acid on carbonates. In this case, therefore, both bicarbonate and CO_2 derive from $CaCO_3$ with a δ^{13} value of +1½ ‰. Isotopic exchange between an excess of this CO_2 and the dissolved HCO_3^- can further enrich the latter with δ^{13} up to a maximum value of +11 ‰.

The δ^{13} values from Friesland and Drente show that in the infiltration areas, down to depths of as much as 200 m, the δ^{13} values can be regarded as normal; in the areas covered by the Holocene clay and peat sequence more positive values appear. In the Pleistocene strata peat and humic layers occur frequently, and these layers with a high vertical hydraulic resistance will have to be passed when vertical movement of ground-water takes place. It is probable that during this process humic acid is added to the ground-water. Subsequently, reacting with $CaCO_3$, this water forms HCO_3^- ions with a high

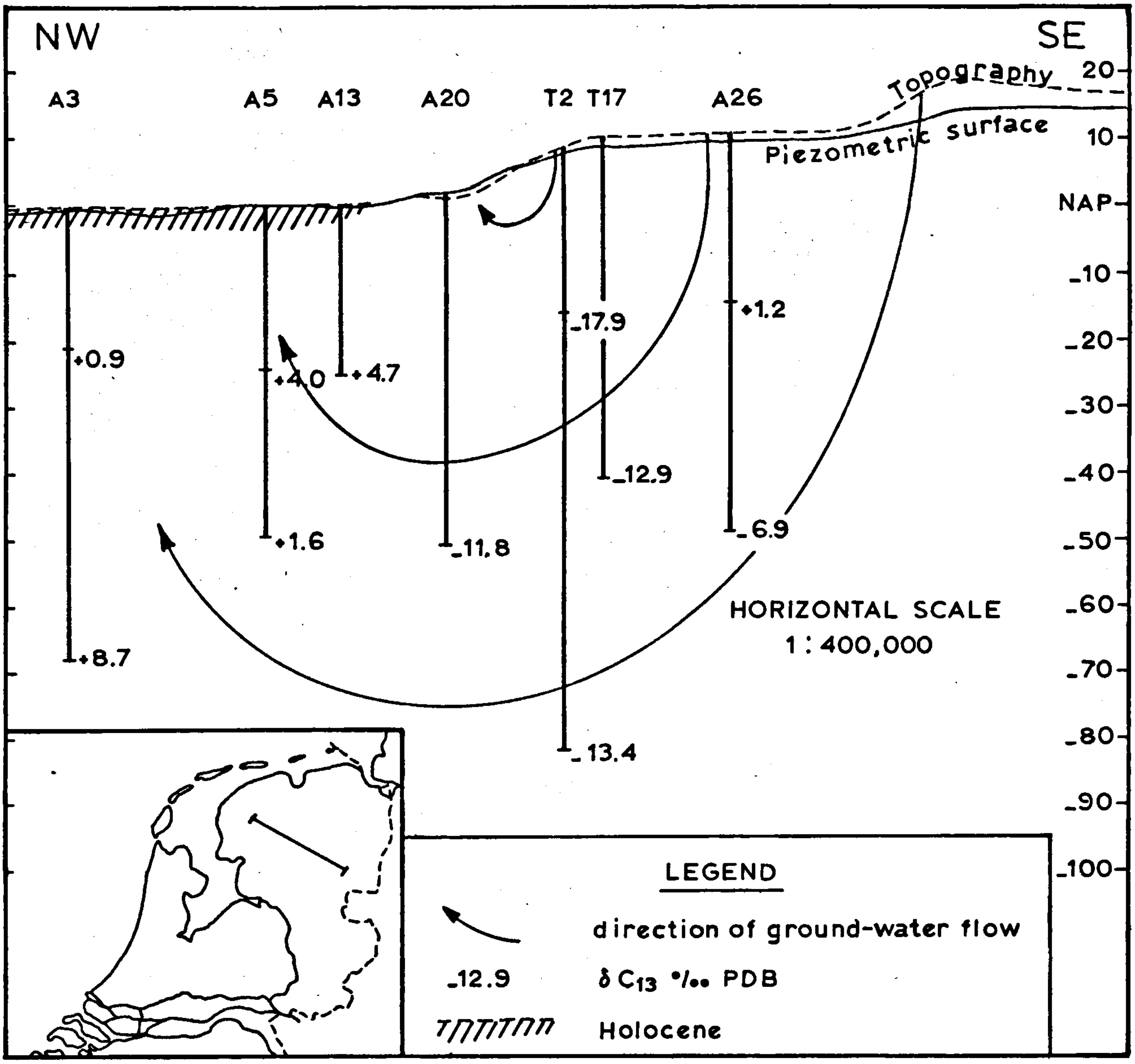

Fig. 21. Schematic section through the provinces of Friesland and Drente. ^{13}C values after Vogel (1963) and Mook (1968).

δ^{13} value. Due to the leaching in the infiltration areas, this process will apply mainly to the vertical upward movement in the low-lying polderlands. Fig. 21 shows a schematic section through Friesland and Drente.

In the areas where horizontal flow predominates, such as the IJsselmeer area before the reclamation projects, the δ^{13} values are normal (Vogel, 1967). The samples from Leerdam, Lexmond, and Lienden also show δ^{13} values between −11 and −12.8‰.

At the same depth, the samples from Bleskensgraaf, i. e. 38D262 and p14, which were taken about 1 km apart, show δ^{13} values of −10.25 and −.56‰. Since the latter sample was taken at a pumping station, the difference in ^{13}C content might be explained by the stronger upward movement of ground-water induced by the pumping.

Age determinations. – The age determinations made in the ground-water samples are difficult to interpret. From Lexmond and Leerdam, at about the same depth, $NaHCO_3$ waters with Cl^- contents of 8 and 16 mg/litre, and a hardness of 10 and 4 °D, respectively, were dated. The low degree of hardness in Leerdam indicates a more advanced cation exchange and, as compared with Lexmond, a slower replacement process. This is reflected in the difference in age between the two samples.

The other samples, which show high Cl^- concentrations, derive from mixed waters whose components are unknown. The Bleskensgraaf sample is mixed with older NaCl water (with a ^{14}C content of 0 %), the dating therefore reflecting a maximum age. If we assume the mixture to consist of sea-water with a total ion concentration of 1180 meq/litre and $NaHCO_3$ water with a concentration equal to the concentration at Leerdam (12 meq/litre), the sea-water component would be 6 %. However, it is more likely that the sea-water component is NaCl water with a lower total ion content.

The samples from Delft and Waddinxveen probably represent mixing of 'fresh' Calais water with younger salt Duinkerke water. The age would accordingly be minimal. The fresh-water component was calculated for the three samples on the basis of the total ion concentration in the sample and in sea-water. For Delft 1, Delft 2, and Waddinxveen, the 'fresh' water components were 50, 32, and 19 meq/litre, respectively. In this case the sea-water component would be 2–3 %. Since the Duinkerke and Calais waters differ in age by only about 3,000 years, the correction will be very small.

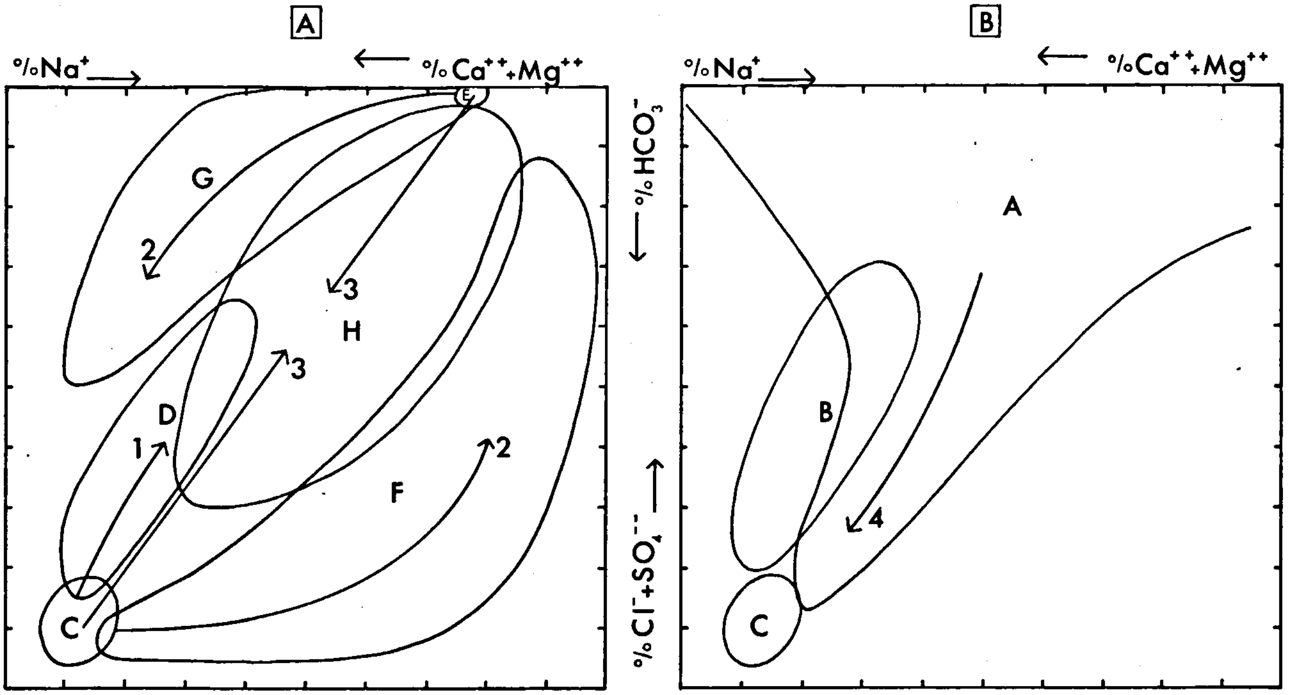

Fig. 22. Schematic subdivision of waters, shown as Piper diagrams. A: western part of the area; B: eastern part. A-H: watertypes, arrow 1: increasing pollution, arrow 2: cation exchange, arrow 3: mixing, arrow 4: solution of $CaCO_3$ and Sulphate reduction.

PRESENTATION OF MAP AND SECTIONS

Classification

The classification of ground-water types used for this paper is based primarily on the $Na^+ : (Ca^{2+} + Mg^{2+})$ and $(Cl^- + SO_4^{2-}) : HCO_3^-$ concentration ratios. The total ion concentration, the hardness, and the Cl^- concentration are also taken into account. The concentration ratios are shown in the Piper diagrams in Fig. 22. Fig. 22A concerns the western part of the area, Fig. 22B the eastern part.

Type A. – Infiltration water is characterized by a low total ion concentration ($<$ 6 meq/litre). Hardness is below 6 °D, Cl^- and SO_4^{2-} concentrations are less than 20 mg/litre.

Type B. – Polluted infiltration water has a relatively low Na^+ concentration as compared with type A. Total ion concentration is higher and the hardness is generally more than 6 °D. Cl^- or SO_4^{2-} concentrations are higher than 20 mg/litre.

Type C. – $Ca(HCO_3)_2$ water occupies a small area in the lower lefthand region of the modified Piper diagram. Hardness in the high-lying areas is below 12 °D, but in the low areas is normally higher. Cl^- concentrations are less than 20 mg/litre; the SO_4^{2-} concentration in the high-lying areas is between 10–20 mg/litre and generally lower in the low areas.

Type D. – Polluted $Ca(HCO_3)_2$ water has the same characteristics as type B but occurs only in low areas. The percentage of SO_4^{2-} in total anion concentration is between 5 and 25. The Cl^- concentration varies between 20 and 150 mg/litre.

Type E. – NaCl water occurs in the upper righthand region of the Piper diagram. The Cl^- concentration is usually higher than 10,000 mg/litre.

Type F. – $NaHCO_3$ water is characterized by an excess of Na^+ over $Cl^- + SO_4^{2-}$. Hardness and Cl^- concentrations are low but increase in the direction of the arrow, due to mixing with water of type E. SO_4^{2-} concentrations are generally under 5 mg/litre.

Type G. – $CaCl_2$ water is characterized by an excess of Ca^{2+} over HCO_3^- + SO_4^{2-}. The Cl^- concentration is generally higher than 1000 mg/litre. SO_4^{2-} concentrations lie below 5 mg/litre.

Type H. – Mixed water lies in the central region of the Piper diagram. No appreciable excess of Na^+ over Cl^- + SO_4^{2+} or of Ca^{2+} over HCO_3^- + SO_4^{2-} is found. The Cl^- concentrations vary considerably. The SO_4^{2-} concentration is generally low.

Distribution of ground-water types

The map shown in Enclosure I indicates the water types of the upper part of the aquifer. In the areas covered by the Holocene clay and peat sequence the map represents the confined water, and in the high-lying areas the phreatic water in the Pleistocene sediments. For changes occurring with depth, the reader is referred to the sections shown in Enclosures II and III. On the map and sections the fresh/salt water boundary is also indicated, defined by a Cl^- concentration of 150 mg/litre.

In the high-lying areas the normal type of ground-water is infiltration water. Especially near the towns and in agricultural areas, the water is generally polluted. An example of this is offered by the town of Nijmegen, where to a depth of 50 m, Cl^- concentrations of more than 100 mg/litre occur. In the sand dunes, $Ca(HCO_3)_2$ water occurs; around The Hague the ground-water is polluted. Near the boundary between the high-lying areas and the polder lands, the infiltration water changes to $Ca(HCO_3)_2$ water. West of Utrecht Hills, the $Ca(HCO_3)_2$ water changes to $NaHCO_3$ water, which is the normal type of ground-water in the western part of the area. North of Leiden and around the Groot Mijdrecht polder mixed waters occur locally. Between The Hague and Rotterdam there is a large zone of mixed waters surrounded by $NaHCO_3$ water.

The fresh/salt water boundary runs more or less parallel to the boundary of $Ca(HCO_3)_2$ and $NaHCO_3$ water on the map.

In the Alblasserwaard region $CaCl_2$ water occurs locally, and the fresh/salt water boundary rises sharply. Application of the geo-electrical method enabled Csonka (1964) to trace this anomaly to the SE; south of Gorcum he found a comparable sharp rise of the fresh/salt water boundary (see also Fig. 23). Recent results obtained by the Groundwater Survey TNO point to a further extension of this anomaly eastward.

Along the rivers there is a zone of polluted water. West of Rotterdam, along the rivers, mixed water was found.

CHAPTER V

DISCUSSION

We may now discuss the occurrence of the different types of water, first in the western region formed by the Holocene marine area and part of the peri-marine area, and then in the eastern part formed by the Holocene fluviatile area and another part of the peri-marine area.

WESTERN REGION

In the western part of the area under study the marine transgressions of the younger Pleistocene and the Holocene strongly influenced the composition of the ground-water. The Eemian Sea covered only the SW part of the area and a narrow zone along the coast, but the Calais transgression reached further to the east, to a line over Dordrecht and Gouda. The Duinkerke Sea covered only the SW part of the area and a small zone near Katwijk. Since a long continental period preceded the Eemian transgression, we can assume that the aquifer contained $Ca(HCO_3)_2$ water at the onset of the Eemian. In part of the marine Plio-Pleistocene sediments the NaCl water was probably also replaced by fresh water. In the SW part of the area, where Eemian marine sediments were deposited, we now find $CaCl_2$ water (see section 3). Since no $CaCl_2$ water was found to be related to the Calais or Duinkerke transgressions, it is probable that the $CaCl_2$ water is of Eemian origin. The infiltrating sea-water was enriched with Ca^{2+} due to cation exchange. In the narrow band of marine Eemian deposits along the coast we only find $Ca(HCO_3)_2$ and $NaHCO_3$ waters, formed after the Eemian transgression. The $NaHCO_3$ and $Ca(HCO_3)_2$ waters probably replaced the Eemian $CaCl_2$ water.

The occurrence of $CaCl_2$ water indicates that the horizontal flow of ground-water from the east towards this area is very small.

In the northern part of the area $NaHCO_3$ water predominates (see sections 1 and 2). This region was covered only by the Calais Sea. The $NaHCO_3$ water extends somewhat farther to the east than the geological boundary of the Calais deposits. During the Calais transgression the fresh water in the aquifer must have been completely replaced by NaCl water. After the sea receded, a fresh ground-water flow from the high-lying areas (Utrecht Hills) flushed out the NaCl water and subsequent cation exchange enriched the water with Na^+. The occurrence of $NaHCO_3$ water to the east of the geological boundary shows that although no marine sediments were deposited, sea-water could still infiltrate the aquifer. This intrusion could have been in the form of a salt wedge, but a more probable explanation is infiltration during storm floods. In Zeeuws Vlaanderen (Geirnaert, 1970) historically known floods were recognized by the composition of the ground-water.

In a large zone of the SW Netherlands lying partly in the area of deposition of the Duinkerke sediments, mixed waters occur, and around this zone $NaHCO_3$ water is found. The mixed waters were probably formed during the Duinkerke transgression, which developed in this area an erosional creek pattern (de Jong, 1967). Some of the creeks cut into the Calais sediments and thus infiltration of sea-water could take place. The Calais Formation also contains sand-filled gullies through which sea-water could infiltrate in the Duinkerke period. After the Calais transgression, by a process of cation exchange, $NaHCO_3$ water was probably formed in the upper part of the aquifer in this area. Later, in the Duinkerke period, the infiltrated sea-water with the $NaHCO_3$ water formed the mixed water type. The extension of the mixed water to the NE, outside the boundary of the Duinkerke deposits, may be related to the Calais gullies described by Pons et al. (1963).

In the area south of Rotterdam, which was also covered by the Duinkerke Sea, only $NaHCO_3$ water occurs. Here the clayey Calais sediments probably prevented the infiltration of sea-water. Another possible explanation for the occurrence of the $NaHCO_3$ water is that mixed water was originally formed here too, but at a later time flushing with fresh water and subsequent cation exchange changed the composition back to the $NaHCO_3$ type of water.

North of Leiden and under the Groot Mijdrecht polder mixed water occurs locally (see section 1). For the centre of the mixed-water area of Groot Mijdrecht, the results of a few analyses indicate the presence of NaCl water. The upward movement of ground-water due to the large pressure difference between the polder level and the piezometric surface must have caused NaCl water of Calais origin and also water from the marine Plio-Pleistocene strata to ascend. Around this zone of NaCl water, mixing of NaCl and $Ca(HCO_3)_2$ water occurred. To the east of the NaCl water, the zone of mixture is larger than the corresponding zone to the west; this is consistent with the main ground-water flow, which is directed E-W.

North of Leiden, upward movement of ground-water also occurs, and mixing of NaCl water with $Ca(HCO_3)_2$ water from the sand dunes has taken place. It is supposed that the upward movement of ground-water in the low-lying polder lands is much more general than the few cases described here (see Table 1, samples from Delft and Waddinxveen).

EASTERN REGION

The eastern part of the area is characterized by the horizontal flow of ground-water from the Utrecht Hills and the southern part of the Veluwe in the north and from the Pleistocene of Noord-Brabant in the south. Due to agriculture – which is much more important in Noord-Brabant than in the southern Veluwe and Utrecht Hills – the ground-water in the south is polluted.

The ground-water in the north changes from the infiltration type to the $Ca(HCO_3)_2$ type at depths varying from 50–150 m below the surface. This conversion generally occurs close to the boundary of the high-lying areas. Only south of the southern Veluwe does the infiltration type of water extend far under the Holocene clay and peat sequence. Here, the ground-water moves under the northern branch of the Rhine. No hydraulic connection between the river and the underlying aquifer exists, as can be concluded from the absence of pollution in the neighbourhood of the river. Further to the west, some pollution is found, probably indicating a deeper incision of the river into the Holocene sequence.

Below the high-lying areas the fresh/salt water interface is generally located at a depth of more than 200 m. Due to a horizontal flow of ground-water from both the north and the south, an upward movement of ground-water occurs in between the two flows. Gischler (1964) described a similar situation near Amersfoort, where two distinct ground-water flows come together. Here, he also found a rise of the fresh/salt water interface.

The gradient of the interface in the south is steep as compared to the northern gradient, which indicates a preponderance of flow from the north over the flow from the south. This is in accordance with the good hydraulic conductivity of the Harderwijk Formation as compared to the Kedichem Formation in the south.

In Fig. 23 the depth of the fresh/salt water boundary, inferred from the chemical analyses, is indicated schematically. The 100-m depth lines delineate an elongated zone extending from west to east. Within this zone, $CaCl_2$ water, $NaHCO_3$ water, and mixed water are occasionally found. This is consistently the case in an area within the Alblasserwaard. To the east, $CaCl_2$ water, $NaHCO_3$ water, or mixed water is found only at a few bore-holes (see sections 5–8). The Cl^- concentrations of these samples vary between 100 and 300 mg/litre.

Apart from the general upward movement of ground-water in this zone, the locally occurring steep rises of the fresh/salt water boundary must be related to patches in the Holocene clay and peat sequence with a low vertical hydraulic resistance.

Previously, another explanation was offered for the occurrence of salt water in the Alblasserwaard region (Geirnaert, 1969). This water was thought to be a remnant of salt water infiltrated during the Holocene, but the occasional occurrence of salt water far to the east now makes this explanation less plausible.

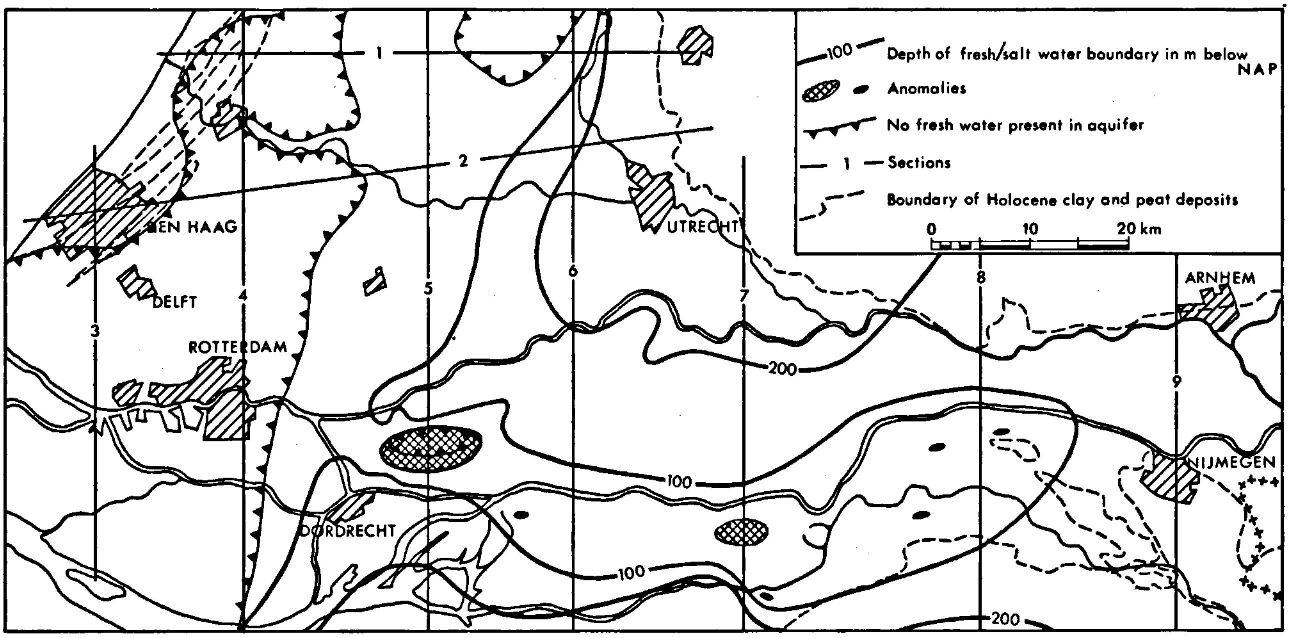

Fig. 23. Depth of the boundary between fresh and salt water (in the Alblasserwaard region; after Csonka, 1964).

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