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CONTRIBUTION TO THE GEOCHEMISTRY OF GROUNDWATER IN NORTHERN GERMANY

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ABSTRACT

Moderately saline groundwaters, which are still usable for drinking and industrial purposes, occur in Northern Germany until depths of approximately 500 meters below the surface. Apart from local saline water intrusions along the North Sea coast and rivers, the saline components of groundwater are derived from deep groundwaters, which can be related to salt bodies mainly of Zechstein age. Sulfate waters are found in the immediate vicinity of salt domes. In contrast chloride salt waters and brines are also found further away from the salt bodies, and show indications of reduction and base-exchange. The relationships of the groundwater types toward each other should be clarified by means of isotope research.

A chemical classification of groundwater has been proposed, which bears in mind the absolute as well as the relative contents of main ions (fig. 2).

1. INTRODUCTION

This paper concerns the chemical composition of groundwaters of deep aquifers of Tertiary and Quaternary age down to 500 meters below the surface in Northern Germany. These unconsolidated aquifers are medium to very good permeability and are generally not very extensive. The Miocene "Lignite Sand" and Pliocene "Kaolin Sand" were deposited in synsedimentary depressions and troughs between salt bodies. Pleistocene aquifers owe their existence to erosion and accumulation processes in deep cut channels and gullies or outwash plains in front of glaciers.

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We have used about 1000 analyses of different origin and completeness. The geological circumstances in Northern Germany are well known because of the abundance of drillings and wells, but not the hydrology and hydrochemistry. The quality and quantity of the data is dependent on the distribution of exploratory holes in the area. We are taking the Hamburg region as an example and applying the data found to other areas of Northern Germany (see publications of the author in the references). In the last few years the data of Northern Niedersachsen (Richter and others, 1968, p. 823-826) and Southern Schleswig-Holstein (Johannsen & Löhnert, 1971) were systematically studied. These areas are similar to the Hamburg region.

2. GENERAL REVIEW OF HYDROCHEMISTRY

Generally in humid climatic conditions fresh water at shallow depth is underlain by groundwater of increasing salinity. The transition between fresh and salt waters both vertically and horizontally is very complex. Definition and more detailed explanation of the term "fresh water" will be given in chapter 3.

According to the *origin of saline components* we can distinguish the following:

a) *Invaded sea water* is found in a 10-15 km broad strip along the North Sea coast. In the cation diagram (fig. 1) after the ion relationship, the oceanic water occupies a distinct position. Owing to dilution, base-exchange, adsorption and reduction the position

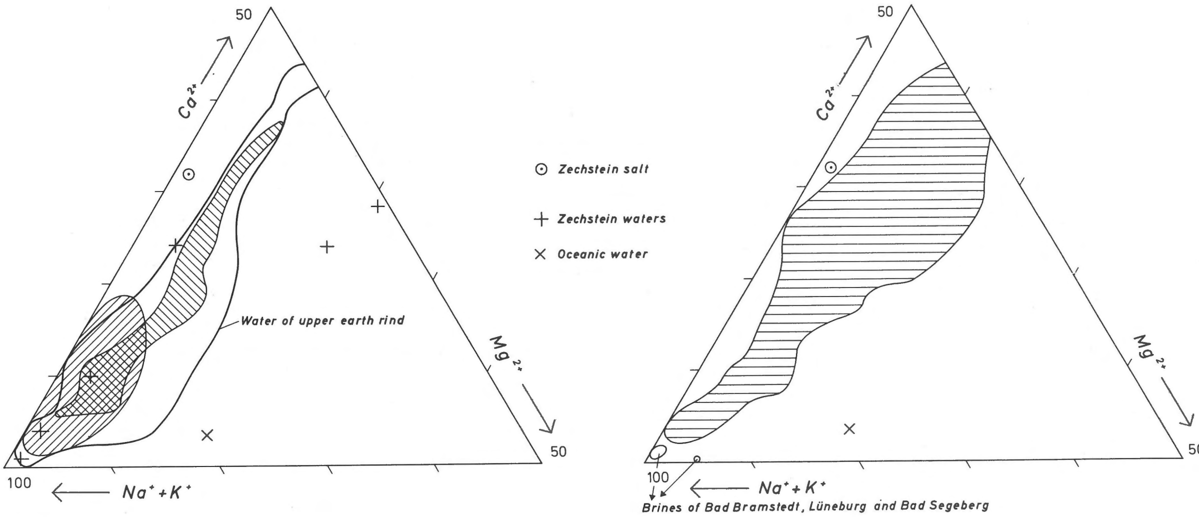

Fig. 1
Kation diagram of North German saline groundwater. Shaded fields on the left = waters from Pretertiary formations, on the right = waters from Tertiary and Quarternary aquifers. For further details see text.

changes rapidly, if a shallow aquifer is infiltrated. On a deeper level the so altered sea water interfingers with the deeper groundwater of the interior. Bearing in mind the unsuccessful methods by means of ion ratios to find a division (O d u m & C h r i s t e n s e n, 1936) it is difficult or almost impossible to achieve a division on hand of simple chemical methods.

In connection with International Hydrological Decade investigations were carried out in the area of Wittmund/Ostfriesland (J. H a h n, 1970, personal communication). Thereby many rare components (lithium, bromide, iodine, heavy metals, borax) were determined and also carbon, oxygen and sulfur-isotope analyses were made. The results of these analyses are not yet published.

b) *Groundwater of bank storage* on the North German plain sometimes has a considerable saline component, which is influenced by the waste load of rivers. In the case of the river Weser (B ö s e n b e r g & L ü t t i g, 1959) and the river Elbe (L ö h n e r t, 1969) a successful separation of anthropogenic water of bank storage and natural saline groundwater was made.

c) *Deep groundwater* at relatively shallow depth shows concentrations, which are higher than those of oceanic water (35 g/kg resp. 1.2 val/kg). Maximal concentrations are reached, which almost approach saturation point (for comparison: NaCl saturation = 358 g/kg resp. 12.2 val/kg). For the origin of brines, according to W a g e r (1955), basically the above mentioned salt bodies are responsible, to the extent that some authors speak of "subrosion waters". Relatively little is known about the chemical composition of these waters, which were taken from oil drillings (socalled reservoir waters or formation waters). Among the anions chloride (Cl^-) is dominant and among the cations Na^+ but to a lesser degree. On the left side of figure 1 the chemistry of deep waters of several stratigraphical ages (pretertiary formations) is drawn in shaded fields. The values according to W a g e r (1955) and R ü d d i g e r (1963) lie at smaller than 20 mval-% Ca, than those according to V o n E n g e l h a r d t (1960) and A n r i c h (1964) partly greater than 20 mval-% Ca (calcareous formations as Malm and Lower Cretaceous). In comparison to the average composition of Zechstein salt and some (Mg rich) Zechstein waters the composition of the formation waters differs quite clearly. Increased Ca contents (and Mg) can be primarily affected by the original composition of salt solution or secondary by diagenetic alterations of the solution (for details see V o n E n g e l h a r d t, 1960).

On the one hand the above mentioned saline *groundwaters of Tertiary and Quaternary aquifers* are

Fresh waters			Salt waters	
< 1000 mg/l dissolved solids			> 1000 mg/l dissolved solids	
pure fresh water <1 mval Cl^-	sulfate diluted water	ca.>3 mval SO_4^{2-}	sulfate salt water	> 20 mval-% SO_4^{2-}
	chloride diluted water	1 - 10 mval Cl^-	chloride salt water	> 10 mval Cl^-

Exchange waters

> 90 mg/l $NaHCO_3$		with Na_2SO_4	Regeneration water
fresh exchange water < 1 mval Cl^-	salt exchange water > 1 mval Cl^-	mval $SO_4^{2-} \gg \frac{\text{perm. hardness}}{2.8}$	mol ratio $\frac{Cl}{Na} \gg 1$

Fig. 2
Types of groundwater distinguished in the Hamburg region.

diluted deep waters representing fossil, diagenetically altered subrosion waters and occasionally connate waters, on the other hand they are subfossil to recent subrosion waters. Their concentration is found to be mainly below that of oceanic water (with the exception of NaCl brines in immediate contact to salt domes, shown on the right of fig. 1).

Qualitatively there exists the following difference to recent oceanic and deep formation water: in the upper half of the *cation* diagram the greater width of alkaline-earth metals can be determined, without the Mg content of the oceanic water will be reached (fig. 1 on the right). This fact depends on base-exchange processes, by which NaCl solutions have influence on calcareous strata and Na is exchanged for Ca ("regeneration" of the exchange layer and hardening of the solution respectively). In comparison to Mg the Ca ion is preferred in a dissolved state, so that the Ca/Mg mol ratio in a regeration water is 1-6 (in contrast to oceanic water where it is 0.2). A reversed exchange process takes place with a lower concentration of dissolved solids: dehardening of the groundwater and formation of sodium hydrogencarbonate. As scale for these exchange reactions one can apply the Cl/Na mol ratio (Von Engelhardt, 1960). In this case we use chloride/alkali metals ratio because only the equivalent amount $Na^+ + K^+$ is known. This value is in regeneration waters greater than 1 (according to available data maximally 5.1), in $NaHCO_3$ water smaller than 1 (in "fresh" exchange waters even smaller than 0.5). In deep waters however this value amounts to 1.0-1.4 (rarely up to 2).

Also the *anions* show differences between deep water and saline groundwater in the Tertiary/Quaternary aquifers. Sulfate ions appear in groundwater of Tertiary and Quaternary sediments in the neighbourhood of dissolved gypsum bodies; often it is only possible to derive gypsum if dissolved SO_4^{2-} is present (fig. 3; Johannsen & Löhnert, 1971). Sulfate contents decrease with increasing distance from the place of solution (Löhnert 1967b). There are many indications that bacterial reduction of sulfate plays a dominant role. By this sulfate

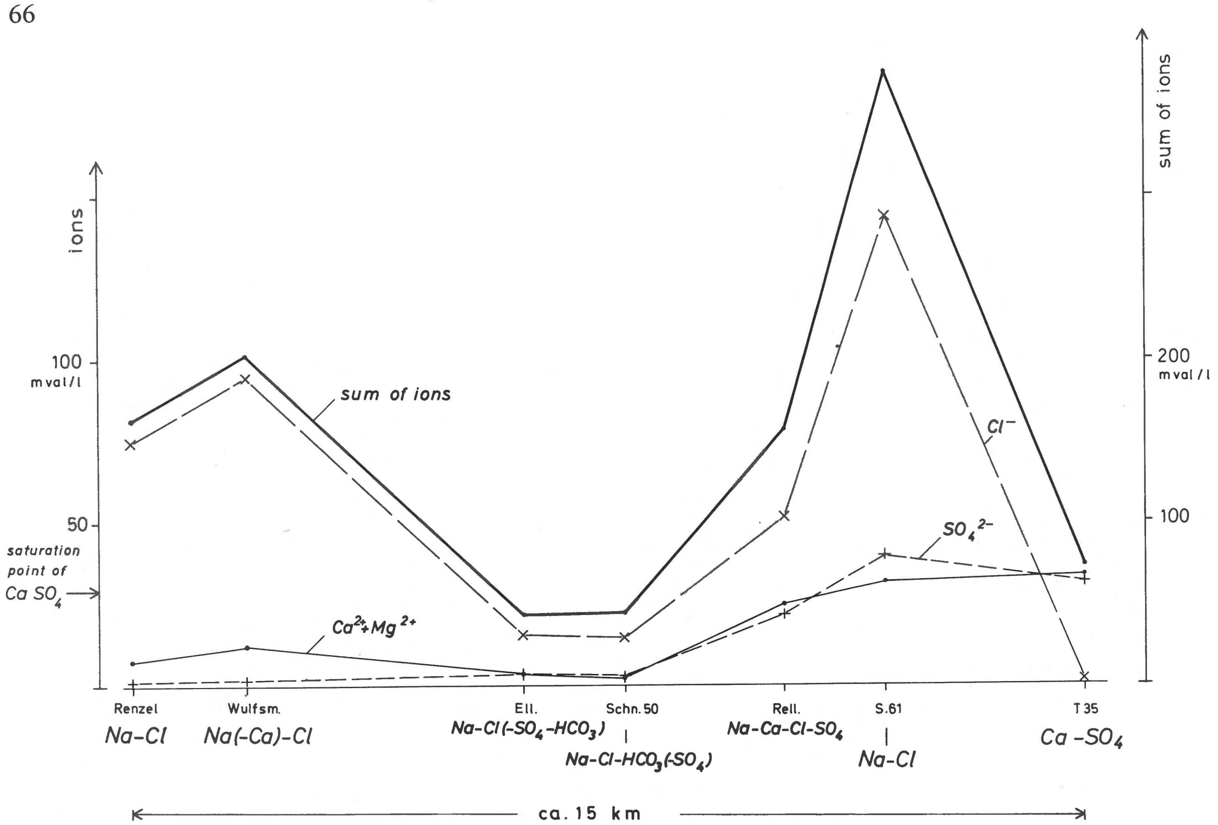

Fig. 3
Hydrochemical cross section through a part of the "Hamburg Scholle".

reduction many authors explain the small contents of sulfate in deep water. Maybe one can interpret in this way the origin of sulfur isotope values in North German deep water, which are generally higher than the standard of Zechstein evaporates (i.e. greater than 10-13‰ $\delta^{34}S$, Müller, Nielsen & Ricke, 1966). Investigations of (younger) subrosion water of Miocene and Pleistocene beds have been started accordingly.

3. TYPES OF GROUNDWATER

The classification of groundwater assumes the availability of complete chemical analyses. With partial water analyses determinations of SO_4^{2-}, Ca^{2+} and Mg^{2+} are often missing. An indication of the amount of sulfate is given by the noncarbonate or permanent hardness respectively; especially in exchange waters a correct evaluation of SO_4 ist mostly impossible. The alkaline earth metals are known as a sum total (total hardness divided by 2.8 = mval Ca + Mg).

In each case however it is necessary to convert the ions to equivalent amounts (mval/1 resp. mval/kg). In the majority of cases the main anions are determined. Therefore one can ascertain the amount of alkali metals by an *ion balance* (mval Na+K = mval anions minus Ca + Mg). The errors of this method in practice are insignificant.

A proposed classification by the author of the groundwaters of the Hamburg region (1967a) takes into account the absolute as well as the relative contents of ions. This method has practical applications to waters for drinking and industrial usage. On figure 2 the main and subtypes are depicted schematically. Specifically one can give the following explanation:

3.1 Fresh waters

The emphasis lies with those fresh waters, which are not affected by oxidation from the surface because of depth or confinement by clay layers. In confined layers anaerobic properties are found relatively near the surface and components of high oxygen value (sulfate, nitrate) are reduced. An exception is made by Pleistocene channels predominantly filled with sand several hundred meters thick. In this material increased groundwater movement can be observed. In these channels the groundwaters are sometimes not in a carbonate-carbon dioxide equilibrium.

In fresh water calcium and hydrogencarbonate ions are predominant and are present in approximately equivalent amounts. Maximal contents (ca. 10 mval)are found in the calcareous moraine deposits of East Holstein. A total dissolved solid content (residue) of 1000 mg/l, which we use as a limit against salt water, includes also chloride and sulfate diluted waters. The latter are rare, whilst chloride diluted waters are fairly frequent. Of special importance is the separation of "pure" fresh water: contents of chloride higher than 1 mval are generally the first indications of subsoil salinisation, i.e. these waters are interdigitating with others of higher Cl concentration. The value of 1 mval (= 35.5 mg/l) Cl identifies itself in our waters with 20 mval-% (L ö h n e r t, 1967a), so that chloride appears even after balneological nomenclature (lists of cations and anions in order of their frequency if represented by more than 20 mval-%; in brackets on fig. 3: ca. 10-20 mval-%).

3.2 Salt waters

Chloride waters are predominant; their origin has already been mentioned. Next to NaCl waters regeneration waters with high contents of $CaCl_2$ are often found. The last mentioned types should be treated under section 3.3, but they belong to the overall subject of "salt water". The author has given an example (1968a, Abb. 4), in which "deep water" of the type of regeneration water reaches right to the surface. In the area of the Ostholstein Scholle, where salt domes are missing, the saline groundwaters are of the same type. The cross section in the area of the Hamburg Scholle however, shown on figure 3, passes the neighbourhood of salt diapires in which subrosion has taken place. In a concentrated area chloride and sulfate waters up to pure gypsum solutions and also mixtures are found. In the lower half of figure 3 all the various types of the balneological nomenclature are given. The disadvantage of this classification is clearly recognisable in borehole location "S 61": SO_4 is surpressed, although the amount has reached saturation point of $CaSo_4$ solution, indicated in the left of the diagram. However after balancing the ions it appears that 20% of the SO_4 ions are combined with alkali metals.

On figure 4 the vertical hydrochemical change is to be seen, which has been proven by 3 different pumping levels of the drilling location "Rell". All ions show an increase with depth, the only exception being hydrogen carbonate; the relatively fast increase of chloride between the top and middle filter can be explained by the presence of a thick layer of clay.

The separation from fresh water with 1 g/l dissolved solids was already mentioned before. In chloride salt waters the Cl amount of 10 mval (= 355 mg/l) is approximately equal. In this degree the perception of taste becomes apparent and this fact underlines the practical application of our classification. Further aspects are the "Begriffsbestimmungen für Kurorte, Erholungsorte und Heilbrunnen des Deutschen Bäderverbandes" (1968), whereby in a defined mineral water at least 1 g/kg dissolved solids must be contained.

A part of the North German interior has been mapped by J o h a n n s e n & L ö h n e r t (1971) which shows an isoline plan where the defined boundary of 1 g/l dissolved solids is depicted for the first time. This boundary itself differs by more than 250 meters in the observed area!

3.3 Exchange waters

On figure 2 a separation of 3 subtypes is shown. Of these the subtype with sodium hydrogencarbonate is the most significant in practice. The author has already reported extensively on this subject (1970). The temporary hardness exceeds the total hardness in these waters. Often the temporary hardness has to be calculated from the alkalinity. By multiplication of the difference between both hardnesses with the factor 30 the amount of $NaHCO_3$ is determined.

As shown on figure 2 the dissolved solids of $NaHCO_3$ exchange waters are comprised of an amount of fresh as well as salt water. Fresh and salt exchange waters are differentiated, which contain 700 mg/l $NaHCO_3$ maximally in Miocene aquifers. The base-exchange process takes place preferentially

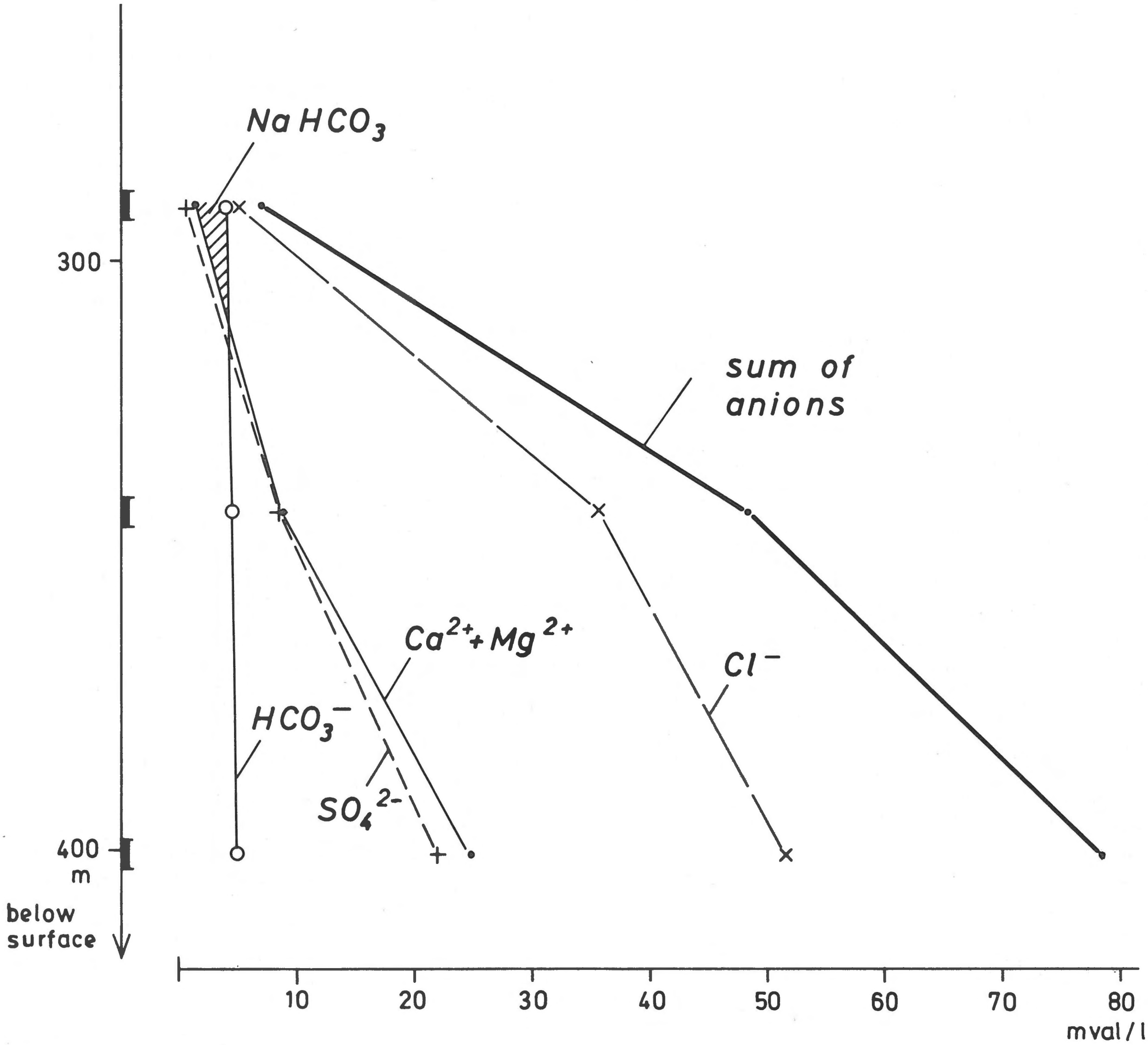

Fig. 4
Vertical hydrochemical section of the drilling "Rell." (see fig. 3).

by contact of fresh and salt water. This exchange zone, several kilometers in size, has been proven to be in the horizontal. For the exploitation of groundwater it is important to know, that also *fresh* exchange waters exist in areas of saline groundwaters. The Na deposit of the permutites ensues by salt solution secondary, which seem to have been more extended in former times. Permutites are mainly mica and humus in difficult permeable fine sand and silt.

Figure 5 shows in the above mentioned area of Ostfriesland salt exchange water with max. 342 mg/l $NaHCO_3$ above chloride salt water. As in other parts of Northern Germany the exchange zone developed in the Miocene strata; it probably extends upwards into fresh exchange water. The hydrochemical configuration is typical for the transition of fresh water into saline deep water (*not* invaded recent sea water). This is an argument for the existence of a relatively old fixed balance.

4. CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

The investigation of the geochemistry of North

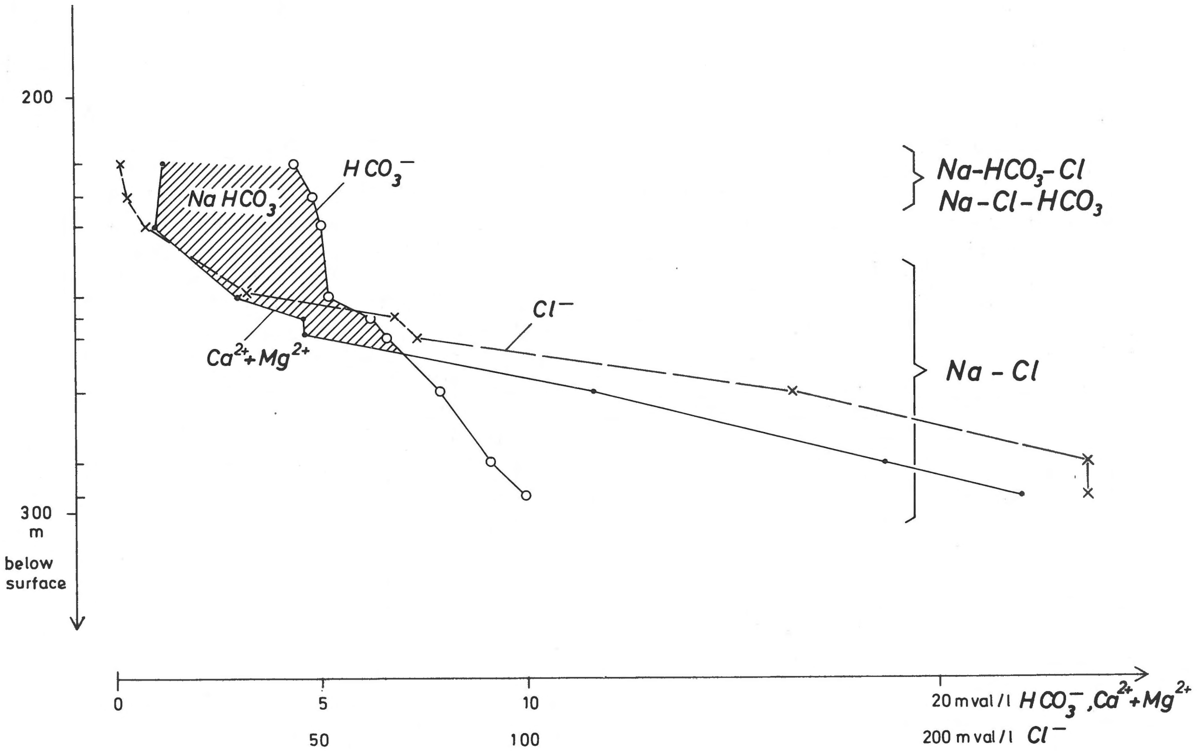

Fig. 5
Vertical hydrochemical section showing the transition exchange/salt water in a drilling of Wittmund/Ostfriesland. For this data I am indepted to my colleague J. HAHN, Niedersächsisches Landesamt für Bodenforschung, Hannover.

German groundwaters is still lacking final results. To obtain more valuable information in the future about the origin and genesis of various types of groundwater a data collection program in specific regions is desirable. Apart from the routine water analyses *trace constituents* should also be determined as it is usual in balneology.

Isotope research (^{14}C and $\delta^{34}S$) has started. The $\delta^{34}S$– values (deviation of the content of heavy sulfur isotope ^{34}S from the terrestrial average) may show, whether apart from Zechstein younger evaporates have been dissolved and are contained in the amount of salt of the groundwaters. First results of ^{14}C–age determinations (Johannsen & Löhnert, 1971) show the possibility of clarifying the important question, to which extent strongly saline groundwater is involved in the hydrologic cycle.

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