OPERA

The composition of deep groundwater in the Netherlands in relation to disposal of radioactive waste

OPERA-PU-TNO521-2

Radioactive substances and ionizing radiation are used in medicine, industry, agriculture, research, education and electricity production. This generates radioactive waste. In the Netherlands, this waste is collected, treated and stored by COVRA (Centrale Organisatie Voor Radioactief Afval). After interim storage for a period of at least 100 years radioactive waste is intended for geological disposal. There is a world-wide scientific and technical consensus that geological disposal represents the safest long-term option for radioactive waste.

Geological disposal is emplacement of radioactive waste in deep underground formations. The goal of geological disposal is long-term isolation of radioactive waste from our living environment in order to avoid exposure of future generations to ionising radiation from the waste. OPERA (OnderzoeksProgramma Eindberging Radioactief Afval) is the Dutch research programme on geological disposal of radioactive waste.

Within OPERA, researchers of different organisations in different areas of expertise will cooperate on the initial, conditional Safety Cases for the host rocks Boom Clay and Zechstein rock salt. As the radioactive waste disposal process in the Netherlands is at an early, conceptual phase and the previous research programmes OPLA and CORA have ended more than a decade ago, in OPERA a first preliminary or initial safety case will be developed to structure the research necessary for the eventual development of a repository in the Netherlands. The safety case is conditional since only the long-term safety of a generic repository will be assessed. OPERA is financed by the Dutch Ministry of Economic Affairs and the public limited liability company Electriciteits-Produktiemaatschappij Zuid-Nederland (EPZ) and coordinated by COVRA. Further details on OPERA and its outcomes can be accessed at www.covra.nl.

OPERA-PU-TNO521-2
Title: The composition of deep groundwater in the Netherlands in relation to disposal of radioactive waste
Author: J. Griffioen (TNO)
Supporting activities: André Cinjee, Dianne den Hamer, Marc Verheul (Deltares)
Date of publication: April 2015
Keywords: groundwater quality, characterisation, geochemistry

Contents

Summary

This report presents a general characterisation of the composition of deep Dutch groundwater above and below the Boom Clay. Here, the vertical distance between sampled groundwater and the Boom Clay is often considerable; very few data is present for the surrounding Paleogene aquifers. 26 samples from existing, deep groundwater wells were collected and analysed on a broad suite of compounds. Additionally, four regional data-sets were obtained from DINO database and literature was collected to obtain data on groundwater below the Boom Clay or iodide concentrations in groundwater. The data show regional differences for groundwater below 100 m depth and either above or below the Boom Clay. Fresh to saline groundwater is found below 100 m depth and above the Boom Clay, with different general characteristics among the regions studied. This deep groundwater likely has an age from 500 y up to ten thousands of years. Below the Boom Clay, hypersaline groundwater is often present in the northern half of the country (related to the occurrence of evaporite deposits) and saline groundwater in the southern half. Here, brines not only coincide with deep gas and oil reservoirs but also with Paleogene aquifers in the vicinity of salt diapirs. Special attention is paid to iodine and selenium because these elements have mobile, long-living radioisotopes that become produced as daughther products. Few data is available for these elements. It shows that iodide ranges from 1 – 1000 µg/l with highest concentrations related to marine sediments and/or saline groundwater, whereas selenium is often below detection limit and does not exceed 1 µg/l.

Samenvatting

Een algemene studie is verricht naar de samenstelling van diep grondwater onder en boven de Paleogene Boomklei. 26 grondwatermonsters zijn genomen uit bestaande diepe putten en geanalyseerd op een breed spectrum aan opgeloste stoffen. Daarnaast zijn voor 4 regionale gebieden waarbinnen deze putten zich bevinden, analyses uit de DINO database opgevraagd en zijn analyses verzameld van jodium in grondwater of grondwater onder de Boomklei.Het blijkt dat er niet meer dan ca. 25 analyses beschikbaar zijn van grondwater in Paleogene aquifers, waarvan een aanzienlijk deel afkomstig is van een Limburgse studie uit 1963. De beschikbare analysegegevens geven aan dat grondwater dieper dan 100 m en boven de Boomklei regionale verschillen vertoont in o.a. zoutgehalte en kalkverzadiging. Dit grondwater heeft waarschijnlijk een verblijftijd van meer dan 500 tot tienduizenden jaren. Op grotere diepte onder de Boomklei, wordt extreem zout grondwater gevonden in de noordelijke helft van Nederland door de aanwezigheid van zoutlagen in de diepere ondergrond. Het extreem zoute grondwater komt niet alleen voor in de olie- en gasreservoirs maar ook in Paleogene watervoerende pakketten in de buurt van zoutdiapieren. In de zuidelijke helft is vaker sprake van zout grondwater dat waarschijnlijk tienduizenden jaren oud is. Speciale aandacht ging uit naar jodium en seleen omdat deze elementen radioisotopen kennen die geproduceerd worden bij verval van radioactief afval, relatief mobiel zijn en een zeer lange halfwaardetijd hebben. Betrekkelijk weinig I en Se analyses zijn beschikbaar. Deze geven aan dat jodide varieert tussen 1 en 1000 µg/l met de hoogste concentraties in zout grondwater of in mariene afzettingen terwijl selenium vaak beneden de detectielimiet ligt en nooit 1 µg/l overschrijdt.

1. Introduction

1.1. Background

OPERA (OnderzoeksProgramma Eindberging Radioactief Afval) is the five-year Dutch research programme on geological disposal of radioactive waste. Within OPERA, conditional Safety Cases for the host rocks Boom Clay (or Rupel Clay according to the Dutch geological stratigraphy) and Zechstein rock salt will be established. As the radioactive waste disposal process in the Netherlands is at an early, conceptual phase and the previous research programme has ended more than a decade ago, in OPERA a first preliminary or initial safety case will be developed to structure the research necessary for the eventual development of a repository in the Netherlands. The Boom Clay is selected as potential host rock for geological waste disposal in the Netherlands and Belgium because of the isolating potential of low permeable, clay-rich rocks.

One of the topics to be addressed is a prognosis on the long-term fate of radionuclides that may disappaer out of the Boom Clay towards the biosphere at the geological time scale under anticipated future geological evolution of the Netherlands. Another topic is the boundary condition at the upper and lower boundaries of the Boom Clay as set by the groundwater composition. In the current Dutch disposal concept, waste is disposed at appr. 500 m depth or more within a clay layer of about 100 m (Verhoef et al., 2014). In OPERA, a disposal concept is investigated in Boom Clay. A depth of 500 meter is chosen in order to accomodate possible erosion by glaciers. Similarly as in the Belgian disposal concept, a width of 100 meters is used as a start. This implies that their are two interests for the groundwater composition at depth: first, as boundary condition for the pore water composition *within* the Boom Clay and, second, as background composition with respect to both the background concentration of the most mobile and long-living radioisotopes and major characteristics as salinity and redox state.

1.2. Objectives

The objective of this activity is to characterise the groundwater composition above and below the Boom Clay in relation to the not site-specific potential disposal of radioactive waste in this Tertiary clay layer. Special attention is devoted to I and Se because these elements have long-living radioisotopes that become produced as daughther products: ^{129}I has a half life of 1.61E7 y and ^{79}Se has 3.27E5 y.

1.3. Realization

This study is performed within task 5-2-1 of the OPERA programma, which focal point is “geochemical properties and long-term evolution of the Boom Clay”. Furthermore, the resulting geochemical characteristics will be used as input in several tasks under WP 6 and WP 7, which will investigate reactive transport of radionuclides. The data is also relevant for WP3 and WP 5, which consider physico-chemical properties and geomechanical aspects of the Boom Clay, respectively.

TNO did set-up the field campaign with respect to groundwater sampling. The actual sampling was subcontracted to Deltares. The groundwater analysis were performed by TNO where the carbon isotope analysis were subcontracted to HydroIsotop and the analysis of CH_4 and I were subcontracted to Vitens. TNO performed the data interpretation as well as the literature search, with some assistance by employees of Deltares.

1.4. Explanation contents

The set-up of the field and laboratory campaigns as well as the data collection and handling are presented in Chapter 2. In Chapter 3, a brief discussion is presented of the hydrogeology of the regions from which groundwater was sampled. Chapter 4 presents the results were attention is paid to the data from the present campaign, regional data of deep groundwater above the Boom Clay and national data of deep groundwater under the Boom Clay. Chapter 5 presents the conclusions. The newly obtained chemical data is presented in the Enclosure together with illustrative hydrogeological cross-sections of the studied regions.

2. Collection of groundwater quality data

2.1. *New analysis*

A selection has been made of groundwater screens at large depth that preferably lie as close as possible to the Boom Clay. 26 screens were selected from 18 wells, which were majorly situated in the northern part of the Netherlands, the middle part of Limburg and western part of North-Brabant (Fig. 2-1). Table 2-1 provides details on screen depths, geological formation in which the screen is present, etc. The depth of the screens varied from 180 m to 510 m-NAP. Note that two sampled screens in western Brabant are situated in Paleogene aquifers below the Boom Clay and all others are situated in Miocene to Middle Pleistocene aquifers above the Boom Clay.

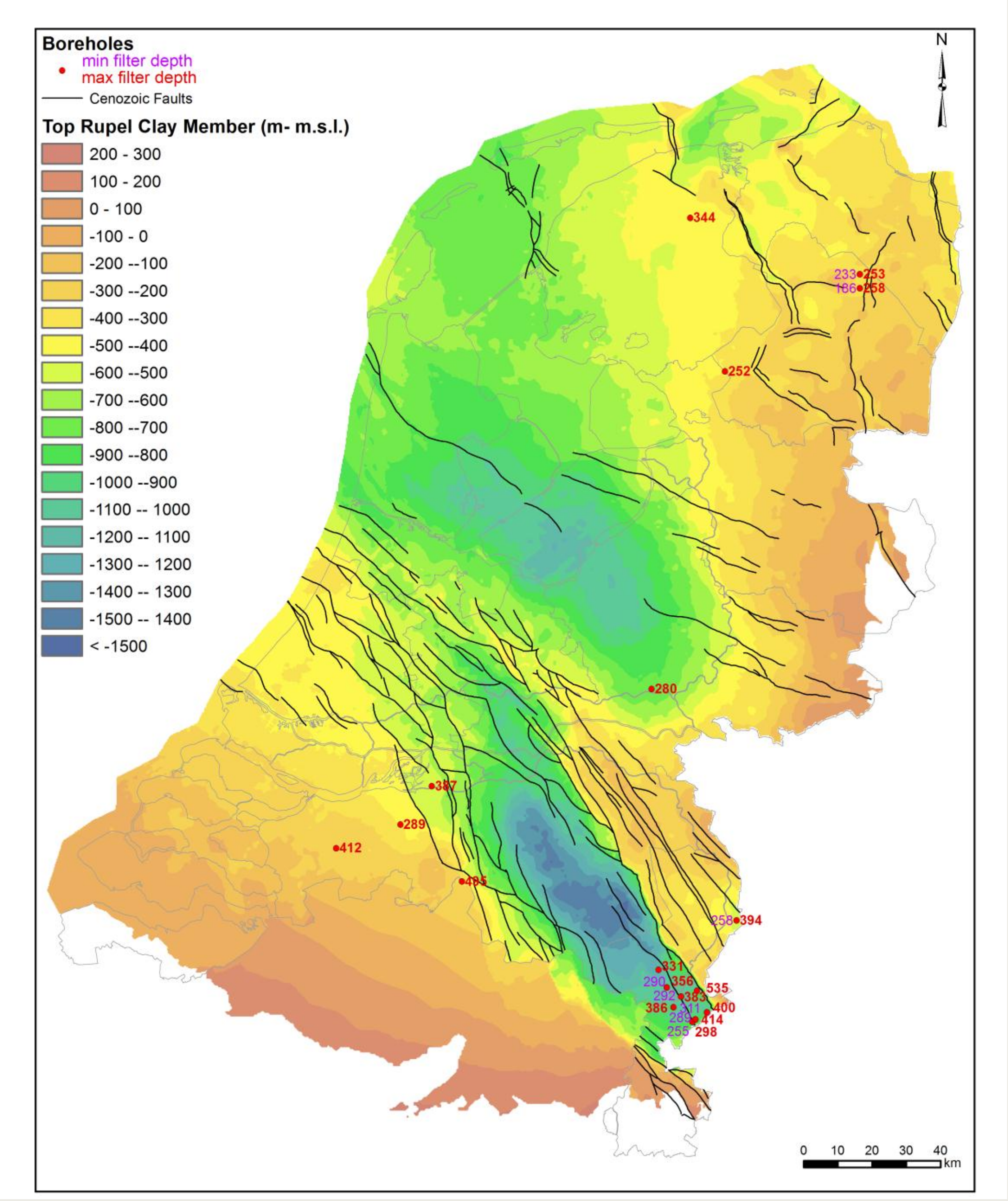


Fig. 2-1. Map of the Netherlands with the locations of the wells sampled and the depth (m below sea level) of the top of the Rupel Clay Member (derived from Vis & Verweij, 2014) in the background.

Table 2-1. Geographical information about the screens that were sampled.

Well	screen	x-coord	y-coord	Altitude (m+NAP)	Depth top filter (m+NAP)	Depth bottom filter (m+NAP)	Formation
Northern Netherlands							
B06D0213	007	198167	581083	1.17	-340.80	-342.80	Peelo
B12E0266	010	247740	564610	1.74	-231.26	-233.26	Peelo
B12E0266	011	247740	564610	1.74	-248.76	-250.76	Peelo
B12G0119	009	247740	560480	4.00	-180.00	-182.00	Oosterhout
B12G0119	010	247740	560480	4.00	-252.00	-254.00	Breda
B16G0088	005	208340	536270	1.17	-248.79	-250.79	Oosterhout
Central Gelderland and northern Limburg							
B40A0551	006	186928	443516	14.45	-263.89	-265.89	Breda
B52H0235	006	211710	375964	43.56	-209.44	-214.44	Breda
B52H0235	007	211710	375964	43.56	-345.44	-350.44	Veldhoven
Western Brabant							
B44E0146	008	122712	415122	0.96	-383.77	-385.77	Oosterhout
B44D0484	010	113521	403932	0.32	-286.18	-288.18	Breda
B49F1427	009	94798	397060	5.92	-403.08	-406.08	Tongeren; Zelzate Member
B50H0373	009	131471	387296	22.40	-469.26	-472.26	Tongeren
Middle Limburg							
B58C0734	004	188982	361521	26.83	-301.17	-304.17	Kiezelooliet
B58D0688	006	195520	353710	25.46	-264.54	-266.54	Kiezelooliet
B58D0688	007	195520	353710	25.46	-355.54	-357.54	Kiezelooliet
B58D0885	003	191361	356425	29.60	-258.17	-260.17	Kiezelooliet
B58D0885	004	191361	356425	29.60	-324.17	-326.17	Kiezelooliet
B58D1609	009	193314	350639	27.57	-353.40	-358.40	Kiezelooliet
B58G0191	005	200181	355411	23.40	-507.05	-512.05	Breda
B60B0107	004	198800	346390	33.16	-219.74	-221.74	Inden
B60B0107	005	198800	346390	33.16	-262.74	-264.74	Breda
B60B0123	004	199701	347040	30.56	-255.44	-258.44	Kiezelooliet
B60B0123	005	199701	347040	30.56	-380.44	-383.44	Inden
B60E0017	005	203044	349069	28.97	-279.24	-282.24	Kiezelooliet
B60E0017	006	203044	349069	28.97	-366.24	-371.24	Inden

Six screens in middle Limburg were artesian wells and they were sampled under overflow conditions. The others were sampled using a submersible pump, which was lowered in the tube as much as possible (Fig. 2-1). Two screens that were earlier selected, could not be sampled in the course of the field campaign because of technical difficulties (screen 12 of B37D0134 and screen 6 of B43H0063).

Samples were collected after the pH, temperature, dissolved O_2 and electrical conductivity were stable. Often several hunderds to a few thousands liters of groundwater were pumped prior to sampling.

Figure 2-2. Sampling of a deep screen using a submersible pump

The groundwater sampled was collected in different bottles using routine procedures for the conservation measures related to the various analyses performed (Fig. 2-3). The following analyses were performed:

- Major and trace metals using ICP-MS
- Chloride, sulphate, bromide, fluoride and nitrate using ion chromatography
- PO_4 and NH_4 using auto-analyser procedure
- DOC as non-purgeable organic carbon and infrared detection of CO_2
- Iodide using liquid chromatography
- Methane using gas chromatography and flame ionisation detection
- Carbon-14 of dissolved inorganic carbonate using fluid scintillation spectrometry
- Carbon-13 of dissolved inorganic carbonate using isotope ratio mass spectrometry

Due to an error in communication, no alkalinity was measured. This was calculated from the electroneutrality condition, where alkalinity is assumed to be equal to the difference between the sum of analysed cations and the sum of analysed anions (in meq/l).

2.2. *Archive data*

Groundwater analyses were also retrieved from the DINO database. Analyses were retrieved for samples that were collected deeper than 100 m for four regions that coincided with the regions from which the new samples were collected.
Analyses were only considered when they contained several major compounds and single solute analyses (in particular chloride) were discarded. When a complete analyses was available (pH, Ca, Mg, Na, Cl, SO4, alkalinity, preferably K, NH4, Mn and Fe as well while Al and NO3 are commonly below detection limit), the analyses which had a good electroneutrality condition were selected.

Here, a good electroneutrality condition (EN) is defined as follows:

$$-5.0\% < EN = (\text{sum cations} - \text{sum anions}) / \text{sum cations} + \text{sum anions}) < 5.0\%$$

Figure 2-3. The series of bottles that were filled per sample.

Repeatedly, several analyses were available for one screen. All samples were used for a speciation calculation using PHREEQC (Parkhurst & Appelo, 1999). Only one analysis was selected per screen for graphical purposes, which contained the most complete analyses having as few as possible variables below detection limit. In general, the agreement among the different analyses per screen was very good. Upon result, the following amounts of screens and samples were selected per region (Fig. 2-4):

1. The northern part with eastern Friesland and Drenthe Plateau: 110 screens with 384 samples
2. area around Arnhem, i.e., Central Gelderland: 39 screens with 49 analyses
3. The middle stretch of Limburg: 117 screens with 496 analyses
4. western North Brabant: 135 screens with 290 analyses

A small series of about 40 groundwater samples with isotope analyses was also retrieved for these regions from the DINO database. These data deal with $\delta^{18}O$, $\delta^{2}H$, ^{3}H of water and $\delta^{13}C$, ^{14}C of TIC. The last two were often not combined with a complete analysis of the major groundwater composition which makes these isotope analysis unsuitable for further correction from apparent groundwater age to true groundwater age. Finally, five Se analyses were found for the northern region and 361 for the middle Limburg region; no Se analyses were found for the other two regions.

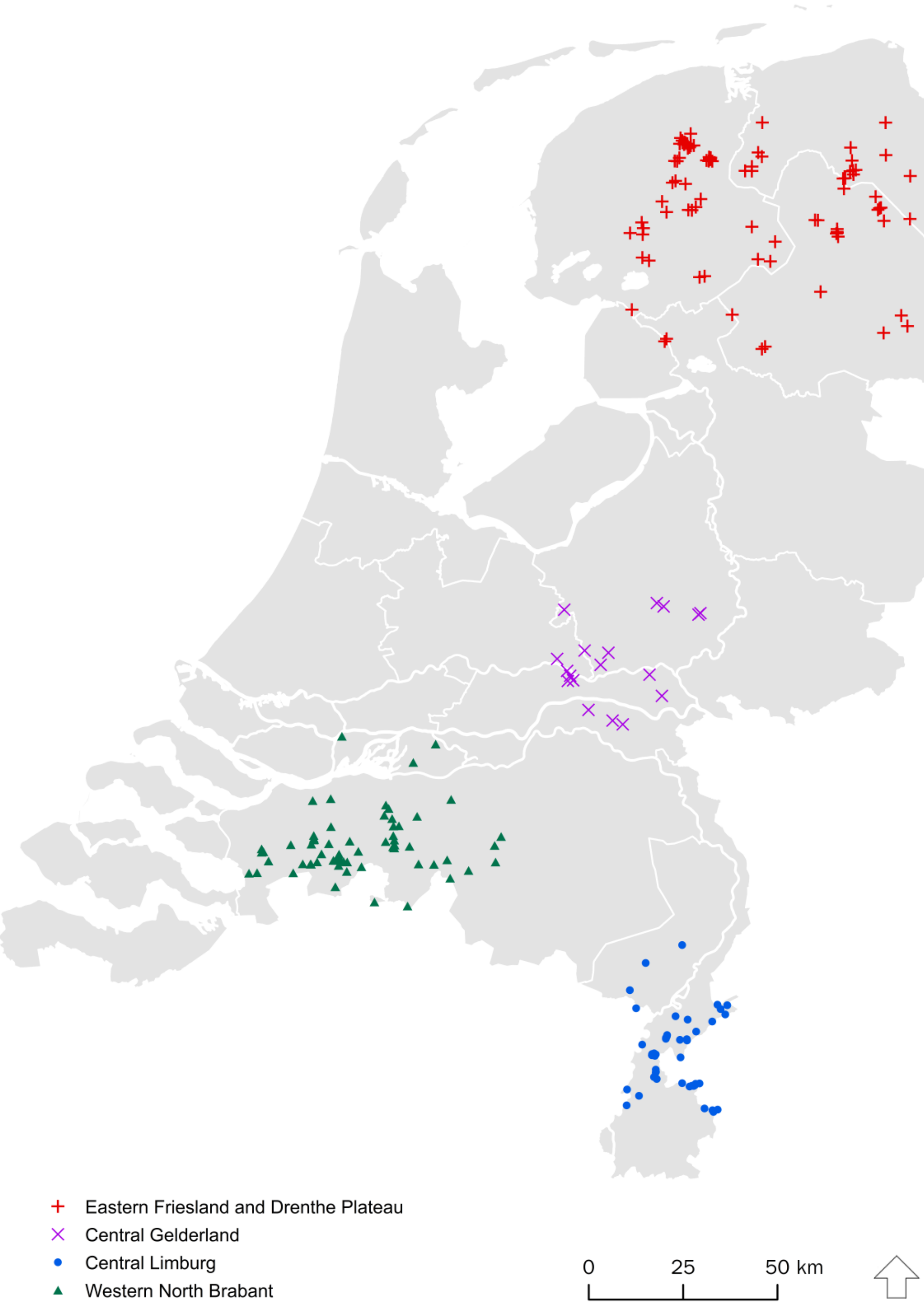


Figure 2-4. Map showing the locations of the wells with multiple or not sampling screens below 100 m depths and above the Boom Clay for which the groundwater analyses were considered in this study.

Four studies were considered that contain data on iodine in groundwater and that deal with groundwater above the Boom Clay: Heymann (1925), Engelen (1969), Geirnaert (1972) and Stuyfzand (1993). The last study also contains some data on Se. Data on iodine and selenium is interesting within the present framework because ^{129}I and ^{79}Se are long-living radioisotopes (half lifes of 1.61E7 y and 3.27E5 y, respectively) that become produced during decay of radioactive waste. These three studies were performed in the western, Holocene part of the Netherlands and dealt with groundwater down to several tens of meters. Additionally, Huurdeman (1986) was consulted to collect data on Cl concentrations in the Miocene Breda Formation. This marine formation lies closely on top of the Boom Clay in many parts of the Netherlands and is frequently the deepest aquifer unit where groundwater flow is driven by hydrological controls at the surface, i.e., it is the deepest aquifer unit above the hydrological basis.

A series of other studies was consulted that deal with the composition of groundwater below the Boom Clay: Jongmans & Driessen (1932), Kimpe (1963), Bless (1981), Van der Weijden (1983), Glasbergen (1981, 1984), Coenegracht et al. (1984), Zuurdeeg et al. (1984), Zuurdeeg & Coenegracht (1986), Core Lab (1987), Heederik (1989), CMEO (1991), Beaucaire et al. (2000) and Verweij (2003). Not all data on the gas and oil reservoirs in South-Holland was included because the compositions are near-similar and a bias would be obtained when all avaliable data would be included. The samples having the highest and lowest concentrations were selected per field. No averaging was preferred as this may obscure interrelationships among equilibrium-controlled concentrations. This data was extended with some analyses available within the framework of re-injection of formation water produced during gas or oil exploitation. The data of Beaucaire (2000) deal with groundwater in the Belgium Oligocene aquifer where the Boom Clay lies within relatively short distance under the surface. The Boom Clay as well as the sampled groundwater lies at depths larger than 400 m for the other studies, except for the studies of Jongmans & Driessen (1932) and Kimpe (1963) in Limburg. The analytical quality of the data was remarkably good when checked for electroneutrality condition: most samples had an electroneutrality condition smaller than 0.5%.

2.3. Geochemical calculations

Speciation calculations for the groundwater analyses were performed with PHREEQC (Parkhurst & Appelo, 1999). Both the Pitzer procedure and the regular procedure were used to calculate the aqueous activities of ions from the total concentrations for analyses of groundwater under the Boom Clay. Groundwater under the Boom Clay is repeatedly a brine with Cl concentrations up to 200,000 mg/l. The Pitzer procedure is more suitable to correct for aqueous activity than the regular procedure for brines, but the associated database on solubility of minerals and temperature dependency of chemical equilibria is rather small. A drawback of the Pitzer database is thus the small database whereas a drawback of the regular database is the incorrect calculation procedure to correct the concentration to activity. Both databases were employed for the data-set of groundwater under the Boom Clay. Figure 2-5 compares the results for the saturation indices of halite and anhydrite as the difference between the two SI-values per sample versus its Cl concentration. The data show that the discrepancy is in the order of several tenths of unit for halite and varies between several tenths of units to several units for anhydrite. The biggest discrepancy happens for the brines having a high temperature of about 100-130°C (i.e., the deep samples) and a smaller discrepancy is found when temperature is around 25°C (i.e., shallower samples). This illustrates that the temperature correction of the thermodynamic equilibria is important in addition to the way in which the activity is calculated. Here, the findings for calcite are comparable to those for anhydrite. Upon result, preference was given to use the normal calculation procedure including temperature correction instead of using the Pitzer procedure.

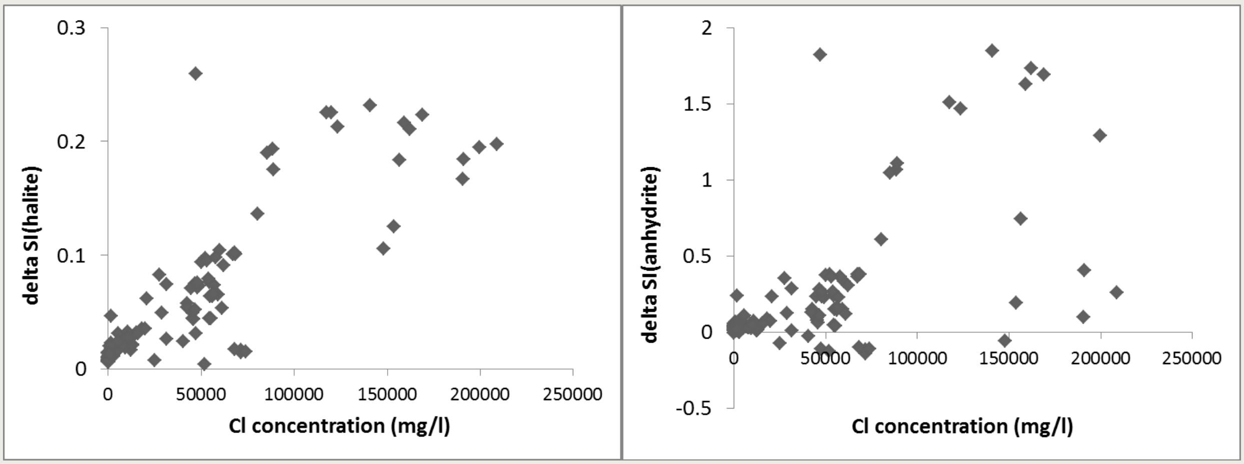


Fig. 2-5 Dependency on the Cl concentration of the difference between the saturation indices of halite and anhydrite as calculated according to the normal procedure and the Pitzer procedure for analyses of groundwater under the Boom Clay.

No temperature data was available for many analyses of groundwater under the Boom Clay. It was, therefore, calculated as:

Temp(sample) = 10°C + depth(sample) x 30°C/km

where depth is given in km and 30°C/km represents the average temperature gradient for the Dutch subsurface (Verweij, 2003). When the calculated temperature was compared with the few observations, the latter were repeatedly considerably lower. This suggests erroneous measurement due to cooling during pumping or so. Preference was given to the calculated temperature instead of the reported temperature as being more robust.

The SO_4 reduction state was calculated as follows:

$$R\text{-}SO_4 = 1 - [Cl_{(sw)} * SO_{4(s)}] / [Cl_{(s)} * SO4_{(sw)}]$$

where (s) refers to the sample and (sw) to seawater. Sulphate reduction is complete when the value is 1. The SO_4 concentration lies on the seawater dilution line when the value is 0. Values below 0 imply that the water sample is enriched in SO_4 relative to Cl, which is likely due to anthropogenic pollution.

3. Hydrogeology

The four regional study areas have an essentially different hydrogeology as shown by the hydrogeological cross-sections across the wells sampled (Enclosure 1). Note that these cross-sections were prepared with REGIS version II.1 (2008) and the geological classification of the filters was performed with the latest Digital Geological Model. Some differences in classification may therefore be noted, which must, for example, be attributed to the meanwhile introduction of the new Inden Formation. The lithostratigraphic formations that are distinguished in the Netherlands are presented in the figure below. Reference is frequently made to these geologial units.

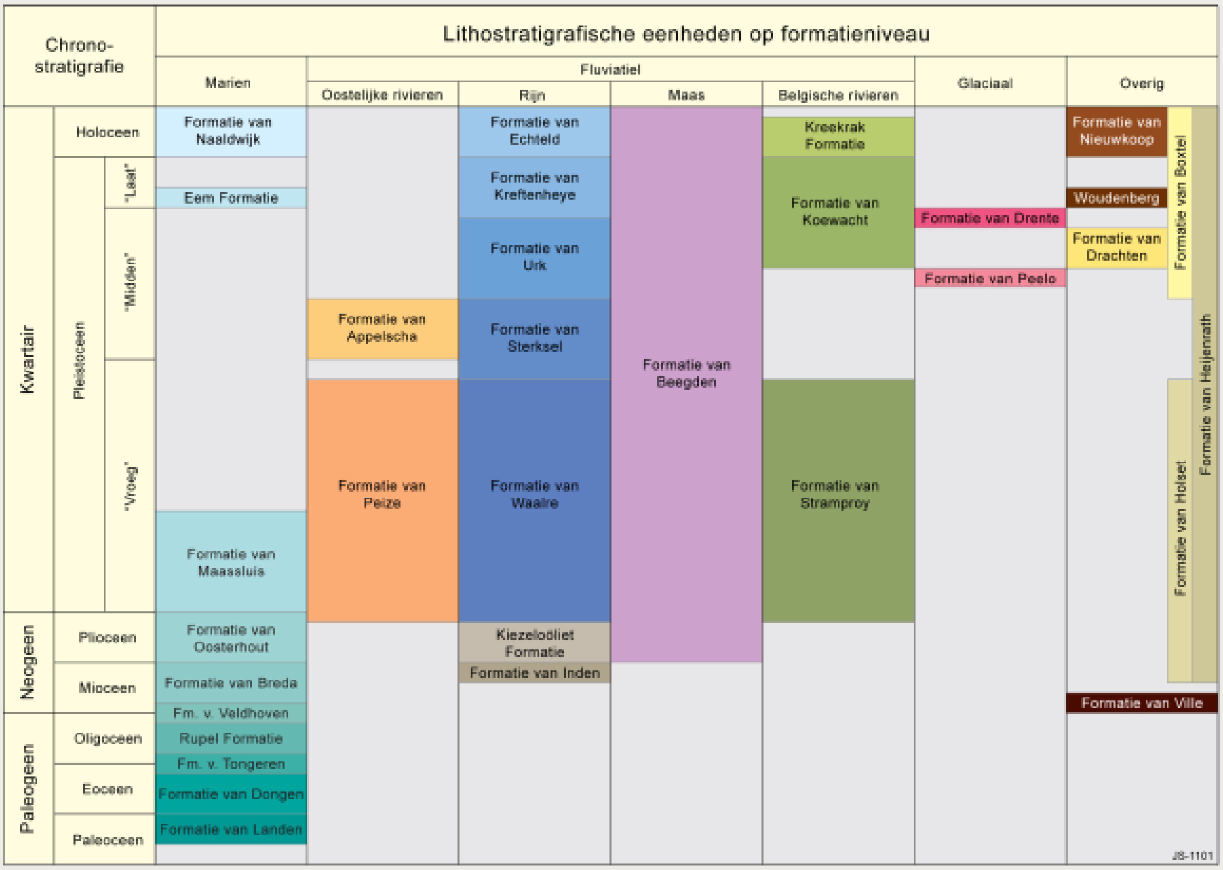


Figure 3-1. Scheme of the lithostratigraphic units that are distinguished in the Netherlands for the Cenozoicum.

In western Brabant, marine deposits of the Maasluis, Oosterhout and Breda Formations are present from 50-100 m-NAP down to several hunderds of meters. These formations dip to the north. Fluvial deposits are predominantly present at more shallow depth. The Rupel Formation, which includes the Rupel or Boom Clay, lies under the Breda Formation. The sampled screens from the wells B49F1427 and B50H0373 lie under the Boom Clay in the Tongeren Formation at 412 and 495 m-NAP. For these two wells, the Rupel Formation has a depth range of 236-388 m and 334 – 487 m-NAP, respectively. The other two wells sampled in this region are situated more northern with screens in the Breda and Oosterhout Formations. This area borders the Belgian Kempen region, where the underground laboratory of Mol is situated. In Flanders two aquifer systems are distinguished above the Boom Clay (VVM, 2008): the Quaternary aquifer system and the Kempen aquifer system of Miocene to Pleistocene age.

The first is not thicker than about ten meters and the last has an increasing thickness up to about 300 m towards the north. Below the Boom Clay, the Oligocene aquifer system is present comprising the Ruisbroek and Berg sands (Beaucaire et al., 2000; VVM, 2008).

The wells in middle Limburg are located in the Roer Valley Graben where 400 m of fluvial deposits dominate the upper part of the subsurface. The top of the Boom Clay lies at a considerable depth of 1300 to 1500 m, which is much deeper than the deepest screens sampled. Most screens sampled lie within the fluvial Kiezelooliet Formation or otherwise the Inden Formation and once in the marine Breda Formation.

Well B52H0235 close to Venlo in northern Limburg (Fig. 2-1) lies at the Peel Horst where the marine Breda Formation can already be present at 25 m-NAP and its thickness is around 200 m. The sampled screens at about 258 and 394 m depth are situated in the marine Breda and Veldhoven Formations, respectively. Here, the Breda Formation is classified as an aquifer in REGIS and the Veldhoven Formation has not been considered. The Breda Formations dips to the north(west) in the Central Gelderland area, where the upper part is classified as an aquitard and the lower part as aquifer. The marine Oosterhout and Maassluis Formations also become present at a depth of 30-90 m-NAP. The sampled screen B40A0551-006 at about 280 m is situated in the Breda Formation.

The situation for the northern region is rather different because of the presence of glaciers during Pleistocene. The Breda Formation is present at a depth below 125 m and it is, here, classified as an aquitard. The marine Oosterhout and Maasluis Formations are found on top of the Breda, being more clayey or sandy. Early Pleistocene fluvial sediments from in particular the Peize or Waalre Formations may be present on top of the marine sediments. Glacial gullies were formed during the Elsterian ice age and these gullies were filled up with fluvioglacial sediments of the Peelo Formation. The gullies had eroded the fluvial, Early and Middle Pleistocene sediments and may also have eroded the marine, Early Pleistocene and Tertiary sediments. The permeability of the fluvioglacial sediments in these gullies can be higher than the surrounding marine sediments, when they occur as sand. This would imply that a higher flux of groundwater happens within these gullies than outside. Relatively young groundwater may thus also become transported to a greater depth within these gullies. The fluvioglacial sediments also occur as so-called Pot Clay, which is very impermeable. The occurrence of clay versus sand in these glacial gullies is not fully clear at the regional scale and so is the groundwater flow situation.The screen from B06D0213 and two screens from B12E0266 are present in the fluvioglacial Peelo Formation. The two sampled screens from B12G0119 and the one from B16G0088 are situated in the marine Oosterhout or Breda Formations. The wells B12E0266 and B12G0119 are situated near each other, but the screens for the first are situated in a deep glacial gully and those for the last not. One should note that the cross-section presented in Enclosure 1 does not illustrate this. However, this cross-section was prepared using REGIS version II.1 from 2008; when using the latest version of the Digital Geological Model the screens become correctly classified on the geological formation in which they are situated (Table 2-1).

4. Results

The results of the study are split into three parts. First, the results of the field and laboratory campaign will be presented. Next, the composition of deep groundwater above the Boom Clay will be considered with special attention to concentrations of I and Se, and the groundwater age dating. Finally, the composition of groundwater below the Boom Clay will be considered. Both the major composition and the concentration ranges observed for the elements I and Se will be presented. This information is relevant within the framework of the fate of the long-lasting radioisotopes of I and Se: isotopic exchange between radioisotopes and stable isotopes of the same element may cause retardation of the radioisotopes during their groundwater transport. Besides, it is interesting to know possible precipitation/dissolution processes of these elements although the occurrence of these processes in the overburden is not part of the current Safety Case concept.

4.1.Hydrogeochemical interpretation of the new analyses

The new analyses can be grouped into three classes that are strongly regionally controlled (Fig. 4-1): 1. groundwater having very low Cl concentrations of about 5 mg/l are predominantly found in middle Limburg where undersaturation for calcite also happens, 2. fresh groundwater (Cl < 200 mg/l) that is mostly undersaturated to saturated with respect to calcite, which is found in the northern Netherlands and two screens in Limburg, and 3. brackish or salt groundwater that is saturated to supersaturated with respect to calcite, which is found in western Brabant, the screen near Arnhem and the deepest screen near Venlo.

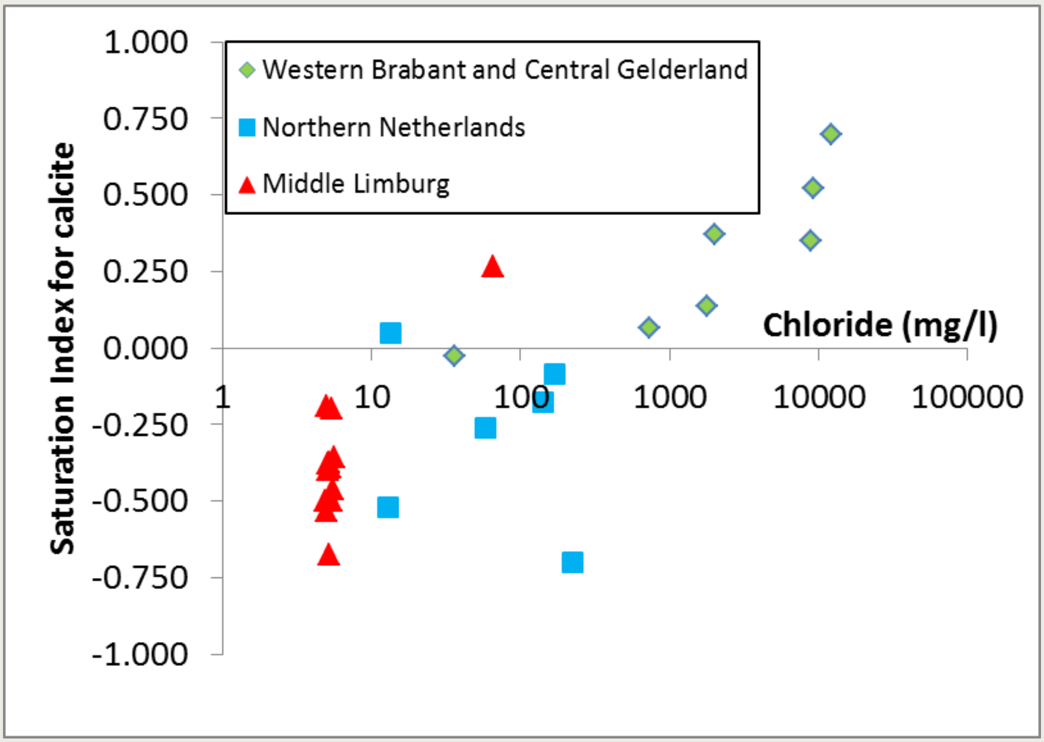


Figure 4-1. The chloride concentration versus the saturation index for calcite for the 26 newly collected samples of deep groundwater.

All groundwater samples are anaerobic but the three groups can be recognised in the redox chemistry as well (Fig. 4-2). The low Cl samples from middle Limburg contain about 5 mg

SO_4/l and no SO_4 reduction is indicated (as does the B52H0235-006 sample from near Venlo). This is quiet remarkable when we assume that the groundwater originates from infiltrated old rain water: they are enriched in SO_4 as indicated by the negative values for R-SO_4. Dissolved methane is near or below the detection limit of 10 µg/l. Oppositely, the samples from northern Netherlands and the one from Gelderland show mostly complete SO_4 reduction and intermediate to high CH_4. The highest detected CH_4 concentration of 7600 µg/l equals a partial gas pressure of 0.26 atm. This is equal to the lower criterium set by Fortuin and Willemsen (2005) for CH_4-rich groundwater as observed by them down to 81 m-surface at most in the Netherlands. The high CH_4 concentrations observed in this study at depths of 250-350 m are thus rather exceptional and it is interesting whether this CH_4 has a thermogenic or biogenic source. The related $\delta^{13}C$ values for DIC vary between -6.77 and -16.78 ‰. Methanogenesis will result into values close or above zero, which values have been observed for groundwater down to 100 m-NAP in the western Netherlands (Beekman, 1991). The lowest values now observed do not indicate methanogenesis and the highest values might be impacted by methanogenesis but dissolution of marine carbonate (typically having values around 0‰) may also explain such values. The samples for western Brabant and the deepest screen near Venlo show complete or near-complete SO_4 reduction and low to intermediate CH_4 concentrations. The dichotomy between the low Cl samples in Limburg and the other samples is also reflected in other compounds:

- Fe is often above 3.5 mg/l for the first and below for the last,
- DOC is mostly below 1 mg/l for the first and above for the last,
- NH_4 is always below 0.25 mg/l for the first and above for the last,
- pH is around 6.7-6.8 for the first and varies from 6.8 to 8.2 for the last.

Additionally, all samples are supersaturated for siderite, $FeCO_3$, except two that are undersaturated and one that is saturated. These three samples also have the lowest Fe concentrations. All samples are undersaturated for gypsum so equilibrium for this mineral does not play a role. The CO_2 partial pressure varies between $10^{-3.0}$ to $10^{-1.2}$ atm. Here, the highest partial pressures are associated with the lowest pH's, which are mostly found in middle Limburg. One saline sample (B52H0235-007) contained 12 mg NO_3/l, which must be an artefact.

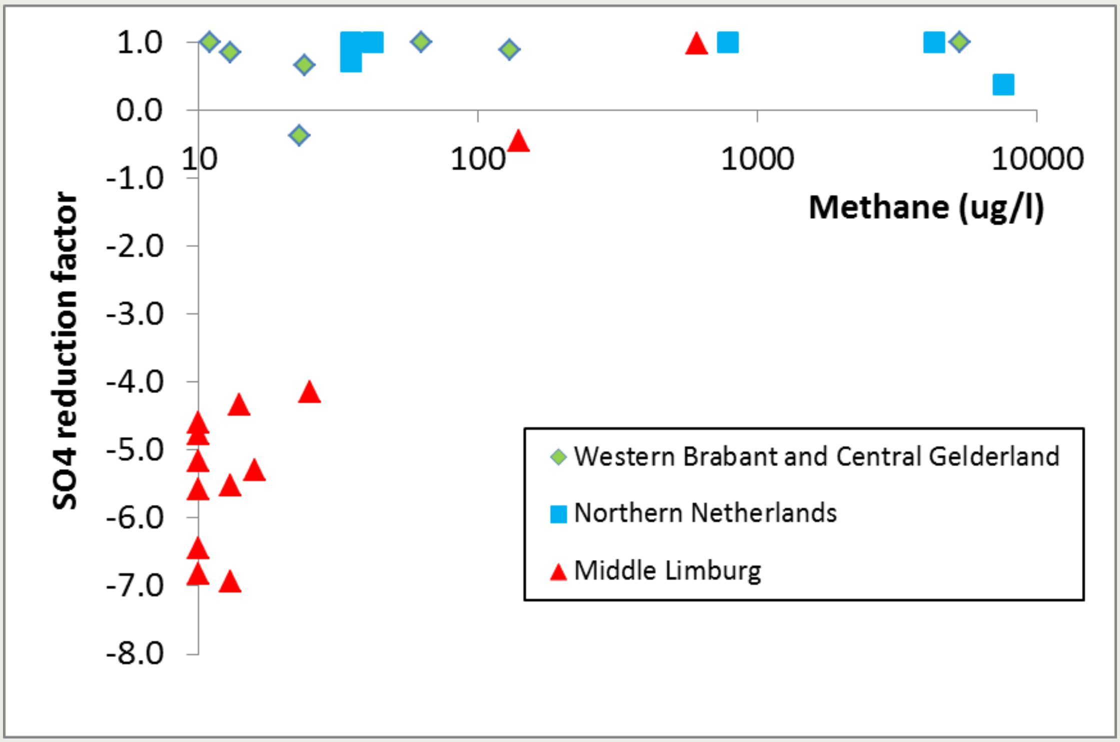


Figure 4-2. The SO_4 reduction state of the samples versus the dissolved CH_4 concentration, where the detection limit for the latter was 10 µg/l.

4.2. Deep groundwater above the Boom Clay

4.2.1. Major composition

Figure 4-3 shows concentration-depth profiles for wells that have multiple screens in the Breda or related Formations. Some of the screens characterised by Huurdeman (1986) are now considered to be present in the related marine Pliocene Oosterhout or Early Pleistocene Maassluis Formations. Such samples were not discarded for further interpretation. The concentrations range from a few mg/l in, in particular, Limburg to over 10,000 mg/l near Den Bosch, Luijksgestel and Haaksbergen. The concentrations do never exceed the seawater concentration of 19,000 mg/l. It is clear that the fresh/brackish - saline interface lies often within the Breda Formation. This means that the salinity of groundwater above the Boom Clay may vary strongly in vertical direction.

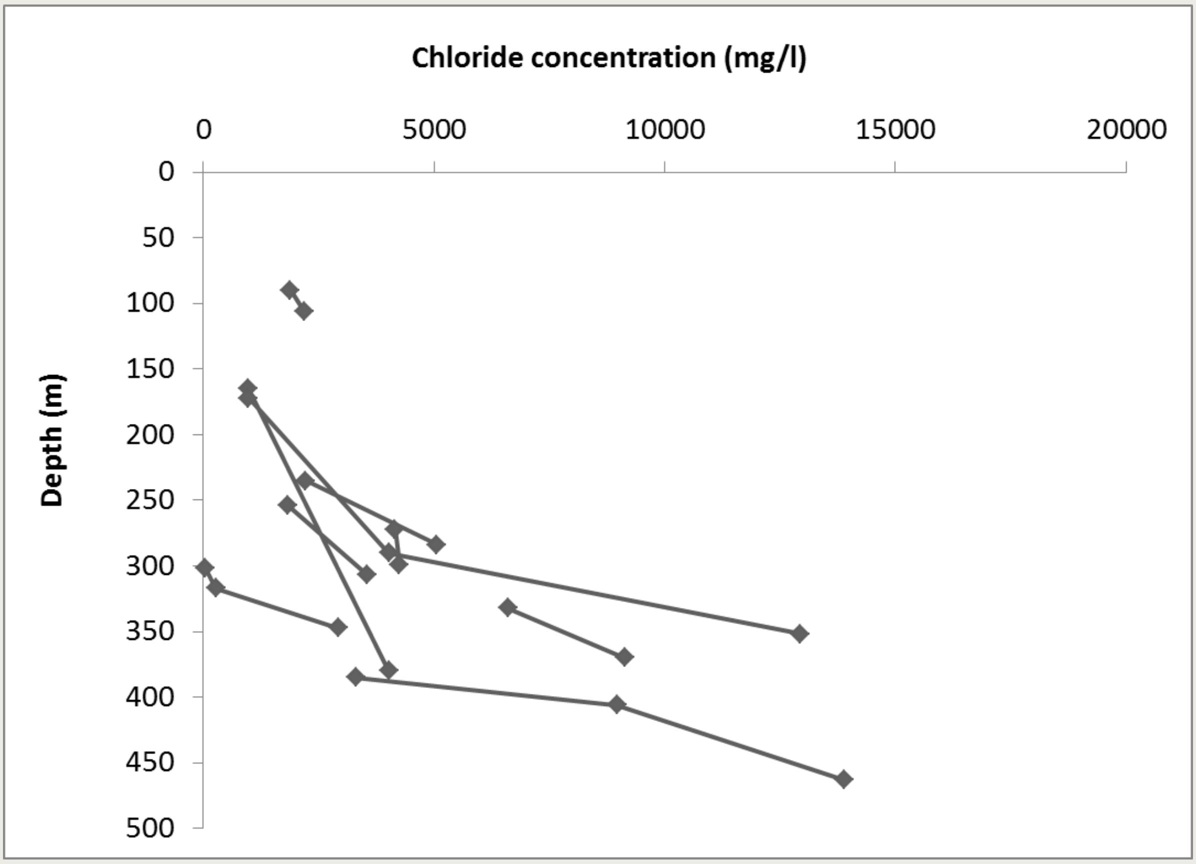


Figure 4-3. Depth profiles of the Cl concentration for wells in eastern and southern Netherlands that have multiple screens in the Breda Formation (or comparable Pliocene/Early Pleistocene marine formations; data obtained from Huurdeman, 1986).

The results for the newly collected samples fit well among the series of analyses as retrieved from the DINO database for the four regions studied (which locations are presented in Fig. 2-4). The hydrogeochemistry of the regions will now be discussed along main lines (Table 4-1). Deep groundwater in Middle Limburg typically has a low Cl concentration and it is frequently undersaturated for calcite (Fig. 4-4). The origin will thus be meteoric and only one sample reaches a Cl concentration above 1000 mg/l. The groundwater is saturated for siderite, few analyses indicate SO_4

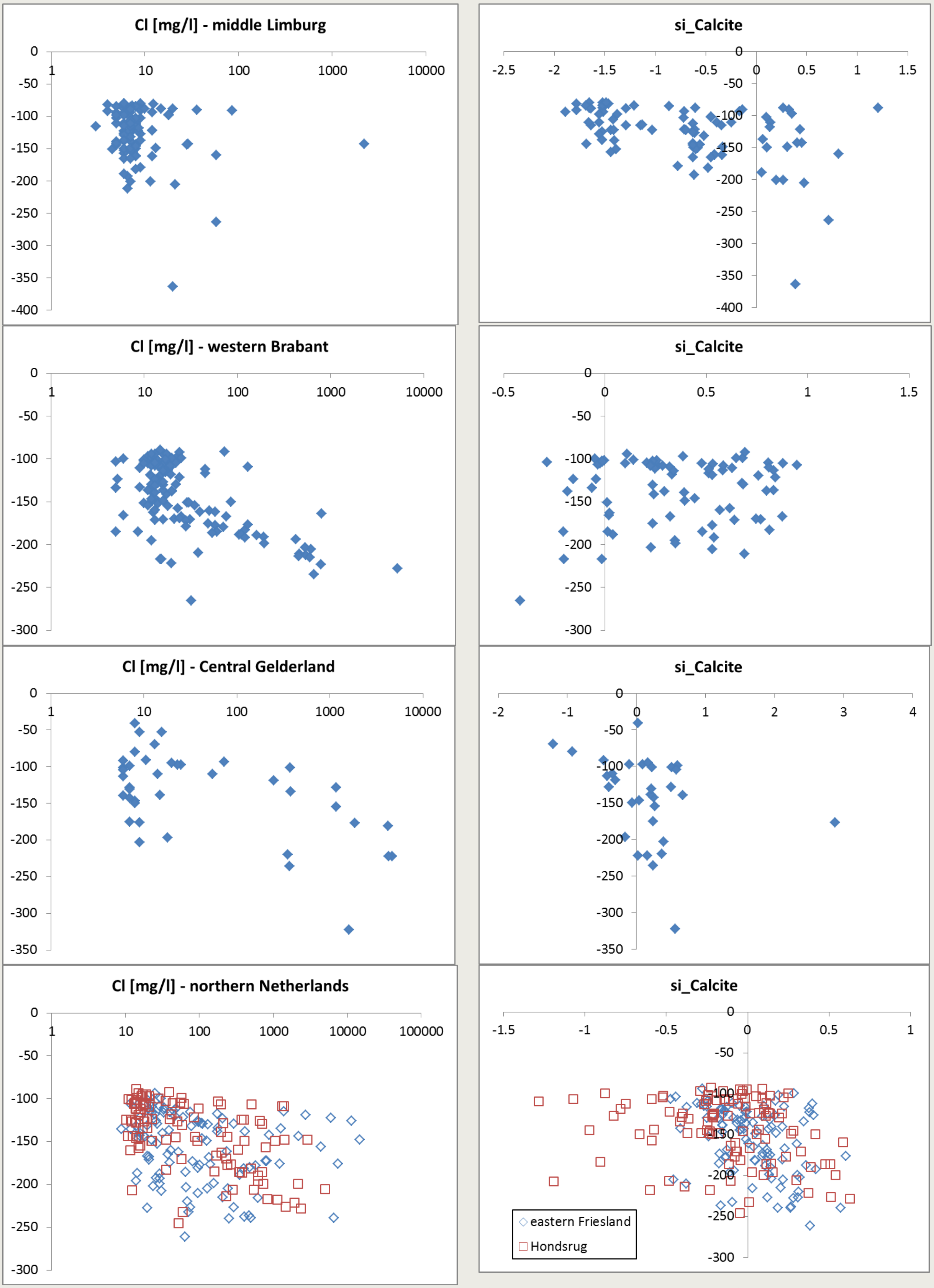


Fig. 4-4. Chloride concentration and saturation index for calcite versus depth (in m+NAP, meters relative to sealevel) for deep groundwater in the four regions studied.

below detection limit, NH_4 is mostly present in low concentrations around 0.1 mg/l, Fe is present in concentrations around 2.5 mg/l and the log value of the CO_2 partial pressure varies around -2.0. Fig. 4-5 show that for the fresh samples a strong linear relationship exists between Ca and alkalinity with an equivalent ratio of 1.2 between alkalinity and Ca. The equivalent ratio becomes 1.0 when Mg is included which brings forward that dissolution of a Mg-rich Ca-carbonate controls alkalinity, Ca and Mg for these samples. The Ca-carbonate must be sparsely present because no calcite saturation is reached for most groundwater samples even down to 200 m depth. The data points that lie to the right of this Ca/alkalinity relationship often have a higher Cl concentration. The enrichment in alkalinity is associated with an enrichment in Na versus Cl, which indicates a freshening of the aquifer with displacement of the more brackish groundwater by fresher groundwater and associated cation-exchange between Ca and Na.

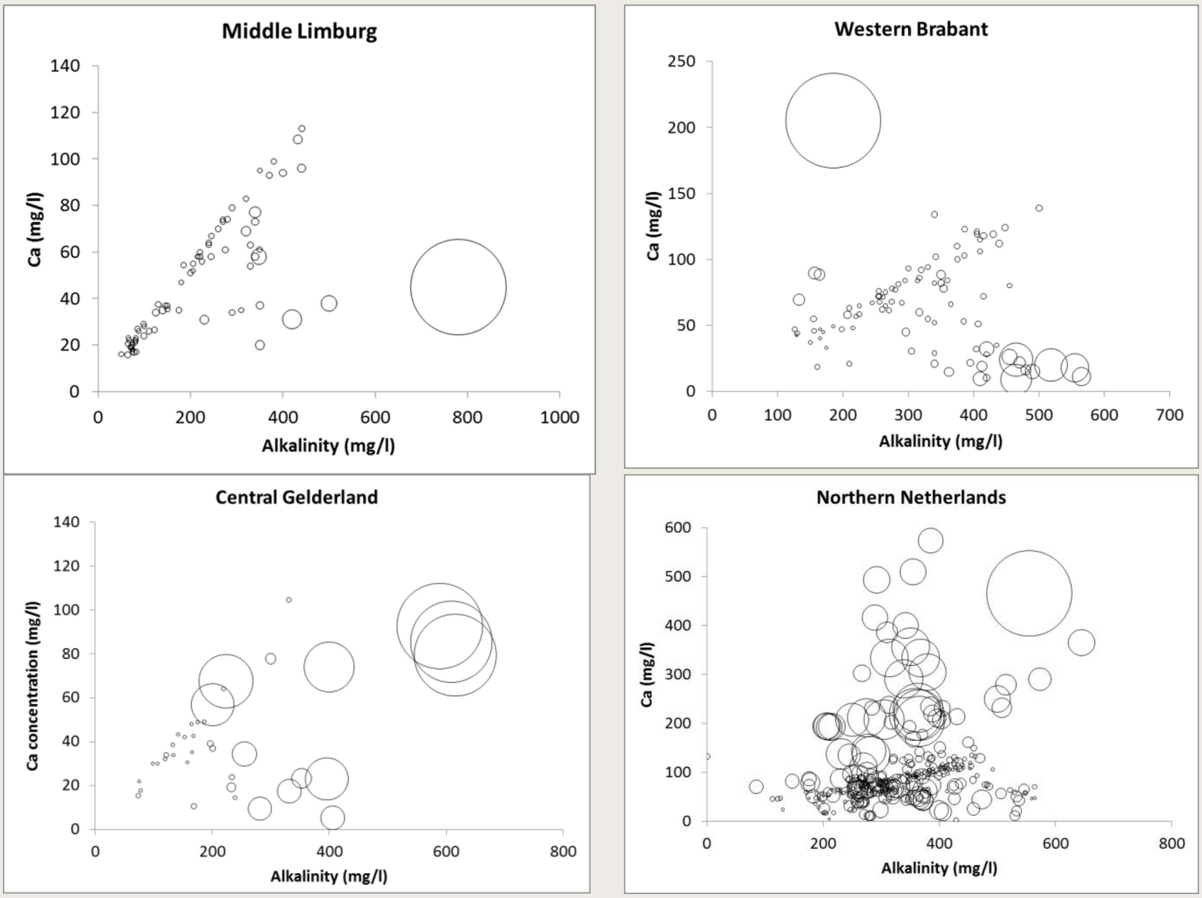


Fig. 4-5. Bubble plot of Ca versus alkalinity for the four regions studied where the radius indicates the Cl concentration. Note the different axes and the differences in maximum Cl concentration, as illustrated in Fig. 4-4.

Deep groundwater in western Brabant is mosly fresh but brackish groundwater is also frequently found (Fig. 4-4). A relationship with depth is present. It is typically supersaturated for calcite and siderite and the CO2 partial pressure of around $10^{-2.5}$ atm is relatively low (Table 4-1). Strong SO4 reduction has happened in many cases, and Fe and NH4 are elevated. Many samples plot along a single line, which indicates the carbonate dissolution line. A series of samples often having higher Cl concentrations, lie to the right of this line and a smaller series to the left. These sampling points indicate cation-exchange processes during groundwater flow. The samples to the right are subject to freshening of the aquifer (Na,Mg-HCO3 type) and those to the right (incl. the most saline sample having 5250 mg Cl/l) are subject to salinisation (CaCl2 type). Groundwater in Central Gelderland is about the same, but a few distinct differencs exist.

First, brackish and saline groundwater is more frequently found: the 75-percentile is higher and more samples are found that contain more than 1000 mg Cl/l. All samples that deviate from the carbonate dissolution line lie to the right of it, i.e., freshening is dominant. Saturation for calcite or siderite is less common and so is intense SO4 reduction. The subsurface in this region is thus less reactive than in western Brabant. The presence of brackish or saline groundwater points to mixing of meteoric water and seawater.

Table 4-1. Statistical data (p is percentile) about the composition of groundwater in Pleistocene and Neogene aquifers and deeper than 100 m for the regions studied (in mg/l for the dissolved compounds).

	Cl		SO4		Fe		NH4	
	p25	p75	p25	p75	p25	p75	p25	p75
Middle Limburg	6.0	9.5	5.0	12.0	0.95	3.4	0.05	0.18
Western Brabant	13	34	1	7.7	0.74	4.23	0.43	0.84
Central Gelderland	7.3	364	3.3	13.8	0.14	0.73	0.14	1.4
Eastern Friesland	24.8	238	< d.l.	2	2	11	0.8	2.0
Hondsrug area	17	377	.8	6.3	2.2	6.8	0.49	1.92
	pH		Log(P_{CO2})		SI(calcite)		SI(siderite)	
Middle Limburg	6.9	7.5	-2.30	-1.77	-1.52	-0.05	-0.22	0.53
Western Brabant	7.6	8.1	-2.67	-2.20	0.06	0.64	0.60	1.30
Central Gelderland	7.7	8.1	-3.04	-2.47	-0.14	0.39	-0.17	0.64
Eastern Friesland	6.9	7.4	-1.93	-1.48	-0.14	0.19	0.56	0.99
Hondsrug area	7.1	7.6	-2.24	-1.66	-0.28	0.11	0.54	1.03

In northern Netherlands, saline and brackish groundwater is much more frequently found. A relationship with depth is not clear as down to 250 m depth the complete range from 10 to about 10,000 mg Cl/l is found. The highest Cl concentration of 14,635 mg/l is not far from the seawater concentration of 19,000 mg/l. Groundwater is mostly saturated for calcite and siderite, but undersaturation for calcite frequently happens. Reduction of SO_4 has been intense with the majority of the samples close to or at complete SO_4 reduction. The NH_4 and Fe concentrations are the highest compared to the other regions. The reactivity of the subsurface is thus high with respect to redox processes whereas this is not self-evident for calcite dissolution. The carbonate dissolution line can be recognised for the groundwater data set but many samples deviate from this relationship in both directions. Both freshening and salinisation are thus on-going processes, where salinisation is more frequent for more brackish or saline groundwater as depicted by the larger circles in the lower right graph of Fig. 4-5. The samples at the carbonate dissolution line are mostly associated with eastern Friesland and not Hondsrug area. The overall data suggest mixing between meteoric and seawater although a contribution by subrosion, i.e., dissolution of NaCl from salt diapirs in groundwater, cannot be ruled out. The latter is more intensively discussed in the next section on groundwater under the Boom Clay.

4.2.2. Iodide and selenium in Dutch groundwater

For groundwater above the Boom Clay, the data on iodide are plotted in Figure 4-6 against chloride together with that of Br. The Br data clearly show that all samples plot along the seawater dilution line, which indicates that Br has a seawater origin and the concentration is determined by mixing (in the subsurface or not) between the end members rain water and seawater. No significant subsurface source or sink is indicated. The data for I are entirely different. The concentrations range from less than 1 to over 1000 µg/l. There is an overall correlation with chloride, but the highest I concentrations are more than one order of magnitude higher than the seawater concentration of 60 µg/l. The behaviour of I can thus not be set equal to that of Br.

Unfortunately, the detection limit of 50 µg/l for the current, new data is high when compared to the concentration range encountered in groundwater. Stuyfzand’s data on groundwater in the coastal dunes lie below the other data on relatively shallow groundwater in the South-Holland polder landscape (Engelen, 1969; Geirnaert, 1972) or deep groundwater in majorly the Pleistocene landscape (present data). Additionally, Krul (1933) presents graphical data on I in groundwater across the Netherlands within the framework of the endemic occurrence of goiter[a]. He observed that I is lowest in Pleistocene Netherlands and highest in the western Netherlands. A few exceptions exist at Zutphen and Elst that were coupled to the near-presence of (reworked) marine sediments.

Iodine happens as iodide, iodate and organic iodine in natural waters and their hydrochemical controls vary. Heymann (1925) performed a unique study on iodine in which he analysed its contents in shells, peat and clay as well as shallow and deep groundwater in the coastal dunes and the Gooi area. Here, he also determined the speciation of I in groundwater at three wells down to more than 100 m-NAP (Fig. 4-7). The data show increasing concentrations with depth and variable ratios between organic and inorganic iodine. It is generally accepted that iodine in groundwater majorly originates from degradation of predominantly marine plants as the related organic compounds contain iodine, although the potential role of carbonates has often been overlooked (Heymann, 1925; Krul, 1933; Geirnaert, 1972; Claret, 2010; Li et al., 2014). The present investigation confirm this observation since an overall correlation with chloride is found and groundwater chloride is also coupled to the presence or neighbouring presence of marine sediments. The difference between shallow groundwater in the dunes versus deep groundwater or other areas may be explained by stronger leaching of the aeolian sands and/or lower presence of remains of marine plants or carbonates in these sands. Summarising, the I concentration in Dutch groundwater varies three orders of magnitude and a coarse relationship with salinity exists. The latter may be more due to the presence of marine sediments than the saline water itself.

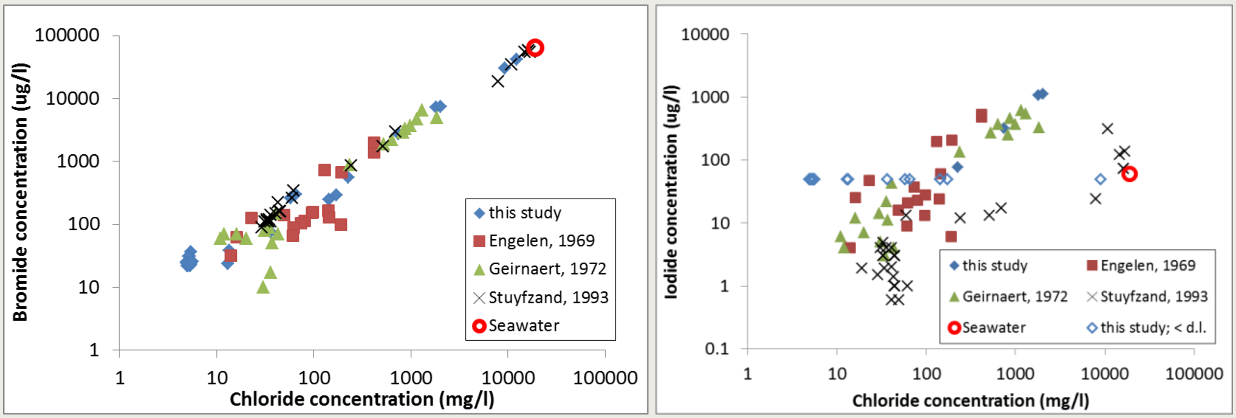


Fig. 4-6. The Br and I concentrations versus the Cl concentration for a several series of groundwater data sets and compared to the seawater composition.

---

[a] Goiter is a swelling in the neck just below Adam's apple due to an enlarged thyroid gland. The enlargement usually occurs due to a deficiency of iodine.

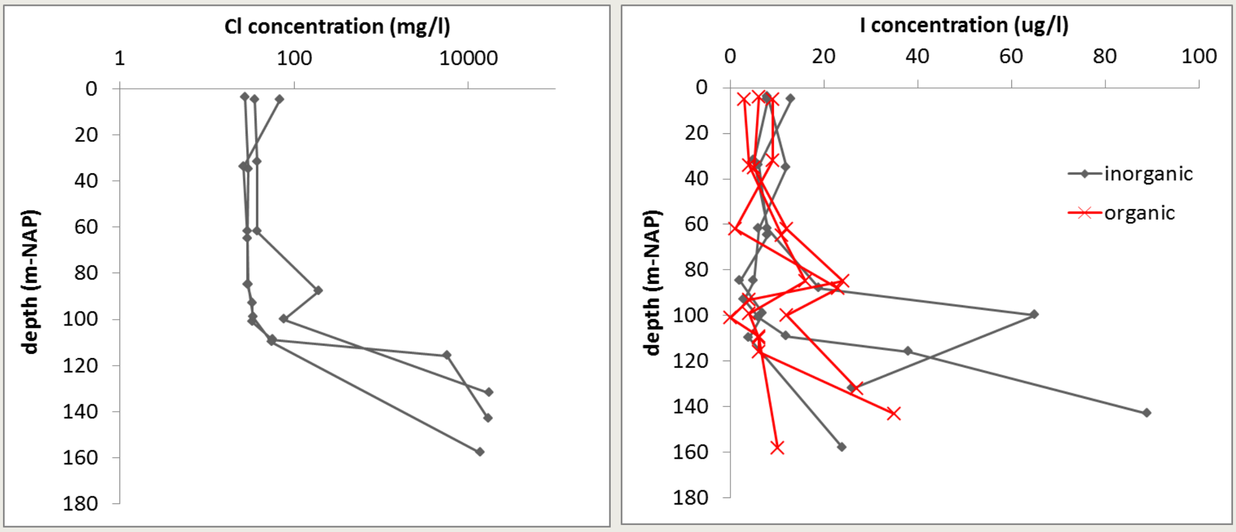


Fig 4-7. Depth profiles of Cl, inorganic and organic I concentrations in groundwater at three wells in the dunes near Leiduin (data obtained from Heymann, 1925).

The Se concentration in deep groundwater varies from below detection limit of around 0.01 µg/l to close to 0.6 µg/l (Fig. 4-8). The two highest concentrations are found in salt groundwater of the screens B50H0373-009 and B52H0235-007, which are several factors above the North Sea concentration. Different concentrations around 0.1 µg/l have been reported for the North Sea, which vary in a similar range as that for other open seas and oceans (Conde & Sanz Alaejos, 1997). The low-Cl samples from middle Limburg show a range in concentration from below detection limit to 0.034 µg/l. Stuyfzand's data on groundwater in the dunes indicate a similar concentration range as the data for the deep groundwater. Both series indicate no good correlation with chloride.

361 Se analyses for deep groundwater in middle Limburg are present in the DINO database. Most samples had a concentration below the high detection limits of 1 or 2 µg/l. Thirteen samples with Cl is 6 mg/l had a concentration of 1.5 or 2 µg/l and one sample with Cl is 29 mg/l had 6 µg/l. Five samples of deep groundwater from northern Netherlands contained a Se analysis. Three fresh samples had a Se concentration of about 20 µg/l and a fresh and a brackish sample had Se below 0.5 µg/l. For the latter data set one may wonder whether the unit shouldn't be ng/l instead of µg/l, when compared to the other available data. Meinardi et al. (2003) found an average concentration of 0.30 ± 0.12 µg/l for springs at the Veluwe. Finally, Fraters et al. (2001) observed that 77% of the screens of the national groundwater quality monitoring network (having its screens between 8 and 25 m-surface) had a concentration below the detection limit of 0.005 µg/l and the maximum was 0.056 µg/l.

Chemically, Se can be compared with S or As, which are in the periodic table immediately above it and to the left of it, respectively. Selenium happens as Se(-II), Se(0), Se(IV) and Se(VI) in aqueous environments and organic selenium compounds may exist in natural water in addition to inorganic solutes (Conde & Sanz Alaejos, 1997). Note that none of the studies mentioned above deals with the speciation of Se. The two major geochemical processes that cause mobilisation/immobilisation of Se are adsorption to oxides and incorporation in sulphides (Basu et al., 2007). Se(IV) as selenite sorbs more strongly to oxides than Se(VI) as selenate; it is also thermodynamically unstable but it persists for long times due to kinetic controls. As both sulphide production and reductive dissolution of Fe-oxides are operational in the groundwater environments studied, the differences in Se concentrations may be explained by different intensities of these geochemical processes. Summarising, the Se concentrations in deep groundwater typically vary between 0.004 and 0.1 µg/l with outliers to about 0.5 µg/l. The hydrogeochemical controls nor its speciation are clear for the Dutch situation.

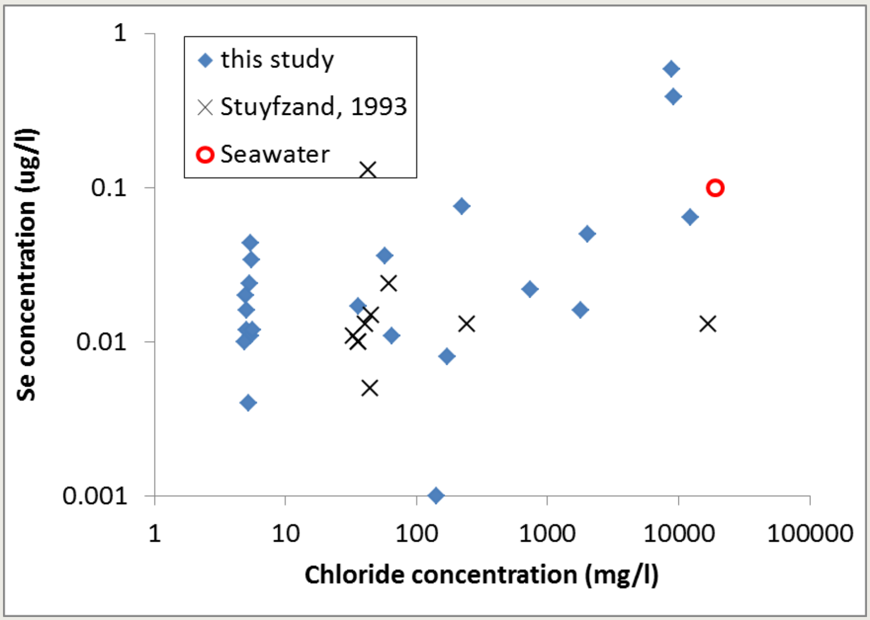


Fig. 4-8. Se concentration versus Cl concentration for two groundwater data series and compared to seawater.

4.2.3. Dating of deep groundwater

Radioisotope analysis of carbon-14 was performed for dating of the groundwater samples. Laboratory analysis of the activity of ^{14}C yields the ‘’apparent age’’ of groundwater, because the activity is determined of total inorganic carbon (TIC) and the TIC concentration is the result of all hydrogeochemical processes that have happened from the infiltration area to the monitoring point.For example, the carbon-14 signal from the infiltration area gets diluted by dissolution of dead carbon from carbonate minerals in the aquifer. A correction must be made to transfer the analysis from apparent age to true age. This may be very complicated depending on the hydrogeological settings and the supporting data present. It is common to combine carbon-14 analysis with stable carbon-13 analysis to verify the correction procedure from apparent to true age. This was also performed in this study.

The laboratory analysis indicate that 6 samples had a carbon-14 activity smaller than the detection limit of 2 PMC (percent modern carbon). This yields an apparent age of at least 32,000 years according to the following formula:

$$apparent\ age = \frac{-5736 \ln(\frac{analysis}{100})}{\ln 2}$$

where apparent refers to a calculation without correction for hydrochemical processes folowing infiltration in the subsurface and analysis refers to the measured ^{14}C activity of the sample in Percent Modern Carbon. Three of these samples were collected in western Brabant (incl. the two samples under the Boom Clay) and the other three close to Arnhem, close to Venlo and in Central Limburg. The fourth sample from western Brabant has a carbon-14 activity of 2.8 PMC, which is equivalent to an apparent age of 29,500 y. The interplay of the hydrogeochemical processes that control the carbon-14 activity is complicated for most of these samples, because mixing of fresh and saline groundwater, cation-exchange, redox processes and carbonate equilibria with calcite and siderite all play a role.

Besides, it is hard to determine when the individual processes did happen, which may affect the release of dead or radiogenic carbon from organic matter or carbonate minerals: radiogenic carbon may get mobilised from the sediment when the processes happen in the Holocene or Late Pleistocene sediments whereas all mobilised carbon will be dead carbon when the processes happen in Middle Pleistocene and older sediments. The correction for these processes is thus also hard without additional insights on the evolution of the groundwater composition along the groundwater flow paths and isotopic information about the reactive components encountered.

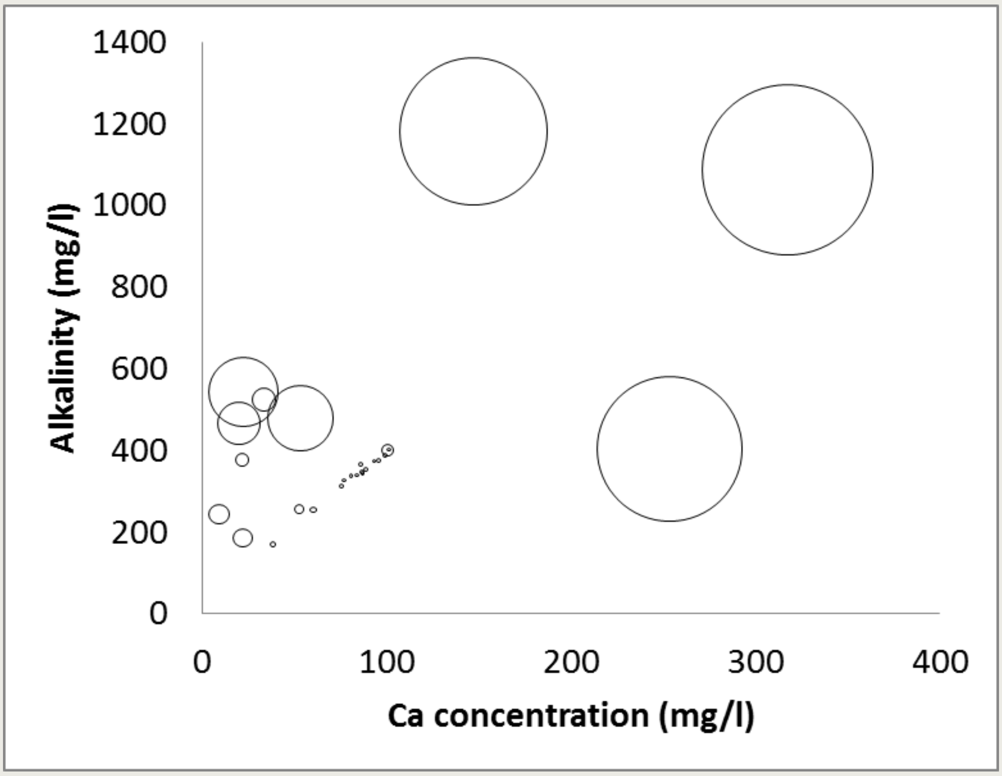


Figure 4-9. Bubble plot of Ca versus alkalinity for the 26 new analyses, where the radius indicates the Cl concentration (max. is 12,321 mg/l).

The other 19 samples were considered for further correction from apparent to true age. Twelve of these samples originate from middle Limburg, 1 from northern Limburg and 6 from the northern Netherlands. The hydrogeochemistry of these samples is more simple, partly due to the fact that all these samples are fresh with at most 1% seawater contribution (Fig. 4-9). Most of these samples are also undersaturated for calcite and dolomite and subject to freshening, which implies that precipitation of Ca-carbonate and related isotope fractionation does not play a role. All samples except two are, however, supersaturated for siderite; the role of siderite precipitation/dissolution was further neglected in the calculations because the Fe-concentration are low and the nature of this process is not straightforward. The following hydrochemical reactions were considered:

$H_2CO_3 + Ca_xMg_yCO_3 \leftrightarrow x\,Ca^{2+} + y\,Mg^{2+} + 2\,HCO_3^-$
$2\,CH_2O + SO_4^{2-} \rightarrow 2\,HCO_3^- + H_2S$
$2\,CH_2O \rightarrow H_2CO_3 + CH_4$
$CaCO_3 + (Na_m,Mg_nK_p)\text{-}X_2 \leftrightarrow Ca\text{-}X_2 + m\,Na^+ + n\,Mg^{2+} + p\,K^+ + CO_3^{2-}$ with $½m+n+½p = 1$

Next, molar mass-balances for the aqueous carbonate system can be stoichiometrically determined from the concentrations of Ca, Mg, Na, SO_4 and CH_4. Combined with the Cl concentration, the deviations of Na, Mg and SO_4 from the seawater dilution line are used to determine the extent of cation-exchange or SO_4 reduction. Further, extent of carbonate dissolution is calculated by means of Ca and remaining Mg, where it is assumed that H_2CO_3 as reactant originates from organic matter and $Ca_xMg_yCO_3$ as reactant is marine carbonate.

Thus, the mass balance for alkalinity is:

$$\text{alkalinity} = 2^*(Ca)_{carb} + 2^*(Mg)_{carb} + Ca\text{-}X_2 + 2^*(SO_4)_{OrgM}$$

where (x) refers to the molar concentration of compound x, $Ca\text{-}X_2$ refers to the amount of Ca-carbonate dissolution that balances cation-exchange of Ca versus Na, Mg and K due to freshening of the aquifer (no salinisation is observed for these samples), and subscripts carb and OrgM refer to alkalinity production by Ca,Mg-carbonate dissolution and mineralisation of sedimentary organic matter, respectively. The data-set contains a series of samples from majorly middle Limburg with a pH between 6.5 and 7.0 and thus a substantial amount of dissolved $H_2CO_3^*$ in addition to HCO_3^-. Mass balance calculations show that this concentration cannot be explained by methanogenesis. A necessary assumption was therefore to introduce extra $H_2CO_3^*$, that was calculated as follows:

$$TIC_{sample} - \text{alkalinity} - (CH_4)_{OrgM} = H_2CO_3{}^*{}_{extra}$$

where subscripts sample and extra refer to the groundwater sample and the extra amount of non-alkalinity TIC present in the sample. We assume that the extra amount of non-alkalinity TIC originates from organic matter. The $\delta^{13}C$ values of the source materials were assumed to be -25‰ for organic matter under non-methanogenic conditions, +10% for carbonate from organic matter during methanogenesis and +1‰ for Ca-carbonate. The related values for ^{14}C activity were 0 PMC for carbonate from Ca,Mg-carbonate dissolution, 100 PMC for carbonate originating from mineralisation of organic matter in the infiltration area and 0 PMC for carbonate originating from anaerobic degradation of organic matter in the subsurface in association with SO_4-reduction or methanogenesis.

The results are presented in Fig. 4-10: the modelled and analysed $\delta^{13}C$-values do not match well for 7 out of the 22 samples. Five of these samples lie in the northern Netherlands. The model is thus erroneous for these samples and these samples show elevated methane concentration, cation-exchange and/or calcite saturation. Two more samples from Brabant do not match on alkalinity, where a difference between analysed and modelled value of more than 5 meq/l was noted. The remaining 13 samples show satisfactory agreement on $\delta^{13}C$ and alkalinity, which all lie in middle Limburg except one. The true age was calculated from the apparent age taking into account the established model. The sample outside obtained a negative true age, so the model established is incorrect and the model was rejected for this sample. As expected, the results for the remaining samples from middle Limburg show that true age is always younger than apparent age and varies from 1,117 to 6,894 y. The results also indicate that on average the age increases with depth (Fig. 4-11). The isotopic model of carbon was rejected for five samples from the northern Netherlands. It is, however, worth comparing the apparent ages of the four samples from the two wells that lie within 5 km from each other (Enclosure 1). The two sampled screens of B12E0266 which are located in the glacial gully have apparent ages of 7160 and 7370 y, whereas the two sampled screens of B12G0119, which are located in the Oosterhout and Breda Formations have apparent ages of 3095 and 4140 y. The latter have Cl concentrations of about 13 mg/l and the first of 143 and 171 mg/l. These data suggest that mixing with old, marine groundwater plays a role for the first but not for the latter.

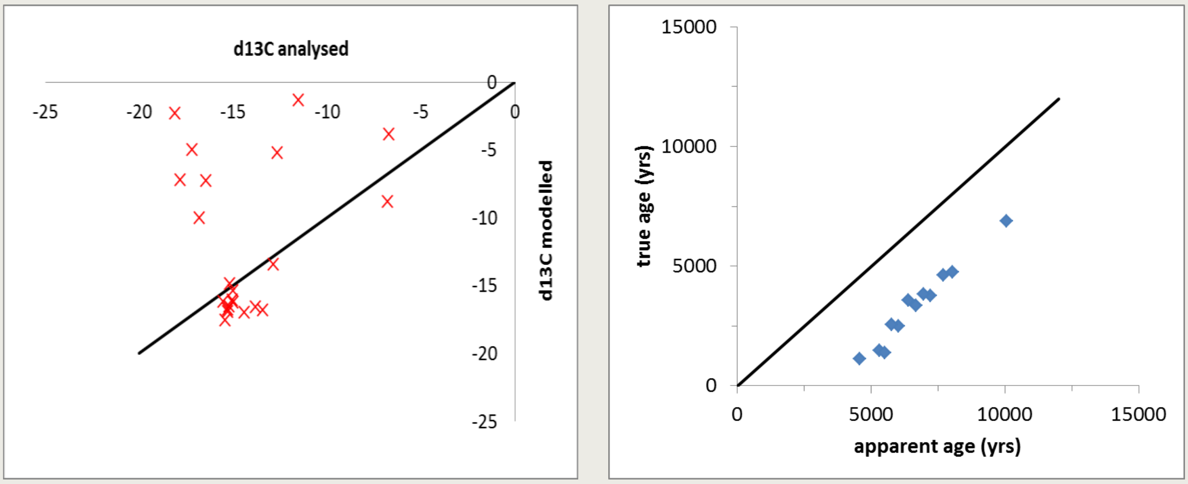


Fig. 4-10. Results for the isotopic modelling of the carbonate chemistry of those samples that have a ^{14}C activity above the detection limit of 2 PMC. The seven samples that are not close to the 1 to 1 line for δ^{13}C (left graph) were not considered for ^{14}C modelling and thus not plotted in the right graph.

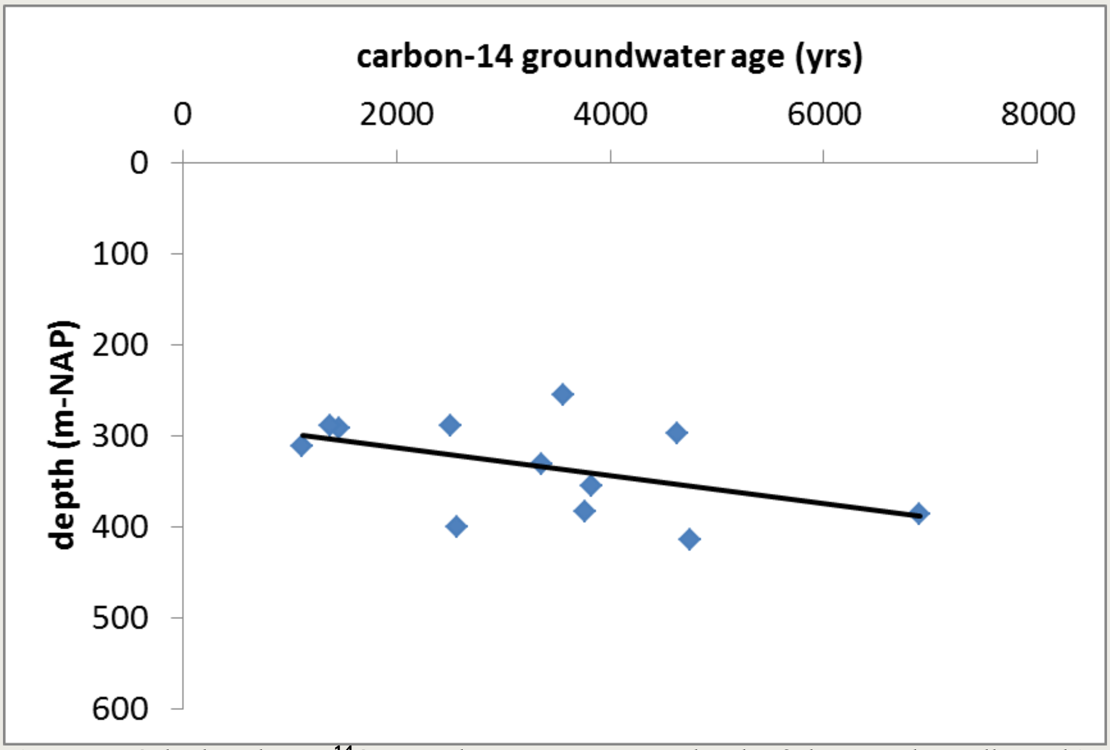


Fig. 4-11. Calculated true ^{14}C groundwater age versus depth of the samples collected in middle Limburg with the linear regression line. Sample B58G0191-005 at 510 m-NAP is not plotted, which has an apparent ^{14}C age larger than 32,000 y.

4.3. Groundwater under the Boom Clay

The quality data available for groundwater under the Boom Clay can be clustered into three groups: 1. data on formation waters in oil and gas reservoirs below 900 m depth (‘’reservoirs’’ from Permian to Lower Cretaceous age), 2. data on shallow (< 100 m) to deep (> 400 m) groundwater in southern Limburg and the Belgium Kempen region, where Cretaceous and older sediments lie close to or at the surface and 3. other data on groundwater several hunderds to appr. 1500 m depth in mostly western Brabant and middle Limburg (‘’deep buried aquifers’’ from Devonian to Paleogene age).

Within the framework of potential disposal of radioactive waste in the Boom Clay, the third group is most relevant when it concerns Paleogene or Upper Cretaceous aquifers. For sake of completeness, all publicly available information is summarised here. The complete information provides best insights in the variability in groundwater composition in Paleogene and older formations.

Figure 4-12 shows a plot of the chloride versus sodium concentration. The seawater composition and brine as observed close to the Permian salt diapir in Gorleben, Germany (Kloppmann et al., 2001), are also plotted. The reservoirs in South Holland, Broad Fourteens basin (which lies off the coast of North-Holland and is southeast-northwest oriented) and northeastern Netherlands have Cl concentrations above 40,000 mg/l, i.e., more than twice as high as seawater. Water containing such high Cl concentrations will henceforth be referred to as hypersaline. The highest concentrations observed equal the Cl concentrations close to the salt dome in Gorleben. Groundwater in the relatively shallow Belgian Rupelian aquifer and the Carboniferous aquifer in southern Limburg shows variable Cl concentrations from around 10 mg/l to 3300 or 15,000 mg/l (except one outlier), respectively. Fresh groundwater is thus present when the pre-Miocene units lie close to the surface. This is illustrated in Fig. 4-13 for groundwater in the Carboniferous unit in southern Limburg, where a shallower, fresh and a deeper, saline groundwater type can be recognised. The Cl concentrations for the four Belgian wells in the Paleogene aquifer and close to the border vary considerably from 95 to 3357 mg/l, which implies that the fresh/saline interface in groundwater immediately below the Boom Clay does not match regionally with the Dutch/Belgian border. For the third groundwater data group (majorly from Cretaceous and Paleogene aquifers in Brabant and middle Limburg), the concentrations range from about 300 mg/l to 30,000 mg/l (except one low Cl sample). Here, the highest concentration exceeds the seawater concentration less than a factor 2.

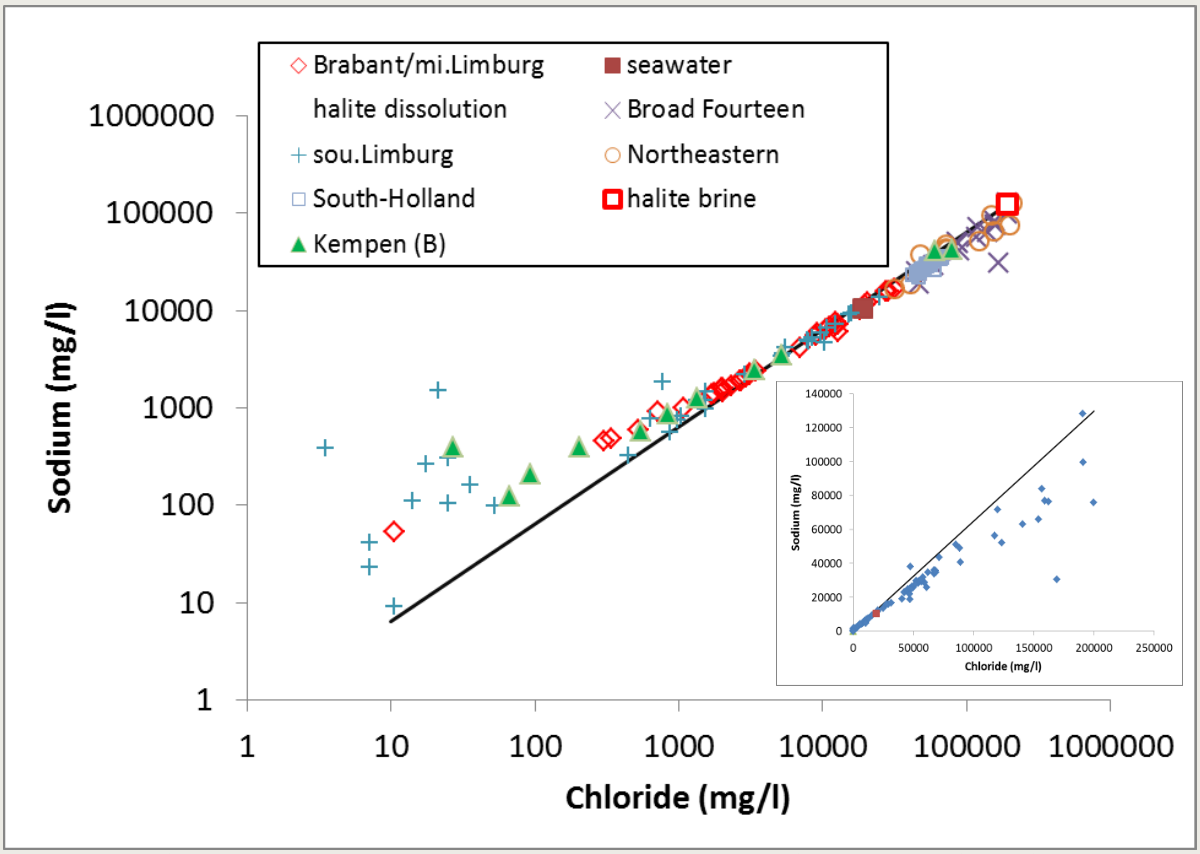


Fig. 4-12. Chloride versus sodium concentration plot for groundwater in geological units of Oligocene and older age. The line is the halite dissolution line.

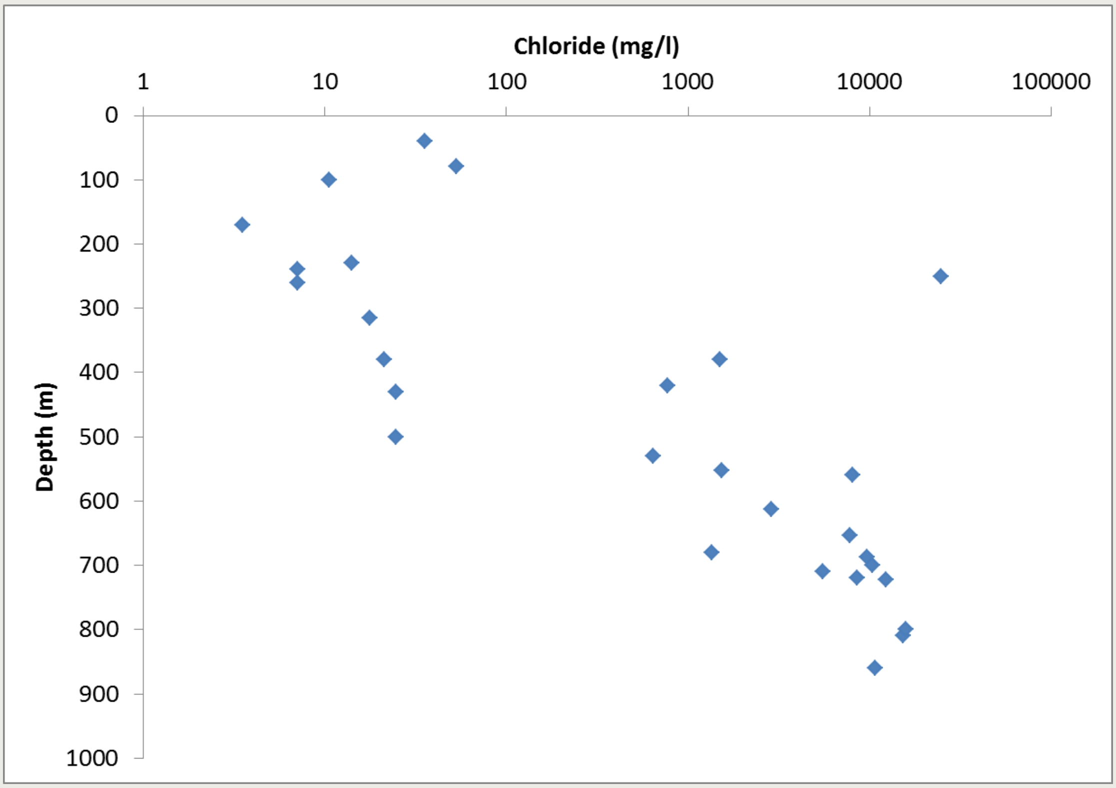


Fig. 4-13. Chloride concentration versus depth for groundwater in the Carboniferous unit in southern Limburg (data obtained from Kimpe, 1963).

Groundwater having more than 70,000 mg Cl/l has only been encountered in the northeastern Netherlands and deep (> 2800 m) reservoirs in Broad Fourteens basin, except for one sample from the Carboniferous Limestone Group at 2250 m depth in Turnhout (B), having 80,300 mg Cl/l. No such hypersaline water has been observed elsewhere in the southern part of the Netherlands including the reservoirs at about 900-1800 m depth in South-Holland. Verweij (2003) attributes this to a combination of two reasons: 1. absense of major halite deposits in this part of the country and 2. meteoric flushing during Tertiary and Quaternary times. Figure 4-14 shows the distribution of Permian Zechstein salt in the Netherlands. This is the most widespread and thickest halite deposit in the Netherlands. Halite deposits are also known for the Triassic Röt, Muschelkalk and Keuper Formations and Late Jurassic Weiteveen Formation (Geluk et al., 2007). The distribution is most widespread for the Röt Formation and overlaps considerably with that of Zechstein salt (Geluk, 2007). The Muschelkalk Evaporite Member also contains halite more southward than the Zechstein (Fig. 4-14): local occurrences are found in the West Netherlands basin and in the Roer Valley Graben. The depth of the latter is more than 2000 m and likely of small relevance with respect to disposal of radioactive waste in the Boom Clay because it will likely be too deep. In Broad Fourteens basin, hypersaline groundwater is observed in both the Permian Rotliegend deposits below and the Lower Triassic or Lower Cretaceous deposits above the Permian Zechstein evaporites.

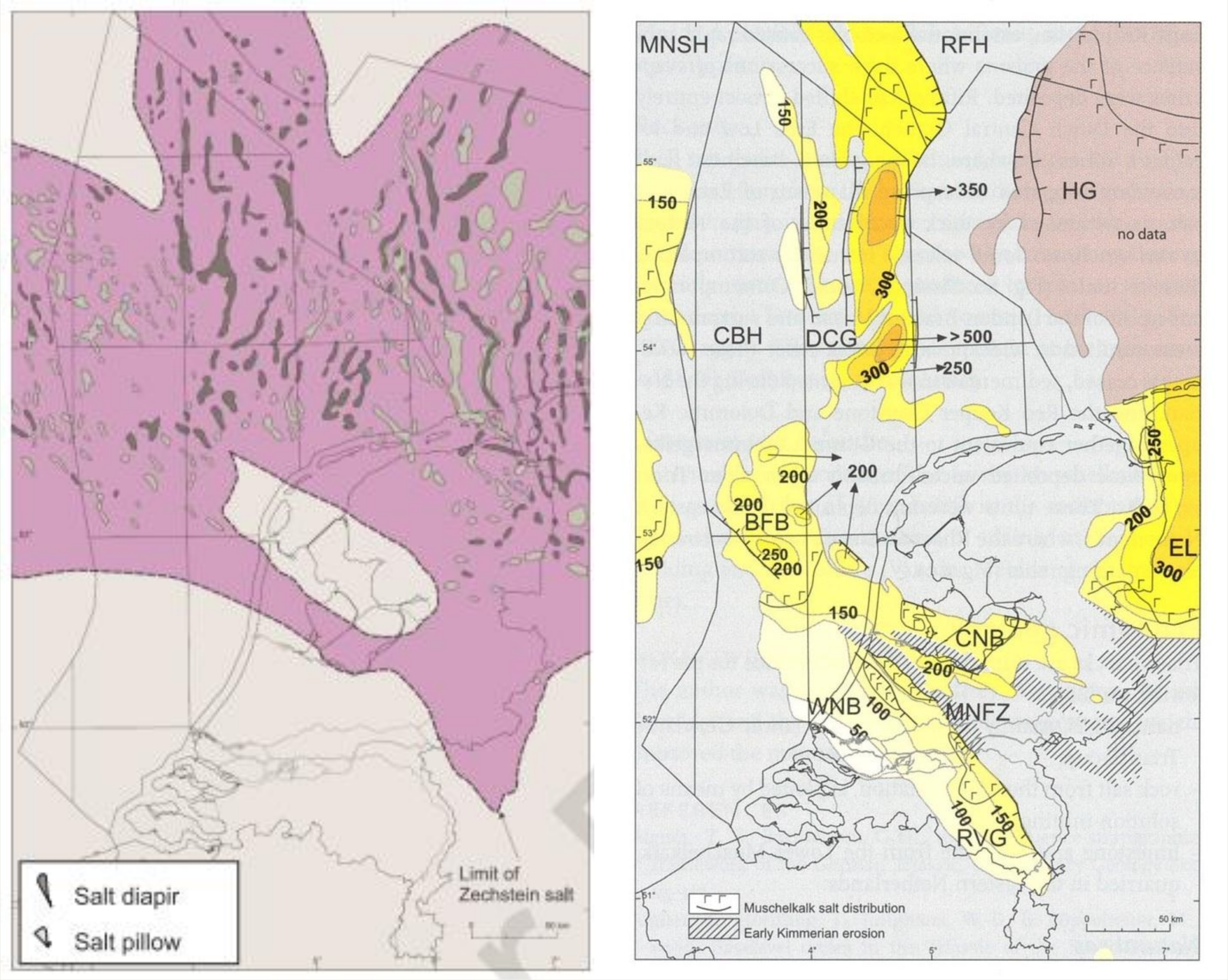


Fig. 4-14. Maximum distribution of Zechstein salt (left; derived from Verweij et al. 2011 and based on Lokhorst, 1998) and halite-bearing Muschalkalk (right; derived from Geluk, 2007) in the Netherlands.

The Cl to Br ratio may give a clue on the hydrogeological mechanism responsible for the brine compositions because this is equal to the seawater weigth ratio of 292 for brines as a result of evaporation, lower for interstitial water when precipitation of rock salt has happened and exceeds 1000 when natural rocksalt dissolves into alongflowing groundwater (Kloppmann et al., 2001). Kloppmann et al. (2001) observed Br concentrations of 55-65 mg Br/l for brines having 182,000-192,000 mg Cl/l in the vicinity of the Gorleben salt dome and around 20-25 mg Br/l for brines having 40,000-65,000 mg Cl/l. Two hypersaline Dutch samples from ‘’a salt diapir’’ fit in this picture (Fig. 4-15).

Unfortunately, no data on Br is present for the brines in the oil and gas reservoirs. No clue can thus be obtained on the origin of the brines from the Cl to Br ratio. δ^2H and δ^{18}O isotopic analyses of formation water are only present for four samples from South-Holland (Fig. 4-15; Van der Weijden, 1983): the data vary around -3 for δ^{18}O and -22 for δ^2H, which suggest a mixture between seawater and rain water. These samples have a Cl concentration close to 60,000 mg/l. Groundwater flow in the reservoirs is induced by either sedimentary loading or topography-driven flow (Verweij et al., 2003). Sedimentary loading will likely expel residual brines from the evaporite deposits and topography-driven flow may introduce fresh groundwater in the reservoirs aquifer under palaeoenvironmental and present conditions.

The palaeohydrological and diagenetic evolution of the reservoirs in the southern North Sea basin is very complicated and varies among the individual subbasins (Verweij et al., 2003; 2011; Gaupp & Okkerman, 2011). Diagenetic evidence exists that meteoric water has entered the Permian Rotliegend reservoir in the northern part of the Netherlands during Early Cretaceous, which has given rise to flushing of this aquifer (Lee et al., 1989). Paleohydrological evidence also exists that topography-driven flow could reach great depths in the Triassic and Lower Cretaceous reservoirs above the Zechstein evaporites during Late Cretaceous in the northern Broad Fourteens basin (Bouw & Oude-Essink, 2003). Evidence also exists that the Permian Rotliegend reservoir is overpressurised under present conditions, where the dregree of overpressurisation increases from southeastern to northwestern direction under the southern North Sea (Verweij et al., 2011). This suggests the presence of compaction-driven flow and absence of topography-driven flow under current conditions for this reservoir. The paleo-fluid movements are difficult to reconstruct: the situation is further complicated by the influx of groundwater and hydrocarbons from the deeper Carboniferous formations in the course of the palaeoenvironmental evolution of the Rotliegend reservoir (Gaupp & Okkerman, 2011). Whether residual brine is still present in this reservoir under the Zechstein evaporites cannot be ascertained based on the available hydrochemical data. Dissolution of rock salt, however, seems a plausible phenomenon for the reservoirs above the Zechstein evaporites.

Few data on Br is present for the regular groundwater aquifers. The data show that a series of samples lies on the seawater dilution/evaporation line, incl. the two samples from the drilling in Asten that have Cl concentrations above that of seawater (and around 100 mg Br/l). This brings forward evaporation of seawater prior to infiltration for this groundwater. The samples from the former Oranje Nassau mine, Arcen, Broekhuizenvorst, Nieuweschans and one more deviate from the Cl/Br seawater ratio (where all of them except the first originate from Paleogene aquifers). The Br concentration of 140 mg/l versus the Cl concentration of 71,500 mg/l for Nieuweschans is remarkable within this perspective. The saline nature of this groundwater just below the Boom Clay in the Dongen aquifer at 582 m depth has been attributed to rocksalt dissolution (Glasbergen, 1981). This should normally yield a lower Br concentration: in addition to an analytical error, dissolution in evaporated sea water or local presence of Br-containing salt that typically precipitate in the last evaporative stages, may explain this observation. Note that for the two samples from Nieuweschans as well as the four samples from South-Holland a mixture between rain water and seawater is indicated. The isotopic data of δ^2H and δ^{18}O vary around -25‰ and -3‰, respectively. This indicates that the fraction of rain water varied from one third to almost half. Alternatively, the Paleogene samples from Broekhuizenvorst lie on the GMWL but are somewhat heavier than recent average Dutch rain while the two Devonian and Carboniferous samples from Maastricht are somewhat lighter than average present-day rain and also fit well on the global meteoric water line. The latter implies a meteoric origin in a colder climate when rain and groundwater that originates from it were isotopically somewhat lighter than nowadays. This all indicates different hydrogeological origins of the groundwater (Fig. 4-15). This is a relevant finding within the framework of the disposal of radioactive waste in the Oligocene Boom Clay as it indicates different recharge mechanisms of these aquifers across the Netherlands.

Even less data is present for I, where all data plot above the seawater I/Cl ratio (Fig. 4-15). These groundwater samples are thus also enriched in I as the more shallow groundwaters studied for I above the Boom Clay (Fig. 4-6). The two groundwater samples from the Paleogene Rupel and Cretaceous Houthem Formations at Asten show high concentrations above 10 mg/l. The other few samples originate from the Paleogene Dongen aquifer at Nieuweschans (2.5/3.7 mg/l), the Devonian/Carboniferous aquifers in Limburg (0.07 – 1.3 mg/l) and the salt diapirs (1.3-12 mg/l). The two samples from the Paleogene formations suggest that the I concentration may be naturally high immediately below the Boom Clay.

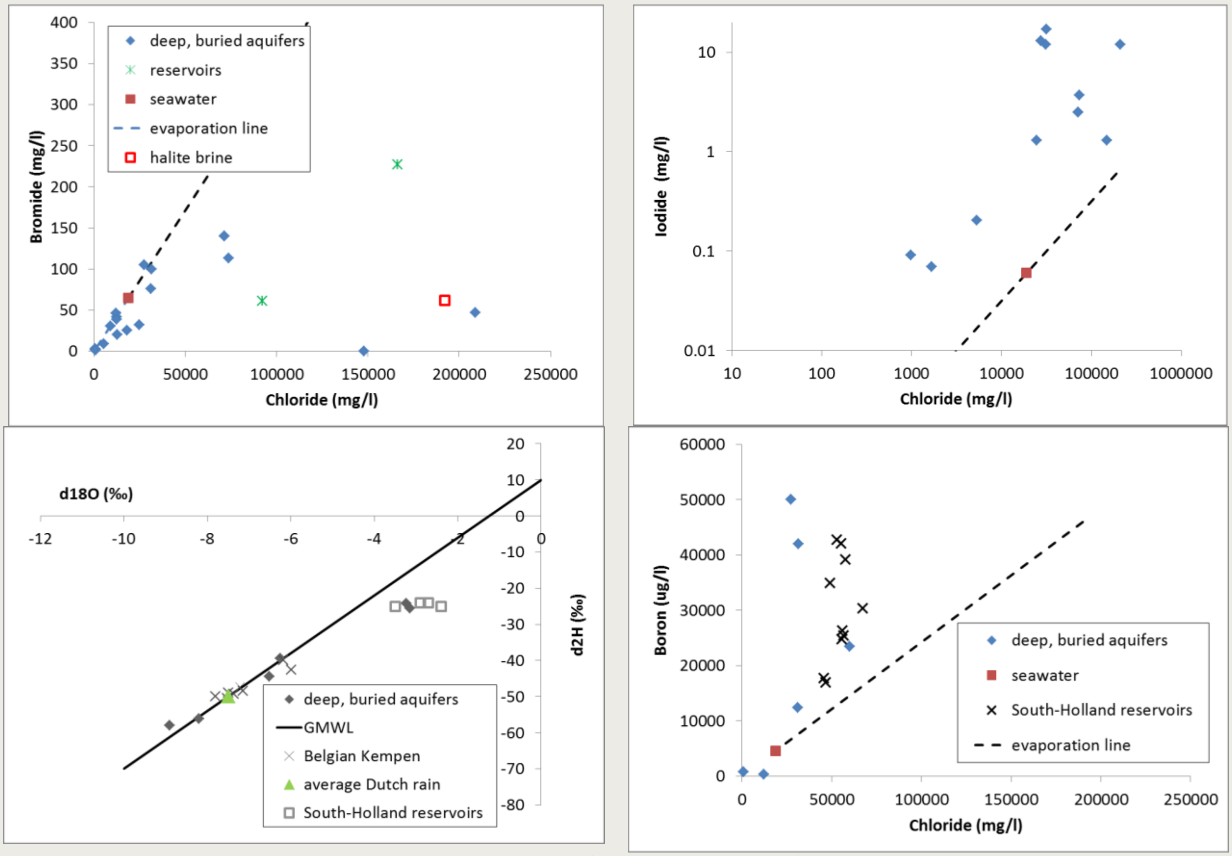


Fig. 4-15. Br, I and B concentrations versus chloride for groundwater under the Boom Clay together with the results of isotope analysis of H_2O in some saline groundwaters under the Boom Clay. The dashed line is the seawater dilution/evaporation line, the brown square represents seawater and the red open square represents halite brine according to Kloppmann (2001).

Figure 4-12 also shows that fresh groundwater is enriched in Na relative to Cl, the molar ratio is about 1 to 1 when Cl is between 2000 and 70,000 mg/l and may be depleted in Na relative to Cl above this concentration. Figure 4-16 shows concentrations plots for the four other main compounds versus Cl. Sulphate ranges from below detection limit to 2000 mg/l, except one outlier. This outlier may be meaningful as the electroneutrality condition for this sample is better when this analysis is included than when not. The highest SO_4 concentrations for fresh groundwater must be related to pyrite oxidation under open conditions in the Carboniferous unit in southern Limburg. The Ca concentrations outrange the SO_4 concentrations by far for the most saline brines, when dissolution of gypsum or anhydrite as evaporites is assumed to be the principal source. The brines in Broad Fourteens basin usually have 43 to 2620 mg SO_4/l (except the outlier), whereas the brines in South Holland or southern Limburg have repeatedly SO_4 below detection limit. It is also known that the natural gas may contain up to 7 ppm H_2S in the reservoirs at South-Holland (Core lab, 1987). This means that the gas is not classified as sour (criterium > 1% H_2S; Lokhorst, 1998) as happens in the Slochteren and Schoonebeek reservoirs (De Jager & Geluk, 2007). All SO_4 concentrations (except one) lie below that of both the seawater and the halite brine composition, i.e., the groundwater is always depleted with SO_4 compared to two end-member solutions. Reduction of sulphate is microbially mediated below 80°C and thermochemically above 100°C or even 160°C (Machel, 2001). To reach 100°C, the corresponding depth must be about 3 km as the thermal gradient is about 25°C/km in the first several hunderds meters below surface and increases to 30-35°C/km at larger depth in the Netherlands (Verweij, 2003). The gas and oil fields in South Holland lie at a depth of

900-1800 m with corresponding temperatures around 30-60°C. One may thus wonder whether thermochemical SO_4 reduction could have played a role for these reservoirs, which would imply that the reduction of SO_4 was microbially controlled or the pore water originates from deeper.

Near comparable patterns are observed for Ca, Mg and K: the data points lie above the seawater dilution line for fresh groundwater, a linear pattern is observed up to Cl concentration of 70,000 mg/l that lies above (Ca) or below (K, Mg) the seawater evaporation line and more elevated concentrations are observed for higher Cl concentration. The latter still remain below the seawater evaporation line for K and Mg. For the part of this data at Cl is around 50,000 mg/l, a near-linear relationship can be recognised that runs under (K) or above (Mg) the data point for halite brine. The Ca concentrations are substantially higher than the K or Mg concentrations for the most saline groundwater and also exceed by far the seawater and halite brine concentrations. Two mechanisms may give rise to brines in the oil and gas reservoirs of the North Sea basin and elsewhere: mixing with connate water expelled from evaporites under compaction that underwent evaporation beforehand (‘’residual brines’’) or dissolution of evaporite minerals as rocksalt. Egeberg & Aagaard (1989) attributed the brines in oil fields on the Norwegian shelf to the first and Verweij (2003), following Hanor (1994), attributed the brines in the Dutch Fourteen Basin and province of South-Holland to the latter. Bonnesen et al. (2009) also deduced for deep groundwater (having Cl concentrations up to 30,000 mg/l) in Upper Cretaceous Chalk at Zealand (Denmark) an origin from mixing between residual brine and meteoric water. Alternatively, Worden et al. (2006) found for a Triassic oil-bearing sandstone in the Wessex Basin (southern Engeland) that the high Cl concentrations around 120,000 mg/l must be explained by dissolution of Upper Triassic evaporites. Both mechanisms thus seem operational in northwestern Europe.

Speciation calculations using PHREEQC (Parkhurst & Appelo, 1999) indicate that only the most hypersaline solutions are supersaturated for halite (Fig. 4-17). This brings forward that the production of dissolved Na^+ and the immobilisation of Na^+ are spatially and temporally decoupled, because otherwise halite saturation could be maintained. The hypersaline groundwater is also saturated or supersaturated for anhydrite (Fig. 4-17; and also gypsum). Strong supersaturation with respect to calcite and dolomite is found for many samples, whereas the saturation state for siderite varies (Fig. 4-17). Precipitation of dolomite may play a role during diagenesis in the oil and gas bearing formations as the Rotliegend sandstone (Purvis, 1992; Gluyas et al., 1997; Gaupp & Okkerman, 2011), which is more unlikely in more shallow groundwater aquifers. Precipitation of siderite and calcite happens under many geochemical conditions.

The more disperse concentration patterns for the four major cations above 70,000 mg Cl/l versus below have been attributed to dissolution of halite with minor secondary reactions for Na below 70,000 mg Cl/l and important secondary reactions above. One mechanism that has been proposed is albitisation of feldspars in the reservoirs containing NaCl brine:

$$NaCl \rightarrow Na^+ + Cl^-$$

and subsequently for Ca-feldspar

$$Na^+ + CaSi_2Al_2O_8 + H_4SiO_4 + ½\ H^+ \rightarrow NaSi_3AlO_8 + Ca^{2+} + 2\ H_2O + ½\ Al_2O_3 + ½\ OH^-$$

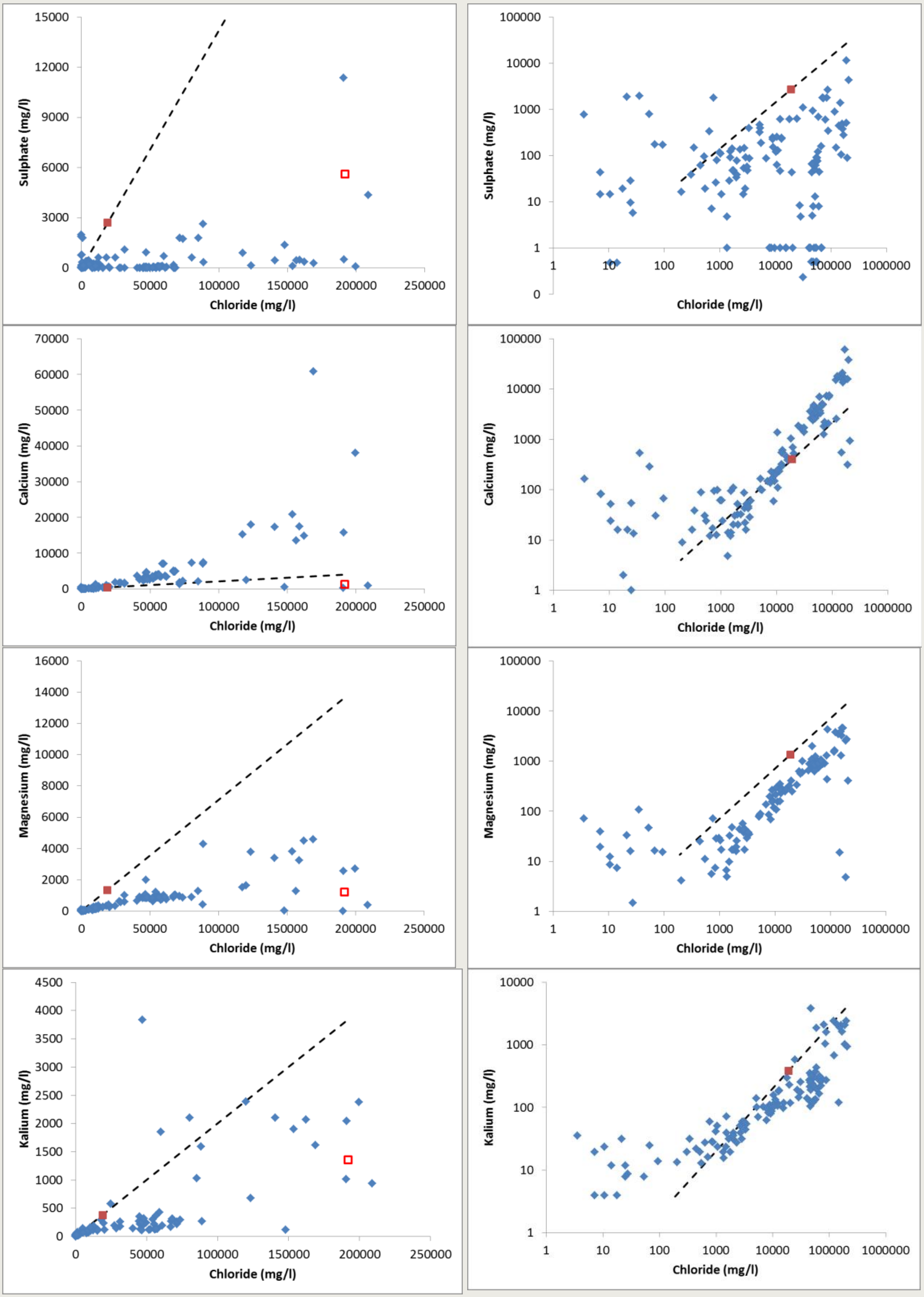


Figure 4-16. Concentration plots of the main compounds SO_4, Ca, Mg and K versus Cl for groundwater in geological units under the Boom Clay at linear (left) and logarithmic scale (right). The dashed line is the seawater dilution/evaporation line, the brown square represents seawater and the red open square represents halite brine according to Kloppmann (2001).

Egeberg & Aagaard (1989) argued that transformation of K-feldspar is unlikely both thermodynamically and in relation to the depletion of K below the seawater evaporation line. Illitisation of the reservoirs is commonly observed and the temperature under which it formed varied strongly. The source of the K-bearing fluid is still uncertain: both non-correlation between feldspar dissolution and amount of authigenic clay as well as increasing feldspar dissolution with precipitation of illite and/or kaolinite has been observed as has the source of the K-fluid been interpreted from the Zechstein rock salt (Gaupp & Okkerman, 2011).

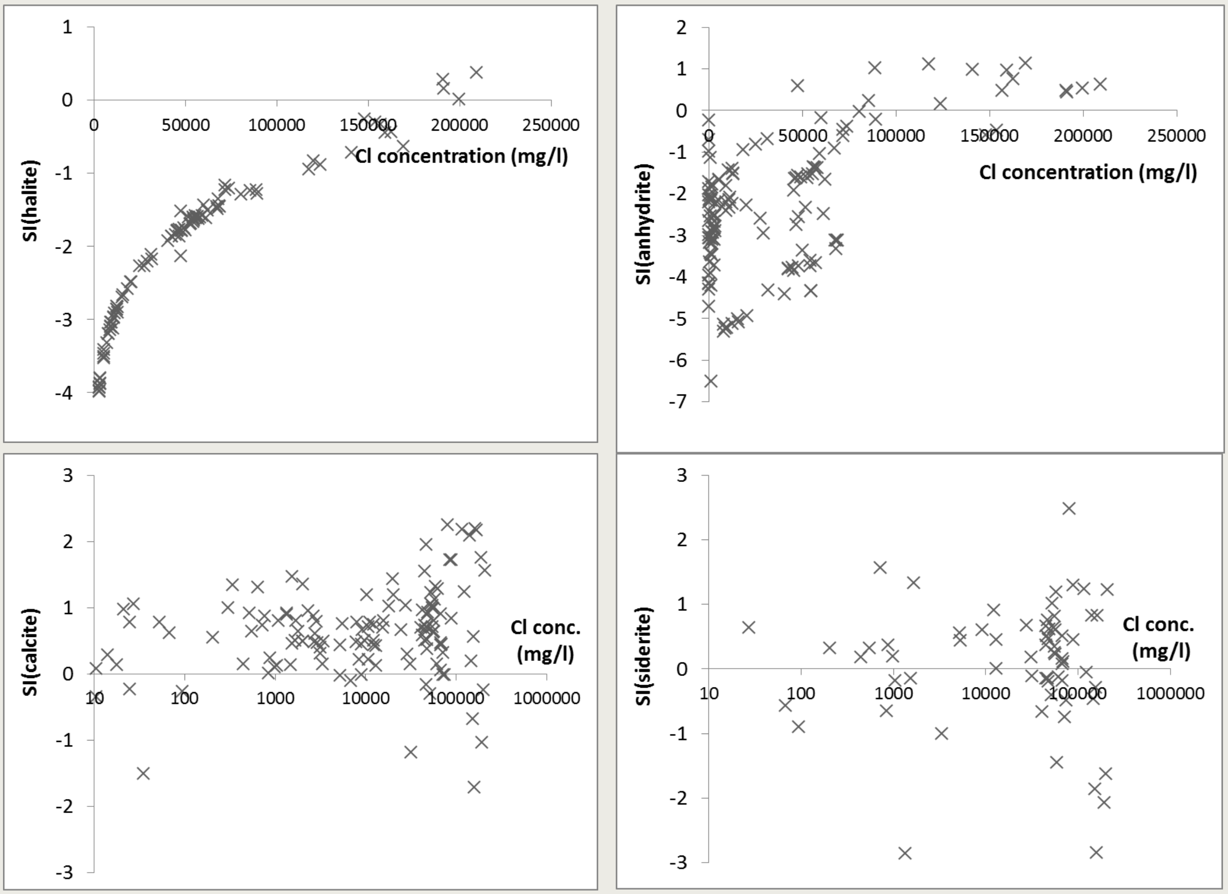


Fig. 4-17. Saturation indices of halite, anhydrite, calcite and siderite versus the Cl concentration of groundwater in geological formations under the Boom Clay.

Calcium concentrations above the seawater evaporation line are observed. Weathering of Ca-feldspars may be plausible although the Rotliegend Sandstone in the southern part of the North Sea basin is usually poor in Ca-feldspars but not in K-feldspar (e.g. Purvis, 1992; Gluyas et al., 1997; Ziegler, 2006). Diagenetic overgrowths of K- and Na-feldspars are even found in this reservoir rock (Gaupp & Okkerman, 2011; Fischer, 2012). The Ca concentrations are not balanced by SO_4 concentrations which suggests in first instance that gypsum or anhydrite dissolution does not a play, whereas these evaporites are commonly found as precursors when halite as evaporite is also found. However, anaerobic oxidation of methane in association with SO_4 reduction has been observed at elevated temperatures in hydrothermal systems (Holler et al., 2011; Biddle et al., 2012; Adams et al., 2013). These observations raise the question whether transformation of anhydrite to calcite may happen in association with methane oxidation (Holler et al., 2011):

$$CaSO_4 + CH_4 \rightarrow CaCO_3 + H_2S + H_2O$$

Preliminary modelling using PHREEQC showed that this process may give rise to high Ca, low SO_4 water but no removal of Na happens. It must also be remembered that anhydrite is not only found as early-stage evaporite mineral but also as late or intermediate stage diagenetic mineral (Purvis, 1992; Lanson et al., 1996; Gluyas et al., 1997; Gauss & Okkerman, 2011) in the Rotliegend sandstone. The environmental conditions for the latter are however not clear: the effects of uplift or mixing of groundwater close to faults has not been exemplified.

The behaviour of Sr and Ba is also relevant in brines because celestite ($SrSO_4$) or barite ($BaSO_4$) may precipitate and contribute to the cementing of grains (Gluyas et al., 1997). Both cations have been frequently analysed in the hypersaline solutions. Figure 4-18 shows the observed Ba and Sr concentrations versus SO_4. An inverse relationship with a 1 to 1 slope at logarithmic scale can be recognised for the data points in the upper right side. This could be indicative for an equilibrium relationship with a solubility control by SO_4 minerals for these two divalent cations. Supersaturation for barite ($BaSO_4$) is usually found for saline or hypersaline and for celestite ($SrSO_4$) also for the hypersaline groundwater, but the saturation index of celestite varies from -3 to 1 for saline groundwater.

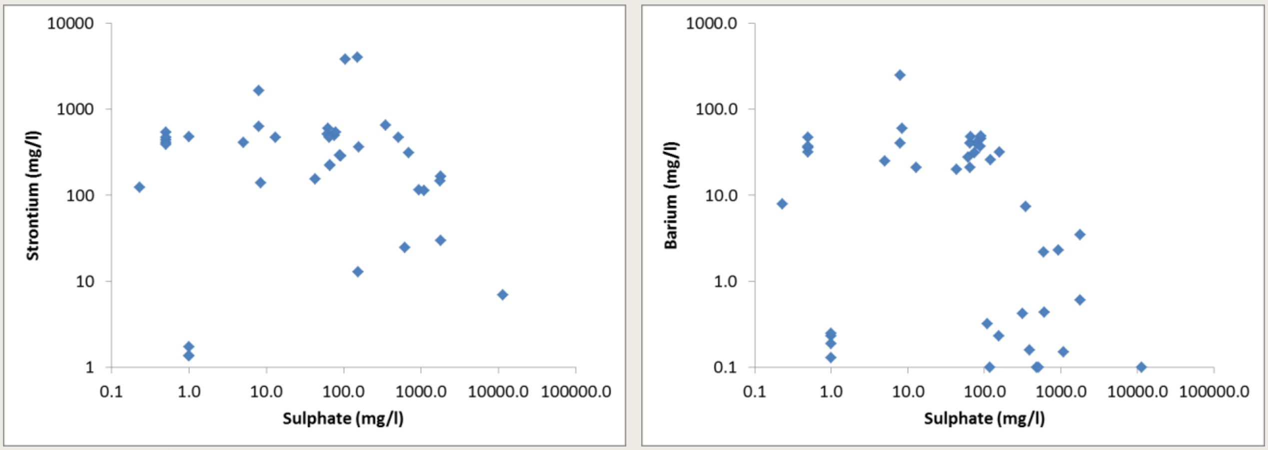


Fig. 4-18. Relationship between SO_4 and Sr or Ba for groundwater in geological formations under the Boom Clay

The previous text discussed the composition of groundwater below the Boom Clay at a national scale irrespective of the vertical distance from the Boom Clay layer. Now, we will focus on those samples that were collected rather close to the Boom Clay. Several analyses are available which are presented on the major compounds of interest in Table 4-2. Based on the few isotope analysis, it was concluded that the origin of groundwater immediately under the Boom Clay varies among 1. rain water infiltrated during a glacial period (at Asten, but with remarkable high Cl concentration), 2. recent rain water (at Broekhuizen-vorst) and 3. a mixture between rain water and seawater where hydrological contact with a salt dome also plays a role and maybe evaporation as well (at Nieuweschans). The chemical data indicate groundwater is usually saline or hypersaline, varies in SO_4 concentration, has high I concentration and is mostly near-saturated or supersaturated for carbonates. Its apparent carbon-14 age is ‘’old’’ with values below 10 PMC. Here, it is surprising that the analysis for Asten does not indicate ‘’below the detection limit’’. The sampling depth was about 1500 m depth and a value of 3 PMC indicates an apparent age of 29,000 y. The true age will be lower, suggesting a travel time of a few tens of thousands of years at maximum.

Table 4-2. Composition of groundwater (in mg/l, except when stated otherwise) immediately below the Boom Clay layer and the reference for groundwater close to rocksalt in Gorleben, Germany (Kimpe, 1963; Glasbergen, 1981; 1984; Heederik, 1989; Kloppmann et al., 2001; own data).

Sample	B08D0034	B49F1427	B50H0373	B52E0114	B52C0234		GoHy674
Location	Nieuweschans	Zegge	Maarle	Broekhuizen-vorst	Asten	Middle Limburg	Gorleben (D)
Geology	Paleogene	Paleogene	Paleogene	Paleogene	Paleogene	Paleogene	
Depth (m below sealevel)	582	412	494.5	539	1520	480 – 650	208
pH	6.51	7.36	7.42	6.64	5.8	7.2 / 8.6	7.1
Na	43500	7595	5967	7200	16769	1000 / 4175	126000
Ca	1250	317	147	610	1400	20 / 146	1240
Mg	950	344	160	290	599	17 / 135	1210
Cl	71500	12321	9211	12939	31500	1078 / 6913	192000
Br	140	41.7	30.5	20.2	100		
SO_4	1800	613	153	230	< 0.23	4814,4/144	5600
Alkalinity	183	$1087^{@}$	$1182^{@}$	514	44	232 / 964	135
δ^{18}O (‰)	-3.23/-3.15			-6.52/-6.25			-8.8
δ^{2}H (‰)	-24.2/-25.6			-44.5/-39.5			-60
^{14}C act. (PMC)	9	< 2	< 2	1/3.4	3		
Calcite	-0.01	0.74	0.66	0.12	-1.19	-0.11/ 0.80	1.62
Dolomite	0.21	1.88	1.74	0.33	-2.14	0.17/ 1.91	4.02
Anhydrite	-0.45	-1.39	-2.20	-1.52	-4.32	-3.10/ -2.31	1.08
Halite	-1.17	-2.83	-3.05	-2.84	-2.18	-4.32/ -3.32	0.42
Log P_{CO2}	-1.56	-1.44	-1.49	-1.10	-1.22	-2.41/ -1.71	-2.25

5. Conclusions

Insight into the composition of groundwater deeper than 100 m is obtained by 1. sampling and analysis of groundwater from 26 deep screens (between 180 and 500 m-NAP) in different regions of the Netherlands, 2. asking for existing analyses of groundwater piezometers deeper than 100 m below surface and above the Boom Clay from the DINO database for these regions and 3. collecting studies that present either analyses of groundwater sampled from geological formations older than the Boom Clay or analyses of iodide in groundwater. An overview on the composition of deep groundwater is obtained from this, with a slight focus on the eastern and southern part of the Netherlands.

The first conclusion must be that very few groundwater analyses exist for groundwater in the Paleogene aquifers immediately above and below the Boom Clay: about 25 where the majority refers to a coal exploration study in the beginning 1960’s (Kimpe, 1963). More frequently, samples were collected from the Miocene Breda Formation.

The overall results indicate that important regional differences are observed for deep groundwater both under and above the Boom Clay layer. The differences are present with respect to: salinity, groundwater age, extent of SO_4 reduction and methanogenesis, carbonate chemistry, and the infiltration origin. The pH is almost always near-neutral, the redox state is always anaerobic and it is often saline or even hypersaline. Deep groundwater above the Boom Clay has a Cl concentration that varies from a few mg/l to close to the seawater concentration of 19,300 mg/l. It is not self-evident that saturation for Ca-carbonates holds even for groundwater down to 250 m-NAP. Methane concentrations run up to several mg/l, which is less high than for the first tens of meters of the Dutch subsurface (in the western Netherlands). Although complications arise in correcting the apparent carbon-14 groundwater age to the true age, it seems justified to conclude that the true age of this deep groundwater is usually above 500 y up to ten thousands of years.

Deep groundwater under the Boom Clay is generally saline or hypersaline: Cl concentrations above the seawater concentration happen frequently in the northern half of the Netherlands. This highly saline groundwater is related to the major occurrence of Permian and Triassic evaporite deposits in this part of the Netherlands. Due to the occurrence of salt diapirs, hypersaline groundwater can also be found in Paleogene aquifers just below the Boom Clay. Saturation or supersaturation for carbonates holds for most groundwater, saturation for anhydrite happens for hypersaline groundwater and near-saturation for halite holds when the Cl concentration is close to 200,000 mg/l.

Limited data is available for iodine and selene, which is relevant within the context of the fate of the slowly decaying radioisotopes iodine-129 (half life 1.61E7 y) and selene-79 (half life 3.27E5 y). Most data on I is related to studies of groundwater aquifers in the coastal lowlands of the Netherlands. The concentrations range from less than 1 to over 1000 µg/l. Here, the iodide concentrations are highest in aquifers having a marine origin and/or where marine groundwater is present. The Se concentration is often below detection limit (usually around 0.01 µg/l) and does not exceed 1 µg/l. No information is present on the speciation of Se or I, except an old study that presents some analyses of organic I for a dune aquifer.

Hydrochemical analysis of groundwater under the Boom Clay is only present for some regional areas across the Netherlands. No complete, national overview can thus be obtained. Analysis of compounds that reveal insights into the hydrological and geochemical processes controlling the composition of deep groundwater (either below or above the Boom Clay) is lacking in almost all data available. This hinders interpretation of the data that goes beyond a characterisation of the composition. Better insights would be obtained when frequent analysis would happen of compounds such as Br and isotopes such as δ^2H-H_2O and $\delta^{18}O$-H_2O. This limits considerations on the impact of deep subsurface activities and the related potential environmental risks.

6. References

Adams, M.M., Haorfrost, A.L., Bose, A., Joye, S.B. & Girguis, P.R. (2013). Anaerobic oxidation of short-chain alkanes in hydrothermal sediments: potential influences on sulfur cycling and microbial diversity. Fron. Microbiol. (4), article 110.

Basu, R., Haque, S.E., Tang, J., Ji, J., Johannesson, K.H. (2007). Evolution of selenium concentrations and speciation in groundwater flow systems: Upper Floridan (Florida) and Carrizo Sand (Texas) aquifers. Chem. Geol. (246), 147-169.

Beaucaire, C., Pitsch, H., Toulhoat, P., Motellier, S. & Louvat, D. (2000). Regional fluid characterisation and modelling of water-rock equilibria in the Boom Clay Formation and in the Rupelian aquifer at Mol, Belgium. Appl. Geochem. (15), 667-686.

Beekman, H.E. (1991). Ion chromatography of fresh and salt water intrusion. Ph.D-thesis, Free University, Amsterdam, 198 pp.

Biddle, J.F., Cardman, Z., Mendlovitz, H., Albert, D.B., Lloyd, K.G., Boetius, A. & Teske, A. (2012). Anaerobic oxidation of methane at different temperature regimes in Guaymas Basin hydrothermal sediments. ISME J. (6), 1018-1031.

Bless, M.J.M. (1981). De mineraalwaterboringen te Maastricht. Natuurhistorisch Museum Maastricht, 31-12-1981, 32 pp.

Bonnesen, E.P., Larsen, F., Sonnenborg, T.O., Klitten, K. & Stemmerik, L. (2009). Deep saltwater in Chalk of North-West Europe: origin, interface characteristics and development over geological time. Hydrogeol. J. (17), 1643-1663.

Bouw, L. & Oude-Essink, G.H.P. (2003). Development of a freshwater lens in the inverted Broad Fourteens basin, Netherlands offshore. J. Geochem. Expl. (78-79), 321-325.

Claret, F., Lerouge, C., Laurioux, T., Bizi, M., Conte, T., Ghestem, J.P., Wille, G., Sato, T., Gaucher, E.C., Giffaut, E. & Tournassat, C. (2010). Natural iodine in a clay formation: Implications for iodine fate in geological disposals. Geochim. Cosmochim. Acta (74), 16-29.

Coenegracht, Y.M.A., Van Rooijen, P. & Zuurdeeg, B.W. (1984). Het mineraalwater van Klein Vink, Arcen. Rijksuniversiteit Utrecht, afd. Geochemie, en Rijks Geologische Dienst, 49 pp.

Conde, J.E. & Sanz Alaejos, M. (1997). Selenium concentrations in natural and environmental waters. Chem. Rev. (97), 1979-2003.

Core Lab (1987). Wellsite sampling and analysis of produced water and gas. Field Ijsselmonde/Ridderkerk. Core Laboratories UK Ltd, Aberdeen, Scotland,

De Jager, J. & Geluk, M.C. (2007). Petroleum geology. In ‘’Geology of the Netherlands’’, eds. Th.E Wong, D.A.J. Batjes & J. de Jager. Royal Netherlands Academy of Arts and Sciences, Amsterdam, the Netherlands, 241-264.

Egeberg, P.K. & Aagaard, P. (1989). Origin and evolution of formation waters from oil fields on the Norwegian shelf. Appl. Geochem. (4), 131-142.

Fischer, C., Dunkl, I., Von Eynatten, H., Wijbrans, J.R. & Gaupp, R. (2012). Products and timing of diagenetic proceses in Upper Rotliegend sandstones from Bebertal (North German Basin, Parchim Formation, Flechtingen High, Germany). Geol. Mag. (149), 827-840.

Fortuin, N.P.M. & Willemsen, A. (2005). Exsolution of nitrogen and argon by methanogenesis in Dutch ground water. J. Hydrol. (301), 1-13.

Fraters, B., Boumans, L.J.M. & Prins, H.P. (2001). Achtergrondconcentraties van 17 sporenmetalen in het grondwater van Nederland. RIVM, rapportno. 711701017/2001, 136 pp.

Gaupp, R. & Okkerman, J.A. (2011). Diagenesis and reservoir quality of Rotliegend sandstones in the northern Netherlands – A review. SEPM Spec. Publ. (98), 193-226.

Geirnaert, W. (1973). The hydrogeology and hydrochemistry of the lower Rhine fluvial plain. Leidse Geol. Medel. (49), 59-84.

Geluk, M.C. (2007). Triassic. In ''Geology of the Netherlands'', eds. Th.E Wong, D.A.J. Batjes & J. de Jager. Royal Netherlands Academy of Arts and Sciences, Amsterdam, the Netherlands, 85-106.

Geluk, M.C., Paar, W.A. & Fokker, P.A. (2007). Salt. In ''Geology of the Netherlands'', eds. Th.E Wong, D.A.J. Batjes & J. de Jager. Royal Netherlands Academy of Arts and Sciences, Amsterdam, the Netherlands, 283-294.

Glasbergen, P. (1981). Extreme salt concentrations in deep aquifers in the Netherlands. Sci. Total Environ. (21), 251-260.

Glasbergen, P. (1984). Enkele voorbeelden van de grondwaterkwaliteit in paleogene watervoerende lagen. RIVM-mededeling 84-1, 31 pp.

Gaupp, R. & Okkerman, J.A. (2011). Diagenesis and reservoir quality of Rotliegend sandstones in the northern Netherlands – a review. SEPM Spec. Publ. (98), 193-226.

Gluyas, J., Jolley, L. & Primmer, T. (1997). Element mobility during diagenesis: sulphate cementation of Rotliegend sandstones, Southern North Sea. Marine Petrol. Geol. (14), 1001-1011.

Heederik, J.P. (1989). Geothermal resources in the Central Graben area, the Netherlands. TNO – Dienst Grondwater Verkenning, report OS89-18.

Heymann, J.A. (1925). Het jodium in het waterleidingbedrijf. Water en Gas (9/4), 39-54.

Holler, T., Widdel, F., Knittel, K., Amann, R., Kellermann, M.Y., Hinrichs, K.U., Teske, A., Boetius, A. & Wegener, G. (2011). Thermophilic anaerobic oxidation of methane by marine microbial consortia. ISME J. (5), 1946-1956.

Huurdeman, A.J.M. (1986). Onderzoek naar adiabatische persluchtopslag in Nederland. TNO – Dienst Grondwater Verkenning, report OS86-43.

Jones, B.F., Hanor, J.S. & Evans, W.R. (1994). Sources of dissolved salts in the central Murray Basin, Australlia. Chem. Geol. (111), 135-154.

Jongmans, W.J. & Driessen, Cl.G. (1932). De mineraalwaterbron te Maastricht. Water (16/13), 137-145.

Kimpe, W.F.M. (1963). Geochimie des eaux dans le houiller du Limbourg (Pays-Bas). Verh. Kon. Ned. Geol. Mijnbouwk. Gen., Geol. Serie (21), 25-45

Kloppmann, W., Négrel, Ph., Casanova, J., Klinge, H., Schelkes, K. & Guerrot, C. (2001). Halite dissolution derived brines in the vicinity of a Permian salt dome (N German Basin). Evidence from boron, strontium, oxygen, and hydrogen isotopes. Geochim. Cosmochim. Acta (65), 4087-4101.

Krul, W.F.J.M. (1933). Het jodiumgehalte van het grondwater in verband met de hydrologische geschiedenis. De Ingenieur (25), A. 216-219.

Lanson, B., Beaufort, D., Berger, G., Baradat, J. & Lacharpagne, J.C. (1996). Illitization of diagenetic kaolinite-to-dickite conversion series : Late-stage diagenesis of the Lower Permian Rotliegend sandstone reservoir, offshore of the Netherlands. J. Sed. Petrol. (66), 501-518.

Lee, M., Aronson, J.L. & Savin, S.M. (1989). Timing and conditions of Permian Rotliegende sandstone diagenesis, souther North Sea: K/Ar and oxygen isotopic data. Am. Ass. Petrol. Geol. Bull. (73), 195-213.

Li, J., Wang, Y., Guo, W., Xie, X., Zhang, L., Liu, Y. & Kong, S. (2014). Sci. Total Environ. (468-469), 738-745.

Lokhorst, A., ED . (1998). The Northwest European Gas Atlas. Netherlands Institute of Applied Geoscience TNO, ISBN 90-72869-60-5.

Machel, H.G. (2001). Bacterial and thermochemical sulfate reduction in diagenetic settings – old and new insights. Sed. Geol. (140), 143-175.

Meinardi, C.R., Groot, M.S.M. & Prins, H.F. (2003). Basiswaarden voor spoorelementen in het zoete grondwater van Nederland; gegevens uit de landelijke en provinciale meetnetten (LMG, PMG, LMB, sprengen Veluwe). RIVM, rapportno. 714801028/2003, 43 pp.

Parkhurst, D.L. & Appelo, C.A.J. (1999). User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geol. Survey, Water-Resour. Investigations Report 99-4259, 312 pp.

Purvis, K. (1992). Lower Permian Rotliegend sandstones, southern North Sea: a case study of sandstone diagenesis in evaporite-associated sequences.

Stuurman, R. (2004). Een verkenning naar de interactie tussen diep, paleogeen grondwater en ondiep grondwater in de provincie Noord-Brabant. TNO-NITG, rapportno. NITG 04-222-B0909, 76 pp.

Stuyfzand, P. (1993). Hydrochemistry and hydrology of coastal dunes of the Western Netherlands, Ph.D. Thesis, Free University, Amsterdam, the Netherlands.

Van der Weijden, M.J.J. (1983). Een hydrogeochemisch onderzoek in verband met de winning van aardwarmte uit het West-Nederland bekken, toegespitsts op het demonstratieproject Delfland. Rijksuniversiteit Utrecht.

Verhoef, E, Neeft, E., Grupa, J. & Poley, A. (2014). Outline of a disposal concept in clay. Report OPERA-PG-COV008.

Verweij, J.M. (2003). Fluid flow systems analysis on geological timescales in onshore and offshore Netherlands. With special reference to the Broad Fourteens Basin. Ph.D thesis, Vrije Universiteit, Amsterdam, the Netherlands, 278 pp.

Verweij, J.M., Simmelink, H.J., Van Balen, R.T. & David, P. (2003). History of petroleum systems in the southern part of the Broad Fourteens basin. Neth. J. Geosci. (82), 71-90.

Verweij, H., Simmelink, E. & Underschultz, J. (2011). Pressure and fluid flow systems in the Permian Rotliegend in the Netherlands onshore and offshore. SEPM spec. publ. (98), 247-263.

Vis, G.J. & Verweij, J.M. (2014). Geological and hydrogeological characterzation of the Boom Clay and its overburden. Report OPERA-PU-TNO411.

VVM (2008). Het Centraal Kempisch systeem. Grondwater in Vlaanderen. Vlaamse Milieumaatschappij, Aalst, 110 pp.

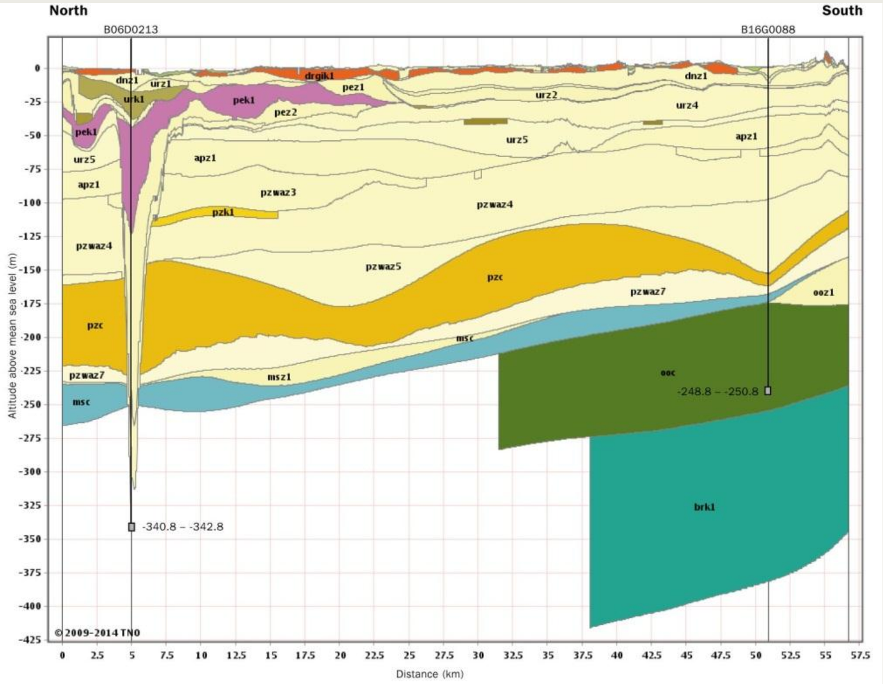
Worden, R.H., Manning, D.A.C. & Bottrell, S.H. (2006). Multiple generations of high salinity formation water in the Triassic Sherwood Sandstone: Wytch Farm oilfield, onshore UK. Appl. Geochem. (21), 455-475.

Ziegler, K. (2006). Clay minerals of the Permian Rotliegend Group in the North Sea and adjacent areas. Clay. Miner. (41), 355-393

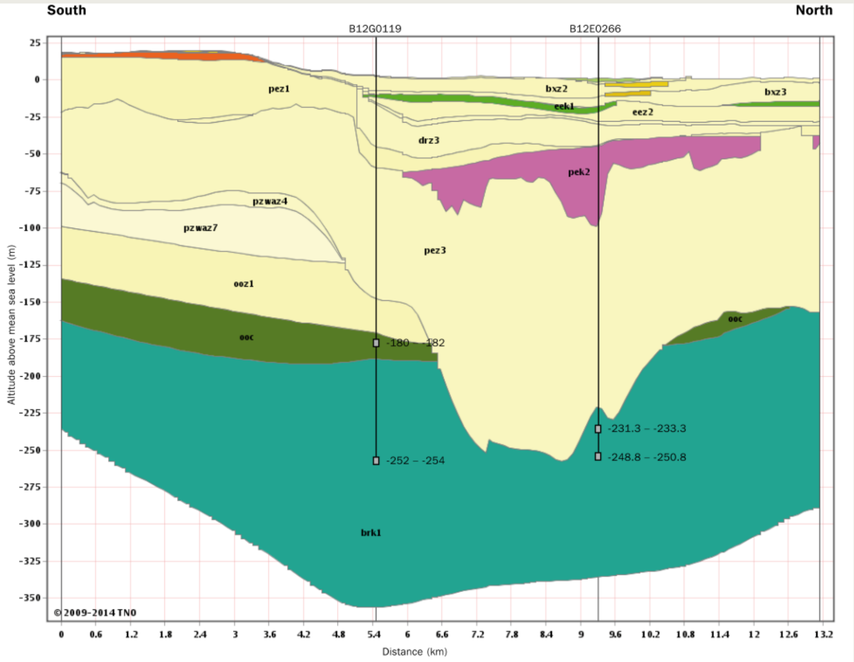
Zuurdeeg, B.W., Coenegracht, Y.M.A., Mebius, J.E. & Van der Weiden, M.J.J. (1984). Het mineraalwater van Winterswijk. Rijksuniversiteit Utrecht, afdeling Geochemie, 21 pp.

Zuurdeeg, B.W. & Coenegracht, Y.M.A. (1986). Genesis of the mineral water of Nieuweschans. Dep. of Geochemistry, University of Utrecht.

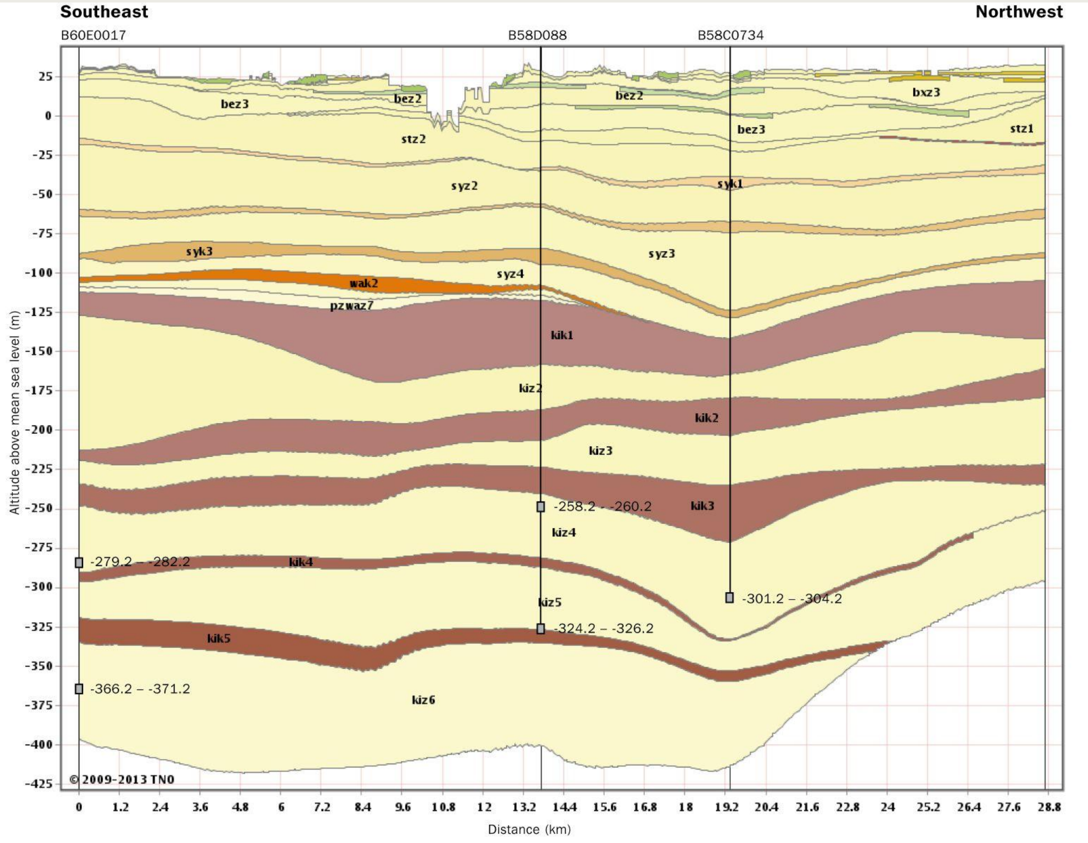
Appendix 1. Hydrogeological cross-sections for the studied areas as obtained from REGIS version II.1 (2008) with indication of sampled screens.



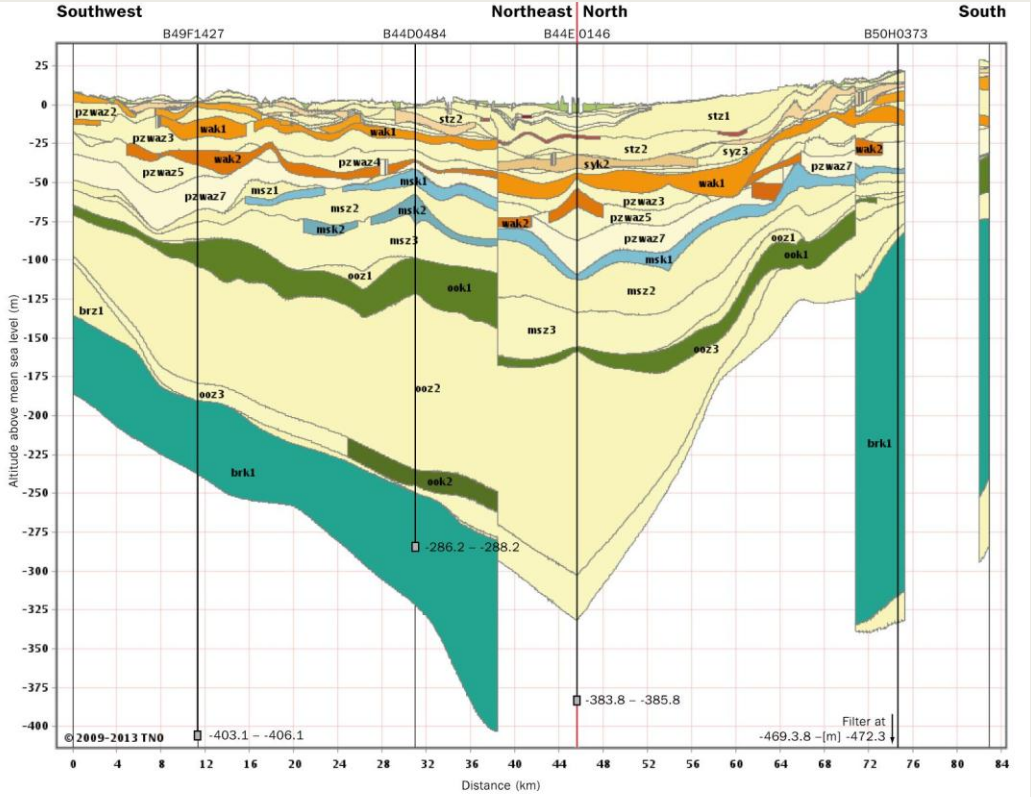
Eastern Friesland



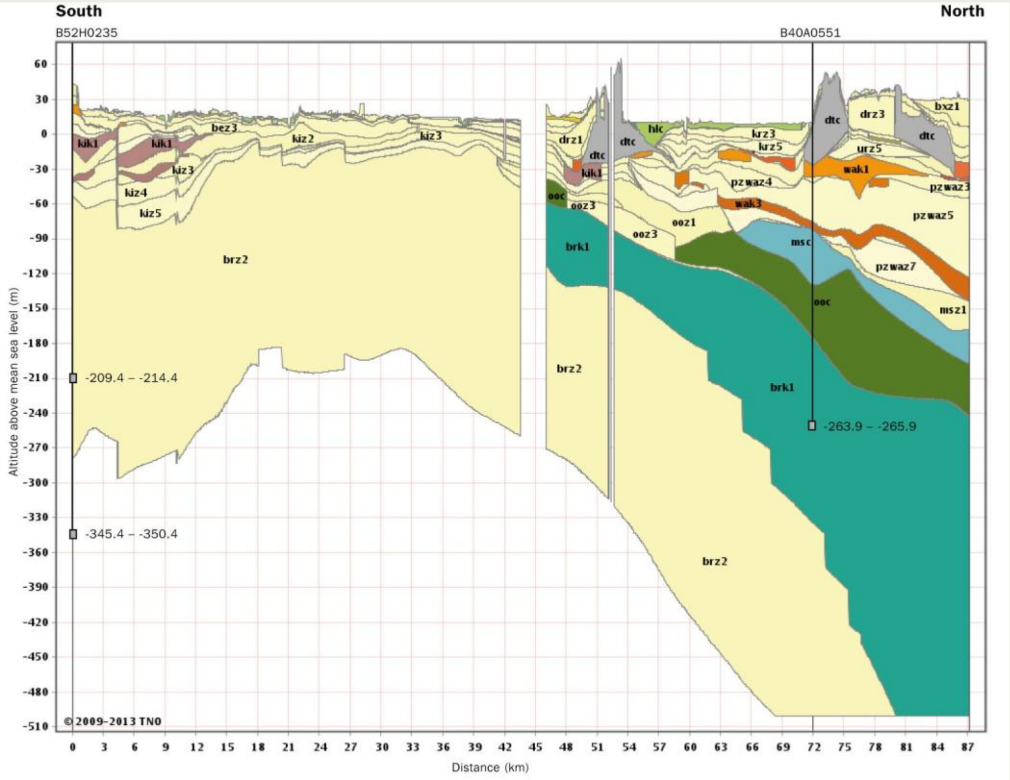
Hondsrug – Drenthe



Middle Limburg



Western Brabant (note the kink in the cross-section)



Northern Limburg and Central Gelderland - Venlo-Arnhem

Appendix 2. Results of the analysis of the groundwater samples collected in this study.

Well		B50H0373	B44D0484	B44E0146	B49F1427	B52H0235	B52H0235	B40A0551	B12E0266	B12E0266
Screen		9	10	8	9	6	7	6	10	11
X-coord.		131471	113521	122712	94798	211710	211710	186928	247740	247740
Y-coord.		387296	403932	415122	397060	375964	375964	443516	564610	564610
filter bottom	m bs	494.5	288.5	386.73	412	258	394	280.34	233	252.5
pH field		7.42	7.89	7.59	7.36	7.43	7.46	8.24	7.87	8.24
pH lab		7.41	8.02	7.5	7.29	7.23	7.21	8	7.71	8.02
Elec.Cond.	ms/cm	27300	32300	6430	35400	535	25800	7220	819	970
temp.	oC	15.5	13.8	16.1	15.6	16.4	14.7	12.1	11.9	11.9
oxygen	mg/l	0.16	0.3	0.02	0.1	0.07	0.07	0.08	0.1	0.12
Al	mg/l	< 0.015	0.004	0.002	< 0.004	0.001	0.027	0.004	0.005	0.006
Sb	µg/l	0.364	0.03	0.051	0.29	0.014	0.523	0.132	0.015	0.016
As	µg/l	3.28	23.496	5.946	4.498	0.736	5.27	81.87	7.241	1.283
Ba	µg/l	231.35	209.3	145.62	439	112.2	571.25	239.37	58.49	12.3
Be	µg/l	< 0.437	< 0.006	0.05	< 0.342	< 0.03	0.304	0.016	0.025	0.034
Cd	µg/l	< 0.07	0	0.005	0.03	0.006	0.086	0.006	< 0.005	0.006
Ca	mg/l	147.125	20.29	53.61	317.25	52.5	253.25	22.308	22.27	9.422
Cr	µg/l	< 0.314	0.222	0.132	0.017	0.106	0.384	0.375	0.324	0.305
Co	µg/l	0.267	3.867	0.059	2.793	0.048	0.148	2.894	1.382	0.508
Fe	mg/l	1.149	0.371	0.812	3.793	0.177	1.685	1.881	0.725	0.206
K	mg/l	78.625	34.64	62.22	114.525	5.717	83.5	42.87	6.434	5.852
Cu	µg/l	0.812	0.047	0.043	1.417	0.023	1.22	0.118	0.182	0.217
Li	µg/l	728.8	57.72	179.7	1263	87.97	3740	102.3	19.7	20.928
Pb	µg/l	0.427	0.023	0.03	0.3	0.026	0.629	0.132	0.687	0.511
Mg	mg/l	160.1	36.62	77.1	343.75	8.23	189.125	41.31	5.497	2.676
Mn	µg/l	198.675	1978	41.04	3590	54.62	108.375	2584.2	119.6	47.32
Na	mg/l	5967	552.4	1109	7595	44.49	5214	1395	122.7	184.2
Ni	µg/l	1.598	0.958	0.339	1.448	0.102	2.558	1.295	0.579	0.143
Se	µg/l	0.387	0.022	0.016	0.064	0.017	0.588	0.05	0.001	0.008
Sr	µg/l	12815	1702.2	2051.4	24857.5	1045.5	14085	428.1	344.8	183.9
Tl	µg/l	0.156	0.003	0.002	0.096	0.006	0.026	0.002	0.01	0.003
tot_P	mg/l	0.084	0.802	1.671	0.397	0.155	0.044	1.921	0.307	0.381
V	µg/l	0.695	0.373	0.542	0.628	0.065	1.14	1.423	5.951	4.557
Zn	µg/l	15.325	2.505	4.674	14.095	0.62	17.69	8.991	6.089	2.224
Br	mg/l	30.525	2.768	7.168	41.731	0.076		7.455	0.249	0.292
Cl	mg/l	9211	742	1808	12321	36.2	8902	2030	143	171
F	mg/l	0.4798	1.4452	0.4747	0.296	0.1281	0	1.0407	0.1063	0.1574
NO3	mg/l	0	0	0	0	0.04	12.004	0	0	0
SO4	mg/l	153.355	15.099	2.013	612.55	7.403	0	0	0.019	0.045
PO4 (acid)	mg/l	0.259	2.433	0.101	1.138	0.378	0.089	5.625	1.045	1.289
NH4	mg/l	11.265	2.261	7.218	11.889	0.559	10.705	3.881	0.638	0.766
DOC	mg/l C	3.65	2.96	3.06	3.08	0.82	1.94	4.42	4.08	3.92
Iodide	mg/l		0.317	1.08		< 0.05	< 0.05	1.18	< 0.05	< 0.05
CH4	ug/l	130	13	11	24	23	63	5300	42	35
d13C-DIC	promille	-18.4	-6.7	-12.87	-14.78	-12.66	-15.5	-16.78	-17.17	-18.1
C14-DIC	PMC	< 2	< 2	2.8	< 2	12.9	< 2	< 2	42.1	41.1

Well		B12G0119	B12G0119	B06D0213	B16G0088	B58C0734	B58D0688	B58D0688	B58D0885	B58D0885
Screen		10	10	7	5	4	6	7	3	4
X-coord.		247740	247740	198167	208340	188982	195520	195520	191361	191361
Y-coord.		560480	560480	581083	536270	361521	353710	353710	356425	356425
filter bottom	m bs	186	258	343.97	251.96	331	292	383	289.77	355.77
pH field		7.52	7.28	6.8	6.8	6.71	6.88	6.77	6.78	6.68
pH lab		7.26	7.39	7.02	7.53	6.8	7.01	7.16	6.8	6.7
Elec.Cond.	ms/cm	458	327	813	17900	571	688	580	537	529
temp.	oC	11	11.6	14.6	11.7	14.1	13.6	14.3	14.7	16.1
oxygen	mg/l	0.2	0.08	0.5	0.12	0.2	0.1	0.08	0.8	0.9
Al	mg/l	0	0	0.002	0.026	0.001	< 0.002	< 0.002	0.001	0.001
Sb	µg/l	0.006	0.013	0.009	0.123	0.004	0.018	0.019	0.012	0.016
As	µg/l	0.417	0.269	5.215	2.432	0.792	8.893	4.356	0.939	9.085
Ba	µg/l	7.966	5.904	56.36	12.84	110.4	412.4	433.6	102.7	256.9
Be	µg/l	0.01	< 0.004	0	0.012	< 0.011	0.006	< 0.004	< 0.019	< 0.019
Cd	µg/l	< 0.005	< 0.005	0.002	0.026	0.004	< 0.001	< 0.002	0.003	0.01
Ca	mg/l	60.3	38.63	100.8	33.72	93.34	99.38	89.09	86.86	80.88
Cr	µg/l	0.019	0.025	0.095	0.429	0.123	0.076	0.042	0.137	0.155
Co	µg/l	0.073	0.069	0.178	0.326	0.081	15.79	9.398	0.111	14.64
Fe	mg/l	1.613	2.195	7.904	0.315	5.767	5.164	5.849	5.041	7.197
K	mg/l	4.906	3.177	5.673	27.28	2.179	1.75	2.376	2.136	2.605
Cu	µg/l	0.022	< 0.003	0.05	3.142	0.05	0.081	0.014	0.078	0.069
Li	µg/l	16.73	10.09	22.092	32.07	11.28	9.525	15.45	11.18	15.03
Pb	µg/l	0.078	0.015	0.012	2.254	0.081	0.278	0.051	0.028	0.065
Mg	mg/l	8.497	4.915	11.84	11.48	14.24	14.45	12.04	13.28	12.61
Mn	µg/l	40.44	80.11	244.5	52.29	231.9	1692	873.1	196.6	621.4
Na	mg/l	15.69	15.68	40.53	276.99	6.639	5.569	7.275	6.733	9.009
Ni	µg/l	< 0.053	< 0.043	0.159	1.016	0.214	12.23	4.813	0.142	5.62
Se	µg/l	< 0.017	< 0.014	0.036	0.076	0.016	0.044	0.012	0.004	0.011
Sr	µg/l	350.4	163.7	388.9	579.2	276.5	346.2	346.7	267.9	292.9
Tl	µg/l	0.005	0.004	0.02	0.004	0.005	0.051	0.035	0.001	0.069
tot_P	mg/l	0.196	0.204	0.266	0.469	0.035	0.159	0.129	0.04	0.182
V	µg/l	0.121	0.097	0.074	5.154	0.025	0.035	0.012	0.02	0.041
Zn	µg/l	1.006	2.579	1.809	7.789	1.73	44.49	44.71	4.442	143.9
Br	mg/l	0.039	0.024	0.262	0.554	0.022	0.037	0.024	0.031	0.023
Cl	mg/l	13.5	13.0	58.0	225	5.04	5.42	5.07	5.22	5.38
F	mg/l	0.0618	0.0713	0.0544	0.125	0.1393	0.1309	0.1228	0.1508	0.121
NO3	mg/l	0.006	0	0	0.217	0	0.055	0	0.042	0.02
SO4	mg/l	0.023	0.537	0.064	20.735	5.56	6.371	4.731	5.093	4.456
PO4 (acid)	mg/l	0.683	0.645	0.833	1.007	0.084	0.514	0.426	0.098	0.527
NH4	mg/l	0.574	0.458	1.392	5.053	0.098	0.172	0.152	0.119	0.134
DOC	mg/l C	1.99	1	3.47	19.55	0.55	0.66	0.59	0.59	0.66
Iodide	mg/l	< 0.05	< 0.05	< 0.05	0.077	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
CH4	ug/l	780	35	4300	7600	10	13	16	< 10	< 10
d13C-DIC	promille	-16.46	-17.81	-6.77	-11.53	-15.2	-15	-15.01	-15.03	-15.27
C14-DIC	PMC	68.8	60.6	42.3	33.1	44.7	52.7	41.9	48.4	43.2

Well		B58D1609	B58G0191	B60B0107	B60B0107	B60B0123	B60B0123	B60E0017	B60E0017
Screen		9	5	4	5	4	5	5	6
X-coord.		193314	200181	198800	198800	199701	199701	203044	203044
Y-coord.		350639	355411	346390	346390	347040	347040	349069	349069
filter bottom	m bs	385.97	535.45	254.9	297.9	289	414	311.21	400.21
pH field		6.69	8.02	6.6	6.69	7.01	6.78	6.73	6.69
pH lab		6.82	7.3	6.61	6.69	6.86	6.75	6.77	6.67
Elec.Cond.	ms/cm	619	770	538	513	552	518	570	554
temp.	oC	14.5	14.3	12.8	11.4	11.9	11.5	12.5	14.3
oxygen	mg/l	1	0.05	1.7	0.3	0.4	0.5	0.25	0.4
Al	mg/l	0.001	0.001	0	0.002	0.001	0.002	0.002	0.001
Sb	µg/l	0.003	0.009	0.009	0.136	0.004	0.01	0.006	0.009
As	µg/l	0.306	0.771	0.341	0.828	10.79	0.581	0.873	0.213
Ba	µg/l	396.3	213	371.2	499.9	445.8	297.8	648.1	735.2
Be	µg/l	< 0.019	< 0.022	< 0.007	0.001	0.001	< 0.016	< 0.004	< 0.011
Cd	µg/l	0.007	0	0.001	0.006	0.001	0.001	0	0.003
Ca	mg/l	101.2	21.64	75.54	84.1	87.21	77.15	95.82	86.25
Cr	µg/l	0.059	0.053	0.043	0.069	0.086	0.082	0.082	0.024
Co	µg/l	0.759	0.019	0.015	0.248	8.384	4.236	0.133	0.074
Fe	mg/l	1.755	0.123	7.468	5.455	4.268	7.69	3.27	6.29
K	mg/l	3.399	12.83	2.487	2.837	1.478	2.88	1.868	2.892
Cu	µg/l	0.061	0.033	0.01	0.017	< 0.022	0.045	0.106	0.054
Li	µg/l	32.97	213.875	17.24	24.861	11.52	29.802	7.814	16.557
Pb	µg/l	0.008	0.001	0.038	0.138	0.006	0.011	0.02	0.059
Mg	mg/l	12.63	8.422	11.9	11.43	13.49	11.02	15.22	15.71
Mn	µg/l	1209	12.95	296.8	410.9	896.3	352.9	156.4	342.8
Na	mg/l	13.15	136.9	6.648	8.423	4.814	9.494	5.036	7.672
Ni	µg/l	0.397	0.122	0.029	0.237	2.692	2.67	0.282	0.227
Se	µg/l	0.012	0.011	< 0.006	0.02	< 0.001	0.01	0.024	0.034
Sr	µg/l	728.2	1401.6	305.8	441.3	238.5	432.6	282.8	372.2
Tl	µg/l	0.01	0.002	0.048	0.006	0	0.036	0.005	0.003
tot_P	mg/l	2.5656	0.066	0.05	0.109	0.129	0.172	0.028	0.04
V	µg/l	0.026	0.054	0.01	0.113	0.025	0.022	0.024	0.015
Zn	µg/l	1.517	0.481	3.146	1.524	7.866	2.349	2.769	1.114
Br	mg/l	0.026	0.296	0.031	0.024	0.022	0.025	0.022	0.025
Cl	mg/l	5.64	65.03	5.18	5.01	4.98	4.90	5.32	5.53
F	mg/l	0.1205	0.9671	0.1139	0.1089	0.1644	0.0894	0.191	0.1391
NO3	mg/l	0	1.022	0.038	0	0	0	0	0
SO4	mg/l	4.451	0.249	5.004	3.818	4.551	1.057	6.162	4.727
PO4 (acid)	mg/l	0.074	0.177	0.072	0.229	0.293	0.407	0.019	0.033
NH4	mg/l	0.229	1.993	0.196	0.142	0.125	0.16	0.102	0.179
DOC	mg/l C	0.65	1.87	0.63	0.73	0.63	1.12	0.45	0.58
Iodide	mg/l	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
CH4	ug/l	14	610	13	25	< 10	140	< 10	< 10
d13C-DIC	promille	-13.43	-12.67	-15.43	-14.41	-15.18	-13.82	-15.52	-15.3
C14-DIC	PMC	29.7	< 2	46.2	39.4	51.4	37.9	57.6	49.9

Note: grey shaded result is considered to be unreliable

OPERA

Meer informatie:

Postadres
Postbus 202
4380 AE Vlissingen

T 0113-616 666
F 0113-616 650
E info@covra.nl

www.covra.nl