

## **Geochemical analyses of Boom Clay pore water and underlying aquifers in the Essen-1 borehole**

M. De Craen, I. Wemaere, S. Labat and M. Van Geet

November, 2006

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## Introduction

The Essen-1 borehole is part of the data acquisition campaign hydro/05neb that has been commissioned by ONDRAF/NIRAS to SCK•CEN (contract C0-90 01 1467.19). The purpose of this data acquisition campaign is to provide additional data required for the hydrogeological models that are running in the framework of the performance assessment of possible disposal of high-level and long-lived radioactive waste in the Boom Clay, in Belgium. The regional hydrogeological system in north-east Belgium needs indeed to be well understood in present-day, past and future conditions and numerous data have to be gathered to build and further develop the hydrogeological models as e.g. the north-eastern Belgium model (Gedeon *et al.*, 2003). This hydro/05neb campaign focuses on the further characterization of the Boom Clay and the deeper layers as the Lower Rupelian, Lede-Brussel aquifers and the Asse Clay. Indeed, up to now, no information was available on the characteristics of the Boom Clay and the deeper layers in this region.

In particular, the Essen-1 borehole has to provide information on the hydrostratigraphic limits, the hydraulic properties of the Boom Clay, the Lower Rupelian aquifer and the Lede-Brussel aquifer, as well as the hydrogeochemical properties of these two deep aquifers. It has to allow monitoring of the water levels in the deep aquifers.

On the other hand, the drilling of Essen-1, located at the western border of the Campine basin, provided the opportunity to assess the transferability aspects of the migration and geomechanical properties of the Boom Clay, which were up to now essentially studied at the Mol site. The pore water chemistry of the Boom Clay could be thoroughly examined in order to compare it with other location in the Campine, as the Mol site, Zoersel and Doel and to provide natural tracer profiles that could be studied in the framework of the CLAYTRAC project (Mazurek *et al.*, in preparation).

This report presents the results of the geochemical analyses performed on samples from the Essen-1 borehole, in Belgium, during the period February to September 2006. The analysed samples are pore water samples extracted from cores and groundwater samples pumped through piezometers from the Lower Rupelian and from Lede-Brussel aquifers. The results are interpreted and for the Boom Clay pore water composition, a comparison is made with the reference Boom Clay pore water composition at the Mol site (De Craen *et al.*, 2004).

## 1 General information on the Essen-1 borehole

The Essen-1 borehole is located in north Belgium, in the north-western part of the Campine (see Figure 1). It has been drilled from January to February 2006 down to a depth of 508.6 m below drilling table (BDT) or 508.4 m below the ground surface. It has a cored section between 145.00 and 301.94 m BDT, essentially through the Boom Formation. The borehole has been equipped with two PVC piezometers: piezometer "e" in the Lower Rupelian aquifer with filter intervals between 285.35 and 381.75 m BDT and piezometer "f" in the Lede-Brussel aquifer with filter intervals between 402.40 m and 500.00 m BDT. The piezometers received the number 52e and 52f in the regional piezometric network monitored by SCK•CEN. The technical description and all detailed information are provided in the drilling report of the borehole (Lie *et al.*, 2006).

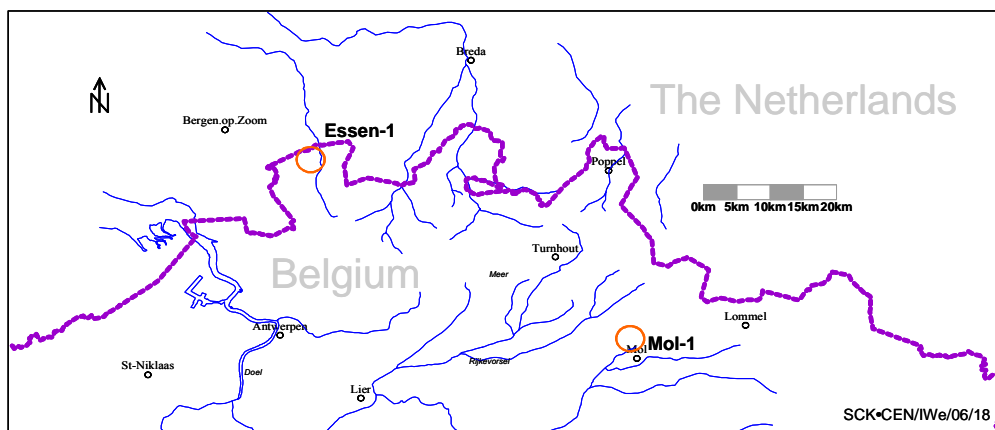


Figure 1: Location of the Essen-1 and Mol-1 borehole.

## 2 Pore water sampling

### 2.1 Pore water sampling from clay cores

Samples for pore water analyses were selected in the Berchem Sands, the Boom Clay, and the Ruisbroek Sands. The location (depth) of these samples is given in Figure 2.

The sampling and preservation of clay cores for geochemical purposes is performed in such a way that all possible geochemical perturbations are minimised. Since Boom Clay is sensitive to oxidation by air, the clay cores are immediately vacuum-packed in sample-bags made of aluminium-coated poly-ethylene sheets. This protects the clay core as much as possible from oxidation and also from drying out. Long-term storage is done in dark and cooled facilities with a temperature around 4 °C.

Pore water sampling is done by the mechanical squeezing of clay cores. The sample preparation is always performed in a nitrogen-filled glove-box (oxygen level < 10 ppm). The aluminium-coated poly-ethylene sheet is removed from the clay core. The outer rim of the clay core, which has been inevitably in contact with air during the drilling, is removed to eliminate possible effects of oxidation. Subsequently, the clay core is transferred to the 'squeezing cell', made of stainless steel type 316 (resistant to corrosion and high tensile strength). The sample chamber has a diameter of 8 cm and a height of 10 cm. The squeezing cell is then removed from the glove box and is put under a hydraulic press (COMPAC EMAC HP100). All samples were squeezed at a constant pressure of 30 MPa during one week. After the squeezing, the water samples were stored at 4 °C before chemical analyses.

### 2.2 Groundwater sampling from the piezometer

Groundwater has been sampled in the Lower Rupelian and the Lede-Brussel in respective piezometer e and f, see Figure 2. The samples were taken after that the piezometers were cleaned and rinsed several times by pumping (Lie *et al.*, 2006). Sampling was performed in February 2006. The samples were then stored at 4°C before chemical analyses.

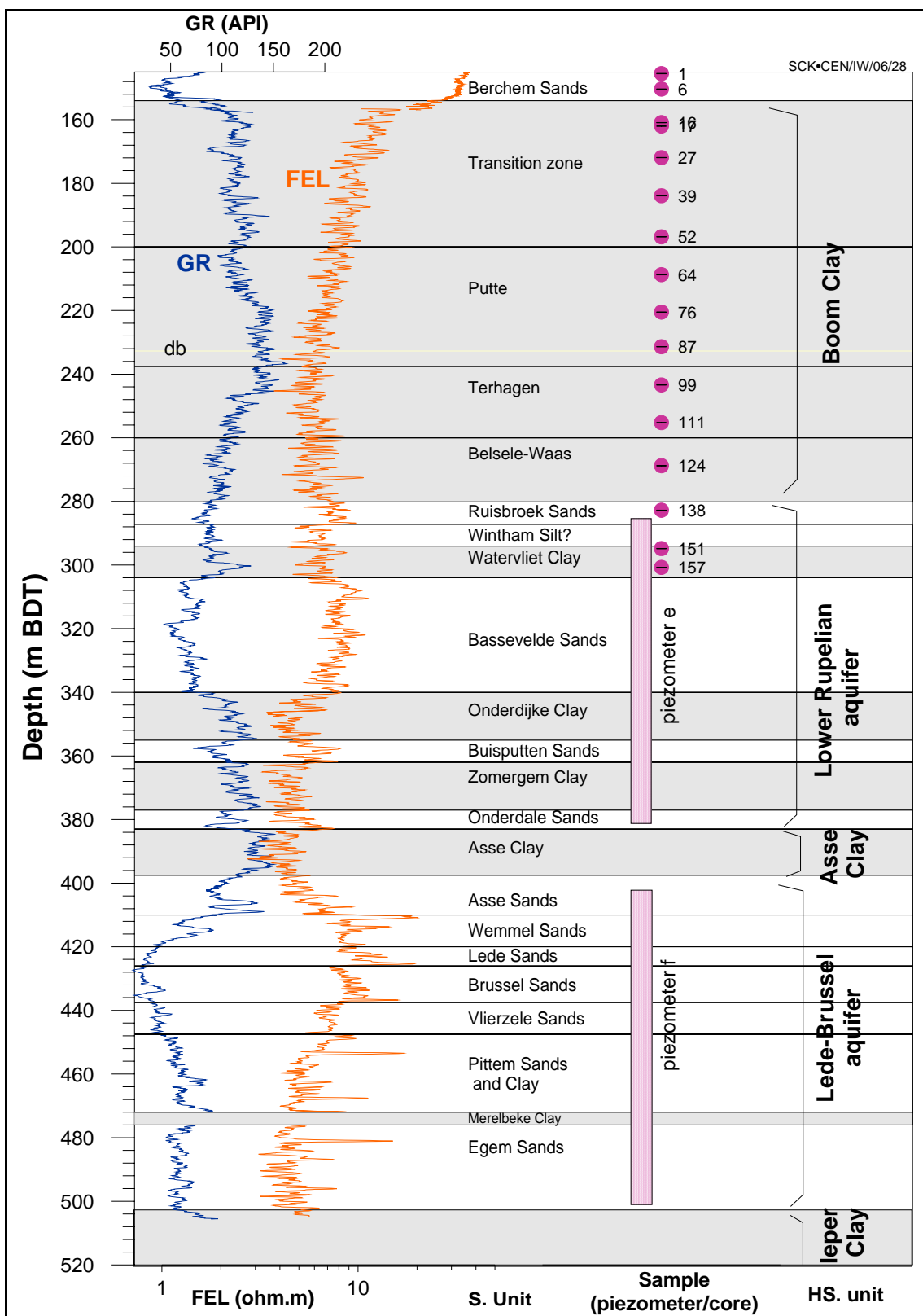


Figure 2: Location of the samples used for geochemical analyses (chemical analyses and stable isotope analyses) of pore waters in the Essen-1 borehole. Clay cores used for the squeezing of the pore waters are indicated by their number. The location of piezometer e and piezometer f is also indicated. GR: natural gamma ray expressed in American Petroleum Institute units (API); FEL: focussed electrical log; S. unit: Stratigraphic unit; HS. unit: Hydrostratigraphic unit.

### 3 Analytical methods

#### 3.1 Chemical analyses

Chemical analyses of the pore water and ground water samples were performed in the period March-July 2006 by the laboratory of Radiochemistry and Analysis (RA) of SCK•CEN, using the classical techniques: ICP-AES for the analyses of the cations, Ion Chromatography for the analyses of the anions, except for F<sup>-</sup> which was analysed by the Ion selective Electrode. ICP-MS was used for the analyses of the trace elements. The total organic carbon content (TOC) was measured with a high-temperature TOC analyser. A detailed description of these techniques is described in De Craen *et al.* (2004).

#### 3.2 Stable isotope analyses

The stable hydrogen isotope composition ( $\delta^2\text{H}$  or  $\delta\text{D}$ ) of the pore water samples were analysed in the period July-August 2006 at the Leibniz Institute for Applied Geosciences (GGA) S3: Geochronology and Isotopehydrology, Hannover, Germany. Water samples were analysed for  $\delta\text{D}$  using a fully automated chromium reduction system at 800 °C (H/Device, ThermoFinnigan) directly coupled to the dual inlet system of a Thermo Finnigan Delta XP isotope ratio mass spectrometer. All samples were measured at least in duplicates and the reported value is the mean value. All values are given in the standard delta notation in per mille (‰) vs. VSMOW (Vienna Standard Mean Ocean Water) according to  $\delta[\text{‰}] = (\text{R}_{\text{sample}}/\text{R}_{\text{reference}} - 1) \times 1000$ . External reproducibility – defined as standard deviation of a control standard during all runs – was better than 0.7 ‰.

The stable oxygen isotope composition ( $\delta^{18}\text{O}$ ) of the pore water samples were analysed in the period July-August 2006 at the Vakgroep Geologie, onderzoeksgroep 'Isotopengeologie en evolutie van het paleomilieu' (GEOL), Vrije Universiteit Brussel. Water samples were analysed for  $\delta^{18}\text{O}$  using H<sub>2</sub>O-CO<sub>2</sub>-equilibration at 25 °C for 12 to 18 hours. After equilibration CO<sub>2</sub> was separated and collected in high vacuum extraction lines and analysed with a Delta E Finnigan MAT) double inlet isotope ratio mass spectrometer. All samples were independently analysed at least in duplicates and the reported value is the mean value. All values are given in the standard delta notation in per mille (‰) vs. VSMOW (Vienna Standard Mean Ocean Water) according to  $\delta[\text{‰}] = (\text{R}_{\text{sample}}/\text{R}_{\text{reference}} - 1) \times 1000$ . External reproducibility – defined as standard deviation calculated on duplicate analyses – was better than 0.1 ‰.

## 4 Results and discussion

### 4.1 Chemical composition of the pore waters

#### 4.1.1 Chemical composition of the pore waters in Essen

The chemical composition of all analysed samples of the Essen-1 borehole is given in Table 1 and visualised in a piper diagram in Figure 3. Table 2 is focussed on the Boom Clay pore water composition and gives the minimum, maximum, and average values of the ionic concentrations in the Boom Clay pore water.

The aquifer above the Boom Clay (*i.e.* the Berchem Sands) is a (Na-Ca)(HCO<sub>3</sub>-Cl) – type water and is clearly different from all other samples in the Essen-1 borehole (Figure 3).

The Boom Clay pore water in Essen is NaCl – type water (Figure 3). In fact there is a strong variation in chemical composition from the top to the bottom with a progressive change from a 6 mM Na(HCO<sub>3</sub>-Cl) – type water at the top to a 108 mM NaCl – type water at the bottom. By average, the Boom Clay pore water in Essen is a 55 mM NaCl solution, containing 21 mg C / l of dissolved organic matter (Table 2).

The pore water is characterised by a relatively high salinity, ranging from 1470 mg/l to 7249 mg/l from the top to the bottom of the clay. The trend of continuous enrichment in salinity from the top to the bottom of the clay, is clearly visible in Figure 4. The trend is present for most anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Br<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, I<sup>-</sup>) and for Na; the other cations show a different behaviour.

The trend of increasing salinity is further continued in the underlying aquifers (except for SO<sub>4</sub><sup>2-</sup>). This is shown in Figure 4. The underlying aquifers are also NaCl – type waters with increasing salinity with depth.

Table 1: Analytical results on Boom Clay pore water samples and groundwater samples of underlying aquifers in the Essen-1 borehole

pore water obtained by the squeezing of clay cores:																										
core nr	depth (m BDT) from	depth (m BDT) to	depth (m BDT) clay core centre		TIC	TOC	B	Ca	Fe	K	Mg	Na	Si	Sr	Al	F-	Cl-	Br-	I-	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	alkalinity	salinity	
					mg C / l	mg C / l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	meq/l	mg/l		
1	145.47	145.57	145.52	Berchem Sands	Essen sq01	34.97	4.64	1.3	42	< 0.02	32	7.9	44	8.2	0.31	0.007	0.5	53	< 0.25	< 0.1	< 0.25	52	< 1	177.764	2.84	419
6	150.32	150.42	150.37	Berchem Sands	Essen sq02	28.62	4.40	1.5	24	0.47	32	6.5	49	6.9	0.18	0.185	0.74	31.2	0.4	< 0.1	< 0.25	60	< 1	145.485	2.47	298
17	161.92	162.09	162.01	BC / Transition zone	Essen sq03b	58.71	20.60	5.6	19	1.11	21	18.7	440	9	0.38	0.008	1.12	510	1.9	0.21	1.38	125	18.6	298.443	5.27	1470
27	171.88	171.98	171.93	BC / Transition zone	Essen sq04	69.87	27.02	5.0	29	3.8	40	29	570	7.5	0.56	0.072	1.72	660	2.4	0.36	< 1	190	24	355.173	5.54	1918
39	183.86	183.96	183.91	BC / Putte Member	Essen sq05	73.46	15.44	7.9	25	0.08	49	34	900	4.2	0.68	n.a.	1.74	1070	3.9	n.a.	0.66	324	13.5	373.422	6.56	2807
52	196.77	196.87	196.82	BC / Putte Member	Essen sq06	72.64	21.40	8.5	18.7	1.09	22	29	1100	6.5	0.54	< 0.005	1.26	1250	4.2	0.55	(1.6)	390	13.8	369.253	6.98	3214
64	208.67	208.77	208.72	BC / Putte Member	Essen sq07	87.28	16.93	9.9	15.3	0.26	22	30	1300	7.5	0.55	n.a.	1.16	1580	5.6	n.a.	< 0.25	373	5.1	443.673	7.41	3794
76	220.46	220.54	220.50	BC / Putte Member	Essen sq08	85.88	27.66	9.4	20	2.2	22	33	1500	7.5	0.69	< 0.005	1.23	1840	6.2	0.73	< 1	450	7.2	436.557	7.30	4336
87	231.33	231.43	231.38	BC / Putte Member	Essen sq09	90.13	29.37	9.2	22	1.03	26	36	1770	7.3	0.90	< 0.005	1.10	2180	7.3	0.80	< 1	550	5.8	458.161	8.12	5075
99	243.35	243.45	243.40	BC / Terhagen Member	Essen sq10	83.27	19.73	8.5	23	0.73	23	41	1890	7.2	1.04	< 0.005	1.07	2360	7.8	0.79	< 1	580	6.0	423.289	7.22	5373
111	255.19	255.29	255.24	BC / Belsele-Waas Member	Essen sq11	84.96	14.27	8.0	26	0.37	24	44	1970	7.5	1.20	< 0.005	1.01	2540	8.4	0.78	< 1	610	22	431.88	7.46	5694
124	268.73	268.83	268.78	BC / Belsele-Waas Member	Essen sq12	109.20	14.06	9.6	36	0.39	55	52	2500	7.7	2	n.a.	0.99	3100	11.0	n.a.	< 0.25	790	129	555.1	9.99	7249
138	282.72	282.82	282.77	Ruisbroek Sands	Essen sq13	n.a.	n.a.	9.0	40	1.41	52	49	2500	9.8	2	0.7	n.a.	3400	11.7	0.90	0.46	600	29	> 6704		
151	294.78	294.88	294.83	Ruisbroek Sands	Essen sq14	109.30	13.41	9.0	45	1.21	57	56	2700	7.4	2.4	0.036	n.a.	3700	12.8	0.99	0.89	630	43	555.608	9.42	7819
average in BC centre						86.58	22.30	9.6	17.70	1.21	22.08	31.50	1400.00	7.52	0.62	< 0.005	1.19	1710.00	5.89	0.73	n.a.	411.50	6.13	440.12	7.36	4065.11
average BC in Terhagen - Base Putte						86.64	23.42	9.23	20.24	1.04	23.37	35.00	1615.00	7.39	0.80	< 0.005	1.14	1990.00	6.70	0.77	n.a.	488.25	6.00	440.42	7.51	4644.58
average in Boom Clay						81.54	20.65	8.1	23.46	1.10	30.42	34.63	1394.00	7.20	0.84	0.04	1.24	1709.00	5.9	0.60	n.a.	438.20	24.52	414.50	7.19	4093
minimum value BC						58.71	14.06	4.96	15.30	0.08	21.00	18.70	440.00	4.20	0.38	0.01	0.99	510.00	1.91	0.21	0.66	125.00	5.10	298.44	5.27	1469.86
maximum value BC						109.20	29.37	9.90	36.00	3.83	55.00	52.00	2500.00	9.00	1.87	0.07	1.74	3100.00	11.00	0.80	1.38	790.00	129.00	555.10	9.99	7248.65
pore water obtained by piezometers:																										
piezo nr	depth (m BDT) from	depth (m BDT) to	depth (m BDT) clay core centre		TIC	TOC	B	Ca	Fe	K	Mg	Na	Si	Sr	Al	F-	Cl-	Br-	I-	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	alkalinity	salinity	
					mg C / l	mg C / l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	meq/l	mg/l		
52e	285	383	334	Lower Rupelian aquifer	141.60	12.60	n.a.	50	0.86	48	53	2800	5.6	n.a.	n.a.	0.69	3800	12.7	1.10	< 0.25	520	n.a.	719.8	11.40	7491	
52f	400	500	450	Lede-Brussel aquifer	190.40	10.70	n.a.	73	0.45	55	57	3300	12.4	n.a.	n.a.	0.70	4900	16.6	1.35	< 0.25	171	n.a.	967.867	14.61	9553	

The HCO<sub>3</sub><sup>-</sup> is calculated from the total inorganic carbon content (TIC).

The *alkalinity* is a measure of the acid neutralizing capacity (ANC) of a solution. This neutralizing capacity is equal to the stoichiometric sum of the bases in solution. In the natural environment carbonate alkalinity tends to make up most of the total alkalinity due to the common occurrence and dissolution of carbonate rocks and presence of carbon dioxide in the atmosphere. Other common natural components that make up alkalinity include borate, hydroxide, phosphate, silicate, nitrate, and sulphide. Alkalinity is given in the unit meq/l. (From Wikipedia, the free encyclopedia).

The *salinity* is the saltiness or the dissolved salt content in water. It is calculated as the sum of all ions and cations present in the water. The salinity is given in the unit mg/l.

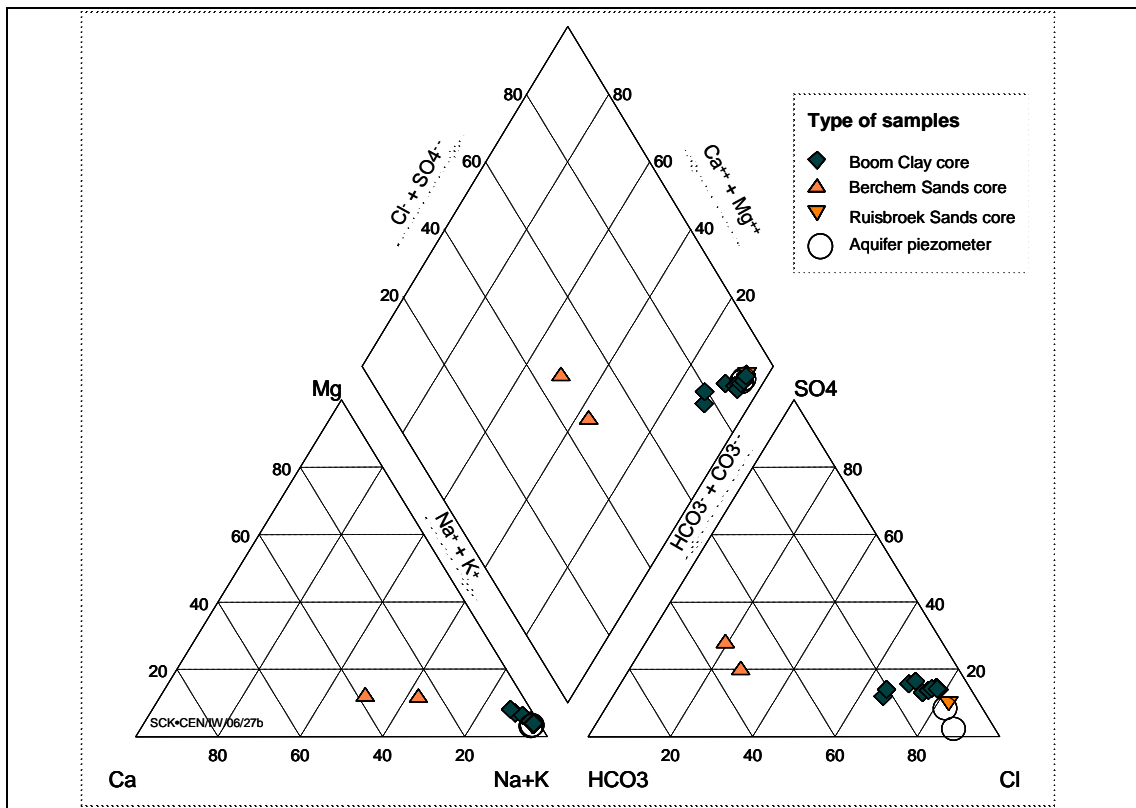


Figure 3: Piper diagram showing the Boom Clay pore water composition and the groundwater composition of the surrounding aquifers in the Essen-1 borehole.

Table 2: Chemical composition of the Boom Clay pore water in Essen. Pore water samples are obtained by the mechanical squeezing of clay cores from the Essen-1 borehole.

Boom Clay pore water composition in Essen		Minimum values	Maximum values	Average Boom Clay pore water composition in Essen	
Water type		Na-HCO <sub>3</sub> -Cl	NaCl	NaCl	
F <sup>-</sup>	mg/l	0.62	1.74	mg/l 1.2	mmol/l 0.06
Cl <sup>-</sup>		106	3100	1563	44.09
Br <sup>-</sup>		1.9	11	5.9	0.07
SO <sub>4</sub> <sup>2-</sup>		27	790	400	4.16
HCO <sub>3</sub> <sup>-</sup>		298	555	414	6.79
Na	mg/l	137	2500	mg/l 1280	mmol/l 55.68
K		10	55	29	0.74
Ca		4.9	36	22	0.55
Mg		6.5	52	32	1.32
Fe		0.08	3.83	1.0	0.02
Si		4.20	10.20	7.5	0.27
Al		< 0.005	0.07	< 0.005	< 0.0002
TOC	mgC/l	14	29	21	
Alkalinity	meq/l	5.3	10.0	7.2	
Salinity	mg/l	1470	7249	4093	

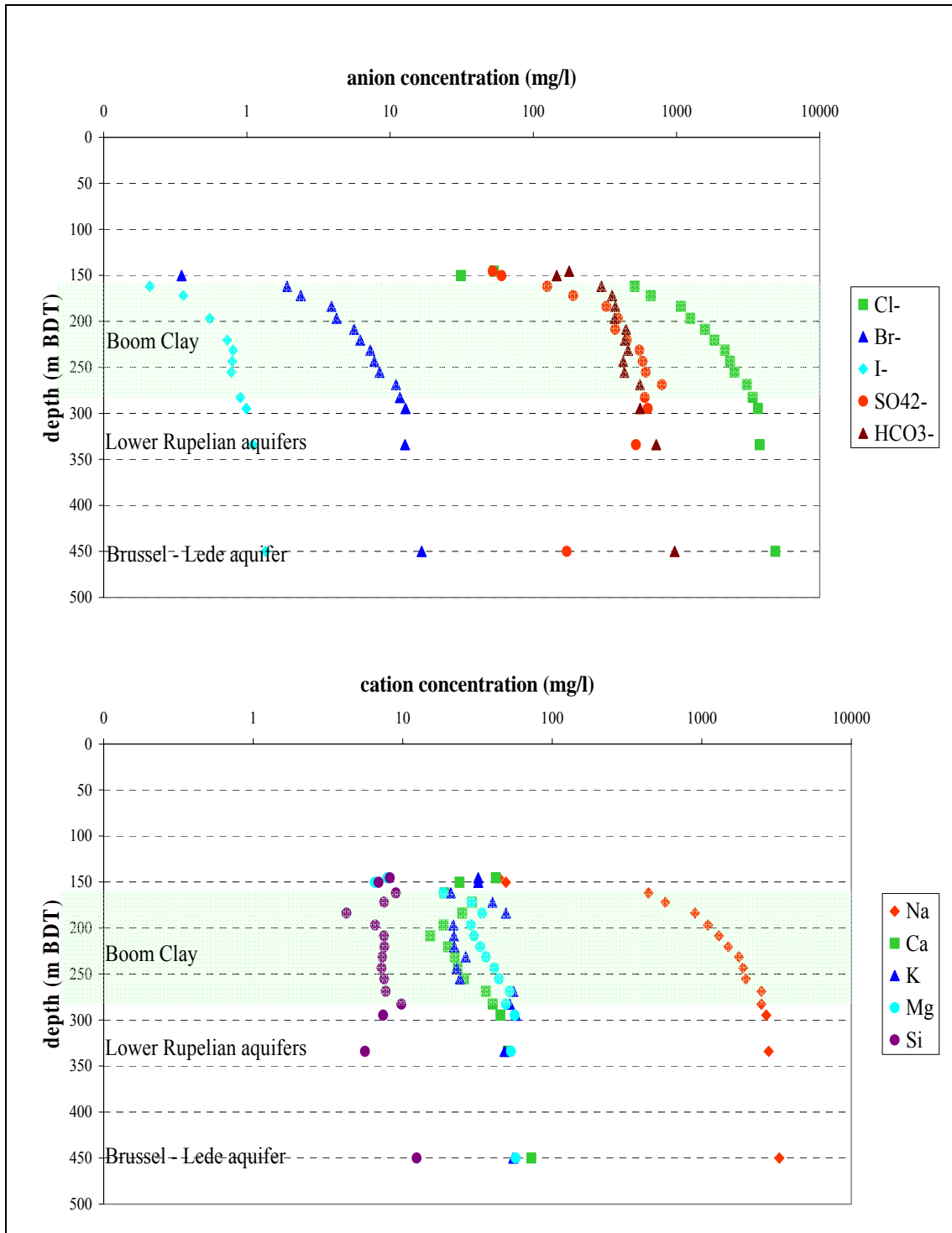


Figure 4: Depth profile showing the variation in pore water composition in the Boom Clay and the underlying aquifers (Essen).

#### 4.1.2 Comparison of the Boom Clay pore water composition in Essen with the reference Boom Clay pore water composition at the Mol site

The Boom Clay pore water composition in Essen is clearly different from the reference Boom Clay pore water composition at the Mol site (Table 3). The most important differences are the type of pore water, the salinity, and the vertical variations in chemical composition.

Table 3: Comparison of the Boom Clay pore water composition in Essen with the reference Boom Clay pore water composition at the Mol site

		<b>Mol</b> Reference Boom Clay pore water composition	<b>Essen</b> Average Boom Clay pore water composition
Water type		<b>NaHCO<sub>3</sub></b>	<b>NaCl</b>
F <sup>-</sup>	mg/l	3.0	1.2
Cl <sup>-</sup>		26	1563
Br <sup>-</sup>		0.6	5.9
SO <sub>4</sub> <sup>2-</sup>		2.2	400
HCO <sub>3</sub> <sup>-</sup>		880	414
Na	mg/l	359	1280
K		7.2	29
Ca		2.0	22
Mg		1.6	32
Fe		0.2	1.0
Si		3.4	7.5
Al		0.0006	< 0.005
TOC	mgC/l	150	21
Alkalinity	meq/l	15	7.2
Salinity	mg/l	1287	4093

##### The type of pore water

For the Mol site, a reference Boom Clay pore water composition has been defined (De Craen *et al.*, 2004). In Mol, the Boom Clay pore water is a NaHCO<sub>3</sub> – type water of 15 mM, containing about 115 mg C / l of dissolved organic matter. In Essen, the Boom Clay pore water is a NaCl – type water of about 55 mM, containing 21 mg C / l of dissolved organic matter.

##### The salinity

In Mol, the salinity of the Boom Clay pore water is rather low (salt content < 1300 mg/l). In Essen the salinity is ranging from 1470 mg/l to 7249 mg/l with an average salt content of 4093 mg/l water.

An important component of these salts is Cl<sup>-</sup>. While only 26 mg/l Cl<sup>-</sup> is present in the reference Boom Clay pore water at the Mol site, up to 3100 mg/l Cl<sup>-</sup> is measured in the pore water in Essen. This is important to mention since Cl<sup>-</sup> can play an important

role regarding corrosion of the metal overpack used in the Belgian reference design for geological disposal of radioactive waste (Wickham, 2005). The impact of such high chloride concentration on the corrosion behaviour of the carbon steel overpack will have to be assessed.

Another major component of the Boom Clay pore water in Essen is  $\text{SO}_4^{2-}$ . In the reference Boom Clay pore water at the Mol site, the  $\text{SO}_4^{2-}$  content is lower than 10 mg/l. In Essen, up to 790 mg/l  $\text{SO}_4^{2-}$  can be present.

#### Vertical variations in pore water composition

As mentioned above, a clear vertical trend of increasing salinity is recognized in the Essen samples. This trend is further continued in the underlying aquifers. Possibly, this means that the observed trend in the Boom Clay pore water composition is influenced by the underlying aquifers. This should however be studied in more detail.

In contrast, this trend of increasing salinity towards the underlying aquifers is not observed at the Mol site. Here, no trend is present at all and only very small variations in the Boom Clay pore water composition are recognised (De Craen *et al.*, 2004). These small variations are not related to depth.

#### **4.1.3 Regional variations in the Boom Clay pore water composition**

The above reported results from the Essen-1 borehole are compared to the Boom Clay pore water composition from squeezed clay cores of various boreholes: the Doel-2b borehole, the Zoersel borehole, the Mol-1 borehole, the HADES borehole 2001/4 (also at Mol). The location of these boreholes is shown in Figure 5.

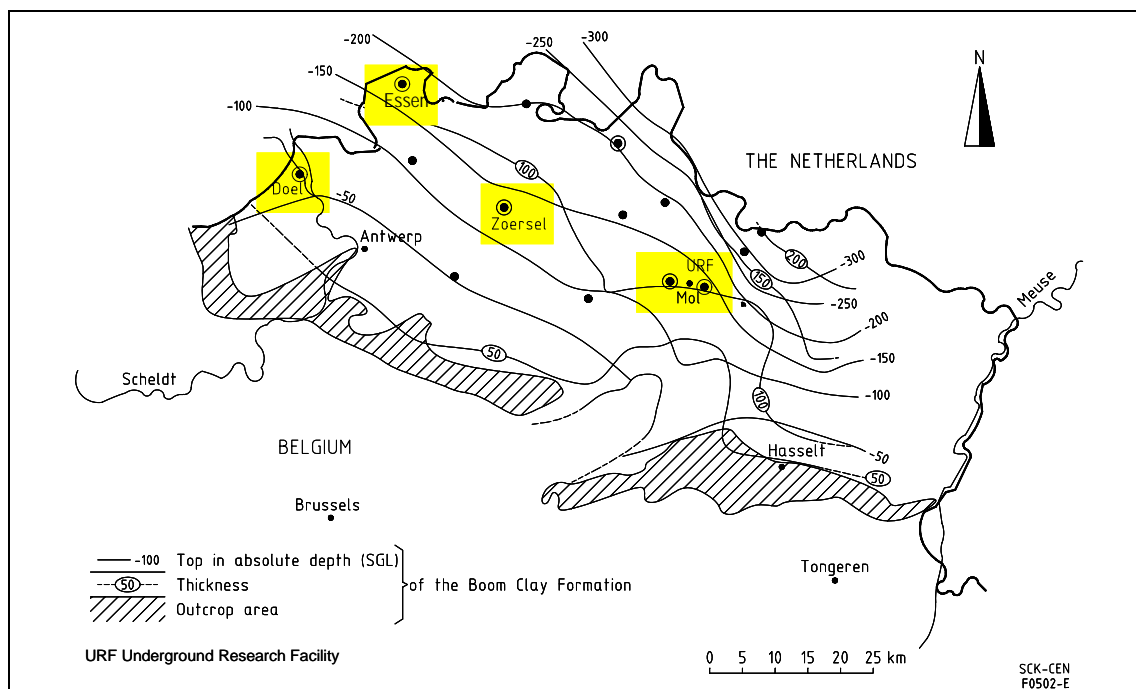


Figure 5: Location of the boreholes used in the study of the lateral variability of the Boom Clay pore water composition: the Doel-2b borehole (in Doel), the Zoersel borehole (in Zoersel), the Mol-1 borehole (in Mol), the HADES borehole 2001/4 (also in Mol), and the Essen-1 borehole (in Essen).

In Figure 6, the depth interval of the Boom Clay considered for pore water analyses in the various boreholes is shown. The average Boom Clay pore water composition at different locations is shown in Table 4. For comparison, the same depth interval was considered (Terhagen – Base Putte). Note that, for Essen, the average composition of this interval (Table 4) is slightly different from the overall average composition of the pore water (Table 2 and Table 3)

The lateral variability in salinity is clearly visible from these results. A general trend of increasing salinity is present from the east (Mol) to the northwest (Doel and Essen). The water composition varies from a  $\text{NaHCO}_3$  – type water in Mol over a  $\text{Na}(\text{SO}_4\text{-HCO}_3\text{-Cl})$  – type water in Zoersel, and a  $\text{NaCl}$  – type water in Doel and in Essen.

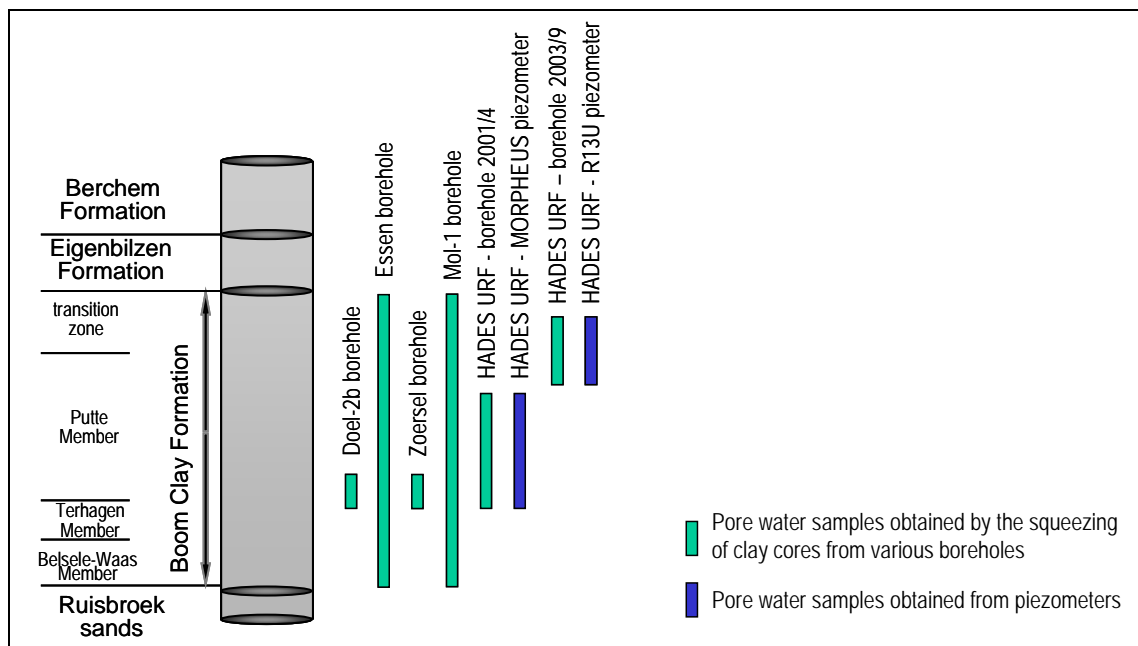


Figure 6: Depth interval of the Boom Clay considered for pore water analyses from squeezed clay cores from various boreholes.

Table 4: Average Boom Clay pore water composition at different locations. For comparison, the same depth interval was considered (Terhagen – Base Putte). Note that, for Essen, the average composition of this interval is slightly different from the overall average composition of the pore water.

	<b>Mol</b> Reference BC pore water composition	<b>Zoersel</b> Average BC pore water composition <i>Terhagen - Base Putte</i>	<b>Doel</b> Average BC pore water composition <i>Terhagen - Base Putte</i>	<b>Essen</b> Average BC pore water composition <i>Terhagen - Base Putte</i>
Water type	<b>NaHCO<sub>3</sub></b>	<b>Na(SO<sub>4</sub>-HCO<sub>3</sub>-Cl)</b>	<b>NaCl</b>	<b>NaCl</b>
F <sup>-</sup> mg/l	3.0	1.6	1.1	1.1
Cl <sup>-</sup>	26	320	1400	1990
Br <sup>-</sup>	0.6	1.6	4.5	6.7
SO <sub>4</sub> <sup>2-</sup>	2.2	640	370	488
HCO <sub>3</sub> <sup>-</sup>	880	680	450	440
Na mg/l	359	680	1060	1615
K	7.2	15	40	23
Ca	2.0	21	66	20
Mg	1.6	32	95	35
Fe	0.2	2.8	2.4	1.0
Si	3.4	8.3	7.2	7.4
Al	0.0006	0.6*	0.6*	< 0.005
TOC mgC/l	150	50	30	23
Alkal. meq/l	15	n.m.	n.m.	7.5
Salinity mg/l	1287	2400	3500	4645
Reference	<i>De Craen et al., 2004</i>	<i>De Craen et al., 2000</i>	<i>De Craen et al., 2000</i>	<i>This report</i>

\* Not filtered before analyses

## 4.2 Stable isotope composition of the pore waters

### 4.2.1 Stable isotope composition of the pore waters in Essen

The stable isotope composition of hydrogen ( $\delta^2\text{H}$  or  $\delta\text{D}$ ) and oxygen ( $\delta^{18}\text{O}$ ) of all analysed samples of the Essen-1 borehole is given in Table 5. Vertical variations in the isotopic composition are shown in Figure 7.

The hydrogen isotope data of Boom Clay pore water in Essen show a general enrichment of  $^2\text{H}$  from the top towards the bottom of the Boom Clay.  $\delta^2\text{H}$  values range from -47.5 ‰ vs VSMOW at the top to -39.3 ‰ vs VSMOW at the bottom of the Boom Clay. This trend is further continued in the underlying aquifer. The enrichment of  $^2\text{H}$  is associated with the increasing salinity towards the bottom of the clay and the underlying aquifer. As mentioned above, the aquifer above the Boom Clay is another type of water, and this is also reflected in the stable isotope composition.

The oxygen isotope composition of Boom Clay pore water in Essen ranges from  $\delta^{18}\text{O} = -6.41$  ‰ vs VSMOW at the top to  $-5.74$  ‰ vs VSMOW at the bottom of the Boom Clay. In Figure 7, it is not clear whether a vertical variation of the  $\delta^{18}\text{O}$  composition is present. However, enlarging the scale of the figure shows that a similar vertical variation is present for the  $\delta^{18}\text{O}$  composition as for the  $\delta^2\text{H}$  composition. Thus with increasing salinity, both the  $^2\text{H}$  and  $^{18}\text{O}$  are enriched in the pore water.

*Table 5: Stable isotope composition of hydrogen ( $\delta^2\text{H}$  or  $\delta\text{D}$ ) and oxygen ( $\delta^{18}\text{O}$ ) of the pore waters from the Essen-1 borehole. Errors for  $\delta^2\text{H}$  are less than 0.7 ‰ and for  $\delta^{18}\text{O}$  less than 0.1 ‰.*

depth (m BDT) from	depth (m BDT) to	depth (m BDT) clay core centre	Lithological unit	Sample code	delta O ‰ VSMOW	delta D ‰ VSMOW
145.47	145.57	145.52	Berchem Sands	Essen sq01	-6.07	-42.8
150.32	150.42	150.37	Berchem Sands	Essen sq02	-5.99	-42.6
161.92	162.09	162.01	BC / Transition zone	Essen sq03b	-6.08	-44.9
171.88	171.98	171.93	BC / Transition zone	Essen sq04	-6.41	-47.5
183.86	183.96	183.91	BC / Putte Member	Essen sq05	-6.31	-46.2
196.77	196.87	196.82	BC / Putte Member	Essen sq06	-6.25	-44.9
208.67	208.77	208.72	BC / Putte Member	Essen sq07	-6.19	-44.2
220.46	220.54	220.50	BC / Putte Member	Essen sq08	-6.04	-42.9
231.33	231.43	231.38	BC / Putte Member	Essen sq09	-6.01	-42.0
243.35	243.45	243.40	BC / Terhagen Member	Essen sq10	-6.15	-40.9
255.19	255.29	255.24	BC / Belsele-Waas Member	Essen sq11	-5.89	-40.0
268.73	268.83	268.78	BC / Belsele-Waas Member	Essen sq12	-5.74	-39.3
282.72	282.82	282.77	Ruisbroek Sands	Essen sq13	-5.69	-39.1
294.78	294.88	294.83	Ruisbroek Sands	Essen sq14	-5.61	-37.7

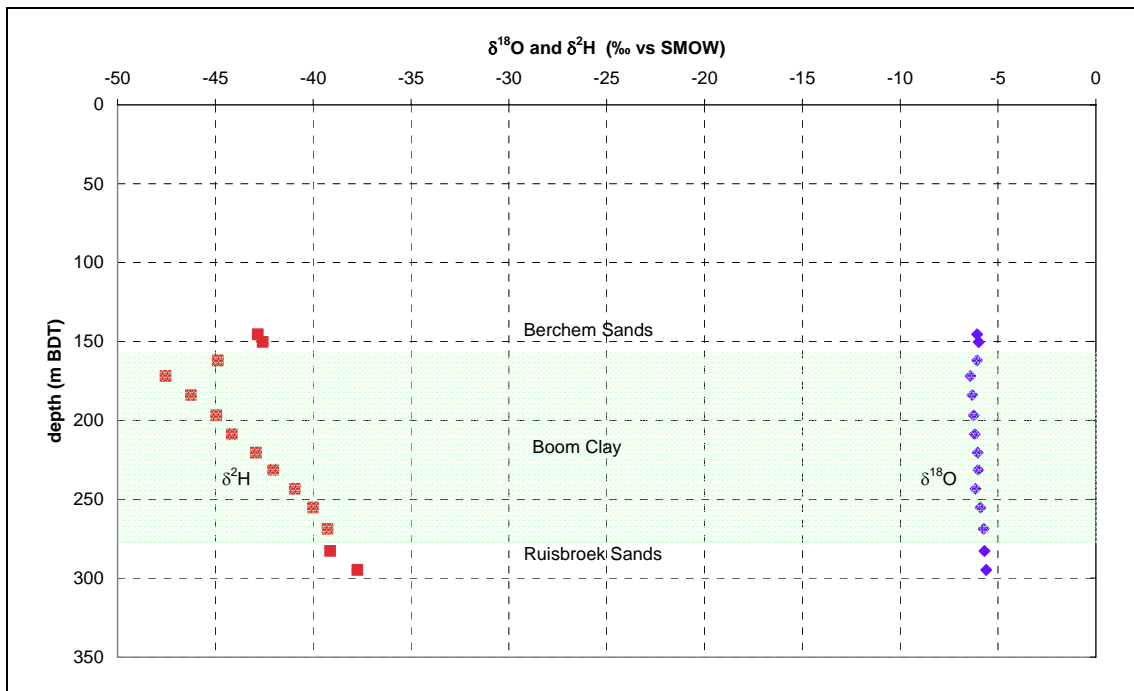


Figure 7: Depth profile showing the variation in the isotopic composition of the pore waters in Essen.

Based on the stable isotope composition, the origin of the Boom Clay pore water can be studied.

Ocean water with 3.5 % salinity exhibits a very narrow range in isotopic composition. The present day isotope composition of ocean water is more or less constant with  $\delta$ -values very near to zero (Hoefs, 1997). There is, however, a strong correlation with salinity because evaporation which increases salinity also concentrates  $^{18}\text{O}$  and  $^2\text{H}$ .

In contrast, the isotope composition of meteoric waters vary linearly on a global scale and are dependent on geographic location. This linear relationship is described as the "meteoric water line" IAEA (1992). The isotope composition of the mean worldwide precipitation is estimated to be  $\delta^{18}\text{O} = -4 \text{‰}$  and  $\delta^2\text{H} = -22 \text{‰}$  (Craig and Gordon, 1965).

Formation waters exhibit a wide range of stable isotope compositions. The change in the  $^2\text{H}$  and  $^{18}\text{O}$  contents of pore fluids depend on the type of initial fluid (ocean water, meteoric water), the temperature, and the lithology of rocks with which the fluids are or have been associated. Generally, formation waters with the lowest temperatures and salinity have the lowest  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values, approaching those of meteoric waters.

In order to study the origin of the pore waters in Essen, the isotopic composition of the pore water is plotted in a  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  diagram (Figure 8). All pore water samples plot very close to the Meteoric Water Line. However, a slight  $^2\text{H}$ -depletion can be recognised for the Boom Clay pore water samples.  $^2\text{H}$ -depletion is a common observation in water extracted from clayey formations and is therefore considered as an artefact of the extraction technique, causing stable isotope fractionation (Griffault *et al.*, 1996). Nevertheless, as suggested in Figure 8, the pore waters in Essen can be

considered as being mainly of meteoric origin, although some mixing with waters of marine origin seems likely (see the salinity). This is the case for both the Boom Clay and the aquifers. During the ARCHIMEDE-argile project (Griffault *et al.*, 1996), similar observations were made for groundwaters of Lower Rupelian aquifers at various locations. The authors concluded that the recharged conditions are either those of present day or climatically little different from these.

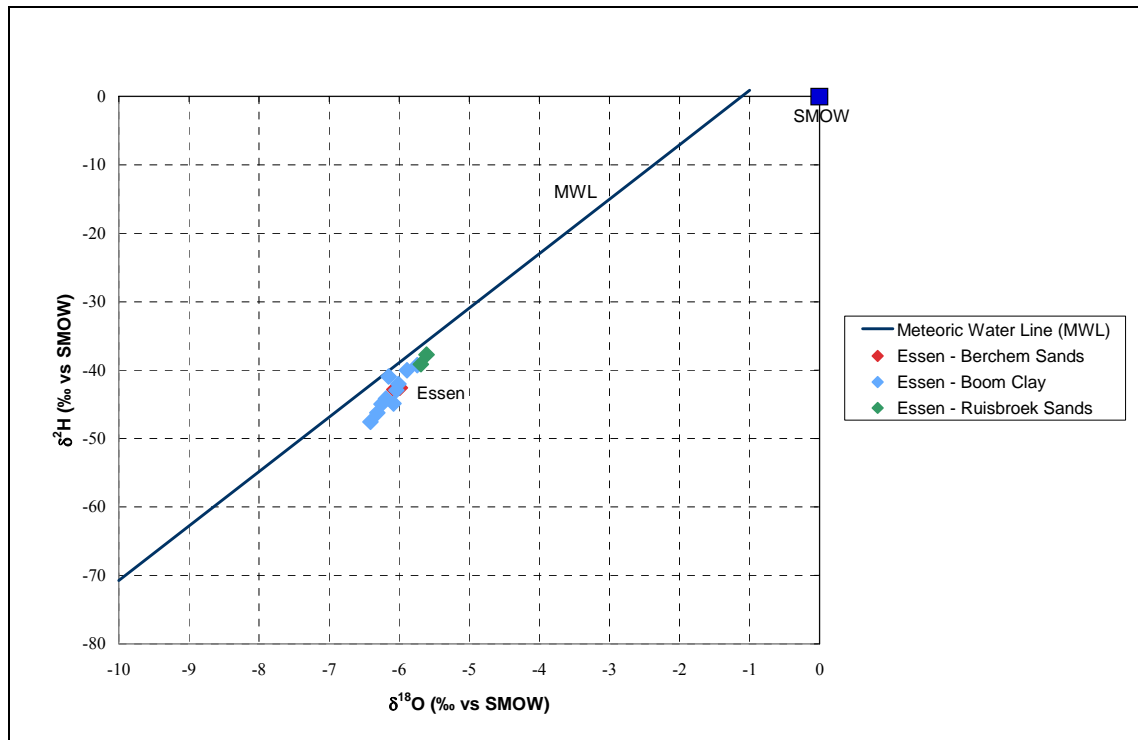


Figure 8: Plot of  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  of Boom Clay pore water and aquifers in Essen (squeezed samples). SMOW is Standard Mean Ocean Water; MWL is Meteoric Water Line.

#### 4.2.2 Comparison of the stable isotope composition of the Boom Clay pore water in Essen with the stable isotope composition of the Boom Clay pore water at the Mol site

The stable isotope composition of the Boom Clay pore water in Essen has been compared with the stable isotope composition of the Boom Clay pore water at the Mol site. The latter data were reported in Griffault *et al.* (1996). New data on pore water from various piezometers installed in the HADES URF are also included in Figure 9.

In Mol, the isotopic composition of Boom Clay pore water is  $\delta^{18}\text{O} = -7$  ‰ and  $\delta^2\text{H} = -53$  ‰. This pore water can be considered as purely meteoric in origin (*e.g.* chloride content).

Seawater contains about 19400 mg/l of chlorides (Millero, 1996) and exhibits  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values very near to zero (Hoefs, 1997). The Boom Clay pore water in Essen contains an average chloride content of 1563 mg/l, which is about 8 % of the chloride content in seawater. Therefore, the Boom Clay pore water in Essen can be considered

as a mixture of 8 % of seawater and 92 % of meteoric water. Indeed, calculating the isotopic composition of a pore water with a 8 % marine and 92 % meteoric origin (starting from the isotopic composition in Mol), ends up with an average stable isotopic composition of  $\delta^{18}\text{O} = -6.4 \text{ ‰}$  and  $\delta^2\text{H} = -48.7 \text{ ‰}$ . This is in line with the isotopic composition of the Boom Clay pore water in Essen. The Boom Clay pore water in Essen is thus mainly of meteoric origin, but mixing with some water of marine origin is visible. This explains the higher salinity of the Boom Clay pore water in Essen compared to Mol, as well as the less depleted in  $^2\text{H}$  and  $^{18}\text{O}$  values.

The same reasoning can be applied for the Ruisbroek Sands. A mixture of 20 % of seawater (see chloride content) with 80 % of meteoric water can explain the measured stable isotope composition.

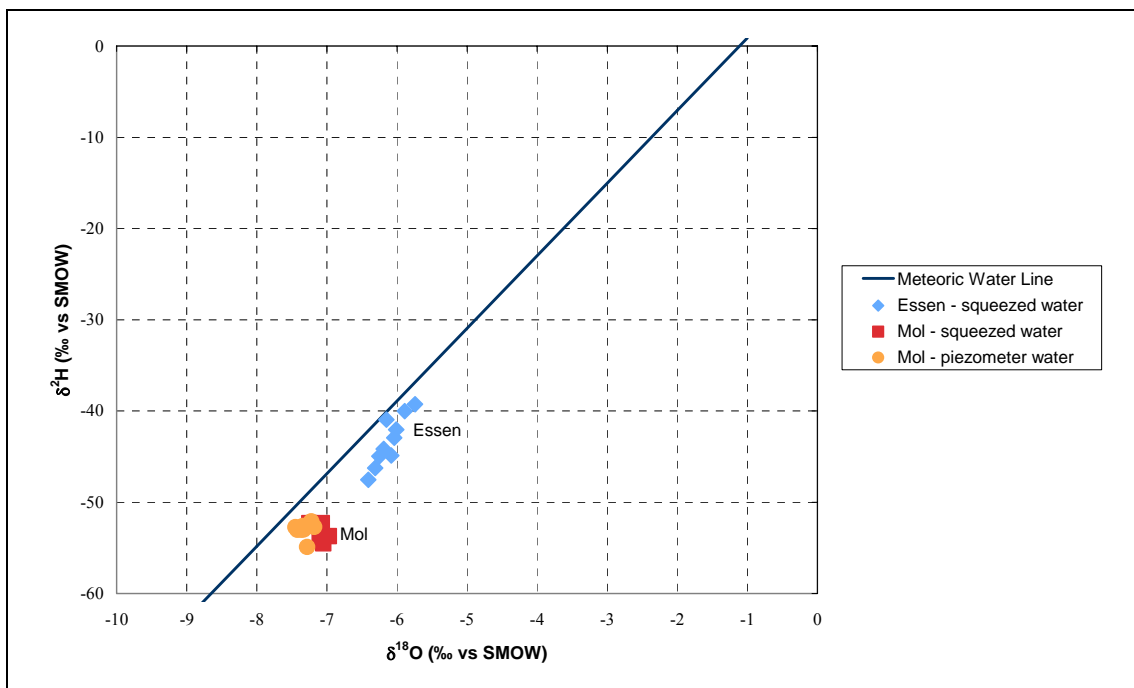


Figure 9: Plot of  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  of Boom Clay pore water in Essen and in Mol.

## 5 Conclusion

The Boom Clay pore water was extracted by squeezing from clay cores of the Essen-1 borehole. The chemical composition and the stable isotope composition of the pore water was then determined and compared to the reference composition at the Mol site.

In Essen, the Boom Clay pore water is a NaCl solution of about 55 mM, containing 21 mg C / l. It is characterised by a relatively high salinity, ranging from 1470 mg/l to 7249 mg/l. The large range in salinity, and thus also in overall chemical composition, reflects an enrichment in salinity from the top to the bottom of the clay, which is continued in the underlying aquifers. The Boom Clay pore water composition in Essen is clearly different from the reference Boom Clay pore water composition at the Mol site. The most important differences are the type of pore water, the salinity, and the vertical variations in chemical composition.

The stable isotope composition of the Boom Clay pore water in Essen is characterised by  $\delta^2\text{H}$  values ranging from -47.5 ‰ vs VSMOW at the top to -39.3 ‰ vs VSMOW at the bottom of the Boom Clay.  $\delta^{18}\text{O}$  values range from -6.41 ‰ vs VSMOW at the top to -5.74 ‰ vs VSMOW at the bottom of the Boom Clay. Thus, with increasing salinity towards the bottom of the clay, both  $^2\text{H}$  and  $^{18}\text{O}$  are enriched in the pore water. These data suggest that these pore waters are mainly from meteoric origin, but some mixing with water of marine origin is visible (most likely from underlying aquifers). The mixing with water of marine origin explains the higher salinity and the enrichment in  $^2\text{H}$  and  $^{18}\text{O}$  in the Essen pore waters compared to the pore waters in Mol.

## 6 References

Craig, H. and Gordon, L. (1965) Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. In: Symposium on marine geochemistry. Graduate school of Oceanography, Univ. Rhode Island, Occ. Publ. No 3:277.

De Craen, M., Delleuze, D., Volckaert, G., Sneyers, A., Put, M. (2000) The Boom Clay as natural analogue. SCK•CEN Final report to NIRAS/ONDRAF for the period 1997-1999, Contract nr. CCHO-98/332, KNT 90 98 1042, R-3444.

De Craen, M., Wang, L., Van Geet, M. and Moors, H. (2004) The geochemistry of Boom Clay pore water at the Mol site, status 2004. SCK•CEN Scientific Report. BLG 990.

Gedeon M. and Wemaere I. (2003) Updated regional hydrogeological model for the Mol site (the North-Eastern Belgium model). Geological disposal of conditioned high-level and long-lived radioactive waste. SCK•CEN report to ONDRAF/NIRAS. R-3751, Mol, Belgium, pp 64

Griffault, L., Merceron, T., Mossmann, J. R., Neerdael, B., De Cannière, P., Beaucaire, C., Daumas, S., Bianchi, A., and Christen, R. (1996) Acquisition et régulation de la chimie des eaux en milieu argileux pour le projet de stockage de déchets radioactifs en formation géologique, Project <Archimède argile>, Rapport final, EUR 17454 FR.

Hoefs, J. (1997) Stable Isotope Geochemistry. Springer, Berlin, 201 pp.

IAEA (1992) Statistical treatment of data and environmental isotopes in precipitations. Technical Report Series 331.

Lie S.F., Broothaers M., and Uyttendaele D. (2006) Drilling and geological report of the Essen-1 well. 1-122. Faninbel report to ONDRAF/NIRAS, Lille, Belgium

Mazurek M., Alt-Epping P., Gimmi T., and Waber H.-N. (in preparation) CLAYTRAC project: Natural tracer profiles across argillaceous formations - review and synthesis. Rock-Water Interaction, Institute of Geological Sciences, University of Bern, Switzerland.

Millero F.J. (1996) Chemical Oceanography. CRC Press, Boca Raton, FL, 469 pp.

Wickham, S.M. (2005) The ONDRAF/NIRAS Supercontainer Concept. Galson Sciences, UK.