

## INFLUENCE OF THE FORMER MARINE CONDITIONS ON GROUNDWATER QUALITY IN THE NEOGENE PHREATIC AQUIFER, FLANDERS

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### Abstract

The Neogene Aquifer is situated in the Campine basin in the northeast of Belgium. The groundwater body consists mainly of sands with some clayey intercalations. The Boom Clay forms the lower impermeable boundary of the aquifer. Groundwater flow has been modelled by means of the MODFLOW code. Calculated piezometric levels show good agreement with the observed piezometric heads. The main processes that influence groundwater quality on his way through the aquifer have been studied. The aquifer is well flushed resulting in low amounts of total dissolved solids. In the recharge areas, infiltrating meteoric water mainly influences the chemical composition of groundwater. Pyrite oxidation raises sulphate and iron contents in the top layers. Groundwater mineralisation increases along a flow line, primarily as a result of silicate and calcite dissolution and cation exchange. Large parts of the aquifer are decalcified. Calcareous deposits are present in the deep parts and to the north. The former marine depositional environment has still influence on the present-day groundwater quality. Cation exchange is the most important witness for this marine depositional environment.

**Keywords:** hydrogeochemistry, cation exchange, geochemical evolution, Belgium

### Introduction

The Neogene Aquifer occurs in the north east of Flanders (Figure 1), more specifically in the provinces of Antwerp and Limburg. The deposits are mainly composed of sands, deposited in shallow marine and sometimes continental conditions. The sediments of the Campine Basin dip gently to the north-northeast with a slope of about 1-2 %. Younger layers gradually crop out in northern direction. The Neogene aquifer is considered as the largest groundwater reservoir in Flanders, containing important drinking water resources. Groundwater extraction mainly takes place in the deeper parts of the aquifer, in the Formations of Diest and Berchem, because of high iron concentrations in the shallow wells.

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The aim of this study is to interpret the groundwater quality evolution and to determine the relevant geochemical processes. Chemical and isotopic data on groundwater was obtained as part of earlier studies (Coetsiers *et al.*, 2003). New chemical data were obtained along a south-north flow line.

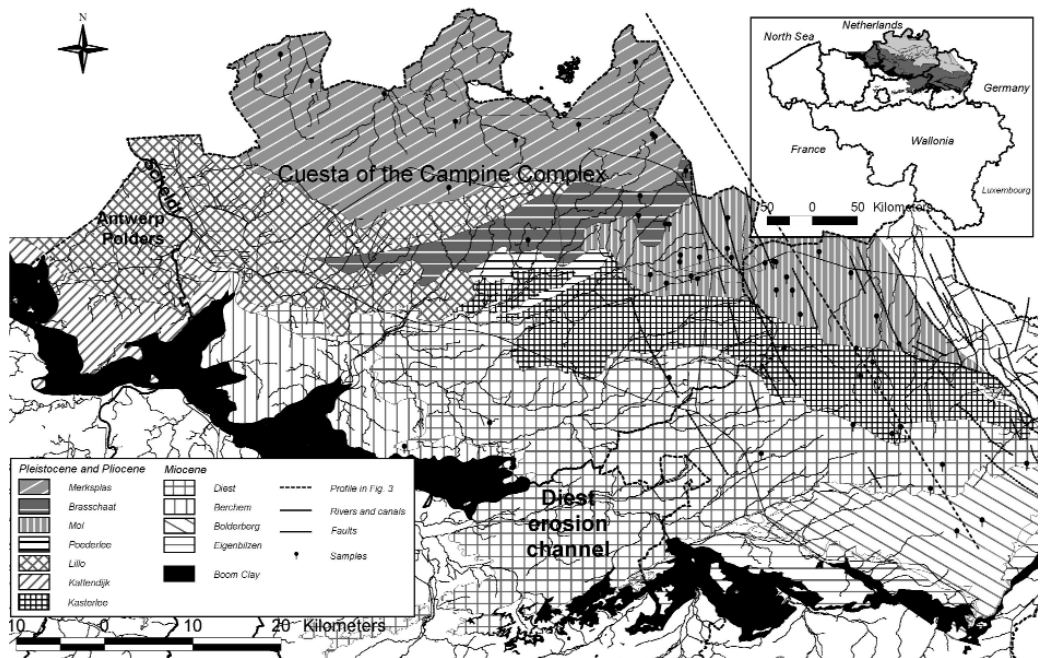
## Geological and hydrogeological setting

The Formation of Boom, consisting of stiff silty clay, forms the substratum of the aquifer. The Boom Clay separates the Neogene Aquifer from underlying Eocene and Palaeocene aquifers. In the area around Diest and Averbode the Boom Clay is completely eroded by the Diest erosion channel, a deep SW-NE orientated erosion trench. In the north of the province of Antwerp the top of the Boom Clay is at a depth of more than 300 m and in certain parts of the Roer Valley Graben the top of the Boom Clay is at a depth of over 800 m.

The marine Formation of Voort is in fact of Late Oligocene age but is hydrogeologically considered as a part of the Neogene Aquifer. It is composed of dark green glauconitic, clayey sands, containing fossils (Laga, 1973; Marechal and Laga, 1988). In westerly direction the Formation of Voort disappears. The Formation of Eigenbilzen is only present in the northeast of the area where it can reach a thickness of 25 m. It is composed of dark green glauconitic, clayey sands (Marechal and Laga, 1988). The Formations of Voort and Eigenbilzen are generally less permeable than the overlying deposits.

The Formation of Bolderberg and the Formation of Berchem represent the Lower Miocene. The Formation of Bolderberg consists of a lower marine unit (dark green, glauconitic and micaceous sands with shells and lignite) and an upper continental unit (white yellowish sands with limonite lenses, lignite layers and quartzite banks) (Laga, 1973). To the west the marine Formation of Berchem (green, fine to medium, strongly glauconitic and slightly clayey sands with shells and phosphate enrichments) replaces the Formation of Bolderberg. In the Diest erosion channel the Sands of Dessel (grey-green, fine, micaceous, glauconitic and calcareous sands) were deposited. Above and outside the trench the Sands of Diest (grey-green to brownish, strongly glauconitic, coarse sands) occur.

The Lower Pliocene occurs as two chronostratigraphic equivalent deposits: the Formation of Kattendijk (dark green to green-grey, fine to medium fine, slightly clayey, glauconitic sands with shells) and the Formation of Kasterlee (grey-green, micaceous, glauconitic, fine sands without fossils). To the north and northwest the Formation of Kasterlee passes gradually into the Formation of Kattendijk. The Upper Pliocene deposits change from fluvial deposits in the east (Formation of Mol), over coastal sands (Formation of Poederlee), to shallow marine clayey sands (Formation of Lillo) in the west. The top of the aquifer system consists of Pleistocene deposits of the Formations of Brasschaat (white-yellow, fine to medium, quartz sand without clay or fossils) and Merksplas (coarse sands with shells at the base) and the heterogeneous Campine Complex (fine to medium fine, locally coarse sands with clay lenses and clay layers). The northeast of the region is disturbed by Oligocene faults, which are mainly oriented NNW-SSE (Figure 1). These faults were formed during the development of the Roer Valley Graben, which is the northwestern branch of the Rhine Graben. The subsidence of the Roer Valley Graben was very strong during Miocene and Pliocene times and is at present still active (Demyttenaere and Laga, 1988).



**Figure 1.** Outcropping geological formations in the study area and localisation of faults.

In Table 1 a hydrogeological schematisation is given for the Neogene deposits based on the HCOV code (Meyus *et al.*, 2000). Although the Neogene deposits are considered as one aquifer unit, different zones can be distinguished. Where the Formations of Diest and Berchem-Bolderberg crop out, the aquifer is phreatic. More towards the north, the groundwater body becomes semi-phreatic by the presence of clayey top layers and limonite banks in the Formation of Diest and the occurrence of clayey layers in the Formations of Lillo, Kattendijk and Kasterlee. Clay layers in the Campine Complex increase the semi-phreatic aspect to the north. Thus three aquifer units can be distinguished: The Miocene Aquifer (Formations of Eigenbilzen, Voort, Bolderberg, Berchem, Diest, Kasterlee and Kattendijk), The Pliocene Aquifer (sandy part of the Formation of Lillo, Formations of Brasschaat, Merksplas, Mol and Poederlee) and the Quaternary Aquifer (sandy part of the Campine Complex).

### Regional groundwater flow model

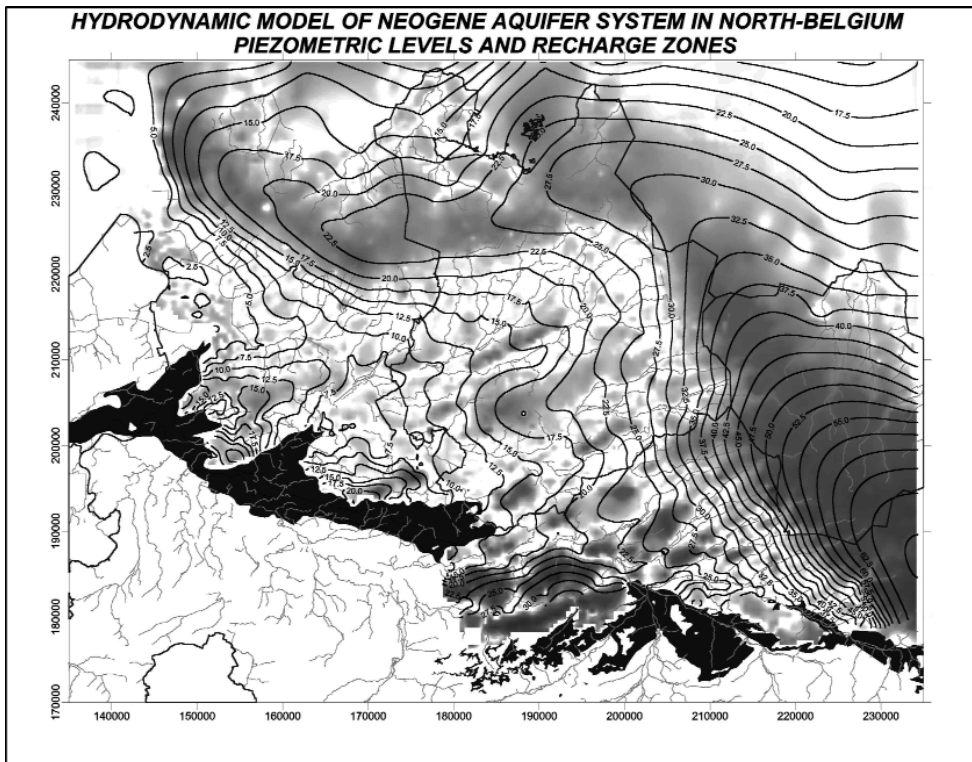
Groundwater flow was simulated using the MODFLOW code, provided by the United States Geological Survey (McDonald and Harbaugh, 1988). The model grid was divided into equal cells of 500 m x 500 m, in 150 rows and 200 columns, encompassing a total area of 7500 km<sup>2</sup>. The groundwater model consists of three layers: the sandy part of the Campine Complex, the clayey part of the Campine Complex and the Miocene Aquifer. In the south and southwest the model area is delimited by the occurrence of the Boom Clay. In the east a zero flow condition is imposed based on the assumption that groundwater flow is essentially oriented from south to north (Figure 2). The boundary conditions used in the hydrodynamical

**Table 1.** Schematisation of the Campine Aquifer System.

	<b>Aquifer / Aquitard</b>	<b>West</b>		<b>East</b>	
<b>Younger</b>	<b>Quaternary Aquifer Systems</b>	Meuse and Rhine deposits			
	<b>Campine Clay Sand Complex</b>	Campine Clay Sand Complex			
	<b>Campine Clay layer</b>	Clay of Rijkevorsel			
	<b>Pleistocene and Pliocene Aquifer</b>	Sands of Brasschaat and/or Merksplas			
—		Sandy top of Lillo	Sands of Poederlee and/or Sandy top of Kasterlee	Sands of Mol	
	Pliocene Aquitard	Clay of Lillo and/or top of Kattendijk		Clayey layers in Sands of Kasterlee	
	<b>Older</b>	Miocene Aquifer	Sands of Kattendijk and/or lower layer of Lillo		Sands of Kasterlee
			Sands of Diest		
			Sands of Dessel		
Sands of Bolderberg					
	Sands of Berchem	Sands of Voort			
		Sands of Eigenbilzen			
	Boom Aquitard	Boom Clay			

model are no-flow to the south, east and west and a constant head boundary in the north. Average groundwater recharge in the region is about 250 mm/year. The Drain package was used to take into account the large amount of rivers and small brooks that drain the area. The numerical implementation of the drain boundary condition is very similar to that for the River and General Head Boundaries. The topography was used as drain elevation.

The calculated piezometric levels in the Miocene aquifer (Figure 2) show good correlation with the observed groundwater heads. Groundwater flow in the Neogene Aquifer is mainly dominated by topography and the present river pattern. The model provided a good localisation of the recharge and discharge areas (Figure 2). Groundwater recharge takes mostly place in the topographically elevated areas. The most important infiltration area lies in the southeast of the model area where topographical elevation is highest and reaches over 80 m above see level. A second important infiltration area and water divide is formed by the elevated cuesta of the Campine Complex in the northwest of the model area. Smaller recharge areas exist in the south where small hills characterize the topography. Groundwater flow will be mainly from the major recharge area in the southeast towards the north-northwest. The cuesta of the Campine Complex causes the regional groundwater flow direction to bend from northern direction to western direction.



**Figure 2.** Positive calculated piezometric heads for the Miocene Aquifer and recharge areas. Gradual grey colours: difference between topography and calculated piezometric level.

## Groundwater chemistry

### *Sampling and analytical methods*

Different sampling campaigns in the period 2001-2004 delivered a total of 77 new samples from the Neogene Aquifer (Figure 1). On-site measurements included temperature, pH, dissolved oxygen, specific electrical conductivity, alkalinity (as  $\text{HCO}_3^-$ ) by titration and redox potential (Eh). Ionic balances were measured for all samples. Determination of cations was carried out by means of Atomic Flame Absorption Spectrophotometry. Additionally, heavy metals and trace elements were analysed. Stable isotopes  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  were analysed for 32 samples. Ten samples were analysed for radiocarbon. Additionally a number of older samples were available. Unfortunately these old samples are not always complete and/or reliable.

### *Classification of groundwater analyses*

Groundwater classification after Stuyfzand (1986) was used to classify groundwater quality. An important advantage of this classification system is that it is able to recognize whether cation exchange has occurred (Walraevens and Lebbe, 1989). Figure 3 shows the distribution of groundwater types on a profile along the direction of groundwater flow. In Figure 4 a Piper diagram is given with indication of groundwater

types. All analysed groundwaters are fresh (code F, Cl < 150 mg/L) and very soft to soft (code \* and 0). In the infiltration areas, where sediments are well flushed, groundwaters are very soft and are mostly CaSO<sub>4</sub>, FeSO<sub>4</sub>, CaMix or NaCl groundwater type. Deeper into the aquifer groundwater becomes CaHCO<sub>3</sub> water type and is still very soft to soft. The cation exchange coefficient  $[(Na+K+Mg)_{corrected} = (Na+Mg+K)_{measured} - 1.061Cl]$  becomes positive indicating water with (Na+K+Mg)-surplus. In the deepest parts of the aquifer MgHCO<sub>3</sub> and NaHCO<sub>3</sub> groundwater types occur (Figure 3).

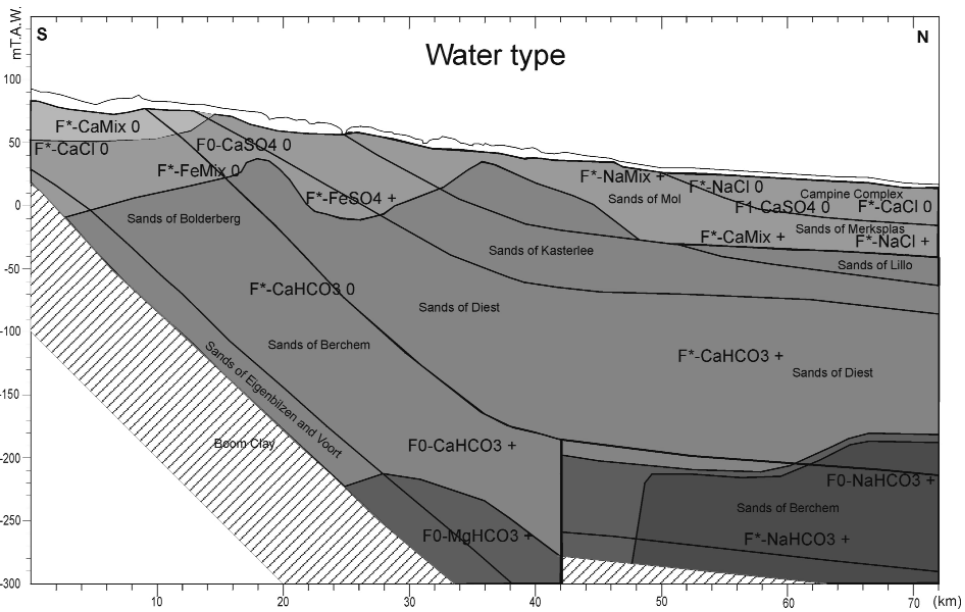


Figure 3. Groundwater types on cross-section along the direction of groundwater flow (see Figure 1).

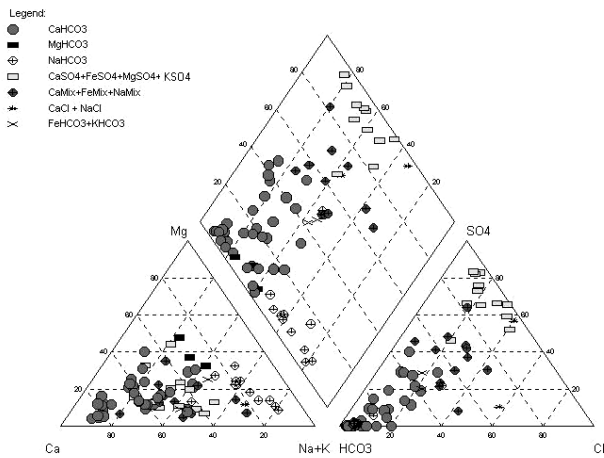


Figure 4. Piper diagram with indication of groundwater types.

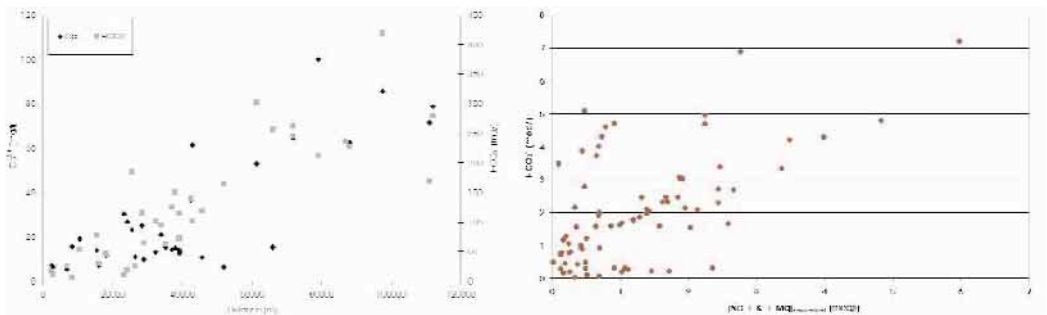
## Reactions

The low reactivity of the deposits in the recharge areas gives rise to a groundwater composition that is very close to evaporated meteoric water. The occurring groundwater types in the recharge zones are NaCl, NaMix, CaCl, and CaMix. Local influence from pollution is noticed, mostly as enhanced levels of nitrate.

### Dissolution reactions

In the decalcified part of the aquifer (where the Formations of Diest and Bolderberg crop out), silicate dissolution is likely the main reaction determining groundwater quality. Silicate dissolution is a very slow process that adds silica and cations ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ ) to the groundwater.  $\text{SiO}_2$ -concentrations increase together with pH and cation content in the direction of groundwater flow. Silica weathering leads to the formation of new secondary minerals like clays (illite, kaolinite and montmorillonite) and iron in silicates usually forms Fe-oxides (Appelo and Postma, 1993). The formation of secondary products is due to the insolubility of the Al-compounds.

Calcite dissolution occurs in the north and northwest, where the calcareous Formation of Lillo is present, and in the deeper parts of the aquifer, where the Formation of Berchem is not yet decalcified. As a consequence of calcite dissolution pH,  $\text{HCO}_3^-$ - and  $\text{Ca}^{2+}$ -concentrations increase (Figure 5) along the direction of groundwater flow and where the Formation of Lillo is present. This gives rise to the occurrence of  $\text{CaHCO}_3$  groundwater types.



**Figure 5.** a)  $\text{Ca}^{2+}$ - and  $\text{HCO}_3^-$ -concentrations along direction of groundwater flow; b)  $\text{HCO}_3^-$  concentrations versus  $(\text{Na} + \text{K} + \text{Mg})_{\text{corrected}}$

### Redox reactions

The oxidation of organic matter progressively consumes oxygen as water percolates in the aquifer. When all dissolved oxygen is consumed the oxidation of organic matter continues. Instead of molecular  $\text{O}_2$ , the agents become  $\text{NO}_3^-$ ,  $\text{MnO}_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{SO}_4^{2-}$  (Figure 6). The succession of different redox processes is well observed in the aquifer. Oxygen, nitrate, iron and sulphate are successively removed from groundwater. In the deeper parts of the groundwater body, water is very poor in nitrate, iron and sulphate (Figure 7).

The oxidation of pyrite and other sulphide minerals can happen by means of oxygen,  $\text{Fe}^{3+}$  or nitrate. Pyrite oxidation mainly occurs in the shallow part of the aquifer where it gives rise to the  $\text{CaSO}_4$  and  $\text{FeSO}_4$  groundwater types. Raising and lowering of the water table provides optimal conditions for the weathering

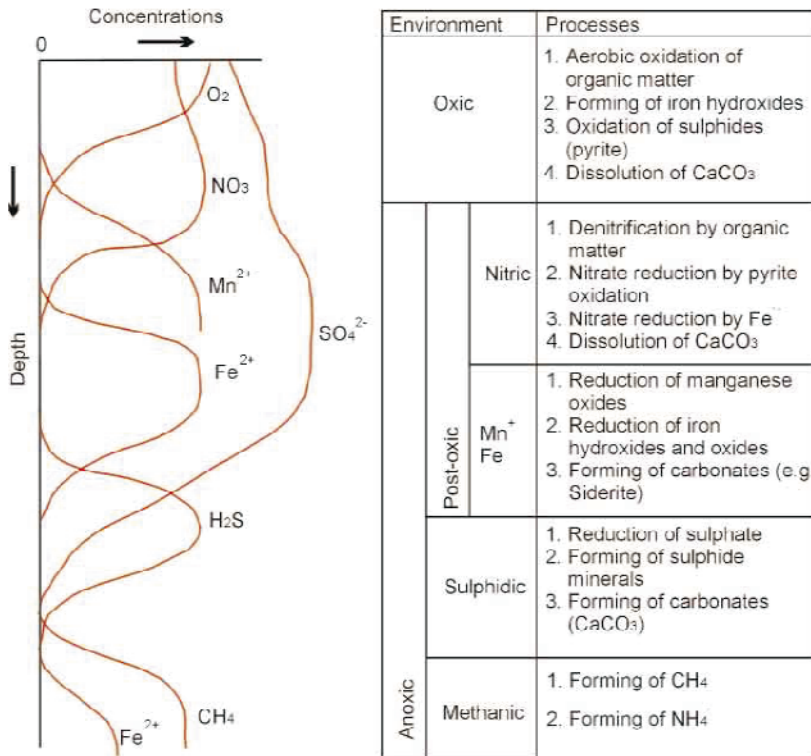


Figure 6. Sequence of reduction processes reflected in groundwater composition (modified after Berner, 1981).

of pyrite. The changes in the geochemical environment, due to the withdrawal of groundwater, results in the decomposition of pyrites and the release of arsenic and other heavy metals. Locally arsenic concentrations over 50 µg/L are observed. The repeated drawdown and recovery pulls oxygen into the dewatered area and causes oxidation of organic matter and the release of CO<sub>2</sub>, oxidation of arsenic bearing pyrite, and the formation of hydroxides and sulphates of iron.

**Ion exchange reactions**

In the deeper parts of the aquifer cation exchange reactions take place. The Na<sup>+</sup>, Mg<sup>2+</sup> and K<sup>+</sup>-cations adsorbed to the clay surfaces are successively being replaced by Ca<sup>2+</sup>-ions in order of increasing affinity for the clay. This results in an increase of marine cations and a depletion of Ca<sup>2+</sup> in the groundwater. The chromatographic sequence of cation exchange is found in the subsequent surplus of Na<sup>+</sup>, followed by K<sup>+</sup> and finally Mg<sup>2+</sup>, resulting in NaHCO<sub>3</sub> and MgHCO<sub>3</sub> water types. High HCO<sub>3</sub><sup>-</sup>-concentrations can result from the depletion of Ca<sup>2+</sup> due to cation exchange, which causes a second stage of calcite dissolution (Walraevens, 1990). This is shown in Figure 5, where the HCO<sub>3</sub><sup>-</sup>-concentration is plotted against the parameter (Na + K + Mg)<sub>corrected</sub>.



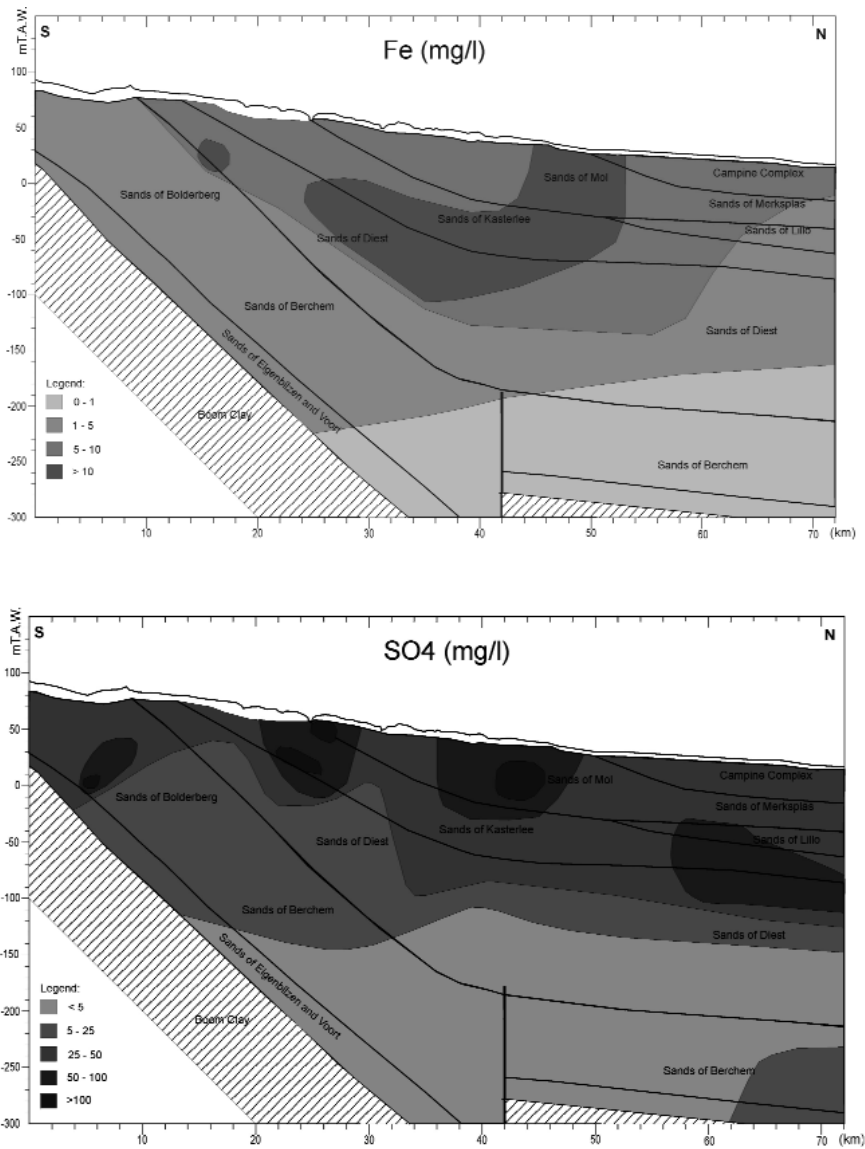


Figure 7. Iron and sulphate concentration based on sampling in cross-sections.

A ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ) surplus can also occur when minerals containing  $\text{Na}^+$ ,  $\text{K}^+$  and/or  $\text{Mg}^{2+}$ , like feldspars, dissolve (Stuyfzand, 1986). But in the deeper parts of the Neogene aquifer the increase in these cations is clearly due to cation exchange as no further increase in silica is observed.

### **Mixing with saline water**

The combined effect of flooding the Antwerp polders during the Middle Ages for strategic reasons and the artificially raising of the terrain by sand in the Antwerp polders has locally made the groundwater to become brackish. The pumping of groundwater near the Scheldt basin has caused infiltration of brackish water. Generally groundwater in the lower Scheldt basin can be considered as brackish.

## **Conclusions**

Regional groundwater flow modelling has allowed locating the recharge and discharge areas. The calculated piezometric heads showed good agreement with the observed groundwater heads. In terms of groundwater quality two important zones can be distinguished in the Neogene Aquifer. Where the Formations of Bolderberg and Diest are outcropping the aquifer is well flushed and completely decalcified. In the top of the groundwater body, where leaching out has been completed, all remnants of the marine environment have disappeared. Groundwater in the recharge area has a composition very close to that of evaporated meteoric water. Pyrite oxidation in these waters causes sulphate and iron to rise, leading to the occurrence of sulphate and sometimes iron water types. Only the deeper parts the Formations of Diest and Berchem contain calcite, which strongly influences groundwater chemistry. The Formation of Lillo also contains important amounts of calcite. Where the Formation of Lillo occurs calcite dissolution will be important in the infiltrating water. Groundwater is of the  $\text{CaHCO}_3$ -watertype in these calcareous parts of the aquifer. The influence of the former marine environment in the sediments is getting clearer in the deep parts of the Neogene Aquifer. Cation exchange is the most important indicator for the old marine environment, leading to the occurrence of  $\text{NaHCO}_3$  and  $\text{MgHCO}_3$  groundwater types.

## **Acknowledgements**

The current work is an extension of the European BASELINE project (Natural Baseline Quality in European Aquifers, EUK1-CT1999-0006).

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