

Identification and quantification of sources of major solutes in a sandy, phreatic aquifer in Central Belgium through ionic ratios and geochemical mass-balance modelling

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Abstract

The processes affecting groundwater chemistry in the Eocene Brussels sands aquifer in Central Belgium are identified based on evaluation of ionic ratios of major solutes. Based on these results and on mineralogic and hydrogeologic information of the aquifer, a conceptual geochemical model for mass-balance modelling is developed, consisting of (1) concentration of precipitation by a factor 1 to 3 due to evaporation, (2) dissolution of a calcite phase with variable magnesium content by both carbonic acid and sulphuric acid, (3) anthropogenic inputs for all major cations and anions except bicarbonate, (4) dissolution of glauconite and (5) a sink for potassium and nitrate.

The mass-balance modelling is carried out by writing mole-balance equations for each considered element based on the stoichiometric reaction coefficients and solving the system of non-linear equations by a least squares optimization, subject to charge balance constraints.

Keywords: Hydrogeochemistry, weathering, anthropogenic influence (*maximum 5 words*)

1. Introduction

The chemical composition of groundwater is the result of chemical reactions between infiltrating water and the minerals present in the unsaturated and saturated zone of the aquifer. In phreatic aquifers in urbanized or agricultural areas the observed groundwater chemistry is not only determined by mixing of different waters and weathering reactions, but a sizeable input of solutes is also derived from anthropogenic activities like fertilizer use, road de-icing, leaking sewage systems, etc.

In order to asses the quality of groundwater it is of importance not only to identify the different processes affecting the chemistry, but also to quantify the contribution of each of these sources. In this paper the identification of processes is carried out by exploring the ionic ratios of major solutes. These findings, combined with information of the mineralogy and hydrogeology of the aquifer will serve as starting point for a conceptual geochemical model. This conceptual model is used for geochemical mass-balance modelling in order to quantify the contribution of each source.

Garrels & Mackenzie (1967) were among the first to use stoichiometric relationships based on mineral weathering reactions to explain the observed changes in groundwater chemistry along a flowpath from precipitation to discharging spring water. Since this paper several authors used and expanded this method to incorporate mixing and concentration of water, cation exchange and redox reactions (Parkhurst, 1997), anthropogenic inputs (Pacheco & Van der Weijden, 1996) and interaction with biomass (Pacheco et al., 2006).

A linear mass balance equation is derived for each element based on the stoichiometric relations, which are known a priori. In reality however some of the reaction coefficients, like the amount of Mg^{2+} in calcite, are unknown a priori. In this study these unknowns are included in the mass balance equations. The resulting system of non-linear equations is solved using a least squares optimization technique.

2. Study Area

The study area is situated in Central Belgium (figure 1). The geology is dominated by the Brussels Sands Formation which is one of the main aquifers in Belgium for drinking water production. This

Brussels Sands aquifer is of Middle Eocene age and consists of a heterogeneous alteration of calcified and silicified coarse sands (Laga et al., 2001), which are locally glauconiferous (Houthuys, 1990).

These sands are deposited on top of a clay formation of Early Eocene age, the Ieper Clay Formation, which forms the base of the aquifer in the study area. On the hilltops, younger sandy formations of Late Eocene to Early Oligocene age cover the Brussels Sands formation. These mainly consist of glauconiferous, fine sands. The entire study area is covered with an eolian loam deposit of Quaternary age. In the north east of the study area, these deposits are sandy loam.

Chemical analyses of the groundwater in this aquifer are obtained from the monitoring networks of the Flemish (VMM) and Walloon government (DGRNE) and from pumping wells from the public drinking water company (VMW).

From this dataset only samples with a charge balance error of less than 5 % are withheld for further analyses. For each of the 98 sampling locations (figure 1) a representative sample is selected, preferably from the first half of 2004. Only concentrations of major ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-} , HCO_3^-) are used in this study.

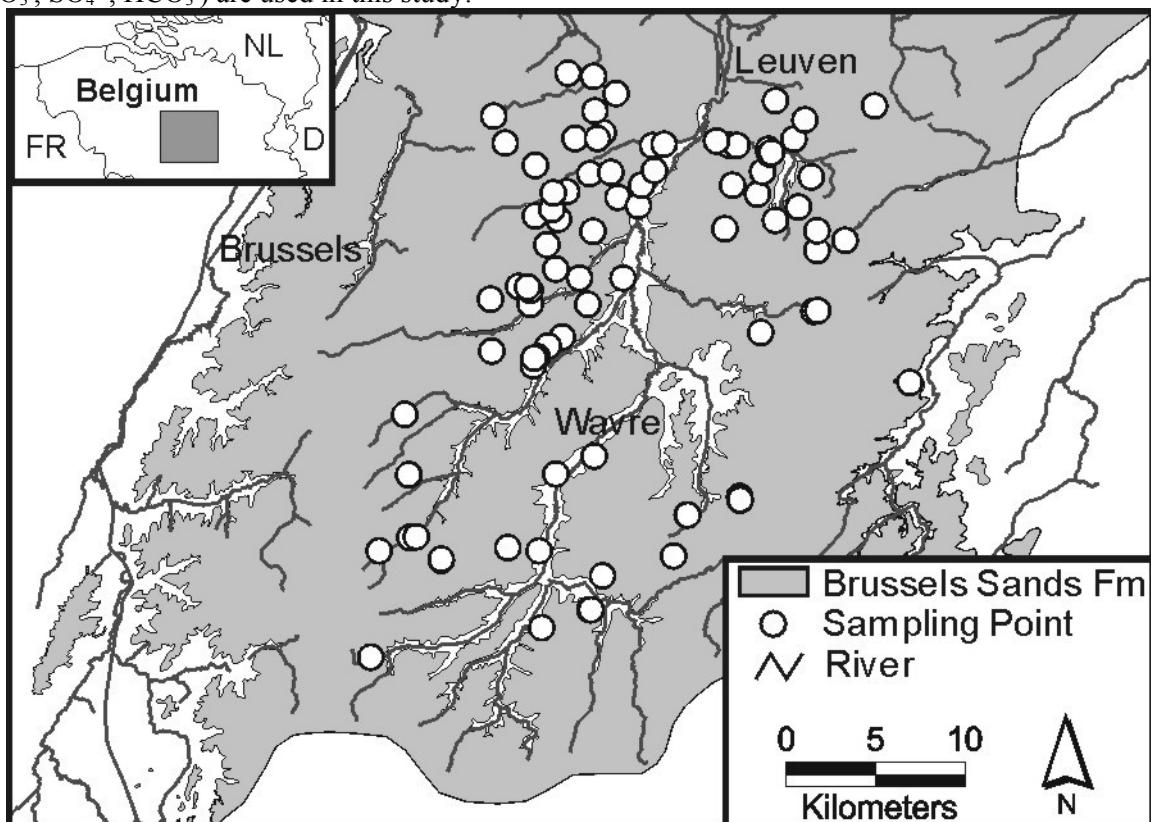


Figure 1: Brussels Sands Aquifer and location of sampling points

3. Ionic ratios

3.1 Piper diagram

A first reconnaissance of groundwater chemistry is provided in figure 2 by plotting the samples in a Piper diagram (Piper, 1944). From this plot it is apparent that the equivalent ratios of cations in the aquifer show little variation and are dominated by calcium and that both contributions of magnesium and sodium plus potassium are below 20 %. The anionic composition shows that bicarbonate is the dominant anion and sulphate contribution is rather low (less than 25%). The contribution of chloride and nitrate however is very variable and shows a range from 2 to 75%. The waters can thus be classified as Ca-HCO₃ and in the central diamond they plot in the carbonate-dissolution zone as defined by Piper (1944).

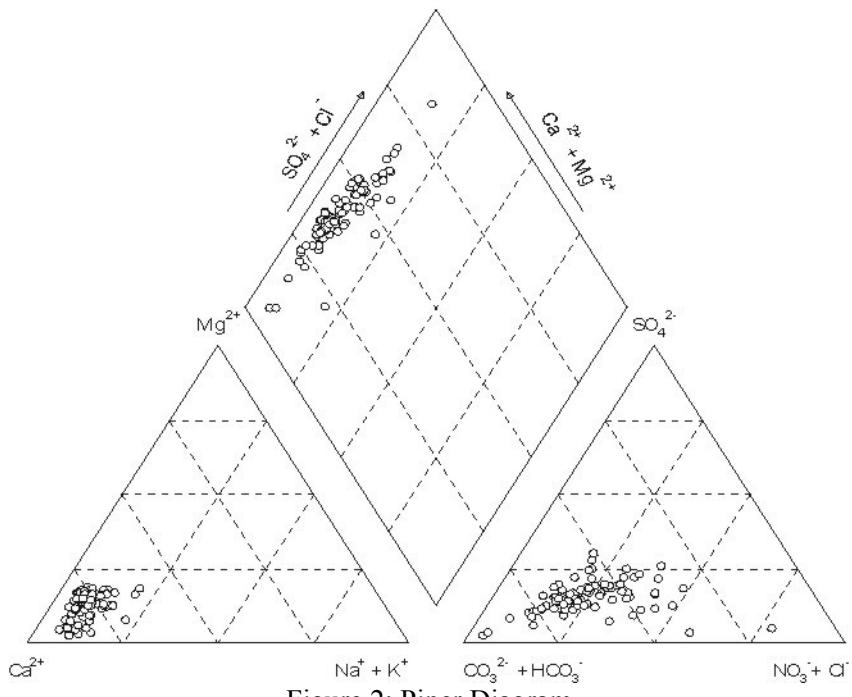


Figure 2: Piper Diagram

3.2 Mineral dissolution

Hydrolysis of silicate minerals as well as the dissolution of carbonates consume carbon dioxide and produce bicarbonate (Bowser & Jones, 2002). The equivalent amounts of cations released by these weathering reactions should balance the equivalent amount of bicarbonate if the aquifer chemistry is dominated by weathering. Figure 3a shows the equivalent moles of bicarbonate versus the sum of equivalent moles of cations. It is clear that all samples plot well above the mineral dissolution line, which means that other sources than mineral dissolution contribute to the cation concentrations.

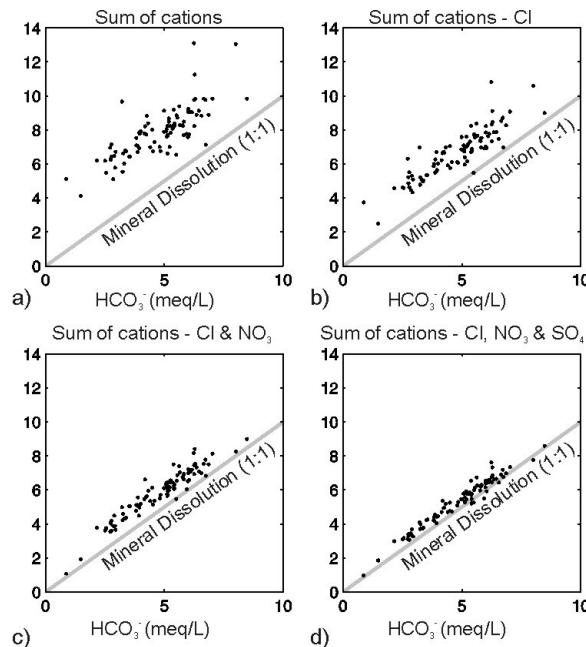


Figure 3: Mineral dissolution

Since no evaporites are present in the aquifer, it is valid to assume that all present chloride, sulphate and nitrate is derived from infiltrating water. Since the infiltrating water has to be charge balanced, cations have to be associated with the chloride, sulphate and nitrate in the infiltrating water. Figures 3

b-d show the chloride, nitrate and sulphate corrected plots of bicarbonate versus sum of cations. It is apparent that the samples plot on the mineral dissolution line only after subtracting the sum of NO_3^- , Cl^- and SO_4^{2-} from the sum of cations.

3.3 Precipitation

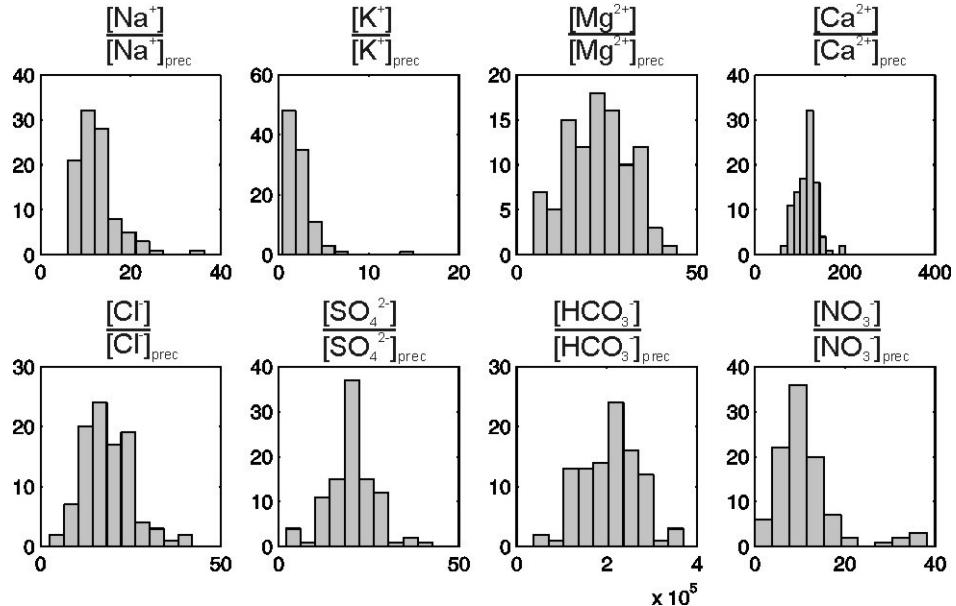


Figure 4: Histograms of ratio of concentration in groundwater over concentration in precipitation

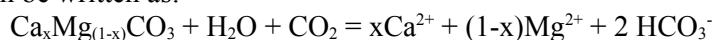
In the previous paragraph is shown that a relatively large part of the total cation concentration is associated with infiltrating water. Since the aquifer under study is phreatic, it is directly fed by infiltrating precipitation, which is the most likely source for these cations. Average precipitation in Central Belgium is 750 mm/yr and the average amount of evapotranspiration can be estimated to be 500 mm/yr. Due to evapotranspiration an increase of all ions is expected with a factor 3. Figure 4 shows the ratio of concentration in the aquifer over the concentration in precipitation for each component. This ratio should be around three if the concentration of the considered ion is only determined by infiltrating evaporated precipitation. For Ca^{2+} and HCO_3^- this ratio is very high, indicating a small contribution from precipitation for these ions. For Cl^- , SO_4^{2-} and NO_3^- the ratios are also elevated. This is also apparent for the sodium and magnesium ratios. The elevated groundwater to precipitation ratios point towards an additional extraneous source. A small portion of nitrate ratios is below one. This can be related to infiltrating water with lower nitrate concentrations or to removal of nitrate due to denitrification.

Potassium ratios are mostly below three, and in some cases even below one. This is an indication of a potassium sink in the aquifer system, probably related to biomass production.

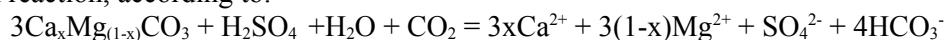
3.4 Carbonate weathering

The Brussels aquifer is characterized by an irregular alteration calcified and decalcified zones while the overlaying Quaternary eolian loam deposits also contain calcite. The Piper diagram and the bicarbonate versus sum of cations plot already indicate calcite dissolution as an important process in this aquifer.

Assuming that calcite contains small amounts of magnesium, the weathering of carbonates by carbon dioxide and water can be written as:



Due to the presence of sulphates and other sulphur species in the atmosphere, partly because of industrial activities, the possibility also exists that sulphuric acid acts as a proton donor in the calcite dissolution reaction, according to:



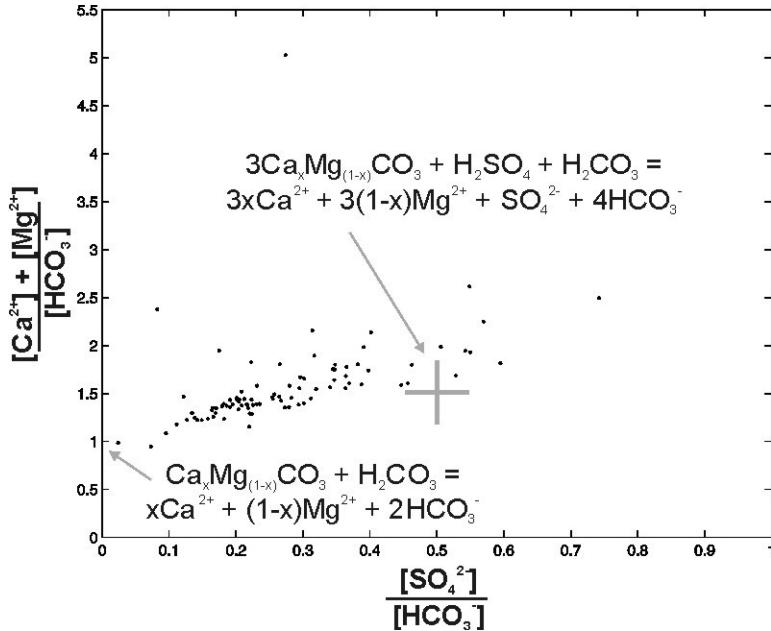


Figure 5: Carbonate weathering by carbonic acid and sulphuric acid

Figure 5 shows the equivalent ratio of sulphate over bicarbonate versus the equivalent ratio of calcium plus magnesium over bicarbonate. A system dominated by dissolution of calcite by carbon dioxide alone would result in an equivalent ratio of Ca^{2+} and Mg^{2+} over HCO_3^- equal to one and small equivalent ratios of sulphate over bicarbonate. A system dominated by calcite dissolution by both carbon dioxide and sulphuric acid would yield equivalent ratios of $[\text{Ca}+\text{Mg}]/[\text{HCO}_3]$ of 1.5 and the equivalent $[\text{SO}_4]/[\text{HCO}_3]$ ratio would be equal to 0.5.

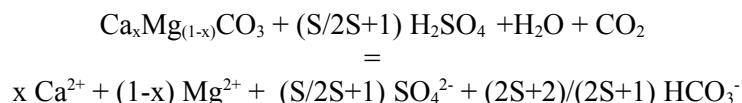
Figure 5 shows that most of the $[\text{SO}_4]/[\text{HCO}_3]$ ratios are below 1.5 and the $[\text{Ca}+\text{Mg}]/[\text{HCO}_3]$ ratios fall between 1 and 2. This indicates that both calcite dissolution by carbon dioxide as dissolution by sulphuric acid are taking place in the aquifer system. The higher ratios for both Ca^{2+} and Mg^{2+} and SO_4^{2-} once again point towards additional sources for these ions.

3.4 Conceptual Geochemical Model

A conceptual geochemical model tries to identify the main geochemical processes contributing to an observed chemical composition of groundwater in an aquifer. The validity of the proposed model can be evaluated through mass-balance modelling.

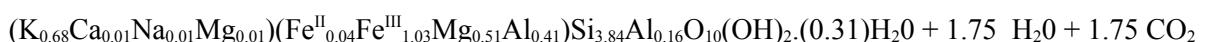
Based on the ionic ratios plots, the mineralogy of the aquifer and the hydrogeologic conditions, following conceptual model is derived for the Brussels Sands Aquifer:

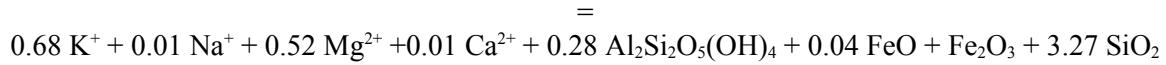
- infiltrating water is concentrated by a factor 1 to 3 by evapotranspiration;
- additional contributions of solutes, with the exception of bicarbonate enter the system through anthropogenic and atmospheric inputs;
- a potassium sink, probably related to biomass production, removes potassium from infiltrating water;
- a carbonate phase containing a small variable amount (x) of Mg^{2+} is dissolved by reaction with carbonic acid and sulphuric acid, according to:



with S the percentage of carbonate weathering by calcite;

- glauconite minerals weather to kaolinite and oxides and provides cations and bicarbonate to the groundwater, according to:





- locally, nitrate concentrations can be lower than nitrate concentration in rainfall due to infiltration of precipitation with lower nitrate concentrations or due to denitrification processes.

4. Mass Balance Modelling

The mass-balance modelling is carried out by writing mole-balance equations for each considered element based on the conceptual model:

$$[\text{X}]_{\text{obs}} = p_{\text{conc}}[\text{X}]_{\text{prec}} + p_{\text{cc}}[\text{Cc}] + p_{\text{gl}}[\text{Gl}] +/ - [\text{X}]_{\text{extra}}$$

with

- $[\text{X}]_{\text{obs}}$: observed concentration of X in groundwater
- $[\text{X}]_{\text{prec}}$: concentration of X in precipitation
- $[\text{X}]_{\text{extra}}$: concentration of X from extraneous sources
- $[\text{Cc}]$: moles of dissolving calcite
- $[\text{Gl}]$: moles of dissolving glauconite
- p_{conc} : concentration factor of precipitation
- p_{cc} : concentration of X produced by weathering 1 mole calcite
- p_{gl} : concentration of X produced by weathering 1 mole glauconite

The equations for Ca^{2+} , Mg^{2+} , SO_4^{2-} and HCO_3^- are non-linear since the percentage of carbonate weathering by sulphuric acid and the percentage of Mg^{2+} in calcite are unknown. The extraneous contributions for potassium and nitrate are allowed to become negative in order to account for the potassium sink and nitrate removal.

This results in an underdetermined system of 8 equations in 12 unknowns. To further constrain this system of equations three additional charge balance equations are formulated to ensure a charge balance for (a) extraneous sources, (b) calcite dissolution and (c) total concentrations;

$$\begin{aligned} 0 &= [\text{Na}^+]_{\text{extra}} + [\text{K}^+]_{\text{extra}} + 2[\text{Ca}^{2+}]_{\text{extra}} + 2[\text{Mg}^{2+}]_{\text{extra}} - [\text{Cl}^-]_{\text{extra}} - [\text{NO}_3^-]_{\text{extra}} - 2[\text{SO}_4^{2-}]_{\text{extra}} \\ 0 &= 2[\text{Ca}^{2+}]_{\text{calcite}} + 2[\text{Mg}^{2+}]_{\text{calcite}} - 2[\text{SO}_4^{2-}]_{\text{calcite}} - [\text{HCO}_3^-]_{\text{calcite}} \\ 0 &= [\text{Na}^+]_{\text{calc}} + [\text{K}^+]_{\text{calc}} + 2[\text{Ca}^{2+}]_{\text{calc}} + 2[\text{Mg}^{2+}]_{\text{calc}} - [\text{Cl}^-]_{\text{calc}} - [\text{NO}_3^-]_{\text{calc}} - 2[\text{SO}_4^{2-}]_{\text{calc}} - [\text{HCO}_3^-]_{\text{calc}} \end{aligned}$$

To ensure that potassium removal only affects the potassium derived from precipitation, an additional constraint is formulated so that the removed concentration of potassium cannot be larger than the concentration in concentrated precipitation.

The system of 12 nonlinear equations in 12 unknowns is solved using a least-squared nonlinear optimization algorithm subject to bounds, based on Coleman and Li (1996), implemented in Matlab®. Table 1 summarizes the chosen bounds for each variable.

Table 1: Upper and lower bounds for nonlinear optimization

Variable	Lower bound	Upper bound
% Mg^{2+} in calcite	0	0.05
% weathering of calcite by H_2SO_4	0	1
p_{conc}	1	3

[Cc]	0 (mol/L)	1 (mol/L)
[Gl]	0 (mol/L)	1 (mol/L)
[Na ⁺] _{extra}	0 (mol/L)	1 (mol/L)
[K ⁺] _{extra}	-1 (mol/L)	1 (mol/L)
[Ca ²⁺] _{extra}	0 (mol/L)	1 (mol/L)
[Mg ²⁺] _{extra}	0 (mol/L)	1 (mol/L)
[Cl ⁻] _{extra}	0 (mol/L)	1 (mol/L)
[SO ₄ ²⁻] _{extra}	0 (mol/L)	1 (mol/L)
[NO ₃ ⁻] _{extra}	-1 (mol/L)	1 (mol/L)

The bounds for percentage of magnesium are based on Fobe (1986) and weathering by sulphuric acid is allowed to vary from 0% to 100 %. The other variables are constrained to be positive, with the exception of potassium and nitrate.

Due to the nonlinearity of the equations an exact solution of the system of equations is seldomly achieved by the optimization process. The quality of the model or parameter set can however be evaluated by the root mean squared error. This also provides a way of comparing models in an objective manner.

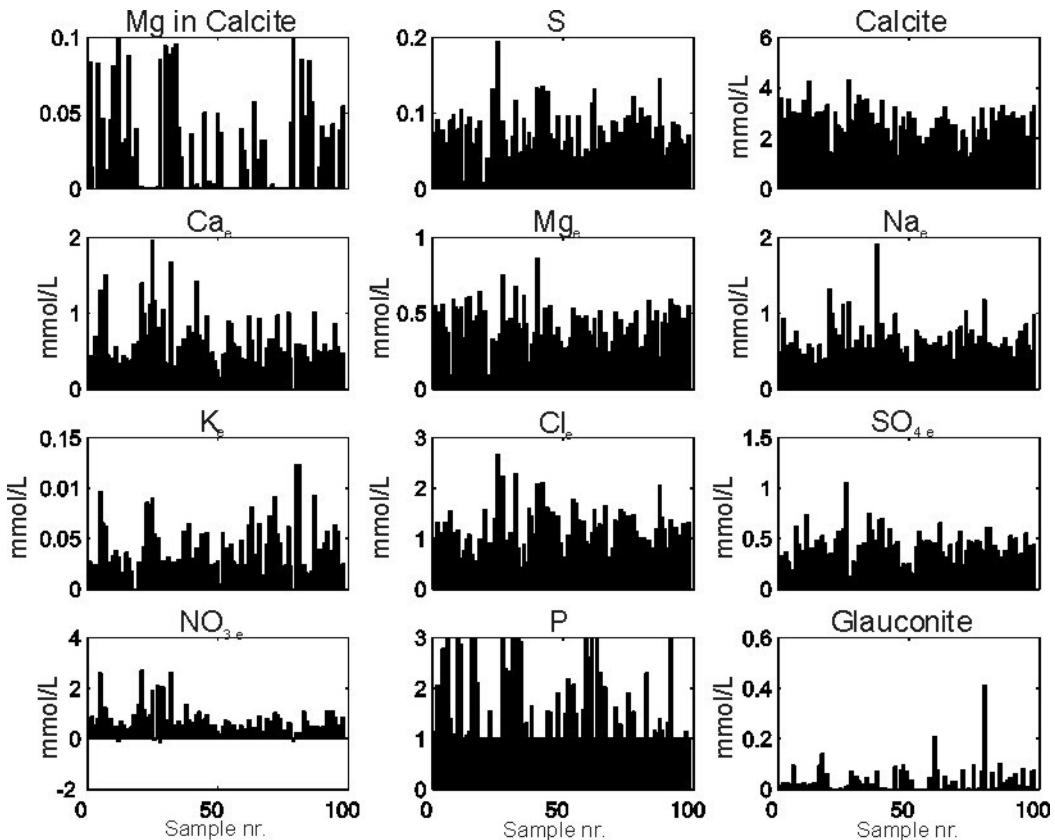


Figure 6: Results of the mass balance modelling per sample

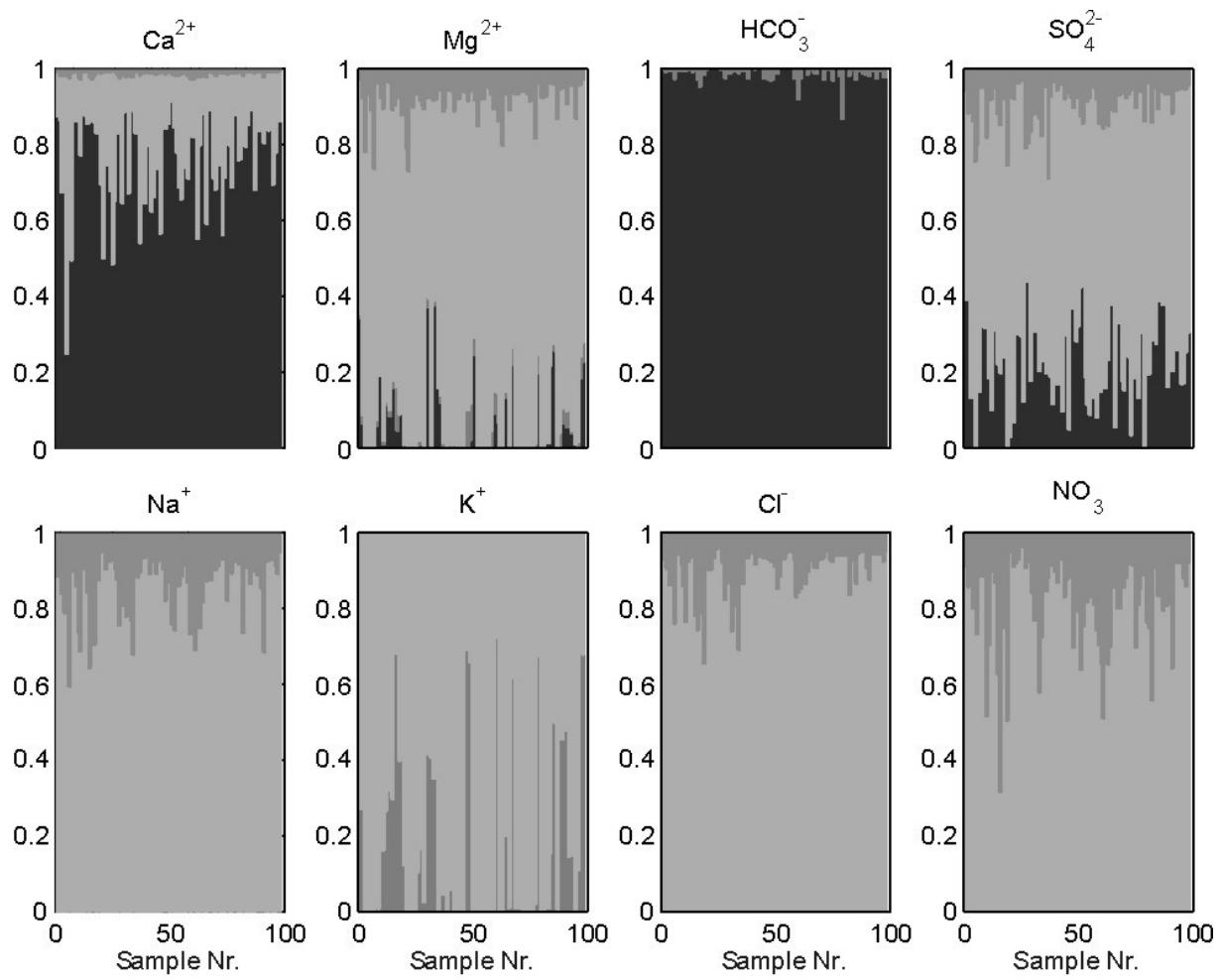


Figure 7: Percent contribution of each process to the calculated chemical composition of each sample

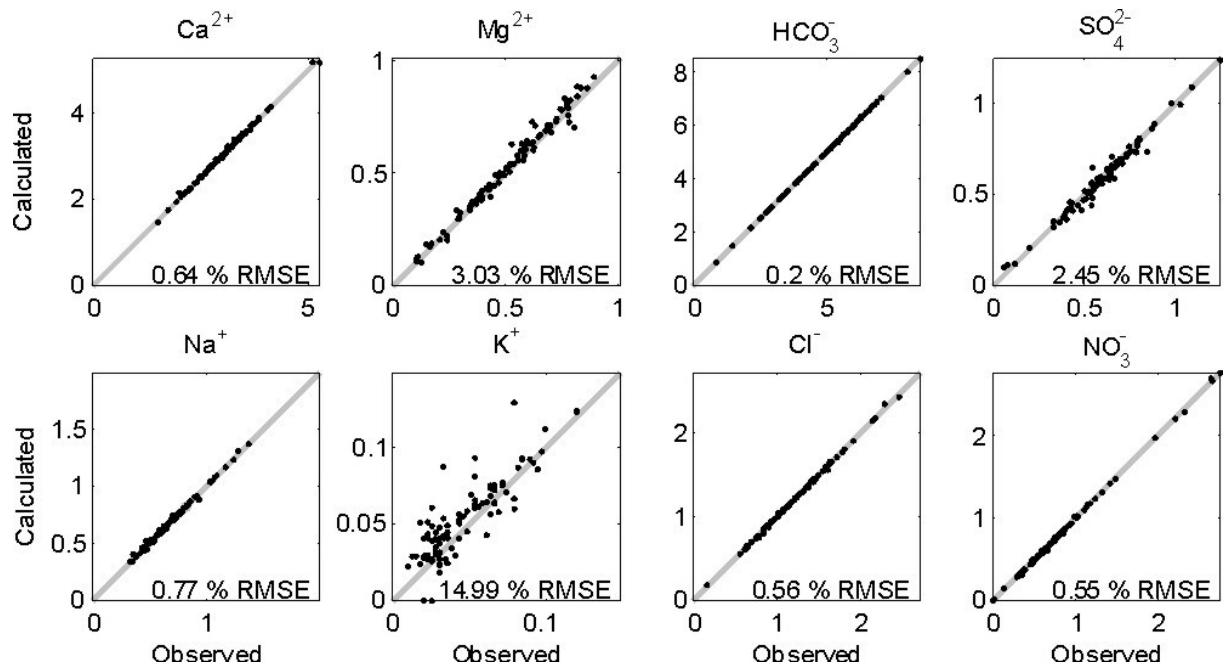


Figure 8: Observed vs calculated concentrations (in mmol/L)

The results of the mass balance modelling are given in figures 6 to 8. Figure 6 shows the calculated value of each variable for each sample while figure 7 shows the relative contribution of each process in the total calculated concentration for each element and for each sample. Figure 8 finally shows crossplots of observed versus calculated total concentrations for each element.

The total root mean squared error for the mass-balance modelling is 2.23×10^{-5} . From figure 8 it can be seen that this is mainly caused by errors associated with magnesium, sulphate and potassium concentrations.

The dissolution of calcite appears to be the major source of solutes for calcium and bicarbonate. It has to be noted however that a considerable part (up to 40%) of the total calcium concentration is derived from extraneous sources.

The magnesium percentage in calcite derived from the mass-balance modelling is low. A large number of samples even do not require any magnesium in the carbonates to account for the observed concentration of magnesium in groundwater. Up to 15% of the weathering of carbonates can be attributed to dissolution by sulphuric acid. This accounts for up to 30% of the observed sulphate concentrations.

Around 10% of the sodium and chloride appear to be derived from precipitation, while precipitation derived nitrate accounts for up to 15% of the total concentration. Although the aquifer is mostly oxic, nitrate levels in groundwater are lower than the concentration in precipitation in a few samples. This probably points towards denitrification, although these samples can also reflect older groundwater, infiltrated when nitrate levels in rainfall were lower.

Glauconite dissolution is a minor contributor of cations to the composition of groundwater in this aquifer, with a maximum of 0.4 mmol/l dissolution. Potassium concentrations however, can locally be dominated by this dissolution process, with a maximum of 60 % of K^+ derived from glauconite. The contribution of glauconite to the magnesium and bicarbonate concentrations is rather low.

5. Conclusions

A mass balance model based on the geochemical processes identified through ionic ratios and mineralogic and hydrogeologic information on the Brussels Sands aquifer in Central Belgium allows a preliminary assessment of the sources of solutes in this aquifer.

Solutes derived from precipitation, concentrated by evapotranspiration, only account up to 10 % of the total concentration of solutes. Weathering of carbonates appear to be the most dominant rock weathering process. The majority of the solutes, however are not provided by precipitation or mineral weathering reactions included in the conceptual model. The unaccounted part of solutes is derived from other processes, of which a part probably is still related to weathering of minerals not included in the model. The major part however is most likely derived from anthropogenic inputs.

Further research will focus on refining the mass-balance model through detailed mineralogic and sedimentological research and on validating the model by comparing the calculated contribution of extraneous sources with chemical data from different anthropogenic sources like road salts, fertilizer and manure. Additionally the role of denitrification reactions in the aquifer will be assessed by evaluating local redox conditions and eventually isotope data.

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References

- Bowser, C. J. & Jones, B. F. (2002) Mineralogic controls on the composition of natural waters dominated by silicate hydrolysis. *American Journal of Science* Vol. 302: 582-662
- Coleman, T.F, Li, Y (1996) An Interior Trust Region Approach for Nonlinear Minimization Subject to Bounds. *SIAM Journal on Optimization* SIAM, Vol. 6: 418-445
- Fobe, B (1986) *Petrografisch onderzoek van de coherente gesteenten van het Eoceen in Laag -en Midden-Belgie* (Petrographic research of the coherent rocks of the Eocene in Lower and Middle Belgium). University Gent

Garrels, RM, Mackenzie, FT (1967) Origin of the chemical composition of springs and lakes. Equilibrium concepts in natural water systems, Am Chem Soc, Advances in Chemistry Series no 67 : 222-242

Houthuys, R (1990) Vergelijkende studie van de afzettingsstructuur van getijdenzanden uit het Eoceen en van de huidige Vlaamse banken.(Comparitive study of the Eocene tidal sands and the current Flemish sand bars). Aardkundige Mededelingen Vol. 5: 55-99

Laga, P, Louwye, S, Geets, S (2001) Paleogene and neogene lithostratigraphic units (Belgium). Geologica Belgica Vol. 4: 135-152

Pacheco, FAL, Sousa Oliveira, A, Van der Weijden, AJ, Van der Weijden, CH (1999) Weathering, Biomass Production and Groundwater Chemistry in an Area of Dominant Anthropogenic Influence, the Chaves-Vila Pouca de Aguiar Region, North of Portugal. Water, Air, & Soil Pollution Vol. 115: 481-512

Pacheco, FAL, van der Weijden, CH (1996) Contributions of water-rock interactions to the composition of groundwater in areas with a sizeable anthropogenic input: A case study of the water of the Fundão area, central Portugal. Water Resources Research Vol. 32: 3553-3570

Parkhurst, DL (1997) Geochemical mole-balance modelling with uncertain data. Water Resources Research Vol. 33: 1957-1970

Piper AM (1944) A graphic procedure in the geochemical interpretation of water-analyses. Transactions-American Geophysical Union Vol. 25: 914-923