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Mobility and removal of nitrate in heterogeneous Eocene aquifers

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Abstract In a study of the principles of lateral and vertical nitrate mobility and removal in unconfined heterogeneous fine sandy Eocene aquifers by long-term observation, no significant nitrate reduction could be observed over short distances (90 m) in the lateral flow direction. Decreasing oxygen contents and limited flow velocity in a downward direction (caused by clay lenses and layers) resulted in a more efficient but incomplete nitrate removal with increasing depth. Chemo-organotrophic and chemo-lithotrophic denitrification coexist in the aquifers. Recharge input of organic matter and the reactivity of sedimentary organic sources, as well as the amounts of pyrite and Fe^{2+}-bearing minerals, control which microbiologically catalysed process finally occurs. Sharp boundaries between different redox zones do not exist due to locally changing availability of organic and inorganic electron donors used for nitrate reduction. Furthermore, preferential flow paths result in a wide spread occurrence of low concentrations of nitrate below the main denitrification zone.

INTRODUCTION

Agriculture, the most extensive anthropogenic source of nitrate to groundwater (Korom, 1992), and water supply installations are often located in the same area; this frequently leads to unacceptable nitrate contamination of drinking water.

Fine sandy layers of the Upper Ypresian age form aquifers that are used for the Flemish drinking water supply. To understand the principles of nitrate mobility and removal in these sediments, four groups of wells consisting of piezometers and multilevel wells were installed in a profile along a slope next to Munte, 15 km southeast of Ghent. The wells are situated in a succession of two unconfined aquifers (the Vlierzele Member and the Mont-Panisel Member) with heterogeneous fine-sandy, iron-rich sediments of marine origin, separated by an almost planar 1 m thick clay layer called Merelbeke clay (see Fig. 1). The total distance of 90 m for the complete profile line and the average of 10 filters per well group results in a high resolution vertical grid of sample points. The recharge area is under cultivation whereas the wells are placed on a field path surrounded by forest and grassland.

Major ion groundwater composition, analysis of trace elements, computer simulation by Visual MODFLOW and column experiments should give detailed information about processes occurring in the survey area.

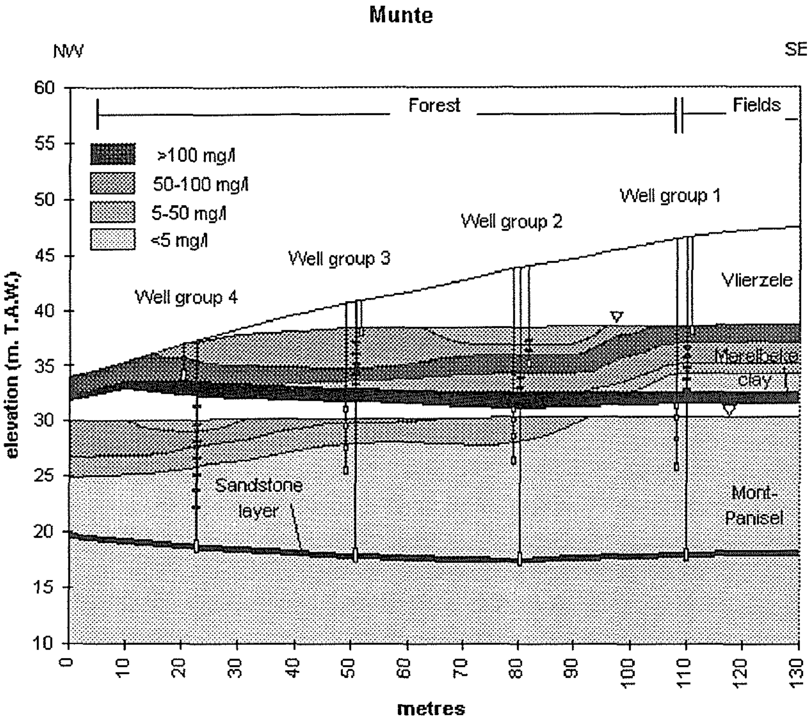

Fig. 1 Profile of the survey area showing the spread of nitrate in groundwater.

MATERIALS AND METHODS

Water samples were taken monthly at 35 filters. Ion concentrations are analysed according to Standard Methods (APHA, 1985) and NBN norms. A Varian Spectra 400 Zeeman graphite tube atomizer was used for the trace elements arsenic, copper and nickel. Redox potential, pH, conductivity and temperature were determined during field sampling with the water quality monitoring system YSI 3560. Oxygen levels were measured with a WTW-OXI 91 instrument. Values of chemical oxygen demand (COD) were analysed by the open reflux method.

The computer simulation program, Visual MODFLOW (Waterloo Hydrogeologic, Inc.), was used to support ideas on groundwater flow and reduction quantities. Column experiments are still in progress. Further results will be available for later publication.

RESULTS

Groundwater quality and especially nitrate as a non-conservative tracer, give a good indication of groundwater flow. Maximum nitrate concentrations of more than 130 mg l^{-1} are measured in the upper (Vlierzele) aquifer at observation point 1, adjacent to the agriculturally used recharge area (see Fig. 1). A zone of higher concentrations is related to the main groundwater flow direction of the upper aquifer.

This interpretation fits with measured water levels and modelling results (Visual MODFLOW). Limited recharge input of nitrate under grassland and forest reduces values at depths shallower than the highly contaminated aquifer zone at observation points 2 and 3 (see Fig. 1). Surface runoff is the reason why remarkable nitrate concentrations are still measured in this area. Due to reduction processes, NO_3^- values below the very contaminated zones of both aquifers decrease. A remarkable lowering of nitrate concentrations occurs in the upper aquifer at observation points 1 and 2, while the main nitrate reduction zones at points 3 and 4 are located in the lower (Mont-Panisel) aquifer (see Fig. 1).

Both aquifers are unconfined. The presence of the less permeable 1 m thick Merelbeke clay causes the appearance of an unsaturated zone at the top of the lower aquifer (see Fig. 1). The hydraulic conductivity of the loamy Merelbeke clay is low at probably 1×10^{-9} m s^{-1}. Nitrate seeps through the clay in high amounts at observation points 3 and 4. It is not clear whether the steep vertical hydraulic gradient of $\Delta i = 8$ allows water to pass through the clay in a reasonably short time. The initial gradient that causes water flow by overpowering electro-molecular forces in water-saturated fine-grained sediments is unknown (Darcy equation: $v = k(\Delta i - i_0$, where v = Darcy velocity (m s^{-1}), k = hydraulic conductivity (m s^{-1}), Δi = hydraulic gradient (-), and i_0 = initial hydraulic gradient (-)). Matthess & Ubell (1983) noted that, for clay, i_0 may have values between 0 and 18. Additional sediment analysis is necessary to determine flow velocities inside the clay. Values between 0 and 5 m $year^{-1}$ are possible. Another aspect is the observed heterogeneity of the clay. Oxidized tubular shapes and voids have been found by analysing cores of shallow hand borings. These rusty brownish canals are probably residues of roots or worm channels. Some parts of the clay are more loamy and a little more sandy. This will lead to a locally higher permeability.

DISCUSSION

Nitrate reduction processes

The ion concentrations of the sampled groundwater reflect that more than one of the following reduction mechanisms for nitrate removal proceeds at the chosen survey site.

Heterotrophic chemo-organotrophic denitrification Obermann (1981), Rödelsperger *et al.* (1992) and Appelo & Postma (1993) have already considered this denitrification by organic matter as the thermodynamically favoured reduction process. The following general reaction is given:

$$5C_{org} + 4NO_3^- + 2H_2O \rightarrow 2N_2 + 4HCO_3^- + CO_2 \qquad (1)$$

Low oxygen contents as well as sufficient quantities and reactivity of organic matter are basic requirements for running this process.

Autotrophic chemolithotrophic denitrification Analysis of the sediment has shown that significant quantities of pyrite are present are present in both aquifers. Postma *et al.* (1991) gives the following reactions for bacterially catalysed nitrate reduction by pyrite oxidation:

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 5Fe^{2+} + 10SO_4^{2-} + 2H_2O \quad (2)$$

$$10Fe^{2+} + 2NO_3^- + 14H_2O \rightarrow 10FeOOH + N_2 + 18H^+ \quad (3)$$

The combination of (2) and (3) leads to the following reaction:

$$2FeS_2 + 6NO_3^- + 2H_2O \rightarrow 3N_2 + 2FeOOH + 4SO_4^{2-} + 2H^+ \quad (4)$$

Rödelsperger *et al.* (1992) consider HCO_3^- and CO_2 as participating reactants causing a change of measured ion concentrations:

$$5FeS_2 + 14NO_3^- + 4CO_2 + 2H_2O \rightarrow 7N_2 + 5Fe^{2+} + 10SO_4^{2-} + 4HCO_3^- \quad (5)$$

$$2FeS_2 + 6NO_3^- + 2HCO_3^- \rightarrow 3N_2 + 2FeOOH + 4SO_4^{2-} + 2CO_2 \quad (6)$$

Nitrate reduction by Fe^{2+} Glauconite as a source of Fe^{2+} is found in relatively high amounts in the sediments of the Vlierzele and Mont-Panisel aquifers. Reaction (3) makes clear that large amounts of Fe^{2+} are necessary to lower nitrate values in an important way. The reaction is inorganically slow but can be quickened by catalytic effects in the presence of Cu^{2+} (Ottley *et al.*, 1997). Furthermore, micro-organisms controlling nitrate reduction after reactions (4) and (6) could use other Fe^{2+} bearing minerals as an additional source.

Groundwater quality at observation point 1 shows excessive nitrate loads at the top of the upper aquifer, whereas NO_3^- is completely reduced over a vertical distance of about 4 m (see Fig. 2(a)). The first sharp decrease in nitrate contents at 2 m below the water table and the increase of bicarbonate by almost constant sulphate concentrations indicates denitrification after reaction (1); this is because the Vlierzele sediments are mainly decalcified. However, only 66% of the increase of bicarbonate

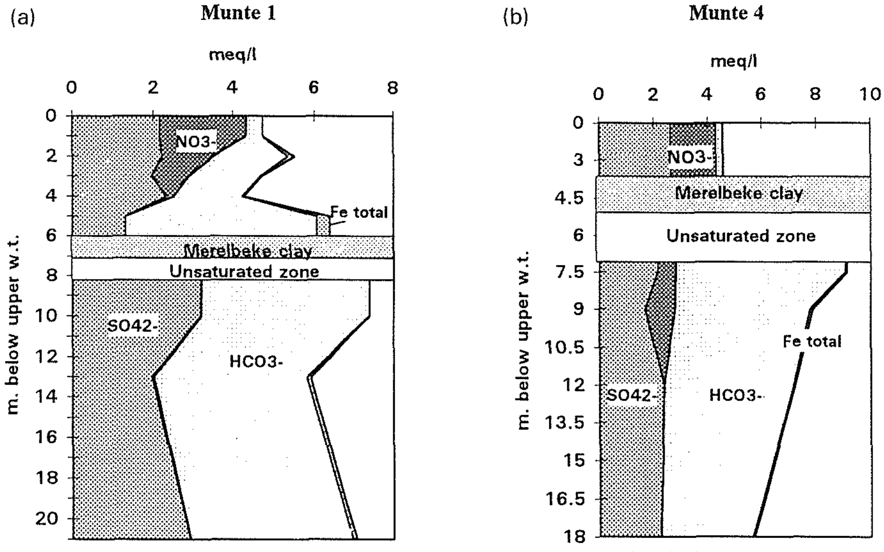

Fig. 2 The change of ion charge equivalents with depth, during participation in nitrate reduction processes, (a) at observation point 1 and (b) at observation point 4.

is correlated to nitrate removal after reaction (1). A lateral mixing of different water types could explain the higher values and so could the solution of residual calcium carbonate. The second sharp decrease in nitrate is located at a depth of 4 m below the water table. Rising sulphate concentrations and almost constant bicarbonate values indicate chemolithotrophic denitrification by pyrite oxidation after reactions (4) and (6). All nitrate has disappeared at 5 m below the water table. Lowering of sulphate values and a heavy increase in bicarbonate and dissolved iron is probably due to an adjacent local source of organic matter. Lignite lenses have been found by during drilling in adjacent regions (Walraevens, 1987).

Bicarbonate contents increase in the groundwater below the Merelbeke clay. The Mont-Panisel Member is not decalcified and the infiltrating water dissolves carbonates. High sulphate concentrations at 10 m below the upper water table (1.5 m below lower water table) are probably due to pyrite oxidation by gaseous O_2 diffusion from the unsaturated zone under the clay (see Fig. 2(a)). Nitrate values of 1–3 mg l^{-1} are still measured in water samples of the Mont-Panisel aquifer at observation point 1 due to preferential flow paths that cause a wide spreading of nitrate below the main reduction zone. An almost planar layering and the highest water levels below the top of the hill indicate that water, present in the lower aquifer, must have passed through the Vlierzele sediments and the Merelbeke clay.

At observation point 4, the main nitrate reduction zone is located in the Mont-Panisel aquifer (see Fig. 2(b)). Denitrification takes places at 7.5 m below the upper water table (0.4 m below lower water table). Nitrite concentrations of almost 2 mg l^{-1} were measured. An extraordinary increase in the bicarbonate concentrations and slightly decreasing sulphate suggest nitrate reduction after reaction (1). COD values of 60 mg O_2 per litre were analysed. The source of organic matter could be located

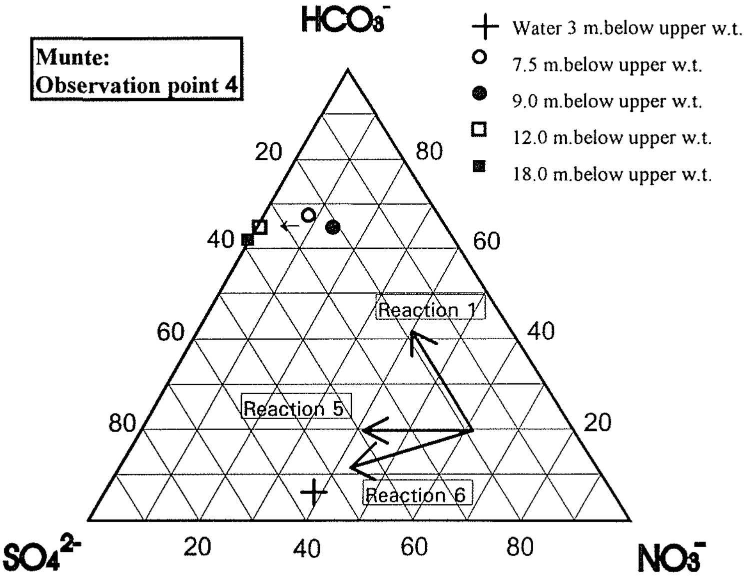

Fig. 3 Ternary system, modified from Rödelsperger *et al.* (1992), representing specific charge equivalents of nitrate, bicarbonate and sulphate and their change in the course of different reactions. An example for groundwater composition at observation point 4 is given.

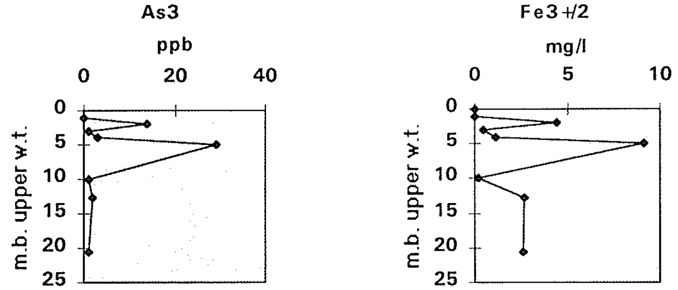

Fig. 4 Example for correlating measured ion concentrations of iron and arsenic in groundwater at observation point 1.

inside the clay that is flushed by infiltrating water. The nitrate concentration rises again at 9 m below the upper water table (1.9 m below the lower water table) probably due to a lateral flow component. Nitrate is completely reduced at a depth of 12 m below the upper water table (4.9 m below lower water table). Additional sulphate and slightly decreasing bicarbonate values indicate a nitrate reduction by pyrite oxidation after reaction (6). The ternary system described by Rödelsperger *et al.* (1992) and used for the interpretation of changing ion compositions of groundwater by nitrate reduction supports this interpretation (see Fig. 3).

Trace elements as indicators

Ion concentrations of the trace elements zinc, arsenic, copper and nickel were analysed to permit quantitative correlations with redox processes occurring inside the aquifers. The Zn^{2+} and Ni^{2+} values do not show any conformity with other measured ions or parameters. Catalytic effects of copper upon nitrate reduction occur according to Ottley *et al.* (1997) at surfaces of precipitated iron oxides. Adsorbed copper in solid phase is preferably catalytically active. Dissolved species have been measured with maximum concentrations of 17 ppb. However, no (anti-) correlation with dissolved ions of iron or other measured parameters was observed. There is no indication of a catalytic enforcement of inorganic nitrate reduction by Fe^{2+}.

Arsenic species show different characteristics. In the Vlierzele aquifer where the pH values are below 7 and the redox potential is higher than 0 mV, As ions correlate extremely well with Fe ions (see Fig. 4), but no increase of sulphate or sulphide concentrations is detectable. Instead of pyrite oxidation as shown by Appelo & Postma (1993), only dissolution of arsenic bearing iron hydroxides occurs. Higher concentrations of dissolved iron are measured in two filters where denitrification by organic matter due to higher bicarbonate and COD values is expected (see Fig. 2(a)). Reaction (7) according to Berner (1981) explains the reduction process occurring.

$$4Fe(OH)_3 + CH_2O + 7CO_2 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O \qquad (7)$$

Nitrate removal

Differences of only a few mg NO_3^- per litre for each filter located in the Vlierzele aquifer were measured in the sampling period from July to December 1997. An almost steady-state situation is given for the groundwater quality of the Vlierzele aquifer. The measured water levels and the modelling with Visual MODFLOW show the flow direction to follow the profile line to the northwest, with a slightly lateral component from south to north. This fits with the observed evolution of groundwater quality. Using a hydraulic permeability for Vlierzele sediments of 5×10^{-5} m s^{-1} (measured by a pumping test in an adjacent region (Walraevens, 1987) and supported by the modelling results) a flow velocity of 35 m $year^{-1}$ is estimated for water transport between observation points 1 and 2 (Darcy equation).

The average lowering of nitrate between filter M1a (observation point 1) and filter M2a (observation point 2) is about 18.5 mg l^{-1}. A half-life of approximately 3.7 years for nitrate under the illustrated conditions is calculated using the degradation formula:

$$\ln(N/N_0) = -\lambda t$$

where N_0 = initial concentration at $t = 0$ (here mg l^{-1} NO_3^-); N = concentration at time t (here mg l^{-1} NO_3^-); t = time; and λ = degradation constant.

The half-life of nitrate for the upper aquifer must be seen as a rough estimate, because lowering O_2 contents, locally changing redox conditions and necessary microbiological adaptation times were not taken into account.

CONCLUSIONS

This example shows that clay layers do not always act as nitrate filters because of retarding downward water transport, electrochemical repulsion or increasing reaction times in contact with electron donors that cause nitrate reduction. Preferential flow paths and steep hydraulic gradients can lead to remarkable vertical transport of nitrate to deeper aquifer zones.

Different nitrate reduction processes occur in the same aquifer system, depending on available electron donor material and its reactivity. Normally, nitrate removal starts by denitrification by organic matter, derived from the recharge input, followed by nitrate reduction by pyrite oxidation. Local sources of reactive organic matter cause a reversed situation. Korom (1992) has already mentioned that further research concerning OC limitation and its impact on the partitioning of nitrate between heterotrophic and autotrophic denitrification will be required.

Concentrations of arsenic species measured in groundwater are not a definite indication of nitrate reduction by pyrite oxidation if iron hydroxides are also regarded as source material for arsenic.

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