

Natural denitrification in groundwater in the presence of pyrite: preliminary results obtained at Naizin (Brittany, France)

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Introduction

Nitrate contamination of groundwater has attracted attention in recent decades because of its toxicity at high levels to infants and livestock. In some areas, denitrification, the biological transformation of nitrate into gaseous N_2 or N_2O , has been inferred from the observed drop in nitrate concentrations with increasing depth or along the flow path of aquifers (cf. the review of Hiscock *et al.*, 1991). Such natural denitrification seems to occur at Naizin where pig-farming and the use of fertilizers lead to high nitrate concentrations in the first meters of the aquifer whereas concentrations decrease as the fluid penetrates down into the fissured medium. In this communication we discuss, based on chemical data, denitrification in the presence of pyrite.

The field site in Naizin is located approximately 70 km southwest of Rennes (Brittany, France). This is an area of about 1200 ha where water flows through schists. In 1993, 7 wells were drilled using the down-the-hole hammer technique. Fluid was sampled during drilling when flowing water was encountered. The wells are located in three main areas: A1, A2 and A3. Fluid samples had also been collected in 1992 from older wells used for water supply (Supply Water Wells, SWW), numbered from 1 to 9.

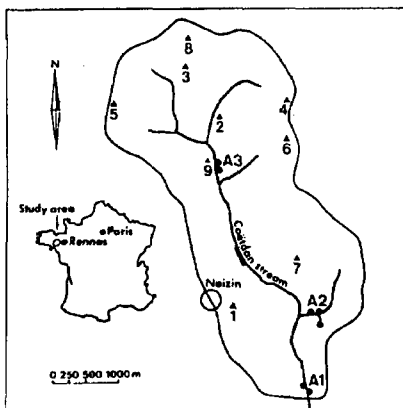
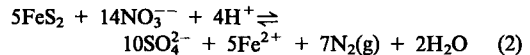
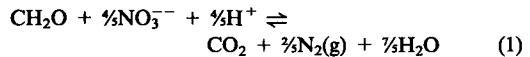


FIG. 1. Location of the study area.

Nitrate concentrations vary according to location. In two areas they decrease abruptly in the first meters from values as high as 150 mg/l to zero. In the third area, surface contents of nitrate seem to be lower. Although this can be partly caused by varying nitrate contribution from the soil surface, it can also be explained by denitrification occurring during organic matter mineralization or pyrite oxidation (equations 1 and 2), which has been detected in the cutting samples collected during drilling:



(CH_2O being a simplified formula for organic matter)

Sulphate concentrations increase with depth (Fig. 3) and with decreasing nitrate concentrations (Fig. 4). This suggests pyrite oxidation reaction. But, according to equation (2), the observed decrease in nitrate concentration would imply higher sulphate concentrations if denitrification during pyrite oxidation were the only process involved. Sulphate cannot have been removed by either the immobilization in a newly formed mineral phase (all the fluids are undersaturated by

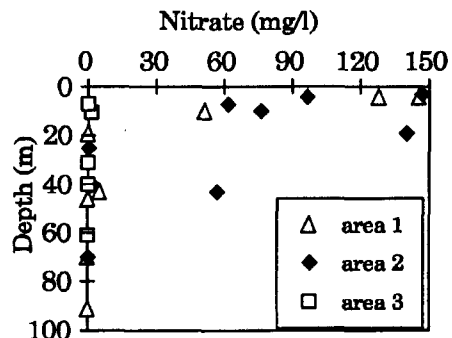


FIG. 2. Variation of nitrate concentration as function of depth in the 7 wells drilled in 1993.

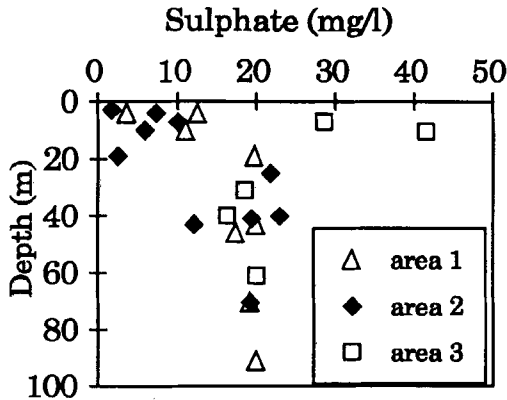


FIG. 3. Variation in sulphate concentration as function of depth in the 7 wells drilled in 1993.

several orders of magnitude with respect to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), or through its reduction via organic matter oxidation because no trace of H_2S has been detected. In areas 1 and 2, SO_4 concentrations only reach values of around 20 mg/l. Assuming that all the sulphate is supplied by denitrification, this would mean that only around 13 mg/l of the nitrate is consumed by the reaction with pyrite whereas concentrations decrease from 150 mg/l to zero. In area 3 and in some fluids collected from the SWW, nitrate concentrations are lower and SO_4 content higher. In these areas, up to 40 mg/l of nitrate may have been consumed by pyrite oxidation.

In some places, therefore, a process other than denitrification during pyrite oxidation is necessary to explain the nitrate decline. Total dissolved CO_2 in the fluids (calculated from pH and alkalinity values) increases with depth (Fig. 5). Its concentration (expressed as $\text{H}_2\text{CO}_3 + \text{HCO}_3^-$) in fluids collected from SWW reaches 111 mg/l.

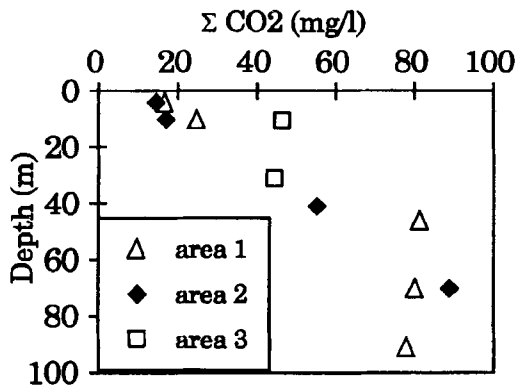


FIG. 5. Total dissolved CO_2 (in mg/l of $\text{H}_2\text{CO}_3 + \text{HCO}_3^-$) vs depth in three of the wells.

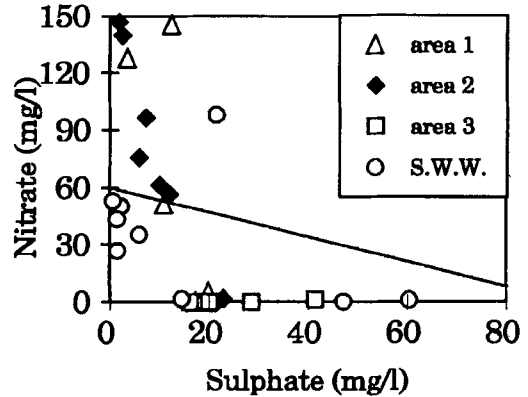


FIG. 4. Nitrate vs. sulphate concentrations of all fluids sampled in this study. SWW: supply water well. The straight line represents the theoretical path followed by a fluid containing 60 mg/L of NO_3 during denitrification through equation (2).

Mineralization of dissolved organic matter by the other electron acceptors present in the aquifer (O_2 , MnO_2) would imply a CO_2 content lower than that which was measured. In the same way, according to the low Ca content, the contribution to CO_2 concentration from dissolution of carbonate minerals would be minimal. Therefore, CO_2 is released during organic matter oxidation via denitrification reaction according to equation (1). Moreover, in areas 1 and 2, the DOC profile decreases with depth until it is completely consumed. On the other hand, in area 3 where NO_3 is removed by equation (2), DOC is still present in the collected fluids.

Conclusion

Denitrification by both pyrite oxidation and dissolved organic matter mineralization has been observed in the area studied. In both cases, pyrite was found in the aquifer material and DOC in the fluids. In further studies, each of these reactions must be quantified and the manner by which one or the other takes place must be determined.

Acknowledgements

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References

- Hiscock, K.M., Lloyd, J.W. and Lerner, D.N. (1991) *Wat. Res.*, **25**(9), 1099–1111.