

INSPIRATION bulletin

CL:AIRE's INSPIRATION bulletins describe practical aspects of research which have direct application to the management of contaminated soil or groundwater in an agricultural context. This bulletin describes an isotopic approach to determine the contribution of nitrate sources in a chalk aquifer in Belgium.

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Analysing N sources and transformation processes in groundwater under agricultural areas (chalk aquifer, Belgium)

1. Introduction

Elevated concentrations of nitrogen (N) in aquifers is one of the major problems in agricultural areas because of the intensive application of mineral fertilisers and manure to increase soil fertility. In such areas, the identification of N sources and, consequently, N pathways is challenging due to the diffuse nature of pollution and the diversity of N sources. However, the study of the stable isotopic compositions of nitrate (NO_3^-) and boron (B) in groundwater is a useful approach for the analysis of pollution sources and interpreting N production and consumption processes (Lasagna and De Luca, 2019; Sacchi *et al.*, 2017).

The present bulletin will inform the reader about the following aspects: 1) the relative contribution of different N sources to groundwater pollution, and 2) the magnitude of N transformation processes. To this end, the stable isotope mixing model SIAR (Stable Isotope Analysis in R) (Parnell, 2008) is applied to the results of NO_3^- and B isotopic compositions in groundwater samples collected during a regional sampling campaign of a chalk aquifer located in Eastern Belgium (Nikolenko *et al.*, 2019).

2. Study Site

The study area corresponds to the unconfined part of the Hesbaye chalk aquifer in the Geer basin, Eastern Belgium. The study area is predominantly characterised by agricultural land use (nearly 65%). Agricultural activities represent the largest source of nitrate input into groundwater, followed by domestic wastewater effluents.

Based on the results of previous investigations (Nikolenko *et al.*, 2019) the study area can be divided into three zones characterised by different hydrochemistry and urbanisation levels (Figure 1). The southern zone corresponds to the unconfined part of the aquifer and the most urbanised land use. The central zone corresponds also to the unconfined part of the aquifer but with a land use dominated by agricultural activities. The north-eastern zone corresponds to the groundwater recharge to the Geer River and predominantly agricultural land use (though sampling wells were located close to the urban areas).

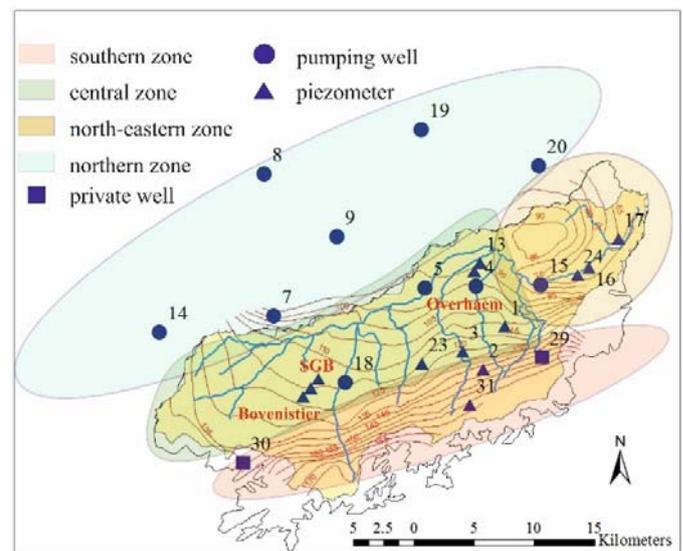


Figure 1: Map of the study area in the Geer basin showing river network, isopiepes and sampling points (wells and piezometers). Colours indicate different zones used to aggregate data.

3. Analysing the Isotopic Data with the SIAR Model

The SIAR mixing model is based on a Bayesian approach which allows uncertainty to be considered in all parameters and uses the Dirichlet distribution for describing prior information. The Dirichlet distribution requires that the total sum of each source input is unity. As input information, the SIAR model requires specifying the mean and standard deviation for each source. This information directs the model simulations according to the user's expert knowledge. The model can be expressed for a set of N mixture measurements on J isotopes with K sources as follows (Jackson *et al.*, 2009;):

$$X_{ij} = \sum_{k=1}^K p_k (S_{jk} + c_{jk}) + \varepsilon_{ij} \quad (1)$$

$$S_{jk} \sim N(\mu_{jk}, \omega_{jk}^2) \quad (2)$$

$$c_{jk} \sim N(\lambda_{jk}, \tau_{jk}^2) \quad (3)$$

$$\varepsilon_{jk} \sim N(0, \sigma_j^2) \quad (4)$$

where X_{ij} is the observed isotope value j of the mixture i, in which $i=1, \dots, N$; $j=1, \dots, J$; S_{jk} is the source value k on isotope j ($k=1, \dots,$

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K) that is assumed normally distributed with a mean μ and standard deviation ω ; p_k is the proportion of source k which is to be estimated by the model; c_{jk} is a fractionation factor for isotope j on source k that is normally distributed with mean λ and standard deviation τ ; and ε_{jk} is the residual error representing additional unquantified variations between individual normally distributed with mean = 0 and standard deviation σ .

The SIAR model was applied to estimate the proportions of N sources contributing to groundwater pollution in the southern, central and north-eastern zones of the studied aquifer. Results of former studies have shown that, in groundwater, N comes from NH_4^+ fertilisers or from manure and sewage which may be transformed by nitrification in the unsaturated zone or the upper part of the aquifer and denitrification in the deeper part of the aquifer. Considering the different possible combinations of N species and processes, the developed model considers five end-members of N: 1) NH_4^+ from inorganic fertilisers; 2) NH_4^+ from manure; 3) NO_3^- from sewage effluent; 4) NO_3^- produced from inorganic fertiliser NH_4^+ (nitrification) and further affected by denitrification, 5) NO_3^- originated from manure and further affected by denitrification. The last two "sources" were introduced to understand the relative intensity of denitrification processes in different zones.

The model input consists of the isotopic signatures of $\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{NO}_3^-$ and $\delta^{11}\text{B}$ of groundwater samples. The isotopic signatures of $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ are suitable for distinguishing inorganic fertilisers from sewage and manure as a source of NO_3^- in groundwater. The isotopic signature of $\delta^{11}\text{B}$ helps to differentiate between sewage and manure pollution sources. Data about the mean and standard deviation values for $\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{NO}_3^-$ and $\delta^{11}\text{B}$ representative of the five selected end-members were obtained from the literature [1] Bateman & Kelly., 2007; Li *et al.*, 2007; Curt *et al.*, 2004; Choi *et al.*, 2003; Kendall *et al.*, 1998; Girard *et al.*, 1997; Wassenaar *et al.*, 1995; Heaton 1986; 2) Nikolenko *et al.*, 2018; Rapisarda *et al.*, 2010; Bateman & Kelly, 2007; Choi *et al.*, 2003; Curt *et al.*, 2004; Fogg *et al.*, 1998; Girard *et al.*, 1997; 3) Divers *et al.*, 2014; Di Lorenzo *et al.*, 2012; Xue *et al.*, 2009; 4) Nikolenko *et al.*, 2018; Bateman & Kelly., 2007; Xue *et al.*, 2009 and 5) Nikolenko *et al.*, 2018; Xu *et al.*, 2016; Michener & Lajtha, 2007]. The average theoretical $\delta^{18}\text{O}-\text{NO}_3^-$ nitrification values were defined from the following equation (Aelion *et al.*, 2009):

$$\delta^{18}\text{O}-\text{NO}_3^- = 2/3(\delta^{18}\text{O}-\text{H}_2\text{O}) + 1/3(\delta^{18}\text{O}-\text{O}_2) \quad (5)$$

with $\delta^{18}\text{O}-\text{H}_2\text{O}$ isotopic signatures taken from a former study (Nikolenko *et al.*, 2019). The fractionation factors and their standard deviations were included in the input information to account for transformations of the first and second N sources due to nitrification and the fourth and fifth sources due to denitrification. (Xu *et al.*, 2016; Li *et al.*, 2014; Otero *et al.*, 2009; Kendall, 1998).

4. Results and Discussion

Figure 2 indicates NH_4^+ from manure as the dominant source of N pollution in the north-eastern and southern zones, accounting for 23 to 42% and from 18 to 37% contribution, respectively. In the central zone, the contributions of NH_4^+ from fertilisers and NH_4^+ from manure are similar – from 21 to 39%, and from 25 to 41%,

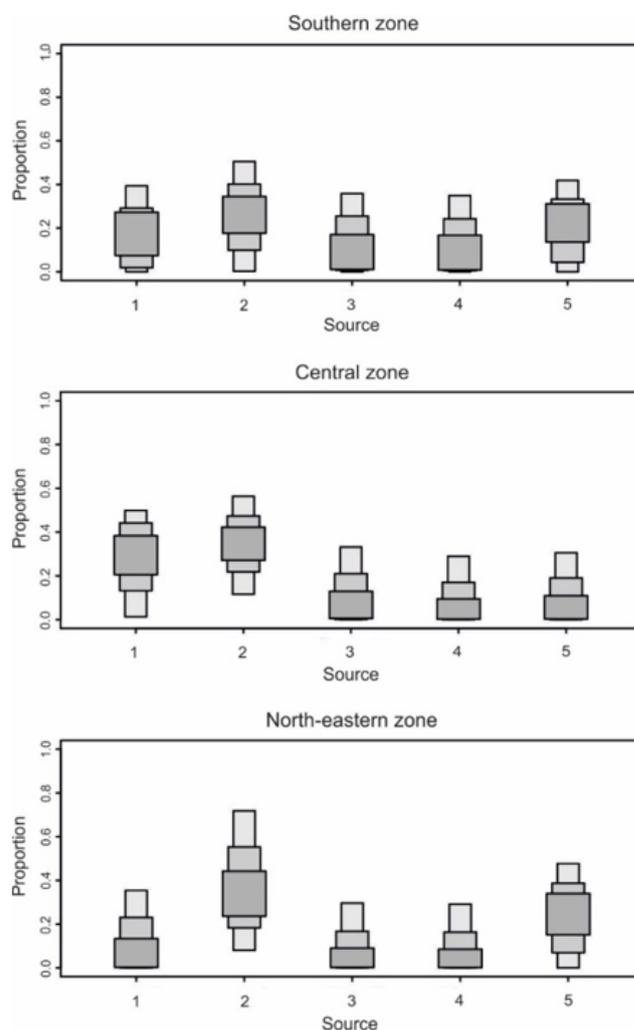


Figure 2: Boxplots of mixing model proportions for each zone, categorised by source. The results shown are the 25%, 75% and 95% Bayesian credible intervals for the probability distribution calculated for each source.

respectively. Household sewage appears to contribute the most to N input into groundwater in the southern zone (3-17%), compared with the other zones. In the central zone, denitrification has a limited influence on the isotopic signature of the $\delta^{15}\text{N}-\text{NO}_3^-$ pool (3-17% contribution for sources 4 and 5) compared to the other zones. In the north-eastern zone, the total NO_3^- pool seems strongly affected by denitrification, as the model estimates that nearly 40-50% of it appears as NO_3^- originating from NH_4^+ in fertilisers and manure, further affected by denitrification.

It can be concluded that the distribution of various N sources is determined by the peculiarities of land use patterns. In particular, more urbanised areas (the southern and north-eastern zones) are characterized with a relatively higher N input from manure and sewage to groundwater, while predominantly agricultural areas show higher proportions of N input coming from inorganic fertilisers. It seems that the hydrogeochemical conditions in the central zone of the study area stimulate the predominance of nitrification, while denitrification occurs to a similar extent as nitrification in the north-eastern and southern zones.

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5. Conclusions

The results of NO₃⁻ and B isotope analyses showed that groundwater conditions in the studied region is affected the most by manure as the dominant source of N pollution. The contribution of mineral fertilisers rises in the zones of intensive agricultural activities. At the same time, sewage seems to be the least important source influencing the groundwater quality; its relative contribution tends to increase in more urbanised areas. To a different extent, both nitrification and denitrification processes affect N dynamics in the subsurface. Their intensity likely depends on the concentration of dissolved oxygen, availability of substrate, residence time of groundwater etc. However, it should be noticed that obtaining the mean and standard deviation values of isotopic composition of N sources from the literature may introduce some uncertainty and affect the accuracy of model outputs. The application of such models should preferably be supported with information about the isotopic composition of sources in the area of study.

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