# **Identification of Multiple Nitrate Sources** in Selected Saudi Arabian Aquifers Using a Multi-Isotope Approach



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### Introduction

Nitrate is one of the principal contaminants of drinking water resources (Widory et al. 2004). Base-level concentrations in the order of a few mg/l occur naturally in groundwater. Elevated concentrations, on the other hand, are mostly associated with anthropogenic impacts such as leaching from synthetic fertilizers or manure used in farmlands and infiltration from wastewater systems. However, there are also several studies which found elevated  $NO_3^-$  concentrations in groundwaters of areas where potential human influence is virtually non-existent, especially in arid and semi-arid environments (e.g. Stadler et al. 2008). Partly, this seems to apply to Saudi Arabian groundwaters as well.

### **Results and Discussion**

Elevated NO<sub>3<sup>-</sup></sub> contents were observed in all of the investigated aquifers (Fig. 1), irrespective of general hydrochemsitry (Fig. 3) or well depth. The maximum concentration was 1180 mg/l (in a highly saline well in an irrigated area) with mean and median values of 66.8 mg/l and 18.6 mg/l, respectively. The WHO drinking water guideline value of 50 mg/l is exceeded in more than a quarter of the investigated wells. Although the highest  $NO_3^-$  concentrations were encountered in groundwaters of the irrigated farms, only 7 out of the 22 wells sampled from these areas contain high levels of NO<sub>3<sup>-</sup>. A relatively high nitrate concentration of 227 mg/l was</sub> found in a well of a rural town. All the other high-NO<sub>3<sup>-</sup></sub> groundwaters were observed in wells located in remote desert settings.









Fig. 1: Map showing the spatial nitrate distribution in the study area.

### **Methods**

To place constraints on potential  $NO_3^-$  sources, a total of 49 groundwater samples were collected from selected wells tapping five major aquifers of the Arabian Platform (Fig. 1). All samples were analysed for major ion composition,  $\delta^{18}O$ , and  $\delta^2$ H. Based on the results of a nitrate rapid test kit, 26 samples were selected for the analysis of the isotopic composition of groundwater NO<sub>3</sub><sup>-</sup> ( $\delta^{15}$ N-NO<sub>3</sub>,  $\delta^{18}$ O-NO<sub>3</sub>). <sup>3</sup>H, <sup>14</sup>C-DIC, and  $\delta^{13}$ C-DIC were determined for 10 selected wells. Most of the sampled wells cater for domestic use and livestock watering purposes in remote villages. In the southern parts of the study area groundwater is used in intensive pivot irrigation systems (Fig. 2).





Fig. 3: Piper plot of the investigated groundwaters. In the diamond, nitrate concentrations are schematically illustrated by the circle size.



Fig. 5: Photographs of a well used for fertigation and a fishfarm, representing potential nitrate sources.

The  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> values fall in a narrow range of 4.4 to 11.5 ‰, while  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> vary between 7.2 and 35.9 % (Fig. 4). Except for a few outliers, most of the data points cluster in the range typical for nitrate derived from biomass in the unsaturated zone. The groundwaters from agricultural areas show  $\delta^{15}N$ - $NO_3^-$  signatures that resemble those from other parts of the study area. The  $\delta^{18}O-NO_3^-$  values, however, are partly higher, suggesting a contamination by  $NO_3^{-}$ -rich irrigation return flow. The well with the highest  $\delta^{18}O-NO_3^-$  value (35.9 ‰) plots between the remaining waters and a tested KNO<sub>3</sub> fertilizer, probably indicating mixing of nitrate from different sources.

A few wells have  $\delta^{15}N-NO_3^-$  and  $\delta^{18}O-NO_3^-$  values, which are in the range expected for septic waste and manure. These are the shallowest wells investigated with static water levels of 40 to 60 m and a couple having relatively high  $NO_3^-$  contents. Substantial contents of  $NO_3^-$  (227 mg/l),  $NH_4^+$  (15.7 mg/l), and B (1.1 mg/l) in one of these wells, which is found in the center of a rural town, give further evidence to potential contamination from septic waste.

Very low <sup>14</sup>C activities and quasi-absence of tritium in most of the studied wells indicate a lack of substantial recent recharge that could leach nitrate into the groundwater. A relatively high <sup>14</sup>C activity of 65.8 pmc was detected in the well suspected of septic waste contamination.

Fig. 2: Typical center pivot irrigation well (center) with fertilizer mix tank (left).



#### $\delta^{15}$ N-NO<sub>3</sub> [‰ AIR]

Fig. 4:  $\delta^{15}N-\delta^{18}O$ -plot for the studied groundwaters and fertilizer samples. For comparison isotopic signatures of potential nitrate sources are displayed (Kendall 1998, Wankel et al. 2010).

## **Conclusions**

The  $\delta^{15}N-NO_3^-$  and  $\delta^{18}O-NO_3^-$  signatures of the investigated groundwaters indicate that both natural and anthropogenic sources contribute to the elevated  $NO_3^-$  concentrations encountered. For remote settings, the main source of contamination is soil  $NO_3^$ which was probably leached into groundwater during past recharge events under wetter climate.

#### References

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