Groundwater contamination by agriculture activities in arid environment: Evidence from $\delta^{15}N$ and $\delta^{18}O$ compositions - Arava Valley, Israel

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Introduction

• The main water resources in the central Arava valley are shallow unconsolidated aquifers.

• Over the last decades these aquifers are undergoing anthropogenic nitrate contamination following the development of modern, water-saving agriculture. The contamination may or may not be accompanied by salinization (Fig. 1).

• In this study we identify the origins and mechanism of the contamination using nitrate isotopic compositions ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$).

• The pumping fields which were studied include: Idan, Hazeva, Zofar-east, Zofar-west, Zofar-alluvium and Paran (Fig. 2b).

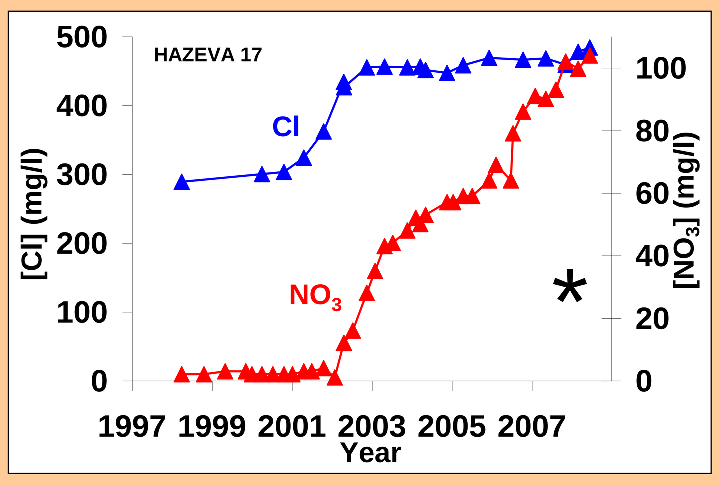

Fig. 1: Nitrate and Chloride concentrations as a function of time in Hazeva-17 well, an example of nitrate contamination accompanied by salinization.

All waters are oxic with no NH_4^+.

* $\delta^{18}O$ of the contaminated water (Hazeva-17) is - 5.82‰ (2008),

$\delta^{18}O$ of the uncontaminated water (Hazeva-12) is - 5.87‰ (2008),

Study area

- The Arava Valley is located in the southern region of Israel, and is part of the arid belt of the northern hemisphere. The valley, shared by Israel and Jordan, is bounded by mountains on both sides (Fig. 2a).
- The area is characterized by moderate winters with very low precipitation (25-50 mm/yr), followed by extremely hot summers.
- The valley serves as a drainage basin for occasional flash floods from both east and west. Some of these flood waters recharge the shallow unconsolidated sediments in the valley.
- The general direction of groundwater flow is NNE (towards the Dead Sea).

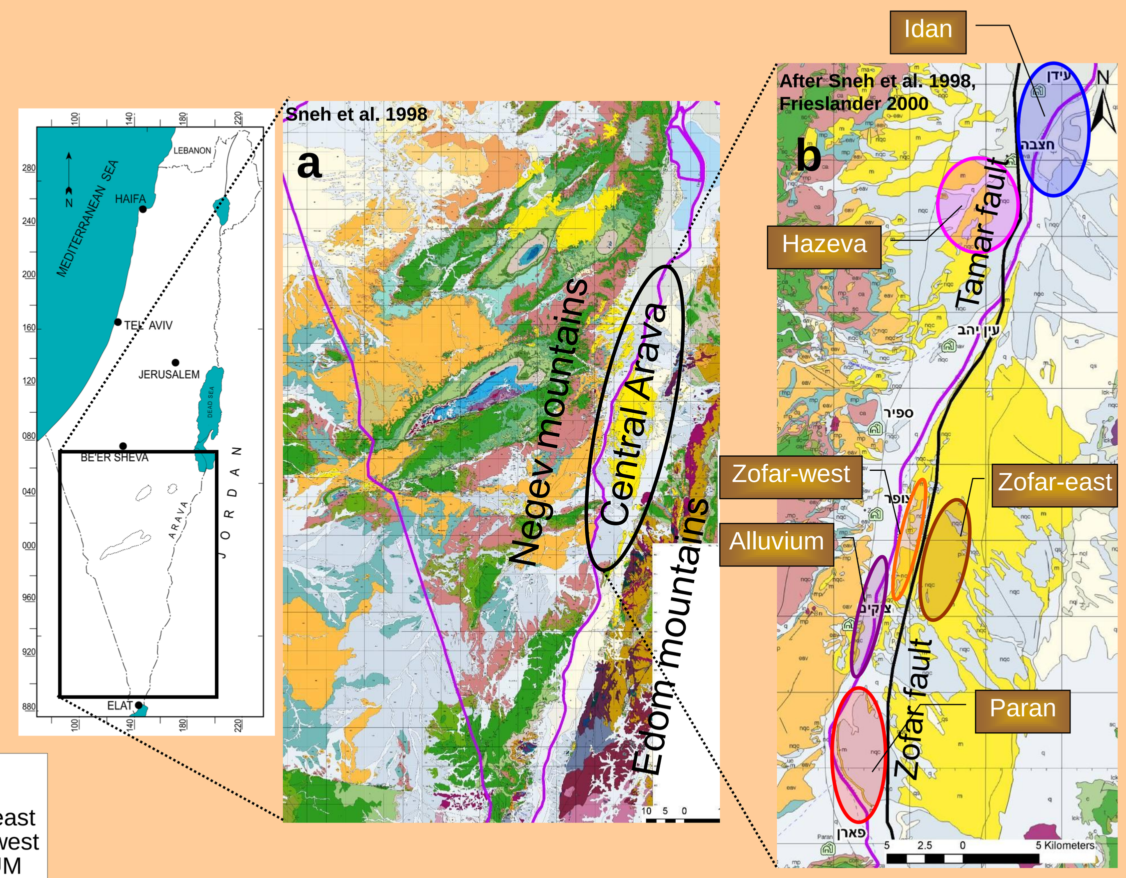

Fig. 2: (a) Geologic map of the Negev (Sneh et al., 1998). (b) Zooming into the central Arava valley. The investigated pumping fields are marked on the map.

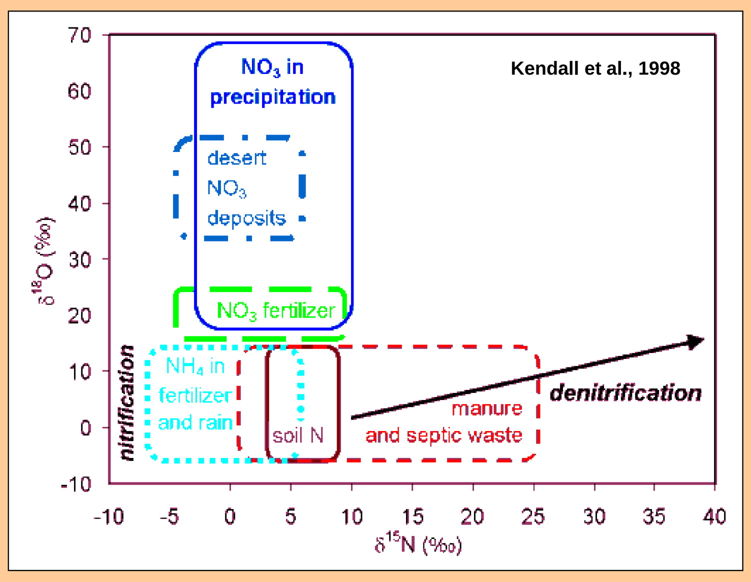

Fig. 3: Isotopic compositions of nitrogen and oxygen of nitrate derived from different sources (Kendall et al. 1998).

Identification of nitrate sources by $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$

• Nitrate sources have different and distinguishable isotopic compositions of nitrogen and oxygen (Fig. 3).

• Generally, nitrate derived from synthetic NO_3^--fertilizers has lower $\delta^{15}N_{NO3}$ and higher $\delta^{18}O_{NO3}$ relative to nitrate derived from soil N.

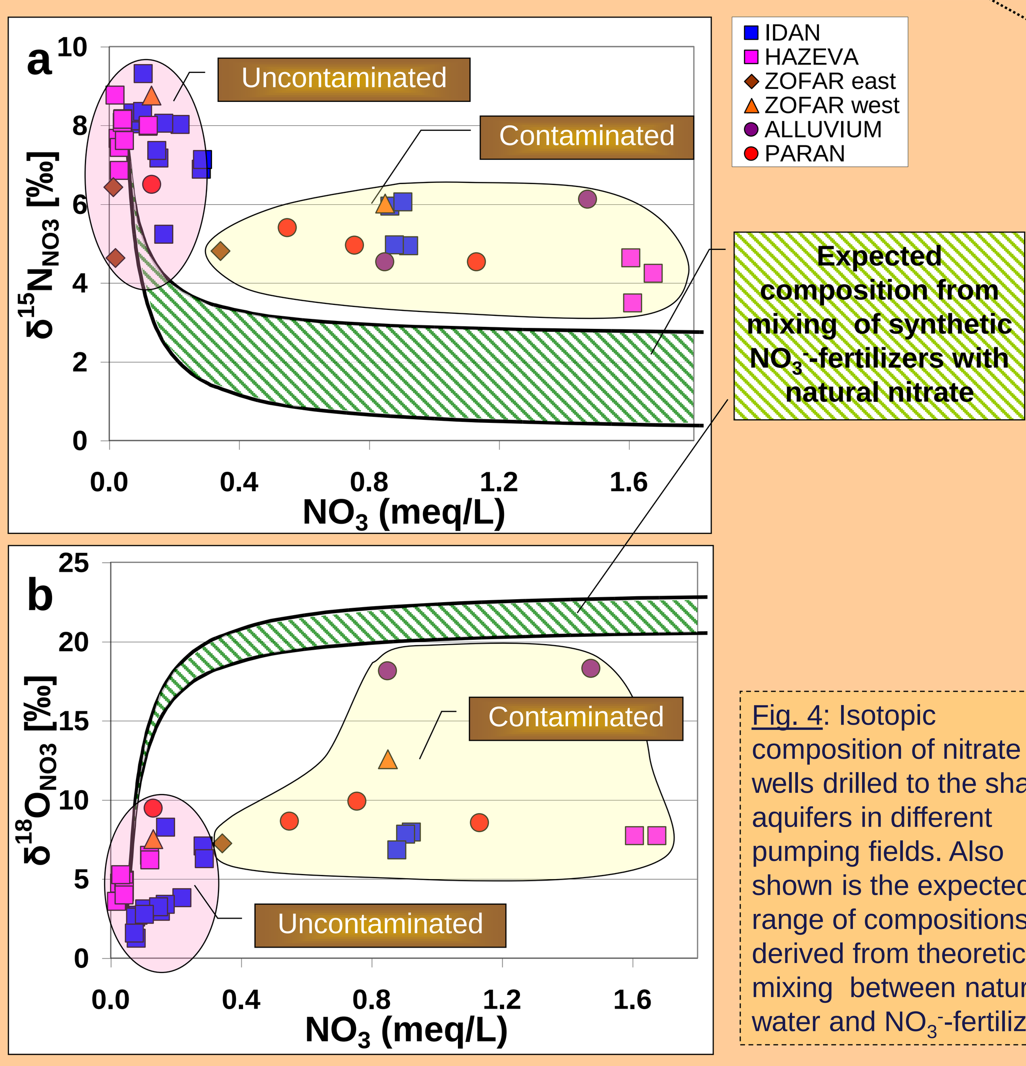

Fig. 4: Isotopic composition of nitrate in wells drilled to the shallow aquifers in different pumping fields. Also shown is the expected range of compositions derived from theoretical mixing between natural water and NO_3^--fertilizers.

The enigma

- Contaminated wells drilled into the shallow aquifers have lower $\delta^{15}N_{NO3}$ and higher $\delta^{18}O_{NO3}$ relative to uncontaminated wells (Fig. 4).
- The measured data does not fit theoretical mixing calculations between synthetic NO_3^--fertilizers and natural nitrate (Fig. 4).
- Hence, additional sources and/or reactions are involved in the nitrate contamination.
- To identify the possible sources a mixing/reaction, a model was developed.

Isotopes mixing/reaction model

Sources of nitrogen in central Arava

The possible sources of anthropogenic nitrogen are (Fig. 5):

1. Synthetic NO_3^--fertilizers.
2. Synthetic NH_4^+-fertilizers.
3. Manure, used as organic fertilizer in the cultivated fields.

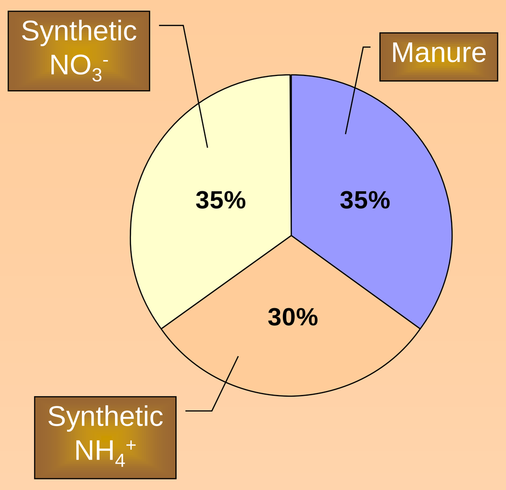

Fig. 5: Available estimated portions of the different N-fertilizer types used in the cultivated fields.

Reactions that fractionate the stable isotopes of nitrate

Nitrogen in the soil has two main species: nitrate and ammonium. Each experiences different reactions (Fig. 6), before reaching the groundwater (always as nitrate). The biogeochemical reactions included in the model and their isotopic effects are:

1. Nitrate or ammonium uptake by plants: $\delta^{15}N$ - Small isotopic fractionation, $\delta^{18}O$ - unknown.
2. Ammonia volatilization which may occur from manure or NH_4^+-synthetic fertilizers: Large isotopic enrichment in the remaining nitrogen.
3. Nitrification: No isotopic fractionation of N (assuming that all remaining NH_3 based fertilizers were nitrified). Nitrate produced by nitrification gains approximately two oxygen atoms from H_2O and one oxygen atom from dissolved (atmospheric) O_2.
4. Evaporation of the water used for irrigation: May enrich the oxygen ^{18}O of the nitrate produced by nitrification.
5. Mixing of the remaining fractions of the nitrate derived from different sources: The final mixing ratios determine the isotopic compositions of the nitrate in the groundwater.

* Scarcity of organic matter in the desert soils prevents denitrification and respiration from being important processes.

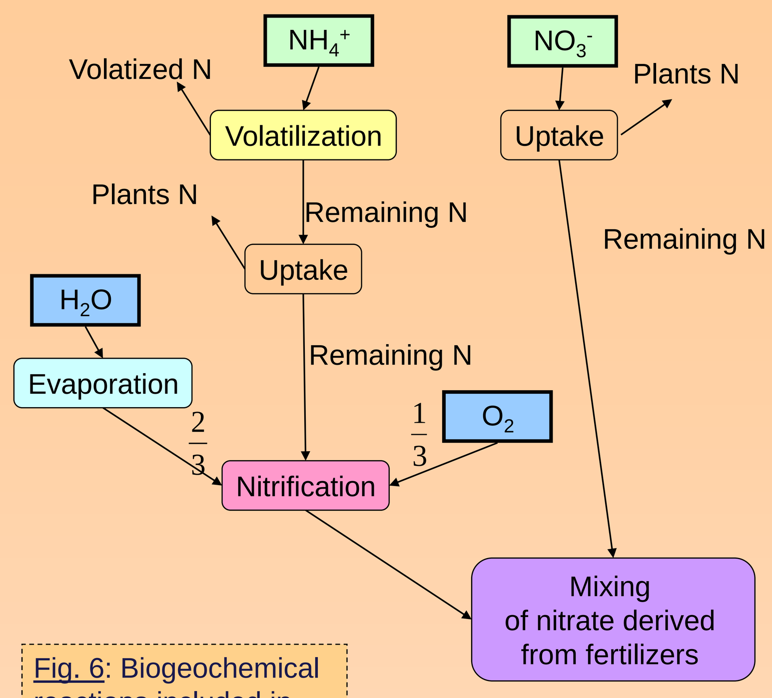

Fig. 6: Biogeochemical reactions included in the model.

Simple three end-members mixing model:

Synthetic NO_3^- and NH_4^+ fertilizers and manure

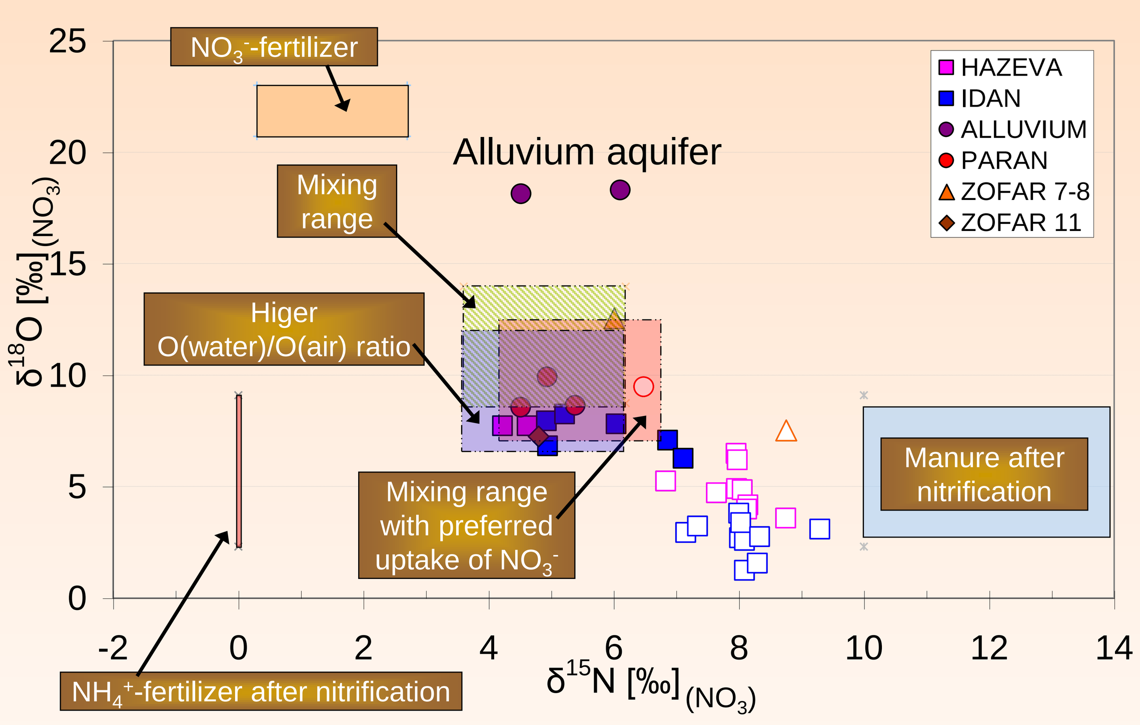

Fig. 7: Mixing of synthetic NO_3^- and NH_4^+ -fertilizers with manure. Empty symbols - uncontaminated wells, solid symbols - contaminated wells.

• Nitrate derived from manure is relatively enriched in ^{15}N due to ammonia volatilization in manure piles. The remaining ammonium is nitrified to nitrate with $\delta^{18}O_{NO3}$ composition similar to the range of nitrate derived from nitrification of the synthetic NH_4^+-fertilizer end-member (Fig. 7).

• The range of $\delta^{18}O_{NO3}$ in the manure and NH_4^+-fertilizer after nitrification depends on the water involved in the nitrification. The higher value (9.1‰) is derived from 50% evaporation of the irrigation water. No evaporation results in the lower value (2.3‰) (Fig. 7).

• No uptake or volatilization are assumed in the geochemical transformations of the synthetic fertilizers.

• The mixing range obtained without any fractionation of the synthetic fertilizers cannot explain the measured isotopic compositions of Idan, Hazeva, Zofar (east and west) and Paran water wells.

• When preferred uptake of NO_3^- is assumed (Fig. 7), the model results fit the measured data. Alternatively, improvement is also achieved when higher O(water)/O(air) ratio in the nitrification is assumed.

• Based on the $\delta^{18}O$ values - neglected evaporation of water occurs in the cultivated fields.

• The $\delta^{18}O$ values in the alluvium aquifer is much higher than expected

Sources of contamination in the shallow alluvium :

Synthetic NO_3^- and synthetic NH_4^+ fertilizers

• The isotopic compositions of nitrate in the alluvium fall within the mixing area of the two synthetic fertilizers (Fig. 8).

• Isotopic fractionation during NO_3^- fertilizer uptake and/or during NH_4^+ fertilizer volatilization is required to explain the different isotopic values of the alluvium (Fig. 7).

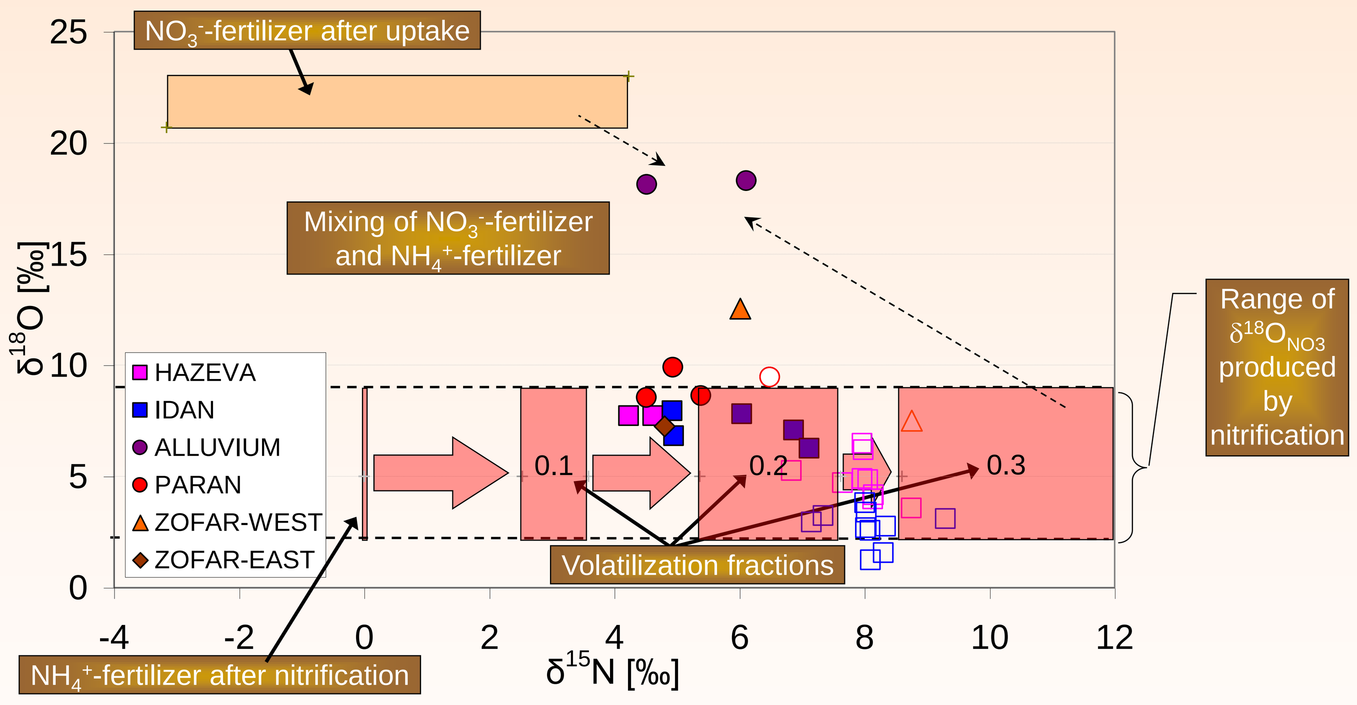

Fig. 8: Two end-members model for the isotopic composition of the alluvial aquifer. The model involves mixing of synthetic NO_3^- fertilizer and synthetic NH_4^+ fertilizer, including isotopic fractionation as a result of NH_3 volatilization and uptake. Empty symbols - uncontaminated wells, solid symbols - contaminated wells.

Conclusions

- Generally, phreatic aquifers in arid zones are sensitive to agriculture contamination. Moreover, since underground water flow is slow the contamination might accumulate and stay for very long periods.
- Simple mixing model explains the isotopic composition of contaminated groundwater in an arid area, the case of the Arava valley, southern Israel:

1. In most of the contaminated groundwater the nitrate is derived from synthetic NO_3^- and NH_4^+-fertilizers and manure in almost equal proportions. These proportions remain constant while seeping from surface to groundwater.
2. The different isotopic values in the alluvial aquifer is explained by mixing of synthetic fertilizers only.

- It is clear from our study that the isotopic tool is very efficient in identifying sources of contaminations in cultivated arid zones.