

## A MULTI-ISOTOPIC APPROACH TO EVALUATE ORIGIN AND FATE OF NITRATE IN GROUNDWATER HOSTED IN A NVZ SARDINIAN AREA

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**Keywords:** Nitrate Pollution, Groundwater, multi-isotopic approach, Arborea (Sardinia)

### Introduction

Water pollution by agriculture nutrients, especially nitrate, has been recognized as one of the most relevant environmental problems in EU. Through the Nitrate Directive (ND, 91/676/EEC), the EU member countries identified Nitrate Vulnerable Zones (NVZ's), developed protocols of good agricultural practices and set up action programs for the management of farm wastes. The understanding of the origin and fate of nitrate, as well as of the biogeochemical processes controlling nitrate attenuation in aquifers, is fundamental for preserving the quality of groundwater supplies, as well as surface waters affected by groundwater inflow. The present study, framed within the KNOW project, aims to evaluate the integrated risk of aquifer pollution by agricultural origin in the dairy farming district of Arborea (W-Sardinia). The area, identified as a NVZ, is one of the most productive agricultural sites in Italy and the productivity of its dairy system is one of the highest in Europe (Mura et al., 2013). Due to the complexity of the study area, the need to identify the potential sources of nitrate (organic and inorganic fertilization, sewage) in groundwater becomes more pressing (Nguyen et al., 2013). The research has been focused in a transect of 2.8 x 1.8 km, taking into account the nitrate seasonal dynamics, and integrating hydrogeochemical, hydrogeological and agronomic approaches (Pittalis et. al., 2013). Hydrogeochemical data were obtained coupling chemical and multi-isotopic approaches, in order to tracing the sources of nitrate pollution and evaluating the chemical reactions related to denitrification processes.

### Material and Methods

The investigated area is located in the northern part of the Campidano Plain (Central-Western

Sardinia, Italy). It occupies the northern part of the Campidano rift in which Quaternary deposits outcrop: littoral sediments (sands), lacustrine deposits (silt and clay), alluvial deposits along the rivers, continental deposits (gravel and sands).

Two Hydrogeological Units (HU) were identified:

- Sandy Hydrogeological Unit (SHU);
- Alluvial Hydrogeological Unit (AHU);

Groundwater from 13 wells were sampled bi-monthly since February 2013, along a transect located in correspondence of the sandy aquifer (SHU). Groundwater samples were stored at 4°C in a dark environment. For each water sample, major anions, cations and metals have been analysed. Isotopic determinations were carried out for water stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), nitrogen and oxygen isotopic composition of dissolved nitrate ( $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ), sulphur and oxygen isotopic composition of dissolved sulphate ( $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ ), and isotopic composition of dissolved boron ( $\delta^{11}\text{B}$ ).

### Results

In the Arborea area, nitrate concentrations in groundwater vary from 1 mg/L to 162 mg/L. The livestock effluents (mostly slurry) are used as organic fertilizers with formal restrictions on maximum rates (up to 170 kg N ha<sup>-1</sup>) and time of their distribution (no spreading from November to February) as by the NVZ rules. Organic effluents represent more than 50% of the crop N input source and are considered the main source of nitrate pollution. In general, the pollution sources cannot be properly identified only considering the isotopic composition of dissolved nitrate (Fig. 1), although some samples appear characterized by a nitrate source from synthetic fertilizers. Preliminary results combining the use of boron and nitrogen isotopic compositions indicate that animal manure should be the dominant pollution source in this area. Water samples with relatively low nitrate concentrations might be related to denitrification

processes (Otero et al., 2009). Indeed, two types of processes that affect the SHU groundwater of Arborea area, have been observed: denitrification (Fig. 1) and sulphate reduction. The former process needs, however, to be further evaluated. In fact, in some surveys at more denitrified samples corresponded higher nitrate concentration.

The samples with the lowest concentrations of nitrate appear subjected to denitrification processes, because the isotopic compositions of dissolved sulphate for these samples, emphasizes the existence of sulphate reduction.

## Conclusion

The case study site provides a number of potential insights about the dynamics of nitrate pollution. Results available so far indicate that nitrate pollution in the Arborea area can be attributed mainly to animal manure and secondary to synthetic fertilizers. Active natural denitrification is occurring in the area, although in some months is recorded an alteration of the process.

Further investigations are planned in order to characterize the seasonal variations in the chemical and isotopic composition of nitrate and to improve our current knowledge on both nitrate pollution sources and the quantification of natural denitrification rates.

## Acknowledgements

This study was funded by the Autonomous Region of Sardinia, in the frame of the "Promotion of scientific and technological

innovation in Sardinia" (LR7/2007, year 2010, project KNOW).

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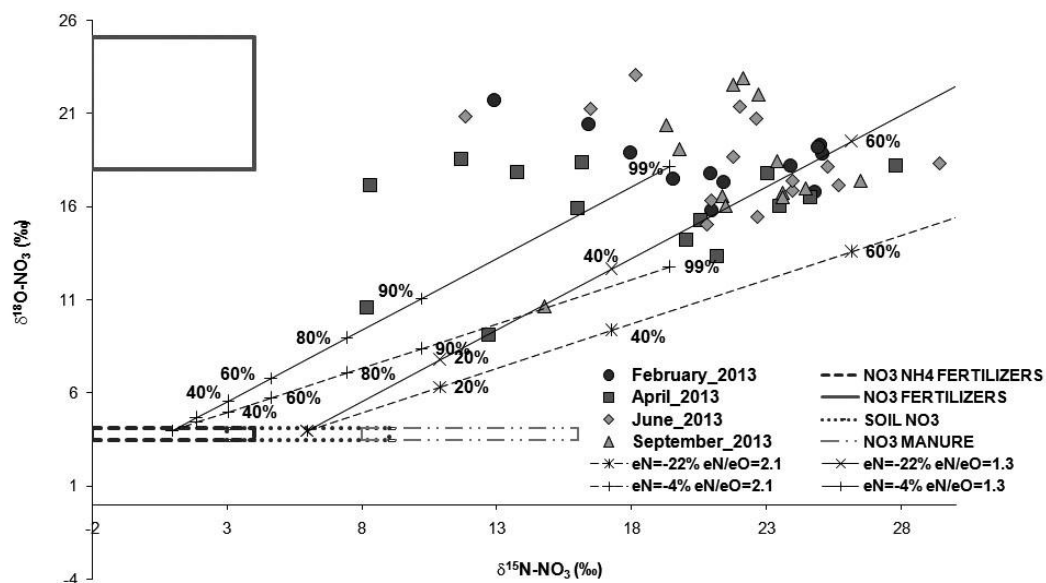


Fig.1 – Diagram  $\delta^{15}N_{NO_3}$  vs  $\delta^{18}O_{NO_3}$  and isotopic composition of the main nitrate sources (rearranged from Otero et al., 2009).