STABLE ISOTOPES OF DISSOLVED NITRATE AS INDICATORS OF THE ORIGIN AND THE MECHANISMS OF TRANSPORT TO/REMOVAL FROM GROUNDWATER: RESULTS FROM THE WESTERN PO PLAIN (NORTHERN ITALY)

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Introduction

Agricultural regions commonly suffer diffuse groundwater pollution by nitrates, resulting from the cumulative effect of day to day activities, including application of synthetic fertilisers, manure spreading and sewage sludge disposal. Locally, point source pollution may arise from discharges from urban or industrial N bearing wastewater and septic leachate in areas not connected to a sewage system When multiple potential nitrate sources exist, identification of the main sources and estimation of their contribution is essential to implement effective, source-oriented remediation measures. In this case, stable isotopes of dissolved nitrates ($\delta^{15}N$ and $\delta^{18}O$) represent a powerful tool, complementary to existing monitoring data, enabling the identification of nitrate sources, the assessment of their relative contribution to nitrate pollution and the quantification of nitrate transport and removal processes.

This contribution aims at presenting groundwater isotope data obtained since 2005 (Pilla et al., 2005; Pilla et al., 2006; Pilla et al, 2007; Sacchi et al., 2007a; 2007b) in an area of approximately 6000 km^2, crossing the Po plain from North to South in correspondence to the Piedmont-Lombardy administrative boundary (Novara, Alessandria, Pavia and Lodi provinces). These are interpreted in conjunction with those available from other regional and local studies. The Po plain alluvial aquifer, of Quaternary age, is constituted by gravels and sands with interbedded clay layers. Agricultural land use includes corn, wheat and rice fields.

Materials and Methods

A preliminary selection of samples, mostly from the phreatic aquifer, for hydrochemical and isotopic characterisation was performed based on available data from groundwater quality monitoring programmes. About 180 monitored wells and natural outflows were selected, considering also rivers and irrigation channels, all with nitrate concentration exceeding 50 mg/l. Samples were analysed for their major ion concentration (especially nitrate, sulphate and chloride content), and stable isotopes $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ of the nitrate molecule. In specific cases, trace metals, stable isotopes of the water molecule and δ^{13}C-DIC were also used.

Results

The isotope composition of dissolved nitrates (Fig. 1) shows very clearly the impact over groundwater resources of intensive agricultural activities. Contamination from synthetic fertilisers is widespread and nitrate accumulation is a threat to large groundwater supplies. On the other hand, peak concentrations are associated to point source pollution and can be attributed to leakage of the sewage network. Very little non-point source contamination seems to originate from manure spreading.

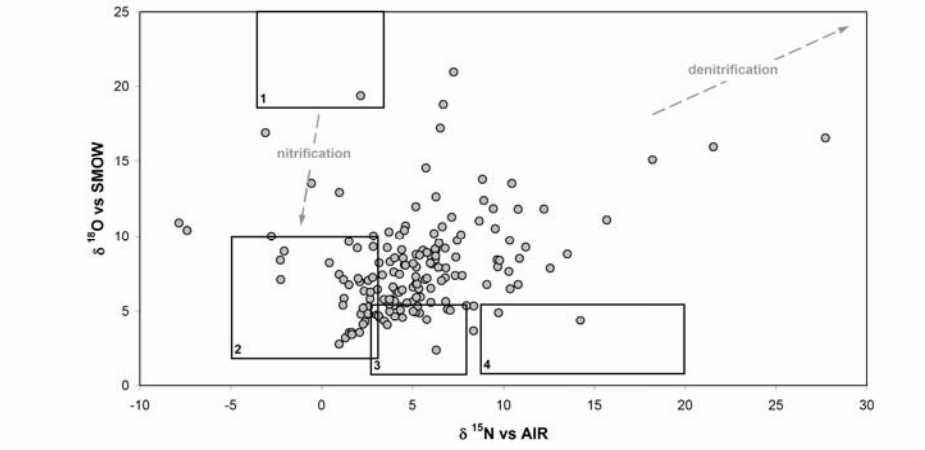

Fig. 1. $\delta^{18}O_{NO3}$ versus $\delta^{15}N_{NO3}$ in groundwater from Western Po Plain. 1 - Synthetic fertilisers; 2 - Mineralised synthetic fertilisers; 3 - Mixed sources; 4 - Manure, septic waste

In addition, it could be shown that the type and distribution of groundwater contamination is closely related to:

- the hydraulic characteristics of the unsaturated zone: clay rich soils reduce infiltration and favour denitrification through the establishment of anoxic conditions;
- the agricultural input: corn and wheat cultivation seems to be mostly responsible for nitrate contribution to groundwater (large use of synthetic fertilisers);
- irrigation practices: the artificial recharge associated with rice cultivation also represents a preferential pathway for input of exotic substances to groundwater, but in this case, the input of nitrogen compounds is partially reduced by denitrification.

Results were integrated with those available for the Milano Province (Arduini et al., 2008) and for the Lombardy plain (ARPA Lombardia, int. rep.). These clearly indicate, for the suburban area of Milano, a conspicuous input from an obsolete and leaking sewage network. By attributing each sample to one of the sources or processes identified in Fig. 1, a regional map highlighting the more vulnerable areas can be obtained.

Conclusions

The implementation of the Water Framework Directive (2000/60/EC) and the Nitrate Directive (91/976/EEC) leads to the designation of areas vulnerable to nitrate pollution, where the use of fertilisers, especially manure, is restricted. On the other hand, the isotopic composition of dissolved nitrates indicates that synthetic fertilisers and leakage from the sewage network represent the main nitrate sources in the investigated area. Therefore the effectiveness of the undertaken mitigation measures is likely to be reduced, as they do not target the actual nitrate sources to groundwater.

References

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