A regional survey on nitrate contamination of the Po valley alluvial aquifer (Northern Italy)

E. Sacchi[a], G. Pilla[b], L. Gerbert-Gaillard[c], G.M. Zuppi[d]

[a] Dipartimento di Scienze della Terra, Università di Pavia and CNR-IGG, Sezione di Pavia, Italy

[b] Dipartimento di Scienze della Terra, Università di Pavia, Italy

[c] ISO4 s.s., Pavia, Italy

[d] Dipartimento di Scienze Ambientali, Università Ca' Foscari di Venezia, Italy

Abstract. The origin, distribution and abatement of nitrate contamination in surface and groundwater are traced by hydrochemical and stable isotope analyses. The studied sector of the Po Valley is approximately 3,600 km^2 wide, extending from the Alps to the Apennine along a N-S transect. The phreatic aquifer is fed by local infiltration and by streams and irrigation channels, while the Po river represents the major discharge axis. The main diffuse source of nitrates is from synthetic fertilisers, exceedingly used for crop raising. Peak concentrations are instead associated to local leakage from sewage network. The distribution of groundwater contamination is closely related to the hydraulic characteristics of the unsaturated zone, to agricultural input and irrigation practices. Denitrification is observed along major draining rivers and below rice fields. Results are interpreted in terms of aquifer vulnerability, groundwater circulation and land use.

1. Introduction

Nitrate concentration in surface and groundwater is an environmental concern. Nitrate pollution may be attributed to point sources, such as landfills, septic tanks or factory farming. Agricultural regions commonly suffer diffuse water pollution, which, in contrast, cannot be attributed to a precise source. Rather, it is the cumulative effect of day to day activities over large areas, including application of synthetic fertilisers, manure spreading and sewage sludge disposal.

Distinction between different sources of nitrates in groundwater can be made using hydrochemistry [1, 2] or/and by determining the isotopic signature of oxygen and nitrogen in the nitrate molecule [3] While the first approach may be useful in simple cases such as point source pollution, the combination of $\delta^{15}N$ and $\delta^{18}O$ data in nitrate allows to evidence cumulative effects in regional contamination problems and, in addition, to recognise nitrification and denitrification processes [4, 5].

The Po plain hosts a multilayer alluvial aquifer, of Quaternary age, is constituted by gravels and sands with interbedded clay layers. The thickness of the sedimentary sequence is strongly conditioned by the presence of buried structures of the marine substratum, which are dislocated and affected by Alpine and Apennine thrusts. The area covered by this study is of approximately 3,600 km^2, crossing the Po plain from N to S in correspondence to the Piedmont-Lombardy administrative boundary (Fig.1). Agricultural land use includes corn, wheat and rice fields (Fig.4).

A preliminary selection of samples for hydrochemical and isotopic characterisation was performed based on available data from groundwater quality monitoring programmes. About 100 monitored wells and natural outflows were selected, considering also rivers and irrigation channels, all with nitrate concentration exceeding 10 mg/l. Groundwater flow direction in the phreatic aquifer is oriented N to S in the pre-alpine sector and S to N in the Apennine one (Fig. 1).

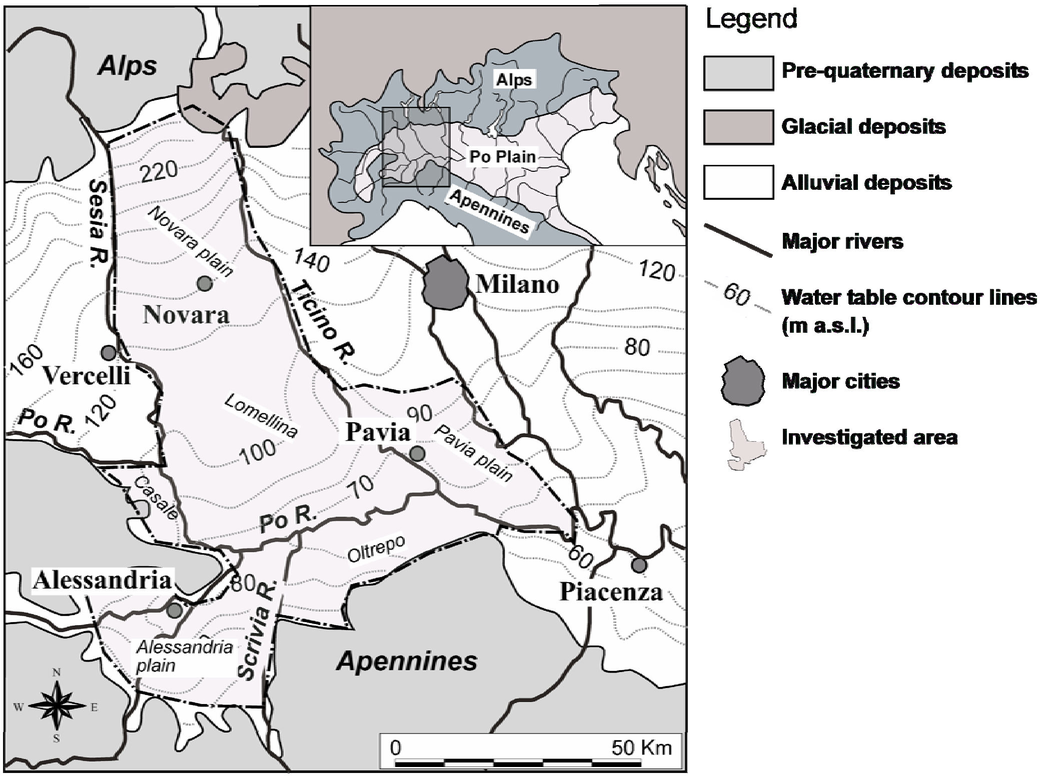

FIG. 1. Location of the investigated area

2. The territorial distribution

2.1. The Novara province

The Novara province is characterised by the presence of a phreatic aquifer of great permeability and thickness. The water table is located few tens of meters below surface, close to the Alps, and becomes shallower moving south, locally originating natural outflows. This is also evidenced by differences in land use: the northern part is intensively cultivated with corn and wheat, while the southern area is covered by rice fields.

Nitrate concentration in groundwater rarely exceeds drinking water limits, and the water quality is generally good. The isotopic composition of dissolved nitrates is chiefly that of mineralised synthetic fertilisers with little denitrification (Fig. 2). Denitrification is also evidenced by a decrease in the NO_3/SO_4 and NO_3/Cl ratios. It is observed in wells tapping deeper portions of the aquifer or experiencing high withdrawal rates (e.g. the Novara municipal wells).

2.2. The Lomellina region and the Pavia plain

The Lomellina region and the Pavia plain are characterised by an elevated potential infiltration and are intensively cultivated with, mainly, rice and corn fields. The water table is only few meters deep. Severe recharge takes place from seepages of channel network and from rice ponds. The phreatic aquifer displays waters of poor quality, with higher nitrate, sulphate and chloride contents and, locally, detectable amounts of pesticides. Indeed, rice cultivation uses ammonium sulphate, urea and potassium chloride as fertilisers.

The isotopic composition of dissolved nitrates confirms the agricultural origin of contaminants due to the nitrification of synthetic fertilisers (Fig. 2) [6]. A seasonal effect, related to soil flooding, can be observed, as the same samples show, at a few months distance, evidence of a strong denitrification occurring. A correlation of isotopic composition with nitrate concentrations (and consequently with depth) is also observed [6]. A detailed investigation on the seasonal variation of nitrate content and isotopic composition in the Lomellina region is reported in a companion paper [7].

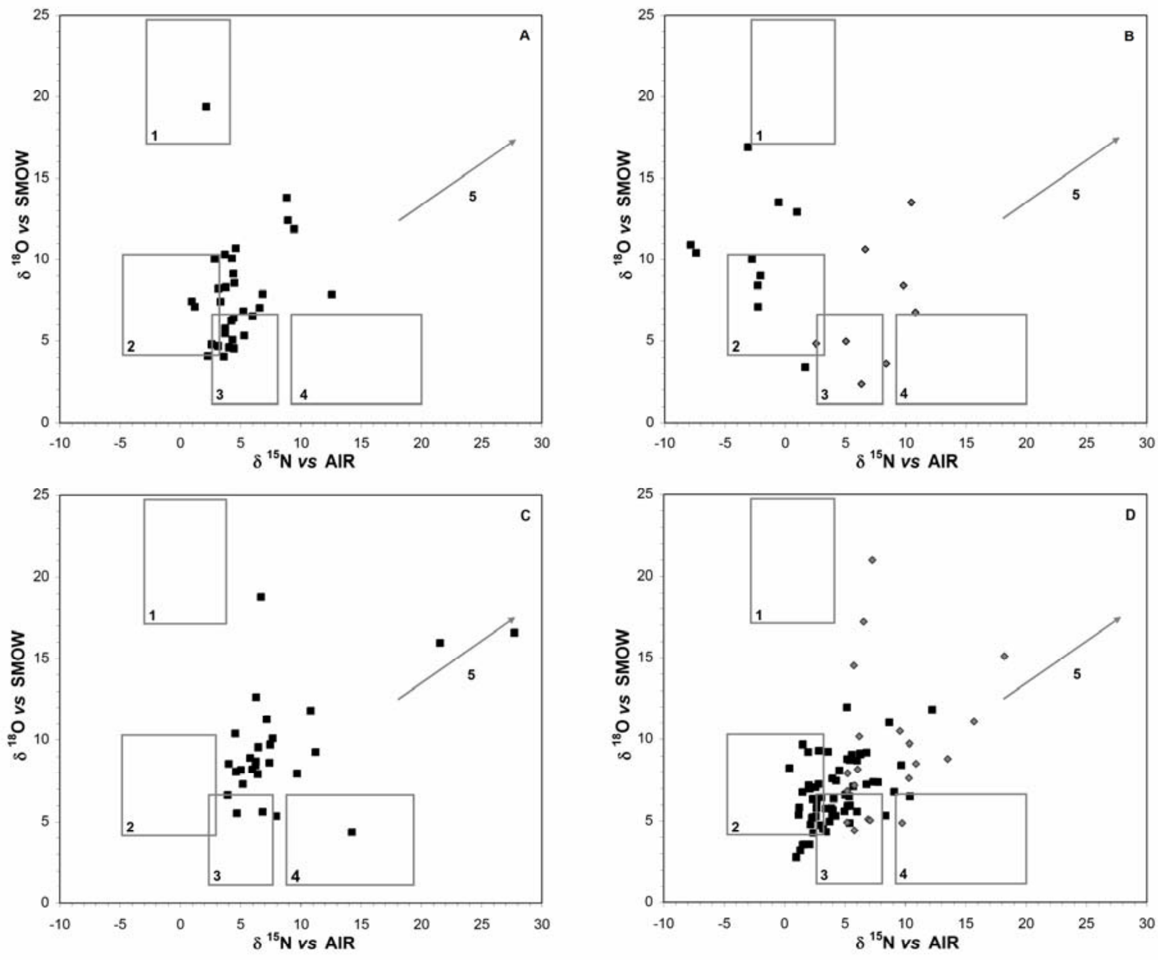

FIG. 2. Isotopic composition of dissolved nitrates. A: Novara province; B: Lomellina region (black squares= fall sampling; grey diamonds = summer sampling); C: Oltrepo region; D: Alessandria province (black squares = Alessandria plain; grey diamonds = Casale area). 1= synthetic fertilisers; 2 = mineralised synthetic fertilisers; 3 = soil organic matter; 4 = manure and septic tank effluents; 5 = slope of the denitrification trend

2.3. The Oltrepo region

In the Oltrepo region, the phreatic aquifer is of limited thickness because of the presence at shallow depth of the dislocated marine substratum. In addition, a clay layer of few meters thickness covering the aquifer formation is present, locally imparting a confined or semi-confined character. Groundwater is high in sulphate (100-250 mg/l) and chloride (locally up to 1600 mg/l) content, while nitrate concentration is generally low. Intensive agricultural activity is hindered by the absence of good quality groundwater and by soil salinisation problems [8].

The isotopic composition of dissolved nitrates confirms the presence, at shallow depth, of an anoxic boundary. Low nitrate concentration would then reflect both a lower agricultural input and denitrification, which is favoured by the hydrogeologic setting and by mixing with anoxic brines. An enriched contribution is also present (Fig. 3): due to the elevated contents (> 90 mg/l) and the position, this is attributed to a leakage from the sewage network.

2.4. *The Alessandria province*

The Alessandria province may be divided into two regions of very different hydrogeologic characteristics, both experiencing very high nitrate contamination. In the Casale area, the hydrogeologic setting closely resembles that of the Oltrepo: the marine substratum is found at shallow depth, as also evidenced by the presence of highly saline groundwater. The dominant land use type is rice cultivation, enhancing recharge and favouring nitrate input in groundwater. The area East of Alessandria also experiences high nitrate contamination: the aquifer is constituted by a great thickness of gravels and sands, originated by the migration eastward of the Scrivia river during Quaternary in response to tectonic deformation. The area is intensively cultivated with corn and wheat.

Surface waters and phreatic groundwater display evidence for regional contamination from agricultural activities. This is indicated by high levels of nitrates (10-160 mg/l), sulphate and chloride contents, and, locally, detectable levels in pesticides. In the Alessandria province, high nitrate contents are positively correlated with Ca^{2+} concentration. This seems to indicate that the acidity associated with nitrate pollution is buffered by the presence of carbonates in the aquifer matrix, this phenomenon increasing water hardness and TDS [2].

The isotopic composition allows identifying the different sources of nitrates: both mineralised synthetic fertilisers and manure contribute to the contamination (Fig. 2). Denitrification phenomena dominantly occur in the Casale area and East of the Scrivia River, because of favourable hydrogeologic settings, while near Alessandria, the high aquifer permeability and thickness do not allow the establishment of anaerobic conditions, favouring the build up of nitrates.

3. Discussion and conclusion

This study dramatically evidences the impact of intense agriculture activities over groundwater resources. Contamination from synthetic fertilisers is widespread and nitrate accumulation is a threat to large groundwater supplies. Peak concentrations are instead associated to point source pollution and can be attributed to leakage of the sewage network. Nitrate concentrations being higher than 10 mg/l, the isotopic compositions in the compositional field of soil organic matter likely correspond to a mixed contribution from both synthetic fertilisers and manure spreading (Fig. 3).

The distribution of groundwater contamination is closely related to:

1. the hydraulic characteristics of the unsaturated zone: clay rich soils reduce infiltration and favour denitrification through the establishment of anoxic conditions

2. the agricultural input: corn and wheat cultivation seems to be mostly responsible for nitrate contribution to groundwater

3. 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, as it is observed in the Casale and Lomellina areas.

The isotopic composition of nitrates confirms the hydrogeologic model of the phreatic aquifer. In the Po plain, the depth of the denitrification zone is strongly conditioned by the presence of buried structures and associated saline waters: it may be as shallow as 15 m below surface, like in the Oltrepo region, or deeper than 100 m, like in the Alessandria plain. Therefore stable isotopes of the nitrate molecule may also represent a useful tool to evidence aquifer overexploitation associated with high withdrawal rates.

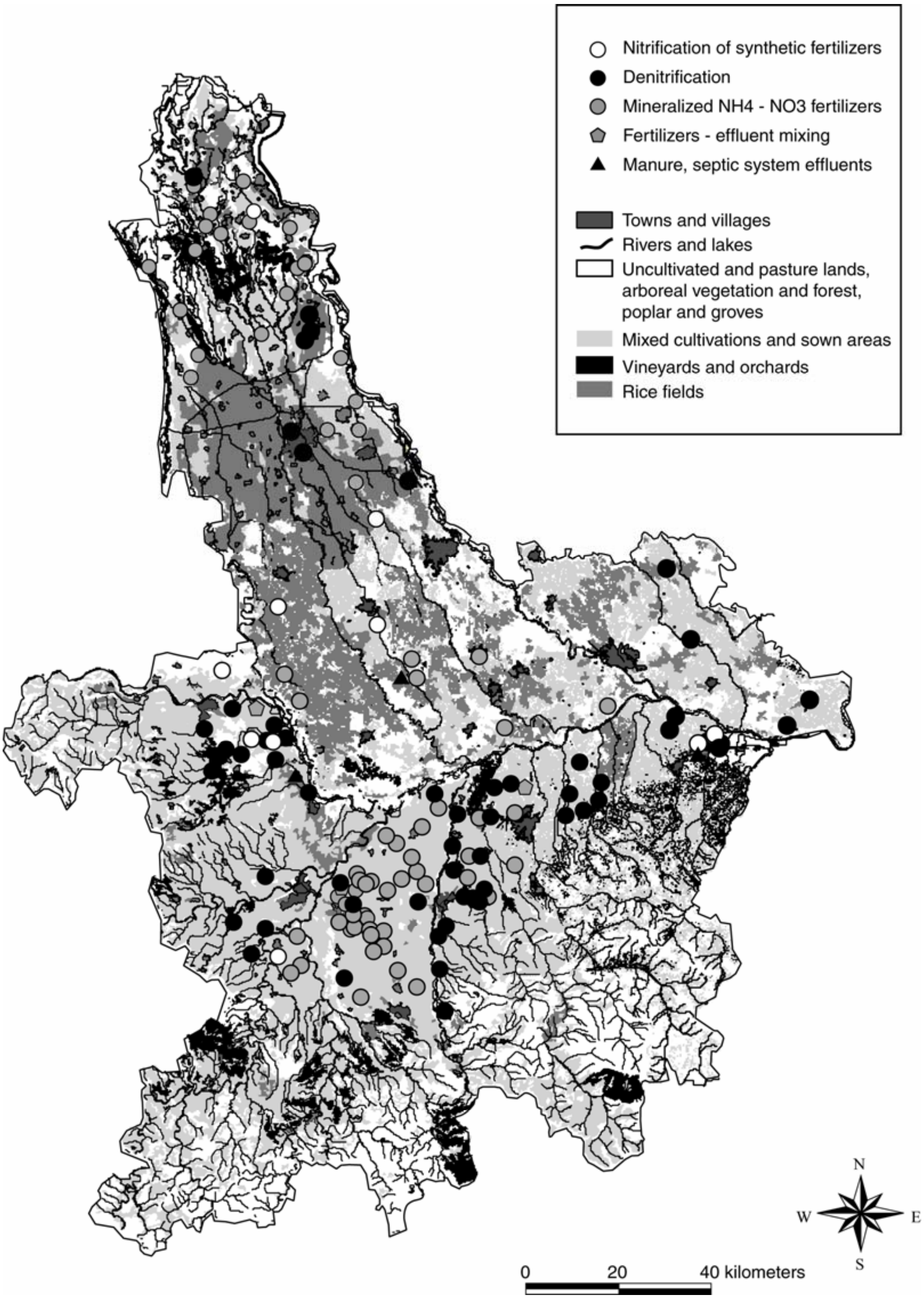

FIG. 3. Origin of and processes affecting dissolved nitrates, derived from their isotopic composition, as a function of location and land use

ACKNOWLEDGEMENTS

This study was supported by the Fondazione CRT and by the local agencies for groundwater management and protection (Amministrazione Provinciale di Pavia, Amministrazione Provinciale di Alessandria, Amministrazione Provinciale di Novara). The work was conducted in close collaboration with the regional environmental monitoring agency (ARPA Piemonte, Dipartimenti di Alessandria e Novara). The authors wish to acknowledge Enrico Allais (ISO4 s.s.) for the analytical effort.

Special thanks go to DISA Raffaele e F.lli, our trustful glass blowers, promptly responding to our desperate requests for more material whenever we would hear explosions in the furnace...

REFERENCES

[1] GRIFFIOEN J., Potassium adsorption ratios as an indicator for the fate of agricultural potassium in groundwater. Journal of Hydrology **254** (2001) 244-254.

[2] SPRUILL T. B., SHOWERS W. J., HOWE S. S., Application of classification-tree methods to identify nitrate sources in ground water. Journal of Environmental Quality **31** (2002) 1538-1549.

[3] CLARK I., FRITZ P., Environmental Isotopes in Hydrogeology. Lewis Publishers, Boca Raton (1997) 328 pp.

[4] ARAVENA R., ROBERTSON W.D., Use of multiple isotope tracers to evaluate denitrification in ground water: study of nitrate from a large-flux septic tank plume. Ground Water **36** (1998) 975-982.

[5] PANNO S.V., HACKLEY K.C., HWANG H.H., KELLY, W.R., Determination of the source of nitrate contamination in karst springs using isotopic and chemical indicators. Chemical Geology **179** (2001) 113-128.

[6] PILLA G., SACCHI E., ZUPPI G.M., BRAGA G., CIANCETTI G., Hydrochemistry and isotope geochemistry as tools for groundwater hydrodynamic investigation in multilayer aquifers: a study case from the Po plain (Lomellina, South-Western Lombardy, Italy). Hydrogeology Journal **14** (2006) 795-808.

[7] SACCHI E., PILLA G., ALLAIS E., GUALLINI M., ZUPPI G.M., Tracing nitrification and denitrification processes in a periodically flooded shallow sandy aquifer. Int. Symp. on Advances in isotope hydrology and its role in sustainable water resources management, IAEA, Vienna, 21/25/05/2007, this volume

[8] PILLA G., SACCHI E., CIANCETTI G., Hydrochemical and isotopic groundwater investigation in the Oltrepo region (Po valley, Northern Italy). Int. Symp. on Advances in isotope hydrology and its role in sustainable water resources management, IAEA, Vienna, 21/25/05/2007, this volume