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Nitrate sources, accumulation and reduction in groundwater from Northern Italy: Insights provided by a nitrate and boron isotopic database

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ABSTRACT

Large volumes of precious water resources are negatively affected by nitrate contamination, and the problem of the world population's exposure to this is becoming an even more pressing issue. To tackle this problem, the application of environmental isotopes has proven to be an effective method to identify the N origins and major transformations in different environments. In this work, nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) and boron ($\delta^{11}B$) isotope analyses performed in the last twenty years in groundwater from shallow aquifers of the Po plain area, a complex hydrogeological system of European relevance, have been compiled in a comprehensive database together with major ionic contents; these data were integrated with additional original results, targeting areas not previously examined or complementing the available information. Such data, previously interpreted on the local scale, are examined at the Po plain scale, providing an understanding of the N sources and dynamics in the shallow aquifers, and defining the most important processes governing nitrate contamination in Northern Italy.

The most impacted groundwater is that hosted in the alluvial fans of the Alpine and Apennine foothills, due to a combination of high soil permeability and presence of intensive agricultural activities. Here, aquifers are characterized by fast circulation and by great water table depths. On the contrary, nitrate contamination is absent in most low plain areas, with shallow water table depths but lower soil permeability, due to the presence of denitrification processes. The $\delta^{15}N$ median values, calculated for each province, are significantly correlated with pig density. Hence, manure represents one of the main nitrate sources in groundwater from agriculture, the other being synthetic fertilizers. Isotopic compositions enriched due to denitrification are present in ~22% of the data, being responsible for nitrate abatement in groundwater affecting up to 70–80% of the original content.

The B systematics, in such a low geogenic-B context, proved the presence in the investigated area of another anthropogenic nitrate source of civil origin (i.e. sewage). While new results on the local B sources are reported, the garnering of all groundwater data allowed us to define the range of the expected geogenic B signature ($\delta^{11}B = +13 \pm 2.5‰$). This contribution is a significant step forward for the use of the coupled $\delta^{15}N$ - $\delta^{11}B$ toolbox in the study area, previously limited by a poor definition of the compositional end-members. This georeferenced set of hydrochemical and isotopic data will lay the foundations for future monitoring activities and advanced data treatment or modelling. In addition, since the hydrogeological setting of the investigated area shows common features to alluvial basins located near mountain ranges, the approach and the results presented in this study serve as a reference for other study areas worldwide.

1. Introduction

In the second half of the 20th century, following the so-called "green revolution", agriculture in developed countries significantly increased crop production and livestock, with a concomitant enhanced use of synthetic and organic matter fertilizers (Tilman et al., 2001;

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Galloway et al., 2008). Although food availability increased, this produced diffuse pollution of nutrients in surface and groundwaters, currently representing a major environmental concern worldwide (Agren and Bosatta, 1988; Vitousek et al., 1997; Galloway et al., 2008). The resultant nitrogen accumulation on land and in waters frequently leads to the deterioration of freshwater and coastal ecosystem services, including water quality, fisheries, and amenity value.

In Europe, nitrate pollution by diffuse sources was first targeted by the Nitrate Directive (European Commission, 1991), followed by the Water Framework Directive (European Commission, 2000). The Nitrates Directive aimed to protect water quality across Europe by preventing nitrates from agricultural sources, also via the designation of "Nitrate Vulnerable Zones" (NVZs). These are territories that drain into polluted waters or waters at risk of pollution and contribute to nitrate pollution. As regards groundwater resources, polluted water, or those at risk of pollution, must be identified in groundwater containing, or that could contain (unless action is taken to reverse the trend), more than 50 mg/l of nitrates. Austria, Denmark, Finland, Germany, Ireland, Lithuania, Luxembourg, Malta, the Netherlands and Slovenia have decided to provide the same level of protection to their whole territory, rather than designate NVZs. In Italy, the Directives have led to the designation of large areas as being vulnerable to nitrate pollution, where the use of fertilizers, especially manure, was significantly restricted (170 and 340 kg N ha^{-1} yr^{-1} for NVZs and non-Nitrate Vulnerable Zones -nNVZs-respectively). Subsequently, and following the evidence collected that manure spreading might not be the only cause of nitrate contamination, the European Commission has granted Italy a derogation for the regions located in the Po plain (European Commission, 2011), allowing for an increase in manure spreading up to 250 kg N ha^{-1} yr^{-1} in NVZs, providing a higher Nitrogen Use Efficiency [NUE] of manure (*i.e.* the percentage of total nitrogen applied in the form of livestock manure that is available to crops in the year of application, considered to be 65% for slurry and 50% for farmyard manure).

One of the major difficulties with water contamination is the identification of the corresponding source(s) of pollution, a prerequisite for properly designing appropriate actions and remediation (Bronders et al., 2012). For this purpose, the application of environmental isotopes of dissolved nitrates (i.e.$\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) has proven to be effective in a large number of cases (e.g. Aravena et al., 1993; Panno et al., 2001; Baily et al., 2011; Matiatos, 2016). More recently, the added value of analyzing the isotopic signature of boron ($\delta^{11}B$) in association with the specific isotope signature of nitrates has been demonstrated (Seiler, 2005; Widory et al., 2004, 2005; Saccon et al., 2013; Puig et al., 2017). Strontium and sulphate isotopes are randomly also used to reinforce this multi-isotopic toolbox (Vitòria et al., 2004; Nestler et al., 2011). In addition to the classical chemical approach, the coupled use of nitrate and boron isotopes - although not yet a routine technique - is gaining interest for policymakers and water quality administrators who are interested in identifying the nitrate sources. This approach is particularly important when the NO_3 concentrations are higher than the threshold value defined by the Water Frame Directive (WFD; 50 mg/l), which implies the definition of the poor chemical status of the quality of the water body. The need to discriminate between the different sources of pollution (i.e. sewage, animal manure, chemical fertilizer, natural soil mineralization) thus becomes crucial for any water exploitation and management (Komor, 1997; Widory et al., 2004, 2005, 2013; Bronders et al., 2012).

The rationale for a coupled use of B and N isotopes is that these elements co-migrate in the groundwater, boron being unaffected by the redox reaction that causes nitrogen transformations (mainly denitrification/nitrification). However, boron is ubiquitous in water and its concentration strongly depends on the aquifer source rock and on the extent of the exchange of water with the fine aquifer matrix (Xiao et al., 2013). Many studies based on the coupled $\delta^{15}N$- $\delta^{11}B$ approach have aimed at defining a well-characterized frame of the geogenic $\delta^{11}B$ background (Palmer and Swihart, 1996 and reference therein), as well as of the anthropogenic components that could represent nitrogen and boron sources (see compilation in ISOBORDAT database; Pennisi et al., 2013).

Numerous studies have been conducted in Northern Italy in the last decade using a variety of hydrochemical and isotopic tools to tackle the sources, the processes and the factors controlling groundwater nitrate contamination. Previous studies on N compounds in groundwater from the Po valley, carried out in the period 1975–1995, considered NH_4, NO_2 and NO_3 molecules (e.g. Giuliano, 1995 and references therein). However, the N distribution in groundwater and its relation with other geochemical compounds often failed to unambiguously identify the nitrate source(s). Therefore, isotopic tools have started to be applied in the last twenty years, leading to a remarkable increase in produced data, nitrogen isotopes also often being associated to oxygen, hydrogen and boron isotopic systematics. As many studies were promoted by provincial or regional authorities, this copious amount of published data was generally interpreted on a local scale and, lacking a wider perspective, did not allow us to draw general conclusions at the Po basin scale, thus being of little interest for an international audience.

Although the watershed level is considered the most appropriate scale for the assessment of nutrient cycling and for the design of effective management and remedial plans (Baker and Schussler, 2007; Billen et al., 2011), nitrate pollution studies are generally local and target only limited portions of large hydrogeological systems. Therefore, the literature lacks examples of regional studies covering areas such as the one investigated here, and based on a substantial amount of isotopic data.

The aim of this paper is to provide an understanding of N dynamics in the shallow aquifers of the Po plain area, representing a hydrogeological system of European relevance (WHYMAP, 2008), and with hydrogeological features common to alluvial basins located near mountain ranges worldwide. In industrialized countries, several sources may contribute to groundwater nitrate contamination, due to complex patterns of coexisting anthropogenic activities insisting on plains (intensive agriculture and farming together with urban and industrial settlements). Here it often occurs that N inventories at the regional scale do not fully match the distribution of nitrates in groundwater, highlighting the need to take into account processes occurring below the surface and within the aquifers. In these situations, the use of an isotopic approach to apportion the contribution of the different nitrate sources to aquifer contamination and to depict the processes governing accumulation and reduction is crucial for stakeholders to implement effective management actions. To achieve this overall objective, a compilation, in a comprehensive database, of all the available hydrochemical and isotopic data, has been performed. This dataset has been integrated with some unpublished data to fill the knowledge gaps in given areas or situations. The interpretation at the watershed scale of data obtained in local scale studies of groundwater hosted in a variety of sedimentary environments allows for the definition of the more relevant processes governing nitrate contamination in Northern Italy with the objective of assisting regulators in devising remediation strategies. This comprehensive picture provides a cost-effective methodology to screen the areas where isotope analyses can be applied, drawing on generally available statistical and groundwater monitoring data.

2. Study area

Northern Italy is characterized by a large alluvial valley comprising the Po and the Veneto plains, bordered by the Alpine and Apennine chains to the N and the S, respectively, and by the Adriatic sea to the E (Fig. 1). The total surface of the Po and Veneto plains is about 100,000 km^2. The Po river, 675 km long, collects the water of 141 tributary rivers from both Alpine and Apennine chains, while the Adige (410 km) and the Tagliamento rivers (170 km) collect 18 relevant tributary rivers from the Eastern Alpine belt. Regions hosting significant