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1 Nitrate sources, accumulation and reduction in groundwater from Northern Italy: insights

2 provided by a nitrate and boron isotopic database

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- 12

13 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.

- 16 To tackle this problem, the application of environmental isotopes has proven to be an effective
- 17 method to identify the N origins and major transformations in different environments. In this
- 18 work, nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) and boron ($\delta^{11}B$) isotope analyses performed in the last twenty
- 19 years in groundwater from shallow aquifers of the Po plain area, a complex hydrogeological
- 20 system of European relevance, have been compiled in a comprehensive database together with
- 21 major ionic contents; these data were integrated with additional original results, targeting areas
- not previously examined or complementing the available information. Such data, previously
- 23 interpreted on the local scale, are examined at the Po plain scale, providing an understanding of

24 the N sources and dynamics in the shallow aquifers, and defining the most important processes

25 governing nitrate contamination in Northern Italy.

26 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
- 29 the contrary, nitrate contamination is absent in most low plain areas, with shallow water table
- 30 depths but lower soil permeability, due to the presence of denitrification processes. The δ^{15} N
- 31 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%
- 35 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
- 40 forward for the use of the coupled $\delta^{15}N \delta^{11}B$ toolbox in the study area, previously limited by a
- 41 poor definition of the compositional end-members. This georeferenced set of hydrochemical and
- 42 isotopic data will lay the foundations for future monitoring activities and advanced data treatment
- 43 or modelling. In addition, since the hydrogeological setting of the investigated area shows
- 44 common features to alluvial basins located near mountain ranges, the approach and the results
- 45 presented in this study serve as a reference for other study areas worldwide.

46 Key-words

47 hydrogeochemistry, contamination, Po plain, pig manure, denitrification, sewage

48 **1. Introduction**

49 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 50 enhanced use of synthetic and organic matter fertilizers (Tilman et al., 2001; Galloway et al., 51 2008). Although food availability increased, this produced diffuse pollution of nutrients in surface 52 53 and groundwaters, currently representing a major environmental concern worldwide (Agren and 54 Bosatta, 1988; Vitousek et al., 1997; Galloway et al., 2008). The resultant nitrogen accumulation 55 on land and in waters frequently leads to the deterioration of freshwater and coastal ecosystem 56 services, including water quality, fisheries, and amenity value.

In Europe, nitrate pollution by diffuse sources was first targeted by the Nitrate Directive (European 57 58 Commission, 1991), followed by the Water Framework Directive (European Commission, 2000). 59 The Nitrates Directive aimed to protect water quality across Europe by preventing nitrates from 60 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 61 62 pollution. As regards groundwater resources, polluted water, or those at risk of pollution, must be 63 identified in groundwater containing, or that could contain (unless action is taken to reverse the 64 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 65 66 protection to their whole territory, rather than designate NVZs. In Italy, the Directives have led to 67 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 68 Vulnerable Zones -nNVZs- respectively). Subsequently, and following the evidence collected that 69 70 manure spreading might not be the only cause of nitrate contamination, the European 71 Commission has granted Italy a derogation for the regions located in the Po plain (European 72 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 73 74 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).

76 One of the major difficulties with water contamination is the identification of the corresponding 77 source(s) of pollution, a prerequisite for properly designing appropriate actions and remediation 78 (Bronders et al., 2012). For this purpose, the application of environmental isotopes of dissolved 79 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. 80 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 81 82 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 83 84 reinforce this multi-isotopic toolbox (Vitòria et al., 2004; Nestler et al., 2011). In addition to the 85 classical chemical approach, the coupled use of nitrate and boron isotopes - although not yet a 86 routine technique - is gaining interest for policymakers and water quality administrators who are 87 interested in identifying the nitrate sources. This approach is particularly important when the NO₃ 88 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. 89 90 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 91 92 management (Komor, 1997; Widory, et al. 2004, 2005, 2013; Bronders et al., 2012).

93 The rationale for a coupled use of B and N isotopes is that these elements co-migrate in the 94 groundwater, boron being unaffected by the redox reaction that causes nitrogen transformations 95 (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 96 97 fine aguifer matrix (Xiao et al., 2013). Many studies based on the coupled δ^{15} N- δ^{11} B approach have aimed at defining a well-characterized frame of the geogenic δ^{11} B background (Palmer and 98 Swihart, 1996 and reference therein), as well as of the anthropogenic components that could 99 100 represent nitrogen and boron sources (see compilation in ISOBORDAT database; Pennisi et al., 101 2013).

Numerous studies have been conducted in Northern Italy in the last decade using a variety of 102 hydrochemical and isotopic tools to tackle the sources, the processes and the factors controlling 103 groundwater nitrate contamination. Previous studies on N compounds in groundwater from the 104 Po valley, carried out in the period 1975-1995, considered NH₄, NO₂ and NO₃ molecules (e.g. 105 106 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 107 108 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, 109 110 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 111 scale and, lacking a wider perspective, did not allow us to draw general conclusions at the Po basin 112 scale, thus being of little interest for an international audience. 113

114 Although the watershed level is considered the most appropriate scale for the assessment of 115 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 120 Po plain area, representing a hydrogeological system of European relevance (WHYMAP, 2008), and 121 122 with hydrogeological features common to alluvial basins located near mountain ranges worldwide. In industrialized countries, several sources may contribute to groundwater nitrate contamination, 123 due to complex patterns of coexisting anthropogenic activities insisting on plains (intensive 124 agriculture and farming together with urban and industrial settlements). Here it often occurs that 125 N inventories at the regional scale do not fully match the distribution of nitrates in groundwater, 126 highlighting the need to take into account processes occurring below the surface and within the 127 aquifers. In these situations, the use of an isotopic approach to apportion the contribution of the 128 129 different nitrate sources to aquifer contamination and to depict the processes governing accumulation and reduction is crucial for stakeholders to implement effective management 130 actions. To achieve this overall objective, a compilation, in a comprehensive database, of all the 131 available hydrochemical and isotopic data, has been performed. This dataset has been integrated 132 with some unpublished data to fill the knowledge gaps in given areas or situations. The 133 interpretation at the watershed scale of data obtained in local scale studies of groundwater 134 135 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 136 137 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 138 available statistical and groundwater monitoring data. 139

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141 **2. Study area**

Northern Italy is characterized by a large alluvial valley comprising the Po and the Veneto plains, 142 143 bordered by the Alpine and Apennine chains to the N and the S, respectively, and by the Adriatic 144 sea to the E (Fig. 1). The total surface of the Po and Veneto plains is about 100,000 km². The Po 145 river, 675 km long, collects the water of 141 tributary rivers from both Alpine and Apennine 146 chains, while the Adige (410 km) and the Tagliamento rivers (170 km) collect 18 relevant tributary 147 rivers from the Eastern Alpine belt. Regions hosting significant plain areas in Northern Italy are 148 (from W to E) Piedmont, Lombardy, Veneto, Emilia Romagna and Friuli Venezia Giulia. More than 149 50% of the Italian Gross National Product is produced in Northern Italy, which hosts more than 20 150 million inhabitants. About one half of total surface is devoted to agriculture and to animal 151 breeding, including mostly cattle, pigs and chickens.

The climate in the western sector is classified as temperate continental, with mean annual
 temperature of ~13°C, cold winters (in January, mean minimum and maximum temperatures of ~ -

154 3° and +3°C) and hot summers (in July, mean minimum and maximum temperatures of ~16° and

 \sim 30°C). In the eastern sector, the continental climate is less accentuated due to the effect of the

156 Adriatic sea (Cati, 1981): the mean annual temperature is ~ 14 °C, with mean minimum and

maximum temperatures of $\sim 0^{\circ}$ and $\sim 7^{\circ}$ C in January, and of $\sim 19^{\circ}$ and $\sim 27^{\circ}$ C in July, respectively

(Brancucci, 2001). Rainy periods are concentrated in spring and autumn, with mean annual rainfall
 in the range of 501-750 mm in the low plain and of 751-1000 mm in the high plain areas (Fratianni

and Acquaotta, 2017). The relative humidity is high, due to intense evapotranspiration (Elmi et al.,

161 2013).

The Po and the Veneto plains were generated during Quaternary by the dismantling of the Alpine 162 163 and Apennine chains, mostly constituted by crystalline basement rocks (Western Alps), and their sedimentary (mostly marine) covers. This large sedimentary basin was significantly affected by 164 165 subsidence in post-Oligocenic periods. Recent continental deposits were deposited during the Lower-Upper Pleistocene to Holocene. The total thickness of Quaternary sediments can reach 166 167 about 0.5 km, being bounded at the bottom by Pliocenic sediments saturated by fossil salty waters in large parts. Coarse sediments generated by rock erosion due to tributaries of the Po river are 168 169 located at the foothills of mountain belts, while finer sediments like sand, silt and clay have been transported by the Po river towards the sea. Alluvial sediments become progressively finer 170 171 towards the centre of the plain and in correspondence with the river deltas along the Adriatic sea coast. A block diagram illustrating the geological and hydrogeological settings of the study area is 172 173 reported in Fig. 1.

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Fig. 1 – Location, simplified geological and hydrogeological settings of the investigated area.
 Piezometric contour lines from Giuliano et al. (1998), modified.

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180 **2.1 Hydrogeological setting**

The aquifer system in the investigated area mostly consists of multilayer aquifers constituted by 181 gravel and sand layered with silt and clay. The shallow aquifers are generally unconfined while the 182 deeper aquifers are semiconfined and confined. Unconfined aquifers are usually poorly connected 183 184 with underlying aquifers in the low plain areas, characterized by a greater presence of fine sediments, while evidence of the effective connections among shallow and deep aquifers are 185 found in alluvial fan areas, characterized by coarser sediments. The thickness of this aquifer 186 system ranges from a few dozen meters to several hundred meters. At different depths, 187 188 depending on the geographic position, a fresh-salt water interface is present, separating freshfrom deeper salt-groundwaters. This is of great importance, as it corresponds to the lower 189 190 boundary of freshwater aquifers that are potentially exploitable for drinking, municipal and farming purposes. 191

The piezometric map of the shallow aquifer (Fig. 1) derives from regional studies (e.g. for the Piedmont plain) and piezometric levels recorded by the Regional Environmental Protection Agencies (ARPAs). The groundwater flow in the unconfined aquifer is directed towards the Po River (i.e. roughly oriented N–S in the pre-alpine sector and S–N closer to the Apennines). In the central western sector, the flow is strongly controlled by the draining action of the Po river and its tributaries, whereas, in the eastern sector, the Po river is not in hydraulic connection with groundwater.

The higher hydraulic gradients are registered close to the Alpine and Apennine chains in alluvial 199 fan areas (high plain). Typical hydraulic gradients of these areas vary from 8‰ to 10‰ in 200 201 Piedmont, and from 4‰ to 8‰ in the other areas of the Po and the Veneto-Friuli high plain. Lower hydraulic gradients characterize low plain aquifers along the Po river (normally ranging 202 from 1‰ to 4‰); in the central-eastern part of the Po Valley they decrease to values of 0.2‰-203 204 1‰. At the transition from the high to low plain, the decrease in the hydraulic gradient is generally associated to the emergence of typical lowland springs (fontanili) (Fig. 1) (Minelli et al. 2002; 205 Vorlicek et al. 2004; De Luca et al. 2009, 2014; Zini et al. 2011; Balderacchi et al. 2016; Fumagalli et 206 al. 2017). The highest hydraulic conductivity (1-10·10⁻³ m/s) is measured in alluvial fan areas, 207 208 whereas lower values (1-10·10⁻⁵ m/s) are measured in low plain areas, although some areas 209 characterized by relatively high permeability coefficients have been identified in the western and the central sectors of the low plain. The water level depth in shallow aquifers is highly variable in 210 the Po plain: minimum values of 1-5 m b.g.l. are recorded in the central part of the plain, whereas 211 closer to the Alps it may reach 30-50 m, and close to the Apennines it is set around 10 m. 212

213 Shallow aquifers and aquifers located in alluvial fans are characterized by relatively high intrinsic 214 vulnerability values, while deep aquifers and shallow aquifers characterized by fine sediments in 215 the unsaturated zone show lower vulnerability.

216

217 **2.2** Groundwater nitrate contents and infiltrability

The existing relationship between the characteristics of the unsaturated zone in the subsoil and groundwater nitrate contents is shown in Fig. 2. The regional infiltrability map was developed through the joint processing of the shallow aquifer textures (gravel, sand and silt) and the thickness of the surface alteration layers and/or loess deposits (Giuliano et al., 1998). Basically, the infiltration parameter, used at regional level, facilitates the identification of those areas where it is easier for substances coming from the surface (in our case, nitrates) to be hydro-transported by recharge waters to the unconfined aquifers.

The plain sector is represented in different colors according to the classification of infiltrability 225 (very high, high, medium, low or negligible). The location of the wells periodically sampled by the 226 ARPAs is also indicated and differentiated based on their nitrate content (lower or higher than 50 227 mg/l, the regulatory limit for drinking water supplies). High values are observed in areas 228 characterized by high infiltrability, mostly at the Alpine and Apennine foothills. This is of particular 229 230 concern since these areas represent the recharge areas for all the Po valley aquifer systems. On the other hand, large portions of the western and central plain (e.g. South of Milan) showing high 231 232 infiltrability values do not record high nitrate concentrations in groundwaters. However, it should be noted that the ARPA network also considers some wells tapping in semi-confined and confined 233

aquifers, where the nitrate concentrations are obviously lower because of the higher protection offered by the overlying low-permeability layers. Nonetheless, in large portions of the central plain, nitrate concentrations do not exceed 50 mg/l in the unconfined aquifer (Pilla et al., 2006; Guffanti et al., 2010), indicating that the aquifer grain size (i.e. the hydraulic conductivity) and the thickness of the surface alteration layers are not the only parameters governing the contamination levels.

Previous studies have indicated that nitrate concentrations in aquifers could depend on different physical-chemical processes. High nitrate contents have been found in areas with high infiltration and/or low aquifer dilution capacity. On the other hand, low nitrate contents have been observed in areas with high dilution capacity, lower infiltration rates from the surface and/or in the presence of enhanced denitrification processes (Debernardi et al. 2008; Lasagna et al. 2013; Lasagna et al. 2016b).



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Fig.2 - Infiltrability map of the Po, Veneto and Friuli plain (after Giuliano et al., 1998, modified). Dots represent wells periodically sampled by regional environmental protection Agencies. Black dots = nitrate concentration <50 mg/l; red dots = nitrate concentration >50 mg/l.

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2.3 Nitrate Vulnerable Zones from agricultural sources

The Nitrates Directive was applied in Italy by national legislation (Decree Law 152/99) and the NVZ designation was undertaken under the competence of the Regional Authorities. The first NVZ designation took place in the late nineteen-nineties, based on the results of monitoring programmes assessing nitrate concentration in surface and groundwaters, and the trophic status of surface waters, and the NVZs were enlarged in different steps between 2000 and 2011. These enlargements were performed in Italian Regions by means of different approaches, and based on multiple parameters (e.g. intrinsic vulnerability of the shallow aquifer obtained with different methods, N-surplus, and soil attenuation capacity). Consequently, these delimitations were performed with a forward-looking approach.

The total designated NVZs in Piedmont, Lombardy, Veneto, Friuli Venezia Giulia and Emilia-261 Romagna represent almost 70% of designated NVZs in Italy (Fig. 3); moreover, they represent a 262 263 percentage ranging between the 50% and 60% of regional plains areas (Ministry for Environment, Land and Sea, Ministry of Agriculture, Food and Forestry Policies, regions of Piedmont, Lombardy, 264 Veneto, Emilia-Romagna and Friuli Venezia Giulia, 2010). In the NVZs, action programmes are to 265 be implemented by farmers on a compulsory basis, including curbs on fertilizer application 266 (mineral and organic) and other measures at farm scale. The costs of these measures in the 267 framework of farm economics can have a negative economic impact, especially for small farm 268 269 holdings (ADAS, 2011).





271 272

273 Fig. 3 – NVZs of Northern Italy (map elaborated with <u>http://fate-</u> 274 <u>gis.jrc.ec.europa.eu/geohub/MapViewer.aspx?id=2</u>)

275

276 **3. Materials and methods**

The compiled database is made up of hydrochemical and isotopic data, retrieved from national and international publications (Pilla et al., 2005; 2006; 2007; Lasagna et al., 2006; 2015; 2016a, 2016b; Debernardi et al., 2008; Guffanti et al., 2010; Sacchi et al., 2013; Saccon et al., 2013;

280 Martinelli et al., 2014a), conference proceedings (Dadomo and Martinelli, 2005; Arduini et al.,

281 2007; Sacchi et al., 2007; Martinelli et al., 2014b; 2014c) and unpublished reports (Provincia di Verona, 2001; ISO4, 2005). These data were all determined in water extracted from shallow 282 283 aquifers during a single campaign. Only in few exceptions groundwater monitoring involved repeated sampling of the same well (Provincia di Verona, 2001; Sacchi et al., 2007; Saccon et al., 284 285 2013). As in many instances this monitoring evidenced a seasonal evolution of both nitrate concentrations and isotopic compositions, all these data were treated as if they were individual 286 287 measurements to avoid the issue of representativeness. Unfortunately, not all the groundwater 288 samples have a correspondingly complete chemical analysis.

- All the data sources are clearly identified in Tab. S1 (Supplementary material), allowing us to refer 289 to the publication in terms of the analytical techniques used. Nitrate isotope data were produced 290 291 using the silver nitrate method (Silva et al., 2000) or the bacterial denitrification method (Sigman et al., 2001), and results are expressed in the standard $\delta^{15}N_{NO3}$ ‰ vs AIR and $\delta^{18}O_{NO3}$ ‰ vs SMOW 292 notation. Boron isotopes were determined by MC-ICP-MS, with results expressed as δ^{11} B‰ with 293 294 respect to the NBS-951 standard. The database is a compilation of results generated in different 295 laboratories, at different times and by different techniques, and no data are available that can be 296 used for inter-laboratory comparison. Nevertheless, isotopic compositions are always expressed 297 with respect to international standards, and therefore, assuming that each laboratory has 298 correctly implemented the analytical protocol, the results should, in principle, be comparable.
- 299 To fill in the knowledge gaps in given areas (e.g. the Parma province in Emilia Romagna) or situations (e.g. the δ^{11} B composition of some compositional end-members), additional original 300 analyses were also performed and reported in Tab. S1 (Supplementary material) and Tab. 1. For 301 302 these samples, nitrate isotopes were determined by IRMS at ISO4, Italy. Samples were prepared and purified according to the method described by Silva et al., 2000. Uncertainties (1σ) are $\pm 0.5\%$ 303 for $\delta^{15}N_{NO3}$ and $\pm 1\%$ for $\delta^{18}O_{NO3}$. Boron isotope ratios in purified fractions of groundwaters were 304 305 measured by MC-ICP-MS Neptune Plus at ALS Scandinavia AB, Luleå (Sweden), with an uncertainty of ± 0.4 to $\pm 1\%$, using a combination of internal standardization and bracketing standards for 306 instrumental mass bias correction. Boron isotopes of relevant anthropogenic sources for the study 307 area (e.g. pig manure, sewage, synthetic fertilizer) were determined by positive TIMS on $Cs_2B_4O_7$ 308 deposited on the ion source filament with graphite and mannitol, which produces CsBO₂ ions, 309 after boron purification through ion exchange resins (Tonarini et al., 1997). Analyses were 310 performed at CNR-IGG in Pisa (Italy) using a VG Micromass 54 E mass spectrometer with an 311
- uncertainty of $\pm 0.5\%$, calculated on replicate analyses of the NBS-951 standard.
- The location of samples included in the database is shown in Fig. 4, with different color codes corresponding to the regions. The distribution of sampling points mostly reflects the areas where nitrate concentrations in groundwater sometimes exceeded the regulatory limits.
- 316 To test the possible correlations of the isotopic composition with anthropogenic pressure
- 317 indicators, data were aggregated by province and the descriptive statistical parameters were
- calculated (Min, Max, Mean, Median; Tab. S2 in Supplementary material). Farm census data
- 319 (number of cattle, number of pigs and Utilized Agronomical Area [UAA] per province) for the year

- 320 2010 were obtained from the National Statistical Institute (ISTAT, 2010), while the number of
- inhabitants and population density were retrieved from the ISTAT database (year 2009). 321
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Fig. 4 - Location of samples included in the hydrochemical and isotopic database. Colors correspond to the different regions.

- 326
- 4. Results and discussion 327

4.1 Groundwater hydrochemistry 328

Previous studies have indicated that in the Po plain, most of the waters hosted in alluvial fans of 329 the Alpine and Apennine chains show a Ca(Mg)-HCO₃ facies, and TDS ranging from 300 to 3500 330 mg/l. Groundwaters with a Na(K)-HCO₃ (TDS range=500-2700 mg/l) facies subordinately occur in 331 the eastern part of the Po plain, characterized by fine sediments. This change in the chemical 332 composition is due to Na-Ca exchange with clays. Ca(Mg)-SO₄ groundwaters (TDS range=750-2400 333 mg/l) occur in limited areas at the foothills of the Apennine chain and are the result of interaction 334 between meteoric waters and evaporitic minerals of Triassic and Messinian age (Giuliano, 1995; 335 Martinelli et al., 2014a). Na (K)-Cl groundwaters (TDS range= 1200-2000 mg/l) occur in the central 336 and eastern part of the Po river plain. They are the result of interactions between meteoric waters 337

- and evaporitic layers formed during Quaternary transgressive episodes (Conti et al., 2000; Pilla et
 al., 2010; Martinelli et al., 2016).
- 340 Ca(Mg)-HCO₃ groundwaters and Ca(Mg)-SO₄ groundwaters are hosted in unconfined and semi-
- 341 confined coarse sediment aquifers characterized by relatively high flow velocities (0.1-5 m/day).
- They are often affected by a significant nitrate contamination (50-100 mg/l) (Pilla et al., 2006;
- 343 Sacchi et al., 2013; Martinelli et al., 2014c). Na(K)-HCO₃ and Na(K)-Cl groundwaters are hosted in
- 344 confined fine sediment aquifers characterized by low groundwater flow velocities (less than 10
- 345 m/yr), which inhibit pollution phenomena.
- Groundwater hydrochemical data, when available in the database (Tab. S1; Supplementary
- material), were represented in the classical Piper diagram (Fig. 5). Most of the samples fall within
- the field of Ca-HCO₃ facies with medium TDS values, reflecting water circulation in shallow
- unconfined aquifers. In areas where the marine substratum is closer to the surface (Fig. 1), the
- 350 groundwater composition is affected by a contribution of Na-Cl waters.





Fig.5 - Piper diagram showing the available compositions of groundwaters.

- 353 Groundwater TDS values in the studied area are strongly determined by mineralogical composition of the substratum, being higher in the eastern and southern parts due to the higher relative 354 355 abundance of carbonates in the aquifer matrix. The relationship between groundwater TDS and nitrate contents is shown in Fig. 6. The plot evidences that the higher nitrate concentrations are 356 357 often found in low TDS waters, mostly hosted in alluvial fans of the Piedmont-Lombardy plain (Fig.1). Since TDS is expected to increase with time due to mineral weathering, this could indicate 358 359 a more recent recharge and a faster circulation in these aquifers. Nevertheless, also high TDS (≥ 360 1000 mg/l) waters in the lower Lombardy and Emilia-Romagna plain show non-negligible nitrate 361 concentrations (~ 30 mg/l), confirming a contribution of present-day recharge for these waters, and suggesting that the differences in groundwater age in unconfined aquifers throughout the 362 363 investigated area should be relatively small.
- 364 An alternative explanation for the nitrate-TDS relationship considers that microbial oxidation of 365 ammonium generates acidity along with nitrate in soils, that is readily buffered by the dissolution of carbonates from the aquifer matrix, if these are present (Spruill et al., 2002). The relationship 366 367 between groundwater nitrate concentrations and hydrochemistry has been recently reviewed by 368 Menció et al. (2016) who demonstrated, in aquifers characterized by different lithologies, that nitrates have an enhancing effect upon the biogeochemical processes that control water-rock 369 370 interactions. This generally leads to an increase in major ions concentrations (therefore in TDS 371 values), but also homogenizes the overall hydrochemistry despite lithological differences, and 372 enhances or reduces the geochemical processes that control groundwater composition at equilibrium. This could be the reason why no clear correlation between nitrate and calcium 373 374 contents could be observed in groundwater from the investigated area, suggesting that other natural processes may mask this relationship (e.g. cation exchange, gypsum dissolution etc.). 375



- 378Fig. 6 –Total Dissolved Solids vs nitrate concentrations of selected groundwaters. The higher379nitrate concentrations are often found in low TDS waters (blue oval).
- 380

381 **4.2 Nitrate sources**

Atmospheric deposition measured in Northern Italy accounts in average for 20-25 kg N ha⁻¹ yr⁻¹ (Rogora et al., 2012). While this represents an important source of reactive N for surface waters, it is a minor component of the total N input to soils compared to agricultural and civil or industrial inputs (EEA, 2005), as indicated by N budgets calculated in several watersheds within the Po river basin (e.g. Bartoli et al., 2012). As most isotopic studies targeted areas with high nitrate concentrations, often located close to the Alpine and Apennine chains (Fig. 2 and Fig. 4), we can reasonably assume to a first approximation that denitrification processes are not very relevant in the study area (see also section 4.3). Therefore, the N isotopic composition should be mostlydetermined by the source of dissolved nitrates.

- The δ^{15} N values recorded in the database vary between -7.84 and +37.50‰ vs AIR (n=818). A
- 392 frequency histogram (Fig. 7) shows that the more common values in groundwater range between
- 393 +6 and +8‰. These values correspond to the isotopic compositions of nitrates naturally generated
- by the degradation of the soil organic matter (Kendall et al., 2007). Nevertheless, the nitrate
- concentrations recorded often largely exceed the expected natural background level (~5 mg/l,
- Edmunds and Shand, 2008), suggesting that this isotopic value derives from anthropogenic
- 397 sources, namely from the mixing between synthetic sources and organic matter-derived nitrates.
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Fig. 7 – Frequency histogram of $\delta^{15}N_{NO3}$ values in groundwater. Values on the x-axis represent the interval's upper limit.

The distribution of δ^{15} N was compared to nitrate concentrations, in order to identify the source(s) 402 that mostly contribute to the observed contamination. Two data modes are present (evidenced by 403 ovals in Fig. 8): one with a relatively depleted value ($\delta^{15}N$ of about +2‰) corresponding to 404 synthetic sources (i.e. fertilizers) and mostly evident in the Piedmont region, and a second, wider 405 mode, around +8‰, displayed by samples from different regions. More interestingly, high nitrate 406 concentrations are mostly recorded in samples with very enriched $\delta^{15}N$, suggesting that these 407 derive from organic matter sources. This is in contrast with the δ^{15} N distribution observed in the 408 409 sole Lombardy plain (Sacchi et al., 2013), where both depleted and highly enriched values were 410 mostly characterized by low nitrate concentrations, the former attributed to synthetic sources and 411 the latter due to the influence of denitrification phenomena.



- Supplementary material) and compared to farm census and population data. All possible
 correlations between δ¹⁵N values and anthropogenic pressure indicators were considered. At the
- basin scale, a significant correlation between the median δ^{15} N values and the number of pigs per
- 424 UAA is observed (n=25; r= 0.478; p=0.015), as shown in Fig. 9, whereas no significant correlations
- 425 could be observed for cattle density, cattle + pig density or population density (Tab.S2;
- 426 Supplementary material). This correlation with pig density, although significant, is not very strong,
- 427 due to some limitations imposed by the dataset, and by the adopted model (linear correlation
- 428 rather than exponential). Nevertheless, it should be noted that the provinces with the highest pig

- densities (i.e. Bergamo, Brescia and Mantua) are poorly correlated with the others. This could be
- due, on one hand, to the low amount of available isotopic data for these provinces, but also to the
- fact that, if denitrification is not occurring, the δ^{15} N enrichment would be limited to the highest
- 432 δ^{15} N values displayed by the contamination source (for example, in the case of pig manure, limited 433 to 16‰, according to Vitòria et al. (2008)). In other words, although the total number of pigs may
- 434 increase, the δ^{15} N content may be constant if it presents the same origin. If these three provinces
- 435 are eliminated from the plot, the correlation significantly improves (Fig. 9), and the correlation
- 436 with the total number of pigs also becomes significant (p<0.01), whereas those with cattle or
- 437 population remain non-significant.
- 438 A correlation between animal husbandry, and particularly with the number of pigs, and
- 439 groundwater nitrate contamination has been observed elsewhere (e.g. Aquilina et al., 2012; Boy-
- 440 Roura et al., 2013), and may be due to the fact that the produced type of excrement is often a
- slurry rather than manure (Lorimor et al., 2004; Mantovi et al., 2006; Risberg et al., 2017).
- 442 Nevertheless, δ^{15} N values could also be enriched due to denitrification, a process that, in absence
- 443 of δ^{18} O data, cannot be ruled out.



445

446Fig. 9 – Number of pigs per UAA versus δ^{15} N median values calculated per each province. Grey line447= all data; black line = excluding the Bergamo (BG), Brescia (BS) and Mantua (MN) provinces.

448

449 **4.3 Processes affecting nitrate contents**

The $\delta^{18}O_{NO3}$ values recorded in the database vary between +1.08 and +25.5‰ vs SMOW (n=412). A frequency histogram (Fig. 10) shows that the more common values in groundwater range between

452 +4 and +10‰.



Fig. 10 – Frequency histogram of $\delta^{18}O_{NO3}$ values in groundwater. Values on the x-axis represent the interval's upper limit.

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Results were plotted on the classical $\delta^{18}O_{NO3}$ vs $\delta^{15}N_{NO3}$ diagram (Fig.11), reporting the expected 457 range of isotopic composition for the different sources. These were derived from the literature 458 (Clark and Fritz, 1997; Kendall et al., 2007), and confirmed by some $\delta^{15}N_{NO3}$ values determined 459 locally and reported in Saccon et al. (2013) and Sacchi et al. (2013). The lowest values of $\delta^{18}O_{NO3}$ of 460 461 the potential sources are calculated, considering that in the nitrate molecule one oxygen atom is provided by atmospheric oxygen ($\delta^{18}O_{02} \approx +23.5\%$) and two are provided by the water molecule 462 (Kendall et al., 2007). Since the isotopic composition of precipitation falling on the plain sector 463 ranges between -6 and -9‰ in $\delta^{18}O_{H2O}$ (Longinelli and Selmo, 2003), a fully equilibrated nitrate 464 should then range between +1.83 and +3.83‰ in $\delta^{18}O_{NO3}$. 465

Two sets of samples characterized by enriched $\delta^{18}O_{NO3}$ can be observed in Fig. 11, one close to the compositional field of synthetic fertilizers, and one related to denitrification processes. The first set, compatible with the nitrification of synthetic fertilizers, accounts for a relatively low number of samples. This process produces nitrates that maintain the atmospheric $\delta^{15}N_{N2}$ signal (see discussion in the previous section 4.2), but are progressively more depleted in $\delta^{18}O_{NO3}$ due to the

- 471 incorporation of oxygen from the water molecules. Nevertheless, the $\delta^{18}O_{NO3}$ is slightly more
- enriched than expected for a full equilibration with $\delta^{18}O_{H2O}$. This enrichment is often observed in
- 473 microbially-produced nitrate, and is attributed to many possible reasons (e.g. nitrification
- occurring in the soil, where the isotopic composition of the available water may be slightly
- enriched by evaporation), although the issue is still being debated (Kendall et al., 2007). The
- 476 presence of isotopic compositions attributable to nitrification of synthetic fertilizers, although not
- 477 so frequent, indicates a fast transfer of nitrates to groundwater, with a low residence time in soils,
- 478 thus confirming for these cases the high permeability, infiltrability and intrinsic vulnerability of the
- 479 aquifer.
- 480 On the other hand, isotopic compositions enriched due to denitrification are present in a relatively
- 481 larger number of samples (\approx 90, corresponding to about 22% of the available data). According to
- 482 Fig. 11, samples plot between two lines with a 0.5 δ^{18} O/ δ^{15} N slope, one with more enriched
- 483 $\delta^{18}O_{NO3}$ values, originating from synthetic fertilizers, and the second from manure and septic
- 484 system effluents. Hence, as both these nitrate sources are present in the area, they are both prone
- 485 to denitrification when favorable environmental conditions are present. The observed isotopic
- 486 enrichment (Fig. 11) allows for the consideration of denitrification as being responsible for nitrate
 487 abatement in groundwater affecting up to 70-80% of the original content, depending on the initial
- 488 isotopic composition and the enrichment factor used (Kendall et al., 2007; Sacchi et al., 2013).
- 489 Denitrification was mostly reported in the lower plain of Piedmont and Lombardy (Pilla et al., 490 2005; Pilla et al., 2007; Debernardi et al. 2008; Guffanti et al., 2010; Sacchi et al., 2013; Lasagna et 491 al. 2016b). Studies indicate that, under different soil and crop types, denitrification occurs when 492 the water table is shallow, within 5 m from the surface, allowing the establishment of reducing 493 conditions at shallow depths. This can occur naturally in low permeability soils, or as a 494 consequence of flood irrigation adopted in rice cultivation. In other cases, denitrification was 495 observed in shallow aquifers characterized by a low-permeability unsaturated zone. In Piedmont, a 496 high denitrification rate was reported in areas with a shallow aquifer of limited thickness (e.g. 497 Poirino Plateau) characterized by low permeability and low dilution degree. In this case, the 498 nitrate input is not diluted in the aquifer, and high nitrate concentrations (even higher than 100
- 499 mg/l) are present in groundwater, despite the denitrification process.
- 500 Indirect evidence for ongoing denitrification can be obtained with hydrochemical tools, as these 501 waters often contain detectable dissolved Fe and Mn contents. Both these metals are geogenic in 502 origin (Maffei et al., 2005), as they derive from the dissolution of Fe(II)-Mn(II)-bearing minerals or the reduction of Fe-Mn oxyhydroxides present in the sediments. In the redox reaction sequence, 503 504 O₂ reduces before nitrate which again is followed by reduction of Mn-oxides and by reduction of Fe-oxides (Appelo and Postma, 2005). Therefore, the presence of nitrates and of Fe/Mn is 505 506 mutually exclusive. In the lower Lombardy plain, Sacchi et al. (2013) mapped groundwater samples with Fe and Mn concentrations above 100 and 50 µg/l respectively, as metals above these 507 508 concentrations may be taken as indicators of reducing environments (McMahon and Chapelle, 2008; Wendland et al., 2008), and compared the distribution with that of nitrates. They concluded 509 510 that in the low plain unconfined aquifers, the input of nitrates from the surface must have been

511 reduced by denitrification due to the presence of an anoxic environment. In other Regions (e.g. Veneto and Emilia Romagna) little isotopic evidence of the presence of denitrification is reported. 512 This is due, on the one hand, to the lack of $\delta^{18}O_{NO3}$ values for these areas. On the other, it should 513 be noted that most isotopic studies targeted areas with high nitrate concentrations, often located 514 515 close to the Alpine and Apennine chains (Fig. 2 and Fig. 4); thus, the lower Veneto plain and the higher Emilia-Romagna plain have not been assessed. Nevertheless, the presence of dissolved Fe 516 517 and Mn, often associated to NH₄⁺ and As, is documented in unconfined aquifers of the low plain throughout the investigated area (e.g. Maffei et al., 2005). Therefore, based on the available 518 519 hydrochemical and isotopic evidence (e.g. Rotiroti et al., 2014, 2017; Giambastiani et al., 2016; Petrini et al., 2014; Castaldelli et al., 2013; Carraro et al., 2013), the absence of nitrates in 520 521 groundwater from the central Po plain can be reasonably ascribed to denitrification, whereas the main factor promoting this permanent loss of reactive nitrogen is the shallowness of the water 522 523 table.



524

525

526

Fig. 11 - $\delta^{18}O_{NO3}$ vs $\delta^{15}N_{NO3}$ values in groundwater. Compositional fields and nitrificationdenitrification trends from Sacchi et al. (2013), modified after Clark and Fritz (1997).

527

528 **4.4 Insights provided by B isotopes**

529 Compared to the consolidated application of δ^{15} N to contamination studies, the associated use of 530 δ^{11} B represents a promising but still subordinated tool, as testified by the very few data available

- 531 in the database of the studied area (both for B concentrations and isotopic compositions),
- 532 compared to the large set of nitrate isotope data.
- 533 Currently, boron concentration values recorded in the database range between b.d.l. to 672 μ g/l,
- and δ^{11} B values vary between -1.4 and +36.3‰ vs NBS-951 (n=27). A frequency histogram for the
- isotopic compositions (Fig. 12) shows the non-normal distribution of the data, with two
- populations characterized by different isotopic compositions, one around +10‰ and a second
- around +22‰. Comparing this distribution of δ^{11} B signatures to that recorded in Italian
- 538 groundwaters (Pennisi et al., 2013), the value of +10% can be considered near to the mean
- 539 geogenic value (+8.2 ‰) that characterizes the Italian alluvial aquifers. On the contrary, the higher
- 540 δ^{11} B mode value (+22‰) clearly evidences inputs either of a sea water or of an animal manure
- 541 component, both characterized by ¹¹B-enriched signatures (Palmer and Swihart, 1996; Widory et
- 542 al., 2005).



543

Fig. 12 – Frequency histogram of δ^{11} B values in groundwater. Values on the x-axis represent the interval's upper limit.

Together with the need to increase the number of values in the database, the application of the B 546 systematics in the study area is challenged by the poor definition of the compositional end-547 548 members, both in terms of natural background and of potential sources of contamination. The application of the coupled δ^{15} N - δ^{11} B toolbox needs to identify the isotopic signature/s of the 549 anthropogenic sources related to the given study site under investigation. As an example, boron in 550 liquid animal manure reflects the boron signature of food and its fractionation eventually 551 552 occurring from ingestion to the excretion pathway (i.e. urine). For piggery, a significant role in the pig manure signature can be played by the origin (marine versus non-marine) of the salt (NaCl with 553

1% boron) supplied with feeding. While concentrations and isotopic compositions of contaminants
are reported for given sites in France and the USA (see ISOBORDAT "Contaminants" database and
references therein), B isotope data on sewage, manure or fertilizer are at present lacking In Italy.

557 As an original contribution of this work we report new data on the main products used in the

agricultural sector in Emilia Romagna (Tab. 1). The values obtained for synthetic fertilizers, sewage

559 water and pig manure are within the ranges defined in the literature for these substances (Widory

560 et al., 2004, 2005; Tirez et al., 2010).

561

Sample	Name	δ^{11} B‰ vs NBS-951	r.s.d (‰)
1	Boric acid	-13.5	0.4
2	Colemanite	-12.8	0.4
3	Colemanite 40	-8.1	0.27
4	Borax pentahydrate	-0.3	0.45
5	Ulexite	-3.5	0.44
6	Nitrophoska Blu Spezial	0.3	0.56
7	Sewage treatment plant (Sassuolo)	8.2	0.56
8	Pig manure	13.9	0.5
9	NaCl Italkali (B=1%)	31.8	0.45

562

Tab. 1 – Isotopic composition of anthropogenic boron sources in the Emilia Romagna region.
Samples 1 to 5 are compounds utilized in the ceramics industry in the Reggio Emilia and Modena
provinces; sample 6 is an industrial fertilizer frequently used in the Po Valley; sample 7 is the
outflow of a sewage treatment plant located in Sassuolo (Modena province); sample 8 is the dry
residue of pig manure collected in the Reggio Emilia area; sample 9 is halite used in pig breeding.

In the highly impacted areas of the Alpine foothills of Lombardy, Sacchi et al. (2013) produced the 568 569 first coupled data on B and N in groundwaters with the aim of discriminating the contamination from agriculture and contamination from civil origin. The authors selected samples where the 570 571 isotopic composition of dissolved nitrates fell in the field of contamination from mixed or anthropogenic organic matter sources, or in the field of denitrification; two waste waters from 572 573 sewage treatment plants were also analysed, whereas the isotopic composition of the other contaminant sources was taken from the literature. In Lombardy, boron concentrations ranged 574 from 20 to 540 μ g/l (displayed as 1/B in Fig. 13) and δ^{11} B values from -1.4‰ to +26.2‰. The 575 sample with the lowest B concentration had a δ^{11} B of +14.6‰, and was assumed to be the 576 geogenic, "uncontaminated" end-member. With the increase of B concentrations, a group of 577 samples shifted towards both more depleted δ^{11} B values, suggesting contamination from sewage 578

and/or fertilizers (Seiler et al., 2005; Widory et al., 2005). Conversely, in other samples, an increase 579 580 in both the B concentration and isotopic composition was observed with respect to the geogenic 581 end-member, attributed to a contribution of anthropogenic boron sourced from animal manure (Widory et al., 2004; 2005). An increase in the geogenic boron concentration controlled by 582 583 increasing water-rock interaction, was also evidenced by the lack of any significant shift in the $\delta^{11}B$ signature of water respect to the un-polluted signature in some Po basin samples (Fig. 13). By 584 comparison, samples from the Emilia Romagna and Veneto regions show a lower range of δ^{11} B but 585 higher B concentrations, suggesting a higher contribution of either sewage or synthetic fertilizers. 586



587

Fig. 13 - δ^{11} B vs 1/B plot of groundwater from Northern Italy (full dots: yellow = Friuli V.G.; orange = Lombardy; red = Emilia Romagna), and literature data from low geogenic-B environments (empty symbols: green squares = Komor, 1997; blue circles = Widory et al., 2004; yellow triangles = Widory et al., 2005; blue diamonds = Seiler, 2005; red squares = Puig et al., 2017). δ^{11} B compositional ranges of contaminants after Widory et al., 2004, 2005; Tirez et al., 2010; range for rainwater from the ISOBORDAT database (Pennisi et al., 2013). Boron concentration in mg/l.

In Fig 13, data from the investigated area are compared to literature data from studies where the 594 δ^{15} N - δ^{11} B tool was applied in low geogenic-B environments. A large isotopic variation of almost 595 50‰ is associated to a boron concentration range of $10 - 1000 \mu g/l$. Three end-members are 596 597 distinguished, most of the samples resulting from a mixing between these sources. The high boron 598 samples span over the whole range of δ^{11} B, and mainly concentrate in the area were the "sewage" 599 and "manure" isotopic signatures overlap. Fig. 13 also identifies a trend in literature data starting 600 from low boron – high δ^{11} B composition (+40‰), indicating a boron enrichment in groundwater that occurs following the infiltration of meteoric water of marine origin. The decrease in δ^{11} B 601 associated to the increase in B concentrations points to the two main anthropogenic boron 602

sources - animal manure and wastewater - recognized in the literature (Widory et al., 2004, 2005; Tirez et al., 2010). In this context, the newly defined isotopic signature of uncontaminated water from the Po alluvial aquifers ($\delta^{11}B = +13 \pm 2.5\%$) appears to be dominated by rainwater nonmarine in origin or already modified during rock interaction.

607 Finally, Fig. 14 shows the δ^{11} B vs δ^{15} N_{NO3} plot of samples from the study area compared to other literature data obtained in groundwater from low geogenic-B environments. The compositional 608 fields of the contaminants are represented as grey boxes (Widory et al., 2004, 2005; Tirez et al., 609 610 2010), and the red box evidences the compositional field defined for uncontaminated water from 611 the Po alluvial aquifers. The plot confirms that both sewage and animal manure contribute to the 612 nitrate pollution in the study area, as already indicated by Sacchi et al. (2013). Although isotopic 613 data suggest that cattle manure is more concerned than pig manure as nitrate supplier to groundwater, this information partially contradicts the results obtained from animal husbandry 614 615 data crossed with N isotopic data (see par. 4.2). Therefore, given the important implications for 616 the agricultural sector, the unequivocal identification of the nitrate contamination sources in the 617 study area still requires a better definition of the isotopic compositions of animal manure applied 618 to agricultural fields, and the coupling of isotopic and farm census data.



619

Fig. 14 - δ^{11} B vs δ^{15} N plot of groundwater from Northern Italy (full dots: orange = Lombardy; red = Emilia Romagna: blue = Veneto), and literature data from low geogenic-B environments (empty symbols: green squares = Komor, 1997; blue circles = Widory et al., 2004; yellow triangles = Widory et al., 2005; blue diamonds = Seiler, 2005; red squares = Puig et al., 2017). δ^{11} B and δ^{15} N compositional ranges: SF = synthetic fertilizers; Sew = sewage; CM = cattle manure; PM = pig manure (after Widory et al., 2004, 2005; Tirez et al., 2010). The red box corresponds to the compositional field defined for uncontaminated water from the Po alluvial aquifers.

627 **5. Conclusions**

- In the last twenty years a remarkable number of nitrate isotopic data, often associated to oxygen, 628 hydrogen and boron isotopic systematics have been produced in the Po plain area, mostly in local 629 investigations. In this work, all the available nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) and boron ($\delta^{11}B$) isotopic 630 data, together with the hydrochemical composition, if available, were compiled in a 631 632 comprehensive database, and some additional analyses were performed to fill the knowledge gaps in given areas or situations. Such an integration of data obtained in the groundwater hosted in a 633 634 variety of sedimentary environments has allowed for their interpretation in a wider perspective, both providing an understanding of the N sources and dynamics in the shallow aquifers at the Po 635 636 basin scale, and defining the more relevant processes governing nitrate contamination in Northern 637 Italy. The conclusions of this work seek to assist regulators in devising sustainable management and remediation strategies. 638
- In the investigated area, the most impacted groundwater is that hosted in the alluvial fans of the 639 640 Alpine and Apennine foothills. This is due to a combination of high soil permeability and presence of intensive agricultural activities. Aquifers in these areas are characterized by fast circulation and 641 642 by great depths of the water table. This finding indicates that, while the input of nitrates in these areas has led to present-day high concentrations, groundwater contamination would be quickly 643 644 remediated if the N excess input were reduced. In addition, it is worth stressing that, in the study 645 area, the general assumption that the deeper the water table, the higher the groundwater 646 protection from contamination, is not verified. On the contrary, nitrate contamination is absent in 647 most low plain areas, where the water table is shallow but soil permeability is lower. This is due to the presence of environmental conditions favourable to denitrification processes, as also indicated 648 by other hydrochemical parameters (Fe, Mn, NH₄⁺). While this is the general case in low plain 649 areas, in certain cases (e.g. Poirino Plateau in Piedmont), denitrification, although present, is not 650 sufficient to fully abate nitrates because of the high input coupled to the low dilution potential of 651 the aquifer. 652
- As the δ^{15} N median values are significantly correlated at the basin scale with pig farming, manure spreading represents one of the main nitrate sources in groundwater from agriculture, the other being synthetic fertilizers. Based on this evidence, pig manure management should be carefully reevaluated and should be favoured in the low plain areas deprived of nitrates in groundwater, since the local hydrogeological setting allows nitrates to be metabolized in the environment with few consequences for the water resources.
- 659 Despite the relatively low number of available B isotope data, this systematics has provided interesting results in terms of nitrate contamination origin in such a low geogenic-B context. 660 661 Indeed, it has proved the presence of another anthropogenic nitrate source, of civil origin, that is sewage in the study area. The garnering of all the data has allowed us to define the range of the 662 expected geogenic B signature, and new results on the local B sources have been produced. This is 663 a significant step forward for the use of the coupled δ^{15} N - δ^{11} B toolbox, as the application of the B 664 665 systematics in the study area was previously limited by a poor definition of the compositional end-666 members, both in terms of natural background and of potential contamination sources. To further

enhance the application of this isotopic systematics, when sampling for nitrate isotopes, it would
be advisable to collect and set aside a water aliquot (< 250 ml of untreated sample) that can be
used for B isotope determinations even years later, should the investigation require it.

This georeferenced set of hydrochemical and isotopic data will lay the foundations for future 670 monitoring activities and allow for an exploitation of already existing data from a different 671 perspective, e.g. by advanced data treatment or modelling. Since the hydrogeological setting is 672 673 similar throughout the Po and Veneto plains (Fig. 1 and Fig. 2), and shows common features to alluvial basins located near mountain ranges, the conceptual model of nitrate circulation and the 674 processes affecting nitrate concentrations revealed by this study can be reasonably extrapolated 675 to other areas of the watershed not yet investigated with isotopic tools, and serve as a reference 676 for other study areas worldwide. In addition, based on the results of this study, different 677 management options could be considered by decision-makers to reduce the impact of nutrients 678 679 on water bodies. These relate to i) the amount of fertilizers used in agriculture, for example by tailoring their use to the actual crop needs. This option has already been adopted in municipalities 680 681 declared as NVZ in order to obtain the derogation to the Nitrate Directive (European Commission, 2012); ii) the type of fertilizer used and the timing of application. This management option should 682 balance the advantages and disadvantages of the use of manure and synthetic fertilizers in 683 agricultural areas characterized by different soil permeabilities and agronomical practices; iii) the 684 amount of water used for irrigation, in order to prevent the leaching of nutrients to the subsurface 685 686 and increase their residence time in the soil; iv) the civil sources of N, for example by connecting isolated households to sewer pipes, checking the integrity of the sewage network and remediating 687 688 leaching septic tanks.

689

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