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(Article begins on next page)

1 **Nitrate sources, accumulation and reduction in groundwater from Northern Italy: insights**  
2 **provided by a nitrate and boron isotopic database**

3 Martinelli G.<sup>1</sup>, Dadomo A.<sup>2</sup>, De Luca D.A.<sup>3</sup>, Mazzola M.<sup>4</sup>, Lasagna M.<sup>3</sup>, Pennisi M.<sup>5</sup>, Pilla G.<sup>6</sup>, Sacchi  
4 E.<sup>6</sup>, Saccon P.<sup>7</sup>

5 <sup>1</sup> *ARPAE Environmental Protection Agency, Emilia Romagna Region, Reggio Emilia, Italy*

6 <sup>2</sup> *Geoinvest Srl, Piacenza, Italy*

7 <sup>3</sup> *Department of Earth Sciences, University of Torino, Italy*

8 <sup>4</sup> *ARPAV Environmental Protection Agency, Veneto Region, Vicenza, Italy*

9 <sup>5</sup> *Institute of Geosciences and Earth Resources (IGG), CNR, Pisa, Italy*

10 <sup>6</sup> *Department of Earth and Environmental Sciences, University of Pavia, Italy*

11 <sup>7</sup> *Waterdrop Consulting, Graz, Austria*

12

13 **Abstract**

14 Large volumes of precious water resources are negatively affected by nitrate contamination, and  
15 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 ( $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ) and boron ( $\delta^{11}\text{B}$ ) 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  
22 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  
27 foothills, due to a combination of high soil permeability and presence of intensive agricultural  
28 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  $\delta^{15}\text{N}$   
31 median values, calculated for each province, are significantly correlated with pig density. Hence,  
32 manure represents one of the main nitrate sources in groundwater from agriculture, the other  
33 being synthetic fertilizers. Isotopic compositions enriched due to denitrification are present in  
34 ~22% of the data, being responsible for nitrate abatement in groundwater affecting up to 70-80%  
35 of the original content.

36 The B systematics, in such a low geogenic-B context, proved the presence in the investigated area  
37 of another anthropogenic nitrate source of civil origin (i.e. sewage). While new results on the local  
38 B sources are reported, the garnering of all groundwater data allowed us to define the range of

39 the expected geogenic B signature ( $\delta^{11}\text{B} = +13 \pm 2.5\%$ ). This contribution is a significant step  
40 forward for the use of the coupled  $\delta^{15}\text{N} - \delta^{11}\text{B}$  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  
50 developed countries significantly increased crop production and livestock, with a concomitant  
51 enhanced use of synthetic and organic matter fertilizers (Tilman et al., 2001; Galloway et al.,  
52 2008). Although food availability increased, this produced diffuse pollution of nutrients in surface  
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.

57 In Europe, nitrate pollution by diffuse sources was first targeted by the Nitrate Directive (European  
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  
61 territories that drain into polluted waters or waters at risk of pollution and contribute to nitrate  
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,  
65 Luxembourg, Malta, the Netherlands and Slovenia have decided to provide the same level of  
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,  
68 especially manure, was significantly restricted (170 and 340 kg N ha<sup>-1</sup> yr<sup>-1</sup> for NVZs and non-Nitrate  
69 Vulnerable Zones -nNVZs- respectively). Subsequently, and following the evidence collected that  
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<sup>-1</sup> yr<sup>-1</sup> in NVZs,  
73 providing a higher Nitrogen Use Efficiency [NUE] of manure (*i.e.* the percentage of total nitrogen  
74 applied in the form of livestock manure that is available to crops in the year of application,  
75 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.  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ) 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  
81 added value of analyzing the isotopic signature of boron ( $\delta^{11}\text{B}$ ) in association with the specific  
82 isotope signature of nitrates has been demonstrated (Seiler, 2005; Widory et al., 2004; 2005;  
83 Saccon et al., 2013; Puig et al., 2017). Strontium and sulphate isotopes are randomly also used to  
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  $\text{NO}_3$   
88 concentrations are higher than the threshold value defined by the Water Frame Directive (WFD;  
89 50 mg/l), which implies the definition of the poor chemical status of the quality of the water body.  
90 The need to discriminate between the different sources of pollution (i.e. sewage, animal manure,  
91 chemical fertilizer, natural soil mineralization) thus becomes crucial for any water exploitation and  
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  
96 strongly depends on the aquifer source rock and on the extent of the exchange of water with the  
97 fine aquifer matrix (Xiao et al., 2013). Many studies based on the coupled  $\delta^{15}\text{N}$ -  $\delta^{11}\text{B}$  approach  
98 have aimed at defining a well-characterized frame of the geogenic  $\delta^{11}\text{B}$  background (Palmer and  
99 Swihart, 1996 and reference therein), as well as of the anthropogenic components that could  
100 represent nitrogen and boron sources (see compilation in ISOBORDAT database; Pennisi et al.,  
101 2013).

102 Numerous studies have been conducted in Northern Italy in the last decade using a variety of  
103 hydrochemical and isotopic tools to tackle the sources, the processes and the factors controlling  
104 groundwater nitrate contamination. Previous studies on N compounds in groundwater from the  
105 Po valley, carried out in the period 1975-1995, considered  $\text{NH}_4$ ,  $\text{NO}_2$  and  $\text{NO}_3$  molecules (e.g.  
106 Giuliano, 1995 and references therein). However, the N distribution in groundwater and its  
107 relation with other geochemical compounds often failed to unambiguously identify the nitrate  
108 source(s). Therefore, isotopic tools have started to be applied in the last twenty years, leading to a  
109 remarkable increase in produced data, nitrogen isotopes also often being associated to oxygen,  
110 hydrogen and boron isotopic systematics. As many studies were promoted by provincial or  
111 regional authorities, this copious amount of published data was generally interpreted on a local  
112 scale and, lacking a wider perspective, did not allow us to draw general conclusions at the Po basin  
113 scale, thus being of little interest for an international audience.

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

116 Schussler, 2007; Billen et al., 2011), nitrate pollution studies are generally local and target only  
117 limited portions of large hydrogeological systems. Therefore, the literature lacks examples of  
118 regional studies covering areas such as the one investigated here, and based on a substantial  
119 amount of isotopic data.

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

140

## 141 **2. Study area**

142 Northern Italy is characterized by a large alluvial valley comprising the Po and the Veneto plains,  
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 km<sup>2</sup>. 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.

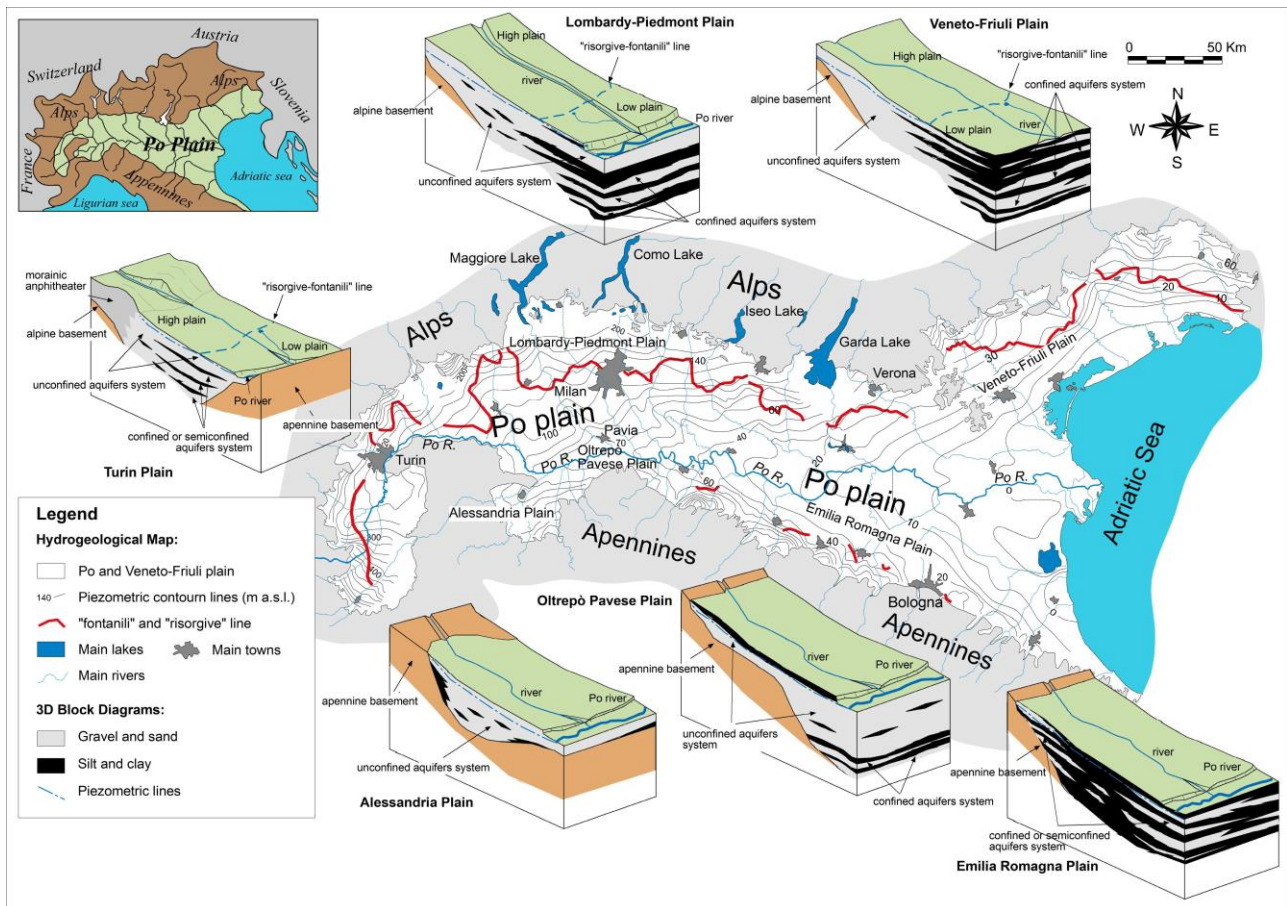
152 The climate in the western sector is classified as temperate continental, with mean annual  
153 temperature of ~13°C, cold winters (in January, mean minimum and maximum temperatures of ~ -  
154 3° and +3°C) and hot summers (in July, mean minimum and maximum temperatures of ~16° and

155 ~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  
157 maximum temperatures of ~ 0° and ~7°C in January, and of ~19° and ~27°C in July, respectively  
158 (Brancucci, 2001). Rainy periods are concentrated in spring and autumn, with mean annual rainfall  
159 in the range of 501-750 mm in the low plain and of 751-1000 mm in the high plain areas (Fратиanni  
160 and Acquaotta, 2017). The relative humidity is high, due to intense evapotranspiration (Elmi et al.,  
161 2013).

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

174

175



176

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

179

180 **2.1 Hydrogeological setting**

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

192 The piezometric map of the shallow aquifer (Fig. 1) derives from regional studies (e.g. for the  
 193 Piedmont plain) and piezometric levels recorded by the Regional Environmental Protection  
 194 Agencies (ARPAs).

195 The groundwater flow in the unconfined aquifer is directed towards the Po River (i.e. roughly  
196 oriented N–S in the pre-alpine sector and S–N closer to the Apennines). In the central western  
197 sector, the flow is strongly controlled by the draining action of the Po river and its tributaries,  
198 whereas, in the eastern sector, the Po river is not in hydraulic connection with groundwater.

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

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***

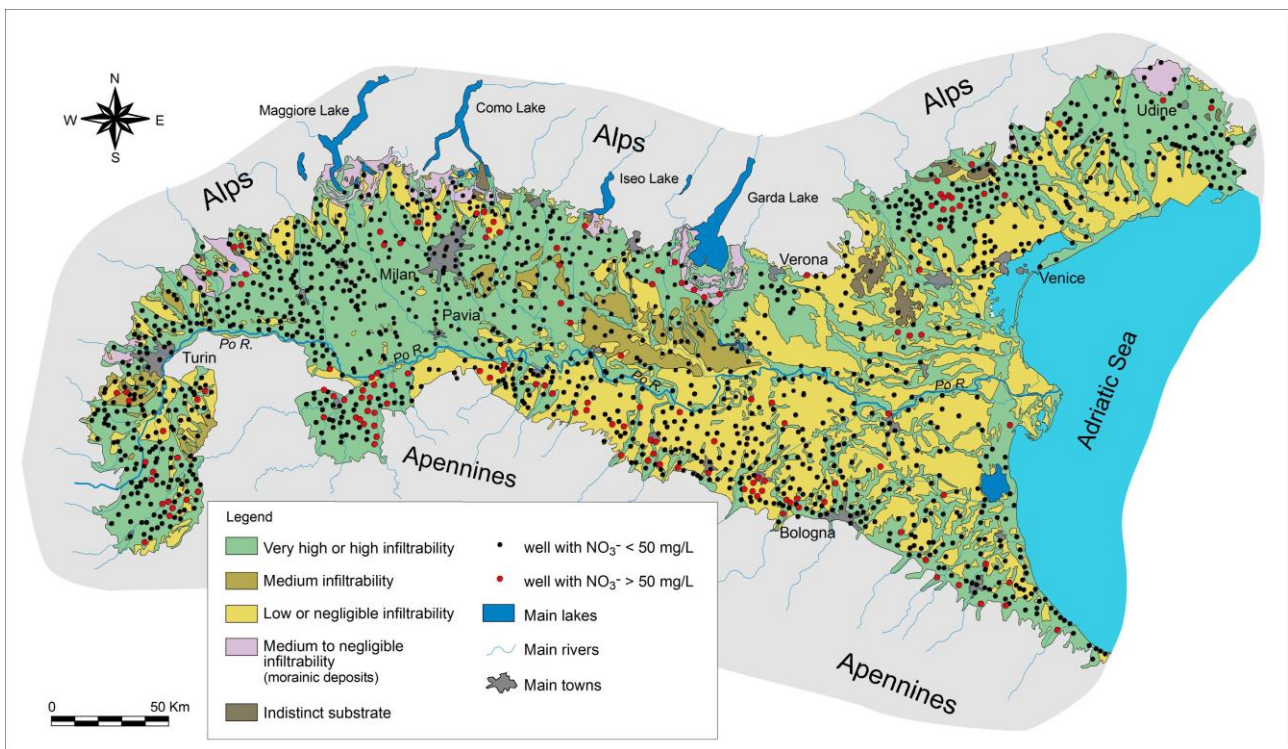
218 The existing relationship between the characteristics of the unsaturated zone in the subsoil and  
219 groundwater nitrate contents is shown in Fig. 2. The regional infiltrability map was developed  
220 through the joint processing of the shallow aquifer textures (gravel, sand and silt) and the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

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



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

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



246  
247 Fig.2 - Infiltrability map of the Po, Veneto and Friuli plain (after Giuliano et al., 1998, modified).  
248 Dots represent wells periodically sampled by regional environmental protection Agencies. Black  
249 dots = nitrate concentration  $< 50 \text{ mg/l}$ ; red dots = nitrate concentration  $> 50 \text{ mg/l}$ .

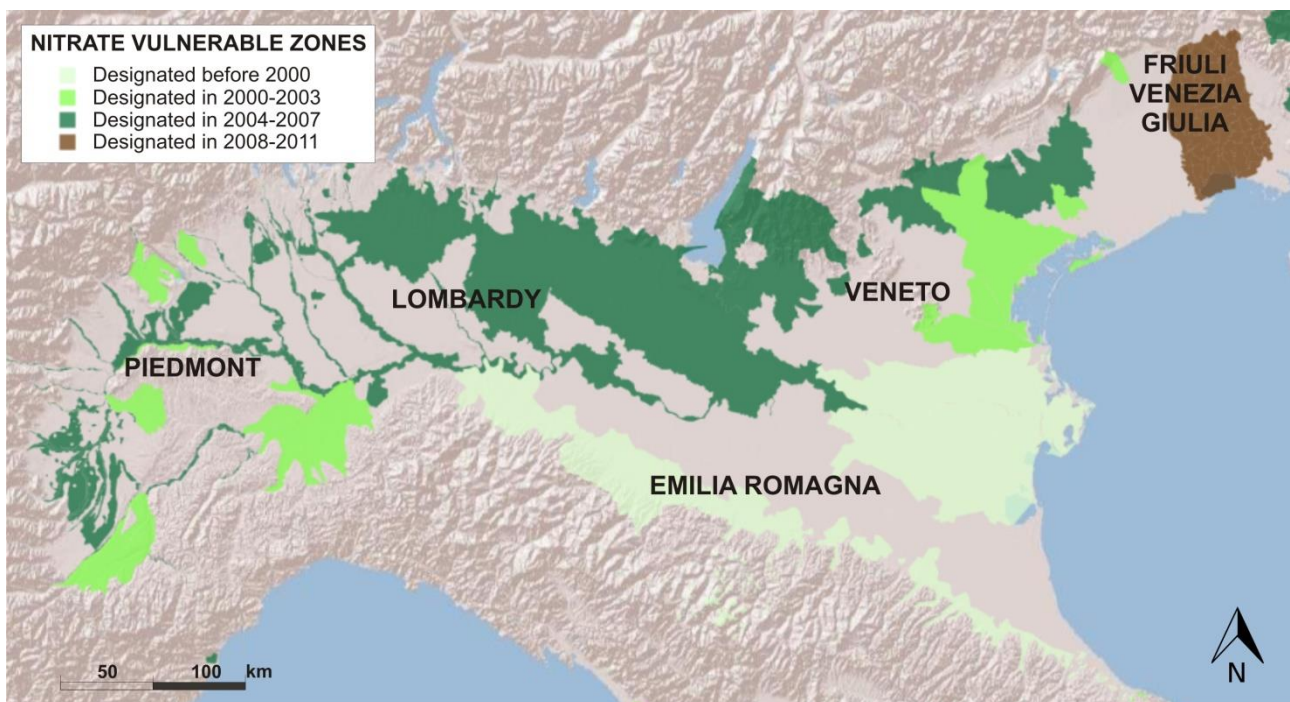
250  
251 **2.3 Nitrate Vulnerable Zones from agricultural sources**

252 The Nitrates Directive was applied in Italy by national legislation (Decree Law 152/99) and the NVZ  
253 designation was undertaken under the competence of the Regional Authorities. The first NVZ  
254 designation took place in the late nineteen-nineties, based on the results of monitoring  
255 programmes assessing nitrate concentration in surface and groundwaters, and the trophic status  
256 of surface waters, and the NVZs were enlarged in different steps between 2000 and 2011.

257 These enlargements were performed in Italian Regions by means of different approaches, and  
258 based on multiple parameters (e.g. intrinsic vulnerability of the shallow aquifer obtained with  
259 different methods, N-surplus, and soil attenuation capacity). Consequently, these delimitations  
260 were performed with a forward-looking approach.

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

270



271

272

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

275

### 276 3. Materials and methods

277 The compiled database is made up of hydrochemical and isotopic data, retrieved from national  
278 and international publications (Pilla et al., 2005; 2006; 2007; Lasagna et al., 2006; 2015; 2016a,  
279 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  
282 Verona, 2001; ISO4, 2005). These data were all determined in water extracted from shallow  
283 aquifers during a single campaign. Only in few exceptions groundwater monitoring involved  
284 repeated sampling of the same well (Provincia di Verona, 2001; Sacchi et al., 2007; Saccon et al.,  
285 2013). As in many instances this monitoring evidenced a seasonal evolution of both nitrate  
286 concentrations and isotopic compositions, all these data were treated as if they were individual  
287 measurements to avoid the issue of representativeness. Unfortunately, not all the groundwater  
288 samples have a correspondingly complete chemical analysis.

289 All the data sources are clearly identified in Tab. S1 (Supplementary material), allowing us to refer  
290 to the publication in terms of the analytical techniques used. Nitrate isotope data were produced  
291 using the silver nitrate method (Silva et al., 2000) or the bacterial denitrification method (Sigman  
292 et al., 2001), and results are expressed in the standard  $\delta^{15}\text{N}_{\text{NO}_3}$  ‰ vs AIR and  $\delta^{18}\text{O}_{\text{NO}_3}$  ‰ vs SMOW  
293 notation. Boron isotopes were determined by MC-ICP-MS, with results expressed as  $\delta^{11}\text{B}$ ‰ with  
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.

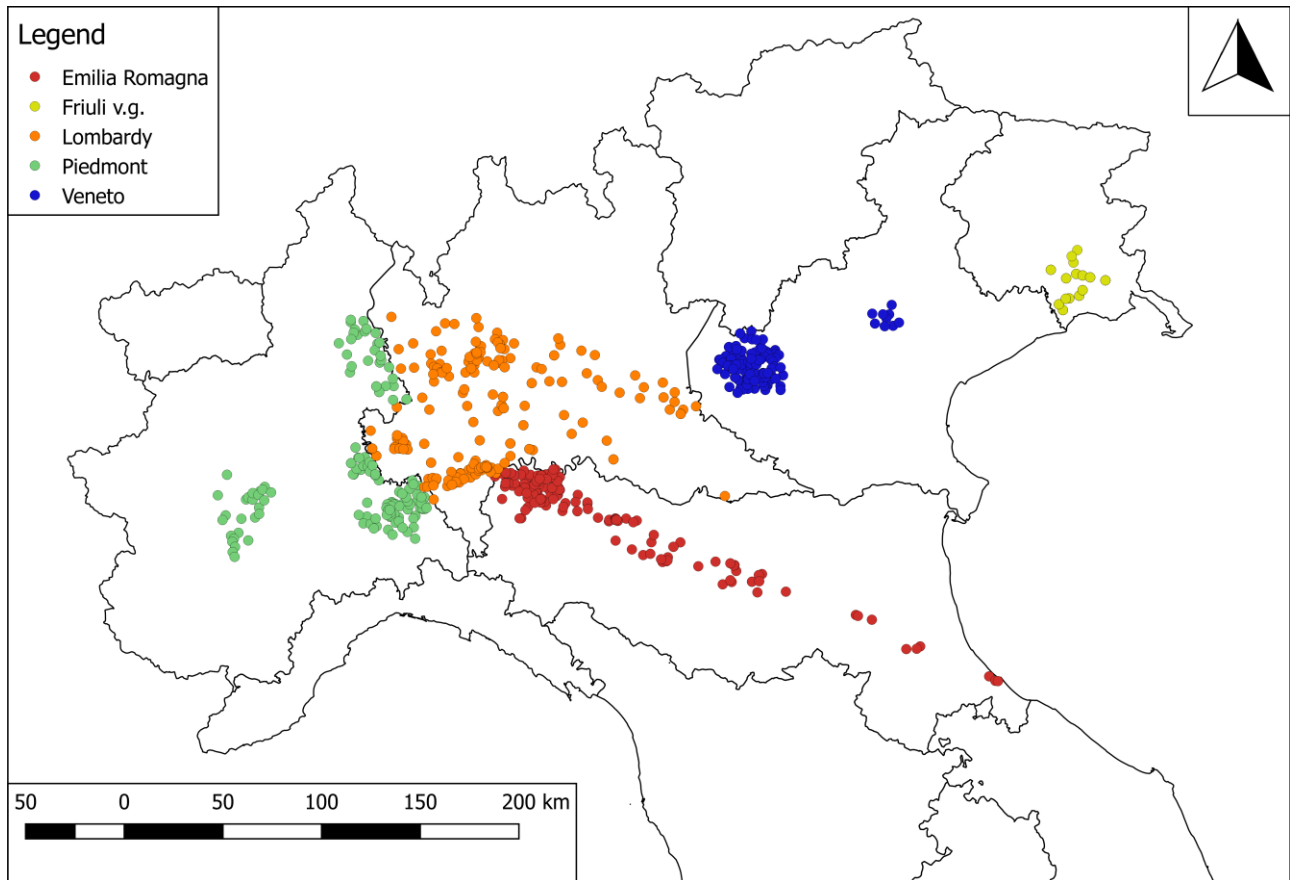
299 To fill in the knowledge gaps in given areas (e.g. the Parma province in Emilia Romagna) or  
300 situations (e.g. the  $\delta^{11}\text{B}$  composition of some compositional end-members), additional original  
301 analyses were also performed and reported in Tab. S1 (Supplementary material) and Tab. 1. For  
302 these samples, nitrate isotopes were determined by IRMS at ISO4, Italy. Samples were prepared  
303 and purified according to the method described by Silva et al., 2000. Uncertainties ( $1\sigma$ ) are  $\pm 0.5$ ‰  
304 for  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\pm 1$ ‰ for  $\delta^{18}\text{O}_{\text{NO}_3}$ . Boron isotope ratios in purified fractions of groundwaters were  
305 measured by MC-ICP-MS Neptune Plus at ALS Scandinavia AB, Luleå (Sweden), with an uncertainty  
306 of  $\pm 0.4$  to  $\pm 1$ ‰, using a combination of internal standardization and bracketing standards for  
307 instrumental mass bias correction. Boron isotopes of relevant anthropogenic sources for the study  
308 area (e.g. pig manure, sewage, synthetic fertilizer) were determined by positive TIMS on  $\text{Cs}_2\text{B}_4\text{O}_7$   
309 deposited on the ion source filament with graphite and mannitol, which produces  $\text{CsBO}_2$  ions,  
310 after boron purification through ion exchange resins (Tonarini et al., 1997). Analyses were  
311 performed at CNR-IGG in Pisa (Italy) using a VG Micromass 54 E mass spectrometer with an  
312 uncertainty of  $\pm 0.5$ ‰, calculated on replicate analyses of the NBS-951 standard.

313 The location of samples included in the database is shown in Fig. 4, with different color codes  
314 corresponding to the regions. The distribution of sampling points mostly reflects the areas where  
315 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  
318 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  
321 inhabitants and population density were retrieved from the ISTAT database (year 2009).

322



323

324 Fig. 4 - Location of samples included in the hydrochemical and isotopic database. Colors  
325 correspond to the different regions.

326

## 327 4. Results and discussion

328

### 328 4.1 Groundwater hydrochemistry

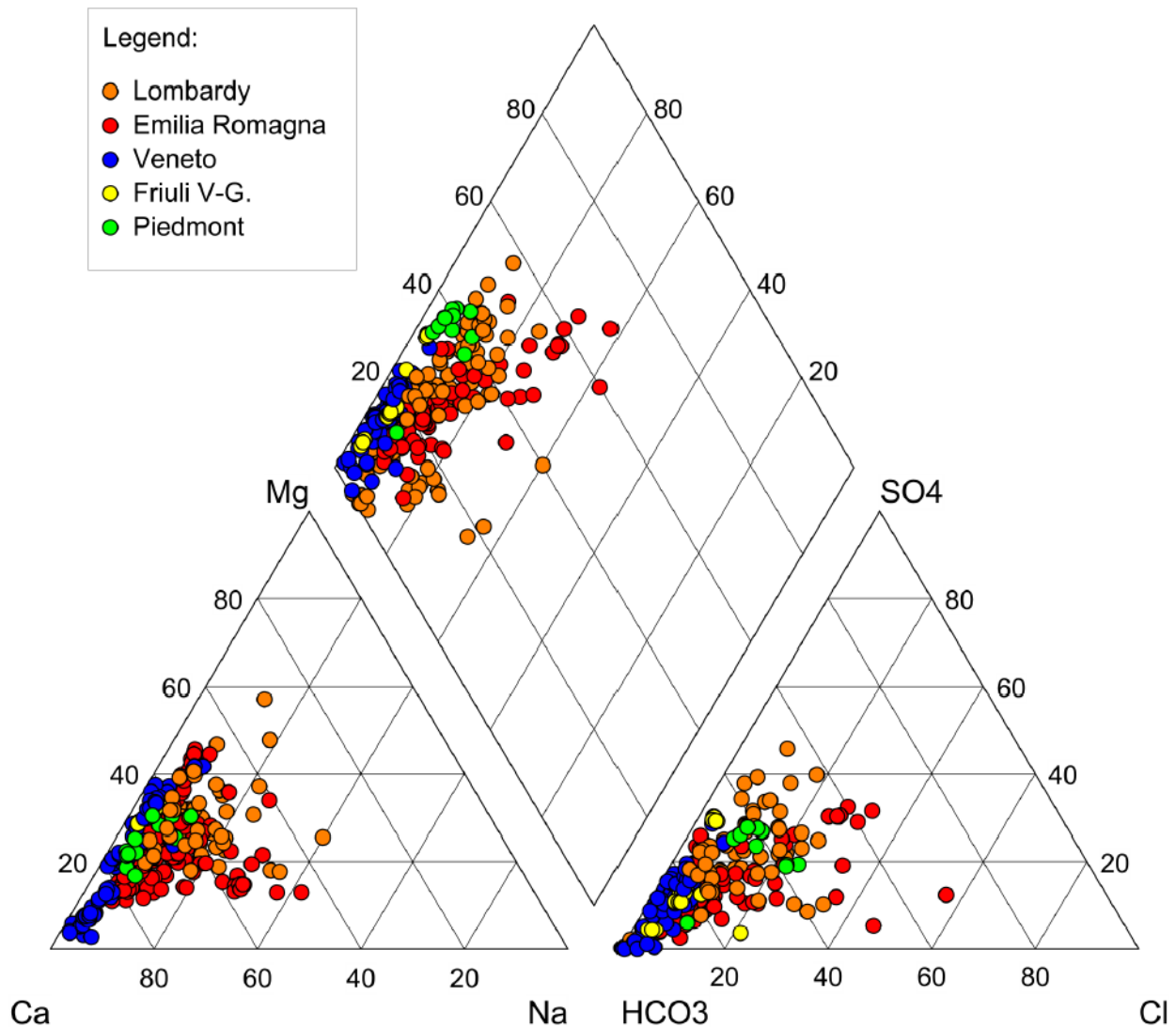
329 Previous studies have indicated that in the Po plain, most of the waters hosted in alluvial fans of  
330 the Alpine and Apennine chains show a Ca(Mg)-HCO<sub>3</sub> facies, and TDS ranging from 300 to 3500  
331 mg/l. Groundwaters with a Na(K)-HCO<sub>3</sub> (TDS range=500-2700 mg/l) facies subordinately occur in  
332 the eastern part of the Po plain, characterized by fine sediments. This change in the chemical  
333 composition is due to Na-Ca exchange with clays. Ca(Mg)-SO<sub>4</sub> groundwaters (TDS range=750-2400  
334 mg/l) occur in limited areas at the foothills of the Apennine chain and are the result of interaction  
335 between meteoric waters and evaporitic minerals of Triassic and Messinian age (Giuliano, 1995;  
336 Martinelli et al., 2014a). Na (K)-Cl groundwaters (TDS range= 1200-2000 mg/l) occur in the central  
337 and eastern part of the Po river plain. They are the result of interactions between meteoric waters



338 and evaporitic layers formed during Quaternary transgressive episodes (Conti et al., 2000; Pilla et  
339 al., 2010; Martinelli et al., 2016).

340 Ca(Mg)-HCO<sub>3</sub> groundwaters and Ca(Mg)-SO<sub>4</sub> groundwaters are hosted in unconfined and semi-  
341 confined coarse sediment aquifers characterized by relatively high flow velocities (0.1-5 m/day).  
342 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)-HCO<sub>3</sub> 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.

346 Groundwater hydrochemical data, when available in the database (Tab. S1; Supplementary  
347 material), were represented in the classical Piper diagram (Fig. 5). Most of the samples fall within  
348 the field of Ca-HCO<sub>3</sub> facies with medium TDS values, reflecting water circulation in shallow  
349 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.



351

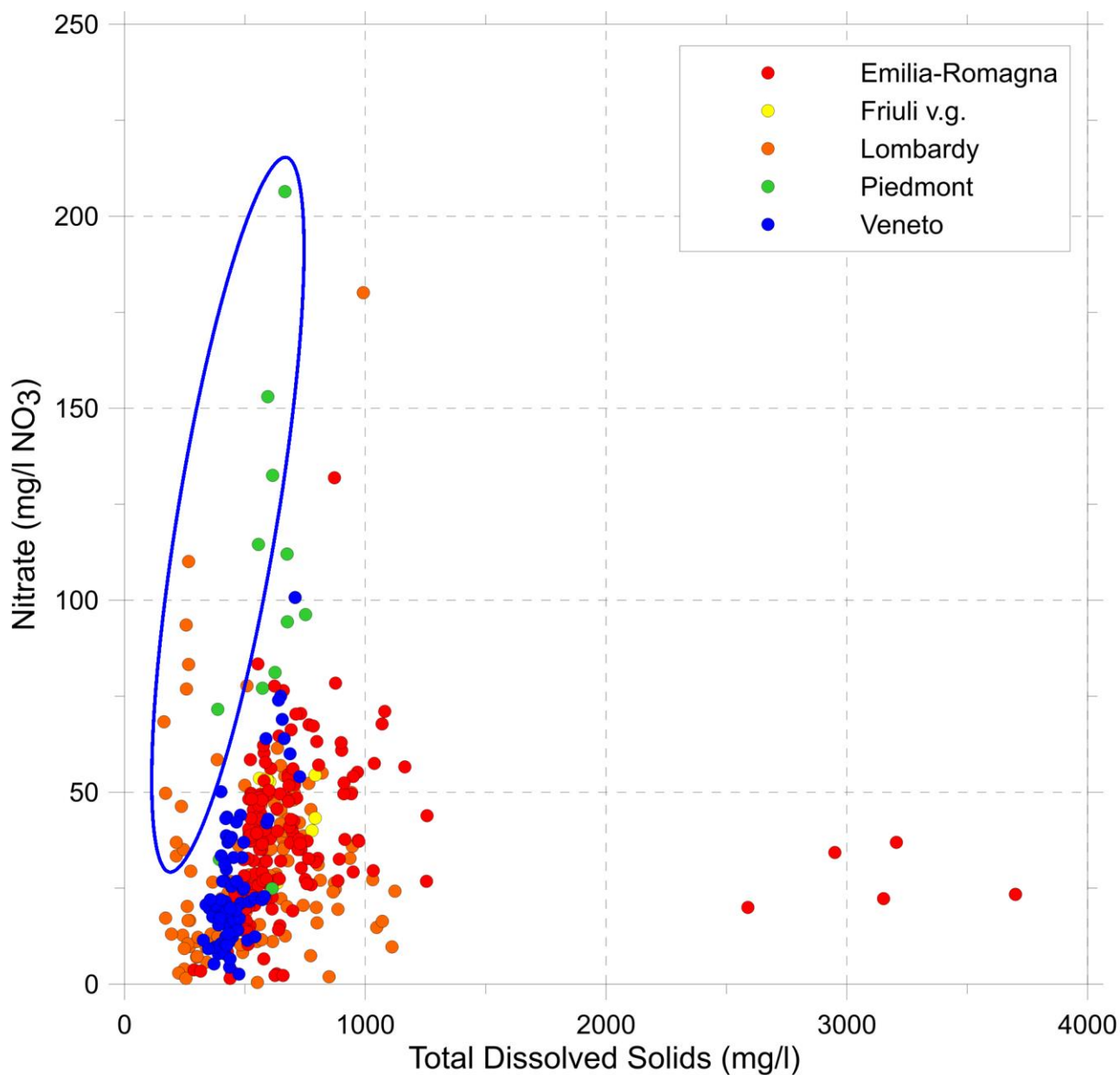
352

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

353 Groundwater TDS values in the studied area are strongly determined by mineralogical composition  
354 of the substratum, being higher in the eastern and southern parts due to the higher relative  
355 abundance of carbonates in the aquifer matrix. The relationship between groundwater TDS and  
356 nitrate contents is shown in Fig. 6. The plot evidences that the higher nitrate concentrations are  
357 often found in low TDS waters, mostly hosted in alluvial fans of the Piedmont-Lombardy plain  
358 (Fig.1). Since TDS is expected to increase with time due to mineral weathering, this could indicate  
359 a more recent recharge and a faster circulation in these aquifers. Nevertheless, also high TDS ( $\geq$   
360 1000 mg/l) waters in the lower Lombardy and Emilia-Romagna plain show non-negligible nitrate  
361 concentrations ( $\sim 30$  mg/l), confirming a contribution of present-day recharge for these waters,  
362 and suggesting that the differences in groundwater age in unconfined aquifers throughout the  
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  
366 of carbonates from the aquifer matrix, if these are present (Spruill et al., 2002). The relationship  
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  
369 nitrates have an enhancing effect upon the biogeochemical processes that control water-rock  
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  
373 equilibrium. This could be the reason why no clear correlation between nitrate and calcium  
374 contents could be observed in groundwater from the investigated area, suggesting that other  
375 natural processes may mask this relationship (e.g. cation exchange, gypsum dissolution etc.).

376



377

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

380

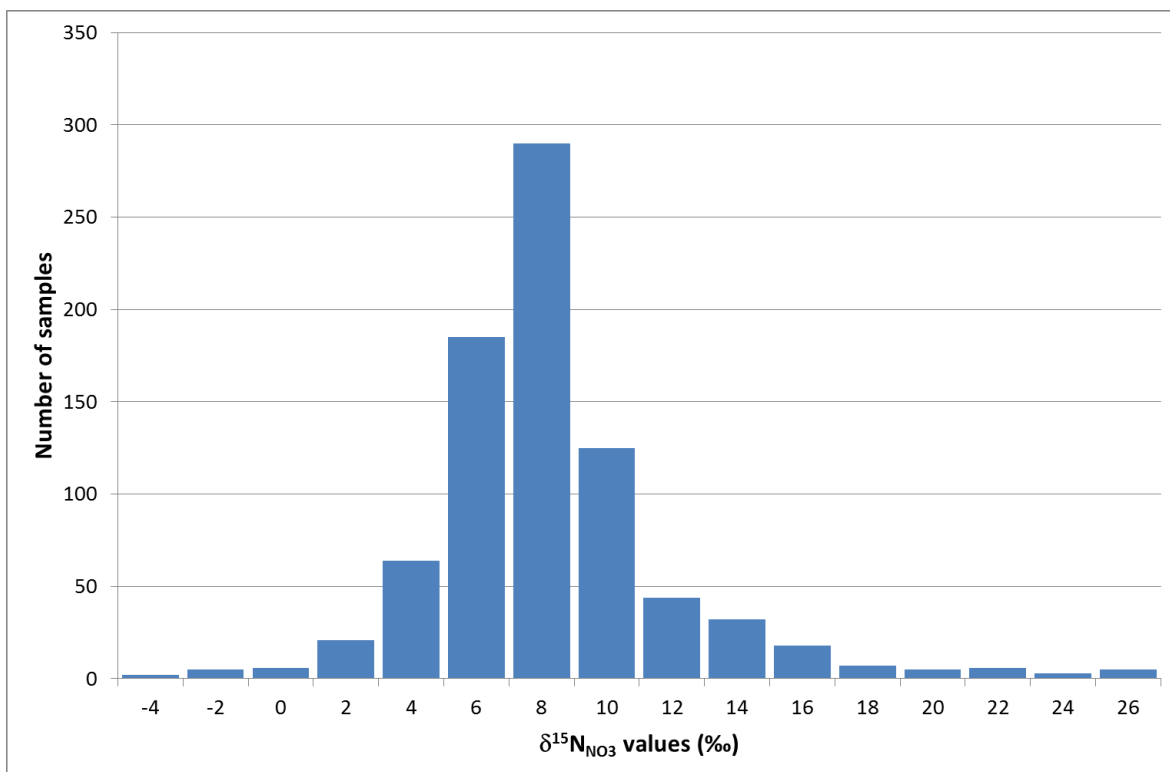
381 **4.2 Nitrate sources**

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

389 the study area (see also section 4.3). Therefore, the N isotopic composition should be mostly  
390 determined by the source of dissolved nitrates.

391 The  $\delta^{15}\text{N}$  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  
394 by the degradation of the soil organic matter (Kendall et al., 2007). Nevertheless, the nitrate  
395 concentrations recorded often largely exceed the expected natural background level (~5 mg/l,  
396 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.

398

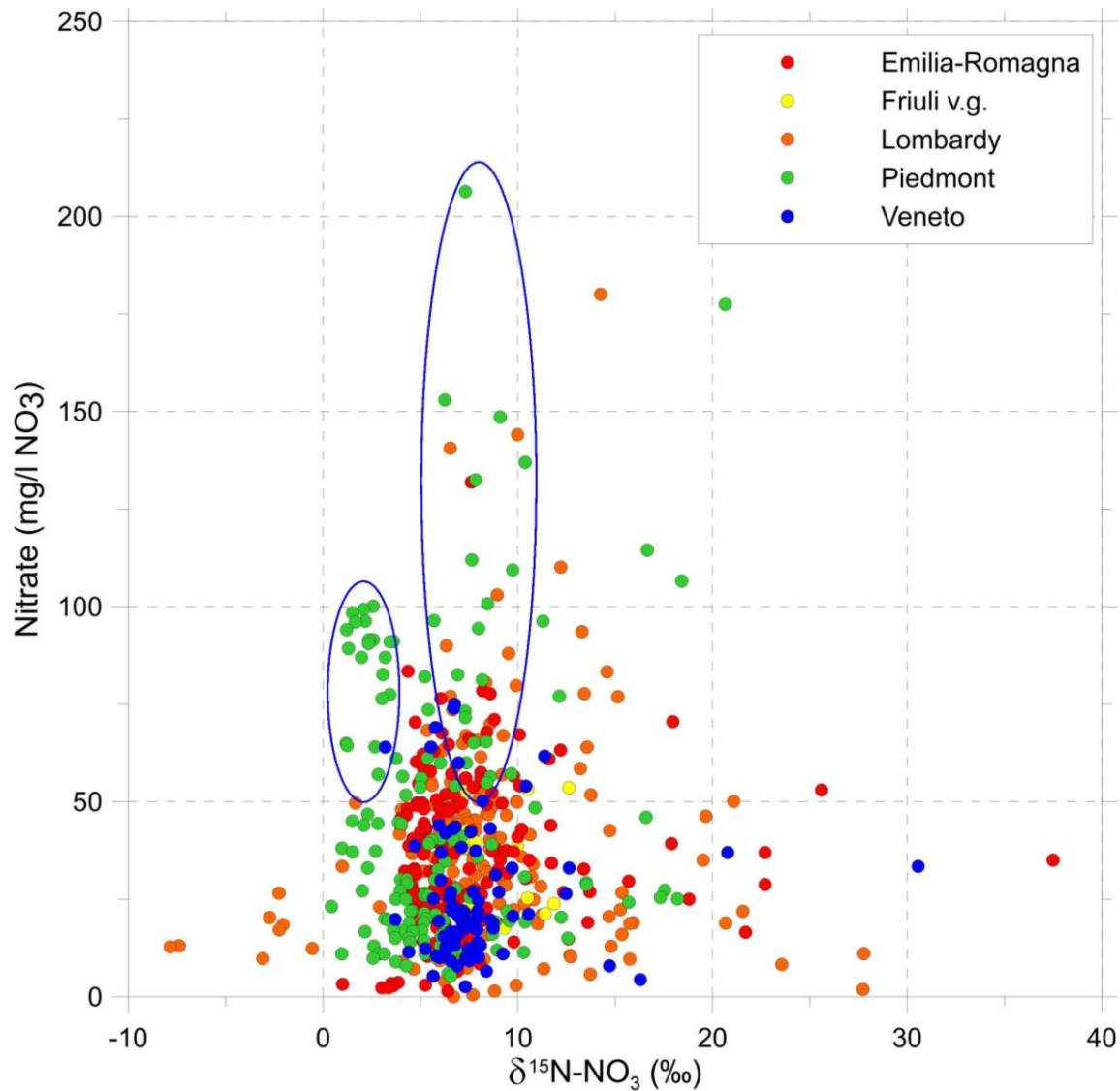


399

400 Fig. 7 – Frequency histogram of  $\delta^{15}\text{N}_{\text{NO}_3}$  values in groundwater. Values on the x-axis represent the  
401 interval's upper limit.

402 The distribution of  $\delta^{15}\text{N}$  was compared to nitrate concentrations, in order to identify the source(s)  
403 that mostly contribute to the observed contamination. Two data modes are present (evidenced by  
404 ovals in Fig. 8): one with a relatively depleted value ( $\delta^{15}\text{N}$  of about +2‰) corresponding to  
405 synthetic sources (i.e. fertilizers) and mostly evident in the Piedmont region, and a second, wider  
406 mode, around +8‰, displayed by samples from different regions. More interestingly, high nitrate  
407 concentrations are mostly recorded in samples with very enriched  $\delta^{15}\text{N}$ , suggesting that these  
408 derive from organic matter sources. This is in contrast with the  $\delta^{15}\text{N}$  distribution observed in the  
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.





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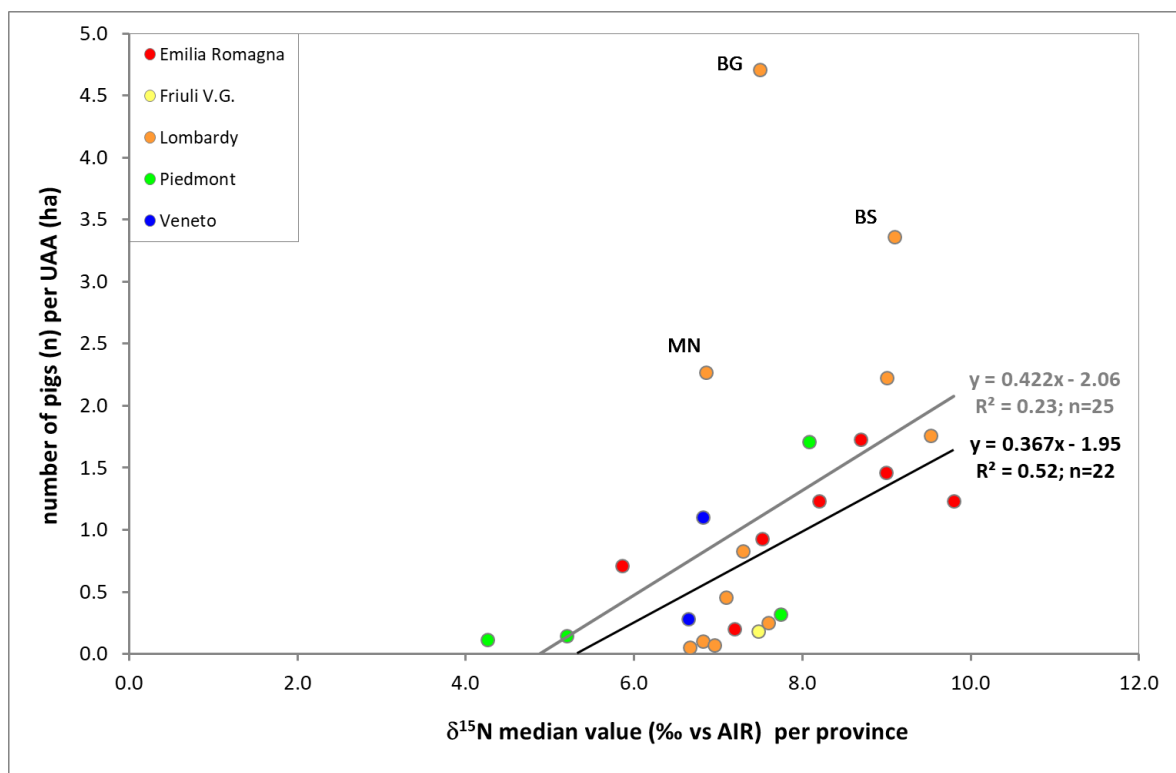
415 Fig. 8 – Nitrate concentrations versus  $\delta^{15}\text{N}$  values in groundwaters. Blue ovals evidence the two  
416 different modes (see text for explanation)

417 In a pioneering study for Italy, Dadomo and Martinelli (2005) in the Piacenza province (Emilia-  
418 Romagna) found a relationship between the distribution of  $\delta^{15}\text{N}$  values and the location of pig  
419 farms in the area. In order to check whether a similar correlation could be observed at the basin  
420 scale, statistical parameters were calculated for each province in the investigated area (Tab. S2;  
421 Supplementary material) and compared to farm census and population data. All possible  
422 correlations between  $\delta^{15}\text{N}$  values and anthropogenic pressure indicators were considered. At the  
423 basin scale, a significant correlation between the median  $\delta^{15}\text{N}$  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

429 densities (i.e. Bergamo, Brescia and Mantua) are poorly correlated with the others. This could be  
 430 due, on one hand, to the low amount of available isotopic data for these provinces, but also to the  
 431 fact that, if denitrification is not occurring, the  $\delta^{15}\text{N}$  enrichment would be limited to the highest  
 432  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  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  
 441 slurry rather than manure (Lorimor et al., 2004; Mantovi et al., 2006; Risberg et al., 2017).  
 442 Nevertheless,  $\delta^{15}\text{N}$  values could also be enriched due to denitrification, a process that, in absence  
 443 of  $\delta^{18}\text{O}$  data, cannot be ruled out.

444



445

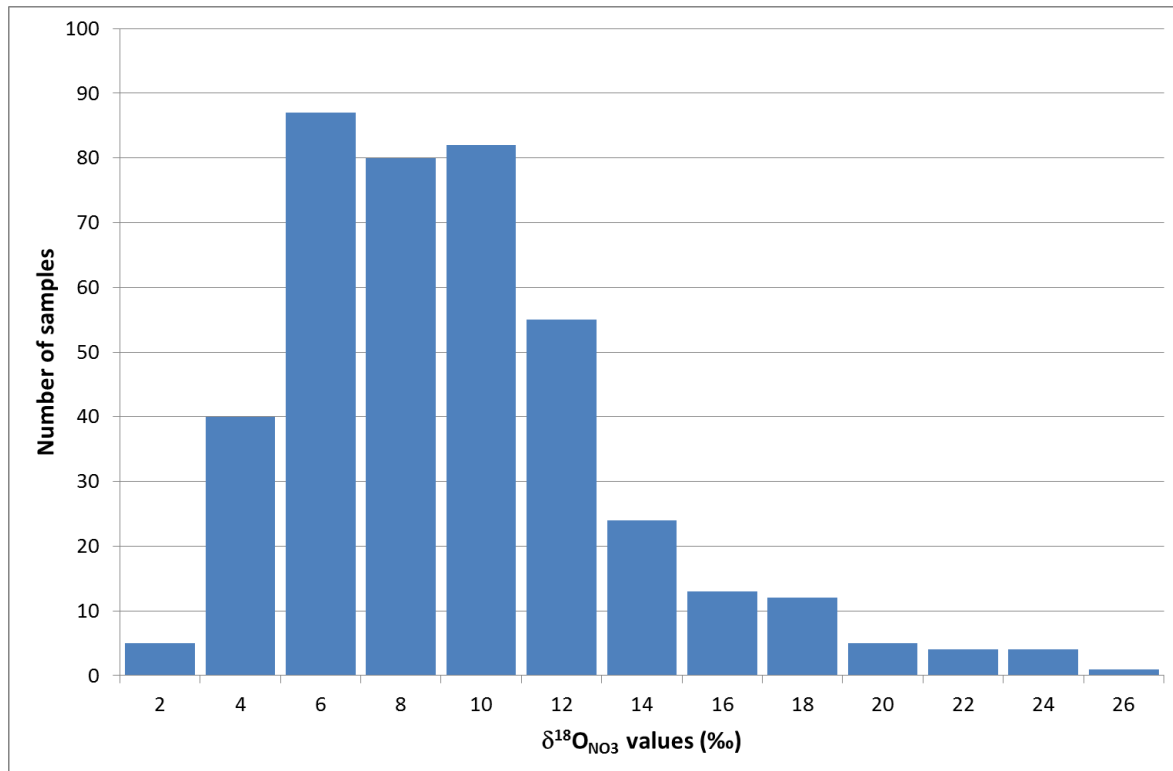
446 Fig. 9 – Number of pigs per UAA versus  $\delta^{15}\text{N}$  median values calculated per each province. Grey line  
 447 = all data; black line = excluding the Bergamo (BG), Brescia (BS) and Mantua (MN) provinces.

448

449

### 4.3 Processes affecting nitrate contents

450 The  $\delta^{18}\text{O}_{\text{NO}_3}$  values recorded in the database vary between +1.08 and +25.5‰ vs SMOW (n=412). A  
451 frequency histogram (Fig. 10) shows that the more common values in groundwater range between  
452 +4 and +10‰.



453

454 Fig. 10 – Frequency histogram of  $\delta^{18}\text{O}_{\text{NO}_3}$  values in groundwater. Values on the x-axis represent the  
455 interval's upper limit.

456

457 Results were plotted on the classical  $\delta^{18}\text{O}_{\text{NO}_3}$  vs  $\delta^{15}\text{N}_{\text{NO}_3}$  diagram (Fig.11), reporting the expected  
458 range of isotopic composition for the different sources. These were derived from the literature  
459 (Clark and Fritz, 1997; Kendall et al., 2007), and confirmed by some  $\delta^{15}\text{N}_{\text{NO}_3}$  values determined  
460 locally and reported in Saccon et al. (2013) and Sacchi et al. (2013). The lowest values of  $\delta^{18}\text{O}_{\text{NO}_3}$  of  
461 the potential sources are calculated, considering that in the nitrate molecule one oxygen atom is  
462 provided by atmospheric oxygen ( $\delta^{18}\text{O}_{\text{O}_2} \approx +23.5\text{‰}$ ) and two are provided by the water molecule  
463 (Kendall et al., 2007). Since the isotopic composition of precipitation falling on the plain sector  
464 ranges between -6 and -9‰ in  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  (Longinelli and Selmo, 2003), a fully equilibrated nitrate  
465 should then range between +1.83 and +3.83‰ in  $\delta^{18}\text{O}_{\text{NO}_3}$ .

466 Two sets of samples characterized by enriched  $\delta^{18}\text{O}_{\text{NO}_3}$  can be observed in Fig. 11, one close to the  
467 compositional field of synthetic fertilizers, and one related to denitrification processes. The first  
468 set, compatible with the nitrification of synthetic fertilizers, accounts for a relatively low number  
469 of samples. This process produces nitrates that maintain the atmospheric  $\delta^{15}\text{N}_{\text{N}_2}$  signal (see  
470 discussion in the previous section 4.2), but are progressively more depleted in  $\delta^{18}\text{O}_{\text{NO}_3}$  due to the

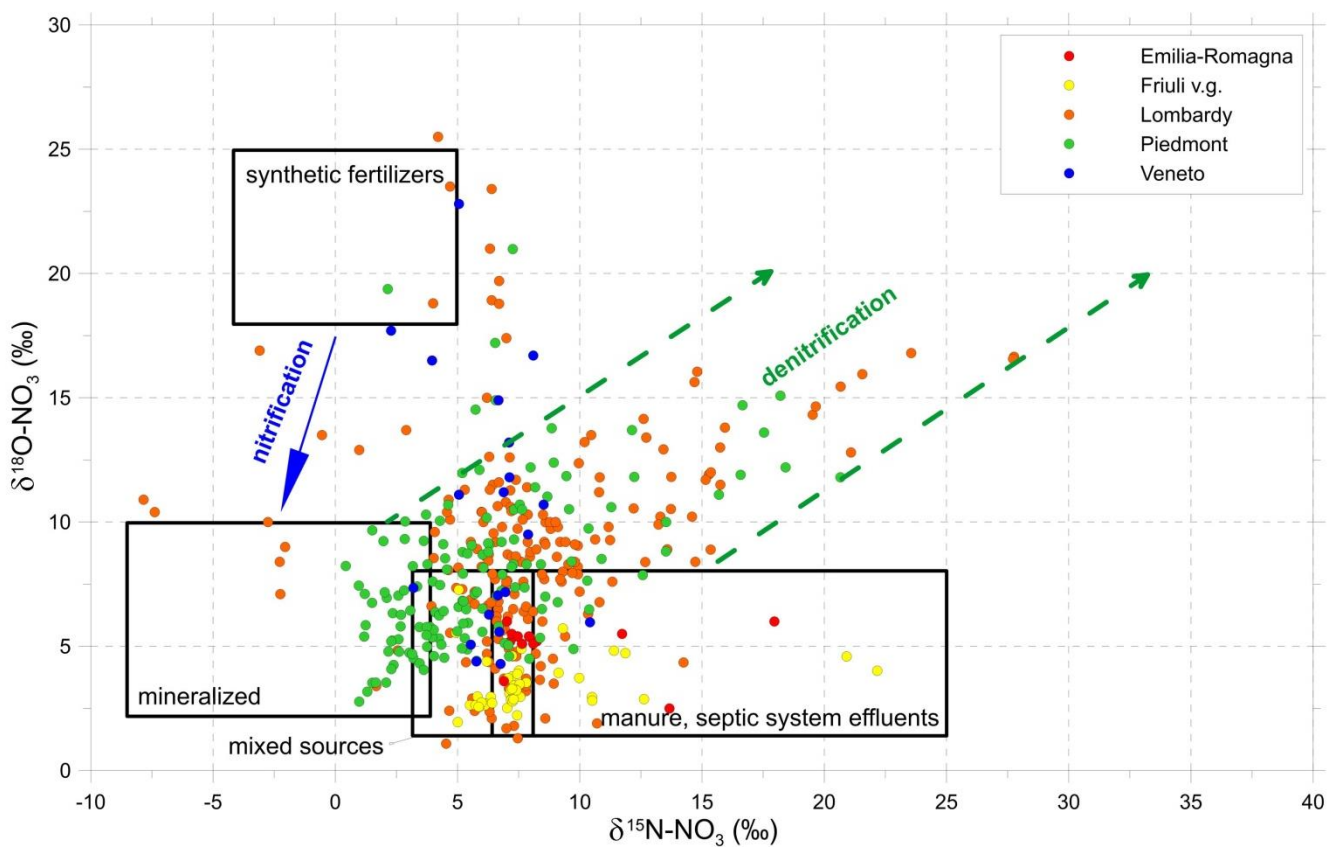
471 incorporation of oxygen from the water molecules. Nevertheless, the  $\delta^{18}\text{O}_{\text{NO}_3}$  is slightly more  
472 enriched than expected for a full equilibration with  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ . This enrichment is often observed in  
473 microbially-produced nitrate, and is attributed to many possible reasons (e.g. nitrification  
474 occurring in the soil, where the isotopic composition of the available water may be slightly  
475 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  $\delta^{18}\text{O}/\delta^{15}\text{N}$  slope, one with more enriched  
483  $\delta^{18}\text{O}_{\text{NO}_3}$  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  
503 the reduction of Fe-Mn oxyhydroxides present in the sediments. In the redox reaction sequence,  
504  $\text{O}_2$  reduces before nitrate which again is followed by reduction of Mn-oxides and by reduction of  
505 Fe-oxides (Appelo and Postma, 2005). Therefore, the presence of nitrates and of Fe/Mn is  
506 mutually exclusive. In the lower Lombardy plain, Sacchi et al. (2013) mapped groundwater samples  
507 with Fe and Mn concentrations above 100 and 50  $\mu\text{g}/\text{l}$  respectively, as metals above these  
508 concentrations may be taken as indicators of reducing environments (McMahon and Chapelle,  
509 2008; Wendland et al., 2008), and compared the distribution with that of nitrates. They concluded  
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.  
 512 Veneto and Emilia Romagna) little isotopic evidence of the presence of denitrification is reported.  
 513 This is due, on the one hand, to the lack of  $\delta^{18}\text{O}_{\text{NO}_3}$  values for these areas. On the other, it should  
 514 be noted that most isotopic studies targeted areas with high nitrate concentrations, often located  
 515 close to the Alpine and Apennine chains (Fig. 2 and Fig. 4); thus, the lower Veneto plain and the  
 516 higher Emilia-Romagna plain have not been assessed. Nevertheless, the presence of dissolved Fe  
 517 and Mn, often associated to  $\text{NH}_4^+$  and As, is documented in unconfined aquifers of the low plain  
 518 throughout the investigated area (e.g. Maffei et al., 2005). Therefore, based on the available  
 519 hydrochemical and isotopic evidence (e.g. Rotiroti et al., 2014, 2017; Giambastiani et al., 2016;  
 520 Petrini et al., 2014; Castaldelli et al., 2013; Carraro et al., 2013), the absence of nitrates in  
 521 groundwater from the central Po plain can be reasonably ascribed to denitrification, whereas the  
 522 main factor promoting this permanent loss of reactive nitrogen is the shallowness of the water  
 523 table.



524

525 Fig. 11 -  $\delta^{18}\text{O}_{\text{NO}_3}$  vs  $\delta^{15}\text{N}_{\text{NO}_3}$  values in groundwater. Compositional fields and nitrification-  
 526 denitrification trends from Sacchi et al. (2013), modified after Clark and Fritz (1997).

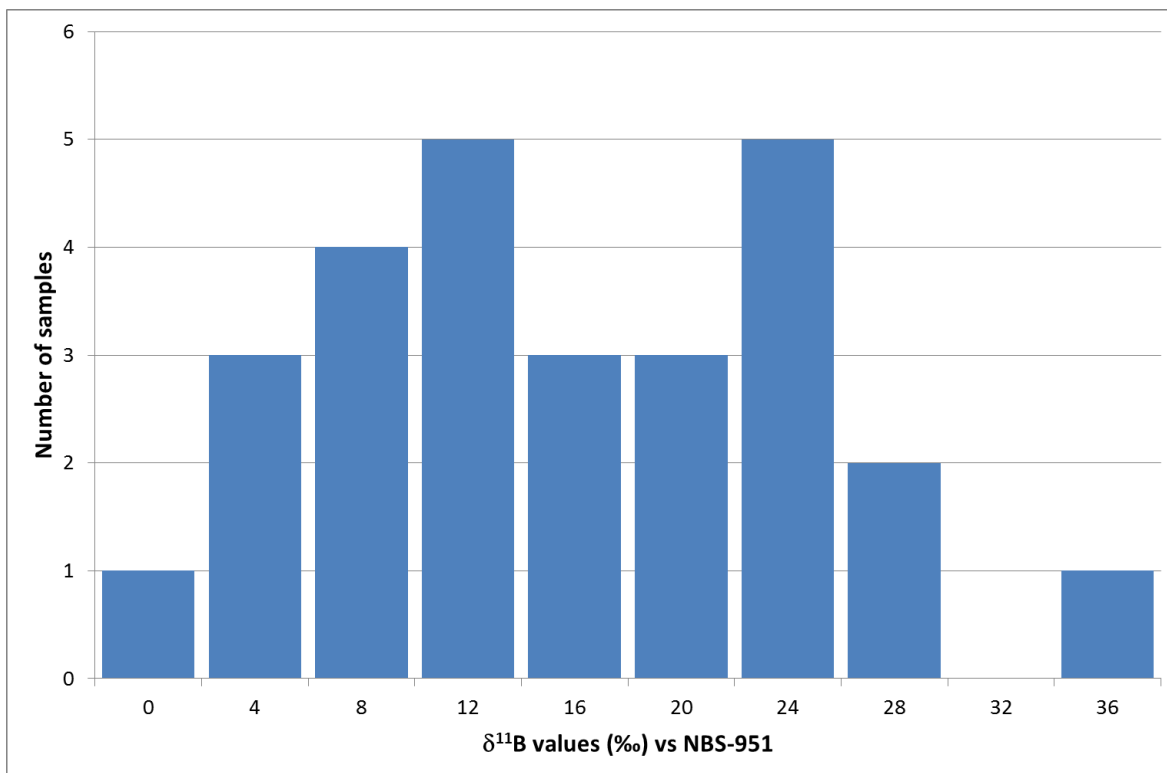
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#### 528 **4.4 Insights provided by B isotopes**

529 Compared to the consolidated application of  $\delta^{15}\text{N}$  to contamination studies, the associated use of  
 530  $\delta^{11}\text{B}$  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  $\mu\text{g/l}$ ,  
534 and  $\delta^{11}\text{B}$  values vary between -1.4 and +36.3‰ vs NBS-951 (n=27). A frequency histogram for the  
535 isotopic compositions (Fig. 12) shows the non-normal distribution of the data, with two  
536 populations characterized by different isotopic compositions, one around +10‰ and a second  
537 around +22‰. Comparing this distribution of  $\delta^{11}\text{B}$  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  $\delta^{11}\text{B}$  mode value (+22‰) clearly evidences inputs either of a sea water or of an animal manure  
541 component, both characterized by  $^{11}\text{B}$ -enriched signatures (Palmer and Swihart, 1996; Widory et  
542 al., 2005).



543  
544 Fig. 12 – Frequency histogram of  $\delta^{11}\text{B}$  values in groundwater. Values on the x-axis represent the  
545 interval's upper limit.

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

554 1% boron) supplied with feeding. While concentrations and isotopic compositions of contaminants  
555 are reported for given sites in France and the USA (see ISOBORDAT “Contaminants” database and  
556 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  
558 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

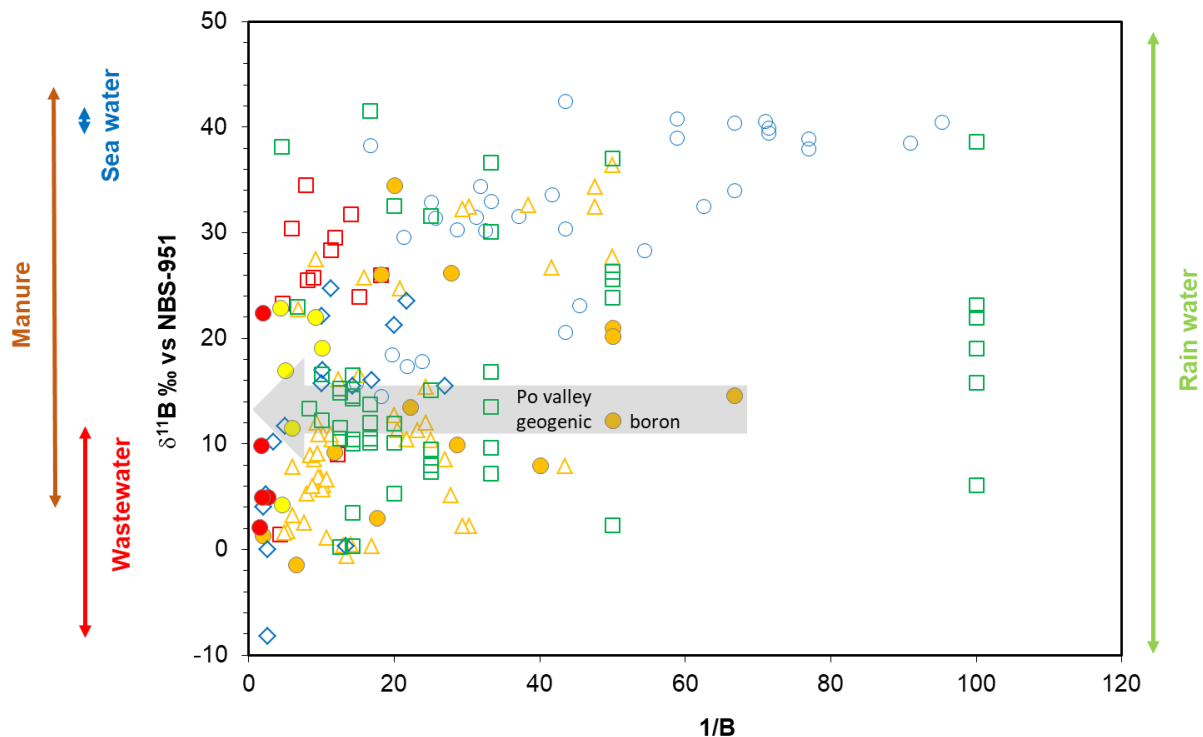
Sample	Name	$\delta^{11}\text{B}\text{‰}$ vs NBS-951	r.s.d (‰)
1	Boric acid	-13.5	0.4
2	Colemanite	-12.8	0.4
3	Colemanite 40	-8.1	0.27
4	Borax pentahydrate	-0.3	0.45
5	Ulexite	-3.5	0.44
6	Nitrophoska Blu Spezial	0.3	0.56
7	Sewage treatment plant (Sassuolo)	8.2	0.56
8	Pig manure	13.9	0.5
9	NaCl Italkali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

562

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

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

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



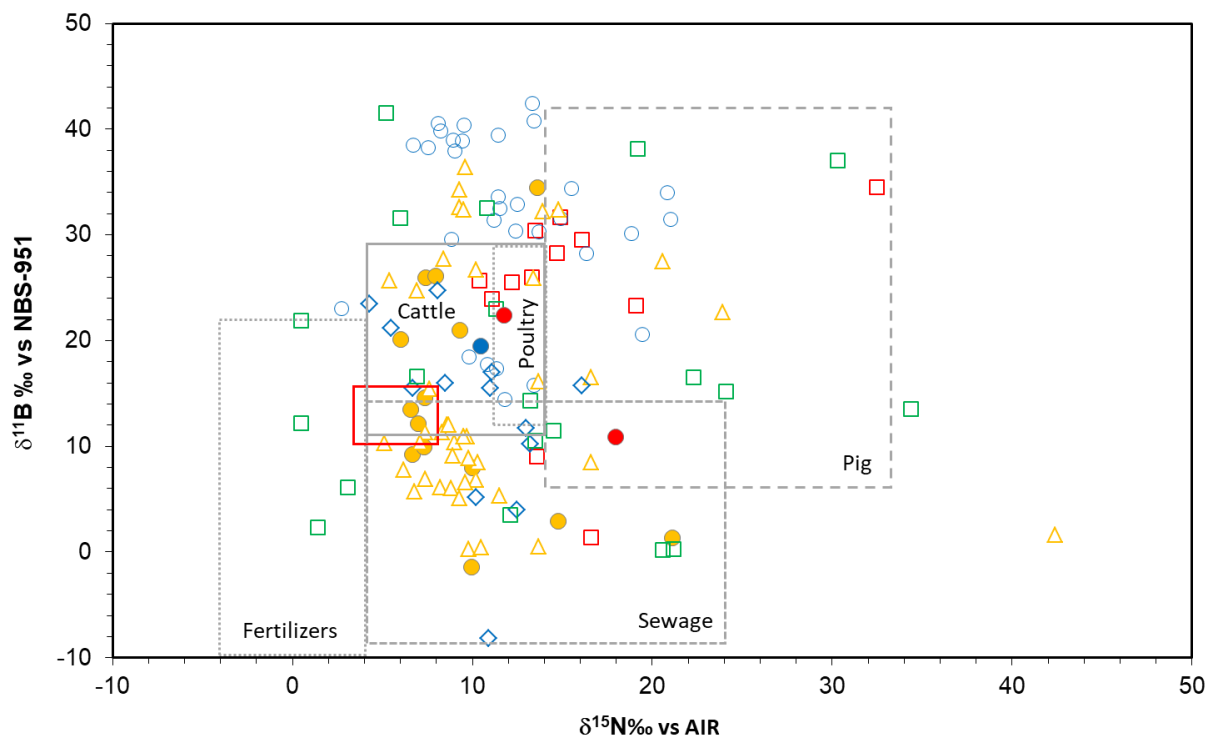
587 Fig. 13 -  $\delta^{11}\text{B}$  vs  $1/\text{B}$  plot of groundwater from Northern Italy (full dots: yellow = Friuli V.G.; orange  
 588 = Lombardy; red = Emilia Romagna), and literature data from low geogenic-B environments  
 589 (empty symbols: green squares = Komor, 1997; blue circles = Widory et al., 2004; yellow triangles  
 590 = Widory et al., 2005; blue diamonds = Seiler, 2005; red squares = Puig et al., 2017).  $\delta^{11}\text{B}$   
 591 compositional ranges of contaminants after Widory et al., 2004, 2005; Tirez et al., 2010; range for  
 592 rainwater from the ISOBORDAT database (Pennisi et al., 2013). Boron concentration in mg/l.  
 593

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



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

607 Finally, Fig. 14 shows the  $\delta^{11}\text{B}$  vs  $\delta^{15}\text{N}_{\text{NO}_3}$  plot of samples from the study area compared to other  
 608 literature data obtained in groundwater from low geogenic-B environments. The compositional  
 609 fields of the contaminants are represented as grey boxes (Widory et al., 2004, 2005; Tirez et al.,  
 610 2010), and the red box evidences the compositional field defined for uncontaminated water  
 611 from 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  
 614 groundwater, this information partially contradicts the results obtained from animal husbandry  
 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  
 620 Fig. 14 -  $\delta^{11}\text{B}$  vs  $\delta^{15}\text{N}$  plot of groundwater from Northern Italy (full dots: orange = Lombardy; red =  
 621 Emilia Romagna; blue = Veneto), and literature data from low geogenic-B environments (empty  
 622 symbols: green squares = Komor, 1997; blue circles = Widory et al., 2004; yellow triangles =  
 623 Widory et al., 2005; blue diamonds = Seiler, 2005; red squares = Puig et al., 2017).  $\delta^{11}\text{B}$  and  $\delta^{15}\text{N}$   
 624 compositional ranges: SF = synthetic fertilizers; Sew = sewage; CM = cattle manure; PM = pig  
 625 manure (after Widory et al., 2004, 2005; Tirez et al., 2010). The red box corresponds to the  
 626 compositional field defined for uncontaminated water from the Po alluvial aquifers.

627

## 5. Conclusions

628 In the last twenty years a remarkable number of nitrate isotopic data, often associated to oxygen,  
629 hydrogen and boron isotopic systematics have been produced in the Po plain area, mostly in local  
630 investigations. In this work, all the available nitrate ( $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ) and boron ( $\delta^{11}\text{B}$ ) isotopic  
631 data, together with the hydrochemical composition, if available, were compiled in a  
632 comprehensive database, and some additional analyses were performed to fill the knowledge gaps  
633 in given areas or situations. Such an integration of data obtained in the groundwater hosted in a  
634 variety of sedimentary environments has allowed for their interpretation in a wider perspective,  
635 both providing an understanding of the N sources and dynamics in the shallow aquifers at the Po  
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  
638 and remediation strategies.

639 In the investigated area, the most impacted groundwater is that hosted in the alluvial fans of the  
640 Alpine and Apennine foothills. This is due to a combination of high soil permeability and presence  
641 of intensive agricultural activities. Aquifers in these areas are characterized by fast circulation and  
642 by great depths of the water table. This finding indicates that, while the input of nitrates in these  
643 areas has led to present-day high concentrations, groundwater contamination would be quickly  
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  
648 the presence of environmental conditions favourable to denitrification processes, as also indicated  
649 by other hydrochemical parameters (Fe, Mn,  $\text{NH}_4^+$ ). While this is the general case in low plain  
650 areas, in certain cases (e.g. Poirino Plateau in Piedmont), denitrification, although present, is not  
651 sufficient to fully abate nitrates because of the high input coupled to the low dilution potential of  
652 the aquifer.

653 As the  $\delta^{15}\text{N}$  median values are significantly correlated at the basin scale with pig farming, manure  
654 spreading represents one of the main nitrate sources in groundwater from agriculture, the other  
655 being synthetic fertilizers. Based on this evidence, pig manure management should be carefully re-  
656 evaluated and should be favoured in the low plain areas deprived of nitrates in groundwater, since  
657 the local hydrogeological setting allows nitrates to be metabolized in the environment with few  
658 consequences for the water resources.

659 Despite the relatively low number of available B isotope data, this systematics has provided  
660 interesting results in terms of nitrate contamination origin in such a low geogenic-B context.  
661 Indeed, it has proved the presence of another anthropogenic nitrate source, of civil origin, that is  
662 sewage in the study area. The garnering of all the data has allowed us to define the range of the  
663 expected geogenic B signature, and new results on the local B sources have been produced. This is  
664 a significant step forward for the use of the coupled  $\delta^{15}\text{N}$  -  $\delta^{11}\text{B}$  toolbox, as the application of the B  
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

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

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

689

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698

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