

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

G. Martinelli<sup>a</sup>, A. Dadomo<sup>b</sup>, D.A. De Luca<sup>c</sup>, M. Mazzola<sup>d</sup>, M. Lasagna<sup>c</sup>, M. Pennisi<sup>e</sup>, G. Pilla<sup>f</sup>, E. Sacchi<sup>f,\*</sup>, P. Saccon<sup>g</sup>

<sup>a</sup> ARPAE Environmental Protection Agency, Emilia Romagna Region, Reggio Emilia, Italy

<sup>b</sup> Geoinvest Srl, Piacenza, Italy

<sup>c</sup> Department of Earth Sciences, University of Torino, Italy

<sup>d</sup> ARPAV Environmental Protection Agency, Veneto Region, Vicenza, Italy

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

<sup>f</sup> Department of Earth and Environmental Sciences, University of Pavia, Italy

<sup>g</sup> Waterdrop Consulting, Graz, Austria

### ARTICLE INFO

Editorial handling by Dr. I. Cartwright

**Keywords:**

Hydrogeochemistry

Contamination

Po plain

Pig manure

Denitrification

Sewage

### ABSTRACT

Large volumes of precious water resources are negatively affected by nitrate contamination, and the problem of the world population's exposure to this is becoming an even more pressing issue. To tackle this problem, the application of environmental isotopes has proven to be an effective method to identify the N origins and major transformations in different environments. In this work, nitrate ( $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ) and boron ( $\delta^{11}\text{B}$ ) isotope analyses performed in the last twenty years in groundwater from shallow aquifers of the Po plain area, a complex hydrogeological system of European relevance, have been compiled in a comprehensive database together with major ionic contents; these data were integrated with additional original results, targeting areas not previously examined or complementing the available information. Such data, previously interpreted on the local scale, are examined at the Po plain scale, providing an understanding of the N sources and dynamics in the shallow aquifers, and defining the most important processes governing nitrate contamination in Northern Italy.

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

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

### 1. Introduction

In the second half of the 20th century, following the so-called

"green revolution", agriculture in developed countries significantly increased crop production and livestock, with a concomitant enhanced use of synthetic and organic matter fertilizers (Tilman et al., 2001;

\* Corresponding author.

E-mail address: [elisa.sacchi@unipv.it](mailto:elisa.sacchi@unipv.it) (E. Sacchi).

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

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

One of the major difficulties with water contamination is the identification of the corresponding source(s) of pollution, a prerequisite for properly designing appropriate actions and remediation (Bronders et al., 2012). For this purpose, the application of environmental isotopes of dissolved nitrates (i.e.  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ) has proven to be effective in a large number of cases (e.g. 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 ( $^{11}\text{B}$ ) in association with the specific isotope signature of nitrates has been demonstrated (Seiler, 2005; Widory et al., 2004, 2005; Saccoccia et al., 2013; Puig et al., 2017). Strontium and sulphate isotopes are randomly also used to reinforce this multi-isotopic toolbox (Vitòria et al., 2004; Nestler et al., 2011). In addition to the classical chemical approach, the coupled use of nitrate and boron isotopes - although not yet a routine technique - is gaining interest for policymakers and water quality administrators who are interested in identifying the nitrate sources. This approach is particularly important when the  $\text{NO}_3^-$  concentrations are higher than the threshold value defined by the Water Frame Directive (WFD; 50 mg/l), which implies the definition of the poor chemical status of the quality of the water body. The need to discriminate between the different sources of pollution (i.e. sewage, animal manure, chemical fertilizer, natural soil mineralization) thus becomes crucial for any water exploitation and management (Komor, 1997; Widory et al., 2004, 2005, 2013; Bronders et al., 2012).

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

background (Palmer and Swihart, 1996 and reference therein), as well as of the anthropogenic components that could represent nitrogen and boron sources (see compilation in ISOBOARD database; Pennisi et al., 2013).

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

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

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

## 2. Study area

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

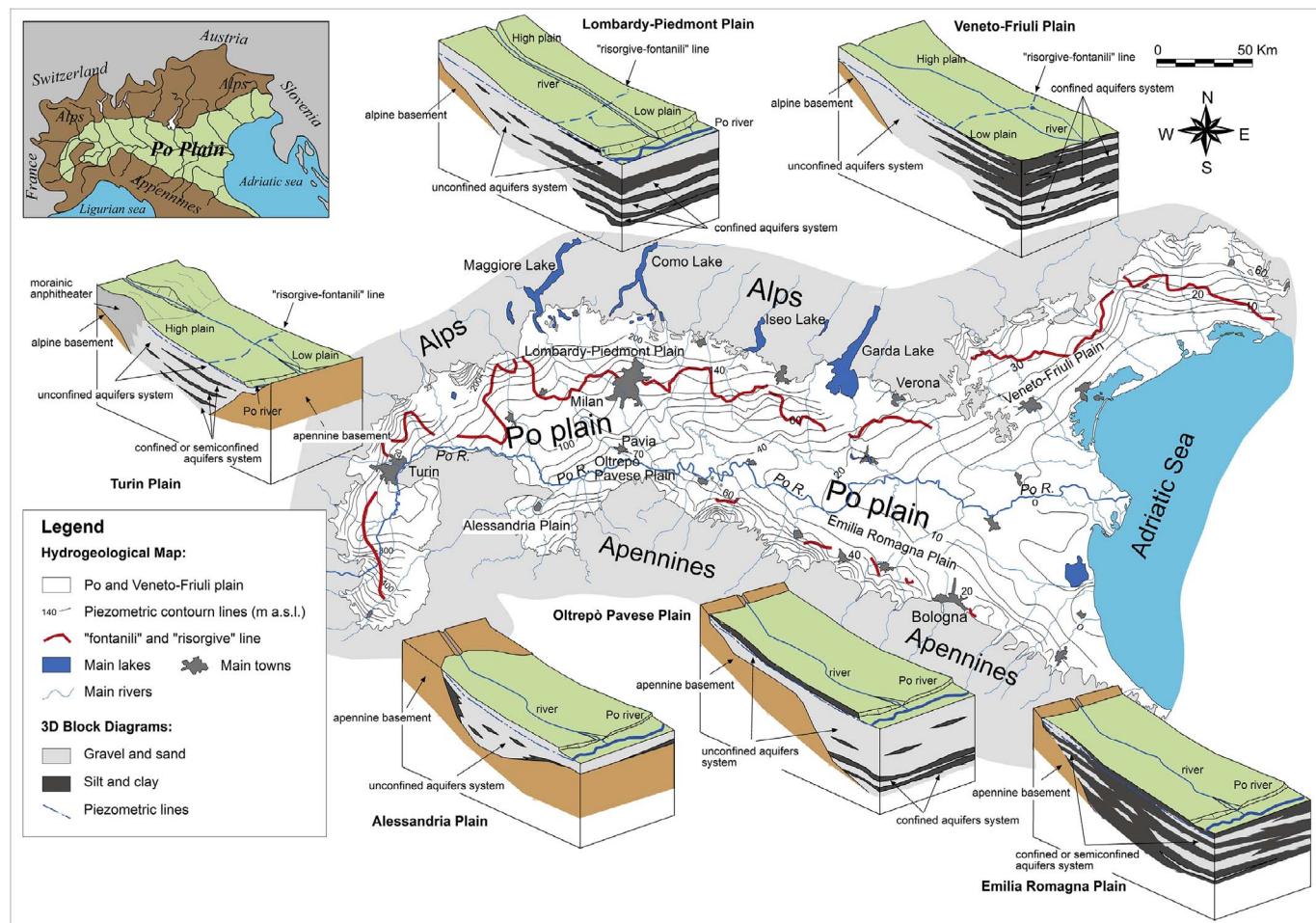


Fig. 1. Location, simplified geological and hydrogeological settings of the investigated area. Piezometric contour lines from Giuliano et al. (1998), modified.

plain areas in Northern Italy are (from W to E) Piedmont, Lombardy, Veneto, Emilia Romagna and Friuli Venezia Giulia. More than 50% of the Italian Gross National Product is produced in Northern Italy, which hosts more than 20 million inhabitants. About one half of total surface is devoted to agriculture and to animal breeding, including mostly cattle, pigs and chickens.

The climate in the western sector is classified as temperate continental, with mean annual temperature of  $\sim 13^{\circ}\text{C}$ , cold winters (in January, mean minimum and maximum temperatures of  $\sim -3^{\circ}$  and  $+3^{\circ}\text{ C}$ ) and hot summers (in July, mean minimum and maximum temperatures of  $\sim 16^{\circ}$  and  $\sim 30^{\circ}\text{ C}$ ). In the eastern sector, the continental climate is less accentuated due to the effect of the Adriatic sea (Cati, 1981): the mean annual temperature is  $\sim 14^{\circ}\text{C}$ , with mean minimum and maximum temperatures of  $\sim 0^{\circ}$  and  $\sim 7^{\circ}\text{C}$  in January, and of  $\sim 19^{\circ}$  and  $\sim 27^{\circ}\text{C}$  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., 2013).

The Po and the Veneto plains were generated during Quaternary by the dismantling of the Alpine 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 subsidence in post-Oligocene periods. Recent continental deposits were deposited during the Lower-Upper Pleistocene to Holocene. The total thickness of Quaternary sediments can reach about 0.5 km, being bounded at the bottom by Pliocene sediments saturated

by fossil salty waters in large parts. Coarse sediments generated by rock erosion due to tributaries of the Po river are 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 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 reported in Fig. 1.

## 2.1. Hydrogeological setting

The aquifer system in the investigated area mostly consists of multilayer aquifers constituted by gravel and sand layered with silt and clay. The shallow aquifers are generally unconfined while the deeper aquifers are semiconfined and confined. Unconfined aquifers are usually poorly connected 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 found in alluvial fan areas, characterized by coarser sediments. The thickness of this aquifer system ranges from a few dozen meters to several hundred meters. At different depths, depending on the geographic position, a fresh-salt water interface is present, separating fresh- from deeper salt-groundwaters. This is of great importance, as it corresponds to the lower boundary of freshwater aquifers that are potentially exploitable for drinking, municipal and farming purposes.

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 fan areas (high plain). Typical hydraulic gradients of these areas vary from 8‰ to 10‰ in 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 from 1‰ to 4‰); in the central-eastern part of the Po Valley they decrease to values of 0.2‰–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; Vorlichek et al., 2004; De Luca et al., 2009, 2014; Zini et al., 2013; Balderacchi et al., 2016; Fumagalli et al., 2017). The highest hydraulic conductivity ( $1\text{--}10 \cdot 10^{-3}$  m/s) is measured in alluvial fan areas, whereas lower values ( $1\text{--}10 \cdot 10^{-5}$  m/s) are measured in low plain areas, although some areas 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 the Po plain: minimum values of 1–5 m b.g.l. are recorded in the central part of the plain, whereas closer to the Alps it may reach 30–50 m, and close to the Apennines it is set around 10 m.

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

## 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 (very high, high, medium, low or negligible). The location of the wells periodically sampled by the ARPA is also indicated and differentiated based on their nitrate content (lower or higher than 50 mg/l, the regulatory limit for drinking water supplies). High values are observed in areas characterized by high infiltrability, mostly at the Alpine and Apennine foothills. This is of particular 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 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 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, 2016b).

## 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.

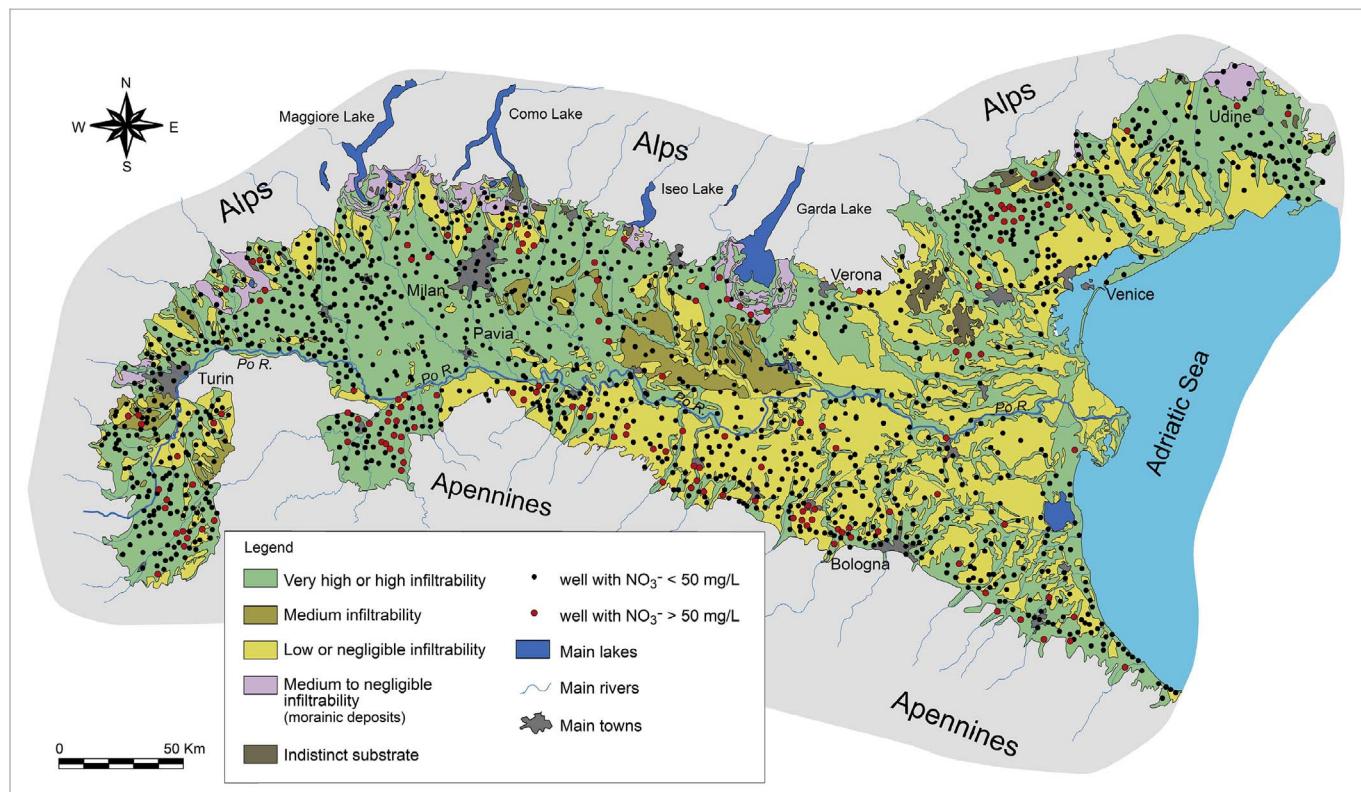
The total designated NVZs in Piedmont, Lombardy, Veneto, Friuli Venezia Giulia and Emilia-Romagna represent almost 70% of designated NVZs in Italy (Fig. 3); moreover, they represent a percentage ranging between the 50% and 60% of regional plains areas (Ministry for Environment, Land and Sea, Ministry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

## 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; Martinelli et al., 2014a), conference proceedings (Dadomo and Martinelli, 2005; Arduini et al., 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 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., 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 measurements to avoid the issue of representativeness. Unfortunately, not all the groundwater samples have a correspondingly complete chemical analysis.

All the data sources are clearly identified in Table S1 (Supplementary material), allowing us to refer to the publication in terms of the analytical techniques used. Nitrate isotope data were produced 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  $\delta^{15}\text{N}_{\text{NO}_3}$ ‰ vs AIR and  $\delta^{18}\text{O}_{\text{NO}_3}$ ‰ vs SMOW notation. Boron isotopes were determined by MC-ICP-MS, with results expressed as  $\delta^{11}\text{B}$ ‰ with respect to the NBS-951 standard. The database is a compilation of results generated in different laboratories, at different times and by different techniques, and no data are available that can be used for inter-laboratory comparison. Nevertheless, isotopic compositions are always expressed with respect to international standards, and therefore, assuming that each laboratory has correctly implemented the analytical protocol, the results should, in principle, be comparable.

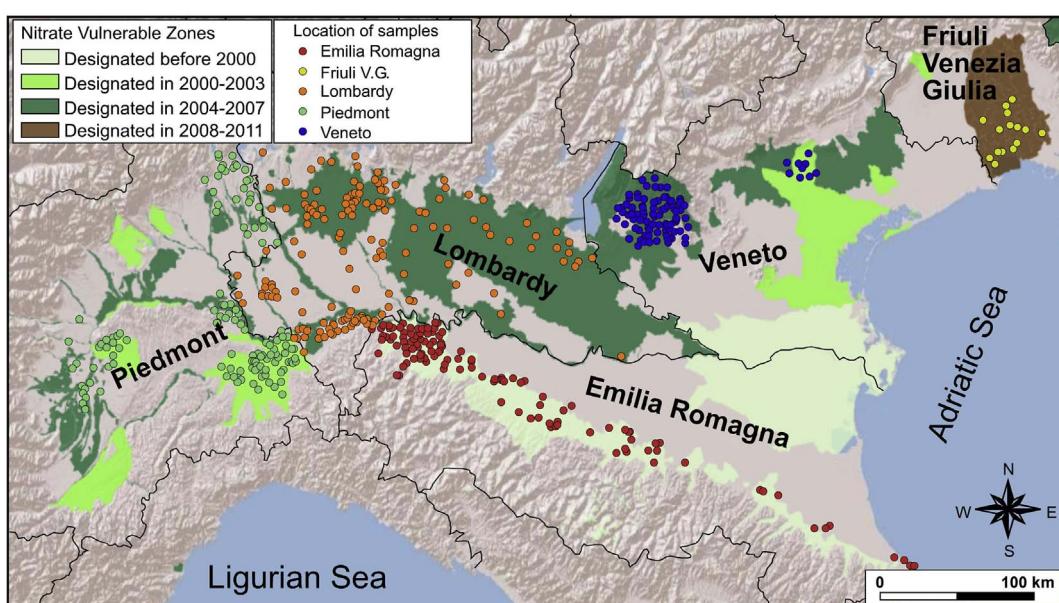
To fill in the knowledge gaps in given areas (e.g. the Parma province in Emilia Romagna) or situations (e.g. the  $\delta^{11}\text{B}$  composition of some



**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  $< 50 \text{ mg/l}$ ; red dots = nitrate concentration  $> 50 \text{ mg/l}$ . (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

compositional end-members), additional original analyses were also performed and reported in Table S1 (Supplementary material) and Table 1. For 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 ( $1\sigma$ ) are  $\pm 0.5\%$  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 measured by MC-ICP-MS Neptune Plus

at ALS Scandinavia AB, Luleå (Sweden), with an uncertainty of  $\pm 0.4$  to  $\pm 1\%$ , using a combination of internal standardization and bracketing standards for instrumental mass bias correction. Boron isotopes of relevant anthropogenic sources for the study area (e.g. pig manure, sewage, synthetic fertilizer) were determined by positive TIMS on  $\text{Cs}_2\text{B}_4\text{O}_7$  deposited on the ion source filament with graphite and mannitol, which produces  $\text{CsBO}_2$  ions, after boron purification through ion



**Fig. 3.** NVZs of Northern Italy (map elaborated with <http://fate-gis.jrc.ec.europa.eu/geohub/MapViewer.aspx?id=2>) and location of samples included in the hydrochemical and isotopic database. The colors of the dots correspond to the different regions. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

**Table 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.

Sample	Name	$\delta^{11}\text{B}\text{\textperthousand}$ 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

exchange resins (Tonarini et al., 1997). Analyses were performed at CNR-IGG in Pisa (Italy) using a VG Micromass 54 E mass spectrometer with an uncertainty of  $\pm 0.5\text{\textperthousand}$ , calculated on replicate analyses of the NBS-951 standard.

The location of samples included in the database is shown in Fig. 3, 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.

To test the possible correlations of the isotopic composition with anthropogenic pressure indicators, data were aggregated by province and the descriptive statistical parameters were calculated (Min, Max, Mean, Median; Table S2 in Supplementary material). Farm census data (number of cattle, number of pigs and Utilized Agronomical Area [UAA] per province) for the year 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).

## 4. Results and discussion

### 4.1. Groundwater hydrochemistry

Previous studies have indicated that in the Po plain, most of the waters hosted in alluvial fans of the Alpine and Apennine chains show a Ca(Mg)-HCO<sub>3</sub> facies, and TDS ranging from 300 to 3500 mg/l. Groundwaters with a Na(K)-HCO<sub>3</sub> facies (TDS range = 500–2700 mg/l) subordinately occur in the eastern part of the Po plain, characterized by fine sediments. This change in the chemical composition is due to Na-Ca exchange with clays. Ca(Mg)-SO<sub>4</sub> groundwaters (TDS range = 750–2400 mg/l) occur in limited areas at the foothills of the Apennine chain and are the result of interaction between meteoric waters and evaporitic minerals of Triassic and Messinian age (Giuliano, 1995; Martinelli et al., 2014a). Na (K)-Cl groundwaters (TDS range = 1200–2000 mg/l) occur in the central and eastern part of the Po river plain. They are the result of interactions between meteoric waters and evaporitic layers formed during Quaternary transgressive episodes (Conti et al., 2000; Pilla et al., 2010; Martinelli et al., 2017).

Ca(Mg)-HCO<sub>3</sub> groundwaters and Ca(Mg)-SO<sub>4</sub> groundwaters are hosted in unconfined and semi-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; Sacchi et al., 2013; Martinelli et al., 2014c). Na(K)-HCO<sub>3</sub> and Na(K)-Cl groundwaters are hosted in confined fine sediment aquifers characterized by low groundwater flow velocities (less than 10 m/yr), which inhibit pollution phenomena.

Groundwater hydrochemical data, when available in the database (Table S1; Supplementary material), were represented in the classical Piper diagram (Fig. 4). Most of the samples fall within the field of Ca-

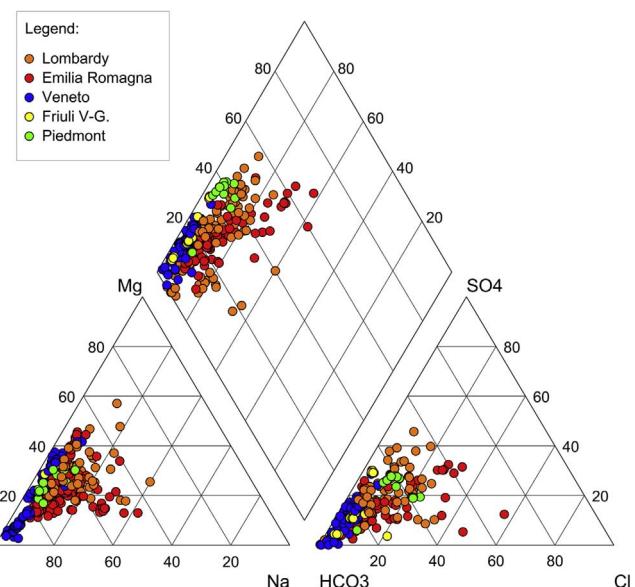


Fig. 4. Piper diagram showing the available compositions of groundwaters.

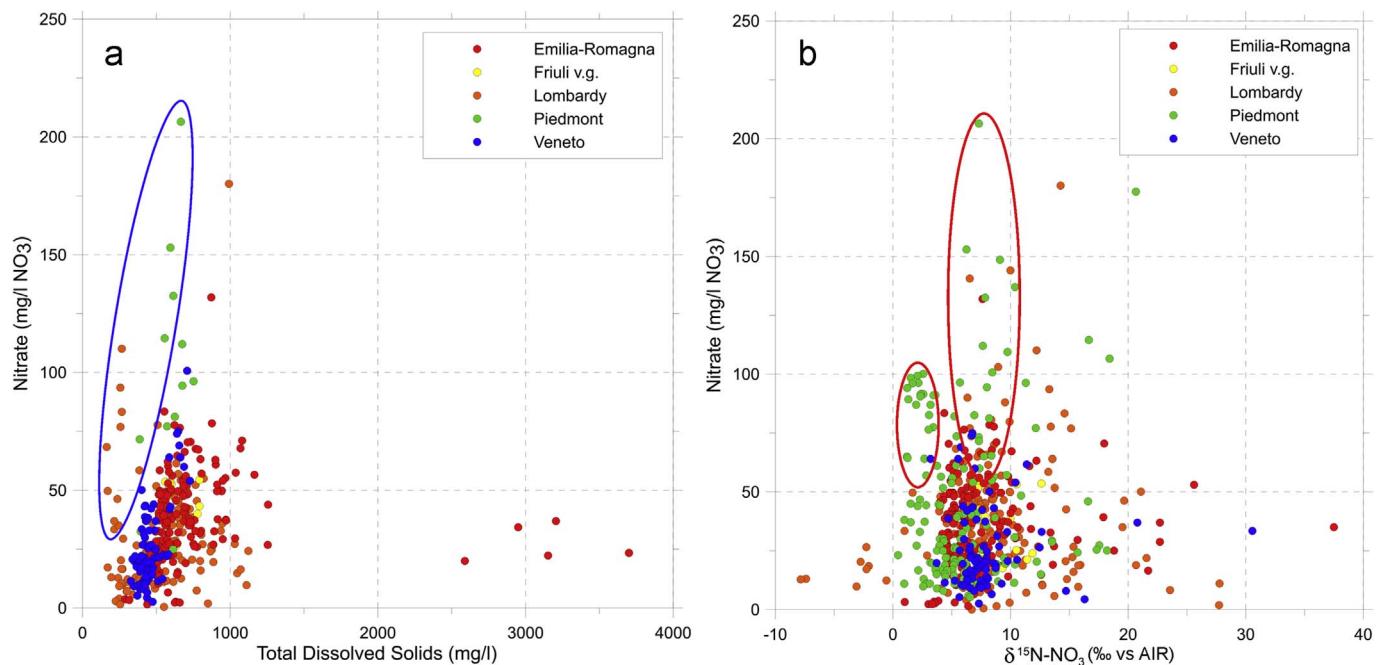
HCO<sub>3</sub> facies with medium TDS values, reflecting water circulation in shallow unconfined aquifers. In areas where the marine substratum is closer to the surface (Fig. 1), the groundwater composition is affected by a contribution of Na-Cl waters.

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 abundance of carbonates in the aquifer matrix. The relationship between groundwater TDS and nitrate contents is shown in Fig. 5a. The plot evidences that the higher nitrate concentrations are 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 a more recent recharge and a faster circulation in these aquifers. Nevertheless, also high TDS ( $\geq 1000$  mg/l) waters in the lower Lombardy and Emilia-Romagna plain show non-negligible nitrate concentrations ( $\sim 30$  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 investigated area should be relatively small.

An alternative explanation for the nitrate-TDS relationship considers that microbial oxidation of 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 between groundwater nitrate concentrations and hydrochemistry has been recently reviewed by Mencio 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 interactions. This generally leads to an increase in major ions concentrations (therefore in TDS values), but also homogenizes the overall hydrochemistry despite lithological differences, and 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 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.).

### 4.2. Nitrate sources

Atmospheric deposition measured in Northern Italy accounts in average for 20–25 kg N ha<sup>−1</sup> yr<sup>−1</sup> (Rogora et al., 2012). While this represents an important source of reactive N for surface waters, it is a



**Fig. 5.** a) Nitrate concentrations vs Total Dissolved Solids of selected groundwaters. The higher nitrate concentrations are often found in low TDS waters (blue oval). b) Nitrate concentrations versus  $\delta^{15}\text{N}$  values in groundwaters. Red ovals evidence the two different modes (see text for explanation). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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 (Figs. 2 and 3), 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 mostly determined by the source of dissolved nitrates.

The  $\delta^{15}\text{N}$  values recorded in the database vary between  $-7.8\text{‰}$  and  $+37.50\text{‰}$  vs AIR ( $n = 818$ ). A frequency histogram (Fig. 6a) shows that the more common values in groundwater range between  $+6$  and  $+8\text{‰}$ . 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 ( $\sim 5 \text{ mg/l}$ , Edmunds and Shand, 2008), suggesting that this isotopic value derives from anthropogenic sources, namely from the mixing between synthetic sources and organic matter-derived nitrates.

The distribution of  $\delta^{15}\text{N}$  was compared to nitrate concentrations, in order to identify the source(s) that mostly contribute to the observed contamination. Two data modes are present (evidenced by red ovals in Fig. 5b): one with a relatively depleted value ( $\delta^{15}\text{N}$  of about  $+2\text{‰}$ ) corresponding to synthetic sources (i.e. fertilizers) and mostly evident in the Piedmont region, and a second, wider mode, around  $+8\text{‰}$ , displayed by samples from different regions. More interestingly, high nitrate concentrations are mostly recorded in samples with very enriched  $\delta^{15}\text{N}$ , suggesting that these derive from organic matter sources. This is in contrast with the  $\delta^{15}\text{N}$  distribution observed in the sole Lombardy plain (Sacchi et al., 2013), where both depleted and highly enriched values were mostly characterized by low nitrate concentrations, the former attributed to synthetic sources and the latter due to the influence of denitrification phenomena.

In a pioneering study for Italy, Dadomo and Martinelli (2005) in the Piacenza province (Emilia-Romagna) found a relationship between the distribution of  $\delta^{15}\text{N}$  values and the location of pig farms in the area. In order to check whether a similar correlation could be observed at the basin scale, statistical parameters were calculated for each province in

the investigated area (Table S2; Supplementary material) and compared to farm census and population data. All possible correlations between  $\delta^{15}\text{N}$  values and anthropogenic pressure indicators were considered. At the basin scale, a significant correlation between the median  $\delta^{15}\text{N}$  values and the number of pigs per UAA is observed ( $n = 25$ ;  $r = 0.478$ ;  $p = 0.015$ ), as shown in Fig. 7, whereas no significant correlations could be observed for cattle density, cattle + pig density or population density (Table S2; Supplementary material). This correlation with pig density, although significant, is not very strong, due to some limitations imposed by the dataset, and by the adopted model (linear correlation 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  $\delta^{15}\text{N}$  enrichment would be limited to the highest  $\delta^{15}\text{N}$  values displayed by the contamination source (for example, in the case of pig manure, limited to  $16\text{‰}$ , according to Vitòria et al. (2008)). In other words, although the total number of pigs may increase, the  $\delta^{15}\text{N}$  content may be constant if it presents the same origin. If these three provinces are eliminated from the plot, the correlation significantly improves (Fig. 7), and the correlation with the total number of pigs also becomes significant ( $p < 0.01$ ), whereas those with cattle or population remain non-significant.

A correlation between animal husbandry, and particularly with the number of pigs, and groundwater nitrate contamination has been observed elsewhere (e.g. Aquilina et al., 2012; Boy-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). Nevertheless,  $\delta^{15}\text{N}$  values could also be enriched due to denitrification, a process that, in absence of  $\delta^{18}\text{O}$  data, cannot be ruled out.

#### 4.3. Processes affecting nitrate contents

The  $\delta^{18}\text{O}_{\text{NO}_3}$  values recorded in the database vary between  $+1.08$  and  $+25.50\text{‰}$  vs SMOW ( $n = 412$ ). A frequency histogram (Fig. 6b) shows that the more common values in groundwater range between  $+4$

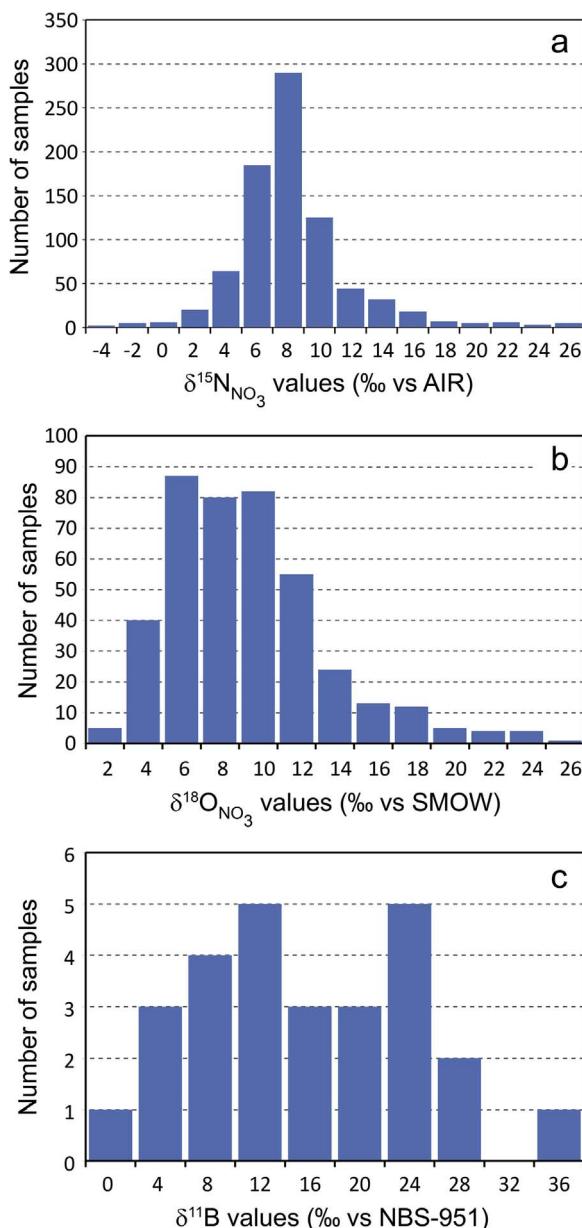


Fig. 6. Frequency histograms of a)  $\delta^{15}\text{N}_{\text{NO}_3}$  values; b)  $\delta^{18}\text{O}_{\text{NO}_3}$  values; c)  $\delta^{11}\text{B}$  values in groundwater. Values on the x-axis represent the interval's upper limit.

and + 10‰.

Results were plotted on the classical  $\delta^{18}\text{O}_{\text{NO}_3}$  vs  $\delta^{15}\text{N}_{\text{NO}_3}$  diagram (Fig. 8), reporting the expected range of isotopic composition for the different sources. These were derived from the literature (Clark and Fritz, 1997; Kendall et al., 2007), and confirmed by some  $\delta^{15}\text{N}_{\text{NO}_3}$  values determined 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 the potential sources are calculated, considering that in the nitrate molecule one oxygen atom is provided by atmospheric oxygen ( $\delta^{18}\text{O}_{\text{O}_2} \approx +23.5\text{\textperthousand}$ ) and two are provided by the water molecule (Kendall et al., 2007). Since the isotopic composition of precipitation falling on the plain sector ranges between -6 and -9‰ in  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  (Longinelli and Selmo, 2003), a fully equilibrated nitrate should then range between +1.83 and + 3.83‰ in  $\delta^{18}\text{O}_{\text{NO}_3}$ .

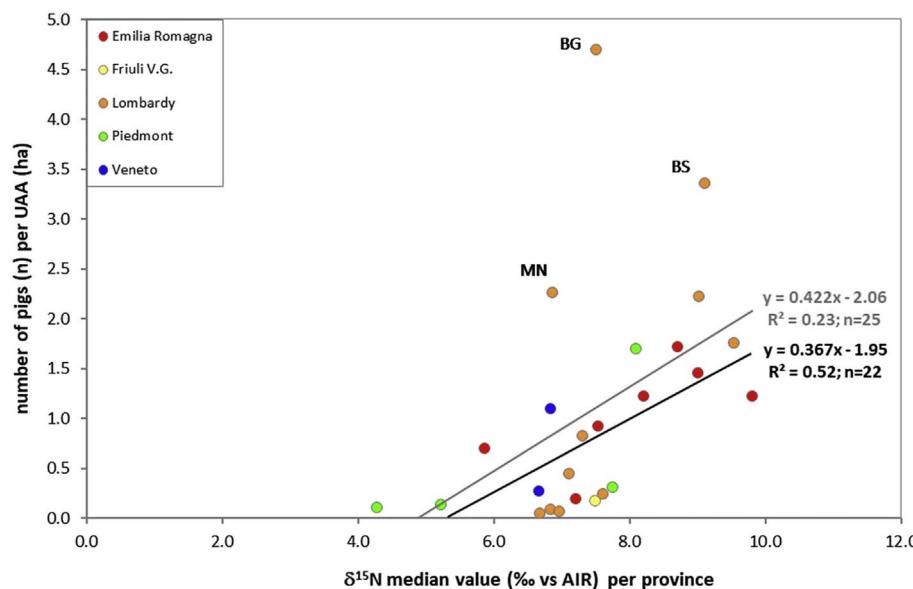
Two sets of samples characterized by enriched  $\delta^{18}\text{O}_{\text{NO}_3}$  can be observed in Fig. 8, one close to the compositional field of synthetic fertilizers, and one related to denitrification processes. The first set, compatible with the nitrification of synthetic fertilizers, accounts for a

relatively low number of samples. This process produces nitrates that maintain the atmospheric  $\delta^{15}\text{N}_{\text{N}_2}$  signal (see discussion in the previous section 4.2), but are progressively more depleted in  $\delta^{18}\text{O}_{\text{NO}_3}$  due to the incorporation of oxygen from the water molecules. Nevertheless, the  $\delta^{18}\text{O}_{\text{NO}_3}$  is slightly more enriched than expected for a full equilibration with  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ . This enrichment is often observed in 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 presence of isotopic compositions attributable to nitrification of synthetic fertilizers, although not so frequent, indicates a fast transfer of nitrates to groundwater, with a low residence time in soils, thus confirming for these cases the high permeability, infiltrability and intrinsic vulnerability of the aquifer.

On the other hand, isotopic compositions enriched due to denitrification are present in a relatively larger number of samples ( $\approx 90$ , corresponding to about 22% of the available data). According to Fig. 8, samples plot between two lines with a 0.5  $\delta^{18}\text{O}/\delta^{15}\text{N}$  slope, one with more enriched  $\delta^{18}\text{O}_{\text{NO}_3}$  values, originating from synthetic fertilizers, and the second from manure and septic system effluents. Hence, as both these nitrate sources are present in the area, they are both prone to denitrification when favorable environmental conditions are present. The observed isotopic enrichment (Fig. 8) allows for the consideration of denitrification as being responsible for nitrate abatement in groundwater affecting up to 70–80% of the original content, depending on the initial isotopic composition and the enrichment factor used (Kendall et al., 2007; Sacchi et al., 2013).

Denitrification was mostly reported in the lower plain of Piedmont and Lombardy (Pilla et al., 2005, 2007; Debernardi et al., 2008; Guffanti et al., 2010; Sacchi et al., 2013; Lasagna et al., 2016b). Studies indicate that, under different soil and crop types, denitrification occurs when the water table is shallow, within 5 m from the surface, allowing the establishment of reducing conditions at shallow depths. This can occur naturally in low permeability soils, or as a consequence of flood irrigation adopted in rice cultivation. In other cases, denitrification was observed in shallow aquifers characterized by a low-permeability unsaturated zone. In Piedmont, a high denitrification rate was reported in areas with a shallow aquifer of limited thickness (e.g. Poirino Plateau) characterized by low permeability and low dilution degree. In this case, the nitrate input is not diluted in the aquifer, and high nitrate concentrations (even higher than 100 mg/l) are present in groundwater, despite the denitrification process.

Indirect evidence for ongoing denitrification can be obtained with hydrochemical tools, as these waters often contain detectable dissolved Fe and Mn contents. Both these metals are geogenic in 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,  $\text{O}_2$  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 mutually exclusive. In the lower Lombardy plain, Sacchi et al. (2013) mapped groundwater samples with Fe and Mn concentrations above 100 and 50  $\mu\text{g/l}$  respectively, as metals above these 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 that in the low plain unconfined aquifers, the input of nitrates from the surface must have been 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. 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 be noted that most isotopic studies targeted areas with high nitrate concentrations, often located close to the Alpine and Apennine chains (Figs. 2 and 3); thus, the lower Veneto plain and the higher Emilia-Romagna plain have not been assessed.



**Fig. 7.** Number of pigs per UAA versus  $\delta^{15}\text{N}$  median values calculated per each province. Grey line = all data; black line = excluding the Bergamo (BG), Brescia (BS) and Mantua (MN) provinces.

Nevertheless, the presence of dissolved Fe and Mn, often associated to  $\text{NH}_4^+$  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 hydrochemical and isotopic evidence (e.g. Rotiroti et al., 2014, 2017; Giambastiani et al., 2015; Petrini et al., 2014; Castaldelli et al., 2013; Carraro et al., 2013), the absence of nitrates in 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 table.

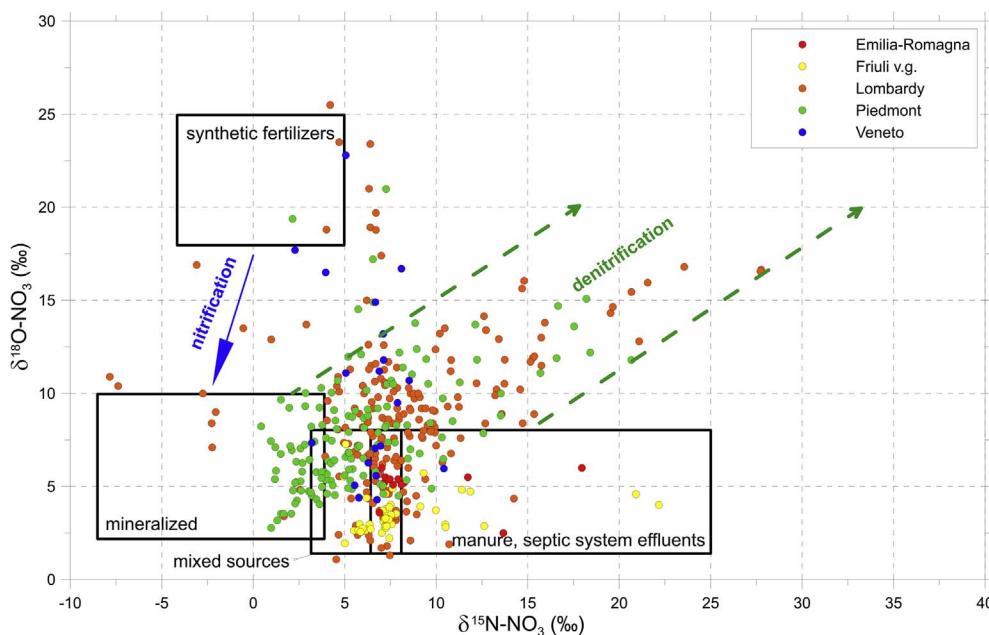
#### 4.4. Insights provided by B isotopes

Compared to the consolidated application of  $\delta^{15}\text{N}$  to contamination studies, the associated use of  $\delta^{11}\text{B}$  represents a promising but still subordinated tool, as testified by the very few data available in the database of the studied area (both for B concentrations and isotopic compositions), compared to the large set of nitrate isotope data.

Currently, boron concentration values recorded in the database range between b.d.l. to 672  $\mu\text{g/l}$ , and  $\delta^{11}\text{B}$  values vary between  $-1.4$

and  $+36.3\text{\textperthousand}$  vs NBS-951 ( $n = 27$ ). A frequency histogram for the isotopic compositions (Fig. 6c) shows the non-normal distribution of the data, with two populations characterized by different isotopic compositions, one around  $+10\text{\textperthousand}$  and a second around  $+22\text{\textperthousand}$ . Comparing this distribution of  $\delta^{11}\text{B}$  signatures to that recorded in Italian groundwaters (Pennisi et al., 2013), the value of  $+10\text{\textperthousand}$  can be considered near to the mean geogenic value ( $+8.2\text{\textperthousand}$ ) that characterizes the Italian alluvial aquifers. On the contrary, the higher  $\delta^{11}\text{B}$  mode value ( $+22\text{\textperthousand}$ ) clearly evidences inputs either of a sea water or of an animal manure component, both characterized by  $^{11}\text{B}$ -enriched signatures (Palmer and Swihart, 1996; Widory et al., 2005).

Together with the need to increase the number of values in the database, the application of the B systematics in the study area is challenged by the poor definition of the compositional end-members, both in terms of natural background and of potential sources of contamination. The application of the coupled  $\delta^{15}\text{N}$  -  $\delta^{11}\text{B}$  toolbox needs to identify the isotopic signature/s of the anthropogenic sources related to the given study site under investigation. As an example, boron in liquid animal manure reflects the boron signature of food and its fractionation



**Fig. 8.**  $\delta^{18}\text{O}_{\text{NO}_3}$  vs  $\delta^{15}\text{N}_{\text{NO}_3}$  values in groundwater. Compositional fields and nitrification-denitrification trends from Sacchi et al. (2013), modified after Clark and Fritz (1997).

eventually 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 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.

As an original contribution of this work we report new data on the main products used in the agricultural sector in Emilia Romagna (Table 1). The values obtained for synthetic fertilizers, sewage water and pig manure are within the ranges defined in the literature for these substances (Widory et al., 2004, 2005; Tirez et al., 2010).

In the highly impacted areas of the Alpine foothills of Lombardy, Sacchi et al. (2013) produced the 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 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 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 from 20 to 540 µg/l (displayed as 1/B in Fig. 9) and δ<sup>11</sup>B values from −1.4‰ to +26.2‰. The sample with the lowest B concentration had a δ<sup>11</sup>B of +14.6‰, and was assumed to be the geogenic, “uncontaminated” end-member. With the increase of B concentrations, a group of samples shifted towards both more depleted δ<sup>11</sup>B values, suggesting contamination from sewage and/or fertilizers (Seiler, 2005; Widory et al., 2005). Conversely, in other samples, an increase in both the B concentration and isotopic composition was observed with respect to the geogenic 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 increasing water-rock interaction, was also evidenced by the lack of any significant shift in the δ<sup>11</sup>B signature of water respect to the un-polluted signature in some Po basin samples (Fig. 9). By comparison, samples from the Emilia Romagna and Veneto regions show a lower range of δ<sup>11</sup>B but higher B concentrations, suggesting a higher contribution of either sewage or synthetic fertilizers.

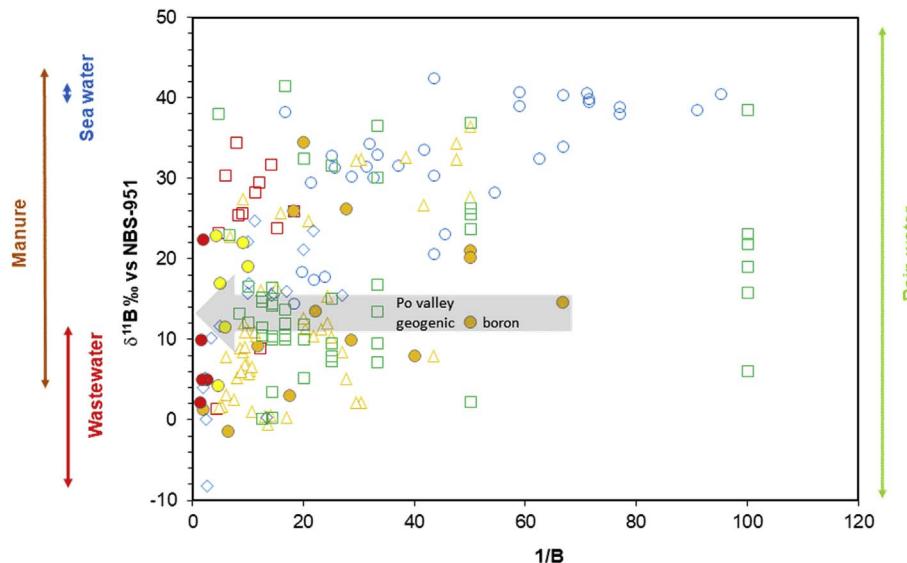
In Fig. 9, data from the investigated area are compared to literature data from studies where the δ<sup>15</sup>N - δ<sup>11</sup>B tool was applied in low geogenic-B environments. A large isotopic variation of almost 50‰ is associated to a boron concentration range of 10–1000 µg/l. Three end-members are distinguished, most of the samples resulting from a mixing

between these sources. The high boron samples span over the whole range of δ<sup>11</sup>B, and mainly concentrate in the area where the “sewage” and “manure” isotopic signatures overlap. Fig. 9 also identifies a trend in literature data starting from low boron – high δ<sup>11</sup>B composition (+40‰), indicating a boron enrichment in groundwater that occurs following the infiltration of meteoric water of marine origin. The decrease in δ<sup>11</sup>B associated to the increase in B concentrations points to the two main anthropogenic boron 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 (δ<sup>11</sup>B = +13 ± 2.5‰) appears to be dominated by rainwater non-marine in origin or already modified during rock interaction.

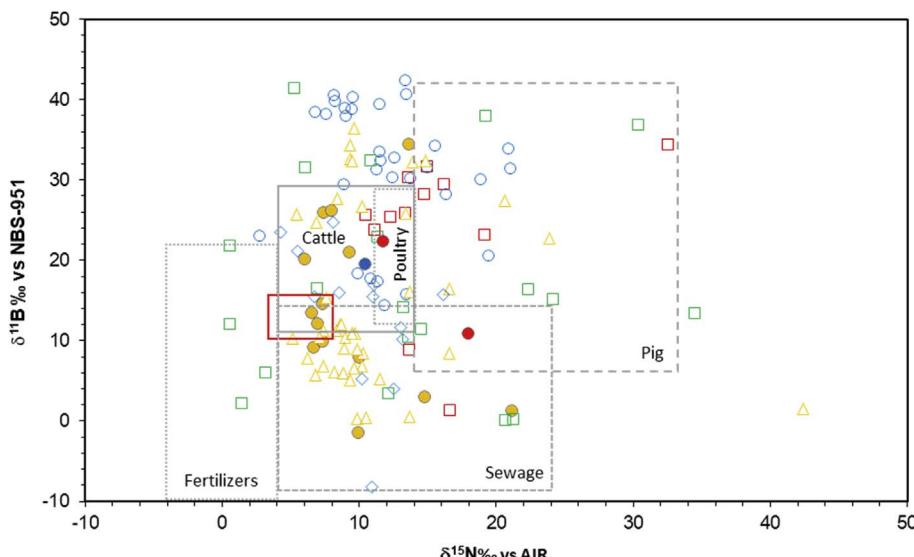
Finally, Fig. 10 shows the δ<sup>11</sup>B vs δ<sup>15</sup>N<sub>NO3</sub> plot of samples from the study area compared to other literature data obtained in groundwater from low geogenic-B environments. The compositional fields of the contaminants are represented as grey boxes (Widory et al., 2004, 2005; Tirez et al., 2010), and the red box evidences the compositional field defined for uncontaminated water from the Po alluvial aquifers. The plot confirms that both sewage and animal manure contribute to the nitrate pollution in the study area, as already indicated by Sacchi et al. (2013). Although isotopic 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 data crossed with N isotopic data (see par. 4.2). Therefore, given the important implications for the agricultural sector, the unequivocal identification of the nitrate contamination sources in the study area still requires a better definition of the isotopic compositions of animal manure applied to agricultural fields, and the coupling of isotopic and farm census data.

## 5. Conclusions

In the last twenty years a remarkable number of nitrate isotopic data, often associated to oxygen, hydrogen and boron isotopic systematics have been produced in the Po plain area, mostly in local investigations. In this work, all the available nitrate (δ<sup>15</sup>N<sub>NO3</sub> and δ<sup>18</sup>O<sub>NO3</sub>) and boron (δ<sup>11</sup>B) isotopic data, together with the hydrochemical composition, if available, were compiled in a 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 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



**Fig. 9.** δ<sup>11</sup>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<sup>11</sup>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. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 10.**  $\delta^{11}\text{B}$  vs  $\delta^{15}\text{N}$  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).  $\delta^{11}\text{B}$  and  $\delta^{15}\text{N}$  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. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

shallow aquifers at the Po basin scale, and defining the more relevant processes governing nitrate contamination in Northern Italy. The conclusions of this work seek to assist regulators in devising sustainable management and remediation strategies.

In the investigated area, the most impacted groundwater is that hosted in the alluvial fans of the 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 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 remediated if the N excess input were reduced. In addition, it is worth stressing that, in the study area, the general assumption that the deeper the water table, the higher the groundwater protection from contamination, is not verified. On the contrary, nitrate contamination is absent in most low plain areas, where the water table is shallow but soil permeability is lower. This is due to the presence of environmental conditions favorable to denitrification processes, as also indicated by other hydrochemical parameters (Fe, Mn,  $\text{NH}_4^+$ ). While this is the general case in low plain areas, in certain cases (e.g. Poirino Plateau in Piedmont), denitrification, although present, is not sufficient to fully abate nitrates because of the high input coupled to the low dilution potential of the aquifer.

As the  $\delta^{15}\text{N}$  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 re-evaluated 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.

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. Indeed, it has proved the presence of another anthropogenic nitrate source, of civil origin, that is sewage in the study area. The gathering of all the data has allowed us to define the range of the expected geogenic B signature, and new results on the local B sources have been produced. This is 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 systematics in the study area was previously limited by a poor definition of the compositional end-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 monitoring activities and allow for an exploitation of already existing data from a different perspective, e.g. by advanced data treatment or modelling. Since the hydrogeological setting is similar throughout the Po and Veneto plains (Figs. 1 and 2), and shows common features to alluvial basins located near mountain ranges, the conceptual model of nitrate circulation and the processes affecting nitrate concentrations revealed by this study can be reasonably extrapolated to other areas of the watershed not yet investigated with isotopic tools, and serve as a reference for other study areas worldwide. In addition, based on the results of this study, different management options could be considered by decision-makers to reduce the impact of nutrients 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 declared as NVZ in order to obtain the derogation to the Nitrate Directive (European Commission, 2011); ii) the type of fertilizer used and the timing of application. This management option should balance the advantages and disadvantages of the use of manure and synthetic fertilizers in agricultural areas characterized by different soil permeabilities and agronomical practices; iii) the amount of water used for irrigation, in order to prevent the leaching of nutrients to the subsurface 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 leaching septic tanks.

## Acknowledgements

The authors wish to acknowledge Enrico Allais (ISO4 s.n.c.), Lia Barazzoni and Milena Repetti (ARPAE Emilia Romagna, Dept. of Piacenza), and Adriano Fava (ARPAE Emilia Romagna, Dept. of Reggio Emilia) for their analytical support. Additional thanks are due to the ISOBORDAT Team (Daniela Andreani, Alessandra Adorni-Braccesi and Lorenzo Gori) for the implementation and maintenance of the boron isotope database. Henry Monaco is acknowledged for the English text editing. Finally, local studies were supported by the Alessandria, Novara, Pavia, Verona and Treviso provinces, and by the CRT Foundation.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2018.01.011>.

## References

- ADAS, 2011. Economics Report for NIT18 NVZ Action Programme Impact Assessment 41 Available at: [https://www.gov.uk/government/uploads/system/uploads/attachment\\_data/file/82410/2011220nitrates-directive-consult-evid3.pdf](https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/82410/2011220nitrates-directive-consult-evid3.pdf).
- Agren, G.I., Bosatta, E., 1988. Nitrogen saturation of terrestrial ecosystems. *Environ. Pollut.* 54, 185–197.
- Appelo, C.A.J., Postma, D., 2005. *Geochemistry, Groundwater and Pollution*, second ed. A.A. Balkema Publishers, pp. 649.
- Aquilina, L., Vergnaud-Aryaud, V., Labasque, T., Bour, O., Molenat, J., Ruiz, L., de Montety, V., De Ridder, J., Roques, C., Longuevergne, L., 2012. Nitrate dynamics in agricultural catchments deduced from groundwater dating and long-term nitrate monitoring in surface- and groundwaters. *Sci. Total Environ.* 435, 167–178.
- Aravena, R., Evans, M.L., Cherry, J.A., 1993. Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic tanks. *Ground Water* 31, 180–186.
- Arduini, C., Dadomo, A., Martinelli, G., Porto, G., Sogni, R., Zelioli, A., 2007. Isotopic prospection in high vulnerability area of the Milano province (Northern Italy). In: Ribeiro, L., Chambel, A., Condesso de Melo, M.T. (Eds.), Proc. of the XXXV IAH Congress "Groundwater and Ecosystems", <http://dx.doi.org/10.13140/RG.2.1.4889.9289>. Lisbon.
- Baily, A., Rock, L., Watson, C.J., Fenton, O., 2011. Spatial and temporal variations in groundwater nitrate at an intensive dairy farm in south-east Ireland: insights from stable isotope data. *Agric. Ecosyst. Environ.* 144, 308–318.
- Baker, L.A., Schussler, J., 2007. Whole Watershed Balances. Lakeline Magazine, pp. 17–20 Summer 2007.
- Balderacchi, M., Perego, A., Lazzari, G., Muñoz-Carpena, R., Acutis, M., Laini, A., Giussani, A., Sanna, M., Kane, D., Trevisan, M., 2016. Avoiding social traps in the ecosystem stewardship: the Italian Fontanile lowland spring. *Sci. Total Environ.* 1 (539), 526–535.
- Bartoli, M., Racchetti, E., Delconte, C.A., Sacchi, E., Soana, E., Laini, A., Longhi, D., Viaroli, P., 2012. Nitrogen balance and fate in a heavily impacted watershed (Oglio River, Northern Italy): in quest of the missing sources and sinks. *Biogeosciences* 9 (1), 361–373.
- Billen, G., Silvestre, M., Grizzetti, B., Leip, A., Garnier, J., Voss, M., Howarth, R., Bouraoui, F., Darracq, H., Lepisto, A., Kortelainen, P., Johnes, P., Curtis, C., Humborg, C., Smedberg, E., Kaste, O., Ganeshram, R., Beusen, A., Lancet, C., 2011. Nitrogen flows from European regional watersheds to coastal marine waters. In: Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B. (Eds.), *The European Nitrogen Assessment*. Cambridge University Press, Cambridge, UK, pp. 271–297.
- Boy-Roura, M., Nolan, B.T., Menció, A., Mas-Pla, J., 2013. Regression model for aquifer vulnerability assessment of nitrate pollution in the Osuna region (NE Spain). *J. Hydrol.* 505, 150–162.
- Brancucci, G., 2001. Brief climatic framework of the Po Plain. In: Castiglioni, G.B., Pellegrini, G.B. (Eds.), *Illustrative Notes of the Geomorphological Map of Po Plain*, pp. 13–15 Ch. 2, *Geogr. Fis. Din. Quat. Suppl.* IV.
- Broders, J., Tirez, K., Widory, D., Petelet-Giraud, E., 2012. Use of compound-specific nitrogen ( $\delta^{15}\text{N}$ ), oxygen ( $\delta^{18}\text{O}$ ), and bulk boron ( $\delta^{11}\text{B}$ ) isotope ratios to identify sources of nitrate-contaminated waters: a guideline to identify polluters. *Environ. Forensics* 13, 32–38.
- Carraro, A., Fabri, P., Giaretti, A., Peruzzo, L., Tateo, F., Tellini, F., 2013. Arsenic anomalies in shallow venetian plain (northeast Italy) groundwater. *Environ. Earth Sci.* 70, 3067–3084.
- Castaldelli, G., Soana, E., Racchetti, E., Pierobon, E., Mastrocicco, M., Tesini, E., Fano, E.A., Bartoli, M., 2013. Nitrogen budget in a lowland coastal area within the Po river basin (northern Italy): multiple evidences of equilibrium between sources and internal sinks. *Environ. Manag.* 52, 567–580.
- Cati, L., 1981. Idrografia e idrologia del Po. *Ministero dei Lavori Pubblici, Servizio Idrografico, Istituto Poligrafico e Zecca dello Stato*, Roma, pp. 310.
- Clark, I., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, Boca Raton.
- Conti, A., Sacchi, E., Chiarle, M., Martinelli, G., Zuppi, G.M., 2000. Geochemistry of the formation waters in the Po plain (Northern Italy): an overview. *Appl. Geochem.* 15, 51–65.
- Dadomo, A., Martinelli, G., 2005. Aspetti di idrologia isotopica in Emilia-Romagna. In: *Acqua e copertura vegetale*, vol. 216. Atti dei Convegni Lincei, Roma, pp. 157–166.
- Debernardi, L., De Luca, D.A., Lasagna, M., 2008. Correlation between nitrate concentration in groundwater and parameters affecting aquifer intrinsic vulnerability. *Environ. Geol.* 55, 539–558.
- De Luca, D.A., Dell'Orto, V., Destefanis, E., Forno, M.G., Lasagna, M., Masciocci, L., 2009. Assetto idrogeologico dei fontanili della pianura torinese (Hydrogeological structure of the "fontanili" in Turin plain). *Rendiconti Online Società Geologica Italiana* 6, 199–200.
- De Luca, D.A., Destefanis, E., Forno, M.G., Lasagna, M., Masciocci, L., 2014. The genesis and the hydrogeological features of the Turin Po Plain fontanili, typical lowland springs in Northern Italy. *Bull. Eng. Geol. Environ.* 73, 409–427.
- Edmunds, W.M., Shand, P. (Eds.), 2008. *Natural Groundwater Quality*. Wiley-Blackwell, pp. 488.
- Elmi, G., Sacchi, E., Zuppi, G.M., Cerasuolo, M., Allais, E., 2013. Isotopic estimation of the evapo-transpiration flux in a plain agricultural region (Po plain, Northern Italy). *Appl. Geochem.* 34, 53–64.
- European Commission, 1991. Directive 91/676/EEC. Council directive of 12 december 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. *Off. J. Eur. Commun.* L 375, 1–8. Available at: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1991:375:0001:0008:EN:PDF>.
- European Commission, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Offic. J. Eur. Commun.* L 327, 1–72. Available at: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2000:327:0001:0072:EN:PDF>.
- European Commission, 2011. Commission implementing decision of 3 November 2011 on granting a derogation requested by Italy with regard to the Regions of Emilia Romagna, Lombardy, Piedmont and Veneto pursuant to Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources (2011/721/EU). *Offic. J. Eur. Union* L 287, 36–41. Available at: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:287:0036:0041:EN:PDF>.
- EEA European Environment Agency, 2005. EEA Report. Source Apportionment of Nitrogen and Phosphorus Inputs into the Aquatic Environment, vol. 7. pp. 48. [http://www.eea.europa.eu/publications/eea\\_report\\_2005\\_7](http://www.eea.europa.eu/publications/eea_report_2005_7).
- Fratanni, S., Acquaotta, F., 2017. The climate of Italy. In: Soldati, M., Marchetti, M. (Eds.), *Landscapes and Landforms of Italy, World Geomorphological Landscapes*. Springer International Publishing AG, pp. 29–38.
- Fumagalli, N., Senes, G., Ferrario, P.S., Toccolini, A., 2017. A minimum indicator set for assessing fontanili (lowland springs) of the Lombardy Region in Italy. *Eur. Countries* 9, 1–16.
- Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., Sutton, M.A., 2008. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. *Science* 320, 889–892.
- Giambastiani, B.M.S., Colombani, N., Mastrocicco, M., 2015. Detecting small-scale variability of trace elements in a shallow aquifer. *Water Air Soil Pollut.* 226, 7.
- Giuliano, G., 1995. Ground water in the Po basin: some problems relating to its use and protection. *Sci. Total Environ.* 171, 17–27.
- Giuliano, G., Mari, G.M., Cavallin, A., De Amicis, M., 1998. Ricerca sulla vulnerabilità naturale e sul rischio di inquinamento delle acque sotterranee nella pianura padana e veneto-friulana: carta della infiltrabilità regionale, carta idrogeologica regionale, carta della vulnerabilità regionale (scala 1:500000). *Mem. Descr. Ia Carta Geol. Italia* 56, 1–102.
- Guffanti, S., Pilla, G., Sacchi, E., Ughini, S., 2010. Characterization of the quality and origin of groundwater of Lodigiano (Northern Italy) with hydrochemical and isotopic instruments. *Ital. J. Eng. Geol. Environ.* 1, 65–78.
- ISO4, 2005. Monitoraggio isotopico delle acque sotterranee in Provincia di Treviso, mediante l'analisi degli isotopi stabili di ossigeno, idrogeno, carbonio e dei nitrati. Unpublished report, Provincia di Treviso. .
- ISTAT, 2010. 2010 Agricultural Census. Available at: <http://dati-censimentoagricoltura.istat.it/Index.aspx?lang=en&SubSessionId=e907b55d-8514-4899-880d-cb62d6106cec&methtable=-200>.
- Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen in ecosystems. In: Michener, R., Lajtha, K. (Eds.), *Stable Isotopes in Ecology and Environmental Science*, second ed. Blackwell Publishing Inc., Oxford UK, pp. 375–449.
- Komor, S.C., 1997. Boron content and isotopic composition of hog manure, selected fertilizer, and water in Minnesota. *J. Environ. Qual.* 26, 1212–1222.
- Lasagna, M., De Luca, D.A., Debernardi, L., Clemente, P., 2013. Effect of the dilution process on the attenuation of contaminants in aquifers. *Environ. Earth Sci.* 70, 2767–2784.
- Lasagna, M., Franchino, E., De Luca, D.A., 2015. Areal and vertical distribution of nitrate concentration in Piedmont plain aquifers (North-western Italy). In: Lollino, G. (Ed.), *River Basins, Reservoir Sedimentation and Water Resources*, vol. 3. Engineering Geology for Society and Territory, Springer International Publishing Switzerland, pp. 389–392.
- Lasagna, M., De Luca, D.A., Franchino, E., 2016a. Nitrate contamination in the western Po Plain (Italy): the effects of groundwater and surface water interactions. *Environ. Earth Sci.* 75, 1–16.
- Lasagna, M., De Luca, D.A., Franchino, E., 2016b. The role of physical and biological processes in aquifers and their importance on groundwater vulnerability to nitrate pollution. *Environ. Earth Sci.* 75, 961.
- Lasagna, M., De Luca, D.A., Franchino, E., 2006. Studio dell'origine dei nitrati nelle acque sotterranee piemontesi mediante gli isotopi dell'azoto. *Giornale di Geologia Applicata* 2, 137–143.
- Longinelli, A., Selmo, E., 2003. Isotopic composition of precipitation in Italy: a first overall map. *J. Hydrol.* 270, 75–88.
- Lorimor, J., Powers, W., Sutton, A., 2004. Manure Characteristics, second ed. Manure Management Systems Series MWPS-18, Section 1 Available at: <http://msue.anr.msu.edu/uploads/files/ManureCharacteristicsMWPS-18.1.pdf> last accessed May 2017.
- Maffei, M., Vigliotti, L., Martinelli, G., 2005. Misure di suscettività magnetica e analisi degli isotopi stabili in carote della pianura padana dati tramite Cabonio 14. In: Scialoja, M.G. (Ed.), *Presenza e diffusione dell'arsenico nel sottosuolo e nelle risorse idriche italiane, nuovi strumenti di valutazione delle dinamiche di mobilizzazione*. ARPA, Agenzia Regionale Prevenzione e Ambiente dell'Emilia-Romagna. I Quaderni di ARPA, Bologna, pp. 181–196.
- Mantovì, P., Fumagalli, L., Beretta, G.P., Guermandi, M., 2006. Nitrate leaching through the unsaturated zone following pig slurry applications. *J. Hydrol.* 316, 195–212.
- Martinelli, G., Chahoud, A., Dadomo, A., Fava, A., 2014a. Isotopic features of Emilia-Romagna region (North Italy) groundwaters: environmental and climatological

- implications. *J. Hydrol.* 519, 1928–1938.
- Martinelli, G., Castagna, M., Pennisi, M., 2014b. Il monitoraggio del Boro nel sito contaminato nazionale Sassuolo-Scandiano (Area del Distretto Ceramicco di Modena e Reggio Emilia). In: Farina, M., Marcaccio, M., Zavatti, A. (Eds.), *Esperienze e prospettive nel monitoraggio delle acque sotterranee: il contributo dell'Emilia-Romagna*. Pitagora Editrice, Bologna, pp. 332–354.
- Martinelli, G., Fava, A., Chahoud, A., Dadomo, A., 2014c. Il monitoraggio isotopico nelle acque sotterranee in Emilia-Romagna. In: Farina, M., Marcaccio, M., Zavatti, A. (Eds.), *Esperienze e prospettive nel monitoraggio delle acque sotterranee: il contributo dell'Emilia-Romagna*. Pitagora Editrice, Bologna, pp. 332–354.
- Martinelli, G., Dadomo, A., Italiano, F., Petriani, R., Slezko, F.F., 2017. Geochemical monitoring of the 2012 Po Valley seismic sequence: a review and update. *Chem. Geol.* 469, 147–162. <https://doi.org/10.1016/j.chemgeo.2016.12.013>.
- Matiatis, I., 2016. Nitrate source identification in groundwater of multiple land-use areas by combining isotopes and multivariate statistical analysis: a case study of Asopos basin (Central Greece). *Sci. Total Environ.* 541, 802–814.
- McMahon, P.B., Chapelle, F.H., 2008. Redox processes and water quality of selected principal aquifer systems. *Ground Water* 46, 259–271.
- Menció, A., Mas-Pla, J., Otero, N., Regás, O., Boy-Roura, M., Puig, R., Bach, J., Domènec, C., Zamorano, M., Brusí, D., Folch, A., 2016. Nitrate pollution of groundwater; all right..., but nothing else? *Sci. Total Environ.* 539, 241–251.
- Minelli, A., Ruffo, S., Stoch, F., Cosentino, A., La Posta, A., Morandini, C., Muscio, G., Lapini, L., Paradisi, S., Sburlino, G., Solari, M., 2002. Risorgive e fontanili. In: *Acque sorgenti di pianura dell'Italia Settentrionale*, Ministero dell'Ambiente, Museo Friulano di Storia Naturale, pp. 13–28 Comune di Udine.
- Ministry for Environment, Land and See, Ministry of Agriculture, Food and Forestry Policies, regions of Piedmont, Lombardy, Veneto, Emilia-Romagna and Friuli Venezia Giulia, 2010. Request from Italy for a derogation under paragraph 2(b) of Annex III to Directive 91/676/EEC from the limit of 170 kilograms of Nitrogen per hectare per year from livestock manure. Available at: [http://www.regione.piemonte.it/ambiente/valutazioni\\_ambientali/dwd/nitrati/documento%20tecnico%20scientifico%20CRPA.pdf](http://www.regione.piemonte.it/ambiente/valutazioni_ambientali/dwd/nitrati/documento%20tecnico%20scientifico%20CRPA.pdf) last accessed March 2017.
- Nestler, A., Berglund, M., Accoe, F., Duta, S., Xue, D., Boeckx, P., Taylor, P., 2011. Isotopes for improved management of nitrate pollution in aqueous resources: review of surface water field studies. *Environ. Sci. Pollut. Res.* 18, 519–533.
- Palmer, M.R., Swihart, G.H., 1996. Boron isotope geochemistry: an overview. *Rev. Mineral.* 33, 1–862.
- Panno, S.V., Hackley, K.C., Hwang, H.H., Kelly, W.R., 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. *Chem. Geol.* 179, 113–128.
- Pennisi, M., Adorni-Braccesi, A., Andreani, D., Gori, L., Sciuto, P.F., Gonfiantini, R., 2013. Isobordat: an online database on boron isotopes. In: *Isotopes in hydrology, marine ecosystems and climate change studies. In: Proceedings from an International Symposium*, Monaco, 2011, vol. 2 IAEA, Vienna.
- Petrini, R., Pennisi, M., Antisari, L.V., Cidu, R., Vianello, G., Aviani, U., 2014. Geochemistry and stable isotope composition of surface waters from the Ravenna plain (Italy): implications for the management of water resources in agricultural lands. *Environ. Earth Sci.* 71, 5099–5111.
- Pilla, G., Sacchi, E., Gerbert-Gaillard, L., Zuppi, G.M., Peloso, G.F., Ciancetti, G., 2005. Origine e distribuzione dei nitrati in falda nella Pianura Padana occidentale (Province di Novara, Alessandria e Pavia). *Giornale di Geologia Applicata* 2, 144–150.
- Pilla, G., Sacchi, E., Zuppi, G.M., Braga, G., Ciancetti, G., 2006. Hydrochemistry and isotope geochemistry as tools for groundwater hydrodynamic investigation in multilayer aquifers: a case study from Lomellina, Po plain, South Western Lombardy, Italy. *Hydrogeol. J.* 14, 795–808.
- Pilla, G., Sacchi, E., Ciancetti, G., 2007. Studio idrogeologico, idrochimico ed isotopico delle acque sotterranee del settore di pianura dell'Oltrepò Pavese (pianura lombarda meridionale). *Giornale di Geologia Applicata* 59–74.
- Pilla, G., Torrese, P., Bersan, M., 2010. Application of hydrochemical and preliminary geophysical surveys within the study of the saltwater uprising occurring in the Oltrepò Pavese plain aquifer. *Boll. Geofis. Teor. Appl.* 51, 301–323.
- Provincia di Verona, 2001. Rapporto Tecnico, Provincia di Verona-Settore Ecologia, Verona. Indagine idrogeologica, geochimica e geochimico-isotopica sugli acquiferi della Lessinia, vol. 97.
- Puig, R., Soler, A., Widory, D., Mas-Pla, J., Domènec, C., Otero, N., 2017. Characterizing sources and natural attenuation of nitrate contamination in the Baix Ter aquifer (NE Spain, using a multi-isotope approach). *Sci. Total Environ.* 580, 518–532.
- Risberg, K., Cederlund, H., Pell, M., Arthurson, V., Schnürer, A., 2017. Comparative characterization of digestate versus pig slurry and cow manure – chemical composition and effects on soil microbial activity. *Waste Manag.* 61, 529–538.
- Rogora, M., Arisci, S., Marchetto, A., 2012. The role of nitrogen deposition in the recent nitrate decline in lakes and rivers in Northern Italy. *Sci. Total Environ.* 417–418, 214–223.
- Rotiroti, M., McArthur, J., Fumagalli, L., Stefania, G.A., Sacchi, E., Bonomi, T., 2017. Pollutant sources in an arsenic-affected multilayer aquifer in the Po Plain of Italy: implications for drinking-water supply. *Sci. Total Environ.* 578, 502–512.
- Rotiroti, M., Sacchi, E., Fumagalli, L., Bonomi, T., 2014. Origin of arsenic in groundwater from the multilayer aquifer in cremona (northern Italy). *Environ. Sci. Technol.* 48, 5395–5403.
- Sacchi, E., Pilla, G., Allais, E., Guallini, M., Zuppi, G.M., 2007. Tracing nitrification and denitrification processes in a periodically flooded shallow sandy aquifer. In: *Int. Symp. On Advances in Isotope Hydrology and its Role in Sustainable Water Resources Management*, vol. 2. IAEA, pp. 461–469 Vienna 21–25 May 2007, IAEA-CN-151/33.
- Sacchi, E., Acutis, M., Bartoli, M., Brenna, S., Delconte, C.A., Laini, A., Pennisi, M., 2013. Origin and fate of nitrates in groundwater from the central Po plain: insights from isotopic investigations. *Appl. Geochem.* 34, 164–180.
- Saccon, P., Leis, A., Marca, A., Kaiser, J., Campisi, L., Bottcher, M.E., Savarino, J., Escher, P., Eisenhauer, A., Erbland, J., 2013. Multi-isotope approach for the identification and characterization of nitrate pollution sources in the Marano lagoon (Italy) and parts of its catchment area. *Appl. Geochem.* 34, 75–89.
- Seiler, R.L., 2005. Combined use of  $^{15}\text{N}$  and  $^{18}\text{O}$  of nitrate and  $^{11}\text{B}$  to evaluate nitrate contamination in groundwater. *Appl. Geochem.* 20, 1626–1636.
- Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M., Bolke, J.K., 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal. Chem.* 73, 4135–4153.
- Silva, S.R., Kendall, C., Wilkison, D.H., Ziegler, A.C., Chang, C.C.Y., Avanzino, R.J., 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. *J. Hydrol.* 228, 22–36.
- Spruill, T.B., Showers, W.J., Howe, S.S., 2002. Application of classification-tree methods to identify nitrate sources in ground water. *J. Environ. Qual.* 31, 1538–1549.
- Tilman, D., Fargione, J., Wolff, B., D'Antonio, C., Dobson, A., Howarth, R., Schindler, D., Schlesinger, W.H., Simberloff, D., Swackhamer, D., 2001. Forecasting agriculturally driven global environmental change. *Science* 292, 281–284.
- Tirez, K., Brusten, W., Widory, D., Petelet, E., Bregnot, A., Xue, D., Boeckx, P., Bronders, J., 2010. Boron isotope ratio ( $\delta^{11}\text{B}$ ) measurements in Water Framework Directive monitoring programs: comparison between double focusing sector field ICP and thermal ionization mass spectrometry. *J. Anal. At. Spectrom.* 25, 964–974.
- Tonarini, S., Pennisi, M., Leeman, W.P., 1997. Precise boron isotopic analysis of complex silicate (rock) samples using alkali carbonate fusion and ion-exchange separation. *Chem. Geol.* 142, 129–137.
- Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: sources and consequences. *Ecol. Appl.* 7, 737–750.
- Vitòria, L., Otero, N., Soler, A., Canals, A., 2004. Fertilizer characterization: isotopic data (N, S, O, C and Sr). *Environ. Sci. Technol.* 38, 3254–3262.
- Vitòria, L., Soler, A., Canals, A., Otero, N., 2008. Environmental isotopes (N, S, C, O, D) to determine natural attenuation processes in nitrate contaminated waters: example of Osuna (NE Spain). *Appl. Geochem.* 23, 3597–3611.
- Vorlichek, P.A., Antonelli, R., Fabbri, P., Rausch, R., 2004. Quantitative hydrogeological studies of the Treviso alluvial plain, NE Italy. *Q. J. Eng. Geol. Hydrogeol.* 37, 1–7.
- Wendland, F., Berthold, G., Blum, A., Elsass, P., Fritzsche, J.G., Kunkel, R., Wolter, R., 2008. Derivation of natural background levels and threshold values for groundwater bodies in the Upper Rhine Valley (France, Switzerland and Germany). *Desalination* 226, 160–168.
- WHYMAP World-wide Hydrogeological Mapping and Assessment Programme, 2008. Groundwater resources map of Europe. Available at: [https://www.whymap.org/whymap/EN/About/about\\_node\\_en.html](https://www.whymap.org/whymap/EN/About/about_node_en.html) last accessed August 2017.
- Widory, D., Kloppmann, W., Chery, L., Bonnin, J., Rochdi, H., Guinamant, J., 2004. Nitrate in groundwater: an isotopic multi-tracer approach. *J. Contam. Hydrol.* 72, 165–188.
- Widory, D., Petelet-Giraud, E., Brenot, A., Bronders, J., Tirez, K., Boeckx, P., 2013. Improving the management of nitrate pollution in water by the use of isotope monitoring: the  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{11}\text{B}$  triptych. *Isot. Environ. Health Stud.* 49 (1), 29–47.
- Widory, D., Petelet-Giraud, E., Negrel, P., Ladouce, B., 2005. Tracking the sources of nitrates in groundwater using coupled nitrogen and boron isotopes: a synthesis. *Environ. Sci. Technol.* 39, 539–548.
- Xiao, J., Xiao, J.K., Jin, Z.D., He, M.Y., Liu, C.Q., 2013. Boron isotope variations and its geochemical application in nature. *Aust. J. Earth Sci.* 60, 431–447.
- Zini, L., Calligaris, C., Treu, F., Zavagno, E., Iervolino, D., Lippi, F., 2013. Groundwater sustainability in the Friuli Plain. *AQUA mundi Am07058*. pp. 041–054.

Tab.S1

ID	ID_Ref	Region	X_utrm32_wgs84	Y_utrm32_wgs84	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	HCO3- mg/l	Cl- mg/l	NO3 <sup>-</sup> mg/l	SO4 <sup>2-</sup> mg/l	B µg/L	Sr mg/L	δ11B	δ <sup>15</sup> N <sub>NO3</sub>	δ <sup>18</sup> O <sub>NO3</sub>	1/B
a01	a	Lombardy	484874	5004680	44,5	10,1	9,4	1,8	134,0	12,4	20,3	48,6			-2,75	10,00		
a02	a	Lombardy	480272	5009278	39,3	7,3	9,6	2,6	100,0	17,3	33,4	39,1			0,98	12,90		
a03	a	Lombardy	494034	5004963	65,2	13,3	10,2	2,2	217,0	7,6	13,1	43,9			-7,39	10,40		
a04	a	Lombardy	511327	4998198	73,2	9,1	8,5	2,3	224,0	11,0	26,6	38,1			-2,27	8,40		
a05	a	Lombardy	497502	4995398	45,3	12,3	9,4	2,9	100,0	0,5	49,7	0,5			1,67	3,40		
a06	a	Lombardy	467669	5002569	107,2	17,9	10,8	4,6	349,0	0,5	18,5	0,5			-2,05	9,00		
a07	a	Lombardy	469773	4998875	65,6	10,9	8,6	8,5	76,0	0,5	17,2	0,5			-2,25	7,10		
a08	a	Lombardy	466861	5011602	63,5	40,5	14,4	1,9	266,0	0,5	12,4	0,5			-0,55	13,50		
a09	a	Lombardy	485581	5002067	51,5	11,9	8,2	1,3	168,0	0,5	12,8	0,5			-7,84	10,90		
a10	a	Lombardy	480152	5023501	40,9	12,6	14,1	2,3	142,0	12,7	9,8	45,4			-3,09	16,90		
b01	b	Lombardy	480315	5007629	49,1	21,2	18,1	69,6	245,2	23,9	8,3	63,4			23,56	16,80		
b02	b	Lombardy	482016	5005047	51,3	13,8	7,9	2,5	162,3	18,0	11,1	44,3			27,77	16,65		
b03	b	Lombardy	481751	5007436	39,2	13,3	8,6	4,2	126,9	19,4	35,1	33,7			19,52	14,31		
b04	b	Lombardy	482953	5007808	53,0	11,1	11,3	1,7	141,5	7,2	7,1	73,6			4,67	2,40		
b05	b	Lombardy	479068	5003306	53,2	13,8	9,4	1,7	133,0	14,3	29,4	49,8			4,53	1,08		
b06	b	Lombardy	481533	5002533	42,1	13,7	12,4	68,9	203,7	27,7	26,7	72,1			15,36	8,89		
b07	b	Lombardy	481751	5007436	43,7	13,3	8,3	3,9	112,2	21,8	46,3	32,8			19,66	14,65		
b08	b	Lombardy	482953	5007808	45,1	9,5	9,9	1,5	130,5	7,9	10,6	59,0			12,68	8,39		
b09	b	Lombardy	483364	5006275	34,3	8,6	7,0	9,7	52,5	13,0	68,3	38,8			5,35	4,35		
b10	b	Lombardy	479068	5003306	49,0	12,8	9,0	1,6	130,5	12,6	16,6	55,0			8,60	9,99		
b11	b	Lombardy	481533	5002533	42,9	12,7	11,9	65,4	186,7	18,8	22,3	63,3			15,27	11,91		
b12	b	Lombardy	483342	5006354	43,7	10,7	10,7	2,7	90,3	14,8	36,9	41,5			6,29	4,36		
b13	b	Lombardy	481751	5007436	48,9	16,2	10,5	4,4	117,1	25,0	76,9	35,3			15,15	11,70		
b14	b	Lombardy	483364	5006275	31,5	7,1	7,2	9,0	87,8	10,2	13,1	41,7			5,54	6,87		
b15	b	Lombardy	480315	5007629	49,7	22,1	16,9	60,3	274,5	22,6	51,8	54,2			13,75	11,81		
b16	b	Lombardy	481751	5007436	52,7	17,3	9,4	4,2	122,0	26,1	83,3	34,6			14,59	10,21		
b17	b	Lombardy	479068	5003306	46,7	11,8	9,4	1,6	134,2	12,6	16,6	47,9			7,03	7,63		
b18	b	Lombardy	480315	5007629	53,4	24,6	16,5	76,1	256,2	27,8	77,7	53,8			13,42	12,92		
b19	b	Lombardy	481751	5007436	52,6	16,2	7,9	4,2	109,8	27,9	93,6	37,2			13,30	10,21		
b20	b	Lombardy	482953	5007808	60,6	12,2	10,0	1,7	201,3	7,8	10,7	48,5			7,43	4,78		
b21	b	Lombardy	483364	5006275	37,6	8,8	7,6	9,2	136,6	8,7	3,9	39,5			6,24	6,63		
b22	b	Lombardy	479068	5003306	38,0	9,3	8,2	1,5	113,5	12,2	2,9	42,0			9,92	9,05		
b23	b	Lombardy	481533	5002533	47,1	15,4	10,9	62,1	159,8	27,5	58,5	62,0			13,21	9,90		
b24	b	Lombardy	481533	5002533	46,7	16,0	11,3	49,7	162,3	20,7	18,8	79,7			15,75	13,00		
b25	b	Lombardy	481751	5007436	59,6	20,0	10,1	5,2	101,3	30,6	110,1	39,8			12,21	10,55		
b26	b	Lombardy	482953	5007808	60,2	14,1	9,9	1,4	203,7	10,9	5,8	41,2			13,73	10,52		
b27	b	Lombardy	483364	5006275	40,3	10,5	6,1	9,5	135,4	9,8	9,3	37,3			5,99	10,41		
b28	b	Lombardy	478828	5002330	42,4	10,9	10,2	6,2	145,2	12,6	1,5	28,0			8,81	9,72		
b29	b	Lombardy	481533	5002533	35,2	9,6	7,1	40,6	126,9	9,3	7,2	72,4			11,33	7,59		
c01	c	Lombardy	537693	5005134	77,7	27,6	9,4	1,7	268,4	10,1	23,8	35,8			10,34	6,30		
c02	c	Lombardy	549085	5001796	79,2	38,1	14,0	0,6	256,2	30,8	36,1	55,1			6,67	5,30		
c03	c	Lombardy	544290	5014369	52,9	18,8	7,3	2,1	183,0	8,9	12,2	32,1			7,87	10,30		
c04	c	Lombardy	533275	5024612	56,4	21,1	4,7	0,7	217,2	9,4	9,6	30,8			8,27			
c05	c	Lombardy	534332	5022963	76,7	25,7	6,6	1,1	266,0	10,2	16,0	32,6			8,46	7,90		
c06	c	Lombardy	547287	5002311	82,4	29,0	11,9	1,4	307,4	12,9	10,3	37,3			12,72	13,40		
c07	c	Lombardy	533951	5028705	91,0	32,4	5,9	1,1	331,8	11,0	18,8	31,0			9,01	10,00		
d01	d	Lombardy	481058	5052889						19,6	39,8	28,0				4,64	10,90	
d02	d	Lombardy	498994	5036486						6,0	9,0	33,0				4,07	9,60	
d03	d	Lombardy	625303	5022240						49,0	73,6	67,0	85,0	0,20	9,25	6,66	6,50	0,0117647
d04	d	Lombardy	576423	5040659						8,5	32,0	37,4			6,68	6,80		
d05	d	Lombardy	550960	5043677						20,0	56,0	44,0	35,0	0,41	9,94	7,28	6,50	0,0285714
d06	d	Lombardy	615365	5028468						36,0	55,0	57,0			4,96	7,35		
d07	d	Lombardy	559892	5049743						25,0	55,0	37,0	20,0	0,33	12,20	6,97	7,40	0,05
d08	d	Lombardy	618522	5022276						25,0	67,0	46,0	15,0	0,28	14,60	7,33	7,10	0,0666667
d09	d	Lombardy	563866	5036331						15,0	67,0	42,0	20,0	0,85	20,98	9,26	7,60	0,05
d10	d	Lombardy	605364	5033595						22,3	144,1	42,8	25,0	0,47	7,98	9,99	7,20	0,04
d11	d	Lombardy	574391	5015701						26,0	55,0	62,0				5,54	9,20	
d12	d	Lombardy	531930	5047331						10,3	43,4	32,0	20,0	0,22	20,18	6,00	10,40	0,05
d13	d	Lombardy	537696	5048310						14,0	50,0	21,0				6,06	10,00	
d14	d	Lombardy	624063	5020094						38,0	63,2	62,0				6,17	8,60	
d15	d	Lombardy	500062	5061949						12,0	37,5	12,8				6,44	11,50	
d16	d	Lombardy	620940	5026211						56,0	140,6	60,0	45,0	0,15	13,49	6,53	7,70	0,0222222
d17	d	Lombardy	488882	5043510						23,0	77,0	43,0				6,55	9,20	
d18	d	Lombardy	488412	5055819						18,3	36,6	23,9				6,69	11,60	
d19	d	Lombardy	504597	5065969						29,0	59,3	34,2				6,82	9,80	
d20	d	Lombardy	482247	5043024						18,0	45,0	36,0				6,97	10,80	
d21	d	Lombardy	534800	5043750						14,8	41,6	31,0	0,0	0,17		7,05	8,70	#DIV/0!
d22	d	Lombardy	499999	4986651						48,0	50,0	84,0				7,13	12,60	
d23	d	Lombardy	534708	5052923						17,0	65,0	34,0				7,18	10,60	
d24	d	Lombardy	502832	5052080						17,1	51,5	22,4				7,23	8,60	
d25	d	Lombardy	517804	5044121						21,5	40,7	46,0	55,0	0,36	26,01	7,39	11,70	0,0181818
d26	d	Lombardy	514970	5041096						20,1	37,5	43,1				7,60	8,40	
d27	d	Lombardy	548548	5035688						17,0	27,0	44,0				7,69	7,60	
d28	d	Lombardy	509322	5065629						20,8	42,7	38,9				7,85	11,40	
d29	d	Lombardy	501905	5045399						23,3	45,2	32,0	0,0	0,24</td				

Tab.S1

ID	ID_Ref	Region	X_utrm32_wgs84	Y_utrm32_wgs84	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	HCO3- mg/l	Cl- mg/l	NO3 <sup>-</sup> mg/l	SO4 <sup>2-</sup> mg/l	B µg/L	Sr mg/L	δ11B	δ <sup>15</sup> N <sub>NO3</sub>	δ <sup>18</sup> O <sub>NO3</sub>	1/B
d38	d	Lombardy	580541	5049899					8,8	30,0	40,0				9,20	9,20		
d39	d	Lombardy	614994	5035965					9,6	46,6	22,7				9,42	9,20		
d40	d	Lombardy	564911	5019500					32,0	88,0	54,0				9,53	8,30		
d41	d	Lombardy	603397	5028059					42,7	79,8	62,9	155,0	0,66	-1,42	9,92	8,20	0,0064516	
d42	d	Lombardy	557472	5036608					55,0	50,0	67,0				9,93	7,90		
d43	d	Lombardy	584041	5033823					15,4	41,6	44,8				10,63	9,30		
d44	d	Lombardy	531422	5021560					20,0	34,0	43,0				10,79	11,20		
d45	d	Lombardy	631820	5023951					25,0	42,6	47,0	57,0	0,05	2,98	14,73	8,40	0,0175439	
d46	d	Lombardy	586561	5006541					7,0	19,0	34,0				15,94	13,80		
d47	d	Lombardy	477393	5069239				1,0	11,2	18,9	36,1				20,67	15,45		
d48	d	Lombardy	646460	4978522					318,0	50,1	58,0	540,0	0,88	1,35	21,09	12,80	0,0018519	
d49	d	Lombardy	589971	4997061					41,0	64,0	97,0	50,0		34,52	13,57	8,90	0,02	
e001	e	Piedmont	478446	4969805						87,0						1,97	9,23	
e002	e	Piedmont	479377	4974506						89,3						1,31	3,18	
e003	e	Piedmont	477550	4975478						82,6						3,08	6,44	
e004	e	Piedmont	477886	4974705						87,0						3,20	4,51	
e005	e	Piedmont	478646	4974239						91,0						3,45	4,32	
e006	e	Piedmont	479167	4967967						98,4						1,52	3,53	
e007	e	Piedmont	479364	4967116						96,1						1,65	3,54	
e008	e	Piedmont	481130	4967746						99,3						2,09	3,54	
e009	e	Piedmont	475369	4973886						73,6						5,40	4,87	
e010	e	Piedmont	476628	4968018						90,5						2,33	5,23	
e011	e	Piedmont	476912	4971335						26,0	19,0					5,20	8,79	
e012	e	Piedmont	475321	4974354						60,0	71,0					7,37	7,37	
e013	e	Piedmont	479349	4967213						96,3						2,17	4,79	
e014	e	Piedmont	476954	4968766						100,1						2,58	7,04	
e015	e	Piedmont	478848	4969525						57,0						2,84	9,31	
e016	e	Piedmont	477171	4968277						91,1						3,62	9,24	
e017	e	Piedmont	476951	4970085						91,5						2,39	4,25	
e018	e	Piedmont	477332	4973367						38,1						0,97	2,77	
e019	e	Piedmont	474876	4972485						30,0	55,0					3,98	7,60	
e020	e	Piedmont	475866	4971445						30,0	33,0					4,29	7,46	
e021	e	Piedmont	485714	4971734						44,7	63,6					3,88	5,78	
e022	e	Piedmont	483592	4974899						45,0	49,2					1,50	6,75	
e023	e	Piedmont	486335	4981931						76,5	57,0					3,03	4,74	
e024	e	Piedmont	481370	4980644						44,4	44,1					2,81	7,25	
e025	e	Piedmont	481641	4973327						23,2	15,6					0,43	8,23	
e026	e	Piedmont	494564	4972121						65,4						8,37	5,34	
e027	e	Piedmont	489580	4968415						56,1	137,0					5,04	6,58	
e028	e	Piedmont	490526	4976124						39,3	126,6					5,44	5,94	
e029	e	Piedmont	485714	4971734						40,5	71,8					6,01	5,58	
e030	e	Piedmont	491973	4972515						60,0	122,8					6,02	8,69	
e031	e	Piedmont	494663	4973492						53,7	150,3					4,99	5,60	
e032	e	Piedmont	486784	4974179						64,1	70,0					2,67	5,80	
e033	e	Piedmont	493372	4971916						61,2	199,5					5,36	6,49	
e034	e	Piedmont	493928	4971812						39,1	220,4					8,68	11,02	
e035	e	Piedmont	493083	4972303						57,2	265,4					9,67	8,42	
e036	e	Piedmont	487973	4986395						27,6	97,6					6,81	9,20	
e037	e	Piedmont	489423	4956922						148,6	89,0					9,10	6,77	
e038	e	Piedmont	488561	4967123						40,0	60,2					5,58	9,06	
e039	e	Piedmont	488706	4962620						26,0	104,9					5,40	8,73	
e040	e	Piedmont	491124	4983669						20,4	116,8					12,23	11,81	
e041	e	Piedmont	490436	4979385						17,0	50,3					6,30	9,08	
e042	e	Piedmont	485656	4975804						51,7	56,2					4,25	5,31	
e043	e	Piedmont	494196	4977943						34,7	136,7					6,25	9,15	
e044	e	Piedmont	492494	4974964						27,2						3,96	5,35	
e045	e	Piedmont	495232	4972492						44,3	103,4					4,02	5,67	
e046	e	Piedmont	492587	4977994						44,0	75,2					2,10	6,95	
e047	e	Piedmont	488583	4984465						22,1	68,5					4,56	8,08	
e048	e	Piedmont	484862	4977827						64,4	44,2					1,24	5,84	
e049	e	Piedmont	482842	4979641						56,5	66,6					4,09	6,37	
e050	e	Piedmont	465045	4968123						137,0	241,1					10,38	6,48	
e051	e	Piedmont	479650	4965004						77,5	49,3					3,44	5,77	
e052	e	Piedmont	463244	4964633						82,1	57,9					5,22	5,92	
e053	e	Piedmont	475761	4961435						65,1	46,2					7,74	7,36	
e054	e	Piedmont	460854	4968958						96,4	72,1					5,70	7,10	
e055	e	Piedmont	465119	4975128						54,1	41,2					6,80	7,23	
e056	e	Piedmont	466835	4964359						21,4	87,9					5,19	11,97	
e057	e	Piedmont	469912	4963199						61,1	44,5					3,75	4,98	
e058	e	Piedmont	468484	4962097						37,1	50,2					1,51	9,67	
e059	e	Piedmont	469408	4967126						27,2	31,4					2,02	7,18	
e060	e	Piedmont	475037	4968962						91,4	42,5					2,35	6,33	
e061	e	Piedmont	481167	4965702						91,5	45,3					2,59	5,28	
e062	e	Piedmont	477974	4958894						37,3	20,7					2,69	6,26	
e063	e	Piedmont	485523	4960304						46,8	49,4					2,29	5,20	
e064	e	Piedmont	483024	4962478						65,0	33,9					1,18	5,38	
e065	e	Piedmont	466464	4990993						19,0						5,18	4,92	
e066	e	Piedmont	466326	4995649						19,5	55,0					6,19	10,18	
e067	e	Piedmont	467813	4993952		9,6	1,1			19,5	37,9					9,56	10,51	
e068	e	Piedmont	459189	5003082		9,0	1,6			11,4	50,0					10,31	7,63	
e069	e	Piedmont	471018	4986500						30,7	111,0					10,36	9,74	
e070	e	Piedmont	458300	4989452						48,4						10,89	8,51	
e071	e	Piedmont	457903	4989515						29,3						13,53	8,81	

Tab.S1

ID	ID_Ref	Region	X_utm32_wgs84	Y_utm32_wgs84	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	HCO <sub>3</sub> - mg/l	Cl- mg/l	NO <sub>3</sub> <sup>-</sup> mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	B μg/L	Sr mg/L	δ11B	δ <sup>15</sup> N <sub>NO3</sub>	δ <sup>18</sup> O <sub>NO3</sub>	1/B
e072	e	Piedmont	461870	4991775							24,3					15,70	11,09	
e073	e	Piedmont	459782	4992323	139,0	30,0	17,8	1,4			25,1	72,0				18,20	15,09	
e074	e	Piedmont	466224	4993515							11,3					7,26	20,98	
e075	e	Piedmont	459189	5003082							12,0					6,54	17,21	
e076	e	Piedmont	463923	4998150							21,1					5,78	4,42	
e077	e	Piedmont	463234	4993784							30,0					5,74	14,52	
e078	e	Piedmont	456933	4995141							82,6	128,0				6,93	5,12	
e079	e	Piedmont	463234	4993784							38,3					7,08	5,05	
e080	e	Piedmont	469195	4988981							109,4	145,0				9,74	4,88	
e081	e	Piedmont	460628	4997925							14,4					5,20	6,83	
e082	e	Piedmont	465337	4993582							26,6	55,0				5,22	7,93	
e083	e	Piedmont	456933	4995141							10,1					5,80	7,19	
e084	e	Piedmont	466464	4990993							15,7					6,06	8,16	
e085	e	Piedmont	456828	5066556							11,0	4,0				0,97	7,44	
e086	e	Piedmont	460240	5060179							25,0	16,0				3,74	5,77	
e087	e	Piedmont	465592	5047028							17,0	12,0				3,77	8,30	
e088	e	Piedmont	470340	5055679							17,0	7,0				4,04	4,60	
e089	e	Piedmont	454870	5050168							25,0	26,0				4,25	6,24	
e090	e	Piedmont	478555	5034192							29,0	32,0				4,34	5,06	
e091	e	Piedmont	478138	5038012							19,0	22,0				4,44	6,42	
e092	e	Piedmont	478252	5027190							14,0	22,0				4,45	4,54	
e093	e	Piedmont	458840	5062793							19,7	17,5				3,35	7,41	
e094	e	Piedmont	468954	5052339							15,0					4,41	9,10	
e095	e	Piedmont	471442	5056239							22,0					4,49	8,54	
e096	e	Piedmont	476204	5043776							33,0	26,0				2,29	4,08	
e097	e	Piedmont	471509	5046136							16,7	14,4				4,62	10,69	
e098	e	Piedmont	474493	5034184							7,9					4,28	10,05	
e099	e	Piedmont	458239	5061171							94,1	59,5				1,21	7,10	
e100	e	Piedmont	471509	5046136							13,0	7,0				6,01	6,51	
e101	e	Piedmont	469736	5034064							15,0	20,0				6,60	7,03	
e102	e	Piedmont	471196	5031197							22,0	62,0				9,45	11,84	
e103	e	Piedmont	485082	5027522							15,0	23,0				12,58	7,86	
e104	e	Piedmont	456833	5067760							12,0					6,83	7,88	
e105	e	Piedmont	485082	5027522							19,3	34,9				8,85	13,77	
e106	e	Piedmont	463236	5067150							13,0	9,0				2,61	4,78	
e107	e	Piedmont	472261	5047318							11,0					5,24	6,81	
e108	e	Piedmont	471956	5049539							20,0	10,0				5,30	5,32	
e109	e	Piedmont	471196	5031197							12,0					8,94	12,39	
e110	e	Piedmont	464736	5063151							16,7	14,4				2,15	19,37	
e111	e	Piedmont	456398	5041139							11,0	13,0				2,86	10,02	
e112	e	Piedmont	457015	5057958							11,0	8,0				3,14	4,69	
e113	e	Piedmont	463996	5061877							20,0	18,0				3,17	8,22	
e114	e	Piedmont	469416	5061101							17,0	17,0				3,62	4,05	
e115	e	Piedmont	450748	5055887							15,0	17,0				3,71	10,30	
e116	e	Piedmont	457259	5044236							9,0	9,0				3,73	5,45	
e117	e	Piedmont	469736	5034064							6,0					6,41		
e118	e	Piedmont	464753	5063201							9,9	18,8				2,57		
e119	e	Piedmont	466326	4995649							16,2	55,0				6,28		
e120	e	Piedmont	461039	4997766							16,1	52,0				8,72		
e121	e	Piedmont	467813	4993952							19,2	51,0				10,37		
e122	e	Piedmont	469234	4989508							25,4					17,33		
e123	e	Piedmont	476520	4971479							17,0					5,07		
f01	f	Lombardy	493041	5028324							9,0	22,0	28,0			7,46	1,30	
f02	f	Lombardy	528822	5029930							14,1	18,7	33,4			7,88	6,10	
f03	f	Lombardy	513617	5030717							22,3	18,4	65,1			9,30	8,00	
f04	f	Lombardy	514355	5032577							34,0	18,4	92,0			9,31	8,00	
f05	f	Lombardy	514970	5041096							20,0	37,1	45,0			7,80	3,20	
f06	f	Lombardy	496616	5022281							5,0	15,0	17,0			6,40	2,10	
f07	f	Lombardy	515822	5024218							16,1	28,3	66,7			11,18	9,80	
f08	f	Lombardy	563866	5036331							15,0	70,0	41,0			8,59	2,10	
f09	f	Lombardy	559892	5049743							22,0	47,0	30,0			7,26	4,60	
f10	f	Lombardy	548548	5035688							20,0	29,0	47,0			7,31	1,80	
f11	f	Lombardy	562001	5058360							21,0	32,0	27,0			8,47	6,00	
f12	f	Lombardy	553596	5042830							24,0	38,0	41,0			6,20	15,00	
f13	f	Lombardy	539545	5055784							11,0	23,0	10,0			2,90	13,70	
f14	f	Lombardy	568803	5009996							58,0	90,0	49,0			6,33	21,00	
f15	f	Lombardy	544971	5024210							9,0	19,0	33,0			4,70	23,50	
f16	f	Lombardy	589971	4997061							41,0	64,0	97,0			13,57	8,90	
f17	f	Lombardy	615365	5028468	126,5	40,9	17,5	1,7	556,0	15,0	20,0	39,0			7,06	6,20		
f18	f	Lombardy	624058	5020051	133,9	41,1	26,9	2,7	543,1	29,0	55,0	44,0			6,54	4,10		
f19	f	Lombardy	620940	5026211							101,0	103,0	48,0			8,94	3,50	
f20	f	Lombardy	520438	5068626							11,3	27,2	33,9			7,00	17,40	
f21	f	Lombardy	531007	5061247	107,9	27,9	14,7	1,4	438,8	12,6	28,7	25,8			6,40	23,40		
f22	f	Lombardy	529908	5057897							15,3	43,8	32,4			4,00	18,80	
f23	f	Lombardy	533899	5057514							13,7	44,3	37,7			6,93	5,70	
f24	f	Lombardy	537693	5005134							12,0	30,8	49,0			10,71	1,90	
f25	f	Lombardy	533951	5028705							12,0	28,6	44,0			9,40	5,40	
f26	f	Lombardy	537693	5005134							10,1	23,8	35,8			10,34	6,30	
f27	f	Lombardy	549085	5001796							30,8	36,1	55,1			6,67	5,30	
f28	f	Lombardy	544290	5014369							8,9	12,2	32,1			7,87	10,30	
f29	f	Lombardy	533275	5024612							9,4	9,6	30,8			8,27		
f30	f	Lombardy	534332	5022963							10,2	16,0	32,6			8,46	7,90	
f31	f	Lombardy	547287	5002311							12,9	10,3	37,3			12,72	13,40	

Tab.S1

ID	ID_Ref	Region	X_utrm32_wgs84	Y_utrm32_wgs84	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	HCO <sub>3</sub> -mg/l	Cl- mg/l	NO <sub>3</sub> <sup>-</sup> mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	B μg/L	Sr mg/L	δ11B	δ <sup>15</sup> N <sub>NO3</sub>	δ <sup>18</sup> O <sub>NO3</sub>	1/B
f32	f	Lombardy	533951	5028705	114,2	29,6	13,6	1,2	420,5	35,0	22,3	36,0			9,01	10,00		
f33	f	Lombardy	525988	5046721	114,2	28,3	37,3	3,8	496,4	13,0	42,1	34,0			9,80	9,10		
f34	f	Lombardy	532141	5055504	114,2	28,3	19,3	14,7	1,4	415,7	2,0	0,5	7,0			6,60	6,20	
f35	f	Lombardy	522342	5053228	91,0	19,3	14,7									7,70		
f36	f	Lombardy	522337	5053228														
f37	f	Lombardy	531106	5045918	114,9	28,3	14,8	1,4	452,6	11,0	41,8	25,0			5,30	11,30		
f38	f	Lombardy	533405	5047226														
f39	f	Lombardy	531930	5047331	119,7	27,3	21,4	2,0	450,8	12,0	54,2	32,0			5,60	2,90		
f40	f	Lombardy	497294	5050263	101,3	23,4	14,9	1,5	399,9	13,0	46,8	13,0			8,50	10,30		
f41	f	Lombardy	517804	5044121	105,6	22,2	36,9	3,7	436,1	18,0	37,8	36,0			6,90	3,70		
f42	f	Lombardy	519374	5044675	127,0	28,7	9,0	0,8	443,5	20,0	39,9	37,0			4,70	10,10		
f43	f	Lombardy	516441	5046496	108,7	21,1	19,7	2,0	401,6	18,0	35,0	31,0			7,70	6,40		
f44	f	Lombardy	534800	5043750	111,0	31,0	10,2	1,1	426,6	14,0	49,2	30,0			5,70	6,70		
f45	f	Lombardy	501905	5045399	102,3	23,1	9,6	1,0	367,8	15,0	44,6	27,0			7,40	3,20		
f46	f	Lombardy	522803	5054423	108,3	20,2	36,2	3,5	472,0	14,0	20,2	21,0			7,60	8,40		
f47	f	Lombardy	519490	5050757	118,6	27,6	12,8	1,2	418,5	24,0	45,5	32,0			7,40	4,60		
f48	f	Lombardy	518964	5046347	100,3	21,2	11,6	1,2	410,5	6,0	15,6	10,0			6,20	4,70		
f49	f	Lombardy	520250	5048953	118,5	30,2	16,8	1,6	413,4	31,0	45,3	38,0			7,80	3,70		
f50	f	Lombardy	521555	5048668	100,1	20,7	8,6	0,7	393,6	14,0	11,1	13,0			5,70	7,20		
f51	f	Lombardy	522578	5051352	111,3	22,6	12,8	1,2	357,7	24,0	48,0	42,0			8,60	9,10		
f52	f	Lombardy	520272	5047203	80,4	18,2	63,9	6,3	396,9	26,0	46,9	32,0			8,40	4,20		
f53	f	Lombardy	516997	5048940	114,4	25,7	14,7	1,3	435,4	17,0	27,7	27,0			7,80	3,40		
f54	f	Lombardy	497553	5045600	115,7	27,2	18,6	1,9	447,4	12,0	41,2	41,0			7,00	7,60		
f55	f	Lombardy	498916	5043857	114,9	28,4	19,5	2,0	451,4	19,0	35,7	26,0			5,70	2,40		
f56	f	Lombardy	506569	5039111	103,6	23,4	13,0	1,4	352,5	26,0	35,4	41,0			6,20	6,50		
f57	f	Lombardy	529324	5044669	115,6	28,9	54,3	5,4	524,9	32,0	31,1	43,0			7,80	6,60		
f58	f	Lombardy	500523	5043121	121,5	26,4	42,8	4,2	512,6	25,0	52,3	32,0			8,20	4,70		
f59	f	Lombardy	502417	5041234	107,9	20,4	10,0	1,0	368,7	16,0	42,0	38,0			7,10	4,90		
f60	f	Lombardy	502975	5040918	86,7	19,9	75,3	7,5	431,8	32,0	49,7	52,0			8,90	4,50		
f61	f	Lombardy	505454	5043333	97,5	24,5	40,5	4,0	430,5	29,0	35,2	34,0			6,20	5,20		
f62	f	Lombardy	531370	5056292	114,5	26,5	21,2	2,1	419,2	20,0	56,9	45,0			9,20	7,70		
f63	f	Lombardy	519407	5041093	101,3	29,4	37,8	3,8	440,9	23,0	43,0	44,0			7,10	3,30		
f64	f	Lombardy	517812	5043240	93,2	20,5	12,6	1,3	353,8	10,0	28,5	26,0			4,20	25,50		
f65	f	Lombardy	532711	5053357	118,2	27,9	10,9	1,0	420,1	18,0	61,5	39,0			8,10	6,40		
f66	f	Lombardy	520178	5056657	95,1	24,1	28,9	2,9	406,4	17,0	28,3	28,0			6,70	19,70		
f67	f	Lombardy	498592	5040230	92,7	18,2	42,3	4,2	394,1	18,0	35,2	39,0			6,60	6,00		
f68	f	Lombardy	520577	5050592														
f69	f	Lombardy	520672	5051200	95,4	18,2	33,2	3,3	424,2	14,0	11,1	27,0			7,00	1,70		
g01	g	Emilia Romagna	576781	4974605	122,0	12,0	11,6	0,9	378,0	12,0	38,7	27,1			4,40			
g02	g	Emilia Romagna	562232	4982593	68,0	37,0	8,7	1,1	344,0	7,1	26,4	33,9			4,70			
g03	g	Emilia Romagna	599308	4951457	116,0	15,0	14,5	2,2	388,0	20,8	31,5	18,9			4,80			
g04	g	Emilia Romagna	538697	4989136	149,0	16,0	14,4	1,1	424,0	12,8	54,6	62,4			4,90			
g05	g	Emilia Romagna	564126	4970912	124,0	12,0	13,1	0,9	367,0	15,9	49,4	31,2			5,10			
g06	g	Emilia Romagna	556345	4987168	96,0	33,0	9,7	1,2	381,0	19,1	37,8	33,9			5,20			
g07	g	Emilia Romagna	553569	4985083	75,0	33,0	8,7	1,0	350,0	15,5	25,4	19,8			5,30			
g08	g	Emilia Romagna	601777	4966075	111,0	32,0	14,9	2,3	410,0	49,6	32,1	28,7			5,50			
g09	g	Emilia Romagna	543267	4989422	108,0	20,0	17,8	2,2	355,0	11,4	27,4	72,5			5,70			
g10	g	Emilia Romagna	596389	4967092	94,0	23,0	18,7	2,2	322,0	49,5	22,9	37,3			5,70			
g11	g	Emilia Romagna	600018	4965233	101,0	30,0	21,2	2,4	350,0	46,9	39,8	46,0			5,70			
g12	g	Emilia Romagna	587645	4965709	132,0	23,0	20,9	2,9	418,0	23,7	40,5	74,2			6,10			
g13	g	Emilia Romagna	587835	4966475	132,0	24,0	21,3	2,9	420,0	24,3	39,5	74,1			6,10			
g14	g	Emilia Romagna	534577	4989122	142,0	15,0	29,8	1,3	429,0	24,8	51,9	64,9			6,30			
g15	g	Emilia Romagna	549941	4975079	91,0	20,0	13,2	0,9	363,0	13,2	15,3	19,4			6,50			
g16	g	Emilia Romagna	712815	4918280	136,0	26,0	39,2	1,3	512,0	45,2	57,1	46,5			6,60			
g17	g	Emilia Romagna	780409	4887176	93,0	18,0	33,4	2,4	271,0	27,3	25,6	98,8			7,00			
g18	g	Emilia Romagna	677371	4930065	180,0	34,0	24,2	3,8	501,0	43,3	49,6	155,7			7,10			
g19	g	Emilia Romagna	720960	4915864	126,0	33,0	36,0	1,9	508,0	38,9	25,9	30,9			7,30			
g20	g	Emilia Romagna	713915	4917802	137,0	31,0	37,8	3,5	453,0	51,6	32,8	89,3			7,50			
g21	g	Emilia Romagna	565600	4974911	154,0	18,0	12,1	1,7	417,0	24,8	66,3	64,5			7,50			
g22	g	Emilia Romagna	609194	4955105	153,0	13,0	19,8	2,1	411,0	32,8	42,6	71,6			7,60			
g23	g	Emilia Romagna	620369	4952777	129,0	13,0	15,7	2,5	377,0	27,5	26,4	43,6			7,90			
g24	g	Emilia Romagna	652199	4940532	156,0	47,0	44,1	2,6	524,0	82,0	55,2	111,7			8,10			
g25	g	Emilia Romagna	651337	4943547	163,0	30,0	93,5	3,4	486,0	99,5	57,5	162,6			8,10			
g26	g	Emilia Romagna	783535	4884930	152,0	24,0	75,5	3,5	422,0	90,9	78,4	108,8			8,20			
g27	g	Emilia Romagna	623882	4955056	122,0	18,0	13,6	1,6	405,0	17,7	19,6	35,5			8,30			
g28	g	Emilia Romagna	650966	4943383	167,0	27,0	104,5	3,1	478,0	106,3	67,8	183,9			8,40			
g29	g	Emilia Romagna	620316	4952802	127,0	14,0	13,1	1,5	393,0	26,5	22,7	37,6			8,40			
g30	g	Emilia Romagna	641709	4945274	156,0	24,0	89,0	2,7	332,0	133,6	29,2	212,0			8,40			
g31	g	Emilia Romagna	617540	4947473	154,0	19,0	21,6	3,9	455,0	31,4	37,3	73,7			8,70			
g32	g	Emilia Romagna	738412	4901001	175,0	44,0	88,0	2,7	471,0	260,3	71,1	40,6			8,80			
g33	g	Emilia Romagna	605029	4948612	122,0	14,0	22,1	2,4	365,0	33,6	37,9	46,1			8,80			
g34	g	Emilia Romagna	649232	4944424	152,0	21,0	87,3	2,8	351,0	114,3	37,7	186,2			8,90			
g35	g	Emilia Romagna	745455	4902363	150,0	42,0	34,4	4,2	526,0	52,5	32,6	83						

Tab.S1

ID	ID_Ref	Region	X_utm32_wgs84	Y_utm32_wgs84	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	HCO <sub>3</sub> -mg/l	Cl- mg/l	NO <sub>3</sub> <sup>-</sup> mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	B μg/L	Sr mg/L	δ <sub>118</sub> B	δ <sup>15</sup> N <sub>NO3</sub>	δ <sup>18</sup> O <sub>NO3</sub>	1/B
g46	g	Emilia Romagna	632964	4942926	176,0	26,0	40,8	1,9	509,0	86,3	60,9	62,2			11,60			
g47	g	Emilia Romagna	582112	4967511	151,0	76,0	108,0	2,7	584,0	230,5	43,9	104,3			11,70			
g48	g	Emilia Romagna	649899	4934980	144,0	28,0	41,0	3,6	433,0	62,9	63,2	85,3			12,20			
g49	g	Emilia Romagna	649207	4935883	141,0	22,0	30,5	1,8	446,0	39,2	70,5	50,8			10,93	17,96	6,00	
g50	g	Emilia Romagna	614094	4946483	150,0	22,0	16,4	2,0	494,0	23,4	32,7	56,4				13,40		
g51	g	Emilia Romagna	610407	4958830	139,0	18,0	15,8	3,1	430,0	30,0	19,1	62,6				13,60		
g52	g	Emilia Romagna	591039	4955932	141,0	44,0	32,9	2,0	525,0	49,1	26,9	91,7				13,70		
h01	h	Emilia Romagna	548256	4983171	70,0	38,0	10,3	1,2	347,0	20,3	26,0	26,7				7,60		
h02	h	Emilia Romagna	558124	4978424	83,0	19,5	9,8	1,1	300,0	8,1	16,4	32,7				6,80		
h03	h	Emilia Romagna	556368	4987175	96,0	33,0	9,2	1,0	379,0	18,8	35,0	33,2				10,60		
h04	h	Emilia Romagna	553328	4989133	76,1	38,6	11,3	1,4	381,6	21,2	35,1	31,6				37,50		
h05	h	Emilia Romagna	554013	4987077	71,0	38,4	9,9	1,3	365,7	21,0	32,2	27,1				4,20		
h06	h	Emilia Romagna	554636	4983242	99,0	27,0	13,7	1,5	375,0	23,0	37,0	32,5				22,70		
h07	h	Emilia Romagna	558819	4982684	89,2	17,9	11,4	1,2	318,7	17,1	14,1	37,9				9,80		
h08	h	Emilia Romagna	561560	4982936	88,0	29,0	10,1	1,5	330,0	11,9	39,3	47,4				17,90		
h09	h	Emilia Romagna	551433	4980393	112,0	20,8	14,3	1,6	400,1	23,7	56,2	35,0				8,10		
h10	h	Emilia Romagna	561657	4979721	100,8	26,5	11,0	1,3	406,5	7,6	49,7	32,7				5,10		
h11	h	Emilia Romagna	555762	4973718	91,5	18,5	9,8	1,2	341,7	9,0	16,6	33,2				21,70		
h12	h	Emilia Romagna	545283	4987098	92,4	20,2	18,4	1,3	361,0	18,8	28,8	31,6				22,70		
h13	h	Emilia Romagna	550216	4988139	88,5	21,4	10,6	1,3	345,4	15,8	25,0	27,1				18,80		
h14	h	Emilia Romagna	547015	4987207	72,4	19,4	10,2	1,4	296,3	17,2	3,2	32,5				1,00		
h15	h	Emilia Romagna	550894	4981544	82,0	21,1	8,8	1,4	319,3	18,8	23,0	30,1				6,90		
h16	h	Emilia Romagna	549316	4979415	105,2	19,7	17,8	1,6	384,5	21,3	53,0	29,4				25,60		
h17	h	Emilia Romagna	557404	4981514	99,2	27,2	12,3	1,3	410,4	12,5	49,3	30,0				8,40		
i001	i	Emilia Romagna	544501	4991342	126,0	29,0	15,0	2,2	425,0	19,8	48,4	59,4				6,52		
i002	i	Emilia Romagna	543035	4989248	108,0	21,0	17,8	2,1	356,0	11,6	26,3	71,3				5,87		
i003	i	Emilia Romagna	541800	4983036	108,0	15,0	20,6	1,7	322,0	7,0	25,7	80,7				6,32		
i004	i	Emilia Romagna	541800	4983036	110,0	15,0	20,0	1,6	334,0	10,0	29,1	82,5				6,33		
i006	i	Emilia Romagna	550223	4985279	60,0	30,0	9,4	1,0	299,0	17,3	19,3	18,2				5,15		
i007	i	Emilia Romagna	550223	4985279	59,0	30,0	9,4	1,0	308,0	16,1	18,1	17,8				5,02		
i008	i	Emilia Romagna	544821	4984662	101,0	16,0	13,2	1,5	352,0	19,8	22,9	30,1				5,36		
i009	i	Emilia Romagna	544821	4984662	102,0	16,0	14,2	1,4	347,0	18,8	23,0	29,0				5,29		
i010	i	Emilia Romagna	539677	4989142	174,0	20,0	18,0	1,9	409,0	64,8	67,6	78,4				6,10		
i012	i	Emilia Romagna	548256	4983171	70,0	34,0	9,8	1,3	328,0	20,1	26,8	26,9				4,60		
i013	i	Emilia Romagna	548256	4983171	70,0	33,0	11,0	1,4	332,0	20,9	28,3	29,1				4,56		
i014	i	Emilia Romagna	558124	4978424	81,0	20,0	9,8	1,1	310,0	6,5	17,7	34,4				5,85		
i015	i	Emilia Romagna	571876	4979122	97,0	21,0	18,4	1,4	334,0	30,4	20,6	38,2				7,67		
i016	i	Emilia Romagna	561560	4982936	90,0	30,0	10,6	1,6	333,0	12,2	37,2	46,3				6,12		
i017	i	Emilia Romagna	561560	4982936	91,0	28,0	10,2	1,6	341,0	12,8	45,4	50,2				5,92		
i018	i	Emilia Romagna	561748	4979167	85,0	31,0	9,6	1,0	353,0	9,1	38,9	28,8				4,85		
i019	i	Emilia Romagna	561748	4979167	86,0	33,0	8,8	1,0	354,0	9,7	49,7	32,7				4,82		
i020	i	Emilia Romagna	561748	4979167	85,0	33,0	9,0	1,1	354,0	10,0	49,1	33,4				4,79		
i021	i	Emilia Romagna	564576	4973062	104,0	19,0	17,4	2,8	374,0	13,4	6,6	47,7				6,90		
i022	i	Emilia Romagna	570745	4975518	71,0	13,0	18,4	1,1	292,0	9,0	8,4	22,8				8,06		
i023	i	Emilia Romagna	576776	4975262	141,0	15,0	14,8	2,4	400,0	18,7	45,7	40,8				4,00		
i024	i	Emilia Romagna	576776	4975262	140,0	14,0	13,4	2,3	404,7	21,8	49,6	50,5				4,95		
i025	i	Emilia Romagna	576992	4971935	152,0	17,0	14,2	1,3	417,0	26,4	53,7	51,8				7,71		
i026	i	Emilia Romagna	576992	4971935	156,0	16,0	13,2	1,3	431,0	27,1	56,1	54,8				7,34		
i027	i	Emilia Romagna	571666	4970802	139,0	8,0	8,4	1,0	384,0	16,1	41,5	30,5				6,38		
i028	i	Emilia Romagna	571666	4970802	144,0	8,0	8,6	1,0	383,0	18,2	50,5	36,4				5,83		
i029	i	Emilia Romagna	545052	4982678	88,0	13,0	12,0	0,9	301,0	16,6	25,2	15,1				4,82		
i030	i	Emilia Romagna	545052	4982678	88,0	14,0	11,8	1,0	307,0	17,9	24,1	18,0				5,13		
i031	i	Emilia Romagna	535348	4990175	132,0	17,0	42,0	2,9	465,0	45,8	27,3	45,8				7,80		
i032	i	Emilia Romagna	529901	4988453	127,0	25,0	31,0	1,3	459,0	30,8	48,5	41,3				6,77		
i033	i	Emilia Romagna	547842	4989286	48,0	10,0	10,4	1,0	182,0	14,9	3,7	21,9				3,86		
i035	i	Emilia Romagna	554672	4986795	80,0	34,0	11,2	1,3	332,0	27,5	40,0	31,3				4,91		
i036	i	Emilia Romagna	554672	4986795	78,0	35,0	10,8	1,3	341,0	25,9	38,3	30,9				4,89		
i037	i	Emilia Romagna	556115	4987071	92,0	33,0	9,8	1,5	373,0	22,7	40,2	32,7				5,35		
i038	i	Emilia Romagna	552510	4987232	75,0	42,0	9,0	1,2	367,0	20,3	42,2	29,0				5,00		
i039	i	Emilia Romagna	560598	4984311	75,0	21,0	9,2	1,3	290,0	10,7	18,9	35,5				5,98		
i040	i	Emilia Romagna	560598	4984311	73,0	21,0	9,6	1,3	287,0	10,7	18,8	35,4				6,27		
i042	i	Emilia Romagna	552038	4988753	76,0	36,0	10,8	1,3	337,0	21,7	40,5	33,1				4,62		
i043	i	Emilia Romagna	552038	4988753	76,0	36,0	10,6	1,3	344,0	20,9	38,8	32,6				4,57		
i045	i	Emilia Romagna	549936	4975082	88,0	20,0	12,8	0,9	354,0	13,0	14,2	18,5				7,05		
i046	i	Emilia Romagna	546455	4977666	55,0	25,0	22,0	0,7	319,0	11,4	3,0	11,4				5,25		
i047	i	Emilia Romagna	554636	4983242	101,0	26,0	15,2	1,7	360,0	25,8	44,5	35,0				5,18		
i048	i	Emilia Romagna	554636	4983242	100,0	27,0	14,2	1,5	373,0	24,6	40,7	33,9				5,15		
i049	i	Emilia Romagna	538757	4983742	110,0	22,0	23,6	3,0	387,0	16,3	27,1	64,4				6,11		
i050	i	Emilia Romagna	538757	4983742	111,0	22,0	22,8	2,7	403,0	17,0	27,4	64,9				6,09		
i051	i	Emilia Romagna	535397	4985202	140,0	13,0	25,6	1,3	441,0	23,6	36,8	44,7				6,71		
i052	i	Emilia Romagna	542157	4980882	103,0	20,0	23,8	2,4	335,0	12,3	26,9	79,0				7,62		
i053	i	Emilia Romagna	539875	4985107	88,0	18,0	20,8	2,6	302,0	10,3	13,7	76,8				5,74		

Tab.S1

ID	ID_Ref	Region	X_utrm32_wgs84	Y_utrm32_wgs84	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	HCO3- mg/l	Cl- mg/l	NO3- mg/l	SO4 <sup>2-</sup> mg/l	B μg/L	Sr mg/L	δ11B	δ <sup>15</sup> N <sub>NO3</sub>	δ <sup>18</sup> O <sub>NO3</sub>	1/B
i054	i	Emilia Romagna	545955	4979996	78,0	19,0	15,0	0,9	315,0	20,8	14,2	16,1				5,13		
i055	i	Emilia Romagna	537913	4990148	150,0	16,0	18,2	1,2	454,0	19,5	35,1	61,8				5,89		
i056	i	Emilia Romagna	533497	4977012	95,0	27,0	31,0	4,1	374,0	7,5	15,3	106,1				7,40		
i057	i	Emilia Romagna	546514	4972736	55,0	11,0	11,0	1,1	198,0	13,7	3,4	26,6				3,50		
i058	i	Emilia Romagna	552398	4984614	88,5	32,1	11,4	1,3	331,0	20,9	48,2	30,8				5,18		
i059	i	Emilia Romagna	553378	4989016	72,0	37,0	9,0	1,2	343,0	20,1	32,8	29,7				4,70		
i060	i	Emilia Romagna	551660	4988894	97,2	34,1	14,4	1,5	364,9	26,9	60,2	40,2				4,80		
i061	i	Emilia Romagna	559034	4989406	74,0	33,0	11,0	1,5	353,0	18,6	20,1	24,3				5,68		
i062	i	Emilia Romagna	562766	4988133	80,0	25,0	11,0	1,4	309,0	13,7	19,7	46,8				6,03		
i063	i	Emilia Romagna	562766	4988133	81,0	26,0	10,8	1,4	320,0	13,6	19,5	47,6				5,90		
i064	i	Emilia Romagna	561569	4986047	73,0	24,0	10,6	1,9	300,0	12,1	24,3	41,4				6,48		
i065	i	Emilia Romagna	554932	4975673	86,0	20,6	13,3	1,6	363,0	10,9	10,4	17,4				5,36		
i066	i	Emilia Romagna	551948	4985997	100,0	38,0	15,4	1,8	440,1	27,5	76,5	37,2				6,04		
i067	i	Emilia Romagna	553353	4988857	62,8	32,3	8,6	1,2	317,1	17,0	21,6	22,9				4,59		
i068	i	Emilia Romagna	549946	4984346	87,1	37,7	10,4	1,4	364,7	21,5	46,6	36,0				4,28		
i069	i	Emilia Romagna	536651	4984891	166,3	13,4	14,8	1,8	431,0	15,8	70,4	68,4				4,73		
i070	i	Emilia Romagna	553008	4975209	123,0	16,6	11,4	1,0	379,8	14,1	40,1	37,2				5,20		
i071	i	Emilia Romagna	558969	4982654	118,3	29,9	14,2	3,1	393,6	20,1	64,7	62,6				6,45		
i072	i	Emilia Romagna	561237	4978554	84,1	33,2	9,5	1,6	362,8	14,6	83,4	48,2				4,37		
i073	i	Emilia Romagna	560615	4991967	161,9	28,0	16,1	47,6	500,2	22,8	131,9	94,8				7,61		
i074	i	Emilia Romagna	559437	4982821	99,7	24,8	11,3	2,4	359,8	12,9	48,6	50,7				5,99		
i075	i	Emilia Romagna	559437	4982821	108,0	26,0	11,2	2,5	356,9	15,0	47,9	52,7				6,05		
i076	i	Emilia Romagna	559637	4983125	84,5	20,9	11,4	1,9	301,2	14,4	22,6	40,3				5,95		
i077	i	Emilia Romagna	551025	4985950	90,0	35,4	13,9	1,5	323,0	23,0	58,5	36,0				5,15		
i078	i	Emilia Romagna	557905	4989982	93,8	34,2	8,5	1,4	380,0	13,2	36,5	40,9				5,16		
i079	i	Emilia Romagna	559439	4976916	111,3	26,5	7,9	1,5	381,0	10,2	62,2	39,0				5,14		
i080	i	Emilia Romagna	562813	4981618	87,8	31,2	8,2	1,2	354,0	8,9	48,2	35,7				4,34		
i081	i	Emilia Romagna	562403	4981800	117,2	33,0	8,7	1,6	397,0	8,2	77,7	57,4				8,58		
i082	i	Emilia Romagna	553402	4977083	131,0	16,0	14,4	1,0	412,0	20,6	14,2	44,7				5,97		
i083	i	Emilia Romagna	555813	4989214	150,0	35,0	32,5	20,5	529,0	45,6	52,4	99,1				8,68		
i084	i	Emilia Romagna	555682	4989449	124,0	32,0	40,0	16,0	410,0	84,4	67,2	77,5				10,08		
i085	i	Emilia Romagna	556062	4989347	137,0	37,0	98,5	2,6	557,0	122,5	29,6	79,0				15,70		
i086	i	Emilia Romagna	529901	4988453	126,0	26,0	31,0	1,3	470,0	33,0	37,8	37,4				6,10		
i087	i	Emilia Romagna	544501	4991342	125,9	28,0	15,0	2,1	431,0	19,6	47,6	59,2				6,42		
i088	i	Emilia Romagna	543035	4989248	110,0	20,0	17,0	2,1	358,0	11,9	27,4	70,8				5,72		
i089	i	Emilia Romagna	539677	4989142	190,0	22,0	44,0	2,5	372,0	151,0	62,9	117,6				5,72		
i090	i	Emilia Romagna	537913	4990148	156,0	16,0	16,9	1,1	457,0	20,3	36,6	62,6				6,02		
i091	i	Emilia Romagna	535348	4990175	133,0	17,0	44,0	2,9	468,0	46,4	26,2	46,2				8,14		
i092	i	Emilia Romagna	558819	4982684	96,0	30,0	9,5	1,4	388,0	13,9	57,8	45,8				5,52		
i093	i	Emilia Romagna	549936	4975082	88,0	20,0	11,8	0,9	356,0	12,7	13,6	18,4				6,94		
i094	i	Emilia Romagna	553436	4977177	178,0	28,0	153,0	7,4	374,0	397,0	26,8	117,5				12,35		
i095	i	Emilia Romagna	552985	4976907	124,0	16,0	11,2	2,7	376,0	13,2	32,0	46,2				5,75		
i096	i	Emilia Romagna	561569	4986047	79,0	23,0	10,9	2,8	289,0	12,7	23,1	42,3				6,36		
i097	i	Emilia Romagna	553378	4989016	72,0	36,0	9,8	2,7	326,0	19,3	32,4	29,7				4,58		
i098	i	Emilia Romagna	557969	4987833	105,0	30,0	9,1	1,4	362,0	14,5	43,0	42,6				5,24		
i099	i	Emilia Romagna	559034	4989406	78,0	33,0	10,7	1,4	341,0	18,4	21,5	25,4				5,71		
i100	i	Emilia Romagna	534992	4983271	121,0	24,0	10,6	1,3	420,9	12,3	39,8	44,9				6,95		
i101	i	Emilia Romagna	535257	4985016	130,0	33,0	10,2	1,3	430,7	23,4	51,7	54,8				6,73		
i102	i	Emilia Romagna	553353	4988857	109,0	20,0	9,6	1,4	403,2	18,4	22,3	24,2				4,61		
i103	i	Emilia Romagna	543247	4967247	126,0	21,0	8,8	1,1	422,5	11,9	2,7	40,2				3,59		
i104	i	Emilia Romagna	542347	4967194	114,0	28,0	9,0	1,2	415,6	12,5	2,3	44,4				3,02		
i105	i	Emilia Romagna	545303	4971331	131,0	32,0	12,0	1,3	416,9	24,8	2,3	39,8				3,35		
i106	i	Emilia Romagna	556115	4987071	97,0	31,0	9,9	1,3	357,0	18,5	39,3	35,4				5,26		
i107	i	Emilia Romagna	552510	4987232	76,0	41,0	9,6	1,2	348,0	20,2	43,2	29,2				5,30		
i108	i	Emilia Romagna	559524	4992002	54,0	31,0	11,3	1,3	312,0	21,1	1,5	7,0				6,41		
I001	I	Veneto	657689	5039736	132,0	8,7	5,6	7,7	216,0	7,7	26,8	38,0				9,03		
I002	I	Veneto	657689	5039736	165,0	8,9	9,9	8,2	218,0	6,3	33,0	72,0				9,71		
I003	I	Veneto	648740	5033715	73,0	28,1	6,4	24,9	272,0	7,9	12,3	36,0				5,26		
I004	I	Veneto	648740	5033715	79,0	28,8	7,3	27,3	276,0	3,0	16,7	35,0				6,85		
I005	I	Veneto	650907	5038100	130,0	6,8	4,7	5,8	242,0	5,3	38,7	28,0				4,72		
I006	I	Veneto	650907	5038100	180,0	8,2	6,2	7,6	250,0	6,1	37,0	37,0				6,07		
I007	I	Veneto	660704	5034831	84,0	12,7	3,9	12,0	265,0	4,2	10,6	19,0				5,82		
I008	I	Veneto	660704	5034831	102,0	14,8	4,8	13,9	264,0	3,8	15,8	19,0				6,89		
I009	I	Veneto	661470	5032885	85,0	21,0	2,4	18,3	236,0	5,4	7,9	22,0				6,91		
I010	I	Veneto	661470	5032885	85,0	19,0	17,9	2,7	229,0	4,2	9,7	18,0				7,41		
I011	I	Veneto	657978	5032777	79,0	16,7	6,5	14,9	246,0	5,6	10,1	29,0				6,00		
I012	I	Veneto	657978	5032777	85,0	17,5	6,6	16,4	251,0	5,9	10,6	36,0				7,75		
I013	I	Veneto	654769	5035525	84,0	14,2	4,3	12,0	215,0	7,2	5,3	35,0				5,65		
I014	I	Veneto	654769	5035525	74,0	13,8	6,0	12,7	209,0	3,3	9,2	30,0				6,55		
I015	I	Veneto	654395	5033104	87,0	21,9	3,9	21,0	246,0	5,6	12,3	35,0				6,37		
I016	I	Veneto	654395	5033104	98,0	21,5	4,9	19,8	248,0	3,9	14,5	38,0				6,73		

Tab.S1

ID	ID_Ref	Region	X_utrm32_wgs84	Y_utrm32_wgs84	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	HCO3- mg/l	Cl- mg/l	NO3- mg/l	SO4 <sup>2-</sup> mg/l	B μg/L	Sr mg/L	δ11B	δ <sup>15</sup> N <sub>NO3</sub>	δ <sup>18</sup> O <sub>NO3</sub>	1/B
I017	I	Veneto	655542	5032441	88,0	22,6	3,9	20,9	251,0	11,4	12,8	29,0				6,29		
I018	I	Veneto	655542	5032441	93,0	22,3	4,5	21,1	255,0	6,1	13,2	37,0				6,76		
I019	I	Veneto	652877	5030752	97,0	26,2	6,0	24,8	250,0	5,7	16,7	43,0				6,56		
I020	I	Veneto	652877	5030752	97,0	27,9	6,7	26,6	248,0	4,5	19,4	40,0				7,14		
I021	I	Veneto	661764	5038626	121,0	3,8	3,9	3,5	245,0	2,4	33,4	22,0				30,56		
I022	I	Veneto	661764	5038626	163,0	3,4	9,7	2,4	226,0	11,8	43,6	9,0				6,79		
I023	I	Veneto	661764	5038626	121,0	2,2	10,0	2,4	227,0	9,0	50,2	29,0				8,20		
I024	I	Veneto	656411	5041887	90,0	3,4	1,5	3,1	226,0	2,4	11,4	1,0				4,40		
I025	I	Veneto	656411	5041887	115,0	4,9	4,5	3,2	220,0	3,4	19,8	1,0				3,72		
I026	I	Veneto	656411	5041887	126,0	3,3	2,6	3,0	219,0	5,0	17,6	7,0				8,74		
I027	I	Veneto	653152	5037507	137,0	20,9	4,8	12,4	281,0	3,3	14,1	11,0				7,95		
I028	I	Veneto	653152	5037507	139,0	21,1	4,9	11,2	276,0	4,2	2,6	18,0				7,31		
I029	I	Veneto	651567	5038638	133,0	12,2	7,8	10,5	216,0	2,6	21,6	36,0				7,95		
I030	I	Veneto	651567	5038638	177,0	18,5	11,0	12,2	212,0	4,7	17,2	42,0				7,91		
I031	I	Veneto	651567	5038638	190,0	18,6	10,9	9,6	211,0	13,4	24,6	39,0				7,98		
I032	I	Veneto	657714	5034800	118,0	10,5	7,3	9,1	283,0	2,5	33,0	22,0				12,64		
I033	I	Veneto	657714	5034800	109,0	9,5	8,8	10,2	278,0	3,8	37,0	10,0				20,78		
I034	I	Veneto	657714	5034800	143,0	13,9	9,6	11,2	277,0	8,3	21,1	20,0				10,56		
I035	I	Veneto	657714	5034800	152,0	14,7	11,7	9,0	280,0	15,6	11,4	28,0				7,89	9,50	
I036	I	Veneto	653360	5042683	85,0	2,9	3,4	2,5	232,0	2,6	20,7	10,0				9,76		
I037	I	Veneto	653360	5042683	117,0	4,1	4,7	2,2	230,0	5,2	20,2	20,0				7,92		
I038	I	Veneto	653360	5042683	119,0	4,3	5,3	2,2	229,0	8,7	20,7	12,0				6,97		
I039	I	Veneto	669766	5040167	95,0	35,3	2,9	30,2	286,0	2,6	44,0	30,0				5,94		
I040	I	Veneto	669766	5040167							10,1					7,98		
I041	I	Veneto	665778	5040861							18,9					8,74		
I042	I	Veneto	669708	5037394	94,0	32,1	6,3	30,8	208,0	6,5	22,0	23,0				7,95		
I043	I	Veneto	668067	5034456	136,0	3,2	3,2	24,4	206,0	5,7	26,8	29,0				6,56		
I044	I	Veneto	674615	5034190	113,0	19,5	6,9	16,4	229,0	2,6	18,9	35,0				7,47		
I045	I	Veneto	674615	5034190	147,0	24,8	10,5	16,0	222,0	14,7	25,1	62,0				5,67		
I046	I	Veneto	674615	5034190	139,0	21,9	8,5	20,8	275,0	13,6	21,6	41,0				7,27		
I047	I	Veneto	674692	5032201	82,0	17,3	7,5	11,2	306,0	11,9	4,4	1,0				16,30		
I048	I	Veneto	674692	5032201	80,0	17,2	7,8	10,5	300,0	1,2	7,9	0,0				14,72		
I049	I	Veneto	666954	5034102	104,0	16,1	2,6	13,9	215,0	2,3	22,0	3,0				6,65		
I050	I	Veneto	666954	5034102	122,0	19,7	3,3	12,0	210,0	4,8	15,4	19,0				6,21		
I051	I	Veneto	666954	5034102	137,0	19,8	3,2	11,6	207,0	15,8	29,9	29,0				6,05		
I052	I	Veneto	666934	5032214	123,0	20,3	8,2	29,1	212,0	4,0	17,2	0,0				7,18		
I053	I	Veneto	666181	5034276	106,0	54,0	21,4	13,1	231,0	6,4	11,0	2,0				9,23		
I054	I	Veneto	666181	5034276	81,0	39,8	12,7	38,5	230,0	5,6	10,1	18,0				7,34		
I055	I	Veneto	665611	5036208	100,0	16,2	2,4	14,0	276,0	2,3	13,2	21,0				8,08		
I056	I	Veneto	665611	5036208	127,0	21,9	4,9	15,0	263,0	3,7	19,4	27,0				5,95		
I057	I	Veneto	665611	5036208	129,0	22,7	4,4	2,2	256,0	5,6	25,5	24,0				6,51		
I058	I	Veneto	658040	5037729	143,0	6,6	7,6	6,1	240,0	2,1	19,8	35,0				8,56		
I059	I	Veneto	658040	5037729	138,0	6,9	4,8	6,2	238,0	2,0	43,1	25,0				8,58		
I060	I	Veneto	658040	5037729	159,0	8,6	6,9	6,4	220,0	10,5	37,4	25,0				7,84		
I061	I	Veneto	658040	5037729	156,0	7,1	7,9	6,6	222,0	10,1	38,3	34,0				7,12	11,80	
I062	I	Veneto	658176	5037666	135,0	6,9	5,3	6,2	245,0	13,6	6,6	27,0				8,39		
I063	I	Veneto	658176	5037666	123,0	6,3	4,9	5,6	241,0	12,2	31,2	23,0				8,87		
I064	I	Veneto	658176	5037666	158,0	8,3	7,6	6,1	243,0	6,4	26,8	35,0				7,71		
I065	I	Veneto	658176	5037666	161,0	9,1	7,5	6,4	243,0	10,7	42,2	27,0				7,58		
I066	I	Veneto	649205	5043029	120,0	9,4	6,2	8,6	355,0	14,6	12,3	28,0				7,46		
I067	I	Veneto	649205	5043029	121,0	9,9	6,0	8,6	347,0	12,9	22,4	36,0				6,57		
I068	I	Veneto	649205	5043029	145,0	14,6	8,3	8,8	349,0	12,6	22,0	34,0				7,18		
I069	I	Veneto	649205	5043029	148,0	13,6	9,2	8,2	351,0	12,5	22,9	38,0				6,76		
I070	I	Veneto	646542	5040279							61,7					11,38		
I071	I	Veneto	646542	5040279							26,4					6,72		
I072	I	Veneto	646542	5040279							18,0					12,48		
I073	I	Veneto	656442	5058434							9,2					7,40		
I074	I	Veneto	656442	5058434							9,2					7,51		
m001	m	Friuli V.G.	811678	5093084	88,4	28,0	4,1	1,0	273,0	6,6	24,5	96,4	110,0	22,00		0,0090909		
m002	m	Friuli V.G.	811678	5093084	88,4	28,0	4,1	1,0	273,0	7,1	21,8	96,4				5,50	2,63	
m003	m	Friuli V.G.	811678	5093084	88,4	28,0	4,1	1,0	273,0	7,1	23,2	96,4				6,13	2,68	
m004	m	Friuli V.G.	811678	5093084	88,4	28,0	4,1	1,0	273,0	7,1	23,9	96,4				11,86	4,73	
m010	m	Friuli V.G.	824547	5090978	98,6	31,3	6,6	3,5	357,0	11,5	40,0	49,6	220,0	4,22		0,0045455		
m011	m	Friuli V.G.	824547	5090978	98,6	31,3	6,6	3,5	357,0	10,2	37,9	49,6				7,19	2,86	
m012	m	Friuli V.G.	824547	5090978	98,6	31,3	6,6	3,5	357,0	11,0	40,9	49,6				7,57	2,96	
m013	m	Friuli V.G.	824547	5090978	98,6	31,3	6,6	3,5	357,0	11,7	39,6	49,6				7,81	3,54	
m014	m	Friuli V.G.	824547	5090978	98,6	31,3	6,6	3,5	357,0	14,4	53,6	49,6				12,63	2,87	
m015	m	Friuli V.G.	819431	5088775	86,4	28,6	4,4	1,1	268,0	7,1	27,5	91,7	100,0	19,11		0,01		
m016	m	Friuli V.G.	819431	5088775	86,4	28,6	4,4	1,1	268,0	7,5	23,0	91,7				6,36	2,96	
m017	m	Friuli V.G.	819431	5088775	86,4	28,6	4,4	1,1	268,0	9,5	22,1	91,7				6,14	2,68	
m018	m	Friuli V.G.	819431	5088775	86,4	28,6	4,4	1,1	268,0	7,1	24,0	91,7				6,11	2,62	

Tab.S1

ID	ID_Ref	Region	X_utrm32_wgs84	Y_utrm32_wgs84	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	HCO3- mg/l	Cl- mg/l	NO3 <sup>-</sup> mg/l	SO4 <sup>2-</sup> mg/l	B μg/L	Sr mg/L	δ11B	δ15N <sub>NO3</sub>	δ18O <sub>NO3</sub>	1/B
m019	m	Friuli V.G.	819431	5088775	86,4	28,6	4,4	1,1	268,0	8,6	25,3	91,7			10,51	2,96		
m020	m	Friuli V.G.	827794	5090231	106,0	33,2	9,9	1,4	379,0	14,4	54,4	47,4	200,0	16,96		7,24	3,79	0,005
m021	m	Friuli V.G.	827794	5090231	106,0	33,2	9,9	1,4	379,0	13,1	51,7	47,4			7,31	3,42		
m022	m	Friuli V.G.	827794	5090231	106,0	33,2	9,9	1,4	379,0	26,1	52,7	47,4			7,52	4,02		
m023	m	Friuli V.G.	827794	5090231	106,0	33,2	9,9	1,4	379,0	14,2	53,6	47,4			10,51	2,82		
m024	m	Friuli V.G.	827794	5090231	106,0	33,2	9,9	1,4	379,0	16,1	53,2	47,4						
m025	m	Friuli V.G.	839364	5087751	85,9	21,6	3,8	1,4	332,0	7,0	26,4	12,5	170,0	11,55				0,0058824
m026	m	Friuli V.G.	839364	5087751	85,9	21,6	3,8	1,4	332,0	6,2	21,9	12,5			7,24	4,61		
m027	m	Friuli V.G.	839364	5087751	85,9	21,6	3,8	1,4	332,0	9,5	17,6	12,5			9,31	5,71		
m028	m	Friuli V.G.	839364	5087751	85,9	21,6	3,8	1,4	332,0	8,1	23,1	12,5			7,62	4,90		
m029	m	Friuli V.G.	839364	5087751	85,9	21,6	3,8	1,4	332,0	54,7	21,3	12,5			11,40	4,82		
m030	m	Friuli V.G.	831611	5089267	99,2	30,7	8,0	1,4	371,0	14,3	43,3	37,6	230,0	22,90				0,0043478
m031	m	Friuli V.G.	831611	5089267	99,2	30,7	8,0	1,4	371,0	12,8	39,8	37,6			7,45	3,88		
m032	m	Friuli V.G.	831611	5089267	99,2	30,7	8,0	1,4	371,0	12,9	40,7	37,6			7,54	3,47		
m033	m	Friuli V.G.	831611	5089267	99,2	30,7	8,0	1,4	371,0	15,0	42,7	37,6			7,38	3,25		
m034	m	Friuli V.G.	831611	5089267	99,2	30,7	8,0	1,4	371,0	16,2	38,7	37,6			9,98	3,72		
m065	m	Friuli V.G.	822225	5099951											7,44	2,22		
n01	n	Piedmont	403721	4976780	89,8	28,5	21,6	28,9	347,1	46,6	206,4	103,6			7,31	9,30		
n02	n	Piedmont	404802	4977819	98,5	26,0	12,0	1,3	314,2	30,9	153,0	111,8			6,26	8,80		
n03	n	Piedmont	407060	4976652	71,2	21,3	11,1	0,6	185,6	47,3	71,6	50,5			7,31	10,50		
n04	n	Piedmont	410724	4980876	128,3	19,1	10,4	0,4	280,2	62,4	77,1	72,8			12,14	13,70		
n05	n	Piedmont	413178	4983149	81,2	11,0	9,9	0,9	258,9	17,6	32,5	14,5			5,90	12,10		
n06	n	Piedmont	407096	4979994	96,5	23,5	20,2	2,5	280,6	62,3	114,5	71,0			16,66	14,70		
o1	o	Veneto	731006	5075308	98,0	34,0	2,8	1,0	390,0	9,0	42,0	55,9			6,29	6,27		
o2	o	Veneto	721144	5070880	99,0	33,0	6,1	1,0	380,0	13,0	43,0	63,7			6,65	7,05		
o3	o	Veneto	729725	5070493	100,0	32,0	4,2	1,2	375,0	13,0	64,0	62,1			3,2	7,35		
o4	o	Veneto	731724	5064718	115,0	31,0	6,3	1,1	415,0	12,0	75,0	68,3			6,76	4,29		
o5	o	Veneto	728323	5068483	115,0	34,0	5,7	1,0	425,0	15,0	64,0	67,0			5,54	5,06		
o6	o	Veneto	722525	5065844	112,0	34,0	7,4	1,0	415,0	15,0	69,0	71,2			5,77	4,39		
o7	o	Veneto	734717	5066341	110,0	33,0	6,2	1,2	405,0	10,0	74,0	74,6			6,71	5,58		
o8	o	Veneto	726589	5070548	115,0	37,0	7,4	1,1	450,0	17,0	60,0	60,0			6,96	7,18		
o9	o	Veneto	727461	5064486	122,0	39,0	8,6	1,3	465,0	19,0	54,0	72,7		19,49	10,42	5,96		
q01	q	Emilia Romagna	591113	4967079											7,45	5,40		
q02	q	Emilia Romagna	591057	4966908											8,24	5,20		
q03	q	Emilia Romagna	590937	4967128											7,92	5,40		
q04	q	Emilia Romagna	590979	4966760											7,64	5,10		
q05	q	Emilia Romagna	591166	4966640											7,63	5,10		
q06	q	Emilia Romagna	591105	4967061											6,90	3,60		
q07	q	Emilia Romagna	591170	4966625											7,16	5,20		
q08	q	Emilia Romagna	591049	4966331											7,22	5,50		
q09	q	Emilia Romagna	592194	4965891											7,02	6,00		
q10	q	Emilia Romagna	591479	4966387											8,10	5,10		
q11	q	Emilia Romagna	591479	4966387											13,67	2,50		
q12	q	Emilia Romagna	591479	4966387											7,46	5,40		
r2	r	Emilia Romagna	660167	4935114	163,0	26,0	97,0	3,0	410,0	151,0	36,9	228,0	672,0	1,46	2,10		0,0014881	
r3	r	Emilia Romagna	649232	4944424	163,0	24,0	99,0	4,8	398,0	148,0	34,3	224,0	534,0	1,36	22,40	11,73	5,50	0,0018727
r4	r	Emilia Romagna	663870	4935331	185,0	30,0	114,0	4,9	395,0	211,0	22,3	274,0	386,0	0,16	5,00		0,0025907	
r5	r	Emilia Romagna	617342	4945891	115,0	20,0	123,0	5,2	335,0	153,0	20,0	192,0	553,0	1,09	5,00		0,0018083	
r6	r	Emilia Romagna	614094	4946483	192,0	44,0	125,0	10,8	544,0	196,0	23,4	300,0	599,0	1,69	9,90		0,0016694	
s01	s	Lombardy	530338	4990127	133,1	30,9	34,7	1,0	433,1	28,8	20,6	79,9			14,69	15,63		
s02	s	Lombardy	511793	4985372	155,6	43,9	45,9	4,7	390,4	65,1	35,9	241,2			10,20	13,21		
s03	s	Lombardy	507730	4986419	160,2	60,3	67,5	3,9	555,1	196,5	24,2	79,8			6,32	11,30		
s04	s	Lombardy	516605	4991760	104,4	42,5	62,9	4,2	312,3	37,5	27,1	249,6			6,40	18,92		
s05	s	Lombardy	525259	4994044	144,6	35,0	26,5	1,7	531,6	23,6	0,0	138,8			6,70	18,78		
s06	s	Lombardy	525872	4992373	145,3	29,3	21,3	0,8	470,9	38,8	45,5	67,5			6,28	8,69		
s07	s	Lombardy	522984	4991544	149,8	42,9	68,1	34,7	463,6	90,0	180,1	142,8			14,25	4,35		
s08	s	Lombardy	519307	4994294	101,9	46,6	17,9	1,9	439,2	37,3	16,0	58,8			14,80	16,05		
s09	s	Lombardy	524301	4993125	157,2	42,5	70,7	1,9	536,8	101,9	27,2	119,7			4,63	8,06		
s10	s	Lombardy	508668	4984542	129,9	39,4	50,0	4,0	431,9	43,7	24,8	176,7			6,83	5,62		
s11	s	Lombardy	505722	4983534	162,9	35,7	18,6	0,6	524,6	39,1	26,4	89,8			7,46	9,73		
s12	s	Lombardy	498823	4976781	123,6	20,6	16,8	1,5	390,4	32,7	26,7	29,5			4,69	5,54		
s13	s	Lombardy	494058	4983086	120,6	29,5	22,1	2,8	368,4	16,4	41,8	88,3			3,93	6,61		
s14	s	Lombardy	496134	4987181	113,2	36,0	16,0	2,4	390,4	13,6	12,6	95,9			7,16	11,27		
s15	s	Lombardy	498340	4987688	128,0	45,2	15,4	3,6	451,4	14,1	38,6	83,5			5,04	8,17		
s16	s	Lombardy	500262	4987364	142,6	45,2	21,6	5,5	549,0	26,9	19,5	95,3			7,97	5,35		
s17	s	Lombardy	495555	4983233	115,3	30,2	18,3	3,0	402,6	13,3	32,2	95,7			5,19	7,30		
s18	s	Lombardy	498772	4983852	113,5	35,6	15,7	2,3	440,2	33,2	48,0	61,5			4,03	8,55		
s19	s	Lombardy	528117	4992890	145,2	24,8	47,3	1,3	444,1	80,0	16,0	57,1			15,36	12,00		
s20	s	Lombardy	531543	4992324	52,4	60,2	25,7	1,6	256,2	45,2	24,9	98,7			7,20	10,44		
s21	s	Lombardy	527595	4990604	160,4	29,8	24,7	0,9	536,8	42,6	24,0	71,7			6,37	6,76		
s22	s	Lombardy	512309	4990113	171,5	42,9	51,9	6,1	524,6	59,4	14,8	190,7			12,61	14,15		

Tab.S1

ID	ID_Ref	Region	X_utrm32_wgs84	Y_utrm32_wgs84	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	Na <sup>+</sup> mg/l	K <sup>+</sup> mg/l	HCO <sub>3</sub> - mg/l	Cl- mg/l	NO <sub>3</sub> <sup>-</sup> mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	B μg/L	Sr mg/L	δ11B	δ <sup>15</sup> N <sub>NO<sub>3</sub></sub>	δ <sup>18</sup> O <sub>NO<sub>3</sub></sub>	1/B
s23	s	Lombardy	512486	4989799	154,8	44,8	66,3	9,6	610,0	96,9	9,7	128,3			15,75	11,50		
s24	s	Lombardy	510539	4987898	68,9	59,1	43,5	43,5	385,5	93,6	1,9	155,4			27,72	16,56		
s25	s	Lombardy	517485	4987834	130,7	61,8	21,3	39,9	531,9	28,4	49,9	129,4			9,96	12,36		
s26	s	Lombardy	507744	4990709	119,2	65,2	72,8	8,3	575,8	154,4	16,4	75,6			6,47	9,55		
s27	s	Lombardy	506283	4986444	147,4	62,9	16,6	2,7	561,2	29,1	32,8	116,1			9,69	7,95		
s28	s	Lombardy	537747	4998771	77,3	34,5	102,1	4,0	390,4	120,7	7,4	44,3			7,39	8,61		
s29	s	Lombardy	534802	4995219	99,0	36,4	25,2	5,3	348,9	44,4	24,9	54,4			10,82	11,80		
s30	s	Lombardy	469773	4998875											10,81	6,77		
s31	s	Lombardy	497502	4995398											6,31	2,36		
s32	s	Lombardy	485581	5002067											2,56	4,83		
s33	s	Lombardy	467669	5002569											9,80	8,40		
s34	s	Lombardy	480272	5009278											6,64	10,64		
s35	s	Lombardy	514062	4987056											10,47	13,50		
s36	s	Lombardy	483440	5002243											8,37	3,64		
s37	s	Lombardy	510097	4985599											6,26	8,44		
s38	s	Lombardy	508086	4984214											5,98	8,20		
s39	s	Lombardy	525533	4992984											7,21			
s40	s	Lombardy	518339	4991493											13,88			
s41	s	Lombardy	520188	4989475											16,41			
s42	s	Lombardy	520013	4996431											5,80	8,92		
s43	s	Lombardy	521437	4991536											20,56			
s44	s	Lombardy	525442	4994148											11,03			
s45	s	Lombardy	518092	4992719											16,70			
s46	s	Lombardy	519225	4994713											21,56	15,95		
s47	s	Lombardy	521909	4992335											21,35			
s48	s	Lombardy	526025	4992927											4,57	10,40		
s49	s	Lombardy	525708	4992881											6,43	7,92		
s50	s	Lombardy	523022	4992959											6,29	12,63		
s51	s	Lombardy	524791	4993392											7,67	10,09		
s52	s	Lombardy	525643	4993178											13,71			
s53	s	Lombardy	522187	5006687											11,24	9,27		
s54	s	Lombardy	518922	5015995											14,55			
t01	t	Piedmont	408290	4967630											7,55	10,70		
t02	t	Piedmont	410297	4972658	46,0	34,8									17,54	13,60	0,0176678	
t03	t	Piedmont	409951	4979071											13,53	10,00		
t04	t	Piedmont	412077	4981762											16,58	11,90		
t05	t	Piedmont	410360	4969424											23,60			
t06	t	Piedmont	412938	4976317											20,66	11,80		
t07	t	Piedmont	416407	4980329											18,42	12,20		
t08	t	Piedmont	401348	4966980											7,29	8,30		
t09	t	Piedmont	393365	4968729											6,56	14,90		
t10	t	Piedmont	396100	4958332											8,59	7,00		
t11	t	Piedmont	399861	4959872											8,41	8,30		
t12	t	Piedmont	391779	4966365											7,21	8,20		
t13	t	Piedmont	404822	4956027											6,68	5,80		
t14	t	Piedmont	394050	4989295											7,94	4,50		
t15	t	Piedmont	389400	4978896											7,11	4,60		
u1	u	Piedmont	396099	4958336	116,5	32,9	9,4	1,4	345,0	46,4	112,0	123,2			7,64	10,50		
u2	u	Piedmont	397537	4956831	129,8	23,7	7,0	1,6	334,2	27,3	81,2	100,8			8,18	11,40		
u3	u	Piedmont	396708	4955321	141,2	24,6	8,8	1,3	344,1	34,4	94,4	121,4			7,99	12,20		
u4	u	Piedmont	398109	4952734	117,2	21,7	10,2	1,8	312,3	38,4	132,5	112,8			7,83	8,30		
u5	u	Piedmont	396920	4950141	145,1	31,0	9,0	4,9	398,0	36,2	96,3	128,0			11,29	10,60		
u6	u	Piedmont	397920	4947697	146,8	26,1	9,5	1,6	361,0	36,2	100,7	127,6			8,45	6,50		

## References

ID_Ref	Reference
a	Pilla, G., Sacchi, E., Zuppi, G.M., Braga, G., Ciancetti, G., 2006. Hydrochemistry and isotope geochemistry as tools for groundwater hydrodynamic investigation in multilayer aquifers: a case study from Lomellina, Po plain, South Western Lombardy, Italy. <i>Hydrogeol. J.</i> 14, 795-808.
b	Sacchi, E., Pilla, G., Allais E., Guallini, M., Zuppi, G.M., 2007. Tracing nitrification and denitrification processes in a periodically flooded shallow sandy aquifer. <i>Int. Symp. on Advances in Isotope Hydrology and its role in Sustainable Water Resources Management</i> , IAEA, Vienna 21-25 May 2007, IAEA-CN-151/33, vol. 2, 461-469
c	Guffanti, S., Pilla, G., Sacchi, E., Ughini, S., 2010. Characterization of the quality and origin of groundwater of Lodigiano (Northern Italy) with hydrochemical and isotopic instruments. <i>Italian Journal of Engineering Geology and Environment</i> 1, 65-78
d	Sacchi, E., Acutis, M., Bartoli, M., Brenna, S., Delconte, C.A., Laini, A., Pennisi, M., 2013. Origin and fate of nitrates in groundwater from the central Po plain: Insights from isotopic investigations. <i>Appl. Geochem.</i> 34, 164-180
e	Pilla, G., Sacchi, E., Gerbert-Gaillard, L., Zuppi, G.M., Peloso, G.F., Ciancetti, G., 2005. Origine e distribuzione dei nitrati in falda nella Pianura Padana occidentale (Province di Novara, Alessandria e Pavia). <i>Giornale di Geologia Applicata</i> 2, 144-150
f	Arduini, C., Dadomo, A., Martinelli, G., Porto, G., Sogni, R., Zelioli, A., 2007. Isotopic prospection in high vulnerability area of the Milano province (Northern Italy). In: L. Ribeiro, A. Chambel, M.T. Condesso de Melo (Eds), Proc. of the XXXV IAH Congress "Groundwater and ecosystems", Lisbon, DOI: 10.13140/RG.2.1.4889.9289
g	Arduini, C., Dadomo, A., Martinelli, G., Porto, G., Sogni, R., Zelioli, A., 2007. Isotopic prospection in high vulnerability area of the Milano province (Northern Italy). In: L. Ribeiro, A. Chambel, M.T. Condesso de Melo (Eds), Proc. of the XXXV IAH Congress "Groundwater and ecosystems", Lisbon, DOI: 10.13140/RG.2.1.4889.9289
h	Martinelli, G., Fava, A., Chahoud, A., Dadomo, A., 2014c. Il monitoraggio isotopico nelle acque sotterranee in Emilia-Romagna. In: Farina M., Marcaccio M., Zavatti A.(Eds) Esperienze e prospettive nel monitoraggio delle acque sotterranee: il contributo dell'Emilia-Romagna, 332-354, Pitagora Editrice, Bologna
i	Martinelli, G., Chahoud, A., Dadomo, A., Fava, A., 2014a. Isotopic features of Emilia-Romagna region (North Italy) groundwaters: Environmental and climatological implications. <i>J. Hydrol.</i> 519, 1928-1938
j	Dadomo, A., Martinelli, G., 2005. Aspetti di idrologia isotopica in Emilia-Romagna. In: "Acqua e copertura vegetale". Atti dei Convegni Lincei 216, 157-166, Roma
k	Provincia di Verona, 2001. Indagine idrogeologica, geochimica e geochimico-isotopica sugli acquiferi della Lessinia. Rapporto Tecnico, Provincia di Verona-Settore Ecologia, Verona, 97
l	Saccon, P., Leis, A., Marca, A., Kaiser, J., Campisi, L., Bottcher, M.E., Savarino, J., Escher, P., Eisenhauer, A., Erbland, J., 2013. Multi-isotope approach for the identification and characterization of nitrate pollution sources in the Marano lagoon (Italy) and parts of its catchment area. <i>Appl. Geochem.</i> 34, 75-89
m	Debernardi, L., De Luca, D.A., Lasagna, M., 2008. Correlation between nitrate concentration in groundwater and parameter affecting aquifer intrinsic vulnerability. <i>Environ. Geol.</i> 55, 539-558
n	ISO4, 2005. Monitoraggio isotopico delle acque sotterranee in Provincia di Treviso, mediante l'analisi degli isotopi stabili di ossigeno, idrogeno, carbonio e dei nitrati. Unpublished report, Provincia di Treviso
o	Unpublished original data, A. Dadomo, 2016
p	Martinelli, G., Castagna, M., Pennisi, M., 2014b. Il monitoraggio del Boro nel sito contaminato nazionale Sassuolo-Scandiano (Area del Distretto Ceramico di Modena e Reggio Emilia. In: Farina M., Marcaccio M., Zavatti A.(Eds) Esperienze e prospettive nel monitoraggio delle acque sotterranee: il contributo dell'Emilia-Romagna, 332-354, Pitagora Editrice, Bologna
q	Pilla, G., Sacchi, E., Ciancetti, G., 2007. Studio idrogeologico, idrochimico ed isotopico delle acque sotterranee del settore di pianura dell'Oltrepò Pavese (pianura lombarda meridionale). <i>Giornale di Geologia Applicata</i> , 59-74
r	Lasagna, M., De Luca, D.A., Franchino, E., 2016b. The role of physical and biological processes in aquifers and their importance on groundwater vulnerability to nitrate pollution. <i>Environ. Earth Sci.</i> 75, 961
s	Lasagna, M., De Luca, D., Sacchi, E., Bonetto, S., 2006. Studio dell'origine dei nitrati nelle acque sotterranee piemontesi mediante gli isotopi dell'azoto. <i>Giornale di Geologia Applicata</i> 2, 137-143

Tab.S2

Region	Province														
		$\delta^{15}\text{N}$ data					husbandry data (ISTAT)			UAA (plain)	cattle density	pig density	cattle + pig density	population data (ISTAT)	
		n	min	max	mean	median	cattle	pigs	cattle + pigs	ha	n/ha	n/ha	n/ha	n	n/km2
Piedmont	AL	89	0,43	18,20	5,54	5,20	9333	12414	21747	86512,86	0,11	0,14	0,2514	440613	123
Lombardy	BG	12	2,90	9,93	7,53	7,50	44613	176921	221534	37608,90	1,19	4,70	5,8905	1098740	399
Emilia Romagna	BO	4	6,6	7,5	7,125	7,2	16031	22871	38902	113221,97	0,14	0,20	0,3436	991924	266
Lombardy	BS	11	6,68	10,63	8,98	9,10	188083	336642	524725	100152,85	1,88	3,36	5,2392	1256025	260
Piedmont	CN	6	7,64	11,29	8,56	8,09	149954	197170	347124	115477,43	1,30	1,71	3,0060	592303	85
Lombardy	CO	3	6,44	7,85	7,04	6,82	4018	319	4337	3277,37	1,23	0,10	1,3233	594988	458
Lombardy	CR	7	4,70	15,94	9,88	9,53	91383	237042	328425	134658,74	0,68	1,76	2,4389	363606	204
Emilia Romagna	FC	3	8,80	9,50	9,10	9,00	7994	57832	65826	39585,14	0,20	1,46	1,6629	395489	165
Lombardy	LC	4	4,00	7,00	6,08	6,67	2856	292	3148	5549,21	0,51	0,05	0,5673	340167	414
Lombardy	LO	17	6,67	12,72	9,27	9,01	36528	120309	156837	54052,17	0,68	2,23	2,9016	227655	289
Lombardy	MB	21	5,60	9,80	7,44	7,60	1571	2027	3598	8223,92	0,19	0,25	0,4375	849636	n.a.
Lombardy	MI	32	4,07	11,18	7,13	7,10	22598	29632	52230	65283,08	0,35	0,45	0,8001	3156694	1998
Lombardy	MN	10	4,96	21,09	9,00	6,86	125147	347213	472360	153323,73	0,82	2,26	3,0808	415442	176
Emilia Romagna	MO	12	8,10	17,96	10,37	9,80	44881	106504	151385	86436,12	0,52	1,23	1,7514	700913	259
Piedmont	NO	34	0,97	12,58	4,66	4,27	5562	5924	11486	52947,96	0,11	0,11	0,2169	371802	276
Emilia Romagna	PC	130	1,00	37,50	6,92	5,86	29626	36195	65821	51031,51	0,58	0,71	1,2898	289875	111
Emilia Romagna	PR	24	4,80	13,70	8,16	7,53	86216	55887	142103	60325,70	1,43	0,93	2,3556	442120	127
Lombardy	PV	86	-7,84	27,77	8,60	7,30	16236	121340	137576	146408,43	0,11	0,83	0,9397	548307	184
Emilia Romagna	RE	9	7,90	13,40	9,58	8,70	65464	117216	182680	67796,16	0,97	1,73	2,6945	530343	229
Emilia Romagna	RN	3	7,00	9,20	8,13	8,20	4125	13801	17926	11215,92	0,37	1,23	1,5983	329302	576
Piedmont	TO	20	5,90	20,66	10,48	7,75	61334	32851	94185	103473,58	0,59	0,32	0,9102	2302353	336
Veneto	TV	9	3,20	10,42	6,48	6,65	53324	25868	79192	91755,81	0,58	0,28	0,8631	888249	357
Friuli V.G.	UD	24	5,50	12,63	8,16	7,48	11700	17315	29015	94997,15	0,12	0,18	0,3054	541522	110
Lombardy	VA	4	4,64	20,67	9,81	6,96	2265	289	2554	4033,48	0,56	0,07	0,6332	883285	731
Veneto	VR	244	-1,39	30,56	7,07	6,82	83387	133407	216794	121143,25	0,69	1,10	1,7896	920158	293

Tab.S2

