Hydrochemical and isotopic analyses to identify groundwater nitrate contamination. The alluvial-pyroclastic aquifer of the Campanian plain (southern Italy)

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This paper concerns the evolution of the quality of the groundwater bodies over space and time, with special focus on nitrate. This case study deals with the qualitative status in alluvial-pyroclastic groundwater bodies located near Naples (southern Italy). The study is based on a significant hydrochemical database, gathered through: (i) groundwater sampling and water level monitoring, (ii) chemical analyses (Mg, Ca, K, Na, Cl, HCO_3, SO_4, NH_4, F, Li, Br, metals) and (iii) isotopic analyses ($\delta^{15}N$ and $\delta^{18}O$ in NO_3, $\delta^{18}O$ and δD in water). Such data, processed using maps and graphical elaborations, has been very useful for identifying groundwater nitrate contamination. Finally, the application of isotope techniques has been important for understanding and following the trend of possible attenuation processes of nitrate content in groundwater.

Keywords: *groundwater nitrate contamination, isotopic analyses, groundwater protection.*

Analisi idrochimiche e isotopiche per la definizione della contaminazione da nitrati nelle acque sotterranee. L'acquifero alluvionale-piroclastico della Piana Campana (Italia meridionale). *Questo lavoro è incentrato sull'evoluzione della qualità delle acque sotterranee dei corpi idrici sotterranei nello spazio e nel tempo, con particolare attenzione ai nitrati. Il caso di studio si occupa dello stato qualitativo dei corpi idrici sotterranei, di tipo alluvionale-piroclastico, presenti nei dintorni di Napoli (Italia meridionale). Lo studio si basa su un database idrochimico significativo, ottenuto attraverso: un campionamento delle acque sotterranee e il monitoraggio del livello piezometrico (i), nonché analisi chimiche (Mg, Ca, K, Na, Cl, HCO_3, SO_4, NH_4, F, Li, Br, metalli) (ii) ed isotopiche ($\delta^{15}N$ e $\delta^{18}O$ in NO_3, $\delta^{18}O$ e δD in acqua) (iii). Tali dati, elaborati mediante mappe e grafici, hanno consentito di definire la contaminazione da nitrati nelle acque sotterranee. Infine, l'applicazione di tecniche isotopiche ha consentito di comprendere e seguire l'evoluzione dei processi di attenuazione dei nitrati nelle acque sotterranee.*

Parole chiave: *contaminazione delle falde da nitrati, analisi isotopiche, protezione delle falde.*

1. Introduction

Nitrate contamination in groundwater, produced by the over-application of mineral and organic nitrogen fertilizers in agriculture or by anthropogenic sources as animal manures, industrial wastewater and leaks from sewage systems, is an important and growing risk to water quality in major *groundwater bodies* (here and after GWBs) around the world (Burow *et al.*, 2010; Capri *et al.*, 2009; Kammoun *et al.*, 2018; Nemčić-Jurec *et al.*, 2007; US EPA, 2000).

Recently, stable isotopes of oxygen and nitrogen have been used as valuable tools to determine natural and anthropogenic sources of nitrates (Aravena *et al.*, 1993; Kendall, 1998; D'Antonio *et al.*, 2009; Xue *et al.*, 2012; Heaton *et al.*, 2012; Stellato *et al.*, 2016; Cossu *et al.*, 2018). In general, isotopic composition of nitrogen can vary between –20 and +30 ‰; in particular: i) $\delta^{15}N$ values around zero ‰ (-5; +5) are characteristic of synthetic fertilizers; ii) $\delta^{15}N$ values between +3 and +25 ‰ are characteristic of animal dejection, since biometabolic processes and volatilization of urea and ammonia cause the enrichment of ^{15}N into the residue; iii) nitrogen compounds in precipitation do not generate an increase in nitrate concentration in agricultural soils and generally show very high variations in isotopic composition. As a consequence, nitrates derived from fertilizers can be distinguished from those coming from animal dejection or sewage (Kendall, 1998).

The $\delta^{18}O$ of nitrate originating from nitrification can vary from –10 to +10 ‰, while the $\delta^{18}O$ interval of nitric fertilizers is very narrow around +23.5 ‰ and finally the $\delta^{18}O$ of nitrate in precipitation spans over a wide range from +30 to about +80 ‰ (Xue *et* *al.*, 2012). Hence, the coupled use of $\delta^{15}N$ and $\delta^{18}O$ of nitrate allows to characterize nitrate sources in groundwater as well as to identify the occurrence of microbes mediated reactions such as denitrification, which is an important process able to reduce nitrate concentration in groundwater (Bottcher *et al.*, 1990; Sanders and Trimmer, 2006; Widory *et al.*, 2011).

In 2017, 23% of the Campania region (3,160 Km^2) was classified as nitrate vulnerable zone (NVZ), according to the EU's Nitrate Directive (91/676/CEE); two coastal GWBs of the Campanian plain the "Volturno-Regi Lagni" plain (P-VLTR) and the "Eastern plain of Naples" (P-NAP) are entirely classified as NVZ (fig. 1).

In these areas, the agricultural activities are very intensive and create a strong impact on groundwater. In particular, in the Volturno plain the land use shows a strong agricultural development, with a high percentage (81%) of cultivated fields (grain cereals and grass cultivations), mostly in association to the numerous livestock activities, predominantly composed of buffalo farming companies. Nevertheless, the urbanized environment represents a relevant percentage of the area (7.4%) and extends mainly along the coast (Aucelli *et al.*, 2016). Moreover, the studied areas can be identified as peri-urban areas, where, around a big city (Naples), industrial sett-

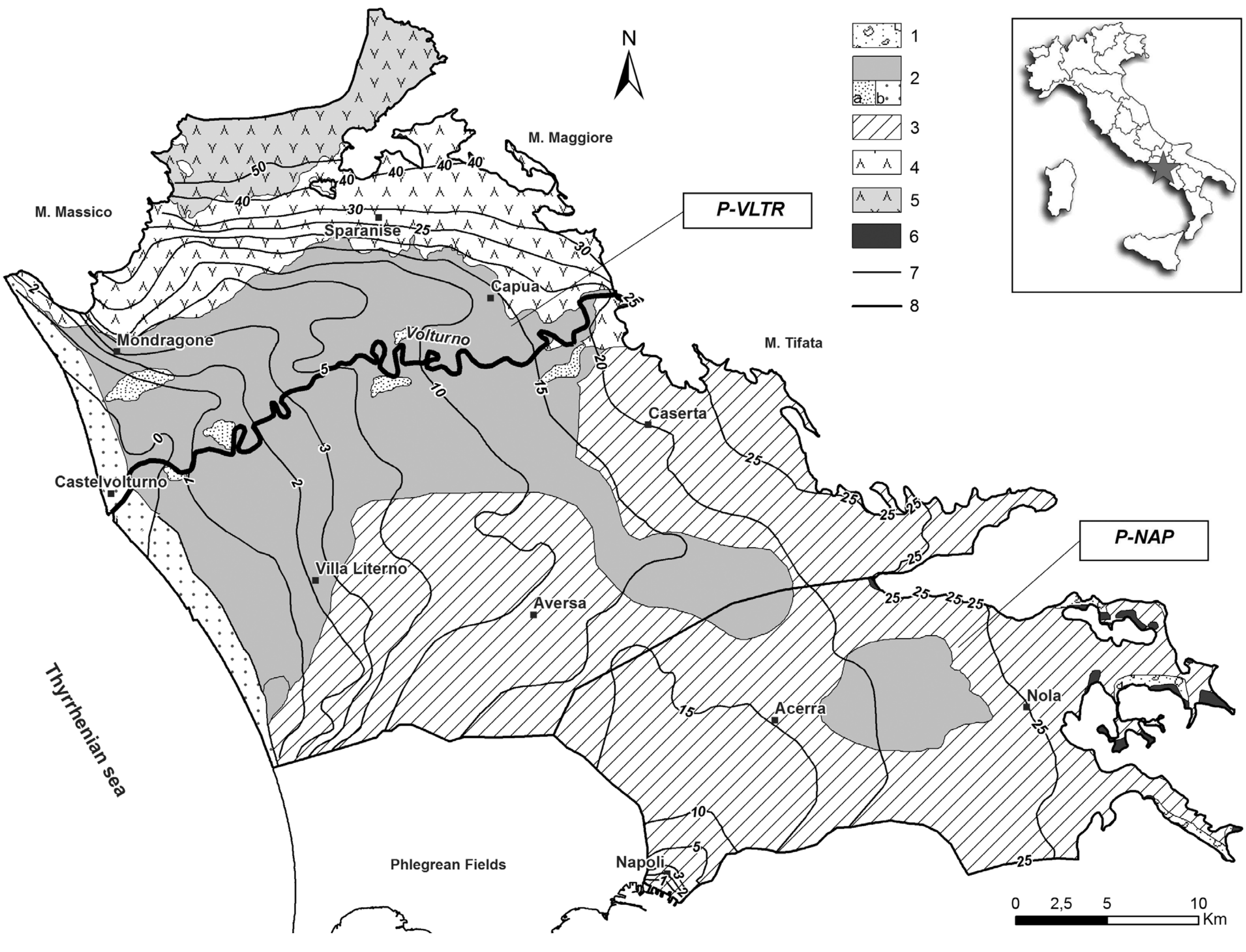

Fig. 1. Location of the study area in Italy (upper right corner). Hydrogeological map of the "Volturno-Regi Lagni" plain (P-VLTR) and "Eastern plain of Naples" (P-NAP) groundwater bodies: 1) Calcareous debris deposits. Medium-high permeability; 2) Alluvial, lacustrine and marine clayey – silty deposits (2a: sand deposits; 2b: of marine origin). Low-medium permeability; 3) Pyroclastic deposits. Medium-low permeability; 4) Campanian Ignimbrite, often covered by pyroclastic deposits. Low permeability; 5) Old tuffs. Low permeability; 6) Limestones and dolomitic limestones. High permeability; 7) Piezometric contour lines of the main aquifer (m a.s.l.;2004-2006); 8) limit of the GWBs.
Ubicazione dell'area di studio (in alto a destra). Carta idrogeologica dei Corpi Idrici Sotterranei della "Piana del Volturno-Regi Lagni" e della "Piana a Oriente di Napoli" 1) Detriti carbonatici. Permeabilità medio-alta; 2) Depositi alluvionali, lacustri, e marini limosi e argillosi (2a: sabbiosi, 2b: di origine marina). Permeabilità da bassa a media; 3) Depositi piroclastici. Permeabilità media-bassa; 4) Ignimbrite Campana, sovente coperta da piroclastiti sciolte. Permeabilità bassa; 5) Tufi antichi. Permeabilità bassa; 6) Calcari e calcari dolomitici. Permeabilità alta; 7) Isopiezometriche della falda principale (in m s.l.m. 2004-2006); 8) limite dei Corpi Idrici Sotterranei.

lements, natural and agricultural landscapes, and landscape between urban spaces coexist (Corniello *et al.*, 2007), causing many ecological disturbances. On top of that, in some areas there are illegal building developments with illicit sewage connections or on-site sewage disposal.

Since the nineties, for the two considered GWBs high nitrate contents in groundwater have been recorded (Corniello and Ducci, 2009; 2014; Corniello *et al.*, 2010; Ducci *et al.*, 2017a, 2017b). These high values, up to 300 mg/L in the shallow aquifer and until 150 mg/L in the deeper aquifer, were confirmed in next decade (Corniello and Ducci, 2009). In the P-VLTR GWB an increasing trend was recorded in the period 2011-2015 (Ducci *et al.*, 2017b). Isotopic studies carried out in a small sector of the area revealed that high contents of nitrate were prevalently due to the farming and the buffaloes breeding (Corniello and Ducci, 2009).

The aim of the present study is to advance the knowledge in the area on the qualitative status of GWBs, especially with respect to nitrate content (tab. 1) actualizing a very great number of previous datasets adding only a few monitoring wells measurements located at key locations, where additional isotopic analyses were performed ($\delta^{15}N$ and $\delta^{18}O$ of dissolved nitrates and $\delta^{18}O$ and δD of water), in order to better constrain the sources of nitrate contamination and to effectively plan proper protection measures.

2. Geological and hydrogeological characterization of the study area

The stratigraphy of the Campanian Plain is the result of marine, fluvial, and volcanic processes. Marine-transitional deposits are the deepest ones (Romano *et al.*,

Tab. 1. Groundwater samples collected in the wells shown in Figure 2 and used for isotopic analysis ($\delta^{15}N$ and $\delta^{18}O$ of dissolved nitrates and $\delta^{18}O$ and δD of water). (-) The symbols refer to the not executed analyses.
Acque sotterranee campionate nei punti d'acqua di Figura 2 usate per le analisi isotopiche ($\delta^{15}N$ e $\delta^{18}O$ dei nitrati e $\delta^{18}O$ e δD dell'acqua) e relativi valori. (–) I simboli si riferiscono alle analisi non eseguite.

Sample ID	*GWB*	NO_3	δD (‰ vs VSMOW) – H_2O	$\delta^{18}O$ (‰ vs VSMOW) – H_2O	*d-excess*	$\delta^{15}N$ (‰ vs AIR) – NO_3	$\delta^{18}O$ (‰ vs VSMOW) – NO_3
PC_V	P-VLTR	10.7	-40	-6.6	13	-	-
PC_U	P-VLTR	5.9	-26	-4.7	12	-	-
PC_T	P-VLTR	138	-36	-5.6	8	-	-
SMF_1	P-VLTR	1.7	-35	-5.7	10	-	-
SMF_2	P-VLTR	5.2	-36	-5.8	10	-	-
SMF_3	P-VLTR	1.4	-32	-5.6	12	-	-
SMF_4	P-VLTR	50.6	-37	-5.3	5	-	-
SMF_5	P-VLTR	63.5	-35	-5.3	8	-	-
VIL_1	P-VLTR	42.0	-30	-4.8	8	-	-
VIL_3	P-VLTR	59.5	-29	-5.2	12	6.3	6.7
VIL_4	P-VLTR	80.9	-33	-4.8	6	-	-
VIL_5	P-VLTR	77.3	-31	-5.3	11	-	-
PC_E	P-VLTR	55.7	-41	-8.2	24	8.8	5.1
PC_466	P-VLTR	96.9	-36	-8.0	28	7.4	6.6
PC_B	P-VLTR	55.3	-40	-7.3	18	6.3	5.3
PC_G	P-VLTR	62.8	-43	-8.5	25	8.5	5.2
PC_S	P-NAP	47.5	-	-	-	6.7	1.4
PC_H	P-NAP	147.0	-37	-5.5	7	6.4	4.5
PC_O	P-NAP	12.2	-35	-5.9	12	5.9	2.6
PC_L	P-NAP	175.0	-31	-5.5	13	8.3	7.2
PC_I	P-NAP	95.4	-37	-5.2	5	9.7	9.0
PC_R	P-NAP	130.0	-42	-8.5	26	7.0	0.5

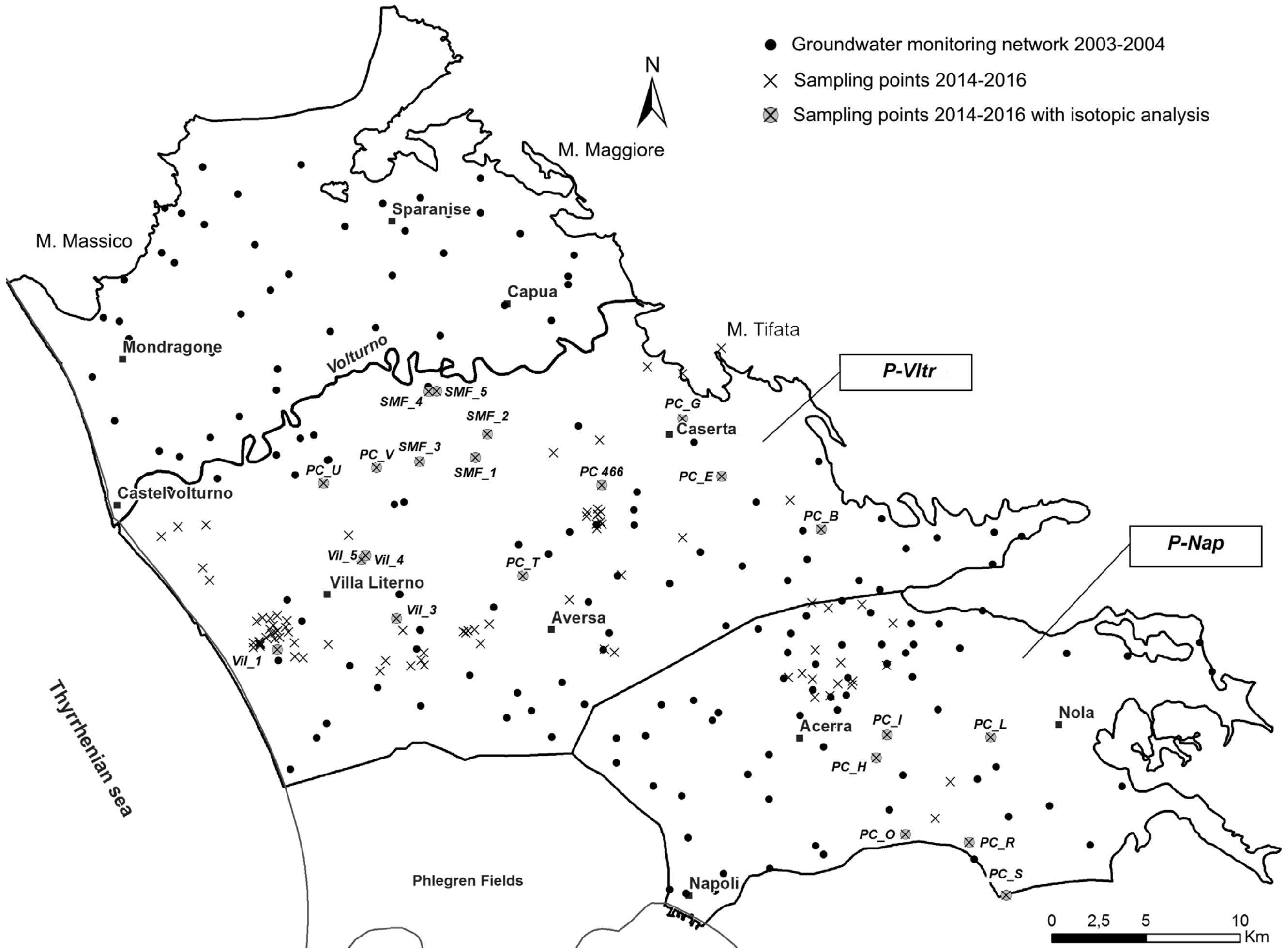

Fig. 2. Groundwater monitoring network 2003-2004 and 2014-2016. Isotopic analysis are labelled (seeTable 1).
Rete di monitoraggio delle acque sotterranee 2003-2004 e 2014-2016. Le etichette delle analisi isotopiche rimandano a tabella 1.

1994; Bellucci, 1998; Aprile *et al.*, 2004). Campanian Ignimbrite (also known as Grey Campanian Tuff) is the most widespread volcanic product across the Plain and it is located above transitional-marine deposits (fig. 1). The Campanian Ignimbrite extends over an area of about 30,000 km^2, including the Volturno river plain with thickness between 30-60 m (Corniello and Ducci, 2014). The Campanian Ignimbrite is absent close to the Volturno river, due to river erosion and there is a widespread presence of peat lenses, that determines negative redox conditions in groundwater (Corniello *et al.*, 2010).

In the Campanian Plain there are two GWBs. In the first, the P-VLTR GWB, the main aquifer is located in the alluvial, pyroclastic and marine porous sediments underlying the Campanian Ignimbrite, which plays, where present, the role of a semi-confining or confining bed; the aquifer is phreatic only near the coast.

In the southern part of the plain, in the P-NAP GWB, corresponding to the eastern plain of Naples (fig. 1), the stratigraphy and the hydrogeological setting are similar to those of the P-VLTR, except in the S sector. Here, the aquifer is located in the pyroclastic reworked deposits and is phreatic, locally confined by peat levels or by most impervious levels as Vesuvian or Phleagrean tuffs. Despite the local differences in the stratigraphy, the permeable layers of the P-NAP GWB are in hydrogeological continuity, constituting a single aquifer (Corniello and Ducci, 2013).

The hydrochemical patterns reflects the groundwater flow patterns in the plain, as could be expected. Near the limestone mountains (NE of the plain), where there is a conspicuous groundwater outflow (Corniello and Ducci, 2014), the r(Ca^{2+} + Mg^{2+})/r(Na^+ + K^+) ratio, and the HCO_3^- content are high, while along the coastal areas more alkaline conditions occur (Ducci *et al.*, 2016).

In the P-VLTR and P-NAP GWBs different types of “natural contamination”, due to volcanic formations, are observed, such as high fluoride (almost everywhere > 1.5 mg/L, and often exceeding 3 mg/L) and high arsenic content (close to the Phlegrean Fields, where As >10 μg/L). The high As values derive mainly from water–rock interaction, and its mobility is favoured by the presence of steam-heated groundwater (Aiuppa *et al.*, 2003). In the sectors close to the Volturno river in the P-VLTR and close to the sea in the P-NAP, groundwater shows lower nitrate content (fig. 3), related to reducing conditions, also testified by low SO_4 and high Fe and Mn (Corniello *et al.*, 2010; Ducci and Sellerino, 2012; Ducci *et al.*, 2016).

3. Materials and methods

The groundwater quality database used in this study includes more than 300 samples collected in 180 sampling points in different time (2003-2004) and with different purposes (Corniello and Ducci, 2009; 2014; Corniello *et al.*, 2007; Ducci and Sellerino, 2012). 25 water points of this dataset belong to the groundwater monitoring network of the Agency for Environmental Protection of Campania Region (ARPAC) that started in autumn 2002 and was implemented in 2015 (Adamo *et al.*, 2007; Ducci *et al.*, 2017b). This database (fig. 2) constituted the background for planning the new sampling campaign.

The groundwater levels measurements and groundwater sampling were planned with the aim to investigate sectors with scarce knowledge of the piezometric pattern and geochemistry or where very high levels of nitrate measured in the past required to check the evolution of the contamination (fig. 2).The present study includes 107 new measurements of piezometric levels and sampling of the groundwater from the deep aquifer, collected in wells located in the southern part of P-VLTR and in the P-NAP GWBs (fig. 2).

In this new campaign, the coordinates (X-Y-Z) of groundwater monitoring point were recorded using a Garmin GPS. Before sampling, the wells were purged for removing stagnant water. All the groundwater monitoring points were analysed on site for EC, pH, alkalinity, temperature and piezometric levels. Subsequently, the samples were stored for metals and isotopes analysis in PE bottles, while in glass bottles for the analysis of dissolved elements (HCO_3, NO_x, NH_3, F, Cl, Br, SO_4, Li, Na, K, Ca, Mg).

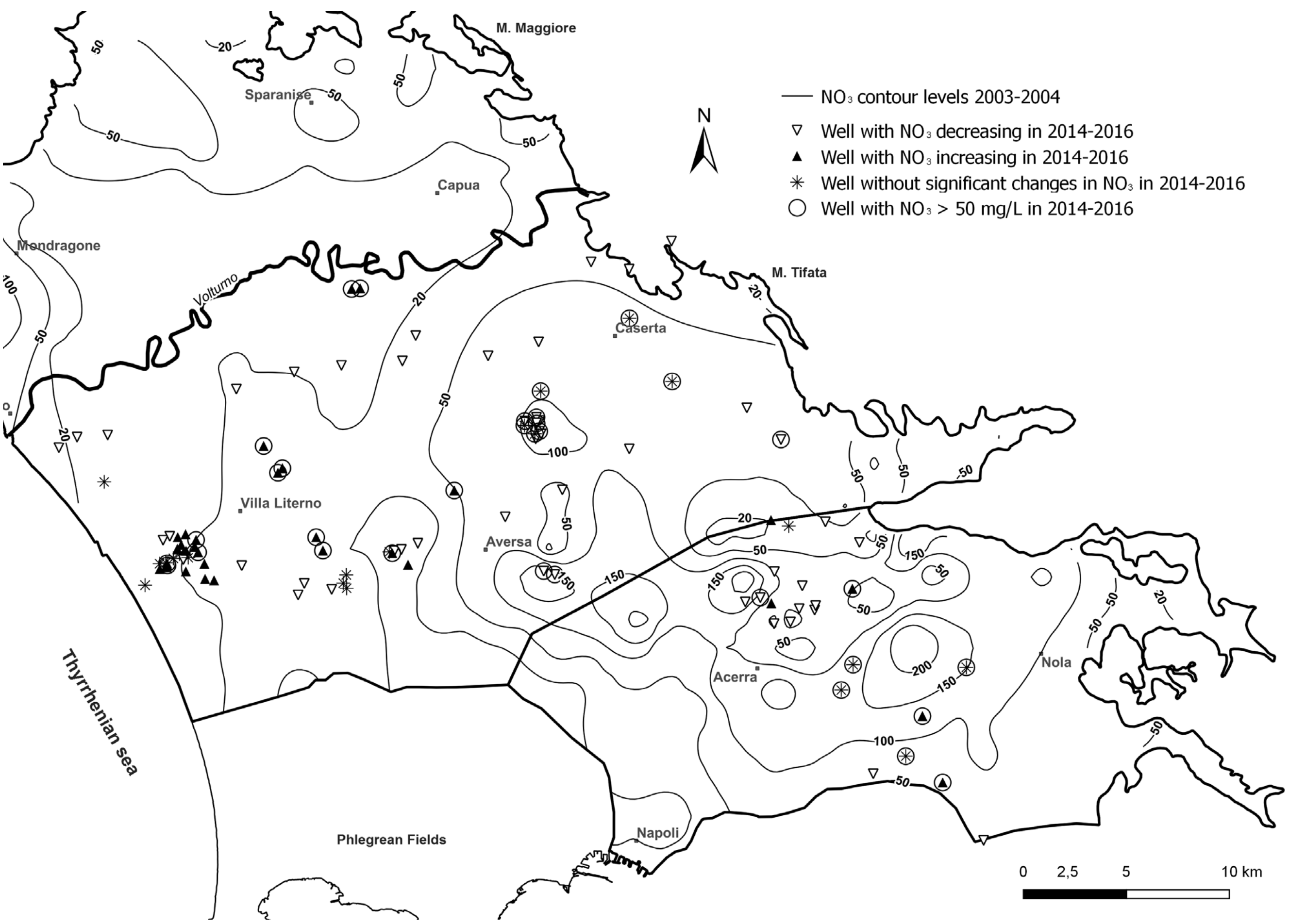

Fig. 3. Variation of the nitrate concentration in groundwater from 2003-2004 to 2014-2016.
Variazione delle concentrazioni di nitrati nelle acque sotterranee dal 2003-2004 al 2014-2016.

Chemical analysis, including major cations (Na, K, Ca, Mg), anions (Cl, SO_4, NO_3, HCO_3) and metals (Al, Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Sb, Se, Sn, Te, Tl, V, Zn) were performed by the laboratories of the University of Naples Federico II (Department of Chemical Sciences), by using ion chromatography and mass spectrometry on unfiltered samples stored at 4 °C. Most of the analyses (70%) show a charge balance error of less than 5%. The data obtained were organized in a database purposely designed to satisfy the analytical needs of GIS (ArcGIS 10 and QGIS 2.14.18), also used for the drawn up of the thematic maps.

22 water points (fig. 2), selected on the basis of their availability and significance, were also sample for isotopic analysis ($\delta^{15}N$ and $\delta^{18}O$ of dissolved nitrates and $\delta^{18}O$ and δD of water) in order to identify either the source of the high contents of nitrates and the groundwater origin. The samples were analysed at the CIRCE (Centre for Isotopic Research on the Cultural and Environmental heritage) laboratory of the Department of Mathematics and Physics of the University of Campania "Luigi Vanvitelli" (Caserta, Italy).

$\delta^{15}N$ and $\delta^{18}O$ of dissolved nitrate, reported as ‰ versus AIR and VSMOW, were measured in 11 wells by means of the silver nitrate protocol (Silva *et al.*, 2000) and analysed by a TC/EA-CF-IRMS system (Delta V Thermo Fisher). The precision of the whole procedure involving the preparation protocol of aqueous samples, reference materials and the isotopic analysis, reported as standard deviation (1 σ) of $AgNO_3$ measurements, is 0.7 ‰ and 1.2 ‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively.

Water stable isotopes (δD and $\delta^{18}O$, reported as ‰ versus VSMOW) were measured in 21 wells by means of a TC/EA-CF-IRMS system (Delta V Thermo Fisher) with an analytical precision of 0.2 ‰ and 1 ‰, for $\delta^{18}O$ and δD, respectively.

The mean infiltration altitude can be estimated by means of the equation reported in Zuppi *et al.* (1974) for the peri-Tyrrhenian areas of Italy: Height (m)= $-1000*(\delta^{18}O + 5.14)/3.44$.

4. Results and discussion

The range of nitrate content measured in groundwater samples is 0.2-175.0 mg/L, with mean value of 40.0 mg/L and standard deviation 37.5 mg/L. The number of exceedances of the 50.0 mg/L threshold value (EU's nitrate directive) is 33 on 107 samples; the wells with groundwater exceeding the threshold are located in the central part of the P-VLTR and in the SW sector of the P-NAP. Despite the high levels of nitrate detected, comparing these data with those recorded during 2004, it is possible to assert that the contamination level has not worsened over time; the nitrate concentration is equal or less that in 2004 for 70% of the monitoring points (fig. 3). The remaining 30% of wells are located near the coast; here, there is no reduction in nitrate contamination, but rather a moderate increase (usually between 1% and 3%) due to the widespread presence of holyday's houses, mainly used in summer periods and not always connected to the sewer system.

In Figure 4 $\delta^{18}O$ and δD values for 21 wells sampled in the two GWBs are shown. All the values fall between the Global Meteoric Water Line (Craig, 1961) and the Eastern Mediterranean Meteoric Water Line (Gat and Carmi, 1970). As a reference, also the Southern Italy Meteoric Water Line presented by Giustini *et al.* (2016) has been reported. From the analysis of the isotopic results (tab. 1), all the piedmont wells (PC_G, PC_E, PC_466 and PC_B for the P-VLTR and PC_R for P-NAP) are characterized by more depleted values of $\delta^{18}O$ and δD and high deuterium excess values, indicating that the recharge of this area is originated by water infiltrating at high altitude from vapour masses formed in conditions of low humidity (65-70%) (Clark and Fritz, 1997). From the piedmont areas towards central areas of the plain more enriched values (SMF and PC wells) are observed, becoming even more enriched from central to coastal areas (i.e., VIL wells). The observed trend towards more enriched values is due to the mixing with water recharged locally at a lower altitude formed by humid (humidity 80-90 %) air masses, close to the sea, and therefore characterized by enriched values of water stable isotopes.

The mean value of $\delta^{18}O$ of piedmont wells (8.0 ± 0.5 ‰) can be used to estimate the mean infiltration altitude. The estimated elevation of the recharge area of the NE part of P-VLTR aquifer results between 680 and 980 m a.s.l., well supporting the hypothesis that the infiltration occurs mainly on carbonate mountains located at the NE border of the plain.

The diagram of Figure 5 shows the characteristic ranges of possible nitrate sources in surface water and groundwater (atmospheric depositions, nitric or ammonium fertilizers, manure, etc.) (Kendall, 1998). The two GWBs are contaminated mainly by nitrate originating from natural nitrification processes occurring in the soils and by manure spreading and/or sewage leaking from collectors or septic tanks. All the collected samples have a NO_3> 50.0 mg/L, except a sector of the P-VLTR GWB located on the left side of the Volturno River, where nega-

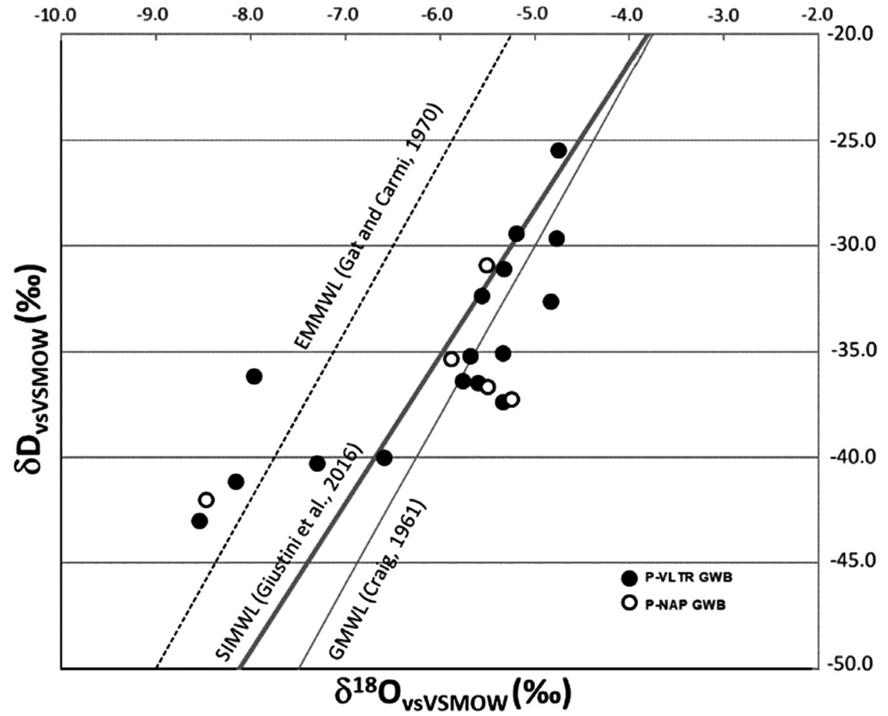

Fig. 4. δD vs. δ^{18}O diagram of the groundwater samples of Table 1and Figure 2. EMMWL: Eastern Mediterranean Meteoric Water Line (Gat and Carmi, 1970); SIMWL: Southern Italy Meteoric Water Line (Giustini *et al.*, 2016); GMWL: Global Meteoric Water Line (Craig, 1961).

Diagramma δD -. δ^{18}O dei campioni d'acqua di Tabella 1 e Figura 2. EMMWL: Eastern Mediterranean Meteoric Water Line (Gat and Carmi, 1970); SIMWL: Southern Italy Meteoric Water Line (Giustini et al., 2016); GMWL: Global Meteoric Water Line (Craig, 1961).

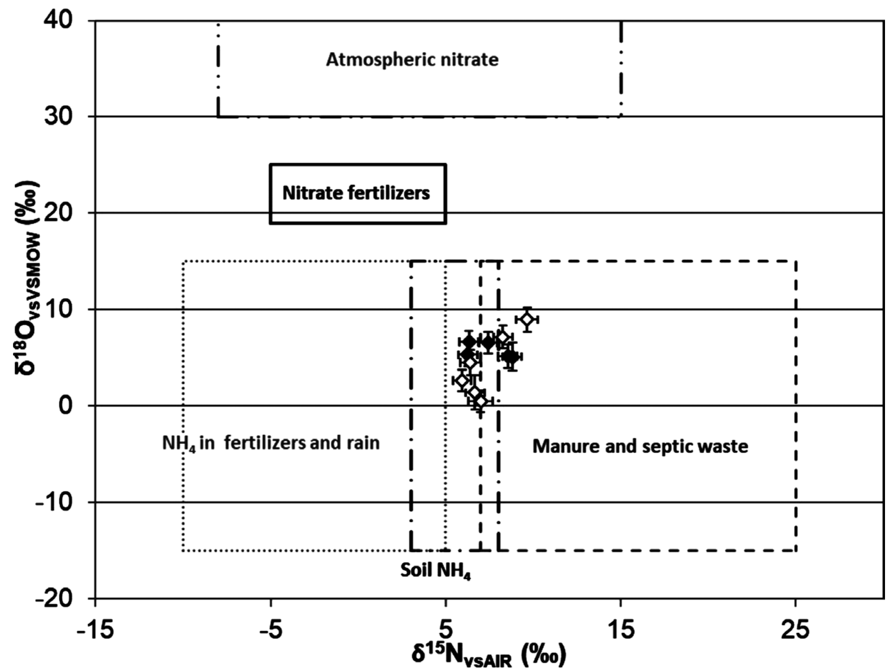

Fig. 5. δ^{18}O-δ^{15}N diagram (Kendall, 1998) of the groundwater samples of Table 1 and Figure 2. The black symbols refer to the P-VLTR GWB and the white symbols to the P-NAP GWB.

Diagramma δ^{18}O-δ^{15}N (Kendall, 1998) dei campioni d'acqua di Tabella 1 e Figura 2. I simboli neri si riferiscono al CIS P-VLTR, quelli bianchi al CIS P-NAP.

tive redox conditions occur (Corniello and Ducci, 2014), promoting a natural attenuation of the dissolved nitrate (i.e., denitrification). The denitrification process is evidenced in the observation points SMF_1, PC_U and PC_V in Figure 2, having NO_3<1 mg/L. On the other side, the P-NAP GWB is characterized by NO_3 always higher than 150.0 mg/L; in these areas, no self-purification processes are evidenced by isotopic and chemical data.

5. Conclusions

Hydrogeochemical and isotope data collected and acquired in two groundwater bodies located in Campania region (southern Italy) provided information about the persistence of the high levels of nitrate content recorded in past years, that gave a bad quality status to these GWBs.

The results of the hydrogeochemical study show that the application of rules and actions in the last 10 years has led to a control of the nitrate problem but not to a resolution; in the two GWBs the NO_3 content in groundwater seem generally decreased, probably thanks to the improvement of good agricultural practices and land use restrictions, to the control of the sewerage systems and to the prohibition of use of certain chemicals (EU's Nitrate Directive – 91/676/CEE). It is important to highlight the dilution effect operated by the groundwater inflow from carbonate mountains, as demonstrated by the elevation of the recharge area (between 680 and 980 m a.s.l.) individuated on the basis of δ^{18}O and δD and by the persistence of the nitrate contamination in the coastal sectors. The source of nitrate, investigated using the isotopic ratios of nitrogen and oxygen of dissolved nitrate, seems prevalently due to the spreading manure application to crops and to the urban sewage leakage. Indeed, this hypothesis seems confirmed by the changes in land use showing an increase of peri-urban areas, often not connected to the sewer systems (Corniello *et al.*, 2007; Ducci *et al.*, 2017b).

The application of isotope techniques has given an important support to understand and follow the trend of possible attenuation processes in nitrate content. In a near future, to better constrain the sources of nitrate contamination, the isotopic signature of the possible sources present in the study area should be determined. This could give also the possibility to apportion quantitatively the different contributes to the mixing (Xue *et al.*, 2012).

In conclusion, the dimension of the area and the very complex land use require a deeper monitoring and analysis, not viable without a purposed funding provided by new projects aimed to protect groundwater from nitrate contamination.

References

Adamo, N., Imperatrice, M.L., Mainolfi, P., Onorati, G., Scala, F. 2007. *Acqua. Il Monitoraggio in Campania 2002-2006*. ARPAC, Napoli, 95-160.

Aiuppa, A., D'Alessandro, W., Federico, C., Palumbo, B., Valenza, M., 2003. *The aquatic geochemistry of arsenic in volcanic groundwaters from southern Italy*. Applied Geochemistry, 18(9), 1283-1296.

Aprile, F., Sbrana, A., Toccaceli, R. M., 2004. *Il ruolo dei depositi piroclastici nell'analisi cronostratigrafica dei terreni quaternari del sottosuolo della Piana Campana (Italia meridionale).* Il Quaternario, 17, 547-554.

Aravena, R., Evans, M.L., Cherry, J.A., 1993. *Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems*. Ground Water 31, 180-186.

Aucelli, C.P.P., Di Paola, G., Incontri, P., Rizzo, A., Vilardo, G., Benassai, G., Buonocore, B., Pappone, G., 2016. *Coastal inundation risk assessment due to subsidence and sea level rise in a Mediterranean alluvial plain (Volturno coastal plain e southern Italy).* Estuarine, Coastal and Shelf Science, 198, 597-609.

Bellucci, F., 1998. *Nuove conoscenze stratigrafiche sui depositi effusivi ed esplosivi nel sottosuolo dell'area del Somma-Vesuvio*. Bollettino della Società geologica italiana, 117(2), 385-405.

Böttcher, J., Strebel, O., Voerkelius, S., Schmidt, H.L., 1990. *Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer*. Journal of Hydrology, 114, 413-424.

Burow, K.R., Nolan, B.T., Rupert, M.G., Dubrovsky, N.M., 2010. *Nitrate in groundwater of the United States, 1991-2003*. Environ Sci Technol 44(13), 4988-4997.

Capri, E., Civita, M., Corniello, A., Cusimano, G., De Maio, M., Ducci, D., Fait, G., Fiorucci, A., Hauser, S., Pisciotta, A., Pranzini, G., Trevisan, M., Delgado Huertas, A., Ferrari, F., Frullini, R., Nisi, B., Offi, M., Vaselli, O., Vassallo, M., 2009. *Assessment of nitrate contamination risk: the Italian experience*. Journal of Geochemical Exploration 102(2), 71-86.

Clark, I.D., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. CRC Press/Lewis Publishers, Boca Raton, FL.

Corniello, A., Ducci, D., 2013. *Hydrogeological features. From groundwater problem to groundwater opportunity. In Planning storm water resilient urban open space*. Ed. F.D. Moccia & F. Palestino. 106-118.

Corniello, A., Ducci, D., 2009. *Origine dell'inquinamento da nitrati nelle falde dell'area di Acerra (Piana Campana)*. Engineering Hydro Environmental Geology, 12, 157-166.

Corniello, A., Ducci, D., 2014. *Hydrogeochemical characterization of the main aquifer of the "Litorale Domizio-Agro Aversano NIPS" (Campania – southern Italy)*. Journal of Geochemical Exploration, 137, 1-10.

Corniello, A., Ducci, D., Ruggieri, G., 2007. *Areal identification of groundwater nitrate contamination sources in periurban areas*. Journal of Soils and Sediments 7(3), 159-166.

Corniello, A., Ducci, D., Trifuoggi, M., Rotella, M., Ruggieri, G., 2010. *Hydrogeology and hydrogeochemistry of the plain between Mt. Massico and the river Volturno (Campania region, Italy)*. Italian Journal of Engineering Geology and Environment, 10(1), 51-64.

Craig, H., 1961. *Isotopic variations in meteoric waters*. Science 133, 1702-1703.

Cossu, R., Zuffianò, L. E., Limoni, P. P., De Giorgio, G., Pizzardini, P., Miano, T., Mondelli, D., Garavaglia, R., Carella, C., and Polemio, M., 2018, How can the role of leachate on nitrate concentration and groundwater quality be clarified? An approach for landfills in operation (Southern Italy). Waste Management, 77, 156-165.

D'Antonio, A., Mottola, A., Stellato, L., Di Meo, T., Ingenito, M.R., Lubritto, C., Onorati, G., 2009. *Impiego di tecniche analitiche isotopiche per l'individuazione delle fonti di inquinamento da nitrati nelle acque sotterranee in due aree della Campania (Nitrate pollution sources in groundwater of two alluvial plains in Campania region (Italy) discriminated by means of isotopic methodologies)*. Giornale di Geologia Applicata, 12, 71-78, doi: 10.1474/EHEGeology.2009-12.0-06.0267.

Ducci, D., Albanese, S., Boccia, L., Celentano, E., Cervelli, E., Corniello, A., Crispo, A., De Vivo, B., Iodice, P., Langella, C., Lima, A., Manno, M., Palladino, M., Pindozzi, S., Rigillo, M., Romano, N., Sellerino, M., Senatore, A., Speranza, G., Fiorentino, N., Fagnano, M., 2017a. *An Integrated Approach for the Environmental Characterization of a Wide Potentially Contaminated Area in Southern Italy*. International Journal of Environ-

mental Research and Public Health, 14(7), 693.
Ducci, D., Condesso de Melo, M. T., Preziosi, E., Sellerino, M., Parrone, D., Ribeiro, L., 2016. *Combining natural background levels (NBLs) assessment with indicator kriging analysis to improve groundwater quality data interpretation and management*. Science of the Total Environment, 569, 569-584.
Ducci, D., Della Morte, R., Mottola, A., Onorati, G., Pugliano, G., 2017b. *Nitrate trends in groundwater of the Campania region (southern Italy)*. Environmental Science and Pollution Research, 1-12.
Ducci, D., Sellerino, M., 2012. *Natural background levels for some ions in groundwater of the Campania region (southern Italy)*. Environonmental Earth Science 67, 683-693.
Gat, J.R., Carmi, H., 1970. *Evolution of the isotopic composition of atmospheric waters in the Mediterranean sea area.* Journal of Geophysical Research, 75, 3039-3040.
Giustini, F., Brilli, M., Patera, A., 2016. *Mapping oxygen stable isotopes of precipitation in Italy*. Journal of Hydrology: Regional Studies 8, 162-181.Heaton, T.H.E., Stuart, M.E., Sapiano, M., Micallef Sultana, M., 2012. An isotope study of the sources of nitrate in Malta's groundwater. J. Hydrol. 414-415, 244-254.
Kammoun, S., Trabelsi, R., Re, V., Zouari, K., Henchiri, J., 2018. *Groundwater quality assessment in semi-arid regions using integrated approaches: the case of Grombalia aquifer (NE Tunisia)*. Environmental monitoring and assessment, 190(2), 87.
Kendall, C. 1998. *Tracing nitrogen sources and cycling in catchments*. In Kendall, C., and McDonnell, J.J. (Eds), 1998. *Isotope tracers in catchment hydrology*. Elsevier, Amsterdam, 517-576.
Nemčić-Jurec, J., Mesić, M., Bašic, F., Kisić, I., Zgorelec, Z., 2007. *Nitrate concentration in drinking water from wells at three different locations in northwest Croatia*. Cereal Research Communications, 35(2), 845-848.
Nitrate Directive, 1991. *91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources*. Official Journal L, 375(31), 12.
Romano, P., Santo, A., Voltaggio M., 1994. *L'evoluzione geomorfologica della pianura del Fiume Volturno (Campania) durante il tardo Quaternario (Pleistocene medio-superiore-Olocene)*. Il Quaternario, 7, 41-56.
Sanders, A., Trimmer, M., 2006. *In situ application of the $^{15}NO_3$–isotope pairing technique to measure denitrification in sediments at the surface water–groundwater interface*. Limnol. Oceanogr.: Methods 4, 2006, 142-152.
Silva, S.R., Kendall, C., Wilkinson, D.H., Ziegler, A.C., Chang, C.C.Y., and Avanzino, R.J., 2000. *A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios*. Journal of Hydrology, 228, 22-36.
Stellato, L., Di Rienzo, B., Di Fusco, E., Rubino, M., Marzaioli, F., Allocca, V., Salluzzo, A., Rimauro, J., Romano, N., Celico, F., 2016. *Surface water-groundwater connectivity implications on nitrate cycling assessed by means of hydrogeologic and isotopic techniques in the Alento river basin (Salerno, Italy): preliminary data*. Rendiconti Online Società Geologica Italiana, 41, 80-83.
US EPA 2000. *Drinking water standards and health advisories*. U.S. Environmental Protection Agency. EPA-822-B-00-001.
Widory, D., Petelet-Giraud, E., Brenot, A., Bronders, J., Tirez, K., Boeckx, P., 2011. *Improving the management of nitrate pollution in water by the use of isotope monitoring: the $\delta^{15}N$, $\delta^{18}O$ and $\delta^{11}B$ triptych*. Isotopes in Environmental and Health Studies, DOI: 10.1080/10256016.2012.666540.
Xue, D., De Baets, B., Van Cleemput, O., Hennessy, C., Berglund, M., Boeckx, P., 2012. *Use of a Bayesian isotope mixing model to estimate proportional contributions of multiple nitrate sources in surface water*. Environmental Pollution, 161, 43-49.
Zuppi, G.M., Fontes, J.C., Letolle, R., 1970. *Isotopes du milieu et circulation d'eaux sulfurées dans le Latium.* In: Isotope Techniques in Groundwater Hydrology. Proceedings of a Symposium, IAEA, Vienna, I, 341-361.

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