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, HCO₃, SO₄, NH₄, F, Li, Br; metals) and (iii) isotopic analyses (δ¹⁵N and δ¹⁸O in NO₃, δ¹⁸O 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.

**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 (Burov 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; Costi et al., 2018). In general, isotopic composition of nitrogen can vary between −20 and +30 ‰; in particular: i) δ¹⁵N values around zero ‰ (-5; +5) are characteristic of synthetic fertilizers; ii) δ¹⁵N values between +3 and +25 ‰ are characteristic of animal dejection, since biometabolic processes and volatilization of urea and ammonia cause the enrichment of ¹⁵N 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 δ¹⁸O of nitrate originating from nitrification can vary from −10 to +10 ‰, while the δ¹⁸O interval of nitric fertilizers is very narrow around +23.5 ‰ and finally the δ¹⁸O of nitrate in precipitation spans over a wide range from +30 to about +80 ‰ (Xue et
Hence, the coupled use of δ¹⁵N and δ¹⁸O 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 Km²) 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-

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 $\deltaD$ 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, fluviatile, and volcanic processes. Marine-transitional deposits are the deepest ones (Romano et al.,

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### 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 $\deltaD$ of water). (-) The symbols refer to the not executed analyses.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>GWB</th>
<th>NO$_3$</th>
<th>$\delta D$ (% vs VSMOW)</th>
<th>$\delta^{18}O$ (% vs VSMOW)</th>
<th>d-excess</th>
<th>$\delta^{15}N$ (% vs AIR)</th>
<th>$\delta^{18}O$ (% vs VSMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC_V</td>
<td>P-VLTR</td>
<td>10.7</td>
<td>-40</td>
<td>-6.6</td>
<td>13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PC_U</td>
<td>P-VLTR</td>
<td>5.9</td>
<td>-26</td>
<td>-4.7</td>
<td>12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PC_T</td>
<td>P-VLTR</td>
<td>15.8</td>
<td>-36</td>
<td>-5.6</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SMF_1</td>
<td>P-VLTR</td>
<td>1.7</td>
<td>-35</td>
<td>-5.7</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SMF_2</td>
<td>P-VLTR</td>
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<td>-36</td>
<td>-5.8</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SMF_3</td>
<td>P-VLTR</td>
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<td>-5.6</td>
<td>12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SMF_4</td>
<td>P-VLTR</td>
<td>50.6</td>
<td>-37</td>
<td>-5.3</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SMF_5</td>
<td>P-VLTR</td>
<td>63.5</td>
<td>-35</td>
<td>-5.3</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VIL_1</td>
<td>P-VLTR</td>
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<td>-30</td>
<td>-4.8</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VIL_3</td>
<td>P-VLTR</td>
<td>59.5</td>
<td>-29</td>
<td>-5.2</td>
<td>12</td>
<td>6.3</td>
<td>6.7</td>
</tr>
<tr>
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<td>P-VLTR</td>
<td>80.9</td>
<td>-33</td>
<td>-4.8</td>
<td>6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>-31</td>
<td>-5.3</td>
<td>11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PC_E</td>
<td>P-VLTR</td>
<td>55.7</td>
<td>-41</td>
<td>-8.2</td>
<td>24</td>
<td>8.8</td>
<td>5.1</td>
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<tr>
<td>PC_466</td>
<td>P-VLTR</td>
<td>96.9</td>
<td>-36</td>
<td>-8.0</td>
<td>28</td>
<td>7.4</td>
<td>6.6</td>
</tr>
<tr>
<td>PC_B</td>
<td>P-VLTR</td>
<td>55.3</td>
<td>-40</td>
<td>-7.3</td>
<td>18</td>
<td>6.3</td>
<td>5.3</td>
</tr>
<tr>
<td>PC_G</td>
<td>P-VLTR</td>
<td>62.8</td>
<td>-43</td>
<td>-8.5</td>
<td>25</td>
<td>8.5</td>
<td>5.2</td>
</tr>
<tr>
<td>PC_S</td>
<td>P-NAP</td>
<td>47.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.7</td>
<td>1.4</td>
</tr>
<tr>
<td>PC_H</td>
<td>P-NAP</td>
<td>147.0</td>
<td>-37</td>
<td>-5.5</td>
<td>7</td>
<td>6.4</td>
<td>4.5</td>
</tr>
<tr>
<td>PC_O</td>
<td>P-NAP</td>
<td>12.2</td>
<td>-35</td>
<td>-5.9</td>
<td>12</td>
<td>5.9</td>
<td>2.6</td>
</tr>
<tr>
<td>PC_L</td>
<td>P-NAP</td>
<td>175.0</td>
<td>-31</td>
<td>-5.5</td>
<td>13</td>
<td>8.3</td>
<td>7.2</td>
</tr>
<tr>
<td>PC_I</td>
<td>P-NAP</td>
<td>95.4</td>
<td>-37</td>
<td>-5.2</td>
<td>5</td>
<td>9.7</td>
<td>9.0</td>
</tr>
<tr>
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<td>P-NAP</td>
<td>130.0</td>
<td>-42</td>
<td>-8.5</td>
<td>26</td>
<td>7.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>
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 km², 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(Ca²⁺ + Mg²⁺)/r(Na⁺ + K⁺) ratio, and the HCO₃⁻ 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 Phleagrean 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 SO₄ 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 (HCO₃, NOₓ, NH₃, F, Cl, Br, SO₄, Li, Na, K, Ca, Mg).

![Map of the study area](image)

Fig. 3. Variation of the nitrate concentration in groundwater from 2003-2004 to 2014-2016.

Chemical analysis, including major cations (Na, K, Ca, Mg), anions (Cl, SO₄, NO₃, HCO₃) and metals (Al, Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Sb, Se, Sn, Te, TI, 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 (Δ¹⁵N and Δ¹⁸O of dissolved nitrates and Δ¹⁸O 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).

Δ¹⁵N and Δ¹⁴O 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) with an analytical precision of 0.2 ‰ and 1 ‰, for Δ¹⁸O 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*(Δ¹⁸O + 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 Δ¹⁸O 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 Δ¹⁸O 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 Δ¹⁸O 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 NO₃ > 50.0 mg/L, except a sector of the P-VLTR GWB located on the left side of the Voltumno River, where nega-
5. Conclusions

Hydrogeochemical and isotopic 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 $\delta^{18}$O and $\delta^D$ 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 preva-
lently 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


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Author Contributions: All the authors participated in the study, contributed to writing the paper and agreed with the results and conclusions. Daniela Ducci is the coordinator of the paper. She supervised, together with Alfonso Corniello, who is the coordinator of the study, the entire draft of the article and organized the various contributions of the authors. Elena Del Gaudio and Mariangela Sellerino, executed the huge field work and organized chapters and figures of the paper, carefully revising them. Luisa Stellato performed the isotopic analysis and wrote the parts of the paper concerning the isotopes.