Hydrogeological and multi-isotopic approach to define nitrate pollution and denitrification processes in a coastal aquifer (Sardinia, Italy)

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Abstract

Agricultural coastal areas are frequently affected by the superimposition of various processes, with a combination of anthropogenic and natural sources, which degrade groundwater quality. In the coastal multi-aquifer system of Arborea (Italy) – a reclaimed morass area identified as a nitrate vulnerable zone, according to Nitrate Directive 91/676/EEC – intensive agricultural and livestock activities contribute to substantial nitrate contamination. For this reason, the area can be considered a bench test for tuning an appropriate methodology aiming to trace the nitrate contamination in different conditions. An approach combining environmental isotopes, water quality and hydrogeological indicators was therefore used to understand the origins and attenuation mechanisms of nitrate pollution and to define the relationship between

27   contaminant and groundwater flow dynamics through the multi-aquifer characterized by sandy (SHU),

28   alluvial (AHU), and volcanic hydrogeological (VHU) units. Various groundwater chemical pathways were

29   consistent with both different nitrogen sources and groundwater dynamics. Isotope composition suggests a

30   mixed source for nitrate (organic and synthetic fertilizer), especially for the AHU and SHU groundwater.

31   Moreover, marked heterotrophic denitrification and sulfate reduction processes were detected, although,

32   for the contamination related to synthetic fertilizer, the attenuation was inefficient at removing NO_3^- to less

33   than the human consumption threshold of 50 mg L^{-1}. Various factors contributed to control the distribution

34   of the redox processes, such as the availability of carbon sources (organic fertilizer and the presence of

35   lagoon-deposited aquitards), well depth, and groundwater flow paths. The characterization of these

36   processes supports water-resource management plans, future actions, and regulations, particularly in

37   nitrate vulnerable zones.

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1. Introduction

Water pollution by agricultural nutrients has been recognized as one of the most important environmental problems in the European Union (EU) (Kallis and Buttler 2001). Through Nitrates Directive 91/676/EEC, EU member countries have identified nitrate vulnerable zones (NVZs), developed protocols of good agricultural practice, and set up action programs for the management of farm wastes. However, the Nitrates Directive is emblematic of asymmetries between its objectives and the effectiveness of its implementation, and nitrate pollution of EU groundwater has not decreased in more than 20 years of Nitrate Directive implementation (Howden et al. 2011).

Nutrient loss pathways between soils and groundwater are complex (Collins and McGonigle 2008) and vary with soil type (van Beek et al. 2009), geology (Meinardi et al. 1995), hydrogeology, climate, and ecological interaction between farmer and environment. Such conditions mean that the Directive cannot consider site-specific occurrence of nitrate groundwater pollution and is not targeting the principal sources of nitrate in groundwater (Sacchi et al. 2013).

This paper considers the case of Arborea, one of the most productive agricultural areas in Italy. It has one of the greatest dairy system productivities in Europe. This area, identified as a NVZ through the Nitrates Directive, has a complexity that is mainly related to geomorphological conditions (because historically it was an insalubrious morass, reclaimed afterwards), frequent nitrate groundwater pollution (Nguyen et al. 2013), and is in proximity to seawater associated with the coastal aquifer (Cau and Paniconi 2007). In an anthropogenic environment within a coastal region, degradation of groundwater quality generally occurs because of the superimposition of more than one process. This often leads to both salinization by seawater intrusion (Pittalis et al. 2016) and strong contamination of groundwater, particularly by nitrate (Rajmohan et al. 2009).

In this complex scenario, the reconstruction of a reliable hydrogeological conceptual model that defines groundwater flow paths and thereby predicts the nitrate (NO_3^-) spatial distribution is necessary to better understand nitrate pollution dynamics and related biogeochemical processes. In this case, chemical and isotopic tracers are useful tools to distinguish sources of nitrate in groundwater (Aravena et al. 1993; Panno et al. 2001; Xue et al. 2009; Baily et al. 2011) and to distinguish between dilution and denitrification

73   phenomena (Grischek et al. 1998; Mengis et al. 1999; Cey et al. 1999). $\delta^{15}N_{NO3}$, taking into account the

74   conservative behavior of nitrate in sub-surface environments, has been widely used for identification of NO_3

75   sources in groundwater (Pasten-Zapata et al., 2014 and reference therein). However, because $\delta^{15}N_{NO3}$

76   values are often modified by isotopic fractionation, their use alone is often inconclusive for identification of

77   the origin of NO_3^- in aquatic systems (Zhang et al., 2015). Combinations of $\delta^{15}N$ and $\delta^{18}O$ of nitrate

78   measurements have been utilized to trace (point and nonpoint) N sources. Specifically, by means of $\delta^{15}N_{NO3}$

79   measurements it is possible to distinguish nitrate derived from ammonium fertilizers, organic matter, and

80   animal manure/septic waste, whereas use of $\delta^{18}O_{NO3}$ can distinguish the nitrate content derived from N-

81   fertilizers and atmospheric deposition (Vystavna et al., 2017 and reference therein). In addition, nitrate

82   isotope measurements constitute a viable tool to trace nitrate transformation processes such as

83   denitrification (Puig et al., 2017 and reference therein). Notwithstanding this, the use of only $\delta^{15}N$ and $\delta^{18}O$ of

84   NO_3 and nitrate concentrations in areas characterized by multiple sources of nitrogen, may result in

85   inconclusive outcomes. Indeed, to provide a useful means for identifying the origin of NO_3^- and related

86   transformation processes in groundwater, several authors have combined different types of isotope

87   measurements according to multi-isotopic approaches (Aravena and Robertson 1998; Rock and Mayer

88   2002; Marimon et al. 2007; Urresti-Estala et al., 2015). The isotopes $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate, and

89    $\delta^{13}C$ of dissolved inorganic carbon (Otero et al. 2009; Hosono et al., 2014), can be used because of their

90   involvement in denitrification reactions. Specifically, the contributions of these isotopes allow determination

91   of the role of heterotrophic and autotrophic processes in groundwater denitrification. It is well known that

92   there are two main denitrification reactions in aquifers, i.e., heterotrophic denitrification by oxidation of

93   organic compounds and autotrophic denitrification by oxidation of inorganic compounds such as sulfide

94   (Rivett et al. 2008). In the first case, the denitrification involves an isotopic relationship between $\delta^{13}C_{DIC}$ with

95    $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$. In contrast, autotrophic denitrification implies an isotopic relationship between $\delta^{15}N_{NO3}$

96   and $\delta^{18}O_{NO3}$ with $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$. In addition, the application of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ is a powerful tool for

97   identifying sources of dissolved sulfate and its biogeochemical evolution in groundwater flow systems (Li et

98   al. 2011; Caschetto et al., 2017). In particular, dissolved sulfate in groundwater may originate from

99   dissolution of evaporitic deposits (mainly gypsum), oxidation of reduced S minerals, atmospheric deposition,

100   and seawater intrusion, as well as from anthropogenic sources such as fertilizers, manure, sewage and mine

101   drainage, among others (Puig et al. 2013; Mongelli et al., 2013; Petelet-Giraud et al., 2016).

102   The present study investigates groundwater dynamics and both sources and processes controlling nitrate

103   contamination of groundwater in an agricultural coastal area of western Sardinia. Environmental isotopes

and water quality indicators were combined with hydrogeological observations to characterize the recharge path and trace the sources of nitrate pollution, evaluating chemical reactions related to denitrification processes. The evaluation of redox zonation is critical to understand the key controls on the fate of nitrate pollution in the area.

The case study site provides a number of potential insights regarding the following.

- The dynamics of both groundwater and nitrogen cycles and nitrate pollution, which would ideally support strategies for the mitigation of nitrate pollution in NVZs in the Mediterranean region.
- Assessment of the state of the aquifer, which apparently is much less polluted than expected from the nitrogen surplus caused by the existing concentration of dairy livestock and associated activities.

2. Study Area

The study area is in the northern part of the Campidano Plain (central-western Sardinia, Italy). The northern and eastern borders are the volcanic complexes of Montiferru and Monte Arci. The area is bounded on the south by the Rio Mogoro, the Marceddì and San Giovanni lagoons, and on the west by the Oristano Gulf. A portion of this area (~60 km^2) is occupied by the Arborea District (Figure 1).

Historically, this area was an insalubrious morass, sparsely populated, and largely used for pastoral activities. The first reclamation started in 1812 and continued through 1912, when the Santa Giusta pond (one of the largest in the region) was dredged and the material used to cover marshlands. Because of the reclamation work, drainage of the entire area was regulated by means of addition of sandy soil and a network of channels that convey the water to a dewatering pump system. In 1956, the Assegnatari Associati Arborea (3A) cooperative was established on the Arborea Plain, and soon became the main economic player in the area (Cau and Paniconi, 2007). The cooperative, in fact, manages the rearing of 28,000 bovine livestock units on a 5000 ha irrigated plain, representing one of the most productive agricultural sites in Italy, and the productivity of its diary system is one of the highest in Europe (Mura et al., 2015; Demurtas et al. 2016).

Fig 1

134   The forage cropping systems are based on double-cropping silage corn – Italian ryegrass (representing >

135   80% of the irrigated land), and ~35,600 dairy livestock are raised in a narrow area (Giola et al. 2012).

136   Consequently, the Arborea area was identified as a NVZ in 2005 (Ghiglieri et al. 2009).

137   The climate is Mediterranean, and mean annual temperature and precipitation are 16.7 °C and 568 mm,

138   respectively (1959–2012). Some 73% of annual rainfall occurs between October and March (Demurtas et al.

139   2016), and the average annual aridity index (rainfall / reference evapotranspiration) is 0.49 (semiarid area).

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141   The study area occupies the northern part of the Campidano rift, with a landscape characterized by

142   Quaternary deposits such as littoral-marine (mainly sands) and fluvial-deltaic material (mainly silt, clay, sand

143   and gravel). The former outcrop corresponds with the Arborea Plain and the latter with its eastern side

144   (Ghiglieri et al. 2016).

145   Three hydrogeological units (HU) have been identified:

146   •   Sandy Hydrogeological Unit (SHU);

147   •   Alluvial Hydrogeological Unit (AHU);

148   •   Volcanic Hydrogeological Unit (VHU).

149   The SHU is represented by an unconfined aquifer hosted in the Holocene littoral sands. It shows thicknesses

150   of 20–25 m, with depth decreasing eastward (Figure 2). It is bounded at its base by a layer of lagoonal

151   deposits made up of silt clays and peaty mud, which outcrop at the reclaimed Sassu Lagoon (Ghiglieri et al.

152   2016). The local lagoonal clay deposits include perched sandy lenses, in some cases hosting fossil

153   seawater. The thickness of this impermeable boundary is consistently between 25 and 30 m in the central

154   and northern part of the Arborea Plain. The geologic setting dominated by aggradational stacking causes an

155   increase of the thickness and presence of Holocene lagoon deposits toward the sea. However, as reported

156   in Ghiglieri et al. (2016), in the southern part of the plain, lagoonal clays that delimit the bottom of the sandy

157   aquifer are lacking, such that Holocene sands of the SHU and alluvial aquifers of the AHU (Pleistocene

158   continental deposits) are in hydraulic communication with each other.

159   The AHU is a multilayer aquifer hosted in Pleistocene continental deposits (Figure 2). It consists of gravels,

160   with some sands or clayey sand outcrops throughout the area surrounding the Arborea Plain up to the Monte

161   Arci. This aquifer is confined in the plain because of the aforementioned clay layer, which separates it from

162   the sandy aquifer (SHU). The impermeable layers are represented by the lagoonal clays, which characterize

163   each depositional sequence.

164 Finally, the VHU is an aquifer hosted in basalt, rhyolite and rhyodacite of the Monte Arci formations (Plio-

165 Pleistocene). The volcanic rocks sink rapidly westwards, reaching a sufficient depth to prevent access from

166 any well on the plain (Figure 2).

167

168   **Fig 2**

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171 **3.   Methodology**

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173 Samples for chemical and isotopic characterization were collected in October 2011 from 45 wells in a

174 monitoring network (Figure 2). The wells were distinguished in three groups as a function of SHU, AHU and

175 VHU. Depths range from 2.3 to 52 m below ground (b.g.; median 20 m b.g.; n = 25) in the SHU wells, from

176 14 to 100 m b.g. (median 40 m b.g.; n = 15) in the AHU wells, and from 60 to 110 m b.g. (median 102 m b.g.;

177 n = 5) in the VHU wells. The spatial distribution of the hydraulic head was reconstructed based on 125 data

178 points affiliated to SHU and AHU in September 2011 (Ghiglieri et al. 2016). Temperature, pH, Eh, dissolved

179 oxygen (DO) and electrical conductivity were measured in situ, using a flow-through cell (AP-5000 -

180 Eijkelkamp) to avoid contact with the atmosphere, and sampling was done when values was stabilized.

181 Samples were filtered at 0.2 μm (for the elements that can be influenced by bacteria activity, such as $\delta^{15}N$

182 and $\delta^{18}O_{NO3}$ isotopes), and at 0.45 µm (for the others elements) and transported in 1 L polythene bottles and

183 kept at 4 °C for subsequent chemical and isotopic analyses. Major anions and cations were analyzed

184 according to standard methods (APHA, 1992). Major ions were determined by atomic absorption

185 spectrometry (Perkin Elmer model AAnalyst 200) and ion chromatography (Alltech Allsep anion column 7

186 µm, 100 mm). Nitrate concentration was detected as NO_3 by ion chromatography. Alkalinity was determined

187 by titration (Titrator Orion 950 - Thermo Scientific) and NH_4^+, NO_2^- and SiO_2 content by colorimetry (Cary 60

188 UV-VIS, Agilent Technologies). Replicate analyses of water samples and standards allowed estimation with

189 analytical errors within 5 % for both anion and cation contents. Non-purgeable dissolved organic carbon

190 (NPDOC) was measured using organic matter combustion (TOC-5000, Shimadzu Scientific Instruments).

191 Chemical analyses were performed at the laboratory of the Engineering Department of Sassari University,

192 Italy.

193 The isotopic characterization included the $\delta^{18}O$ and δ^2H of H_2O, $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-, $\delta^{34}S$ and $\delta^{18}O$ of

194 SO_4^{2-}, and $\delta^{13}C$ of DIC (dissolved inorganic carbon). δ^2H_{H2O} and $\delta^{18}O_{H2O}$ were analyzed at the University of

195 Málaga (Spain) with Wavelength-Scanned Cavity Ringdown Spectroscopy for isotopic water measurements

196 with L2120-i Picarro® equipment. Six replicates for each sample were done, although the last three were

197 selected for statistical treatment. The $\delta^{15}N$ and $\delta^{18}O$ of dissolved nitrate were determined using a modified

198 cadmium reduction method (McIlvin and Altabet 2005; Ryabenko et al. 2009). Briefly, nitrate was converted

199 to nitrite through spongy cadmium reduction and then to nitrous oxide using sodium azide in an acetic acid

200 buffer. Simultaneous $\delta^{15}N$ and $\delta^{18}O$ analysis of the N_2O produced was done using a Pre-Con (Thermo

201 Scientific) coupled to a Finnigan MAT-253 Isotope Ratio Mass Spectrometer (IRMS, Thermo Scientific). For

202 $\delta^{34}S$ and $\delta^{18}O$ analyses, dissolved SO_4^{2-} was precipitated as $BaSO_4$ by adding $BaCl_2 \cdot 2H_2O$ after acidifying

203 the sample with HCl and boiling it to prevent $BaCO_3$ precipitation, following standard methods (Dogramaci et

204 al. 2001). The $\delta^{34}S$ was analyzed with the Carlo Erba EA - Finnigan Delta C IRMS. The $\delta^{18}O$ was analyzed

205 in duplicate using a ThermoQuest high-temperature conversion elemental analyzer coupled in continuous

206 flow with a Finnigan MAT Delta X IRMS. For $\delta^{13}C_{DIC}$, carbonates were converted to CO_2 gas by adding a

207 phosphoric acid solution in a GasBench (Thermo Scientiific) and the isotope ratio was measured in a MAT-

208 253 IRMS (Thermo Scientific) coupled to the GasBench. Isotopic results are expressed in terms of delta (δ)

209 per mil relative to the following international standards: Vienna Standard Mean Oceanic Water for $\delta^{18}O$ and

210 δ^2H, Vienna Canyon Diablo Troillite for $\delta^{34}S$, Air for $\delta^{15}N$, and Vienna Pee Dee Belemnite for $\delta^{13}C$.

211 Reproducibility (1σ) was calculated using international and internal laboratory standards systematically

212 interspersed in the analytical batches: ±0.15 ‰ for $\delta^{18}O_{H2O}$, ±1 ‰ for δ^2H_{H2O}, ±0.2 ‰ for $\delta^{34}S_{SO4}$, ±0.5 ‰ for

213 $\delta^{18}O_{SO4}$, ±0.6 ‰ for $\delta^{15}N_{NO3}$, ±1.0 ‰ for $\delta^{18}O_{NO3}$, and ±0.2 ‰ for $\delta^{13}C_{DIC}$. The international and internal

214 laboratory standards used are: for ^2H and ^{18}O in water isotopic analyses OH13, OH14 and OH15

215 (Wassenaar et al., 2012); for ^{34}S in sulfate: NBS127 (+20.3‰); UB-YCEM (+12.8‰) and SO-5 (+0.5‰); for

216 ^{18}O in sulfate: UB-YCEM (+17.6‰); UB-ASC (+13.2‰) and NBS127 (+9.3‰); for ^{15}N in nitrate USGS-32

217 (+180‰); USGS-34 (-1.8‰); USGS-35 (+2.7‰) and UB-IWS (+16.9‰); for ^{18}O in nitrate USGS-32

218 (+25.3‰); USGS-34 (-27.9‰); USGS-35 (+57.3‰) and UB-IWS (+28.5‰); and for ^{13}C in DIC: UB-NA (-

219 4.36‰), UB-NAK (-18.7‰) and UB-K (-29.16‰) calibrated with NBS-18 and NBS-19. Where not otherwise

220 specified, the preparation of samples for isotopic analyses was done at the laboratory of the Mineralogia

221 Aplicada i Geoquímica de Fluids (MAG-UB) research group, and the analysis was done at the Centres

222 Científics i Tecnològics of the Universitat de Barcelona (CCiT-UB), Spain. Bulk isotopic results of the survey

223 are presented in the Appendix (Tables 1 and 3).

224

225 **4. Results**

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4.1. Groundwater flow path

The groundwater mainly flows from east to west, confirming the results of previous investigations (Ghiglieri et al. 2016). In detail, the SHU is recharged laterally from the AHU in the southern part of the Arborea Plain and by zenithal infiltration from local precipitation and irrigation. According to the spatial distribution of the hydraulic head within the SHU, a groundwater divide was recognized in the area from Arborea village to the NVZ central area (Figure 2). The SHU can be considered a homogeneous system in which the water table shows subdued adaptation to the topography, from the groundwater divide area westward to the sea and eastward to the Sassu lagoon.

Within the AHU, the groundwater flows: (i) from east to west, i.e., from the volcanic area toward the sea; (ii) from southeast to northwest in the southern portion of the Sassu lagoon, with the hydraulic gradient decreasing at the border of continental deposits with the alluvial one from about 1% to 0.3%.

The AHU is recharged laterally from the VHU and by zenithal infiltration from both precipitation and irrigation return flow, owing to extensive agricultural activities also in the portion of the plain on the eastern side of the Sassu lagoon.

Therefore, groundwater flows in unconfined conditions within the SHU and part of the AHU (specifically from the Monte Arci formation toward the eastern edge of the Sassu lagoon), highlighting the influence of the drainage channels that, intercepting the aquifer, convey the groundwater toward a pumping station (Figures 2 and 3). In addition, in the AHU (Figure 3), the groundwater flows under confined conditions within a deeper heterogeneous subsystem composed of discontinuous aquitards.

Fig 3

4.2. Hydrochemical facies definition

Groundwater samples showed near neutral or slightly alkaline pH (6.4–8.3). Redox potential values ranged from oxidizing to reducing conditions (Eh = 227 to -180 mV) and dissolved oxygen varied between 9.2 and < 0.1 mg/L for the complete dataset. Conductivity values were between 537 and 7410 µS/cm. Groundwater with electrical conductivity > 2000 µS/cm generally occurred along the coast, but also inland (> 10 kilometers from the coast) where the hydraulic head is > 10–12 m above sea level. In spite of small numbers, VHU samples showed geochemical variability less than that observed in SHU and AHU samples. AHU

256   groundwater showed the greatest variance for almost all considered parameters. Relatively high silica in

257   VHU wells and alkalinity in SHU wells pinpoint the respective contributions of silicate and carbonate minerals

258   in those aquifers.

259   Electrical conductivity, chloride and sodium concentration in SHU and AHU wells strongly revealed the

260   effects of saline sources in a coastal region. At the same time, elevated concentrations of nitrate in the SHU

261   wells (reaching 243 mg/L) and in part of the unconfined AHU (up to 143 mg/L) reflect the influence of

262   anthropogenic activities in the area.

263   Hydrochemical facies was deduced according to the classification of Stuyfzand (2008), modified as indicated

264   in Fig. 4 to consider the nitrate pollution grade. The Stuyfzand classification is well known for its application

265   to coastal areas for the determination of water type and evaluation of geochemical processes

266   (Vandenbohede and Lebbe 2012; Ghiglieri et al. 2012; Mollema et al. 2013), and is useful for systems

267   experiencing excessive application of manure and other fertilizers (Stuyfzand 1986). The classification was

268   based on Cl^- content, alkalinity, major cations and anions, Base Exchange Index (BEX), and NO_3 content, in

269   order to define water type as a combination of various parameters considered in a hierarchical structure with

270   five levels of subdivision (Figure 4).

271

272   **Fig 4**

273

274   Table 2 of the Appendix shows a synthesis of main water types identified in each aquifer, grouped on the

275   basis of nitrate content. The terms of the classification (Cl^- content, alkalinity, major cations and anions, and

276   BEX) are listed following relative abundances. According to the classification, hydrochemical facies in the

277   study area range from fresh (F) to brackish-salt (b) waters. There was high nitrate content in both fresh-

278   brackish (f) and brackish-salt water (b), with variable alkalinity.

279   Fresh waters show nitrate concentrations < 50 mg/L. When the NO_3 pollution grade is low (L), these waters

280   show greater alkalinity and a Na mixed character, whereas with nitrate increase (M), groundwater shows a

281   NaCl character.

282   Brackish-salt-water occurrences are limited to a few wells on the coast (SHU) and inland in the AHU.

283   These waters showed a Ca/HCO_3 ratio > 1. However, waters on the coast had high chloride and were

284   oversaturated with respect to calcite, whereas inland waters showed SO_4 up to 340 mg/L and

285   undersaturation with respect to calcite.

286   Brackish waters were mainly found in the SHU, in the southern part of the reclamation area. Chemical

287   compositions range from NaCl to CaCl types, with very variable nitrate content (L, M, HH) and high HCO_3.

288

289   *4.3. Isotopic data*

290   The plot in Fig. 5 shows values of $\delta^{18}O$ and δ^2H ranging from −6.7 ‰ to −4.7 ‰ and −37.9 ‰ to −28.1 ‰,

291   respectively (Table 3). Most of the SHU and AHU samples fall on the Local Meteoric Water Line (LMWL, δD

292   = 7.46 ^{18}O + 7.22), indicating that they are of meteoric origin. In contrast, water isotopic compositions of VHU

293   and some of the AHU samples are more depleted. In this case, recharge may derive from: (i) rainwater

294   affected by an altitude gradient that causes an isotopically depleted precipitation, owing to lower average

295   temperature at higher altitudes (Clark and Fritz 1997; Williams 1997); (ii) rainwater conditions cooler than at

296   present (Edmunds et al. 2003; Zhu et al. 2007).

297

298   **Fig 5**

299

300   Most SHU samples collected from wells drilled to large depths of 30–53 m b.g. showed values similar to the

301   AHU samples, reflecting the likely existence of a link to various aquifer zones (Clark and Fritz 1997).

302   According with the water isotope values of groundwater, no significant influence of seawater intrusion is

303   observed. Also the relationship between chlorine content and water isotopic values points out that seawater

304   intrusion is not occurring in the studied area. Some evaporative processes in the unsaturated zone can

305   explain the displacement of some data from the water meteoric line to the global meteoric line.

306

307   The isotopic composition of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ was from +4.3 ‰ to +43.0 ‰, and +0.9 ‰ to +24.6 ‰,

308   respectively (Table 3). In Figure 6, $\delta^{15}N$ and $\delta^{18}O$ in dissolved NO_3^- is represented together with the isotopic

309   composition of the main NO_3^- sources, i.e., synthetic fertilizers (NO_3^-, nitrified NH_4^+), soil-N, and animal

310   manure (organic fertilizer) or sewage (Vitòria et al. 2004; Kendall et al. 2007; Xue et al. 2009). The $\delta^{18}O_{NO3}$

311   derived from nitrification of NH_4^+ was calculated following the experimental equation 1 (Anderson and

312   Hooper, 1983):

313

314                            $\delta^{18}O_{NO3} = 2/3\delta^{18}O_{H2O} + 1/3\delta^{18}O_{O2}$ (1)

315

316 where $\delta^{18}O_{H2O}$ represents the range obtained from the field survey (−4.7 ‰ to −6.7 ‰), and $\delta^{18}O_{O2}$ was

317 assumed to be that of atmospheric O_2 (+23.5 ‰). Hence, NO_3^- in the study area should have $\delta^{18}O_{NO3}$ values

318 between +3.2 ‰ and +4.5 ‰. Nonetheless, $\delta^{15}N$ and $\delta^{18}O$ values in most of the samples from that area were

319 larger than theoretically expected, suggesting nitrate attenuation processes.

320 NO_3^- concentration measured in the VHU was from 1.9 to 23.1 mg/L, with median 8.6 mg/L ($n = 5$).

321

322 **Fig 6**

323

324 Samples collected in the AHU show substantial variation in NO_3^- concentration (0.5–143.4 mg/L; mean 31

325 mg/L). Specifically, samples from the eastern AHU (P146, P331, P264, P165 and P184), adjacent to the

326 Monte Arci formation, show a lower NO_3^- concentration (< 25 mg/L) related to soil-N (Figure 6) and isotopic

327 compositions similar to the VHU, possibly representing a natural endmember.

328 Samples that according to the flow path were located closely up-gradient with reference to Sassu lagoon

329 (P292, P296, P257, P324, P342, and P361) showed variable nitrate contents, from below the detection limit

330 (P257) to 134 mg/L (observed in the shallowest well, P296). Finally, samples from the confined AHU below

331 the reclaimed lagoon (P253 and P293) and below the Arborea NVZ (P85 and P211) showed NO_3^-

332 concentrations < 1 mg/L. About the SHU, the samples show a wide range of NO_3^- content, between 0.3 and

333 216 mg/L, with a mean value of 74.1 mg/L.

334 All samples showed higher $\delta^{15}N$ and $\delta^{18}O$ values than theoretical values for the sources defined above

335 (Figure 6). Nevertheless, these heavier values can indicate that some denitrification processes are occurring,

336 even if an uncertainty about the theoretical values for the $\delta^{18}O_{NO3}$ of the sources has to be considered.

337 The increases in the $\delta^{15}N$ and $\delta^{18}O$ of the residual nitrate, in fact, is caused by denitrification and produce a

338 distinctive isotopic signature recognizable within a range (Figure 6) defined from denitrification studies by

339 Böttcher et al. (1990) and Aravena et al. (1998). In addition, as detailed below, the presence of a redox

340 gradient, disappearance of dissolved O_2 and increases in alkalinity (mostly bicarbonate), are usually

341 associated with significant denitrification (Kendall, 1998).

342 The $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate ranges from +4.3 ‰ to +43.0 ‰, and +0.9 ‰ to +24.6 ‰, respectively

343 (Table 3). Three sources can be related to SO_4^{2-} (Figure 7): intrusion of marine water and aerosol, influence

344 of soil-derived SO_4^{2-} content and agrochemical products and manure.

345

346 **Fig 7**

347

5. DISCUSSION

349 Hydrochemical results highlighted a variability in geochemical features reflecting the occurrence of different

350 hydrosomes (water bodies with a specific origin; Stuyfzand 1999) affected by multiple processes. Brackish-

351 salt waters, showing a molar Na/Cl ratio lower than sea water, suggest that Na removing processes

352 occurred. Cation exchange processes between Na and Ca has been reported in other aquifers affected by

353 salinization (Appelo and Postma, 2005). High alkalinity in brackish water may result from denitrification

354 processes (Otero et al. 2009). However, stratigraphic information from boreholes in the SHU in this area

355 have revealed remains of shells and limestone strata interbedded with sands (Ghiglieri et al. 2016).

356 Most groundwater showed a molar SO_4/Cl ratio higher than seawater, indicating additional sulfate other than

357 marine sources. Despite the lack of a strong correlation between NO_3^- and SO_4^{2-}, other sources of sulfates

358 could be related to fertilization practice (Mahlknecht et al., 2017). Therefore, the enhanced concentrations of

359 major ions and nitrate indicate that groundwater quality is impaired by both saline sources and pollutant

360 influx from anthropogenic activities. Specifically, nitrate contamination may result from fertilizer, manure,

361 septic tank effluent, municipal and animal waste, and landfill.

362

5.1. Sources of Nitrate

364 Different sources of nitrate were detected for the groundwater of the study area according to the dissolved

365 nitrate isotopic composition (Fig 6). In detail, VHU samples show a relationship with soil-N (even if influence

366 of NH_4 fertilizer slightly volatilized cannot be excluded), except the sample P166 that, due to the $\delta^{15}N$ and

367 $\delta^{18}O$ values coupled with low Eh and relatively high NPDOC, suggest the existence of denitrification

368 processes. About the AHU, the samples located up-gradient with reference to Sassu lagoon (P292, P296,

369 P257, P324, P342, and P361) show an isotopic composition attributable to synthetic fertilizers. Denitrification

370 processes may have occurred also in these waters. Some processes can be supposed also for the samples

371 from the confined AHU below the reclaimed lagoon (P253 and P293) and below the Arborea NVZ (P85 and

372 P211) supported by conditions favorable to denitrification (DO ranged from 0.1 to 3.6 mg/L and Eh as low as

373 −138 mV).

374 The isotope composition of SHU samples suggests a mixed source of nitrate. Most samples (P112, P28,

375 P41, P133, P12, P124, P132, P116, P13, P354 and P118) are within the area defined by synthetic fertilizer

376 whereas the samples P14, P205 and P88 showed nitrate isotopic composition attributable to manure or

377 sewage. In contrast, no precise sources of nitrate were recognized in samples P26, P77, P48, P215 and

378   P283. On the whole, all the SHU samples appear influenced by denitrification processes, even if with

379   different magnitude. Specifically, for the samples affected by synthetic fertilizer the attenuation was not

380   efficient enough to remove nitrate (concentrations from 49 to 202 mg/L). Exceptions were observed in

381   samples P112, P28 and P133 which showed lower nitrate concentration (< 8 mg/L). Instead, for those

382   samples in which organic fertilizer sources have been defined, the denitrification processes have contributed

383   to decrease nitrate concentration below 34 mg/L. Also for the samples with no clear nitrate origin definition

384   (mean nitrate concentration ~146 mg/L), a high load of NO_3^- appeared to overcome the natural capacity to

385   promote denitrification. Indeed, the fate of nitrate in SHU is influenced by the sandy soils texture. Lower

386   contents of silt and clay, in fact, can reduce cation exchange capacity, which in turn allows faster nitrate

387   leaching into groundwater (Biddau et al. 2016). In addition, an influence is attributable to the recent change

388   of fertilizer management systems, i.e. higher use of inorganic instead of organic fertilizer in the Arborea NVZ

389   (Demurtas et al. 2016) may have contributed to the isotopic signature.

390

391   ***5.2. Sources of Sulfate***

392   Figure 7 shows that sulfate can be related to different sources. Some samples can be attributed to marine

393   sulfate, with isotopic signature +20 ‰ for $\delta^{34}S_{SO4}$ and +9 ‰ for $\delta^{18}O_{SO4}$ (Utrilla et al. 1992). Specifically,

394   $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ from VHU samples showed values that can be related to seawater sulfate. As shown in

395   Figure 8, this influence was in agreement with the observed SO_4^{2-}/Cl^- ratio in VHU samples near the

396   seawater ratio. However, sulfate concentration in these samples was low (< 40 mg/L). Because of this low

397   concentration, the distance from the coast of wells and the meteoric water isotopic values of groundwater

398   without seawater influence, the existence of seawater intrusion related to water extraction can be discarded.

399   One hypothesis explaining a seawater source of sulfate is the presence of some deep saline paleo-waters

400   that could have been recharged during past transgressions, which have evolved through mixing with sulfate-

401   free freshwater (Aquilina et al. 2013, Duriez et al. 2008, Edmunds and Milne 2001, Cary et al. 2015). Another

402   hypothesis is related to dissolution of evaporites present in lagoon deposits. Evaporites may have been

403   precipitated during regression periods when the lagoon was isolated from the sea. Similar evaporitic

404   minerals have been observed in salt marsh environments, because of direct precipitation from seawater

405   (Warren et al. 2006). The presence of evaporite materials in the lagoon deposits could also be responsible

406   for the weak seawater influence on $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ in some AHU and SHU samples (Figure 7). In any

407   case, further research is needed to characterize different sources of sulfate related to seawater in the study

408   area, with the aims of identifying the source of sulfate in groundwater.

409   Other sources of sulfate (Figure 7) can be ascribed to soil-derived SO_4^{2-} (groundwater with $\delta^{34}S_{SO4}$ and

410    $\delta^{18}O_{SO4}$ between 0 ‰ and 6 ‰, Krouse and Mayer 2000) and agrochemical and manure products. The latter,

411   considering potential anthropogenic SO_4^{2-} sources, show isotopic compositions with mean $\delta^{34}S_{SO4}$ = +5 ‰

412   and $\delta^{18}O_{SO4}$ = +12 ‰ respectively, according to similar environmental conditions reported by Vitòria et al.

413   (2004). Moreover, part of SHU and AHU samples are characterized by sulfate reduction processes,

414   specifically for the samples that have availability of an organic C source.

415

416

417   **Fig 8**

418

419

420   ***5.3. Evidence of Denitrification processes***

421   The nitrate isotopic composition confirms the occurrence of denitrification, particularly for the SHU and some

422   AHU samples. Denitrification processes are consistent with other geochemical indicators such as DO

423   concentrations < 2.0 mg/L and low Eh values, indicating conditions suitable for denitrification in the aquifer

424   (Korom 1992). The observed denitrification can be promoted by autotrophic bacteria, which use inorganic

425   compounds such as sulfide as electron donors, or heterotrophic bacteria that use organic carbon as a source

426   of electrons. Denitrification produced by sulfide should increase sulfate concentration, contemporaneous with

427   a shift of sulfate isotopic composition. The $\delta^{15}N_{NO3}$ vs. $\delta^{34}S_{SO4}$ diagram (Figure 9) illustrates that samples

428   affected by strong denitrification ($\delta^{15}N_{NO3}$ > +15 ‰) do not show evidence of SO_4^{2-} originating from sulfide

429   oxidation ($\delta^{34}S$ < −5 ‰). An exception is represented by the sample P283 from SHU, located in the

430   southeast of Arborea NVZ. This sample, with $\delta^{34}S_{SO4}$ values around 0 per mil, is consistent with a sulfate

431   originated from sulfide oxidation that was not able to discard autotrophic denitrification. Nevertheless, neither

432   chemical nor isotopic data confirm the role of sulfide in NO_3^- attenuation observed in the Arborea NVZ.

433

434   **Fig 9**

435

436   Alternatively, the presence of peaty mud sediments from Holocene deposits can act as a source of organic

437   matter to develop heterotrophic denitrification in the AHU and SHU. In addition, livestock effluents (mostly

438   slurry) used as organic fertilizer in Arborea constitute large amounts of organic input (Pinna et al., 2014) and,

439   despite the predominant sandy composition of soils in the study area, their long-term application contributed

440   to greater soil organic carbon in the soil (Cappai 2013).

441   The relationship between $\delta^{13}C_{DIC}$ and bicarbonate concentrations, as well as NPDOC concentration, is

442   typically used to explain the role of organic matter oxidation in denitrification. In the study area, measured

443   $\delta^{13}C_{DIC}$ had values from −6.6‰ to −24.6 ‰ (median −12.4 ‰). Most samples (Figure 10) had values in

444   agreement with the known range of $\delta^{13}C_{DIC}$ for groundwater (−16 ‰ to −11 ‰; Vogel and Ehhalt 1963),

445   although the larger values detected could have had some influence from marine carbonates. Hence,

446   chemical equilibria among the dissolved carbonate species mask any chemical and isotopic variation caused

447   by heterotrophic denitrification.

448

449   **Fig 10**

450

451   Referring to NPDOC concentration, degradation and leaching of organic matter can increase electron donor

452   availability in water, and may therefore promote denitrification. In the study area, NPDOC concentration

453   varied from a minimum in the VHU (1.4 mg/L) to a maximum in the SHU (22.1 mg/L). High NPDOC

454   concentrations matched large values of $\delta^{15}N_{NO3}$ (Figure 11). The variation in NPDOC concentration and

455   denitrification can be attributed to the heterogeneous distribution of both, organic matter, and NO_3^- inputs. If

456   NPDOC contents is the limitation of the denitrification reactions, biostimulation, adding dissolved organic

457   matter to the aquifer, would enhance the nitrate attenuation.

458

459   **Fig 11**

460

461   ***5.4. Evidence of sulfate reduction***

462   As clearly shown in Fig. 7, sulfate reduction processes were detected in some SHU (P8, P10, P65, P72,

463   P83) and AHU (P85, P211, P253, P324) samples that simultaneously showed large values of both $\delta^{34}S_{SO4}$

464   and $\delta^{18}O_{SO4}$ and low NO_3^- concentrations (< 1 mg/L). These samples had DO ranging from 0.2 to 4.1 mg/L

465   and Eh from +51 to −180 mV. These parameters, with low DO and reducing groundwater conditions, are

466   favorable to sulfate reduction. In general, once NO_3^- is completely removed by denitrification, the excess

467   organic carbon could be used to promote SO_4^{2-} reduction according to reaction 2:

468

469   $$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad (2)$$

470

471 An exception was the sample P324, which had a nitrate concentration of 110 mg/L. This sample was

472 collected from a fully screened deep well (50 m b. g.), where it is possible that shallow groundwater polluted

473 by nitrate is mixed with deep groundwater.

474 Overall, the AHU and SHU aquifers, composed of alluvial-lacustrine and littoral deposits, may provide a

475 potential reductive environment for SO_4^{2-} consumption in groundwater, although the samples affected by

476 sulfate reduction did not show any sign of depletion in terms of SO_4^{2-} concentration.

477 The effect of net SO_4^{2-} changes on isotopic compositions and concentration can be evaluated by the

478 normalization of SO_4^{2-} to Cl^- in groundwater (Li et al. 2011). In fact, considering the conservative behavior of

479 Cl^-, the decrease of SO_4^{2-}/Cl^- ratio can indicate sulfate removal associated with biogeochemical processes

480 (Dogramaci et al. 2001; Berner et al. 2002). As shown in Fig. 8, a decreasing (SO_4^{2-}/Cl^-) ratio coupled with an

481 increase of $\delta^{34}S_{SO4}$ suggests that isotopically light SO_4^{2-} was progressively removed and the residual SO_4^{2-}

482 became enriched in ^{34}S and ^{18}O during sulfate reduction. In general, the samples with smaller $\delta^{34}S_{SO4}$ and

483 $\delta^{18}O_{SO4}$ values and large SO_4^{2-}/Cl^- ratios can be linked to an initial SO_4^{2-} pool, such as marine or

484 anthropogenic sulfate.

485

486 **5.5. Spatial distribution of Redox reactions**

487 Denitrification and sulfate reduction processes have been specifically identified for the AHU and SHU. For

488 the AHU, denitrification has not been identified in groundwater collected from the area adjacent to the

489 volcanic massif. On the contrary, moving from the eastern side of the Sassu lagoon toward the Arborea NVZ,

490 denitrification processes have been identified. The occurrence of denitrification, especially when

491 groundwater flows in confined conditions, is supported by indicators such as dissolved oxygen

492 concentrations (3.5 mg/L) and Eh (–180 mV). Samples such as P85 and P211 (within the NVZ) and P253

493 and P293 (corresponding to Sassu lagoon) show evidence of reduction processes, suggesting the

494 availability of an organic C source within the lagoon deposit aquitard. This provides the basis for enhanced

495 reduction of nitrate and sulfate in this area. Also, the geologic setting supports the presence of Holocene

496 lagoon deposits toward the sea, revealing the importance of this material in the control of the attenuation

497 observed in the AHU.

498   In the SHU, the variation in NO_3^- content is related to the heterogeneous nitrate load and the degree of

499 denitrification, the latter being modulated by well depth, the availability of organic C, and the groundwater

500 flow path. In general, a lower content of nitrate in groundwater, imputable to denitrification processes, has

been observed when nitrate comes from organic rather than synthetic fertilizers. It is reasonable to assume that the high NO_3^- load from synthetic fertilizer overwhelms the capacity to promote efficient denitrification. This is in line with the situation in the study area over recent decades, in which organic effluents (representing > 50 % of the crop N input source) have been progressively replaced by mineral fertilizer not reducing, *de facto*, nitrate leaching.

The wells with depths < 10 m b.g. had higher nitrate concentrations, especially when the origin was clearly attributable to synthetic fertilizers (Figure 12). In addition, those wells showed evidence of sulfate reduction (Figure 13).

Fig 12

The SHU groundwater intercepted at depths > 10 m b.g. showed strong variability in terms of redox reaction distribution in the area. Some samples in the southern portion of the area (e.g. P124), located on the flow path down-gradient from the groundwater divide, had high NO_3^- concentrations (up to 123 mg/L) as a result of nitrate loading from sources upstream. Furthermore, the thin and discontinuous layers of Holocene lagoon deposits permit the mixing of SHU and AHU groundwater, limiting the efficiency of denitrification. In contrast, the deepest SHU groundwater, adjacent to the coast (P8, P10, P65 and P83), showed NO_3^- concentrations below the detection limit, with even evidence of sulfate reduction (Figures 12–13). In this case, in addition to the presence of clay lenses of lagoonal origin, this reduction is attributable to the absence of drainage from up-gradient contaminated wells.

In the central-east part of the NVZ, near Sassu lagoon, it has not been possible to clearly define reduction process paths. In fact, some SHU deep samples (P219 and P72) showed almost complete nitrate attenuation (NO_3^- < 7 mg/L; $\delta^{15}N$ > 30 ‰), whereas shallower wells (< 12 m b.g) such as P215 and P77, with large $\delta^{15}N$ and $\delta^{18}O$ values (>15.9 ‰ and >12.5 ‰, respectively), had high nitrate concentrations (> 137 mg/L).

Fig 13

6. CONCLUSIONS

This paper presented an analysis of multiple isotopes, water chemistry, and hydrogeologic results to identify the sources and fate of NO_3^- in an agricultural coastal area in western Sardinia. According to the results, the

532 presence of reclaimed lagoons is a key factor in the groundwater flow path, for both the phreatic aquifer and

533 confined conditions within a deeper heterogeneous subsystem composed of discontinuous aquitards.

534 Various groundwater chemical paths were consistent with different nitrogen sources and groundwater

535 dynamics, moving from the mountain area (eastern study area) to the coast. According to δ^2H_{H2O} and $\delta^{18}O_{H2O}$

536 groundwater values, in the studied area, groundwater is mainly originating from local precipitation and no

537 significant seawater intrusion is occurring. Groundwater quality is affected by multiple processes associated

538 with saline (sea spray deposition on topsoil and input of sea salts trapped in lagoonal sediments) and

539 anthropogenic sources (linked to agriculture and livestock raising). Nitrate sources were clearly differentiated

540 by the use of $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ isotopes in soil-N, mineral, and organic fertilizers. The $\delta^{34}S_{SO4}$ and

541 $\delta^{18}O_{SO4}$ isotopes supported the above results, showing mixing between anthropogenic sources (linked to

542 agricultural and livestock raising activities) and marine sulfate. That sulfate is most likely related to saline

543 paleo-waters recharged during past transgressions, or to the dissolution of evaporites occurring in the lagoon

544 deposits as salt precipitation. In addition, nitrate and sulfate isotopes revealed the existence of denitrification

545 and sulfate reduction processes, in agreement with chemical indicators (i.e., Eh values, dissolved oxygen,

546 and NPDOC concentration). By contrast, $\delta^{13}C_{DIC}$ was not suitable to explain the role of organic matter

547 oxidation in the natural nitrate attenuation. Heterotrophic denitrification was specifically highlighted for the

548 AHU and SHU, owing to the presence of peaty mud sediments from Holocene deposits and organic

549 fertilizers (livestock effluents). Regarding the distribution of nitrate and natural attenuation processes in the

550 study area, the eastern side (reaching the reclaimed lagoon) generally showed lower nitrate concentrations

551 in the VHU and part of the AHU, attributable to soil-N. The AHU samples closely located up-gradient from the

552 reclaimed lagoon pointed to a nitrate origin from synthetic fertilizers and heterotrophic denitrification

553 processes. From that lagoon to the sea, AHU groundwater flow in confined conditions had the lowest NO_3^-

554 concentrations, owing to conditions favorable to heterotrophic denitrification and sulfate reduction processes.

555 In the SHU west of the reclaimed lagoon, a mixed source for nitrate was defined, which in some cases

556 increased according to the flow path. Also in this groundwater, there were heterotrophic denitrification and

557 sulfate reduction processes. However, high nitrate concentrations in samples influenced by synthetic

558 fertilizer indicate attenuation insufficient to remove NO_3^- to below the human consumption threshold. For

559 SHU groundwater, therefore, the change from organic to inorganic fertilizer application did not reduce the

560 nitrate pollution in groundwater. As in the study area natural attenuation processes are taking place, it would

561 be suitable to promote biostimulation to add dissolved organic matter and, consequently, electron donor

562 availability to the aquifer therefore promoting denitrification.

563   In conclusion, the present study demonstrates that the combination of multi-isotope, chemical and

564   hydrogeological approaches facilitates nitrate source identification and the evaluation of nitrate removal via

565   biogeochemical transformation processes in a multi-aquifer system under Mediterranean conditions.

566   However, characterization of potential nitrate and marine source terms as well as the enrichment factor for

567   aquifers should be acquired to better define the evolution of contamination and to implement remediation

568   techniques.

569

570

Acknowledgments

576

577 **Appendix 1**

578

579 **Table 1** Hydrochemical data of sampled groundwater in Arborea area, October 2011. Dissolved oxygen (DO), cations

580 and anions are in mg/L; temperature (T) is in °C; Electrical Conductivity (EC) in μS/cm; Redox potential (Eh) is in mV

581

Sample ID	T	pH	EC	Eh	DO	Cl^-	SO_4^{2-}	HCO_3^-	NO_2^-	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SiO_2	DOC
SHU																	
P8	20.0	7.7	5030	-180	0.2	1525.0	74.5	181.8	-	1.0	0.10	750.0	27.5	125.0	75.0	26.8	-
P10	19.6	8.0	1243	-49	0.1	269.8	31.3	205.4	-	0.5	0.00	170.0	14.4	40.0	21.0	27.1	-
P12	20.5	7.0	1034	33	3.9	170.2	72.6	144.5	0.20	49.3	n.d.	122.5	28.0	27.0	19.0	41.7	8.0
P13	19.2	7.5	1575	95	0.2	247.8	83.1	245.2	0.20	205.1	n.d.	120.0	7.0	130.0	40.0	29.6	-
P14	23.0	7.3	723	96	3.8	114.6	35.4	181.5	0.00	1.4	0.10	76.0	12.8	48.0	12.0	31.2	8.6
P26	21.3	6.9	3180	160	0.8	647.7	171.4	642.5	0.10	49.9	0.10	310.0	42.0	165.0	105.0	28.0	-
P28	19.6	7.8	1216	152	2.3	217.8	88.2	236.9	0.00	3.7	0.10	190.0	8.1	34.0	17.0	23.0	11.4
P41	19.4	7.5	1483	139	4.1	201.8	97.1	293.1	0.70	136.9	0.10	125.0	6.5	120.0	36.0	28.0	14.9
P48	22.3	7.0	1809	179	6.9	214.8	102.7	481.1	1.40	146.4	0.20	140.0	88.0	132.0	38.0	36.1	21.2
P65	19.6	7.9	1121	-135	2.5	237.9	23.7	237.4	-	0.4	n.d.	150.0	6.7	48.0	17.0	21.7	-
P72	19.4	7.9	1808	8	4.1	406.5	32.0	312.4	-	1.1	n.d.	290.0	11.5	31.0	26.0	28.7	-
P77	20.2	6.9	2000	148	3.0	367.8	155.4	277.0	0.10	168.5	0.10	190.0	12.5	116.0	65.0	22.6	-
P83	19.8	7.5	4060	-33	2.8	1195.0	82.3	177.3	-	0.8	n.d.	500.0	20.3	144.0	80.0	23.0	-
P88	20.8	7.4	2330	144	2.8	384.3	118.9	577.7	0.10	34.1	0.30	245.0	54.0	138.0	50.0	41.4	22.1
P112	18.8	7.7	1518	190	4.1	308.1	47.0	248.7	0.00	7.6	n.d.	170.0	13.8	64.0	40.0	26.6	-
P116	19.3	7.5	1219	162	0.0	199.1	46.2	232.7	-	71.3	n.d.	130.0	8.8	69.0	26.0	29.4	-
P118	19.9	7.1	1560	178	3.5	236.9	77.0	298.1	-	119.4	n.d.	130.0	9.8	128.0	34.0	34.9	-
P124	19.8	7.9	1845	165	4.3	339.6	83.9	212.5	1.20	122.7	n.d.	285.0	8.5	36.0	18.0	21.5	-
P132	21.5	6.9	2100	185	3.3	304.1	108.8	448.3	0.20	202.2	0.10	190.0	15.8	170.0	55.0	32.8	-
P133	20.1	7.7	2140	155	0.3	544.9	64.6	212.8	0.00	4.4	n.d.	220.0	14.5	113.0	50.0	25.0	-
P205	22.0	6.9	537	155	6.2	77.0	26.4	124.9	-	6.4	0.10	54.0	12.2	28.5	10.5	26.2	-
P215	21.1	6.4	2160	160	1.4	370.0	116.9	256.0	0.20	215.8	0.10	200.0	20.0	88.0	70.0	29.8	12.4
P219	20.4	8.0	1344	-75	0.2	270.9	56.5	295.7	-	0.3	n.d.	230.0	6.6	24.0	13.0	25.9	-
P283	21.0	7.5	1464	177	9.2	186.6	108.8	277.4	-	156.3	n.d.	115.0	12.3	126.0	32.0	33.1	-
P354	18.9	6.9	2510	199	1.7	411.7	181.2	477.8	-	147.6	n.d.	280.0	9.0	180.0	47.5	41.9	-
AHU																	
P85	21.9	8.3	1929	-138	3.2	468.0	103.1	172.9	-	0.5	n.d.	350.0	3.5	28.0	11.0	18.9	-
P146	21.1	6.6	1846	174	5.2	446.1	52.4	126.5	-	6.0	n.d.	180.0	14.5	61.0	50.0	97.4	-
P165	20.4	6.8	7410	85	3.6	2260	217.8	374.2	-	27.2	1.20	675.0	41.8	330.0	300.0	76.5	-
P184	19.2	7.1	2700	136	5.0	611.0	123.3	275.1	-	72.3	n.d.	360.0	18.0	82.0	60.0	78.0	-
P211	20.9	7.8	2040	-97	0.3	476.8	92.7	220.0	-	0.5	n.d.	340.0	9.8	44.0	17.0	24.2	-
P253	21.0	7.3	2370	51	0.1	566.8	70.7	182.0	-	0.5	n.d.	320.0	17.5	74.0	30.0	56.9	-
P257	22.2	8.0	836	67	0.7	118.8	25.0	249.8	-	0.6	n.d.	136.0	7.0	14.0	7.0	57.1	-
P264	22.9	6.8	5270	110	4.0	1450.0	256.6	227.8	-	24.9	n.d.	600.0	28.8	196.0	150.0	79.2	-
P292	21.0	6.7	1061	227	1.5	215.5	41.3	146.3	-	14.3	n.d.	140.0	8.2	32.0	18.0	52.2	-
P293	21.0	7.6	1299	125	1.0	238.1	86.3	224.1	-	0.5	n.d.	190.0	9.1	40.0	13.0	40.2	5.5
P296	19.8	6.5	1460	227	1.4	251.8	97.9	135.9	-	143.4	n.d.	185.0	7.8	43.0	30.0	46.1	-
P324	19.3	7.0	6650	25	4.2	1809.9	343.5	222.6	0.10	110.3	0.10	875.0	23.8	218.0	125.0	55.3	4.7
P331	19.8	6.4	751	199	4.6	132.3	49.3	102.2	-	22.3	n.d.	84.0	9.4	20.0	20.0	74.8	7.5
P342	19.8	7.4	1557	180	1.9	245.5	101.7	332.2	-	31.6	n.d.	185.0	9.1	74.0	40.0	34.5	-
P361	19.3	7.4	1245	165	0.9	195.5	60.6	296.8	-	11.2	n.d.	185.0	7.6	27.0	17.0	39.2	1.4
VHU																	
P138	21.2	6.6	743	162	6.2	141.0	27.4	119.3	0.00	23.1	n.d.	90.0	10.6	19.0	16.0	63.3	-
P142	23.6	7.4	1050	141	3.4	223.5	23.9	165.1	-	1.9	n.d.	180.0	8.6	7.0	6.5	97.7	-
P156	21.3	7.4	1692	157	6.5	387.1	41.1	226.1	-	3.1	n.d.	300.0	12.3	25.0	20.0	89.8	4.3
P159	20.7	6.9	1196	170	3.5	264.3	35.7	161.1	-	7.3	n.d.	175.0	12.2	21.0	19.0	96.1	-
P166	21.6	7.8	1073	43	5.1	204.7	32.0	201.4	-	7.8	n.d.	180.0	11.0	20.0	14.0	91.7	-

Table 2 Synthesis of main water types for the aquifer in Arborea area, grouped on the basis of nitrate content

Hosting aquifer	NO$_3$ pollution grade	No. of wells	Water Classification
SHU	HH	11	(f-B)(3-2)(CaMIX-CaCl-NaMIX-NaCl)(+)
SHU	M	3	(B-F)(4-2)(NaCl-CaCl-NaMIX)(+)
SHU	L	11	(f-B-b-F)(2-3)(NaCl-NaMIX)(+ -)
AHU	HH	3	(f-B-b)(2-3)(NaCl)(+ -)
AHU	M	6	(F-b-F)(3-2-1)(NaCl-NaMIX-CaCl)(+ -)
AHU	L	6	(B-F-f)(2-3)(NaCl-NaMIX)(+ *)
VHU	M	1	(F)(1)(Na-Cl)(+)
VHU	L	4	(f-B)(2)(NaCl)(+)

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611　**Table 3** Isotopic data (‰) of sampled groundwater in Arborea area, October 2011

Sample ID	$\delta^{15}N\text{-}NO_3$	$\delta^{18}O\text{-}NO_3$	$\delta^{34}S\text{-}SO_4$	$\delta^{18}O\text{-}SO_4$	$\delta^{13}C\text{-}DIC$	$\delta^2H\text{-}H_2O$	$\delta^{18}O\text{-}H_2O$
SHU							
P8	-	-	24.3	19.3	-8.4	-29.9	-5.1
P10	-	-	28.4	19.0	-14.2	-30.5	-5.4
P12	10.8	13.6	11.2	10.2	-18.4	-29.9	-5.1
P13	12.5	9.4	8.1	7.7	-12.7	-31.0	-5.2
P14	27.7	14.6	10.8	9.0	-15.7	-31.9	-5.6
P26	29.2	20.8	12.0	12.2	-7.9	-31.3	-5.1
P28	16.2	16.0	11.6	11.6	-6.6	-34.2	-5.6
P41	15.9	15.1	8.2	7.8	-11.4	-31.0	-5.2
P48	24.3	17.0	7.3	7.8	-13.8	-28.1	-4.9
P65	-	-	22.8	16.1	-13.0	-32.3	-5.7
P72	-	-	29.3	18.6	-11.9	-32.3	-5.4
P77	25.7	17.7	10.8	8.8	-10.3	-28.9	-5.0
P83	-	-	21.4	16.4	-11.6	-31.8	-5.4
P88	43.0	15.0	9.1	11.1	-15.5	-28.6	-5.0
P112	19.2	17.6	14.9	15.2	-14.9	-32.1	-5.6
P116	11.7	8.5	13.5	10.9	-13.3	-35.0	-5.9
P118	15.3	11.2	10.2	9.6	-12.9	-32.3	-5.4
P124	10.7	9.5	15.2	13.5	-8.2	-33.6	-5.6
P132	14.7	11.2	9.3	9.0	-7.8	-29.3	-4.7
P133	14.9	14.3	16.8	16.3	-12.5	-32.7	-5.4
P205	30.3	13.7	10.1	7.8	-13.6	-35.7	-5.5
P215	19.4	12.5	8.6	8.1	-9.9	-28.9	-4.7
P219	-	-	18.3	9.7	-13.1	-36.4	-6.1
P283	12.6	7.0	-0.6	8.3	-13.7	-31.2	-5.2
P354	11.6	8.6	11.1	9.8	-13.8	-32.8	-5.5
AHU							
P85	-	-	21.2	15.3	-13.2	-32.9	-5.6
P146	7.1	4.4	18.1	7.2	-15.8	-35.8	-6.4
P165	9.2	5.3	18.5	5.9	-15.6	-33.1	-5.7
P184	13.1	6.9	13.9	8.4	-16.7	-30.7	-5.4
P211	-	-	23.2	14.3	-13.3	-33.4	-5.5
P253	-	-	20.4	11.7	-14.3	-34.8	-5.8
P257	9.6	2.7	18.4	9.2	-10.8	-37.9	-6.3
P264	9.5	5.2	17.6	9.4	-14.3	-33.4	-5.2
P292	8.7	7.1	17.5	9.6	-13.4	-35.7	-5.7
P293	-	-	18.9	10.0	-11.3	-37.8	-6.3
P296	6.8	7.1	13.3	9.5	-14.6	-32.8	-5.4
P324	13.5	10.5	17.3	16.1	-14.2	-30.6	-5.0
P331	9.1	4.9	10.7	7.8	-16.0	-32.1	-5.6
P342	8.6	7.4	7.3	8.8	-16.5	-32.5	-5.3
P361	18.9	13.4	13.6	9.0	-13.0	-34.1	-6.1
VHU							
P138	7.5	4.5	14.9	7.4	-15.8	-37.0	-6.5
P142	6.2	2.6	18.5	7.6	-17.7	-36.1	-6.7
P156	6.7	0.9	18.0	7.7	-17.2	-35.3	-6.5
P159	8.4	5.5	17.7	9.9	-24.6	-35.7	-6.1
P166	14.0	6.8	17.4	9.5	-16.1	-35.8	-6.6

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FIGURE CAPTIONS:

Fig 1 Geographic location of the study area

Fig 2 Piezometric contours, and locations of wells for the hydrogeological survey and for the monitoring

sampling of October 2011; in red, position of the geologic cross-section A-A'.

Fig 3 Hydrogeological cross section and detail of the land west of Sussu Lagoon.

Fig 4 Hydrochemical facies definition for study area (modified from Stuyfzand, 2008).); c=cations, a=anions

Fig 5 Plot of ^{2}H vs. ^{18}O content. The Mediterranean Sea Water (MSW) was defined according to Otero et al.

(2011), and the Local Meteoric Water Line (LMWL) was defined following Cidu et al. (2008)

Fig 6 δ^{15}N vs. δ^{18}O$_{NO3}$, together with isotopic composition of the main nitrate sources in the study area: (a)

SHU, (b) AHU and VHU

Fig 7 δ^{34}S vs. δ^{18}O$_{SO4}$ of dissolved sulfate

Fig 8 δ^{34}S$_{SO4}$ values as a function of (SO$_4^{2-}$)/(Cl$^-$) ratio for samples from the study area

Fig 9 Denitrification driven by the sulfur oxidation model calculated using extreme values of ℰN (−4 to −30)

using initial ^{34}S of +15 and sulfate concentration 90 mg/L

Fig 10 HCO$_3^-$ concentration vs. δ^{13}C of studied samples and groundwater range of δ^{13}C$_{DIC}$, represented by

dotted lines

Fig 11 Non-purgeable dissolved organic carbon (NPDOC) concentration vs. δ^{15}N$_{NO3}$ of studied samples

Fig 12 Variation in nitrate concentration for SHU related to depth and origin. *Vertical and horizontal dashed*

lines representing the human water supply threshold of 50 mg/L (nitrate) and depth 10 m.b.g., respectively

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845   **Fig 13** Sulfate reduction processes related to depth: (a) δ^{34}S, (b) δ^{18}O. *Gray areas* represent wells deeper

846   than 10 m.b.g. affected by sulfate reduction

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