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

alluvial (AHU), and volcanic hydrogeological (VHU) units. Various groundwater chemical pathways were consistent with both different nitrogen sources and groundwater dynamics. Isotope composition suggests a mixed source for nitrate (organic and synthetic fertilizer), especially for the AHU and SHU groundwater. Moreover, marked heterotrophic denitrification and sulfate reduction processes were detected; although, for the contamination related to synthetic fertilizer, the attenuation was inefficient at removing NO_3^- to less than the human consumption threshold of 50 mg/L. Various factors contributed to control the distribution of the redox processes, such as the availability of carbon sources (organic fertilizer and the presence of lagoon-deposited aquitards), well depth, and groundwater flow paths. The characterization of these processes supports water-resource management plans, future actions, and regulations, particularly in nitrate vulnerable zones.

Résumé: Les zones côtières agricoles sont fréquemment touchées par la superposition de divers processus, avec une combinaison de sources anthropiques et naturelles, qui dégradent la qualité des eaux souterraines. Dans le système côtier aquifère multi-couches d'Arborea (Italie)—une zone marécageuse identifiée comme une zone vulnérable aux nitrates, selon la directive Nitrate 91/676 /CEE—les activités intensives de l'agriculture et de l'élevage contribuent de manière significative à la contamination en nitrate. Pour cette raison, cette zone est. considérée comme un banc d'essai pour la détermination d'une méthodologie appropriée ayant pour objectif de tracer la contamination en nitrate pour différentes conditions. Une approche combinant des isotopes environnementaux, la qualité de l'eau et des indicateurs hydrogéologiques a ainsi été utilisée pour comprendre les origines et les mécanismes d'atténuation de la pollution aux nitrates et pour définir la relation entre les contaminants et les dynamiques d'écoulements d'eaux souterraines au travers de l'aquifère multi-couches composé d'unités hydrogéologiques sableuses (SHU), alluviales (AHU) et volcaniques (VHU). Diverses voies chimiques des eaux souterraines sont compatibles avec les différentes sources d'azote et la dynamique des eaux souterraines. La composition isotopique suggère une source mixte pour le nitrate (engrais organique et de synthèse), en particulier pour les eaux souterraines AHU et SHU. De plus, des processus marqués de dénitrification hétérotrophe et de réduction des sulfates ont été détectés, bien que pour la contamination liée à l'engrais de synthèse, l'atténuation ait été inefficace pour éliminer le NO_3^- à une valeur inférieure au seuil de 50 mg/L fixé pour la consommation humaine. Divers facteurs ont contribué à contrôler la distribution des processus de réduction, tels que la disponibilté des sources en carbone (engrais organique et présence d'aquitards associés aux dépôts des lagunes), la profondeur des puits, et les voies d'écoulement des eaux souterraines. La caractérisation de ces processus est. en faveur des plans de gestion des ressources en eau, des actions futures, et

les réglementations, particulièrement dans les zones vulnérables aux nitrates.

Resumen: Las áreas costeras dedicadas a la agricultura se ven frecuentemente afectadas por la superposición de varios procesos, con una combinación de fuentes antropogénicas y naturales, que degradan la calidad del agua subterránea. En el sistema costero multi-acuífero de Arborea (Italia), una zona de marisma recuperada, que identificada como zona vulnerable a los nitratos, de acuerdo con la Directiva de Nitratos 91/676 / EEC, las actividades agrícolas y ganaderas intensivas contribuyen a una sustancial contaminación por nitratos. Por esta razón, el área se puede considerar como un área de ensayo de laboratorio para ajustar una metodología apropiada con el objetivo de rastrear la contaminación por nitratos en diferentes condiciones. Por lo tanto, se utilizó un enfoque que combina isótopos ambientales, calidad del agua e indicadores hidrogeológicos para comprender los orígenes y mecanismos de atenuación de la contaminación por nitratos y definir la relación entre la dinámica del contaminante y del flujo de agua subterránea a través del acuífero múltiple (SHU), aluvial (UTA), y unidades hidrogeológicas volcánicas (VHU). Diversas trayecctorias químicas de aguas subterráneas fueron consistentes con las diferentes fuentes de nitrógeno y la dinámica del agua subterránea. La composición de isótopos sugiere una fuente mixta de nitratos (fertilizante orgánico y sintético), especialmente para las aguas subterráneas de AHU y SHU. Además, se detectaron procesos marcados de desnitrificación heterotrófica y reducción de sulfato, aunque, para la contaminación relacionada con el fertilizante sintético, la atenuación fue ineficaz para eliminar el NO_3^- a un nivel inferior al umbral de consumo humano de 50 mg/L. Diversos factores contribuyeron a controlar la distribución de los procesos redox, como la disponibilidad de fuentes de carbono (fertilizante orgánico y la presencia de acuitardos depositados en la laguna), la profundidad del pozo y las trayectorias de flujo del agua subterránea. La caracterización de estos procesos respalda los planes de gestión de los recursos hídricos, las acciones futuras y las reglamentaciones, particularmente en las zonas vulnerables a los nitratos.

摘要：农业沿海地区经常受到各种过程叠加的影响,结合了人为源和自然源,降低了地下水质量。根据硝酸盐指令91/676 / EEC,在意大利的Arborea沿海多含水层系统－一个被认定为硝酸盐脆弱区的再生沼泽区,密集的农业和畜牧业活动导致了大量的硝酸盐污染。由于这个原因,这个区域可以被认为是一个实验室测试,用来调整一个适当的方法来追踪不同条件下的硝酸盐污染。结合环境同位素,水质和水文地质指标的方法被用来了解硝酸盐污染的起源和衰减机制,并通过以含沙(SHU),冲积(AHU)为特征的多含水层来定义污染物与地下水流动态之间的关系)和火山水文地质(VHU)单位。各种地下水化学途径与不同的氮源和地下水动态是一致的。同位素组成表明硝酸盐(有机和合成肥料)的混合来源,尤其是AHU和SHU地下水。此外,显着的异养反硝化作用和硫酸盐还原过程被发现,尽管

对于合成肥料的污染,减少NO$_3^-$的效率低于50 mg/L的人类消耗阈值。各种因素有助于控制氧化还原过程的分布,如碳源(有机肥料和浮湖沉积的防渗剂的存在)的可用性,井深和地下水流动路径。这些过程的表征支持水资源管理计划,未来行动和法规,特别是在硝酸盐脆弱地区。

Resumo: Áreas agrícolas costeiras são frequentemente afetadas pela sobreposição de vários processos, com uma combinação de fontes antropogênicas e naturais, que degradam a qualidade da água. Em um sistema multiaquífero em Arborea (Itália)—uma área pantanosa recuperada identificada como uma zona vulnerável ao nitrato de acordo com a Diretiva de Nitrato 91/676 /EEC—atividades de agricultura e pecuária intensivas contribuem para uma contaminação por nitrato substancial. Por essa razão, a área pode ser considerada um ensaio para ajustar uma metodologia apropriada com o objetivo de rastrear a contaminação por nitrato em diferentes condições. Uma abordagem que combina isótopos ambientais, qualidade da água e indicadores hidrogeológicos foi, portanto, utilizada para compreender as origens e os mecanismos de atenuação da poluição por nitrato e para definir a relação entre a dinâmica dos fluxos de contaminantes e águas subterrâneas através do multiaquífero caracterizado por unidades hidrogeológicas arenosas (SHU), aluviais (AHU) e vulcânicas (VHU). Várias vias químicas das águas subterrâneas foram consistentes com ambas diferentes fontes de nitrogênio e dinâmica das águas subterrâneas. A composição isotópica sugere uma fonte mista de nitrato (fertilizante orgânico e sintético), especialmente para as águas subterrâneas das AHU e SHU. Além disso, detectaram-se processos marcantes de denitrificação heterotrófica e de redução de sulfato, embora, para a contaminação relacionada ao fertilizante sintético, a atenuação tenha sido ineficiente na remoção de NO$_3^-$ para menos do que o limite de consumo humano de 50 mg/L. Vários fatores contribuíram para controlar a distribuição dos processos redox, como a disponibilidade de fontes de carbono (adubo orgânico e a presença de aquitardos depositados em lagunas), bem como profundidade e caminhos de fluxo de águas subterrâneas. A caracterização desses processos apoia os planos de gerenciamento de recursos hídricos, ações futuras e regulamentos, particularmente nas zonas vulneráveis ao nitrato.

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85	Foot note information	

REPORT

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 live-stock 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 contaminant and groundwater flow dynamics through the multi-aquifer characterized by sandy (SHU), alluvial (AHU), and volcanic hydrogeological (VHU) units. Various groundwater chemical pathways were consistent with both different nitrogen sources and groundwater dynamics. Isotope composition suggests a mixed source for nitrate (organic and synthetic fertilizer), especially for the AHU and SHU groundwater. Moreover, marked heterotrophic denitrification and sulfate reduction processes were detected; although, for the contamination related to synthetic fertilizer, the attenuation was inefficient at removing NO_3^- to less than the human consumption threshold of 50 mg/L. Various factors contributed to control the distribution of the redox processes, such as the availability of carbon sources (organic fertilizer and the presence of lagoon-deposited aquitards), well depth, and groundwater flow paths. The characterization of these processes supports water-resource management plans, future actions, and regulations, particularly in nitrate vulnerable zones.

Keywords Nitrate · Italy · Coastal aquifers · Denitrification · Groundwater management

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).

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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, which 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 phenomena (Grischek et al. 1998; Mengis et al. 1999; Cey et al. 1999). $\delta^{15}N_{NO3}$, taking into account the conservative behavior of nitrate in sub-surface environments, has been widely used for identification of NO_3 sources in groundwater (Pasten-Zapata et al. 2014 and reference therein). However, because $\delta^{15}N_{NO3}$ values are often modified by isotopic fractionation, their use alone is often inconclusive for identification of the origin of NO_3^- in aquatic systems (Zhang et al. 2015). Combinations of $\delta^{15}N$ and $\delta^{18}O$ of nitrate measurements have been utilized to trace (point and nonpoint) N sources. Specifically, by means of $\delta^{15}N_{NO3}$ measurements it is possible to distinguish nitrate derived from ammonium fertilizers, organic matter, and animal manure/septic waste, whereas use of $\delta^{18}O_{NO3}$ can distinguish the nitrate content derived from N-fertilizers and atmospheric deposition (Vystavna et al. 2017 and reference therein). In addition, nitrate isotope measurements constitute a viable tool to trace nitrate transformation processes such as denitrification (Puig et al. 2017 and reference therein). Notwithstanding this, the use of only $\delta^{15}N$ and $\delta^{18}O$ of NO_3 and nitrate concentrations in areas characterized by multiple sources of nitrogen, may result in inconclusive outcomes. Indeed, to provide a useful means for identifying the origin of NO_3^- and related transformation processes in groundwater, several authors have combined different types of isotope measurements according to multi-isotopic approaches (Aravena and Robertson 1998; Rock and Mayer 2002; Marimon et al. 2007; Urresti-Estala et al. 2015). The isotopes $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate, and $\delta^{13}C$ of dissolved inorganic carbon (Otero et al. 2009; Hosono et al. 2014), can be used because of their involvement in denitrification reactions. Specifically, the contributions of these isotopes allow determination of the role of heterotrophic and autotrophic processes in groundwater denitrification. It is well known that there are two main denitrification reactions in aquifers, i.e., heterotrophic denitrification by oxidation of organic compounds and autotrophic denitrification by oxidation of inorganic compounds such as sulfide (Rivett et al. 2008). In the first case, the denitrification involves an isotopic relationship between $\delta^{13}C_{DIC}$ with $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$, whereas in contrast, autotrophic denitrification implies an isotopic relationship between $\delta^{15}N_{NO3}$ 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 identifying sources of dissolved sulfate and its biogeochemical evolution in groundwater flow systems (Li et al. 2011; Caschetto et al. 2017). In particular, dissolved sulfate in groundwater may originate from dissolution of evaporitic deposits (mainly gypsum), oxidation of reduced S minerals, atmospheric deposition, and seawater intrusion, as well as from anthropogenic sources such as fertilizers, manure, sewage and mine drainage, among others (Puig et al. 2013; Mongelli et al. 2013; Petelet-Giraud et al. 2016).

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

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 (Fig. 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) co-operative 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 5,000-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).

The forage cropping systems are based on double-cropping silage corn—Italian ryegrass (representing >80% of the irrigated land), and ~35,600 dairy livestock are raised in a narrow area (Giola et al. 2012). Consequently, the Arborea area was identified as a NVZ in 2005 (Ghiglieri et al. 2009).

The climate is Mediterranean, and mean annual temperature and precipitation are 16.7 °C and 568 mm, respectively (1959–2012). Some 73% of annual rainfall occurs between October and March (Demurtas et al. 2016), and the average annual aridity index (rainfall/reference evapotranspiration) is 0.49 (semiarid area).

The study area occupies the northern part of the Campidano rift, with a landscape characterized by Quaternary deposits such as littoral-marine (mainly sands) and fluvial-deltaic material (mainly silt, clay, sand and gravel). The former outcrop corresponds with the Arborea Plain and the latter with its eastern side (Ghiglieri et al. 2016).

Three hydrogeological units (HU) have been identified:

- Sandy hydrogeological unit (SHU)
- Alluvial hydrogeological unit (AHU)
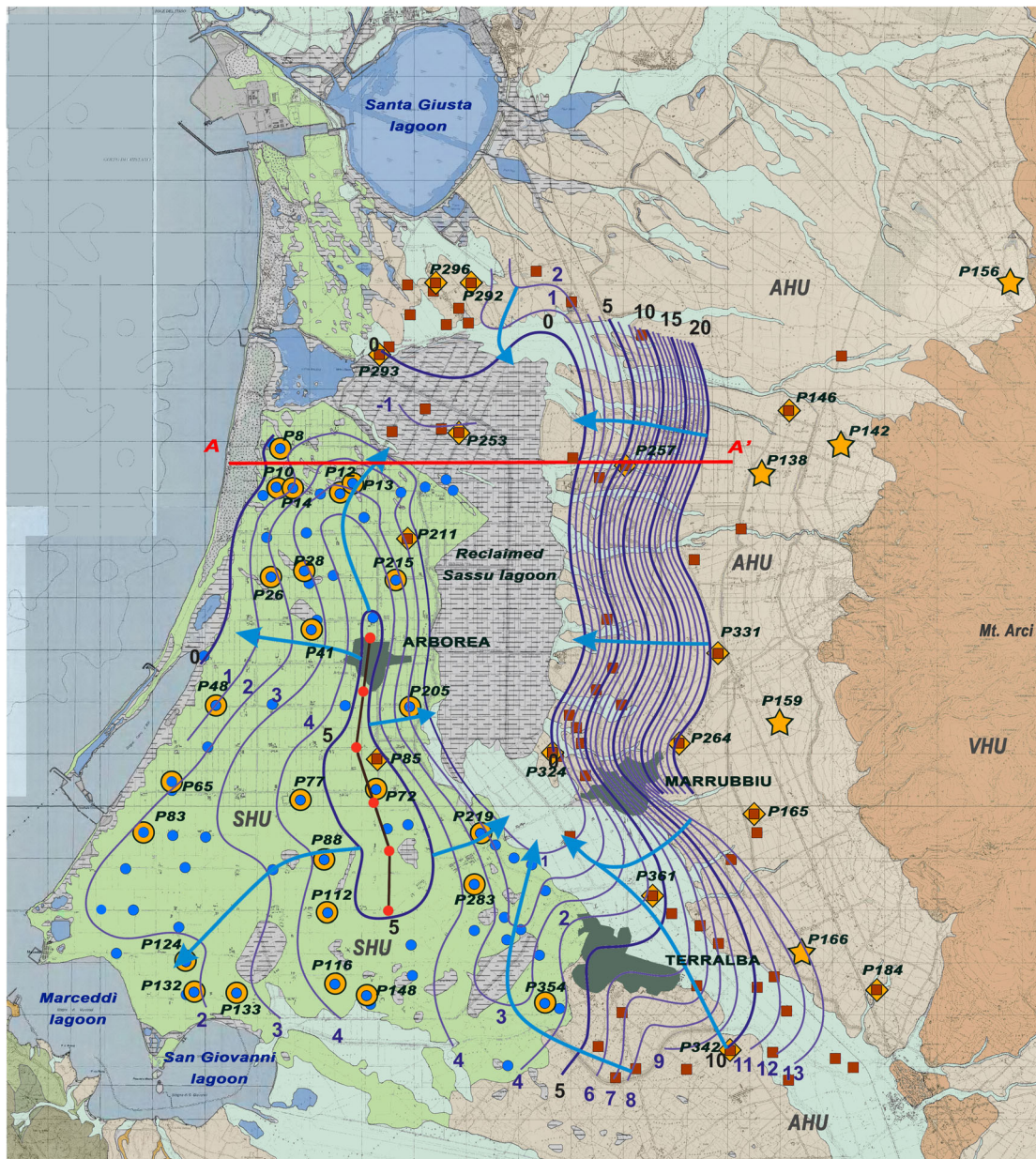- Volcanic hydrogeological unit (VHU)

Fig. 1 Geographic location of the study area

189 The SHU is represented by an unconfined aquifer hosted in
190 the Holocene littoral sands. It shows thicknesses of 20–25 m,
with depth decreasing eastward (Fig. 2). It is bounded at its 191
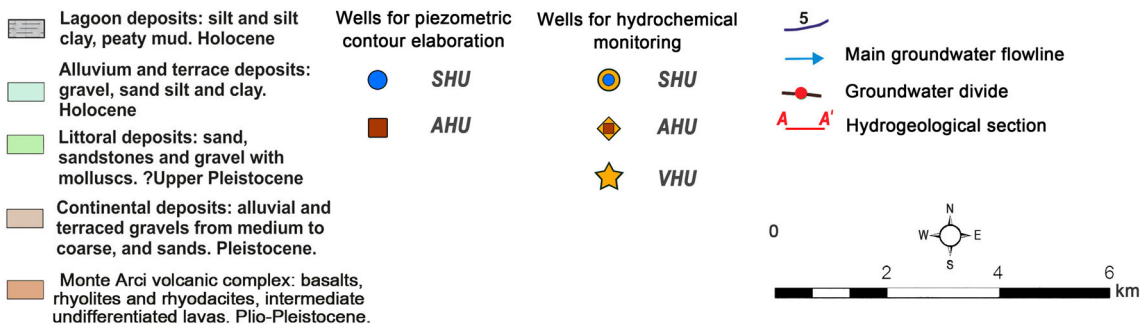base by a layer of lagoonal deposits made up of silt clays and 192

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'

peaty mud, which outcrop at the reclaimed Sassu Lagoon (Ghiglieri et al. 2016). The local lagoonal clay deposits include perched sandy lenses, in some cases hosting fossil seawater. The thickness of this impermeable boundary is consistently between 25 and 30 m in the central and northern part of the Arborea Plain. The geologic setting dominated by aggradational stacking causes an increase of the thickness and presence of Holocene lagoon deposits toward the sea; however, as reported in Ghiglieri et al. (2016), in the southern part of the plain, lagoonal clays that delimit the bottom of the sandy aquifer are lacking, such that Holocene sands of the SHU and alluvial aquifers of the AHU (Pleistocene continental deposits) are in hydraulic communication with each other.

The AHU is a multilayer aquifer hosted in Pleistocene continental deposits (Fig. 2). It consists of gravels, with some sands or clayey sand outcrops throughout the area surrounding the Arborea Plain up to the Monte Arci. This aquifer is confined in the plain because of the aforementioned clay layer, which separates it from the sandy aquifer (SHU). The impermeable layers are represented by the lagoonal clays, which characterize each depositional sequence. Finally, the VHU is an aquifer hosted in basalt, rhyolite and rhyodacite of the Monte Arci formations (Plio-Pleistocene). The volcanic rocks sink rapidly westwards, reaching a sufficient depth to prevent access from any well on the plain (Fig. 2).

Methodology

Samples for chemical and isotopic characterization were collected in October 2011 from 45 wells in a monitoring network (Fig. 2). The wells were distinguished in three groups as a function of SHU, AHU and 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 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.; $n = 5$) in the VHU wells. The spatial distribution of the hydraulic head was reconstructed based on 125 data points affiliated to SHU and AHU in September 2011 (Ghiglieri et al. 2016). Temperature, pH, Eh, dissolved oxygen (DO) and electrical conductivity were measured in situ, using a flow-through cell (AP-5000 - Eijkelkamp) to avoid contact with the atmosphere, and sampling was done when values was stabilized. Samples were filtered at 0.2 μm (for the elements that can be influenced by bacteria activity, such as $\delta^{15}N$ and $\delta^{18}O_{NO3}$ isotopes), and at 0.45 μm (for the others elements) and transported in 1-L polythene bottles and kept at 4 °C for subsequent chemical and isotopic analyses. Major anions and cations were analyzed according to standard methods (APHA, 1992). Major ions were determined by atomic absorption spectrometry (Perkin Elmer model AAnalyst 200) and ion chromatography (Alltech Allsep anion column 7 μm, 100 mm). Nitrate concentration was detected as

NO$_3$ by ion chromatography. Alkalinity was determined by titration (Titrator Orion 950 - Thermo Scientific) and NH$_4^+$, NO$_2^-$ and SiO$_2$ content by colorimetry (Cary 60 UV-VIS, Agilent Technologies). Replicate analyses of water samples and standards allowed estimation with analytical errors within 5% for both anion and cation contents. Nonpurgeable dissolved organic carbon (NPDOC) was measured using organic matter combustion (TOC-5000, Shimadzu Scientific Instruments). Chemical analyses were performed at the laboratory of the Engineering Department of Sassari University, Italy.

The isotopic characterization included the $\delta^{18}O$ and δ^2H of H$_2$O, $\delta^{15}N$ and $\delta^{18}O$ of NO$_3^-$, $\delta^{34}S$ and $\delta^{18}O$ of 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 Málaga (Spain) with Wavelength-Scanned Cavity Ringdown Spectroscopy for isotopic water measurements with L2120-i Picarro equipment. Six replicates for each sample were done, although the last three were selected for statistical treatment. The $\delta^{15}N$ and $\delta^{18}O$ of dissolved nitrate were determined using a modified cadmium reduction method (McIlvin and Altabet 2005; Ryabenko et al. 2009). Briefly, nitrate was converted to nitrite through spongy cadmium reduction and then to nitrous oxide using sodium azide in an acetic acid buffer. Simultaneous $\delta^{15}N$ and $\delta^{18}O$ analysis of the N$_2$O produced was done using a Pre-Con (Thermo Scientific) coupled to a Finnigan MAT-253 Isotope Ratio Mass Spectrometer (IRMS, Thermo Scientific). For $\delta^{34}S$ and $\delta^{18}O$ analyses, dissolved SO$_4^{2-}$ was precipitated as BaSO$_4$ by adding BaCl$_2$·2H$_2$O after acidifying the sample with HCl and boiling it to prevent BaCO$_3$ precipitation, following standard methods (Dogramaci et al. 2001). The $\delta^{34}S$ was analyzed with the Carlo Erba EA - Finnigan Delta C IRMS. The $\delta^{18}O$ was analyzed in duplicate using a ThermoQuest high-temperature conversion elemental analyzer coupled in continuous flow with a Finnigan MAT Delta X IRMS. For $\delta^{13}C_{DIC}$, carbonates were converted to CO$_2$ gas by adding a phosphoric acid solution in a GasBench (Thermo Scientiific) and the isotope ratio was measured in a MAT-253 IRMS (Thermo Scientific) coupled to the GasBench. Isotopic results are expressed in terms of delta (δ) per mil relative to the following international standards: Vienna Standard Mean Oceanic Water for $\delta^{18}O$ and δ^2H, Vienna Canyon Diablo Troillite for $\delta^{34}S$, Air for $\delta^{15}N$, and Vienna Pee Dee Belemnite for $\delta^{13}C$. Reproducibility (1σ) was calculated using international and internal laboratory standards systematically 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 $\delta^{18}O_{SO4}$; ±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 laboratory standards used are: for ^2H and ^{18}O in water isotopic analyses OH13, OH14 and OH15 (Wassenaar et al. 2012); for ^{34}S in sulfate: NBS127 (+20.3‰); UB-YCEM (+12.8‰) and SO-5 (+0.5‰); for

^{18}O in sulfate: UB-YCEM (+17.6‰); UB-ASC (+13.2‰) and NBS127 (+9.3‰); for ^{15}N in nitrate USGS-32 (+180‰); USGS-34 (−1.8‰); USGS-35 (+2.7‰) and UB-IWS (+16.9‰); for ^{18}O in nitrate USGS-32 (+25.3‰); USGS-34 (−27.9‰); USGS-35 (+57.3‰) and UB-IWS (+28.5‰); and for ^{13}C in DIC: UB-NA (−4.36‰), UB-NAK (−18.7‰) and UB-K (−29.16‰) calibrated with NBS-18 and NBS-19. Where not otherwise specified, the preparation of samples for isotopic analyses was done at the laboratory of the Mineralogia Aplicada i Geoquímica de Fluids (MAG-UB) research group, and the analysis was done at the Centers Científics i Tecnològics of the Universitat de Barcelona (CCiT-UB), Spain. Bulk isotopic results of the survey are presented in Tables 1 and 2.

Results

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 (Fig. 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: (1) from east to west, i.e., from the volcanic area toward the sea; (2) 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 (Figs. 2 and 3). In addition, in the AHU (Fig. 3), the groundwater flows under confined conditions within a deeper heterogeneous subsystem composed of discontinuous aquitards.

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 7,410 μS/cm. Groundwater with electrical conductivity >2,000 μS/cm generally occurred along the coast, but also inland (> 10 km 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 groundwater showed the greatest variance for almost all considered parameters. Relatively high silica in VHU wells and alkalinity in SHU wells pinpoint the respective contributions of silicate and carbonate minerals in those aquifers.

Electrical conductivity, chloride and sodium concentration in SHU and AHU wells strongly revealed the effects of saline sources in a coastal region. At the same time, elevated concentrations of nitrate in the SHU wells (reaching 243 mg/L) and in part of the unconfined AHU (up to 143 mg/L) reflect the influence of anthropogenic activities in the area.

Hydrochemical facies was deduced according to the classification of Stuyfzand (2008), modified as indicated in Fig. 4 to consider the nitrate pollution grade. The Stuyfzand classification is well known for its application to coastal areas for the determination of water type and evaluation of geochemical processes (Vandenbohede and Lebbe 2012; Ghiglieri et al. 2012; Mollema et al. 2013), and is useful for systems experiencing excessive application of manure and other fertilizers (Stuyfzand 1986). The classification was based on Cl$^-$ content, alkalinity, major cations and anions, base exchange index (BEX), and NO$_3$ content, in order to define water type as a combination of various parameters considered in a hierarchical structure with five levels of subdivision (Fig. 4).

Table 3 shows a synthesis of main water types identified in each aquifer, grouped on the basis of nitrate content. The terms of the classification (Cl$^-$ content, alkalinity, major cations and anions, and BEX) are listed following relative abundances. According to the classification, hydrochemical facies in the study area range from fresh (F) to brackish-salt (b) waters. There was high nitrate content in both fresh-brackish (f) and brackish-salt water (b), with variable alkalinity.

Fresh waters show nitrate concentrations <50 mg/L. When the NO$_3$ pollution grade is low (L), these waters show greater alkalinity and a Na-mixed character, whereas with nitrate increase (M), groundwater shows a NaCl character.

Brackish-salt-water occurrences are limited to a few wells on the coast (SHU) and inland in the AHU. These waters showed a Ca/HCO$_3$ ratio > 1; however, waters on the coast had high chloride and were oversaturated with respect to calcite, whereas inland waters showed SO$_4$ up to 340 mg/L and

Table 1 Hydrochemical data of sampled groundwater in Arborea area, October 2011. Dissolved oxygen (*DO*), cations and anions are in mg/L; temperature (*T*) is in °C; electrical conductivity (*EC*) in µS/cm; redox potential (*Eh*) is in mV

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	5,030	−180	0.2	1,525.0	74.5	181.8	–	1.0	0.10	750.0	27.5	125.0	75.0	26.8	–
P10	19.6	8.0	1,243	−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	1,034	33	3.9	170.2	72.6	144.5	0.20	49.3	ND	122.5	28.0	27.0	19.0	41.7	8.0
P13	19.2	7.5	1,575	95	0.2	247.8	83.1	245.2	0.20	205.1	ND	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	3,180	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	1,216	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	1,483	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	1,809	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	1,121	−135	2.5	237.9	23.7	237.4	–	0.4	ND	150.0	6.7	48.0	17.0	21.7	–
P72	19.4	7.9	1,808	8	4.1	406.5	32.0	312.4	–	1.1	ND	290.0	11.5	31.0	26.0	28.7	–
P77	20.2	6.9	2,000	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	4,060	−33	2.8	1,195.0	82.3	177.3	–	0.8	ND	500.0	20.3	144.0	80.0	23.0	–
P88	20.8	7.4	2,330	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	1,518	190	4.1	308.1	47.0	248.7	0.00	7.6	ND	170.0	13.8	64.0	40.0	26.6	–
P116	19.3	7.5	1,219	162	0.0	199.1	46.2	232.7	–	71.3	ND	130.0	8.8	69.0	26.0	29.4	–
P118	19.9	7.1	1,560	178	3.5	236.9	77.0	298.1	–	119.4	ND	130.0	9.8	128.0	34.0	34.9	–
P124	19.8	7.9	1,845	165	4.3	339.6	83.9	212.5	1.20	122.7	ND	285.0	8.5	36.0	18.0	21.5	–
P132	21.5	6.9	2,100	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	2,140	155	0.3	544.9	64.6	212.8	0.00	4.4	ND	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	2,160	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	1,344	−75	0.2	270.9	56.5	295.7	–	0.3	ND	230.0	6.6	24.0	13.0	25.9	–
P283	21.0	7.5	1,464	177	9.2	186.6	108.8	277.4	–	156.3	ND	115.0	12.3	126.0	32.0	33.1	–
P354	18.9	6.9	2,510	199	1.7	411.7	181.2	477.8	–	147.6	ND	280.0	9.0	180.0	47.5	41.9	–
AHU																	
P85	21.9	8.3	1,929	−138	3.2	468.0	103.1	172.9	–	0.5	ND	350.0	3.5	28.0	11.0	18.9	–
P146	21.1	6.6	1,846	174	5.2	446.1	52.4	126.5	–	6.0	ND	180.0	14.5	61.0	50.0	97.4	–
P165	20.4	6.8	7,410	85	3.6	2,260	217.8	374.2	–	27.2	1.20	675.0	41.8	330.0	300.0	76.5	–
P184	19.2	7.1	2,700	136	5.0	611.0	123.3	275.1	–	72.3	ND	360.0	18.0	82.0	60.0	78.0	–
P211	20.9	7.8	2,040	−97	0.3	476.8	92.7	220.0	–	0.5	ND	340.0	9.8	44.0	17.0	24.2	–
P253	21.0	7.3	2,370	51	0.1	566.8	70.7	182.0	–	0.5	ND	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	ND	136.0	7.0	14.0	7.0	57.1	–
P264	22.9	6.8	5,270	110	4.0	1,450.0	256.6	227.8	–	24.9	ND	600.0	28.8	196.0	150.0	79.2	–
P292	21.0	6.7	1,061	227	1.5	215.5	41.3	146.3	–	14.3	ND	140.0	8.2	32.0	18.0	52.2	–
P293	21.0	7.6	1,299	125	1.0	238.1	86.3	224.1	–	0.5	ND	190.0	9.1	40.0	13.0	40.2	5.5
P296	19.8	6.5	1,460	227	1.4	251.8	97.9	135.9	–	143.4	ND	185.0	7.8	43.0	30.0	46.1	–
P324	19.3	7.0	6,650	25	4.2	1,809.9	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	ND	84.0	9.4	20.0	20.0	74.8	7.5
P342	19.8	7.4	1,557	180	1.9	245.5	101.7	332.2	–	31.6	ND	185.0	9.1	74.0	40.0	34.5	–
P361	19.3	7.4	1,245	165	0.9	195.5	60.6	296.8	–	11.2	ND	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	ND	90.0	10.6	19.0	16.0	63.3	–
P142	23.6	7.4	1,050	141	3.4	223.5	23.9	165.1	–	1.9	ND	180.0	8.6	7.0	6.5	97.7	–
P156	21.3	7.4	1,692	157	6.5	387.1	41.1	226.1	–	3.1	ND	300.0	12.3	25.0	20.0	89.8	4.3
P159	20.7	6.9	1,196	170	3.5	264.3	35.7	161.1	–	7.3	ND	175.0	12.2	21.0	19.0	96.1	–
P166	21.6	7.8	1,073	43	5.1	204.7	32.0	201.4	–	7.8	ND	180.0	11.0	20.0	14.0	91.7	–

Table 2 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
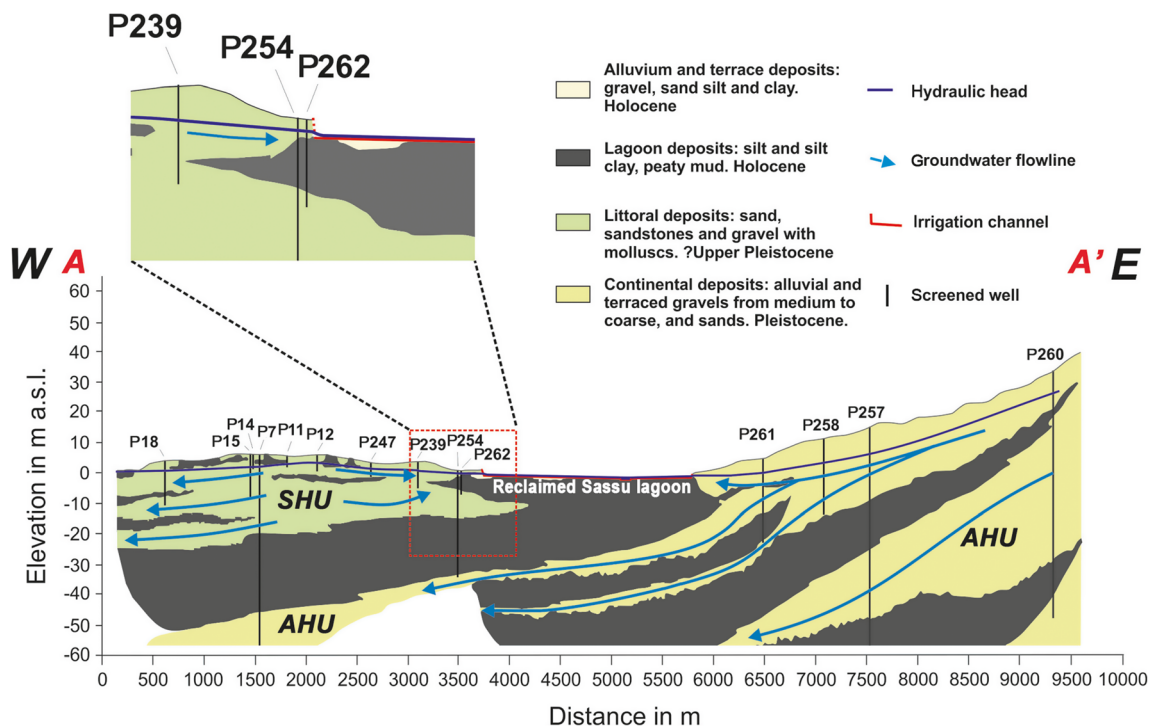
Fig. 3 Hydrogeological cross section and detail of the land west of Sussu Lagoon
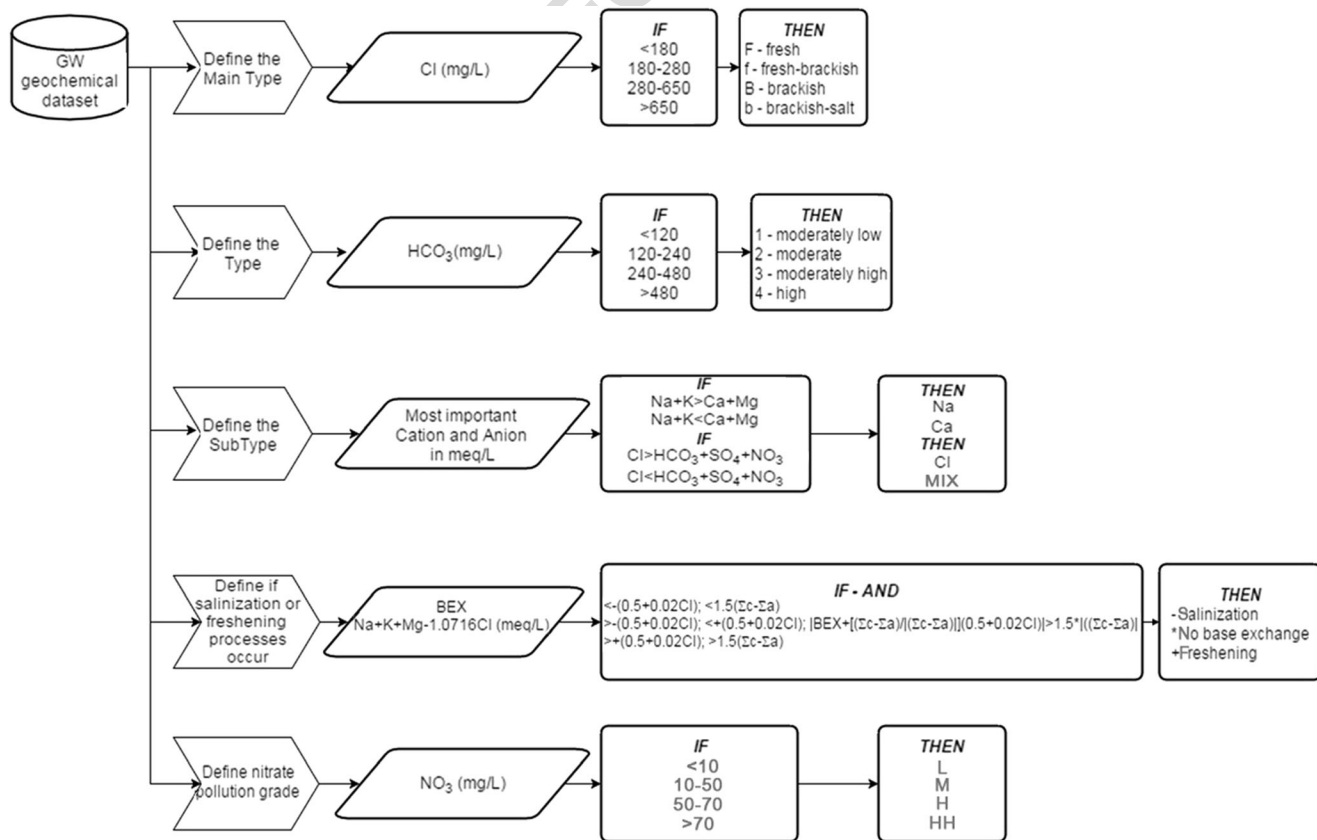
Q3   **Fig. 4** Hydrochemical facies definition for study area (modified from Stuyfzand 2008). c cations, a anions

Table 3 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)[a]
SHU	M	3	(B-F)(4–2)(NaCl-CaCl-NaMIX)[a]
SHU	L	11	(f-B-b-F)(2–3)(NaCl-NaMIX)[b]
AHU	HH	3	(f-B-b)(2–3)(NaCl)[b]
AHU	M	6	(F-b-F)(3–2-1)(NaCl-NaMIX-CaCl)[b]
AHU	L	6	(B-F-f)(2–3)(NaCl-NaMIX)[b,c]
VHU	M	1	(F)(1)(Na-Cl)[a]
VHU	L	4	(f-B)(2)(NaCl)[a]

[a] Identifies groups of water n which salinization processes occur

[b] Identifies groups of water n both salinization and refreshening processes occur

[c] No cations exchange occurring

undersaturation with respect to calcite. Brackish waters were mainly found in the SHU, in the southern part of the reclamation area. Chemical compositions range from NaCl to CaCl types, with very variable nitrate content (L, M, HH) and high HCO$_3$.

Isotopic data

The plot in Fig. 5 shows values of δ^{18}O and δ^2H ranging from −6.7 to −4.7 ‰ and −37.9 to −28.1 ‰, respectively (Table 3). Most of the SHU and AHU samples fall on the local meteoric water line (LMWL, δD = 7.46 ^{18}O + 7.22), indicating that they are of meteoric origin. In contrast, water isotopic compositions of VHU and some of the AHU samples are more depleted. In this case, recharge may derive from: (1) rainwater affected by an altitude gradient that causes an isotopically depleted precipitation, owing to lower average temperature at higher altitudes (Clark and Fritz 1997; Williams 1997); (2) rainwater conditions cooler than at present (Edmunds et al. 2003; Zhu et al. 2007). Most SHU samples collected from wells drilled to large depths of 30–53 m b.g. showed values similar to the AHU samples, reflecting the likely existence of a link to various aquifer zones (Clark and Fritz 1997).

According to the water isotope values of groundwater, no significant influence of seawater intrusion is observed. Also, the relationship between chlorine content and water isotopic values points out that seawater intrusion has not occurred in the studied area. Some evaporative processes in the

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)
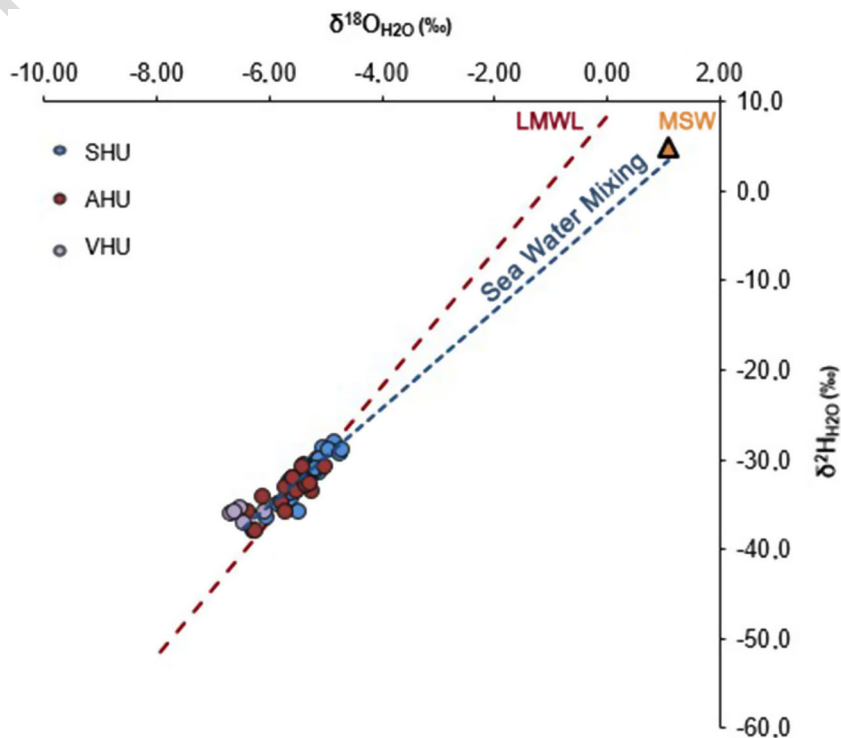
unsaturated zone can explain the displacement of some data from the water meteoric line to the global meteoric line.

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 ‰, respectively (Table 3). In Fig. 6, $\delta^{15}N$ and $\delta^{18}O$ in dissolved NO_3^- is represented together with the isotopic composition of the main NO_3^- sources, i.e., synthetic fertilizers (NO_3^-, nitrified NH_4^+), soil-N, and animal manure (organic fertilizer) or sewage (Vitòria et al. 2004; Kendall et al. 2007; Xue et al. 2009). The $\delta^{18}O_{NO3}$ derived from nitrification of NH_4^+ was calculated following the experimental Eq. (1) (Anderson and Hooper 1983):

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

where $\delta^{18}O_{H2O}$ represents the range obtained from the field survey (−4.7 to −6.7 ‰), and $\delta^{18}O_{O2}$ was assumed to be that of atmospheric O_2 (+23.5 ‰). Hence, NO_3^- in the study area should have $\delta^{18}O_{NO3}$ values between +3.2 and +4.5 ‰; nonetheless, $\delta^{15}N$ and $\delta^{18}O$ values in most of the samples from that area were larger than theoretically expected, suggesting nitrate attenuation processes. NO_3^- concentration measured in the VHU was from 1.9 to 23.1 mg/L, with median 8.6 mg/L ($n = 5$).

Samples collected in the AHU show substantial variation in NO_3^- concentration (0.5–143.4 mg/L; mean 31 mg/L). Specifically, samples from the eastern AHU (P146, P331, P264, P165 and P184), adjacent to the Monte Arci formation, show a lower NO_3^- concentration (< 25 mg/L) related to soil-N (Fig. 6) and isotopic compositions similar to the VHU, possibly representing a natural endmember.

Samples that, according to the flow path were located closely upgradient with reference to Sassu lagoon (P292, P296, P257, P324, P342, and P361), showed variable nitrate contents, from below the detection limit (P257) to 134 mg/L (observed in the shallowest well, P296). Finally, samples from the confined AHU below the reclaimed lagoon (P253 and P293) and below the Arborea NVZ (P85 and P211) showed NO_3^- concentrations <1 mg/L.

About the SHU, the samples show a wide range of NO_3^- content, between 0.3 and 216 mg/L, with a mean value of 74.1 mg/L. All samples showed higher $\delta^{15}N$ and $\delta^{18}O$ values than theoretical values for the sources previously defined (Fig. 6). Nevertheless, these heavier values can indicate that some denitrification processes are occurring, even if an uncertainty about the theoretical values for the $\delta^{18}O_{NO3}$ of the sources has to be considered.

The increases in the $\delta^{15}N$ and $\delta^{18}O$ of the residual nitrate, in fact, are caused by denitrification and produce a distinctive isotopic signature recognizable within a range (Fig. 6) defined from denitrification studies by Böttcher et al. (1990) and Aravena and Robertson (1998). In addition, as detailed in the following section, the presence of a redox gradient, disappearance of dissolved O_2 and increases in alkalinity (mostly bicarbonate) are usually associated with significant denitrification (Kendall 1998). 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 (Table 2). Three sources can be related to SO_4^{2-} (Fig. 7): intrusion of marine water and aerosol, influence of soil-derived SO_4^{2-} content and agrochemical products and manure.

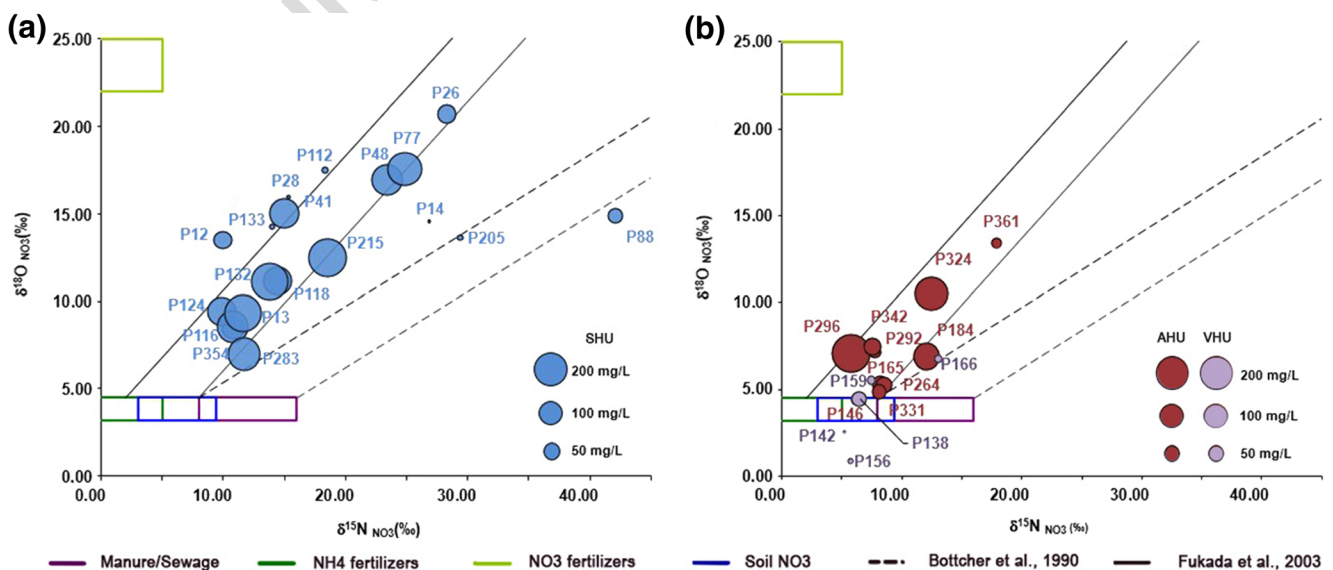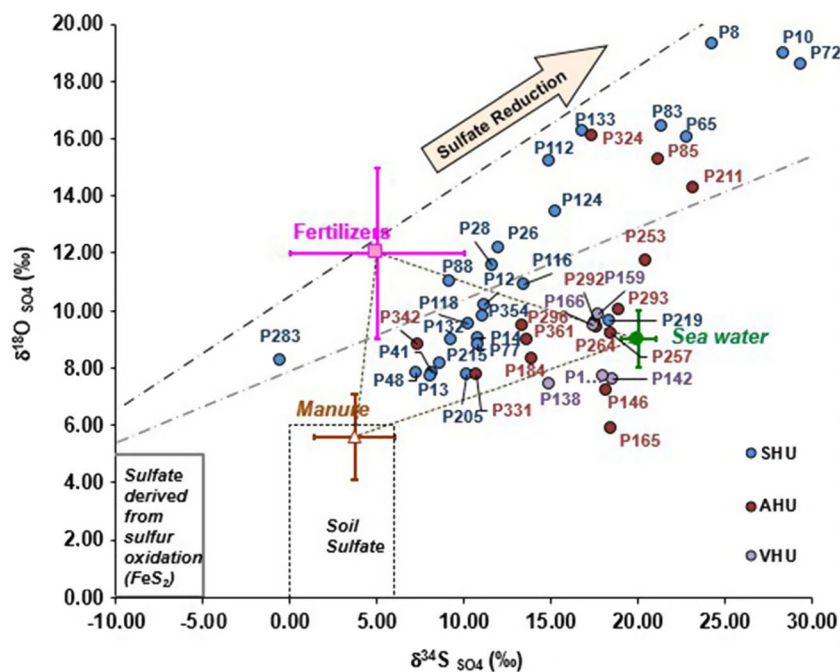Fig. 6 $\delta^{15}N$ vs. $\delta^{18}O_{NO3}$, together with isotopic composition of the main nitrate sources in the study area: **a** SHU, **b** AHU and VHU

Fig. 7 $\delta^{34}S$ vs. $\delta^{18}O_{SO4}$ of dissolved sulfate

Discussion

Hydrochemical results highlighted a variability in geochemical features reflecting the occurrence of different hydrosomes (water bodies with a specific origin; Stuyfzand 1999) affected by multiple processes. Brackish-salt waters, showing a molar Na/Cl ratio lower than sea water, suggest that Na removing processes occurred. Cation exchange processes between Na and Ca has been reported in other aquifers affected by salinization (Appelo and Postma 2005). High alkalinity in brackish water may result from denitrification processes (Otero et al. 2009); however, stratigraphic information from boreholes in the SHU in this area have revealed remains of shells and limestone strata interbedded with sands (Ghiglieri et al. 2016).

Most groundwater showed a molar SO_4/Cl ratio higher than seawater, indicating additional sulfate other than marine sources. Despite the lack of a strong correlation between NO_3^- and SO_4^{2-}, other sources of sulfates could be related to fertilization practice (Mahlknecht et al. 2017). Therefore, the enhanced concentrations of major ions and nitrate indicate that groundwater quality is impaired by both saline sources and pollutant influx from anthropogenic activities. Specifically, nitrate contamination may result from fertilizer, manure, septic tank effluent, municipal and animal waste, and landfill.

Sources of nitrate

Different sources of nitrate were detected for the groundwater of the study area according to the dissolved nitrate isotopic composition (Fig. 6). In detail, VHU samples show a relationship with soil-N (even if influence of NH_4 fertilizer slightly volatilized cannot be excluded), except the sample P166 that, due to the $\delta^{15}N$ and $\delta^{18}O$ values coupled with low Eh and relatively high NPDOC, suggest the existence of denitrification processes. About the AHU, the samples located upgradient with reference to Sassu lagoon (P292, P296, P257, P324, P342, and P361) show an isotopic composition attributable to synthetic fertilizers. Denitrification processes may have occurred also in these waters. Some processes can be supposed also for the samples from the confined AHU below the reclaimed lagoon (P253 and P293) and below the Arborea NVZ (P85 and P211) supported by conditions favorable to denitrification (DO ranged from 0.1 to 3.6 mg/L and Eh as low as −138 mV).

The isotope composition of SHU samples suggests a mixed source of nitrate. Most samples (P112, P28, P41, P133, P12, P124, P132, P116, P13, P354 and P118) are within the area defined by synthetic fertilizer, whereas the samples P14, P205 and P88 showed nitrate isotopic composition attributable to manure or sewage. In contrast, no precise sources of nitrate were recognized in samples P26, P77, P48, P215 and P283. On the whole, all the SHU samples appear influenced by denitrification processes, even if with different magnitude. Specifically, for the samples affected by synthetic fertilizer the attenuation was not efficient enough to remove nitrate (concentrations from 49 to 202 mg/L). Exceptions were observed in samples P112, P28 and P133 which showed lower nitrate concentration (< 8 mg/L). Instead, for those samples in which organic fertilizer sources have been defined, the denitrification processes have contributed to decrease nitrate concentration below 34 mg/L. Also for the samples with no clear nitrate origin definition (mean nitrate concentration ~146 mg/

543 L), a high load of NO_3^- appeared to overcome the natural
544 capacity to promote denitrification. Indeed, the fate of nitrate
545 in SHU is influenced by the sandy soils texture. Lower con-
546 tents of silt and clay, in fact, can reduce cation exchange ca-
547 pacity, which in turn allows faster nitrate leaching into
548 groundwater (Biddau et al. 2016). In addition, an influence
549 is attributable to the recent change of fertilizer management
550 systems, i.e. higher use of inorganic instead of organic fertil-
551 izer in the Arborea NVZ (Demurtas et al. 2016) may have
552 contributed to the isotopic signature.

Sources of sulfate
553

554 Figure 7 shows that sulfate can be related to different sources.
555 Some samples can be attributed to marine sulfate, with isoto-
556 pic signature +20 ‰ for $\delta^{34}S_{SO4}$ and +9 ‰ for $\delta^{18}O_{SO4}$
557 (Utrilla et al. 1992). Specifically, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ from
558 VHU samples showed values that can be related to seawater
559 sulfate. As shown in Fig. 8, this influence was in agreement
560 with the observed SO_4^{2-}/Cl^- ratio in VHU samples near the
561 seawater ratio; however, sulfate concentration in these sam-
562 ples was low (< 40 mg/L). Because of this low concentration,
563 the distance from the coast of wells and the meteoric water
564 isotopic values of groundwater without seawater influence,
565 the existence of seawater intrusion related to water extraction
566 can be discarded. One hypothesis explaining a seawater
567 source of sulfate is the presence of some deep saline paleo-
568 waters that could have been recharged during past transgres-
569 sions, which have evolved through mixing with sulfate-free
570 freshwater (Aquilina et al. 2013; Duriez et al. 2008, Edmunds

571 and Milne 2001; Cary et al. 2015). Another hypothesis is
572 related to dissolution of evaporites present in lagoon deposits.
573 Evaporites may have been precipitated during regression pe-
574 riods when the lagoon was isolated from the sea. Similar
575 evaporitic minerals have been observed in salt marsh environ-
576 ments, because of direct precipitation from seawater (Warren
577 2006). The presence of evaporite materials in the lagoon de-
578 posits could also be responsible for the weak seawater influ-
579 ence on $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ in some AHU and SHU samples
580 (Fig. 7). In any case, further research is needed to characterize
581 different sources of sulfate related to seawater in the study
582 area, with the aims of identifying the source of sulfate in
583 groundwater.

584 Other sources of sulfate (Fig. 7) can be ascribed to soil-
585 derived SO_4^{2-} (groundwater with $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ be-
586 tween 0 and 6 ‰, Krouse and Mayer 2000) and agrochemical
587 and manure products. The latter, considering potential anthro-
588 pogenic SO_4^{2-} sources, show isotopic compositions with
589 mean $\delta^{34}S_{SO4} = +5$ ‰ and $\delta^{18}O_{SO4} = +12$ ‰ respectively,
590 according to similar environmental conditions reported by
591 Vitòria et al. (2004). Moreover, part of SHU and AHU sam-
592 ples are characterized by sulfate reduction processes, specifi-
593 cally for the samples that have availability of an organic C
594 source.

Evidence of denitrification processes
595

596 The nitrate isotopic composition confirms the occurrence of
597 denitrification, particularly for the SHU and some AHU sam-
598 ples. Denitrification processes are consistent with other

Fig. 8 $\delta^{34}S_{SO4}$ values as a function of $(SO_4^{2-})/(Cl^-)$ ratio for samples from the study area
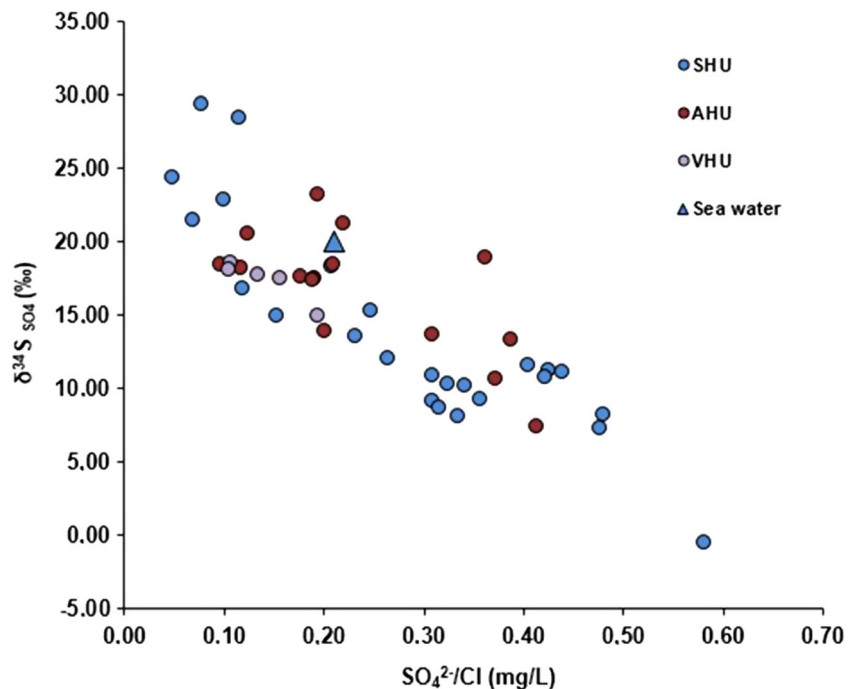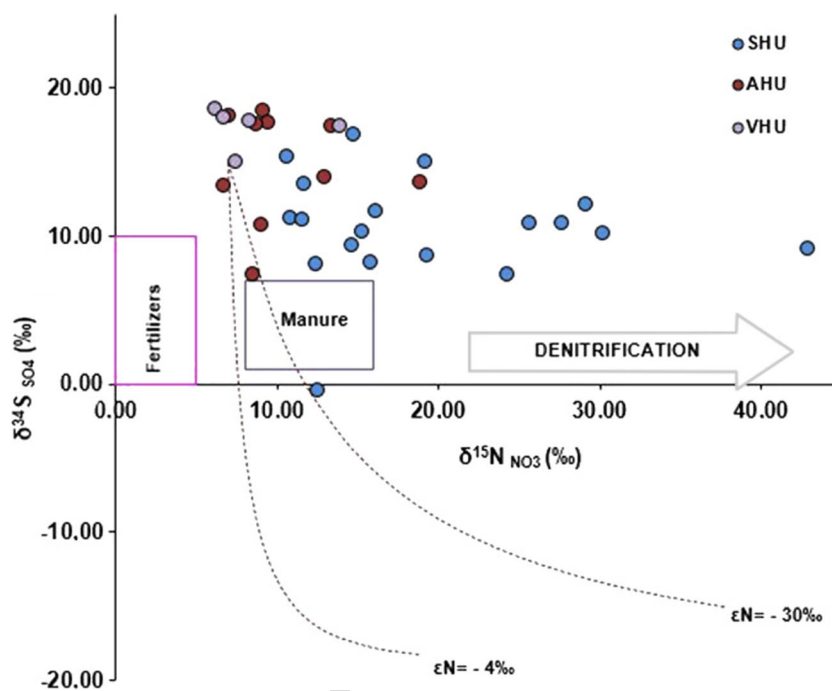
Fig. 9 Denitrification driven by the sulfur oxidation model calculated using extreme values of N (−4 to −30) using initial ^{34}S of +15 and sulfate concentration 90 mg/L

geochemical indicators such as DO concentrations <2.0 mg/L and low Eh values, indicating conditions suitable for denitrification in the aquifer (Korom 1992). The observed denitrification can be promoted by autotrophic bacteria, which use inorganic compounds such as sulfide as electron donors, or heterotrophic bacteria that use organic carbon as a source of electrons. Denitrification produced by sulfide should increase sulfate concentration, contemporaneous with a shift of sulfate isotopic composition. The $\delta^{15}N_{NO3}$ vs. $\delta^{34}S_{SO4}$ diagram (Fig. 9) illustrates that samples affected by strong denitrification ($\delta^{15}N_{NO3}$ > +15 ‰) do not show evidence of SO_4^{2-} originating from sulfide oxidation ($\delta^{34}S$ < −5 ‰). An exception is represented by the sample P283 from SHU, located in the southeast of Arborea NVZ. This sample, with $\delta^{34}S_{SO4}$ values around 0 per mil, is consistent with a sulfate originated from sulfide oxidation that was not able to discard autotrophic denitrification; nevertheless, neither chemical nor isotopic data confirm the role of sulfide in NO_3^- attenuation observed in the Arborea NVZ.

Alternatively, the presence of peaty mud sediments from Holocene deposits can act as a source of organic matter to develop heterotrophic denitrification in the AHU and SHU. In addition, livestock effluents (mostly slurry) used as organic fertilizer in Arborea constitute large amounts of organic input (Pinna et al. 2014) and, despite the predominant sandy composition of soils in the study area, their long-term application contributed to greater soil organic carbon in the soil (Cappai 2013).

The relationship between $\delta^{13}C_{DIC}$ and bicarbonate concentrations, as well as NPDOC concentration, is typically used to explain the role of organic matter oxidation in denitrification.

In the study area, measured $\delta^{13}C_{DIC}$ had values from −6.6 to −24.6 ‰ (median − 12.4 ‰). Most samples (Fig. 10) had values in agreement with the known range of $\delta^{13}C_{DIC}$ for groundwater (−16 to −11 ‰; Vogel and Ehhalt 1963), although the larger values detected could have had some influence from marine carbonates. Hence, chemical equilibria among the dissolved carbonate species mask any chemical and isotopic variation caused by heterotrophic denitrification.

Referring to NPDOC concentration, degradation and leaching of organic matter can increase electron donor availability in water, and may therefore promote denitrification. In the study area, NPDOC concentration varied from a minimum in the VHU (1.4 mg/L) to a maximum in the SHU (22.1 mg/L). High NPDOC concentrations matched large values of $\delta^{15}N_{NO3}$ (Fig. 11). The variation in NPDOC concentration and denitrification can be attributed to the heterogeneous distribution of both, organic matter, and NO_3^- inputs. If NPDOC contents is the limitation of the denitrification reactions, biostimulation, adding dissolved organic matter to the aquifer, would enhance the nitrate attenuation.

Evidence of sulfate reduction

As clearly shown in Fig. 7, sulfate reduction processes were detected in some SHU (P8, P10, P65, P72, P83) and AHU (P85, P211, P253, P324) samples that simultaneously showed large values of both $\delta^{34}S_{SO4}$ 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 and Eh from +51 to −180 mV. These parameters, with low DO and reducing groundwater conditions, are favorable to sulfate reduction. In general, once NO_3^- is

Fig. 10 HCO_3^- concentration vs. $\delta^{13}C$ of studied samples and groundwater range of $\delta^{13}C_{DIC}$, represented by dotted lines
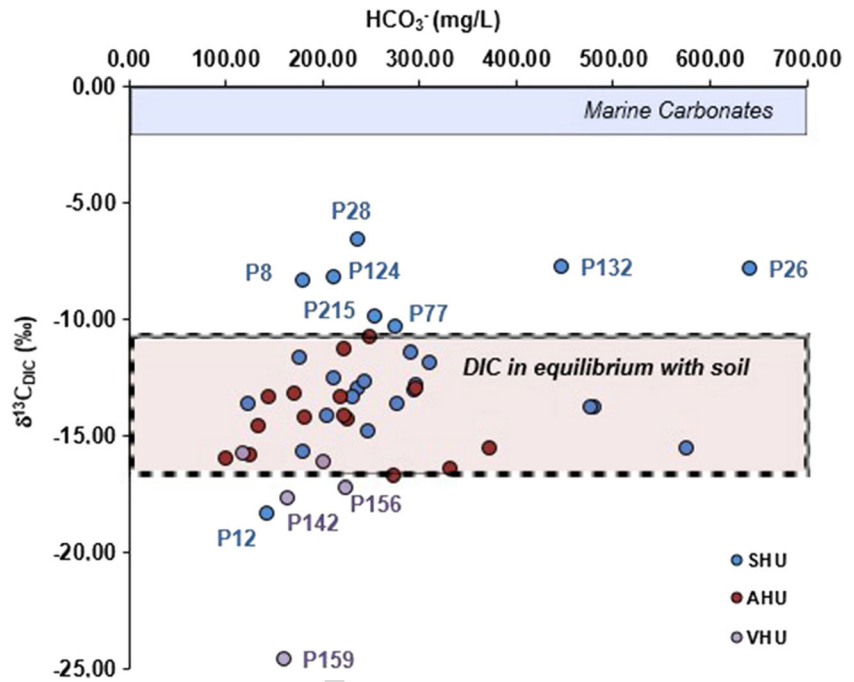
659 completely removed by denitrification, the excess organic car-
660 bon could be used to promote SO_4^{2-} reduction according
661 toEq. (2):

662

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

665

666 An exception was the sample P324, which had a nitrate
667 concentration of 110 mg/L. This sample was collected from
668 a fully screened deep well (50 m b.g.), where it is possible that

669 shallow groundwater polluted by nitrate is mixed with deep
670 groundwater.
671 Overall, the AHU and SHU aquifers, composed of alluvial-
672 lacustrine and littoral deposits, may provide a potential reduc-
673 tive environment for SO_4^{2-} consumption in groundwater, al-
674 though the samples affected by sulfate reduction did not show
675 any sign of depletion in terms of SO_4^{2-} concentration.
676 The effect of net SO_4^{2-} changes on isotopic compositions
677 and concentration can be evaluated by the normalization of

Fig. 11 Nonpurgeable dissolved organic carbon (NPDOC) concentration vs. $\delta^{15}N_{NO3}$ of studied samples
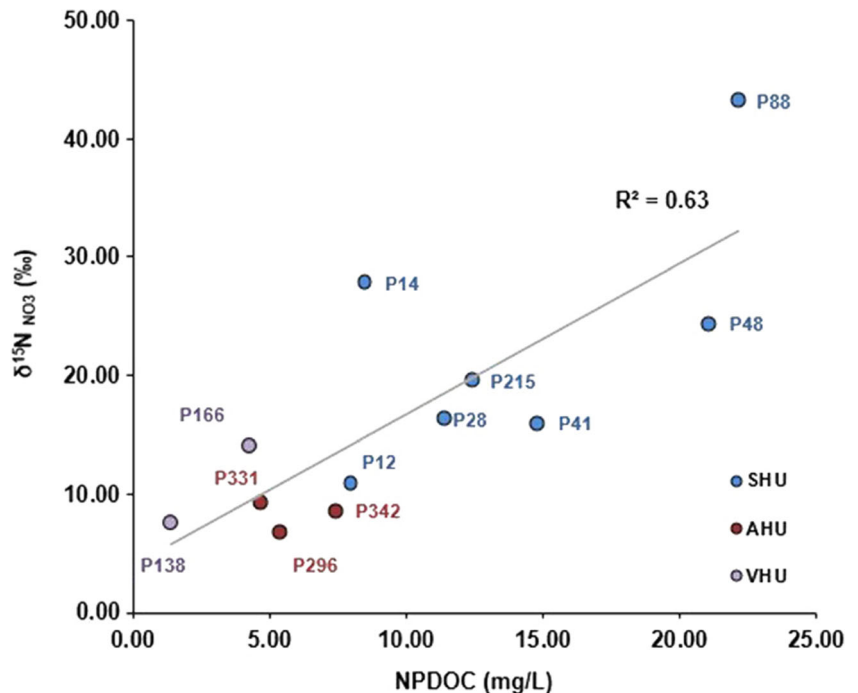
678 SO_4^{2-} to Cl^- in groundwater (Li et al. 2011). In fact, consid-
679 ering the conservative behavior of Cl^-, the decrease of SO_4^{2-}
680 $/Cl^-$ ratio can indicate sulfate removal associated with bio-
681 geochemical processes (Dogramaci et al. 2001; Berner et al.
682 2002). As shown in Fig. 8, a decreasing (SO_4^{2-}/Cl^-) ratio
683 coupled with an increase of $\delta^{34}S_{SO4}$ suggests that isotopically
684 light SO_4^{2-} was progressively removed and the residual SO_4^{2-}
685 became enriched in ^{34}S and ^{18}O during sulfate reduction. In
686 general, the samples with smaller $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values
687 and large SO_4^{2-}/Cl^- ratios can be linked to an initial SO_4^{2-}
688 pool such as marine or anthropogenic sulfate.

Spatial distribution of redox reactions

690 Denitrification and sulfate reduction processes have been
691 specifically identified for the AHU and SHU. For the
692 AHU, denitrification has not been identified in ground-
693 water collected from the area adjacent to the volcanic
694 massif. On the contrary, moving from the eastern side
695 of the Sassu lagoon toward the Arborea NVZ, denitrifi-
696 cation processes have been identified. The occurrence of
697 denitrification, especially when groundwater flows in
698 confined conditions, is supported by indicators such as
699 dissolved oxygen concentrations (3.5 mg/L) and Eh
700 (−180 mV). Samples such as P85 and P211 (within the
701 NVZ) and P253 and P293 (corresponding to Sassu la-
702 goon) show evidence of reduction processes, suggesting
703 the availability of an organic C source within the lagoon
704 deposit aquitard. This provides the basis for enhanced
705 reduction of nitrate and sulfate in this area. Also, the
706 geologic setting supports the presence of Holocene la-
707 goon deposits toward the sea, revealing the importance
708 of this material in the control of the attenuation observed
709 in the AHU.
710 In the SHU, the variation in NO_3^- content is related to
711 the heterogeneous nitrate load and the degree of denitrifi-
712 cation, the latter being modulated by well depth, the
713 availability of organic C, and the groundwater flow path.
714 In general, a lower content of nitrate in groundwater,
715 imputable to denitrification processes, has been observed
716 when nitrate comes from organic rather than synthetic
717 fertilizers. It is reasonable to assume that the high
718 NO_3^- load from synthetic fertilizer overwhelms the ca-
719 pacity to promote efficient denitrification. This is in line
720 with the situation in the study area over recent decades,
721 in which organic effluents (representing >50% of the
722 crop N input source) have been progressively replaced
723 by mineral fertilizer not reducing, de facto, nitrate
724 leaching.
725 The wells with depths <10 m b.g. had higher nitrate
726 concentrations, especially when the origin was clearly at-
727 tributable to synthetic fertilizers (Fig. 12). In addition,
728 those wells showed evidence of sulfate reduction (Fig. 13).
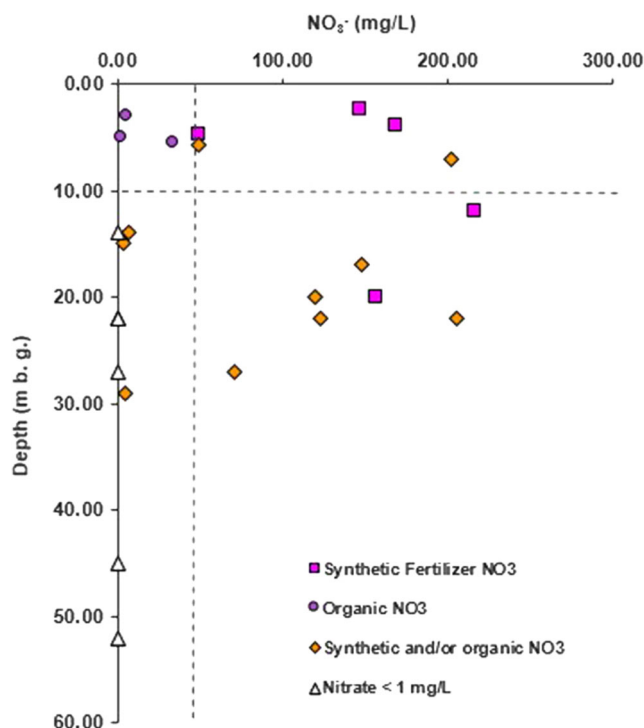
Fig. 12 Variation in nitrate concentration for SHU related to depth and origin. Vertical and horizontal dashed lines representing the human water supply threshold of 50 mg/L (nitrate) and depth 10 m b.g., respectively

729 The SHU groundwater intercepted at depths >10 m
730 b.g. showed strong variability in terms of redox reaction
731 distribution in the area. Some samples in the southern
732 portion of the area (e.g. P124), located on the flow path
733 down-gradient from the groundwater divide, had high
734 NO_3^- concentrations (up to 123 mg/L) as a result of
735 nitrate loading from sources upstream. Furthermore, the
736 thin and discontinuous layers of Holocene lagoon de-
737 posits permit the mixing of SHU and AHU groundwater,
738 limiting the efficiency of denitrification. In contrast, the
739 deepest SHU groundwater, adjacent to the coast (P8,
740 P10, P65 and P83), showed NO_3^- concentrations below
741 the detection limit, with even evidence of sulfate reduc-
742 tion (Figs. 12 and 13). In this case, in addition to the
743 presence of clay lenses of lagoonal origin, this reduction
744 is attributable to the absence of drainage from upgradient
745 contaminated wells.
746 In the central-east part of the NVZ, near Sassu lagoon,
747 it has not been possible to clearly define reduction pro-
748 cess paths. In fact, some SHU deep samples (P219 and
749 P72) showed almost complete nitrate attenuation
750 ($NO_3^- < 7$ mg/L; $\delta^{15}N > 30$ ‰), whereas shallower wells
751 (< 12 m b.g) such as P215 and P77, with large $\delta^{15}N$ and
752 $\delta^{18}O$ values (>15.9 and >12.5 ‰, respectively), had high
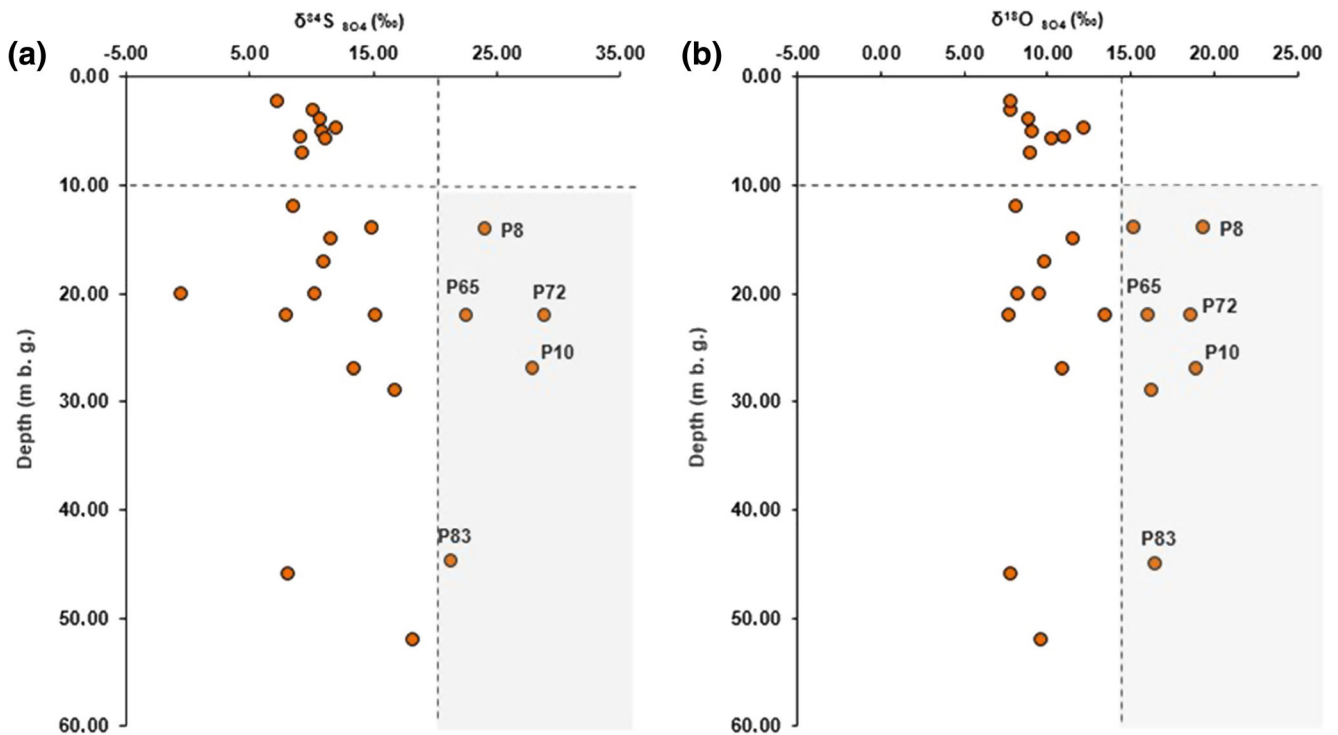753 nitrate concentrations (> 137 mg/L).

Fig. 13 Sulfate reduction processes related to depth: **a** δ^{34}S, **b** δ^{18}O. Gray areas represent wells deeper than 10 m b.g. affected by sulfate reduction

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 presence of reclaimed lagoons is a key factor in the groundwater flow path, for both the phreatic aquifer and confined conditions within a deeper heterogeneous subsystem composed of discontinuous aquitards. Various groundwater chemical paths were consistent with different nitrogen sources and groundwater dynamics, moving from the mountain area (eastern study area) to the coast. According to δ^2H_{H2O} and $\delta^{18}O_{H2O}$ groundwater values, in the studied area, groundwater is mainly originating from local precipitation and no significant seawater intrusion is occurring. Groundwater quality is affected by multiple processes associated with saline (sea spray deposition on topsoil and input of sea salts trapped in lagoonal sediments) and anthropogenic sources (linked to agriculture and livestock raising). Nitrate sources were clearly differentiated 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 $\delta^{18}O_{SO4}$ isotopes supported the aforementioned results, showing mixing between anthropogenic sources (linked to agricultural and livestock raising activities) and marine sulfate. That sulfate is most likely related to saline paleo-waters recharged during past transgressions, or to the dissolution of evaporites occurring in the lagoon deposits as salt precipitation. In addition, nitrate and sulfate

isotopes revealed the existence of denitrification and sulfate reduction processes, in agreement with chemical indicators (i.e., Eh values, dissolved oxygen, and NPDOC concentration).

By contrast, $\delta^{13}C_{DIC}$ was not suitable to explain the role of organic matter oxidation in the natural nitrate attenuation. Heterotrophic denitrification was specifically highlighted for the AHU and SHU, owing to the presence of peaty mud sediments from Holocene deposits and organic fertilizers (livestock effluents). Regarding the distribution of nitrate and natural attenuation processes in the study area, the eastern side (reaching the reclaimed lagoon) generally showed lower nitrate concentrations in the VHU and part of the AHU, attributable to soil-N. The AHU samples closely located upgradient from the reclaimed lagoon pointed to a nitrate origin from synthetic fertilizers and heterotrophic denitrification processes. From that lagoon to the sea, AHU groundwater flow in confined conditions had the lowest NO_3^- concentrations, owing to conditions favorable to heterotrophic denitrification and sulfate reduction processes. In the SHU west of the reclaimed lagoon, a mixed source for nitrate was defined, which in some cases increased according to the flow path. Also in this groundwater, there were heterotrophic denitrification and sulfate reduction processes; however, high nitrate concentrations in samples influenced by synthetic fertilizer indicate attenuation insufficient to remove NO_3^- to below the human consumption threshold. For SHU groundwater, therefore, the change from organic to inorganic fertilizer application did

809 not reduce the nitrate pollution in groundwater. As in the study
810 area, natural attenuation processes are taking place, it would
811 be suitable to promote biostimulation to add dissolved organic
812 matter and, consequently, electron donor availability to the
813 aquifer therefore promoting denitrification.

814 In conclusion, the present study demonstrates that the com-
815 bination of multi-isotope, chemical and hydrogeological ap-
816 proaches facilitates nitrate source identification and the eval-
817 uation of nitrate removal via biogeochemical transformation
818 processes in a multi-aquifer system under Mediterranean con-
819 ditions. However, characterization of potential nitrate and ma-
820 rine source terms as well as the enrichment factor for aquifers
821 should be acquired to better define the evolution of contami-
822 nation and to implement remediation techniques.

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