Science of the Total Environment 954 (2024) 176015

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Investigating pollution input to coastal groundwater-dependent ecosystems in dry Mediterranean agricultural regions

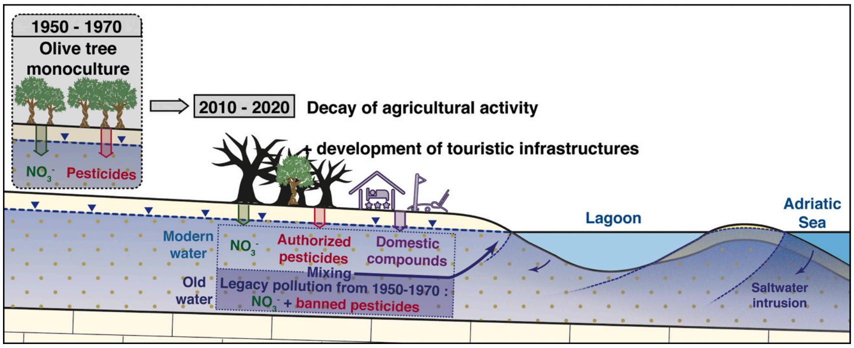
E. Crayol [a,b], F. Huneau [a,b,*], E. Garel [a,b], L.E. Zuffianò [c], P.P. Limoni [c], A. Romanazzi [c], A. Mattei [a,b], V. Re [d], K. Knoeller [e,f], M. Polemio [c]

[a] Université de Corse Pascal Paoli, Département d'Hydrogéologie, Campus Grimaldi, BP 52, 20250 Corte, France
[b] CNRS, UMR 6134, SPE, BP 52, 20250 Corte, France
[c] CNR-IRPI, National Research Council—Research Institute for Hydrogeological Protection, 70126 Bari, Italy
[d] Università di Pisa, Dipartimento di Scienze della Terra, Via Santa Maria 53, 56126 Pisa, Italy
[e] UFZ-Helmholtz Centre for Environmental Research, Isotope Tracer Group, Theodor-Lieser-Str. 4, 06120 Halle, Germany
[f] Technical University of Darmstadt, Institute of Applied Geosciences, Schnittspahnstr. 9, 64287 Darmstadt, Germany

HIGHLIGHTS

- Coastal groundwater-dependent ecosystems (GDE) of the Mediterranean are endangered.
- Pollution sources to coastal GDE are mainly from agricultural and wastewater origin.
- Isotope hydrology can be used with organic tracers for better pollution tracking.
- Legacy-pollution stored in groundwater can limit the regulations implementation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jurgen Mahlknecht

Keywords:
Coastal aquifer
Lagoon
Isotope hydrology
Emerging contaminants
Nitrate
Italy

ABSTRACT

The insufficient taking into account of groundwater as a basis for implementing protection measures for coastal wetlands can be related to the damage they are increasingly exposed to. The aim of this study is to demonstrate the pertinence of combining hydrogeological tools with assessment of pollutant fluxes and stable isotopes of O, H and N, as well as groundwater time-tracers to identify past and present pollution sources resulting from human activities and threatening shallow groundwater-dependent ecosystems. A survey combining physico-chemical parameters, major ions, environmental isotopes (^{18}O, ^{2}H, ^{15}N and ^{3}H), with emerging organic contaminants including pesticides and trace elements, associated with a land use analysis, was carried out in southern Italy, including groundwater, surface water and lagoon water samples. Results show pollution of the shallow groundwater and the connected lagoon from both agricultural and domestic sources. The N-isotopes highlight nitrate sources as coming from the soil and associated with the use of manure-type fertilizers related to the historical agricultural context of the area involving high-productivity olive groves. Analysis of EOCs has revealed

---

* Corresponding author at: Université de Corse Pascal Paoli, CNRS UMR 6134 SPE, Equipe Hydrogéologie, Bâtiment Dumenicu Alfonsi, Campus Grimaldi, BP 52, 20250 Corte, France.
E-mail address: huneau_f@univ-corse.fr (F. Huneau).

https://doi.org/10.1016/j.scitotenv.2024.176015
Received 26 March 2024; Received in revised form 13 August 2024; Accepted 2 September 2024

the presence of 8 pesticides, half of which have been banned for two decades and two considered as pollutant legacies (atrazine and simazine), as well as 15 molecules, including pharmaceuticals and stimulants, identified in areas with human regular presence, including rapidly degradable compounds (caffeine and ibuprofen). Results show that agricultural pollution in the area is associated with the legacy of intensive olive growing in the past, highlighting the storage capacity of the aquifer, while domestic pollution is sporadic and associated with regular human presence without efficient modern sanitation systems. Moreover, results demonstrate the urgent need to consider groundwater as a vector of pollution to coastal ecosystems and the impact of pollutant legacies in planning management measures and policies, with the aim of achieving 'good ecological status' for waterbodies.

1. Introduction

Groundwater-dependent ecosystems (GDEs) are among the Earth's most productive ecosystems, delivering a wide range of goods and services which human society benefits from (Velasco et al., 2018; Mehvar et al., 2018). Groundwater-dependent coastal wetlands are well represented on Mediterranean coasts, with >50 coastal lagoons of major environmental interest (Pérez-Ruzafa et al., 2011). However, most Mediterranean coastal wetlands do not achieve satisfactory ecological status, particularly with regard to trophic states (Souchu et al., 2010; Fabres et al., 2012; Pérez-Ruzafa et al., 2019). Damage to wetland areas over the last 100 years worldwide has been attributed to drainage and land conversion, mainly for urban development and agriculture (Gardner and Finlayson, 2018). The Mediterranean region faces climate change involving increasing temperatures and decreasing precipitation during spring and summer, leading to surface water scarcity most of the year (García-Ruiz et al., 2011) with only a minor contribution of river water, while groundwater supplies GDEs throughout the year. In addition, half of the population is concentrated in coastal hydrological basins, intensifying environmental pressures (UNEP/MAP, 2017). Moreover, land use changes, associated with hydrological alterations, further complicate already inadequate water resources management increasing the risk of groundwater salinization, especially in coastal areas, and adding further difficulties in the treatment of several pollution types (Andreu et al., 2016; Polemio and Zuffianò, 2020; Ruiz and Sanz-Sánchez, 2020).

In relation with those pressures, many different kinds of pollutants affect Mediterranean wetlands, degrading their status, including nutrients introduced by human activities, emerging organic compounds (EOCs), trace elements and hydrocarbons, among others (Fabres et al., 2012). In addition, the ecological role of groundwater supplying GDEs is rarely taken into account in scientific investigations and management policies (Rockström et al., 2014), nor is their role as a vector of pollution (Huang et al., 2013; Erostate et al., 2018; Huang et al., 2018; Zhang et al., 2019; Zhang et al., 2020; Balestrini et al., 2021; Huang et al., 2022; Crayol et al., 2023). While groundwaters are exposed to various forms of anthropogenic pollution, the most common appears to be nitrate contamination from the use of fertilizers and manure in agricultural areas, or from wastewater effluents from the surrounding watershed, leading to the ecosystem's eutrophication (Rodellas et al., 2018; Ligorini et al., 2022). The occurrence of EOCs (e.g. pharmaceuticals, pesticides, additives, personal care products, etc) (Pietrzak et al., 2020; Szymczycha et al., 2020) in aquatic environments, has become a major research topic due to advances in analytical techniques (Muter and Bartkevics, 2020; Richardson and Kimura, 2020). EOCs are increasingly being investigated in coastal ecosystems (Lorenzo et al., 2019; Girones et al., 2021; Sadutto et al., 2021; Castaño-Ortiz et al., 2023), but their environmental behavior, fate and potential ecotoxicity are still poorly known. This lack of knowledge has led to a weak regulatory framework on EOCs worldwide (Lapworth et al., 2019). EOCs display a wide range of molecules and pollution sources in groundwater, and thus the use of such anthropogenic tracers enables the characterization of the hydrosystem's functioning by precisely identifying the pollution sources and estimating groundwater residence time as well as the residence time of molecules in groundwater (e.g. recent infiltration vs. legacy) (White et al., 2016; McCance et al., 2020; Currell et al., 2022). Molecules such as caffeine and ibuprofen, under certain conditions, are generally associated with recent infiltration due to rapid degradation in groundwater (a few days) (Hillebrand et al., 2012, 2015; Schübl et al., 2021), while molecules such as pesticides will remain persistent in soil and groundwater for decades, e.g. atrazine, simazine, and tend to be considered as legacies (Reberski et al., 2022). So far, few studies (Robertson et al., 2013; McCance et al., 2018; Erostate et al., 2019; Shishaye et al., 2021; Crayol et al., 2023) have associated organic anthropogenic pollution with age dating techniques such as radioisotopes like ^{3}H, in order to better identify pollutant legacies in groundwater and to predict the progression of organic pollutant levels which is essential for the implementation of sustainable water resources policies (Roy et al., 2014).

Despite the growing concern at global scale regarding anthropogenic pollution affecting groundwater, associated with long-term effects, studies focusing on groundwater as a vector of pollution towards dependent ecosystems are still underrepresented, especially in coastal areas. Although necessary for sustainable water resources management, studies considering anthropogenic pollution related to past and present land use transformations are essential due to the variety of pollution sources threatening coastal GDEs. Moreover, they contribute to filling a knowledge gap by identifying anthropogenic molecules in areas with already implemented protection measures and restricted access.

Thus, a comprehensive and integrated approach that qualitatively accounts for the importance of land use changes that generate pollutants that are transferred to groundwater and explains the pollution legacy inherited from historical agriculture is lacking. In the Mediterranean region, olive growing is historically one of the major agricultural resources in most countries (Recept et al., 2011), adapted to lowlands. Over the past decades olive growing has rapidly intensified on a large scale, inducing environmental impacts (Rodríguez Sousa et al., 2019; Michalopoulos et al., 2020; Morgado et al., 2022), especially through the use of fertilizers impacting groundwater, which is poorly documented in scientific literature. Puglia is one of Italy's longest-established olive-growing regions (Caracuta, 2020), making it a sentinel site for studying the impact of olive-growing on groundwater resources and dependent ecosystems, in the same way as in other olive groves with Mediterranean climates around the world.

The aim of the present study is 1) to investigate the hydrogeological functioning of a coastal GDE, and determine the groundwater residence time, 2) to evidence the impact of historical agricultural practices on a coastal aquifer, 3) to trace back and identify pollution fluxes from the watershed to the lagoon, using several hydrogeological tracers, 4) to fill the knowledge gap on the presence of compounds and their fate in aquatic environments increasing the vulnerability of Mediterranean GDEs. A multi-tracer approach is used, integrating chemical elements, stable isotopes of the water molecule ($\delta^{18}O_{H2O}$ and $\delta^{2}H_{H2O}$), stable nitrate isotopes ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$), EOCs including pesticides and domestic molecules, trace elements and the radioactive isotope tritium (^{3}H), associated with a land uses analysis.

2. Material and methods

2.1. Study site: Location, climatology, geomorphology and land uses

The study was carried out at the Le Cesine wetland, located in southern Italy, in the Apulia Region, along the Adriatic coast and 17 km east of Lecce city (94,500 inhabitants, ISTAT, 2023) (Fig. 1). The site is a coastal basin with interconnected waterbodies with two perennial lagoons, Li Salapi (0.14 km^2) and Pantano Grande (0.68 km^2) connected with each other by an artificial channel. They are both shallow brackish coastal lagoons with a maximum depth of 0.8 m, and a total area of 0.9 km^2 (Caldararu et al., 2010; De Giorgio et al., 2018). The lagoons are separated from the Adriatic Sea by a narrow sand bar ($<$10 m in some parts). Seawater exchanges occur through small openings along the sand bar, mainly in winter and during storms and violent winds (Mancinelli et al., 2008).

The site is characterized by a typical Mediterranean climate. The mean annual temperature and the precipitation measured at the Lecce weather station are 17.5 °C and 490 mm respectively, and the potential evapotranspiration is 1020 mm, from the average calculated from 2014 to 2022 periods (ARPA Puglia, 2023). The site does not present a natural drainage network, but there is an artificial drainage channels network all around the wetland which drains a small fraction of shallow groundwater directly into the sea. Shallow groundwater is mainly discharged in the lagoons (De Giorgio et al., 2018).

The site is of major environmental interest for the nesting, staging and wintering of numerous species of waterbirds. The Convention on Wetlands of International Importance (Ramsar Convention), declared Le Cesine an area of international importance (De Giorgio et al., 2018). In 1980, a Decree of the Ministry of Agriculture and Forestry declared the Le Cesine wetland an Italian State Nature Reserve. Le Cesine is also a Site of Community Interest, a Special Area of Conservation and a Special Protection Area. The managing agency of the reserve is WWF Italia (ONG/ONLUS), which receives funding through a special agreement with the Italian Ministry for Environment (MATTM). The protected area extends over 6.2 km^2, with very restricted access for the public subject to authorization. The area is preserved from any urbanization processes with only a few old constructions, including the visitor center of the reserve and some private houses on isolated cultivated plots. There is a golf club as well as a large resort complex inland and immediately upstream of the wetland, bordering the National Park.

In the past, the Le Cesine site was a very dynamic agricultural area with a monoculture of olive groves. Over the past decade, the Apulia Region has been devastated by the bacterium *Xylella fastidiosa*, decimating thousands hectares of olive plantations (EFSA, 2015), including the study site, where the agricultural landscape is mostly composed of dead olive trees. Still, a small amount of agricultural activity still continues, with some spared olive trees and some scattered farming here and there, mainly for vegetable production.

2.2. Geology and hydrogeology

Le Cesine is located on the eastern part of the Salento peninsula (Fig. 1), part of the Apulian carbonate platform. It is constituted of a thick sequence of Mesozoic carbonate of the Bari and Altamura limestone formations, overlaid by Tertiary to Pleistocene deposits (Ricchetti et al., 1988). The geological framework appears as a multilayer system of calcarenite and fine limestone, affected in some parts by significant karst dissolution features and deep fracturing. The site's geology and lithological features are described in detail in De Giorgio et al. (2018).

The area is composed of three overlaying aquifer levels. They are identified, from bottom to top, as follows: deep, intermediate and shallow aquifers (De Giorgio et al., 2018). The deep aquifer is a very wide aquifer, locally confined and located at a depth of about −160 m (in the area P1 and S1 of Fig. 1). It is hundreds of meters thick and corresponds to the fissured and karstic regional carbonate Mesozoic aquifer of the Murgia and Salento peninsula (Romanazzi et al., 2015). The hydraulic conductivity was assumed as equal to 4 10^{-4} m/s (De Giorgio et al., 2018) in the area but shows wide variability at aquifer scale (Cotecchia et al., 2005). The Salento aquifer portion is known to be impacted by seawater intrusion from the Adriatic coast to the Ionian coast (Polemio et al., 2009). The semi-confined intermediate aquifer

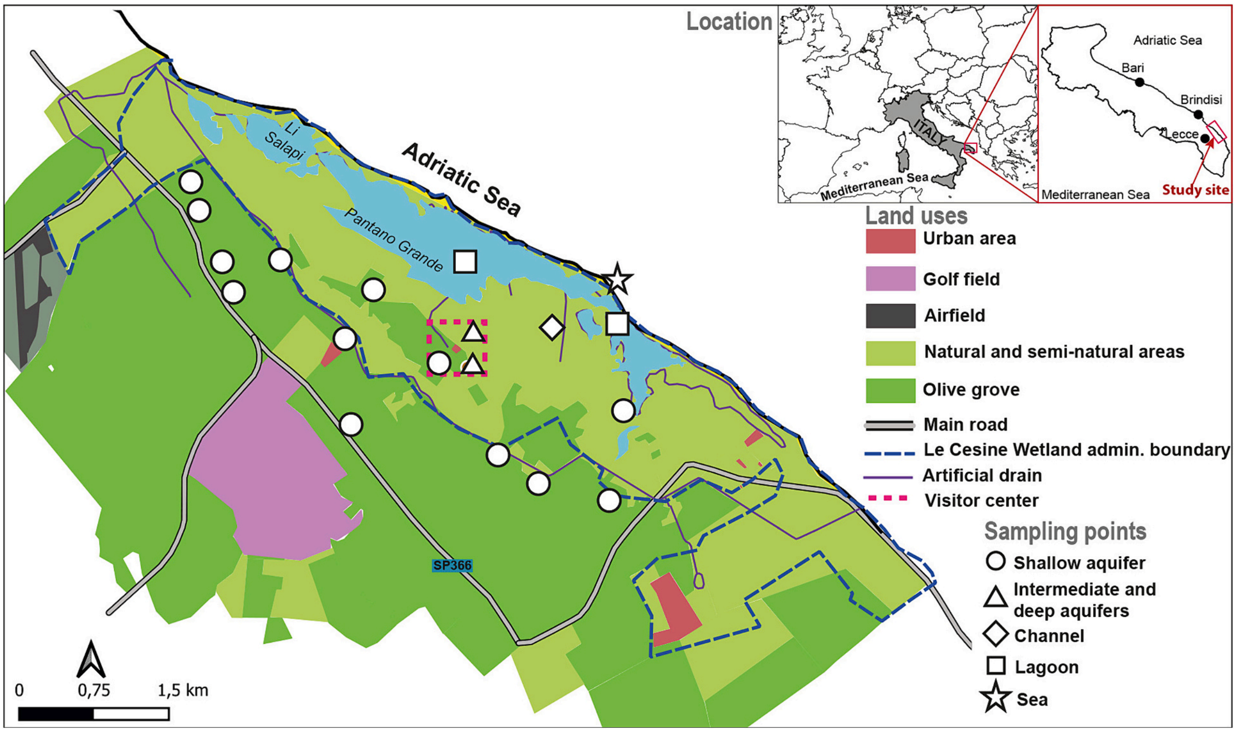


Fig. 1. Study site location, land uses over the studied area and sampling points types and location.

corresponds to the calcarenite and limestone complex of the Pliocene and Miocene. It is 90 m thick and shows hydraulic conductivity of 3 10^{-5} m/s; and is impacted by saline intrusion even if its coastal boundaries are not well known. Finally, there is a 20–25 m thick shallow phreatic aquifer, of calcarenite and sand from the Pleistocene, that can show high variability of hydraulic conductivity, with values up to 10^{-3} m/s (De Giorgio et al., 2018), and mainly recharged by local rainfall infiltration.

On the coastal part of the plain, silty Quaternary deposits can be found near the lagoons. The geological-structural relationships between the geological formations and boundaries along the coast are still uncertain (Fig. 2a), but it is certain that the hydrogeological pattern permits water exchanges between groundwater from the shallow aquifer and the lagoons and it is realistic to suppose that seawater intrusion can involve all aquifers, to varying degrees.

The shallow groundwater level map (Fig. 2b) clearly shows flow direction from inland towards the lagoons, being the main fresh water input to the hydrosystem. The shallow aquifer is hydraulically connected to the main drainage channel and to the wetland, providing a continuous input of freshwater and making Le Cesine a groundwater dependent ecosystem (GDE) (De Giorgio et al., 2018).

In addition, De Giorgio et al. (2018) investigated groundwater residence time using temporal tracers such as tritium within the aquifers, drainage network and lagoon waters. Results show that the deep and intermediate aquifers are characterized by a long residence time (> 50 years), while the shallow aquifer behaves as a fast-recharging system.

3. Investigations

A monitoring network has been designed selecting private wells, boreholes or piezometers used for the study of the impact of a geothermal power plan on the GDE (De Giorgio et al., 2018), as well as surface water samples for survey purposes. Then the present study established a sampling network tailored to the ecosystem protection objectives and complementary to the previous study.

3.1. Field sampling and analytical procedures

In order to provide reliable information, both in time and space, about the hydrosystem, the field campaigns were organized over two timeframes: in a first step, pre-sampling campaigns for the analyses of the stable isotopes of the water molecule and major ions were carried out quarterly between January 2021 and October 2021, at 17 sampling points to investigate the seasonal variability of main hydrochemical and isotopic parameters of waters. Then, in a second step a major sampling campaign comprising the analyses of $\delta^{15}N_{NO3}$, ^{3}H, EOCs and trace elements was carried out in October 2022, at the end of the dry period in order to gain information on groundwater residence time and pollutants occurrence and origin at the moment of the lowest dilution of the hydrosystem, allowing for the detection of reliable and more clear signals. This strategy permits the characterization of this poorly know hydrosystem, for which access restrictions exist to protect the biodiversity of the site.

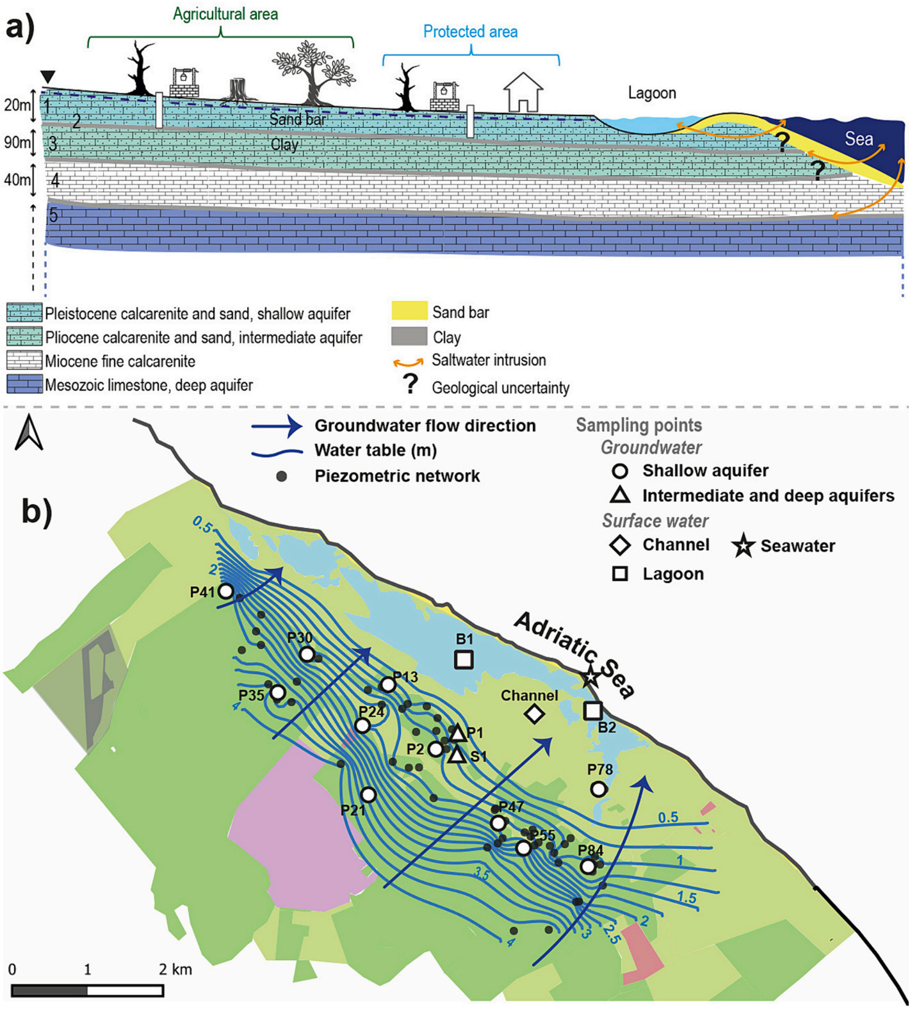


Fig. 2. a) Spatial distribution of groundwater levels at the le Cesine site, b) Le Cesine site schematic cross-section: (1) Pleistocene calcarenite and sand, shallow aquifer, (2) clay, (3) Pliocene calcarenite and sand, intermediate aquifer, (4) Miocene fine calcarenite, (5) Mesozoic limestone, deep aquifer.

A total of 17 samples were collected as follows: 13 groundwater samples (10 in the shallow aquifer, 2 in the in the deep aquifer (S1 and P1), 1 surface sample in an artificial drain (channel), 2 samples from the lagoon and a sample from the sea (Table 1 and Fig. 1). Samples from shallow-dug wells were pumped by means of a Low Flow Whale 12-V PVC device, while samples from drilled wells (P1, P2 and S1) were sampled after purging 3 wellbore volumes to remove standing water in contact with the atmosphere using Grundfos BMI/MP1–230 V pump. In situ measurements of EC, pH, T, Eh, and dissolved oxygen (O_2) were performed using a flow-through cell unit associated to a multiparametric probe AP-5000 Aquameter®. Alkalinity was determined in the field by volumetric titration, using a digital titrator HACH (Hach Company, Loveland, CO, U.S.A). Samples for major ions analysis were filtered on site through a 0.45 μm cellulose membrane and collected in two pre-cleaned 150 mL polyethylene bottles. Major ion analysis was carried out at CNR-IRPI (Research institute for hydrogeological protection, Bari, Italy), using a Dionex ICS 1100 chromatograph. The margin of error, based on the charge balance, was validated to be <5 %. The limit of detection is <0,1 mg/L.

Water samples for trace elements analysis were filtered through 0.20 μm nitrocellulose membranes, acidified using ultrapure HNO_3, and collected in 50 mL polyethylene bottles. The analyses were carried out at the AETE technical platform, University of Montpellier (France), using a Q-ICPMS X series II Thermo Fisher (Thermo Fisher Scientific, Bremen, Germany), with an analytical precision better than 8 %. The full dataset is displayed in Supplementary Material as Table S1 and Table S2.

3.2. Environmental isotopes analysis

A rain collector from the company PALMEX was deployed on the rooftop of the visitor' center (40.350090, 18.336046), at the beginning of the monitoring campaign in winter 2020. Samples for water stable isotope analyses were collected every month in pre-cleaned 20 mL amber glass bottles without head-space. Analyses were performed using a DLT-100 laser-based liquid–vapor stable isotope analyzer (Los Gatos Research, San Jose, CA, USA) according to the analytical procedure recommended by the International Atomic Energy Agency (IAEA, 1992; Penna et al., 2010) at the Hydrogeology Department (CNRS UMR 6134 SPE), University of Corsica, France. Ratios of $\delta^{18}O$ and $\delta^{2}H$ are expressed in permil (‰) relative to the Vienna Standard Mean Ocean Water (VSMOW) reference material. The analytical precision was better than 2 ‰ for $\delta^{2}H$ and 0.2 ‰ for $\delta^{18}O$.

Table 1
Sampling points description.

Sampling points	Aquifer	Type	Location (WGS 84)	Depth (m)
P2	Shallow	Drilled well	40.350084, 18.336407	25
S1	Intermediate	Drilled well	40.350018, 18.336383	200
P1	Deep	Drilled well	40.350069, 18.336307	167
P13	Shallow	Drilled well	40.355241, 18.330047	6.50
P21	Shallow	Drilled well	40.346484, 18.325719	>50
P24	Shallow	Shallow-dug well	40.352285, 18.326667	5.47
P30	Shallow	Shallow-dug well	40.358848, 18.322194	5.40
P35	Shallow	Shallow-dug well	40.357462, 18.316834	6.97
P35bis	Shallow	Shallow-dug well	40.356177, 18.318238	n.a.
P41	Shallow	Shallow-dug well	40.363675, 18.315146	3.73
P41bis	Shallow	Shallow-dug well	40.365406, 18.314804	6.47
P47	Shallow	Shallow-dug well	40.342065, 18.338972	3.80
P55	Shallow	Drilled well	40.339679, 18.341061	10
P78	Shallow	Drilled well	40.343327, 18.350190	9.20
P84	Shallow	Shallow-dug well	40.337149, 18.347544	6
Channel	Shallow	Surface	40.350462, 18.345091	n.a.
B1	Shallow	Lagoon	40.355958, 18.338697	n.a.
B2	Shallow	Lagoon	40.349734, 18.351339	n.a.

n.a.: not applicable.

Samples for $\delta^{15}N_{NO3}$ – $\delta^{18}O_{NO3}$ analysis were filtered through 0.20 μm nitrocellulose membrane filters, collected in 50 mL polyethylene bottles, and frozen. Analyses of nitrate (N) and oxygen (O) isotope ratios were carried out at the Helmholtz Center for Environmental Research-UFZ at Halle/Saale in Germany. Dual stable isotope analysis was carried out in duplicate for each sample on a Gasbenchll/delta V plus combination (Thermo Scientific, USA) using the denitrifier method for a simultaneous determination of $\delta^{15}N$ and $\delta^{18}O$ (Sigman et al., 2001; Casciotti et al., 2002). The measuring gas N_2O is produced by controlled reduction of any sample nitrate by a bacterial strain of *Pseudomonas chlororaphis* (ATCC #13985) lacking an active N_2O reductase. Nitrogen and oxygen stable isotopes results are reported in delta (δ) notation ($\delta_{sample} = [(R_{sample}/R_{standard}) - 1] \times 1000$) as part permil (‰) deviation relative to the standards AIR for nitrogen and VSMOW for oxygen, where R is the ratio of the heavy to light isotope. Four international standards (USGS32, USGS34, USGS35, IAEA-NO3) and one working standard (KNO_3) were used for calibration and quality control of the routine measuring runs. The calibration standards covered isotopic ranges of −1.8 ‰ to +180 ‰ (vs. AIR) and − 27.9 ‰ to +57.5 ‰ (vs. VSMOW) for nitrogen and oxygen isotopes, respectively. The standard deviation of the described analytical measurement was ±0.4 ‰ for $\delta^{15}N$ and ± 1.6 ‰ for $\delta^{18}O$.

Water collected for tritium (^{3}H) analysis was sampled in pre-cleaned 500 mL polyethylene bottles. Tritium analyses were done by liquid scintillation counting (Thatcher et al., 1977) after electrolytic enrichment (Kaufman and Libby, 1954) at Eurofins Analytical Services in Hungary. The concentrations are expressed in tritium units (TU). The full dataset is displayed in Supplementary Material as Table S3.

3.3. Emerging organic compounds

A total of 16 samples (except the seawater) were collected for the analyses of domestic compounds and pesticides. Analyses were carried out according to valid procedures and EPA method 1694 in the Povodi Vltavy laboratory, Pilsen, Czech Republic. Replicated water samples ($n = 2$) were taken in pre-cleaned 60 mL amber glass vials, filled only halfway and immediately frozen in an inclined position. For domestic compounds analysis, a total of 114 molecules and metabolites were analyzed on a screening basis including among the main molecules 15 antibiotics, 8 beta blockers, 7 antidepressants, 6 anti-inflammatories, 5 contrast agents, and other pharmaceuticals and cosmetics. For pesticide analysis a total of 240 molecules and metabolites were analyzed on a screening basis including, 1 biocide, 1 UV filter, 2 PFAs, 2 plant growth regulators, 3 corrosion inhibitors, 36 insecticides and 3 metabolites, 45 fungicides and 4 metabolites and 113 herbicides and 31 metabolites. The full list of the analyzed organic molecules is provided in Supplementary Material as Table S4. The samples were defrosted at a maximum temperature of 30 °C on the day of analysis. Analyses were done using LC-MS/MS with combined ESI+ and ESI- mode. The water samples were centrifuged in headspace vials for 10 min at about 3500 rpm. Subsequently 1.50 g of each sample were weighed in a 2 mL vial on an analytical balance. Then 5 μL of ammonium thiosulphate, and 1.5 μL of acetic acid was added to each sample. An isotope dilution was performed in the next step. Isotopically labeled internal standards were used (for example triclosan C12, acesulfame D4, Saccharin C6, telmisartan D7, valsartan acid D4, and others). Molecules were separated and detected by LC–MS/MS methods based on direct injection of the sample into a chromatograph. A 1290 ultra-high-performance liquid chromatograph (UHPLC) coupled with an Agilent 6495B Triple Quad Mass Spectrometer (MS/MS) of Agilent Technologies, Inc. (Santa Clara, CA, USA) were used. The separation was carried out on a Waters Xbridge

C18 analytical column (100 mm × 4.6 mm, 3.5 μm particle size for domestic compounds and 100 mm × 2.1 mm, 2.5 μm particle size for pesticides). The mobile phase consisted of methanol and water with 0.5 mM ammonium fluoride and 0.02 % acetic acid as the mobile phase additives. The flow rate was 0.3 mL/min and the injection volume was 0.050 mL. The full dataset is provided in Supplementary Material as Table S5).

3.4. Statistical analysis

The statistical treatment of the hydrogeochemical dataset was performed on XLSTAT v.2022.4.1 software by Addinsoft™. Multivariate statistical analyses are often used in karst hydrogeology (Long and Valder, 2011; Gil-Márquez et al., 2019; Liu et al., 2020); they can be used to reduce the variance of multidimensional dataset with principal component factors (Melloul and Collin, 1992), in order to explain correlations between chemical parameters, and to determine the hydrogeological functioning. PCA (Principal Component Analysis) was applied to 82 water samples based on 11 physical and chemical parameters. Data were normalized by Pearson's correlation coefficient.

4. Results and discussion

4.1. Field parameters and hydrochemistry

During the pre-sampling campaigns between January 2021 and October 2021 (Table S1), the groundwater temperature in the area ranged from 12 °C to 28 °C (average 18 °C), which is close to the annual air temperature trends in Lecce (mean 17.5 °C) meteorological station, (ARPA Puglia, 2023). Water temperature in the lagoon ranged from 6.15 °C (in January 2021) to 21 °C (in October 2021), with an average of 15.5 °C.

Groundwater and surface water (channel) displayed EC values between 472 μS/cm (October 2021) and 4910 μS/cm (January 2021), with an average value of 1106 μS/cm. Brackish water, including the lagoon and the seawater intrusion samples (P1, S1) showed EC values from 1990 μS/cm (January 2021) to 42,700 μS/cm (January 2021). The samples impacted by saline intrusion (P1 and S1, 39,700 to 42,700 μS/cm respectively) always present a higher EC than the lagoon itself. The saline intrusion samples are from intermediate and deep aquifer (P1, S1).

The pH in groundwater and surface water varies from 7 to 8.6, indicating the alkaline nature of the water; the higher pH values may reflect a marine influence locally, but are more generally showing the influence of the limestone nature of the underground. The pH in the lagoon varies from acidic to slightly basic (from 6.1 to 7.8).

During the main campaign of October 2022, the groundwater temperature in the area ranged from 18.5 °C to 21.8 °C (average 20 °C), and the water temperature in the lagoon ranged from 22.4 °C to 26.8 °C. These values are higher than those from the pre-campaigns, certainly due to the end of the summer season. Groundwater and surface water (channel), displayed EC values between 206 μS/cm and 2675 μS/cm. Brackish water, including lagoon and the seawater intrusion samples (P1, S1) showed EC values from 5456 μS/cm to 28,520 μS/cm. The pH in groundwater and surface water varies from 6.29 to 8.5, indicating acidic to alkaline nature of the water, while the pH in the lagoon is more alkaline than during pre-campaigns (from 8 to 8.7).

During the campaign of October 2022, lagoon (B1 and B2), channel waters and several groundwater samples (S1, P1, P2, P13, P21, P24, P30) presented a negative redox potential, from −56 mV (B1) to −250 mV (P24) indicating a reductive environment.

The hydrochemical water-type is displayed on a Piper Diagram in

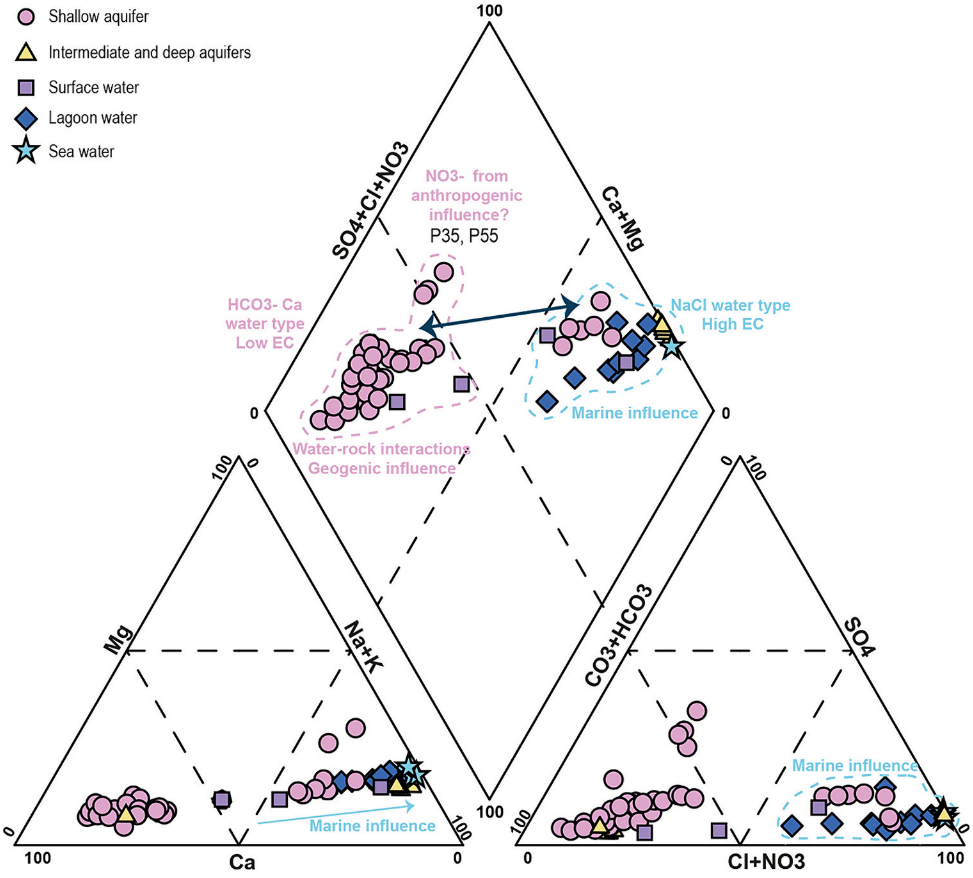


Fig. 3. Piper diagram of all the water samples collected in the study area.

Fig. 3. Two distinct water-types have been identified in the study area: the HCO_3^--Ca^{2+} type related to the carbonated geology of the area and the Na^+-Cl^- type for the samples affected by seawater intrusion (P1, S1) and brackish waters of the lagoon (B1, B2). The surface water sample (channel), is affected by a mixing with lagoon water in July and October, presenting a Na^+-Cl^- profile during these periods.

The Piper diagram reveals important information on nitrate concentrations in groundwater. Some samples (P35, P55) appear on the diagram to display high nitrate concentrations well above the natural baseline concentration for groundwater, estimated between 5 and 7 mg/L maximum (Appelo and Postma, 2010), hence nitrate concentrations exceeding this threshold can be related to an anthropogenic influence, potentially degrading the groundwater quality. The results of hydrochemical investigations have then been by a statistical treatment in order to confirm the observations.

4.2. *Statistical analysis*

The generated correlation matrix (Table S6) shows a highly positive relationship (> 0.8 and > 0.9) between the following ions: Cl^-, Br^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}. It indicates that those elements strongly contribute to the water mineralization. The PCA, on Fig. 4, suggests that two main factors could explain 79.25 % of the total variance of the hydrochemical changes in the groundwater sample set of the Le Cesine site. The first (F1, 65.08 %) is defined by high loading of Cl^-, Br^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}. Thus, this factor reflects the mineralization within the aquifer impacted by seawater mixing or influence (direct seawater intrusion or sea spray). Bicarbonates, apart from this tendency, represent the major influence of the carbonated matrix of the regional aquifer on the groundwater mineralization (Santoni et al., 2018).

The second factor (F2, 14.17 %) is defined by NO_3^- and PO_4^{3-} loadings, in relation with Eh. Those loadings are not explained by the water mineralization, suggesting another origin, potentially anthropogenic.

The projection of variables and individuals on a factorial plane (F1, F2) shown in Fig. 4, classifies water in two distinct groups. The first group on the left factorial side of the plane, corresponds to continental freshwater and the second group on the right factorial side, corresponds to seawater and samples impacted by seawater intrusion. In order to identify the nitrate origin, samples with high or low redox are represented on the plot. The persistence of nitrogen in groundwater is governed by biological reactions of nitrification and denitrification, which are a function of environmental redox conditions. Without oxygen, reducing conditions favor the denitrification (conversion of nitrate into gas), while in presence of oxygen, nitrite can oxidize into mobile nitrate (McMahon and Chapelle, 2008). Therefore, several samples have been identified with oxidative conditions (high redox) associated with high concentration of nitrates (P35bis, P41bis, P47, P55, P84).

4.3. *Groundwater origin*

The $\delta^{18}O_{H2O}$ and δ^2H_{H2O} values for groundwater, channel and lagoon water samples are listed in Table S3. The isotopic signature of groundwater ranges between −6.7 ‰ and 4.2 ‰ for $\delta^{18}O_{H2O}$ and between −37.9 ‰ and 23.7 ‰ for δ^2H_{H2O} (Fig. 5). The oxygen and deuterium isotopic signatures of the freshwater samples are plotted between the Global Meteoric Water Line (GMWL) from Craig, 1961, the Western Mediterranean Meteoric Water Line (WMMWL) from Celle-Jeanton et al., 2001, and the local southern Italy water line (LMWL, Local Meteoric Water Line) from Longinelli and Selmo, 2003.

The groundwater isotopic signatures are plotted along the LMWL, very close to the annual weighted mean of isotope in rainfall, collected from the Le Cesine pluviometer (4 m asl, −33.9 ‰ for δ^2H_{H2O} and − 5.9 ‰ for $\delta^{18}O_{H2O}$). This is consistent with a low altitude of the water recharge source, and displays a similar meteoric origin for all samples, highlighting an autochthonous recharge. Moreover, there is no significant isotope shift for groundwater, suggesting a rapid runoff and infiltration rate.

The $\delta^{18}O_{H2O}$ and δ^2H_{H2O} signatures of the lagoon water range from −29.5 ‰ to 24.8 ‰ and from −5.4 ‰ to 5.1 ‰, respectively. The lagoon water isotopes data fall slightly below the local evaporation line, calculated from Gibson et al., 2008, showing significant isotopic evaporation in summer when the contribution of the sea to the lagoon is highest.

Lagoon water displays seasonal variations: during low groundwater inputs (July 2021 and October 2022) lagoon water shows the highest evaporation, and an isotopic signal beyond that of the seawater (mean values from 9.0 ‰ for δ^2H_{H2O} and 1.4 ‰ for $\delta^{18}O_{H2O}$), while during winter and autumn 2021 the lagoon waters show a mixing with groundwater and seawater. In January 2021, the groundwater contribution vs seawater contribution in B1 and B2 was 63 % and 82 % respectively. In October 2021, the groundwater contribution in B2 was up to 82 % (Fig. 5).

Most of the time B1 presents an isotopic signature closer to that of the sea (less groundwater inputs), while B2 on the contrary presents an

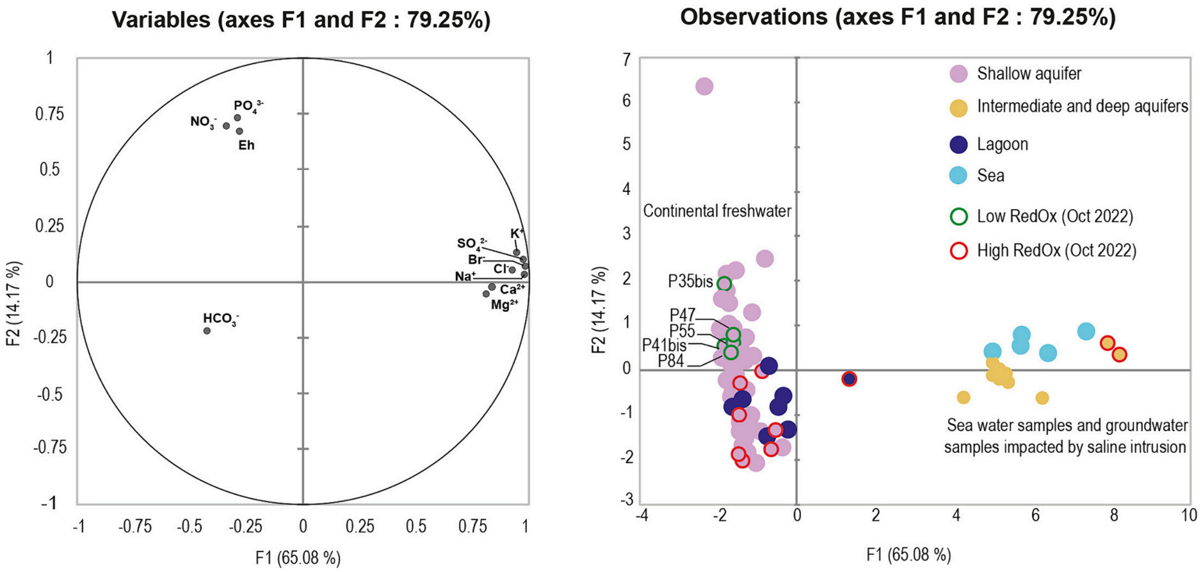


Fig. 4. left) Distribution of the two principal components, right) Variables' projection on the factorial plane ($F_1 \times F_2$).

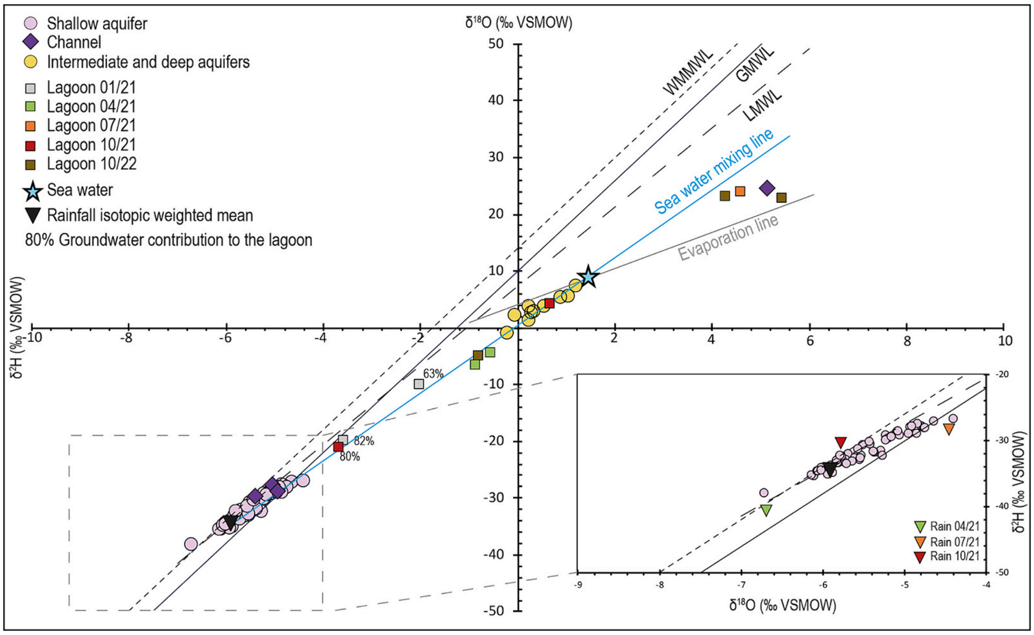


Fig. 5. $\delta^{18}O_{H2O}$ vs $\delta^{2}H_{H2O}$ plot with groundwater, lagoon water and seawater, with weighted mean values of rainwater collected at the Le Cesine site. Also the Global Meteoric Water Line (GMWL) from Craig (1961), the Western Mediterranean Meteoric Water Line (WMMWL) from Celle-Jeanton et al. (2001) and the Local Meteoric Water Line from Longinelli and Selmo (2003). The evaporation line is calculated from Gibson et al. (2008).

isotopic signature more linked to a mixing with groundwater than seawater, especially during January and October 2021 and 2022. This can be explained by the geomorphology of the lagoon. B1 is located in the widest part of the lagoon and the sand bar is very narrow, inducing regular sea overflows (especially in seasons with storm events); in consequence seawater inputs dilute groundwater inputs and decrease the isotopic signal of groundwater discharge. B2 presents a different configuration, located in a narrower part of the lagoon and further inland, limiting the seawater inputs in favor of groundwater inputs.

In a general way, the channel displays a more enriched isotopic signal than that of the groundwater. Its isotopic signal is close to groundwater in January, April and October 2021, corresponding to high water periods, while the signature is more evaporated in October 2022 and close to the lagoon water signature in July 2021. On that basis, channel water can be considered as groundwater standing on the surface, particularly evaporated during the summer, with an isotopic signature close to the lagoon's indicating a possible mixing with seawater.

Tritium content of water samples ranged from <0.5 TU (not detected) to 3.0 ± 0.3 TU, with an average of 1.9 ± 0.2 TU (Table S3). Overall, ^{3}H contents <0.8 TU correspond to old groundwater recharge (before 1950) (Clark and Fritz, 1997). For the western Mediterranean area, modern water, corresponding to rainfall inputs, is estimated at about 3.9 TU (Juhlke et al., 2020), therefore tritium activities in between submodern and modern groundwater recharge correspond to a mixing of different types of groundwaters. For samples P1, S1, P13 and P78, no ^{3}H content has been detected (<0.5 TU), indicating a long water residence time (> 70 years). Samples P2 and P55 display very low ^{3}H content (0.9 ± 0.2) The absence of tritium content in the shallow aquifer (P13, P78) could be explained by vertical mixing with the intermediate aquifer (S1). The physical properties of the carbonate rocks as well as the aquifer heterogeneity and deep fracturing are factors that can influence the water mixing in some parts (Petrella and Celico, 2013; Raco and Battaglini, 2022). For the other samples, including the channel and the lagoon (B1, B2), tritium contents range from 1.3 ± 0.2 TU to 3.0 ± 0.3 TU, close to the rainfall content in the western Mediterranean region, indicating a mixing between formerly recharged groundwater and recently infiltrated rainwater, and in line with the rapid rainfall infiltration in the area evidenced by the stable isotopes of the water molecule.

But going into a more detailed characterization of pollutant sources can be also a way to improve the behavior of the groundwater system.

4.4. Groundwater quality and changes in land use: nitrate contamination sources

Nitrates are naturally present in groundwater, in maximum concentrations estimated at 5 up to 7 mg/L (Appelo and Postma, 2010). Concentrations well above this threshold are markers of ongoing anthropogenic pressures degrading groundwater quality, most of the time related to synthetic or organic fertilizers and septic waste (Re et al., 2017; Vystavna et al., 2017; Cossu et al., 2018; Ligorini et al., 2023).

During the hydrogeological monitoring of the site, for some sampling points, nitrate concentrations clearly above the natural baseline were encountered varying from 8.4 mg/L up to 79.9 mg/L (P24, P30, P35, P35bis, P41bis, P47, P55, P78, P84) (Table S1). The only sample exceeding the drinking water standard of 50 mg/L (World Health Organization, 2011) was P78 (except in October 2021 and 2022).

In April and July 2021, the lagoon waters at B2 display nitrate concentrations around 15 mg/L. This can be explained by the narrowness, reducing the dilution processes, of the lagoon at B2, accentuated by the fact that the sample is in hydraulic connectivity with groundwater samples upstream (P47, P55, P78, P84) and having nitrate concentrations between 18 and 23 mg/L Fig. 6b), constituting a direct nitrogen input into the lagoon. Groundwater being the only freshwater inputs towards the lagoon, it has therefore a predominant impact on nitrogen supply to the lagoon, and can play a major role in the occurrence of dystrophic crisis.

In order to identify the precise origin and fate of nitrate, the isotopic composition of nitrogen and oxygen ($\delta^{15}N_{NO3}$ VS $\delta^{18}O_{NO3}$), were measured at all the sampling points for the October 2022 survey, results displayed on Fig. 6a). The isotopic composition correlation plot (Kendall, 1998; Xue et al., 2009; Zhang et al., 2015), shows values for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ ranging from −3.0 ‰ to 16.7 ‰ and from 2.7 ‰ to 33.6 ‰ respectively (Table S3).

To distinguish the possible ranges of local nitrate sources, the

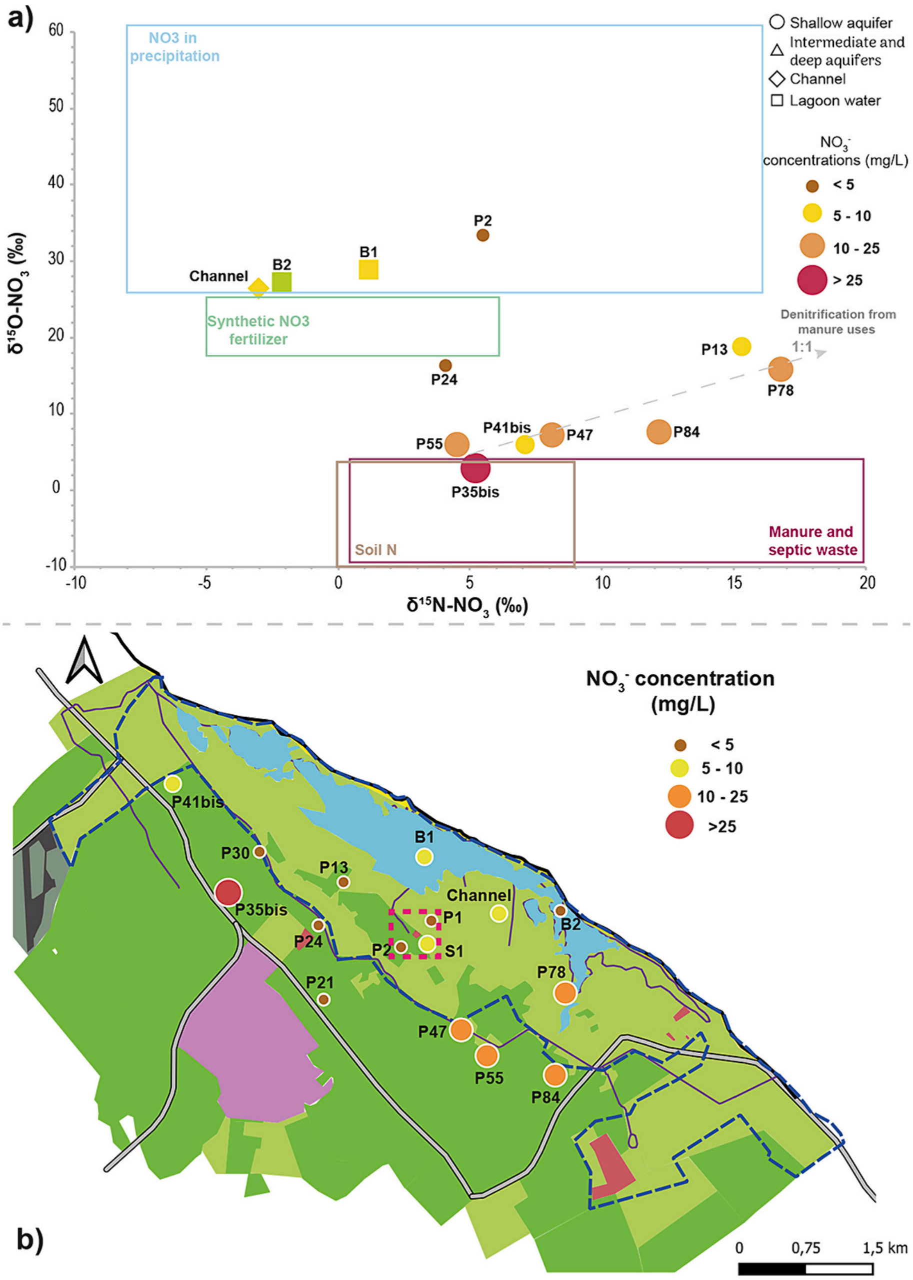


Fig. 6. a) $\delta^{15}N_{NO3}$ vs $\delta^{18}O_{NO3}$ plot for all analyzed samples. Dominant compositional ranges of δ^{15}N and δ^{18}O data for nitrate from different sources (Kendall, 1998; Mayer et al., 2001), b) Spatial distribution of nitrate concentration in mg/L, over the study area.

$\delta^{18}O_{NO3}$ were calculated according to the local δ^{18}O of groundwater (Mayer et al., 2001), using the local weighted mean isotopic rainfall value (−5.90 ‰ $\delta^{18}O_{H2O}$), mean values were calculated and the plot was adjusted accordingly, using the atmospheric $\delta^{18}O\text{-}O_2$ value of 23.5 ‰ (Kroopnick and Craig, 1972; Horibe et al., 1973).

By comparing the data with literature values, the plot suggests the presence of different processes controlling the nitrate concentration in water samples, including nitrate from 1) the soil in agricultural areas ($\delta^{15}N_{NO3}$ from 4.5 ‰ to 8 ‰), 2) the use of manure and septic waste influence ($\delta^{15}N_{NO3}$ from 12.2 ‰ to 16.7 ‰) associated with denitrification processes, 3) the use of synthetic fertilizers ($\delta^{15}N_{NO3}$ from −3 ‰ to 4.1 ‰) with denitrification processes. In addition, the lagoon waters (B1, B2), P2 and P24 seem to be impacted by nitrates of atmospheric origin. Mean annual nitrate concentration in rainfall can be considered locally as very low, around 0.2 mg/L (Santoni et al., 2018); considering that <1/5 of precipitation is infiltrated into groundwater due to evapotranspiration under such climatic and hydrogeological conditions (Polemio and Romanazzi, 2013; Marković et al., 2022), it restricts the impact of atmospheric inputs in groundwater to about 2 mg/L maximum. Atmospheric nitrate can originate in this part of the eastern Mediterranean Sea bordered by highly industrialized regions from atmospheric deposition such as NOx, which can dominate other external nitrogen inputs (Mara et al., 2009; Emeis et al., 2010), and can subsequently enrich rainfall and accumulate in groundwater.

For a long time, the agricultural activities of the region have been dominated by the monoculture of olive groves. Both organic and synthetic fertilizers are of benefit to olive trees (Mazeh et al., 2021); in the Apulia Region organic fertilizers such as cattle, pig and sheep manure are usually used with a maximum authorized quantity of 30 kg/ha, and synthetic fertilizers, cheaper and with higher amount of nutrients, can be used up to 70 kg/ha (Regione Puglia, 2022). Samples P13, P35bis, P41bis, P47, P55, P78 and P84 have a $\delta^{15}N_{NO3}$ signature indicating nitrogen originating from manure denitrification and present notable nitrate concentrations (≈ 20 mg/L). This can be explained by past intensive agricultural activities at the Le Cesine site, drastically reduced since 2013 mainly due to the *Xylella fastidiosa* epidemic (Ali et al., 2021; Bajocco et al., 2023). Therefore, the origin of N from the soil can be associated with the use of large amounts of organic fertilizers in the past (Serio et al., 2018), as was the case in Greece (Chatzistathis et al., 2016; Solomou and Sfougaris, 2021; Platis et al., 2023), which is more documented as Europe's third largest olive producer (Eurostat, 2019). These past agricultural activities can lead to consider nitrates from the use of manure as a nutrient legacy pollution in the area (Chen et al., 2019; Ator et al., 2020; Martin et al., 2023).

For these samples (mainly P13 and P41), the isotopic enrichment allows us to consider denitrification as responsible for nitrate abatement in groundwater (Kendall et al., 2007; Sacchi et al., 2013; Re et al., 2017). In the present case, denitrification occurs naturally because the water table is shallow and in some places with low permeability can present reducing conditions (Martinelli et al., 2018). This is also the case for the use of synthetic fertilizers, probably occurring in P24 and channel, displaying a low nitrate concentration and plotting at the limit of

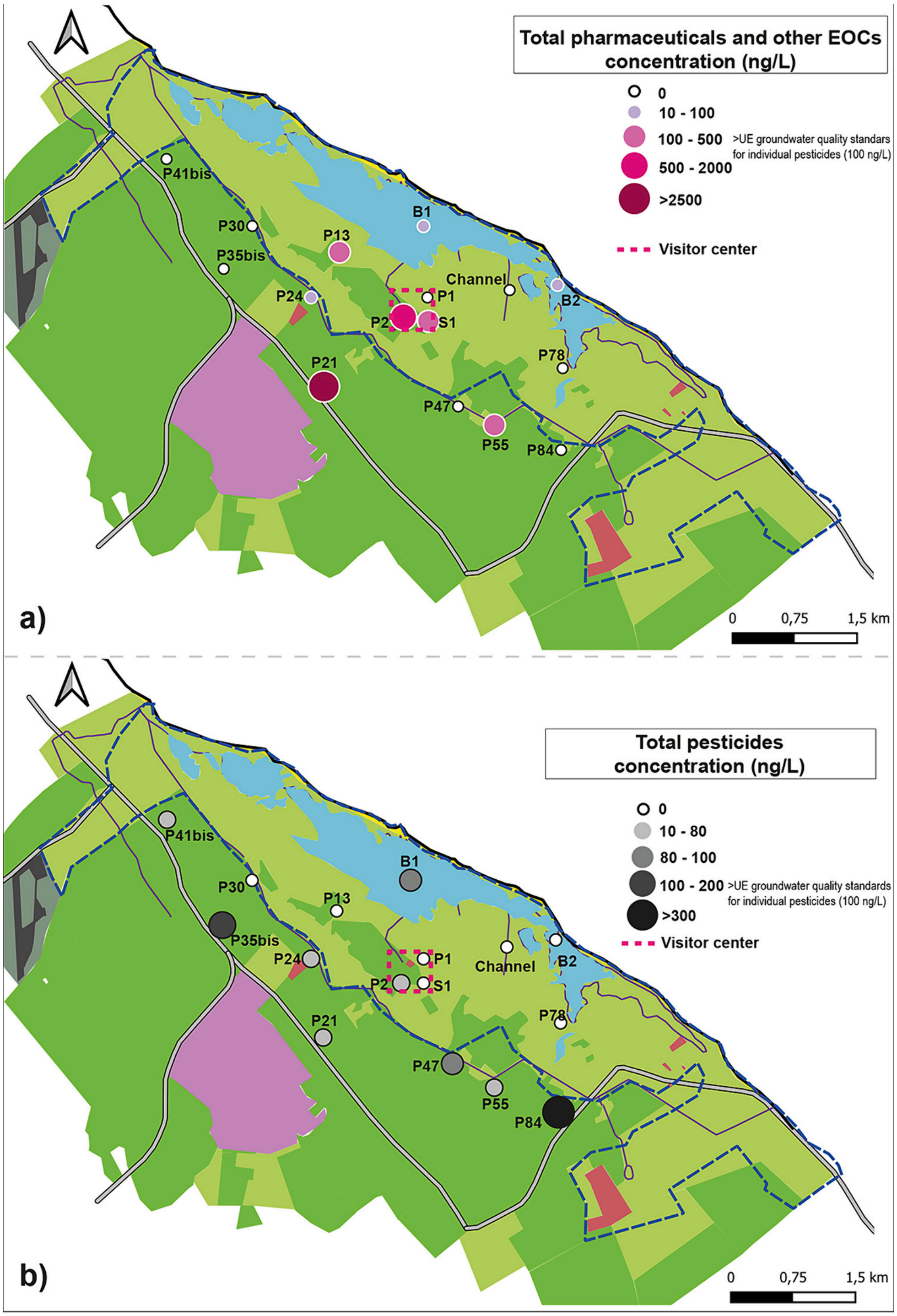


Fig. 7. a) Spatial distribution of total pharmaceuticals and other EOCs measured throughout the Le Cesine site (ng/L), b) Spatial distribution of total pesticides and metabolites measured throughout the site (ng/L).

synthetic fertilizers due to ongoing denitrification processes from another N source. The plot of $\delta^{15}N_{NO3}$ VS $\delta^{18}O_{NO3}$ allows identification of major trends in the potential origin of nitrate pollution in the study area.

But used alone, it does not allow the precise identification of pollution sources. For that, it must be complemented by the use of additional tracers such as EOCs and groundwater residence time indicators such as ^{3}H.

4.5. *Emerging organic compounds: compounds identified*

EOCs are good tracers to identify pollution sources (Jurado et al., 2012; Stuart et al., 2014) because they are not naturally present in the environment unlike conventional tracers. Some EOCs are source specific indicators (e.g. caffeine) and can be particularly useful for the identification of hydrogeological processes.

The spatial distribution of the total EOCs concentrations over the study site is shown in Fig. 7. Among a screening of 236 pesticides and metabolites, 8 were identified in both groundwater and lagoon waters, with concentrations above 10 ng/L in most of the samples (9/16 samples), including 4 herbicides, 3 insecticides and 1 fungicide. In addition, among a screening of 113 domestic compounds, 15 were detected in half of the samples, including 8 pharmaceuticals, 3 stimulants, 2 plasticizers and a corrosion inhibitor (Table S5). This diversity of molecules identified in ground and lagoon waters demonstrate an anthropogenic footprint with a two-fold origin, both agricultural and domestic.

4.5.1. *Agricultural origin*

The pesticides have mainly been identified in agricultural plots, at the edge of the natural reserve area, and in the lagoon in B1 (Fig. 7b). They mainly correspond to non-crop-specific compounds.

Among the molecules identified, half correspond to pesticides banned in Europe for several decades, including atrazine, simazine and associated metabolites, cyhalothrin that could have been used in olive groves and small farming plots in the area in the past decades (Hasaneen, 2012), and imidacloprid, a pesticide more recently banned, in 2018. Atrazine and simazine, banned in 2003, are frequently detected in European groundwaters (Loos et al., 2010; Lapworth et al., 2012). They are very persistent in soil and water, (Lewis et al., 2016) and are considered as pesticide legacies in Europe (Lapworth and Gooddy, 2006; Reberski et al., 2022; Becker et al., 2023). In P35bis, the concentration of atrazine exceeds the European groundwater quality standard for individual pesticides, of 100 ng/L (Directive 2006/118/EC). Those molecules can therefore be considered as legacies from historical agricultural practices on the site, such as olive growing and small farming. In addition, in P41bis, and P47, atrazine and simazine (Fig. 8b) are also present.

Cyhalothrin is an insecticide that is particularly effective on olive trees; it was banned in 1994 in Europe (Lewis et al., 2016). This molecule has been identified in the lagoon waters only (B1) at a detectable concentration (93 ng/L), and can result from the archiving capacity of groundwater supplying the lagoon, and/or from illegal uses (Yang et al., 2014). In addition, this molecule is certainly present in groundwater but below the limit of detection of 30 ng/L. Moreover, EOCs may not be detected in water samples, but be present in sediments and biota (Capolupo et al., 2017) and therefore released to lagoon waters after storm events with strong swell (Castaño-Ortiz et al., 2023).

Finally, imidacloprid was found in P84 in a large amount (279 ng/L), greatly exceeding the quality standard. This neonicotinoid is the most widely used insecticide in the world (Goulson, 2013), no longer allowed in Europe since 2018 (Reg. (EU) 2018/783–4-5). In Italy, it is the most frequently reported insecticide in groundwater (ISPRA, 2018). However, the Apulia Region authorizes its use, in the particular context of the fight against *Xylella fastidiosa* (Regione Puglia, 2014). It can be suspected that this large amount of imidacloprid is associated with a local attempt to control this bacterium, in view of the intensively cultivated plots near the sampling point. As previously observed, P84 displays a noticeable concentration in nitrate which is also associated with the highest total pesticide concentration (358.6 ng/L), indicating a coupled use of both manure fertilizers and pesticides.

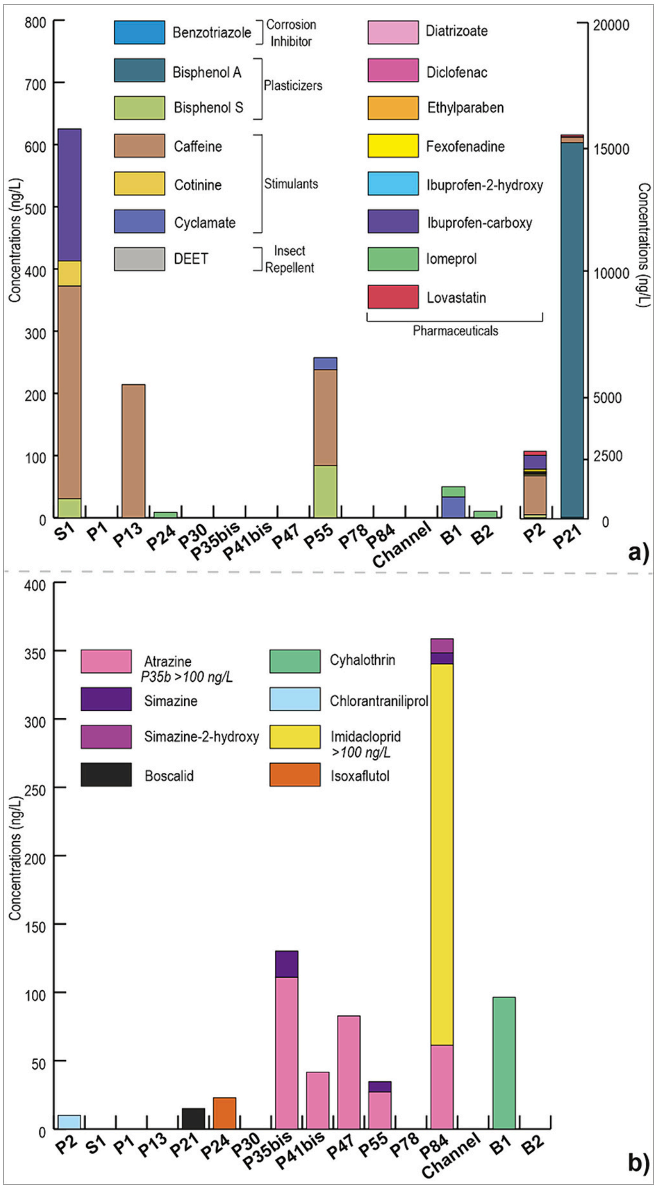


Fig. 8. a) Concentrations of pharmaceuticals in all water samples throughout the area, b) Concentrations of pesticides metabolites in all water samples throughout the area.

The other pesticides identified in P2, P21, 24, are currently authorized molecules (respectively chlorantraniliprol, boscalid, isoxaflutol). They are considered as a “new generation” of pesticides developed as an alternative to highly toxic molecules such as neonicotinoids or atrazine, for example (Ramanarayanan et al., 2005; Avenot and Michailides, 2007; Meyer et al., 2007; Sandstrom et al., 2022). All three are identified in amounts not exceeding 25 ng/L, and except isoxaflutol remain very persistent in the environment (Lewis et al., 2016), so they can be considered as a serious threat for the future as well as those banned several decades ago.

4.5.2. *Domestic origin*

Domestic EOCs in groundwater have mainly been identified in S1, P2, P13, P21, P24, and P55. Except for P55, all are downstream of the golf club, two of these are close to the visitor centre area (P2, S1), three are in agricultural plots associated with past or present human presence (P13, P24, P55) (Fig. 7a). Stimulants and pharmaceuticals only have been identified in the lagoon (B1, B2). Most of the time domestic EOCs are good indicators of the connectivity of groundwater with wastewater from sewage effluents or septic tanks (Lapworth et al., 2012). The present study reveals 5 compounds out of the 20 most frequently detected in carbonate groundwater in general, namely caffeine, bisphenol A, diclofenac, ibuprofren, 1-H-benzotriazole, indicating a potential risk to aquatic ecosystems. The presence of rapidly degrading compounds due to biodegradation, such as ibuprofen and caffeine, under specific conditions, with half-lives of 4 and 3 days respectively in karst systems (Hillebrand et al., 2012, 2015) but with significant half-life variability (Schübl et al., 2021), could indicate a short residence time of the molecules associated with a connectivity with wastewater effluents, evidencing the high aquifer vulnerability. Samples close to the visitor centre show the highest diversity of domestic EOCs. P2 is the most impacted with the highest concentration in caffeine (1570 ng/L) and ibuprofen (547 ng/L). Other compounds are mainly pharmaceuticals (Fig. 8a), which could suggest contamination from the septic tank of the visitor's centre, that could be no longer effective. The same explanation may be proposed for S1, close to P2. Samples S1 and P2 also display arsenic values of 12 μg/L and 28 μg/L respectively, above the international quality standard in groundwater of 10 μg/L (WHO, 2022). Arsenic can come from raw wastewater again owing to problems with the wastewater collecting system (Shankar and Shanker, 2014).

The sampling point P21 also displays a noteworthy total concentration of 15,100 ng/L of bisphenol A. This compound is an endocrine disruptor used in plastics, resins, etc., and mainly comes from sewage water (Vandenberg et al., 2007; Lapworth et al., 2012), but it is not expected to be persistent in the environment (USEPA, 2010) and the principal cause of the concentration decreasing in groundwater can be attributed to biodegradation (Heinz et al., 2009; Hillebrand et al., 2015). Associated with this compound benzotriazole, caffeine, ibuprofen and lovastatin, a pharmaceutical used to lower the cholesterol, all indicate a connection with wastewater and a continuous input, possibly related to the golf club's sewage system located immediately upstream along the groundwater flow line towards the visitor centre and the lagoon system.

The other samples with domestic EOCs, P13, P24, P55, contain mainly caffeine and can be related to human presence on the plots for cultivation, as also shown by the presence of pesticides, and/or the upstream activities carried out at the Golf Club (except for P55). The sampling point P55 displays both pesticides legacies and organic compounds including caffeine suggesting a recently infiltrated mixing with sewage water.

The lagoon in B1 presents 33.5 ng/L of cyclamate, a sweetener, which indicates an input of raw sewage (Zirlewagen et al., 2016). Cyclamate has a half-life of 57 days (Reberski et al., 2022) and when it was identified without recently infiltrated compounds such as caffeine, it did not necessarily indicate a recent infiltration according to Hillebrand et al. (2015). B1 is located in the widest part of the lagoon. The sampling point presents domestic molecules and a pesticide with a long residence time, which does not indicate a recent infiltration and shows limited dilution processes with contaminated groundwater. We could hypothesize that in this part of the lagoon, there is an input of groundwater having stored pollution over time, threatening the good quality of the lagoon waters over the long term.

The timing of the pollutant dispersion process can be now confirmed by investigations on the residence time of groundwater within the hydrosystem.

4.6. Groundwater residence time and mixing processes

In order to identify the legacy contaminations in a chronological way, a plot of $\delta^{15}N_{NO3}$ vs ^{3}H is proposed in Fig. 9. Groundwater samples P35bis, P41bis, P47, P55 and P84 display ^{3}H values between 0.9 ± 0.2 TU and 2.0 ± 0.3 TU, associated with $\delta^{15}N_{NO3}$ signature coming from a denitrification of manure and septic waste origin and displays pesticides banned for decades, suggesting a long residence time with a progressive accumulation of nitrate and pesticide concentrations, related to past agricultural activities, making them pollutant legacies. The hypothesis of the nutrient inputs from manure use is here the most likely. Soils in the Apulia region have been subject to major land use changes, inducing conversion of natural pastures into cultivation areas, notably for olive growing. The conversion processes involve the fragmentation of the carbonate rocks of the topsoil in order to increase the soil depth (Zdruli

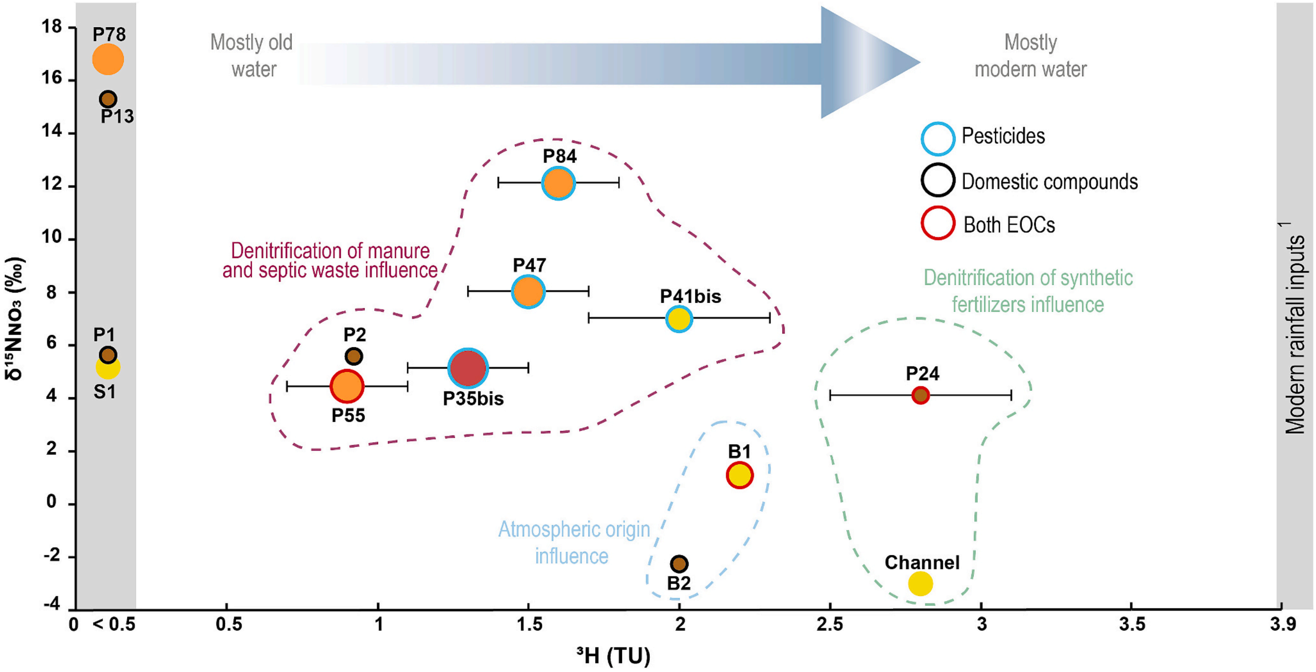
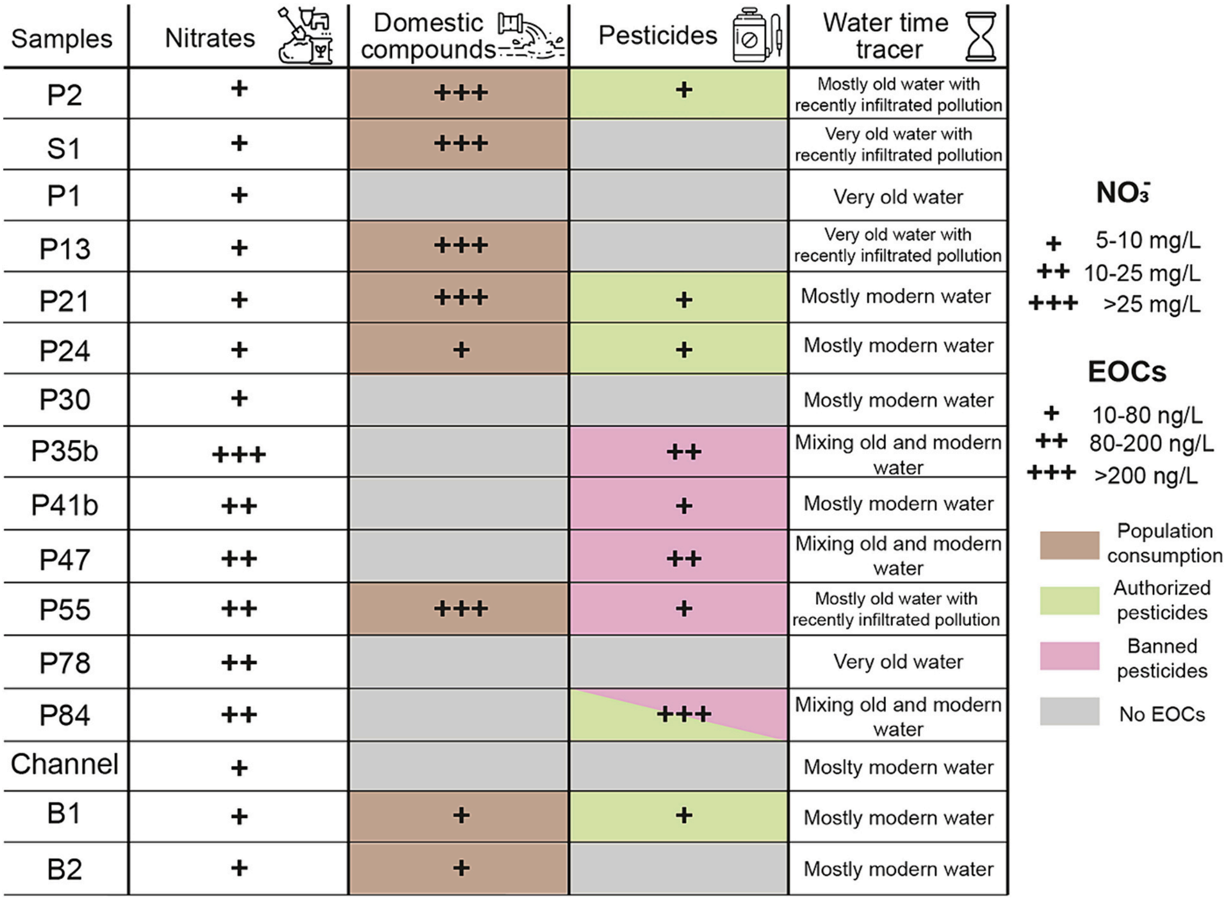


Fig. 9. $\delta^{15}N_{NO3}$ vs ^{3}H concentrations in water samples. The symbol size is proportional to NO_3- concentrations measured in water samples. Black outline indicates a presence of EOCs in samples. Samples with values of <0.5 TU can be considered as tritium-free (Juhlke et al., 2020).

et al., 2014). However, these transformations tend to decrease the biological diversity in soils (Geri et al., 2010) and the organic matter content but increase the soil erosion leading to a loss of pedodiversity (Cerdà, 2001; Lo Papa et al., 2011; Ferrara et al., 2012). Under olive groves, carbonate soils appear to be eroded and poor in organics, requiring an input of organic nutrients to improve the soil quality (Zdruli et al., 2014; Shelef et al., 2016; Serio et al., 2018). Therefore, at the Le Cesine site the use of manure mainly from cattle, pigs and sheep as nutrient inputs could have been practiced for decades and especially in olive groves, in large amounts (Serio et al., 2018; Regione Puglia, 2022). The use of manure fertilizers seems to have been in the process of reduction at the Cesine site for several decades, therefore this might explain the large amount of nitrates accumulated in groundwater associated with very low ^{3}H corresponding to an old recharge (S1, P55, P78). For P35bis, P47, P84 the same process can be suspected but involving less old groundwater to remain in agreement with the moderate ^{3}H content observed. Samples P13, S1 and P55 present very low ^{3}H values, indicating an old groundwater recharge. But these samples display EOCs concentration (Fig. 9.), including the caffeine molecule, which is considered as a tracer of modern and rapid infiltration of raw sewage (Hillebrand et al., 2012; Reberski et al., 2022). This can be explained by small leakages of untreated sewage water, due to the absence of sanitation, not sufficient to impact the ^{3}H signature.

4.7. Groundwater pollution in time

The multi-tracer approach using isotopes of nitrate, domestic compounds and pesticides associated with time tracers, in addition to hydrogeological parameters and a land uses survey, provides a robust methodology for an integrated approach to tackle pollution legacies impacting a coastal GDE, which is summarized in Fig. 10. It provides a basis for building a synoptical summary of the molecules identified in each sample according to groundwater residence time by identification of the precise pollution sources in P13, P35bis, P41bis, P47, P55 and P84. This pollution source identification was enabled by the combination of $\delta^{15}N_{NO3}$ VS $\delta^{18}O_{NO3}$ with EOCs, otherwise the nitrate pollution sources would have remained incomplete and hypothetical. Furthermore, the combination of EOCs with time tracers highlights the presence of pollutant legacies such as atrazine and simazine, and suggests that other pesticides banned more recently e.g. imidacloprid, could become legacies in their turn, within a few decades (Goulson, 2013), constituting a latent threat to the groundwater and the lagoon. This multi-tracer investigation can provide a basis for better management to preserve the quality of water resources, in compliance with the WFD requirements. In particular, taking into account past agricultural practices in the area, using manure fertilizers and pesticides leading to accumulation of nitrates and organic molecules in groundwater during decades (Caracuta, 2020), and particularly from the 1950–1960, groundwater inputs towards the lagoon play the role of legacy vector. Even if the region is strongly impacted by the *Xylella fastidiosa* crisis from 2013, the olive production activity remains very important and the contamination process can be considered as still active. In addition, the area does not possess sanitation systems, leading to leakages of raw wastewater to the aquifers, degrading the water quality and threatening the lagoon by nutrient enrichment. The south of Italy can also be considered as a good illustration of the coastal Mediterranean regions combining huge olive industry with dynamic tourism economy and suffering from both impacts on groundwater and connected ecosystems, this is for instance the case in Tunisia in the Sfax region (Ben Nasr et al., 2024), in Greece (Panagopoulos et al., 2023) or in the South of Spain (González-Ramón



Samples	Nitrates	Domestic compounds	Pesticides	Water time tracer
P2	+	🟫 +++	🟩 +	Mostly old water with recently infiltrated pollution
S1	+	🟫 +++	⬜	Very old water with recently infiltrated pollution
P1	+	⬜	⬜	Very old water
P13	+	🟫 +++	⬜	Very old water with recently infiltrated pollution
P21	+	🟫 +++	🟩 +	Mostly modern water
P24	+	🟫 +	🟩 +	Mostly modern water
P30	+	⬜	⬜	Mostly modern water
P35b	+++	⬜	🟥 ++	Mixing old and modern water
P41b	++	⬜	🟥 +	Mostly modern water
P47	++	⬜	🟥 ++	Mixing old and modern water
P55	++	🟫 +++	🟥 +	Mostly old water with recently infiltrated pollution
P78	++	⬜	⬜	Very old water
P84	++	⬜	🟩🟥 +++	Mixing old and modern water
Channel	+	⬜	⬜	Moslty modern water
B1	+	🟫 +	🟩 +	Mostly modern water
B2	+	🟫 +	⬜	Mostly modern water

NO_3^-

+	5-10 mg/L
++	10-25 mg/L
+++	>25 mg/L

EOCs

+	10-80 ng/L
++	80-200 ng/L
+++	>200 ng/L

🟫	Population consumption
🟩	Authorized pesticides
🟥	Banned pesticides
⬜	No EOCs

Fig. 10. Summary of sampling points associated with anthropogenic tracers and water time tracer. "Mixing" indicates a mixing between old and modern water.

et al., 2013).

4.8. Management implications

Due to inherent geological parameters, the Le Cesine aquifer and associated ecosystems are highly vulnerable to emerging forms of contamination and to changes in land use over time (White, 2002). The use of various anthropogenic tracers combined with conventional indicators has enabled the identification of a dual source of contamination in the area, namely agricultural and domestic inputs. The results provide information on past and current land uses. Nitrate from the soil indicates a historic pollution legacy and evidences the storage capacity of the aquifer, which is also confirmed by the presence of pesticides banned for several years and considered as pollution legacy. The identification of domestic compounds highlights the rapid infiltration and the continuous input of sewage water within the aquifer. Actual pollution (domestic EOCs) and legacies (nitrate concentrations resulting from manure fertilizers, pesticide legacies) constitute a serious threat towards groundwater quality and the Le Cesine lagoon-dependent ecosystem. The domestic influence is clearly identified close to areas with regular human presence (golf club, visitor center, some cultivated crops), without an efficient sewage system. Deep groundwater is also vulnerable to pollution, presenting compounds that can transit quickly from the surface to the bedrock (S1 the intermediate aquifer) (Reberski et al., 2022), and the absence of EOCs does not necessary indicate low vulnerability.

This original work provides essential information on nutrient legacies from past use of manure fertilizers in olive groves to enrich the poor carbonate soils of the area. These legacies associated with the use of triazine herbicides have been poorly investigated in the Apulia Region and in the literature. But they constitute a potential threat to groundwater and dependent ecosystems, especially in a protected area.

Moreover, to correctly assess the sources of contamination, it is essential to include socio-economic and historical data, retrieved from the local population, regarding land use changes over time and their groundwater uses. The purpose of this survey is to cross-check this data with hydrogeological data, in order to promote the sustainable management of groundwater resources and dependent ecosystems in the carbonate domain. This methodology is one of the bases of the socio-hydrogeological approach (Re, 2015), which has shown its relevance in very different contexts (Re et al., 2017; Carrión-Mero et al., 2021; Frommen and Moss, 2021; Musacchio et al., 2021), and more recently for a highly anthropized Mediterranean GDE of strong environmental interest (Crayol et al., 2023).

The intention was to transpose the methodology used by Crayol et al. (2023) to the Le Cesine site; however, certain limitations meant that complete transposition could not be achieved. The site has been a National Natural Park for four decades with very restricted and regulated access, resulting in the presence of very few people in the area. It was therefore difficult to interview local water users; only two people were available to answer our questions. Despite common environmental interests, some GDEs may present very different local management policies. When access is very restricted, this can be an obstacle to a proper understanding of the socio-hydro-ecosystem because information on actual and past land uses needs to be retrieved from discussion with local users, but their recollections are not easily accessible to researchers, just as there can be little awareness of water resources among the local population.

The Water Framework Directive (WFD) of 2000 (European Union, 2000), defined GDEs as dependent on the groundwater quality and quantity for a significant period of the year (European Commission, 2012). Thus, the chemical composition of the groundwater must not degrade the ecological or chemical quality of dependent ecosystems. The fact is that so far, there is no suitable method implemented to link the pollutant legacy of groundwater impacting the quality of a dependent ecosystem, such as the one developed in the present work, leading to inconsistencies in GDE management policies. This lack can lead to unsatisfactory management of waterbodies, e.g. the absence of an efficient sanitation system inside a Natural Park, or the presence of impactful activities upstream of a protected area, which makes it difficult to achieve the ‘good status’ required by the WFD (ARPA Puglia, 2021; Collectivité de Corse, 2022).

Local application of the WFD in European countries giving priority to protecting hydrosystems through sustainable management usually does not consider waterbodies as a continuum, where they are interconnected, and does not integrate local specificities (Ligorini et al., 2023) in order to improve the application of EU standards in each country. Moreover, these GDEs should be considered as socio-hydroecosystems and protection measures should combine scientific and technical expertise associated with the perception of stakeholders (De Wit et al., 2020) and the local population (Re et al., 2017, 2021, 2023). Despite the protection measures, coastal GDEs are highly vulnerable to anthropogenic pollution. The lack of maintenance/deployment of sewage systems on plots with human activities is a major cause of the deterioration of the water quality by domestic pollutants and nitrates. In addition, the scarcity of knowledge regarding pollutant legacies and the storage capacity of the aquifer contributes to the ongoing deterioration of the water quality. This is why improvement of knowledge of the hydrosystem's behavior and efficient communication must be established between the scientists, the local population and the local stakeholders, in order to reduce the vulnerability of the system, by sharing knowledge in order to implement sustainable management measures for Mediterranean groundwater-dependent ecosystems (Re, 2015; Crayol et al., 2023).

5. Conclusions

Coastal GDEs are facing various global threats inducing land use transformation associated with pollutant fluxes. The consideration of waterbodies in a space and time continuum is essential for the sustainable management of water resources. Groundwater can act as a vector of pollution towards dependent ecosystems, threatening their ecological status. In this context, the present study demonstrated the value of using a multi-tracer approach to improve the knowledge and make good a gap regarding the hydrogeological functioning of a shallow groundwater dependent ecosystem in carbonate domain under the impact of anthropogenic pollution, as well as offering a precise identification of contaminant sources. Conventional hydrogeological tracers were combined with the use of nitrate concentrations associated with $\delta^{15}N_{NO3}$ VS $\delta^{18}O_{NO3}$, trace elements and EOCs, whose environmental behavior, toxic effects and degradation processes are still poorly known. Results indicated a two-fold pollution affecting groundwater resources and the Le Cesine lagoons of both agricultural and domestic origin. The main nitrate sources appear to be N from the use of manure fertilizers related to the past agricultural context of the area. Animal manure fertilizers were applied in olive groves as nutrient surplus on poor soils. Nitrates accumulate in groundwater and appear as pollutant legacies constituting a potential threat to the GDE. In addition, EOCs help to clarify the identification of more recent pollution sources, highlighting both recently infiltrated compounds, rapidly degradable, related to human consumption habits, and typical of raw sewage identified in samples with regular human presence, without efficient sanitation facilities, and legacy compounds, more persistent, from the use of pesticides further back in time, such as triazine herbicides associated with olive growing. This study is also innovative in the combination of groundwater time-tracer (^{3}H) with anthropogenic pollutant fluxes. It has made it possible to increase the time scale of hydrological processes highlighted by the study of pollutant and their state with regard to the fate of those pollutant legacies. The under-investigated or even ignored legacy effect of compounds in groundwater related to historical Mediterranean olive groves is cause for concern regarding the resilience and sustainable management of GDEs, particularly in coastal areas. Multi-tracer approaches and dialogue between actors at different levels could provide a proper basis for management policies in the future. Furthermore, this study allows the use of multi-tracer approaches in groundwater to be considered as the most reliable strategy for the assessment and prospection of relevant anthropogenic pollution flows.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.176015.

Funding

This research is part of the GERHYCO interdisciplinary project dedicated to water management, ecology and hydro-ecosystem services in island context and was financially supported by the 'Culletività di Corsica'.

CRediT authorship contribution statement

E. Crayol: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **F. Huneau:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **E. Garel:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Data curation, Conceptualization. **L.E. Zuffianò:** Writing – review & editing, Investigation, Formal analysis, Data curation, Conceptualization. **P.P. Limoni:** Writing – review & editing, Investigation, Formal analysis, Data curation, Conceptualization. **A. Romanazzi:** Writing – review & editing, Investigation, Data curation. **A. Mattei:** Writing – review & editing, Investigation, Formal analysis, Data curation. **V. Re:** Writing – review & editing, Methodology, Conceptualization. **K. Knoeller:** Writing – review & editing, Investigation, Formal analysis, Data curation. **M. Polemio:** Writing – review & editing, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors wish to thank all the people from WWF managing Le Cesine wetland for welcoming us, answering all our questions and completing the questionnaire. We also wish to thank all the well and borehole owners who have contributed to the project by answering the questionnaire and allowing the research team to collect samples on their property. The authors thank all the people who have facilitated the progress of this research work, including the CNR-IRPI research fellow Giorgio De Giorgio.

References

Ali, B.M., van der Werf, W., Oude Lansink, A., 2021. Assessment of the environmental impacts of Xylella fastidiosa subsp. pauca in Puglia. Crop Prot. 142, 105519 https://doi.org/10.1016/j.cropro.2020.105519.

Andreu, V., Gimeno-García, E., Pascual, J.A., Vazquez-Roig, P., Picó, Y., 2016. Presence of pharmaceuticals and heavy metals in the waters of a Mediterranean coastal wetland: potential interactions and the influence of the environment. Science of The Total Environment, 5th Special Issue SCARCE: River Conservation under Multiple stressors: Integration of ecological status, pollution and hydrological variability, 540, pp. 278–286. https://doi.org/10.1016/j.scitotenv.2015.08.007.

Appelo, C.A.J., Postma, D., 2010. Geochemistry, Groundwater and Pollution, 2nd ed., 5th corr. repr. ed. CRC Press, Boca Raton.

ARPA Puglia, 2021. Agenzia Regionale per la Prevenzione e la Protezione dell'Ambiente - II CICLO SESSENNALE 2016–2021 [WWW Document]. URL. https://www.arpa.puglia.it/pagina2975_ii-ciclo-sessennale-2016-2021.html.

ARPA Puglia, 2023. ARPA Puglia Dati Meteo.

Ator, S.W., Blomquist, J.D., Webber, J.S., Chanat, J.G., 2020. Factors driving nutrient trends in streams of the Chesapeake Bay watershed. J. Environ. Qual. 49, 812–834. https://doi.org/10.1002/jeq2.20101.

Avenot, H.F., Michailides, T.J., 2007. Resistance to Boscalid Fungicide in Alternaria alternata Isolates from Pistachio in California. Plant Dis. 91, 1345–1350. https://doi.org/10.1094/PDIS-91-10-1345.

Bajocco, S., Raparelli, E., Bregaglio, S., 2023. Assessing the driving role of the anthropogenic landscape on the distribution of the Xylella fastidiosa-driven "olive quick decline syndrome" in Apulia (Italy). Sci. Total Environ. 896, 165231 https://doi.org/10.1016/j.scitotenv.2023.165231.

Balestrini, R., Delconte, C.A., Sacchi, E., Buffagni, A., 2021. Groundwater-dependent ecosystems as transfer vectors of nitrogen from the aquifer to surface waters in agricultural basins: the fontanili of the Po plain (Italy). Sci. Total Environ. 753, 141995 https://doi.org/10.1016/j.scitotenv.2020.141995.

Becker, R.W., Araújo, D.S., Jachstet, L.A., Ruiz-Padillo, A., do Amaral, B., de Souza, J.E., Müller Athayde, C. de V., Athayde, G.B., Sirtori, C., 2023. Classifying micropollutants by environmental risk in groundwater using screening analysis associated to a hybrid multicriteria method combining (Q)SAR tools, fuzzy AHP and ELECTRE. Sci. Total Environ. 892, 164588 https://doi.org/10.1016/j.scitotenv.2023.164588.

Ben Nasr, W., Huneau, F., Trabelsi, R., Zouari, K., Garel, E., Leydier, T., 2024. Emerging organic compounds as markers of the degradation of groundwater qualitative and quantitative equilibrium in a context of rapid urban expansion. Sci. Total Environ. 915, 170068.

Caldararu, A., Rosati, I., Barbone, E., Georgescu, L., Iticescu, C., Basset, A., 2010. Implementing european water framework directive: uncertainty degree of metrics for macroinvertebrates intransitional waters. Environ. Eng. Manag. J. 9 (1259), 1267.

Capolupo, M., Franzellitti, S., Kiwan, A., Valbonesi, P., Dinelli, E., Pignotti, E., Birke, M., Fabbri, E., 2017. A comprehensive evaluation of the environmental quality of a coastal lagoon (Ravenna, Italy): integrating chemical and physiological analyses in mussels as a biomonitoring strategy. Sci. Total Environ. 598, 146–159. https://doi.org/10.1016/j.scitotenv.2017.04.119.

Caracuta, V., 2020. Olive growing in Puglia (southeastern Italy): a review of the evidence from the Mesolithic to the middle ages. Veget. Hist. Archaeobot. 29, 595–620. https://doi.org/10.1007/s00334-019-00765-y.

Carrión-Mero, P., Morante-Carballo, F., Vargas-Ormaza, V., Apolo-Masache, B., Jaya-Montalvo, M., 2021. A conceptual socio-hydrogeological model applied to sustainable water management. Case study of the Valdivia River basin. Southwestern Ecuador. IJSDP 16, 1275–1285. https://doi.org/10.18280/ijsdp.160708.

Casciotti, K.L., Sigman, D.M., Hastings, M.G., Böhlke, J.K., Hilkert, A., 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Anal. Chem. 74, 4905–4912. https://doi.org/10.1021/ac020113w.

Castaño-Ortiz, J.M., Gil-Solsona, R., Ospina-Alvarez, N., García-Pimentel, M.M., León, V. M., Santos, L.H.M.L.M., Barceló, D., Rodríguez-Mozaz, S., 2023. Bioaccumulation and fate of pharmaceuticals in a Mediterranean coastal lagoon: temporal variation and impact of a flash flood event. Environ. Res. 228, 115887 https://doi.org/10.1016/j.envres.2023.115887.

Celle-Jeanton, H., Travi, Y., Blavoux, B., 2001. Isotopic typology of the precipitation in the Western Mediterranean region at three different time scales. Geophys. Res. Lett. 28, 1215–1218. https://doi.org/10.1029/2000GL012407.

Cerdà, A., 2001. Effects of rock fragment cover on soil infiltration, interrill runoff and erosion. Eur. J. Soil Sci. 52, 59–68. https://doi.org/10.1046/j.1365-2389.2001.00354.x.

Chatzistathis, T., Tsiolis, A., Papaioannou, A., Tsirakoglou, V., Molassiotis, A., 2016. Can sustainable management models for olive groves adequately satisfy their nutritional needs? Sci. Hortic. 207, 48–56. https://doi.org/10.1016/j.scienta.2016.04.036.

Chen, N., Valdes, D., Marlin, C., Blanchoud, H., Guerin, R., Rouelle, M., Ribstein, P., 2019. Water, nitrate and atrazine transfer through the unsaturated zone of the chalk aquifer in northern France. Sci. Total Environ. 652, 927–938. https://doi.org/10.1016/j.scitotenv.2018.10.286.

Clark, I., Fritz, P., 1997. Environmental Isotopes in Hydrology. Lewis Publishers, p. 328.

Collectivité de Corse, 2022. Programme de mesures 2022–2027, bassin de Corse (Directive cadre européenne sur l'eau pour le bon état des milieux aquatiques).

Cossu, R., Zuffianò, L.E., Limoni, P.P., De Giorgio, G., Pizzardini, P., Miano, T., Mondelli, D., Garavaglia, R., Carella, C., Polemio, M., 2018. How can the role of leachate on nitrate concentration and groundwater quality be clarified? An approach for landfills in operation (southern Italy). Waste Manag. 77, 156–165. https://doi.org/10.1016/j.wasman.2018.05.014.

Cotecchia, V., Grassi, D., Polemio, M., 2005. Carbonate aquifers in Apulia and seawater intrusion. https://doi.org/10.1474/GGA.2005-01.0-22.0022.

Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702–1703. https://doi.org/10.1126/science.133.3465.1702.

Crayol, E., Huneau, F., Garel, E., Mattei, A., Santoni, S., Pasqualini, V., Re, V., 2023. Socio-hydrogeological survey and assessment of organic pollutants to highlight and trace back pollution fluxes threatening a coastal groundwater-dependent ecosystem. Sci. Total Environ. 165343 https://doi.org/10.1016/j.scitotenv.2023.165343.

Currell, M., McCance, W., Jones, O.A.H., 2022. Novel molecular tracers for the assessment of groundwater pollution. Curr. Opin. Environ. Sci. Health 26, 100331. https://doi.org/10.1016/j.coesh.2022.100331.

De Giorgio, G., Chieco, M., Zuffianò, L.E., Limoni, P.P., Sottani, A., Pedron, R., Vettorello, L., Stellato, L., Di Rienzo, B., Polemio, M., 2018. The compatibility of geothermal power plants with groundwater dependent ecosystems: the case of the Cesine wetland (southern Italy). Sustainability 10, 303. https://doi.org/10.3390/su10020303.

De Wit, R., Leruste, A., Le Fur, I., Sy, M.M., Bec, B., Ouisse, V., Derolez, V., Rey-Valette, H., 2020. A multidisciplinary approach for restoration ecology of shallow coastal lagoons, a case study in South France. Front. Ecol. Evol. 8.

EFSA, P. on P.H. (PLH), 2015. Scientific opinion on the risks to plant health posed by Xylella fastidiosa in the EU territory, with the identification and evaluation of risk reduction options. EFSA J. 13 https://doi.org/10.2903/j.efsa.2015.3989.

Emeis, K.-C., Mara, P., Schlarbaum, T., Möbius, J., Dähnke, K., Struck, U., Mihalopoulos, N., Krom, M., 2010. External N inputs and internal N cycling traced by isotope ratios of nitrate, dissolved reduced nitrogen, and particulate nitrogen in the eastern Mediterranean Sea. J. Geophys. Res. 115, G04041. https://doi.org/10.1029/2009JG001214.

Erostate, M., Huneau, F., Garel, E., Lehmann, M.F., Kuhn, T., Aquilina, L., Vergnaud-Ayraud, V., Labasque, T., Santoni, S., Robert, S., Provitolo, D., Pasqualini, V., 2018. Delayed nitrate dispersion within a coastal aquifer provides constraints on land-use evolution and nitrate contamination in the past. Sci. Total Environ. 644, 928–940. https://doi.org/10.1016/j.scitotenv.2018.06.375.

Erostate, M., Huneau, F., Garel, E., Vystavna, Y., Santoni, S., Pasqualini, V., 2019. Coupling isotope hydrology, geochemical tracers and emerging compounds to evaluate mixing processes and groundwater dependence of a highly anthropized coastal hydrosystem. J. Hydrol. 578, 123979 https://doi.org/10.1016/j.jhydrol.2019.123979.

European Commission, 2012. Technical report on groundwater dependent terrestrial ecosystems. Technical report. No 6. [WWW document]. Publications office of the EU. URL. https://op.europa.eu/en/publication-detail/-/publication/f7bd5cf8-c62c-41f6-8138-fe922a1f6410.

European Union, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 Establishing a Framework for Community Action in the Field of Water Policy.

Eurostat, 2019. Olive trees cover 4.6 million hectares in the EU.

Fabres, J., Kurvits, T., Nilsen, R., Pravettoni, R., Agardy, T., 2012. State of the Mediterranean Marine and Coastal Environment. https://doi.org/10.13140/RG.2.1.3013.2648.

Ferrara, G., Farrag, K., Brunetti, G., 2012. The effects of rock fragmentation and / or deep tillage on soil skeletal material and chemical properties in a Mediterranean climate. Soil Use Manag. 28, 394–400. https://doi.org/10.1111/j.1475-2743.2012.00423.x.

Frommen, T., Moss, T., 2021. Pasts and presents of urban socio-hydrogeology: groundwater levels in Berlin, 1870–2020. Water 13, 2261. https://doi.org/10.3390/w13162261.

García-Ruiz, J.M., López-Moreno, J.I., Vicente-Serrano, S.M., Lasanta-Martínez, T., Beguería, S., 2011. Mediterranean water resources in a global change scenario. Earth Sci. Rev. 105, 121–139. https://doi.org/10.1016/j.earscirev.2011.01.006.

Gardner, R.C., Finlayson, C., 2018. Global Wetland Outlook: State of the World's Wetlands and their Services to People.

Geri, F., Amici, V., Rocchini, D., 2010. Human activity impact on the heterogeneity of a Mediterranean landscape. Appl. Geogr. 30, 370–379. https://doi.org/10.1016/j.apgeog.2009.10.006.

Gibson, J.J., Birks, S.J., Edwards, T.W.D., 2008. Global prediction of δ a and δ 2 H- δ 18 O evaporation slopes for lakes and soil water accounting for seasonality: predicting evaporation line slopes. Global Biogeochem. Cycles 22. https://doi.org/10.1029/2007GB002997 n/a-n/a.

Gil-Márquez, J.M., Andreo, B., Mudarra, M., 2019. Combining hydrodynamics, hydrochemistry, and environmental isotopes to understand the hydrogeological functioning of evaporite-karst springs. An example from southern Spain. J. Hydrol. 576, 299–314. https://doi.org/10.1016/j.jhydrol.2019.06.055.

Girones, L., Oliva, A.L., Negrin, V.L., Marcovecchio, J.E., Arias, A.H., 2021. Persistent organic pollutants (POPs) in coastal wetlands: a review of their occurrences, toxic effects, and biogeochemical cycling. Mar. Pollut. Bull. 172, 112864 https://doi.org/10.1016/j.marpolbul.2021.112864.

González-Ramón, A., Rodríguez-Arévalo, J., Martos-Rosillo, S., Gollonet, J., 2013. Hydrogeological research on intensively exploited deep aquifers in the 'Loma de Úbeda' area (Jaén, southern Spain). Hydrogeol. J. 21, 887–903.

Goulson, D., 2013. REVIEW: an overview of the environmental risks posed by neonicotinoid insecticides. J. Appl. Ecol. 50, 977–987. https://doi.org/10.1111/1365-2664.12111.

Hasaneen, M.N., 2012. Herbicides: Properties, Synthesis and Control of Weeds. BoD –. Books on Demand.

Heinz, B., Birk, S., Liedl, R., Geyer, T., Straub, K.L., Andresen, J., Bester, K., Kappler, A., 2009. Water quality deterioration at a karst spring (Gallusquelle, Germany) due to combined sewer overflow: evidence of bacterial and micro-pollutant contamination. Environ. Geol. 57, 797–808. https://doi.org/10.1007/s00254-008-1359-0.

Hillebrand, O., Nödler, K., Licha, T., Sauter, M., Geyer, T., 2012. Caffeine as an indicator for the quantification of untreated wastewater in karst systems. Water Res. 46, 395–402. https://doi.org/10.1016/j.watres.2011.11.003.

Hillebrand, O., Nödler, K., Sauter, M., Licha, T., 2015. Multitracer experiment to evaluate the attenuation of selected organic micropollutants in a karst aquifer. Sci. Total Environ. 506–507, 338–343. https://doi.org/10.1016/j.scitotenv.2014.10.102.

Horibe, Y., Shigehara, K., Takakuwa, Y., 1973. Isotope separation factor of carbon dioxyde - water system and isotopic composition of atmospheric oxygen. J. Geophys. Res. 78, 2625–2629. https://doi.org/10.1029/JC078i015p02625.

Huang, G., Sun, J., Zhang, Y., Chen, Z., Liu, F., 2013. Impact of anthropogenic and natural processes on the evolution of groundwater chemistry in a rapidly urbanized coastal area, South China. Sci. Total Environ. 463–464, 209–221. https://doi.org/10.1016/j.scitotenv.2013.05.078.

Huang, G., Zhang, M., Liu, C., Li, L., Chen, Z., 2018. Heavy metal(loid)s and organic contaminants in groundwater in the Pearl River Delta that has undergone three decades of urbanization and industrialization: distributions, sources, and driving forces. Sci. Total Environ. 635, 913–925. https://doi.org/10.1016/j.scitotenv.2018.04.210.

Huang, G., Pei, L., Li, L., Liu, C., 2022. Natural background levels in groundwater in the Pearl River Delta after the rapid expansion of urbanization: a new pre-selection method. Sci. Total Environ. 813, 151890 https://doi.org/10.1016/j.scitotenv.2021.151890.

IAEA, 1992. Statistical Treatment of Data on Environmental Isotopes in Precipitation No. 331. Technical Reports Series.

ISPRA, 2018. Pesticides in water Italian monitoring 2016.

ISTAT, 2023. Popolazione residente al 1° gennaio : Puglia [WWW Document]. URL. http://dati.istat.it/Index.aspx?QueryId=18550 (accessed 5.30.23).

Juhlke, T.R., Sültenfuß, J., Trachte, K., Huneau, F., Garel, E., Santoni, S., Barth, J.A.C., van Geldern, R., 2020. Tritium as a hydrological tracer in Mediterranean precipitation events. Atmos. Chem. Phys. 20, 3555–3568. https://doi.org/10.5194/acp-20-3555-2020.

Jurado, A., Vàzquez-Suñé, E., Carrera, J., López de Alda, M., Pujades, E., Barceló, D., 2012. Emerging organic contaminants in groundwater in Spain: a review of sources, recent occurrence and fate in a European context. Science of The Total Environment, Integrated modelling and monitoring at different river basin scales under global change 440, 82–94. https://doi.org/10.1016/j.scitotenv.2012.08.029.

Kaufman, S., Libby, W.F., 1954. The natural distribution of tritium. Phys. Rev. 93, 1337–1344. https://doi.org/10.1103/PhysRev.93.1337.

Kendall, C., 1998. Chapter 16 - tracing nitrogen sources and cycling in catchments. In: Kendall, C., McDonnel, J.J. (Eds.), Isotope Tracers in Catchment Hydrology. Elsevier, Amsterdam, pp. 519–576. https://doi.org/10.1016/B978-0-444-81546-0.50023-9.

Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen to ecosystems. In: Stable Isotopes in Ecology and Environmental Science. John Wiley & Sons, Ltd, pp. 375–449. https://doi.org/10.1002/9780470691854.ch12.

Kroopnick, P., Craig, H., 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. Science 175, 54–55. https://doi.org/10.1126/science.175.4017.54.

Lapworth, D.J., Gooddy, D.C., 2006. Source and persistence of pesticides in a semi-confined chalk aquifer of Southeast England. Environ. Pollut. 144, 1031–1044. https://doi.org/10.1016/j.envpol.2005.12.055.

Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environ. Pollut. 163, 287–303. https://doi.org/10.1016/j.envpol.2011.12.034.

Lapworth, D.J., Lopez, B., Laabs, V., Kozel, R., Wolter, R., Ward, R., Amelin, E.V., Besien, T., Claessens, J., Delloye, F., Ferretti, E., Grath, J., 2019. Developing a groundwater watch list for substances of emerging concern: a European perspective. Environ. Res. Lett. 14, 035004 https://doi.org/10.1088/1748-9326/aaf4d7.

Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A., 2016. An international database for pesticide risk assessments and management. Hum. Ecol. Risk Assess. Int. J. 22, 1050–1064. https://doi.org/10.1080/10807039.2015.1133242.

Ligorini, V., Malet, N., Garrido, M., Four, B., Etourneau, S., Leoncini, A.S., Dufresne, C., Cecchi, P., Pasqualini, V., 2022. Long-term ecological trajectories of a disturbed Mediterranean coastal lagoon (Biguglia lagoon): ecosystem-based approach and considering its resilience for conservation? Front. Mar. Sci. 9, 937795 https://doi.org/10.3389/fmars.2022.937795.

Ligorini, V., Crayol, E., Huneau, F., Garel, E., Malet, N., Garrido, M., Simon, L., Cecchi, P., Pasqualini, V., 2023. Small Mediterranean coastal lagoons under threat: hydro-ecological disturbances and local anthropogenic pressures (size matters). Estuar. Coasts. https://doi.org/10.1007/s12237-023-01182-1.

Liu, J., Wang, H., Jin, D., Xu, F., Zhao, C., 2020. Hydrochemical characteristics and evolution processes of karst groundwater in carboniferous Taiyuan formation in the Pingdingshan coalfield. Environ. Earth Sci. 79 https://doi.org/10.1007/s12665-020-8898-4.

Lo Papa, G., Palermo, V., Dazzi, C., 2011. Is land-use change a cause of loss of pedodiversity? The case of the Mazzarrone study area, Sicily. Geomorphology, Driving Forces for Global Pedodiversity 135, 332–342. https://doi.org/10.1016/j.geomorph.2011.02.015.

Long, A.J., Valder, J.F., 2011. Multivariate analyses with end-member mixing to characterize groundwater flow: wind cave and associated aquifers. J. Hydrol. 409, 315–327. https://doi.org/10.1016/j.jhydrol.2011.08.028.

Longinelli, A., Selmo, E., 2003. Isotopic composition of precipitation in Italy: a first overall map. J. Hydrol. 270, 75–88. https://doi.org/10.1016/S0022-1694(02)00281-0.

Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M., Gawlik, B.M., 2010. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Res. 44, 4115–4126. https://doi.org/10.1016/j.watres.2010.05.032.

Lorenzo, M., Campo, J., Morales Suárez-Varela, M., Picó, Y., 2019. Occurrence, distribution and behavior of emerging persistent organic pollutants (POPs) in a Mediterranean wetland protected area. Sci. Total Environ. 646, 1009–1020. https://doi.org/10.1016/j.scitotenv.2018.07.304.

Mancinelli, G., Pinna, M., Basset, A., 2008. Spatio-temporal variability of macrozoobenthos size structure of a coastal lagoon: the influence of spectrum resolution. Transit. Waters Bull. 2 https://doi.org/10.1285/i1825229Xv1n4p81.

Mara, P., Mihalopoulos, N., Gogou, A., Daehnke, K., Schlarbaum, T., Emeis, K.-C., Krom, M., 2009. Isotopic composition of nitrate in wet and dry atmospheric deposition on Crete in the eastern Mediterranean Sea: ISOTOPIC COMPOSITION OF NITRATE IN DEPOSITION. Global Biogeochem. Cycles 23, n/a-n/a. https://doi.org/10.1029/2008GB003395.

Marković, T., Karlović, I., Orlić, S., Kajan, K., Smith, A.C., 2022. Tracking the nitrogen cycle in a vulnerable alluvial system using a multi proxy approach: case study Varaždin alluvial aquifer. Croatia. Sci. Total Environ. 853, 158632 https://doi.org/10.1016/j.scitotenv.2022.158632.

Martin, S., Hamlin, Q., Kendall, A., Wan, L., Hyndman, D., 2023. The land use legacy effect: looking back to see a path forward to improve management 12.

Martinelli, G., Dadomo, A., De Luca, D.A., Mazzola, M., Lasagna, M., Pennisi, M., Pilla, G., Sacchi, E., Saccon, P., 2018. Nitrate sources, accumulation and reduction in groundwater from northern Italy: insights provided by a nitrate and boron isotopic database. Appl. Geochem. 91, 23–35. https://doi.org/10.1016/j.apgeochem.2018.01.011.

Mayer, B., Bollwerk, S.M., Mansfeldt, T., Hütter, B., Veizer, J., 2001. The oxygen isotope composition of nitrate generated by nitrification in acid forest floors. Geochim. Cosmochim. Acta 65, 2743–2756. https://doi.org/10.1016/S0016-7037(01)00612-3.

Mazeh, M., Almadi, L., Paoletti, A., Cinosi, N., Daher, E., Tucci, M., Lodolini, E.M., Rosati, A., Famiani, F., 2021. Use of an organic fertilizer also having a biostimulant action to promote the growth of young olive trees. Agriculture 11, 593. https://doi.org/10.3390/agriculture11070593.

McCance, W., Jones, O.A.H., Edwards, M., Surapaneni, A., Chadalavada, S., Currell, M., 2018. Contaminants of emerging concern as novel groundwater tracers for delineating wastewater impacts in urban and peri-urban areas. Water Res. 146, 118–133. https://doi.org/10.1016/j.watres.2018.09.013.

McCance, W., Jones, O.A.H., Cendón, D.I., Edwards, M., Surapaneni, A., Chadalavada, S., Wang, S., Currell, M., 2020. Combining environmental isotopes with contaminants of emerging concern (CECs) to characterise wastewater derived impacts on groundwater quality. Water Res. 182, 116036 https://doi.org/10.1016/j.watres.2020.116036.

McMahon, P.B., Chapelle, F.H., 2008. Redox processes and water quality of selected principal aquifer systems. Ground Water 46, 259–271. https://doi.org/10.1111/j.1745-6584.2007.00385.x.

Mehvar, S., Filatova, T., Dastgheib, A., Ruyter, De, van Steveninck, E., Ranasinghe, R., 2018. Quantifying economic value of coastal ecosystem services: a review. J. Mar. Sci. Eng. 6, 5. https://doi.org/10.3390/jmse6010005.

Melloul, A., Collin, M., 1992. The 'principal components' statistical method as a complementary approach to geochemical methods in water quality factor identification; application to the coastal plain aquifer of Israel. J. Hydrol. 140, 49–73. https://doi.org/10.1016/0022-1694(92)90234-M.

Meyer, M.T., Scribner, E.A., Kalkhoff, S.J., 2007. Comparison of fate and transport of Isoxaflutole to atrazine and Metolachlor in 10 Iowa Rivers. Environ. Sci. Technol. 41, 6933–6939. https://doi.org/10.1021/es070903t.

Michalopoulos, G., Kasapi, K.A., Koubouris, G., Psarras, G., Arampatzis, G., Hatzigiannakis, E., Kavvadias, V., Xiloyannis, C., Montanaro, G., Malliaraki, S., Angelaki, A., Manolaraki, C., Giakoumaki, G., Reppas, S., Kourgialas, N., Kokkinos, G., 2020. Adaptation of Mediterranean olive groves to climate change through sustainable cultivation practices. Climate 8, 54. https://doi.org/10.3390/cli8040054.

Morgado, R., Ribeiro, P.F., Santos, J.L., Rego, F., Beja, P., Moreira, F., 2022. Drivers of irrigated olive grove expansion in Mediterranean landscapes and associated biodiversity impacts. Landsc. Urban Plan. 225, 104429 https://doi.org/10.1016/j.landurbplan.2022.104429.

Musacchio, A., Andrade, L., O'Neill, E., Re, V., O'Dwyer, J., Hynds, P.D., 2021. Planning for the health impacts of climate change: flooding, private groundwater contamination and waterborne infection – a cross-sectional study of risk perception, experience and behaviours in the Republic of Ireland. Environ. Res. 194, 110707 https://doi.org/10.1016/j.envres.2021.110707.

Muter, O., Bartkevics, V., 2020. Advanced analytical techniques based on high-resolution mass spectrometry for the detection of micropollutants and their toxicity in aquatic environments. Current Opinion in Environmental Science & Health, Environmental Chemistry: Innovative Approaches and Instrumentation in Environmental Chemistry 18, 1–6. https://doi.org/10.1016/j.coesh.2020.05.002.

Panagopoulos, G.P., Katsanou, K.N., Barouchas, P.E., 2023. Assessment of groundwater vulnerability to nitrates using the GIS-based DRASTIC and SI methods: a case study in Zacharo area. Greece. Environ. Monit. Assess. 195, 286.

Penna, D., Stenni, B., Šanda, M., Wrede, S., Bogaard, T.A., Gobbi, A., Borga, M., Fischer, B.M.C., Bonazza, M., Chárová, Z., 2010. On the reproducibility and repeatability of laser absorption spectroscopy measurements for δ2H and δ18O isotopic analysis. Hydrol. Earth Syst. Sci. 14, 1551–1566. https://doi.org/10.5194/hess-14-1551-2010.

Pérez-Ruzafa, A., Marcos, C., Pérez-Ruzafa, I.M., 2011. Mediterranean coastal lagoons in an ecosystem and aquatic resources management context. Phys. Chem. Earth, Parts A/B/C 36, 160–166. https://doi.org/10.1016/j.pce.2010.04.013.

Pérez-Ruzafa, A., Pérez-Ruzafa, I.M., Newton, A., Marcos, C., 2019. Chapter 15 - coastal lagoons: Environmental variability, ecosystem complexity, and goods and services uniformity. In: Day, J.W., Elliott, M., Ramachandran, R. (Eds.), Wolanski, E. Elsevier, Coasts and Estuaries, pp. 253–276. https://doi.org/10.1016/B978-0-12-814003-1.00015-0.

Petrella, E., Celico, F., 2013. Mixing of water in a carbonate aquifer, southern Italy, analysed through stable isotope investigations. Int. J. Speleol. 42 https://doi.org/10.5038/1827-806X.42.1.4.

Pietrzak, D., Kania, J., Kmiecik, E., Malina, G., Wątor, K., 2020. Fate of selected neonicotinoid insecticides in soil–water systems: current state of the art and knowledge gaps. Chemosphere 255, 126981. https://doi.org/10.1016/j.chemosphere.2020.126981.

Platis, D.P., Menexes, G.C., Kalburtji, K.L., Mamolos, A.P., 2023. Energy budget, carbon and water footprint in perennial agro and natural ecosystems inside a Natura 2000 site as provisioning and regulating ecosystem services. Environ. Sci. Pollut. Res. 30, 1288–1305. https://doi.org/10.1007/s11356-022-22231-5.

Polemio, M., Romanazzi, A., 2013. Modelling of Coastal Karst Aquifer for Management Support: Study of Salento (Apulia, Italy). https://doi.org/10.4408/IJEGE.2013-01.O-05.

Polemio, M., Zuffianò, L.E., 2020. Review of utilization Management of Groundwater at risk of salinization. J. Water Resour. Plan. Manag. 146, 03120002. https://doi.org/10.1061/(ASCE)WR.1943-5452.0001278.

Polemio, M., Dragone, V., Limoni, P.P., 2009. Monitoring and methods to analyse the groundwater quality degradation risk in coastal karstic aquifers (Apulia, southern Italy). Environ. Geol. 58, 299–312. https://doi.org/10.1007/s00254-008-1582-8.

Raco, B., Battaglini, R., 2022. Tritium as a tool to assess leachate contamination: an example from Conversano landfill (southern Italy). J. Geochem. Explor. 235, 106939 https://doi.org/10.1016/j.gexplo.2021.106939.

Ramanarayanan, T., Narasimhan, B., Srinivasan, R., 2005. Characterization of fate and transport of Isoxaflutole, a soil-applied corn herbicide, in surface water using a watershed model. J. Agric. Food Chem. 53, 8848–8858. https://doi.org/10.1021/jf0508596.

Re, V., 2015. Incorporating the social dimension into hydrogeochemical investigations for rural development: the Bir Al-Nas approach for socio-hydrogeology. Hydrogeol. J. 23, 1293–1304. https://doi.org/10.1007/s10040-015-1284-8.

Re, V., Sacchi, E., Kammoun, S., Tringali, C., Trabelsi, R., Zouari, K., Daniele, S., 2017. Integrated socio-hydrogeological approach to tackle nitrate contamination in groundwater resources. The case of Grombalia Basin (Tunisia). Sci. Total Environ. 593–594, 664–676. https://doi.org/10.1016/j.scitotenv.2017.03.151.

Re, V., Thin, M.M., Tringali, C., Mya, M., Destefanis, E., Sacchi, E., 2021. Laying the groundwork for raising awareness on water related issues with a socio-hydrogeological approach: the Inle Lake case study (southern Shan State, Myanmar). Water 13, 2434. https://doi.org/10.3390/w13172434.

Re, V., Rizzi, J., Tuci, C., Tringali, C., Mancin, M., Mendieta, E., Marcomini, A., 2023. Challenges and opportunities of water quality monitoring and multi-stakeholder management in small islands: the case of Santa Cruz, Galápagos (Ecuador). Environ. Dev. Sustain. 25, 3867–3891. https://doi.org/10.1007/s10668-022-02219-4.

Reberski, J.L., Terzić, J., Maurice, L.D., Lapworth, D.J., 2022. Emerging organic contaminants in karst groundwater: a global level assessment. J. Hydrol. 604, 127242 https://doi.org/10.1016/j.jhydrol.2021.127242.

Recept, E., Soykan, A., Cürebal, I., Sönmez, S., 2011. Olive and olive oil culture in the Mediterranean region, pp. 54–64.

Regione Puglia, 2014. Linee guida per il contenimento della diffusione di "xylella fastidiosa" subspecie pauca ceppo codiro e la prevenzione e il contenimento del complesso del disseccamento rapido dell'olivo (codiro).

Regione Puglia, 2022. Bollettino ufficiale della Regione Puglia (No. 38 del 31–03–2022).

Ricchetti, G., Ciaranfi, N., Luperto Sinni, E., Mongelli, F., Pieri, P., 1988. Geodinamica ed evoluzione sedimentaria e tettonica dell'avampaese Apulo 41, 57–82.

Richardson, S.D., Kimura, S.Y., 2020. Water analysis: emerging contaminants and current issues. Anal. Chem. 92, 473–505. https://doi.org/10.1021/acs.analchem.9b05269.

Robertson, W.D., Van Stempvoort, D.R., Solomon, D.K., Homewood, J., Brown, S.J., Spoelstra, J., Schiff, S.L., 2013. Persistence of artificial sweeteners in a 15-year-old septic system plume. J. Hydrol. 477, 43–54. https://doi.org/10.1016/j.jhydrol.2012.10.048.

Rockström, J., Falkenmark, M., Allan, T., Folke, C., Gordon, L., Jägerskog, A., Kummu, M., Lannerstad, M., Meybeck, M., Molden, D., Postel, S., Savenije, H.h.g., Svedin, U., Turton, A., Varis, O., 2014. The unfolding water drama in the Anthropocene: towards a resilience-based perspective on water for global sustainability. Ecohydrology 7, 1249–1261. https://doi.org/10.1002/eco.1562.

Rodellas, V., Stieglitz, T.C., Andrisoa, A., Cook, P.G., Raimbault, P., Tamborski, J.J., van Beek, P., Radakovitch, O., 2018. Groundwater-driven nutrient inputs to coastal lagoons: the relevance of lagoon water recirculation as a conveyor of dissolved nutrients. Sci. Total Environ. 642, 764–780. https://doi.org/10.1016/j.scitotenv.2018.06.095.

Rodríguez Sousa, A.A., Barandica, J.M., Rescia, A., 2019. Ecological and economic sustainability in olive groves with different irrigation management and levels of Erosion: a case study. Sustainability 11, 4681. https://doi.org/10.3390/su11174681.

Romanazzi, A., Gentile, F., Polemio, M., 2015. Modelling and management of a Mediterranean karstic coastal aquifer under the effects of seawater intrusion and climate change. Environ. Earth Sci. 74, 115–128. https://doi.org/10.1007/s12665-015-4423-6.

Roy, J.W., Van Stempvoort, D.R., Bickerton, G., 2014. Artificial sweeteners as potential tracers of municipal landfill leachate. Environ. Pollut. 184, 89–93. https://doi.org/10.1016/j.envpol.2013.08.021.

Ruiz, I., Sanz-Sánchez, M.J., 2020. Effects of historical land-use change in the Mediterranean environment. Sci. Total Environ. 732, 139315 https://doi.org/10.1016/j.scitotenv.2020.139315.

Sacchi, E., Acutis, M., Bartoli, M., Brenna, S., Delconte, C.A., Laini, A., Pennisi, M., 2013. Origin and fate of nitrates in groundwater from the central Po plain: Insights from isotopic investigations. Applied Geochemistry, Special issue dedicated to Giovanni Maria (Gian Maria) Zuppi (1947–2011) 34, 164–180. https://doi.org/10.1016/j.apgeochem.2013.03.008.

Sadutto, D., Andreu, V., Ilo, T., Akkanen, J., Picó, Y., 2021. Pharmaceuticals and personal care products in a Mediterranean coastal wetland: impact of anthropogenic and spatial factors and environmental risk assessment. Environ. Pollut. 271, 116353 https://doi.org/10.1016/j.envpol.2020.116353.

Sandstrom, M.W., Nowell, L.H., Mahler, B.J., Van Metre, P.C., 2022. New-generation pesticides are prevalent in California's central coast streams. Sci. Total Environ. 806, 150683 https://doi.org/10.1016/j.scitotenv.2021.150683.

Santoni, S., Huneau, F., Garel, E., Celle-Jeanton, H., 2018. Multiple recharge processes to heterogeneous Mediterranean coastal aquifers and implications on recharge rates evolution in time. J. Hydrol. 559, 669–683. https://doi.org/10.1016/j.jhydrol.2018.02.068.

Schübl, M., Kiecak, A., Hug, K., Lintelmann, J., Zimmermann, R., Stumpp, C., 2021. Sorption and biodegradation parameters of selected pharmaceuticals in laboratory column experiments. J. Contam. Hydrol. 236, 103738 https://doi.org/10.1016/j.jconhyd.2020.103738.

Serio, F., Miglietta, P.P., Lamastra, L., Ficocelli, S., Intini, F., De Leo, F., De Donno, A., 2018. Groundwater nitrate contamination and agricultural land use: a grey water footprint perspective in southern Apulia region (Italy). Sci. Total Environ. 645, 1425–1431. https://doi.org/10.1016/j.scitotenv.2018.07.241.

Shankar, S., Shanker, U., Shikha, 2014. Arsenic contamination of groundwater: a review of sources, prevalence, health risks, and strategies for mitigation. Sci. World J. 2014, 304524 https://doi.org/10.1155/2014/304524.

Shelef, O., Stavi, I., Zdruli, P., Rachmilevitch, S., 2016. Land use change, a case study from southern Italy: general implications for agricultural subsidy policies. Land Degrad. Dev. 27, 868–870. https://doi.org/10.1002/ldr.2343.

Shishaye, H.A., Tait, D.R., Maher, D.T., Befus, K.M., Erler, D., Jeffrey, L., Reading, M.J., Morgenstern, U., Kaserzon, S., Mueller, J., De Verelle-Hill, W., 2021. The legacy and drivers of groundwater nutrients and pesticides in an agriculturally impacted quaternary aquifer system. Sci. Total Environ. 753, 142010 https://doi.org/10.1016/j.scitotenv.2020.142010.

Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M., Böhlke, J.K., 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Anal. Chem. 73, 4145–4153. https://doi.org/10.1021/ac010088e.

Solomou, A.D., Sfougaris, A., 2021. Contribution of agro-environmental factors to yield and plant diversity of olive grove ecosystems (Olea Europaea L.) in the mediterranean landscape. Agronomy 11. https://doi.org/10.3390/agronomy11010161.

Souchu, P., Bec, B., Smith, V., Thierry, L., Fiandrino, A., Laurent, B., Valerie, O., Collos, Y., Andre, V., 2010. Patterns in nutrient limitation and chlorophyll a along an anthropogenic eutrophication gradient in French Mediterranean coastal lagoons. Canadian Journal Of Fisheries And Aquatic Sciences (0706-652X) (National Research Council Canada), 2010–04, Vol. 67, N. 4, P. 743–753 67. https://doi.org/10.1139/F10-018.

Stuart, M.E., Lapworth, D.J., Thomas, J., Edwards, L., 2014. Fingerprinting groundwater pollution in catchments with contrasting contaminant sources using microorganic compounds. Sci. Total Environ. 468–469, 564–577. https://doi.org/10.1016/j.scitotenv.2013.08.042.

Szymczycha, B., Borecka, M., Białk-Bielińska, A., Siedlewicz, G., Pazdro, K., 2020. Submarine groundwater discharge as a source of pharmaceutical and caffeine residues in coastal ecosystem: bay of Puck, southern Baltic Sea case study. Sci. Total Environ. 713, 136522.

Thatcher, L.L., Janzer, V.J., Edwards, K.W., 1977. Methods for determination of radioactive substances in water and fluvial sediments (USGS Numbered Series No. 05-A5), Methods for determination of radioactive substances in water and fluvial sediments, Techniques of Water-Resources Investigations. U.S. Government Printing Office. https://doi.org/10.3133/twri05A5.

UNEP/MAP, 2017. Quality status report for the Mediterranean - MED QSR 2017 [WWW Document]. URL. https://www.medqsr.org/population-and-development (accessed 6.7.23).

USEPA, 2010. Bisphenol a Action Plan. U.S. Environmental Protection Agency, Washington.

Vandenberg, L.N., Hauser, R., Marcus, M., Olea, N., Welshons, W.V., 2007. Human exposure to bisphenol a (BPA). Reprod. Toxicol. 24, 139–177. https://doi.org/10.1016/j.reprotox.2007.07.010.

Velasco, A.M., Pérez-Ruzafa, A., Martínez-Paz, J.M., Marcos, C., 2018. Ecosystem services and main environmental risks in a coastal lagoon (mar Menor, Murcia, SE Spain): the public perception. J. Nat. Conserv. 43, 180–189. https://doi.org/10.1016/j.jnc.2017.11.002.

Vystavna, Y., Diadin, D., Yakovlev, V., Hejzlar, J., Vadillo, I., Huneau, F., Lehmann, M.F., 2017. Nitrate contamination in a shallow urban aquifer in East Ukraine: evidence from hydrochemical, stable isotopes of nitrate and land use analysis. Environ. Earth Sci. 76, 463. https://doi.org/10.1007/s12665-017-6796-1.

White, D., Lapworth, D.J., Stuart, M.E., Williams, P.J., 2016. Hydrochemical profiles in urban groundwater systems: new insights into contaminant sources and pathways in the subsurface from legacy and emerging contaminants. Sci. Total Environ. 562, 962–973. https://doi.org/10.1016/j.scitotenv.2016.04.054.

White, W.B., 2002. Karst hydrology: recent developments and open questions. Eng. Geol. Eng. Environ. Impacts of Karst 65, 85–105. https://doi.org/10.1016/S0013-7952(01)00116-8.

WHO, 2022. Arsenic in Drinking Water.

World Health Organization, 2011. Guidelines for Drinking-Water Quality, 4th Edition, Incorporating the 1st Addendum.

Xue, D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O., Berglund, M., Boeckx, P., 2009. Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. Water Res. 43, 1159–1170. https://doi.org/10.1016/j.watres.2008.12.048.

Yang, X., Wang, F., Meng, L., Zhang, W., Fan, L., Geissen, V., Ritsema, C.J., 2014. Farmer and retailer knowledge and awareness of the risks from pesticide use: a case study in the Wei River catchment, China. Sci. Total Environ. 497–498, 172–179. https://doi.org/10.1016/j.scitotenv.2014.07.118.

Zdruli, P., Calabrese, J., Ladisa, G., Otekhile, A., 2014. Impacts of land cover change on soil quality of manmade soils cultivated with table grapes in the Apulia region of South-Eastern Italy. CATENA 121, 13–21. https://doi.org/10.1016/j.catena.2014.04.015.

Zhang, F., Huang, G., Hou, Q., Liu, C., Zhang, Y., Zhang, Q., 2019. Groundwater quality in the Pearl River Delta after the rapid expansion of industrialization and urbanization: distributions, main impact indicators, and driving forces. J. Hydrol. 577, 124004 https://doi.org/10.1016/j.jhydrol.2019.124004.

Zhang, M., Huang, G., Liu, C., Zhang, Y., Chen, Z., Wang, J., 2020. Distributions and origins of nitrate, nitrite, and ammonium in various aquifers in an urbanized coastal area, South China. J. Hydrol. 582, 124528 https://doi.org/10.1016/j.jhydrol.2019.124528.

Zhang, Y., Zhou, A., Zhou, J., Liu, C., Cai, H., Liu, Y., Xu, W., 2015. Evaluating the sources and fate of nitrate in the alluvial aquifers in the Shijiazhuang rural and suburban area, China: Hydrochemical and multi-isotopic approaches. Water 7, 1515–1537. https://doi.org/10.3390/w7041515.

Zirlewagen, J., Licha, T., Schiperski, F., Nödler, K., Scheytt, T., 2016. Use of two artificial sweeteners, cyclamate and acesulfame, to identify and quantify wastewater contributions in a karst spring. Sci. Total Environ. 547, 356–365. https://doi.org/10.1016/j.scitotenv.2015.12.112.