Quali-Quantitative Assessment and Protection to Pollution of Fissured Aquifers' Strategic Groundwater Resources of the Lucanian and Calabrian Apennines in the Framework of the Tech4You Research Project

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Abstract. This study is related to the activities carried out in the Pilot Project PP2 belonging to the Tech4You research project, still in progress, whose objective is to apply innovative methods and tools for the quali-quantitative assessment and protection to pollution of selected fissured aquifers' strategic groundwater resources of the Lucanian and Calabrian Apennines.

The activities involved the definition of the geological setting of the northern sector of the Lauria Mountains; the Calabrian sector of the Pollino Chain, located in the area of the springs of the Raganello stream; the San Severino Lucano municipality area where the Pollino Massif ophiolites outcrop; the Lauria Mountains and the Pollino area hydrogeological characterization, and the geochemical characterization of the San Severino Lucano area.

Keywords: Strategic Groundwater Resources · Aquifer Vulnerability Assessment · Purification of Groundwater

1 Introduction

This paper describes the activities carried out under the larger interest of the Tech4You Research Project, Spoke1, Goal2, PP2, which aims to apply innovative methods and tools for the quali-quantitative assessment and protection to pollution of the fissured aquifers' strategic groundwater resources of the Lucanian and Calabrian Apennines.

The first objective of the Pilot Project is to identify, quantify, and protect the strategic good-quality groundwater resources of fissured aquifers belonging to the Lucanian and Calabrian Apennines uncollected or not adequately exploited to be used as strategic water resources in cases of drought or particular conditions of water emergency.

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The second one regards the purification of natural polluted groundwater by using membrane technologies intending to develop a membrane prototype based on renewable energy to test in a selected pilot area.

Nowadays, the availability of water is a crucial issue for social development worldwide. Increased demography, agricultural land use and irrigation demand, and modifications in lifestyle, under climate changes, lead to ever-increasing water scarcity with serious implications for future sustainable development [1–3]. In this context, groundwater represents an important resource for different uses. In some cases, uncollected groundwater may represent favorable conditions for strategic water resources.

Fractured carbonate hydrostructures in the regions of Basilicata and Calabria are distinguished by the abundance of high-quality springs. A thorough methodological approach was used in this work to help advance knowledge of the hydrogeological setting and the groundwater hydrogeological characterization of these aquifer systems. Geological and hydrogeological field research was part of the investigations to comprehend the unique features of the systems.

The Pilot Areas were identified in different sites, such as the Northern sector of the Lauria Mountains; the Calabrian sector of the Pollino Chain, located in the area of the springs of the Raganello stream; the San Severino Lucano municipality area where the Pollino Massif ophiolites outcrop.

The ongoing work of the research group, focused primarily on the identification of the potential study sites, was related to the definition of the geostructural setting of the identified areas, the hydrogeological characterization of the northern sector of the Lauria Mountains and the Calabrian sector of Pollino.

The hydrogeological characterization of the hydrostructure located in the northern sector of the Lauria Mountains began with the collection of available topographic, climate, geological, and hydrogeological data. The schematic hydrogeological map and the hydrogeological complexes map were elaborated, and the main springs were identified. All the cartography and data were implemented in the GIS environment. The data provided by the regional agencies were implemented in a geodatabase in the QGIS software in order to elaborate the inverse hydrogeological balance. Furthermore, the aquifer vulnerability assessment was carried out.

Moreover, the work also focused on the areas of the Pollino Chain where ophiolitic rocks outcrop to identify potentially polluted waters. The attention focused on Chromium (Cr), a toxic element that can be released during water-rock interaction processes, making unusable groundwater discharging in these areas [4, 5]. A multidisciplinary study was initiated starting with the collection of water samples to identify Cr-rich water to be treated using membrane technologies in a laboratory environment. Treatment tests allowed to identify a promising membrane to solve this specific environmental issue.

Future activities will concern the discharge monitoring of the selected springs, the groundwater hydrogeochemical characterization, the design, implementation, and updating of a WebGIS platform in which the processed and monitoring data will be implemented, and also the development of a membrane prototype for water purification to test in situ.

2 The Lauria Mountains Northern Sector Study Area

2.1 Geological Setting

The morphostructure of the Lauria Mountains northern sector is located in the southernmost part of the Basilicata region close to the Calabrian region border. In detail, the study area covers an area of 90 km^2 between Lauria, Castelluccio Superiore, and Latronico towns, where the mountain peaks of Serra La Rotonda, Starsia, La Spina, and La Zaccana, with heights ranging between 1000 and 1650 m, are present.

The geological setting of the study area is typical of the southernmost sector of the Apennine chain. The Southern Apennine chain is a fold and thrust belt formed after a series of compressional and extensional phases that determined its geological-structural evolution [6]. The post-Oligocene evolution led to the tectonic superposition with a NE-vergence of the different sedimentary units that make up the fold and thrust belt. Afterwards, during the late Pliocene-Pleistocene, the contractional structures were deformed by the formation of important sets of normal and strike-slip faults [7].

The tectonic units involved in the deformation chain, from the innermost to the outermost, are the Liguride complex, composed of ophiolitic and metasedimentary rocks, and the Sicilide complex, which is entirely made up of sedimentary units [8]. Large exposures of the carbonate successions of the Apennine Platform Unit are present eastwards. These, in turn, are divided into subunits, such as the Bulgheria-Capri Unit, the Alburno-Cervati-Pollino Unit, and the Maddalena Mountains Unit, mainly consisting of Mesozoic carbonate successions covered by Miocene terrigenous formations [6, 9–11]. The Lagonegro Units, of the Triassic-Oligocene age, consist of basinal calcareous-silico-marly successions, divided into two tectonic Units by Scandone [12, 13]. The two superposed Units have an overall thickness of up to 3 km and are separated by regional thrust. The Lagonegro Units overthrust Miocene syn-orogenic Units [14, 15], which is the lowermost thrust sheet of the allochthonous pile. This latter covers tectonically the autochthonous unit represented by carbonate and siliciclastic successions of the Apulian Platform [6]. Later extensional deformation affecting the contractional structures is responsible for the formation of crests and depressions in the axial portion of the chain.

The study area is mainly characterized by exposures of the Apennine Platform Unit. These are represented by Triassic dolostones, Jurassic limestones of the Monte Foraporta subunit, Cretaceous limestones, and the Bifurto formation of the Alburno-Cervati-Pollino subunit, which are exposed in the Lauria, Castello Starsia, Monte Serra La Rotonda, and Monte La Zaccana areas. The remaining lithologies belonging to the Lagonegro 1 Unit, occurring in the northern sector of the area, are tectonically covered by the Apennine Platform Units. The formations of the Sicilide and Liguride Units, exposed mostly in the northern and eastern sectors of the study area, are the Argille Varicolori formation, the Frido and the Nemoli Units. The Quaternary deposits of the Mercure basin, the "Villafranchian" Breccias, and the most recent slope debris cover the older successions in various sectors of the study area.

The study area is affected by different sets of low- to high-angle tectonic contacts connected to the complex Miocene to Pleistocene tectonic evolution. Thrusts are the most common medium and low-angle contacts separating tectonic Units and subunits. Low-angle extensional contacts are also present on the South and East slopes of La Zaccana

Mountain that highlight the detachment of the Liguridi formations with respect to the carbonate platform Units. Instead, high-angle faults mainly oriented NW-SE and NE-SW, associated with minor N-S sets, separate different mountain ridges. These affected mainly Apennine platform formations. High-angle E-W faults are rare in the study area and show minor displacements (Fig. 1).

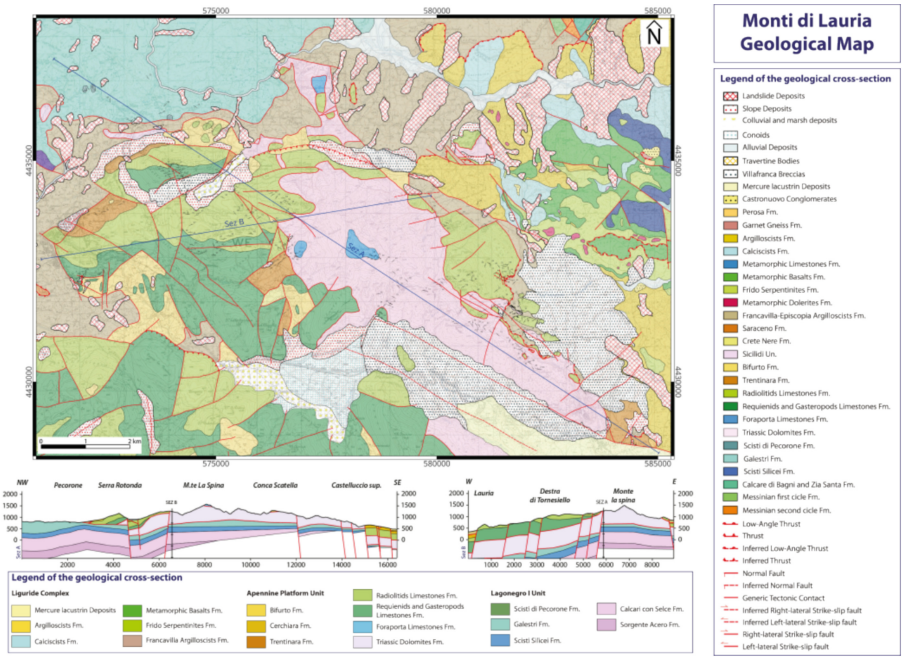

Fig. 1. Monti di Lauria geological map.

2.2 Hydrogeological Characterization

The hydrogeological setting of the Lauria Mountains northern sector hydrostructure, and in particular the groundwater flow pathways and the springs' emergency hydrogeological conditions, reflects the peculiar geostructural arrangement of the morphostructure.

The hydrogeological characterization carried out shows that the geometrical configuration of the carbonate hydrostructure is structured according to the major faults, the presence of thrusts and fracturing conditions defining two hydrogeological basins, characterized by water interchanges and peculiar hydrogeological features, and organizing in the carbonate lithologies different groundwater flow directions.

The hydrogeological features are characterized by subsurface boundaries related to the peculiar geostructural setting that conditions the groundwater flow directions and the springs emergencies, distinguishing two aquifers with different hydrogeological and hydrodynamic characteristics (Fig. 2) [16].

Karst morphologies are present on the dolomitic limestones and are identifiable in evolved fractures and karstic conduits. Their presence suggests a local prevalence of the calcareous component on the dolomite and represents the surface traces of the probably developed underground karst network [17].

The major groundwater emergencies, located on the eastern and western sides of the carbonate massif, belong to the aquifers of the La Spina-Zaccana and Lauria; some of them aren't correctly exploited or uncollected and might constitute strategic groundwater for the Basilicata region (Fig. 2).

The presence of important faults that cut across the hydrostructure is the primary determinant of the groundwater pathways, which have a preferred flow direction aligned NE-SW. Caffaro-Mandarino, Caffaro, and Arena Bianca are the three principal springs in the Lauria aquifer. The clayey-marly flysch formations of the Sicilidi-Affinity Unit tampon the Caffaro-Mandarino spring, which is situated on the border of the carbonate structure and has a flow rate of about 0.81 $m^3\ s^{-1}$. It serves as a groundwater delivery point for the deep aquifer. The Caffaro spring, which has a flow rate of 25 L s^{-1}, is a draining tunnel that was created for a hydroelectrical system rather than a naturally occurring spring.

The flow rate of the Arena Bianca spring is 11 L s^{-1} [18]. Located at varying elevations, the minor springs Alagia, Martino, Montepesco, Starsia, and Menavoli are associated with shallow water pathways and are distinguished by paltry flow rates and changeable regimes (Fig. 2).

The central-eastern region of the northern Lauria Mountains is made up of the substructure of the La Spina-Zaccana Mounts Aquifer.

Dolostones, dolomitic limestones, and a monotonous succession of grey, micro, and macro-crystalline dolomites make up the prevailing geological formations. Coarse clays and marls and subordinately fine clastic sediments constitute the continental quaternary deposits and fluvio-lacustrine deposits of the Mercure basin. These deposits are primarily outcropping in the southern boundary of the La Spina-Zaccana aquifer and certain peripheral sectors of the ridge.

This carbonate aquifer is surrounded by tectonic contacts of various kinematics and stratigraphic locations in nearly all directions. The anticlinal hinge zone of the Castello Starsia-La Spina Mount is where the hydrostructure's northwest limit is situated. However, a thrust that is depressed by some normal faults surrounds the aquifer at its northeastern edge, superimposing the argillite-marly formations on top of the carbonates. The Castelluccio Fault, a significant fault with a high inclination, orientated in the N120° direction, and submerged towards SSO, borders the La Spina-Zaccana sub-structure along its southern boundary. With left strike-slip kinematics, it was developed during the Pleistocene and then reactivated as a normal fault during the upper Pleistocene.

The high rate of activity of this fault and its significant vertical throw are highlighted by the high and steep slope that defines the southern side of the La Spina-Monte Zaccana ridge. From a hydrogeological perspective, the Castelluccio Fault marks the superimposed permeability threshold of the San Giovanni spring front and serves as the structure's morpho-structural southern boundary.

Significant groundwater resources are present in the La Spina-Zaccana aquifer, which is mostly drained from the San Giovanni spring; the southeast sector of the structure has

modest springs with lower potentiality (Fig. 2). The geostructural and karst arrangement conditions the aquifer's geometry, groundwater circulation, and spring existence. Along the eastern edge of Monte Zaccana, the San Giovanni spring front, Acqua del Lavatoio, and Pantanello springs are fed by groundwater that flows primarily in a NW-SE direction.

The San Giovanni springs (at least seven normal permanent springs, with a mean discharge of 450 L s^{-1}) [18] are located along a steep slope at an altitude between 480 m and 504 m. Groundwater is partly exploited for drinking purposes and irrigation use from the Acquedotto Lucano (about 150 L s^{-1}). Shallow groundwater flow paths are the main features of several groundwater emergencies, including Sorgituro, Salice di Sopra, Salice di Sotto, and Peschiera.

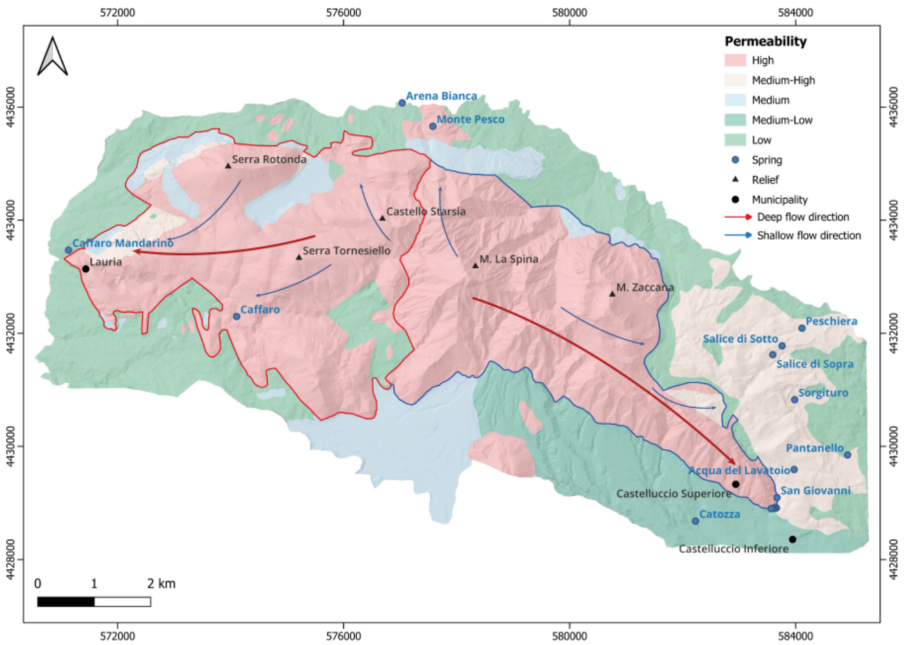

Fig. 2. Schematic hydrogeological map of the northern sector of the Lauria hydrostructure, in which the Lauria aquifer (red line) and La Spina-Zaccana Mounts Aquifer (blue line) with relative permeability classes were identified (modified from [16]).

Different hydrogeological complexes and their relative permeability have been identified, taking into account the distinct geo-lithological and structural characteristics of the area [16, 19, 20].

Dolomites, limestones, and dolomitic limestones that constitute the Carbonate Complex host the aquifers.

The southeastern portion of the study area is constituted by the Conglomerate Complex, which is made up of conglomerates and breccias. It permits the formation of smaller springs and stores a portion of the groundwater. Its relative permeability degree ranges from medium-low to medium-high. The cementation and fracturing of the rock affect its permeability.

Grey, well-layered calcarenite succession with regular marl intercalations makes up the Calcarenite Complex. With a medium level of relative permeability, it plays a secondary role in the local hydrogeological framework.

The Detritical Complex of the debris cones and alluvial fans, comprising clastic and detritical deposits with a medium relative permeability.

The Fluvio-Lacustrine Complex includes clays, marly clays, layered clayey marls with sandy layers, and polygenic conglomerates rich in a sandy matrix. It is distinguished by a medium-low degree of relative permeability. It is identified in the quaternary deposits of the Mercure basin, which form the southern boundary of the carbonate hydrostructure.

The Clayey-Marly Complex consists of pelagic and chaotic sequences of the Argille Varicolori; marls, and marly limestone of the Sicilidi-Affinity and Lagonegro Units; clays and marls from the Frido Unit; and arenaceous-pelitic alternation that is part of the Flysch of Albidona. This complex, which borders the carbonate hydrostructure and represents the limit of permeability in some areas of the system, is distinguished by a low degree of relative permeability.

The quantitative assessment of groundwater in the studied carbonate aquifers strongly depends on the geostructural and hydrogeological setting. To assess the annual groundwater recharge (i.e., effective infiltration) of the Lauria northern sector hydrostructure, the inverse hydrogeological water balance approach was applied [21–23]. This method was implemented in the QGIS environment [24, 25], and the domain of the study area was discretized in grid cells of 5 x 5 m.

The effective infiltration amount was evaluated on daily thermo-pluviometric series collected from the gauging stations located inside or immediately outside of the basin in the period 1992–2022, data provided by the Regional Department of Civil Protection and Lucanian Agency for Development and Innovation in Agriculture (ALSIA).

The balance equation is a ratio of conservation of mass in which the system inputs are equal to the output plus the change in storage [26]:

$$P = ET_r + \Delta S + R \tag{1}$$

where: P indicates the precipitation (mm), ET_r is the amount of actual evapotranspiration (mm), ΔS is the change in total storage (mm), and R is the direct runoff (mm).

Based on these assumptions and Eq. (1), the net flux of water to the surface, or the rate at which the total amount of rainfall is subtracted from the actual amount of evapotranspiration, can be defined as the effective rainfall (Pe) based on these assumptions. This term includes both direct runoff and effective infiltration, which is helpful in comprehending the effective recharge:

$$P_e = P - ET_r = I + R \tag{2}$$

where I is the effective infiltration (mm).

From the daily termo-pluviometric data and by Eq. (2), for each gauging station, the monthly and annual averages of these data were computed in the reference period (1992–2022).

Due to the limited availability of temporal and spatial meteorological datasets, the empirical Turc's formula was applied to evaluate the actual evapotranspiration [27]. This empirical model is based on annual precipitation and air temperature; its reliability has

been confirmed by many studies conducted in the Mediterranean basin and European areas [27, 28]:

$$ET_r = \frac{P}{\sqrt{0.9 + \left(\frac{P}{300+25T_c+0.05T_c^3}\right)^2}} \tag{3}$$

The temperature data were used to calculate the mean annual corrected temperature T_c (°C), depending on the precipitation. The corrected temperature T_c is necessary to evaluate the actual evapotranspiration [27]. The T_c was calculated for each station by using (4):

$$T_c = \frac{\sum P_i T_i}{\sum P_i} \tag{4}$$

where: P_i is the average monthly precipitation (mm), and T_i is the temperature (°C) of the i-th month, referred to the reference period (1992–2022).

The effective infiltration, related to the infiltration capacity of the hydrogeological complexes, is expressed by the identification of the potential infiltration coefficients χ [23]. The effective rainfall P_e and potential infiltration coefficients were used to compute the effective infiltration:

$$I = P_e \cdot \chi \tag{5}$$

The effective infiltration was determined in each grid cell with the previously mentioned Eq. (5). The difference between effective rainfall and infiltration indirectly determine the runoff rate.

The hydrogeological water balance terms in the study basin were defined using the inverse hydrogeological water balance, which was elaborated by means QGIS software. Over the 1992–2022 reference period of data, these values were averaged (Table 1).

Table 1. Annual average amount of the inverse hydrogeological water balance terms.

Variable	mm y^{-1}	L s^{-1}
Direct Precipitation (P)	1878	3573
Actual Evapotranspiration (ET_r)	501	953
Effective Infiltration (I)	787	1497
Direct Runoff (R)	591	1124

The amount of effective infiltration (i.e., annual recharge) is approximately 1497 L s^{-1} according to the application results to the hydrogeological basin with an extension of about 60 km^2.

The groundwater discharge amounts provided to the springs, almost 1470 L s^{-1}, agree with the inflows derived by calculating the effective infiltration (i.e., active recharge).

Since the comparison yields an error of less than 10%, the inverse groundwater balance that was performed can be regarded as trustworthy [21].

The reliefs, situated at high elevations of the hydrostructure with W-E direction, represent the recharge area.

2.3 Aquifer Vulnerability Assessment

A methodological approach was used in this study to evaluate the vulnerability to pollution of the Lauria Mountains northern sector hydrostructure. It represents an effective tool for managing and safeguarding groundwater resources from pollution. Its assessment in the study area has been defined by the GNDCI-CNR (National Group for Defense from Hydrogeological Catastrophes (GNDCI) of the National Research Council (CNR)) method [23, 24] based on a survey of the hydrogeological complexes, characteristics, and setting [24, 29, 30].

Several hydrogeological scenarios, from medium to large scale, have been identified for the qualitative GNDCI-CNR technique; each of these scenarios is linked to a certain level of vulnerability.

According to the main determinants of the aquifer vulnerability, such as, aquifer geometry, lithology, and particular hydrogeological features, the hydrogeological scenarios of reference, as specified in the methodological protocol, are determined. This approach's benefit is its accurate intrinsic vulnerability assessment for large hydrogeological basins, particularly those situated in mountainous environments with limited and dispersed specific hydrogeological data.

The applied protocol does not require numerical input parameters, and the assessment of the hydrogeological intrinsic vulnerability was conducted by overlaying the maps on different levels of data [30, 31].

Geological and hydrogeological field studies, detailed field geostructural investigations of the limestone rocks, the application of the hydrogeological water balance, and the intrinsic vulnerability assessment aimed at the groundwater quali-quantitative safeguarding and protection were among the studies conducted. The structural and lithological features, the fracturing distribution of the carbonate complex, the feeding modes, the carbonate hydrogeological complex hydraulic conductivity, and the definition of preferential flow directions were the most important hydrogeological factors for assessing the intrinsic vulnerability degree of the aquifer.

The vulnerability to pollution of the carbonate hydrostructure was assessed using the qualitative GNDCI method based on hydrogeological homogeneous areas zoning after being suitably calibrated with consideration of the reliable data of the local hydrogeological complex characteristics and comparing the situation of interest to the standard specific hydrogeological scenarios [30]. This considered the lack of information related to the direct field hydrogeological measurements, such as piezometers and wells data and permeability tests, and the orography of the area.

The vulnerability assessment was carried out as follows: the hydrogeological conceptual model was defined based on surveys and investigations; the methodological approach for estimating vulnerability was chosen with consideration for the hydrogeological setting of the area; the geological and hydrogeological conditioning factors were identified for the vulnerability assessment; the hydrogeological situations recognized in

the area were compared to the GNDCI-CNR protocol scenarios; the relative qualitative vulnerability levels were assigned; and the intrinsic vulnerability map to pollution of the hydrogeological basin was elaborated.

Hydrogeological complexes and hydrogeological characteristics, as well as homogenous zones with comparable features, were identified based on the data elaboration and the overlaying of the geo-structural context using GIS techniques. The vulnerability level for each of the locations was then assessed by comparing their characteristics with typical reference scenarios.

The result is the map of intrinsic vulnerability to pollution of the Lauria Mountains northern sector hydrostructure (Fig. 3).

The elaboration permitted to distinguish various classes of the vulnerability to pollution of this hydrogeological system, defined by numerous contributing factors, including the lithological environment and the distribution of fracturing, contributing to the spatial distribution of these classes.

Six classes of intrinsic vulnerability, ranging from low to extremely high, were identified by the technique. The Clayey-Marly Complex is referred to as the low vulnerability class. The medium-low degree is attributable to the fluvio-lacustrine detritical successions and the Conglomerate Complex. The medium vulnerability degree concerns the areas where the Detritical Complex and the Calcarenite Complex outcrop. The high degree of vulnerability refers to the fissured calcareous-dolomitic succession of the Carbonate Complex of the Monte La Spina-Monte Zaccana aquifer. The very high degree belongs to the fissured limestones of the Carbonate Complex of the Lauria aquifer southern part. The extremely high vulnerability was assigned to the fractured and karstified limestone of the Carbonate Complex of the Lauria aquifer northern part.

3 The San Severino Lucano Study Area

3.1 Environmental Issues

In specific geological settings, like ophiolitic areas, chromium (Cr) occurs naturally in rocks and derived soil, and due to water-rock interaction processes, it can be enriched in natural waters. The World Health Organization (WHO) has set a limit of 50 μg/L for total Cr in drinking water. However, due to recent studies on the toxicity of Cr(VI), the Italian government has lowered the acceptable level of total Cr to 25 μg/L (D.M. 30/06/2021, which revises the Italian Law D.Lgs 31/2001) [32].

The removal of hexavalent chromium (Cr(VI)) from contaminated water can be achieved using various techniques like chemical precipitation, ion flotation and ion exchange, adsorption, photocatalysis, Electrochemical Methods, bioremediation, membrane filtration which employing techniques such as ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [33]. Among all techniques, membrane technologies represent a promising and effective alternative in recent decades due to their numerous benefits, including enhanced product quality, elimination of chemical use, and energy independence through integration with renewable energy sources [34, 35]. For these reasons, nanofiltration (NF) was selected as a suitable technique to address the environmental issue of Cr-polluted waters in the Basilicata region, where ophiolite-bearing terrains outcrop [36].

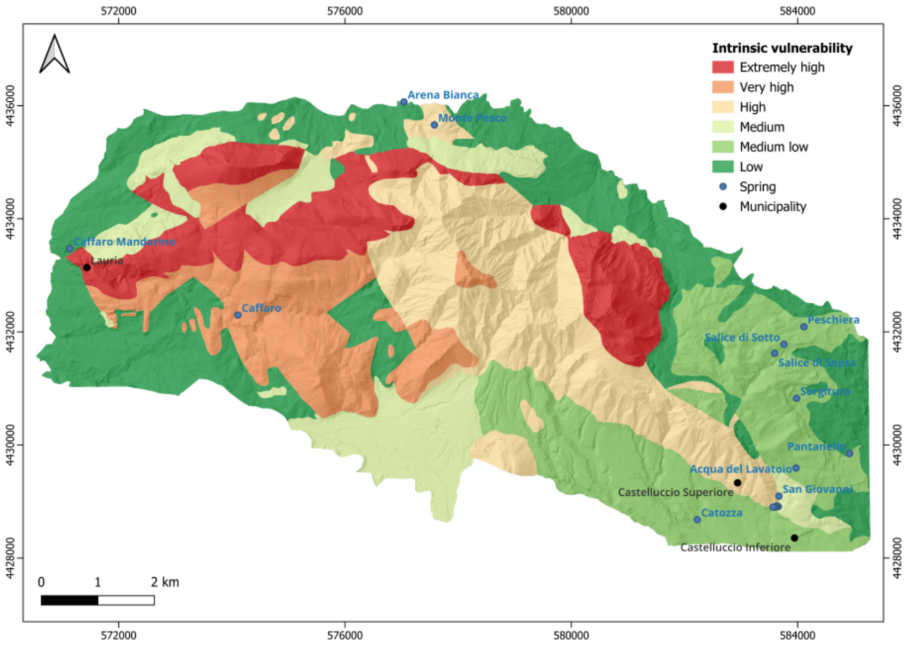

Fig. 3. Map of the intrinsic vulnerability to pollution of the Lauria Mountains northern sector with the different classes.

3.2 Geological Setting

The Pollino Massif area is located at the Calabria–Lucania border zone (Southern Apennines), which consists of tectonically juxtaposed thrust belts derived from the deformation of the African passive margin. This deformation occurred between the Oligocene and the Pleistocene time and involved the Ligurian ocean ophiolitic crust and its sedimentary cover (e.g., [37]). The Ligurian Complex cropping up in the Pollino Massif is affected by an intense tectonic deformation and consists of two ophiolite-bearing units named Calabro-Lucanian Flysch Unit and Frido Unit, unconformably overlain by turbiditic syn-orogenic sequences [38]. As depicted in Fig. 4, ophiolitic lithotypes (predominantly serpentinite and metabasic rocks) outcrop across diverse sectors of the Basilicata region. However, the area of interest for this research falls within the territory of San Severino Lucano municipality.

Generally, from the bottom to the top, it is possible to discern: (i) the Calabro-Lucanian Flysch [39], a non-metamorphosed ophiolitic complex, partially corresponding to the North-Calabrian Complex defined by Bonardi et al. [40]; (ii) the metamorphic lithologies of the Frido Unit [41]; (iii) syn-orogenic turbidite strata, including the Saraceno Formation, the Albidona Formation, and a sequence of alternating shales, mudstones and sandstones [42]. Notably, the ophiolitic lithotypes of the Frido Unit consist of lenticular metabasic rocks interspersed with cataclastic and intensely fractured serpentinites, extensively characterized through petrological and mineralogical analyses [43–45]. The metabasite rocks are frequently interlayered with serpentinites, phyllites,

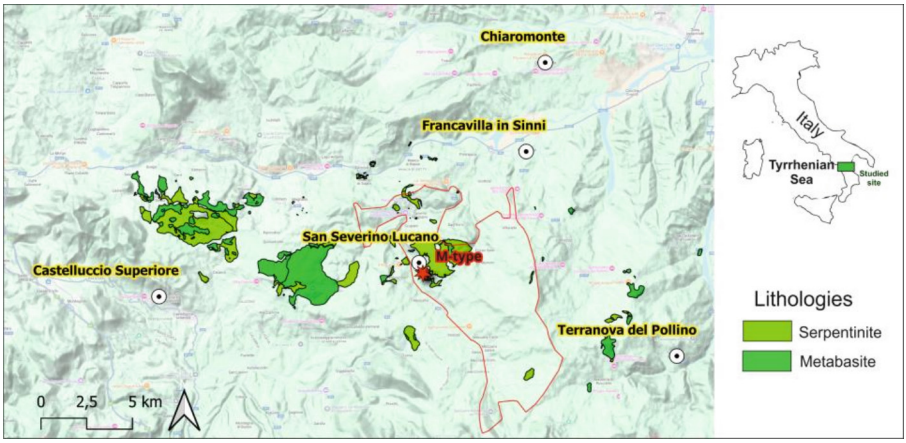

Fig. 4. Lithological map reporting the lithologies of interest (serpentinite and metabasite). In the map, the location of M-type water was also reported.

and metalimestones. The serpentinite rocks represent serpentinized greenish-bluish mantle peridotites. From a hydrogeological point of view, the Frido Unit terrains act as an aquitard for springs emerging in these zones. The aquifers consist of conglomerates, carbonates, metabasites, gneiss, and serpentinites. Typically, the aquifers are attenuated and laterally discontinuous, due to the lenticular and spatially restricted nature of the ultramafic rocks within the impermeable lithologies of the Frido Unit. Therefore, groundwater circulation in these areas is influenced by weather and, thus, by seasonal variations, with a fast mobilization and dilution of chemical elements [46].

3.3 Field and Laboratory Activities

A geochemical prospection started in the San Severino Lucano territory, and several water samples were collected. In the field, labile parameters were measured. The samples were collected, stabilized, and stored after filtration through a 0.45 μm pore-size filter. For each sample, the concentrations of chromium were determined using an iCAP PRO XP Duo ICP-OES.

A NF/RO laboratory pilot unit was used for water treatment tests (see [47] for further details on system components). Tests were performed by using a nanofiltration membrane, not already tested for chromium removal from waters, named Trisep TS40 and composed of polypiperazine (Mann + Hummel) (Table 2), two types of waters (distilled water and Cr-contaminated water) and four operating pressures: 3 bar, 6 bar, 9 bar, 12 bar. The aim is to obtain the best results concerning water decontamination and an adequate ionic load after treatment.

3.4 Results of Treatment Tests

The analysis identified a sample with a Cr concentration equal to 30 ppb, named M-type, which was selected for treatment tests (Table 3). Water flux tests were performed using

Table 2. Membrane's characteristics ([a] Typical NaCl rejection: 40%, [b] Test conditions: 2,000 ppm $MgSO_4$, 7.6 bar (110 psi), 25 °C (77 °F), 15% recovery, pH 8.0, 30 min operation. Membrane specifications may change without notice as design revisions occur [48]).

Membrane type	Thin-film Polupeperazine
MWCO	200–300 Da
Maximum Operating pressure	41 bar (600 psi)
Maximum Operating Temperature	45 °C
pH Range	1.0–12.0
Stabilized $MgSO_4$ Rejection[a]	99%
Minimum $MgSO_4$ Rejection	98.50%
Flux Range LMH (GFD)[b]	40.8–61.2 (24.0 36.0)

both distilled and M-type waters. Trisep TS40 showed permeate fluxes of distilled water ranging from 15.1 L/hm^2 (3 bar) to 85,1 L/hm^2 (12 bar). These values are comparable with the fluxes obtained by using M-type, which are as follows: 3 bar = 13.7 L/hm^2; 6 bar = 39.4 L/hm^2; 9 bar = 57.1 L/hm^2; 12 bar = 83.6 L/hm^2 (Fig. 5a). The selected membrane can lower Cr concentration below the law limit already at low operating pressures as shown in Fig. 5b, with Cr rejection values ranging from 90% to 95%.

Table 3. Physical- chemical parameters of M-type water.

pH_{field}	7.6
EC_{field}	473 µS/cm
T_{field}	14 °C
Eh_{field}	241 mV
Cr	30 ppb

During the tests in operating conditions, the measurement of electrical conductivity was used as an indirect measure of the amount of dissolved ions, allowing us to understand the total dissolved load before and after treatment. Considering this parameter (Fig. 5c), it is possible to note that the TS40 membrane represents a selective membrane type, as it significantly lowers the ionic load, especially at pressures of 12 bar. Nevertheless, water is never fully demineralized, but retains an ionic load in solution even after treatment at 12 bar TMP (the lowest EC value is equal to ~ 110 µS/cm). The decrease of EC values is the follows 53%, 71%, 75%, and 77% at 3 bar, 6 bar, 9 bar, and 12 bar respectively.

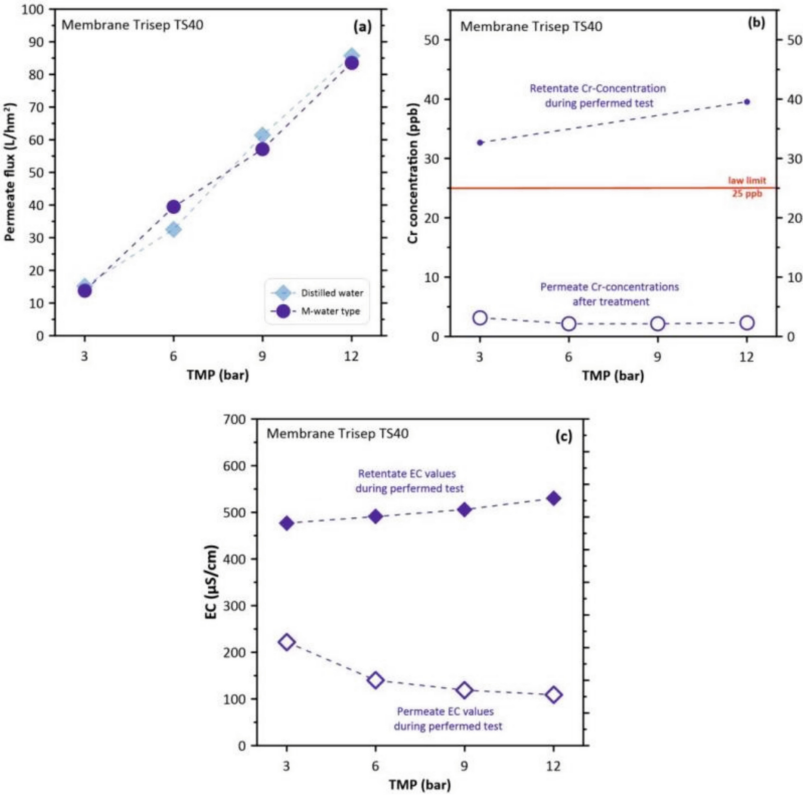

Fig. 5. (a) Permeate water fluxes; (b) Cr concentrations of M-type before and after treatment; (c) EC values of M-type before and after treatment.

Considering all results, the membrane TS40 can be considered a good solution for Cr removal from natural polluted waters. These findings add to the available knowledge on the treatment of chromium-contaminated natural waters (e.g., [5]), providing useful data for future scientific multidisciplinary studies involving geochemical research and new membrane applications in similar geological settings worldwide. Moreover, these data, together with the results of the other treatment tests in progress, will support the development of a membrane-based purification system to be installed in a strategic area and used during water emergency time, allowing water reuse.

4 Conclusions

This study, started with the definition of the geological setting of the selected study areas in the framework of the PP2 Tech4You project, the hydrogeological characterization of the Lauria Mountains, and the application of membrane technology, has as the main goal the quali-quantitative assessment and protection to pollution of selected fissured aquifers' strategic groundwater resources of the Lucanian and Calabrian Apennines.

The geological and hydrogeological setting and the vulnerability assessment were carried out for the Lauria Mountains. This carbonate hydrostructure hosts significant amounts of groundwater, which can be used mainly for human consumption and represent strategic groundwater resources for the region.

Performed water treatment tests give a chance to fill the current data gap concerning the treatment of natural Cr-contaminated groundwater by using membrane processes, providing useful data for future scientific and application developments. Moreover, the in situ development of a membrane prototype integrated with solar energy panels for the purification of contaminated waters from specific toxic pollutants will be a sustainable solution, allowing to produce safe waters for consumers living in these areas to be used during water emergency periods.

The study, still in progress, aims to proceed with investigations such as geoelectrical resistivity tomographies and new boreholes to deeply understand the subsurface, the discharge of the main springs and precipitations monitoring to define the amount of groundwater to allocate as strategic resources. Hydrogeochemical investigations will be performed to characterize the quality status and the geochemical composition of the groundwater; the WebGIS platform and in situ membrane purification activities will be realized.

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