Unravelling the salinity origins in the coastal aquifer/aquitard system of the Volturno River (Italy)

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ABSTRACT

To counteract the ongoing salinization of coastal aquifers, which poses a significant environmental and socio-economic challenge to local communities, it is necessary to first understand the origin and mechanisms of this phenomenon. This study investigates the origins of salinity in the Volturno River lowland in Southern Italy and reveals that the primary source in the area is paleo-seawater entrapped within sediments that were subject to evapoconcentration processes. By systematically collecting sediment samples at variable depths and locations and extracting porewaters, a comprehensive understanding of the interplay between freshwater and saline water was gained, including complex patterns of vertical stratification of groundwater salinity. The study highlights the limitations of traditional methods that rely on salinity monitoring via integral depth sampling, particularly in capturing the vertical redox and salinity gradients characteristics of layered aquifer/aquitard systems. On the contrary, environmental tracers, like chloride and bromide, provide valuable insights into the sources of groundwater salinity, distinguishing between current seawater intrusion and other causes, such as paleo-seawater and return flow from drained agricultural land. Results suggest that the majority of salinity does not originate from modern seawater intrusion or recent evaporation. Instead, it can be attributed to paleo-seawater affected by evapoconcentration processes. This study has broader implications for the sustainable management of coastal aquifers and the safeguarding of freshwater resources. While our findings are specific to the Volturno River coastal area, the methodologies and insights here presented can be reproduced in every coastal region facing similar salinity challenges.

1. Introduction

The ongoing salinization of freshwater resources is a ubiquitous and alarming phenomenon, with profound implications for coastal areas (Li et al., 2020). Evapoconcentration, leaching of evaporites, mobilization of salts stored in the unsaturated zone, infiltration of surface waters contaminated by sewage, influx of sluggish saline waters of marine origin, highly mineralized waters from geothermal fields, sea spray, excessive filtration from aquitards, agricultural practices, and other human activities collectively represent the most prominent sources and processes contributing to global salt accumulation (Cartwright et al., 2004; Li et al., 2020). In coastal plains, characterized by small hydraulic gradients and intensive drainage (Rahmawati et al., 2013), current seawater intrusion is pointed out as the main cause of groundwater salinization, although recent studies (Alessandrino et al., 2023; Colombani et al., 2017; Dang et al., 2022; Giambastiani et al., 2021; Schiavo et al., 2023; Seibert et al., 2023; Yu et al., 2023) have shown that paleo-seawater is often a major issue, especially in lowland deltaic areas hosting shallow Holocene aquifers. Furthermore, the depletion of groundwater resources in areas of high human activity, along with prolonged periods of subpar rainfall, is exacerbating the salinization of groundwater (Ashraf et al., 2017; Mastrocicco and Colombani, 2021). To optimize the economical stewardship of water resources, it is imperative to gain an in-depth comprehension of the governing

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mechanisms dictating the interplay between freshwater and saline water, encompassing the vertical stratification of groundwater salinity. This understanding is fundamental for quantifying both the magnitude and the spatial distribution of saline groundwater infiltration within low-lying coastal regions (de Louw et al., 2010). The monitoring of the saltwater-freshwater interface in unconfined aquifers often relies on the profiling of electrical conductivity (EC) using data loggers installed in fully screened wells. However, this method comes with certain limitations stemming from intraborehole mixing processes that have the potential to smear the saltwater-freshwater interface and to alter the redox gradients (González-Quirós and Comte, 2020; Shalev et al., 2009). Depth-dependent sampling is thus inevitable to gain a reliable reconstruction of salinity distribution. Multi-level sampling via packers' sampler, socks' sampler, and nested piezometers are among the most common methods used to collect groundwater samples at different depths (Goode et al., 2014; Weatherill et al., 2014). Their employment is more expensive and time-consuming compared to the integral depth sampling procedure. An alternative reliable approach, if the drilling material of an undisturbed borehole is available, involves extracting porewater from sediment cores. This is a valuable method for examining the source of groundwater salinity, particularly when analysing non-reactive species like chloride (Cl^-) and bromide (Br^-), to be used as environmental tracers (Alcalá and Custodio, 2008; Mirzavand et al., 2020). Cl^-/Br^- ratio is an established method for determining salinity sources in groundwater (Rao et al., 2005). These anions are generally conservative, since they do not undergo chemical reactions that alter their original ratio (Eggenkamp 2014). Furthermore, this ratio allows a worthy differentiation between seawater intrusion, deep groundwater input, trapped ancient salinity, and anthropogenic contamination (Faye et al., 2005). Indeed, a similar approach was recently used by Alessandrino et al. (2023) to assess the salinity origin in the coastal aquifer of the Southern Venice lowland, discriminating among current seawater intrusion and other causes such as trapped paleo-seawater, evapoconcentrated salts, and agricultural activities. But here a more comprehensive database has been used with major ions and trace elements, combined with a detailed stratigraphic description and with a robust geostatistical analysis via Principal Component Analysis (PCA).

This study aims to assess the salinity origin of the Volturno River coastal aquifer addressing the research gap concerning the complex dynamics of salinity in response to both natural and anthropogenic stressors (Mastrocicco et al., 2021), and the worrying scenarios depicted by Busico et al. (2021), that reported the potential degradation of approximately 4000 hectares of agricultural land as a consequence of salinization. The widespread presence of saline groundwater has been reported recently also using geophysical methods (Tarallo et al., 2023), as well as the seawater encroachment within the Volturno River terminal part (Gaiolini et al., 2023). In this light, delving into the origin of groundwater salinity in this area becomes paramount to implement the necessary strategies to safeguard groundwater resources (Hussain et al., 2019). In this study, the porewater extraction method was applied by systematically collecting sediment samples at different depths and locations. This helped validate the conceptual model illustrating the origin of salinity and locate hot spots of salinity cross-referenced with sedimentary facies associations and hydrogeological data.

2. Study area

The study area is located in the coastal floodplain of the Volturno River, within the Campana Plain (CP) in Southern Italy (Fig. 1). The CP is a key component of a vast basin system, formed during the Quaternary, situated between the western boundary of the southern Apennines and the eastern edge of the Tyrrhenian continental margin (Casciello et al., 2006; Ferranti et al., 1996). The CP, which emerged during the Early Pleistocene as part of the Campania continental shelf, was shaped by post-orogenic extensional processes related to strike-slip tectonics along the Eastern Tyrrhenian margin (Milia and Torrente, 2003). During
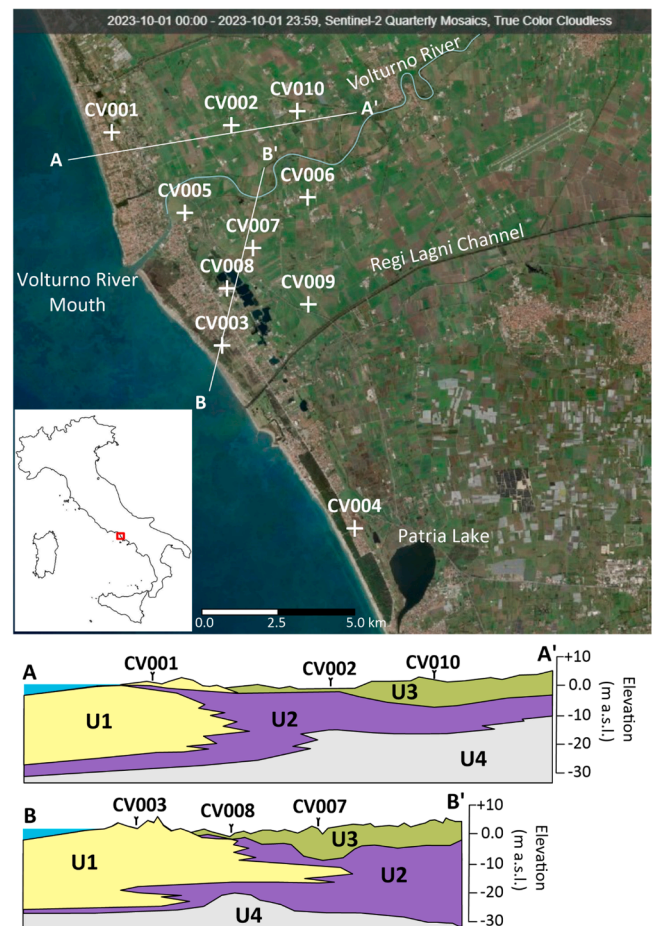
Fig. 1. Upper Panel: Sentinel-2 true colour mosaic of the study area showing the locations of the sediment cores used for the present study and the track of the two stratigraphic profiles reconstructed in the lower panel. Note the mixed agricultural and urban land use of the area. Lower Panel: Stratigraphic profiles of the lower alluvial-delta plain showing the Late Quaternary evolution of the recognized depositional units described in Table 1.

the Late Pleistocene, the entire CP was exposed to subaerial conditions due to reduced subsidence rates (Sacchi et al., 2014) and the concurrent sea level regression of the last glacial period. Subsequently, in the Holocene, the CP underwent extensive flooding, coinciding with the post-glacial transgression, whose maximum ingression occurred about 7–6.5 ky BP (Amorosi et al., 2012). As sea levels stabilized, the coastline advanced seaward, leading to the formation of a well-developed beach-dune system that enclosed lagoon and swamp systems rich in peaty lenses and characterized by elevated sedimentary organic matter (SOM) content that spanned several kilometres from the present coastline (Ruberti et al., 2022).

In the 16th century, substantial reclamation works transformed this area, facilitating agricultural and urban development, particularly in the coastal zone (Ruberti and Vigliotti, 2017). The CP experiences ongoing subsidence, particularly in coastal areas with swamp and lacustrine deposits, which results from both natural processes and human activities, such as urbanization, water extraction, and drainage practices associated with intensive agriculture (Matano et al., 2018). The natural subsidence component, due to the presence of compressible materials subjected to primary and secondary consolidation, is prevailing over the anthropogenic component (Buffardi et al., 2021). The irrigation of agricultural fields relies heavily on diversions from artificial canals, leading to a consistent decrease in river discharge, particularly during the summer season, which in turn results in sporadic saltwater intrusion events along the Volturno River (Gaiolini et al., 2023).

3. Materials and methods

3.1. Sample collection and sediment analysis

Ten sediment cores, perforated down to a depth of 30 m (b.g.l.) and drilled with a continuous coring system, were designed to capture local-scale subsurface variability of the study area (Fig. 1). The cores were sub-sampled in the field when changes in grain size, colour, or presence of fragments (e.g., shells or vegetation) occurred. A total number of 116 samples were collected for porewater analyses.

The 10 sedimentary cores were thoroughly analysed for the assessment of various parameters, including lithology, grain size, sedimentary structures, colour, sorting, as well as the identification of fossils, vegetal remains, and bioturbation. This comprehensive analysis facilitated the identification of depositional units (U) based on homogeneous sedimentological and paleontological criteria. The primary lithological characteristics of these units are summarized in Table 1.

Batch leaching experiment was chosen as extraction method because the shallow aquifer's samples were not fully saturated. Therefore, this method ensured that all samples were consistently extracted. The experiments, on the 116 samples collected from the 10 cores, followed the saturation soil extraction (SSE) method (Schuwirth and Hofmann, 2006). Each batch featured a liquid/solid (L/S) ratio of 5:1, and a 40-day contact duration allowed the solid matrix to reach equilibrium with the liquid phase, that consists of Milli-Q deionized water (18.2MΩ). This L/S was chosen to ensure that all ions passed into the liquid phase, since lower L/S can lead to an incomplete extraction (Alessandrino et al., 2022) The HDPE containers for the batches were sealed to prevent external influences and maintained in darkness at a controlled temperature of 20±1 °C.

Total Dissolved Solids (TDS) and pH were monitored weekly using a HANNA multiparametric probe (model HI98194) to determine when equilibrium was achieved between the solid and liquid phases. Prior to each measurement set, the probe underwent calibration for EC, pH, and ORP using HANNA solution standards. After 40 days, water samples were collected from the batches and subsequently filtered for analysis. Anions (F^-, Cl^-, Br^-, PO_4^{3-}, and SO_4^{2-}) were determined by an isocratic dual pump ion chromatography (IC) with an ICS-1000 Dionex (Thermo-Fisher, USA), equipped with an AS14 250 mm high-capacity column and guard column, an ASRS-ULTRA 4 mm self-suppressor. An AS-40 Dionex auto-sampler was employed to run the analyses. Quality Control (QC) samples were integrated into the analysis routine, with QC samples analysed every ten samples to ensure the accuracy and reliability of the results. An ICP-OES (PerkinElmer, USA) was used to quantify major cations (Na, K, Mg, Ca) and trace metals (Cu, Cd, Fe, Li, Mn, Ni, Pb, Zn) in leachate water samples after acidification with ultrapure 1 M nitric

acid and filtering on 0.45 μm. Dissolved Total N (DTN) in water was analysed with LCK 238 LatoN cuvette tests (Hach-Lange, UK) and a UV/Vis spectrophotometer. Dissolved Total S (DTS) in water was determined as SO_4^{2-} via IC after complete oxidation in 30 % H_2O_2 and UV radiation (λ=254 nm), following the procedure of Prietzel et al. (1996). DOC and DIC were determined with a C analyser (Carbon Analyzer Shimadzu TOC-V-CSM).

Porewater concentrations (C_{pw}) were calculated using the formula (Jiao et al., 2010):

$$C_{pw} = C_w * \left(\frac{V_w + S*SWC}{1000}\right) \Big/ \left(\frac{S*SWC}{1000}\right) \quad (1)$$

where V_w is the volume of water used (mL) in the batch, C_w (mg/L) is the concentration of the analysed species in the batch liquid phase, S is the sediment weight (g) and SWC is the measured sediment water content (mL/mL).

The end-members of non-reactive freshwater-saltwater mixing were characterized using the chemical composition of Volturno River, Tyrrhenian Sea, and rainwater. Volturno River and Tyrrhenian Sea samples were collected using polyvinylchloride transparent disposable bailers, while rainwater was collected using an HDPE flask with a funnel.

3.2. Data elaboration

Cl^-/Br^- ratio was assessed to distinguish between anthropogenic and natural causes of salinization (Hudak, 2003). Cl^- and Br^- are considered non-reactive ions because their concentrations are not significantly affected by redox reactions or the precipitation of low-solubility minerals. As a result, when both Cl^- and Br^- originate from the same source, their ratio should remain constant (Alcalá and Custodio, 2008). In addition, mixing lines among end-members were drawn fitting the data on precipitation, rivers, Tyrrenian Sea, and halite (Herrmann et al., 1973).

Base Exchange (BEX) index serves as a valuable tool for comprehending the dynamics of salinization/freshening within a coastal aquifer and could be assessed using the following equations (Stuyfzand, 2008) for Ca and Mg rich aquifers, respectively:

$$BEX_{Ca} = Na + K + Mg - 1.0716\ Cl \quad (2)$$

$$BEX_{Mg} = Na + K - 0.8768\ Cl \quad (3)$$

where 1.0716 and 0.8768 equal to [Na + K + Mg]/Cl and [Na + K]/Cl for mean ocean water (meq/L), respectively. BEX_{Ca} could not be applied to dolomitic aquifer system, because significant amount of Mg derives from dolomite dissolution. Because of the non-negligible presence of dolomite minerals in the study area, BEX_{Mg} was also employed. Samples were categorized into three distinct classes: positive BEX, indicating freshening trends; negative BEX, indicating salinization trends; and zero, indicating stable conditions. The BEX index describes cation exchange processes caused by water-rock interactions when salt water enters a freshwater aquifer or vice versa (Vandenbohede and Lebbe, 2012). BEX was already effectively used in this area by Mastrocicco et al. (2021), although using fully screened wells and not depth profiles via porewater, to investigate the spatial and temporal evolution of the freshwater/saltwater interface providing useful information about significant changes imposed by both natural and anthropic stressors.

Principal Component Analysis (PCA) was performed via IBM SPSS Statistics software, to identify and separate the main biogeochemical processes. Principal components (PCs) were extracted using the varimax rotation option, following Kaiser normalization, i.e. only factors with eigenvalues greater than 1.0 were retained. 19 independent numerical variables were employed (F, Cl, Br, Li, Na, K, Mg, Ca, Cd, Ni, Zn, Cu, Fe, Mn, DOC, DIC, pH, DTS, DTN), while Pb was excluded since always below detection limits. Moreover, the analysis considered the major depositional environments as nominal variables, aiming to correlate the

Table 1
Simplified depositional units identified in this study, based on Amorosi et al. (2012) and Ruberti et al. (2018).

Units (n° of samples)	Description	Depositional Environment
U1 (35)	Well sorted, medium to coarse grey or yellowish sand, with abundant marine shell fragments, plant and rare pumice fragments	Shoreface-beach-dune-ridge complex
U2 (29)	Grey to dark grey clay with abundant organic matter and freshwater gastropods. Peat intercalations and sandy layers with mollusc and pumice fragments	Lagoon/estuary, Coastal plain/swamp
U3 (44)	Rooted and pedogenized, brown to grey clay and silty clay with abundant whitish pumices and plant fragments. Gravel with sand lens locally occurs	Alluvial plain
U4 (8)	Alternations of pumice and ash beds, zeolitized yellow tuff, volcanic sand, cinerite deposits, sometimes reworked by fluvial erosion	Volcaniclastics

type and origin of sediments with local observed porewater concentrations.

4. Results and discussion

4.1. Salinity distribution and origin

TDS and Cl⁻ vertical concentration profiles along two transects almost perpendicular to the coastline at the northern and southern flanks of the Volturno River are shown in Fig. 2. The highest TDS are not located in the highly permeable sandy sediments of the U1, but are consistently found in U2 that forms local aquitards. In fact, back-barrier and lagoonal depositional environments create the typical conditions for trapping salts via evapoconcentration processes and the low permeability of such horizons does not allow the complete flushing of the accumulated salts (Alessandrino et al., 2023; Carol et al. 2024; Schiavo et al., 2023; Sheng et al., 2024). Furthermore, organic matter dissolution and degradation (Tfaily et al., 2014) combined with pumices pyrite oxidation (Bonnissel-Gissinger et al., 1998; Naimo et al., 2005) result in significant concentrations of DOC, SO_4^{2-}, and Fe^{2+} (Supplementary Information), which contribute to the high TDS detected. On the contrary, the more permeable sandy lenses are characterized by freshwater in the shallow part of the aquifer even near the coastline (CV001 and CV003).

This is due to the high regional groundwater flow coming from the surrounding hills that generates submarine groundwater discharge (SGD) rather than seawater intrusion along the whole Campania coastline (Gaiolini et al., 2022). Since freshwater is less dense than seawater, SGD takes place near to the beach face (Bakhtyar et al., 2012), while the actual seawater intrusion creates a wedge in the lower part of the aquifer. It can be noticed that the above-mentioned classical seawater process is occurring just near to the coast with groundwater that becomes brackish with depth, but never reaching TDS values of typical modern seawater concentration of 36.2 g/L (Iacono et al., 2021) or of the Tyrrhenian Sea in the Volturno bay of 38.0 g/L (Sorgente et al., 2020). Another clue that groundwater salinity is not due to actual seawater intrusion is that Cl⁻ vertical gradients do not follow TDS gradients in inland cores. This is particularly evident in CV002 and CV010 where the TDS peaks are characterized by low Cl⁻ concentrations.

Analysing the relationship between Cl⁻ and Br⁻ (Fig. 3a), it is evident that most of the samples do not plot along the seawater-freshwater mixing lines but are rather a ternary mixture of rain, Volturno River, and seawater. Besides, a considerable number of samples fall along the rain-halite mixing line, confirming the hypothesis of evapoconcentration as main salinizing mechanism in this area, due to the ability of salts to crystallise, especially where precipitation is low and evaporation high (Bell, 2005). Results depicted in Fig. 3b suggest
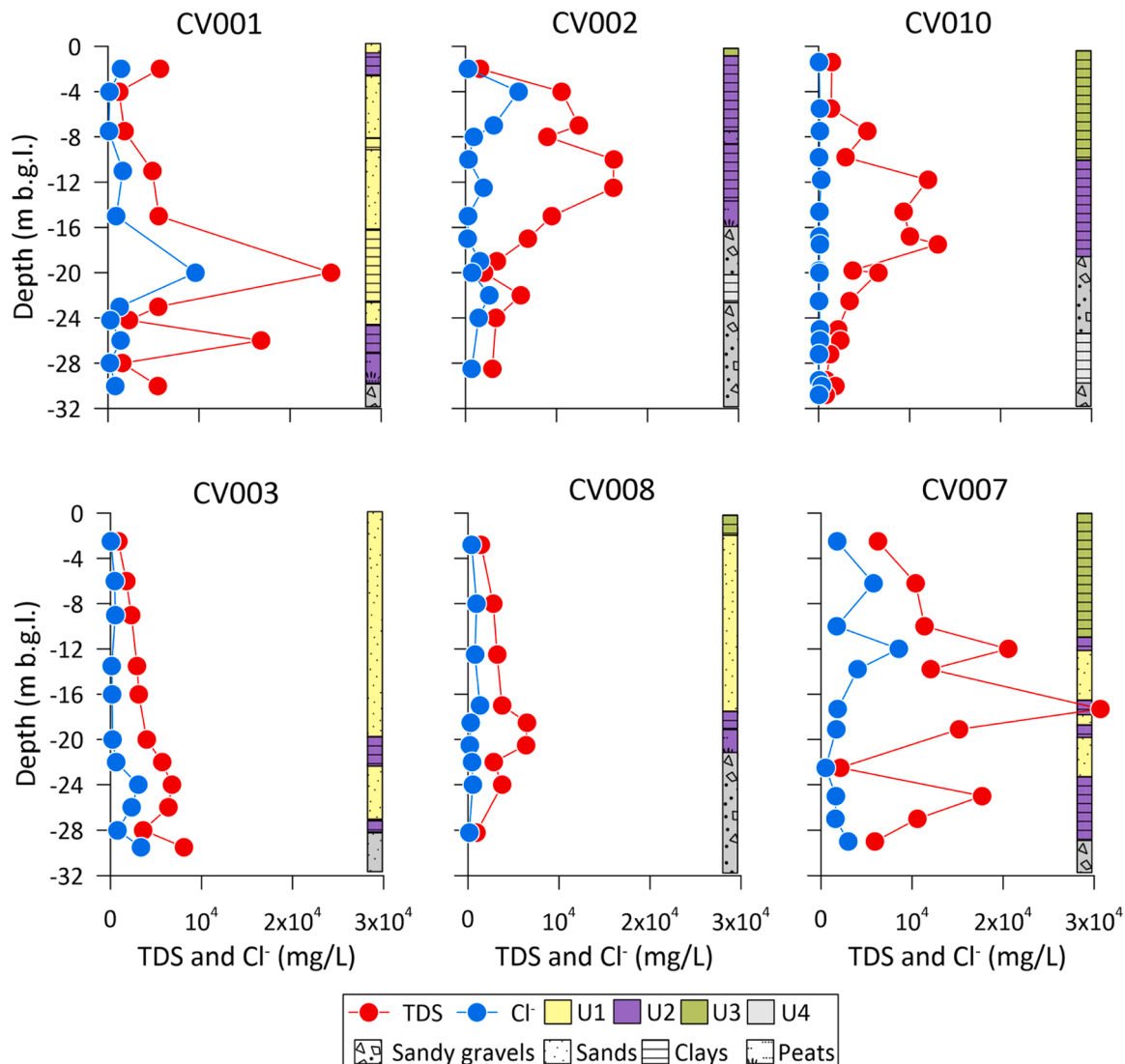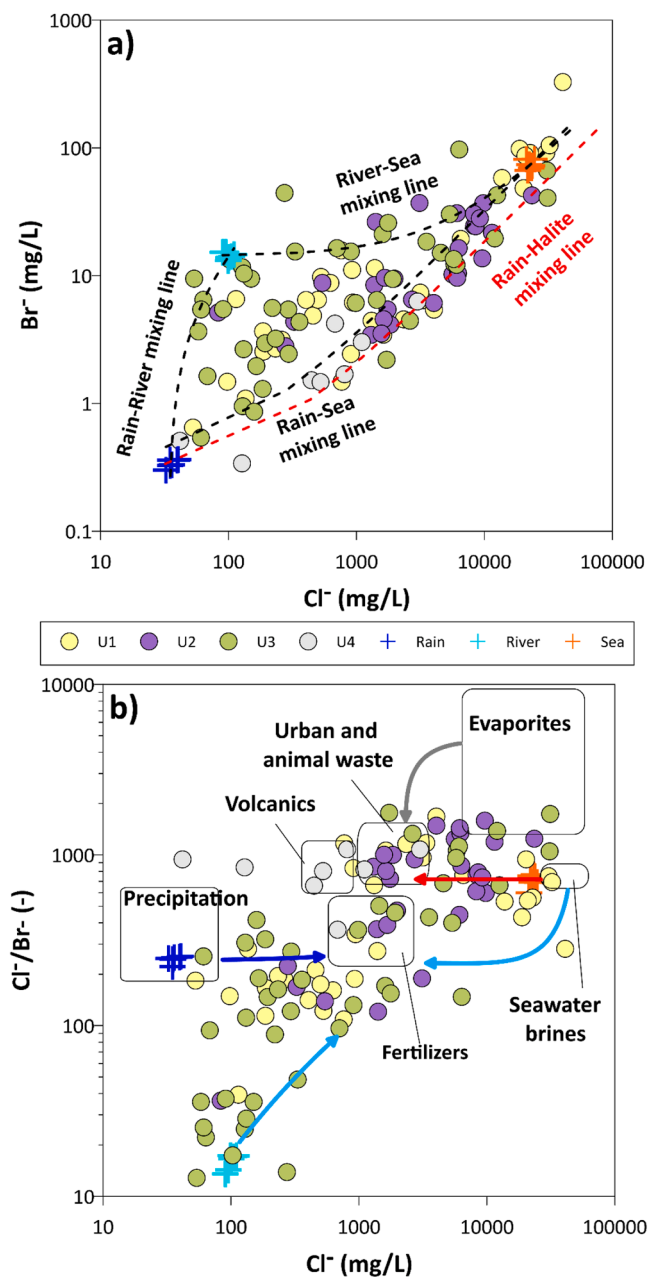

Fig. 2. TDS and Cl⁻ distribution along two transects almost perpendicular to the coastline (refer to Fig. 1 for the location).

Fig. 3. a). Cl⁻ vs Br⁻ plot; b) Cl⁻/Br⁻ molar ratio vs Cl⁻ plot. In plot (a), the dashed lines are linear mixing among end-members, data on halite Cl⁻ and Br⁻ composition were sourced from Herrmann et al. (1973); mixing lines appear not straight due to the axis log-scale. In plot (b), the arrows indicate the different mixing lines among the end-members, while rectangular boxes are reported from Alessandrino et al. (2023).

that the majority of salinity does not originate from modern seawater intrusion or recent evaporation. Instead, it can be attributed to paleo-seawater affected by evapoconcentration processes. In reality, samples are not aligned along Cl⁻/Br⁻ value of 655, which is characteristic of marine water (Grilli et al., 2020), but exhibit a broader spectrum of distribution, indicating the presence of alternative salinity sources.

The subsequent mixing with recharge waters have diluted the initial hypersaline waters, with most samples positioned between evaporite leaching and samples collected from the Tyrrhenian Sea. Samples can be classified into three distinct groups based on their Cl⁻/Br⁻ ratios. Samples with extremely low Cl⁻/Br⁻ ratios, predominantly from the Volturno River, are associated with the alluvial plain unit U3. Samples

with low Cl⁻/Br⁻ ratios originated from precipitation and fertilizers leaching. As shown in Fig. 1, the intensive agricultural activities and the urban settlements scattered in the area have a substantial impact on the groundwater quality of this aquifer as previously reported (Busico et al., 2018; Ducci et al., 2019); in fact, many samples fall within the urban and animal waste and fertilizers boxes. Finally, samples at greater depths exhibit a high Cl⁻/Br⁻ ratio of approximately 1100, indicating their association with processes involving the intrusion of paleo-seawater and mixing with evaporitic layers. This phenomenon has been already documented by Alessandrino et al. (2023) and Colombani et al. (2017) in similar environments, but the interesting point is that the same processes have been recognized in a different deltaic system respect to the Po river delta, and potentially these features could be recognizable in the whole Mediterranean basin On the other hand, the shallower samples exhibiting an exceptionally low Cl⁻/Br⁻ ratio are indicative of agricultural leaching (Panno et al., 2006). Finally, it must be highlighted that some of the most saline samples are from U1 and precisely from CV004, located near to the coastline. Here salinities of up to 77 g/L and Cl⁻ concentrations up to 41 g/L were measured trough the profile, values that are almost twice the actual Tyrrenian seawater (see Supplementary Information). The reason why this borehole has so high salinities, is probably due to the fact that the CV004 is located downgradient respect to the regional groundwater flow that is directed from inland towards the coast and is passing through the Soglitelle Oasis (Gaiolini et al., 2022). The latter is a hypersaline reclaimed area forming the remnant of the Patria Lake, where fine layers of evaporitic muds have been recognized and dated around 3 ky BP (Sacchi et al., 2014).

Many samples exhibited Br⁻ concentrations extremely low in comparison with Cl⁻ concentrations. This phenomenon is attributed to the dissolution of halite, a mineral known for its low Br⁻ content (Herrmann, 1972), which precipitated in lagoonal and marsh environments marked by shallow ponds during a drier climatic phase, namely the post-Last Glacial Maximum (LGM) marine transgression. This concept is illustrated with more details in the following section.

4.2. Salinization/freshening pathways

Since the aquifer is composed of mixtures of sediments coming from the Carbonate and Dolomitic Massifs bordering the CP, Figs. 4a and 4b show both BEX indices. In both cases, the BEX values observed across the cores' profiles exhibit a common freshening trend for most of the extracted samples, again suggesting that high salinities are attributable to evapoconcentrated paleo-seawater entrapped within sediments then flushed by recharge waters from rain and rivers (Meyer et al., 2019). The BEX_{Ca} plot shows the highest absolute values with freshening trends with increasing ionic strength for U2 and U3, while U1 and U4 show values around zero. U2 freshening trend is a further confirmation that high TDS detected in this layer could be attributed to paleo-seawater combined with redox processes. In fact, recharge water, that have a higher redox potential, trigger U2 SOM dissolution and pumices pyrite oxidation. Only a few samples display salinizing values, these pertain to CV004 which is close to the coast and possibly affected by actual seawater intrusion, or to CV007 and CV009 which are characterized by agricultural and farming activities. However, the scattered distribution of BEX_{Mg} reflects the natural scattered distribution of dolomitic limestone in this area, which is mostly $CaCO_3$ dominant (Corniello et al., 2018).

Fig. 4c shows that the dissolution of halite is the major driver of Na^+ and Cl^- presence in groundwater. The Na^+ deviation from the expected 1:1 NaCl line is likely due to cation-exchange (Mastrocicco et al., 2021).

Data plotted in Fig. 4d provide additional information on the pivotal role played by carbonates in the hydrogeochemistry of the CP aquifer. The majority of the values fall below the bisectrix and could be attributed to the abundance of bicarbonate in the aquifer matrix. Their dissolution buffers the pH decrease arising from the mineralization
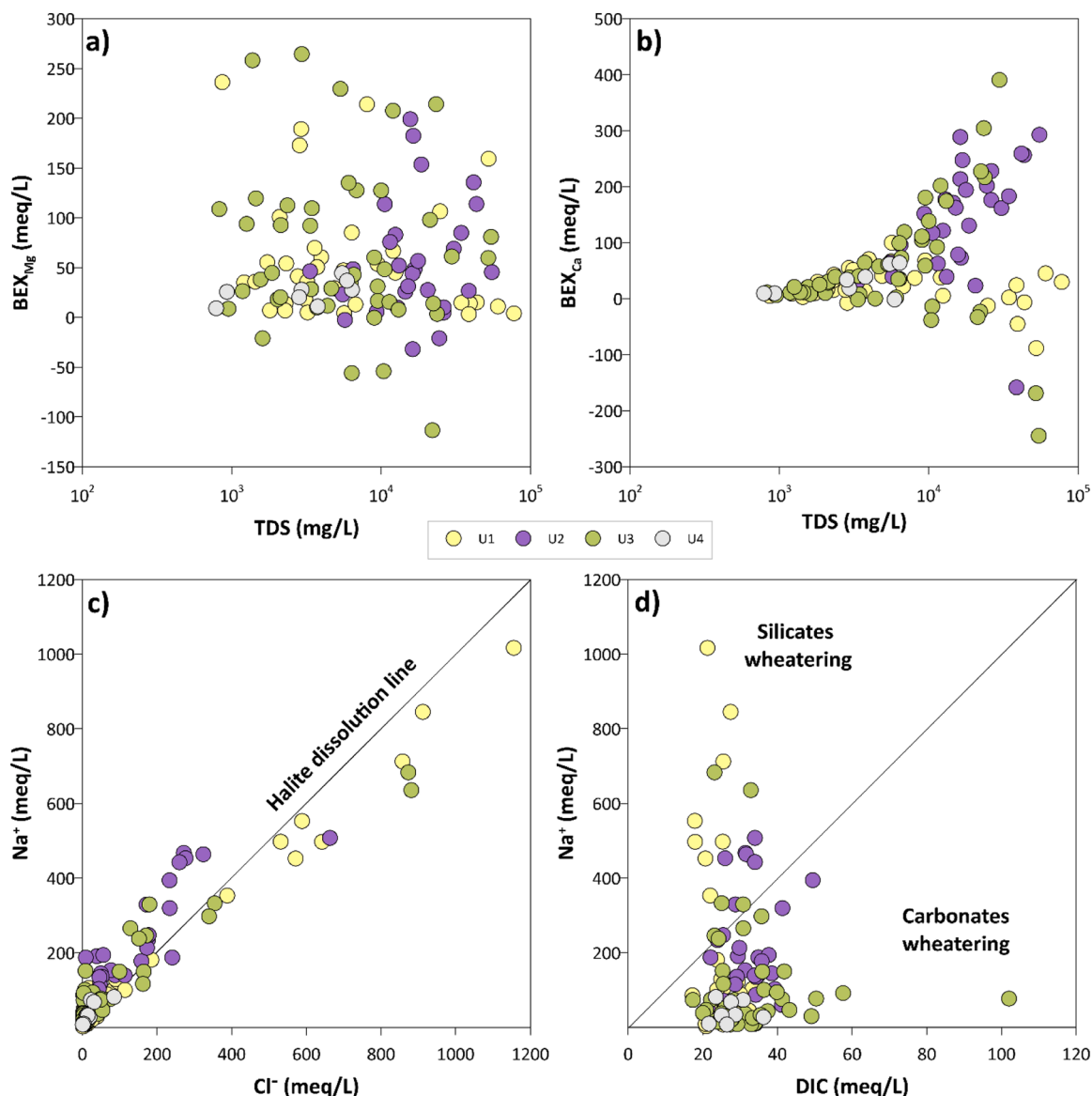
Fig. 4. a). BEX_{Mg} vs TDS plot; b) BEX_{Ca} vs TDS plot; c) Na^+ vs Cl^- plot; d) Na^+ vs DIC plot.

processes of the SOM, found abundantly in the peaty lenses and in the back-barrier silty clay sediments. Indeed, the dissolution of carbonates within the aquifer matrix often contributes to the alkalinity increase in groundwater (Caschetto et al., 2017; Jiao et al., 2010). The few samples that exhibit a clear silicate weathering pattern are those located in CV004, the borehole is located closer to the Phlegraean Field volcanic area and thus characterized by layers with an abundance of silicates over carbonates. While the CV009 borehole is located in the terminal part of the ancient Patria Lake that was extending over here before the construction of the Regi Lagni reclamation channel in the XVI century, thus the Na^+ excess over DIC is imputable to the high salinities developed during short-lived evaporitic events (Sacchi et al., 2014), rather than to volcanic sediments deposition. Finally, it has been emphasized by Cai et al. (2003) that CO_2 inputs from SOM degradation via SO_4^- reduction seriously modified groundwater DIC composition across the entire salinity range, while fermentation and $CaCO_3$ dissolution modified the groundwater DIC composition in the low-salinity region. This is in agreement with the results here exposed, thus the use of DIC in combination with Na^+ can provide some constraints to identify the salinity sources, although it could be difficult to interpret when volcanic deposits are concomitantly present with calcareous deposits and

hypersaline environments.

4.3. PCA results

While specific information on dissolution mechanisms from aquifer matrix and salinization processes can be gained from the classical geochemical tools and the graphs previously reported, the PCA often provides unexpected insights on trace elements distribution and major geochemical processes occurring in coastal aquifers (Colombani et al., 2017; Huang et al., 2023). PCA results are reported in Table 2, where significant loadings ($\geq \pm 0.6$) have been highlighted. Components extracted following the Kaiser criterion are five and their total explained variance is 75 %.

The first component explaining the 24.3 % of the variance encloses the conservative (Cl^- and Br^-) and the most soluble cation (Na^+) providing the relative importance of the salinization process in the area. The high ionic strength also brings into the solution some trace elements (Li, Cd, and Zn). The second component, which is also important since it explains the 17.4 % of the total variance, is related to the presence of SOM (mainly in peaty lenses) with very high loadings of DTS and Ca and with lower loadings of DTN and K. The third component, still explaining

Table 2
Principal component loadings (varimax rotated) for the different variables and their explained variance. Bold values are > 0.60, bold and italics values are < −0.60.

i.d.	Component				
	1	2	3	4	5
F	0.356	−0.212	0.097	0.053	**0.761**
Cl	**0.895**	0.108	0.007	−0.088	−0.048
Br	**0.888**	0.085	0.073	−0.062	0.175
Li	**0.657**	0.143	−0.091	−0.039	0.275
Na	**0.881**	0.304	0.052	−0.035	−0.036
K	0.394	**0.666**	0.063	0.009	−0.168
Mg	0.567	0.442	0.571	0.018	0.065
Ca	0.211	**0.883**	0.020	0.130	0.003
Cd	**0.613**	0.209	0.037	0.389	−0.304
Ni	0.017	0.018	**0.938**	0.148	−0.032
Zn	**0.844**	0.115	0.029	0.098	−0.237
Cu	0.407	0.556	−0.004	0.552	−0.152
Fe	0.020	−0.343	0.044	0.526	0.215
Mn	0.000	0.011	**0.940**	−0.015	0.030
DOC	−0.003	0.330	0.090	**0.817**	−0.028
DIC	−0.133	0.125	−0.002	**0.835**	0.111
pH	0.006	−0.172	*−0.800*	0.022	−0.167
DTS	0.173	**0.898**	0.110	0.163	0.017
DTN	0.019	**0.658**	0.488	0.055	0.021
Dep Env	−0.344	0.086	0.119	0.167	**0.640**
% Var.	24.34	17.40	15.18	11.11	6.966
Cum. Var.	24.34	41.74	56.92	68.03	74.99

a high percentage of the total variance (15.2 %), is related to the development of the main redox process in the aquifer/aquitard system, the Mn reduction which is also accompanied by Ni desorption (Larsen and Postma, 1997) in decreasing pH, as testifying by the negative loading of this latter. However, it must be stressed that Ni concentrations were always low (see Supplementary Information). The fourth component (explaining the 11.1 % of the variance) is again related to the SOM mineralization with high loadings for DOC and DIC and low loadings for Fe and Cu, witnessing the high reducing conditions of the mineralization processes. The last component and the less important (only 7 % of the variance explained) is related to the volcanic sediments rich in F, as already pointed out by previous research in this area (Busico et al., 2018; Corniello and Ducci, 2014).

5. Conclusions

The porewater salinity distribution in the complex aquifer/aquitard system of the Volturno River plain and the potential degradation of agricultural land due to salinization, underline the urgency of understanding the origin of groundwater salinity and implementing strategies to mitigate its detrimental effects. The findings of this study have broader implications for the sustainable management of coastal aquifers. Results clearly express how the actual seawater intrusion does not represent the main driver of groundwater salinization in this area. Alternatively, a combined process, including trapped paleo-seawater and redox related processes occurring in U2, appears to be the key factor of the widespread groundwater salinity. Thus, understanding the sources and processes of salinization is essential for safeguarding freshwater resources and mitigating the environmental and economic consequences of salinization. The systematic collection and analysis of sediment samples at different depths and locations, along with porewater extraction, have enabled to better understand the interplay between freshwater and saline water in such a cumbersome environment. This knowledge is crucial for quantifying the magnitude and spatial distribution of saline groundwater infiltration in low-lying coastal regions. The results highlight the limitations of traditional saltwater-freshwater interface monitoring methods which rely merely on salinity logging in fully screened wells. Intraborehole mixing processes can affect these measurements and introduce uncertainty in the assessment

of salinity origin. The use of non-reactive species like Cl^- and Br^- as environmental tracers has proven valuable for identifying the sources of groundwater salinity as well as the PCA, which highlighted that the prevailing redox process is Mn reduction via SOM degradation. This approach has provided insights into the complex interplay of various processes, such as modern vs paleo-seawater intrusion, evapoconcentration processes, and human activities. While our findings are specific to the Volturno River coastal area, the methodologies and insights here presented can be reproduced in every coastal region facing similar salinity challenges. However, spatial and temporal distribution of samples may not fully represent the geochemical variability of the studied area. Obviously, the use of isotopic analysis would ensure greater accuracy of results, but it would increase the costs of research by far. Future studies could focus on the possibility of using innovative tracers to better understand groundwater flow paths and interactions between waters of different origins.

CRediT authorship contribution statement

Nicolò Colombani: Writing – review & editing, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Luigi Alessandrino:** Writing – original draft, Data curation. **Mattia Gaiolini:** Writing – review & editing, Software, Investigation, Formal analysis, Data curation. **Maria Pia Gervasio:** Investigation, Formal analysis. **Daniela Ruberti:** Writing – review & editing, Validation, Conceptualization. **Micòl Mastrocicco:** Writing – review & editing, Validation, Resources, Methodology, Funding acquisition, 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.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.122145.

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