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Seawater intrusion and hydrogeochemical processes in the Ischia Island groundwater system

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Abstract:	Ischia is a volcanic island located NW of the Gulf of Naples (South Italy). The island of Ischia is a structurally complex hydrothermal active system that hosts a fractured aquifer system whose geometry and hydraulic properties are still partly unknown. The aquifer system of Ischia, composed mainly of Quaternary volcanic deposits and marine sediments, exhibits physically and chemically heterogeneous waters. The intense seismicity and hydrothermal activity are expressed by numerous fumaroles and thermal springs, which have been exploited since ancient times, promoting and supporting the world-renowned tourist activities that constitute the main economic activity of the island. The aim of this study is to determine the hydrogeochemical processes in the Ischia aquifer system. Also, we calculated the proportion of seawater in the aquifer system of Ischia using historical hydrogeochemical data relative to two sampling campaigns. Sixty-nine groundwater and thermal spring samples collected in July 2000 were analyzed and compared with previously published data to identify the changes in seawater contribution. The sample analysis shows that different physicochemical processes occur in the groundwater of Ischia Island, where recharge water, seawater and deep fluids interact and overlap with different intensity. The calculated saline factor indicates a seawater content of up to 70% in some samples near the coast, suggesting that seawater intrusion is the main process in these areas. Later data show that seawater intrusion increases around the coastline with up to 93% seawater content. Finally, data analysis shows that although a change in chemical composition is observed, no variation in thermal water temperature is recorded over time.
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Universidad Austral de Chile
Conocimiento y Naturaleza

Valdivia (Chile), December 28th, 2021

Dr. Stefano Albanese
Editor-in-Chief
Journal of Geochemical Exploration

Dear Dr. Albanese,

Please find attached the second revision for the manuscript "Seawater intrusion and hydrogeochemical processes in the Ischia Island groundwater system" by Linda Daniele and co-authors, accepted for publication in Journal of Geochemical Exploration with pending revision.

We have carefully revised the manuscript considering the reviewer observations. Also, we have addressed a number of minor changes.

Again, we would like to express our gratitude for the time and effort that you have devoted to the review of our manuscript. On the "Reviewers reply" document we address the comments and suggestions by the reviewers.

Thank you and best regards,

Dr. Daniele Tardani
(Corresponding author)
Earth Science Institute
Austral University of Chile, Valdivia

On the following pages, we present the response to the second review of our manuscript. We have carefully considered every observation from the reviewer and addressed the changes suggested by the reviewer.

Reviewer #1:

General comment

Reviewer #1:

In general, the authors have made modifications according to the suggestions made and the work has been improved. However, there are two important issues that were suggested that have not been taken into account by the authors.

1. The suggestion to quantify some of the processes involved, for example, ion exchange. It is not a fundamental question because the hydrogeochemical scenario will probably not change but the work would have been more in-depth.

Reply: We are grateful for the suggestion and we agree with that. The present contribution is focused on quantifying the saline intrusion and on disentangling the solute origin in groundwater aquifer. The quantification of ion exchange is beyond the purpose of this article, nevertheless we are aware that it would be an interesting contribution, so we are working on a reactive transport model in Ischia aquifer that will include also a quantification of ion exchange process, as well as element sorption, mineral precipitation/dissolution and fluid mixing.

2. The second question is the boron concentration in seawater. And after the second revision the strontium coul be added Regarding boron, all the existing data on the concentration of boron in seawater are between 4.5 and 5 mg / L. The authors state that in their seawater the concentration is 5.27 microg / L, that is, a thousand times lower than the standard one. The authors' answer "The boron value for SW sample corresponds to a seawater sample collected and measured by the authors and is not a theoretical value" is not convincing and helps to think about the existence of analytical errors. I think it is necessary to review this question and, in any case, explain why the sea water near Ischia is so different from the rest of the world.

Reply: Thanks for the comment. The boron value was certainly incorrect. The correct value is 5.27 mg/l, as previously published in Morell et al. (2008). We have corrected the value in the table and figures. We also add this sentence to the Result and Discussion section (Page 11-12):"The B value of SW sample is slightly higher than mean values in seawater (4.5 mg/l; Morell et al., 2008), but this value agrees with the average value of 5.1 mg/l calculated by Gofiantini et al. (2003) for the Mediterranean Sea".

Something similar occurs with strontium, whose usual concentration in seawater is of the order of 8 mg / L, while the analysis carried out for this work is 4.8 mg / L.

Reply: Strontium value for seawater near Ischia is the same published by Morell et al. (2008). At the time two samples were collected and analyzed in two different laboratories and the results obtained were consistent. We are aware that the value is lower than other samples collected in the Mediterranean Sea, but is a confiable value, already published by other authors. We addressed a new sentence in Results and Discussion section (page 12): “The Sr contents of the seawater sample (4.8 mg/l), already published in Morell et al. (2008), is lower than Sr concentrations measured in the mediterranean sea (8.4 mg/l; Daniele et al., 2011). The FW sample presents relatively high Sr, Ca and Mg values of 0.57 mg/l, 86 mg/l and 16.8 mg/l. Strontium follows a similar trend of Mg and Ca and presents positive correlation with Cl (fig. 5c, d, h), according to a Sr, Ca and Mg origin mainly related to carbonate dissolution and water-rock interaction (Musgrove, 2021)”.

In conclusion, the work has improved, but its publication cannot be recommended until the mystery of boron and strontium is solved and, where appropriate, the corresponding corrections are made.

Reply: Again, we are really grateful for the comments and observations that have substantially improved the quality of the manuscript.

Seawater intrusion and hydrogeochemical processes in the Ischia Island groundwater system

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Revised version to *Journal of Geochemical Exploration*

Abstract

Ischia is a volcanic island located NW of the Gulf of Naples (South Italy). The island of Ischia is a structurally complex hydrothermal active system that hosts~~forms~~ a fractured aquifer system whose geometry and hydraulic properties are still partly unknown. The aquifer system of Ischia, composed mainly of Quaternary volcanic deposits and marine sediments, exhibits physically and chemically heterogeneous waters. The intense seismicity and hydrothermal activity are expressed by numerous fumaroles and thermal springs, which have been exploited since ancient times, promoting and supporting the world-renowned tourist activities that constitute the main economic activity of the island. The aim of this study is to determine the hydrogeochemical processes in the Ischia aquifer system. Also, we calculated the proportion of seawater in the aquifer system of Ischia using historical hydrogeochemical data relative to two sampling campaigns. Sixty-nine groundwater and thermal spring samples collected in July 2000 were analyzed and compared with previously published data to identify the changes in seawater contribution. The sample analysis shows that different physicochemical processes occur in the groundwater of Ischia Island, where recharge water, seawater and deep fluids interact and overlap with different intensity. The calculated saline factor indicates a seawater content of up to 70% in some samples near the coast, suggesting that seawater intrusion is the main process in these areas. Later data show that seawater intrusion increases around the coastline with up to 93% seawater content. Finally, data analysis shows that although a change in chemical composition is observed, no variation in thermal water temperature is recorded over time.

Keywords: seawater intrusion; water-rock interaction; thermal waters; Ischia Island

1. Introduction

Seawater intrusion (i.e., the landward incursion of seawater) is a widely recognized process in coastal aquifers and islands (Custodio, 2010) and is usually caused by several factors, such as prolonged changes in coastal groundwater levels, climate variations or sea-level fluctuations, among others (Werner et al., 2013). In many coastal hydrogeological settings, seawater intrusion occurs normally due to overexploitation of freshwater resources. As a result, the lowering of the water table level allows the sea water intrusion that progressively causes the salinization of the aquifer, which may become inappropriate for drinking and agricultural use. Groundwater salinization induced by seawater intrusion is generally regarded to be practically irreversible and leads to the complete degradation of freshwater reservoirs. During the last decades, considerable research efforts have been performed, in economically developed regions, to improve the knowledge about seawater intrusion occurrence and timing (Russak and Sivan, 2010; Ferguson and Gleeson, 2012; Werner et al., 2013; Lu and Werner, 2013).

Coastal aquifers provide a water source for more than one billion people in the world living in coastal regions (Small & Nicholls, 2003). The population growth in most of the coastal areas and the increase of water demand make seawater intrusion a global threat.

Ischia Island is an active volcano located in southern Italy, hosting a geothermal system. The groundwater system of Ischia consists of several permeable aquifers, interbedded with low-permeability levels (Celico et al., 1999). In natural conditions, the Ischia’s aquifers are recharged by rainfall with a variable contribution of deep hydrothermal fluids (Di Napoli et al., 2009; Piscopo et al., 2020). Due to this interplay, many thermal springs are present on the island.

The thermal waters were known and used from the Roman age, but during the last thirty years the growing spas-related touristic activity, representing the main economic income of the island, encouraged the drilling of pumping wells to obtain a constant thermal water flow rate.

Nowadays, more than 200 spas are operating at Ischia Island, most of them located near the coast. As a consequence of the intensive groundwater pumping, it is known that seawater intrusion is present in the volcanic rock aquifer of the island (Corniello et al., 1994). The hydrogeological setting of Ischia Island is complex due to geological and structural factors, as well as human activities that have deeply changed the groundwater flow circulation. Ischia Island is characterized by the main groundwater body lying above sea level and in natural conditions groundwater flows towards the sea (Celico et al., 1999; Ducci and Sellerino, 2012).

Numerous studies have been focused on the hydrothermal system of the island, focusing on thermal fluids composition and origin, providing important information for geothermal energy exploration and volcanic risk assessment. These studies allowed refining knowledge on hydrothermal fluid circulation (De Gennaro et al., 1984; Panichi et al., 1992; Caliro et al., 1999; Celico et al., 1999a; Inguaggiato et al., 2000; Lima et al., 2003; Chiodini et al., 2004; Daniele, 2004; Milano et al., 2004; Aiuppa et al., 2006; Morell et al., 2008; Di Napoli et al., 2009; 2011; 2013; Carlino et al., 2012; 2015).

On the other hand, the groundwater system, presenting a wide range of chemical compositions (from calcium-bicarbonate to alkali-chloride waters), has been previously explained by a mixing process among meteoric water, seawater and deep geothermal fluids (De Gennaro et al. 1984; Panichi et al. 1992; Aiuppa et al. 2006; Di Napoli et al. 2009). Despite these fundamental advances, the hydrogeochemical processes governing the groundwater composition and the magnitude and extension of the saline intrusion process in the island are still unknown. (Corniello et al., 1994; Di Napoli et al., 2009; Piscopo et al., 2020).

The main goals of this paper are: a) to assess the hydrogeochemical processes, as water-rock interaction and deep fluids input in the Ischia groundwater; and b) to estimate the extension and magnitude of saltwater contribution in the Ischia aquifer system.

The results of this study provide critical information for programming upcoming sustainable management strategies for Ischia water resources and represent essential knowledge for future groundwater studies and environmental decisions. Furthermore, considering the growing interest in geothermal energy exploitation in the island, improving the aquifer comprehension and its physicochemical processes, acquires particular relevance in this social and hydrogeological context.

2. The study area

Ischia Island is the westernmost active volcanic complex of the Campania region and belongs to the Phlegrean volcanic district of Southern Italy (Fig. 1) (Carlino et al., 2012; Troise et al., 2019). The local geology is composed of landslide deposits, marine sediments and volcanic rocks, represented by alkali-trachytes, trachybasalt, latites and phonolites, reflecting a complicated sequence of alternating constructive and destructive volcano-tectonic, erosion and sedimentation phases (Vezzoli, 1988; Orsi et al., 1991; Tibaldi and Vezzoli, 1997). Although the island (~45 k~~K~~m^2) is dominated by the structural block of Mount Epomeo (786 m a.s.l.), several volcanic structures are still present, such as the rim of a caldera (~55 ka BP), partially recognizable (Carlino et al., 2014). Ischia is an active volcano, indicated by the occurring of historical eruptions (Vezzoli, 1988), intense and diffuse hydrothermal features (Chiodini et al., 2004), and seismic activity (Luongo et al., 1987; De Natale et al., 2019, Nappi et al., 2021). Ischia volcanic historical activity dates approximately 150 ka BP and it is characterized by lava domes and hydromagmatic eruptions. The largest-scale volcanic event is the alkali-trachytic ignimbrite eruption of Mt. Epomeo Green Tuff (MEGT), which caused the caldera collapse (~55 ka BP) that partially destroyed the previous eruptive history of the island and marks the transition between volcanic cycle phases (Vezzoli, 1988; Orsi et al., 1991; Tibaldi and Vezzoli, 1998). The volcanic cycle of the island consists in two phases, the first one mainly characterized by pyroclastic activity and the second one by a lava dome emplacement (Carlino et al., 2006). During the second cycle, as a result of the caldera collapse, several phreatomagmatic eruptions and strong pyroclastic activity filled the caldera with ignimbrite deposits that in turns favored the sea intrusion in the central part of the present island (Vezzoli, 1988). Carlino et al. (2006) proposed that a laccolith (10 km large and up to 1 km deep) in the center of the island triggered the caldera resurgence (~33 ka BP) after the Mount Epomeo Green Tuff (MEGT) eruption. The tectonic deformation cutting the oldest volcanic rock, part of the seismic activity and the widespread landslides have been associated with the Mt. Epomeo block uplift (Tibaldi and Vezzoli, 1997; Tibaldi and Vezzoli, 1998; Tibaldi and Vezzoli, 2004; Chiocci and de Alteriis, 2006; Capuano et al., 2015), resulting in the horst of Mt. Epomeo, in the central part of the island, while the east side is dominated by a graben structure. The uplift of Mt. Epomeo has also been explained by different mechanical and geophysical models, most of them involving a shallow magma body as the source of deformation, together with local tectonics, high geothermal gradients and volcanism (Vezzoli, 1988; Fusi et al., 1990; Orsi et al., 1991; Acocella et al., 1997; Cubellis and Luongo, 1998; Acocella and Funiciello, 1999; Molin et al., 2003; Tibaldi and Vezzoli, 2004; Carlino et al., 2006; Carlino, 2012). De Martino et al. (2011) and Del Gaudio et al. (2011) reported present-day subsidence, especially in the areas with active landsliding and faulting (Manzo et al., 2006).

The geothermal system of Ischia has been the subject of several investigations. De Gennaro et al. (1984) proposed a geothermal model where the deep source of fluids is represented by a large magmatic body located at a depth greater than 3000 m and with a temperature over 200 °C. Carapezza et al. (1988) suggested the existence of two intermediate magmatic systems, and Panichi et al. (1992) estimated the temperature of the magmatic reservoir in the range of 160–240 °C. Inguaggiato et al. (2000) concluded the existence of a magmatic reservoir liquid dominated at 280

°C, supported by carbon isotope data. However, the authors do not discard the possibility of the existence of a second magma body (more than 4 km deep), as suggested by Tedesco (1996). Recently, Di Napoli et al. (2009; 2011), based on studies from integrated geophysical (electrical resistivity) and geochemical properties (CO_2, TDS in thermal springs) infer that the circulation of the hydrothermal fluids, in the south-west of the island, takes place within two overlapped and different geothermal reservoirs. These reservoirs are localized at a depth of ~200 and ~1000 m with temperatures of ~150 ºC and ~270 ºC, respectively, and are connected through fractures generated by the resurgence. Carlino et al. (2014) made a critical review of the geothermal system of Ischia Island and concluded that the geothermal system is vapor dominated and related to the intrusion of a shallow magma body, occurred after the MEGT eruption (55 ka BP), whose top is migrated up to about 2 km depth. Carlino et al. (2014) proposed that the two shallow geothermal reservoirs may be geologically separated. The first one is supposed to be located in the western sector at depths between 150 m to at least 600 m, with a temperature ranging between 150 °C and 200 °C, and pressure of about 4 MPa (40 bar). The second, deeper reservoir is hypothesized to be at depth >900 m, with a temperature between 270 to 300 °C and pressure of 9 MPa (90 bar). All the authors agree that the geothermal system of Ischia is fed by meteoric water, seawater and hydrothermal fluids.

The hydrogeological setting of Ischia Island is highly complex due to both geological and structural features, and human activities that have deeply changed the territory and influenced the groundwater flow circulation. The groundwater system of Ischia consists of several permeable horizons (fracturation and/or porosity), interbedded with low-permeability levels (Celico et al., 1999). This composite system reflects the contrasting lithologies and geometries of the volcanic deposits, the pervasive hydrothermal circulation with the consequent self-sealing processes, and the complex volcano-tectonic and gravitational events that occurred over time (Celico et al. 1999; Di Napoli et al., 2009). Ischia Island is characterized by the main groundwater body lying above sea level and in natural conditions groundwater flows towards the sea (Celico et al., 1999; Ducci and Sellerino, 2012).

According to Celico et al. (1999) and Carlino et al. (2014), two different hydraulic areas can be identified (Fig. 2): the first one is the graben in the northeast of the island, which is highly transmissive and can be pictured as a single aquifer fed by meteoric waters and seawater ingression; the other area is Mount Epomeo and its border zone, which is intensively fractured and consists of very heterogeneous materials forming complex geometries that mainly affects the vertical component of groundwater flow. The hydrogeology reflects the complex tectonics and lithology settings and suggests the presence of a multilayer aquifer (Celico et al., 1999).

Variations in the chemical composition and temperature of the groundwater are related to the complex hydrogeological setting. Groundwater circulating in the shallow aquifer has temperatures up to boiling, and ranges in composition from diluted bicarbonate waters to more saline and chlorine-rich waters, interpreted as evidence of dual (meteoric and seawater) recharge to the aquifer (Panichi et al., 1992; Inguaggiato et al., 2000; Aiuppa et al., 2006; Di Napoli et al., 2009; Di Napoli et al., 2013). There are also several fresh springs in the higher and inner part of the island and their discharge is usually 1-3 l/s (Celico et al., 1999; Carlino et al., 2014).

3. Materials and Methods

A total of 69 samples, retrieved from 56 boreholes less than 100 m deep, 11 thermal springs and 2 cold springs, were collected during the period 1999 – 2000 (Fig. 2). It is important to remark that some of the data used in this paper have been already published in previous works (Lima et al., 2003; Daniele, 2004). The wells were pumped for at least 30 min before the samples were taken and electrical conductivity, pH, and water temperature were measured in situ. The samples were filtered using 0.45 µm Millipore® membranes in double-capped, polyethene bottles of 100 ml volume and stored at 4°C. Samples for cations and trace elements analysis were also acidified to 1% with pure nitric acid. The analytical procedure is detailed in previously published works (Lima et al., 2003; Daniele, 2004). The samples labelled as SW and FW represent the end-members for seawater and freshwater, respectively and are used to calculate the saline factor in each groundwater sample. The SW sample proceeds from Morell et al., 2008, FW is a low-chlorine water sample, selected among the 2001 cold temperature samples and presenting the lowest EC.

Table 1 summarizes the ionic composition of the sampled waters. The following variables were considered in this work: Cl, Na, K, Ca, Mg, Br, Si, B, Sr, Li, Mo, W, T°, E.C. and pH.

The seawater content (fsea) for each sample was calculated using the ionic deviation from a conservative seawater–freshwater mixture, assuming Cl to be a conservative tracer:

$$fsea = (C_{Cl,sample} - C_{Cl,f})/(C_{Cl,sea} - C_{Cl,f}) \times 100 \quad (1)$$

where $C_{Cl,\ sample}$ represents the Cl concentration of the sample, $C_{Cl,f}$ the freshwater Cl concentration and $C_{Cl,sea}$ the seawater Cl concentration. These values were compared with seawater fraction for the period 2002-2007, fsea (2002- 2007), calculated using the water chemistry data published by Di Napoli et al. (2009).

The statistical analyses used in this study are multivariate methods, which provide several venues for exploratory assessment of water quality data sets. Water chemistry is subject to complex interactions, whose impacts may be impossible to isolate and to study individually.

In this study, using the IBM SPSS Statistics Software V26 we performed the factorial analysis (FA), over the same database of water chemical analysis. FA is a useful method, largely used in hydrogeological studies (Moeck et al., 2016; Negri et al., 2018; Taucare et al., 2020; Daniele et al., 2013, 2020). Factors were extracted from the correlation matrix of the variables using the

Principal Component Analysis (PCA) method. The selected factors have eigenvalues higher than one and were subsequently rotated orthogonally using the quartimax method to minimize the number of factors needed to explain each variable. The variable weights in each factor are relevant if it is >0.50. The variance of the geochemical variables has been determined by the KMO test (Kayser, 1960) whose value of 0.81 ensures the quality of the FA in this study. In addition, this method also allows us to calculate the factor score, which represents the intensity of the factor on each sample.

4. Results and Discussion

Ischia groundwaters present a wide range of physicochemical parameters that vary from diluted cold waters (e.g., #44 and #69) to highly saline boiling waters (e.g., #48). Water temperature ranges between 11.0 °C and 99.5 °C, with the highest values registered in the western part of the island (Fig. 3), and pH values vary from slightly acidic to alkaline values, between 4.3 to 8.8. Electrical conductivity varies from 1.3 mS/cm to 52.7 mS/cm, with the minimum value recorded in cold spring (#44) in the south part of the island and far from the coastline, and the maximum value measured in a high-temperature spring (#48), 100 m far from the coast. Despite that, a linear correlation between T and EC is absent. In general, more saline samples are located close to the coastline (Fig. 3).

The chemical composition of water samples is largely dominated by Cl and Na, followed in decreasing order by K, Mg, Ca, Br, B, Sr, Li and W. Chloride shows a poor correlation with temperature and its maximum concentrations are located along the coastal areas (Fig. 4a and b). Cl contents are mainly related to seawater contribution to the Ischia groundwater system, in agreement with Di Napoli et al., (2012).

Figure 5 shows binary plots of major and minor ions versus Cl. The positive correlations of

Na, K, ~~and~~ Br and B with Cl (Figs. 5a, b, e), lying on the theoretical FW-SW mixing line, suggest a common origin for these chemical species, mainly related to seawater intrusion. The B concentration of the SW sample~~of SW sample~~ is slightly higher than mean values in seawater (4.5 mg/l; Morell et al., 2008), but this value agrees with the average value of 5.1 mg/l calculated by Gofiantini et al. (2003) for the Mediterranean Sea. The Sr contents of the seawater sample (4.8 mg/l), already published in Morell et al. (2008), is lower than Sr concentrations measured in the mediterranean sea (8.4 mg/l; Daniele et al., 2011). The FW sample presents relatively high Sr, Ca and Mg values of 0.57 mg/l, 86 mg/l and 16.8 mg/l. Strontium follows a similar trend of Mg and Ca and presents positive correlation with Cl (fig. 5c, d, h), according to a Sr, Ca and Mg origin mainly related to carbonate dissolution and water-rock interaction (Musgrove, 2021).

On the other hand~~, B and~~ Li (Figs. 5f, g,) presenting a poor correlation with Cl, diverges from the theoretical mixing curve, showing values higher than the SW end-member, and suggest an origin for Li~~these elements~~ that could be related to the mixing between FW and a hydrothermal endmember (Aiuppa et al., 2006; Morell et al., 2008).

4.1 Seawater intrusion

To quantify the seawater contribution in the chemical composition of each sample, the seawater fraction (fsea) was calculated. This method is considered ~~a~~ valid ~~one~~, since Cl is a conservative tracer, and his concentration in Ischia waters is mainly due to marine origin (Di Napoli et al., 2012), mostly related to seawater intrusion and subordinate marine aerosol. The calculated values range from <1% to 70%, with most of them being <10%. The spatial distribution (Fig. 6a) shows high values (>10% wt) toward the coast, with particularly high values (>60% wt) along the western portion of the island (Lacco, Citara, St. Angelo), indicating the presence of water of marine origin. Towards the central part of the island the values are generally lower than 2%, indicating that the phenomenon of seawater intrusion is almost absent. In Lacco and Citara, the high variability of fsea values in sampled wells suggests a complex hydrogeological setting, where the aquifer may be controlled by an irregular fracture network, forming overlapped aquifer (multilayer) or perched aquifer (impermeable layer) that can exert a strong control on the seawater intrusion.

Figure 6b and c shows the fsea values calculated with water samples collected between 2002-2007, based on the work of Di Napoli et al. (2009). To have a direct comparison, in Figure 6b, the fsea was calculated with the samples from Di Napoli et al. (2009) collected in the same wells of the present work. In Figure 6c, we calculated the fsea with all the samples from Di Napoli et al. (2009). Comparing the time variation of the seawater intrusion, calculations indicate an increase all along the coast, with fsea values up to 93%, while lower values are maintained towards the center of the island, indicating that the saline intrusion has not extended inland during about 10 years. The increasing over pumping in wells near the coastline, where most of the spas and thermal wells are located, has enhanced the saltwater intrusion in the island. On the other hand, the aquifer geometry controlled by the fault-fracture meshes, and maybe the intense withdrawal near the coastline have limited the intrusion to the coastal areas, preventing the saltwater from reaching the inner part of the island. The input of cold seawater has not generated any changes in water temperatures as shown in Figure 6, where our data are compared with data from Di Napoli et al. (2009), indicating a thermal system highly active.

4.2 Factorial Analysis

The use of the multivariate geostatistical methods is common in hydrogeochemical studies (Join et al., 1997; Meng and Maynard, 2001; Swanson et al., 2001; Cruz et al., 2006; Daniele et al., 2008), being a reliable tool to unravel the relationship among the whole group of variables. This helps to obtain a more complete hydrogeochemical interpretation of the controlling processes or the origin of the single variables. The Factorial Analysis (FA) is a statistical method used to underlie the interrelationship between the variables and to infer the geochemical processes controlling the water chemistry.

A total of three principal factors were extracted (Figure 7), with eigenvalues greater than 1, explaining 84% of the total variance. Variables with loadings near to 1 form the factor, while near to 0 they don't form the factor.

Factor 1 (F1) accounts for 52% of the total variance, being the most relevant factor in the composition of these waters. It has positive loading values for Cl, Na, K, Mg, Ca, Br, Sr, with moderate positive loadings for B and Li. These variables, responsible for the major percentage of the observed chemistry, can be associated with the seawater intrusion process (Daniele, 2007; Daniele et al., 2008; Panda et al., 2006; Morell et al., 2008).

Factor 2 (F2) accounts for 18% of the total variance and shows fairly positive loadings for T° (C), Si, Mo and W. Silica, Mo and W are usually related to either uptake by secondary minerals or non-stoichiometric dissolution of primary rocks. Their alteration minerals have not been identified in the geothermal surface environments in Ischia, but Mo and W have been found associated with sulfides and (hydr)oxides elsewhere, in wells scales and subsurface alteration (Kaasalainen and Stefánsson, 2012). The processes influencing the geochemistry of Mo and W in geothermal waters can be related to water-rock interaction and mixing between condensed steam and non-thermal surface waters.

Factor 3 (F3) accounts for 14% of the total variance and shows fairly positive loading for Li, B and K. Boron is considered to be a highly mobile element and a good indicator of rock leaching in geothermal waters (Arnórsson and Andrésdóttir, 1995). Also, B may be transported by ascending steam (Morell et al., 2008; Kaasalainen and Stefánsson, 2012) and the B enrichment in geothermal waters may be the result of its close proximity to the magmatic source and the absorption of magmatic vapors rich in B in non-thermal surface waters (Kaasalainen and Stefánsson, 2012; Wrage et al., 2017 and references therein). Lithium and K are considered to be dominated by water-rock interaction processes and to a lesser extent to mixing between condensed steam and non-thermal surface waters (Markússon and Stefánsson, 2011; Kaasalainen and Stefánsson, 2012). Aqueous concentrations of these elements are considered to be controlled by the equilibrium of thermal waters with aluminum silicates such as K-feldspar, zeolites and clays (Stefánsson and Arnórsson, 2000). Pure alkali minerals are not common, but these elements are more commonly incorporated into major secondary minerals like clays, zeolites, and feldspar as well as Li into quartz (Goguel, 1983).

Also, B, Li and K may have a marine origin and are considered a tracer for seawater intrusion assessment (Sanchez-Martos et al., 1999). The variables present similar loadings in F1 and F3, suggesting that both seawater and hydrothermal contribution may be reasonable for K, B and Li in Ischia waters.

According to our interpretation, samples with high saline factors have positive F1 values, suggesting that seawater intrusion is the main hydrogeochemical process. Nevertheless, some of these samples also show positive factor scoring for F2 and F3, indicating the existence and superposition of different geochemical processes in the analyzed samples. Samples #43, #64 and #65 show a highly positive factor scoring for F3, and also for F1, indicating superposition of processes for these samples.

Other samples show negative F1 values, indicating low or no seawater influence. These samples present positive factor scoring for F2, indicating a hydrothermal influence from the active geothermal reservoir. Finally, we obtained the spatial distribution of the factor scoring of each sample, using the inverse weighted distance interpolation. The method assumes that each measured value has local influences diminishing with the distance. The absence of data in the central and southeast parts of the island has to be considered in the obtained spatial distribution. The distribution maps represent a synthesis of the physicochemical processes identified at the Ischia Island geothermal system.

The F1 spatial distribution (Figure 7a), associated with the seawater intrusion process, presented positive scoring along the coastline (north, center and south) of the western Ischia sector and the north-east coastline, with the highest value in the western area. Towards inland, and in the south-east (Forio), F1 presents negative scores, according to the fact that seawater intrusion moves from the coast toward inland, with a limited extension. The spatial distribution of F2 (Figure 7b), associated with the hydrothermal water-rock interaction and mixing of deep geothermal fluids with meteoric recharge, presents positive scoring from Mt. Epomeo towards the north (Casamicciola) and south-west (south Citara and St. Angelo), far from the coast, associated with fracture systems and the deepest faults delimiting Mt. Epomeo. The F3 spatial distributions (Figure 7c), associated with superposition of processes, show a high intensity at the coastal fracture system at north-west (Lacco), where the deep fluids rise (enhancing water volcanic/saline rock interaction) and mix with superficial recharge waters, meteoric and seawater. This location also presents a high intensity for F1, corroborating the superposition of processes in that zone. Forio coastal area shows negative scoring for all factors, indicating that these waters have not been significantly affected by the processes just mentioned, due to scarce hydraulic connection, or waters just infiltrated, hosted in perched or small confined aquifers.

5. Conclusions

The Ischia hydrothermal system is characterized by a great complexity in its geometry, fluid circulation and hydrogeochemical processes which is reflected in the vast physicochemical heterogeneity of the waters. The low correlation between Cl and temperature indicates that the Cl origin is mainly related to seawater. Also, its spatial distribution shows higher concentrations towards coastal zones diminishing towards inland, being the marine source (seawater intrusion) the most likely origin. Considering a conservative mixture between FW and SW, most of the ionic concentrations deviate from this theoretical mix line, showing enrichment in B, Li and depletion in Mg, Ca and Sr due to ionic exchange processes, water-rock interaction and mixing with deep hydrothermal fluids. The water-rock interaction process is enhanced by the high temperature of the system that allows the dissolution of volcanic rock minerals and the precipitation of secondary minerals, such as calcite and other carbonates.

The statistical and geostatistical methods used allowed us to identify different hydrogeochemical processes in the Ischia groundwater. Seawater intrusion, for the first time quantified in the Ischia groundwaters by this study, water-rock interaction, and deep fluid mixing processes are present. The calculated saline factor rises up to 69.6% in samples collected near the coastline. Results indicate that the determined processes act with different intensity and are superimposed in most of the analyzed waters, with clear spatial distribution. Each sample presents a dominant process, and we assess three main water types based on identified hydrogeochemical processes.

The Ischia groundwater system is fed by meteoric recharge and the water samples with neutral pH, low E.C, temperature and saline factor, with low or no interaction with the hydrothermal system and seawater intrusion can be considered as FW proceeding from this process.

Waters with low to moderate salinity, with Cl content less than 2000 mg/l, Br lower than 11,47 mg/l and lower Ca and Mg concentrations, show B and Li content and higher concentrations of Si, Mo and W compared with the rest of the samples. Their temperature ranges widely from 15,8°C to 77,4°C. The dominant processes in these samples are the hydrothermal water-rock interaction and the mixing of deep-seated fluids.

Finally, the last water type is formed by samples with high Cl > 15733 mg/l and Br [17,3 – 90,9 mg/l] content, but with the lowest concentrations of Si, Mo and W. The temperature is generally high [43.3 – 99.5°C]. The dominant geochemical process in this group is the seawater intrusion (i.e., high fsea).

The factorial analysis corroborates these results and suggests that the main physicochemical process in the analyzed samples is the seawater intrusion. The F1, which explains most of the data variability, has been interpreted as the seawater intrusion factor, and positive scores are associated with the coastal zone samples. The deep fluids and water-rock interaction processes (F2 and F3) are less responsible for the water chemistry of the Ischia Island. Samples along fractured zones, associated with lower salinity water (north and south-west zones) show the highest scores of F2 and F3, except for the Punta Caruso-Lacco area. Here seawater and deep fluids overlap in sampled chemistry water. This distribution of the hydrogeochemical processes reveals a highly complex hydrogeological scenario, with waters highly different in the composition being collected very close due to strong control played by fractures and faults.

The complex lithological/structural system indicates that towards the center of the island the principal groundwater source is the meteoric recharge, which infiltrates to deeper levels where a mixture with hot fluids occurs. The groundwater flows towards the coast where seawater intrusion occurs due to boreholes pumping. The water-rock interaction (precipitation/dilution) is enhanced by high temperature in fractures, and towards the coast where the seawater intrusion promotes the ionic exchange process.

From a temporal point of view, the samples from Di Napoli et al. (2007) establish that the seawater intrusion has increased over time all along the coastline reaching values up to 90%. While low values of fsea continue in the central part of the island. Despite this extra input of cold seawater, the temperature of the system is stable, at high temperatures, suggesting a very efficient heat transport in this active geothermal system.

Acknowledgements

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Figure Captions

Figure 1. Structural and geological map of Ischia Island. Modified from Paoletti et al. (2015); Nocentini et al. (2015) and Lima et al. (2003).

Figure 2. Hydrological zonation of Ischia Island, modified from Celico et al. (1999). Blue squares and circles represent the locations of sampled springs and boreholes, respectively. Blue stars SW and FW identify the sample location of the reference seawater and groundwater samples, respectively.

Figure 3. Spatial distribution of sample temperatures (colors) and electric conductivity (size) in the area of study.

Figure 4. Linear correlation (a) and spatial distribution (b) of temperature and chloride contents in water samples from Ischia Island.

Figure 5. Chloride contents versus elemental concentrations of Na (a), K (b), Ca (c), Mg (d), Br (e), B (f), Li (g) and Sr (h) for the springs (blue square) and borehole (blue circles) samples of Ischia Island. SW and FW end-members are also reported.

Figure 6. Spatial distribution of saline factor calculated with data from this work (a) and from Di Napoli et al. (2009) (b and c). In Figure 6b are presented the fsea calculated with only the samples from Di Napoli et al. (2009) collected in the same wells of the present work. In Figure 6c, the fsea are calculated with all samples from Di Napoli et al. (2009).

Figure 7. Spatial distribution of calculated factors F1 (a), F2 (b) and F3 (c) scoring for each sample.

Highlights

- Seawater intrusion has been quantified for the first time in the Ischia groundwaters
- Chlorine origin in Ischia waters is mainly related to seawater intrusion
- Water-rock interaction processes are less responsible for the groundwater chemistry
- The seawater intrusion has increased over time all along the coastline

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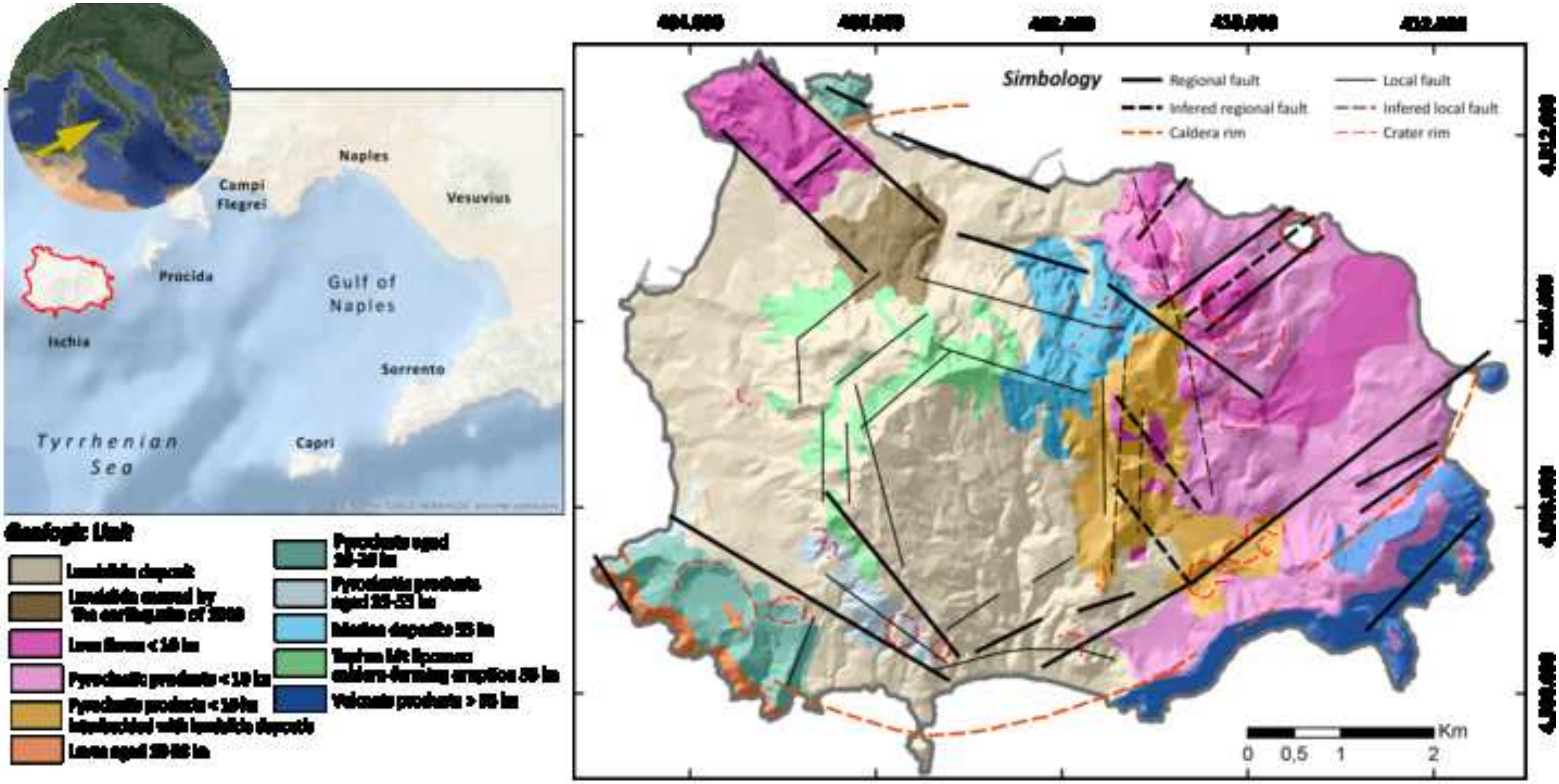

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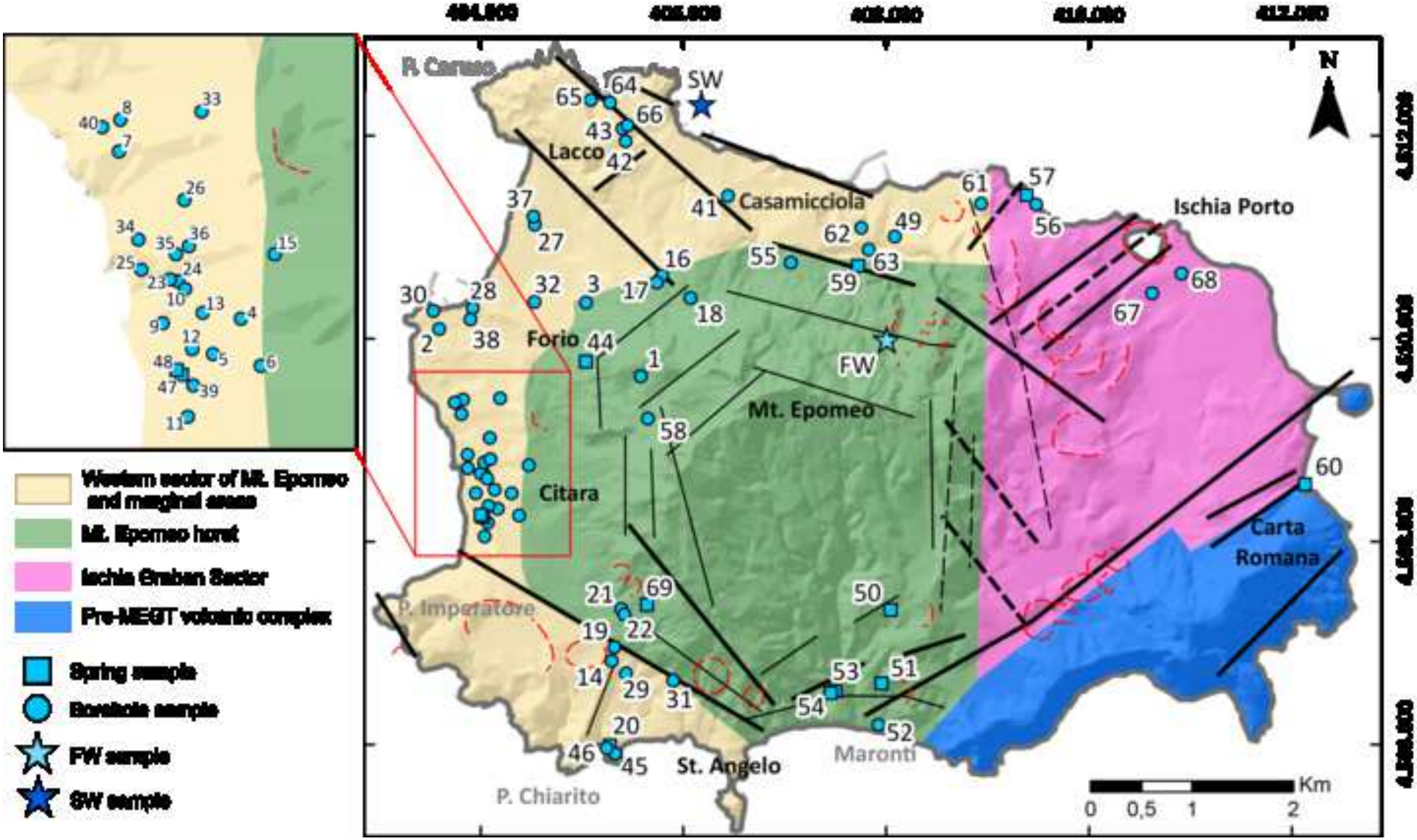

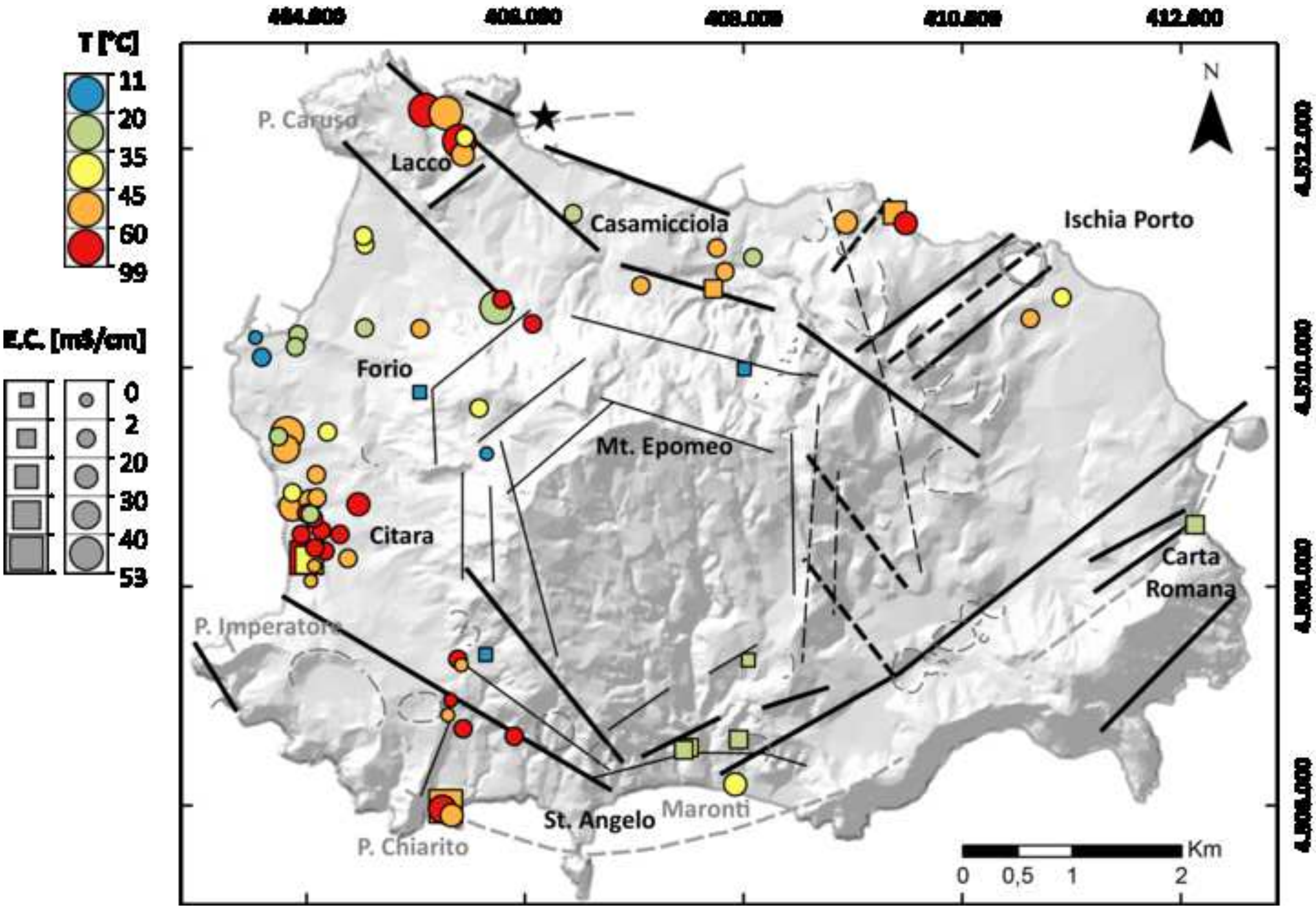
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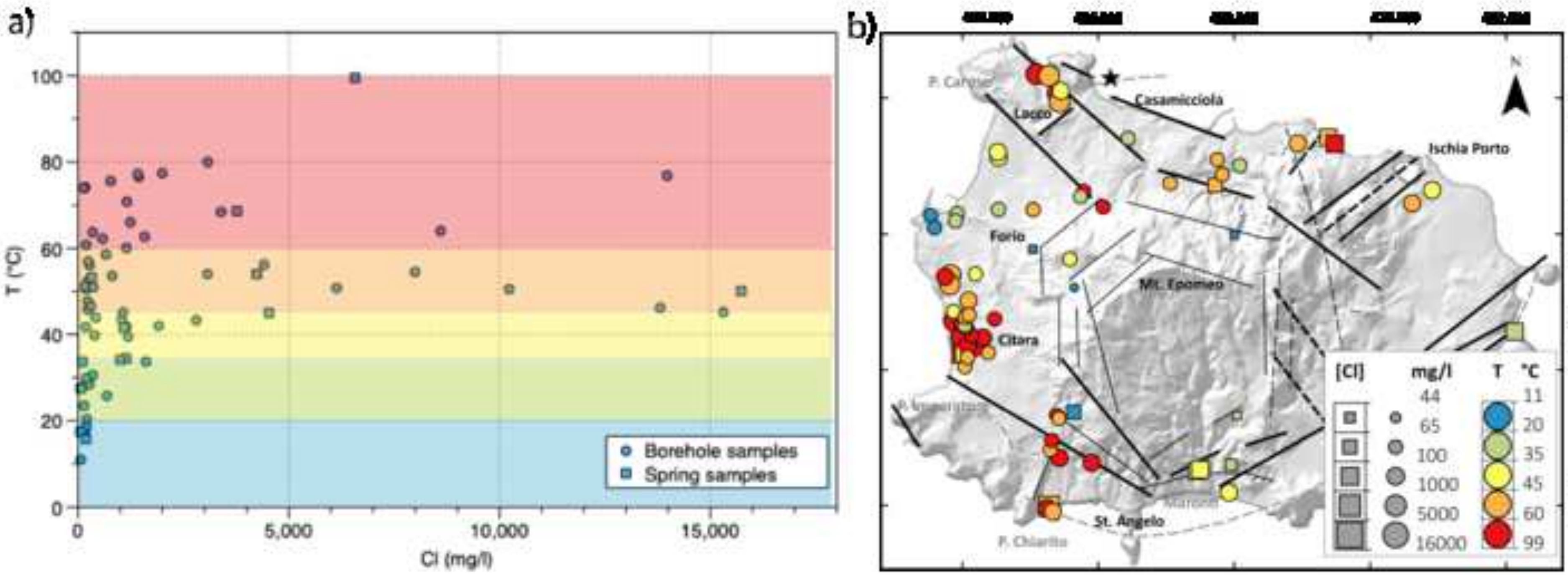

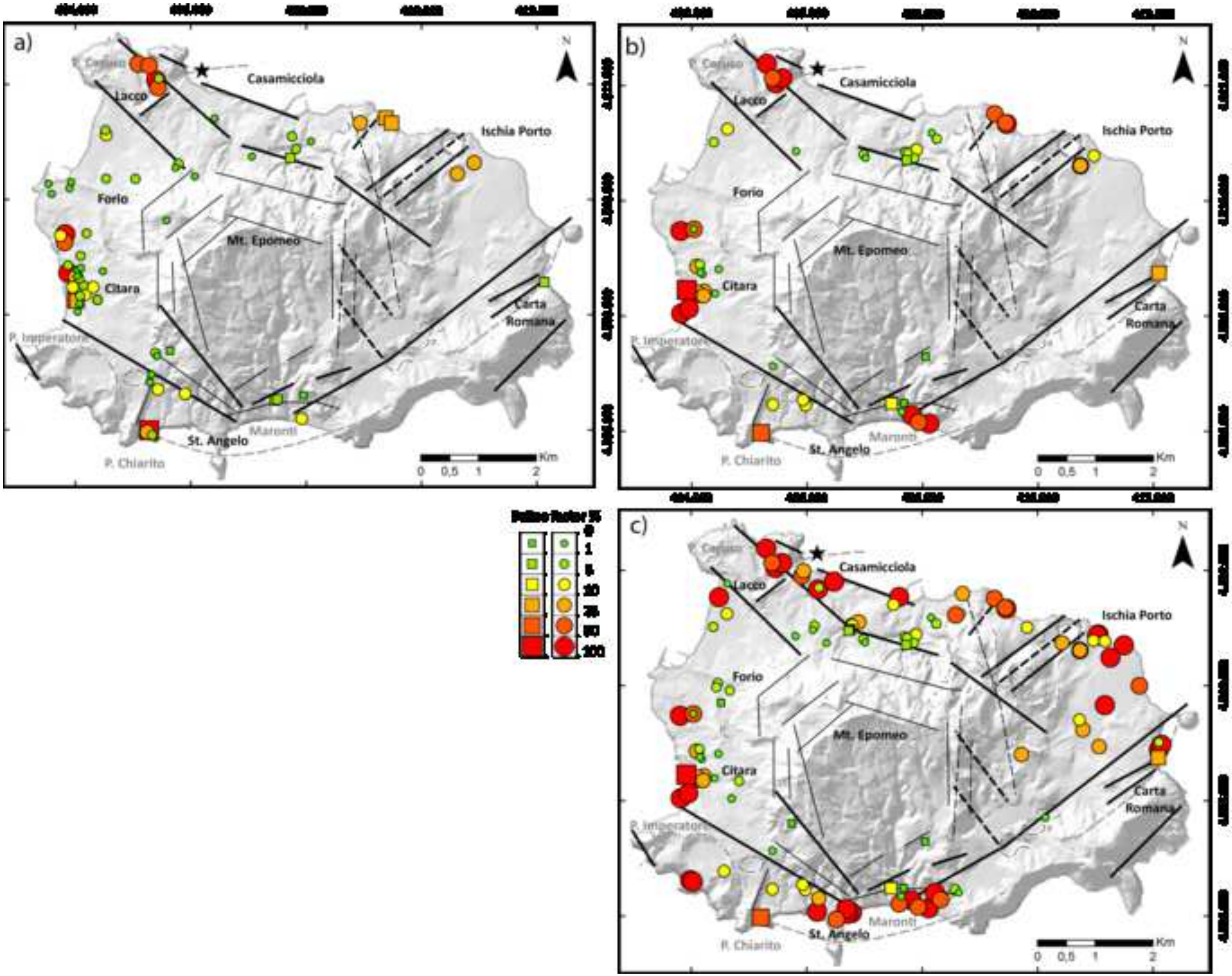
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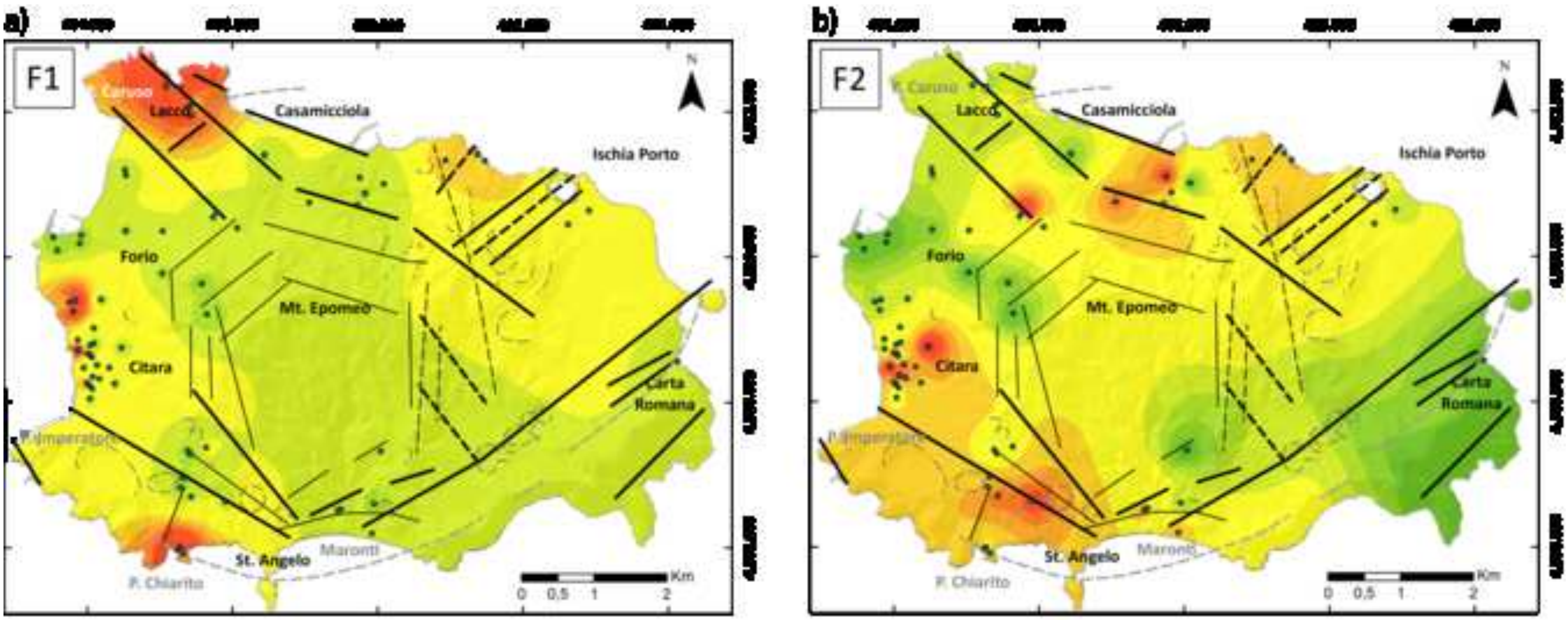
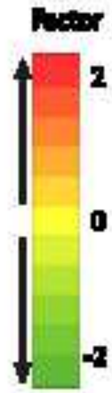
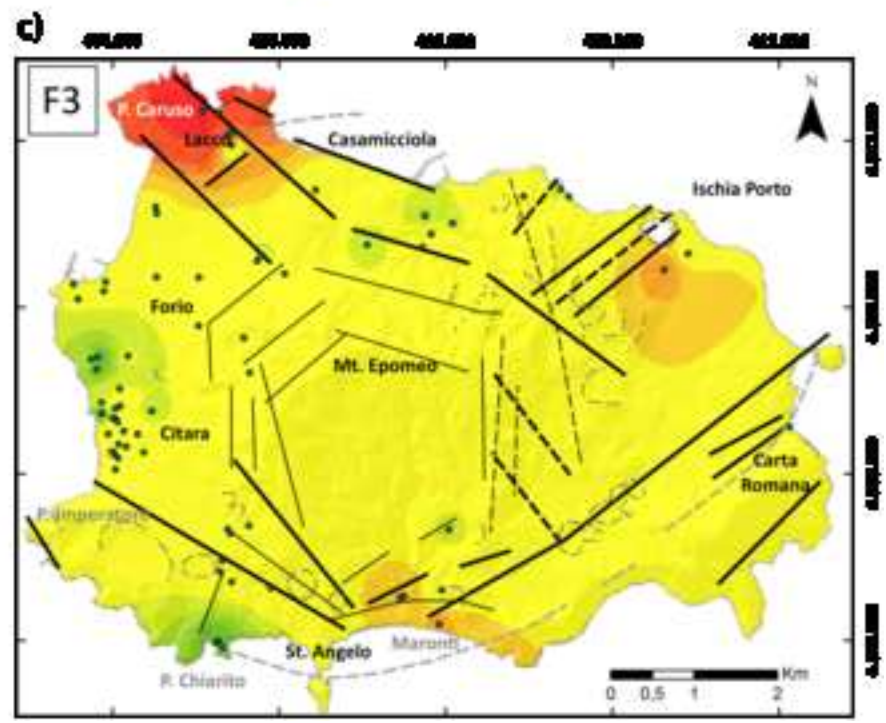


	Component		
	F1	F2	F3
T°	0,22	0,78	0,17
Cl	0,98	-0,02	0,00
Na	0,95	0,03	0,10
K	0,78	0,01	0,57
Mg	0,95	-0,11	-0,13
Ca	0,98	-0,16	-0,08
B	0,53	0,10	0,73
Br	0,98	-0,02	0,05
Sr	0,91	-0,08	0,22
Li	0,49	0,03	0,84
Si	-0,19	0,75	0,22
Mo	-0,17	0,71	-0,15
W	-0,16	0,78	-0,06
Total	6,72	2,34	1,81
% of Var	51,70	17,98	13,91
Cum %	51,70	69,68	83,59





Figure

Click here to access/download;Figure;Figure 5.png

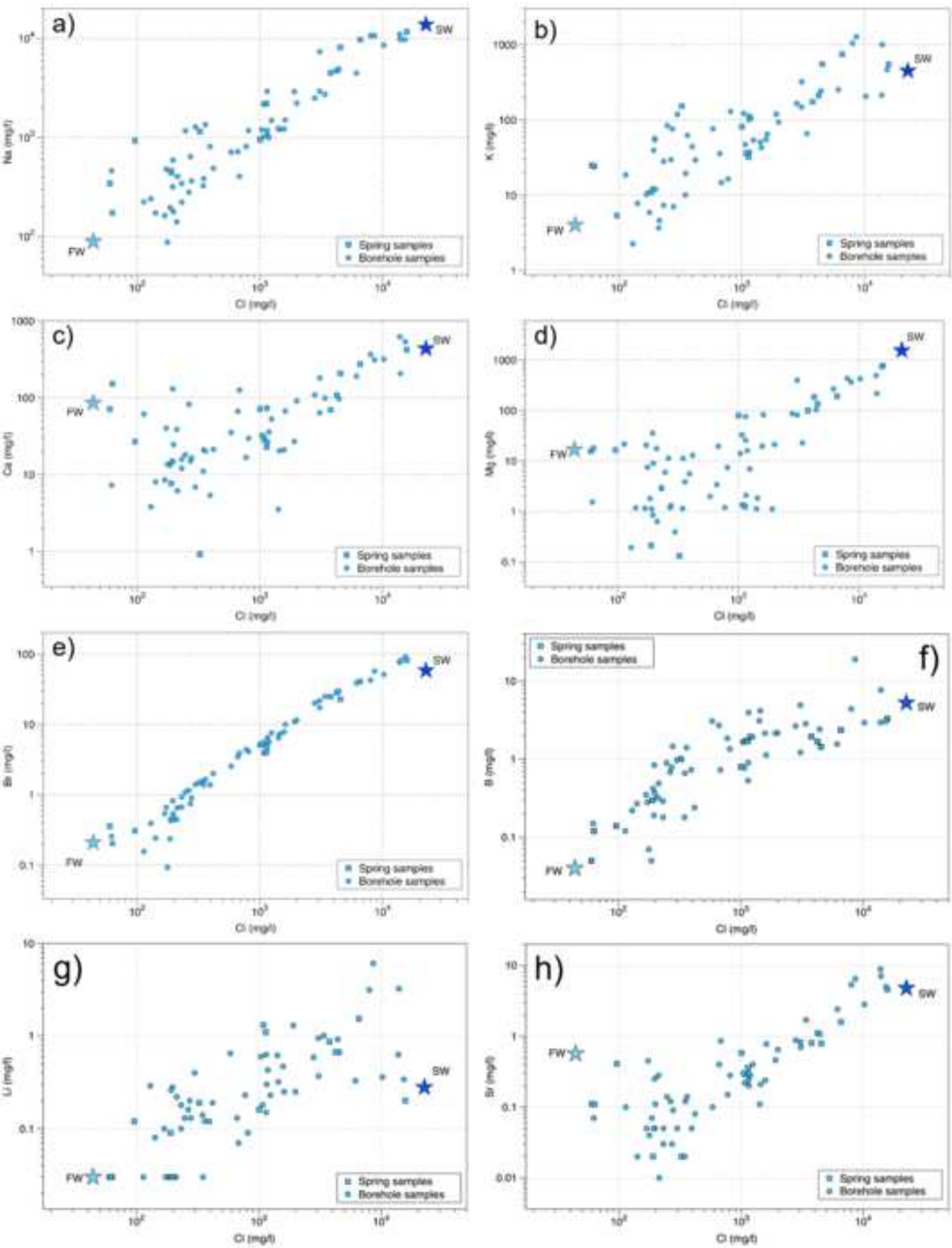


Table 1. Ions concentration in water samples from Ischia Island.

Sample ID		E	N	T	ph	EC	Cl	Na
		UTM WGS84 33N		°C	-	mS/cm	mg/l	mg/l
SW		406181	4512306	26.4	8.2	56.9	22561	13848
FW		408006	4509988	19	7.5	0.65	44	89
1	Well	405580	4509630	41.7	7.3	15.9	186	196
2	Well	403590	4510096	18.0	7.6	7.6	177	88
3	Well	405040	4510357	53.6	7.1	9.1	811	1180
4	Well	404306	4508476	66	6.3	12	1245	1490
5	Well	404170	4508323	77.4	6.6	18.5	1997	2228
6	Well	404380	4508255	58.5	6.4	6.6	662	721
7	Well	403811	4509258	50.5	7.2	37.9	10228	8580
8	Well	403827	4509399	46.2	7.0	45.2	13812	11000
9	Well	403954	4508476	76.5	7.5	8.9	1444	1212
10	Well	404035	4508659	56	7.1	2.7	272	642
11	Well	404038	4508049	53	7.1	2	278	366
12	Well	404078	4508351	70.8	7.2	8.4	1157	1073
13	Well	404137	4508510	75.6	7.4	6.1	774	811
14	Well	405293	4506825	52.1	7.0	1.88	213	406
15	Well	404474	4508751	60.7	7.0	27.5	196	591
16	Well	405789	4510624	62.2	6.9	6.3	584	715
17	Well	405737	4510552	27.9	6.9	40.4	114	224
18	Well	406069	4510399	74.1	6.7	4	173	480
19	Well	405318	4506959	74	7.3	1.7	130	242
20	Hot spring	405276	4505993	50.1	7.2	45.7	15733	11700
21	Well	405387	4507335	63.7	7.3	2.2	346	325
22	Well	405418	4507281	47.7	6.9	2	231	223
23	Well	404000	4508670	68.4	6.5	16.3	3395	2736
24	Well	404065	4508622	25.8	7.1	3.56	682	407
25	Well	403875	4508722	45.2	6.3	31.2	15314	9784
26	Well	404089	4509021	45.1	7.2	7.51	1071	1022
27	Well	404534	4511123	39.5	7.6	7.65	1186	1002
28	Well	403923	4510302	20.4	7.6	14	211	141
29	Well	405432	4506700	62.7	7.5	9.2	1577	1220
30	Well	403533	4510273	18.7	7.8	1.6	198	179
31	Well	405901	4506629	77.2	7.9	9.64	1417	1242
32	Well	404531	4510362	30.6	7.8	3	349	385
33	Well	404193	4509411	39.8	7.5	4.28	394	813
34	Well	403871	4508858	43.9	7.0	4.04	419	490
35	Well	404035	4508781	45.7	7.0	26.7	231	344
36	Well	404095	4508813	50.5	7.5	3	192	466
37	Well	404521	4511204	43.4	7.5	7.5	1038	1202
38	Well	403899	4510192	23.5	7.8	12.8	142	174
39	Well	404072	4508188	51.2	7.6	1.6	168	163
40	Well	403743	4509372	33.7	7.4	10.7	1612	1506
41	Well	406440	4511407	28.5	7.4	19.1	265	281
42	Well	405430	4511947	50.8	7.0	25.5	6134	4485
43	Well	405400	4512070	76.8	6.7	46.7	13974	9763
44	Cold spring	405035	4509776	17.5	7.5	1.36	60	345
45	Well	405330	4505909	60	7.0	23	1147	2932
46	Well	405244	4505962	80	6.5	34	3077	7365
47	Hot spring	404024	4508240	45	6.0	35.9	4530	8182
48	Hot spring	404002	4508263	99.5	7.1	52.7	6571	9740
49	Well	408084	4511008	29.9	7.5	2.08	195	318
50	Hot spring	408043	4507326	27.5	6.4	1.27	63	173

51	Hot spring	407954	4506601	33.7	7.5	3.24	96	933
52	Well	407924	4506193	42	8.0	22.2	1913	2907
53	Hot spring	407499	4506528	41.6	7.8	8.33	1089	2180
54	Hot spring	407454	4506508	34.5	7.8	7.05	1138	2221
55	Well	407059	4510748	57	7.3	5.6	247	1171
56	Hot spring	409481	4511327	68.6	7.1	20.7	3771	4511
57	Hot spring	409385	4511418	54	6.9	24	4240	4732
58	Well	405649	4509211	11	8.6	1.34	62	462
59	Hot spring	407722	4510720	53.2	8.8	4.77	325	1151
60	Hot spring	412131	4508563	34.2	6.1	7.22	1005	958
61	Well	408935	4511330	56.2	7.0	20.4	4415	4924
62	Well	407755	4511094	51	7.1	5.18	361	1351
63	Well	407828	4510877	46.6	8.1	5.1	299	1283
64	Well	405275	4512328	54.5	7.1	47.9	7994	10700
65	Well	405088	4512353	64	4.3	51	8605	10700
66	Well	405449	4512103	41.8	6.1	5.38	1147	1178
67	Well	410623	4510449	54	7.6	12.5	3071	2934
68	Well	410913	4510641	43.3	6.6	9.98	2800	2504
69	Cold spring	405639	4507376	15.8	8.1	1.47	190	445

K	Ca	Mg	Br	Si	B	Sr	Li	Mo	W
mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	µg/l	µg/l
449	437	1556	58.3	b.d.	5.27	4.81	0.28	b.d.	b.d.
4	86	16.8	0.2	13.8	0.04	0.57	0.03	8.7	0.5
11	13	1.8	0.2	18.5	0.05	0.07	0.03	4.2	0.5
6	14	7.5	0.1	6.9	0.07	0.04	0.03	9.1	0.5
130	30	7.4	4.1	21.4	1.35	0.28	0.09	80	2.1
54	53	6.9	7.5	37.5	1.93	0.40	0.23	20.1	33.1
93	90	21.2	11.5	36.9	2.17	0.65	0.25	22.9	20.1
36	67	3.4	3.5	45.5	2.71	0.40	0.13	32.7	19
206	319	427	51.1	11.9	2.94	2.82	0.36	23.5	1.6
213	622	493	76.7	16.1	2.95	8.92	0.63	19.1	1
43	20	1.8	7.3	41.9	4.16	0.21	0.32	64.2	139.8
76	15	1.2	0.7	66.5	0.79	0.03	0.20	63.4	41.6
7	16	1.3	0.9	42.8	1.46	0.09	0.13	16.2	11.9
38	27	2.1	6.5	34	3.95	0.20	0.30	53.3	127.6
16	17	1.2	4.4	40	1.85	0.15	0.23	41.8	63.9
5	6	0.6	0.7	64.2	0.49	0.01	0.22	17.2	21
55	15	0.8	0.5	79.7	0.84	0.05	0.28	156.3	87.6
76	35	2.0	2.5	52.7	3.08	0.10	0.65	203.4	73.6
19	61	21.5	0.2	22.6	0.12	0.10	0.03	2.9	0.3
11	40	20.6	0.7	33.3	0.28	0.45	0.03	14.1	1.5
2	4	0.2	0.4	50.6	0.22	0.00	0.29	16	10.7
551	422	773	82.3	12.4	3.29	4.60	0.20	23.1	4.4
10	11	1.1	1.6	46.5	0.18	0.02	0.14	13.3	1.7
7	12	2.8	0.9	39.3	0.18	0.03	0.10	13.2	3.7
66	99	22.8	25	55	2.84	1.71	1.01	35.2	35.4
15	126	19.5	3.9	16.9	0.73	0.86	0.07	4	0.4
466	537	741	90.9	5.4	3.04	5.02	0.34	5.2	0.5
47	31	32.9	5.2	25.4	0.77	0.22	0.18	45.3	4.4
106	36	16	5.6	13.9	1.97	0.28	0.43	24.5	25.4
4	39	17.6	0.4	5.2	0.32	0.28	0.03	4.9	0.1
55	21	19.6	7.8	30.5	2.15	0.24	0.47	63	67.3
12	25	8.9	0.5	7.1	0.37	0.11	0.03	15.6	0.2
51	4	1.1	6.4	34.2	3.10	0.11	0.62	22.4	90.8
19	21	11.2	1.4	13	0.66	0.12	0.03	28.9	1.8
44	5	5.6	1.4	22.4	0.73	0.05	0.12	36.4	23
29	21	12.9	2.0	28.6	0.24	0.08	0.19	25	6.3
28	16	3	0.7	32.1	0.29	0.05	0.18	28	9.8
39	15	1.1	0.4	46.4	0.42	0.05	0.26	43.9	18.7
122	32	14	5.5	19.6	1.65	0.30	0.60	23.5	40
8	8	1.2	0.2	12.3	0.27	0.02	0.08	11.6	12.9
10	9	1.1	0.5	29.5	0.35	0.05	0.10	11.8	35.2
65	67	82.6	10	14	1.13	0.78	0.25	20.4	5.9
30	82	11.4	1.2	23.2	0.68	0.12	0.16	12.5	17.2
252	190	268.4	38.7	8.9	1.56	2.41	0.33	20.6	8
1000	206	219	80.5	45.5	7.70	7.12	3.25	6.2	9.5
25	71	15.4	0.4	18.2	0.05	0.11	0.03	6.6	0.5
100	74	75.9	5.9	25.2	0.53	0.30	0.15	14.1	59.9
320	181	402.3	17.3	33.3	1.22	0.70	0.37	14.7	50.1
551	207	135.4	22.8	43.1	1.44	0.79	0.67	2.2	4.3
742	276	193.3	40.5	48.5	2.36	1.60	1.54	3.9	4.9
57	131	35.6	0.8	18.9	0.19	0.25	0.03	14.9	2
24	151	17.8	0.2	18.4	0.12	0.11	0.03	15.6	0.2

5	27	16.4	0.3	29.1	0.14	0.41	0.12	30.4	14.2
119	27	1.1	10.9	38.8	2.15	0.46	1.30	16.8	78
36	28	1.3	3.9	38.4	1.71	0.29	1.32	75.1	15.3
32	23	1.2	4.1	48.2	1.69	0.36	1.10	80.2	12.9
84	18	5.9	1.1	33	0.89	0.14	0.13	101.2	27.6
174	70	99.0	24.7	23.8	1.95	0.81	0.87	58.8	28
212	109	185	28.5	25.3	1.68	1.11	0.67	49.4	28.3
25	7	1.5	0.3	21.3	0.15	0.07	0.03	2.2	0.3
153	1	0.1	1.5	39.8	1.00	0.02	0.19	44.8	41.5
81	71	79.4	5.1	20.3	0.80	0.58	0.16	6.5	0.1
244	97	103.4	29.7	32.3	2.42	1.07	0.92	45.5	29.4
62	20	3.8	1.7	36	1.40	0.14	0.12	133.7	48.7
119	7	0.4	1.4	38.6	0.97	0.05	0.40	39.3	30.1
1041	367	431.1	42.5	16	4.40	5.40	3.15	4.1	3.5
1270	311	364.8	57.1	41.4	18.95	6.52	6.08	5.5	9.5
113	72	25.7	4.7	33.3	0.90	0.24	0.63	26.9	13.1
148	64	81.5	21.7	31.4	4.90	0.83	0.95	47	15.2
165	109	86.3	20.1	25.2	2.65	0.88	0.59	46.5	8.1
12	8	0.2	0.4	19.8	0.30	0.02	0.09	11.2	0.5

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0.4

Sample	Sample ID		E	N	T	ph	EC	Cl
			UTM WGS84 33N		°C	-	mS/cm	mg/l
	SW		406181	4512306	26.4	8.19	56.9	22561
	FW		408006	4509988	19	7.49	0.65	44
LD 1	1	Well	405580	4509630	41.7	7.31	15.9	185.8
LD 2	2	Well	403590	4510096	18.0	7.56	7.6	177
LD 3	3	Well	405040	4510357	53.6	7.11	9.1	811.3
LD 4	4	Well	404306	4508476	66	6.33	12	1244.8
LD 5	5	Well	404170	4508323	77.4	6.59	18.5	1996.5
LD 6	6	Well	404380	4508255	58.5	6.43	6.6	662.3
LD 7	7	Well	403811	4509258	50.5	7.17	37.9	10228.4
LD 8	8	Well	403827	4509399	46.2	7.02	45.2	13811.7
LD 9	9	Well	403954	4508476	76.5	7.50	8.9	1443.5
LD 10	10	Well	404035	4508659	56	7.05	2.7	272
LD 11	11	Well	404038	4508049	53	7.09	2	277.5
LD 12	12	Well	404078	4508351	70.8	7.21	8.4	1157.3
LD 13	13	Well	404137	4508510	75.6	7.44	6.1	773.7
LD 14	14	Well	405293	4506825	52.1	7.04	1.88	213.1
LD 15	15	Well	404474	4508751	60.7	6.99	27.5	196.2
LD 16	16	Well	405789	4510624	62.2	6.91	6.3	583.8
LD 17	17	Well	405737	4510552	27.9	6.93	40.4	113.7
LD 18	18	Well	406069	4510399	74.1	6.74	4	172.7
LD 19	19	Well	405318	4506959	74	7.33	1.7	129.6
LD 20	20	Hot spring	405276	4505993	50.1	7.19	45.7	15733.4
LD 21	21	Well	405387	4507335	63.7	7.29	2.2	346.2
LD 22	22	Well	405418	4507281	47.7	6.89	2	231.1
LD 23	23	Well	404000	4508670	68.4	6.48	16.3	3395.2
LD 24	24	Well	404065	4508622	25.8	7.10	3.56	682.2
LD 25	25	Well	403875	4508722	45.2	6.31	31.2	15313.9
LD 26	26	Well	404089	4509021	45.1	7.20	7.51	1070.5
LD 27	27	Well	404534	4511123	39.5	7.56	7.65	1185.9
LD 28	28	Well	403923	4510302	20.4	7.59	14	210.6
LD 29	29	Well	405432	4506700	62.7	7.46	9.2	1577.3
LD 30	30	Well	403533	4510273	18.7	7.75	1.6	198.2
LD 31	31	Well	405901	4506629	77.2	7.88	9.64	1417.4
LD 32	32	Well	404531	4510362	30.6	7.81	3	349.1
LD 33	33	Well	404193	4509411	39.8	7.52	4.28	393.7
LD 34	34	Well	403871	4508858	43.9	7.02	4.04	418.8
LD 35	35	Well	404035	4508781	45.7	7.02	26.7	230.9
LD 36	36	Well	404095	4508813	50.5	7.50	3	191.7
LD 37	37	Well	404521	4511204	43.4	7.50	7.5	1037.5
LD 38	38	Well	403899	4510192	23.5	7.77	12.8	141.5
LD 39	39	Well	404072	4508188	51.2	7.59	1.6	168.3
LD 40	40	Well	403743	4509372	33.7	7.35	10.7	1611.5
LD 41	41	Well	406440	4511407	28.5	7.41	19.1	264.6
LD 42	42	Well	405430	4511947	50.8	6.95	25.5	6133.9
SDF 43	43	Well	405400	4512070	76.8	6.71	46.7	13974.2
SDF 44	44	Cold spring	405035	4509776	17.5	7.50	1.36	60
SDF 45	45	Well	405330	4505909	60	6.97	23	1147
SDF 46	46	Well	405244	4505962	80	6.52	34	3077
SDF 47	47	Hot spring	404024	4508240	45	6.02	35.9	4530
SDF 48	48	Hot spring	404002	4508263	99.5	7.05	52.7	6571
SDF 49	49	Well	408084	4511008	29.9	7.48	2.08	195
SDF 50	50	Hot spring	408043	4507326	27.5	6.38	1.27	63
SDF 51	51	Hot spring	407954	4506601	33.7	7.54	3.24	96
SDF 52	52	Well	407924	4506193	42	8.00	22.2	1913

SDF 53	53	Hot spring	407499	4506528	41.6	7.81	8.33	1089
SDF 54	54	Hot spring	407454	4506508	34.5	7.82	7.05	1138
SDF 55	55	Well	407059	4510748	57	7.34	5.6	247
SDF 56	56	Hot spring	409481	4511327	68.6	7.08	20.7	3771
SDF 57	57	Hot spring	409385	4511418	54	6.85	24	4240
SDF 59	58	Well	405649	4509211	11	8.63	1.34	62
SDF 60	59	Hot spring	407722	4510720	53.2	8.82	4.77	325
SDF 61	60	Hot spring	412131	4508563	34.2	6.07	7.22	1005
SDF 62	61	Well	408935	4511330	56.2	6.95	20.4	4415
SDF 66	62	Well	407755	4511094	51	7.09	5.18	361
SDF 67	63	Well	407828	4510877	46.6	8.14	5.1	299
SDF 68	64	Well	405275	4512328	54.5	7.14	47.9	7994
SDF 69	65	Well	405088	4512353	64	4.30	51	8605
SDF 70	66	Well	405449	4512103	41.8	6.10	5.38	1147
SDF 71	67	Well	410623	4510449	54	7.60	12.5	3071
SDF 72	68	Well	410913	4510641	43.3	6.60	9.98	2800
SDF 73	69	Cold spring	405639	4507376	15.8	8.10	1.47	190

Na	K	Mg	Ca	Br	Si	B	Sr	Li	Mo
mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	ug/l	ug/l	ug/l	ug/l
13848.3	448.5	1556.4	436.6	58.28	b.d.	5.27	4810	280	b.d.
89.2	4.01	16.82	85.51	0.21	13.80	0.04	570	30	8.7
196	10.98	1.80	13.23	0.237	18.51	49	65.34		4.2
87.9	5.9	7.5	13.7	0.093	6.95	73	36.87		9.1
1180.4	129.6	7.4	29.6	4.122	21.41	1354	280.24	88	80
1489.9	53.75	6.93	52.93	7.548	37.46	1933	397.6	226	20.1
2228.2	93.18	21.19	90.46	11.466	36.88	2172	647.5	254	22.9
721.4	35.69	3.38	66.56	3.458	45.52	2708	397.56	128	32.7
8579.6	205.78	427.06	318.60	51.125	11.88	2936	2822.04	355	23.5
11000	213.46	493.28	622.49	76.709	16.13	2948	8917.02	625	19.1
1212	42.75	1.83	20.30	7.266	41.92	4161	209.36	315	64.2
642.2	75.85	1.19	15.04	0.743	66.54	789	31.25	203	63.4
365.6	7.04	1.31	16.48	0.895	42.82	1463	87.32	129	16.2
1073.3	37.81	2.08	26.54	6.469	33.95	3953	195.45	303	53.3
810.5	16.44	1.19	16.72	4.4	40.03	1851	154.4	232	41.8
406	4.62	0.63	6.17	0.653	64.16	491	14.9	218	17.2
591.4	54.84	0.84	14.83	0.54	79.70	835	46.35	278	156.3
714.9	76.08	1.98	35.33	2.546	52.69	3081	101.64	650	203.4
224.4	18.60	21.51	61.40	0.156	22.64	121	104.57		2.9
479.7	10.77	20.62	40.16	0.664	33.29	277	446.22		14.1
241.5	2.26	0.19	3.82	0.393	50.59	221	3.18	285	16
11700	550.96	773.00	421.70	82.305	12.39	3291	4602.51	195	23.1
325.3	10.08	1.14	11.05	1.576	46.49	184	16.48	141	13.3
222.5	7.34	2.82	12.04	0.928	39.30	180	26.71	102	13.2
2735.9	65.83	22.78	98.76	24.963	55.04	2839	1707.79	1009	35.2
407	14.72	19.53	125.55	3.899	16.89	733	857.96	72	4
9784.3	465.5	741.1	536.7	90.872	5.44	3041	5022.38	336	5.2
1021.5	47.3	32.9	31.3	5.211	25.40	767	217.89	175	45.3
1001.7	106.1	16.0	35.9	5.592	13.94	1974	283.81	426	24.5
141.2	3.68	17.60	38.67	0.447	5.19	323	275.15		4.9
1220.4	54.81	19.58	20.98	7.847	30.52	2145	242.57	468	63
179	12.02	8.92	24.62	0.47	7.06	372	113.17		15.6
1241.9	50.79	1.12	3.53	6.42	34.18	3096	111.13	624	22.4
385.2	19.48	11.24	20.81	1.386	13.02	661	120.21		28.9
813.4	44.12	5.55	5.39	1.389	22.42	725	51.11	124	36.4
490	29.23	12.92	21.28	2.000	28.60	238	76.35	187	25
344	28.15	2.99	15.79	0.671	32.11	290	45.52	178	28
466.4	39.49	1.12	14.92	0.438	46.35	420	49.17	263	43.9
1201.9	122.1	14.0	32.4	5.474	19.60	1648	302.3	598	23.5
173.5	7.77	1.17	8.05	0.242	12.33	265	24.85	80	11.6
163.1	10.26	1.15	8.52	0.54	29.52	350	53.85	100	11.8
1506.1	65.05	82.63	67.00	10.006	14.01	1131	779.79	251	20.4
281.0	29.66	11.39	82.14	1.161	23.19	677	123.71	161	12.5
4484.6	252.3	268.4	190.0	38.738	8.93	1564	2412.33	329	20.6
9763.1	1000	219	206	80.456	45.49	7701	7123.11	3248	6.2
345.4	24.94	15.44	71.48	0.359	18.19	49	105.54		6.6
2931.8	100.39	75.88	73.76	5.865	25.17	525	299.39	150	14.1
7364.6	320.4	402.3	181.2	17.288	33.30	1219	695.81	368	14.7
8182.3	550.66	135.35	207.07	22.823	43.15	1438	794.27	674	2.2
9739.5	742.34	193.31	275.54	40.518	48.45	2364	1598.61	1535	3.9
318.4	56.94	35.59	130.74	0.821	18.94	191	248.64		14.9
173.5	24.09	17.82	151.43	0.204	18.44	119	107.03		15.6
933.4	5.38	16.42	26.93	0.308	29.07	144	407.49	117	30.4
2907	118.73	1.11	26.99	10.939	38.81	2151	459.71	1297	16.8

2180.4	36.33	1.34	28.27	3.941	38.43	1709	291.54	1319	75.1
2220.5	32.01	1.23	22.77	4.123	48.17	1693	361.56	1103	80.2
1171.4	84.24	5.94	18.11	1.082	33.02	885	137.99	125	101.2
4511	174.21	99.03	69.56	24.687	23.84	1953	806.44	873	58.8
4732	212	185	109	28.468	25.32	1683	1108.67	670	49.4
462.21	24.93	1.52	7.27	0.256	21.33	153	73.62		2.2
1151.3	152.94	0.13	0.92	1.484	39.76	1002	15.44	192	44.8
957.8	81.21	79.37	71.31	5.058	20.29	799	580.98	159	6.5
4924.1	243.7	103.4	96.7	29.677	32.30	2422	1069.13	923	45.5
1350.8	62.28	3.84	20.32	1.654	36.01	1400	136.8	118	133.7
1282.7	118.63	0.39	6.88	1.405	38.58	973	53.64	398	39.3
10700	1041.05	431.07	366.52	42.528	15.96	4399	5395.96	3154	4.1
10700	1270.44	364.84	311.22	57.117	41.42	18951	6516.73	6076	5.5
1178.5	112.86	25.73	72.11	4.731	33.32	897	241.26	625	26.9
2933.7	148.16	81.54	63.69	21.698	31.39	4897	831.36	951	47
2504	165.02	86.32	108.63	20.081	25.16	2650	880.72	589	46.5
444.7	12.07	0.21	7.66	0.441	19.84	304	17.13	94	11.2

W	f.sea
ug/l	%
b.d.	100
0.5	0
0.5	0.4
0.5	0.4
2.1	3.2
33.1	5.1
20.1	8.5
19	2.5
1.6	45.1
1	61.1
139.8	6.0
41.6	0.8
11.9	0.8
127.6	4.7
63.9	3.0
21	0.5
87.6	0.5
73.6	2.2
0.3	0.1
1.5	0.4
10.7	0.2
4.4	69.6
1.7	1.1
3.7	0.6
35.4	14.7
0.4	2.6
0.5	67.7
4.4	4.4
25.4	4.9
0.1	0.5
67.3	6.6
0.2	0.5
90.8	5.9
1.8	1.1
23	1.3
6.3	1.5
9.8	0.6
18.7	0.4
40	4.2
12.9	0.2
35.2	0.3
5.9	6.8
17.2	0.8
8	26.9
9.5	61.8
0.5	0.0
59.9	4.7
50.1	13.3
4.3	19.8
4.9	28.8
2	0.5
0.2	0.0
14.2	0.0
78	8.1

15.3	4.4
12.9	4.7
27.6	0.7
28	16.4
28.3	18.5
0.3	0.0
41.5	1.0
0.1	4.1
29.4	19.2
48.7	1.2
30.1	0.9
3.5	35.2
9.5	37.9
13.1	4.7
15.2	13.3
8.1	12.1
0.5	0.4

The authors declare that there is no conflict of interest.

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Seawater intrusion and hydrogeochemical processes in the Ischia Island groundwater system

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Abstract

Ischia is a volcanic island located NW of the Gulf of Naples (South Italy). The island of Ischia is a structurally complex hydrothermal active system that hosts a fractured aquifer system whose geometry and hydraulic properties are still partly unknown. The aquifer system of Ischia, composed mainly of Quaternary volcanic deposits and marine sediments, exhibits physically and chemically heterogeneous waters. The intense seismicity and hydrothermal activity are expressed by numerous fumaroles and thermal springs, which have been exploited since ancient times, promoting, and supporting the world-renowned tourist activities that constitute the main economic activity of the island. The aim of this study is to determine the hydrogeochemical processes in the Ischia aquifer system. Also, we calculated the proportion of seawater in the aquifer system of Ischia using historical hydrogeochemical data relative to two sampling campaigns. Sixty-nine groundwater and thermal spring samples collected in July 2000 were analyzed and compared with previously published data to identify the changes in seawater contribution. The sample analysis shows that different physicochemical processes occur in the groundwater of Ischia Island, where recharge water, seawater and deep fluids interact and overlap with different intensity. The calculated saline factor indicates a seawater content of up to 70% in some samples near the coast, suggesting that seawater intrusion is the main process in these areas. Later data show that seawater intrusion increases around the coastline with up to 93% seawater content. Finally, data analysis shows that although a change in chemical composition is observed, no variation in thermal water temperature is recorded over time.

Keywords: seawater intrusion; water-rock interaction; thermal waters; Ischia Island

1. Introduction

Seawater intrusion (i.e., the landward incursion of seawater) is a widely recognized process in coastal aquifers and islands (Custodio, 2010) and is usually caused by several factors, such as prolonged changes in coastal groundwater levels, climate variations or sea-level fluctuations, among others (Werner et al., 2013). In many coastal hydrogeological settings, seawater intrusion occurs normally due to overexploitation of freshwater resources. As a result, the lowering of the water table level allows the sea water intrusion that progressively causes the salinization of the aquifer, which may become inappropriate for drinking and agricultural use. Groundwater salinization induced by seawater intrusion is generally regarded to be practically irreversible and leads to the complete degradation of freshwater reservoirs. During the last decades, considerable research efforts have been performed, in economically developed regions, to improve the knowledge about seawater intrusion occurrence and timing (Russak and Sivan, 2010; Ferguson and Gleeson, 2012; Werner et al., 2013; Lu and Werner, 2013).

Coastal aquifers provide a water source for more than one billion people in the world living in coastal regions (Small & Nicholls, 2003). The population growth in most of the coastal areas and the increase of water demand make seawater intrusion a global threat.

Ischia Island is an active volcano located in southern Italy, hosting a geothermal system. The groundwater system of Ischia consists of several permeable aquifers, interbedded with low-permeability levels (Celico et al., 1999). In natural conditions, the Ischia’s aquifers are recharged by rainfall with a variable contribution of deep hydrothermal fluids (Di Napoli et al., 2009; Piscopo et al., 2020). Due to this interplay, many thermal springs are present on the island.

The thermal waters were known and used from the Roman age, but during the last thirty years the growing spas-related touristic activity, representing the main economic income of the island, encouraged the drilling of pumping wells to obtain a constant thermal water flow rate.

Nowadays, more than 200 spas are operating at Ischia Island, most of them located near the coast. As a consequence of the intensive groundwater pumping, it is known that seawater intrusion is present in the volcanic rock aquifer of the island (Corniello et al., 1994). The hydrogeological setting of Ischia Island is complex due to geological and structural factors, as well as human activities that have deeply changed the groundwater flow circulation. Ischia Island is characterized by the main groundwater body lying above sea level and in natural conditions groundwater flows towards the sea (Celico et al., 1999; Ducci and Sellerino, 2012).

Numerous studies have been focused on the hydrothermal system of the island, focusing on thermal fluids composition and origin, providing important information for geothermal energy exploration and volcanic risk assessment. These studies allowed refining knowledge on hydrothermal fluid circulation (De Gennaro et al., 1984; Panichi et al., 1992; Caliro et al., 1999; Celico et al., 1999a; Inguaggiato et al., 2000; Lima et al., 2003; Chiodini et al., 2004; Daniele, 2004; Milano et al., 2004; Aiuppa et al., 2006; Morell et al., 2008; Di Napoli et al., 2009; 2011; 2013; Carlino et al., 2012; 2015).

On the other hand, the groundwater system, presenting a wide range of chemical compositions (from calcium-bicarbonate to alkali-chloride waters), has been previously explained by a mixing process among meteoric water, seawater and deep geothermal fluids (De Gennaro et al. 1984; Panichi et al. 1992; Aiuppa et al. 2006; Di Napoli et al. 2009). Despite these fundamental advances, the hydrogeochemical processes governing the groundwater composition and the magnitude and extension of the saline intrusion process in the island are still unknown. (Corniello et al., 1994; Di Napoli et al., 2009; Piscopo et al., 2020).

The main goals of this paper are: a) to assess the hydrogeochemical processes, as water-rock interaction and deep fluids input in the Ischia groundwater; and b) to estimate the extension and magnitude of saltwater contribution in the Ischia aquifer system.

The results of this study provide critical information for programming upcoming sustainable management strategies for Ischia water resources and represent essential knowledge for future groundwater studies and environmental decisions. Furthermore, considering the growing interest in geothermal energy exploitation in the island, improving the aquifer comprehension and its physicochemical processes, acquires particular relevance in this social and hydrogeological context.

2. The study area

Ischia Island is the westernmost active volcanic complex of the Campania region and belongs to the Phlegrean volcanic district of Southern Italy (Fig. 1) (Carlino et al., 2012; Troise et al., 2019). The local geology is composed of landslide deposits, marine sediments and volcanic rocks, represented by alkali-trachytes, trachybasalt, latites and phonolites, reflecting a complicated sequence of alternating constructive and destructive volcano-tectonic, erosion and sedimentation phases (Vezzoli, 1988; Orsi et al., 1991; Tibaldi and Vezzoli, 1997). Although the island (~45 k m^2) is dominated by the structural block of Mount Epomeo (786 m a.s.l.), several volcanic structures are still present, such as the rim of a caldera (~55 ka BP), partially recognizable (Carlino et al., 2014). Ischia is an active volcano, indicated by the occurring of historical eruptions (Vezzoli, 1988), intense and diffuse hydrothermal features (Chiodini et al., 2004), and seismic activity (Luongo et al., 1987; De Natale et al., 2019, Nappi et al., 2021). Ischia volcanic historical activity dates approximately 150 ka BP and it is characterized by lava domes and hydromagmatic eruptions. The largest-scale volcanic event is the alkali-trachytic ignimbrite eruption of Mt. Epomeo Green Tuff (MEGT), which caused the caldera collapse (~55 ka BP) that partially destroyed the previous eruptive history of the island and marks the transition between volcanic cycle phases (Vezzoli, 1988; Orsi et al., 1991; Tibaldi and Vezzoli, 1998). The volcanic cycle of the island consists in two phases, the first one mainly characterized by pyroclastic activity and the second one by a lava dome emplacement (Carlino et al., 2006). During the second cycle, because of the caldera collapse, several phreatomagmatic eruptions and strong pyroclastic activity filled the caldera with ignimbrite deposits that in turns favored the sea intrusion in the central part of the present island (Vezzoli, 1988). Carlino et al. (2006) proposed that a laccolith (10 km large and up to 1 km deep) in the center of the island triggered the caldera resurgence (~33 ka BP) after the Mount Epomeo Green Tuff (MEGT) eruption. The tectonic deformation cutting the oldest volcanic rock, part of the seismic activity and the widespread landslides have been associated with the Mt. Epomeo block uplift (Tibaldi and Vezzoli, 1997; Tibaldi and Vezzoli, 1998; Tibaldi and Vezzoli, 2004; Chiocci and de Alteriis, 2006; Capuano et al., 2015), resulting in the horst of Mt. Epomeo, in the central part of the island, while the east side is dominated by a graben structure. The uplift of Mt. Epomeo has also been explained by different mechanical and geophysical models, most of them involving a shallow magma body as the source of deformation, together with local tectonics, high geothermal gradients and volcanism (Vezzoli, 1988; Fusi et al., 1990; Orsi et al., 1991; Acocella et al., 1997; Cubellis and Luongo, 1998; Acocella and Funiciello, 1999; Molin et al., 2003; Tibaldi and Vezzoli, 2004; Carlino et al., 2006; Carlino, 2012). De Martino et al. (2011) and Del Gaudio et al. (2011) reported present-day subsidence, especially in the areas with active landsliding and faulting (Manzo et al., 2006).

The geothermal system of Ischia has been the subject of several investigations. De Gennaro et al. (1984) proposed a geothermal model where the deep source of fluids is represented by a large magmatic body located at a depth greater than 3000 m and with a temperature over 200 °C. Carapezza et al. (1988) suggested the existence of two intermediate magmatic systems, and Panichi et al. (1992) estimated the temperature of the magmatic reservoir in the range of 160–240 °C. Inguaggiato et al. (2000) concluded the existence of a magmatic reservoir liquid dominated at 280

°C, supported by carbon isotope data. However, the authors do not discard the possibility of the existence of a second magma body (more than 4 km deep), as suggested by Tedesco (1996). Recently, Di Napoli et al. (2009; 2011), based on studies from integrated geophysical (electrical resistivity) and geochemical properties (CO_2, TDS in thermal springs) infer that the circulation of the hydrothermal fluids, in the south-west of the island, takes place within two overlapped and different geothermal reservoirs. These reservoirs are localized at a depth of ~200 and ~1000 m with temperatures of ~150 ºC and ~270 ºC, respectively, and are connected through fractures generated by the resurgence. Carlino et al. (2014) made a critical review of the geothermal system of Ischia Island and concluded that the geothermal system is vapor dominated and related to the intrusion of a shallow magma body, occurred after the MEGT eruption (55 ka BP), whose top is migrated up to about 2 km depth. Carlino et al. (2014) proposed that the two shallow geothermal reservoirs may be geologically separated. The first one is supposed to be located in the western sector at depths between 150 m to at least 600 m, with a temperature ranging between 150 °C and 200 °C, and pressure of about 4 MPa (40 bar). The second, deeper reservoir is hypothesized to be at depth >900 m, with a temperature between 270 to 300 °C and pressure of 9 MPa (90 bar). All the authors agree that the geothermal system of Ischia is fed by meteoric water, seawater and hydrothermal fluids.

The hydrogeological setting of Ischia Island is highly complex due to both geological and structural features, and human activities that have deeply changed the territory and influenced the groundwater flow circulation. The groundwater system of Ischia consists of several permeable horizons (fracturation and/or porosity), interbedded with low-permeability levels (Celico et al., 1999). This composite system reflects the contrasting lithologies and geometries of the volcanic deposits, the pervasive hydrothermal circulation with the consequent self-sealing processes, and the complex volcano-tectonic and gravitational events that occurred over time (Celico et al. 1999; Di Napoli et al., 2009). Ischia Island is characterized by the main groundwater body lying above sea level and in natural conditions groundwater flows towards the sea (Celico et al., 1999; Ducci and Sellerino, 2012).

According to Celico et al. (1999) and Carlino et al. (2014), two different hydraulic areas can be identified (Fig. 2): the first one is the graben in the northeast of the island, which is highly transmissive and can be pictured as a single aquifer fed by meteoric waters and seawater ingression; the other area is Mount Epomeo and its border zone, which is intensively fractured and consists of very heterogeneous materials forming complex geometries that mainly affects the vertical component of groundwater flow. The hydrogeology reflects the complex tectonics and lithology settings and suggests the presence of a multilayer aquifer (Celico et al., 1999).

Variations in the chemical composition and temperature of the groundwater are related to the complex hydrogeological setting. Groundwater circulating in the shallow aquifer has temperatures up to boiling, and ranges in composition from diluted bicarbonate waters to more saline and chlorine-rich waters, interpreted as evidence of dual (meteoric and seawater) recharge to the aquifer (Panichi et al., 1992; Inguaggiato et al., 2000; Aiuppa et al., 2006; Di Napoli et al., 2009; Di Napoli et al., 2013). There are also several fresh springs in the higher and inner part of the island and their discharge is usually 1-3 l/s (Celico et al., 1999; Carlino et al., 2014).

3. Materials and Methods

A total of 69 samples, retrieved from 56 boreholes less than 100 m deep, 11 thermal springs and 2 cold springs, were collected during the period 1999 – 2000 (Fig. 2). It is important to remark that some of the data used in this paper have been already published in previous works (Lima et al., 2003; Daniele, 2004). The wells were pumped for at least 30 min before the samples were taken and electrical conductivity, pH, and water temperature were measured in situ. The samples were filtered using 0.45 μm Millipore® membranes in double-capped, polyethene bottles of 100 ml volume and stored at 4°C. Samples for cations and trace elements analysis were also acidified to 1% with pure nitric acid. The analytical procedure is detailed in previously published works (Lima et al., 2003; Daniele, 2004). The samples labelled as SW and FW represent the end-members for seawater and freshwater, respectively and are used to calculate the saline factor in each groundwater sample. The SW sample proceeds from Morell et al., 2008, FW is a low-chlorine water sample, selected among the 2001 cold temperature samples and presenting the lowest EC.

Table 1 summarizes the ionic composition of the sampled waters. The following variables were considered in this work: Cl, Na, K, Ca, Mg, Br, Si, B, Sr, Li, Mo, W, T°, E.C. and pH.

The seawater content (fsea) for each sample was calculated using the ionic deviation from a conservative seawater–freshwater mixture, assuming Cl to be a conservative tracer:

$$fsea = (C_{Cl,sample} - C_{Cl,f})/(C_{Cl,sea} - C_{Cl,f}) \times 100 \quad (1)$$

where $C_{Cl,\ sample}$ represents the Cl concentration of the sample, $C_{Cl,f}$ the freshwater Cl concentration and $C_{Cl,sea}$ the seawater Cl concentration. These values were compared with seawater fraction for the period 2002-2007, fsea (2002- 2007), calculated using the water chemistry data published by Di Napoli et al. (2009).

The statistical analyses used in this study are multivariate methods, which provide several venues for exploratory assessment of water quality data sets. Water chemistry is subject to complex interactions, whose impacts may be impossible to isolate and to study individually.

In this study, using the IBM SPSS Statistics Software V26 we performed the factorial analysis (FA), over the same database of water chemical analysis. FA is a useful method, largely used in hydrogeological studies (Moeck et al., 2016; Negri et al., 2018; Taucare et al., 2020; Daniele et al., 2013, 2020). Factors were extracted from the correlation matrix of the variables using the

Principal Component Analysis (PCA) method. The selected factors have eigenvalues higher than one and were subsequently rotated orthogonally using the quartimax method to minimize the number of factors needed to explain each variable. The variable weights in each factor are relevant if it is >0.50. The variance of the geochemical variables has been determined by the KMO test (Kayser, 1960) whose value of 0.81 ensures the quality of the FA in this study. In addition, this method also allows us to calculate the factor score, which represents the intensity of the factor on each sample.

4. Results and Discussion

Ischia groundwaters present a wide range of physicochemical parameters that vary from diluted cold waters (e.g., #44 and #69) to highly saline boiling waters (e.g., #48). Water temperature ranges between 11.0 °C and 99.5 °C, with the highest values registered in the western part of the island (Fig. 3), and pH values vary from slightly acidic to alkaline values, between 4.3 to 8.8. Electrical conductivity varies from 1.3 mS/cm to 52.7 mS/cm, with the minimum value recorded in cold spring (#44) in the south part of the island and far from the coastline, and the maximum value measured in a high-temperature spring (#48), 100 m far from the coast. Despite that, a linear correlation between T and EC is absent. In general, more saline samples are located close to the coastline (Fig. 3).

The chemical composition of water samples is largely dominated by Cl and Na, followed in decreasing order by K, Mg, Ca, Br, B, Sr, Li and W. Chloride shows a poor correlation with temperature and its maximum concentrations are located along the coastal areas (Fig. 4a and b). Cl contents are mainly related to seawater contribution to the Ischia groundwater system, in agreement with Di Napoli et al., (2012). Figure 5 shows binary plots of major and minor ions versus Cl. The positive correlations of Na, K, Br and B with Cl (Figs. 5a, b, e), lying on the theoretical FW-SW mixing line, suggest a common origin for these chemical species, mainly related to seawater intrusion. The B concentration of the SW sample is slightly higher than mean values in seawater (4.5 mg/l; Morell et al., 2008), but this value agrees with the average value of 5.1 mg/l calculated by Gofiantini et al. (2003) for the Mediterranean Sea. The Sr contents of the seawater sample (4.8 mg/l), already published in Morell et al. (2008), is lower than Sr concentrations measured in the Mediterranean Sea (8.4 mg/l; Daniele et al., 2011). The FW sample presents relatively high Sr, Ca and Mg values of 0.57 mg/l, 86 mg/l and 16.8 mg/l. Strontium follows a similar trend of Mg and Ca and presents positive correlation with Cl (fig. 5c, d, h), according to a Sr, Ca and Mg origin mainly related to carbonate dissolution and water-rock interaction (Musgrove, 2021). On the other hand, Li (Figs. 5f, g,) presenting a poor correlation with Cl, diverges from the theoretical mixing curve, showing values higher than the SW end-member, and suggest an origin for Li that could be related to the mixing between FW and a hydrothermal endmember (Aiuppa et al., 2006; Morell et al., 2008).

4.1 Seawater intrusion

To quantify the seawater contribution in the chemical composition of each sample, the seawater fraction (fsea) was calculated. This method is considered valid, since Cl is a conservative tracer, and his concentration in Ischia waters is mainly due to marine origin (Di Napoli et al., 2012), mostly related to seawater intrusion and subordinate marine aerosol. The calculated values range from <1% to 70%, with most of them being <10%. The spatial distribution (Fig. 6a) shows high values (>10% wt) toward the coast, with particularly high values (>60% wt) along the western portion of the island (Lacco, Citara, St. Angelo), indicating the presence of water of marine origin. Towards the central part of the island the values are generally lower than 2%, indicating that the phenomenon of seawater intrusion is almost absent. In Lacco and Citara, the high variability of fsea values in sampled wells suggests a complex hydrogeological setting, where the aquifer may be controlled by an irregular fracture network, forming overlapped aquifer (multilayer) or perched aquifer (impermeable layer) that can exert a strong control on the seawater intrusion.

Figure 6b and c shows the fsea values calculated with water samples collected between 2002-2007, based on the work of Di Napoli et al. (2009). To have a direct comparison, in Figure 6b, the fsea was calculated with the samples from Di Napoli et al. (2009) collected in the same wells of the present work. In Figure 6c, we calculated the fsea with all the samples from Di Napoli et al. (2009). Comparing the time variation of the seawater intrusion, calculations indicate an increase all along the coast, with fsea values up to 93%, while lower values are maintained towards the center of the island, indicating that the saline intrusion has not extended inland during about 10 years. The increasing over pumping in wells near the coastline, where most of the spas and thermal wells are located, has enhanced the saltwater intrusion in the island. On the other hand, the aquifer geometry controlled by the fault-fracture meshes, and maybe the intense withdrawal near the coastline have limited the intrusion to the coastal areas, preventing the saltwater from reaching the inner part of the island. The input of cold seawater has not generated any changes in water temperatures as shown in Figure 6, where our data are compared with data from Di Napoli et al. (2009), indicating a thermal system highly active.

4.2 Factorial Analysis

The use of the multivariate geostatistical methods is common in hydrogeochemical studies (Join et al., 1997; Meng and Maynard, 2001; Swanson et al., 2001; Cruz et al., 2006; Daniele et al., 2008), being a reliable tool to unravel the relationship among the whole group of variables. This helps to obtain a more complete hydrogeochemical interpretation of the controlling processes or the origin of the single variables. The Factorial Analysis (FA) is a statistical method used to underlie the interrelationship between the variables and to infer the geochemical processes controlling the water chemistry.

A total of three principal factors were extracted (Figure 7), with eigenvalues greater than 1, explaining 84% of the total variance. Variables with loadings near to 1 form the factor, while near to 0 they don't form the factor.

Factor 1 (F1) accounts for 52% of the total variance, being the most relevant factor in the composition of these waters. It has positive loading values for Cl, Na, K, Mg, Ca, Br, Sr, with moderate positive loadings for B and Li. These variables, responsible for the major percentage of the observed chemistry, can be associated with the seawater intrusion process (Daniele, 2007; Daniele et al., 2008; Panda et al., 2006; Morell et al., 2008).

Factor 2 (F2) accounts for 18% of the total variance and shows positive loadings for T° (C), Si, Mo and W. Silica, Mo and W are usually related to either uptake by secondary minerals or non-stoichiometric dissolution of primary rocks. Their alteration minerals have not been identified in the geothermal surface environments in Ischia, but Mo and W have been found associated with sulfides and (hydr)oxides elsewhere, in wells scales and subsurface alteration (Kaasalainen and Stefánsson, 2012). The processes influencing the geochemistry of Mo and W in geothermal waters can be related to water-rock interaction and mixing between condensed steam and non-thermal surface waters.

Factor 3 (F3) accounts for 14% of the total variance and shows positive loading for Li, B and K. Boron is considered to be a highly mobile element and a good indicator of rock leaching in geothermal waters (Arnórsson and Andrésdóttir, 1995). Also, B may be transported by ascending steam (Morell et al., 2008; Kaasalainen and Stefánsson, 2012) and the B enrichment in geothermal waters may be the result of its close proximity to the magmatic source and the absorption of magmatic vapors rich in B in non-thermal surface waters (Kaasalainen and Stefánsson, 2012;

Wrage et al., 2017 and references therein). Lithium and K are dominated by water-rock interaction processes and to a lesser extent to mixing between condensed steam and non-thermal surface waters (Markússon and Stefánsson, 2011; Kaasalainen and Stefánsson, 2012). Aqueous concentrations of these elements are controlled by the equilibrium of thermal waters with aluminum silicates such as K-feldspar, zeolites and clays (Stefánsson and Arnórsson, 2000). Pure alkali minerals are not common, but these elements are more commonly incorporated into major secondary minerals like clays, zeolites, and feldspar as well as Li into quartz (Goguel, 1983).

Also, B, Li and K may have a marine origin and are considered a tracer for seawater intrusion assessment (Sanchez-Martos et al., 1999). The variables present similar loadings in F1 and F3, suggesting that both seawater and hydrothermal contribution may be reasonable for K, B and Li in Ischia waters.

According to our interpretation, samples with high saline factors have positive F1 values, suggesting that seawater intrusion is the main hydrogeochemical process. Nevertheless, some of these samples also show positive factor scoring for F2 and F3, indicating the existence and superposition of different geochemical processes in the analyzed samples. Samples #43, #64 and #65 show a highly positive factor scoring for F3, and for F1, indicating superposition of processes for these samples.

Other samples show negative F1 values, indicating low or no seawater influence. These samples present positive factor scoring for F2, indicating a hydrothermal influence from the active geothermal reservoir. Finally, we obtained the spatial distribution of the factor scoring of each sample, using the inverse weighted distance interpolation. The method assumes that each measured value has local influences diminishing with the distance. The absence of data in the central and southeast parts of the island must be considered in the obtained spatial distribution. The distribution maps represent a synthesis of the physicochemical processes identified at the Ischia Island geothermal system.

The F1 spatial distribution (Figure 7a), associated with the seawater intrusion process, presented positive scoring along the coastline (north, center and south) of the western Ischia sector and the north-east coastline, with the highest value in the western area. Towards inland, and in the south-east (Forio), F1 presents negative scores, according to the fact that seawater intrusion moves from the coast toward inland, with a limited extension. The spatial distribution of F2 (Figure 7b), associated with the hydrothermal water-rock interaction and mixing of deep geothermal fluids with meteoric recharge, presents positive scoring from Mt. Epomeo towards the north (Casamicciola) and south-west (south Citara and St. Angelo), far from the coast, associated with fracture systems and the deepest faults delimiting Mt. Epomeo. The F3 spatial distributions (Figure 7c), associated with superposition of processes, show a high intensity at the coastal fracture system at north-west (Lacco), where the deep fluids rise (enhancing water volcanic/saline rock interaction) and mix with superficial recharge waters, meteoric and seawater. This location also presents a high intensity for F1, corroborating the superposition of processes in that zone. Forio coastal area shows negative scoring for all factors, indicating that these waters have not been significantly affected by the processes just mentioned, due to scarce hydraulic connection, or waters just infiltrated, hosted in perched or small confined aquifers.

5. Conclusions

The Ischia hydrothermal system is characterized by a great complexity in its geometry, fluid circulation and hydrogeochemical processes which is reflected in the vast physicochemical heterogeneity of the waters. The low correlation between Cl and temperature indicates that the Cl origin is mainly related to seawater. Also, its spatial distribution shows higher concentrations towards coastal zones diminishing towards inland, being the marine source (seawater intrusion) the most likely origin. Considering a conservative mixture between FW and SW, most of the ionic concentrations deviate from this theoretical mix line, showing enrichment in B, Li and depletion in Mg, Ca and Sr due to ionic exchange processes, water-rock interaction and mixing with deep hydrothermal fluids. The water-rock interaction process is enhanced by the high temperature of the system that allows the dissolution of volcanic rock minerals and the precipitation of secondary minerals, such as calcite and other carbonates.

The statistical and geostatistical methods used allowed us to identify different hydrogeochemical processes in the Ischia groundwater. Seawater intrusion, for the first time quantified in the Ischia groundwaters by this study, water-rock interaction, and deep fluid mixing processes are present. The calculated saline factor rises to 69.6% in samples collected near the coastline. Results indicate that the determined processes act with different intensity and are superimposed in most of the analyzed waters, with clear spatial distribution. Each sample presents a dominant process, and we assess three main water types based on identified hydrogeochemical processes.

The Ischia groundwater system is fed by meteoric recharge and the water samples with neutral pH, low E.C, temperature, and saline factor, with low or no interaction with the hydrothermal system and seawater intrusion can be considered as FW proceeding from this process.

Waters with low to moderate salinity, with Cl content less than 2000 mg/l, Br lower than 11,47 mg/l and lower Ca and Mg concentrations, show B and Li content and higher concentrations of Si, Mo and W compared with the rest of the samples. Their temperature ranges widely from 15,8°C to 77,4°C. The dominant processes in these samples are the hydrothermal water-rock interaction and the mixing of deep-seated fluids.

Finally, the last water type is formed by samples with high Cl > 15733 mg/l and Br [17,3 – 90,9 mg/l] content, but with the lowest concentrations of Si, Mo and W. The temperature is generally high [43.3 – 99.5°C]. The dominant geochemical process in this group is the seawater intrusion (i.e., high fsea).

The factorial analysis corroborates these results and suggests that the main physicochemical process in the analyzed samples is the seawater intrusion. The F1, which explains most of the data variability, has been interpreted as the seawater intrusion factor, and positive scores are associated with the coastal zone samples. The deep fluids and water-rock interaction processes (F2 and F3) are less responsible for the water chemistry of the Ischia Island. Samples along fractured zones, associated with lower salinity water (north and south-west zones) show the highest scores of F2 and F3, except for the Punta Caruso-Lacco area. Here seawater and deep fluids overlap in sampled chemistry water. This distribution of the hydrogeochemical processes reveals a highly complex hydrogeological scenario, with waters highly different in the composition being collected very close due to strong control played by fractures and faults.

The complex lithological/structural system indicates that towards the center of the island the principal groundwater source is the meteoric recharge, which infiltrates to deeper levels where a mixture with hot fluids occurs. The groundwater flows towards the coast where seawater intrusion occurs due to boreholes pumping. The water-rock interaction (precipitation/dilution) is enhanced by high temperature in fractures, and towards the coast where the seawater intrusion promotes the ionic exchange process.

From a temporal point of view, the samples from Di Napoli et al. (2007) establish that the seawater intrusion has increased over time all along the coastline reaching values up to 90%. While low values of fsea continue in the central part of the island. Despite this extra input of cold seawater, the temperature of the system is stable, at high temperatures, suggesting a very efficient heat transport in this active geothermal system.

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Figure Captions

Figure 1. Structural and geological map of Ischia Island. Modified from Paoletti et al. (2015); Nocentini et al. (2015) and Lima et al. (2003).

Figure 2. Hydrological zonation of Ischia Island, modified from Celico et al. (1999). Blue squares and circles represent the locations of sampled springs and boreholes, respectively. Blue stars SW and FW identify the sample location of the reference seawater and groundwater samples, respectively.

Figure 3. Spatial distribution of sample temperatures (colors) and electric conductivity (size) in the area of study.

Figure 4. Linear correlation (a) and spatial distribution (b) of temperature and chloride contents in water samples from Ischia Island.

Figure 5. Chloride contents versus elemental concentrations of Na (a), K (b), Ca (c), Mg (d), Br (e), B (f), Li (g) and Sr (h) for the springs (blue square) and borehole (blue circles) samples of Ischia Island. SW and FW end-members are also reported.

Figure 6. Spatial distribution of saline factor calculated with data from this work (a) and from Di Napoli et al. (2009) (b and c). In Figure 6b are presented the fsea calculated with only the samples from Di Napoli et al. (2009) collected in the same wells of the present work. In Figure 6c, the fsea are calculated with all samples from Di Napoli et al. (2009).

Figure 7. Spatial distribution of calculated factors F1 (a), F2 (b) and F3 (c) scoring for each sample.