



UNIVERSITÀ POLITECNICA DELLE MARCHE  
Repository ISTITUZIONALE

Natural and anthropogenic factors driving groundwater resources salinization for agriculture use in the Campania plains (Southern Italy)

This is a pre print version of the following article:

*Original*

Natural and anthropogenic factors driving groundwater resources salinization for agriculture use in the Campania plains (Southern Italy) / Mastrocicco, M.; Gervasio, M. P.; Busico, G.; Colombani, N.. - In: SCIENCE OF THE TOTAL ENVIRONMENT. - ISSN 0048-9697. - ELETTRONICO. - 758:(2021). [10.1016/j.scitotenv.2020.144033]

*Availability:*

This version is available at: 11566/286825 since: 2024-07-17T09:58:34Z

*Publisher:*

*Published*

DOI:10.1016/j.scitotenv.2020.144033

*Terms of use:*

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. The use of copyrighted works requires the consent of the rights' holder (author or publisher). Works made available under a Creative Commons license or a Publisher's custom-made license can be used according to the terms and conditions contained therein. See editor's website for further information and terms and conditions.

This item was downloaded from IRIS Università Politecnica delle Marche (<https://iris.univpm.it>). When citing, please refer to the published version.

(Article begins on next page)

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/347240579>

# Natural and anthropogenic factors driving groundwater resources salinization for agriculture use in the Campania plains (Southern Italy)

Article in Science of The Total Environment · December 2020

DOI: 10.1016/j.scitotenv.2020.144033

CITATIONS

0

READS

89

4 authors:



**Micòl Mastrocicco**

Università degli Studi della Campania "Luigi Vanvitelli"

218 PUBLICATIONS 1,473 CITATIONS

[SEE PROFILE](#)



**Maria Pia Gervasio**

Università degli Studi della Campania "Luigi Vanvitelli"

2 PUBLICATIONS 1 CITATION

[SEE PROFILE](#)



**Gianluigi Busico**

Aristotle University of Thessaloniki

33 PUBLICATIONS 175 CITATIONS

[SEE PROFILE](#)



**Nicolò Colombani**

Università Politecnica delle Marche

208 PUBLICATIONS 1,512 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Special Issue "Salinization of Water Resources: Ongoing and Future Trends" [View project](#)



Special Issue "Salinization of Coastal Aquifer Systems". A special issue of Water (ISSN 2073-4441). [View project](#)

1 **Natural and anthropogenic factors driving groundwater resources**  
2 **salinization for agriculture use in the Campania plains (Southern Italy)**

3 Micol Mastrocicco<sup>1</sup> Maria Pia Gervasio<sup>2,3</sup>, Gianluigi Busico<sup>1</sup>, Nicolò Colombani<sup>2#</sup>

4

5 <sup>1</sup>DiSTABiF - Department of Environmental, Biological and Pharmaceutical Sciences and  
6 Technologies, Campania University “Luigi Vanvitelli”, Via Vivaldi 43, 81100 Caserta, Italy

7 <sup>2</sup>SIMAU - Department of Materials, Environmental Sciences and Urban Planning, Polytechnic University of  
8 Marche, Via Breccie Bianche 12, 60131 Ancona, Italy

9 <sup>3</sup>SVeB - Department of Life Sciences and Biotechnology, University of Ferrara, Via L. Borsari 46,  
10 44121 Ferrara, Italy

11

12 #Corresponding author: Dr. Nicolò Colombani (n.colombani@univpm.it)

13

14 **Highlights**

15 Mechanisms of groundwater salinization are studied at the coastal aquifer scale

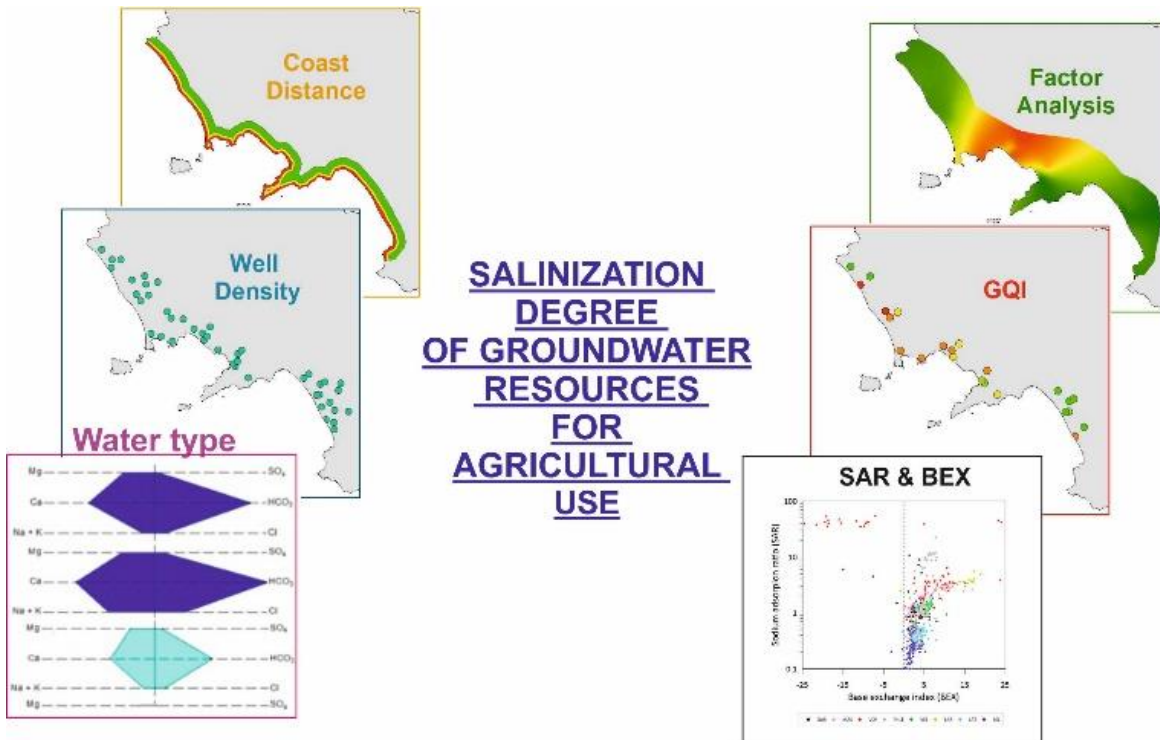
16 Withdrawals in greenhouses areas near the coast led to groundwater salinization

17 BEX and SAR temporal-spatial trends discriminate natural Vs. anthropic salinization

18

19 **Graphical abstract**

20



**SALINIZATION  
DEGREE  
OF GROUNDWATER  
RESOURCES  
FOR  
AGRICULTURAL  
USE**

21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37

**ABSTRACT**

The Mediterranean region is under pressure for a more sustainable use of water resources in view of the actual and future climate change. Under this pressure, the need to better assess the links between groundwater availability and quality and irrigated agriculture, is becoming urgent. Through the hydrogeologic and hydrochemical characterization of the coastal aquifers of a representative Mediterranean study area (the Campania Region in southern Italy), this study strengthened the analysis of basic components of the groundwater cycle and their temporal variability, including hydrologic, environmental and socio-economic aspects. Selected physiochemical properties of groundwater in 52 monitoring wells were considered from the Campania Environmental Protection Agency database. A total of 626 samples were collected from 2004 to 2018 to capture the water quality variability. Factor analysis and a specific groundwater quality index were also applied on 23 samples in two different timelines (2006, 2016) to capture the hydro-chemistry evolution through year. Moreover, land use and active pumping wells locations were used in the analysis. Spatial and temporal trends of base exchange indices (BEX) and sodium adsorption ratio (SAR) were computed along with Pearson coefficient among different variables, like well densities and distance from the coast. The

38 variation in the distribution of salinity between 2006 and 2016, along with highly positive and highly negative  
39 BEX and groundwater quality index values, indicate unstable conditions for the future. In the greenhouse's  
40 areas, where groundwater exploitation is elevated, an increase of salinity was recorded due to seawater  
41 intrusion. In volcanic districts water rock interaction is the main driver of groundwater salinization, while  
42 mixing processes with carbonate freshwaters diminish groundwater salinities in the alluvial plains. This study  
43 demonstrates that groundwater over pumping can have a major impact on groundwater quality used for  
44 irrigation, despite the dominant influence that local geological and morphological features exert on the area.

45

## 46 **Keywords**

47 Regional hydrology; salinization; irrigation and drainage; water-rock interaction; freshwater-seawater mixing,  
48 GQI, factor analysis.

49

50

## 51 **1. INTRODUCTION**

52 The Mediterranean region is undergoing intensive demographic, social, economic, and environmental changes.  
53 Almost a third of the Mediterranean basin's population (about 170 million in 2020) actually lives within coastal  
54 plains covering less than 12% of the surface area of the Mediterranean countries (<https://ec.europa.eu/eurostat>).  
55 In addition to the widespread ongoing urbanization, the Mediterranean coastal areas are also intensively  
56 exploited for agriculture purpose. Cereals, vegetables, and citrus fruits account for over 85% of the  
57 Mediterranean's total agricultural production. Moreover, cultivation of other products, such as olives and  
58 grapes, also occupies a significant amount of agricultural land (Leff et al., 2004). In this context, water  
59 resources play a crucial role, so that in the Mediterranean basin, agriculture accounts for 70% of total water  
60 use. So, crop irrigation represents the main water utilization, reaching the higher intensity especially in summer  
61 (80% of total water use), when crops grow, precipitation decreases, and evapotranspiration consequently  
62 increases. As a main consequence, the Water Exploitation Index (WEI) shows that many Mediterranean  
63 regions are currently classified as water-stressed, with several countries showing a WEI higher than 40%  
64 (<https://www.eea.europa.eu/data-and-maps>). Almost the 30% of Mediterranean regions are classified as water

65 stressed with a WEI  $\geq$  20% (Turkey, Belgium, Italy, Cyprus, and Malta) that is widely considered as a warming  
66 threshold (Alcamo et al., 2010). The increasing need of freshwater for irrigation has progressively put more  
67 pressure onto groundwater resources, also because of the loss of surface water resources due to contamination  
68 (Arnell, 1999; Priyantha Ranjan et al., 2006). In the next years, the phenomenon of Climate Change (CC) will  
69 most probably exacerbate this issue. For the Mediterranean Region, recent studies predicted sea level rise  
70 (SLR), an increase in temperature, especially in summer, a probable decrease in precipitation and a change in  
71 the in-year recharge and evapotranspiration patterns (Cramer et al., 2018). So far, most of the studies have  
72 been done on the above ground components of the hydrologic cycle, both on historical and projected changes.  
73 On the other hand, for the subsurface components (recharge, groundwater levels, aquifer fluxes and  
74 groundwater quality), the scientific knowledge is still incomplete. In lowland coastal area, a small rate of sea-  
75 level rise will cause an inland shift of saline groundwater (Colombani et al., 2016; Yechieli et al., 2010). In  
76 addition, changing precipitation regimes and groundwater recharge rates may cause a similar landward shift  
77 of the saltwater-freshwater interface (Chang and Yeh, 2010; Werner et al., 2013). Under this pressure, the need  
78 to better assess the links between groundwater availability and quality and irrigated agriculture, especially on  
79 a regional scale, is becoming urgent (Romanelli et al., 2012). The concept of groundwater “quality” is strongly  
80 related to its chemical composition and destination of use. Generally, a water classified as excellent in chemical  
81 and biological quality is mainly retained for human consumption, while agricultural needs can be usually met  
82 by water of lesser quality. So, it is important to properly evaluate the water (superficial or groundwater) quality  
83 in accordance with its main use. To achieve this target several methodologies have been developed, and a brief  
84 description is available in Machiwal et al. (2018). Among these, groundwater quality indices (GQIs) and Fit  
85 for purpose (FFT) evaluations have been the more widely applied methods due to their relative ease of use  
86 (Bui et al., 2020; Rufino et al., 2019; Karim et al 2020; Jha et al., 2020). These methodologies involve the  
87 evaluation of all those variables responsible of groundwater quality (i.e. chemical, physical, and microbial)  
88 finally summarizing them in an lumped numerical index in relation to the various water quality thresholds such  
89 as the i) World Health Organization (WHO) standards, ii) FAO guidelines or iii) regional standards. The  
90 concept of water quality is moreover directly linked with the sustainability of irrigated agriculture that is  
91 questioned in many coastal areas for a combination of factors, but above all for the risk of salinization. In fact,  
92 salinization affects almost 10% of irrigated land (Tanji and Kielen, 2002). The salt accumulation in

93 Mediterranean soils and aquifers is a natural process favoured by the region's ecological conditions, which can  
94 however be modified by human activities, especially in flat arable lands. In fact, once groundwater become  
95 saline, its fate within the aquifers is most of the times long lasting (Foster and Chilton, 2003). Moreover, when  
96 groundwater resources with high salinity content are used for irrigation, they can cause water stress leading to  
97 yield reduction, especially for crops with limited salt tolerance. Thus, understanding the salinization processes  
98 within coastal aquifers at regional and long-term scales among with groundwater quality evolution is a  
99 prerequisite to evaluate the sustainability of irrigated agriculture. The recognition of groundwater salinization  
100 origin in coastal aquifers is not a straightforward task; in fact, beside actual seawater intrusion (SWI),  
101 groundwater salinization can result from other natural salt sources or from human activities. The most relevant  
102 salt sources/processes are: i) water rock interaction, ii) the mobilization of salts stored in the unsaturated zone  
103 (Walter et al., 2017), iii) evapoconcentration (Colombani et al., 2018), iv) slow-moving saline/saltwater of  
104 marine origin (Meyer et al., 2019), v) highly mineralised waters from geothermal fields (Regenspurg et al.,  
105 2010), and finally vi) the agricultural practices mainly as return flow (Foster et al., 2018). The salt sources may  
106 have different geochemical imprints, thus an approach by multiple natural tracers is required for their  
107 recognition (de Montety et al., 2008). Whatever the salt source, its recognition is often masked by mixing of  
108 fresh and saline waters and by water-rock interactions due to increase in water ionic strength (Belkhiri et al.,  
109 2010). On one hand, the mixing processes are normally enhanced by human actions as over-exploitation  
110 (causing lateral SWI and/or upconing) and presence of drainage systems for land reclamation (Barlow and  
111 Reichard, 2010; Custodio, 2010). On the other hand, the main processes that might occur during water-rock  
112 interactions are cation exchange, redox reactions, dissolution/precipitation, evapoconcentration, and  
113 leakage/seepage of saltwater (de Montety et al., 2008; Mollema et al., 2013). Accordingly, to define the  
114 ongoing hydrogeochemical processes within an aquifer system can be a difficult task, and sometimes the  
115 analyses of large data sets among with the utilization of advanced statistical methodologies is required. In this  
116 scenario multivariate statistical analysis such as factor analysis (FA) and principal component analysis (PCA)  
117 has proven to be a useful and a worldwide applied tool that allow to properly explain the main  
118 hydrogeochemical factors responsible for the chemical groundwater composition (Hynds et al., 2014; Kazakis  
119 et al., 2017; Zanolini et al., 2019). For example, Busico et al. (2018, 2020) successfully utilized the FA to  
120 identify all the hydrochemical factors in two coastal plains within the Campania plain, stating how this

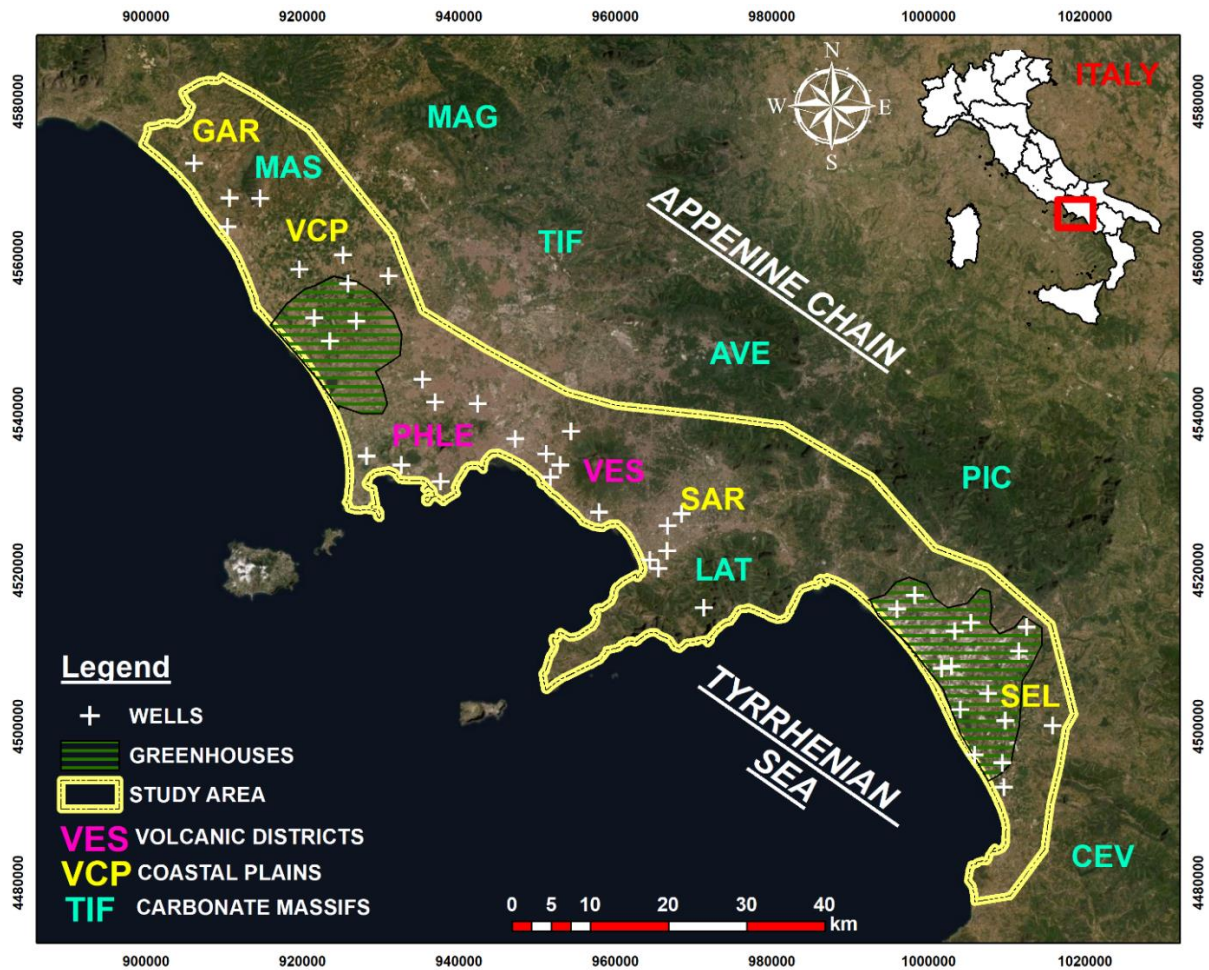
121 methodology can be useful in discriminate and identify the different mineralization processes. Through the  
122 hydrogeologic and hydrochemical characterization of the coastal aquifers of a representative Mediterranean  
123 study area (the Campania Region in southern Italy), this study aims at strengthening the understanding of the  
124 analysis of basic components of the groundwater cycle and their temporal variability, including hydrologic,  
125 environmental and socio-economic aspects. This was achieved identifying the origin and the mechanism of  
126 groundwater salinization, taking into account the main drivers (e.g. subsidence, coastal erosion, sea level rise,  
127 meteo-climate variability, lowering of the water table) and verifying whether the current irrigation strategies  
128 have created imbalances to the fresh/salt water interface and assess their sustainability in the future, also in  
129 view of possible climate and land use changes. Multivariate statistical analysis along with a Specific  
130 Groundwater Quality Index (SGQI) has been utilized to identify the main hydrochemical processes that  
131 characterize the study area and to define the groundwater salinization degree for the irrigation water utilization  
132 for cereals (corn, wheat and oath) production. Moreover, a time series analysis has been conducted to describe  
133 the intensification/lessening of the salinization process and the corresponding changes in water quality  
134 accordingly with the climate, land cover, and management variation that has interested the last twenty years.

## 135 **2. MATERIAL AND METHODS**

### 136 **2.1. Study Area**

137 The Campania Region (southern Italy) with its nearly 6 million of inhabitants, of whom 50% live in coastal  
138 plains, with 15% of urban areas and more than 50% of agricultural land, could be considered a representative  
139 study area to address the issues previously described (Minolfi et al., 2016). The Campania region, surrounded  
140 by the Apennine to the west and the Tyrrhenian Sea to the east (Fig. 1), has a Mediterranean climate with cold  
141 winters and dry summers. The minimum average temperature is 10.2 °C and the maximum average temperature  
142 is 19.6 °C.





143

144 **Figure 1:** Geographical setting of the Campania Region and location of the monitoring wells and of the  
 145 greenhouse areas in the VCP and SEL coastal plains.

146

147 Precipitations happen primarily in the period between October and May, showing strong patterns in terms of  
 148 elevation and proximity to the sea (Ducci and Tranfaglia, 2008). The highest precipitation occurs in the  
 149 Apennine, with values up to 2000 mm/y, while in the coastal plains values around 800 mm/y are registered  
 150 (Busico et al., 2017). From a geological point of view, the Apennine is characterized by sedimentary rocks like  
 151 limestones, dolomites and terrigenous sediments of Mesozoic age, buried under variable thicknesses of  
 152 Neogene units, mainly made of volcanoclastic materials coming from the Roccamonfina Volcano, the Somma-  
 153 Vesuvio and Campi Flegrei districts; the plains are characterized by Quaternary sediments (alluvial and  
 154 lacustrine deposits). The Campania region includes many hydrogeological systems: quaternary alluvial  
 155 deposits, pyroclastic deposits, carbonate karstified systems and silico-clastic systems (Ducci et al., 2019).

156 Since the present study was intended to address the salinization of water resources only in coastal plains, the  
 157 Campania Region was not entirely considered but a coastal strip of 2300 km<sup>2</sup> (approximately 150 km along  
 158 the coast x 15 km inland, highlighted with the yellow bold line in Fig. 1) was selected, where the pressure of  
 159 agricultural activities and urbanization are particularly high (see Table 1). From NW to SE the Campanian  
 160 coastal area presents the graben of the Garigliano Plain (GAR), the horst of Monte Massico (MAS), the graben  
 161 of the Campana Plain, the horst of Monti Lattari (LAT), the graben of the Sele plain (SEL). The Campana  
 162 Plain is further divided, by two topographic highs of the Phlegraean Fields (PHLE) and the Vesuvius volcanoes  
 163 (VES), into the Volturno coastal plain (VCP), the Sebeto coastal plain (here discussed together with the VES  
 164 group) and the Sarno River coastal plain (SAR) (Fig. 1).

165  
 166  
 167  
 168

169 **Table 1.** Extension, elevation, and population density of coastal plains (GAR, VCP, SAR, SEL), volcanic districts  
 170 (PHLE and VES) and carbonate massifs (MAS and LAT) with the relative percentage of land for agricultural use.  
 171 To locate each morphological unit, refer to Figure 1.

172

	<i>Area</i> (Km <sup>2</sup> )	<i>Agric. Area</i> (%)	<i>Median Elev. (min./max.)</i> (m a.s.l.)	<i>Pop. Dens.</i> (inhabitants/Km <sup>2</sup> )
<b>GAR</b>	137	87	18 (-1/486)	176
<b>VCP</b>	1068	81.8	7 (-2/528)	776
<b>SAR</b>	198	67.7	22 (0/652)	2232
<b>SEL</b>	430	87	31 (0/312)	363
<b>PHLE</b>	203	43.2	139 (0/460)	4458
<b>VES</b>	430	66.3	289 (0/655)	2704
<b>MAS</b>	29	18.1	370 (29/812)	25
<b>LAT</b>	260	25	713 (2/1428)	583

173

174 The plains result from the aggradation of structural depressions (Pappone et al., 2011): the Campana Plain  
 175 (VCP, VES and SAR) comes from volcano-sedimentary aggradation of the peri-Tyrrhenian graben from the  
 176 Lower Pleistocene (Milia and Torrente, 2003), when most of the Plain was occupied by transitional and  
 177 shallow marine environments; the Sele Plain (SEL) derives from the sedimentary aggradation of a Plio-  
 178 Quaternary depression along the western margin of the southern Apennine extending about 400 km<sup>2</sup>.  
 179 The studied sector of the VCP is characterized by a flat morphology (slope <5°) with a wide lowland area  
 180 reclaimed starting in the XVI century, which allowed for the development of agriculture and farming as well  
 181 as severe urbanization along the coastal zone (Ruberti and Vigliotti, 2017).  
 182 Recently, the VCP plain, experienced a retreat of hundreds of metres of the Volturno delta due to the reduction  
 183 of sediment discharge and to coastal erosion. VCP is also affected by a long-term subsidence that nowadays  
 184 occurs at up to 10 mm/y (where lacustrine deposits are found) due to natural processes, locally accelerated by  
 185 urbanization, water pumping and drainage for the intense agricultural activities (Matano et al., 2018). Even in  
 186 the SAR, subsidence appears to have continued until the historical period. SEL has experienced an erosional  
 187 phase, with a maximum erosion of 4.8 m/y close to the river mouth (Pappone et al., 2011).  
 188 From NW to SE the prevailing soil types according to the Soil Map of the Campania Region 1:250.000  
 189 (<http://agricoltura.regione.campania.it/pedologia/suoli.html>), are reported in Table 2.

190

191 **Table 2.** Main and secondary (according to their extension) soil types found in coastal plains (GAR, VCP, SAR,  
 192 SEL), volcanic districts (PHLE and VES) and carbonate massifs (MAS and LAT). The cation exchange capacity  
 193 (CEC) and the drainage capacity of soil types are also reported.

194

	Main soil type	CEC	Drainage capacity	Secondary soil type	CEC	Drainage capacity
<b>GAR</b>	Deep Vertic & Fluvic Cambisols	high	moderate - good	Eutric Vertisols & Calcic Vertisols	high	moderate - good
<b>VCP</b>	Deep Eutric & Calcic Vertisols, Fluvic Cambisols	high	moderate- good	Deep Vertic & Fluvic Cambisols, Mollic Gleyisols	high- medium	good-low

<b>SAR</b>	Deep Fluvic Cambisols	low	good-high	Deep Vitric Cambisols & Gleyic Andosols	medium-low	good-low
<b>SEL</b>	Shallow Calcaric Fluvisols & Fluvic Cambisols	medium	good-high	Shallow Eutric Fluvisols	medium	moderate
<b>PHLE</b>	Deep Haplic & Mollic Andosols	medium-high	good-high			
<b>VES</b>	Deep Vitric Cambisols & Humic Andosols	medium	good			
<b>MAS</b>	Shallow Epileptic Andosols, Regosols & Mollic Leptosols	high	good-high	Deep Eutric Andosols	high	good
<b>LAT</b>	Shallow Vitric Andosols	medium	good	Eutric & Luvic Andosols	medium	good

195

196 In the coastal area, the mean annual precipitation (2004–2018) is 870 mm and the mean annual  
197 evapotranspiration is 968 mm. From 2004 to 2018 the average precipitation diminished of about 20-25% for  
198 all the coastal plains considered in this study. Nevertheless, Campania is not a highly water stressed region,  
199 but irrigation of agricultural land is essential since this is one of the more productive agricultural areas in Italy,  
200 valuable crops such as vegetables, fruits, olives and grapes. Irrigated land is between 58% and 67%, with an  
201 input of 160-190 mm over the growing season. Water allocation is managed by water districts for irrigation  
202 and drainage. Most of the irrigation water comes from large diversions from the rivers crossing the coastal  
203 plains (see Table 3). For the Volturno river, withdrawals for irrigation (up to 35% of the river discharge)  
204 induced a decrease in river discharge during summer, with minimum values sometimes lower than the  
205 historical minimums recorded in the last decades. This induced a lowering of the piezometric heads, leading  
206 to sporadic saltwater intrusion events, which have already occurred in some coastal areas of VCP. Also, the  
207 Sele river, especially in recent years, is negatively affected by withdrawals granted for irrigation (up to 25%  
208 of the river discharge), with frequent imbalances between the summer river discharge and the active  
209 withdrawal concessions. Groundwater flow direction in the coastal aquifers of Campania is roughly oriented  
210 NE-SW towards the Tyrrhenian Sea. The water table generally lies close to the land surface, facilitating losses  
211 via evapotranspiration (see Table 3).

212

213 **Table 3.** Average Precipitation (P), Potential Evapotranspiration (PET), Water Table (WT) depth and River  
 214 Discharge (RD) during the monitoring period (2004-2018), in coastal plains (GAR, VCP, SAR, SEL), volcanic  
 215 districts (PHLE and VES) and carbonate massifs (MAS and LAT).

	Mean P	Mean PET	Mean WT depth	Mean RD
	(mm)	(mm)	(m b.g.l.)	(Mm <sup>3</sup> /y)
<b>GAR</b>	1011	1095	6-12	3784 (Garigliano)
<b>VCP</b>	937	922	1-6	2586 (Volturno)
<b>SAR</b>	1084	1116	3-18	410 (Sarno)
<b>SEL</b>	1215	1268	5-40	2185 (Sele +Tusciano)
<b>PHLE</b>	847	956	50-250	-
<b>VES</b>	985	1007	10-23	-
<b>MAS</b>	985	973	-	-
<b>LAT</b>	1236	1175	-	-

216

## 217 **2.2. Sampling and analytical methods**

### 218 *2.2.1 Database selection*

219 For this study, selected physiochemical properties of groundwater in 52 monitoring wells (see Fig. 1 for  
 220 location) from the online available dataset of ARPAC (Agenzia Regionale per la Protezione Ambientale in  
 221 Campania) [ARPAC, 2019] were considered. A total of 626 samples were collected in wet and dry seasons  
 222 from 2004 to 2018 to capture the water quality variability (see Table 4). Water samples were grouped with  
 223 respect to their sampling environment into coastal plains (GAR, VCP, VES, SAR and SEL), volcanic districts  
 224 (PHLE and VES) and carbonate massifs (MAS and LAT) (Fig. 1).

225 Among the large ARPAC database, temperature, electrical conductivity (EC), pH, chloride (Cl), bicarbonate  
 226 (HCO<sub>3</sub>), sulphate (SO<sub>4</sub>), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K) and boron (B), were  
 227 selected to carry out this study. Temperature, EC, and pH were measured in situ, while samples intended for  
 228 major ions analyses were collected in HDPE bottles and analysed in a laboratory following the international  
 229 standards guidelines (APHA, 2017). The ionic balance was calculated for all samples and samples with an  
 230 ionic balance exceeding  $\pm 5\%$  were not included in the water type analysis.

231

232 **Table 4.** Summary of the groundwater physiochemical parameters database. N° refers to the number of observations

233 available for the selected parameter; M. is the median value for the selected parameter for each year.

	<b>HCO<sub>3</sub> (mg/l)</b>		<b>B (µg/l)</b>		<b>Ca (mg/l)</b>		<b>Cl (mg/l)</b>		<b>EC (µS/cm)</b>		<b>Mg (mg/l)</b>		<b>K (mg/l)</b>		<b>Na (mg/l)</b>		<b>SO<sub>4</sub> (mg/l)</b>	
	N°	M.	N°	M.	N°	M.	N°	M.	N°	M.	N°	M.	N°	M.	N°	M.	N°	M.
<b>2004</b>	52	415	26	218	52	104	47	72	46	947	47	31	47	15	47	49	47	46
<b>2005</b>	62	364	42	159	62	108	62	87	62	947	62	30	62	31	62	57	62	37
<b>2006</b>	62	415	56	45	62	110	56	74	56	1033	56	33	56	29	52	54	56	49
<b>2007</b>	63	4151	56	126	63	104	57	85	57	1086	57	36	57	35	57	52	57	55
<b>2008</b>	43	274	37	46	43	110	40	80	40	1093	40	36	40	30	40	43	40	34
<b>2009</b>	71	410	58	150	71	84	64	86	64	1024	64	34	63	31	64	56	64	51
<b>2010</b>	44	488	42	207	44	107	42	95	42	1110	42	35	42	46	42	78	42	58
<b>2011</b>	24	455	20	17	24	117	20	23	20	751	20	32	20	6	20	18	20	24
<b>2012</b>	69	439	62	67	70	113	62	52	62	1028	62	35	62	13	62	50	62	44
<b>2013</b>	59	366	63	44	71	94	63	55	62	998	63	30	63	26	63	50	63	54
<b>2014</b>	64	468	54	69	65	104	67	81	67	1120	55	34	55	30	55	58	67	76
<b>2015</b>	47	463	47	97	47	114	42	67	41	1100	42	33	42	27	42	53	42	61
<b>2016</b>	28	439	24	63	28	166	26	37	24	805	24	42	24	21	24	47	33	38
<b>2017</b>	37	427	36	77	37	135	42	45	40	845	37	35	37	15	37	57	46	22
<b>2018</b>	37	488	33	66	89	37	43	40	42	885	37	30	37	13	37	32	43	23

234

235

236 *2.2.2. Data Analyses*

237 Groundwater samples were assigned to a given hydro-chemical class considering the major dissolved cations

238 and anions, by using Stiff diagrams via the Excel macro PiperStiff-QW-2019.v5, freely available on-line

239 (<https://halfordhydrology.com/piper-and-stiff/>). Salinity was subdivided into four classes according to Rhoades

240 et al. (1992) (Fig. 4). The long-term effect of irrigation water on physical and chemical properties of soil and

241 crop productivity depends on several factors, like Na and alkaline earth elements (Ca and Mg) content,

242 electrical conductivity, and initial physical properties of soil. In this study, to assess the degree of salinization

243 for irrigation groundwater of Campania Plains, the following parameters were used: Sodium Adsorption Ration  
244 (SAR), electrical conductivity (EC) and Base Exchange index (BEX).

245 There is a significant relationship between SAR values and the effect on soils: at high SAR, the cation exchange  
246 complex may become saturated with Na, leading to a loss of soil structure due to the dispersion of clay  
247 particles. SAR is computed from the following equation (Oster and Sposito, 1980):

248

$$249 \quad SAR = \frac{Na^+}{\sqrt{\frac{1}{2}(Ca^{2+}+Mg^{2+})}} \quad (1)$$

250

251 where  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  concentrations are expressed in meq/L.

252 The identification of spatial and temporal changes in the position of the freshwater/saltwater interface may be  
253 obtained applying the BEX, which defines cation exchange reactions due to water–rock interactions when  
254 saline water enters a freshwater aquifer and vice versa (Vandenbohede and Lebbe, 2012). For instance, during  
255 salinization sea water (with high Cl, Na, K and Mg) displaces fresh water with high Ca and  $HCO_3$  and Na is  
256 adsorbed, conversely during freshening Ca is adsorbed. BEX was calculated according to the following  
257 formulas, for Ca and Mg rich aquifers, respectively (Stuyfzand, 2008):

258

$$259 \quad BEX = Na + K + Mg - 1.0716 Cl \quad (2)$$

260

$$261 \quad BEXD = Na + K - 0.8768 Cl \quad (3)$$

262

263 where 1.0716 and 0.8768 equal to  $[Na+K+Mg]/Cl$  and  $[Na+K]/Cl$  for mean ocean water in meq/L, respectively  
264 (Riley and Skirrow, 1975). The BEX application subdivided groundwater samples into three classes: positive  
265 during freshening, negative during salinization and zero when there is no base exchange, and the situation is  
266 stable. Saturation indices (SI) for various mineral phases and ionic balances were calculated with PHREEQC-3  
267 (Parkhurst and Appelo, 2013). When SI of a given mineral is negative the solution is undersaturated and the mineral  
268 (if present in the aquifer) may dissolve, while if SI is positive the mineral may precipitate. Finally, the groundwater  
269 dataset together with some representative drivers of groundwater salinization (e.g. distance from the coastline, well

270 density) were analysed using Pearson correlation via Excel 2016 (Microsoft, Redmond, WA, USA) without data  
271 normalization. Linear mixing lines were created for freshwater/seawater and for freshwater/geothermal waters;  
272 using for the freshwater end-member the less saline groundwater present in the database, for the seawater end-  
273 member the mean Tyrrhenian seawater composition (Pennisi et al., 2006) and for the geothermal end-member the  
274 composition found by Cuoco et al. (2017b).

275

### 276 *2.2.3. Multivariate statistical analysis and GQI.*

277 For this study, a multivariate statistical approach through the application of FA has been applied to: i) discriminate  
278 all the hydrogeochemical processes occurring in the studied aquifer in two different time period (2006 and 2016)  
279 and ii) to evaluate the evolution intensity of the main salinization process through time. A 10-years interval has been  
280 chosen i) to involve at least a decadal climate variability in the analysis which is considered the minimum time laps  
281 to appreciate a variation in the climate regime and its effect (Kim et al., 2012, Dono et al., 2013), and ii) to obtain a  
282 proper evaluation considering the same sampling wells accordingly to the data availability, as the monitoring  
283 database suffer of several missing analysis and only few years allow a comparative assessment. The FA has become  
284 a robust approach worldwide applied in all the geoscience fields allowing to highlight the relationships between  
285 observed variables creating a list of few significant factors which include them. The number of factors are chosen  
286 following the Kaiser criterion (Kaiser, 1960) hence considering significant those factors with an eigenvalue higher  
287 than 1, while the overall meaningfulness are considered significant with the Kaiser-Meyer-Olkin (KMO) coefficient  
288 higher than 0.5 (Kumar, 2014). The average values of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{B}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , EC and SAR within  
289 the same twenty-three sample for the 2006 and the 2016 has been utilized as variables. The GQI evaluation instead,  
290 has been calculated following the methodology proposed by Babiker et al. (2007). The SGQI for this study,  
291 has been created utilizing the threshold values suggested from Food and Agricultural Organization (Ayers and  
292 Westcot, 1994.) and reported in Table 5 for the optimal cereals grow. Accordingly, a salinization assessment  
293 has been carried out based on GQI structure for 24 monitoring wells. Similarly for FA, the GQI has been  
294 calculated for 2006, 2016 and its decadal evolution.

295



296 **Table 5:** Water Quality Criteria for GSIQ

<i>Parameters</i>	<i>Units</i>	<i>Cereals</i>
<i>Boron (B)</i>	mg/L	2
<i>Chloride (Cl)</i>	mg/L	300
<i>Electrical Conductivity (EC)</i>	μS/cm	1100
<i>Sodium (Na)</i>	mg/L	300
<i>Sodium Absorption Ratio (SAR)</i>	-	10
<i>Total Dissolved Solid (TDS)</i>	mg/L	704

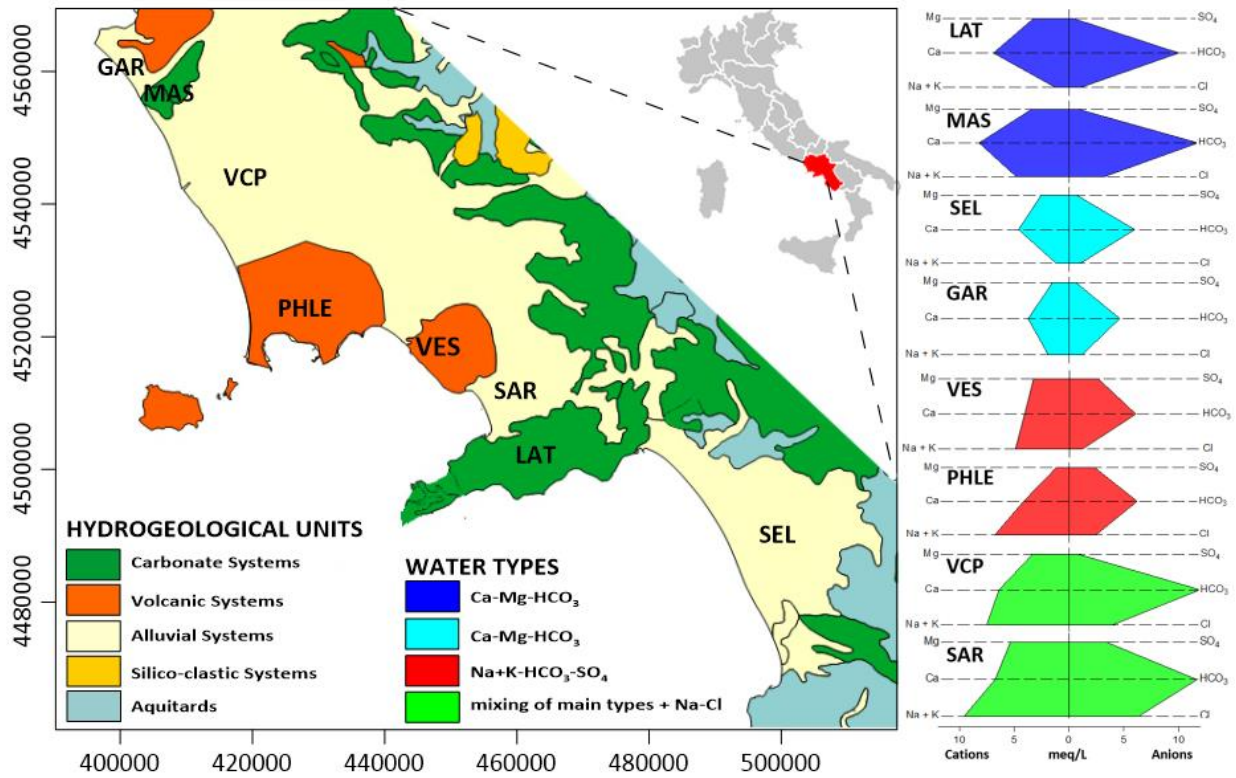
297

### 298 **3. RESULTS**

#### 299 **3.1 General hydro-geochemistry.**

300 Water-rock interaction processes dominate the composition of most of groundwater samples (Buondonno et  
 301 al., 2007; Cuoco et al., 2017a). From the chemical results of the 626 water samples, 4 main water types were  
 302 identified (Fig. 2). In summary, 57% are of the Ca-Mg-HCO<sub>3</sub> type (where Ca is largely prevailing on Mg),  
 303 23% are Na+K-HCO<sub>3</sub>-SO<sub>4</sub> type (where HCO<sub>3</sub> is largely prevailing on SO<sub>4</sub>), 1% are Na-Cl type and 19% are a  
 304 mixing between the two dominant types and the Na-Cl type. Among the Ca-Mg-HCO<sub>3</sub> type that is found in  
 305 correspondence of the carbonate massifs and the plains delimited by them (Fig. 2), two groups are evident: on  
 306 one hand LAT and MAS show a saturation index (SI) of Calcite of 3.6 and a SI of Dolomite of 6.1, on the  
 307 other hand SEL and GAR have a SI of Calcite of 2.4 and a SI of Dolomite of 3.7. The Na+K-HCO<sub>3</sub>-SO<sub>4</sub> type  
 308 which includes the volcanic districts of PHLE and VES is characterize by a SI of Gypsum of 0.81. Finally, the  
 309 alluvial systems of VCP and SAR are a variable mix of the previous water types with some samples showing  
 310 a large interaction with Na-Cl water type. The pH values of all the aquifers considered in this study ranges  
 311 between 6.5 and 8.3. Spatial and temporal variations of pH are controlled by the quality and the infiltration  
 312 rate of recharge water, the replenishing water rate and water-rock interaction in the aquifer. These pH values  
 313 are all in the desirable limits set by the World Health Organization (WHO). The temperature values of  
 314 groundwater varied from 12.2°C to 22.6°C.

315



316

317 **Figure 2:** Hydrogeological units and water types of the coastal zone of the Campania region.

318

### 319 3.2. FA applications

320 Both the results of FAs for 2006 and 2016 well agree with the above discussed geochemistry evaluation. The  
 321 same three factors have been identified in the two different timelines (2006 and 2016) (Table 6). The results  
 322 of FA have been spatialized using the Ordinary Kriging (OK). The OK is a geostatistical technique widely  
 323 utilized to spatial interpolate the values of a certain field in unobserved locations starting from nearby  
 324 observations points. In this study the factor scores belonging to each groundwater monitoring wells have been  
 325 considered as input variables to interpolate and consequently display the range and the degree of groundwater  
 326 salinization influenced by the common factors. This procedure has been commonly worldwide utilized with  
 327 excellent results (Busico et al., 2018, 2020, Shyu et al., 2011, Wang et al., 2001). The F1 explains the 34% of  
 328 the total variance and shows a positive correlation between  $\text{Na}^+$ , SAR,  $\text{Cl}^-$ ,  $\text{B}^+$  and EC highlighting the presence  
 329 of a persistent salinization probably due to phenomena of actual SWI, and to the water rock interaction with  
 330 shallow marine sediments and reworked volcanic materials (Busico et al., 2018). In F2, the chemical species  
 331 of  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  are strongly correlated, indicating the carbonate water-rock interaction, and

332 describing the 33% of the total variance. Finally, the F3, explaining the 22% of the total variance, strongly  
333 correlate  $K^+$  and  $SO_4^{2-}$ . Both elements are ascribable to intensive feldspar weathering process and magmatic  
334 fluid contact (Thivya et al. 2013). Among the three factors, F1 has been chosen as describer of SWI and saline  
335 water mixing process. In Figure 3 is shown the spatial distribution of F1 in the two different years (Fig. 3a, b)  
336 and its evolution through the decadal timeline (Fig. 3c). The legends of Figure 3a and 3b express the values of  
337 factor scores calculated through FA of the F1. Negative and positive values indicate low and strong magnitude  
338 of the process respectively, allowing the identification of those areas more prone to SWI. Specifically, for the  
339 2006 (Fig. 3a) the areas more affected are the whole coastal plains of VCP and SAR along with the northern  
340 part of SEL and volcanic districts of PHLE and VES. For the 2016, instead, a different situation was portrayed  
341 (Fig. 3b): the VCP showed a reduction of the process going far from the coastline accompanied by a slightly  
342 increase along the coastline. The SEL plain, instead, suffered of a general magnitude increase, especially in  
343 the southern sector of the plain. In Figure 3c is possible to appreciate the F1 evolution from 2006 to 2016. This  
344 map has been created realizing a spatial difference among 2016 and 2006 F1's maps, processing both the raster  
345 files in ArcGIS environment using raster calculator tool. The result highlighted where the process's magnitude  
346 has increased, decreased, or remained constant through the decadal timeline. Summarizing, those areas that  
347 have registered a SWI increase are the PHLE field along with GAR and SEL plains while no significative  
348 differences are verifiable near the main carbonate massifs (LAT and MAS). The spatial distribution of F2 and  
349 F3, responsible of carbonate influx and volcanic water rock interaction respectively, are shown in Figure S1  
350 and S2. These two factors are further contributing to the salinization degree of the local groundwater resources.  
351 The F2 characterized the whole VCP in the 2006 (Fig. S1a) due to the later influx from MAS carbonate relief,  
352 while in the 2016 it will be also more evident in the LAT reliefs and SAR plain (Fig. S1b). F3 instead, is  
353 perfectly localized within PHLE and VES volcanic centres (Fig. S1) with a lower lateral influence also within  
354 SAR and VCP plain. The main differences among 2006 and 2016 distribution is only related to the PHLE area  
355 where the magnitude of F3 slightly decrease (Fig. 3b) concurrently with the increase of F1 in the same area  
356 (Fig. 3c). The spatial distribution of FA's results further confirmed how each specific area is characterized by  
357 multiple processes of salinization aside of SWI, responsible of the main groundwater chemistry.

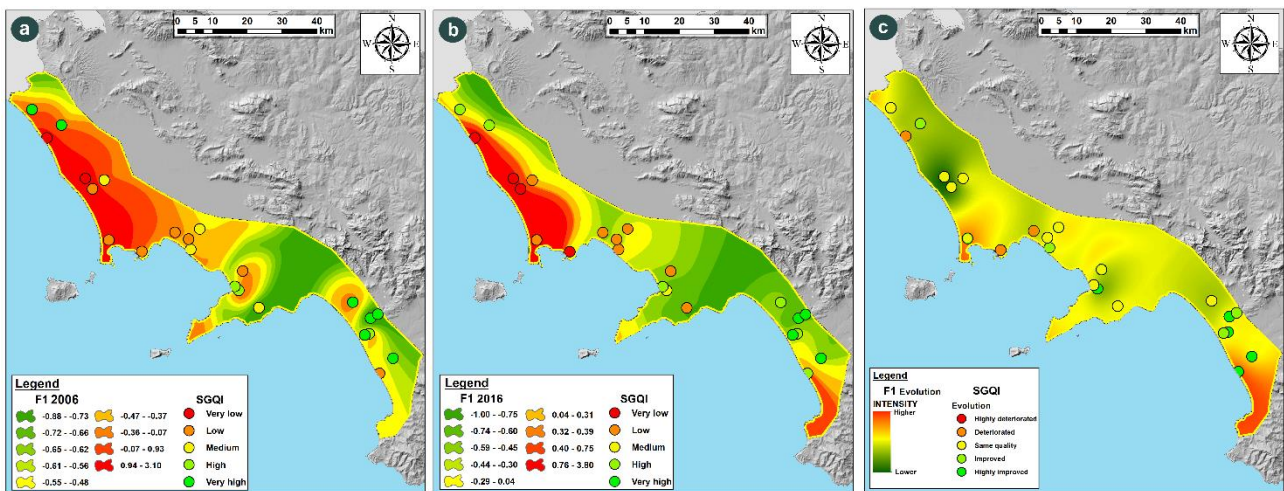
358

359

360 **Table 6.** Factors score for the applied FAs.

	FACTORS - 2006			FACTORS - 2016		
	F1	F2	F3	F1	F2	F3
HCO <sub>3</sub>	0.445	0.846	-0.181	0.163	0.771	-0.084
Na	0.908	0.354	0.158	0.900	0.290	0.258
SAR	0.936	-0.204	0.176	0.949	-0.226	0.107
Cl	0.669	0.542	0.297	0.643	0.531	0.408
K	0.267	0.106	0.928	0.234	0.270	0.821
Mg	-0.040	0.862	0.096	-0.076	0.907	0.180
B	0.761	0.410	0.410	0.644	0.515	0.258
SO <sub>4</sub>	0.179	-0.076	0.960	0.167	-0.201	0.831
Ca	0.108	0.893	-0.025	0.017	0.903	-0.122
EC	0.684	0.575	0.318	0.736	0.449	0.402
KMO	0.657			0.653		

361

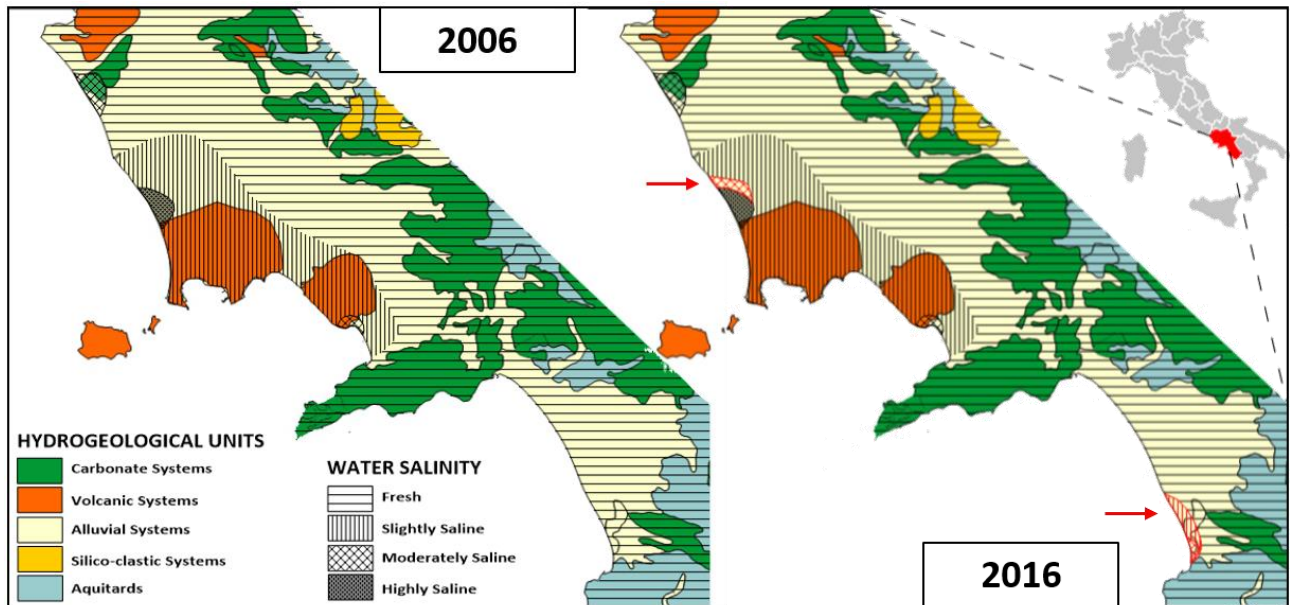


362

363 **Figure 3:** Spatial distribution of F1 for 2006 (a) and 2016 (b) along with correspondent SGQI. The figure 3  
 364 (c) shows the F1 and SGQI evolution trough time.

365 Similar results to F1 are represented in Figure 4, using the previous described salinity indices (BEX and SAR),  
 366 where the increasing salinity is magnified for the two coastal areas further confirming the phenomena. In VCP

367 an area that in 2006 was characterized by slightly saline waters, in 2016 become moderately saline.  
 368 Furthermore, in the southernmost part of SEL a large area shifted from freshwater to slightly saline.  
 369



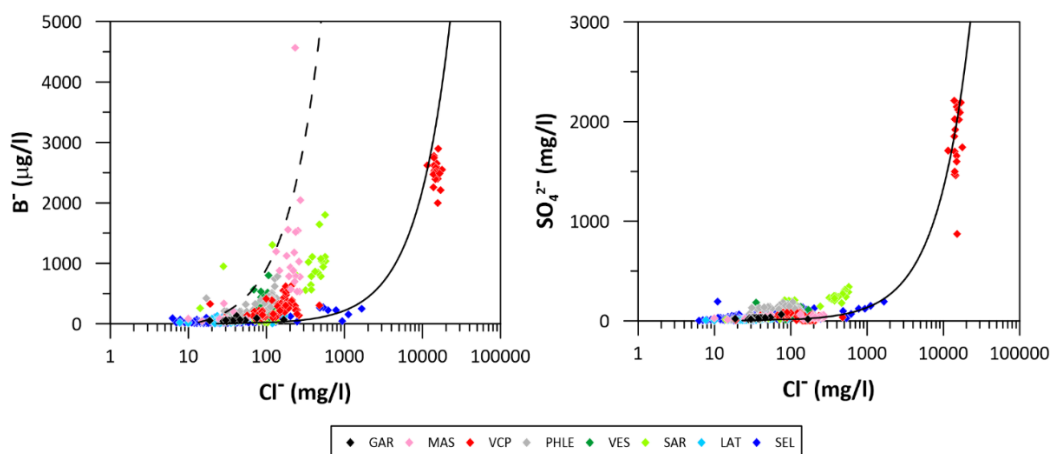
370  
 371 **Figure 4:** Hydrogeological units and water salinity classes (according to Rhoades et al., 1992) of the coastal  
 372 zone of the Campania region, for 2006 (left plot) and 2016 (right plot), where the expansion of areas with high  
 373 salinity are highlighted by red arrows.

374  
 375 *3.2.1 Water quality evaluation.*

376 Many water quality parameters affect the suitability of groundwater for irrigation, but in this study, the most  
 377 concerning parameter is salinity. Salinization eventually makes groundwaters inadequate for the growth and  
 378 productivity of many crops (Moujabber et al., 2006). For example, for an appropriate growth and productivity  
 379 of most crops, EC levels should be less than 2,250  $\mu\text{S}/\text{cm}$ . But 10% of the coastal groundwater exceeded the  
 380 recommended EC value, and 3% of EC values were greater than 15,000  $\mu\text{S}/\text{cm}$ , above which growth is  
 381 impossible or crop yield seriously compromised (Katerji et al., 2003). Accordingly, the 50% of groundwaters  
 382 investigated with the realization of a SGQI are subjected to a high salinization degree which made them  
 383 unsuitable for cereals irrigation (dots in Figure 3). The lower quality waters, and consequently the higher  
 384 salinization degree, are located within VCP and VES districts in agreement with previous investigation done  
 385 by Rufino et al. (2019) while the higher quality waters and lower salinization are found in correspondence of

386 MAS, LAT, and SEL. As major and minor components of salinity from seawater, B and SO<sub>4</sub> concentrations  
 387 were moreover further studied. The maximum concentration for SO<sub>4</sub> for agricultural water is designated at 50  
 388 mg/l (Lee and Song, 2007) and 45% of groundwater samples exceeded this threshold. Irrigation procedure  
 389 with high-sulphate groundwater concentration may result in an increasing salinity in the soil profile, governed  
 390 by the solubility of gypsum (Methochis, 1989). The maximum concentration for B in agricultural water is  
 391 designated at 1000-2000 µg/l (Regulation EC 2003/2003) and 6% of groundwater samples exceeded this  
 392 threshold. Specifically a groundwater B concentration less than 500 µg/l can be satisfactory for all kind of  
 393 crops while yet value higher than 1000 µg/l could generate several negative effect such as leaf burning in some  
 394 sensitive species (Zaman et al., 2018). The diagrams showing the relationship between the seawater markers  
 395 B, Cl and SO<sub>4</sub> (Fig. 5) shows that not all samples follow a simple mixing line between freshwater and seawater.  
 396 In fact, water rock interaction (e.g. cation exchange and precipitation/dissolution) and migration of saline water  
 397 are also important chemical and physical processes determining the water quality. VCP samples are  
 398 characterized by both paleo and actual SWI close to the shoreline and by freshwater recharge inland (Busico  
 399 et al., 2018). Some of the SAR samples show an enrichment in B and SO<sub>4</sub>, due to the interaction with the  
 400 volcanic lithofacies and/or to the circulation of geothermal fluids (like in the MAS, PHLE and VES samples  
 401 showing high B concentrations). The remaining samples show a large interaction with fresh water from  
 402 regional and local recharge.

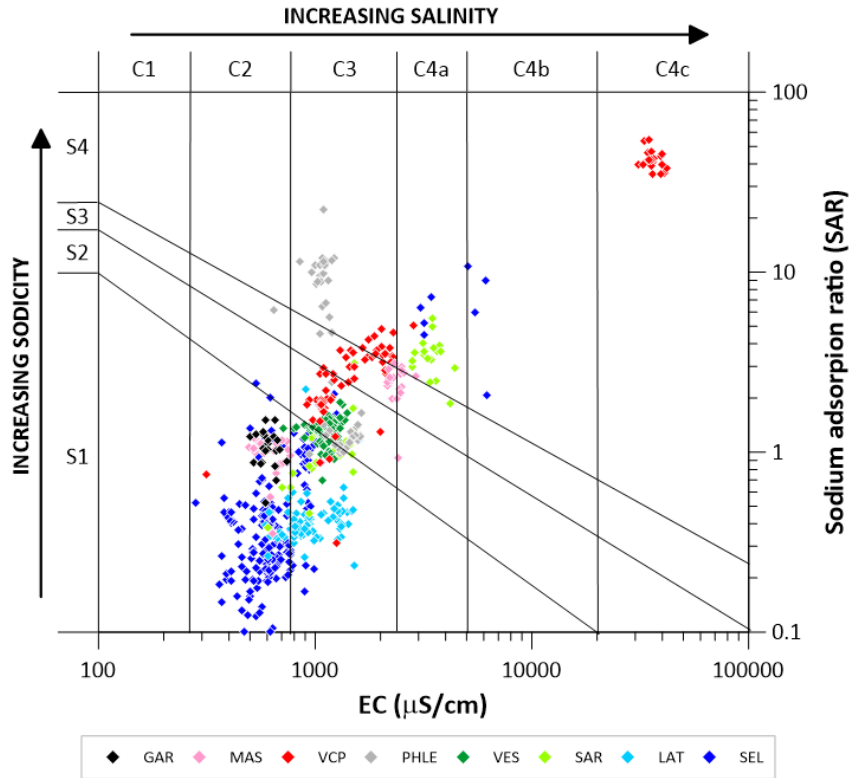
403



404

405 **Figure 5:** The diagrams show the relationship between the groundwater tracers B-Cl (left plot) and between  
 406 SO<sub>4</sub>-Cl (right plot). The black line shows the mixing trend between fresh water and sea water, the dashed line  
 407 shows the mixing trend between geothermal water and fresh water.

408 The sodium hazard of the irrigation water can be evaluated using SAR from Ca, Mg and Na contents. The  
409 SAR values in the study area range between 0.1 and 54.1. A SAR greater than 10 represents a high sodium  
410 hazard (Hem, 1985); 9% of groundwater samples exceeded this threshold. The combination of EC and SAR is  
411 generally used to determine the degree of salinization of water used for irrigation and consequently its  
412 suitability. The Fig. 6 illustrates that most groundwater samples fall into C2S1 (34%) and C3S1 (26%),  
413 indicating water with medium-to-high salinity and low SAR, which is suitable for irrigation. In this group fall  
414 all GAR and LAT samples, almost all SEL samples and a part of MAS and VES samples accordingly with  
415 SGQI spatial distribution (Fig. 3). The remaining VES samples plot into C3S2, together with part of the PHLE,  
416 SAR and VCP samples. The latter group shows very high salinities and medium alkalinity hazards. The C3S3  
417 and C4S3 categories are represented by MAS and BVR samples, indicating strongly mineralized groundwater  
418 presenting important risk of soil salinization and alkalization. Finally, C3S4 and C4S4 (7% and 9%,  
419 respectively) indicate very high salinity waters pertaining to VCP, PHLE, SAR and SEL. This type of waters  
420 is completely unsuitable for irrigation, regardless of the type of plant and soil and especially for cereal  
421 production. To sum up, approximately 16% of the groundwater samples are unsuitable for irrigation, 8% are  
422 suitable only with specific crops (salt tolerant species like cauliflower, sorghum and sunflower), 17% is usable  
423 with special caution (e.g. limited to well drained soils with low CEC) and the remaining 60% is good quality  
424 water accordingly with SAR classification.



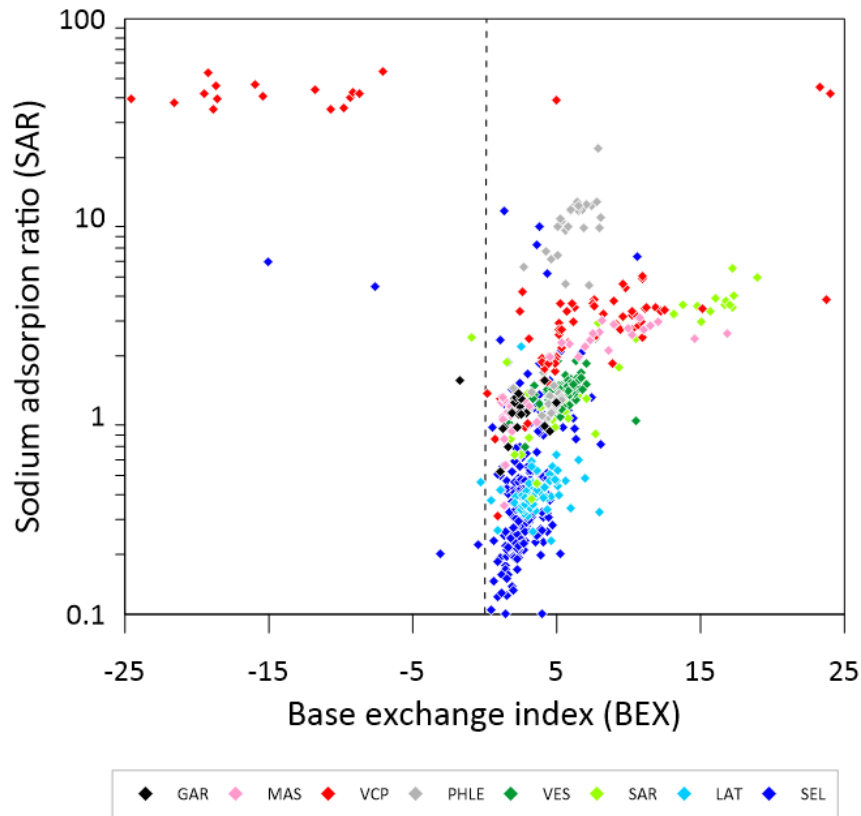
425

426 **Figure 6:** US Salinity Laboratory diagram for classifying irrigation waters on the basis of SAR and EC as  
 427 described by Richards (1968).

428

429 The BEX index classification resulted in 82% of all samples showing a positive BEX, 13% a zero BEX, and  
 430 5% a negative BEX (Fig. 7). Negative BEX, indicating a worsening of the groundwater quality, are located in  
 431 VCP and SEL plains and to a lesser extent in GAR and SAR; most samples plots close to the zero BEX value  
 432 (dashed line in Fig. 7), indicating stable conditions; a clear positive BEX, indicating a freshening trend, is  
 433 shown by some SAR, MAS and VCP samples.





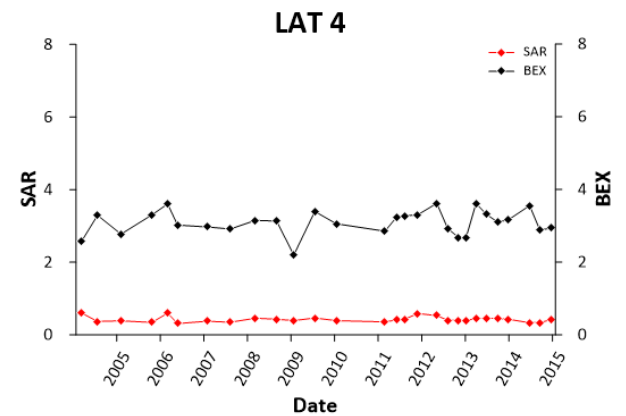
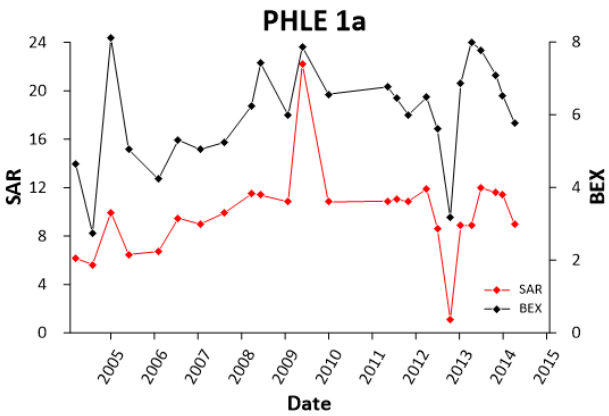
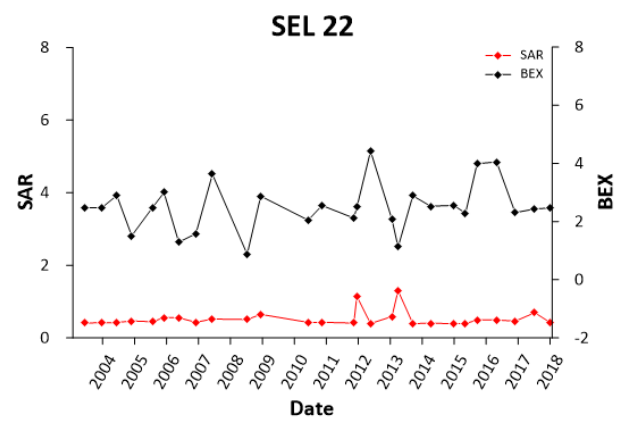
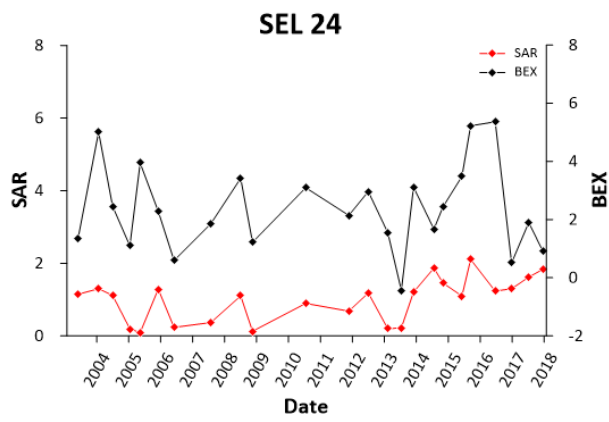
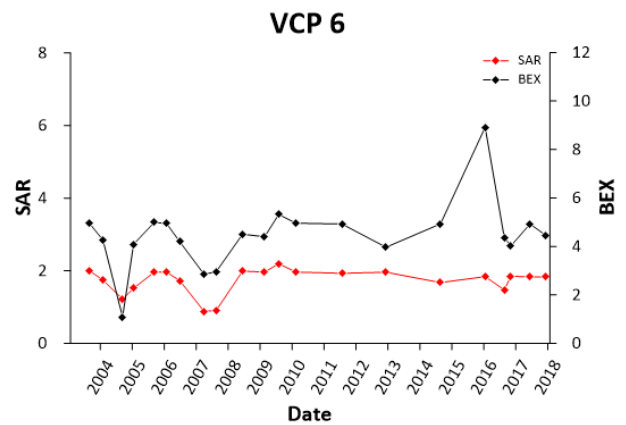
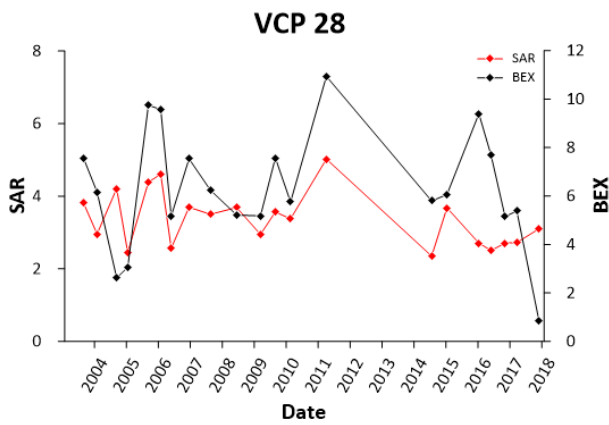
434

435 **Figure 7:** SAR versus BEX distribution for the morphological units of the Campania coastal area. The dashed  
 436 line indicates stable conditions.

437

438 Considering the temporal trend of the BEX for selected monitoring wells in the VCP, SEL, PHLE and LAT  
 439 morphological units (Fig. 8), even within the same unit, wells located in different area may have dissimilar  
 440 behaviour. In VCP, the monitoring wells 28 and 6, both located in the greenhouses area where groundwater  
 441 abstraction is particularly intense, show acceptable SAR values during the whole monitoring period,  
 442 conversely BEX remains positive in well 6 (located 8500 m from the shoreline) with values around 5, but in  
 443 well 28 (located 4250 m from the shoreline) BEX shows a progressive decrease from 9 in 2016 to almost 0 in  
 444 2018. In SEL, the monitoring well 24, located in the greenhouse area at 820 m from the shoreline, shows low  
 445 SAR values but with an increasing trend from 2013 to 2018; its BEX values are often close to zero and a  
 446 negative BEX was recorded in 2013. The monitoring well 22, located at the edge the greenhouses area at 6410  
 447 m from the shoreline and right downstream to the Cervati carbonate massif (see Fig. 1), shows low values of  
 448 SAR, and BEX values are always positive around 3. For the PHLE 1a monitoring well (located 2350 m from  
 449 the shoreline) it is interesting to note that SAR and BEX have concordant trends, meaning that they are not

450 governed by variable boundary conditions (like SWI, groundwater fluctuation and/or local recharge) but rather  
 451 by strong local drivers (like water rock interactions and/or geogenic factors). In PHLE 1a SAR values are  
 452 greater than 10 (high sodium hazard according to Hem, 1985) for most of the monitoring period with a peak  
 453 of 22.3 in 2009; BEX values, though showing large oscillations, remain always positive. In the monitoring  
 454 well LAT 4 (located 2300 m from the shoreline within the Lattari carbonate massif) SAR and BEX have nearly  
 455 constant values of 0.5 and 3, respectively, for the whole monitoring period.



456

457 **Figure 8:** SAR and BEX trend during the monitoring period (2004-2018) for select monitoring wells of the  
458 study area.

459

#### 460 **4. DISCUSSION**

461 From the analysis of the results, specific water rock interaction is the driver responsible for the salinization of  
462 a large coastal area of the Campania Region, especially between the volcanic districts of the Campi Flegrei  
463 (PHLE) and the Somma Vesuvio (VES, which also include the Sebeto Plain), where groundwater is slightly  
464 saline (Fig. 3-4) due to the combined effect of SWI, specific water rock interaction and geothermal fluids. This  
465 result is confirmed both from salinity index, SGQI and FA application. Here the main groundwater type is  
466 Na+K-HCO<sub>3</sub>-SO<sub>4</sub> (see Fig. 2), with medium to high SAR values and high ECs, indicating strongly mineralized  
467 groundwater presenting important risk of soil salinization and alkalization, which makes groundwater  
468 unsuitable for irrigation (Fig. 5-6). Also, the SGQI evaluation showed in these zone and high degree of  
469 salinization and a low water quality for irrigation use. Accordingly with Factor 3 (Fig. S2) distribution, here  
470 the water quality is probably governed by strong local drivers (geogenic factors) and it is almost independent  
471 of the variability of phenomena such recharge, SWI and over pumping. It is evident from Figure S3 how within  
472 these two volcanic areas the continuous water rock interaction with volcanic materials (mainly tuffs) represents  
473 the main salinization factor. This is also witnessed by the statistical analysis (Table. 7) that shows no significant  
474 correlations between salinity, SAR and Na, Cl, well density and distance from the coast, for both PHLE and  
475 VES samples. Anyway, if these SWI phenomena play a role in defining the quality of the water in this area,  
476 they are however largely masked by water rock interactions and this leads to the consideration that even if the  
477 latter drivers should change in the near future due to climate and/or land use changes, groundwater quality  
478 should not undergo major changes. This assumption is also confirmed by the calculated SGQI evolution from  
479 2006 to 2016 (Fig. 3c). Despite an albeit light increase of F1 in these areas, the water quality will be not  
480 subjected to significative changes, showing almost the same SGQI values in the two investigated periods  
481 (yellow dots in figure 3c). D'Alessandro et al. (2011) and Paternoster (2019) found similar behaviour for the  
482 Etnean and Vulture areas, respectively.

483 Even in the Lattari carbonate massif (LAT), groundwater quality is mainly driven by water rock interaction,  
484 with a Ca-Mg-HCO<sub>3</sub> type (where Ca is largely prevailing on Mg, Fig. 2), but in this case groundwater is fresh

485 (Fig. 2) with low SAR and EC values (Fig. 5) and nearly constant BEX values close to zero (Figs. 6 and 7),  
486 indicating a stable situation. Also in this case, the statistical analysis (Table 5) show no relevant correlations.  
487 The good quality and the large amount of groundwater reserves hosted within this massif have ensured that it  
488 is used for drinking purposes. The exploitation of this coastal aquifer did not show any worsening between the  
489 monitoring campaigns of 2006 and 2016 and it is believed that, given the large regional recharge feeding this  
490 aquifer, there will be no considerable variations in the near future. Likewise, the Garigliano Plain (GAR) shows  
491 Ca-Mg-HCO<sub>3</sub> groundwater type with good quality as regards salinity, EC, SAR, BEX and SGQI. This is mostly  
492 due to the positive groundwater/surface water interaction which sees the Garigliano River feeding the highly  
493 permeable aquifer with a considerable discharge (see Table 3) coming from large springs which drain vast  
494 carbonate massifs of the Apennines chain (Saroli et al., 2017). Once again from the statistical analysis (Table  
495 5) no significant correlation was found between salinity, SAR, and the considered parameters. The  
496 groundwater of the Garigliano plain is suitable for irrigation and its suitability it is believed to last on the long  
497 term, given the massive regional freshwater flux.

498 Another relevant process affecting the quality of groundwater in the coastal area of the Campania Region, is  
499 mixing among different water types, which in some cases lead to salinization.

500 The groundwater in the Mount Massico (MAS) is Ca-Mg-HCO<sub>3</sub> type but due to the proximity to the volcanic  
501 district of the Roccamonfina, a high content of Na+K is also recorded (Fig. 2). Moreover, this area is affected  
502 by the circulation of geothermal fluids that rise towards shallow aquifers thanks to the presence of extensive  
503 tectonic lines. like the regional fault Ortona-Roccamonfina; (Cuoco et al., 2017b). This geological setting  
504 favours the mixing of different water end-members which is responsible for the moderate salinity recorded in  
505 this area (Corniello et al., 2018) (Fig. 3), accordingly MAS samples line up along the dashed mixing line of  
506 Figure5, showing an enrichment in B, precisely attributable to deep geothermal fluids (Pennisi et al., 2006).  
507 Most MAS samples show high SAR and EC, indicating strongly mineralized water presenting important risk  
508 of soil salinization and alkalization (Fig. 5). According to the statistical analysis (Table 5), salinity is strongly  
509 correlated to Mg, Na and Cl concentration and negatively related to the distance from the coast and the well  
510 density, indicating that the origin of the salinization is not imputable to the interaction with seawater (proximity  
511 to the coast and over pumping inducing inland migration of the freshwater/saltwater interface) but rather to the

512 mixing with highly mineralized water of geogenic origin. Accordingly, SAR is positively correlated to Cl and  
513 negatively to WD. These features make the water unsuitable for irrigation.

514 Even in the Sarno plain (SAR) mixing is the main driving process of groundwater salinization, as clearly  
515 emphasized by the Stiff diagram in Figure 2. The area is characterized by slightly saline groundwater with  
516 variable SAR and EC contents. A group of SAR samples shows extremely high SAR and EC values (C4S4 in  
517 Fig. 5); these samples are the ones that plot along the freshwater/geothermal mixing line (Fig. 4) indicating the  
518 interaction among the regional groundwater flow coming from the Somma-Vesuvio and the one coming from  
519 the Lattari Massif. In fact, recently has been pointed out that both feed the aquifer hosted in the Sarno Plain  
520 (Lasagna et al., 2020). The remaining SAR samples show much lower SAR and EC values, indicating  
521 groundwater that is usable for irrigation at specific conditions, like in well drained soils with low CEC.  
522 According to Table 2, the main soil type found in the Sarno plain (Deep Fluvic Cambisols) shows these specific  
523 features, so that the groundwater in the inland portion of the plain may be considered suitable for irrigation.  
524 The results of the statistical analysis confirm that salinity is not related to actual SWI (negative values of DC  
525 and WD), but rather to local mixing processes with highly mineralised waters; in the same way, SAR is  
526 positively correlated with Cl and K. It must be admitted that the high values of Na+K and Cl would suggest  
527 that saltwater intrusion may play a role in this area, but like for the water rock interaction in PHLE and VES  
528 areas, if other phenomena play a role in defining the quality of the groundwater in SAR, they are however  
529 largely masked by mixing processes.

530 In the Volturno Coastal Plain (VCP), the area to the left of the Volturno River is characterized by slightly  
531 saline groundwater inland and by highly saline groundwater in proximity to the coast. This latter zone  
532 expanded in the 2016 monitoring campaign, compared to the 2006 one (Fig. 3, 4). SAR and EC show medium  
533 to extremely high values, making most of the coastal groundwater unsuitable for irrigation (Fig. 5). Moreover,  
534 the BEX show negative values for some wells close to the shoreline, indicating that cation exchange with  
535 saline water intruding in the aquifer is still in progress in this area (Fig. 6), as confirmed by the BEX trend of  
536 VCP monitoring well 28 (Fig.7).

537 From the statistical analysis (Tab. 5) it is clear that groundwater salinization in this area should be attributed  
538 to SWI (positive values for Na, Cl, Mg and SO<sub>4</sub>) probably due to overexploitation of resources (positive values  
539 for WD) to be attributed to the high irrigation requirements of the intensive agriculture (e.g. see greenhouse

540 extension in Fig. 1). It is clear that in VCP, local geomorphological features, like below sea-level topography,  
541 natural subsidence and coastal erosion (Tab. 1), worsen by the anthropogenic impact (land reclamation,  
542 urbanization and intensive agriculture) induce a general inland groundwater gradient, which lead to the inland  
543 migration of the freshwater/saltwater interface. What it is not possible to assess is whether the worsening of  
544 the groundwater quality is only due to actual SWI or if paleoseawater upconing is also contributing to  
545 groundwater salinization. The existence of low permeability saline lenses pertaining to the Lower Pleistocene,  
546 when most of the Plain was occupied by transitional and shallow marine environments (Amorosi et al., 2012),  
547 make it reasonable to speculate that even the latter mechanism may play a role, but the information considered  
548 in this study do not make it possible to distinguish between the two processes. A clue of this phenomena can  
549 be given observing the result of F1 evolution and its correlation with groundwater quality. In fact, despite a  
550 decrease F1 intensity in these areas, the GSIQ did not register appreciable variations.

551 In this contest it is clear that not only the intensive use of water resources (both surficial and below ground  
552 ones) for irrigation has impacted groundwater quality in VCP, but also that it will continue to worsen if  
553 alternative strategies to safeguard coastal aquifers are not put in place. The impact of climate and land use  
554 changes (variation in precipitation regime, total rainfall reduction, decrease in the Volturno River discharge,  
555 expansion of the greenhouse area) have already proved to be harmful in VCP, as in many other Mediterranean  
556 coasts (Moutahir et al., 2017; Ertürk et al., 2014), and are believed to show even more negative effects in view  
557 of the forecasted increase of the population and of the irrigation needs in this area (Reimann et al., 2018; Malek  
558 et al., 2018, von Gunten et al., 2015), as already demonstrated by predictive modelling on a small portion of  
559 the VCP coast (Mastrocicco et al., 2019).

560 Similar issues are also affecting the Sele Plain (SEL), were a shift from fresh to slightly saline groundwater  
561 was registered in 2016 (Fig. 3), once again in the greenhouse expansion area. Most of SEL samples show low  
562 SAR and EC, indicative of good quality water, suitable for irrigation, which comes from the regional recharge  
563 of the nearby carbonate masses surrounding the plain (Fig. SM1), as also testified by the prevailing Ca-Mg-  
564 HCO<sub>3</sub> water type (Fig. 2). Anyway, a few monitoring wells (e.g. SEL 24 in Fig. 7), which are not interested  
565 by salinization, show decreasing values of BEX in the last few years suggesting a progressive risk of SWI (Fig.  
566 3c), which seems here the only reason for the deterioration of the water quality for irrigation, as confirmed by  
567 the positive correlation between SAR and Cl (Table 5).

568 **Table 7:** Selected Pearson coefficients representing the variables that most influence Salinity and SAR in  
 569 coastal plains (GAR, VCP, SAR, SEL), volcanic districts (PHLE and VES) and carbonate massifs (MAS and LAT).

	Salinity						SAR		
	Mg	Na	Cl	SO <sub>4</sub>	DC*	WD <sup>#</sup>	K	Cl	WD <sup>#</sup>
<b>GAR</b>									
<b>VCP</b>	0.98	0.99	0.99	0.98		0.94	0.95	0.98	0.94
<b>SAR</b>					-0.87	-0.87	0.92	0.89	
<b>SEL</b>								0.95	
<b>PHLE</b>									
<b>VES</b>									
<b>MAS</b>	0.91	0.90	0.95		-0.99	-0.99		0.92	-0.90
<b>LAT</b>									

570 *\*Distance from the Coastline; <sup>#</sup>Well Density*

571

572 Like for the Volturno Plain, the main drivers of groundwater salinization are attributable to both natural  
 573 (mainly erosion in the SEL area) and anthropic factors (mainly over abstraction due to a vast greenhouses area)  
 574 are believed to be worsen by the climate and land use changes forecasted for the Mediterranean region, with  
 575 the serious risk of making groundwater unsuitable for irrigation also in other coastal areas of SEL.  
 576 Summarizing, especially in those areas characterized by high salinization risk, the implementation of anti-soil  
 577 and groundwater salinization actions are mandatory further considering the various effect of climate and land  
 578 use changes that will characterize the next decades (Uri, 2018). These countermeasures could range from more  
 579 detailed analysis to better characterize SWI within coastal areas (Folch et al., 2020), to delineate suitable zone  
 580 for managed aquifer recharge (Kazakis, 2018) and to the possibility to use natural zeolite as Na-filter  
 581 conditioner in the soil (Ferretti et al., 2018).

582

583

584

585

586

587

## 588 **5. CONCLUSIONS**

589 The development of a conceptual model of a representative Mediterranean coastal area (the Campania Plain)  
590 has led to an improved spatial and temporal understanding of the hydrology and hydrochemistry of the system.  
591 The variation in the distribution of salinity between 2006 and 2016, together with highly positive and highly  
592 negative BEX values indicating unstable conditions for the future, suggest that the groundwater system has  
593 not equilibrated to the significant changes imposed by both natural and anthropic stresses to the system. This  
594 demonstrates the importance of considering the slow temporal dynamics of groundwater responses in coastal  
595 areas. Given the large size of the study area, this demonstrates the major impact that widespread anthropic  
596 activities can have on groundwater system behaviour and quality, despite the dominant influence that local  
597 geological, stratigraphic, and morphological features exert on the area. The rapid, and largely uncontrolled,  
598 expansion in groundwater exploitation in some cases is not physically sustainable in the longer term, and in  
599 numerous others can lead to aquifer degradation. The most evident of these involves aquifer salinization, which  
600 is quasi irreversible, and could be a problem for virtually all uses, and in particular for irrigation. This study  
601 has demonstrated that sound conceptual models and spatial-temporal data analysis can contribute to the  
602 objective understanding required for the design, management, and operation of irrigation strategies in coastal  
603 areas, under changing climate and local environmental pressures.

604

## 605 **ACKNOWLEDGEMENTS**

606 We would like to thank Prof. Daniela Ruberti for the useful discussion about the geological settings of the  
607 Campania plains that helped to construct a robust conceptual hydrogeological model of the coastal aquifers.  
608 Moreover, we would like to thank Dr. Eleonora Grilli for helping to delineate the major soils types in the study  
609 areas.

610

611

612

613



614

615 **REFERENCES**

616 Alcamo, J., Henrich, T., Rösch, T., 2000. World Water in 2025 – Global modeling and scenario analysis for  
617 the World Commission on Water for the 21st Century. Report A0002, Centre for Environmental System  
618 Research, University of Kassel, Germany

619 American Public Health Association (APHA), 2017. Standard Methods for the Examination of Water and  
620 Wastewater. 23rd edition. American Public Health Association, American Water Works Association, and  
621 Water Environment Federation, Washington DC (1268 pp. ISBN: 978-0-87553-287-5).

622 Amorosi, A., Pacifico, A., Rossi, V., Ruberti, D., 2012. Late Quaternary incision and deposition in an active  
623 volcanic setting: The Volturno valley fill, southern Italy. *Sediment. Geol.* 282, 307–320.  
624 <https://doi.org/10.1016/j.sedgeo.2012.10.003>

625 Arnell, N., 1999. Climate change and global water resources. *Glob. Environ. Chang.* 9, S31–S49.  
626 [https://doi.org/10.1016/S0959-3780\(99\)00017-5](https://doi.org/10.1016/S0959-3780(99)00017-5)

627 ARPA Campania. Available online: <http://www.arpacampania.it/web/guest/365> (accessed on 23 December  
628 2018).

629 Ayers, R., Westcot, D., 1994. Water Quality for Agriculture; FAO Irrigation and Drainage Paper 29 Rev. 1;  
630 FAO: Rome, Italy.

631 Babiker, I.S., Hohamed, M.A.A., Hiyama, T., 2007. Assessing groundwater quality using GIS. *Water Resour.*  
632 *Manag.* 21(4), 699–715. <https://doi.org/10.1007/s11269-006-9059-6>.

633 Barlow, P.M., Reichard, E.G., 2010. Saltwater intrusion in coastal regions of North America. *Hydrogeol. J.*  
634 18, 247–260. <https://doi.org/10.1007/s10040-009-0514-3>

635 Belkhiri, L., Boudoukha, A., Mouni, L., Baouz, T., 2010. Application of multivariate statistical methods and  
636 inverse geochemical modeling for characterization of groundwater — A case study: Ain Azel plain  
637 (Algeria). *Geoderma* 159, 390–398. <https://doi.org/10.1016/j.geoderma.2010.08.016>

638 Buondonno, A., Colella, A., Colella, C., Coppola, E., de' Gennaro, B., de' Gennaro, M., Gargiulo, N., Grilli,  
639 E., Langella, A., Rubino, M., 2007. Modeling pedogenization of zeolitized tuffs. II: medium-term  
640 weathering of phlegraean yellow tuff and red tuff with black scoriae by water and humic acids. pp. 2092–  
641 2097. [https://doi.org/10.1016/S0167-2991\(07\)81104-9](https://doi.org/10.1016/S0167-2991(07)81104-9)

642 Bui, D.T., Khosravi, K., Tiefenbacher, J., Nguyen, H., Kazakis, N., 2020. Improving prediction of water  
643 quality indices using novel hybrid machine-learning algorithms. *Sci. Tot.*  
644 *Environ.* 721 <http://doi.org/10.1016/j.scitotenv.2020.137612>.

645 Busico, G., Kazakis, N., Cuoco, E., Colombani, N., Tedesco, D., Voudouris, K., Mastrocicco, M., 2020. A  
646 novel hybrid method of specific vulnerability to anthropogenic pollution using multivariate statistical and  
647 regression analyses. *Water Res.* 171 <http://doi.org/10.1016/j.watres.2019.115386>.

648 Busico, G., Kazakis, N., Colombani, N., Mastrocicco, M., Voudouris, K., Tedesco, D., 2017. A modified  
649 SINTACS method for groundwater vulnerability and pollution risk assessment in highly anthropized  
650 regions based on  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations. *Sci. Tot. Environ.* 609, 1512–1523.  
651 <https://doi.org/10.1016/j.scitotenv.2017.07.257>

652 Busico, G., Cuoco, E., Kazakis, N., Colombani, N., Mastrocicco, M., Tedesco, D., Voudouris, K. (2018).  
653 Multivariate statistical analysis to characterize/discriminate between anthropogenic and geogenic trace  
654 elements occurrence in the Campania Plain, Southern Italy. *Environ. Pollut.* 234, 260–269.  
655 <https://doi.org/10.1016/j.envpol.2017.11.053>

656 Chang, C.-M., Yeh, H.-D., 2010. Spectral approach to seawater intrusion in heterogeneous coastal aquifers.  
657 *Hydrol. Earth Syst. Sci.* 14, 719–727. <https://doi.org/10.5194/hess-14-719-2010>

658 Colombani, N., Osti, A., Volta, G., Mastrocicco, M., 2016. Impact of climate change on salinization of coastal  
659 water resources. *Water Resour. Manage.* 30(7), 2483–2496. <https://doi.org/10.1007/s11269-016-1292-z>

660 Colombani, N., Di Giuseppe, D., Kebede, S., Mastrocicco, M., 2018. Assessment of the anthropogenic fluoride  
661 export in Addis Ababa urban environment (Ethiopia). *J. Geochemical Explor.* 190, 390–399.  
662 <https://doi.org/10.1016/j.gexplo.2018.04.008>

663 Corniello, A., Ducci, D., Ruggieri, G., Iorio, M., 2018. Complex groundwater flow circulation in a carbonate  
664 aquifer: Mount Massico (Campania Region, Southern Italy). Synergistic hydrogeological understanding.  
665 *J. Geochemical Explor.* 190, 253–264. <https://doi.org/10.1016/j.gexplo.2018.03.017>

666 Cramer, W., Guiot, J., Fader, M., Garrabou, J., Gattuso, J.-P., Iglesias, A., Lange, M.A., Lionello, P., Llasat,  
667 M.C., Paz, S., Peñuelas, J., Snoussi, M., Toreti, A., Tsimplis, M.N., Xoplaki, E., 2018. Climate change  
668 and interconnected risks to sustainable development in the Mediterranean. *Nat. Clim. Chang.* 8, 972–  
669 980. <https://doi.org/10.1038/s41558-018-0299-2>

670 Cuoco, E., Colombani, N., Darrah, T.H., Mastrocicco, M., Tedesco, D., 2017a. Geolithological and  
671 anthropogenic controls on the hydrochemistry of the Volturno river (Southern Italy). *Hydrol. Process.*  
672 31, 627–638. <https://doi.org/10.1002/hyp.11055>

673 Cuoco, E., Minissale, A., Di Leo, A. “Magda,” Tamburrino, S., Iorio, M., Tedesco, D., 2017b. Fluid  
674 geochemistry of the Mondragone hydrothermal systems (southern Italy): water and gas compositions vs.  
675 geostructural setting. *Int. J. Earth Sci.* 106, 2429–2444. <https://doi.org/10.1007/s00531-016-1439-4>

676 Custodio, E., 2010. Coastal aquifers of Europe: an overview. *Hydrogeol. J.* 18, 269–280.  
677 <https://doi.org/10.1007/s10040-009-0496-1>

678 D’Alessandro, W., Bellomo, S., Bonfanti, P., Brusca, L., Longo, M., 2011. Salinity variations in the water  
679 resources fed by the Etnean volcanic aquifers (Sicily, Italy): natural vs. anthropogenic causes. *Environ.*  
680 *Monit. Assess.* 173, 431–446. <https://doi.org/10.1007/s10661-010-1397-4>

681 de Montety, V., Radakovitch, O., Vallet-Coulomb, C., Blavoux, B., Hermitte, D., Valles, V., 2008. Origin of  
682 groundwater salinity and hydrogeochemical processes in a confined coastal aquifer: Case of the Rhône  
683 delta (Southern France). *Appl. Geochemistry* 23, 2337–2349.  
684 <https://doi.org/10.1016/j.apgeochem.2008.03.011>

685 Dono, G., Cortignani, R., Doro, L., Giraldo, L., Ledda, L., Pasqui, M., Roggero, P.P., 2013. Adapting to  
686 uncertainty associated with short-term climate variability changes in irrigated Mediterranean farming  
687 systems. *Agric. Syst.* 117, 1-12. <https://doi.org/10.1016/j.agsy.2013.01.005>.

688 Ducci, D., Della Morte, R., Mottola, A., Onorati, G., Pugliano, G., 2019. Nitrate trends in groundwater of the  
689 Campania region (southern Italy). *Environ. Sci. Pollut. Res.* 26, 2120–2131.  
690 <https://doi.org/10.1007/s11356-017-0978-y>

691 Ducci, D., Tranfaglia, G., 2008. Effects of climate change on groundwater resources in Campania (southern  
692 Italy). *Geol. Soc. London, Spec. Publ.* 288, 25–38. <https://doi.org/10.1144/SP288.3>

693 Ertürk, A., Ekdal, A., Gürel, M., Karakaya, N., Guzel, C., Gönenç, E., 2014. Evaluating the impact of climate  
694 change on groundwater resources in a small Mediterranean watershed. *Sci. Total Environ.* 499, 437–  
695 447. <https://doi.org/10.1016/j.scitotenv.2014.07.001>

696 Ferretti, G., Di Giuseppe, D., Faccini, B., Coltorti, M., 2018. Mitigation of sodium risk in a sandy agricultural  
697 soil by the use of natural zeolites. *Environ. Monit. Assess.* 190(11). [https://doi.org/10.1007/s10661-  
698 018-7027-2](https://doi.org/10.1007/s10661-018-7027-2).

699 Folch, A., del Val, L., Luquot, L., Martínez-Pérez, L., Bellmunt, F., Le Lay, H., Rodellas, V., Ferrer, N.,  
700 Palacios, A., Fernandez, S., Marazuela, M.A., Diego-Feliu, M., Pool, M., Goyetche, T., Ledo, J.,  
701 Pezard, P., Bour, O., Queralt, P., Marcuello, A., Garcia-Orellana, J., Saaltink, M.W., Vasquez-Sune,  
702 E., Carrera, J., 2020. Combining fiber optic DTS, cross-hole ERT and time-lapse induction logging to  
703 characterize and monitor a coastal aquifer. *J. Hydrol.* 588. <https://doi/10.1016/j.jhydrol.2020.125050>.

704 Foster, S., Pulido-Bosch, A., Vallejos, Á., Molina, L., Llop, A., MacDonald, A.M., 2018. Impact of irrigated  
705 agriculture on groundwater-recharge salinity: a major sustainability concern in semi-arid regions.  
706 Hydrogeol. J. 26, 2781–2791. <https://doi.org/10.1007/s10040-018-1830-2>

707 Foster, S.S.D., Chilton, P.J., 2003. Groundwater: the processes and global significance of aquifer degradation.  
708 Philos. Trans. R. Soc. London. Ser. B Biol. Sci. 358, 1957–1972. <https://doi.org/10.1098/rstb.2003.1380>

709 Hem JD (1985) Study and interpretation of the chemical characteristics of natural water. 3<sup>rd</sup> edn, USGS,  
710 Alexandria

711 Hynds, P., Misstear, B.D., Gill, L.W., Murphy, H.M., 2014. Groundwater source contamination mechanisms:  
712 Physicochemical profile clustering, risk factor analysis and multivariate modelling. J. Contam. Hydrol.  
713 159, 47-56. <https://doi.org/10.1016/j.jconhyd.2014.02.001>

714 Jha, M.K., Shekhar, A., Jenifer, M.A., 2020. Assessing groundwater quality for drinking water supply using  
715 hybrid fuzzy-GIS-based water quality index. Water Res., 179.  
716 <http://doi.org/10.1016/j.watres.2020.115867>.

717 Kaiser, H.F., 1960. The application of electronic computers to factor analysis. Educational and Psychological  
718 Measurement, 20, 141-151

719 Karim, A., Cruz, M.G., Hernandez, E.A., Uddameri, V., 2020. A GIS-based fit for the purpose assessment of  
720 brackish groundwater formations as an alternative to freshwater aquifers. Water (Switzerland), 12(8)  
721 <http://doi.org/10.3390/w12082299>.

722 Katerji, N., Van Hoorn, J.W., Hamdy, A., Mastrorilli, M., 2003. Salinity effect on crop development and yield,  
723 analysis of salt tolerance according to several classification methods. Agric. Water Manage. 62(1), 37–  
724 66. [https://doi.org/10.1016/S0378-3774\(03\)00005-2](https://doi.org/10.1016/S0378-3774(03)00005-2)

725 Kazakis, N., 2018, Delineation of Suitable Zones for the Application of Managed Aquifer Recharge (MAR)  
726 in Coastal Aquifers Using Quantitative Parameters and the Analytical Hierarchy Process. Water, 10, 804.  
727 <https://doi.org/10.3390/w10060804>.

728

729 Kazakis, N., Kantiranis, N., Kalaitzidou, K., Kaprara, E., Mitrakas, M., Frei, R., Vargemezis, G., Tsourlos, P.,  
730 Zouboulis, A., Filippidis, A., 2017. Origin of hexavalent chromium in groundwater: the example of  
731 Sarigkiol Basin. North. Greece. *Sci. Tot. Environ.* 593, 594, 552, 566.  
732 <https://doi.org/10.1016/j.scitotenv.2017.03.128>.

733 Kim, H.M., Webster, P.J., Curry, J. A., 2012. Evaluation of short-term climate change prediction in multi-  
734 model CMIP5 decadal hindcasts. *Geophys. Res. Lett.* 39(10) <https://doi.org/10.1029/2012GL051644>.

735 Kumar, P., 2014. Evolution of groundwater chemistry in and around Vaniyambadi industrial area:  
736 differentiating the natural and anthropogenic sources of contamination. *Chem. Erde* 74, 641e651.  
737 <https://doi.org/10.1016/j.chemer.2014.02.002>.

738 Lasagna, M., Ducci, D., Sellerino, M., Mancini, S., De Luca, D.A., 2020. Meteorological Variability and  
739 Groundwater Quality: Examples in Different Hydrogeological Settings. *Water* 12, 1297.  
740 <https://doi.org/10.3390/w12051297>

741 Lee, J.-Y., Song, S.-H., 2007. Evaluation of groundwater quality in coastal areas: implications for sustainable  
742 agriculture. *Environ. Geol.* 52, 1231–1242. <https://doi.org/10.1007/s00254-006-0560-2>

743 Leff, B., Ramankutty, N., Foley, J.A., 2004. Geographic distribution of major crops across the world. *Global*  
744 *Biogeochem. Cycles* 18, n/a-n/a. <https://doi.org/10.1029/2003GB002108>

745 Machiwal, D., Cloutier, V., Güler, C., Kazakis, N., 2018. A review of GIS-integrated statistical techniques for  
746 groundwater quality evaluation and protection. *Environ. Earth Sci.* 77(19) [http://doi.org/10.1007/s12665-](http://doi.org/10.1007/s12665-018-7872-x)  
747 [018-7872-x](http://doi.org/10.1007/s12665-018-7872-x).

748 Malek, Ž., Verburg, P.H., R Geijzendorffer, I., Bondeau, A., Cramer, W., 2018. Global change effects on land  
749 management in the Mediterranean region. *Glob. Environ. Chang.* 50, 238–254.  
750 <https://doi.org/10.1016/j.gloenvcha.2018.04.007>

- 751 Mastrocicco, M., Busico, G., Colombani, C., Vigliotti, M., Ruberti, D., 2019. Modelling Actual and Future  
752 Seawater Intrusion in the Variconi Coastal Wetland (Italy) Due to Climate and Landscape Changes.  
753 Water 11, 1502. <https://doi.org/10.3390/w11071502>
- 754 Matano, F., Sacchi, M., Vigliotti, M., Ruberti, D., 2018. Subsidence Trends of Volturno River Coastal Plain  
755 (Northern Campania, Southern Italy) Inferred by SAR Interferometry Data. Geosciences 8, 8.  
756 <https://doi.org/10.3390/geosciences8010008>
- 757 Metochis, C., 1989. Water requirement, yield and fruit quality of grapefruit irrigated with high-sulphate water,  
758 J. Hortic. Sci. 64(6), 733-737. <https://doi.org/10.1080/14620316.1989.11516016>.
- 759 Meyer, R., Engesgaard, P., Sonnenborg, T.O., 2019. Origin and Dynamics of Saltwater Intrusion in a Regional  
760 Aquifer: Combining 3-D Saltwater Modeling With Geophysical and Geochemical Data. Water Resour.  
761 Res. 55, 1792–1813. <https://doi.org/10.1029/2018WR023624>
- 762 Milia, A., Torrente, M.M., 2003. Late-Quaternary volcanism and transtensional tectonics in the Bay of Naples,  
763 Campanian continental margin, Italy. Mineral. Petrol. 79, 49–65. [https://doi.org/10.1007/s00710-003-](https://doi.org/10.1007/s00710-003-0001-9)  
764 [0001-9](https://doi.org/10.1007/s00710-003-0001-9)
- 765 Minolfi, G., Albanese, S., Lima, A., Tarvainen, T., Fortelli, A., De Vivo, B., 2018. A regional approach to the  
766 environmental risk assessment - Human health risk assessment case study in the Campania region. J.  
767 Geochemical Explor. 184, 400–416. <https://doi.org/10.1016/j.gexplo.2016.12.010>
- 768 Mollema, P.N., Antonellini, M., Dinelli, E., Gabbianelli, G., Greggio, N., Stuyfzand, P.J., 2013.  
769 Hydrochemical and physical processes influencing salinization and freshening in Mediterranean low-  
770 lying coastal environments. Appl. Geochemistry 34, 207–221.  
771 <https://doi.org/10.1016/j.apgeochem.2013.03.017>
- 772 Moujabber, M.E., Samra, B.B., Darwish, T., Atallah, T., 2006. Comparison of Different Indicators for  
773 Groundwater Contamination by Seawater Intrusion on the Lebanese Coast. Water Resour. Manag. 20,  
774 161–180. <https://doi.org/10.1007/s11269-006-7376-4>

- 775 Moutahir, H., Bellot, P., Monjo, R., Bellot, J., Garcia, M., Touhami, I., 2017. Likely effects of climate change  
776 on groundwater availability in a Mediterranean region of Southeastern Spain. *Hydrol. Process.* 31, 161–  
777 176. <https://doi.org/10.1002/hyp.10988>
- 778 Oster, J.D., Sposito, G., 1980. The Gapon Coefficient and the Exchangeable Sodium Percentage-Sodium  
779 Adsorption Ratio Relation. *Soil Sci. Soc. Am. J.* 44, 258–260.  
780 <https://doi.org/10.2136/sssaj1980.03615995004400020011x>
- 781 Pappone, G., Alberico, I., Amato, V., Aucelli, P.P.C., Di Paolo, G., 2011. Recent evolution and the present-  
782 day conditions of the Campanian Coastal plains (South Italy): the case history of the Sele River Coastal  
783 plain. pp. 15–27. <https://doi.org/10.2495/CP110021>
- 784 Parkhurst, D.L., Appelo, C.A.J., 2013. Description of input and examples for PHREEQC version 3. A  
785 computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical  
786 calculations: U.S. Geological Survey Techniques and Methods. Book 6, Chap. A43, p. 497.  
787 <https://pubs.usgs.gov/tm/06/a43>.
- 788 Paternoster, M., 2019. Boron Isotopes in the Mount Vulture Groundwaters (Southern Italy): Constraints for  
789 the Assessment of Natural and Anthropogenic Contaminant Sources. *Geofluids* 2019, 1–10.  
790 <https://doi.org/10.1155/2019/9107636>
- 791 Pennisi, M., Bianchini, G., Muti, A., Kloppmann, W., Gonfiantini, R., 2006. Behaviour of boron and strontium  
792 isotopes in groundwater–aquifer interactions in the Cornia Plain (Tuscany, Italy). *Appl. Geochemistry*  
793 21, 1169–1183. <https://doi.org/10.1016/j.apgeochem.2006.03.001>
- 794 Priyantha Ranjan, S., Kazama, S., Sawamoto, M., 2006. Effects of climate and land use changes on  
795 groundwater resources in coastal aquifers. *J. Environ. Manage.* 80, 25–35.  
796 <https://doi.org/10.1016/j.jenvman.2005.08.008>



797 Regensburg, S., Wiersberg, T., Brandt, W., Huenges, E., Saadat, A., Schmidt, K., Zimmermann, G., 2010.  
798 Geochemical properties of saline geothermal fluids from the in-situ geothermal laboratory Groß  
799 Schönebeck (Germany). *Geochemistry* 70, 3–12. <https://doi.org/10.1016/j.chemer.2010.05.002>

800 Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to  
801 fertilisers. *Official Journal L* 304, 21/11/2003 P. 0001 - 0194

802 Reimann, L., Merkens, J.-L., Vafeidis, A.T., 2018. Regionalized Shared Socioeconomic Pathways: narratives  
803 and spatial population projections for the Mediterranean coastal zone. *Reg. Environ. Chang.* 18, 235–  
804 245. <https://doi.org/10.1007/s10113-017-1189-2>

805 Rhoades, J. D., Kandiah, A., Mashali, A. M. (1992). The use of saline waters for crop production-FAO  
806 irrigation and drainage paper 48. FAO, Rome, 133.

807 Richards LA (1968) *Diagnosis and Improvement of Saline and Alkali Soils*, US Dept Agriculture Handbook  
808 # 60, Washington DC, USA

809 Riley, J.P., Skirrow G., 1975. *Chemical oceanography*. Acad. Press, London & NY

810 Romanelli, A., Lima, M.L., Quiroz Londoño, O.M., Martínez, D.E., Massone, H.E., 2012. A Gis-Based  
811 Assessment of Groundwater Suitability for Irrigation Purposes in Flat Areas of the Wet Pampa Plain,  
812 Argentina. *Environ. Manage.* 50, 490–503. <https://doi.org/10.1007/s00267-012-9891-9>

813 Ruberti, D., Vigliotti, M., 2017. Land use and landscape pattern changes driven by land reclamation in a coastal  
814 area: the case of Volturno delta plain, Campania Region, southern Italy. *Environ. Earth Sci.* 76, 694.  
815 <https://doi.org/10.1007/s12665-017-7022-x>

816 Rufino, F., Busico, G., Cuoco, E., Darrah, T.H., Tedesco, D., 2019. Evaluating the suitability of urban  
817 groundwater resources for drinking water and irrigation purposes: An integrated approach in the Agro-  
818 Aversano area of southern Italy. *Environ. Monit. Assess.*, 191(12) [http://doi.org/10.1007/s10661-019-](http://doi.org/10.1007/s10661-019-7978-y)  
819 [7978-y](http://doi.org/10.1007/s10661-019-7978-y).

820 Saroli, M., Lancia, M., Albano, M., Casale, A., Giovinco, G., Petitta, M., Zarlenga, F., dell'Isola, M. 2017. A  
821 hydrogeological conceptual model of the Suio hydrothermal area (central Italy). *Hydrogeol. J.* 25, 1811–  
822 1832. <https://doi.org/10.1007/s10040-017-1549-5>

823 Shyu, G.S., Cheng, B.Y., Chiang, C.T., Yao, P.H, Chang, T.K., 2011. Applying factor analysis combined with  
824 kriging and information entropy theory for mapping and evaluating the stability of groundwater quality  
825 variation in Taiwan. *Int. J. Environ. Res. Public Health.* 8(4), 1084-1109.  
826 <https://doi.org/10.3390/ijerph8041084>.

827 Stuyfzand P.J. (2008) Base Exchange Indices as Indicators of Salinization or Freshening of (Coastal) Aquifers.  
828 20th Salt Water Intrusion Meeting, Florida (USA)

829 Tanji, K.K., Kielen, N.C. (2002) Irrigation and Drainage Paper 61 (Food and Agriculture Organization, Rome).

830 Thivya, C., Chidambaram, S., Singaraja, C., Thilagavathi, R., Prasanna, M.V., Jainab, I., 2013. A study on the  
831 significance of lithology in ground-water quality of Madurai district, Tamil Nadu (India). *Environ.*  
832 *Develop. Sus.* 15 (5), 1365e1387. <https://doi.org/10.1007/s10668-013-9439-z>.

833 Uri, N., 2018. Cropland soil salinization and associated hydrology: Trends, processes and examples. *Water*  
834 (Switzerland), 10(8). <https://doi.org/10.3390/w10081030>.

835 Vandenhede, A., Lebbe, L., 2012. Groundwater chemistry patterns in the phreatic aquifer of the central  
836 Belgian coastal plain. *Appl. Geochemistry* 27, 22–36. <https://doi.org/10.1016/j.apgeochem.2011.08.012>

837 von Gunten, D., Wöhling, T., Haslauer, C.P., Merchán, D., Causapé, J., Cirpka, O.A., 2015. Estimating  
838 climate-change effects on a Mediterranean catchment under various irrigation conditions. *J. Hydrol. Reg.*  
839 *Stud.* 4, 550–570. <https://doi.org/10.1016/j.ejrh.2015.08.001>

840 Walter, J., Chesnaux, R., Cloutier, V., Gaboury, D., 2017. The influence of water/rock – water/clay interactions  
841 and mixing in the salinization processes of groundwater. *J. Hydrol. Reg. Stud.* 13, 168–188.  
842 <https://doi.org/10.1016/j.ejrh.2017.07.004>

843 Wang, Y., Ma, T., Luo, Z., 2001. Geostatistical and geochemical analysis of surface water leakage into  
844 groundwater on a regional scale: a case study in the Liulin karst system, north-western China. *J. Hydrol.*  
845 246 (1e4), 223e234. [https://doi.org/10.1016/S0022-1694\(01\)00376-6](https://doi.org/10.1016/S0022-1694(01)00376-6).

846 Werner, A.D., Bakker, M., Post, V.E.A., Vandenbohede, A., Lu, C., Ataie-Ashtiani, B., Simmons, C.T., Barry,  
847 D.A., 2013. Seawater intrusion processes, investigation and management: Recent advances and future  
848 challenges. *Adv. Water Resour.* 51, 3–26. <https://doi.org/10.1016/j.advwatres.2012.03.004>

849 WHO, 2004 Guidelines for Drinking-Water Quality, World Health Organization, Geneva, Switzerland, 3<sup>rd</sup>  
850 edition.

851 Yechieli, Y., Shalev, E., Wollman, S., Kiro, Y., Kafri, U., 2010. Response of the Mediterranean and Dead Sea  
852 coastal aquifers to sea level variations. *Water Resour. Res.* 46. <https://doi.org/10.1029/2009WR008708>

853 Zaman, M., Shahid, S.A., Heng, L., 2018 Irrigation Water Quality. In: *Guideline for Salinity Assessment,*  
854 *Mitigation and Adaptation Using Nuclear and Related Techniques.* Springer, Cham.  
855 [https://doi.org/10.1007/978-3-319-96190-3\\_5](https://doi.org/10.1007/978-3-319-96190-3_5).

856 Zanotti, C., Rotiroti, M., Fumagalli, L., Stefania, G.A., Canonaco, F., Stefenelli, G., Prevot, A.S.H., Leoni, B.,  
857 Bonomi, T., 2019. Groundwater and surface water quality characterization through positive matrix  
858 factorization combined with GIS approach. *Water Res.* 159, 122, 134.  
859 <http://doi.org/10.1016/j.watres.2019.04.058>.

860