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GEOCHEMICAL CHARACTERIZATION AND HEALTH RISK ASSESSMENT IN TWO DIVERSIFIED ENVIRONMENTAL SETTINGS (SOUTHERN ITALY)

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	<p>Caiazzo plain where statistically significant correlations have been found between major and trace elements and microbiological indicators. The use of a Groundwater Quality Index (GQI) has shown general poor water quality for the majority of analyzed samples due to the high amount of Nitrate and Fecal indicators. The use of a Health Risk Assessment (HRA) highlighted that Nitrate coupled with Fluoride represent the most important concern for human health compared to the all investigated parameters in both sites.</p>
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1 **GEOCHEMICAL CHARACTERIZATION AND HEALTH RISK ASSESSMENT IN TWO**
2 **DIVERSIFIED ENVIRONMENTAL SETTINGS (SOUTHERN ITALY)**

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17 **Abstract**

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19 sites of the Campania Plain (southern Italy) with different land use covering and different
20 hydrogeological features in order: i) to define the water-rock interaction processes, ii) to
21 differentiate sources of pollution in a detailed way iii) to evaluate the degree of water quality in
22 the studied alluvial aquifer and iv) to identify the most worrying elements for human's health.
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24 enrichment in alkali ions have been highlighted moving from the boundary of the plain toward the
25 coastal areas, due to groundwater interaction with volcanic rocks along the flow path. The
26 application of the Factor Analysis allowed to identify different sources of pollution, which were
27 attributed to (a) leaks in the sewer system for the Agro Aversano Area and also the spreading of
28 manure as fertilizers in agricultural activities for the Caiazzo Plain. Furthermore, it has been
29 highlighted that the use of major elements, trace elements and microbiological indicators, allows
30 to accurately differentiate contamination processes in progress. In fact, from the results of the
31 Factor Analysis applied in the Agro Aversano area, no significant statistically relationships
32 between major elements and microbiological indicators of fecal contamination were highlighted,
33 unlike the Caiazzo plain where statistically significant correlations have been found between major
34 and trace elements and microbiological indicators. The use of a Groundwater Quality Index (GQI)
35 has shown general poor water quality for the majority of analyzed samples due to the high amount
36 of Nitrate and Fecal indicators. The use of a Health Risk Assessment (HRA) highlighted that
37 Nitrate coupled with Fluoride represent the most important concern for human health compared to
38 the all investigated parameters in both sites.

39 **Keywords:** Fecal pollution, Alluvial aquifer, Factor analysis, Trace elements, GQI, HRA

40 **1 INTRODUCTION**

41 The continuous increasing demand of water for human utilization (industrial, agricultural
42 and municipal use) has recently moved the worldwide attention on groundwater's protection,
43 management and quality control. The implementation of groundwater's control actions have
44 become extremely urgent especially in those areas characterized by scarce water resources or
45 highly anthropized to correctly achieve the water sustainability purpose and ensure potable water
46 supplies. All types of groundwater pollution, occurring by inorganic and organic compounds, are
47 considered a serious global environmental issue since groundwater resources represent the main
48 sources of drinking and potable water worldwide (Rapant and Krčmová, 2007). Many studies, in
49 the last decades, have focused on shallow aquifers characterization, which represent the main
50 source of water supply for many agricultural areas (Busico et al., 2020; Mastrocicco et al. 2011).
51 Unfortunately, results highlighted the continuous worsening of the chemical and microbial
52 groundwater's quality in many regions (Busico et al. 2018; Celico et al. 2004; Kelly et al. 2009;;
53 Rufino et al. 2019; Zhang et al. 2014). Moreover, the described scenario becomes more troubling
54 since the use of polluted water could represent a serious risk for human health and all living
55 organisms. The continuous intake through drinking waters of several dissolved species (major
56 ions, trace elements) resulted to be one of the main causes of a various number of human's diseases
57 (WHO 2017).

58 Accordingly, the potential use of groundwater for potable purpose can be seriously
59 compromised by several natural or anthropogenic pollutants. Among all chemical species, nitrate
60 (NO_3) is considered one of the main groundwater's pollutants (Ascott et al. 2017). An ever-
61 growing pollution of groundwater by NO_3 and nitrogen compounds could then generate severe
62 side effects on human health (Ward et al. 2018). Nitrate origins were generally linked to various
63 anthropogenic activities such as agricultural or municipal. The intense use of fertilizers,
64 wastewater treatment plant and/or sewers leaching were identified as the main sources of nitrogen
65 in superficial and groundwater bodies (Busico et al. 2017; Shrestha et al. 2017). Nevertheless, NO_3
66 is not the only pollutant which can be usually found inside groundwater bodies. Along with NO_3 ,
67 others chemical toxic pollutants have attracted the attention of the world's scientific community
68 such as As (Brammer and Ravenscroft 2009; Duker et al. 2005; Fendorf et al. 2010; Nadiri et al.
69 2018), Cr (VI) (Kazakis et al. 2017; Oze et al. 2007), F (Chitsazan et al. 2015; Nadiri et al. 2013a;
70 Azizullah et al. 2011; Farooqi et al. 2007; Harrison 2005;) U (Cuoco et al. 2015; Liesch et al.
71 2015), and Al (Frankowski et al. 2011). All these elements can be originated both by geogenic or
72 anthropogenic sources. Water interactions with specific types of rocks can be responsible of
73 releasing several chemical elements. For example, volcanic rocks could free/leak in groundwater
74 important amounts of F, As and U (Casentini et al. 2010; Corniello et al. 2018; Viaroli et al. 2016).
75 On the other hands, human activities (industrial and agricultural) represent the major sources of
76 spreading for all these toxic pollutants, causing an increasing concern on groundwater quality

77 deterioration which could even increase considering climate change effect on water availability
78 and its quality (Busico et al.2020; Kazakis et al. 2017; Wang et al. 2012).

79 Along with the status of chemical pollution, the water microbial condition needs to be also
80 considered for a proper water quality evaluation, especially for drinking water purpose. The
81 consumption of feces-contaminated waters may considerably increase risks of disease, triggering
82 outbreaks of waterborne pathologies, since they represent a source of viruses and pathogenic
83 bacteria (WHO 2017). Generally, groundwater microbial pollution is linked to the introduction of
84 humans and animal fecal materials within the soils and groundwater and/or to the inefficient
85 treatment and inadequate management of the sewage system (Macler et al. 2000; WHO 2017).The
86 widely used indicator of fecal contamination are: i) Total Coliforms (TC), ii) Fecal Coliforms (FC)
87 and iii) Fecal Streptococci (FS) as they are easy and inexpensive to detect.

88 Thus, the correct understanding of the main water-rock interaction influencing water
89 chemistry, along with the determination of the aquifer's pollution sources and consequently the
90 groundwater quality status becomes mandatory for a sustainable management plan of water
91 resources and to regulate its utilization. To achieve this purpose, several tools were recently
92 proposed ranging from more time consuming and expensive ones such as numerical modeling and
93 isotope investigation to more user-friendly application like water quality indices (WQIs) and
94 multivariate statistical analysis. Multivariate statistical techniques, including Factorial Analysis
95 (FA) or Principal Component Analysis (PCA), were widely applied to differentiate the various
96 mineralization processes characterizing groundwater, surface waters and soil bodies(Bove et al,
97 2011; Busico et al, 2018 ; Cuoco et al, 2009, 2013; Nadiri et al, 2013b; Viaroli et al, 2016; Rufino
98 et al, 2020). In the case of quality assessment, WQIs become rapidly popular through scientific
99 community due to the main advantage of aggregating different parameters (i.e. chemical, physical
100 and microbial indicators) into a single numerical index, representing the overall water quality.
101 Since these tools are very flexible in choosing parameters involved for the computation and
102 considering fixed standard threshold values, they can be used to evaluate the suitability of the
103 resource for a specific final intended use. Then using these numerical indices there is a wide range
104 of applications that have been found in studies concerning groundwater bodies in the last decades.
105 An exhaustive review on the evolution of WQIs is given by Lumb et al.(2011), Vadiati et al.(2016),
106 Machiwal et al. (2018) and references therein.

107 For example, Babiker et al. (2007) used chemical parameters to develop a Groundwater
108 Quality Index (GQI) showing the spatial variation of the water quality in a Japanese alluvial basin,
109 El Fadel et al., (2014) developed a GQI incorporating chemical and microbial parameters for
110 evaluating the water quality variation over two different hydrological seasons in a coastal karstic
111 aquifer in Lebanon. Among the most recent applications we mention Rufino et al. (2019) which
112 coupled a GQI with rating methodology in a highly urbanized agricultural plain in southern Italy,
113 and Saleh et al. (2020) which proposed a water quality index for groundwater (WQIG) to assess
114 its quality around a landfill area in Iran.

115 The understanding of various pollution processes and consequently which elements play
116 a more negative role on the water quality allows to specifically calibrate a Health Risk Assessment

117 (HRA) linked to the consumption and/or the utilization of polluted/low quality groundwater. A
118 properly HRA investigation for those elements which can generate noncarcinogenic and
119 carcinogenic problems, was widely considered as an important methodology for determining
120 health risks to humans (Eziz et al. 2018; Krishna and Mohan 2016). It was used to define the hazard
121 quotient for different element exposure such as NO_3 (Qasemi et al. 2018), F (Aravinthasamy et al.
122 2019; Karunanidhi et al. 2020), and As (Murtaza et al. 2019).

123 In the Campania Plain (CP), which is an alluvial plain located in southern Italy, a huge
124 number of studies focused on groundwater bodies, have highlighted over the last decades the
125 continuous deterioration of the groundwater resources from a chemical point of view. Most of
126 these works (Bellucci et al. 1990; Busico et al. 2017, 2018, 2020; Corniello et al. 2006, 2007;
127 Corniello and Ducci 1997; Cuoco et al. 2015; Diodato et al. 2013; Ducci et al. 2019, 2020; Rufino
128 et al. 2019; Tufano et al. 2020) were mainly focused on the high levels of Nitrate found in shallow
129 groundwater, attributing the sources of pollution mainly to human activity such as the use of
130 synthetic fertilizers, farming and seepage from the sewage systems. Conversely, only few works
131 have focused on microbial pollutants in CP as well as throughout the Italy (Bucci et al. 2015;
132 Celico et al. 2005, 2004a, 2004b; De Giglio et al. 2016; Lugoli et al. 2011; Naclerio et al. 2008).

133 To fill this gap, a well-tailored multidisciplinary approach considering both chemical
134 parameters (major elements and traces) and microbiological indicators (TC, FC and SF) in two
135 areas of the CP (Fig. 1) with different geographical, geological/hydrogeological and socio-
136 economic peculiarities has been tested. Firstly, the FA was utilized to identify all processes
137 characterizing the two study areas, then a modified GQI was developed considering only those
138 parameters (chemical and microbial) identified as harmfully for human health. Finally considering
139 the result obtained from FA and GQI in identifying those elements considered to negatively impact
140 on the overall water quality a specific site location HRA for the adult population has been assessed.
141 Specifically, the Agro Aversano site (AAS) is in a highly urbanized area located in the middle of
142 the CP, with a high population density, where urban, suburban and agricultural activities coexist
143 together. On the other hand, the Caiazzo Plain site (CPL) is an intra-mountain alluvial plain,
144 crossed by the Volturno river, located among the southern Apennine chain and characterized by a
145 high degree of naturalness, where the main source of economic income is represented by agricultural
146 activities related to tree plantation. These two sites were chosen because they offer the possibility
147 to test and verify the methodology in two extremely different hydrogeological and socio-economic
148 scenario.

149
150

151 **2 STUDY AREAS**

152 2.1 Agro-Aversano area

153

154 The Agro-Aversano site (AAS), located in the southern part of the Caserta province, is a densely
155 populated area bounded to the North and East by the Regi Lagni Canals, to the South by the Campi

156 Flegrei caldera and to the West by the Tyrrhenian Sea. The main outcropping lithology is made of
157 volcanic and alluvial deposits; the volcanic succession is mainly represented by tuff, trachyte and
158 scoria formation coming from explosive events of the Campanian volcanic centers over the time
159 (Aprile and Ortolani 1979)(Fig. 1b). The Campanian Ignimbrite (CI) is the main pyroclastic
160 deposit of the area consisting of a grey trachytic tuff erupted approximately 40,000 years BP
161 (Giaccio et al. 2017). It is covered by alluvial and volcanic reworked material and its thickness
162 decreases either toward the coastal areas (Allocca et al. 2007) as well toward the Volturno River
163 (Barra et al. 1996; Corniello et al. 2010). Alluvial deposits are principally made of silt and mixed
164 clay/sands derived from the Volturno river course. From a hydrogeological point of view, the CI
165 has an important role since it represents a confining/semi-confining layer dividing the two main
166 aquifers of the area: (i) a shallower one, hosted in reworked material of volcanic and alluvial origin
167 above the CI and (ii) a deeper one confined/semi confined hosted in the alluvial, volcanic and
168 karstic marine sediments below the CI. According to Corine Land Cover (CLC 2018) the 77% of
169 the area is occupied by agricultural fields (wheat, orchards, vegetables, and olive), the 23% is
170 occupied by urban areas (Figure S1b). No significant changes in land use have been highlighted
171 analyzing the CLC over the time (CLC 2006; 2012;2018).

172

173 2.2. Caiazzo Plain

174

175 The Caiazzo plain (CPL),is in the North part of the Caserta city and is bounded to the North- East
176 by the Alife Plain, to the West by the Mt. Maggiore chains, to the South by the Caserta Mountains.
177 The main outcropping lithological units are limestone (at Mt. Maggiore and Caserta Mountains
178 foothills), followed by the CI (in the northern part of the study area) and by the alluvial material
179 derived from the Volturno river (Fig. 1a).Moreover, an arenaceous-clayey flysch formation made
180 of mixed conglomerates, sandstones, marls, and clays outcrops in the external margins of the chain,
181 with an average thickness of a few hundred meters (Budetta et al. 1993). The study area shows
182 different land uses and even in this case no changes have been highlighted analyzing the CLC over
183 the time. According to Corine Land Cover (CLC 2018) the area is for approximately the 81%
184 occupied by agricultural fields, for the 7 % by urban fabric and the remaining 12% by natural areas
185 (mixed and broad-leafed forest) (Figure S1a).

186

187 3 MATERIALS AND METHODS

188 3.1 Groundwater sampling and chemical analysis

189 In this study a total of fifty-three groundwater samples were collected for chemical analysis and
190 microbial enumeration, from agricultural and municipal wells. The first field campaign was
191 performed in the AAS during the spring-summer period of 2017 collecting sixteen samples. For
192 the CPL, instead, thirty-seven samples were collected during the summer-spring period of 2018
193 (Fig. 1). All water samples are representative of the same shallow alluvial aquifer (see Table 1

194 ESM). All the wells' coordinates have been recorded at each surveyed point using a GARMIN
195 GPS device with an accuracy of ± 10 m. Field parameters were measured *in situ* using a multi-
196 parametric probe HANNA (HI991300), calibrated using HANNA standard pH buffers (7.0 and
197 4.0) and a standard of 1413 $\mu\text{S}/\text{cm}$ for EC. Water wells were purged before sampling, avoiding to
198 collect stagnant water, and till physical parameters (T, pH and EC) were stable. Alkalinity was
199 directly measured *in situ* by titration using a portable titrator KARTEL TECHNORATE, titrating
200 100ml of each sample with 0.1 N HCl solution and methyl-orange as indicator. Two aliquots of
201 water for each sample were collected and stored in 50-mL HDPE bottles for ion chromatography
202 (IC) analysis. Samples were finally filtered using a 0.45 μm Millipore filters and acidified ($\approx 2\%$;
203 $\text{pH} < 2.0$) with ultrapure HNO_3 MERCK™ for cations and trace element analysis. All chemical
204 analyses were carried out in the Laboratory of Environmental Geochemistry at the University of
205 Campania "Luigi Vanvitelli". The major anions (F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were
206 analyzed by IC using a Dionex DX-120. Calibration curves were constructed using five calibration
207 standards (1, 5, 10, 25, 50 mg/L) and analysis precision was checked against certified reference
208 water (SANGAMON™). All sample analyses show a charge balance error within 5%. Trace
209 elements analysis were performed only for CPL site by Inductively Coupled Plasma Mass
210 Spectrometry (ICP-MS) using an Agilent 7500 CE ICP-MS. More details concerning
211 methodologies employed for trace elements analysis are given in Cuoco et al. (2015).

212 **3.2 Microbial water indicator**

213 As previously presented TC, FC and FS are the main indicators used for water quality. TC include
214 a wide range of aerobic and facultatively anaerobic, Gram-negative, non-spore-forming bacilli.
215 This group indicate fecal and environmental species that can survive and grow in both sewage and
216 natural waters. Even if some of these bacteria are excreted in human and animal feces, they are
217 ubiquitous and thus cannot be properly considered as indicator of fecal pollution but as a general
218 indicator of the cleanliness and the integrity of distribution systems (WHO 2017). TC able to
219 ferment lactose at 44-45 °C, are known as thermo-tolerant coliform or FC. FC can be considered
220 as an acceptable indicator of fecal pollution since *Escherichia coli* is the most representative specie
221 of this group and it is present in very high numbers in i) human/animal feces, ii) sewage and iii)
222 water subject to recent fecal pollution. Intestinal enterococci instead, are a subgroup of the larger
223 group of organisms defined as FS. These bacteria are Gram-positive, that have been isolated from
224 the feces of both human and warm-blooded animals and are relatively tolerant of sodium chloride
225 and alkaline pH levels. In human feces are detected with an order of magnitude lower than those
226 of *E. coli*, while can be present in larger number in water polluted by sewage or human/animal
227 wastes. The detection of that group indicates recent fecal contamination (WHO 2017). The
228 transport into the groundwater through soil and rock, which are considered as "good but imperfect
229 traps for microbial pollutants" and their movement along the flow path is heavily dependent on
230 both the hydrogeological background and climatic conditions (Taylor et al. 2004).

231

232 **3.3 Microbiological analysis**

233 Samples for microbial analysis were collected in sterilized 2-L glass bottles. Samples were stored
234 in ice and analyzed within 4-6 hours after sampling. The sampling procedure was performed
235 delicately with care to avoid any external contamination. A filtering membrane technique was used
236 to analyze all water samples for bacterial enumeration. The following agar medium were used
237 according to American Public Health Association and Italian D.Lgs n. 152/2006: m-Endo-agar for
238 TC, m-FC-agar for FC, KF-agar for FS. Filtration was done through nitrocellulose membrane with
239 pore size of 0.45 μm and diameter of 47mm. After filtration plates were incubated at 37 °C for 24
240 h and 48 h for TC and FS respectively and at 44 °C for 24 h for FC. All microbial analyses were
241 carried out in the Microbiology Laboratory of the University of Campania “Luigi Vanvitelli”.

242 **3.4 Multivariate statistical analysis**

244 A multivariate statistical approach through Factor Analysis (FA) has been conducted i) to
245 distinguish the hydrogeochemical processes occurring in the studied aquifer, ii) to highlight the
246 relationships between major and/or trace elements and microbial indicators and iii) to differentiate
247 between natural and anthropogenic processes of groundwater mineralization. The FA represents a
248 robust approach worldwide applied in studies concerning hydrochemistry and environmental
249 geochemistry (Busico et al.2020, 2018) which allow to group the detected variables into new
250 synthetic variables called factors. The number of factors can be chosen following the Kaiser
251 criterion (Kaiser, 1960) and the correlations between elements expressed by each factor is
252 considered significant with factor loading ≥ 0.7 . More details concerning the applied statistical
253 method are given in Busico et al. (2018) and Rufino et al. (2020). Two different approaches were
254 tested considering different variables: the first using major ions and microbial pollutants for the
255 AAS (FA-AAS) and the second using major ions, trace elements and microbial pollutants for the
256 CPL (FA-CPL).

257 **3.5 “Groundwater Quality Index”**

259 A site specific GQI has been developed for each site considering only those parameters which can
260 potentially create health problems on human. All the utilized elements are listed in Table1. In this
261 study the methodology proposed by Babiker et al. (2007) and applied by several authors worldwide
262 (El Fadel et al. 2014; Khan et al. 2011; Kouli et al. 2008; Machiwal et al. 2011; Mohebbi et al.
263 2013; Rufino et al. 2019; Singh et al. 2018; Vadiati et al. 2016) was chosen to develop the index.
264 The resulting GQI is a synthetic numerical index incorporating different variables and comparing
265 them with fixed threshold limits. For this work the WHO guidelines for drinking water were
266 considered as threshold limit (WHO 2017). The GQI calculation has been done directly on each
267 sampled well using a multistep process schematized as follow:

268

269 $C = \frac{X-Y}{X+Y}$ (1)

270
271 $R = (0.5 * C^2) + (4.5 * C) + 5$ (2)

272
273 $GQI = 100 - ((R_1W_1 + R_2W_2 + \dots R_nW_n)/N)$ (3)

274
275 Where C is the defined contamination index, which compares the concentration (X) detected in
276 each well to its WHO desired threshold for drinking water (Y) (WHO 2017). The resulting C value
277 ranges between -1 and 1. The corresponding rank value (R) is then calculated using the polynomial
278 equation expressed in Eq. (2). The resulting R value ranges between 1 and 10, where 1 corresponds
279 to the lowest impact of the specific factor on the entire results and 10 corresponds to the highest
280 impact. The final step consists in the GQI calculation using Eq. (3), where W_n represents the
281 relative weight of each parameter and N is the number of parameters involved in the calculation.
282 For the AAS the GQI was built considering F^- , Cl^- , NO_3^- , SO_4^{2-} , TC, FC, FS while for the CPL
283 also Al, Cu, Ni and U have been added to the computation. The effects on human health and their
284 relative thresholds are listed in Table 1. As the computation has been performed using only those
285 parameters that are considered equally able to create potential negative effects on human health,
286 no weight factors were considered in the result. Unlike the standard procedure, the calculation was
287 made only on the sampled points. Finally, the GQIs have been classified in three equal classes of
288 quality (poor, medium and high).
289

290 **3.6 Human Health Risk Assessment (HRA)**

291 For the computation of the HRA two factors need to be calculated: i) the Chronic daily intake
292 (CDI) and ii) the hazard quotient (HQ). The CDI can be calculated following the formula:

293
294 $CDI = \frac{C \times IR \times ED \times EF}{BW \times AT}$ (4)

295 Where C indicates the pollutant concentration (mg/L) in the considered water samples, IR
296 represents the ingestion rate of water per day (L/day) that could vary accordingly with ages, ED
297 specifies the exposure duration for water (years), EF represent the water exposure frequency (365
298 days/year), BW is used for body weight of local individuals (kg), while AT signifies average life
299 expectancy (days). Regarding the HQ instead it calculated as a fraction of indicated dose to the
300 reference dose (RfD) as given in the following equation:

301
302 $HQ = \frac{CDI}{RfD}$ (5)

303 The HQ provides a single effective value for comparison of health risks. The greater the HQ, the
304 more the health risks involved. Based on the USEPA (2013), $HQ < 1$ demonstrates unlikely
305 deleterious health impact to the exposed individual, whereas $HQ \geq 1$ means that there exists the
306 likelihood that non-carcinogenic impacts may occur (Huang et al. 2018; Qasemi et al. 2018).

307

308 **4 Results and discussion**

309 **4.1 Geochemical characterization**

310 The electrical conductivity (EC) and pH in the AAS vary from 470 up to 1575 $\mu\text{S}/\text{cm}$, with an
311 average value of 901 $\mu\text{S}/\text{cm}$ and from 6.23 up to 7.69, with an average value of 6.94, respectively.
312 On the other hand, for the CPL site EC and pH vary from 251 up to 987 $\mu\text{S}/\text{cm}$ with an average
313 value of 586 $\mu\text{S}/\text{cm}$ and from 6.30 up to 7.68 with an average value of 7.10, respectively. The
314 dataset (Table 1 ESM) highlights as within the AAS, the 75% of the collected samples exceed the
315 WHO threshold for Nitrate (fixed at 50 mg/L), ranging between 50 and 342 mg/L, while only 25%
316 of samples are below the WHO threshold (50 mg/L). For the CPL instead, only the 8% of samples
317 exceed the WHO threshold, highlighting the different degree of NO_3 contamination in the two
318 areas of the CP. A statistical summary (mean, median, maximum, minimum, 25th and 75th
319 percentiles, standard deviation) of the detected variables is given in Table 2 ESM. According to
320 Piper diagram (Piper 1944) (Fig.2) the groundwater in the AAS are classified as HCO_3 type with
321 a significant amount of Ca (from 33% up to 55%) and Na+K (from 27 % up to 51%). The CPL
322 groundwater is (also) similarly classified as HCO_3 - Ca type with Ca ranging from 53% up to 84%
323 and HCO_3 ranging from 70% up to 96%. Ternary plot of major cations (Ca-Mg-Na+K) (Fig. 2)
324 shows different chemical signatures detected in the two sites. The 99 % of total samples plot
325 between two Ca-Mg end-members with considerable differences in alkali elements. For the CPL,
326 groundwater maintains the original chemical composition of rich HCO_3 -Ca recharges coming from
327 neighboring carbonate massifs of Mt. Maggiore and Caserta Mountains, with Na+K/Ca ratio
328 ranging from 0.1 up to 0.5. Conversely the AAS groundwater shows a progressive enrichment in
329 alkali elements with a Na+K/Ca ratio ranging from 0.4 up to 1.5 (approximately three times
330 higher than CPL). In function of the well-known local stratigraphy (Aprile and Ortolani 1979), the
331 alkali enrichment should be associated to two main phenomena, i) water-volcanic rock interactions
332 along the flow path (Cuoco et al, 2020) and ii) to lateral Na-K-rich inflows coming from the
333 volcanic aquifer of the Campi Flegrei area (Rufino et al. 2019). The different chemical signature
334 and the different enrichment in alkaline elements (Na + K) is also appreciable in Figure 2 ESM,
335 where the Stiff diagrams representative of the upper and lower ends of the two populations (in
336 term of Na+K/Ca ratio) are presented. The same points are also highlighted in Fig. 2 with red and
337 blue lines. The ternary plot of major anions (HCO_3 -Cl- SO_4) (Fig. 2) shows a natural trend of
338 collected waters and a progressive Cl and SO_4 enrichment moving from the reliefs at the boundary
339 of the CP toward the coastal areas. More details concerning the hydrochemistry of the AAS are

340 given in Rufino et al. (2019). Furthermore, geochemical results of the present study agree with the
341 hydrogeochemical model of the shallow aquifer within the CP proposed by Cuoco et al. (2015).
342 Following the graphical approach already proposed in prior works (Busico et al. 2017; Rufino et
343 al. 2019) here we present a modified NO_3/SO_4 scatter diagram (Fig. 3) integrated with indicators
344 of fecal pollution (FC and FS) made to discriminate the principal sources of these pollutants.
345 Generally, Sulphur is added in variable amounts and in several chemical forms in synthetic
346 fertilizers (Cuoco et al. 2015). It maintains a weight ratio with nitrogen never <1 (Casalicchio and
347 Graziano 1984). Moreover, SO_4/NO_3 ratios (i) approximately of 4 in areas with intensive use of
348 fertilizers (Federico et al. 2004) and (ii) around 0.1-0.4 for local wastewater (Cuoco et al. 2015)
349 were estimated. Results of microbial enumeration are given in Table 1 ESM. The 69% of the AAS
350 samples, collected in private wells within urban area, fall in the range of the organic matter
351 showing fecal pollution by FC along with high level of nitrates and sulphates. Therefore,
352 considering this information, we can assert that the source of the fecal pollution for this group of
353 samples could be linked to leaks from the sewer systems and subsequent percolation of the
354 wastewater within the aquifer. Conversely for the CPL it is possible to note that (i) the SO_4/NO_3
355 ratio tends to shift from very high (>4) to very low value (<0.4) values and (ii) that 75% of this
356 group of samples is characterized by both FC and FS pollution. Hence considering the land use
357 information reported above, it is likely that the spreading of animal manure (which represents a
358 still used agricultural practice throughout the CP) could be the first cause of groundwater pollution
359 for the CPL site.

360 **4.2 Factor analysis application**

361 To further confirm the proposed hydrogeochemical background of the two study areas a FA was
362 applied to evaluate the potential correlation between chemicals and microbial compound for both
363 sites. Results of FA-AAS (Table 2) have highlighted 4 different factors and no correlations
364 between major elements and microbial pollutants were shown. Results of FA-CPL (Table 2) have
365 also highlighted 4 different factors, even correlating microbial pollutants with trace elements.
366 Concerning the AAS, the F1 explains the 47% of the total variance and correlates Cl, NO_3 , SO_4 ,
367 K, Mg, and Ca. This represents the main mineralization factor for the study area confirming how
368 the natural drainage system, along with the intensive farming and agricultural activities can
369 determine the enrichment in solution of these elements (Rufino et al. 2019). The F2 explains about
370 the 14% of the total variance showing an independent nature of the Fluoride. This result was
371 expected because the F is typically associated with water-volcanic rock interaction (Casentini et.
372 al 2010) and the AAS is also characterized by the presence of a buried volcanic complex with the
373 bottom at 1500 mt at depth (Ortolani and Aprile 1985; Rolandi et al. 2003). The F3 explains the
374 11% of the total variance correlating HCO_3 and Na remarking the main hydrogeochemical facies
375 expressed by the Piper diagram. The gradual interaction with volcanites brings to increasing of Na
376 (ion exchange) and HCO_3 hydrolysis reactions with either buried basalts and Phlegrean Field's
377 volcanites. Finally, the F4 explains the 9% of the total variance and see alone the TC, confirming
378 a possible recent microbial pollution but at the same time highlighting no dependencies between

379 biological and chemicals parameters. For CPL instead, the F1 explains the 27% of the total
380 variance and correlates HCO₃, Cl, SO₄, Na, Ca, B, Co, and Sr. This first factor can be correlated
381 to the carbonate nature of the main lithological units in the study area. The F2 explains about the
382 13% of the total variance correlating P, TC and FC with NO₃, K and FS showing eigen values
383 approaching the significance level (0.56, 0.55, 0.68, respectively). In this case, the correlation
384 between biological and chemical elements is evident in as much P, K and NO₃ are the main
385 nutrients for microorganisms. Moreover, the correlation among those parameters could also
386 indicate the proximity to those wells to septic tanks, where sometimes leaching may not be able to
387 percolate through the soil, especially during the wet season, resulting in groundwater
388 contamination (Arnade, 1999, Elangovan et al. 2018). The F3 explains the 10% of the total
389 variance and highlights the independent nature of the U. The F4 explains the 8% of the total
390 variance showing a negative correlation between Ti and Al likely related to interaction with
391 argillaceous rocks where the alteration of secondary mineral brings to the colloids mobilization,
392 in fact Ti and Al are not soluble elements in groundwater but they are found in suspended materials
393 (Viaroli et al. 2016)

394 **4.3 GQI and HR application**

395 The resulting GQI varies between 62.5 and 88.5 for the AAS with an average value of 70.1 while
396 for the CPL it ranges from 73.3 to 91.2 with an average value of 79.3. A representation of GQI
397 classification for each sampled well is shown in Fig. 4. 75 % of samples for the AAS area show
398 poor groundwater quality due to the high amount of NO₃ and the fecal contamination with only
399 the 25 % of the samples with a medium/high quality, NO₃ concentration below the WHO limit (50
400 mg/L) and low/absent fecal contamination. For the CPL instead, the 65% of water samples show
401 poor water quality while the remaining 35% of the samples are characterized by medium/high
402 quality. It is worth noting that the average GQI value in the CPL (79.3) is clearly higher than the
403 AAS (70.1) despite for CPL the GQI calculation also accounted four trace elements potentially
404 toxic for human health (Al, Cu, Ni and U). The different level of quality can be mainly associated
405 with i) different land use coverage and ii) a different human impact in the two study areas. In fact,
406 the CPL alluvial aquifer receives continuous freshwater recharge from the peripheral carbonate
407 massifs, which determine a higher level of dilution and consequently a lower level of
408 contamination, as well as presenting a greater percentage of natural areas, absent in the AAS (Fig.
409 S1a). The R values obtained for the GQI evaluation have been considered identifying those
410 elements suitable for a further HRA evaluation. It is important to specify as in both study areas all
411 microbial parameters showed an average R value higher than six (6) which indicates a
412 medium/high level of fecal contamination that need to be properly considered in the final (overall)
413 quality evaluation. Among the chemical elements, for AAS, NO₃ and F were identified to be the
414 most sensitive elements disrupting water quality for human health, while only NO₃ was considered
415 for the CPL. The HRA was then calculated using the CDI and HQ formulation for non-
416 carcinogenic risk and considering an adult population. The parameters utilized for the HRA
417 evaluation are described in Table 3. The reference ingestion dose for NO₃ and F are 1.6 mg/kg*day

418 and 0.04 mg/kg*day, respectively and were sourced by USEPA (USEPA 2013). For the ASS, the
419 HQ for NO₃ ranges from 0.31 to 8.00 with an average value of 2.8 while the HQ for F ranges from
420 0.62 to 1.18 with an average value of 0.88. Generally, the occurrence of harmful health impacts is
421 found when the HQ value is higher than 1, whereas it is regarded to be safe when the HQ value is
422 less than 1. In this case, considering NO₃, the 95% of water samples were above the safety level
423 while only the 25 % for F. For CLP instead the HQ for NO₃ ranges from 0.01 to 3.37 with an
424 average value of 0.98. In this case the 45% of sample showed a HQ value higher than 1 which
425 could generate harmful effect on human health. The HRA assessment further confirmed how the
426 higher percentage of water belonging to ASS suffer from important quality problem and how the
427 different degree of human impact can significantly decrease the overall groundwater quality posing
428 a serious concern of human health. It is worth to mention how the reduction of the various sources
429 of pollution is mandatory. Such operations like the optimization of a decision-making support
430 system to avoid polluting action (Phan et al. 2016) assisted by an adequate land use planning
431 (Bannenberget al. 2020) could avoid further deterioration of groundwater status.

432 **5 Conclusions**

433 This study proposed a comprehensive groundwater quality status for two study areas characterized
434 by large different environmental conditions. The main findings of the current research are
435 summarized below:

- 436 1) Different chemical groundwater signatures were highlighted for the AAS and CPL. The
437 water hosted within the alluvial aquifer in the middle part of the CP (AAS) undergoes a
438 remarkable enrichment in alkali elements compared to the groundwater in the CPL, which
439 tends to maintain the original chemical composition of the inflows coming from the
440 neighboring karst aquifers. This hydrochemical dynamics is related to the natural evolution
441 of the chemical composition along the groundwater flow-path. The leaching of agricultural
442 soils allows the NO₃ and SO₄ input with the succession of production cycles.
- 443 2) The statistical results of FA highlighted different hydrogeochemical processes confirming
444 the main hydrogeological setting of the two areas and stating apparently no correlations
445 between chemical and microbial compounds for AAS suggesting an independent nature
446 for TC. Conversely, in the FA-CPL a correlation between P, TC and FC was found (with
447 FS, NO₃ and K approaching the significant level fixed at 0.7). Moreover, combining these
448 information with a graphical approach allowed to differentiate the sources of pollution,
449 mainly attributed to i) the leaks in the sewer system for the AAS and to ii) the spreading of
450 manure as fertilizers in agricultural activity for the CPL.
- 451 3) A general poor quality has been highlighted for the majority of analyzed samples in both
452 sites through the GQI application, due to the different high levels of both Nitrate and Fecal
453 indicators. The HRA further confirmed the poor water quality and highlighted that for ASS,
454 the NO₃ could represent an important concern for human health compared to other
455 investigated chemical elements. The same issue has been identified in CLP although with
456 a much lower magnitude due to the higher degree of naturalness of the area.

457 Finally, the proposed assessment remarked how all the applied tools can be easily and widely
458 applied and modified around the world to evaluate current and future issues related to
459 groundwater sustainability.

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464 preparation, data collection, analysis, and data development were performed by Francesco Rufino,
465 Emilio Cuoco and Gianluigi Busico. The first original manuscript draft was written by Francesco
466 Rufino. Dario Tedesco, Sergio Calabrese and Lidia Muscariello provided the language editing. All
467 authors commented on previous versions of the manuscript. All authors read and approved the
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469 **Data availability:** The dataset generated during this study is available and attached to the
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471

472 **Compliance with ethical standards**

473 **Competing interests:** The authors declare that they have no competing interests.

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479 **6 References**

480 Aprile, F., & Ortolani, F. (1979) Sulla struttura profonda della Piana Campana, *Bollettino della*
481 *Società dei Naturalisti in Napoli*, 88, 243-261

482 Alghamdi, A.G., Aly, A.A., Aldhumri, S.A., & Al-Barakaha, F.N. (2020) Hydrochemical and
483 Quality Assessment of Groundwater Resources in Al-Madinah City, Western Saudi Arabia.
484 *Sustainability*, 12(8), 3106 <https://doi.org/10.3390/su12083106>

485 Allocca, V., Celico, F., Celico, P., De Vita, P., Fabbrocino, S., Mattia, C., Monacelli, G., Musilli,
486 I., Piscopo, V., Scalise, A.R., Summa, G., & Tranfaglia, G. (2007) Carta Idrogeologica
487 dell'Italia Meridionale. *Istituto Poligrafico e Zecca dello Stato*.

488 Aravinthasamy, P., Karunanidhi, D., Subramani, T., Srinivasamoorthy, K., & Anand, B. (2019)
489 Geochemical evaluation of fluoride contamination in groundwater from Shanmuganadhi River
490 basin South India: Implication on human health. *Environmental Geochemistry and Health*.
491 <https://doi.org/10.1007/s10653-019-00452-x>

492 Arnade, L.J. (1999). Seasonal correlation of well contamination and septic tank distance. *Ground*
493 *Water*, 37(6), 920-923. <https://doi.org/10.1111/j.1745-6584.1999.tb01191.x>.

494 Ascott, M.J. Gooddy, D.C. Wang, L. Stuart, M.E. Lewis, M.A. Ward, R.S., & Binley, A.M. (2017)
495 Global patterns of nitrate storage in the vadose zone. *Nature Communication* 8(1), 1416.
496 <https://doi.org/10.1038/s41467-017-01321-w>

497 Azizullah, A., Khattak, M.N.K., Richter, P., & Häder, D. (2011) Water pollution in Pakistan and
498 its impact on public health - A review. *Environment International*, 37(2), 479-497.
499 <https://doi.org/10.1016/j.envint.2010.10.007>

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

502 Barra, D., Romano, P., Santo, A., Campajola, L., Roca, V., & Tuniz, C. (1996) The Versilian
503 transgression in the Volturno river plain (Campania, Southern Italy): paleoenvironmental
504 history and chronological data. *Il Quaternario Italian Journal of Quaternary Sciences*, 9(2),
505 445–458

506 Bannenberg, M., Ntona, M. M., Busico, G., Kalaitzidou, K., Mitrakas, M., Vargemezis, G., . . .
507 Voudouris, K. (2020). Hydrogeological and hydrochemical regime evaluation in flamouria
508 basin in edessa (northern greece). *Environments - MDPI*, 7(12), 1-16.
509 <https://doi.org/10.3390/environments7120105>.

510 Bellucci, F., Corniello, A., de Riso, R., & Russo, D. (1990). Idrogeologia della Piana a nord-est di
511 Napoli. *Memorie della Societa Geologica Italiana*, 45, 339–349.

512 Bove, M.A., Ayuso, R.A., De Vivo, B., Lima, A., & Albanese, S. (2011) Geochemical and isotopic
513 study of soils and waters from an Italian contaminated site: Agro Aversano (Campania, Italy).
514 *Journal of Geochemical Exploration*, 109(1-3), 38–50.
515 <https://doi.org/10.1016/j.gexplo.2010.09.013>.

516 Brammer, H., & Ravenscroft, P. (2009) Arsenic in groundwater: A threat to sustainable agriculture
517 in south and south-east Asia. *Environment International*, 35(3), 647-654.
518 <https://doi.org/10.1016/j.envint.2008.10.004>

519 Bucci, A., Petrella, E., Naclerio, G., Allocca, V., & Celico, F. (2015). Microorganisms as
520 contaminants and natural tracers: a 10-year research in some carbonate aquifers (southern
521 Italy). *Environmental Earth Sciences*, 74(1), 173-184. <https://doi.org/10.1007/s12665-015-4043-1>

522

523 Budetta. P., Calcaterra. D., Corniello. A., De Riso. R., Ducci. D. & Santo. A. (1993) Appunti di
524 Geologia dell'Appennino Meridionale con riferimento ai "rischi" ed alle risorse del territorio.
525 *Istituto di Geologia Applicata*, 332, 1-39

526 Busico, G., Kazakis, N., Cuoco, E., Colombani, N., Tedesco, D., Voudouris, K., & Mastrocicco,
527 M., (2020) A novel hybrid method of specific vulnerability to anthropogenic pollution using

528 multivariate statistical and regression analyses. *Water Research*, 171,
529 115386 <https://doi.org/10.1016/j.watres.2019.115386>

530 Busico, G., Cuoco, E., Kazakis, N., Colombani, N., Mastrocicco, M., Tedesco, D., & Voudouris,
531 K. (2018) Multivariate statistical analysis to characterize/discriminate between anthropogenic
532 and geogenic trace elements occurrence in the Campania plain, southern Italy. *Environmental*
533 *Pollution*, 234, 260–269. <https://doi.org/10.1016/j.envpol.2017.11.053>

534 Busico, G., Kazakis, N., Colombani, N., Mastrocicco, M., Voudouris, K., & Tedesco, D. (2017)
535 A modified SINTACS method for groundwater vulnerability and pollution risk assessment in
536 highly anthropized regions based on NO_3^- and SO_4^{2-} concentrations. *Science of The Total*
537 *Environment*, 609, 1512-1523. <https://doi.org/10.1016/j.scitotenv.2017.07.257>

538 Casalicchio G. & Graziano P.L. (1984) Chimica agraria. I Fertilizzanti. *Cooperativa Libreria*
539 *Universitaria Editrice Bologna*.

540 Casentini, B., Pettine, M., & Millero, F., (2010) Release of arsenic from volcanic rocks through
541 interactions with inorganic anions and organic ligands. *Aquatic geochemistry*, 16 (3), 373-
542 393. <https://doi.org/10.1007/s10498-010-9090-3>

543 Celico, F., Musilli, I., Varcamonti, M., & Naclerio, G. (2005). Microbial groundwater pollution in
544 Italian carbonate aquifers. *Giornale di Geologia Applicata*, 1, 213-217.

545 Celico, F., Musilli, I., & Naclerio, G. (2004a) The impacts of pasture- and manure-spreading on
546 microbial groundwater quality in carbonate aquifers. *Environmental Geology*, 46(2), 233-236
547 <https://doi.org/10.1007/s00254-004-0987-2>

548 [Celico, F., Varcamonti, M., Guida, M., & Naclerio, G. \(2004b\). Influence of precipitation and soil](#)
549 [on transport of fecal enterococci in fractured limestone aquifers. *Applied and Environmental*](#)
550 [Microbiology](#), 70(5), 2843-2847.

551 Chitsazan, N., Nadiri, A. A., & Tsai, F. T. C. (2015). Prediction and structural uncertainty analyses
552 of artificial neural networks using hierarchical Bayesian model averaging. *Journal of*
553 *Hydrology*, 528, 52-62. <https://doi.org/10.1016/j.jhydrol.2015.06.007>

554 Corine Land Cover (2018) Available online at: [https://land.copernicus.eu/pan-european/corine-](https://land.copernicus.eu/pan-european/corine-land-cover/clc2018)
555 [land-cover/clc2018](#)

556 Corniello, A., Ducci, D., Rotella, M., Trifuoggi, M., & Ruggieri, G. (2010)
557 Hydrogeology and hydrogeochemistry of the plain between Mt. Massico and the river Volturno
(Campania region, Italy). *Italian Journal of Engineering Geology and Environment*, 1, 51–64.
558 <https://doi.org/10.4408/IJEGE.2010-01.O-04>.

559 Corniello, A., Ducci, D., Ruggieri, G., Iorio, M. (2018). Complex groundwater flow circulation in
560 a carbonate aquifer: Mount Massico (Campania region, southern Italy). synergistic
561 hydrogeological understanding. *Journal of Geochemical Exploration*, 190, 253-264.
562 <http://doi.org/10.1016/j.gexplo.2018.03.017>

563 Corniello, A., Ducci, D., & Ruggieri, G. (2007). Areal identification of groundwater nitrate
564 contamination sources in periurban areas. *Journal of Soils Sediments*, 7(4), 159–166.
565 <https://doi.org/10.1065/jss2007.03.213>

566 Corniello A., Ducci D., Ruggieri G. (2006). Il rischio di Inquinamento da nitrati di origine agricola
567 nella Piana del F. Volturno: il test site di Acerra. Atti Gisday 2006: integrazione in ambiente
568 GIS di dati ambientali. Novembre 2006, Caserta.

569 Corniello A., Ducci D. (1997). La Carta del rischio di inquinamento delle risorse idriche
570 sotterranee: un esempio in Piana Campana. Quaderni di Tecniche di Protezione Ambientale.
571 Quaderni di Geologia Applicata, 1 (1), 117–131, Pitagora, Bologna.

572 Cuoco, E., Sacchi, E., De Francesco, S., Paolucci, V., Maletic, E.L., Darrah, T.H., Sirna, M.,
573 Tedesco, D. (2020) Groundwater mixing in a heterogeneous multilayer aquifer driven by
574 geogenic CO₂ fluxes: Evidence from chemical and isotopic composition of *Ferrarelle* waters
575 (Riardo Plain, southern Italy) *Applied Geochemistry*, 116, 104564.
576 <https://doi.org/10.1016/j.apgeochem.2020.104564>

577 Cuoco, E., Darrah, T.H., Buono, G., Verrengia, G., De Francesco, S., Eymold, W.K., & Tedesco,
578 D. (2015) Inorganic contaminants from diffuse pollution in shallow groundwater of the
579 Campanian plain (southern Italy). Implications for geochemical survey. *Environmental*
580 *Monitoring and Assessment*, 187(2), 46. <https://doi.org/10.1007/s10661-015-4307-y>

581 Cuoco, E., De Francesco, S., & Tedesco, D., (2013) Hydrogeochemical dynamics affecting steam-
582 heated pools at El Chichón Crater (Chiapas - Mexico). *Geofluids*. 13(3), 331–
583 343. <https://doi.org/10.1111/gfl.12028>

584 Cuoco, E., Verrengia, G., De Francesco, S., & Tedesco, D. (2010). Hydrogeochemistry of
585 Roccamonfina volcano (Southern Italy). *Environmental Earth Sciences* 61, 525–538
586 <https://doi.org/10.1007/s12665-009-0363-3>

587 De Giglio, O., Barbuti, G., Trerotoli, P., Brigida, S., Calabrese, A., Di Vittorio, G., ... & Montagna,
588 M. T. (2016). Microbiological and hydrogeological assessment of groundwater in southern
589 Italy. *Environmental Monitoring and Assessment*, 188(11), 638.
590 <https://doi.org/10.1007/s10661-016-5655-y>

591 Diodato, N., Esposito, L., Bellocchi, G., Vernacchia, L., Fiorillo, F., & Guadagno, F. M. (2013).
592 Assessment of the spatial uncertainty of nitrates in the aquifers of the Campania plain (Italy).
593 Ducci, D., Della Morte, R., Mottola, A., Onorati, G., & Pugliano, G. (2019). Nitrate trends in
594 groundwater of the Campania region (southern Italy). *Environmental Science and Pollution*
595 *Research*, 26(3), 2120-2131. <https://doi.org/10.1007/s11356-017-0978-y>

596 Ducci, D., Della Morte, R., Mottola, A., Onorati, G., & Pugliano, G. (2020). Evaluating upward
597 trends in groundwater nitrate concentrations: an example in an alluvial plain of the Campania
598 region (Southern Italy). *Environmental Earth Sciences*, 79(13), 1-10.
599 <https://doi.org/10.1007/s12665-020-09062-8>

600 Duker, A. A., Carranza, E., & Hale, M. (2005) Arsenic geochemistry and health. *Environment*
601 *international*, 31(5), 631-641. <https://doi.org/10.1016/j.envint.2004.10.020>

602 Elangovan, N.S., Lavanya, V., Arunthathi, S. (2018). Assessment of groundwater contamination
603 in a suburban area of Chennai, Tamil Nadu, India. *Environment, Development and Sustainability*,
604 20(6), 2609-2621. <https://doi.org/10.1007/s10668-017-0007-9>.

605 El Fadel, M., Tomaszekiewicz, M., Adra, Y., Sadek, S., & Najm, M.A. (2014) GIS-based
606 assessment for the development of a groundwater quality index towards sustainable aquifer
607 management. *Water Resources Management*, 28, 3471-3487. [https://doi.org/10.1007/s11269-](https://doi.org/10.1007/s11269-014-0683-2)
608 [014-0683-2](https://doi.org/10.1007/s11269-014-0683-2)

609 Emmanuel, E., Pierre, M. G., & Perrodin, Y. (2009) Groundwater contamination by
610 microbiological and chemical substances released from hospital wastewater: Health risk
611 assessment for drinking water consumers. *Environment international*, 35(4), 718-726.
612 <https://doi.org/10.1016/j.envint.2009.01.011>

613 Eziz, M., Mohammad, A., Mamut, A., & Hini G (2018) A human health risk assessment of heavy
614 metals in agricultural soils of Yanqi Basin, Silk Road Economic Belt, China. *Human and*
615 *Ecological Risk Assessment* 24(5), 1–15 <https://doi.org/10.1080/10807039.2017.1412818>

616 Farooqi, A., Masuda, H., & Firdous, N. (2007) Toxic fluoride and arsenic contaminated
617 groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant
618 sources. *Environmental Pollution*, 145(3), 839-849.
619 <https://doi.org/10.1016/j.envpol.2006.05.007>

620 Federico, C., Aiuppa, A., Favara, R., Gurrieri, S., & Valenza, M. (2004) Geochemical monitoring
621 of groundwater (1998–2001) at Vesuvius volcano (Italy). *Journal of Volcanology and*
622 *Geothermal Research*, 133(1–4), 81–104 [https://doi.org/10.1016/S0377-0273\(03\)00392-5](https://doi.org/10.1016/S0377-0273(03)00392-5)

623 Fendorf, S., Michael, H. A., & Van Geen, A. (2010) Spatial and temporal variations of
624 groundwater arsenic in south and southeast Asia. *Science*, 328(5982), 1123-1127.
625 <https://doi.org/10.1126/science.1172974>

626 Frankowski, M., Ziola-Frankowska, A., Kurzyca, I., Novotný K., Vaculovič, T., Kanický, V.,
627 Siepak, M., & Siepak, J. (2011) Determination of aluminum in groundwater samples by GF-
628 AAS, ICP-AES, ICP-MS and modelling of inorganic aluminum complexes. *Environmental*
629 *Monitoring and Assessment*, 182, 71–84 <https://doi.org/10.1007/s10661-010-1859-8>

630 Gangolli, S.D., van den Brandt, P.A., Feron, V.J., Janzowsky, C., Koeman, J.H., Speijers, G.J.A.,
631 Spiegelhalder, B., Walker, R., & Wishnok, J.S., (1994) Nitrate, nitrite and N-nitroso
632 compounds. *European Journal of Pharmacology: Environmental Toxicology and*
633 *Pharmacology*. 292(1), 1-38. [https://doi.org/10.1016/0926-6917\(94\)90022-1](https://doi.org/10.1016/0926-6917(94)90022-1)

634 Giaccio, B., Hajdas, I., Isaia, R., Deino, A., & Nomade, S. (2017) High-precision ^{14}C and $^{40}\text{Ar}/^{39}\text{Ar}$
635 dating of the Campanian Ignimbrite (Y-5) reconciles the time-scales of climaticultural
636 processes at 40 ka. *Scientific Reports*, 7(1). <https://doi.org/10.1038/srep45940>.

637 Kaiser, H. F. (1960) The application of electronic computers to factor analysis. *Educational and*
638 *Psychological Measurement*, 20, 141-151 <https://doi.org/10.1177/001316446002000116>

639 Karunanidhi, D., Aravinthasamy, P., Subramani, T., & Muthusankar, G. (2020) Revealing
640 drinking water quality issues and possible health risks based on water quality index (WQI)
641 method in the Shanmuganadhi River basin of South India. *Environmental Geochemistry and*
642 *Health*. <https://doi.org/10.1007/s10653-020-00613-3>

643 Kazakis, N., Kantiranis, N., Kalaitzidou, K., Kaprara, M., Mitrakas, M., Frei, R., Vargemezis, G.,
644 Tsourlos, P., Zouboulis, A.f., & Filippidis, A. (2017) Origin of hexavalent chromium in

645 groundwater: The example of Sarigkiol basin, northern Greece. *Science of the Total*
646 *Environment*, 593-594, 552-566. <https://doi.org/10.1016/j.scitotenv.2017.03.128>

647 Kelly, W.R., Panno, S.V., Hackley, K.C., Martinsek, A.T., Krapac, I.G., Weibel, C.P., & Storment,
648 E.C. (2009) Bacteria contamination of groundwater in a mixed land-use karst region. *Water*
649 *Quality, Exposure and Health*, 1(2), 69-78. <https://doi.org/10.1007/s12403-009-0006-7>

650 Krishna, A.K., & Mohan, K.R. (2016) Distribution, correlation, ecological and health risk
651 assessment of heavy metal contamination in surface soils around an industrial area, Hyderabad,
652 India. *Environmental Earth Sciences*75:411 <https://doi.org/10.1007/s12665-015-5151-7>

653 Khan, H.H., Khan, A., Ahmed, S., & Perrin, J. (2011) GIS-based impact assessment of land-use
654 changes on groundwater quality: study from a rapidly urbanizing region of South India.
655 *Environment and Earth Science*, 63, 1289-1302. <https://doi.org/10.1007/s12665-010-0801-2>

656 Kouli, M., Lydakis-Simantiris, N., & Soupios, P. (2008), 4th quarter. GIS-based aquifer modeling
657 and planning using integrated geoenvironmental and chemical approaches. In: Groundwater:
658 modeling, management, and contamination. König LF, Weiss JL (eds) Nova Publishers, USA

659 Harrison, P.T.C. (2005) Fluoride in water: a UK perspective. *Journal of Fluorine Chemistry*.
660 126(11-12), 1448-1456 <https://doi.org/10.1016/j.jfluchem.2005.09.009>

661 Huang, Y., Teng, Y., Zhang, N., Fu, Z., Ren, W. (2018) Human health risk assessment of heavy
662 metals in the soil-*Panax notoginseng* system in Yunnan province, China. *Human and*
663 *Ecological Risk Assessment*, 24(5), 1312-1326
664 <https://doi.org/10.1080/10807039.2017.1411782>

665 Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA) (2009), CARG project, Carta
666 geologica d'Italia alla scala 1:50000. Available online at:
667 [http://www.isprambiente.gov.it/en/projects/soil-and-territory/carg-project-geologic-and-](http://www.isprambiente.gov.it/en/projects/soil-and-territory/carg-project-geologic-and-geothematic-cartography)
668 [geothematic-cartography](http://www.isprambiente.gov.it/en/projects/soil-and-territory/carg-project-geologic-and-geothematic-cartography)

669 Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA) (1976) Carta geologica
670 d'Italia alla scala 1:100000. Available online at
671 [http://www.isprambiente.gov.it/it/cartografia/carte-geologiche-e-geotematiche/carta-](http://www.isprambiente.gov.it/it/cartografia/carte-geologiche-e-geotematiche/carta-geologica-alla-scala-1-a-100000)
672 [geologica-alla-scala-1-a-100000](http://www.isprambiente.gov.it/it/cartografia/carte-geologiche-e-geotematiche/carta-geologica-alla-scala-1-a-100000)

673 Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA)
674 http://sgi2.isprambiente.it/arcgis/rest/services/servizi/carta_geologica_100k/MapServer

675 Liesch T., Hinrichsen, S., & Goldscheider, N. (2015) Uranium in groundwater - fertilizers versus
676 geogenic sources. *Science of the Total Environment*, 536, 981-995.
677 <https://doi.org/10.1016/j.scitotenv.2015.05.133>

678 Lugoli, F., Leopizzi, M. I., Bagordo, F., Grassi, T., Guido, M., & De Donno, A. (2011).
679 Widespread microbiological groundwater contamination in the South-eastern Salento (Puglia-
680 Italy). *Journal of Environmental Monitoring*, 13(1), 192-
681 200. <https://doi.org/10.1039/c0em00193g>

682 Machiwal, D., Cloutier, V., Güler, C., Kazakis, N. (2018). A review of GIS-integrated statistical
683 techniques for groundwater quality evaluation and protection. *Environmental Earth Sciences*,
684 77(19). <https://doi.org/10.1007/s12665-018-7872-x>.

685 Machiwal, D., Jha, M. K., & Mal, B. C. (2011) GIS-based assessment and characterization of
686 groundwater quality in a hardrock hilly terrain of Western India. *Environmental Monitoring*
687 *and Assessment*, 174, 645-663. <https://doi.org/10.1007/s10661-0101485-5>

688 Macler B. A., & Merkle, J. C. (2000) Current knowledge on groundwater microbial pathogens and
689 their control. *Hydrogeology Journal*, 8(1), 29–40. <https://doi:10.1007/pl00010972>

690 Mastrocicco, M., Colombani, N., Palpacelli, S., & Castaldelli, G. (2011) Large tank experiment
691 on nitrate fate and transport: the role of permeability distribution. *Environmental Earth*
692 *Sciences*, 63(5), 903–914. <https://doi.org/10.1007/s12665-010-0759-0>

693 Mohebbi, M. R., Saeedi, R., Montazeri, A., Vaghefi, K. A., Labbafi, S., Oktaie, S., Abtahi, M., &
694 Mohagheghian, A. (2013) Assessment of water quality in groundwater resources of Iran using
695 a modified drinking water quality index (DWQI). *Ecological Indicators*, 30, 28-34.
696 <https://doi.org/10.1016/j.ecolind.2013.02.008>

697 Murtaza, B., Natasha, Amjad, M., Shahid, M., Imran, M., Shah, N. S., Abbas, G., Naeem, M.A. &
698 Amjad, M. (2019) Compositional and health risk assessment of drinking water from health
699 facilities of District Vehari, Pakistan. *Environmental Geochemistry and*
700 *Health*<https://doi.org/10.1007/s10653-019-00465-6>

701 Nadiri, A. A., Aghdam, F. S., Khatibi, R., & Moghaddam, A. A. (2018). The problem of identifying
702 arsenic anomalies in the basin of Sahand dam through risk-based ‘softmodelling’. *Science of*
703 *the total environment*, 613, 693-706.<https://doi.org/10.1016/j.scitotenv.2017.08.027>

704 Nadiri, A. A., Fijani, E., Tsai, F. T. C., & Asghari Moghaddam, A. (2013a). Supervised committee
705 machine with artificial intelligence for prediction of fluoride concentration. *Journal of*
706 *Hydroinformatics*, 15(4), 1474-1490.<https://doi.org/10.2166/hydro.2013.008>

707 Nadiri, A. A., Moghaddam, A. A., Tsai, F. T., & Fijani, E. (2013b). Hydrogeochemical analysis
708 for Tasuj plain aquifer, Iran. *Journal of earth system science*, 122(4), 1091-1105.
709 <https://doi.org/10.1007/s12040-013-0329-4>

710 Naclerio, G., Petrella, E., Nerone, V., Allocca, V., De Vita, P., & Celico, F. (2008). Influence of
711 topsoil of pyroclastic origin on microbial contamination of groundwater in fractured carbonate
712 aquifers. *Hydrogeology Journal*, 16(6), 1057-1064. <https://doi.org/10.1007/s10040-008-0297->
713 [y](https://doi.org/10.1007/s10040-008-0297-y)

714 Ortolani, F., & Aprile, F. (1985). Principali caratteristiche stratigrafiche e strutturali dei depositi
715 superficiali della Piana Campana. *Bollettino della Società Geologica Italiana*, 104(2), 195–206.

716 Oze C., Bird, D. K., & Fendorf, S. (2007) Genesis of hexavalent chromium from natural sources
717 in soil and groundwater. *Proceedings of the National Academy of Sciences of the United States*
718 *of America*, 104(16), 6544-6549. <https://doi.org/10.1073/pnas.0701085104>

719 Phan, T. D., Smart, J. C. R., Capon, S. J., Hadwen, W. L., Sahin, O. (2016). Applications of
720 bayesian belief networks in water resource management: A systematic review. *Environmental*
721 *Modelling and Software*, 85, 98-111. <https://doi.org/10.1016/j.envsoft.2016.08.006>.

722 Piper, A.M., (1944) A graphical procedure in the geochemical interpretation of water analysis.
723 *Eos, Transactions American Geophysical Union*. Union 25, 914e923.
724 <https://doi.org/10.1029/TR025i006p00914>

725 Qasemi, M., Farhang, M., Biglari, H., Afsharnia, M., Ojrati, A., Khani, F., Samiee, M., & Zarei,
726 A. (2018) Health risk assessments due to nitrate levels in drinking water in villages of
727 Azadshahr, northeastern Iran. *Environmental Earth Sciences*, 77, 782
728 <https://doi.org/10.1007/s12665-018-7973-6>

729 Rapant, S., & Krčmová, K. (2007) Health risk assessment maps for arsenic groundwater content:
730 application of national geochemical databases. *Environmental Geochemistry and Health*,
731 29(2), 131-141 <https://doi.org/10.1007/s10653-006-9072-y>

732 Rolandi, G., Bellucci, F., Heizler, M.T., Belkin, H.E., & De Vivo, B. (2003) Tectonic controls on
733 the genesis of ignimbrites from the Campanian volcanic zone, southern Italy. *Mineralogy and*
734 *Petrology*, 79(1–2), 3–31. <https://doi.org/10.1007/s00710-003-0014-4>

735 Rufino, F., Cuoco, E., Busico, G., Caliro, S., Maletic, E. L., Avino, R., Darrah T. H., & Tedesco,
736 D. (2020). Deep carbon degassing in the Matese massif chain (Southern Italy) inferred by
737 geochemical and isotopic data. *Environmental Science and Pollution Research*, 1-13.
738 <https://doi.org/10.1007/s11356-020-11107-1>

739 Rufino, F., Busico, G., Cuoco, E., Darrah, T. H., & Tedesco, D. (2019). Evaluating the suitability
740 of urban groundwater resources for drinking water and irrigation purposes: an integrated
741 approach in the Agro-Aversano area of Southern Italy. *Environmental Monitoring and*
742 *Assessment*, 191(12). <https://doi.org/10.1007/s10661-019-7978-y>

743 Saleh, N.H., Valipour, S., Zarei, A., Yousefi, M., Asghari, F.B., Ali Akbar Mohammadi, A.A.,
744 Amiri, F., Ghalehaskar, S., & Khaneghah, A.M. (2020) Assessment of groundwater quality
745 around municipal solid waste landfill by using Water Quality Index for groundwater resources
746 and multivariate statistical technique: a case study of the landfill site, Qaem Shahr City, Iran.
747 *Environmental Geochemistry and Health*, 42, 1305–1319. [https://doi.org/10.1007/s10653-019-](https://doi.org/10.1007/s10653-019-00417-0)
748 [00417-0](https://doi.org/10.1007/s10653-019-00417-0)

749 Shrestha, S., Kafle, R., Pandey, V.P. (2017). Evaluation of index-overlay methods for ground-
750 water vulnerability and risk assessment in Kathmandu valley, Nepal. *Science of the Total*
751 *Environment*, 575,779–790. <https://doi.org/10.1016/j.scitotenv.2016.09.141>

752 Singh, S., Ghosh, N. C., Gurjar, S., Krishan, G., Kumar, S., & Berwal, P. (2018) Index-based
753 assessment of suitability of water quality for irrigation purpose under Indian conditions.
754 *Environmental Monitoring and Assessment*, 190, 29-14. [https://doi.org/10.1007/s10661-017-](https://doi.org/10.1007/s10661-017-6407-3)
755 [6407-3](https://doi.org/10.1007/s10661-017-6407-3)

756 Taylor, R., Cronin, A., Pedley, S., Barker, J., & Atkinson, T. (2004) The implications of
757 groundwater velocity variations on microbial transport and wellhead protection—review of field
758 evidence. *FEMS Microbiology Ecology*, 49(1), 17-
759 26. <https://doi.org/10.1016/j.femsec.2004.02.018>

760 Tufano, R., Allocca, V., Coda, S., Cusano, D., Fusco, F., Nicodemo, F., Pizzolante, A., & De Vita,
761 P. (2020). Groundwater vulnerability of principal aquifers of the Campania region (southern
762 Italy). *Journal of Maps*, 16(2), 565-576. <https://doi.org/10.1080/17445647.2020.1787887>

763 USEPA, United States Environmental Protection Agency, Washington, DC (2013) Integrated risk
764 information system (IRIS). Available online at: <https://www.epa.gov/iris>

765 USEPA, United States Environmental Protection Agency, Washington, DC (2011) Drinking
766 Water Contaminants. National Primary Drinking Water Regulations. Available on line at:
767 <http://water.epa.gov/drink/contaminants/>
768 Vadiati, M., Asghari-Moghaddam, A., Nakhaei, M., Adamowski, J., & Akbarzadeh, A. H. (2016)
769 A fuzzy-logic based decision-making approach for identification of groundwater quality based
770 on groundwater quality indices. *Journal of Environmental Management*, 184, 255–270.
771 <https://doi.org/10.1016/j.jenvman.2016.09.082>
772 Viaroli, S., Cuoco, E., Mazza, R., & Tedesco, D. (2016) Dynamics of natural contamination by
773 aluminium and iron rich colloids in the volcanic aquifers of Central Italy. *Environmental*
774 *Science and Pollution Research*, 23(19), 19958–19977. [https://doi.org/10.1007/s11356-016-](https://doi.org/10.1007/s11356-016-7198-8)
775 [7198-8](https://doi.org/10.1007/s11356-016-7198-8)
776 Wang, J., Liu, J., Li, H., Song, G., Chen, Y., Xiao, T., Qi, J., Zhu, L. (2012). Surface water
777 contamination by uranium Mining/Milling activities in northern Guangdong province, China.
778 *Clean - Soil, Air, Water*, 40(12), 1357-1363. <http://doi.org/10.1002/clen.201100512>.
779 Ward, M.H., Jones, R.R., Brender, J.D., De Kok, T.M., Weyer, P.J., Nolan, B.T., Villanueva,
780 C.M., & Van Breda, S.G. (2018) Drinking Water Nitrate and Human Health: An Updated
781 Review. *International Journal of Environmental Research and Public Health*, 15, 1557.
782 <https://doi.org/10.3390/ijerph15071557>
783 WHO, World Health Organization (2017) Guidelines for drinkingwater quality, 4th edn.
784 Incorporating the first addendum. WHO, Geneva, Switzerland. 145–220. Available online at:
785 [https://www.who.int/water_sanitation_health/publications/drinking-water-quality-guidelines-](https://www.who.int/water_sanitation_health/publications/drinking-water-quality-guidelines-4-including-1st-addendum/en/)
786 [4-including-1st-addendum/en/](https://www.who.int/water_sanitation_health/publications/drinking-water-quality-guidelines-4-including-1st-addendum/en/)
787 Zhang, Y., Kelly, W.R., Panno, S.V., & Liu, W.T. (2014) Tracing fecal pollution sources in karst
788 groundwater by Bacteroidales genetic biomarkers, bacterial indicators, and environmental
789 variables. *Science of The Total Environment*, 490, 1082–1090.
790 <https://doi.org/10.1016/j.scitotenv.2014.05.086>
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807 **Tables**

808 Table 1: Parameters involved in the GQI computation with related effects on human health and
809 WHO thresholds

810 Table 2: FA-AAS and FA-CPL results. Bold emphasis is given to elements correlated in each
811 factor.

812 Table 3: Parameters involved for HRATable 2 ESM: Statistical summary of the detected chemical
813 and microbial variables

814 **Figures**

815 Figure 1: Simplified geological scheme of the CPL (a) and AAS (b).

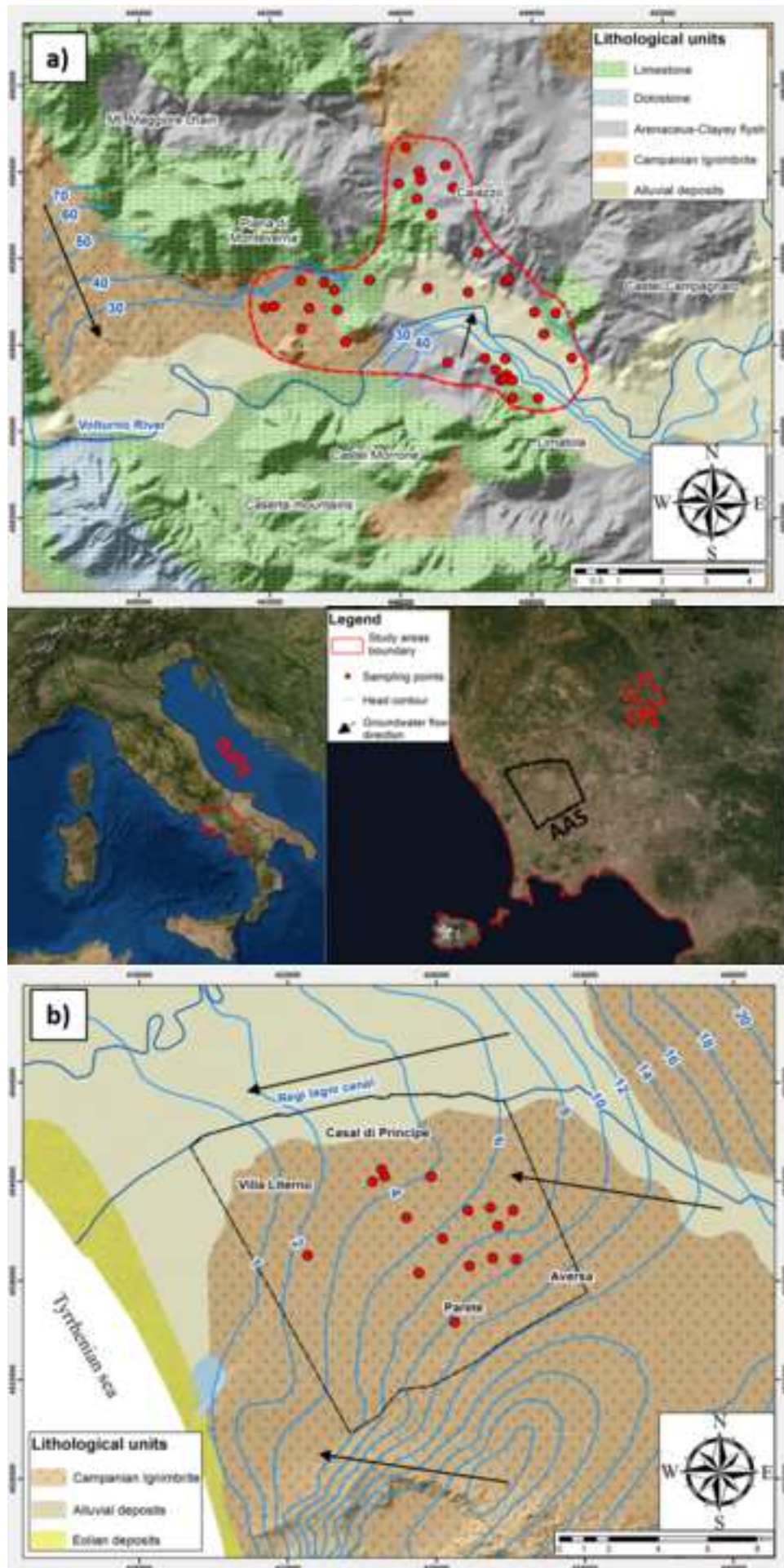
816 Figure 2: Piper diagram and ternary plots for cations and anions

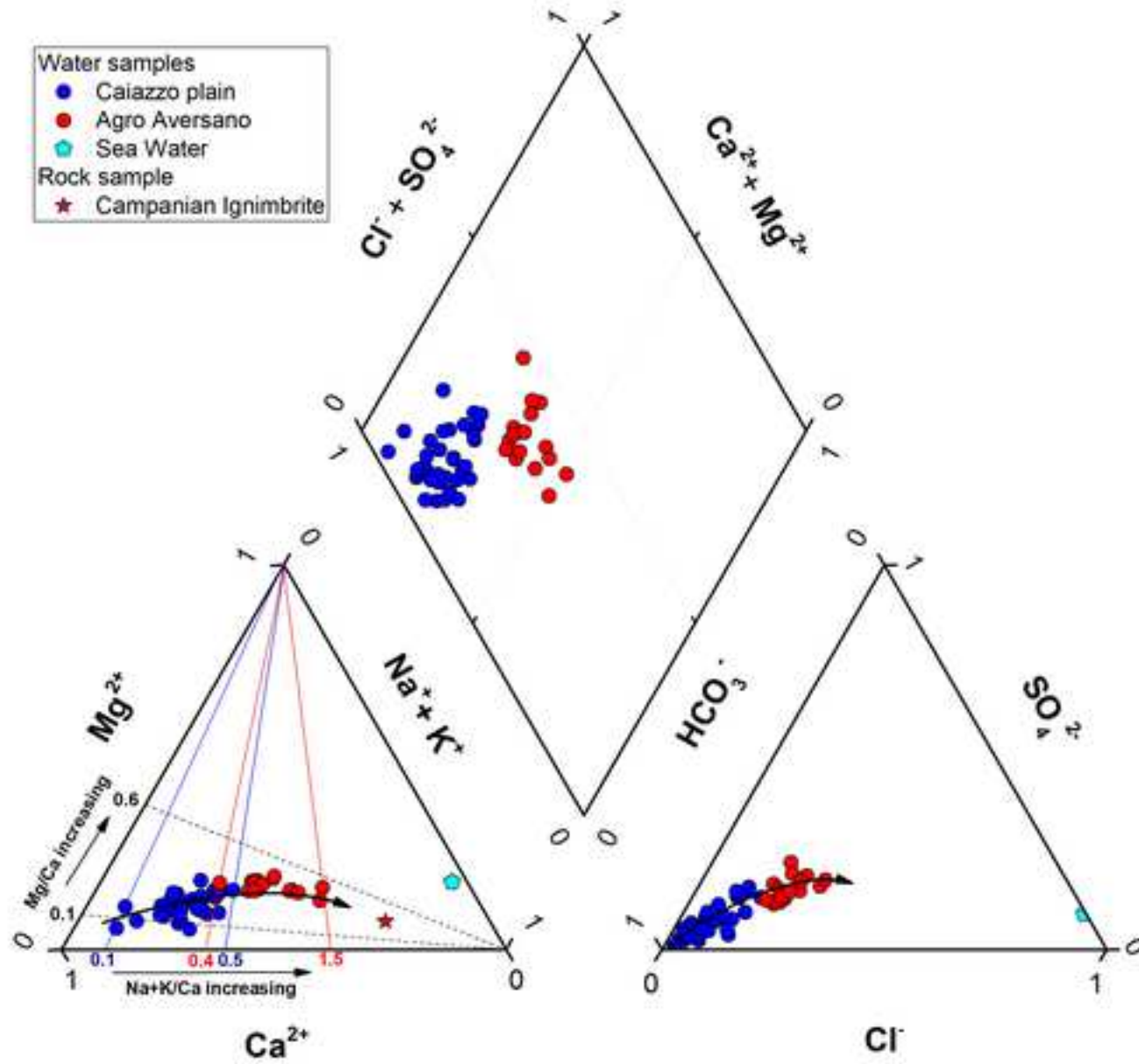
817 Figure 3: SO₄/NO₃ scatterplot integrated with FC (a) and with FS (b). Empty dots represent points
818 where fecal contamination has been detected

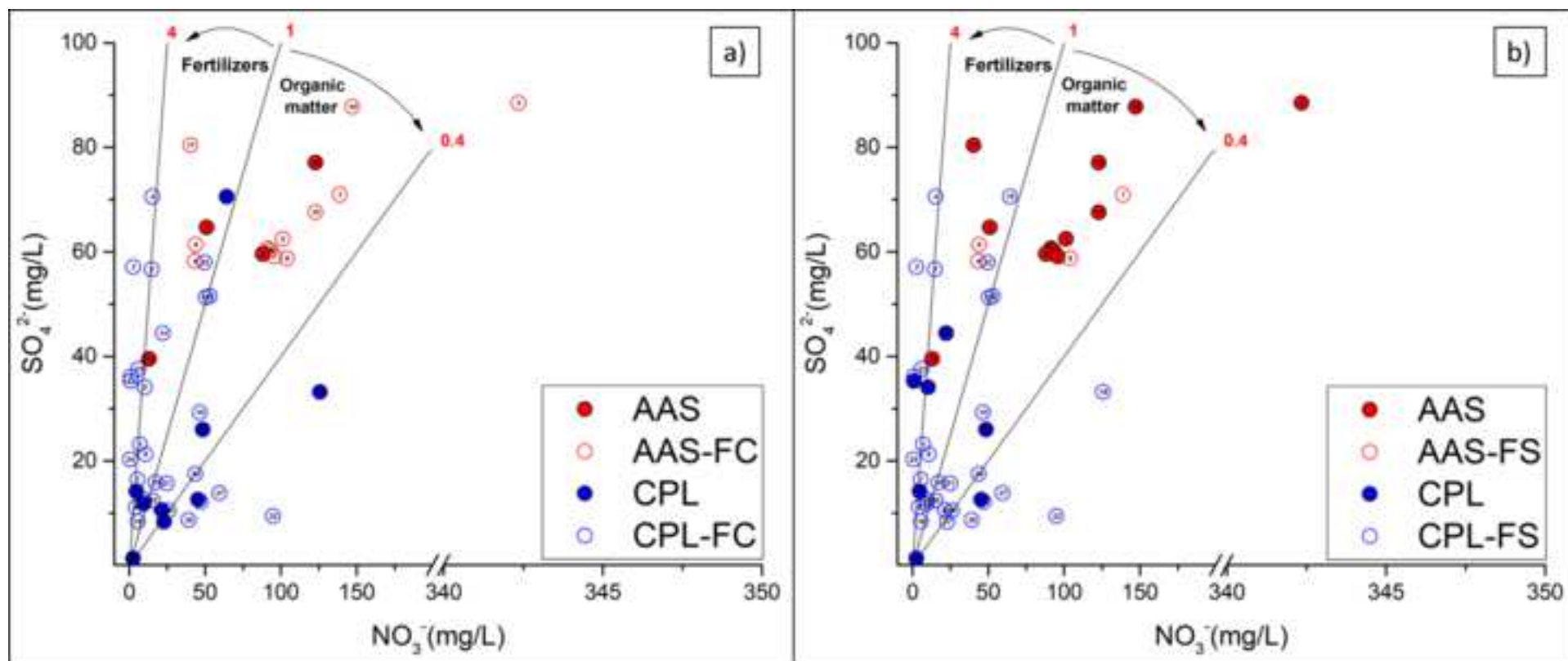
819 Figure 4: GQI maps for AAS (a) and for CPL (b). Red squares indicate general poor quality, yellow
820 squares indicate medium quality and green squares high quality

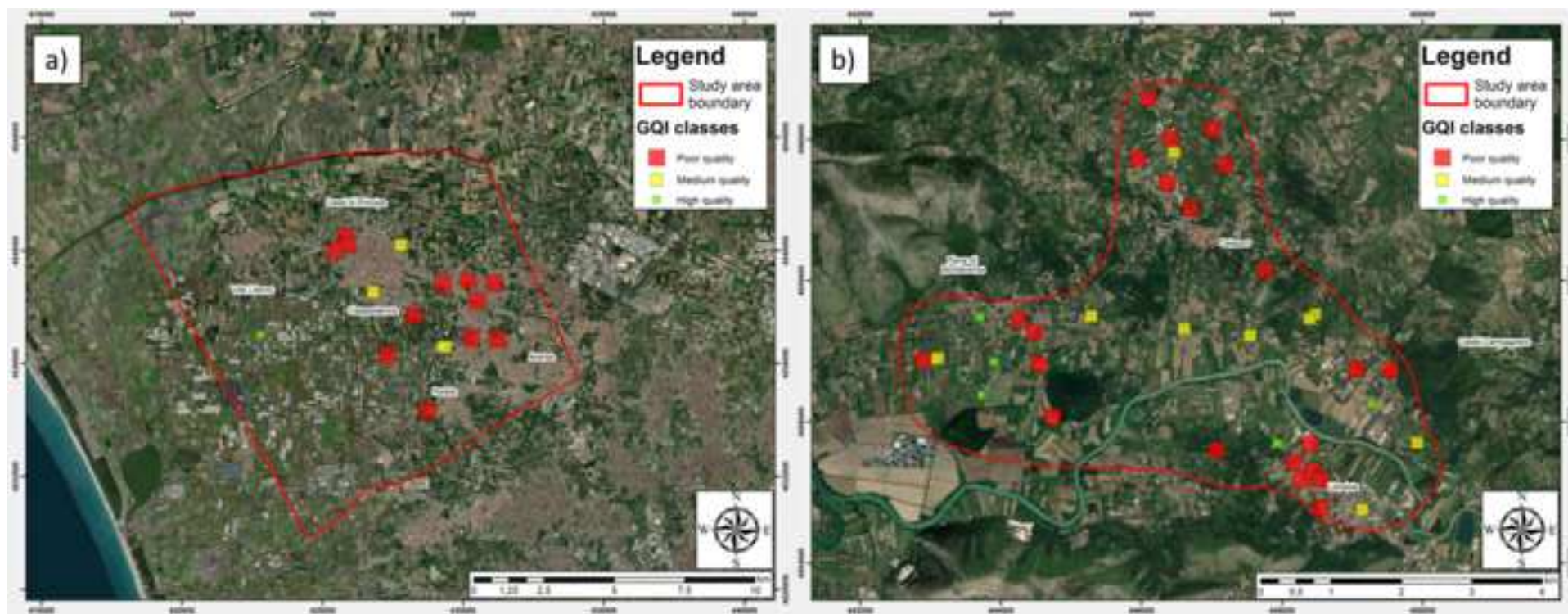
821 Figure 1 ESM: Land use pattern for CPL(a) and for AAS (b) (Corine Land Cover 2018 modified)

822 Figure 2 ESM: Stiff diagrams for Na+K/Ca upper and lower ends of the two populations









Category	Parameters	Effects on human health	References	WHO threshold
Major elements	-NO ₃	-Methemoglobinemia	-Gangolli et al. (1994)	50 (mg/L)
	-SO ₄	- Diarrhea and laxative effects	-WHO (2017)	250 (mg/L)
	-Cl	- Stomach discomfort	-USEPA (2011)	200 (mg/L)
	-F	- Hip and dental Fluorosis	-Harrison (2005)	1.5 (mg/L)
Trace elements	-Al	-Development or acceleration of onset of Alzheimer disease	-WHO (2017)	0.1 (mg/L)
	-Cu	-Direct gastric irritation	-WHO (2017)	2 (mg/L)
	-Ni	-Carcinogenic	-WHO (2017)	0.07 (mg/L)
	-U	-Increased risk of cancer, kidney toxicity	-WHO (2017); USEPA (2011)	0.03 (mg/L)
Microbial indicators	-TC; FC; FS	-Markers of faecal pollution in water: cause of Infectious diseases	- Emmanuel et al. (2009); WHO (2017);	0 (UFC/100ml)

	CPL				AAS			
	F1	F2	F3	F4	F1	F2	F3	F4
HCO ₃	0.85	0.09	0.05	0.36	0.25	-0.26	0.87	0.21
F	0.41	-0.48	0.42	-0.13	-0.39	0.86	0.02	0.00
Cl	0.81	-0.17	0.07	-0.17	0.91	-0.13	0.27	0.08
NO ₃	0.04	0.57	-0.04	0.03	0.96	-0.10	-0.01	-0.03
SO ₄	0.78	0.11	0.21	-0.18	0.76	0.17	0.04	-0.27
Na	0.72	0.02	0.52	0.12	0.20	0.40	0.79	-0.21
K	0.16	0.56	0.47	-0.29	0.79	0.12	0.39	0.12
Mg	0.59	-0.06	0.39	0.19	0.76	-0.19	0.56	0.17
Ca	0.87	0.10	-0.03	0.27	0.94	-0.17	0.24	0.12
TC	0.19	0.76	-0.02	0.00	0.04	0.02	0.02	0.96
FC	0.07	0.81	0.09	0.05	-0.14	0.66	-0.47	0.16
FS	-0.23	0.68	-0.04	-0.01	0.15	0.50	0.06	-0.05
Li	0.68	-0.14	-0.01	-0.19	-	-	-	-
B	0.74	0.16	0.28	0.13	-	-	-	-
Al	-0.13	-0.09	-0.04	-0.82	-	-	-	-
P	0.07	0.83	0.08	-0.16	-	-	-	-
Ti	0.07	-0.12	0.14	-0.87	-	-	-	-
V	-0.22	0.25	0.52	-0.30	-	-	-	-
Fe	0.15	0.27	-0.22	-0.50	-	-	-	-
Co	0.89	0.15	-0.13	0.10	-	-	-	-
Ni	0.50	-0.17	-0.31	0.27	-	-	-	-
Cu	0.16	-0.23	0.40	0.03	-	-	-	-
Zn	0.12	-0.06	-0.07	0.28	-	-	-	-
Rb	-0.14	0.19	0.52	0.03	-	-	-	-
Sr	0.88	-0.05	0.12	0.11	-	-	-	-
Mo	0.10	0.03	0.61	-0.13	-	-	-	-
Ba	0.60	0.15	-0.23	-0.29	-	-	-	-
U	0.26	-0.18	0.76	0.18	-	-	-	-

Parameters	Unit	Nitrate	Fluoride
<i>Ingestion Rate (IR)</i>	L/Day	2.8	2.8
<i>Average Time (AT)</i>	Days	25500	25500
<i>Exposure Frequency (EF)</i>	Day/Year	365	365
<i>Exposure Duration (ED)</i>	Year	70	70
<i>Body Weight (BW)</i>	Kg	75	75
<i>Reference Ingestion Dose (RfD)</i>	mg/kg*day	1.6	0.04

[Click here to view linked References](#)

Dear Editor,

Please find enclosed the paper entitled "*Geochemical characterization and health risk assessment related to the consumption of polluted groundwater: a comparison between two sites in Campania Plain (Southern Italy)*" by Rufino et al. to be considered for publication in *Environmental Geochemistry and Health*.

This study was accepted by the scientific committee of the MINWAT 2020 and we were invited to submit the extended version in the conference special issue.

In this study we conducted a detailed chemical and microbial investigation of 53 water samples collected in two different sites throughout the Campania Plain (Southern Italy) from urban and agricultural water wells. Through the use of a graphical and statistical approach, the of water-rock interaction processes were discriminated. Furthermore, the possible causes of anthropic contamination that persist in the two study areas have been identified. Finally, the entire water quality and the possible implications related to the consumption of contaminated water have been described in detail.

We have full agreement on the current state of the manuscript from all authors and report no conflicts of interest.

We hope our work can be suitable for publication in *Environmental Geochemistry and Health*

Best Regards

[Click here to view linked References](#)

Id	N (WGS84-33T)	E (WGS84-33T)	T (°C)	pH	E.C. (µS/cm)	HCO ₃ (mg/L)	F (mg/L)	Cl (mg/L)	NO ₃ (mg/L)	SO ₄ (mg/L)	Na (mg/L)
1	4536916	430275	24.5	7.41	811	307.34	1.19	87.0	138.8	70.9	73.0
2	4537022	422793	21.8	6.93	658	319.13	1.11	46.6	51.0	64.7	79.1
3	4538944	430175	24	7.25	1575	335.41	0.67	99.8	342.3	88.5	69.3
4	4536311	427294	27.1	7.69	804	311.20	1.15	50.8	43.1	58.2	67.2
5	4540207	425897	20	6.86	1050	388.09	0.95	72.9	101.2	62.5	65.6
6	4534328	428751	18.8	6.23	556	205.23	1.27	35.6	43.7	61.4	64.5
7	4537696	428248	18	6.76	963	435.68	0.88	70.6	95.8	59.1	79.2
8	4538539	426791	17.8	6.6	976	410.66	0.99	72.9	88.1	59.6	77.6
9	4539997	425417	16.6	6.67	945	406.60	0.75	68.2	104.0	58.8	67.7
10	4538842	431091	17.3	6.99	1045	335.81	0.96	77.7	147.2	87.8	68.1
11	4536861	431207	16.8	6.99	719	315.07	0.91	59.2	40.2	80.4	72.8
12	4536588	429342	19.1	7.58	470	200.96	0.82	44.4	13.1	39.5	46.3
13	4538829	429272	16.8	6.56	1126	420.63	1.01	59.8	91.4	60.7	70.7
14	4538207	430480	17	6.9	813	370.19	0.74	66.0	93.1	60.2	61.0
15	4540490	425789	18.9	6.69	985	359.00	0.86	69.0	122.9	67.6	68.1
16	4540198	427781	17.7	7	928	327.68	0.86	71.4	122.9	77.1	68.6

K (mg/L)	Mg (mg/L)	Ca (mg/L)	Err (%)	CT (UFC/100ml)	CF (UFC/100ml)	SF (UFC/100ml)	GQI	Groundwater depth (m.a.s.l)	Depth of wells (m.b.g.l)
42.9	22.4	111.3	1.7	5300	108	7	62.5	7	18
32.6	16.5	56.2	-2.0	0	0	0	88.6	9	34
41.5	31.6	168.2	-2.1	370	75	0	64.6	7	22
23.4	15.1	64.8	-3.1	480	61	2	66.1	7	24
36.0	24.0	107.9	-1.2	123000	136	0	66.3	10	33
22.9	10.2	46.4	1.0	1880	846	1	66.4	13	50
33.5	25.1	96.4	-3.4	2300	120	0	66.5	8	26
32.8	25.4	93.7	-2.3	3	0	0	79.1	8	13
32.9	23.7	104.4	-2.6	174	12	5	64.8	7	14
39.7	21.6	116.4	-1.7	13	3	0	69.0	8	12
22.5	16.0	70.3	-3.6	1800	19	0	68.6	8	16
17.7	9.6	42.2	-2.3	465	0	0	79.5	10	17
31.8	24.3	104.5	-1.2	85	2	0	70.1	15	39
31.7	21.0	94.8	-3.9	5600	25	0	67.1	16	52
43.9	22.8	102.8	-0.8	24	8	0	67.7	16	40
31.8	19.6	103.3	-2.1	255	0	0	75.1	9	10

Id	N (WGS84-33T)	E (WGS84-33T)	T (°C)	pH	E.C. (µS/cm)	HCO ₃ (mg/L)	F (mg/L)	Cl (mg/L)	NO ₃ (mg/L)
1	4560581	446104	11.5	6.74	523	329.5	0.56	25.2	7.1
2	4560152	447015	14.1	6.94	672	406.8	0.37	33.5	14.9
3	4560010	446420	16.2	6.32	622	353.9	0.78	33.5	2.5
4	4559644	447190	12.3	6.30	794	494.3	0.56	37.7	15.1
5	4559818	446465	11	7.24	680	449.5	1.01	28.5	10.4
6	4559730	445946	12	7.20	506	325.0	0.21	17.6	10.7
7	4559383	446370	10.8	7.27	555	400.0	0.21	11.4	5.4
8	4559023	446695	15.4	6.82	725	555.0	0.35	13.3	4.3
9	4556752	449062	15.9	7.42	345	205.4	0.23	18.9	1.0
10	4556739	449543	14.1	7.54	422	195.3	0.26	24.8	46.5
11	4557318	446609	14.8	7.48	657	449.5	0.35	38.4	1.0
12	4557466	448386	15.1	7.45	870	518.7	0.34	55.1	53.2
13	4555600	447067	15.3	6.75	628	347.8	0.24	29.2	50.4
14	4557225	447543	16.5	7.29	742	512.6	0.51	33.7	22.3
15	4557525	448470	15.6	7.68	775	445.4	0.56	31.7	64.2
16	4558142	447766	15	6.96	532	406.8	0.15	18.7	5.5
17	4556252	449271	15.6	7.44	572	386.5	0.47	35.2	4.7
18	4555708	449917	15.4	6.71	396	245.0	0.70	21.1	9.6
19	4555183	448271	9.2	7.21	828	429.2	0.19	16.3	125.9
20	4555694	447932	17.2	7.1	794	473.9	0.17	13.6	48.4
21	4555430	448172	15	7.36	540	345.8	0.15	9.5	24.8
22	4555686	448399	14.4	7.33	987	514.6	0.13	25.4	49.6
23	4555309	448433	14	7.2	683	417.0	0.24	15.2	5.9
24	4555203	448369	15.5	7.53	490	333.6	0.32	6.9	0.6
25	4554783	448561	14.9	7.36	592	343.8	0.12	4.9	17.4
26	4555190	448556	12.3	7.4	338	234.9	0.54	8.5	9.5
27	4554763	449142	15.8	7.01	608	372.2	0.05	5.9	23.0
28	4557491	443708	12.8	7.24	251	195.3	0.24	2.9	2.5
29	4557501	445285	15.2	6.34	538	299.0	0.20	12.4	43.5
30	4556381	443726	14.7	7.11	367	235.9	0.20	6.0	21.4
31	4556851	443905	12.9	7.08	546	358.0	0.16	6.1	45.4
32	4557269	444471	14.7	7.28	484	238.0	0.09	10.8	94.8
33	4557449	444252	10.5	7.14	509	276.6	0.20	14.9	47.1
34	4556899	443097	14.8	7.34	579	370.2	0.25	15.2	26.1
35	4556079	444735	14.7	7.16	604	412.9	0.30	9.9	15.3
36	4556867	442894	14.9	6.52	437	274.6	0.12	6.5	39.1
37	4556815	444542	15.4	6.64	524	280.7	0.22	11.7	59.3

SO₄ (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Err (%)	Li (ppb)	B (ppb)	Al (ppb)	P (ppb)
23.2	35.8	23.8	8.2	84.6	2.4	3.8	54.1	67.4	168.9
56.7	50.1	10.9	17.1	107.0	0.8	4.4	44.2	206.3	102.5
57.1	39.3	20.0	12.6	108.8	4.0	3.4	76.8	61.6	168.1
70.6	52.3	12.1	25.3	137.9	2.8	4.5	56.8	64.8	128.2
34.1	38.8	27.2	14.7	125.1	3.9	3.1	57.6	56.5	91.0
21.3	40.8	8.1	11.7	83.4	4.8	3.0	52.8	220.1	115.7
16.5	30.5	7.0	14.1	107.3	4.6	2.7	72.5	59.0	49.1
11.1	40.4	8.9	18.8	145.0	4.8	2.7	50.5	59.5	18.6
36.1	17.7	10.1	7.1	57.1	-2.4	2.3	22.6	70.6	84.4
29.3	12.8	26.7	8.1	61.7	-2.8	2.1	27.5	458.7	298.6
35.3	34.5	6.8	13.0	115.1	-4.1	2.8	67.5	58.6	3.4
51.5	30.2	4.9	9.8	173.3	-4.9	5.1	48.7	63.6	191.4
51.3	33.5	23.2	10.4	102.4	-2.5	4.8	39.4	60.7	199.6
44.4	36.4	8.6	14.7	135.0	-4.5	7.6	43.4	46.9	0.0
70.6	40.5	30.7	6.3	133.4	-4.9	7.8	68.4	59.6	0.0
8.5	11.8	6.4	4.8	118.7	-3.3	4.2	23.7	138.7	0.0
14.2	38.9	10.0	13.4	98.0	1.4	3.8	51.4	70.0	32.1
11.8	28.4	12.4	10.3	63.0	4.7	4.5	24.2	267.6	0.0
33.2	30.9	17.3	14.8	152.9	2.0	2.4	36.6	75.6	44.5
26.0	41.1	27.7	14.7	131.9	4.1	2.6	48.3	72.0	55.3
15.7	25.3	10.5	8.7	98.9	2.5	2.3	36.2	93.7	238.9
58.0	42.6	38.7	11.4	127.0	-4.9	3.2	74.0	75.4	1366.0
37.6	28.7	17.9	13.4	113.7	2.0	5.9	50.6	80.6	358.1
20.3	23.4	11.9	7.6	82.7	-0.3	2.7	30.2	51.4	0.0
15.9	29.6	20.7	8.7	88.7	4.2	3.9	27.5	68.7	71.3
12.6	16.3	9.2	3.5	58.2	-4.6	2.4	32.2	72.8	107.0
8.4	21.7	25.5	5.9	94.5	-0.1	2.0	43.4	75.4	372.0
1.4	3.5	4.7	4.1	49.3	-4.5	1.0	4.8	84.1	105.9
17.5	29.6	14.0	8.6	84.5	1.9	2.7	31.9	75.6	202.0
10.6	15.1	12.2	4.9	60.6	-2.4	1.0	14.6	88.6	58.9
12.6	20.0	13.2	6.8	94.6	-4.1	1.3	29.1	68.6	99.0
9.4	18.6	9.2	9.3	79.7	-1.3	1.0	37.2	88.1	536.3
12.1	23.3	30.4	10.9	62.2	-1.6	1.1	38.1	76.3	91.5
10.5	35.3	18.9	12.4	85.2	1.0	6.9	42.1	73.2	235.6
12.4	25.9	9.7	8.4	113.3	1.1	1.2	48.6	72.9	103.0
8.7	16.0	8.8	9.3	69.9	-3.1	1.1	11.8	71.3	138.8
13.9	29.4	17.5	11.0	70.9	-0.2	1.4	23.2	68.5	94.0

Ti (ppb)	V (ppb)	Mn (ppb)	Fe (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Rb (ppb)	Sr (ppb)
7.3	7.7	5.1	16.3	2.5	1.9	3.8	24.7	69.2	385.7
6.4	5.7	4.5	18.2	3.0	2.0	1.1	9.4	36.77	504.3
6.1	6.5	108.7	28.7	3.0	2.1	1.9	18.6	26.04	544.1
6.0	7.0	4.3	19.7	3.8	2.3	22.1	72.3	42.96	653.9
4.9	6.1	7.0	12.4	3.5	3.6	129.6	874.0	21.52	488.8
7.7	7.0	2.0	53.2	2.2	1.6	28.2	49.9	17.91	328
4.2	3.8	2.1	6.4	3.0	4.0	3.9	1363.0	17.52	372.4
3.3	0.2	462.4	9.2	4.3	2.2	1.1	29.6	8.302	523.5
6.1	4.8	7.2	8.5	1.8	1.6	4.0	25.2	24.4	221.2
19.0	5.8	6.2	154.8	1.9	1.9	14.7	13.6	28.9	238
2.8	1.3	0.9	8.3	4.0	10.5	6.2	46.6	7.79	511.5
6.2	6.6	12.5	9.8	6.1	5.5	9.8	204.6	12.77	1058
8.1	8.3	4.8	85.6	3.4	1.8	3.5	177.1	49.72	354.1
5.0	4.2	1.3	5.6	4.1	4.0	14.0	4025.0	19.72	633.4
3.4	1.0	0.8	5.5	4.4	3.5	7.2	15.2	3.762	775.5
5.4	2.9	32.8	120.0	3.7	4.6	7.9	1099.0	12.6	157.5
3.2	3.1	17.1	7.4	2.8	1.5	1.0	21.9	16.62	457.5
11.4	6.9	3.1	79.8	1.7	0.8	2.0	6.3	17.2	295.2
4.8	6.1	3.6	7.6	5.1	2.7	5.6	173.4	38.3	486.9
5.0	8.3	2.1	6.2	4.2	1.8	6.5	29.9	45.82	533.7
2.8	4.0	1.2	8.5	3.1	1.4	2.0	9.1	7.546	293.3
4.2	7.9	213.3	104.8	4.4	2.3	1.9	42.8	47.51	485.6
4.1	6.3	54.5	486.5	3.7	1.7	2.3	55.6	12.08	412.3
3.4	3.2	7.4	9.9	3.0	5.7	6.7	22.2	19.38	190
6.6	11.4	1.5	4.7	2.8	1.2	3.4	38.4	30.35	339.8
3.7	9.6	16.3	38.2	1.7	1.9	2.4	20.2	15.88	133.3
4.4	8.5	2.2	5.0	3.3	1.4	5.0	43.3	26.76	215.3
2.2	4.2	0.0	7.0	0.8	1.1	4.9	68.1	7.119	55.32
4.5	6.8	0.0	6.7	1.5	2.0	34.7	120.5	36.92	341.7
2.7	6.5	0.0	7.9	0.9	0.8	4.9	27.6	36.19	147.8
4.5	5.6	0.0	5.8	1.7	1.0	3.0	68.3	29.12	244.1
2.7	5.0	0.0	14.0	1.3	2.6	4.4	30.3	15.45	166.6
2.5	3.7	9.3	10.1	1.3	2.1	3.1	2958.0	52.95	272.5
4.0	5.7	114.5	20.8	1.6	2.2	12.7	63.9	173.3	442.8
3.5	6.5	8.3	6.9	2.1	2.0	14.9	392.8	19.81	444.5
2.8	3.6	0.5	5.9	1.1	0.9	4.0	57.0	32	280.7
5.2	7.1	19.0	4.8	1.1	0.8	1.8	30.0	59.06	382.4

Mo (ppb)	Ba (ppb)	U (ppb)	CT (UFC/100ml)	CF (UFC/100ml)	SF (UFC/100ml)	GQI	Groundwater depth (m.a.s.l)
4.1	4.3	9.3	900	4	111	76.6	46
2.3	18.1	10.3	1100	1	2	78.9	44
6.4	66.7	11.6	1000	100	2	77.4	41
2.2	27.0	13.5	400	6	3	77.3	46
3.5	51.7	11.7	1100	1	0	83.3	41
2.7	14.5	7.1	8400	132	51	74.6	42
1.6	25.0	4.1	1300	5	39	77.1	45
1.4	111.1	6.8	100	4	37	77.3	41
0.8	56.2	0.5	1500	3	8	78.2	28
3.2	75.0	3.3	2700	61	70	73.3	35
2.1	30.8	3.0	600	1	0	84.2	28
1.4	93.1	2.6	1400	1	2	79.4	31
1.7	19.8	3.7	9200	1	19	77.9	44
1.4	22.7	3.6	275	2	0	82.7	27
2.8	140.9	1.6	2700	0	1	82.5	34
0.4	34.9	0.6	4900	17	17	76.0	31
1.6	71.2	4.0	700	0	0	86.2	27
2.0	53.3	1.9	400	0	8	80.0	27
2.5	38.7	7.7	35000	0	150	79.1	42
6.4	71.0	9.3	134	0	0	85.3	44
1.3	49.6	2.7	4100	135	150	75.2	43
2.3	76.4	3.9	35000	6100	150	74.7	41
1.9	79.0	2.3	13300	13	150	76.1	41
5.0	10.7	4.6	12700	3	3	79.2	42
2.4	21.1	3.7	1500	54	16	76.1	48
4.3	7.7	1.8	3400	82	150	75.7	47
3.5	89.4	1.4	155	0	1	83.7	48
1.4	14.9	1.0	32	0	0	86.8	29
1.8	34.2	2.3	300	3	NC	81.9	41
2.0	8.9	5.7	0	0	1	91.2	28
0.7	18.1	2.2	44	0	0	85.9	29
1.2	28.5	2.0	2100	1100	200	74.4	29
3.8	12.6	3.2	4200	2700	200	74.9	29
2.8	36.1	4.1	7	1	1	82.2	29
1.5	14.9	10.1	4700	2	2	79.3	25
0.8	10.1	8.4	1800	2	16	77.3	29
1.0	19.1	4.5	1900	42	121	74.9	26

**Depth of wells
(m.b.g.l)**

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AAS								CPL															
	Mean	Median	Max	Min	25 th percentile	75 th percentile	Sd		Mean	Median	Max	Min	25 th percentile	75 th percentile	Sd		Mean	Median	Max	Min	25 th percentile	75 th percentile	Sd
T	19.5	18.4	27.1	16.6	17.2	20.5	3.2	T	14.2	14.8	17.2	9.2	12.9	15.4	1.9	Li	3.2	2.7	7.8	1.0	2.1	4.2	1.8
pH	6.9	6.9	7.7	6.2	6.7	7.1	0.4	pH	7.1	7.2	7.7	6.3	6.9	7.4	0.4	B	41.7	42.1	76.8	4.8	29.1	51.4	17.5
E.C.	901.5	936.5	1575.0	470.0	782.8	1000.0	256.8	E.C.	586.9	572.0	987.0	251.0	506.0	680.0	159.5	Al	95.2	72.0	458.7	46.9	63.6	80.6	77.5
HCO₃	340.5	335.6	435.7	201.0	314.1	392.7	68.0	HCO₃	363.1	358.0	555.0	195.3	280.7	429.2	98.2	P	160.3	102.5	1366.0	0.0	49.1	191.4	235.6
F	0.9	0.9	1.3	0.7	0.9	1.0	0.2	F	0.3	0.2	1.0	0.1	0.2	0.4	0.2	Ti	5.1	4.5	19.0	2.2	3.4	6.1	3.0
Cl	65.7	68.6	99.8	35.6	57.1	72.9	16.2	Cl	19.2	15.2	55.1	2.9	9.9	28.5	12.1	V	5.6	6.1	11.4	0.2	4.0	7.0	2.4
NO₃	102.4	94.5	342.3	13.1	49.2	122.9	74.7	NO₃	27.8	17.4	125.9	0.6	5.9	46.5	28.0	Mn	30.7	4.5	462.4	0.0	1.3	12.5	84.2
SO₄	66.1	61.9	88.5	39.5	59.5	72.5	12.5	SO₄	26.5	17.5	70.6	1.4	12.1	36.1	19.1	Fe	38.1	9.2	486.5	4.7	6.7	20.8	84.0
Na	68.7	68.3	79.2	46.3	66.8	72.9	7.9	Na	29.4	29.6	52.3	3.5	21.7	38.8	11.1	Co	2.8	3.0	6.1	0.8	1.7	3.7	1.3
K	32.3	32.7	43.9	17.7	29.6	36.9	7.7	K	15.6	12.2	38.7	4.7	9.2	20.7	8.5	Ni	2.5	2.0	10.5	0.8	1.5	2.6	1.8
Mg	20.5	22.0	31.6	9.6	16.3	24.1	5.8	Mg	10.7	10.3	25.3	3.5	8.1	13.4	4.4	Cu	10.4	4.4	129.6	1.0	2.4	7.9	21.5
Ca	92.7	99.6	168.2	42.2	68.9	105.3	31.3	Ca	99.3	98.0	173.3	49.3	79.7	118.7	30.3	Zn	333.2	43.3	4025.0	6.3	24.7	120.5	833.1
CT	8859	418	123000	0	70	1985	30491	CT	4299	1400	35000	0	400	4100	8150	Rb	30.8	24.4	173.3	3.8	15.9	36.9	28.8
CF	88	16	846	0	2	83	207	CF	286	3	6100	0	1	42	1090	Sr	388.4	372.4	1058.0	55.3	244.1	488.8	196.6
SF	1	0	7	0	0	0	2	SF	47	8	200	0	1	80	66	Mo	2.4	2.0	6.4	0.4	1.4	2.8	1.4
	-	-	-	-	-	-	-		-	-	-	-	-	-	-	Ba	42.1	30.8	140.9	4.3	18.1	66.7	32.7
	-	-	-	-	-	-	-		-	-	-	-	-	-	-	U	4.9	3.7	13.5	0.5	2.3	7.1	3.5

ELETTRONIC SUPPLEMENTARY MATERIALS

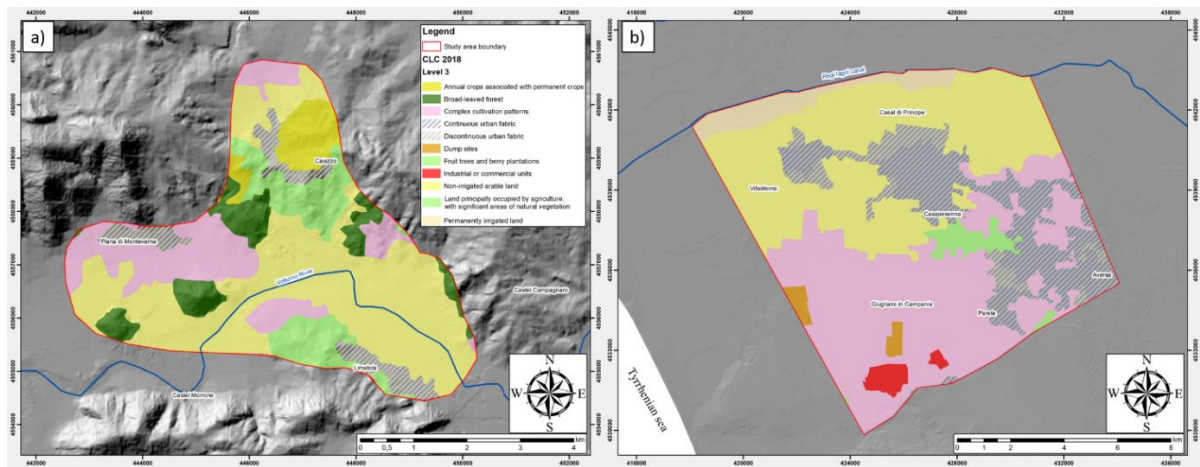


Figure S1: Land use pattern for CPL(a) and for AAS (b) (Corine Land Cover 2018 modified)

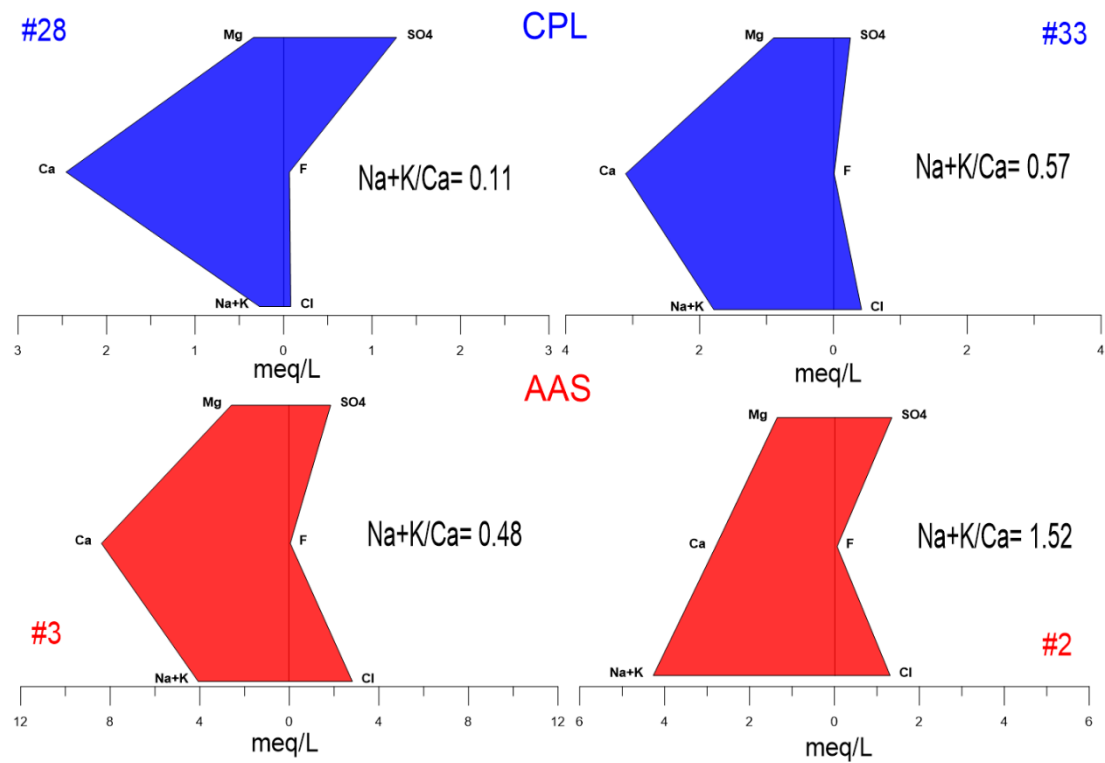


Figure S2: Stiff diagrams for Na+K/Ca upper and lower ends of the two populations

[Click here to view linked References](#)

Dear Editor,

We would like to once again thank the Reviewers for the valuable, helpful and very constructive comments that allowed us to improve the manuscript's quality and clarity. We have carefully considered all of the Reviewer's suggestions and revised the manuscript accordingly. All responses to the last comments are attached in the present document and for completeness (and as requested by Reviewer #2), a language editing has been provided by a native speaker.

Title has been changed as reported below:

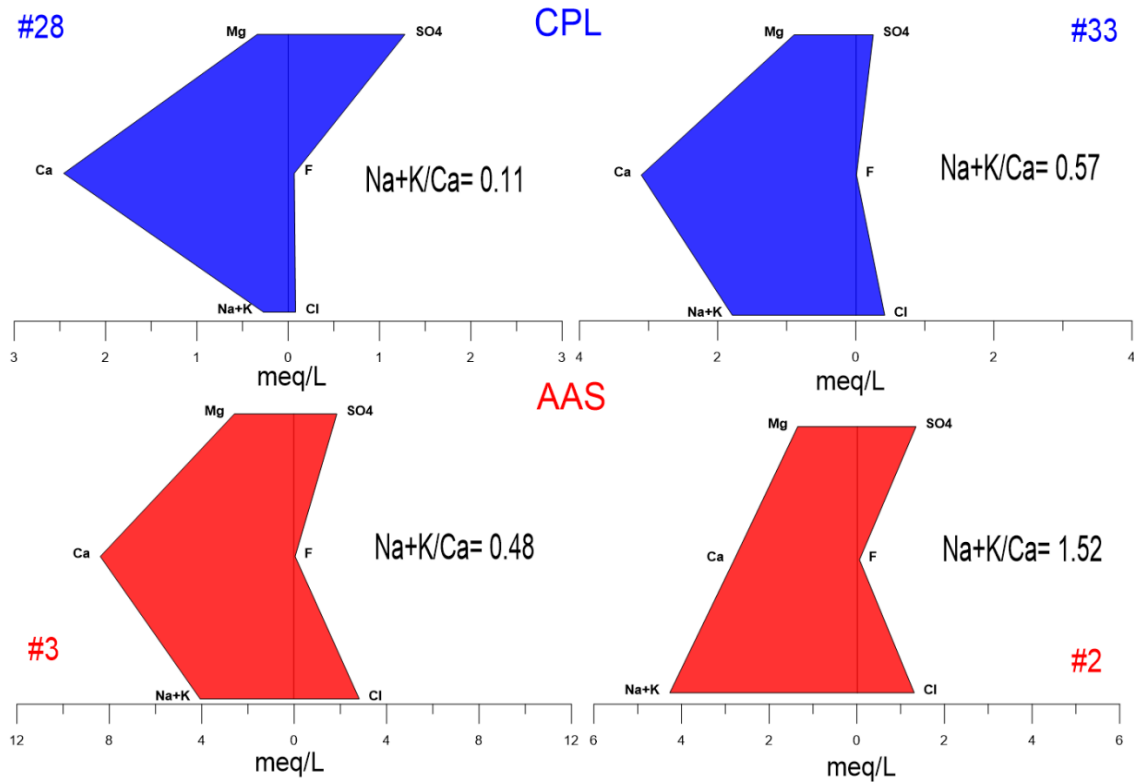
“GEOCHEMICAL CHARACTERIZATION AND HEALTH RISK ASSESSMENT IN TWO DIVERSIFIED ENVIRONMENTAL SETTINGS (SOUTHERN ITALY)

Reviewer #1: Dear Editor,

Most of requested revisions have been done. But I believe that that stiff diagrams and Piper diagram are not right.

Stiff diagram: They may be draw by mg/L unit, so, it is not balance in volume of both side of diagram. Major ions values in meq/L use to draw Stiff diagram.

We apologize but we were not able to understand the reviewer's comment. The stiff diagrams shown in Fig. 2 ESM have been realized by using the values in meq/L, as can also be clearly understood from the values shown in the scales or rather from the data shown in the Table 1 ESM. The diagrams seem unbalanced due to the amounts of calcium (and bicarbonate) resulting of an order of magnitude (sometimes two) greater than other dissolved species. Anyway, to avoid any kind of misunderstanding, the units have been added to the diagrams as reported below.



Piper diagram: Sea water and Campanian Ignimbrite samples are not located in right location in Piper diamond.

The projection of the two endmembers only in the two ternary diagrams is intended (and wanted) in order to (i) show the evolution trends (in terms of mineralization) of these waters and (ii) to avoid any kind of misunderstanding to the readers. For this reason we prefer to keep the diagram in its current form..

Reviewer #2: Dear Authors,

I appreciate your efforts in revising the manuscript according reviewers' indications. Overall all the changes respond to the requests done, even if still some English mistakes are visible here and there. I also appreciate the inclusion of depths info according GW and wells, but maybe a reference in the units adopted is strongly needed (e.g. below/above sea/ground level). Besides, I suggest to publish the present manuscript after few revisions.

We completely agree with the reviewer's comments. A linguistic editing was carried out by a native speaker in order to fix the last errors within the manuscript and the units were corrected in Table 1 ESM.