Hydrogeochemical characterization of the southern sector of the Alburni Massif, Campania region, Italy

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Abstract

The Alburni Massif represents one of the most important karst regions of the Southern Apennines, and it has a high potential as a water resource. This paper reports a hydrogeochemical evaluation of sampled waters from the southern sector of the Alburni Massif (Campania region, Italy). Five water samples were analyzed (three from natural springs and two from wells) to i) evaluate the hydrogeochemical properties of the waters in the study area and ii) understand the groundwater flow in this system. Waters were classified as Ca-Mg type due to enrichment from different alkaline elements (Na⁺, Mg++) and carbonate (HCO₃⁻) classification is in agreement with the lithologies present in this area. Groundwater flow was connected to the fault line passing through the south-west sector of the complex, which divides the Massif into two large structures situated to the east and the west.

Introduction

The Alburni Massif represents one of the most important karst areas in Italy. It is located in the Cilento and Vallo di Diano National Park, which was founded on December 6, 1991 through Law No. 334. In 1973, the necessity of protecting the coast and inland areas from speculation and mass tourism was discussed at the International Conference on Mediterranean Coastal Parks. One result of this conference was the establishment of two nature reserves by the Minister of the Environment, Mt. Cervati and Calore River, respectively. The combined area of these two reserves totalled 36,000 ha. The National Park now covers an area of approximately 180,000 ha and includes eight mountain communities and 80 municipalities. The National Park is bordered by the Sele Valley to the north, the Diano Valley to the east, Policastro Gulf to the south and the Tyrrhenian Sea to the west. In 1991, this area declared an UNESCO World Heritage Site to protect the temples of Paestum and Certosa of Padula. In 1997, the National Park also became part of a prestigious network of “Biosphere Reserves,” which are designated to maintain an equilibrium between man and environment through the conservation of biological diversity, the promotion of economic development and the preservation of cultural values. Within the Park, the Alburni Massif is an area that takes its name from the highest peak (1742 m a.s.l.) in the group. The northern slope of the peak is steep, while the southern slope has a moderate gradient and hosts beech, turkey oak, deciduous forest and meadows dotted with karst features. The Alburni Massif is characterized by a dense arrangement of karst features throughout the highest elevations of the Central and Southern Apennines [1, 2]; these features are related to the tectonic and geomorphic evolution of the Massif. The aims of this study are: i) to perform a geochemical evaluation of the waters in the southern sector of the Alburni Massif; and ii) to understand the groundwater flow in this system.
2. Geological framework

The Alburni Massif is included in topographic sheets No. 198 (Eboli) and 199 (Potenza) of the Italian Geological Map (1:100000; Figu

Figure 1. Geological framework of the Alburni Massif and location of sampling sites (red squares).

The Alburni Massif covers an area of approximately 2 km² and is bordered by major marginal faults responsible for the subrectangular shape and created a large plateau (average altitude approximately 1300 m a.s.l.) [2]. It is located between the Vallo di Diano to the east, the Tanagro Valley to the north-east, the Calore Valley to the south-west and Sele Valley to the north-west. It is characterized by limestone sequences in carbonate platform facies followed by siliciclastic deposits in flysch facies; locally, especially along the edges, there are continental Quaternary formations. The complete stratigraphic sequence is as follows [3, 4, 5, 6, 7, 8, 9, 10]: a) Mesozoic limestone, b) Tertiary limestone, c) residual red clay, d) flysch deposits, e) silicilide deposits and f) continental Quaternary formations. The carbonate Massif represents a hydrogeological structure rized by autonomous groundwater circulation. Outcropping rocks can be grouped into four hydrogeological complexes, each with a different permeability. From bottom to top, they are: a) the carbonate complex, characterized by limestone and dolomite; it outcrops in all study areas, is characterized by different fault and fracture systems and has a high permeability; b) the flysch complex, characterized by clays, marls and arenaceous deposits with varying permeability; c) the detrital complex with variable permeability due to its porosity and d) the lacustrine–alluvial complex, characterized by lacustrine and fluvial deposits. Celico has been found [11] that water flows preferentially from the south-east to the north-west; the major obstacle to this flow is the teconic line corresponding with the incision between the towns of Pertosa and San Rufo. In this sector, compression traces divide the Alburni Massif into two hydrogeological structures (Figure 2) [12].

Figure 2. Hydrogeological maps of the Alburni Massif

The structure located to the east of this fault drains groundwater toward the Pertosa springs (average flow rate 1.1 cm/sec), while the hydrogeological structure located to the west of the fault drains toward the lying Tanagro and Casteleivita springs. Figure 3 shows a schematic sketch of the hydrological relationships in the southern sector of the Alburni Massif [13]. A perched water table and basal aquifer are present and supply water to different springs and wells located in the study area.

Figure 3. Schematic sketch of the hydrological relationships in the southern sector of Alburni Massif (modify from

3. Materials and methods

The geochemistry of the southern sector of Alburni Massif was investigated by sampling three springs and two private wells. The sampling was performed during January and March 2009. In the first month, samples were collected under variable weather conditions and after copious rains, while in March the samples were
taken in sunny weather conditions. In both cases, the sampling period coincided with the charging time of the hydrologic cycle. Groundwater samples were collected at five sites (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Altitude</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>n.a.</td>
<td>W</td>
</tr>
<tr>
<td>A3</td>
<td>n.a.</td>
<td>W</td>
</tr>
<tr>
<td>A4</td>
<td>475</td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>220-263</td>
<td>S</td>
</tr>
</tbody>
</table>

Table 1. Groundwater sampled in the southern sector of the Alburni Massif. Altitude in meters (m asl) S: spring W: well n.a.: data not available.

All samples were collected in laboratory certified clean bottles and labelled with the well depth and location, date and time of sample collection, analyses to be performed and field preservation performed, if any [14]. Water temperature, electrical conductivity and pH values were determined in the field. Bicarbonate was determined by titration with 0.1 N HCl using methyl orange colour turning method [15]. Water samples were filtered through cellulose filters (0.45 µm), and their major and minor constituents were determined with a Dionex DX-120 ion chromatograph (reliability ±2%). A Dionex CS-12 column was used for determining cations (Na⁺, K⁺, Ca²⁺, Mg²⁺), whereas a Dionex AS9 for anions (F⁻, Cl⁻, NO₃⁻, SO₄²⁻) [15, 16]. Trace element concentrations were measured using ICP-MS (X Series 2 Thermo Fisher Scientific); the analytical accuracy of these methods ranged from 2% to 5%. All analyses were conducted in the Earth Science Department, “Sapienza” University of Rome, Italy.

4. Results

- **Physical parameters**

  - Chemical characteristics of the groundwater from the southern sector of the Alburni Massif are reported in Table 2.

  Temperature values ranging from 9.5 (A4) and 11.9 °C (A5); this range of temperature is typical of the sampling period. The pH of the groundwaters ranged between 7.58 (A3) and 8.19 (A1).

  At the end, the electrical conductivity (EC) values ranging from 170 (A4) and 500 µS/cm (A1, A3 and A5).

4.2 Trace elements

Trace element concentrations are reported in Table 3 in accordance with Legislative Decree 152/2006 of National

5. Discussion

- **Chemical parameters**

  In our climate, the pH of natural waters is generally between 7.2 and 7.5. In this case study, the pH values of all samples were greater than average. This is likely the result of an interaction between the water sampled and the limestone it circulated through. As the water circulated, the pH assumed values linked to the equilibrium of the system CO₂ + H₂O ⇌ \( \text{H}_3\text{O}^+ + \text{CO}_3^{2-} \), regulated by the partial pressure of carbon dioxide in the gas phase and temperature.

  The ionic dominance pattern of the water samples for cations and anions was Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, CO₃²⁻, Cl⁻, SO₄²⁻, respectively. The high concentrations of Ca²⁺ connected to the geology of the study area; the sampling sites belong to an important karst system, where calcite dissolution is an important process that leads to the formation of the HCO₃⁻ ion (soluble) and the subsequent release of Ca²⁺.

5.2 Hydrogeochemistry

  The relative abundance of major elements allows us to identify the only geochemical family found, as shown in the Langelier-Ludwig diagram (Figure 4). Tested waters have the Ca-Mg chemical composition as a result of the different enrichment rates of water in alkaline elements (Na⁺, K⁺) and carbonate (HCO₃⁻ + CO₃²⁻).

Figure 4. Ludwig-Langelier diagram of the waters collected in the southern sector of the Alburni Massif.
The samples are homogeneous and consist of only one water type, the composition of which is substantially linked to the lithology of the site examined.

The Schoeller diagram below (Figure 5) illustrates a more detailed characterization of each sample's hydrogeochemistry; this diagram highlights slight anomalies between samples because it is based on the direct relationship of theionic concentrations (expressed in)

As shown in Figure 5, the waters drawn have similar hydrogeochemical characteristics, and all samples have a bicarbonate geochemical profile typical of waters circulating in carbonate rocks. In fact, each sample contains high concentrations of 2\textsuperscript{+} and 3\textsuperscript{+} ions.

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Table 2. Chemical and physical parameters of groundwater samples for the Alburni Massif area. Temperature (T) in °C, electrical conductivity (EC) in $\mu$S cm$^{-1}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T</th>
<th>pH</th>
<th>EC</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Na$^{+}$</th>
<th>K$^+$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
<th>HCO$_3^-$</th>
<th>F$^-$.</th>
<th>NO$_3^-$</th>
<th>NO$_2^-$</th>
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<tbody>
<tr>
<td>A1</td>
<td>10.8</td>
<td>8.10</td>
<td>300</td>
<td>40.5</td>
<td>3.03</td>
<td>8.84</td>
<td>1.56</td>
<td>5.29</td>
<td>5.08</td>
<td>143</td>
<td>0.01</td>
<td>0.06</td>
<td>1.73</td>
</tr>
<tr>
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<td>7.82</td>
<td>180</td>
<td>40.0</td>
<td>0.04</td>
<td>5.04</td>
<td>1.65</td>
<td>3.07</td>
<td>2.06</td>
<td>124</td>
<td>0.06</td>
<td>0.00</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
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<td>11.3</td>
<td>7.50</td>
<td>300</td>
<td>42.9</td>
<td>1.50</td>
<td>8.30</td>
<td>1.0</td>
<td>6.37</td>
<td>3.30</td>
<td>153</td>
<td>0.07</td>
<td>0.00</td>
<td>4.42</td>
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<tr>
<td>A4</td>
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<td>8.01</td>
<td>170</td>
<td>40.6</td>
<td>0.83</td>
<td>5.84</td>
<td>1.68</td>
<td>30.7</td>
<td>2.78</td>
<td>48.8</td>
<td>0.02</td>
<td>0.00</td>
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<tr>
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<td>7.67</td>
<td>300</td>
<td>51.3</td>
<td>10.1</td>
<td>0.56</td>
<td>2.62</td>
<td>7.29</td>
<td>4.83</td>
<td>207</td>
<td>0.13</td>
<td>0.13</td>
<td>6.02</td>
<td></td>
</tr>
</tbody>
</table>

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Table 3 (Continued). Trace elements in groundwater samples of the Alburni Massif area.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li</th>
<th>B</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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<td>ppb</td>
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<td>ppb</td>
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<td>ppb</td>
</tr>
<tr>
<td>MAC (in ppb)</td>
<td>1000</td>
<td>50</td>
<td>50</td>
<td>20</td>
<td>1100</td>
<td>50</td>
<td>50</td>
<td>200</td>
<td></td>
<td></td>
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<tr>
<td>A1</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.29</td>
<td>0.20</td>
<td>0.19</td>
<td>1.98</td>
<td>0.09</td>
<td>1.32</td>
<td>2.20</td>
<td>13.3</td>
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<td>A2</td>
<td>0.08</td>
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<td>0.64</td>
<td>0.56</td>
<td>0.88</td>
<td>3.58</td>
<td>0.12</td>
<td>0.19</td>
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<tr>
<td>A3</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.52</td>
<td>0.21</td>
<td>0.03</td>
<td>4.06</td>
<td>0.09</td>
<td>0.33</td>
<td>1.48</td>
<td>3.22</td>
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<tr>
<td>A4</td>
<td>0.03</td>
<td>0.35</td>
<td>1.26</td>
<td>0.38</td>
<td>2.02</td>
<td>16.8</td>
<td>0.11</td>
<td>0.81</td>
<td>0.36</td>
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<tr>
<td>A5</td>
<td>0.22</td>
<td>0.27</td>
<td>0.86</td>
<td>0.26</td>
<td>1.93</td>
<td>14.7</td>
<td>0.12</td>
<td>0.43</td>
<td>0.48</td>
<td>1.68</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th>Sample</th>
<th>Ga</th>
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<th>Rb</th>
<th>Sr</th>
<th>Cd</th>
<th>Sb</th>
<th>Cs</th>
<th>Ba</th>
<th>Hg</th>
<th>TI</th>
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<tr>
<td></td>
<td>ppb</td>
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<td>ppb</td>
</tr>
<tr>
<td>MAC (in ppb)</td>
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<td>5</td>
<td>1</td>
<td>10</td>
<td>110</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
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<tr>
<td>A1</td>
<td>0.02</td>
<td>0.24</td>
<td>2.68</td>
<td>41.4</td>
<td>0.06</td>
<td>0.07</td>
<td>0.01</td>
<td>15.8</td>
<td>0.15</td>
<td>&lt;0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>A2</td>
<td>&lt;0.01</td>
<td>0.84</td>
<td>1.61</td>
<td>77.1</td>
<td>0.02</td>
<td>0.07</td>
<td>0.02</td>
<td>78.6</td>
<td>0.32</td>
<td>&lt;0.01</td>
<td>0.22</td>
</tr>
<tr>
<td>A3</td>
<td>0.01</td>
<td>0.20</td>
<td>1.87</td>
<td>41.2</td>
<td>&lt;0.01</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>31.8</td>
<td>0.24</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>A4</td>
<td>0.02</td>
<td>1.26</td>
<td>2.40</td>
<td>10.1</td>
<td>0.33</td>
<td>0.23</td>
<td>0.03</td>
<td>77.5</td>
<td>0.10</td>
<td>0.01</td>
<td>3.45</td>
</tr>
<tr>
<td>A5</td>
<td>0.04</td>
<td>0.32</td>
<td>1.98</td>
<td>74.6</td>
<td>0.14</td>
<td>0.13</td>
<td>0.02</td>
<td>24.1</td>
<td>0.70</td>
<td>0.01</td>
<td>1.99</td>
</tr>
</tbody>
</table>
study site, this zoning is not entirely valid because the water is removed quickly from the surface and circulates at depth, where it takes on the characteristics of the aquifer. The Schoeller diagram provides additional information on the groundwaters sampled. The lines of A1 and A3 are similar, except for the Cl/\(\text{SO}_4\) molar ratio.

Figure 5. Schoeller diagram representing the waters collected in the Alburni Massif area.

Both the well and the spring draw from the same shallow groundwater, which is characterized by rapid flow and leaches the same type of rocks. The vertical hydrochemical zonation does not vary between the two water samples, which have a homologous supply mode from the same aquifer. Sample A5, as shown in Figure 8, is dissimilar with respect to the others.

Figure 6. Schoeller diagram for samples A1 and A3.

This sample also belongs to the bicarbonate type, but it has a higher \(\text{Mg}^{2+}\) concentration and lower \(\text{Na}^+\) concentrations than the other samples. The higher \(\text{Mg}^{2+}\) concentration is likely linked to the lithology of the substrate at depth (may be dolomitic-limestone and dolomite). While there are no dolomite formations in this area of the Alburni Massif, the high \(\text{Mg}^{2+}\) concentration in the sample indicates extended circulation of the water at depth and its contact with dolomitic-limestone at the basement of the carbonate stack. This hypothesis is justified by the higher \(\text{Na}^+\) and \(\text{Mg}^{2+}\) concentrations in the A5 sample compared to the concentrations of these ions in the other samples.

5.3 Trace elements

The analysis of minor and trace elements in natural waters has improved substantially following the development of new analytical methodologies that provide better quality measurements. Environmental
geochemistry reveals that the continuous introduction of many trace elements into the environment via atmospheric and hydrological cycles has been strongly disturbed by human activity \[17, 18\]. In addition, a number of natural processes (e.g., volcanic activity, chemical weathering of crustal rocks, etc.) help to determine concentrations of unwanted and/or harmful metals in water.

![Figure 7. Schoeller diagram for samples A2 and A4.](image)

In view of the strong toxicity of many metals, the presence of trace elements and potential pollutants cannot be disregarded from this analysis. From a purely environmental point of view, and with reference to the Maximum Allowable Concentrations (MAC) for various elements defined in Legislative Decree 152/2006, no minor or trace elements exceed their threshold values.

\[Ca^{2+}\] is the only element with a high concentration, but it has no threshold value. This element is an alkaline earth metal and was discovered in 1789 by Adair Crawford. It has a chemical structure similar to calcium and can replace it in some cases.

Figure 9 shows the distribution of \(Sr^{2+}\) with relation to the pH of measured samples.

- rock interaction (WRI) processes justify the general positive correlation between \(Sr^{2+}\) concentrations and pH for samples A2, A3, and A4. The increase of pH concentrations can be explained by a prolonged interactions between the groundwater and sediments/rocks.

Figure 9 also shows the calcite (\(CaCO_3\)) dissolution line at pH value of 7.8; under this line, the solution is undersaturated with respect to \(CaCO_3\), while above the line the solution is oversaturated with respect to \(CaCO_3\).

The A1 sample is located in the oversaturated sector; it's characterized by a low \(Sr^{2+}\) concentration and the highest pH value of the samples examined. Consequently, a higher concentration of \(Ca^{2+}\) exists in solution compared to \(Sr^{2+}\). The pH value of the A1 sample should be relatively lower than the other samples' measured values, but the opposite occurs. This is explained by the presence of a higher concentration of dissolved oxygen in the water, which reacts with \(H_2^+\) ions and lowers their concentration, resulting in a higher pH.

![Figure 8. Schoeller diagram for sample A5.](image)

Sample A5 falls in the undersaturated \(CaCO_3\) sector of the graph; this means that at this site, free \(Ca^{2+}\) exists in low concentration. Additionally, the pH value is high, and consequently, the concentration of \(Sr^{2+}\) increases.

6. Conclusions

The present study aimed to develop a hydrogeochemical profile of the waters located along the southern sector of the Albanian Massif. A geochemical campaign was conducted in January 2009 at five selected sites (three springs and two wells).

Through this study, the waters sampled were classified as \(CaCO_3\) at a result of enrichment in alkaline elements (\(Na^{+}\) and carbonate (\(HCO_3^{-}\) \(\rightarrow\))). It is interesting to note that the lithologies of the area. The sites examined belong to an important karst system, where the calcite dissolution is an important process that leads to
the formation of the HCO₃⁻ ion (soluble) and the subsequent release of Ca²⁺.

Figure 9. Diagram of Sr²⁺ vs. pH for groundwaters of the Alburni Massif.

Groundwater flow within the Alburni Massif is connected to the fault line passing through its south-

This fault line divides the Massif into two large structures situated to the east and west, which drain the waters from the basement to the Pertosa springs and Tanagro and Castelletto springs, respectively.

The Alburni Massif is an important car complex on the edge of Cilento: Cilento possesses few water resources, and in the summer, water demand exceeds availability. Interest in the Alburni Massif mountain complex stems from its potential as a water resource. A management plan should be at protect this water resource, including:

- Qualitative and quantitative monitoring of different springs in this area;
- Analysis to define natural water availability;
- Assessment of the impact of human activity;
- Designation of quality objectives and the organization of a refined sustainability management plan for the study area.

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