

POTENTIAL TOXIC ELEMENTS (PTES) IN GROUND AND SPRING WATERS, SOILS AND SEDIMENTS: AN INTERDISCIPLINARY STUDY IN ANTHEMOUNTAS BASIN, N. GREECE

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Abstract

Ground and spring waters, soils and sediments of Anthemountas basin in Northern Greece were analyzed for Potential Toxic Elements (PTEs). In total, twenty three soil and sediment samples, three groundwater (boreholes) and two spring water samples, were analyzed. Contents of Ni in soils and sediments can be as high as 2169 mg/kg. The high correlation coefficient of Ni and Cr, indicates the geogenic origin of Ni, which originates from ophiolitic rocks. Arsenic concentration ranges from 3 to 110 mg/kg in soils and sediments, with the highest contents observed in travertine. The spring waters are characterized by elevated concentrations of As (up to 235 µg/L), Na, K, Fe and Zn, indicating that hydrothermal fluids are responsible for feldspar alteration of the Monopigado granodiorite. On the contrary, in groundwaters, As contents are low (up to 18 µg/L). Electrical resistivity tomographies performed around the groundwater boreholes, revealed the presence of normal faults, locally allowing the mixing of geothermal fluids with the shallow porous aquifer (SPA). The presence of As in the SPA is probably due to inputs from geothermal waters through normal faulting.

Keywords: Arsenic, Nickel, Travertine, Geothermal water, Faults, Ophiolites.

Περίληψη

Υπόγεια και πηγαία νερά, εδάφη και ιζήματα της λεκάνης του Ανθεμούντα (Βόρεια Ελλάδα) αναλύθηκαν για την πιθανή παρουσία τοξικών στοιχείων (PTEs: Potential Toxic Elements). Συνολικά αναλύθηκαν, 23 δείγματα εδαφών και ιζημάτων, 3 υπόγειων (γεωτρήσεων) και 2 πηγαίων νερών. Η συγκέντρωση του Ni σε εδάφη και ιζήματα έφθασε τιμές έως τα 2169 mg/kg και ο υψηλός συντελεστής συσχέτισής του με το Cr, δηλώνει τη γηγενή προέλευση του Ni από τα οφιολιθικά πετρώματα. Η συγκέντρωση του As κομαίνεται από 3 έως 110 mg/kg σε εδάφη και ιζήματα, με την υψηλότερη συγκέντρωση να παρατηρείται στον τραβερτίνη. Τα πηγαία νερά χαρακτηρίζεται από υψηλές συγκεντρώσεις As (έως 235 µg/L), Na, K, Fe και Zn, δηλώνοντας ότι τα υδροθερμικά ρευστά επηρεάζουν άμεσα και επιδρούν στους αστρίους του γρανοδιωρίτη του Μονοπήγαδου. Αντίθετα, στα υπόγεια νερά, η συγκέντρωση του As έφθασε τιμές έως και 18 µg/L. Οι γεω-ηλεκτρικές τομογραφίες που πραγματοποιήθηκαν γύρω από τις γεωτρήσεις των υπόγειων υδάτων, αποκάλυψαν την παρουσία κανονικών ρηγμάτων, που τοπικά συνδέουν τα γεωθερμικά ρευστά με το

επιφανειακό πορώδη υδροφορέα. Η παρουσία του As στον επιφανειακό πορώδη υδροφορέα, οφείλεται στις εισροές από τα γεωθερμικά νερά διαμέσου αυτών των κανονικών ρηγμάτων.

Λέξεις κλειδιά: Αρσενικό, Νικέλιο, Τραβερτίνη, Γεωθερμικά ρευστά, Ρήγματα, Οφιόλιθοι.

1. Introduction

Natural environments such as water, soil and air are under a constant risk of pollution due to population growth, agricultural activities and accelerated industrialization process (Morrison *et al.*, 1990). Heavy metals are considered as one of the most serious environmental pollutants due to their persistence in the environment, bioaccumulation and high toxicity (Esmaeili *et al.*, 2014; Assubaie, 2015). Heavy metals and Potential Toxic Elements (PTEs) can originate from two primary sources; anthropogenic such as agricultural practices, vehicle exhaust emissions, metalliferous mining and associated industries, whereas rock weathering and thermal springs constitute natural or geological inputs (Zhang *et al.*, 1999; Gallego *et al.*, 2002; Micó *et al.*, 2006, Rodríguez Martín *et al.*, 2007; Esmaeili *et al.*, 2014). However, heavy metals and PTEs pollution in soils, sediments, plants, surface and groundwater is due to both natural processes and human activities and depends, among other things, on rock chemistry and mineral chemistry, the bioavailability of heavy metals and the different metallic and industrial mineral deposits that are exploited by humans (Papastergios *et al.*, 2011; Petrotou *et al.*, 2012; Skordas *et al.*, 2013). Hexavalent chromium and arsenic are two of the most toxic elements in the environment and their consumption leads to carcinogenesis (Mandal and Suzuki, 2002; Linos *et al.*, 2011). Weathering and erosion of ultramafic rocks has been recognized as a natural source of chromium in sediments and groundwater (Fantoni *et al.*, 2002; Kaprara *et al.*, 2015; Kazakis *et al.*, 2015; Dermatas *et al.*, 2015). The release of arsenic in groundwater can be due to the reductive dissolution of arsenic-bearing iron oxides (Harvey *et al.*, 2002), the released As through sulfide oxidation reactions (Chowdhury *et al.*, 1999) and the result of geothermal inputs (Nimik *et al.*, 1998; Pique *et al.*, 2010). Geothermal fluids circulating through faults can also be a source of As on groundwater and soils (Gamaletsos *et al.*, 2013).

The Anthemountas river basin is characterized by a complex hydrogeological and hydrochemical regime with elevated concentrations of arsenic and chromium in groundwater (Kazakis, 2013). The geogenic origin of chromium and its distribution in aquifers has been clarified from previous studies (Kazakis *et al.*, 2015). Nimfopoulos *et al.* (2002) reported elevated concentrations of heavy metals, PTEs and arsenic in the Geothermal springs water of the Anthemountas basin. Additionally, Tzamos *et al.* (2014) and Tziritis *et al.* (2015) reported low concentrations of heavy metals, PTEs and arsenic on tap water of Thermi Municipality.

This study aiming to explain the presence of the PTEs and heavy metal concentrations in soils, sediments, groundwater and geothermal springs' water in the Anthemountas basin. Therefore, previous studies (Kazakis, 2013; Kazakis *et al.*, 2015) and new analytical data of soils, sediments and water were used to study the leaching mechanism of the most toxic elements Cr(VI) and As(III) (McCleskey *et al.*, 2004). Additionally, this study focused in leaching from soils and sediments of the most toxic elements Cr(VI) and As. Moreover, electrical resistivity tomographies (ERT) were performed in selected sites in order to determine the hydrogeological conditions favoring elevated arsenic concentrations.

2. Study site

Anthemountas basin is placed in the eastern part of the Thermaikos Gulf in Northern Greece (Fig. 1). The site is characterized by a complex geological, hydrogeological and hydrochemical status due to the coexistence of various geological formations and aquifer types. Mesozoic igneous and metamorphic rocks, ultramafic rocks, together with granodiorite and recrystallized carbonates rocks are placed in the mountainous area surrounding the basin. The lowland comprises Quaternary and

Neogene sediments of variable thickness. The Quaternary sediments consist of terrace systems (gravels, sands, pebbles and clays) and alluvial deposits (sands, gravels and sands with clay), whereas the Neogene sediments are composed of conglomerates, sandstones, marls and red-clay series. The sedimentary formations are the hosts of confined and unconfined porous aquifers with variable morphological characteristics. Fissured rock aquifers are developed in the crystalline and metamorphic rocks, whereas a karstic aquifer is located in the carbonate rocks. A detailed description of these aquifers' characteristics can be found in previous studies (Kazakis *et al.*, 2015). In the study area, the water demands are met with groundwater resources and therefore aquifers' quality is of the utmost importance for the sustainability of the site. Consequently the origin and spatial distribution of pollutants are essential so as to prevent exposure of the population to toxic elements.

3. Materials and Methods

3.1. Soil and sediment sampling, mineralogical and chemical characterization

The soil and sediment sample sites were the same as those used in the study of Kazakis *et al.* (2015) in order to supplement the geochemical analysis of Cr and Mn. Additionally, a sediment sample of travertine was collected from the Voskina spring. In total, 23 soil and sediment samples were collected at depths up 0.7 m by using a Dutch auger.

For the aluminosilicate mineral samples, a subsample of 0.2 g was placed in an open PTFE beaker where 1 mL of concentrated HClO₄ and 20 mL of concentrated HF (Merck, pro-analysis) were added. The solution was then heated to fully evaporate HF and HClO₄. Subsequently, 20 mL of HCl 6 N were added and the sample was heated for 30 min. The solution was diluted to a final volume of 200 mL (Sparks *et al.*, 1996). Metal concentrations were determined either by flame or graphite furnace atomic absorption spectrophotometry using a Perkin Elmer AAnalyst 800 instrument (GF-AAS). For the determination of water-soluble fraction of As and Cr a 20 g sub-sample of soil was shaken with 60 mL deionized water for 15 min and then was filtered through a 0.45 µm pore-size membrane filter. As and Cr concentrations in filtrate were determined by GF-AAS.

The morphological and mineralogical characteristics of the travertine sample were accurately determined by microprobe analysis of its minerals were determined by Scanning Electron Microscopy (SEM, JEOL JSM-840A) with associated Energy Dispersive Spectroscopy analysis (EDS, Link AN10000). To minimize volatilization of alkalis in the minerals framework, the electron beam spot size was enlarged and the counting time decreased. Different minerals (micas, carbonates, feldspars) and pure metals were used as probe standards.

3.2 Water sampling and analysis

Groundwater samples were collected from 2 springs (Voskina 1S and Agiasma 2S) and three boreholes from the shallow porous aquifer, following a two-hour (at least) pumping session for the boreholes (Fig. 1). All samples were collected in September 2015. The water samples were filtered through 0.45 µm membrane filters. One part of each sample was acidified at pH 2 using HNO₃ and the other was analyzed immediately or refrigerated at 4 °C to be analyzed later. All analyses were conducted according to Clesceri *et al.* (1989). In particular, the parameters pH and electric conductivity (EC) were analyzed according to the methods APHA 4500-H⁺ and 2520 B, respectively. The anions of bicarbonate (HCO₃⁻), chloride (Cl⁻), nitrate (NO₃⁻), nitrite (NO₂⁻), phosphate (PO₄³⁻) and sulfate (SO₄²⁻) were determined according to the methods 2320 B, 4500 Cl⁻ F, 4500 NO₃⁻ C, 4500 NO₂⁻ B, 4500 P C and 4500 SO₄²⁻ B respectively. The ammonium cation NH₄⁺ was determined according to the 4500 NH₃ C method. The concentration of water soluble metals was determined either by flame or GF-AAS. Cr(VI) concentrations were determined by the diphenylcarbazide method (3500-Cr D) using a Perkin Elmer Lambda 2 UV/VIS spectrophotometer version 3.7 equipped with 10 cm path-length measurement cells. Boron determination was

performed by the azomethine H method and total organic carbon (TOC) content was measured to a Shimadzu TOC-V_{CSN} Total Organic Carbon Analyzer.

3.3 Electrical resistivity tomography (ERT)

Three ERT lines were measured during the period of September 2011 near to the groundwater sample sites to detect structure which can facilitate the mixing between geothermal waters and fresh water of the upper aquifers system. Twenty-one stainless steel electrodes were used 50 m apart, forming a total length of 1000 m for each ERT line. Electrical resistivity measurements were performed using a SYSCAL Pro resistivity meter which was located in the center of the electrode array. Wenner array and configuration was used to accurately delineate the predicted horizontal structures and their interfaces (Loke, 2011), whereas dipole-dipole array configuration was also used to examine if lateral changes are significant. The reliability of the ERTs was tested with available lithological profiles and geological data and the best fitting array configuration was selected. The inversion of the mixed resistivity data set was performed using DC2DPRO software (Kim, 2009) and 2-D resistivity images were produced. Finally, the RMS error values of all ERTs ranged between 2 and 8% indicating the reliability of the measured data.

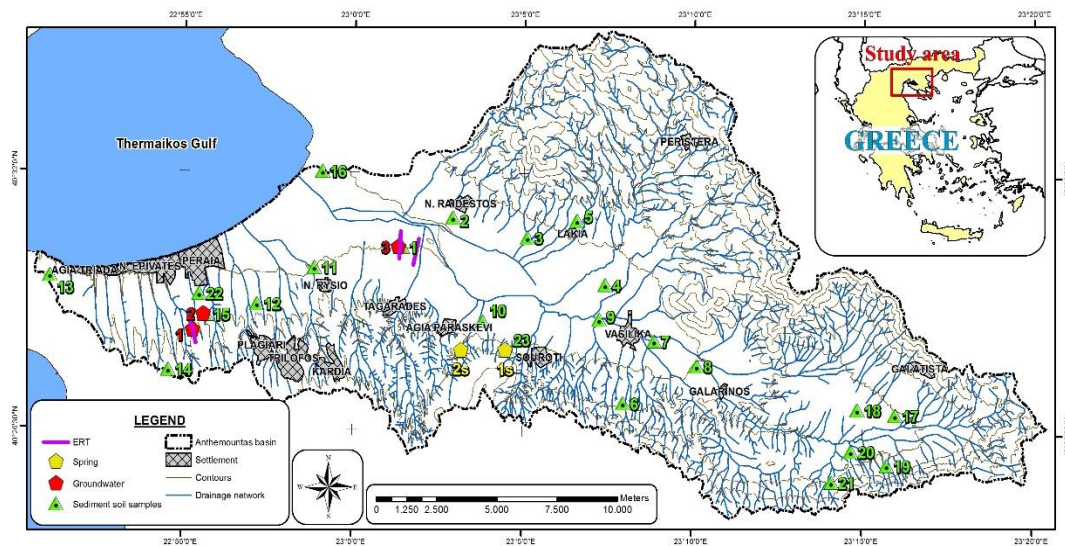


Figure 1 - Topographic map of Anthemountas river basin showing the sampling points.

4. Results and discussion

The minimum, maximum and mean values of the geochemical composition of soils and sediments are shown in Table 1. Total arsenic concentration in soils and sediments varies from 5 to 110 mg/kg, whereas the highest concentration was recorded in the travertine sample, and leachable arsenic ranges between 3 and 58 mg/kg. It is worth mentioning that leachable amounts of As from travertine were below the detection limit. Chromium and manganese content of travertine were 2 and 384 mg/kg respectively which are low in comparison to the rest of samples from the study area. The leachable Cr(VI) concentration of soils and sediments range between 3 and 46 mg/kg; the higher leachable amounts of Cr(VI) were observed in the samples with high serpentine content.

The concentrations of Ni, Pb and Zn range between 7 and 2169 mg/kg, 1 and 35 and 39 and 123 mg/kg, respectively. Mg contents range between 1.6 and 5.6 g/kg, while the higher values for Mg and Ni are located in the areas near the ophiolitic rocks. Sodium and potassium concentrations in soils and sediments range between 8.7 to 27.2 and 2.2 to 16.3 g/kg, respectively. Calcium varies from 13 to 375 g/kg with an average concentration of 194 g/kg. The higher concentrations of calcium

are found in soils and sediments nearby the carbonate rocks of the study area. Lead (Pb) and zinc (Zn) range between 1 to 35 and 39 to 123 mg/kg, respectively.

Table 1 - Leachable As and Cr(VI) and geochemical composition of the studied soils and sediments.

| Values | Cr ¹ | Mn ¹ | Ni | As | Pb | Zn | Al | Ca | Fe | K | Mg | Na | As ² | Cr ² |
|-----------------|-----------------|-----------------|------|-----|-----------------|-----|------|-----|------|------|-----|------|-----------------|-----------------|
| | mg/kg | | | | | | g/kg | | | | | | mg/kg | |
| Min | 2 | 384 | 7 | 5 | ND ³ | 39 | 4.4 | 13 | 1.9 | 2.2 | 1.6 | 8.7 | ND | ND |
| Max | 959 | 1630 | 2169 | 110 | 35 | 123 | 62.0 | 375 | 15.2 | 16.3 | 5.6 | 27.2 | 58 | 46 |
| Mean | 303 | 964 | 350 | 22 | 20 | 74 | 33.2 | 194 | 8.6 | 9.3 | 3.6 | 18.0 | 15 | 8 |
| SD ⁴ | 245 | 314 | 524 | 28 | 9 | 17 | 13 | 78 | 3.2 | 3.4 | 1.2 | 5.9 | 11 | 9 |
| DL ⁵ | 50 | 50 | 1 | 1 | 1 | 1 | 1 | 0.1 | 0.05 | 0.05 | 0.1 | 0.05 | 1 | 1 |

¹ Includes data from Kazakis *et al.*, 2015; ² Leachable As and Cr(VI); ³ Not detected; ⁴ Standard deviation; ⁵ Detection limit.

A correlation analysis was performed between the elements and is shown in Table 2. The high correlation between Cr and Mn has been also referred in the study of Kazakis *et al.* (2015). Ni has high correlation with Cr, Mn, Fe and Mg and thus, it is concluded the geogenic origin of Ni from the weathering products of ophiolitic rocks. In contrast, the highest correlation of As was observed with Na and K. This is probably an indication of the influence of hydrothermal fluids in feldspar-rich clastic sediments and/or directly to the Monopigado granodiorite, causing the alteration of feldspars which enriches these fluids in Na and K. The interaction between the geothermal field of Monopigado granodiorite field and the springs' hydrothermal fluid has been proposed by Nimfopoulos *et al.* (2002) based on Michard *et al.* (1998) study. Furthermore, the existence of a system of faults running through this igneous rock with ESE-NW direction favors the circulation of these fluids and the enrichment of groundwater in As and other heavy metals such as Fe, Mn and Zn. Additionally, high correlation coefficient is observed between Fe and Mn.

Table 2 - Correlation matrix of the elements from soils and sediments of the Anthemountas basin.

| | Cr | Ni | Mn | Pb | Zn | As | Al | Ca | Fe | Mg | Na | K |
|----|--------------|--------------|--------------|--------|--------|--------------|--------|--------|-------|--------|--------------|---|
| Cr | 1 | | | | | | | | | | | |
| Ni | 0.847 | 1 | | | | | | | | | | |
| Mn | 0.859 | 0.764 | 1 | | | | | | | | | |
| Pb | -0.244 | -0.172 | -0.122 | 1 | | | | | | | | |
| Zn | -0.145 | 0.034 | 0.044 | 0.224 | 1 | | | | | | | |
| As | 0.072 | -0.006 | 0.070 | -0.635 | 0.192 | 1 | | | | | | |
| Al | -0.577 | -0.713 | -0.311 | -0.086 | 0.187 | 0.370 | 1 | | | | | |
| Ca | -0.388 | -0.313 | -0.502 | 0.095 | -0.198 | -0.177 | -0.265 | 1 | | | | |
| Fe | 0.798 | 0.737 | 0.837 | -0.470 | 0.177 | 0.539 | -0.201 | -0.450 | 1 | | | |
| Mg | 0.842 | 0.886 | 0.698 | -0.203 | -0.068 | 0.039 | -0.772 | -0.053 | 0.700 | 1 | | |
| Na | -0.094 | -0.161 | -0.040 | -0.555 | 0.219 | 0.968 | 0.531 | -0.180 | 0.414 | -0.146 | 1 | |
| K | -0.277 | -0.302 | -0.226 | -0.422 | 0.351 | 0.901 | 0.570 | -0.108 | 0.222 | -0.306 | 0.943 | 1 |

Scanning electron microscopy (Fig. 2) of the travertine sample revealed the presence of an amorphous Fe-As rich phase deposited as irregular masses scattered throughout the surface of travertine. This denotes the arsenic deposition together with iron oxides-hydroxides (oxidized forms of iron) on

the carbonate phases of travertine (Nimfopoulos *et al.*, 2002). The latter is rich in CaCO₃ phases, especially calcite, as revealed from the X-ray diffraction analysis.

Groundwater samples were collected from two springs and three boreholes. Their statistical values are presented in Table 3. The electrical conductivity varies from 1127 to 6334 µS/cm, the higher values being observed in spring waters. In the spring waters and borehole 3, the pH is slightly acidic (6.2-6.5), while in boreholes 1 and 2 is neutral to slightly alkaline (7.8). Nitrate concentrations are mainly low (<22 mg/L), while the highest concentration was observed in borehole 3. Sodium and potassium concentrations range from 105 to 950 and 2.6 to 70.9 mg/L, respectively, while the highest concentrations were observed in the spring waters. These confirm our opinion that the hydrothermal fluids directly affect and alter the feldspars of the Monopigado granodiorite. Also, the highest concentrations of Cl (up to 1325 mg/L) were observed in spring waters.

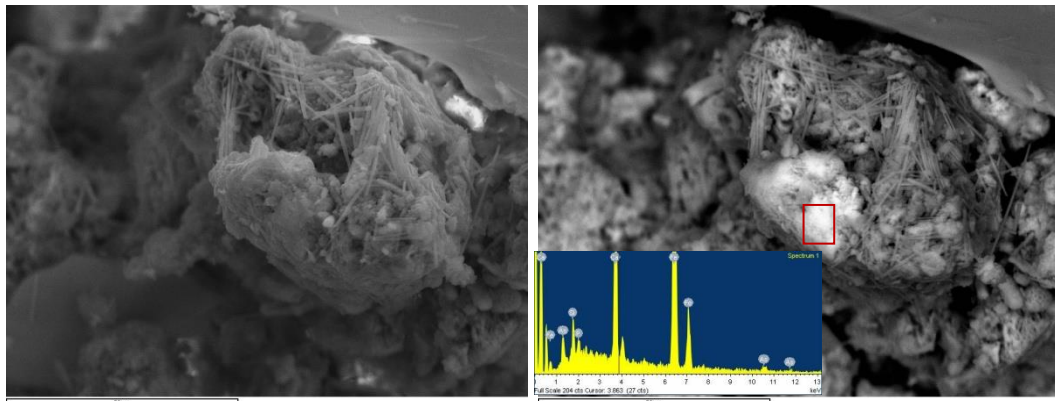


Figure 2 - Microphotograph (normal-left, backscattered-right) of travertine sample and microprobe analysis of Fe-As rich phase deposit on the Ca-rich travertine surface.

The concentrations of Hg, Pb, Cu, Cr, Cr(VI) and Sb were below the corresponding detection limit. Cobalt was detected only in the spring water of Agiasma (6 µg/L). Iron and manganese vary from 204 to 6667 and 96 to 1264 mg/L, respectively. The highest concentration of boron was observed in the borehole 3 (9.5 mg/L), whereas in the Voskina and Agiasma springs the concentrations were 8.3 and 7.8 mg/L, respectively. In borehole 2 the concentration of B was below detection limit, while in borehole 1 the concentration was 2.4 mg/L. Arsenic concentrations in the studied samples range from 3 to 235 µg/L. The highest concentration was observed in Agiasma spring and the lowest in the borehole 3. Concentration in the Voskina spring was 30 µg/L, 18 µg/L in borehole 1 and 7 µg/L in borehole 2.

Electrical resistivity tomographies were performed near the boreholes 1 and 3 in order to detect faults which can serve as paths for geothermal waters in the course of being mixed with the fresh waters of the shallow porous aquifers. Figure 3 depicts the electrical conductivity (Kazakis, 2013) of the boreholes around the ERT lines and the ERT. ERTs confirm the existence of faults with resistivity values up to 10 Ohm-m. The low resistivity value in the fault bodies is due to the circulation of geothermal fluids.

The fault orientation in the site of borehole 3 is ENE-WSW, whereas the faults are normal and parallel to the Anthemountas fault. It is located in the boundary between the alluvial deposits and the terrace system. In the site of borehole 1, the orientation of the fault wasn't determined due to the absence of a second ERT. The fault is located in the sandstone-marl series two kilometres south of the Peraia town.

Summarizing the results of this study, the groundwater quality of the shallow porous aquifer is locally affected by geothermal fluids. The geothermal water connected through the faults with the upper aquifer and mixed with fresh groundwater. The elevated concentrations of As and the related trace elements in groundwater of the study area are probably associated with the geothermal waters.

Table 3 - Statistical characteristics of groundwater and spring water samples.

| Parameter | Units | Detection Limit | Mean | Max | Min | St. Dev |
|----------------------------------|-------|-----------------|-------|--------|-------|---------|
| pH | | | 6.9 | 7.8 | 6.2 | 0.83 |
| E.C. | μS/cm | | 3326 | 6334 | 1127 | 2209 |
| Total Hardness | °F | | 69.5 | 106.7 | 27.3 | 34.6 |
| Carbonate Hardness | °F | | 62.4 | 106.7 | 27.3 | 38.4 |
| Non-Carbonate Hardness | °F | | 17.7 | 24.7 | 10.7 | 10.88 |
| Alkalinity (M) | | | 12.3 | 25.2 | 6.9 | 7.81 |
| Alkalinity (P) | | | ND | ND | ND | ND |
| (HCO ₃ ⁻) | mg/L | 5 | 847 | 1537 | 418 | 547 |
| (CO ₃ ²⁻) | mg/L | 5 | ND | ND | ND | ND |
| (Cl ⁻) | mg/L | 2 | 629.2 | 1325.0 | 110.0 | 518.14 |
| (SO ₄ ²⁻) | mg/L | 2 | 66.8 | 144.0 | 35.0 | 45.21 |
| (NO ₂ ⁻) | mg/L | 0.01 | 0.1 | 0.2 | 0.01 | 0.08 |
| (NO ₃ ⁻) | mg/L | 2 | 8.8 | 22.0 | 2.0 | 8.89 |
| (PO ₄ ³⁻) | mg/L | 0.01 | 0.1 | 0.2 | 0.0 | 0.07 |
| (Na ⁺) | mg/L | | 434 | 950 | 105 | 351 |
| (K ⁺) | mg/L | | 22.9 | 70.9 | 2.6 | 28.96 |
| (Ca ²⁺) | mg/L | | 190 | 375 | 35 | 160 |
| (Mg ²⁺) | mg/L | | 53.5 | 97.0 | 31.4 | 26.77 |
| (Li ⁺) | mg/L | 0.01 | 1.0 | 2.6 | 0.04 | 1.11 |
| (Sr ²⁺) | mg/L | 0.05 | 1.5 | 2.0 | 1.2 | 0.35 |
| (NH ₄ ⁺) | mg/L | 0.05 | 3.1 | 5.0 | 1.2 | 2.17 |
| (Sb) | μg/L | 2 | ND | ND | ND | ND |
| (As) | μg/L | 1 | 58.6 | 235.0 | 3.0 | 99.2 |
| (Cd) | μg/L | 0.1 | 0.2 | 0.2 | 0.2 | 0.09 |
| Cr(VI) | μg/L | 1 | ND | ND | ND | ND |
| (Cr) | μg/L | 1 | ND | ND | ND | ND |
| (Cu) | μg/L | 50 | ND | ND | ND | ND |
| (Fe) | μg/L | 50 | 1594 | 6667 | 204 | 2840 |
| (Pb) | μg/L | 1 | ND | ND | ND | ND |
| (Mn) | μg/L | 20 | 427 | 1264 | 96 | 481 |
| (Ni) | μg/L | 1 | 11.0 | 21.0 | 1.8 | 9.56 |
| (Co) | μg/L | 1 | 6.0 | 6.0 | 6.0 | - |
| (Mo) | μg/L | 2 | 4.1 | 6.3 | 2.0 | 2.48 |
| (Zn) | μg/L | 10 | 70.8 | 194.0 | 22.0 | 72.03 |
| (Hg) | μg/L | 0.2 | ND | ND | ND | ND |
| (B) | mg/L | 0.05 | 7.0 | 9.5 | 2.4 | 4.15 |
| SiO ₂ | mg/L | 2 | 23.8 | 27.0 | 20.0 | 2.77 |
| T.O.C. | mg/L | 0.5 | 3.5 | 7.4 | 0.7 | 3.12 |

The geothermal origin of As is also supported by the elevated concentrations of As, Na, K, Fe and Zn in the travertine sample. The Ni in soils and sediments of the study area has a geogenic origin from the weathering products of the ophiolitic rocks.

The small number of the groundwater samples is the main limitation of this study in order to make a representative map of As concentration in the aquifers of the Anthemountas basin. However, it is important to the origin of As in porous aquifers from geothermal waters. The geological sources of As in Greece are reported by Gamaletsos *et al.* (2013). Geothermal inputs of As in groundwater have been also reported from Mitrakas (2001) and Pique *et al.* (2010) in the Caldes de Malavella geothermal area in Spain. A future study, with a higher number of groundwater samples would be

beneficial for the determination of As distribution in porous aquifers of the study area. In Greece, elevated concentration of arsenic in groundwater have been reported in many regions (Katsoyiannis *et al.*, 2007; Voudouris *et al.*, 2014) indicating the need for a consistent and detailed monitoring of As in groundwater. Additionally, speciation of As should be performed in future studies in order to determine the form of arsenic (As(III) or As(V)) on groundwater considering that the toxicity of As(V) is significantly lower from As(III).

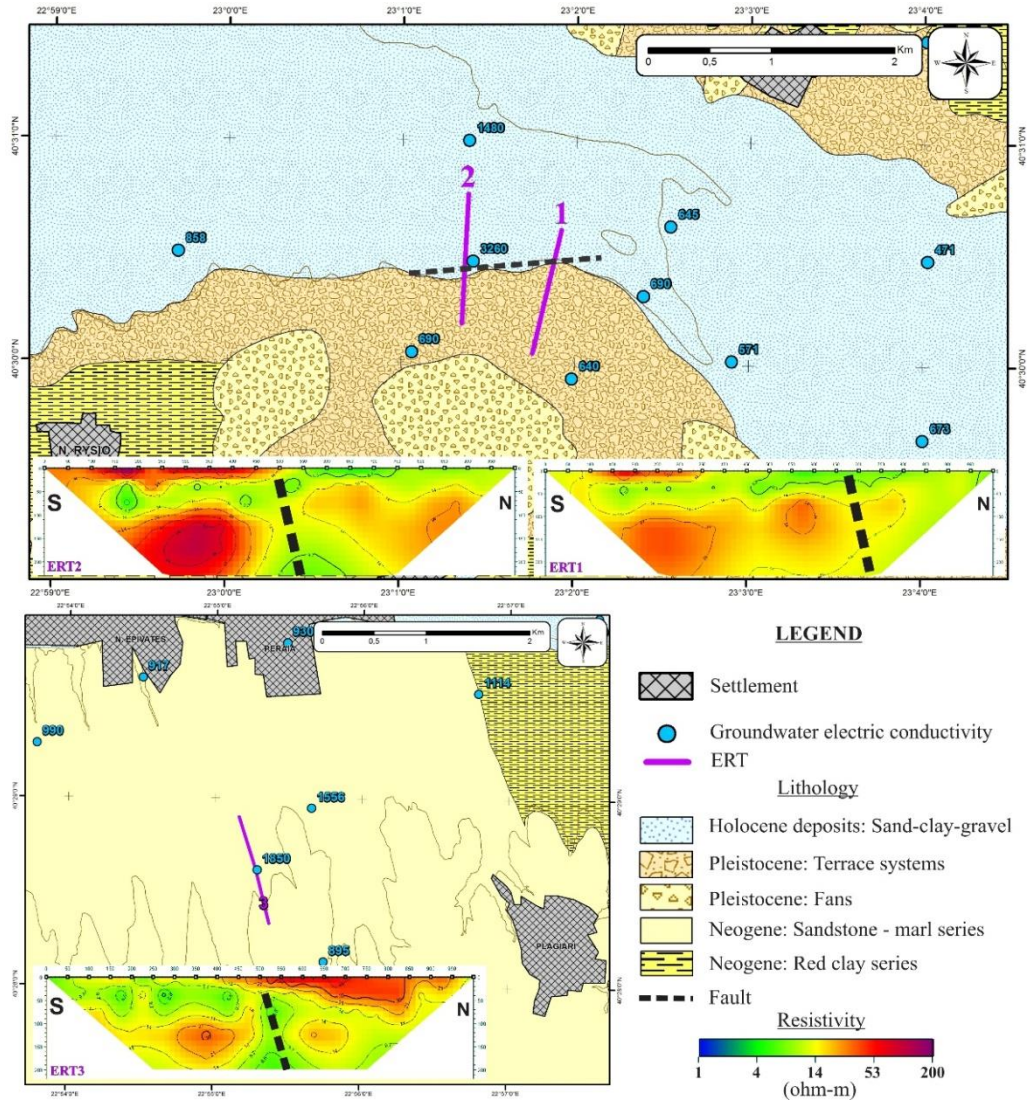


Figure 3 - Geological maps with ERTs and groundwater electrical conductivity.

5. Conclusions

In the Anthemountas river basin, a variable geochemical composition was occurred in soils and sediment samples. Nickel concentrations were up to 2169 mg/kg and the highest values located near to the ophiolitic rocks. The high correlation coefficient between Cr and Ni indicates the geogenic origin of Ni in the Anthemountas basin. Arsenic concentrations range from 3 to 110 mg/kg in soils and sediments, while the highest concentration observed in travertine. Spring waters are characterized by elevated concentrations of As (up to 235 $\mu\text{g/L}$), Na, K, Fe and Zn, and can be

assumed, particularly by the presence of Na and K, that hydrothermal fluids directly affect and alter the feldspars of the Monopigado granodiorite. In groundwater samples from the studied boreholes As concentrations are equal or below 18 µg/L. Electrical resistivity tomographies have revealed the existence of normal faults which facilitate the mixing between geothermal waters and fresh water of the upper porous aquifers.

The interdisciplinary approach and results of this study can be used as a tool to identify aquifers prone to high As concentrations originating from geothermal waters. However, a more detailed mapping of As distribution in the aquifers of Anthemountas basin is necessary in order to prevent exposure of the population to As.

6. Acknowledgements

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