Mobilisation of Arsenic in groundwater, Lesvos Island, Greece

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Abstract
In the present study, a geochemical analysis was conducted to investigate the As occurrence and release in groundwater from two different geological environments on Lesvos island: (i) the volcanic area of Mandamados (ignimbrite) and (ii) the metamorphic area of Tarti that comprises the geologic basement under ignimbrite. Seven sampling campaigns were conducted between October 2010 and October 2011 including 65 groundwater samples from 11 wells and springs. Chemical analyses showed As concentrations exceeding the 10 μg/L national drinking water limit in 46% of the samples from Mandamados. Groundwater composition in Mandamados evolved from Ca-HCO3 type, to mixed type and finally to Na-Cl type along the groundwater flow direction, indicating the contribution of ion exchange in groundwater chemical composition, while Ca-HCO3 type waters were observed in the Tarti area. Arsenic speciation analysis showed that As(V) was the main species in all samples, indicating that As was released under oxidizing conditions. Statistical analysis suggested silicate weathering as the prime mechanism of As release in groundwater in both cases, while, in the Tarti area, carbonate dissolution may represent a secondary mechanism which could be related to the observed relatively low As concentrations in the region. In both areas, pH related desorption of As, primarily from Fe mineral phases, was found to be the most important factor controlling the mobilisation of As, while the contribution of the redox control to As release in groundwater was generally found to be less significant.
Keywords: Arsenic, Groundwater, Volcanic geological substrate, Lesvos, Greece

1. Introduction

Many countries (Banglandesh, West Bengal, Taiwan, Inner Mongolia, Mexico, Hungary, Argentina and Chile) are facing the serious problem of As release in water from natural sources. Arsenic (As) is considered one of the most toxic elements, abundant in the Earth's crust (Smedley and Kinniburgh 2002). Therefore WHO, US-EPA, EU have set the maximum permissible value of As in the potable water to 10 μg/L. Naturally occurring As can be primarily released in water due to weathering of primary As rich minerals, or rocks, redox processes, desorption from mineral phases at increased pH and oxidizing conditions, or due to reductive dissolution of Fe and Mn oxyhydroxides (Smedley and Kinniburgh 2002). The aim of this study was to identify the environmental conditions and examine the mechanisms responsible for the natural As occurrence in groundwater as derived from two different geological regions in the island of Lesvos: (i) a volcanic area, where elevated As concentrations were observed, and (ii) a metamorphic area, where the As levels recorded during the past decade were occasionally relatively high. The study of the metamorphic region aims at exploring its potential contribution to As occurrence in shallower water since it represents the geologic basement underlying the volcanic rocks.

2. Description of the study area

The study areas located in two different geological regions of the island of Lesvos. The first one is the area of the Mandamados village, in the northeast part of the island (Fig. 1), which consists of volcanic rocks, namely ignimbrites of the Neogene period with rhyolithic to rhyodacitic composition. The second study area is located near the small village of Tarti in the southeast part of Lesvos (Fig. 1) within the metamorphic geologic basement of Neopalaeozoic to Triassic Age, that consists mainly of schists and marbles (Hecht, 1971-1974). The two villages have low relief and are close to the sea. The water supply for the two villages originates mainly from public and private groundwater wells and rarely from spring water.

3. Materials and Methods

Seven sampling campaigns between October 2010 and October 2011, at two month interval, were conducted in groundwater from the areas of study. Water samples were collected from 7 wells and 1 spring from the Mandamados area, and 1 well and 2 springs from the area of Tarti, adding up to a total of 79 samples, including field blanks. In-situ measurements of physicochemical parameters, chemical analyses for major anions, trace elements and As species were performed in examined groundwater. Further details on the sampling, the analyses and the analytical performance have been reported in Zkeri et al. 2015.

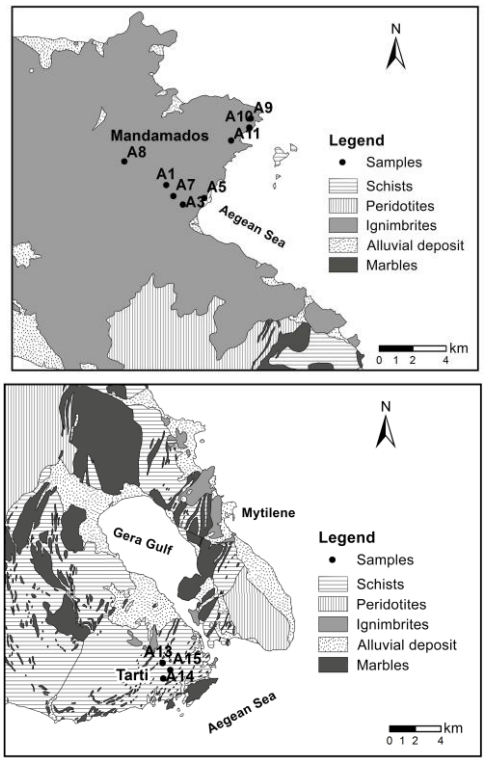

Figure 1. Location of the study areas (upper Mandamados, lower Tarti) on island of Lesvos, and groundwater sampling sites.

4. Results and Discussion

Arsenic concentrations in waters from the volcanic area of Mandamados were higher than those from the metamorphic area of Tarti. In Tarti area, As concentration (ranged between 0.41 μg/L - 8.4 μg/L), in all examined samples was found to be lower than the Drinking Water Standard (10 μg/L). In Tarti, groundwater was of Ca-HCO_3 type and As strongly correlated with Mg^{2+}, HCO_3^-, F, Li, B, Si, Ni, Sr, Ba probably due to their common origin from the metamorphic rocks of this area. On the other hand, in Mandamados area 46% of all examined water samples had As levels higher than the maximum permissible limit for human consumption (ranged from 1.78 to 54.67 μg/L). Arsenic concentration in this area followed an increasing trend from west to east (that is from inland to the coast), as the water quality changes from Ca-HCO_3 type, to mixed type and finally to Na-Cl type. The samples failing to meet the As drinking water standards were 67% and 31% for the coastal wells and the inland wells, respectively. In the wells near the coast, the range of measured As concentration was from 1.78 to 54.7 μg/L (median: 19.1 μg/L), while the respective concentration range in the samples from the inland area was from 4.29 to 17.6 μg/L (median: 8.05 μg/L). This behaviour may be attributed to silicate weathering and ion exchange due to the increase in EC (Nicolli et al. 2012), resulting from the increased residence time and water-rock interaction as groundwater flow becomes slower towards the coast (Smedley and Kinniburgh 2002; Nicolli et al. 2012), or, in the case of well A5, resulting from mixing with seawater (Mukherjee and Fryar 2008).

The strong positive correlation of As with pH, in both areas, indicates that higher pH values may contribute to the desorption of As from mineral phases in contact with the groundwater. The predominant As species is As(V), indicating that As is mainly mobilized under oxidizing conditions.

The contribution of the redox control to As release in groundwater was generally found to be less significant, however, there is an exception of some individual wells from both Mandamados and Tarti where more reducing conditions were found to occur temporarily (Zkeri et al. 2015).

5. Conclusions

Groundwater from two different geological regions (volcanic and metamorphic) on Lesvos Island was examined in order to explore the processes responsible for As occurrence. Arsenic concentrations exceeded the 10 μg/L limit in 46% of the samples collected from the volcanic area of Mandamados (67% and 31% for the coastal wells and the inland wells, respectively), whereas all waters from the metamorphic area of Tarti were below this limit. The predominant As species is As(V), indicating that As is mobilized under oxidizing conditions. In Mandamados, the primary sources of dissolved As and other elements appear to be the rhyolithic volcanic glass and/or volcanic ash which are abundant in Lesvos ignimbrite. Silicate weathering and ion exchange due to increased EC have been identified as factors of major importance in enhancing As mobility in groundwater in this area. The latter process is probably responsible for the higher As concentrations observed in the coastal wells of Mandamados, in comparison to the inland wells. In Tarti, groundwater was of Ca-HCO_3 type and As strongly correlated with Mg^{2+}, HCO_3^-, F, Li, B, Si, Ni, Sr, Ba probably due to their common origin from the metamorphic rocks of this area. In both areas, pH related desorption of As was found to be the most important factor controlling the mobilisation of As in the examined aquifers. The contribution of the redox control to As release in groundwater was generally found to be less significant, however, there is an exception of some individual wells from both Mandamados and Tarti where more reducing conditions were found to occur temporarily. Furthermore, the contribution of the metamorphic geologic basement to the As distribution in the overlying volcanic rocks appear to be minimal since waters from the two geological environments have different geochemical signatures acquired by the different chemical composition of their hosting rocks.

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