

# Seasonal variation and spatial distribution of Arsenic in groundwater in a Rhyolitic Volcanic area of Lesvos Island, Greece

Zkeri E.<sup>1,\*</sup>, Aloupi M.<sup>1</sup>, Gaganis P.<sup>1</sup>

<sup>1</sup> Department of Environment, University of the Aegean, GR-81100 Mytilene, Greece

\*corresponding author: e-mail: e.zkeri@geo.aegean.gr

## Abstract

A research conducted in water wells located in the rhyolitic volcanic area of Mandamados, Lesvos Island, Greece, indicated that significant seasonal variation of arsenic concentration in groundwater exists mainly in wells near the coastal zone. However, there were differences among those coastal wells with regard to the processes and factors responsible for the observed seasonal variability of the element, although they are all located in a small homogeneous area. On the other hand, in wells located in higher relief regions, the concentration of As in groundwater followed a fairly constant pattern throughout the year, which is probably related to the faster groundwater flow in this region due to a higher hydraulic gradient. In general, seasonal variation of As in groundwater in the study area was found to be related to geology, recharge rate, topography—distance from coast, and well depth.

**Keywords:** Arsenic, Groundwater, Volcanic geological substrate, Seasonal variation, Spatial variation

## 1. Introduction

Arsenic is a metalloid, abundant in the Earth's crust and well known as a cancer causing chemical. Elevated levels of naturally occurring As in groundwater used for human consumption is a serious problem for many regions of the globe. 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). Previous studies (Aloupi et al. 2009; Zkeri et al. 2015) and unpublished data from the Regional Union of Municipalities of Lesvos have shown occasionally elevated As levels in groundwater, which vary seasonally and spatially, exceeding the legislation limit of 10 µg/L in areas with volcanic geological substrate. Although, high spatial (e.g. Smedley and Kinniburgh 2002) and seasonal variability (e.g. Ayotte et al. 2015) of the element, even in adjacent boreholes, have been reported in numerous studies. However, there is limited research focusing on the factors and processes involved, especially in volcanic areas and

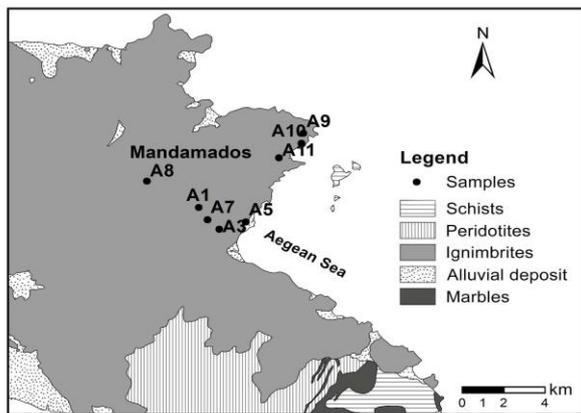
Mediterranean climatic conditions. The aim of this study is to contribute to the understanding of As hydrogeochemistry by examining the seasonal and spatial variability of As in groundwater from a rhyolitic volcanic area on the eastern Mediterranean island of Lesvos in Greece and exploring the environmental conditions that control its occurrence.

## 2. Description of the Study Area

The study area is located at the north eastern part of the Lesvos island, near the Mandamados village (39°18'37.08''N; 26°20'10.52''E). The rainfall events typically occur from October to April. The mean annual rainfall on the island is 648 mm, and the annual mean temperature is 17.6 °C, data provided by the Hellenic National Meteorological Service for the period (1955 - 1997). The geology of the area of study consists of Neogene volcanic rocks of rhyolitic to rhyodacitic composition, namely ignimbrites which overlie a metamorphic basement (serpentine, marbles and schists) in the central and in the southern parts of Lesvos and volcanic products in the northern part of the island (Hecht 1971-1974). The map of the Mandamados study area with the groundwater sampling sites can be found in Figure 1.

## 3. Materials and Methods

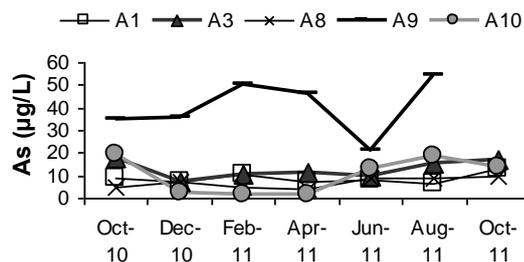
Seven sampling campaigns between October 2010 and October 2011, at two month interval, were conducted in groundwater from the area of Mandamados (a total of 58 groundwater samples) in order to investigate the seasonal variability in chemical characteristics. In-situ measurements of physicochemical parameters, 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 and Zkeri et al. 2018.



**Figure 1** Location of the Mandamados study area on island of Lesvos, and groundwater sampling sites.

#### 4. Results and Discussion

Arsenic ranged from 1.78 to 54.67  $\mu\text{g/L}$ , exceeding the limit of 10  $\mu\text{g/L}$  in 46% of the examined wells. The predominant As species is As(V), indicating that As is mainly mobilized under oxidizing conditions. As concentration followed an increasing trend along the flow direction, that is from west to east. Silicate weathering, ion exchange due to increased EC especially in the coastal wells, as well as pH-related desorption primarily from Fe mineral phases, were found to be the most important factors controlling the mobilization of As in the area.



**Figure 2.** Temporal variation of As during the period October 2010 – October 2011, in wells A1, A3, A8, A9 and A10

In the rhyolitic volcanic area of Mandamados, seasonal variation in As groundwater concentration was observed in three of the examined wells (A3, A9 and A10, figure 1), yet following opposite patterns and driven by different

#### References

- Aloupi, M., Angelidis, M., Gavriil, A., Koulousaris, M., Varnavas, S. (2009), Influence of geology on arsenic concentrations in ground and surface water in central Lesvos, Greece. *Environmental Monitoring and Assessment*, **151**, 383–396.
- Ayotte, J. D., Belaval, [...], Lindsey, B. D. (2015), Factors affecting temporal variability of arsenic in groundwater used for drinking water supply in the United States. *Science of the Total Environment*, **505**, 1370–1379.
- Hecht, J. (1971–1974), Geologic map of Lesvos Island (5 sheets). Athens: (Hellenic) National Institute of Geological and Mining Research (IGME).

processes in each case. In particular the variation of As in these three wells was related to (a) an increase of As concentration due to a higher rate of silicate weathering and ion exchange during the dry period followed by the dilution by the recharge water during the wet period, which, was recorded in well A10, (b) increased As mobility as a result of enhanced desorption promoted by higher pH in summer and subsequent dilution of As by the infiltration of recharge water during the wet period, in the case of the well A3, and (c) high As levels caused by the reductive dissolution of Mn during the wet period and by desorption under high pH values during the dry period, interrupted by the dilution by seawater intrusion in the beginning of the summer, resulting in a fluctuating though not clearly seasonal pattern, in well A9.

As a general trend, higher and seasonally variable As concentrations were found in the low-lying parts of the study area due to the slower flow rate that increases the water residence time. On the contrary, lower and fairly constant As levels observed in the elevated parts of the study area were attributed to the higher flow rates due to the higher hydraulic gradient. Moreover, the type of the aquifer (confined, unconfined) as well as the depth of the wells seems to affect the variation of As, since the shallower wells are recharged more quickly than the deeper ones. Arsenic concentrations showed an increasing trend along the flow path delineated by the wells A1, A8, A3, A7 and A5, as the water quality changes from Ca-HCO<sub>3</sub> type, to mixed type and finally to Na-Cl type. This trend was more intense during summer, when there is no contribution of recharge water. The As levels in wells A9, A10 and A11, which are located in an adjacent flat coastal area, also exhibit this spatial and temporal distribution pattern.

#### 5. Conclusions

The seasonal and spatial variation of As in groundwater from the Mandamados rhyolitic volcanic area is related to the geology, the groundwater recharge rate, the local topography in connection to the distance from coast, as well as with the well depth. These parameters account for the heterogeneity observed among the geochemical conditions that favour the mobilization of As in the examined wells which are located in a relatively small area within a homogeneous geologic environment.

- Smedley, P. L., Kinniburgh, D. G. (2002), A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry*, **17**(5), 517–568.
- WHO (2011), Guidelines for drinking-water quality. (4th ed.).
- Zkeri, E., Aloupi, M., & Gaganis, P. (2015). Natural occurrence of arsenic in groundwater from Lesvos Island, Greece. *Water, Air, & Soil Pollution*, **226**(9), 1–16.
- Zkeri, E., Aloupi M., Gaganis P. (2018). Seasonal and Spatial Variation of Arsenic in Groundwater in Rhyolitic Volcanic area of Lesvos Island, Greece. *Environ Monit Assess*, **190** (1), article number 44