Catena 150 (2017) 206–222

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Assessment of arsenic and associated metals in the soil-plant-water system in Neogene basins of Attica, Greece

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ARTICLE INFO

Article history:
Received 17 February 2016
Received in revised form 10 November 2016
Accepted 14 November 2016
Available online 25 November 2016

Keywords:
Arsenic
Contamination
Risk
Bio-accumulation
Ground water
Neogene basins
Greece

ABSTRACT

This paper presents a study on the soil-plant-water system in the Neogene basins of Attica (Greece), where an uppermost yellow-brown travertine limestone has been deposited. The principal goal of our study is to identify the percentage of arsenic (As) and metal transferred into plants and crops (bio-accumulation) in order to describe the incorporation of As in plants from rocks and soils and to assess potential groundwater contamination. The bio-accumulation factor for plants exhibits a wide range, including relatively low (1.5–7.6%) for As, Pb, Ni, Mn, Cr, Ba, Sb, Fe, much higher (29–67%) for Cu, Zn, Co, Ca and Mg, and exceptionally high (265%) for P. Although acceptable limits for As and heavy metals for plants have not been defined, As contents (dry weight) in plants from the Neogene basins of Attica are often higher than normal or limited values. The bio-accumulation factor for plants (As_{plant} / As_{soil} * 100) in Neogene basins of Attica exhibited a positive correlation between As and Fe, Cr, Mn, Pb and Sb.

The estimated risk assessment maps for As, Na, Cl and Se in water are produced according to the parametric values of Directive 98/83/EC, although these elements showed higher risk values in the southwest and central part of the Mesogeia basin than in the Kalamos-Varnavas basin. The elevated Na, Cl, As, Se, Li and B concentrations, measurement of salinity and factor analysis in groundwater in the Mesogeia basin were attributed to a contribution by seawater in this aquifer.

The estimated risk assessment maps of As in soils and ground waters in Neogene basins of Attica may indicate a potential human health risk and environmental significance of an integrated water-soil-plant investigation of As contamination in similar Neogene lacustrine formations.

1. Introduction

Arsenic (As), which is associated with igneous and sedimentary rocks, and sulphide ores, is the 20th most common element in the earth's crust (0.5–2.5 mg/kg) (Kabata-Pendias and Mukherjee, 2007). Arsenic compounds are observed in rock, soil, water, air and plant and animal tissues. The risk of As entering the food chain through water, soil and plant/crop contaminations has been a topic of global interest (WHO, 2004). The recommended limit of As in drinking water is 10 μgL^{-1} As (USEPA, 2001), although at present, there is no known safe limit for As. Recent research suggests that tuberous vegetables accumulate higher amount of arsenic than leafy vegetables, although leafy vegetables accumulate higher amounts of arsenic than fruity vegetables (Alam et al., 2002; Bhattacharya et al., 2010a, 2010b; Roychowdhury et al., 2002; Samal, 2005). The rate of uptake and the bio-accumulation factor of As in crops usually depends on its availability in soils, the soil pH, organic matter, redox potential and mineral composition (Mandal and Suzuki, 2002).

In aquatic systems, inorganic arsenic occurs primarily in two oxidation states, As(V) and As(III). Both forms generally co-exist, although As(V) predominates under oxidizing conditions and As(III) predominates under reducing conditions, depending on the Eh, pH, salinity, metal concentrations, temperature, and distribution and composition of the biota (USEPA, 1984). Natural levels of arsenic in soil usually range from 1 to 40 mg/kg, with a mean of 5 mg/kg. Arsenic is observed in many foods at contents that usually range from 20 to140 µg/kg.

Elevated As contents were recently recorded for the first time in a limestone quarry in Varnavas basin (NE Attica, Greece) that is exploited for a popular multicolour building material and in the associated soil (Kampouroglou and Economou-Eliopoulos, 2013). The results of a geochemical investigation at Neogene basins, which cover a significant portion of Attica, were presented using the geographical information system (GIS), geostatistical techniques and mapping software to show the extent and intensity of As contamination and other elements (Fe, Mn, Ni, Cr and Ba) in travertine limestone and associated soils (Kampouroglou and Economou-Eliopoulos, 2016). These researchers

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http://dx.doi.org/10.1016/j.catena.2016.11.018
0341-8162/

concluded that the major contamination sources are most likely sulphide and Fe-Mn mineralization in Attica, basement rocks that involve mylonitic ophiolitic blocks and, to a lesser extent, human activities.

Given that the uppermost yellow-brown travertine limestone, which is distributed across Attica, has high contents of As and heavy metals, our present study focused on the investigation of plants and water samples (springs, wells and boreholes) from the major Neogene basins of Attica. Our study aimed to assess the percentage of As and metal transferred into plants/crops (bio-accumulation) in order to describe the incorporation of arsenic in plants from soils and potential groundwater contamination.

1.1. Description of the site-sampling

The study area of Attica is composed of alpine basement, both metamorphic and non-metamorphic rocks, and post-alpine formations. The metamorphic section of the Attica-Cyclades zone occurs in the eastern and southern parts of Attica, where it is transformed by high pressure and low temperature conditions and consists of Triassic schists, metabasic, and quartz-feldspathic rocks (Papanikolaou and Papanikolaou, 2007).

The geomorphology of the area is dominated by the Parnitha and Aegaleo Mountains in the west, and the Penteli and Hymettus Mountains in the east that, border the Athens basin. During the Upper Pliocene-Pleistocene, activation of the Penteli detachment fault lifted the Hymettus Mountain and caused the separation of the Athens basin from the Mesogeia basin (Mposkos, 2008). Maps showing contaminated and potentially contaminated sites coupled with mineralogical and geochemical data confirm the geotectonic literature data suggest the separation of an initially single basin in Attica into smaller basins (Kampouroglou and Economou-Eliopoulos, 2016). Three major drainage basins can be distinguished from the coastal zone of Oropos-Kalamos in the southern Evoikos gulf to the Saronic gulf: 1) The Kalamos-Varnavas basin toward the northwest, 2) The Athens basin in the south with a NNE-SSW flow direction, and 3) The Mesogeia basin with a major W-E flow direction between the Hymettus Mountain in the west and the Penteli Mountain in the north (Fig. 1).

The alpine bedrock is covered by post-alpine Neogene to Quaternary formations. These formations include 1) Upper Pliocenic deposits (marine-coastal) of Southern Athens and Eastern Mesogeia basins, 2) Upper Miocenic deposits (lacustrine formations-travertine limestone, fluvial-lacustrine, fluvial-continental and lacustrine-continental), and 3) Quaternary alluvial deposits (I.G.M.E., 2000, 2002, 2003). The Neogene lacustrine deposits of Kalamos-Varnavas basin consist of marls, marl limestone with lignite intercalations of the Malakasa-Oropos area and travertine, while upward to these, clays, sandstones and conglomerates are developed (Ioakim et al., 2005; Mettos, 1992). In the central part of the Mesogeia basin, alternation marls and marl limestone with lignite intercalations of Rafina are found (Mettos, 1992).

The most important aquifers in the Kalamos-Varnavas basin are constituted by Triassic-Jurassic limestones, Upper Cretaceous limestones, marly limestones and travertine limestones, which are characterized as permeable rocks. The Triassic-Jurassic limestones of the Sub-Pelagonian zone in the Kalamos-Varnavas basin are characterized as karstic aquifer and with outlets through submarine and coastal springs located in the north part of the Kalamos area. The

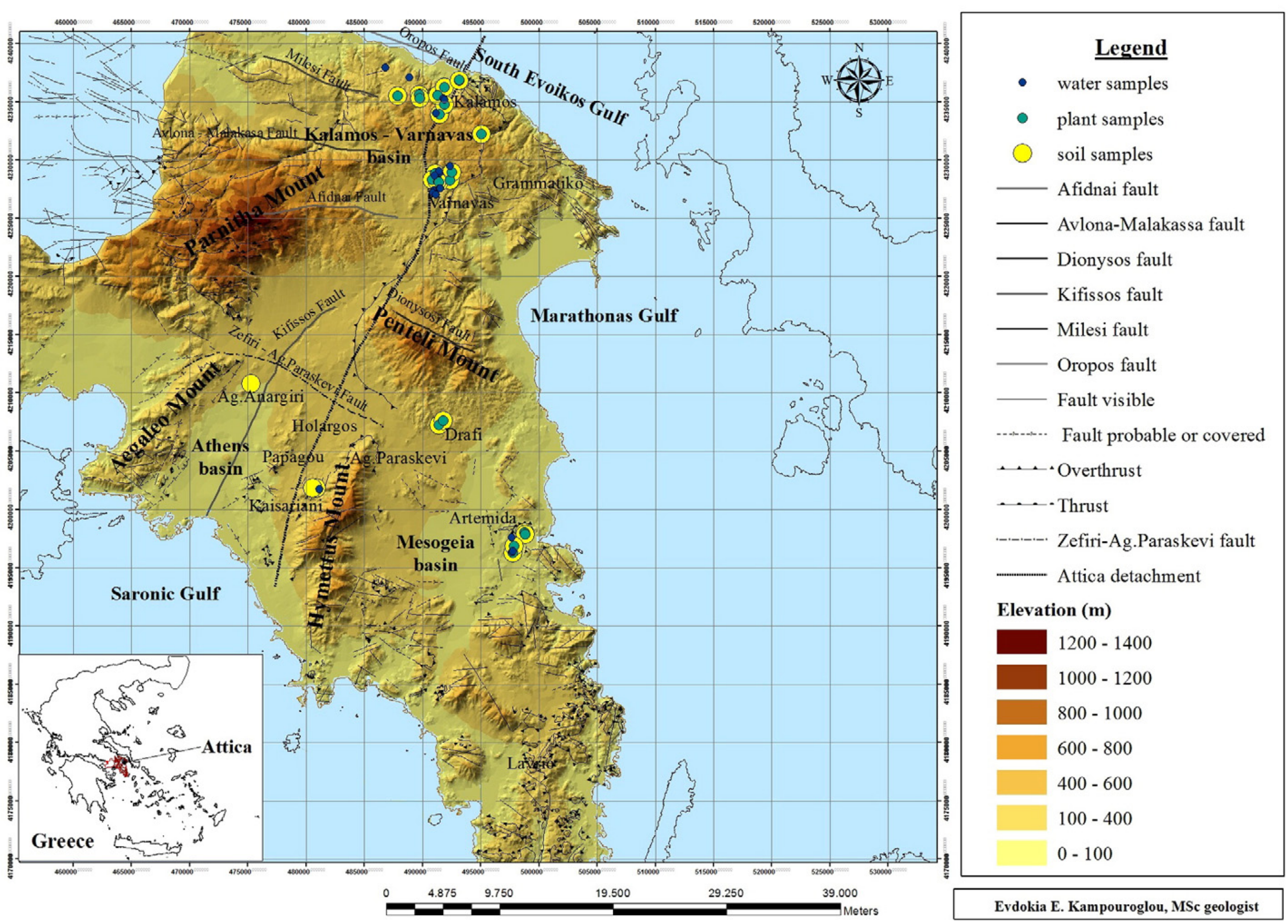

Fig. 1. Topographical map showing the sampling locations in Neogene basins of Attica (Greece).