THE GEOCHEMICAL DISTRIBUTION OF ARSENIC AND ANTIMONY IN THE CULTIVATED SOILS OF THE HYDROLOGIC BASIN OF THE AMYROS RIVER (LARISSA, GREECE)

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Abstract
In this research the concentration and the spatial distribution of elements As and Sb in the soils of the hydrologic basin of the Amyros river in the region of Larissa (Greece) were studied. The main goal of this research was to identify the areas with anomalous concentrations and to determine the spatial distribution of the above elements for potential future environmental restoration, because in this region apple trees are cultivated. One hundred seventy three (173) soil samples were collected and analyzed by ICP-AES after solubilization with $HClO_4$-HNO_3-HCl-HF. The mean concentration values of both elements were higher than the mean values of the world soils. The spatial distribution of the highest As and Sb contents is unbreakably linked to metal sulphide mineralization connected with Tertiary hydrothermal solutions which were emanated from acid sub-volcanic infiltrations.

Introduction
The soil provides to the plant a complex mixture of metallic elements, thus the absorption of a given metal can be influenced by other elements that can either strengthen or inhibit its uptake (Kabata-Pendias and Pendias, 1984; Mervyn, 1980).
Arsenic and antimony are two chemical elements with similar geochemical behaviour, which generally occur in trace amount in the earth surface environment. Their main origin is natural with the highest concentrations located in areas where sulphide mineralization occurs (Kelepertsis, 2000; Kelepertsis et al., 2006). The most common sulphide minerals containing As and Sb are arsenopyrite FeAsS and stibnite Sb_2S_3, respectively.
A lot of incidents of soil and ground water pollution from As and Sb have occurred with consequent diseases in humans (Das et al., 1996; Foy et al., 1978; Gebel, 1997; Gurani et al., 1994) because of their high toxicity.
The goal of this study was the determination of As and Sb spatial distribution in the top soils of the hydrologic basin of the Amyros river in the region of Larissa (Greece) in order to assess the feasibility of environmental restoration of the study area wherein apple trees are cultivated.

Materials and Methods
In an area of 65 km^2, 173 soil samples were collected. During the sampling procedure there was an effort to use a quadrangular grid of 500x500 m. In the areas where this was not possible, because of the cultivations and the mountainous terrain, attention was given in order to cover the area uniformly following the existing rural network of the area.
The sample collection took place after removing the surficial vegetation and then by digging in a depth of 10 cm approximately. The soil sample was stored in a numbered plastic bag. In the laboratory the samples were dried in an oven at 40^0 C, disaggregated in an agate mortar and sieved through a 2 mm screen. The fraction <2 mm was homogenized and pulverized, taking the fraction <100 μm. Then the samples were digested in a mixture of acids $HClO_4$ - HNO_3 - HCl - HF and analyzed for 35 elements included As and Sb (Skordas and Kelepertsis, 2005). The analyses took place in ACME Analytical Laboratories Canada by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy).
For the reproducibility control of the analytical results, 17 samples were randomly selected and analyzed twice (Ramsey et al., 1987). The analytical error was generally smaller than 10%.

Results
Table 1 shows the summary statistics of As and Sb contents in the study area compared to the concentrations in world soils (Connor and Shackelete, 1975; Siegel, 1974), to the phytotoxic levels (Kabata-Pendias and Pendias, 1984) and to the environmental guidelines of the British legislation. The concentrations of As and Sb in the samples from the Eastern side of the study area, wherein sulphide mineralization occurs, range from 15 to 242 and from 7 to 49, respectively. Isoline plots of metal contents were created in SURFER 6 for Windows using Kriging as the interpolation method. The contour maps were projected on the simplified geological map created

using ARCVIEW 3.1 for Windows in order to visualize the spatial relationship between the metal concentrations and the various sources of pollution in the study area. These maps are presented in Figures 1 and 2.

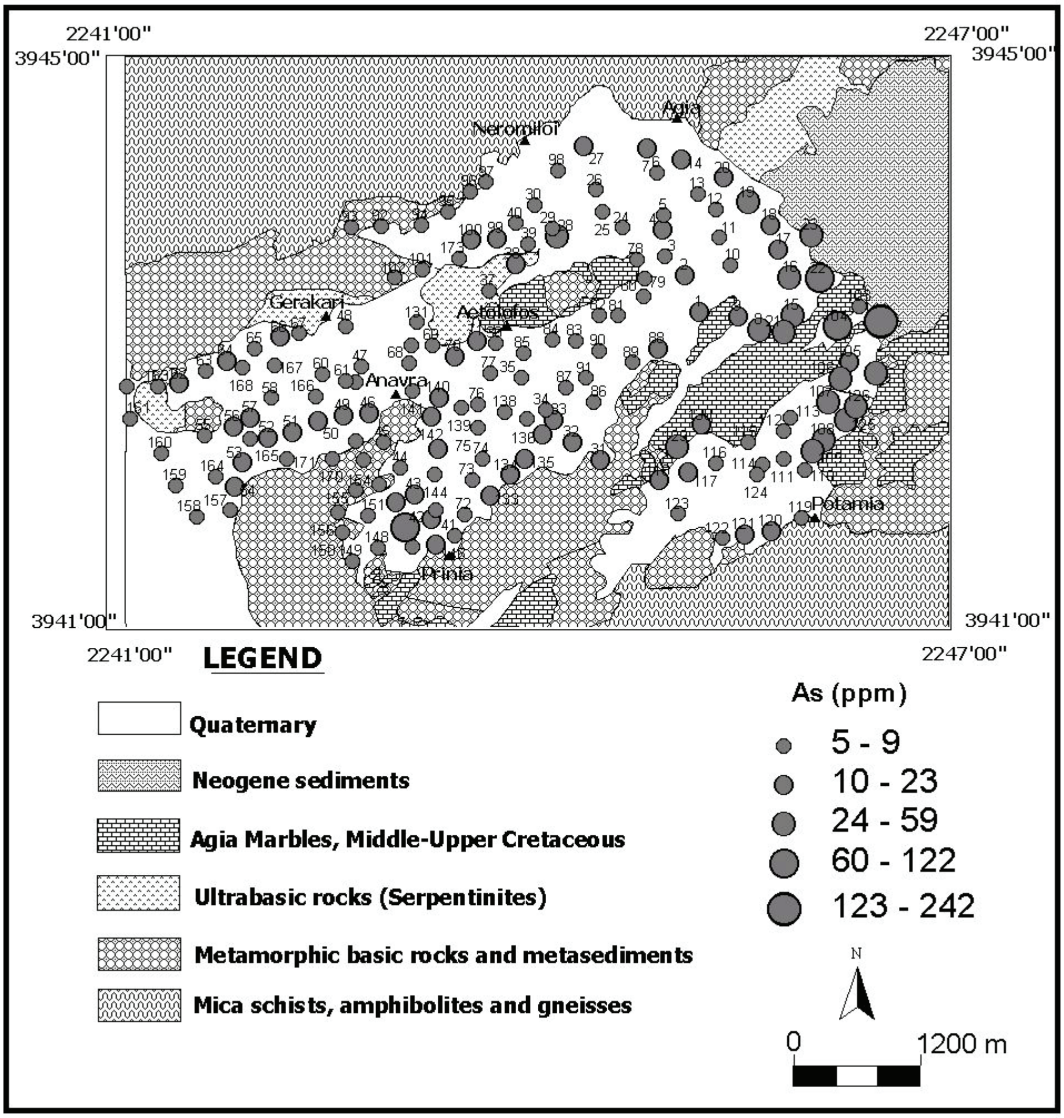

Figure 1. Isoline plot of spatial distribution of As in the study area.

Table 1. Summary statistics for As and Sb concentrations (in µg g^{-1}) in the study area in comparison with average world soil composition, phytotoxic levels and GLC guidelines of British legislation.

Element	Range in the study area	Mean	Average world soil composition	Phytotoxic level (3)	G.L.C. guidelines (4)				
					I	II	III	IV	V
As	5-242	13	7.5 (1)	15-50	30	50	100	500	>500
Sb	5-49	5.8	2 (2)	5-10	-	-	-	-	-

(1) Connor and Shackelete, 1975
(2) Siegel, 1974
(3) Kabata-Pendias and Pendias, 1984
(4) Great London Council suggested range of values in air-dried soils. I: Typical values for uncontaminated soils; II: Slight contamination; III: Contaminated; IV: Heavy contamination; V: Unusually heavy contamination.

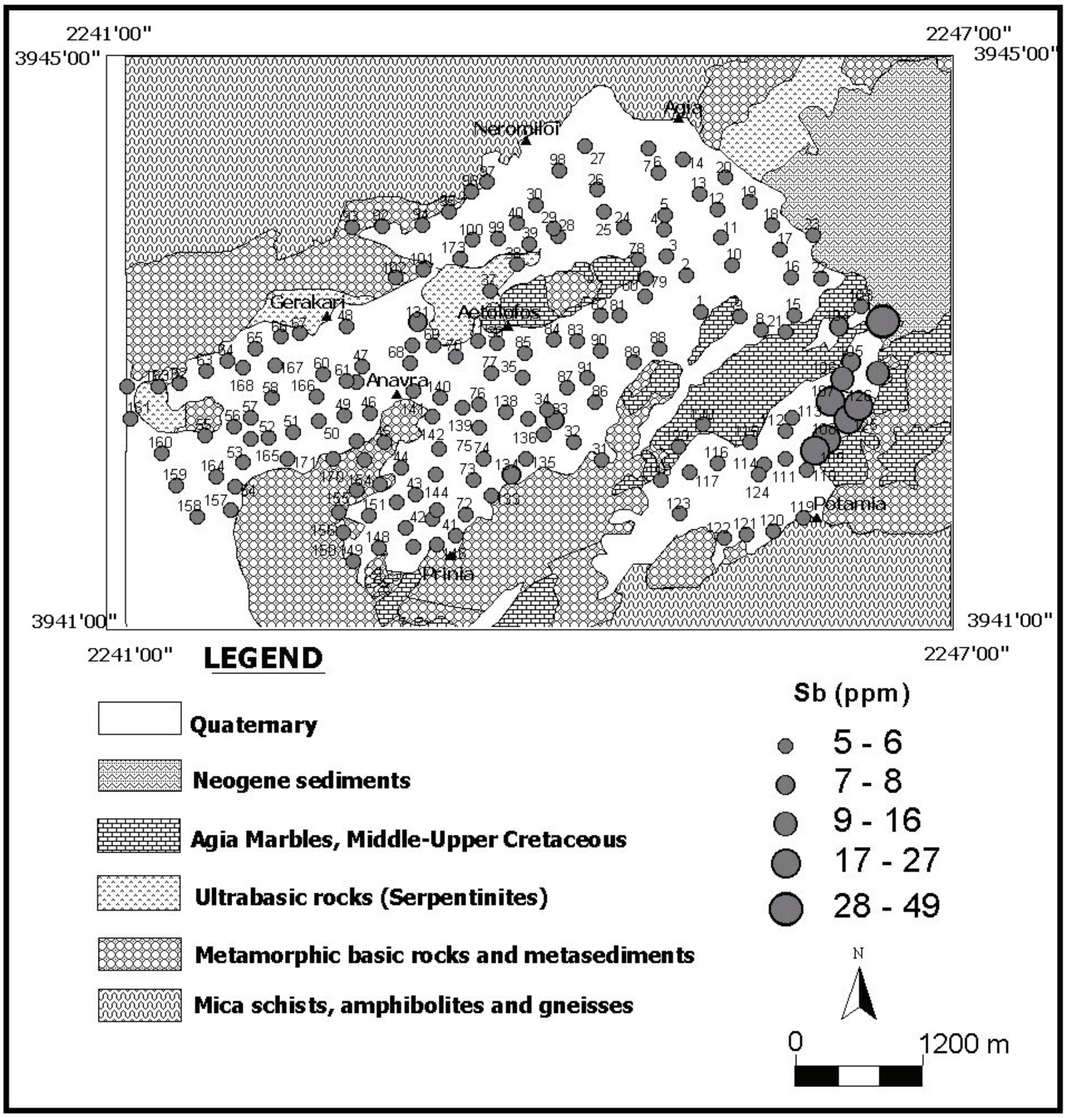

Figure 2. Isoline plot of spatial distribution of Sb in the study area.

Discussion and Conclusions

Table 1 shows that the mean values of As and Sb in the study area are higher than the mean values of world soils. The 47% and the 100% of the As and Sb values, respectively, are higher than the mean values of world soils (Connor and Shackelete, 1975; Siegel, 1974). Also the percentage of the samples that exceed the phytotoxic levels is 3% for As and 4.6% for Sb (Kabata-Pendias and Pendias, 1984). According to the British legislation, 92% of the samples can be characterised as uncontaminated, 5% as slightly contaminated, 2% as contaminated and only 1% as heavy contaminated from As. The samples with high concentrations of both elements are found in the Eastern part of the study area (Fig. 1 and 2). These increased values of As and Sb can be explained by the existence of metal sulphide deposits connected with Tertiary hydrothermal solutions which were emanated from acid sub-volcanic infiltrations (Kelepertsis, 2000; Kelepertsis et al., 2006). They are multi-metal occurrences of orpiment, realgar, arsenopyrite, stibnite and pyrite hosted in fractured serpentinite with intense oxidation and pyritization (Migiros, 1993).

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