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Variability and Enrichment of Metals in Soils and Sediments along Karvounoskala Stream (NE Chalkidiki, Northern Greece)

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The occurrence of metals in the environment originates from various sources including natural processes, as well as anthropogenic activities. Geochemical ratios of metals in soils are based on the chemical and mineralogical associations in the natural environment. Metals mostly adsorb and accumulate in sediments than water or suspended solids. Hence, sediments act as a metals sink in the aquatic environments (Salomons *et al.*, 1984; Zhang *et al.*, 2016).

The present study focuses on element (As, Cd, Cr, Cu, Ni, Pb, Sb, Zn) enrichment along the Karvounoskala stream, which is located near Stratoni village and discharges in Ierissos Gulf. The wider area has a long history concerning the mining activities of Greece (Chalkidiki Peninsula). Geologically, the study area belongs to the Kerdylia formation, part of the Serbomacedonian massif. In this region, the Stratoni granodiorite intrudes marbles, biotite- and hornblende-biotite-gneisses and amphibolites, which are overlain by alluvial deposits (Kockel *et al.*, 1977; Vavelidis *et al*., 1983).

Nine samples were in total collected downstream Karvounoskala stream as follows: 5 soils and 4 sediments. After they were transferred to the laboratory, the samples were dried at 50˚C for 48h in order to remove the moisture. The whole soil and sediment samples were pulverised in a mortar to achieve a homogeneous sample of particle size <0.063 mm. Total element concentrations were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and compared to the global average composition of shales (Turekian *et al*., 1961). Element enrichment was assessed by using the following geochemical indices: enrichment factor (EF), contamination factor (Cf), geo-accumulation index (I_{geo}) and contamination degree (Cd) (Salomons *et al*., 1984; Müller, 1969; Hakanson *et al*., 1980; Sakan *et al*., 2009). For the calculation of these indices, the concentration of each studied element is normalised against a reference element. In this study, Al was used as a reference element, since it revealed low variability. Total Al content in soil and sediment samples was determined by X-Ray Fluorescence (XRF).

According to the results of this study, element concentrations in soil followed the order Pb >Zn > As > Cu > Cr > Sb > Ni > Cd. Geochemical maps were plotted within a GIS environment. The map presenting the variation of Pb concentrations in the studied samples is illustrated in Fig. 1.

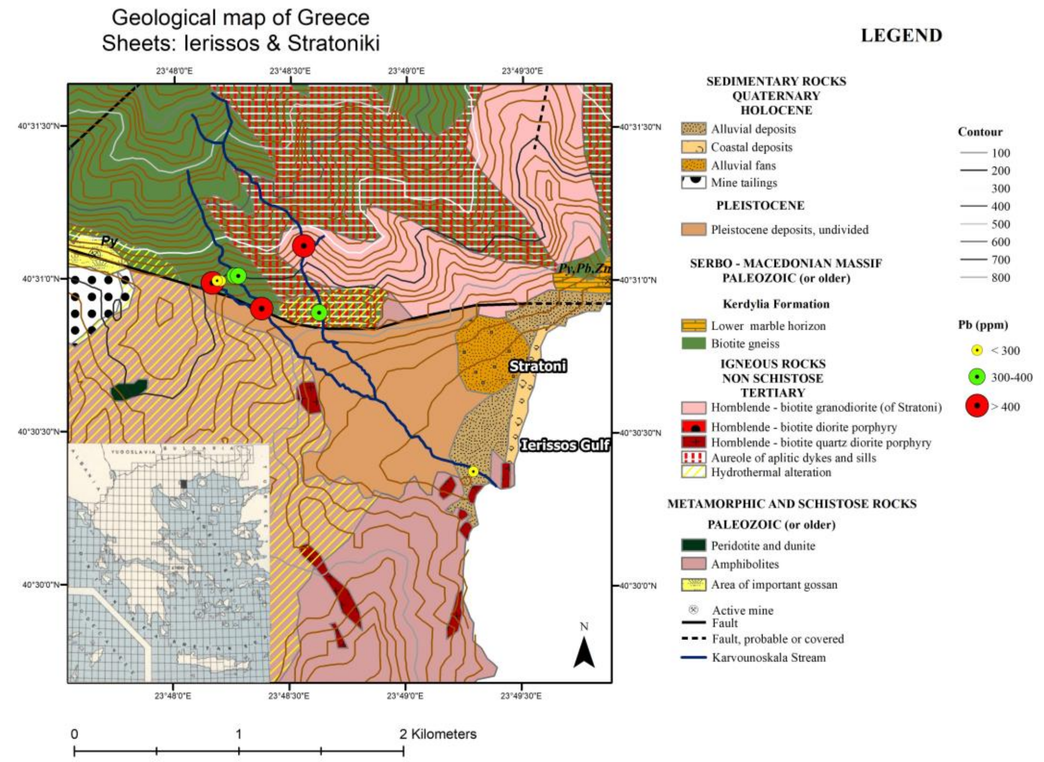

Figure 1. Variation of Pb concentrations in the studied samples along Karvounosklala stream.

Concerning the EF values, Cd revealed the highest (43.96), followed by Pb (32.72), Sb (12.85), As (11.39), Zn (2.55), Cu (1.66), Ni (0.38) and Cr (0.28). According to these values, soil samples revealed very strong enrichment in Pb and Zn, strong enrichment in Sb and As and minor enrichment in Zn, Cu, Ni and Cr. I_{geo} values indicate that in the soil samples Cd levels (4.47-4.85) range from heavily to extremely contaminated, and Pb (0.14-4.43) ranges from uncontaminated-moderately contaminated to heavily-extremely contaminated. A wider range is exhibited by Sb levels (2.15-3.08) since the soils are characterised from moderately-heavily to heavily contaminated. For As ([-0.96]-2.90) and Zn ([-1.32]-0.79) the soils are practically uncontaminated to moderately-heavily contaminated, and for Zn ([-1,32]-0,79) and Cu ([-1.91]-0.17) the soils are practically uncontaminated to uncontaminated-moderately contaminated. The Cr and Ni levels are below 0, demonstrating no contamination. Contamination degree (Cd) values indicate very high contamination for Cd, Pb, Sb and As, while low contamination is indicated for Zn, Cu, Cr and Ni (Fig. 2).

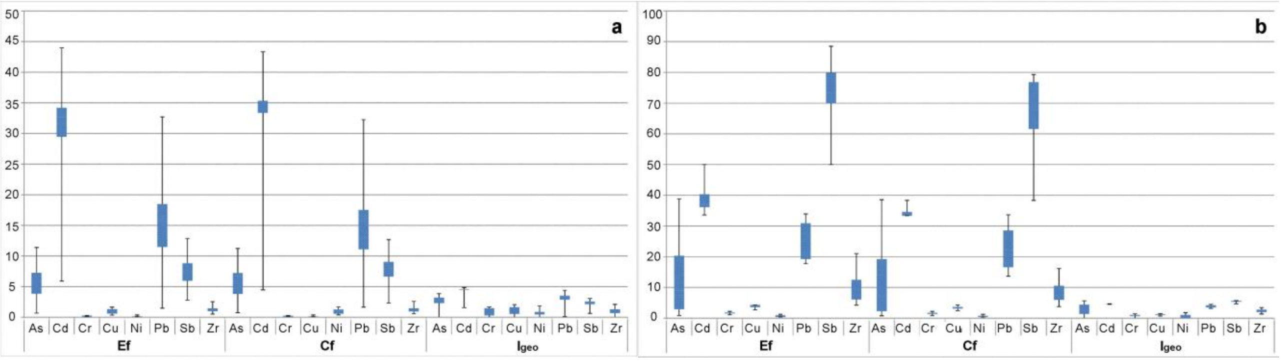

Figure 2. Variation of the geochemical indices, as they were calculated for (a) soil and (b) sediment samples.

Regarding the sediment samples, their element content presented minor differentiation with respect to the soil samples, following the order Zn > Pb > As > Cu > Cr > Sb > Ni > Cd. The highest EF value was recorded at 88.5 for Sb, followed by As (38.8), Cd (50.0), Pb (33.9), Zn (21.1), Cu (4.30), Cr (2.22) and Ni (1.27). Therefore, sediment samples exhibited extremely strong enrichment in Sb, very strong enrichment in As, Cd and Pb and strong enrichment in Zn. Moderate enrichment was revealed for Cu, while the sediments had a minor enrichment in Ni and Cr. I_{geo} values in the sediments presented similar distribution with the respective ones in the soils, indicating that sediment samples are heavily to extremely contaminated with regard to Sb (4.68-5.72), Cd (4.47-4.68) and Pb (3.19-4.49). A wider range is exhibited by As ([-0.96]-4.68), since the samples are characterised from practically uncontaminated to moderately contaminated. Moreover, Zn (1.34-3.43), Cu (0.70-1.51) and Cr ([-0.85]-0.55) levels range from moderately to heavily contaminated, uncontaminated-moderately to moderately contaminated and uncontaminated to uncontaminated-moderately contaminated, respectively. The Ni levels are below 0, indicating no contamination. Contamination degree (Cd) values suggest that the highest contamination in sediments is indicated by Sb, Cd, Pb, As and Zn. Moderate contamination is indicated by Cu, while signs of low contamination were shown by Cr and Ni (Fig. 2).

In general, soil and sediment compositions appear rather uniform. This is expected, since both are derived from the weathering of the rocks in the study area. The studied elements originate from the weathering of the surrounding geological formations, as well as from the element occurrences that they host. All samples are partly enriched in Sb, Pb, As, Cd and Zn due to the presence of polymetallic sulphides, Fe-Mn oxides and slags in the soils and sediments. Traces of Cr and Ni are attributed to amphibolite occurrences (Karetou *et al*., 2018).

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