Distribution of Trace Elements in Old Lignite Disposal Sites and Potential Impact on the Local Environment, Oropos Basin, Northern Attika

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The Oropos Basin was one of the most important lignite-bearing areas in Greece. The lignite deposits in the area of Mavrosouvala, between Markopoulo and Milesi, has been known since 1830 and mining activity in the area lasted for about a century. Numerous waste lignite and spoil heaps have been neglected ever since. Previous research in the area has underlined geogenic contamination of potentially toxic elements in the groundwater and the Neogene sediments bedrock of this basin (Stamatis *et al.*, 2011; Kampouroglou and Economou-Eliopoulos, 2016; Kampouroglou *et al.*, 2017). However, the environmental impact of the neglected lignite wastes has not been evaluated so far. The aim of this research was to sample mining wastes from different disposal sites and perform mineralogical and geochemical analysis. Characterisation of samples includes semi-quantitative mineralogical analysis by SEM/EDS analysis and XRD, bulk waste geochemical analysis for major and trace elements by XRF and ICP-MS and LECO methods.

Based on field observations and the bulk analysis the mine waste material is characterised as highly heterogeneous consisting of variable amounts of waste lignite, soil and waste rock. Total sulphur concentration (LECO measurements) in the all the waste types including the waste rock is high, *i.e.*, from 3.5 up to 10.7 wt.% associated with a high pyrite content (Fig. 1). Organic carbon also shows high variability from 0.1 to 19 wt.%. According to SEM/EDS analysis the sulphides (pyrite, sphalerite) and montmorillonite host significant amounts of As in the waste lignite whereas goethite is the main carrier of As in the waste rock (dolomitic limestone).

Ashing of lignite waste and then dissolution by nitric acid in closed vessels (and microwave heating) was performed in order to minimise loss of volatile elements during the open vessel acid attack at high temperatures. Trace element concentration of the digests were measured by ICP-MS. The total Fe concentration in the lignite waste (XRF analysis) ranges from 5.1 to 7.9 wt.%, being probably associated with the abundance of pyrite; it is also possible to participate in clay minerals (montmorillonite). The average concentration of As, Cr, Co, and Ni in the lignite ash is higher than the respective ash concentration of the main Greek lignite deposits (Table 1). The determination of As in the ash samples is considered accurate, since the digestion test was performed in closed vessels (Lachas *et al.*, 1999).

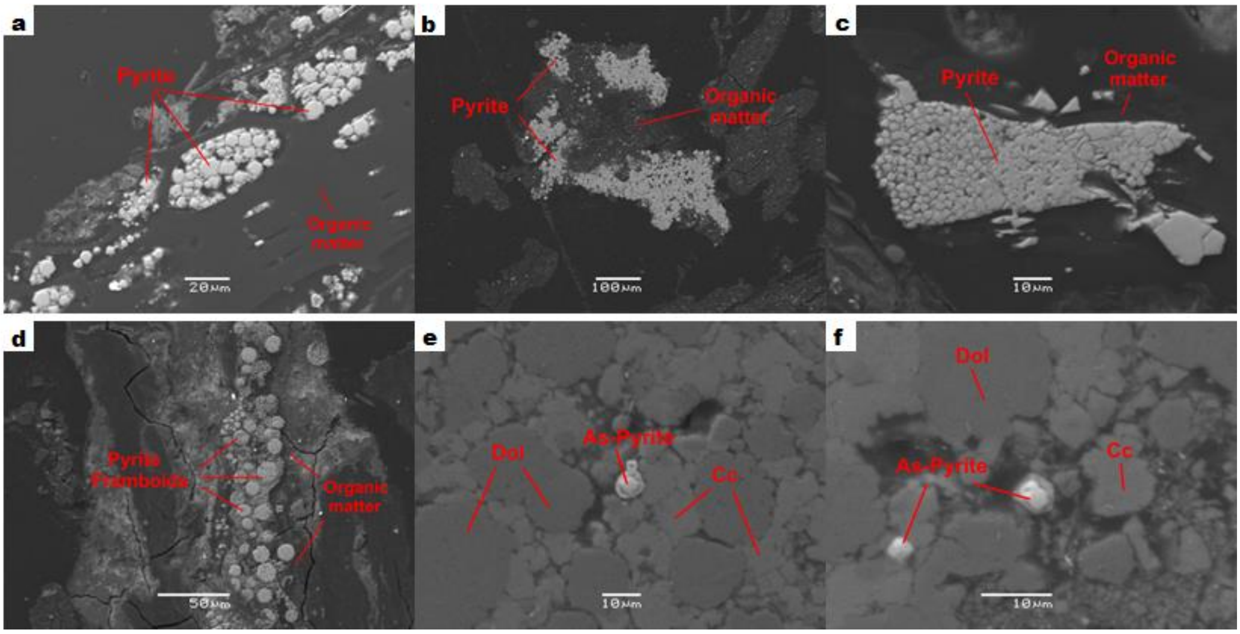

Figure 1. Pyrite occurrence as framboids in the lignite waste (a-d) and As-pyrite in the dolomitic limestone host rock (e-f).

Table 1. Concentrations in ppm of trace elements and iron of lignite waste (bulk analysis by XRF) and lignite ash (ICP-MS analysis) from Oropos basin. For comparison, lignite ash from the main lignite deposits of Greece are shown (Foscolos *et al.*, 1989, 1998).

Element	Oropos Lignite waste (dried bulk, n=3)	Oropos Lignite ash	Ptolemaida/Amyntaio ash	Megalopoli ash	Drama ash
Fe (wt.%)	5.1 – 7.9	4.3	-	-	-
As	80 – 119	168	23.5 – 104	20 – 30	102 – 606
Ba	74 – 544	-	612 – 852	487 – 700	425 – 1323
Cd	2 – 7	2	<3.3	<1.8	<2.1
Cr	610 – 640	535	234 – 591	236 – 351	50 – 290
Co	102 – 216	132	18 – 35	25 – 53	9 – 25
Cu	56 – 98	50	140 – 220	165 – 194	25 – 110
Mo	<15	-	18 – 29	10 – 33	46 – 712
Mn	195 – 576	185	304 – 1172	319 – 531	168 - 1273
Ni	643 – 2752	1842	229 – 651	215 – 226	57 – 246
Pb	14.7 – 40	20	50 – 67	56 – 66	50 – 119
U	15 – 40	-	21 – 97	12 – 13	33 – 313
V	188 – 344	219	267 – 348	227 – 282	116 – 737
Y	21 – 41	-	24 – 26	35 – 47	28 – 298
Zn	116 – 194	83	57 – 98	110 – 185	50 – 242

High concentrations of Cr and Ni ranging from 234 to 591 ppm and 229 and 651 ppm, respectively, have also been recorded in the ash from Ptolemaida – Amyntaio lignite basin (Papanikolaou *et al.*, 2004).

The paste pH test (1 part solid:1 part water) was used to determine the acidic nature of the waste samples and ranged from 2.7 to 4.9. Samples having a paste pH of <4.0 are considered potentially acid forming (PAF), and these samples contain significant acidic sulphate salts. Preliminary results of acid-base accounting tests (ABA) showed Neutralisation Potential Ratio (NPR) values <1and Net Neutralisation Potential (NNP) <-20 kg $CaCO_3$/t indicating potential acid generation from the mine waste material. These conditions could enhance metal leachability and cause an increased risk for the local water and soil.

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