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Trace Elements in the Soil-Plant Systems of Copper Mine Areas-A Case Study From Murgul Copper Mine From the Black Sea Region of Turkey

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Abstract: This study presents a case study on the heavy metal analysis of soil and plant samples around the Murgul copper mine, one of the first and most important mining areas in Turkey. An attempt has been made to investigate the status of trace elements like Al^{3+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} and Cd^{2+} in soils and plants. The sampling localities were taken from 500 m, 600 m, and 1000 m altitudes around the factory and at 1400 m in the forest zone. The aboveground parts and foliage ash of *Silene compacta, Tussilago farfara, Smilax excelsa, Rhododendron ponticum, R. luteum,* and herbal mix were analysed. The results of analysis have revealed the minimum and maximum concentrations measured in the plants as follows; aluminium (20-8985 mg kg^{-1}), cadmium (0.0-0.5 mg kg^{-1}), cobalt (0.0-5.5 mg kg^{-1}), copper (0.0-347.5 mg kg^{-1}), iron (25-9320 mg kg^{-1}), lead (2-51 mg kg^{-1}), nickel (1.5-16.5 mg kg^{-1}), and zinc (13.0-221.0 mg kg^{-1}). In the soil the concentrations of aluminium, cadmium, cobalt, copper, iron, lead, nickel, and zinc vary between 33-457, 0.0-0.0, 0.0-0.4, 0.1-88.7, 14-50, 0.3-4.1, 0.2-0.8, and 4.0-20.3 mg kg^{-1} respectively. These findings enlighten the fact that copper is generally toxic in the soils as well as plants. *Silene compacta* has been recorded as a high copper accumulator, behaving as a healthy plant on the polluted sites of the area alongside the Murgul creek (especially at 600 m). This study stresses the fact that it is imperative to assess and monitor the levels of heavy metals in the environment due to anthropogenic activities, including mining, for evaluation of human exposure and for sustainable environment.

Keywords: Copper mines; environmental pollution; heavy metals; soil-plant interactions; toxicity

1 Introduction

Mining of minerals and metals is known from ancient times and has been the key force for industrial and economic development of societies [1-7]. However, this activity has generated huge amounts of waste in the form of tailings [7-9]. Abandoned underground and surface mining have resulted in untreated wastes forming spoil heaps, which remain at old metal mine sites and are one of the sources of heavy metal contamination in the environment [6,7,10]. Copper from ancient mines is the best example of anthropogenic metal pollution. Its concentration in the surrounding soils provides good opportunity to study the past as well as present impacts [11].

Average copper content in the crust of earth varies between 55-70 mg kg^{-1} [9,12]. The use of copper, cadmium and zinc has substantially increased during the last few decades however, copper is now produced more than any other metal [10]. Copper production per year at present is around 13 million tons. The known global reserves of high-grade ore are around nearly 1 billion tons [13]. Global average copper background value in soils is 14 mg kg^{-1}. But, the values in America are around 5 to 70 mg kg^{-1}. It forms

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strong bonds with sulfur forming covellite [CuS], chalcocite [Cu_2S] and bornite [Cu_5FeS_4]. If weathering occurs these minerals can combine with carbonate and oxygen to form malachite [$Cu_2CO_3(OH)_2$] [9,12]. Total metal concentrations at relic copper mining and smelting sites has revealed that these sites are significantly contaminated [11]. Copper is one of the major contaminants detected in the soils reaching hundreds and sometimes even thousands of mg kg^{-1} levels. The concentrations up to 4,500 mg kg^{-1} copper have been found in the soil samples near a relic mining center dating from 3000 to 1800 BC in Jordan [9].

Basic problem in this connection exposure of humans to heavy metals in the mining areas who suffer from ingestion or inhalation of contaminated particles together with consumption of cultivated crops grown on the soils in such areas [7,14,15]. There is also direct deposition of contaminants onto plant surfaces used as food or fodder [5,7]. Many investigators have published results on the carcinogenic and non-carcinogenic impacts related to the human health risks by consumption of heavy metal-contaminated crops grown on such areas [5,7]. Major intake or ingestion of heavy metals occurs through crop plants cultivated on mine contaminated sites which make their way into the food chain [16-19].

The proper management of tailings can prevent or mitigate the risks in the functioning of ecosystems and human health originating from heavy metal contaminations [5-7,20]. Phytomanagement is cost effective and environmentally friendly technique suitable for decreasing the environmental risks from metal(loid) enriched mine tailings [6,21,22]. Several plants plants are used for the phytomanagement, as these show several edaphic constrains interferring with plant growth including heavy metal toxicity [20,23,24]. Native plant species are preferred because these are adapted not only to the contamination of tailings but also to the local climatic conditions [5,25-28].

Major actively operated copper deposits in Turkey are present in the Black Sea and South-eastern Anatolian regions. The copper is produced from pits in Kure and Murgul and then enriched at the flotation facilities to produce copper concentrates [29].

Significant heavy metal concentrations have been detected around the copper mine areas where dispersion of copper, lead and zinc has occurred downstream the mine workings, affecting waters, soils and vegetation. Metal concentrations in the soils around these mines depict the long working life of the mines [8,9,30]. Generally abandoned mine tailings are left without any proper management, and therefore are unstable and prone to wind and water erosion, as well as to acid mine drainage [31-33]. The tailings pose serious environmental threats affecting water courses, soils and natural ecosystems, ultimately posing serious risk for human health [20,22,24]. A sustainable management is very important [5].

In the light of these observations our major aim during this study was to evaluate the status of heavy metal levels in the soils and their possible uptake by the plants in the Murgul area which is highly rich in biodiversity and one of the important hotspots in the world.

2 Study Site

Murgul copper mine area is located in eastern Black Sea region of Turkey (Fig. 1). This area receives a high rainfall in the country. Murgul copper smelter is situated on the foothills of a deep and very narrow valley near Murgul town, located between latitudes 41° 09´-41° 18´ N and longtides 41° 25´-41° 38´ E. Murgul is surrounded by high mountains with a single opening in the NE direction. There is a stream receiving the domestic and industrial effluents of the area. The climate is mild subtropical arid, average annual temperature being 13.7°C and annual prepitation 1190 mm. The prevailing wind direction is NW. Soil cover in the area has soils mainly derived from albite-dacite and acidic volcanic tuffs, which belong to the group of spodosol with great variability in texture and organic matter contents [34-36].

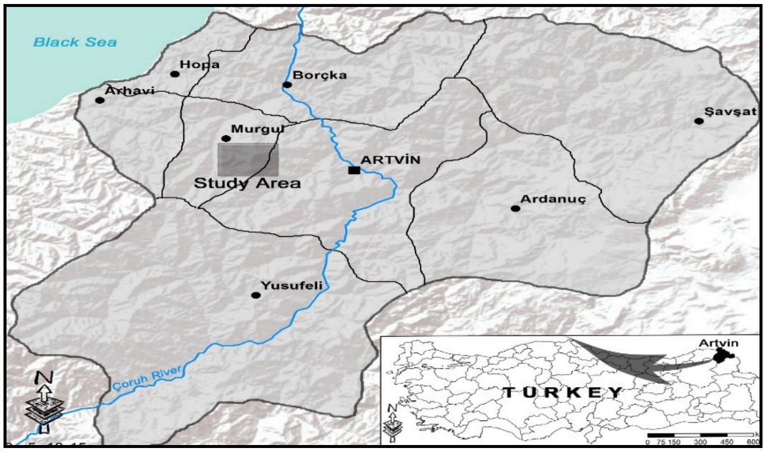

Figure 1: Map showing the location of Murgul area and its environs in Turkey

The history of copper mining dates back to 600 years from today. It was operated by a different firms during 1907-1914. Turkish Etibank Murgul Copper Works has been responsible for its operations from 1951 until its privatization in 2004. Annual ore production is approximately 3 million tonnes, with a copper ratio of 1.31 percent and annual copper concentrate production is around 210.000 tons, 17 percent of this is copper [35,36].

The eastern Black Sea region is a metallogenic belt nearly 5.000 km long, extending from Balkans to the Himalayas. It is a large ore province with most important copper, lead and zinc deposits in Turkey. The host rocks contain high concentrations of various ore elements [37-41]. Largest deposits are found in the Artvin Province at Murgul copper mine area with more than 100 MT of ore production [42-47]. The area has abundant many late cretaceous felsic volcanic and subvolcanic rocksare. The oldest rocks in this area are basalts and its pyroclastics. The rocksare is overlain by footwall dacite and its pyroclastics contain VMS deposits. These are the hanging-wall acidic rocks found on top of footwall rocks. These rocks are overlain by Late Cretaceous andesite, interbedded with sedimentary rocks, followed by tertiary andesite and pyroclastic rocks [48].

3 SO_2-Induced Environmental Problems Around Murgul

Copper, Iron, Zinc and Manganese are the main metallic contaminants of Murgul area. These originate from smelting of sulphide ores chalcopyrite ($CuFeS_2$) and pyrite (FeS). It has also been reported that concentrated copper contains arsenic 600 mg kg^{-1}, bismuth 70 mg kg^{-1}, cadmium 300 mg kg^{-1}, silver 785 mg kg^{-1}, gold 12 mg kg^{-1}, nickle 300 mg kg^{-1}, selenium 200 mg kg^{-1}, lead 3400 mg kg^{-1}, and antimony 60 mg kg^{-1} [35]. The sulphuric acid factory was built here in 1956, to avoid the harmful effects of sulphur on the surroundings. It was not operated till 1963, however, operation took place during 1963-1975. New sulphuric acid factory was established in 1986 which worked until 1994, with about 30-40 percent efficiency. From 1951 to 1978 total amount of SO_2 produced at the copper smelter has been estimated as 795.431 tons. From 1994 onwards smelter was closed and only concentrated copper was produced, which was transported to Samsun Smelter via Hopa Port [35]. Murgul Copper Factory was privatized in 2004 under the name Eti-Bakır who run three open pit mines. They excavate about 2.7 million tons of copper ore containing about 1 percent copper. In all 75.000 tons of concentrated copper is produced. The company has constructed new dams to collect mining wastes for conservation of environment and a large number of saplings have been planted [35]. During the last 6 decades several studies have been carried out on the environmental problems related to SO_2 emissons of Murgul Copper Factory notable among these bing; Çetik [34] and Oruç [35].

3.1 Potential Effects of SO_2 on Natural Plant Cover

Murgul copper mine area is lush green with a densely populated forests and is the best among the Turkish woodlands. These forest are dominated by *Fagus orientalis, Picea orientalis*, and *Pinus sylvestris*. These are mostly located outside the sulphur dioxide effected area. First study on these forests has been carried out by Çetik [34] with emphasis on forest trees away from the factory and those effected by sulphur dioxide lying closer to the factory to see the changes in the vegetation (Tab. 1) [34].

Table 1: SO_2 effects on the natural plant diversity of Murgul area

Plant species	*Localities											
	1	2	3	4	5	6	7	8	9	10	11	12
Trees												
Fagus orientalis	+	+	+		+			+				
Acer colchicum		+	+					+		+	+	
Picea orientalis		+	+					+			+	
Quercus petraea			+								+	
Pinus sylvestris				+							+	
Populus tremula								+			+	
Shrubs												
Rhododendron ponticum	+	+	+		+			+			+	+
Cornus australis		+	+				+	+	+	+		+
Rhododendron luteum		+						+		+	+	+
Smilax excelsa			+	+			+			+		+
Rubus caucasicus		+	+					+				
Vaccinium arctostaphylos								+			+	
Hedera helix										+	+	
Herbs												
Phytolacca americana	+		+	+		+	+		+	+		+
Poa annua	+		+		+			+		+		
Setaria viridis						+	+		+	+		+
Physalis alkekengi	+		+						+	+		
Trifolium repens	+				+	+		+				
Pteridium aquilinum						+			+		+	+
Polygonum bellardii						+			+	+		+
Potentilla reptans	+					+		+				
Urtica dioica	+		+							+		
Calamintha grandiflora	+		+					+				
Plantago major	+					+		+				
Sambucus ebulus			+			+				+		
Convolvulus arvensis			+		+							+
Polygonum convolvulus			+					+		+		
Veronica anagalloides	+		+									
Prunella vulgaris	+							+				
Holcus lanatus			+		+							
Bellis perennis						+		+				
Plantago lanceolata						+		+				
Lolium perenne						+						+
Euphorbia peploides									+	+		

Species with single locality: *Corylus avellana* (1+); *Sambucus nigra* (1+); *Salvia glutinosa* (1+); *Paris incompleta* (1+); *Lapsana communis* (1+); *Polygonum lapathifolium* (1+); *Epilobium hirsutum* (1+); *Festuca* sp. (2+); *Campanula rapunculoides* (3+); *Trifolium pratense* (5+); *Vicia cracca* (5+); *Centaurium erythraea* (5+); *Lotus corniculatus* (5+); *Centaurea jacea* (5+); *Echium vulgare* (6+); *Taraxacum officinale* (6+); *Trifolium arvense* (6+); *Cynoglossum officinale* (6+); *Arctium lappa* (6+); *Circaea lutetiana* (6+); *Medicago lupulina* (6+); *Cynodon dactylon* (7+); *Ilex aquifolia* (8+); *Pyrus communis* (8+); *Fragaria vesca* (8+); *Calystegia sepium* (8+); *Lysimachia verticillaris* (8+); *Hypericum perforatum* (8+); *Sedum hispanicum* (9+); *Anagallis arvensis* (9+); *Castanea sativa* (11+); and *Pyracantha coccinea* (12+).

***Localities**: **1**: The North exposed slopes of the valley; **2**: Skalga village; **3**: The areas below 750 m and the North exposed slopes of Skalga village; **4**: Around the Murgul stream; **5**: The muncipalities of Damar and Maden in the east-west direction of Murgul; **6**: Damar muncipality; **7**: Zansu village; **8**: Around the Petek ranges; **9**: The area between Petek village and copper factory; **10**: Above the Petek village hospital road; **11**: The Durca and Erenköy villages; **12**: Around the Arduç and the factory in Murgul.

3.2 Effects on Fruit Trees

Juglans regia (walnut), *Corylus avellana* (hazelnut), *Castanea sativa* (chestnut), *Prunus avium* (chery) and *Prunus persica* (peach) trees have suffered much in this area as per the report published in the early days by Karaca [49]. SO_2 emissions at Göktaş, Damar, Petek and Kabaca villages; located close to the smelter; has caused great damage to the fruits. Nearly 4000 pear, 2500 cherry, 1500 plums, 700 apple, 450 walnut trees have been destroyed fully in the Petek Village, the most heavily effected from the emissions. The atmosferic SO_2 concentrations higher than 2 mg kg^{-1} are in general recorded as harmful for vegetation [35].

According to Çıtır [50] nearly 80 to 120 tons of SO_2 is emitted by the Murgul Smelter, daily. Inspite of this mulberry and corn have been recorded as almost resistant plant taxa in the face of SO_2 damages. There are necrotic bleached areas, brown or black lesions, spots and blotches visible on the leaves of apple, pear, quince, grape, vine and rose plants in the less affected areas.

3.3 Effects on Forest Trees

Following the operation of Murgul Copper Factory 41 tonnes of sulphur were burnt daily at the smelter and SO_2 emissions affected the environment in the North and South upto 6250 and 9500 meters in the vicinity of factory respectively [51].

False-Color Aerial Photography Technique was used by Eren [52] to study the the effects of sulphur dioxide emitted by the Goktas (Murgul) Copper Establishment on the forests in the vicinity of factory. In all 5428.5 ha were affected. The areas were classified into four groups; most heavily (1099.9 ha), heavily (737.9 ha), less heavily (752.1 ha) and lesser heavily (2838.9 ha) affected. The study has revealed that hazardous effects of SO_2 decreased with the distance from the copper smelter and increase in elevation of terrain. Sulphur contents in the needles collected from control and lesser affected sites were around 0.12-14 and 34-37 percent respectively. SO_2 emitted as 80-100 tons/day from the smelter destroyed nearly 9.000 hectares of 18-20 km long forested area at the height between 400-900 m in the narrow Murgul Basin [53]. Nearly 68000 m^3 of wood production was lost with the effects from stack gases. According to Oruç [35] pH values of the surface soil samples collected from the heavily affected and control sites has shown that it was lower but SO_4 contents were higher in heavily affected sites than control ones.

In 1988 Nuhoğlu and Çanakçıoğlu [54] have reported that more than 900 thousand tons of SO_2 were released to the atmosphere during the period covering 1951 to 1988. As a result of this 1800 hectares of forest area was destroyed and nearly 4000 hectares showed various degrees of destruction. The agricultural lands of 13 villages were badly affected and factory was compelled to pay compensation for their yield losses, totaling upto more than 500 million TL till 1985. Some of the severely effected agricultural lands were purchased by the factory [35,54].

3.4 Effects on Soils

Heavy emissions of SO_2 (80-100 tons/day) effected the surface soils around the smelter [55,56]. The emissions lead to a decrease in the pH value, organic matter content and total microbial activity of polluted soils around the smelter, whereas the SO_4 contents and S-oxidising microorganism counts in the soils were higher compared to the control sites.

Both the soil acidity and SO_4 levels increased with the proximity to the smelter. Organic matter content of the soils decreased in areas close to the smelter. pH values of surface soil samples outside the study area ranged from 5.1 to 5.9 but those collected near the smelter ranged from 4.1 to 5.5. The mean weight diameters of aggregates of soil samples collected near the smelter were lower than those collected from control sites. The aggregate stability of soils was weak due to loss of vegetation. pH values of rain samples in the vicinity of smelter ranged from 3.8 to 5.0, and those collected from 3 and 5 kilometers away from the smelter varied between 4.8 to 5.5 and 5.5 to 6.4 respectively [35]. Atmospheric fallout from ore smelters contributes significantly towards soil contamination with heavy metals which adversely effect the vegetation as well as human health via food chain [57].

The contamination of soils due to copper, iron, zinc and manganese in the surface soils coming from the smelter fallout appear to be centered within 1-3 km of the polluting source. The metal contents in surface layer decrease with increasing distance from the smelter in general. Many investigators have reported similar results on the impacts of heavy metals on environment, emitted by copper smelters [35,58,59].

4 Evaluation of Potential Effects of Environmental Pollution on Plants and Soils Near the Murgul Copper Mine

The species diversity of Murgul Copper factory area has suffered a lot during its operation covering 42 years. An attempt was made to investigate the status of trace elements like Al^{3+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} and Cd^{2+} in soils and plants by atomic absorption spectrophotometry. The collection sites were in the vicinity of the factory at altitudes of 500 and 600 m, 1000 m around the ore extraction site and at 1400 m altitude in the forest zone respectively. The aboveground herbaceous parts and foliage ash of some plant taxa like; *Silene compacta, Tussilago farfara, Smilax excelsa, Rhododendron ponticum, R. luteum,* and *Herbaceous mix* were investigated for the said elements. Species showed considerable differences in their ability to accumulate or exclude the various elements (Tab. 2).

The results of analysis have revealed the minimum and maximum concentrations measured in the plants as follows; aluminium (20-8985 mg kg^{-1}), cadmium (0.0-0.5 mg kg^{-1}), cobalt (0.0-5.5 mg kg^{-1}), copper (0.0-347.5 mg kg^{-1}), iron (25-9320 mg kg^{-1}), lead (2-51 mg kg^{-1}), nickel (1.5-16.5 mg kg^{-1}), and zinc (13.0-221.0 mg kg^{-1}). In the soil the concentrations of aluminium, cadmium, cobalt, copper, iron, lead, nickel, and zinc vary between 33-457, 0.0-0.0, 0.0-0.4, 0.1-88.7, 14-50, 0.3-4.1, 0.2-0.8, and 4.0-20.3 mg kg^{-1} respectively (Tab. 2).

Silene compacta, Tussilago farfara, Smilax excelsa, Rhododendron ponticum, Rhododendron luteum, and *Herbaceous mix* taxa were studied to compare these elements easily in the research area (Tab. 2 and Figs. 2-6). These plants showed considerable differences in their ability to accumulate or exclude various elements. The concentration values of trace elements vary between the species and even in the same species at different sites. An evaluation of the results from different altitudes has revealed that; concentrations of copper are variable, ranging widely from 0.0 to 347.5 mg kg^{-1} in plant samples. The highest is found in *Silene compacta* (125.5 mg kg^{-1} at 500 m, and 347.5 mg kg^{-1} at 600 m), *Tussilago farfara* (97.0 mg kg^{-1} at 1000 m), and *Herbaceous mix* (71.5 mg kg^{-1} at 1400 m) (Fig. 2).

The concentrations of nickel are variable, ranging widely from 1.5 to 16.5 mg kg^{-1} in plant samples. The highest is found in *Silene compacta* (16.5 mg kg^{-1} at 500 m, and 9.0 mg kg^{-1} at 600 m), *Quercus petraea* (bark) (12.0 mg kg^{-1} at 1000 m), and *Herbaceous mix* (16.5 mg kg^{-1} at 1400 m) (Tab. 2 and Fig. 3).

The concentrations of lead are variable, ranging widely from 2.0 to 51.0 mg kg^{-1} in plant samples. The highest is found in *Silene compacta* (46.0 mg kg^{-1} at 500 m), *Smilax excelsa* (24.0 mg kg^{-1} at 600 m), *Quercus petraea* (bark) (47.0 mg kg^{-1} at 1000 m), and *Picea orientalis* (bark) (51.0 mg kg^{-1} at 1400 m) (Tab. 2 and Fig. 4).

The concentrations of zinc vary ranging between 13.0 to 221.0 mg kg^{-1} in plant samples; highest found in *Silene compacta* (221.0 mg kg^{-1} at 500 m, and 210.0 mg kg^{-1} at 600 m), *Tussilago farfara* (108.0 mg kg^{-1} at 1000 m), and Herbaceous mix (179.0 mg kg^{-1} at 1400 m) (Fig. 5).

The concentrations of aluminium are variable, ranging widely from 20 to 8985 mg kg^{-1} in plant samples. The highest is found in *Silene compacta* (8985 mg kg^{-1} at 500 m, and 3715 mg kg^{-1} at 600 m), and Herbaceous mix (5415 mg kg^{-1} at 1000 m, and 7285 mg kg^{-1} at 1400 m) (Fig. 6).

Table 2: Concentrations of some major and trace elements in plant and soil samples in the study area

Localities/Plants-Soils	N	P	K	Ca	Mg	Fe	Cd	Zn	Pb	Cu	Co	Ni	Al
		(%)							(mg kg^{-1})				
500 m													
Silene compacta	1.24	0.24	2.60	1.00	0.48	9320	0.5	221.0	46.0	125.5	5.5	16.5	8985
Smilax excelsa	1.54	0.11	1.50	0.78	0.12	415	0.0	33.0	21.0	14.5	1.0	4.5	445
Tussilago farfara	0.97	0.26	3.70	1.99	0.46	1810	1.0	116.0	30.0	29.0	3.0	13.5	1815
Rhododendron ponticum	0.63	0.09	1.00	1.53	0.18	165	0.0	21.0	13.0	11.5	0.5	6.5	135
Herbaceous mix (*Equisetum arvense, Sedum pallidum, Dorycnium pentaphyllum*)	1.75	0.08	0.90	0.89	0.31	4565	0.0	83.0	9.0	43.5	1.5	8.5	3805
Soils	0.00	0.00	0.11	0.02	0.01	50	0.0	20.3	4.1	88.7	0.1	0.3	457
600 m													
Silene compacta	1.09	0.10	2.30	1.34	0.53	5570	0.0	210.0	16.0	347.5	4.5	9.0	3715
Smilax excelsa	1.65	0.12	1.60	0.95	0.09	590	0.0	94.0	24.0	143.5	1.0	7.0	375
Rhododendron ponticum	0.83	0.10	1.20	1.10	0.27	290	0.0	50.0	14.0	54.5	1.0	8.0	365
Rhododendron luteum	1.15	0.22	1.10	0.58	0.43	250	0.0	37.0	5.0	27.5	1.0	6.5	295
Alnus glutinosa	2.82	0.19	0.60	1.14	0.38	465	0.0	62.0	14.0	47.0	1.5	6.5	405
Herbaceous mix (*Equisetum arvense, Phytolacca america, Dorycnium pentaphyllum*)	2.47	0.25	2.00	0.94	0.46	435	0.0	149.0	9.0	88.0	0.0	5.0	630
Soils	0.00	0.00	0.07	0.00	0.02	16	0.0	15.8	3.7	8.8	0.4	0.2	67
1000 m													
Smilax excelsa	1.93	0.19	1.70	1.01	0.14	205	0.0	39.0	17.0	14.0	1.0	5.0	305
Tussilago farfara	1.87	0.21	3.30	1.99	0.65	3680	0.5	108.0	16.0	97.0	3.0	8.5	3715
Rhododendron ponticum	1.13	0.05	0.30	0.38	0.06	25	0.0	13.0	2.0	0.0	0.0	1.5	20
Rhododendron luteum	1.49	0.29	1.50	0.56	0.32	240	0.0	34.0	8.0	17.0	2.0	4.0	285
Acer cappadocicum	3.25	0.23	1.70	1.30	0.29	215	0.0	29.0	14.0	14.5	0.5	4.5	220
Quercus petraea (shoot)	2.04	0.21	1.10	1.44	0.28	290	0.0	40.0	11.0	15.0	1.0	7.0	415
Quercus petraea (Bark)	0.52	0.08	0.30	1.95	0.06	475	0.0	22.0	47.0	35.0	1.5	12.0	410
Herbaceous mix (*Sedum pallidum, Valeriana alliriifolia, Trifolium pratense, Dorycnium pentaphyllum*)	2.28	0.18	1.80	1.47	0.49	5665	0.0	88.0	34.0	62.0	3.0	6.5	5415
Soils	0.00	0.00	0.14	0.01	0.01	14	0.0	7.4	1.5	16.9	0.0	0.6	33
1400 m													
Rhododendron ponticum	1.01	0.07	1.00	0.90	0.21	85	0.0	24.0	6.0	7.5	0.0	4.5	235
Laurocerasus officinalis	2.03	0.12	0.90	1.47	0.23	100	0.0	54.0	21.0	8.5	1.0	5.5	270
Picea orientalis (shoot)	1.34	0.10	0.50	1.05	0.06	295	0.0	36.0	15.0	18.5	0.0	7.0	590
Picea orientalis (bark)	0.48	0.02	0.50	0.69	0.04	150	0.0	39.0	51.0	10.5	1.0	15.5	225
Carpinus betulus	2.92	0.14	1.30	0.90	0.23	310	0.0	110.0	12.0	35.0	1.5	9.0	520
Herbaceous mix (*Trifolium pratense, Fragaria vesca, Alchemilla* sp.)	2.24	0.18	1.80	1.02	0.33	5215	0.5	179.0	19.0	71.5	3.5	16.5	7285
Soils	0.00	0.00	0.11	0.00	0.00	49	0.0	4.0	0.3	0.1	0.0	0.8	449

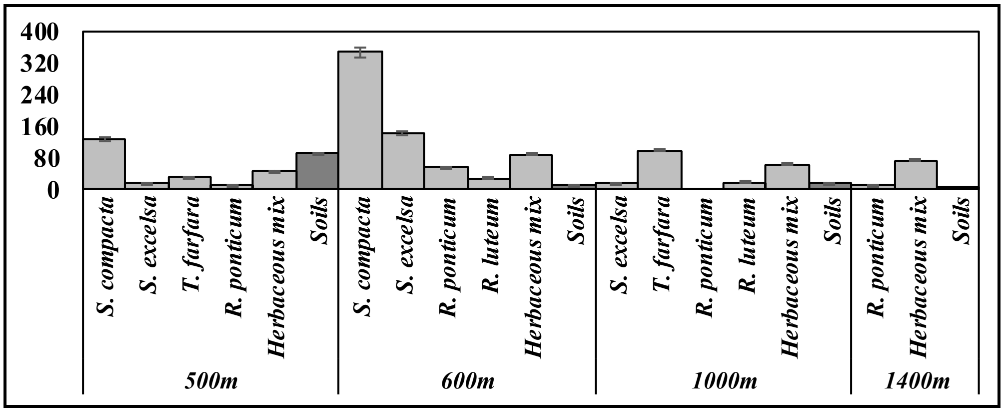

Figure 2: Cu concentrations in plant and soil samples (mg kg^{-1}) in the study area

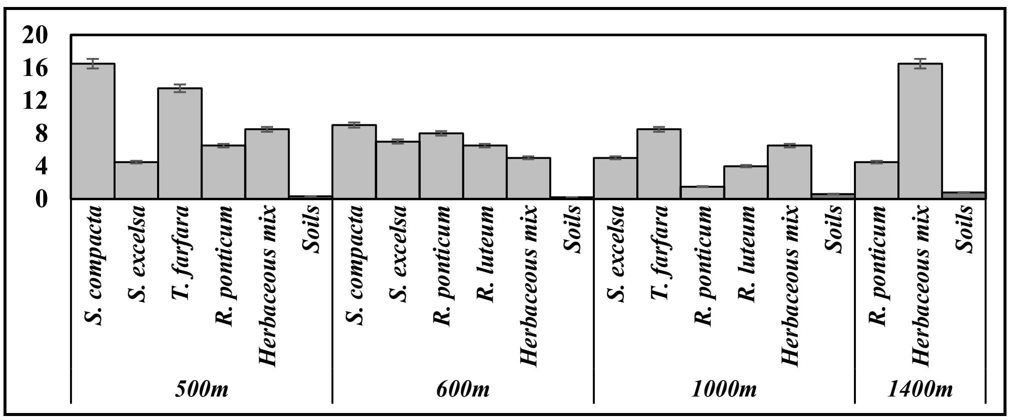

Figure 3: Ni concentrations in plant and soil samples (mg kg^{-1}) in the study area

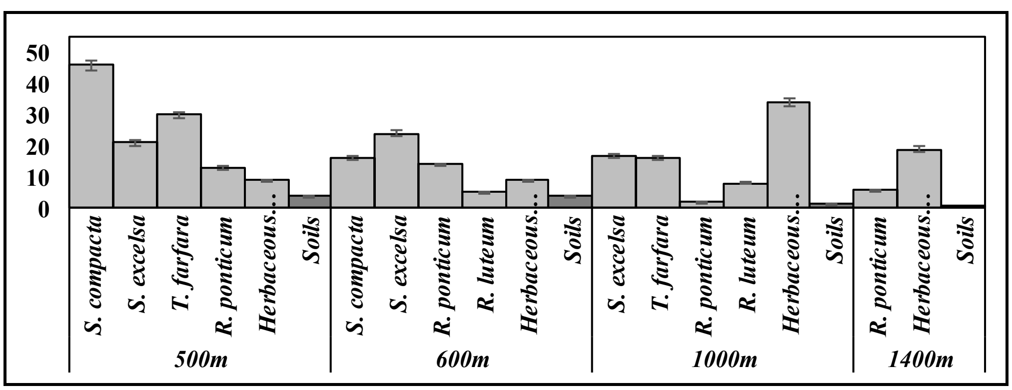

Figure 4: Pb concentrations in plant and soil samples (mg kg^{-1}) in the study area

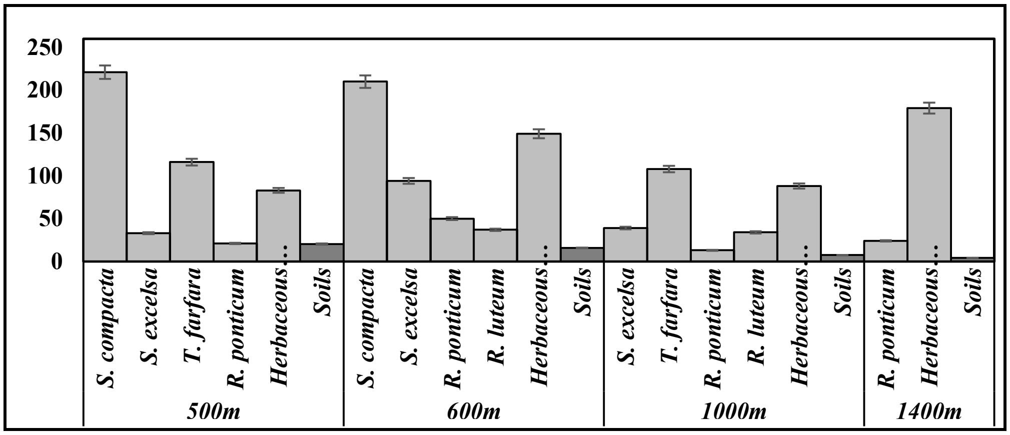

Figure 5: Zn concentrations in plant and soil samples (mg kg^{-1}) in the study area

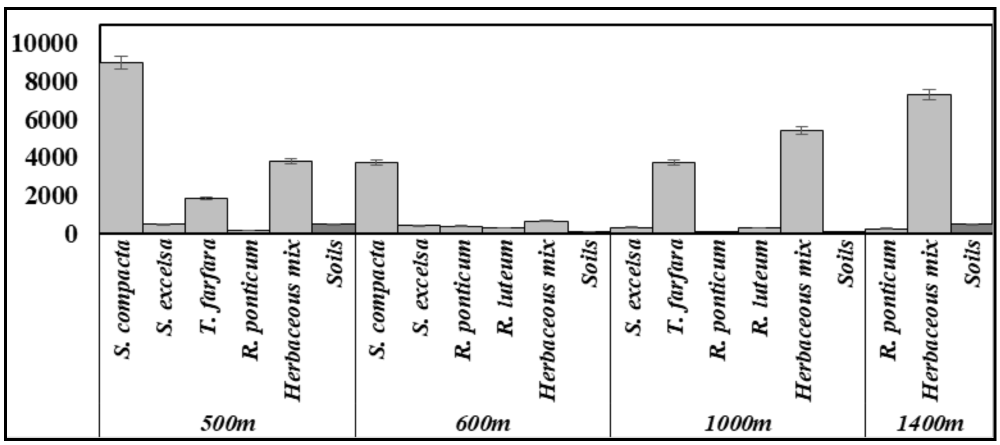

Figure 6: Aluminium concentrations in plant and soil samples (mg kg^{-1}) in the study area

The concentrations of cadmium are variable, ranging between 0.0 to 1.0 mg kg^{-1} in plant samples; highest is found in *Silene compacta* (0.5 mg kg^{-1} at 500 m), *Tussilago farfara* (1.0 mg kg^{-1} at 500 m, and 0.5 mg kg^{-1} at 1000 m), and herbal mix (0.5 mg kg^{-1} at 1400 m). Except for these plants, no traces of cadmium were detected in other samples (Tab. 1). The concentrations of cobalt are variable, ranging widely from 0.0 to 5.5 mg kg^{-1} in plant samples. The highest is found in *Silene compacta* (5.5 mg kg^{-1} at 500 m, and 4.5 mg kg^{-1} at 600 m), *Tussilago farfara* (3.0 mg kg^{-1} at 1000 m), and herbal mix (3.0 mg kg^{-1} at 1000 m, and 3.5 mg kg^{-1} at 1400 m) (Tab. 2). The concentrations of iron vary, ranging widely from 25 to 9320 mg kg^{-1} in plant samples. The highest is found in *Silene compacta* (9320 mg kg^{-1} at 500 m, and 5570 mg kg^{-1} at 600 m), and herbal mix (5665 mg kg^{-1} at 1000 m, and 5215 mg kg^{-1} at 1400 m) (Tab. 2).

Much data is avilable on phytotoxicity of metals and their critical toxicity levels in terrestrial plants. These are in general given as 6-10 mg kg^{-1} dw cadmium; 20-30 mg kg^{-1} dw copper; 10-50 mg kg^{-1} dw nickle; 10-30 mg kg^{-1} dw lead; 40-500 mg kg^{-1} dw aluminyum; > 100 mg kg^{-1} dw zinc; > 0.5 mg kg^{-1} dw cobalt; and > 300-500 mg kg^{-1} dw iron [60-66]. Phytotoxic concentrations of metals in soils are given as 3-8 mg kg^{-1} dw cadmium; 60-125 mg kg^{-1} dw copper; 20-100 mg kg^{-1} dw nickle; 100-400 mg kg^{-1} dw lead; > 10000-40000 mg kg^{-1} dw aluminiyum; > 200 mg kg^{-1} dw zinc; >10 mg kg^{-1} dw cobalt; and > 500-1000 mg kg^{-1} dw iron [61-69].

The values of cobalt, copper, nickle and lead in all plants are above normal values, but copper is found at toxic levels in all plants. The values of copper, cobalt, nickle, lead, zinc, aluminyum and iron in *Silene compacta* and *Herbaceous mix* are toxic. In the case of *Tussilago farfara* available cobalt, copper, nickle, lead, aluminyum and iron values are toxic. The values of cobalt, copper lead and iron are toxic in *Smilax excelsa* as well. *Rhododendron ponticum* shows toxic levels of copper and lead whereas in *Rhododendron luteum* and cobalt and copper values are toxic (Tab. 2 and Figs. 2-6).

Highly acidic pH in the tailing ponds results in the release of trace metals, entering underground waters, surface waters, seawater and nearby-lands. The area has an intense sulphur-like odor. Moreover, the winds carry the dust clouds from the tailing ponds creating environmental pollution rich in trace metals and sulphur [70,71].

The single most important factor affecting trace element availability is soil pH. For cationic species, lower pH values result in higher mobility and thus availability [72-76], while the opposite is true for anionic species [76,77]. Epstein [60] has reported that aluminyum is usually toxic to plants in acid soils. pH vlaues of many soil samples were recorded during this study and these varied between 4.13-7.64, depicting that the area is still showing acidic character (Tab. 3).

According to Sağlam and Akçay [47] sulphate has the highest levels in open pit lakes. It dilutes with distance from the mining site, is very mobile anion and usually shows long dispersion. The sulphate values in the vicinity of Murgul are diluted to background levels within a few hundred metres from the source of pollution. High sulphate values are obtained near the open pit lakes and in flotation discharge fluid. Major source of sulphate enrichment come from the Damar creek as a result of millions of tons of waste dumped into it [47]. Variability of SO_4 concentrations detected in different localities in the study area coincide with the data of Sağlam and Akçay [47] (Tab. 3).

The deposits of copper, lead, zinc and manganese are rich in the Murgul area the State of Artvin [36,47]. The wastes from mine have lead to an increase in the copper and iron concentrations in the area [47]. Impact of Murgul mine in the form of sediments contaminated by waste powder and tailings continues and reaches upto Çoruh River (especially copper, lead, zinc, iron) [47]. These authors have reported that iron minerals like ferrihydrite, schwertmannite, goethite and hematite are very common in the sampled drainages around the Murgul copper mine. According to these workers oxyhydroxides and oxyhydroxysulphates of aluminium, such as jurbanite, alunite, basaluminite, gibbsite and amorphous oxyhydroxides are the ochreous precipitates [47]. Absorption of other elements like cobalt and nickle into the plant varies depending on plant species, soil pH, the form and concentration, and availability of different metals [78]. Very recently increase in population has lead to an increase in the urbanization in the area and as a result of this anthropogenic activities like highway construction and domestic wastes have contributed to the increase in lead concentration [36,47,79]. This stresses the fact that lead pollution is not from the mine but from the anthropogenic activities.

Prasad and Freitas [80], Prasad [81], and Baycu et al. [65] report that native metallophytes, fast-growing and metal-tolerant accumulators or hyperaccumulator plant taxa show great potential for *in-situ* remediation of abandoned mining sites. Hyperaccumulators are the plants which can accumulate more than 100 mg kg^{-1} cadmium; 300-1,000 mg kg^{-1} copper, chromium, cobalt; 1,000 mg kg^{-1} nickle, lead, arsenic; 3,000-10,000 mg kg^{-1} zinc and more than 10,000 mg kg^{-1} manganese in dry foliage while growing in their natural habitats [62,63,65,82]. In our findings *Silene compacta* was found as high copper accumulator, behaving as a healthy plant on the polluted sites of the area alongside the Murgul creek (especially at 600 m) (Tab. 2 and Fig. 2).

All calculations were based on parameters of plant species and soil samples. Pearson's correlation statistical analyses was performed using IBM SPSS Statistics 20 software [83]. The levels of statistical significance were expressed as ** $p < 0.01$ level. The correlation coefficients between the element values determined in the plant species and soil samples at different altitudes examined (Tab. 4) have shown that positive correlation exists between nitrogen and availability of phosphorus as well as magnesium (> 0.52, > 0.68). High positive correlations are found between phosphorus and availability of potassium, calcium, and magnesium elements (> 0.53, > 0.75); between potassium and availability of calcium, magnesium, iron, cadmium, zinc, cobalt, nickle, and aluminium (> 0.51, > 0.80); between calcium and availability of magnesium, lead and nickle (> 0.52, > 0.58); between magnesium and availability of iron, zinc, cobalt and aluminium (> 0.57, > 0.70); between iron and availability of zinc, copper, cobalt, nickle, and aluminum (> 0.57, > 0.97); between cadmium and availability of zinc, cobalt, nickle and aluminium (> 0.52, > 0.60); zinc and availability of copper, cobalt, nickle, and aluminium (> 0.64, > 0.82); lead and availability of cobalt and nickle (> 0.53, > 0.77); between the availability of copper and cobalt (> 0.61); between availability of nickle and aluminiyum (> 0.61); and finally between availability of cobalt and nickle and aluminum (> 0.70, > 0.85).

Table 3: Some physical and chemical parameters in soil samples of different localities in the study area

Location Number	Soil type	pH	EC (mmhos/cm)	$CaCO_3$ (%)	Organic matter (%)	Total N (%)	P_2O_5 (%)	SO_4 (mg kg^{-1})
1	Humus	5.57	0.06	0.00	48.98	2.25	108	60.0
2	Sandy loam	6.51	0.50	0.00	19.29	0.96	116	52.8
3	Sandy loam	6.60	0.32	0.00	8.99	0.45	68	23.0
4	Loamy	6.13	0.20	0.00	2.05	0.10	44	18.0
5	Sandy loam	4.39	0.25	0.00	6.98	0.35	65	60.0
6	Sandy loam	4.73	0.26	0.00	2.76	0.14	54	60.6
7	Sandy loam	4.89	0.23	0.00	1.44	0.07	39	51.6
8	Sandy loam	4.88	0.20	0.00	0.32	0.02	14	48.6
9	Sandy	4.13	0.34	0.00	9.21	0.46	70	102.0
10	Sandy loam	4.46	0.25	0.00	2.01	0.10	53	47.4
11	Sandy loam	4.64	0.25	0.00	1.24	0.06	28	66.0
12	Sandy loam	4.66	0.24	0.00	0.74	0.04	21	66.0
13	Sandy loam	4.58	0.32	0.00	7.28	0.36	62	102.0
14	Sandy loam	4.95	0.25	0.00	4.18	0.21	45	78.0
15	Sandy loam	5.72	0.25	0.00	3.64	0.18	28	70.2
16	Sandy clay	6.34	0.25	0.00	2.12	0.11	17	58.8
17	Sandy loam	7.03	0.36	0.00	2.08	0.10	45	64.5
18	Sandy loam	7.22	0.36	0.00	3.51	0.18	33	45.0
19	Sandy clay	7.42	0.24	0.00	2.48	0.12	31	30.0
20	Clay loam	7.64	0.26	0.00	9.79	0.49	24	27.0
21	Clayey	5.40	0.20	0.00	6.72	0.34	55	24.6
22	Clayey	5.37	0.20	0.00	3.07	0.15	43	16.2
23	Clayey	5.39	0.19	0.00	2.51	0.13	26	21.6
24	Clayey	5.38	0.18	0.00	2.00	0.10	22	16.2
25	Sandy loam	4.45	0.20	0.00	4.76	0.24	40	43.8
26	Sandy loam	4.57	0.22	0.00	5.49	0.28	40	36.6
27	Sandy clay	5.68	0.18	0.00	2.19	0.11	24	37.5
28	Sandy loam	6.06	0.19	0.00	1.34	0.07	19	38.4
29	Clay loam	4.36	0.23	0.00	6.22	0.31	45	174.0
30	Clay loam	4.74	0.41	0.00	4.29	0.21	40	147.0
31	Loamy	4.98	0.44	0.00	1.66	0.08	30	150.0
32	Loamy	5.19	0.35	1.46	0.64	0.03	31	115.5
33	Sandy loam	4.27	0.34	0.74	8.04	0.40	59	90.0
34	Sandy clay	5.47	0.31	0.74	2.27	0.11	45	75.0
35	Clay loam	6.18	0.33	1.11	1.19	0.06	28	55.8
36	Clay loam	6.90	0.28	0.00	0.99	0.05	18	53.7

Table 4: Pearson's correlation coefficients of major and trace elements in plant and soil samples in the study area

Correlation Matrix (R)	P	K	Ca	Mg	Fe	Cd	Zn	Pb	Cu	Co	Ni	Al
N	.676**	.411*	.436*	.516**	.166	.023	.358	.053	.048	.207	.205	.191
P		.734**	.525**	.751**	.296	.430*	.461*	.184	.097	.473**	.367	.315
K			.623**	.802**	.547**	.725**	.701**	.316	.422*	.694**	.505**	.524**
Ca				.576**	.286	.419*	.357	.520**	.195	.454*	.565**	.253
Mg					.618**	.476**	.695**	.155	.465*	.696**	.420*	.573**
Fe						.473**	.803**	.416*	.572**	.881**	.575**	.971**
Cd							.517**	.325	.113	.598**	.572**	.539**
Zn								.353	.729**	.822**	.644**	.783**
Pb									.151	.528**	.768**	.402*
Cu										.607**	.264	.455*
Co											.695**	.846**
Ni												.609**

*Correlation is significant at the 0.05 level (2-tailed); **Correlation is significant at the 0.01 level (2-tailed).

5 Conclusions

Currently our environment is facing increasing anthropogenic influences with polluting effects causing negative changes in natural ecosystems, simplifying the structure and lowering the productivity. All such degradative effects are especially visible to the naked eye in the forest ecosystems. Heavy metals originating from the mining areas are a dangerous group of anthropogenic pollutants. There is need to work towards continuous assessment and monitoring of their levels around the biodiversity hotspots. We need to evaluate plant exposures for the sake of a sustainable environment.

6 Future Prospects

This research has revealed that highest accumulation of heavy metals has been recorded in *Silene compacta*, the values being four to eleven times higher than normal values. Accumulation is found mainly at 500 m and 600 m because of their closeness to the mine area but also to the human dwellings.

Silene compacta may prove as a good candidate for bioremediation.

Lower values of investigated heavy metals in the soils is because of the uptake by plants.

The people living in the area must be careful while using plant products from the area on health grounds.

Effluents from the ore area should be monitored continuously.

Policy formulation is needed for the decontamination of the polluted soil and water at different levels.

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