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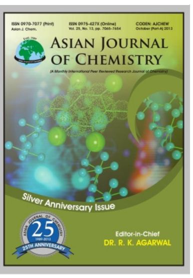

Environmental Impact Assessment of Mining Activities in the Vicinity of Madenköy (Nigde) Using Biogeochemical Modeling

TULIN GEDIK[1] and MUSTAFA AKYILDIZ[2,*]

[1]Mineral Research & Exploration General Directorate Department of Geology, Ankara 06800, Turkey
[2]Department of Geological Engineering, Faculty of Engineering & Architecture, Çukurova University, Adana 01330, Turkey

*Corresponding author: Fax: +90 322 3386715; Tel: +90 322 3387131; E-mail: akyildizm@cu.edu.tr; akyildizmst@gmail.com

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Detection, distribution and assessment of environmental impacts of covered mine ores uses biogeochemical methods in addition to geochemical methods. This study analyzed environmental effects of mineralization and mining activities on plants, using biogeochemical methods. The study also determined spatial distribution of biogeochemical parameters by modeling through geochemical and geostatistical methods. The study used *Astragalus* sp., *Berberis vulgaris, Colutea cilicia, Juniperus oxycedrus, Paliurus spina-christi, Pinus nigra, Rosa canina* plant species, which are abundant and widely distributed in the region. It was found that among plant species, branch of *Juniperus oxycedrus* were found to be indicators for Pb ($r = 0.7541$; $p = < 0.01$; $n = 15$) and branch of *Pinus nigra* were found to be indicators for Zn ($r = 0.79$; $p = < 0.01$; $n = 13$). Analyses showed that metal accumulation varied in each plant. It was observed that biologic absorption coefficients corresponded to strong absorption (BAC = 1-10) values in Zn and Pb elements.

Key Words: Biogeochemistry, Multi-element analysis, Indicator plants, Environmental impact, *Juniperus oxycedrus*, *Pinus nigra*.

INTRODUCTION

Bushes and trees with deep roots in the soil are affected from the heavy metal accumulation in the soil[1]. Tissues of plants that grow in this soil with high heavy metal concentration contain high ratios of those heavy metals. Heavy metal concentration in plants is used in biogeochemical studies[2-4]. This plant is termed as indicator plant and can be used as environmental monitor in mine prospection[5]. Indicator plants are living organisms that provide information about the quality of the environment they grow in.

A biogeochemical study can provide geochemical data on other surface materials, which are not found in substrate. Composition of plants reflects presence of an element near root system, plants' ability of absorption, delivery and accumulation of elements. The procedure in biogeochemical analyses provides dynamic nature of living plant that cause a variation in plant chemistry. In biogeochemical studies, indicator plants, particularly which collect some elements at high ratios, correspond to the concentrations of these elements in substrate[2,3,6-10].

Soil contaminated by these metals due to erosion and operation of ore level creates a direct health problem for the animals and humans living in that region. The animals that feed on the plants growing in these soils can store these poisonous elements in their bodies at high ratios. They can also transfer those elements to other living things, which consume milk and meat of these animals in their daily diet[1].

Madenköy (Nigde/Ulukisla) and its vicinity, which is rich in lead-zinc mineralization was called "Bulgarmaden" in ottoman period. Records of antique mining traces and slag masses which are thought to belong antiquity are found since 19. Century Pb-Zn-Cu-Au-Ag deposits in Bolkar Mountains are considered to be exploited by Hittites, Byzantium and Romans. In addition, it was reported that ore mined in other regions were brought and sheltered in Madenköy[11].

This study analyzed environmental effects of mineralization and mining activities in the region on plants using biogeochemical methods. The study aimed to analyze indicator plants for each element by identifying heavy metal (Al, Fe, Mn, Pb, Cu, Zn) contents in plant and soil based on abundant and widely distributed plant species (*Astragalus* sp., *Berberis vulgaris, Colutea cilicia, Juniperus oxycedrus, Paliurus spina-christi, Pinus nigra*, *Rosa canina)* and soil samples in the region[12]. This paper included biogeochemical behaviours of *Juniperus oxycedrus* and *Pinus nigra* plant species.

EXPERIMENTAL

A total of 83 abundant and widely distributed plant (*Astragalus* sp., *Berberis vulgaris, Colutea cilicia, Juniperus* *oxycedrus, Paliurus spina-christi, Pinus nigra, Rosa canina*) and soil specimens were collected from 39 stations field studies conducted in May and August. Plant specimens with the same age and height were collected to the possible extent. Plant specimens were washed with pure water and were dried. Soil specimens were sieved and made available for analysis.

Chemical and statistical analysis: Plants specimens were dried at 105 °C for 24 h; organic substances were removed and was reduced to ash at 500-550 °C for 8 h using the method developed by Campbell and Plank[13]. Soil and plant specimens were dissolved in aqua regia. Element concentrations were identified using Perkin-Elmer 700 model atomic absorption spectrophotometry (AAS) in the solutions. Obtained data were calculated as ppm in plant sections (ash) and soil. By modeling analysis results using geochemical and geostatistical methods, spatial distribution of biogeochemical parameters were determined.

Correlation coefficients (r) and biological absorption coefficients (BAC) were calculated to determine proximity degrees between element concentrations in soil and plants. Element concentrations in soil and plant were compared and chemical relationship between the soil and plant was calculated.

Biological absorption coefficients is defined as the intensity of absorption of chemical elements by plant substrates. According to Kovalevskii[14] biological absorption coefficient;

$$BAC = C_p / C_s$$

C_p = concentration of an element in plant ash; C_s = concentration of the same element in substrate.

While data obtained in biogeochemical prospection was assessed according to correlation coefficient, theoretical r values, which should depend on number of specimens and experimentally identified r values were compared. $r_{deneysel} > r_{teorik}$ should be reached within desired reliability limits[15].

RESULTS AND DISCUSSION

Metal concentration contained by soil and plants are related with formation of mine deposits in the region or anthropogenic effects. In Bolkar mountain zinc-lead deposits in the study area, principle minerals of primary ores are sfelarite, galenite and pyrite. These minerals are accompanied by minerals such as chalcopyrite, arsenopyrite, native silver, magnetite in small ratios[16]. The fact that Zn, Pb and Fe elements in soil specimens showed high concentrations in some stations in analyses is related with the presence of sfelarite, galenite and pyrite. The region is estimated to have potential ore reserve of 500,000 tons with 3 % Zn, 2.5 % Pb, 0.7 % Cu tenor[17].

Metal (Al, Cu, Fe, Mn, Zn, Pb) concentrations of *Juniperus oxycedrus* and *Pinus nigra* plant specimens growing in the vicinity of Madenköy, which is rich in Zn-Pb, are presented in Table-1. Varying absorption capacities and selectivity of the plants in the study in element intake caused differences in metal concentrations. In addition, element concentrations in various parts of same plant species also showed variations.

Correlation coefficients (r) biological absorption coefficients (BAC) calculated to determine proximity degrees between elements concentrations in soil and plants are presented in Table-2. Specimens outside of the population determined by statistical methods were neglected. Although plant specimens had a high capacity to store some elements there was an insignificant relationship between plants and soil.

TABLE-1
METAL (Al, Cu, Fe, Mn, Zn, Pb) CONCENTRATIONS OF *Juniperus oxycedrus* AND *Pinus nigra* PLANT SPECIES GROWING IN THE VICINITY OF MADENKÖY

Element		*Juniperus oxycedrus*				*Pinus nigra*			
		S	Min	Max	Average	S	Min	Max	Average
Al	Soil	18	5017	20911	12392	16	8000	40880	19361
	Leaf	18	2134	8636	5155	16	2874	12520	7062
	Branch	18	2907	9768	6392	16	3096	20791	11299
	Fruit	–	–	–	–	–	–	–	–
Fe	Soil	18	24955	103445	44936	16	24811	106049	45620
	Leaf	18	1910	7868	4295	16	2694	7825	5256
	Branch	18	2035	12955	5842	16	1867	19115	10739
	Fruit	14	417	2453	817	–	–	–	–
Mn	Soil	18	397	2602	934	16	519	2746	1033
	Leaf	18	466	2500	1063	16	313	3620	1709
	Branch	18	182	606	374	16	310	1732	934
	Fruit	15	222	1203	594	–	–	–	–
Cu	Soil	18	19	412	59	16	40	441	100
	Leaf	18	26	115	62	16	52	149	90
	Branch	18	50	133	86	16	82	201	127
	Fruit	15	56	157	92	–	–	–	–
Zn	Soil	18	71	1076	220	16	71	1106	290
	Leaf	18	120	306	194	16	299	1636	299
	Branch	18	130	314	189	16	540	2070	993
	Fruit	15	190	398	292	–	–	–	–
Pb	Soil	18	55	3540	380	16	25	1551	468
	Leaf	18	30	363	86	16	19	74	50
	Branch	15	80	1025	373	16	44	862	269
	Fruit	11	24	113	43	–	–	–	–

TABLE-2
BIOLOGICAL ABSORPTION COEFFICIENTS (BAC) AND CORRELATION COEFFICIENTS (r) OF *Juniperus oxycedrus* AND *Pinus nigra* PLANT SPECIES GROWING IN THE VICINITY OF MADENKÖY

Element/ Parts of plants		*Juniperus oxycedrus*					*Pinus nigra*				
		S	BAC			r	S	BAC			r
			Min	Max	Average			Min	Max	Average	
Al	Leaf	18	0.16	1.17	0.47	-0.0178	16	0.13	1.03	0.47	-0.2787
	Branch	18	0.21	1.54	0.61	0.1263	16	0.14	2.04	0.81	0.4800
	Fruit	–	–	–	–	–	–	–	–	–	–
Fe	Leaf	16	0.04	0.30	0.14	-0.0944	15	0.07	0.19	0.12	0.3266
	Branch	16	0.04	0.27	0.15	-0.1634	15	0.04	0.57	0.24	0.0362
	Fruit	10	0.01	0.04	0.02	-0.1063	–	–	–	–	–
Mn	Leaf	14	0.61	3.31	1.79	-0.0503	16	0.24	5.04	2.22	0.0207
	Branch	14	0.23	1.15	0.60	-0.1934	16	0.27	2.41	1.18	-0.0529
	Fruit	11	0.28	2.70	1.03	-0.5511	–	–	–	–	–
Cu	Leaf	17	0.88	4.37	1.85	0.0719	13	1.03	2.07	1.65	-0.0234
	Branch	17	1.02	4.85	2.52	0.0294	13	1.17	3.80	2.41	0.1272
	Fruit	14	1.56	4.9	2.87	0.0761	–	–	–	–	–
Zn	Leaf	15	0.80	2.64	1.61	-0.1681	13	3.33	7.66	4.95	0.7900
	Branch	15	0.83	2.47	1.56	0.1941	13	3.22	18.17	6.44	0.1424
	Fruit	12	1.20	3.13	2.20	-0.0793	–	–	–	–	–
Pb	Leaf	14	0.11	1.49	0.44	-0.2344	14	0.06	1.24	0.31	0.5204
	Branch	15	0.47	3.60	1.74	0.7541	14	0.12	3.24	1.10	0.3062
	Fruit	9	0.08	0.34	0.19	-0.0087	–	–	–	–	–

15% of earth's crust is composed of Al_2O_3. According to Chenery[18], Al concentration is plants is approximately 200 ppm. Aluminum concentrations of soil specimens collected from the study area did not correspond to abnormality values. On the other hand, in plant species, branch sections stored aluminum better than other sections. No Al concentration was found in fruit section of *Juniperus oxycedrus*.

Rose *et al.*[19] reported 21000 ppm Fe in soil and 1600 ppm Fe in plant ash. It was observed that Fe concentrations in soil specimens collected from M1 and M35 stations from upper section of Madenköy were higher than those in other stations. This is believed to be caused by iron enrichment in the region. It was found that branch sections of *Juniperus oxycedrus* and *Pinus nigra* plant specimens collected from the vicinity of Madenköy absorbed iron more than other sections.

Normal manganese concentration is 320 ppm in soil and 6700 ppm in plant ash[19]. The fact that soil specimens collected from stations no M1, M2, M10, M16, M18, M35 showed higher values than other specimens can be caused by small-sized mineralization or contamination (mine excavation works). Nagaraju and Karimulla[20] reported that leaves and needle generally contain higher amount of manganese than branches and therefore manganese concentration is higher in leaves in all plant species. In the present study, manganese leaves of the plants had higher concentrations of manganese than other sections (branch and fruit). So, the leaves are the best storing sections in analyzed plant species.

Soil has 15 ppm, plant ash has 130 ppm copper concentration[19]. Copper concentrations in soil specimens collected from station no M18 were higher than 400 ppm. Sandmann and Böger[21] reported that copper can be found in higher amounts in areas with mine quarries or in areas where copper containing plant protection drugs are used. Çevikbas[22] reported presence of copper in ophiolitic rocks. Among plant species which were analyzed according to biological absorption coefficients, branch section of *Pinus nigra* and fruit section of *Juniperus oxycedrus* absorbed copper higher than other sections.

According to Rose *et al.*[19], the soil contains 36 ppm, plant ash contain 570 ppm zinc concentration. Zinc concentrations in soil specimens collected from stations no M15-M18-M5 and M10 contained higher concentrations than other specimens. In a study carried out by Ozdemir and Sagiroglu[23], it was found that zinc concentration in branch section of plant specimens was higher than those in leaves. In plant specimens collected in the vicinity of Madenköy, branch sections of *Pinus nigra* absorbed zinc than other plant sections. Particularly according to biological absorption coefficients it corresponds to high absorption value in M27 (18.17) and M28 (10.46). On the other hand, fruit section of *Juniperus oxycedrus* plant absorbed zinc in higher amounts than other sections. Among these plant species, there was a linear relationship between zinc concentrations in leaf sections of *Pinus nigra* and increasing zinc concentrations in soil. Correlation coefficient at 99 % reliability was r = 0.7900'dur ($r_{experimental} > r_{theoretical}$). Fig. 1 presents the relationship between zinc concentration in soil and zinc concentration in leafsections of *Pinus nigra*. Increasing zinc coefficient in soil also increased in leaf section of *Pinus nigra*. It was found that there was a positive (+) linear relationship between zinc concentration in soil and zinc concentration in leaf section of *Pinus nigra*. This plant species can be defined as *Indicator Plant* for zinc.

Concentration of lead element is 17 ppm in soil, 30 ppm in plant[19]. The fact that lead concentration in soil specimens collected from the study area showed a high distribution is closely related with the formation of lead ore. Lead concentrations in soil specimens collected from the study area can be considered as abnormality. It is believed that the region is contaminated with lead deposits or mine excavation works. Plants store lead element they intake from soil in their roots instead

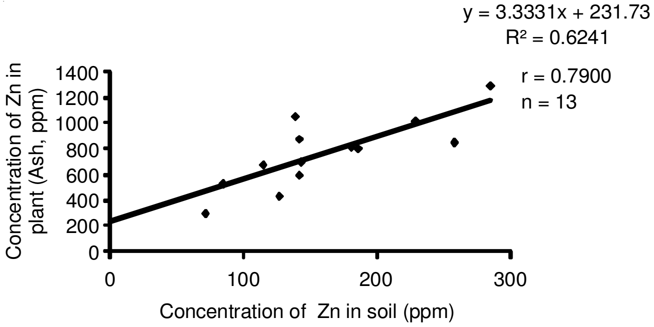

Fig. 1. Relationship between Zn concentration in soil and Zn concentration in leaf section of *Pinus nigra* plant species

of other plant sections such as stem or leaves[24]. Lead concentrations in branch section of *Juniperus oxycedrus*, *Pinus nigra* plant species correspond to abnormal values. According to biological absorption coefficients, branch section of *Juniperus oxycedrus* was the best accumulator. Correlation coefficient for *Juniperus oxycedrus* at 99 % reliability was r = 0.7541 ($r_{experimental} > r_{theoretical}$). Since there is a positive (+) linear relationship between Pb concentration in soil and branch section of *Juniperus oxycedrus* plant species, branch section of this plant species can be defined as *Indicator Plant* for Pb. Fig. 2 shows a linear relationship between plant and soil.

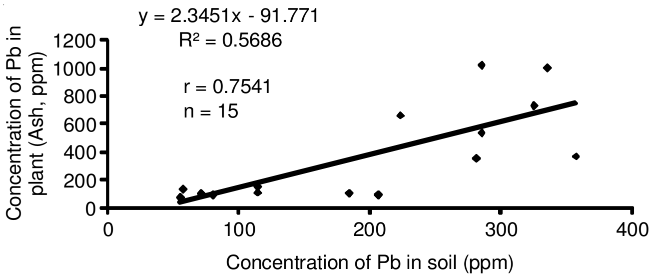

Fig. 2. Relationship between Pb concentration in soil and Pb concentration in leaf section of *Juniperus plant* species

Correlation coefficients of *Juniperus oxycedrus* (branch) and *Pinus nigra* (leaf) which were identified as indicator plants, with other elements (Al-Cu-Fe-Mn-Pb-Zn) in their tissues are presented in Tables 3 and 4. There was a positive linear relationship between Al-Fe and Cu-Zn elements in branch section of *Juniperus oxycedrus*. There was a positive relationship between Al-Fe elements in leaf sections of *Pinus nigra* and a negative linear relationship between Al-Mn elements.

Conclusions

A large section of root can reach 90-150 cm depth in well-drained soil. Some part of roots reach 180-240 cm depth according to the properties of plants. In tree group plants, roots cannot reach more than 100 cm and the roots of only a few of them can reach 3 m depth[25]. In the present study, the fact that roots of tree group plant species which were defined as indicator plants can reach deep in the soil with their roots can give information about covered mineralization. In other words, plants can serve as shallow drilling.

According to multi-elements (Al, Fe, Mn, Cu, Zn, Pb) analysis of plant species in the preset study, each plant had different metal accumulation. This indicates that plant species are selective to intake of necessary elements and prevention of unnecessary elements.

TABLE-3
CORRELATION ANALYSIS BETWEEN ELEMENT (Al-Cu-Fe-Mn-Pb-Zn) CONCENTRATIONS OF *Juniperus oxycedrus* (BRANCH) PLANT SPECIES

	Al	Fe	Mn	Cu	Zn	Pb
Al	1	0.7549	0.3457	-0.1374	0.2692	-0.0396
Fe		1	0.1059	-0.4475	-0.1606	0.0354
Mn			1	0.3485	0.3792	-0.1937
Cu				1	0.7775	-0.1378
Zn					1	-0.1671
Pb						1

TABLE-4
CORRELATION ANALYSIS BETWEEN ELEMENT (Al-Cu-Fe-Mn-Pb-Zn) CONCENTRATIONS OF *Pinus nigra* (LEAD) PLANT SPECIES

	Al	Fe	Mn	Cu	Zn	Pb
Al	1	0.8908	-0.6113	0.0557	-0.0824	0.1946
Fe		1	-0.0708	-0.1234	0.0517	0.2552
Mn			1	-0.1746	-0.2625	-0.2663
Cu				1	-0.4457	0.0103
Zn					1	0.2522
Pb						1

Heavy metal accumulation properties of plants can be used as a source for biogeochemical studies. Leaf section of *Pinus nigra* was found to be an indicator plant for lead while branch section of *Juniperus oxycedrus* was found to be an indicator plant for lead element.

The fact that analyzed heavy metals were found in high concentrations in the soil in some stations and that they are stored by the plants in the study can have a toxic effect for living things. It case a significant problem both in soils contaminated by erosion of mine ores but also in food chain. Furthermore, these plant species can be used in mining prospection, analysis of environmental effects of mine deposits and recycling of contaminated areas.

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