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DETERMINATION OF TRACE ELEMENTS IN THE PLANTS OF MT. BOZDAG, IZMIR, TURKEY

D. YILDIZ[1], I. KULA[1], G. AY[2], S. BASLAR[3] and Y. DOGAN[3*]

[1]*Department of Chemistry, Faculty of Art-Science, Mugla University,* 48000 Mugla, Turkey
[2]*Department of Biology, Faculty of Art-Science, Celal Bayar University,* 45000 Manisa, Turkey
[3]*Department of Biology, Buca Faculty of Education, Dokuz Eylul University,* 35000 Izmir, Turkey

Abstract - The aim of this study was to determine the current level of atmospheric heavy metal content on the Bozdag Mountain of the Aegean Region, Turkey. Twenty nine different plants were selected to study their potential as biomonitors of trace elements such as Ni, Zn, Fe, Pb, Mn and Cd (μg g^{-1}, dry weight). The samples were collected from two different altitudes of Mt. Bozdag. The concentrations of trace elements were determined by atomic absorption spectrometry. The mean concentrations determined at 1000 m altitude ranged from 0.025 to 1.609, 0.232 to 0.731, 0.578 to 5.983, 0.287 to 0.565 and 0.176 to 2.659 (μg g^{-1}, dry weight), for Ni, Zn, Fe, Pb and Mn, respectively. At the altitude of 1600 m, the values ranged from 0.023 to 0.939, 0.258 to 1.254, 0.839 to 5.176, 0.301 to 1.341 and 0405 to 3.351 (μg g^{-1}, dry weight) for Ni, Zn, Fe, Pb and Mn, respectively. No Cd was detected at either altitude. Statistical significance was determined by the independent sample *t*-test and comparisons were made in order to determine if there were any differences between the averages of herbaceous and woody plants.

Keywords: Bozdag Mountain, FAAS, plant, trace element, Turkey

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INTRODUCTION

Human activities have globally affected the biogeochemical cycling of heavy metals, resulting in a progressive increase in the flux of bioavailable chemical forms to the atmosphere (Ng et al., 2005; Yorek et al., 2008). There is evidence that increasing exposure to toxic elements in marine and terrestrial organisms is having adverse toxicological consequences (Rana et al., 2004; Katranitsas et al., 2003). In order to evaluate, minimize and avoid the adverse effects of toxic metals, there has been an emphasis on the use of bioindicators to monitor atmospheric quality in both urban and rural environments (Szczepaniak and Biziuk, 2003; Ng et al., 2005).

Biomonitoring is a means to detect the deposition, accumulation and distribution of trace metals in ecosystems. Through the use of different types of vegetation, the levels of atmospheric trace metallic concentrations have been successfully monitored (El-Hasan et al., 2002; Baslar et al., 2003; Dogan et al., 2007; Onder et al., 2007). Biomonitoring provides the cheapest and simplest method for monitoring trace metal elements in the atmosphere (Kaya and Yaman, 2008; Cayir et al., 2008; Baslar et al., 2009).

Because it is a comparatively simple, cheap and practical method of determining air quality (Cayir et al., 2007), plant biomonitoring is increasingly used as an alternative to the traditional methods, especially in Europe, for studying the regional deposition of natural and anthropogenic pollutants from the atmosphere to the terrestrial environment (Pacheco et al., 2001; Dogan et al., 2007).

A number of studies has been carried out in urban and rural habitats in Turkey (Guleryuz et al., 2002; Baslar et al., 2003; 2005; Samura et al., 2003; Yilmaz and Zengin, 2004; Yilmaz et al., 2006; Dogan et al., 2007; Cayir et al., 2008; Ozturk et al., 2008; Huseyinova et al., 2009). On the assumption that mountainous areas remain unpolluted, the samples collected in some of these studies have been used as a control group (e.i. Baslar et al., 2003;

2005; Yilmaz and Zengin, 2004; Dogan et al., 2007; Dogan et al., 2010). The present study is important, as it determines heavy metal levels in heavy metal-free mountainous areas.

The goal of this study was to present and investigate the concentrations of Pb, Cd, Ni, Zn, Fe and Mn on Mt. Bozdag by using plant species.

MATERIALS AND METHODS

Sampling area

Ecotourism, which has become increasingly popular in recent years, has been expanding especially in mountains. This particular type of tourism, along with the opportunities provided by the environment, makes the culture and agricultural traditions of the locals available to tourism. Therefore, it has been embraced in many parts of the country and is expanding rapidly. Mt. Bozdag, with its summer pastures as well as archeological and cultural heritage, is among the important ecotourism centers of Western Anatolia. Mt. Bozdag (2159 m) is the highest mountain of the Bozdaglar mountain chain which forms a natural border between the provinces of Izmir and Manisa (Fig. 1).

The samples were collected as suggested by Zechmeister (1995), from 1000 m and 1600 m above the sea level, away from the city with negligible traffic and pollution.

Fig. 1. Geographical location of the study area.

Sample collection and preparation

Samples were collected from altitudes of 1000 and 1600 m in July-August 2006. Twenty nine species were collected in total, of which 15 were from 1000 m and 14 were from 1600 m. The taxonomic determination of the plant species was carried out according to Davis (1965-1985), Davis et al., (1988) and Guner et al., (2001).

For analysis purposes, approximately 100 g of the aboveground parts of bushy species and the fully developed leaves of other plants were collected. The samples were dried in an oven at 80ºC for 24 h, ground in a micro-hammer cutter and fed through a 0.2 mm sieve. The samples were stored in self-sealing plastic bags with silica gel desiccant. Since it was washed after every use, first with absolute alcohol then with distilled water, contamination from the micro-hammer cutter was negligible during the grinding.

Wet digestion procedure

The digestion method is described by Perkin Elmer Corporation (Anonymous, 1996). Samples were immediately analyzed following digestion. The digested plant samples were fed into an air-acetylene flame and metal concentrations were determined by flame atomic absorption spectrometry (FAAS). The analyses were carried out in triplicate.

Reagents

Unless otherwise specified, all chemicals used were of analytical reagent grade. Triple distilled water was used throughout the experiments. By diluting the stock standard solution with water, working metal standard solutions were prepared just before use.

Instrumentation

Determination of heavy metals was performed with a Perkin Elmer Analyst 700 model flame atomic absorption spectrometer furnished with deuterium background correction, hollow cathode lamps (HCl) and an acetylene burner. The absorption measurements were performed under the conditions recommended by the manufacturer. Before determination, a Cole-Parmer microfiltration apparatus with a membrane filter (0.45 µm pore size manufactured by Micro Filtration Systems, MFS) was used for aqueous phase filtration.

Data analysis

Concentration values are given as mean±standard error (SE). Statistical significance was determined by the One-sample *t*-test. In the independent *t*-test, comparisons were made in order to determine whether there were any differences between the averages of the sites assumed as polluted and the control region. Differences at $P<0.05$ were considered to be significant. A Statistical Package was used in the analysis of *t*-test for the data.

RESULTS AND DISCUSSION

Levels of the trace elements Cd, Ni, Zn, Fe, Pb and Mn (µg g^{-1}, dry weight) in plant samples collected from different altitudes of Mt. Bozdag are given in Tables 1 and 2. The plants used as biomonitors were sampled with 29 different species at two different altitudes in the Mt. Bozdag. Atomic absorption spectrometry was used in order to determine the concentrations of metals. The following mean concentrations were determined at an average altitude of 1000 m: The contents of Ni, Zn, Fe, Pb and Mn (µg g^{-1}, dry weight) ranged from 0.025 to 1.609, 0.232 to 0.731, 0.578 to 5.983, 0.287 to 0.565 and 0.176 to 2.659, respectively (Table 1). On the other hand, at an average altitude of 1600 m, the contents of Ni, Zn, Fe, Pb and Mn (µg g^{-1}, dry weight) ranged from 0.023 to 0.939, 0.258 to 1.254, 0.839 to 5.176, 0.301 to 1.341 and 0405 to 3.351, respectively (Table 2). No Cd values were determined in the samples collected from either height.

The aggregation of investigated trace elements in plants collected from 1000 m on Mt. Bozdag is presented in Table 1. From the table it can be seen that the Ni content was the highest in *Lapsana communis* (1.609 µg g^{-1}), and the lowest in *Phillyrea latifolia* (0.025 µg g^{-1}). Zn content was the highest in *Cercis siliquastrum* (0.731 µg g^{-1}), and lowest in *Juniperus oxycedrus* subsp. *oxycedrus* (0.232 µg g^{-1}). The Fe content was the highest in *Stachys cretica* subsp. *smyrnaea* (5.983 µg g^{-1}), and lowest in *Pinus brutia* (0.578 µg g^{-1}). The Pb content was the highest in *Urtica dioica* (0.565 µg g^{-1}), and in *Pinus brutia* (0.287 µg g^{-1}) it was the lowest The. Mn content was the highest in *Lapsana communis* (2.659 µg g^{-1}), and lowest in *Pinus brutia* (0,176 µg g^{-1}). At 1000 m, the highest values were recorded for Ni and Mn in *Lapsana communis,* for Zn in *Cercis siliquastrum,* for Fe in *Stachys cretica* subsp. *smyrnaea* and for Pb in *Urtica dioica*.

In the plants collected at 1600 m, Ni content was highest in *Plantago maritime* (0.939 µg g^{-1}), and lowest in *Erysimum caricum* (0.023 µg g^{-1}). The Zn content was highest in *Lamium pisidicum* (1.254 µg g^{-1}), and lowest in *Genista lydia* subsp. *lydia* (0.258 µg g^{-1}). The Fe content was highest in *Plantago maritime* (5.176 µg g^{-1}), and lowest in *Juniperus oxycedrus* subsp. *oxycedrus* (0.839 µg g^{-1}). The Pb content was highest in *Genista lydia* subsp. *lydia* (1.341 µg g^{-1}), and lowest in *Juniperus oxycedrus* subsp. *oxycedrus* (0.301 µg g^{-1}). The highest Mn content was observed in *Salix* sp. (3.351 µg g^{-1}), and the lowest in *Juniperus oxycedrus* subsp. *oxycedrus* (0.405 µg g^{-1}). At 1600 m, the Ni and Fe contents were highest in *Plantago maritime*, Zn was highest in *Lamium pisidicum,* Pb was highest in *Genista lydia* subsp. *lydia* and Mn was highest in *Salix* sp.

The sources for accumulation of some trace elements have been explained by various researchers. For example, anthropogenic activities are the main sources of Pb and Zn according to Alfani et al., (2000), Blok (2005) and Oliva and Rautio (2005). The burning of coal and oil, production of Cu, Ni and Pb, mining operations, steel works and cement industry are cited as major anthropogenic sources of Ni (Nriagu and Pacyna, 1988). Although airborne Mn mainly comes from soil (Bargagli et al., 2003; Oliva and Rautio, 2005), and Fe originates from both anthropogenic and na-

Table 1. Trace element contents in plants growing on Mt. Bozdag (μg g^{-1} dry weight) (1000 m).

Plant	Ni	Zn	Fe	Pb	Mn
Woody					
Castanea sativa Miller.	0.052	0.400	1.995	0.380	1.125
Cercis siliquastrum L.	0.080	0.731	2.855	0.306	0.367
Juniperus oxycedrus L. subsp. *oxycedrus*	0.060	0.232	4.129	0.321	0.352
Juniperus oxycedrus subsp. *oxycedrus*	0.099	0.241	0.593	0.297	0.532
Phillyrea latifolia L.	0.025	0.368	0.762	0.424	0.365
Pinus brutia L.	0.119	0.328	0.578	0.287	0.176
Pistacia terebinthus L.	0.688	0.468	4.378	0.472	0.730
Rubus idaeus L.	0.051	0.685	4.294	0.541	0.412
Sambucus nigra L.	0.112	0.394	2.409	0.387	0.631
Spartium junceum L.	0.282	0.331	3.246	0.469	1.979
Herbaceous					
Dryopteris filix-mas (L.) Schott	0.132	0.353	3.681	0.447	0.301
Lapsana communis L.	1.609	0.644	5.132	0.416	2.659
Ruscus aculeatus L.	0.268	0.414	4.833	0.526	0.413
Stachys cretica subsp. *smyrnaea* Rech. Fil.	0.119	0.387	5.983	0.361	0.550
Urtica dioica L.	0.900	0.550	4.951	0.565	1.475
Min.:	0.025	0.232	0.578	0.287	0.176
Max.:	1.609	0.731	5.983	0.565	2.659
Mean:	0.30±0.11	0.43±0.03	3.32±0.44	0.41±0.02	0.80±0.18

tural sources (Oliva and Rautio, 2005), it was reported that the contamination of soil by Fe and Mn highly affects plants in the Mediterranean climate zone (Loppi et al., 1999).

The accumulation of trace elements in plant parts was investigated by various researchers in different parts of the world, as well as in Turkey. Some of them are given below for comparison with our findings: Dijingova et al., (1995) (Cd: 0.10-31.20 μg g^{-1}, Ni : 0.50-4.9 μg g^{-1}, Zn: 7-302 μg g^{-1}, Fe: 100-283 μg g^{-1}, Pb: 0.80-21.30 μg g^{-1}, Mn: 44-405 μg g^{-1}), Baslar et al., (2003) (Ni: 0.88 μg g^{-1}, Fe: 57.28 μg g^{-1}, Pb: 1.4 μg g^{-1}), Dogan et al., (2007) (Ni: 3.56 μg g^{-1}, Fe: 486.35 μg g^{-1}, Pb: 4.59 μg g^{-1}), Baslar et al., (2005) (Cd: 1.7 μg g^{-1}, Zn: 63.4 μg g^{-1}, Fe: 182.6 μg g^{-1}, Pb: 2.3 μg g^{-1}) and Kapusta et al., (2006) (Cd: 6.44 μg g^{-1}, Pb: 5.64 μg g^{-1}, Zn: 304 μg g^{-1}).

Table 2. Trace element contents in plants growing on Mt. Bozdag (μg g^{-1} dry weight) (1600 m).

Plant	Ni	Zn	Fe	Pb	Mn
Woody					
Juniperus foetidissima Willd.	0.061	0.458	0.839	0.301	0.405
Pyrus amigdaliformis L.	0.640	0.380	3.174	0.325	0.690
Rosa canina L.	0.162	0.575	1.900	0.568	1.548
Quercus cerris L. subsp. *cerris*	0.080	0.641	1.100	0.366	0.525
Salix sp.	0.320	0.823	3.249	0.378	3.351
Herbaceous					
Delphinium peregrinum L.	0.310	0.560	3.811	0.441	1.698
Erysimum caricum L.	0.023	0.611	4.754	0.460	1.327
Euphorbia sp.	0.164	0.690	2.694	0.518	1.416
Genista lydia L. subsp. *lydia*	0.352	0.258	3.482	1.341	0.625
Lamium pisidicum L.	0.370	1.254	3.892	0.540	0.850
Plantago maritima L.	0.939	0.631	5.176	0.362	2.122
Tripleurospermum sp.	0.671	1.139	4.232	0.442	1.064
Verbascum sp.	0.628	0.365	4.575	0.408	1.558
Vincetoxicum tmoleum Boiss.	0.096	0.610	2.504	0.481	0.871
Min.:	0.023	0.258	0.839	0.301	0.405
Max.:	0.939	1.254	5.176	1.341	3.351
Mean:	0.34±0.07	0.64±0.07	3.24±0.35	0.49±0.06	1.28±0.20

Bowen (1979) has reported the normal natural concentration intervals for land plants as Cd: 0.2-2.4 μg g^{-1}, Ni: 1-5 μg g^{-1}, Zn: 20-400 μg g^{-1}, Fe: 70-700 μg g^{-1}, Pb: 1-13 μg g^{-1}, Mn: 20-700 μg g^{-1}. Comparison of our results with these findings (Table 1 and 2) clearly shows that our results are well below the accepted range. Therefore, the area is free from the contamination of heavy metal pollution regarding the trace elements investigated. The level of accumulation we obtained in the plant sample is soil-oriented.

Baslar et al., (2009) have obtained the following results in the study they conducted on Mt. Honaz, another important mountain of the same region: The mean concentrations determined at 1000 m ranged from 0.273 to 0.488, 0.099 to 0.488, 0.306 to 0.682, 1.017 to 3.744, and 0.148 to 0.674 (μg g^{-1}, dry weight), for Pb, Ni, Zn, Fe and Mn, respectively. At 1600 m, the values ranged from 0.225 to 0.534, 0.150 to 0.842, 0.234 to 0.905, 1.082 to 3.864 and 0.023 to 0.982(μg g^{-1}, dry weight) for Pb, Ni, Zn, Fe, Pb and Mn, respectively. No Cd was detected at either altitude.

Table 3. Statistical analysis values of herbaceous and woody plants.

Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Ni	Equal variances assumed	2,110	,158	-1,614	27	,118	-,218975	,135683	-,497374	,059425
	Equal variances not assumed			-1,827	26,975	,079	-,218975	,119848	-,464893	,026944
Zn	Equal variances assumed	2,215	,148	-1,796	27	,084	-,159833	,088990	-,342426	,022759
	Equal variances not assumed			-2,081	26,411	,047	-,159833	,076794	-,317567	-,002100
Fe	Equal variances assumed	4,863	,036	-3,358	27	,002	-1,676247	,499234	-2,700591	-,651904
	Equal variances not assumed			-2,919	13,583	,012	-1,676247	,574228	-2,911401	-,441094
Pb	Equal variances assumed	1,321	,260	-2,323	27	,028	-,157354	,067750	-,296365	-,018342
	Equal variances not assumed			-2,889	20,760	,009	-,157354	,054460	-,270688	-,044019
Mn	Equal variances assumed	8,666	,007	-2,998	27	,006	-,780318	,260279	-1,314367	-,246269
	Equal variances not assumed			-3,703	21,517	,001	-,780318	,210746	-1,217948	-,342688

Kula et al., (2010) have studied trace element concentrations of plants on Mt. Akdag and have obtained following results: The mean concentrations determined at and altitude of 1000 m ranged from 0.011 to 0.882, 0.241 to 0.714, 0.532 to 9.396, 0.329 to 0.487, and 0.155 to 3.439 (μg g^{-1}, dry weight), for Ni, Zn, Fe, Pb and Mn, respectively. At 1600 m, the values ranged from 0.092 to 0.600, 0.272 to 0.834, 1.130 to 8.021, 0.263 to 0.889 and 0.076 to 0.508 (μg g^{-1}, dry weight) for Ni, Zn, Fe, Pb and Mn, respectively. No Cd was detected at either altitude. The similarities of the results obtained from Mt. Honaz, Mt. Akdag and Mt. Bozdag show the validity and credibility of our studies.

The results of statistical analysis show that the comparison of heavy metal pollution values of herbaceous and woody plants for Fe and Mn was meaningful (P<0.05), whereas it was not for Ni, Zn and Pb (Table 3). When the mean values of heavy metal pollution in herbaceous and woody plants were compared, the accumulation was higher in herbaceous plants for Fe and Mn, with a statically meaningful difference.

In this study, 29 different plants that are used as biomonitors were sampled at two different altitudes (1000 m and 1600 m) of Mt. Bozdag in order to investigate the levels of the trace elements Cd, Ni, Zn, Fe, Pb and Mn (μg g^{-1}, dry weight). The obtained trace element values were shown to be below the values of control samples from other studies carried out in clean areas. As a result, low element values are considered to be soil-oriented. We are convinced that this study will contribute to future studies on pollution in the same or similar localities.

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