Some Element Levels in Moss Samples Collected from the Igdir-Nahhicevan International Highway, Turkey

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Twenty-six moss and seven soil samples were collected from near the Igdir- Nahhicevan international highway in Turkey. Seventeen elements (Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe, Cu, Zn, Sr, Cr, Mn, Rb and Pb) were analyzed using X-ray fluorescence spectrometry. The element concentrations were found to be 1000-1862 µg/g (Na), 2174-6578 µg/g (Mg), 1308-30669 µg/g (Al), 11708-73710 µg/g (Si), 91-659 µg/g (P), 45-2680 µg/g (S), 1123-2667 µg/g (K), 5969-13997 µg/g (Ca), 641-1387 µg/g (Ti), 5855-17133 µg/g (Fe), 23-36 µg/g (Cu), 10-93 µg/g (Zn), 29-114 µg/g (Sr), 4-85 µg/g (Cr), 17-326 µg/g (Mn), 6-19 µg/g (Rb), 1-14 µg/g (Pb) for mosses and 324254-402976 µg/g (Si), 35347-92506 µg/g (Na), 28261-76471 µg/g (Ca), 3822-72123 µg/g (Mg), 52731-66335 µg/g (Fe), 28115-39747 µg/g (Al), 9659-11664 µg/g (K), 6928-11617 µg/g (Ti), 936-1385 µg/g (S), 585 µg/g (P), 149-261 µg/g (Sr), 126 µg/g (Zn), 15-240 µg/g (Cr), 42-180 µg/g (Cu), 89 µg/g (Mn), 27-46 µg/g (Rb) and 37 µg/g (Pb) for soil, respectively.

Key Words: Atmospheric deposition, Trace elements, Mosses, EDXRF, Igdir, Turkey.

INTRODUCTION

Most of the elements are essential for biological systems, whereas some metals like lead and cadmium are non-essential metals as they do not have any biological function are toxic even in traces. Iron is part of the structure of the oxygen-carrying protein, hemoglobin, in the red blood cells; calcium, phosphorus and other elements constitute a significant part of the mass of teeth and bones and sodium, potassium, phosphate, sulfate, chloride and many other elements are important constituents of the fluids, both inside and outside all the body cells. Calcium in minute concentrations is necessary for normal blood clotting. Magnesium stimulates the activity of many enzymes and number of trace elements controls the contraction of muscle and the transmission of impulses by nerve cells¹.

Mosses possess many properties that make them suitable bio-monitors for air pollutants²⁻⁴. They do not have real roots. So, they cannot take their nutrient from soil. Nutrient uptake from the atmosphere is promoted by their weakly developed cuticle. Their large surface-to-weight ratio improves adsorption. Slow growth rate lets them accumulate pollutants over a larger time period. Undeveloped vascular bundles allow better adsorption than vascular plants⁴. The attachment of the

particle is affected by the size of the particle and the surface structure of the mosses⁴⁻⁶.

The moss monitoring technique, first introduced in Scandinavia, has shown to be very suitable for studying atmospheric deposition of heavy metals and other elements as well⁷. The usefulness of mosses in determining trace- and heavy-metal concentrations in different geographical areas has been discussed in many studies⁸⁻²⁰.

Several moss species are commonly grown through Igdir-Nahhicevan international highway vicinity. The traffic on this highway is very high and stills the levels of metals in mosses and soils. Thus in present studies, the levels of metals in some moss and soil samples were determined by EDXRF spectrometry.

EXPERIMENTAL

For this study we have used the nine different sampling sites (Table-1). The sampling areas are shown in Fig. 1. This time ten moss species (*Grimmia orbicularis*, *Grimmia laevigata*, *Syntrichia montana*, *Syntrichia virescens*, *Grimmia longirostris*, *Syntrichia ruralis*, *Homalothecium sericeum*, *Hypnum cupressiforme*, *Abietinella abietina*, *Grimmia ovalis*) and six soil samples were collected from vicinity of roadside

TABLE-1
DESCRIPTIONS OF THE NINE STATIONS IN IGDIR PROVINCE

Site No	Localities	Moss samples	Nature	Latitude-longitude	Altitude (m)	Collected Date
1	Igdir: Karakoyunlu district, Melekli town	<i>Grimmia orbicularis</i> <i>Grimmia laevigata</i> <i>Syntrichia montana</i> Soil samples	Polluted	39°57'30.50"N 44°08'58.02"E	860	30.03.2010
2	Igdir: Tuzluca district (between Tuzluca and Kagızman district)	<i>Syntrichia virescens</i> <i>Grimmia longirostris</i> <i>Syntrichia ruralis</i> Soil samples	Polluted	40°06'27.77"N 43°30'16.05"E	1055	31.03.2010
3	Igdir: Tuzluca district, Yukarıcivanlı Village	<i>Grimmia longirostris</i>	Unpolluted	40°00'31.57"N 43°32'526.37"E	1882	16.06.2010
4	Igdir: Aralık district	<i>Grimmia laevigata</i> Soil samples	Polluted	39°58'51.89"N 44°18'05.06"E	831	30.03.2010
5	Igdir: Halfeli	<i>Grimmia longirostris</i> <i>Grimmia laevigata</i> <i>Homalothecium sericeum</i> Soil samples	Unpolluted	39°51'54.84"N 43°56'53.53"E	1180	29.03.2010
6	Igdir: Center of Tuzluca district	<i>Syntrichia ruralis</i> <i>Homalothecium sericeum</i> <i>Hypnum cupressiforme</i> Soil samples	Polluted	40°03'09.53"N 43°39'16.15"E	1074	31.03.2010
7	Igdir: Alibeyköy village	<i>Abietinella abietina</i> <i>Grimmia ovalis</i> <i>Syntrichia montana</i> <i>Hypnum cupressiforme</i> <i>Homalothecium sericeum</i> Soil samples	Unpolluted	39°48'50.92"N 43°55'57.88"E	1850	29.03.2010
8	Igdir: Tuzluca district, Taşköprü Village	<i>Syntrichia virescens</i> <i>Homalothecium sericeum</i> <i>Hypnum cupressiforme</i>	Polluted	39°52'07.40"N 43°28'57.94"E	2134	14.06.2010
9	Igdir: Korhan High Plateau, Ağrı Mountain	<i>Grimmia ovalis</i> <i>Hypnum cupressiforme</i> <i>Homalothecium sericeum</i> <i>Syntrichia ruralis</i>	Unpolluted	39°47'11.09"N 44°16'06.73"E	1904	17.06.2010

Fig. 1. Geographical location of the research area

from Igdir-Nahhichevan (5-100 meters away) during 2010. The samples were dried at 105 °C for 24 h. Dried samples were grinded in a spex mill then the powder obtained was sieved using a 400 mesh sieve and then stirred for 20 min to obtain a well-mixed sample and stored in pre-cleaned polyethylene bottles until analysis. A five tone hydraulic press was used to compress the sample powder into a solid thick pellet

of 40 mm diameter using a boric acid (H_3BO_3 -powder) as a protective cover.

The elements concentration of the samples were determined using a Skyray EDX 3600B spectrometer equipped with an Oxford Rh anode X-ray tube (the spectrometer has a SSD high resolution detector having 145 ± 5 eV energy resolutions and this spectrometer is capable of 0.05 % measurement precision. Besides, 24 elements can be analyzed simultaneously using it).

RESULTS AND DISCUSSION

All element concentrations were determined on a dry weight as $\mu g/g$. The relative standard deviations were less than 10 % for all elements. t-test was used in this study ($p < 0.05$). The mean concentrations of Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe, Cu, Zn, Sr, Cr, Mn, Rb and Pb in moss and soil samples are given in Tables 2 and 3. The order of levels of elements in moss samples were determined as $Si > Al > Fe > Ca > Mg > Na > S > K > Ti > P > Mn > Sr > Zn > Cr > Cu > Rb > Pb$.

Among the elements Fe (1713 $\mu g/g$), Cu (36 $\mu g/g$), Mn (326 $\mu g/g$), Zn (93 $\mu g/g$) and Cr (85 $\mu g/g$) higher concentrations on the traffic roadside were than control areas. Levels of, iron, copper, manganese, zinc and chromium showed highest concentrations on the traffic roadside. Copper, zinc and chromium had approximate similar concentrations on the traffic roadside and control areas. The concentration of trace

TABLE-2
CONCENTRATIONS OF ELEMENTS IN MOSS SPECIES (µg/g)

No	Moss species	Site	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Cu	Zn	Sr	Cr	Mn	Rb	Pb
1	<i>Grimmia orbicularis</i>	1	1152	5001	10482	53990	249	1341	1866	9201	1235	15301	25	42	65	38	17	12	3
2	<i>Grimmia laevigata</i>	1	1237	4748	30669	73710	507	854	2667	9637	1330	17133	27	23	50	49	80	13	3
3	<i>Syntrichia montana</i>	1	1316	3449	17762	42002	600	1280	2406	9978	1032	13604	27	33	52	37	123	10	3
4	<i>Syntrichia virescens</i>	2	1158	4887	15069	69671	214	1300	2334	10804	1387	16306	24	21	81	24	29	11	1
5	<i>Grimmia longirostris</i>	3	1540	5405	6006	74644	225	1730	2559	6106	1154	12752	26	29	57	7	99	16	9
6	<i>Grimmia laevigata</i>	4	1684	6578	1308	40405	432	2000	1708	7574	1150	13298	25	71	57	26	41	7	8
7	<i>Grimmia longirostris</i>	5	1348	4610	1308	42911	196	2103	2182	7628	1318	15305	28	79	67	30	103	14	14
8	<i>Grimmia laevigata</i>	5	1648	5859	1308	47968	91	1705	2124	6952	1338	15159	27	47	55	34	20	12	8
9	<i>Homalothecium sericeum</i>	6	1593	5051	1308	32803	312	1783	2004	13928	1007	11738	25	60	90	36	131	12	8
10	<i>Syntrichia ruralis</i>	6	1459	5695	1308	29607	290	1573	2091	9731	1088	12585	28	72	65	16	242	19	11
11	<i>Hypnum cupressiforme</i>	6	1745	5329	1308	28517	390	1384	2093	10577	974	11177	29	72	55	45	167	10	9
12	<i>Grimmia longirostris</i>	2	1356	5190	9813	38955	202	1306	1262	12119	1083	15200	25	18	86	39	17	6	3
13	<i>Syntrichia ruralis</i>	2	1371	5859	1308	34470	343	1522	2032	13997	1146	16469	27	18	114	33	145	12	1
14	<i>Abietinella abietina</i>	7	1418	2402	11113	27899	659	926	2523	9569	864	8051	32	44	36	59	253	9	1
15	<i>Grimmia ovalis</i>	7	1377	4610	18208	58815	364	1408	2083	7418	1141	10916	29	55	45	4	96	11	6
16	<i>Syntrichia montana</i>	7	1535	3676	14308	36768	611	1002	2275	7703	930	10124	29	77	60	6	168	12	6
17	<i>Hypnum cupressiforme</i>	7	1000	2427	9832	39617	185	1640	1825	5969	804	8300	26	10	28	4	61	9	2
18	<i>Homalothecium sericeum</i>	7	1167	2174	3611	24990	313	45	2065	7510	740	7124	29	29	57	4	115	9	1
19	<i>Syntrichia virescens</i>	8	1707	3600	6508	16937	354	2680	1123	10307	728	5855	36	32	33	85	326	9	3
20	<i>Homalothecium sericeum</i>	8	1862	4433	2886	11708	284	45	2091	7904	641	6819	33	93	29	46	251	9	3
21	<i>Grimmia ovalis</i>	9	1739	3916	24150	50943	488	570	2254	7326	1068	11863	29	69	63	4	237	13	3
22	<i>Hypnum cupressiforme</i>	8	1432	2212	5226	15908	165	45	1912	9314	779	7706	30	76	37	52	278	9	9
23	<i>Hypnum cupressiforme</i>	9	1371	4988	6062	42421	379	1254	2176	7896	991	10012	28	55	36	22	106	11	5
24	<i>Homalothecium sericeum</i>	9	1511	3121	9423	26986	362	102	2066	7690	673	6208	32	64	29	27	202	6	6
25	<i>Syntrichia ruralis</i>	9	1193	3954	13008	43160	252	45	1932	6519	1096	12170	28	63	59	4	134	13	8
26	<i>Syntrichia princeps</i>	9	1102	2528	4409	32376	201	1027	1827	6439	1043	10406	23	17	76	4	17	13	1

TABLE-3
CONCENTRATIONS OF ELEMENTS IN SOIL SAMPLES (µg/g)

Samples	Sites	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Cu	Zn	Sr	Cr	Mn	Rb	Pb
Soil	1	89984	58112	33421	397267	230	936	11131	45173	7184	62098	180	171	149	188	44	38	25
Soil	2	92506	72123	30561	324254	218	1385	10335	76471	7690	66335	144	145	253	240	89	28	8
Soil	4	46835	53961	28115	369166	585	1003	10372	38949	6928	52731	122	128	188	164	49	36	5
Soil	5	89143	51452	36112	402976	218	1184	11304	35099	7183	57878	105	126	173	129	38	27	26
Soil	6	60564	48079	31814	384513	218	1143	11664	45177	7066	55519	163	208	176	122	74	46	37
Soil	7	35347	38220	39754	365441	218	1328	9659	28261	11617	63536	42	154	261	15	38	36	5

metals in the samples are depended on moss species. For example, the high element accumulation levels in the species were found in *Grimmia laevigata* for Si (73710 µg/g), Al (30669 µg/g), Fe (17133 µg/g), Mg (4433 µg/g), K (2667 µg/g), Pb (14 µg/g), *Syntrichia ruralis* for Ca (13997 µg/g), Sr (114 µg/g), Rb (19 µg/g), Sr (114 µg/g), *Syntrichia virescens* for Mn (326 µg/g), Cr (85 µg/g), Cu (36 µg/g), Ti (1387 µg/g), S (2680 µg/g), *Homalothecium sericeum* for Na (1862 µg/g), Zn (93 µg/g) and *Abietinella abietina* for P (659 µg/g), respectively.

The element concentrations in soil samples were found to be 324254-402976, 35347-92506, 28261-76471, 3822-72123, 52731-66335, 28115-39747, 9659-11664, 6928-11617, 936-1385, 585, 149-261, 126, 15-240, 42-180, 89, 27-46 and 37 µg/g for Si, Na, Ca, Mg, Fe, Al, K, Ti, S, P, Sr, Zn, Cr, Cu, Mn, Rb and Pb, respectively. The order of levels of metals in soil samples as Si > Na > Ca > Mg > Fe > Al > K > Ti > S > P > Sr > Zn > Cr > Cu > Mn > Rb > Pb.

Iron is a relatively abundant element in the universe. The main iron emission sources can be coal-burning and intensive traffic^{21,22}. The lowest and highest iron concentrations were found to be 5855 µg/g in *Syntrichia virescens* and 17133 µg/g in *Grimmia laevigata*. Our results were higher than those

reported earlier^{13,20,23-28}. Aluminium concentration was found 30669 µg/g in *Grimmia laevigata*. Aluminium is the second high concentration values after Si in moss samples. Aluminium values have been reported lower for different moss species by Giordano *et al.* and Barandowski *et al.*^{26,27}.

Zinc is involved in the metabolism of energy, proteins, carbohydrates, lipids and nucleic acids and is an essential element for tissue accretion¹. Zinc concentrations were found as 10-93 µg/g in moss samples. Zinc average values are in good agreement with literature values as 14-203 µg/g²⁷.

Average chromium concentration ranged 4-85 µg/g in moss samples. Chromium values are higher than literature values for Serbia, Romania, Bulgaria and quite higher than Norway, Finland, North Spain, Hungary, Poland, France, Germany, Netherlands and Czech Republic^{13,20,24,26-28}. Cr the other emission sources are intensive traffic, coal-fired power plant and coal-mining Works^{29,30}.

Copper concentration was found 23-36 µg/g in the moss samples. Our copper results were higher than literature values^{20,24,31}. Giordano *et al.*, were reported higher values than ours²⁶. Copper mainly originates from the metal industry, mining, coal-fired plants, traffic, copper-containing fungicides and fertilizers used by agriculture and even from soil²¹.

Copper compounds are widely used in the environment as fertilizers and nutritional supplements and, because of their microbicidal properties, as fungicides, algacides, insecticides and wood preservatives¹.

The maximum lead concentration was found as 14 µg/g in unpolluted area. The adding of lead to the petrol increases the concentration of lead. In literature, the high lead concentration has been reported in the samples of high-density traffic areas³². Our lead value is lower than literature values^{13,16,24,26-28}. Combustion of leaded fuel is still a main source of lead pollution, other sources such as metal production, motor vehicles, soils, coal combustions and mining²⁸.

Average Si, Ca, Na, S, K, Ti, P, Mn, Sr and Rb concentrations were found to be 11708-73710, 5969-13997, 1000-1862, 2680, 1123-2667, 91-1387, 14, 326, 114 and 6-19 µg/g in moss samples, respectively.

Average Si, Na, Ca, Mg, Fe, Al, K, Ti, S, P, Sr, Zn, Cr, Cu, Mn, Rb and Pb were found to be 324254-402976, 35347-92506, 28261-76471, 3822-72123, 52731-66335, 28115-39747, 9659-11664, 6928-11617, 936-1385, 585, 149-261, 126, 15-240, 42-180, 89, 27-46 and 37 µg/g, in soil samples, respectively. In this study, the moss samples were found to be the best bioindicator for all elements.

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