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Determination of Elements due to Atmospheric Deposition on *Barbula indica* Moss at Dalat, Vietnam using NAA and TXRF Techniques

(Penentuan Unsur Disebabkan Pemendapan Atmosfera pada Lumut Barbula indica di Dalat, Vietnam menerusi Teknik NAA dan TXRF)

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ABSTRACT

In this paper, two multielement analysis techniques, Neutron Activation Analysis (NAA) and Total Reflection X-ray Fluorescence (TXRF), are combined to detect elemental concentrations in Barbula indica *moss collected at Dalat, Vietnam. Combining these two techniques has improved the qualitative detection of elements due to atmospheric deposition on moss samples. The concentrations of 40 elements, including Na, Mg, Al, Si, P, S, Cl, K, Ar, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Kr, Rb, Y, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Yb, Hf, Ta, Pb, Th, and U in the* Barbula indica *moss samples collected at 19 locations at Dalat have been determined. It is shown that the air in Dalat is suspected of contamination by Na, Mg, Si, P, S, V, Mn, Cu, Se, Br, and U; slightly contaminated by Mg, Cl, K, Cr, Ni, S, and Ni; moderately contaminated by Sc, Fe, Co, Zn, As, Kr, Rb, Y, Sb, Cs, Ba, La, Ce, Sm, Eu, Dy, Yb, Ta, Pb, and Th; and seriously contaminated by Tb. Factor analysis has been used to explain the contamination sources of these elements, including V, As, Fe, Zn, Se, Rb, Sb, Cs, Al, Cu, and Pb in the investigated area. Four factors have been extracted that can explain 86% of the total variance, and the results suggest that the main sources of atmospheric pollution in Dalat originate from traffic and windblown dust.*

Keywords: Atmospheric deposition; Barbula indica*; Dalat; NAA; TXRF*

ABSTRAK

Dalam kajian ini, dua teknik analisis berbilang-unsur iaitu Analisis Pengaktifan Neutron (NAA) dan Pendaflor Sinar-X Pantulan Keseluruhan (TXRF) telah digabungkan untuk mengesan kepekatan unsur dalam lumut Barbula indica *yang diperoleh di Dalat, Vietnam. Penggabungan dua teknik ini telah meningkatkan pengesanan kualitatif unsur kerana terdapat pemendapan atmosfera pada sampel lumut. Kepekatan 40 unsur, iaitu Na, Mg, Al, Si, P, S, Cl, K, Ar, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Kr, Rb, Y, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Yb, Hf, Ta, Pb, Th dan U dalam sampel lumut* Barbula indica *yang diperoleh dari 19 lokasi di Dalat telah ditentukan. Data menunjukkan udara di Dalat disyaki tercemar oleh Na, Mg, Si, P, S, V, Mn, Cu, Se, Br, dan U; sedikit tercemar oleh Mg, Cl, K, Cr, Ni, S, dan Ni; sederhana tercemar oleh Sc, Fe, Co, Zn, As, Kr, Rb, Y, Sb, Cs, Ba, La, Ce, Sm, Eu, Dy, Yb, Ta, Pb dan Th; dan tercemar teruk oleh Tb. Analisis faktor telah digunakan untuk menjelaskan sumber pencemaran unsur-unsur ini, termasuk V, As, Fe, Zn, Se, Rb, Sb, Cs, Al, Cu dan Pb di kawasan yang dikaji. Empat faktor telah diekstrak yang dapat menjelaskan 86% daripada total varians, dan hasilnya menunjukkan bahawa sumber utama pencemaran atmosfera di Dalat berasal daripada lalu lintas dan debu yang ditiup angin.*

Kata kunci: Barbula indica*; Dalat; NAA; pemendapan atmosfera; TXRF*

INTRODUCTION

Air pollution threatens the health of people everywhere in the world. Air pollution exposes people to fine particles in polluted air. These fine particles penetrate deep into the lungs and cardiovascular system, causing strokes, heart disease, lung cancer, chronic obstructive pulmonary disease, and respiratory infections. Therefore, air quality monitoring has been carried out regularly in many countries. Vietnam is one of the countries with very high air pollution levels that continue to increase. What is the air quality in Vietnam today? It is still a controversial issue in the scientific community, and the government and ordinary citizens need to know the air quality in Vietnam. At present, data on air quality are lacking in many parts of Vietnam.

Around the world, the moss biomonitoring method to study air pollution has been frequently implemented because it is cheap and can be easily carried out over a large area. This method provides data on airborne chemical elements needed to assess air quality and is very suitable for developing countries like Vietnam. The application of the moss technique for surveying elemental atmospheric deposition was developed in the late 1960s (Rühling & Tyler 1970, 1969, 1968). Additional work by Gjengedal and Steinnes (1990) showed that mosses have a strong capacity to retain trace elements, especially metals. Normally, two moss techniques are used: Native species and active biomonitoring. Using native bryophyte moss species in assessing temporal or spatial changes in atmospheric deposition, Sucharová and Suchara (1998) determined the atmospheric loads of 13 elements (Al, As, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, S, V, and Zn). Later, mosses were used for active biomonitoring with moss bags. Fernández and Carballeira (2000) used transplanted mosses of the species *Scleropodium purum* to determine levels of Co, Cr, Cu, K, Ni, Pb, Se, and Zn.

The moss biomonitoring method is a low-cost method that might allow Vietnam to collect air quality data to a much greater extent. Recently, the investigation of air pollution using the moss biomonitoring method has been applied in Hanoi and some other big cities (Doan Phan et al. 2019; Khiem et al. 2020; Nguyen et al. 2018). In this report, the results of an investigation of heavy metal air pollution in Dalat using the moss biomonitoring method are presented. Dalat is a popular tourist resort and air quality in Dalat needs to be regularly monitored to help city managers take measures to improve air pollution to the lowest level. The moss biomonitoring method can provide data for this purpose.

The moss species that have been frequently used in Europe are *Pleurozium schreber*, *Hylocomium splendens*, *Scleropodium purum*, and *Hypnum cupressiforme* (Frontasyeva & Harmens 2020; Frontasyeva et al. 2004; Harmens et al. 2010). However, the earlier-mentioned moss species are rarely found in Asia; instead, other mosses are used, such as *Hypnum plumaeforme*, *Taxithelium instratum*, *Thuidium tamariscellum,* and *Barbula indica* (Abdullah et al. 2011; Doan Phan et al. 2019; Khiem et al. 2020; Lee et al. 2005; Munar et al. 2014). In the present investigation, the samples of *Barbula indica* moss were collected at different locations in Dalat. *Barbula indica* moss is widely distributed and easy to collect in the city. The concentrations of 40 chemical elements in the moss samples were determined by two analytical methods, namely, neutron activation analysis and total reflection X-ray fluorescence. The possible sources of heavy metal air pollution have been identified by the application of factor analysis.

Materials and Methods

SAMPLING AREAS

Dalat, a tourist city located in Lam Dong province of Vietnam, is about 390 km² in area. Dalat is located at 11.95° latitude and 108.44° longitude and sits approximately 1500 m above sea level on the Lang Biang Plateau in the southern part of the Central Highlands. Dalat is surrounded by lovely mountains and is in the temperate zone because of the effects of altitude and forest cover. Dalat has dry and rainy seasons each year. Normally, the rainy season is from May to October, and the other months are the dry season.

Nineteen moss samples were taken at different sites in and around Dalat (Figure 1) after the end of the rainy season from October 2018 to May 2019. Some moss samples were collected near roads with different levels of traffic, others were collected near farms, and some were taken near fertilizer factories. This study is intended as a

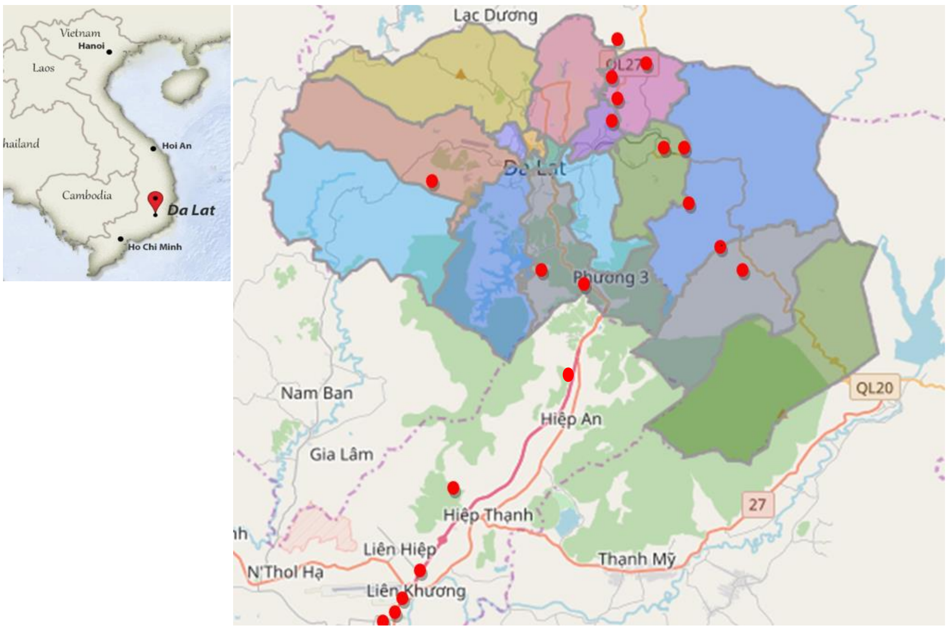

FIGURE 1. Sampling sites in Dalat

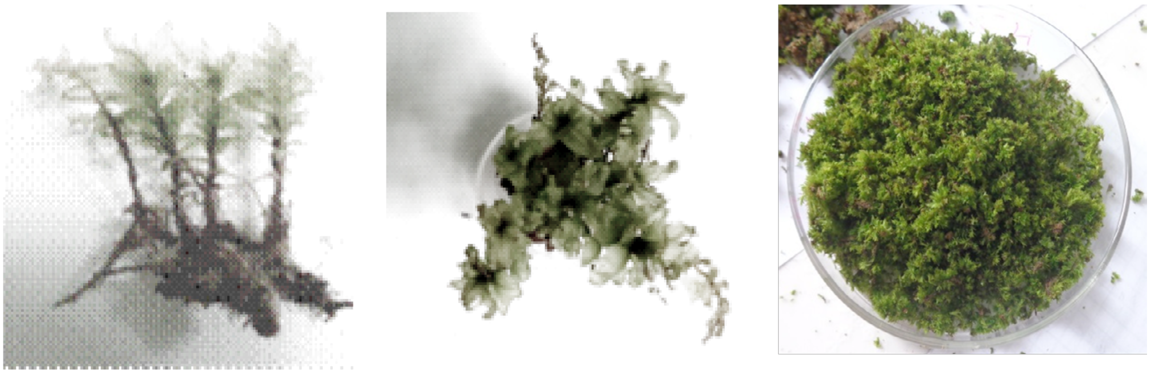

FIGURE 2. Left and Middle: cross section and plan view of *Barbula indica* moss. Right: a raw moss sample

survey. The main purpose of sampling at a variety of sites is to assess a wide range of possible air pollution sources. A typical moss sample is shown in Figure 2.

PREPARING MOSS SAMPLES

We followed moss sampling procedures recommended by the ICP Vegetation protocol (Frontasyeva & Harmens 2020). To minimize the influence of the substrate, moss was collected from trees at least 1.5 m above the ground and only the green part of the moss was used for analysis. Using only the green portion allows us to measure the relatively recent pollutants from the past two-to-three years. After collection, the moss samples were cleaned of soil particles, washed three times with distilled water, and after that dried at 40 °C for 50 h. Next, they were crushed and homogenized to a powder (~0.5 mm) in a Retsch AS 300 control analytical sieve shaker for 30 min. After preparation, the moss powders were stored in sealed polyethylene vials until they were analyzed.

EXPERIMENTAL TECHNIQUES

NAA TECHNIQUE

NAA was carried out at the 500 kW Dalat research reactor (DRR) in Vietnam to determine the concentration of trace elements. Previous work established that NAA at DRR meets the requirements of multielement analysis for 42 elements: Al, As, Au, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Hf, I, In, K, La, Mg, Mn, Mo, Na, Nd, Pr, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn, and Zr (Ho et al. 2016b).

For NAA sample preparation, the moss powder was heat-sealed in polyethylene foil bags and packed in aluminum containers. Sample weights were about 50 and 150 mg for short and long-term irradiation, respectively. Table 1 shows the masses of the NAA moss samples.

TABLE 1. The mass of NAA moss samples in mg

Moss sample name	Mass of moss sample (short irradiation)	Mass of moss sample (long irradiation)
DL01	47.25	148.51
DL02	54.11	139.27
DL03	57.0	189.79
DL04	47.0	150.57
DL05	72.78	159.99
DL06	55.7	151.53
DL07	43.91	152.57
DL08	60.91	181.25
DL09	65.62	156.71
DL10	62.47	157.05
DL11	46.92	121.77
DL12	52.27	171.85
DL13	67.05	173.39
DL14	54.37	164.07
DL15	55.16	122.68
DL16	66.25	157.81

DL17	54.34	165.68
DL18	50.33	117.11
DL19	48.6	111.29

The k0-NAA method was used to analyze the moss samples. This method was developed at the Dalat Nuclear Research Institute and has been officially applied since 2002 as the standard method (Ho & Pham 2003; Ho et al. 2016a).

Short irradiations were conducted for 45 s on Channel 7-1 at a thermal neutron flux of approximately 4.2×10^{12} $cm^{-2}s^{-1}$. To determine short-lived isotopes, every sample was decayed for 1-2 min and then measured for 15 min. Long irradiations were conducted for 1 h on a rotary rack at a thermal neutron flux of approximately 3.5×10^{12} $cm^{-2}s^{-1}$. The samples were allowed to decay for 3 days prior to counting for 1 h. The moss samples were measured with a gamma-ray spectrometer on a Canberra HPGe detector, for which the FWHM is approximately 1.9 keV at 1332 keV and the relative efficiency is ~33%. Genie-2K software was used to analyze the obtained gamma spectra and the K0-Dalat software (Ho et al. 2016a) was used to determine the elemental concentrations from the obtained count rates. Certified international reference materials (SRM-1572, SRM 1547, IAEA-V-10, and SMELS Type I, Type II, and Type III) were analyzed for analytical quality control. The differences between the certified values and those obtained for all analyzed elements are smaller than 7%.

TXRF TECHNIQUE

Along with NAA, we used TXRF to analyze the trace element concentrations in the moss samples. A Bruker S2 PICOFOX spectrometer was used for the TXRF measurements. The spectrometer can detect and measure K-line energy of the following elements: Al, Si, P, Se, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Es, Fm, Md, No, and Lr. With L-line energy, it can measure elements: Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Fr, Ra, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, and U. Difficult or impossible to measure are elements: Na, Mg, Ar, Kr, Xe, Rn, Np, Pu, Am, Cm, Ek, Cf , H, He, Li, Be, B, C, N, O, F, Ne, Zr, Nb, Mo, and Tc (Towett et al. 2013). To prepare the TXRF moss samples, the moss powder samples described above were ground down to a grain size of 50 μm using a Retsch MM 400 mixer mill. Then, the moss powder samples must be liquified by means of digestion. In this investigation, MARS 6 Microwave Acid Digestion made by CEM Corporation was used. A 0.5 g weight of moss powder was placed into the digestion vessel and 10 mL of HNO_3 (65%) were added. The mixture was gently swirled and allowed to sit for approximately 15 min before closing the vessel. The operating time of the Retsch MM 400 mixer mill was 50 min. After finishing this procedure, the moss samples were liquid (the original sample). Then 500 μL of the original sample we retransferred to a polymer container, and a gallium internal standard liquid was added until the sample reached 1 ppm gallium. The sample was then thoroughly homogenized with an automatic sample shaker. After thorough homogenization, 10 μL of the sample were transferred to a sample carrier and then dried at 30 °C. Figure 3 shows an NAA sample and a TXRF sample.

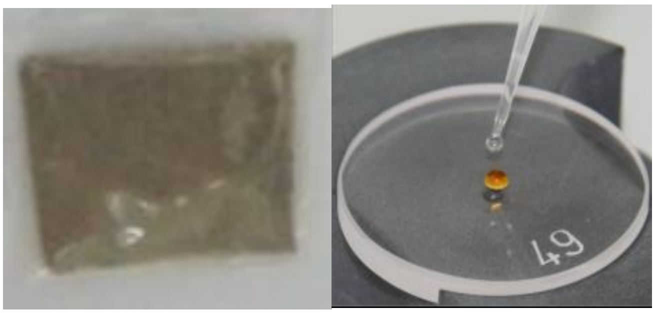

FIGURE 3. Left: NAA sample. Right: TXRF sample

RESULTS AND DISCUSSION

ORIGINAL DATA

The elemental concentration data of the moss samples from the 19 sampling sites were analyzed using NAA and TXRF techniques. In all, 40 elements were detected, including Na, Mg, Al, Si, P, S, Cl, K, Ar, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Kr, Rb, Y, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Yb, Hf, Ta, Pb, Th, and U.

The error in the concentrations for all elements is less than 10%. The experimental data of *Barbula indica* moss at Dalat are presented in Table 2. These results show that more elements were found than in similar studies in Vietnam. Khiem et al. (2020) detected 22 elements in moss samples from Hanoi using the Proton Induced X-ray Emission (PIXE) technique. Doan Phan et al. (2019) found 30 elements in moss samples from Hue, Hoi An, and Ho Chi Minh City using INAA.

TABLE 2. Trace element concentrations for moss samples from Dalat region (in $mg.kg^{-1}$)

Element	Site																		
	DL01	DL02	DL03	DL04	DL05	DL06	DL07	DL08	DL09	DL10	DL11	DL12	DL13	DL14	DL15	DL16	DL17	DL18	DL19
Na*	287	133	389	266	139	138	152	96	183	150	89	216	139	218	234	394	112	150	319
Mg*	236	233	239	252	157	186	179	182	171	170	292	213	290	415	153	339	188	163	218
Al**	2087	2125	4581	2015	1639	2171	3169	861	5209	1885	1197	2320	1636	334	2865	3342	1437	3122	3506
Si**	3210	5210	11330	5341	4202	5339	4524	3675	3755	9386	5425	2872	2975	2678	2826	2875	3246	2846	2759
P**	326	1048	839	591	603	517	1210	1111	1423	851	545	803	958	809	759	1106	1049	565	849
S**	548	1382	1461	1018	1239	703	1056	1401	1493	1223	1011	1211	1197	1481	1124	1428	1326	970	1227
Cl*, **	345	752	297	704	219	781	238	300	216	343	407	924	352	52	1288	90	1042	226	343
K*, **	7522	2926	6208	10670	4716	2526	7985	5792	10940	6047	2036	7099	1858	4491	4729	8856	8295	5427	4584
Sc*	2.36	0.97	1.50	2.10	0.86	0.44	1.25	0.46	1.90	0.34	0.15	1.20	0.70	0.08	0.73	1.83	0.88	0.35	0.58
Ti**	122	139	220	234	119	160	279	95	107	181	84	87	240	28	28	68	44	87	75
V*, **	7.80	9.60	7.60	12.30	5.60	9.10	7.80	5.20	9.50	12.40	5.30	8.00	9.40	5.00	17.60	16.80	10.40	5.00	18.70
Cr*, **	5.90	6.10	11.80	12.70	5.80	2.98	5.69	3.44	12.20	3.86	1.35	11.10	4.50	9.11	8.25	6.90	12.86	3.12	7.97
Mn*, **	138	69	101	58	60	56	50	38	60	47	58	64	77	40	122	84	79	71	163
Fe*, **	4494	2727	5064	2915	2191	948	3244	1178	5065	1018	400	3088	1963	286	2377	2795	2709	1222	2066
Co*, **	1.58	0.80	1.41	0.65	0.66	0.28	1.00	0.77	0.80	0.39	0.21	1.05	1.57	0.30	1.81	1.45	2.19	0.97	1.87
Ni**	1.08	1.46	3.02	2.14	0.86	0.86	1.28	0.68	2.56	1.12	1.15	1.06	1.10	2.50	6.10	2.66	5.58	5.63	5.90
Cu**	12.34	11.94	16.28	6.76	10.78	7.50	10.60	16.80	14.06	8.74	7.12	15.80	8.20	9.21	12.50	11.60	17.86	13.45	16.66
Zn*, **	86	214	176	59	157	80	110	1366	140	83	110	479	157	47	76	220	802	97	191
As*	11.36	2.56	5.30	1.61	1.28	2.78	4.25	1.49	6.47	3.97	0.78	7.06	2.56	0.55	0.70	0.71	0.49	0.77	0.93
Se*	0.34	0.16	0.21	0.25	0.16	0.09	0.21	0.11	0.24	0.19	0.10	0.15	0.15	0.10	0.21	0.25	0.10	0.11	0.20
Br*, **	3.40	2.33	6.88	2.58	2.62	3.05	1.97	3.64	4.51	6.44	2.48	3.79	4.53	2.78	2.96	1.94	2.15	1.62	5.80
Kr**	1.16	0.16	0.87	1.54	1.21	1.78	0.52	1.33	1.16	0.22	1.54	0.22	1.26	1.42	1.57	1.64	1.87	1.59	1.33
Rb*,**	27.40	7.80	17.80	19.20	13.90	5.21	22.20	22.00	25.30	11.10	2.95	29.00	4.70	5.47	3.10	2.70	23.00	2.96	9.20
Y**	28.20	1.28	1.96	7.88	0.78	1.30	1.46	1.56	4.28	1.10	1.36	1.46	1.30	0.42	3.06	7.30	2.66	6.30	6.28
Sb*	0.37	0.08	0.43	0.05	0.16	0.17	0.14	0.44	0.08	0.12	0.36	0.17	0.28	0.24	0.11	0.64	0.30	0.05	0.14
I*	5.90	4.10	10.60	6.00	3.20	6.02	3.10	2.70	2.70	4.74	5.22	6.70	7.10	4.80	4.50	4.74	3.70	2.10	1.24
Cs*	1.76	0.38	0.84	1.64	0.44	0.22	0.82	0.42	1.40	0.45	0.21	0.77	0.30	0.13	0.31	0.86	0.34	0.18	0.29
Ba**	2.52	26.58	22.78	3.60	24.36	18.96	12.56	8.88	14.54	4.20	7.64	7.54	5.48	3.28	4.68	12.45	5.78	20.65	15.45
La*	23.31	2.32	3.29	23.96	1.90	3.90	2.40	1.25	2.80	1.74	1.83	3.64	1.79	0.36	3.20	6.61	1.70	18.40	4.41
Ce*	45.60	5.60	7.50	25.17	4.60	9.80	5.75	3.52	7.00	2.20	2.06	9.70	5.00	0.38	3.37	9.00	3.20	13.74	4.48
Sm*	5.52	0.35	0.67	3.00	0.36	0.54	0.37	0.31	0.37	0.31	0.40	0.75	0.32	0.05	0.68	1.02	0.36	2.75	0.73
Eu*	0.74	0.09	0.09	0.29	0.06	0.05	0.09	0.05	0.09	0.03	0.02	0.09	0.07	0.01	0.11	0.20	0.14	0.27	0.10
Tb*	0.90	0.07	0.09	0.19	0.05	0.04	0.06	0.03	0.09	0.00	0.02	0.14	0.07	0.01	0.08	0.23	0.11	0.15	0.07
Dy*	4.52	0.30	0.35	1.72	0.25	0.50	0.40	0.18	0.43	0.35	0.13	0.73	0.26	0.14	0.70	1.18	0.32	1.33	0.67
Yb*	1.80	0.14	0.46	0.33	0.11	0.08	0.20	0.14	0.30	0.09	0.07	0.50	0.20	0.05	0.12	0.58	0.16	0.24	0.12
Hf*	0.53	0.25	0.60	0.76	0.25	0.20	0.35	0.18	0.70	0.17	0.04	0.60	0.40	0.16	0.26	0.87	0.18	0.14	0.36
Ta*	0.21	0.09	0.27	0.13	0.09	0.05	0.14	0.04	0.18	0.07	0.02	0.22	0.13	0.02	0.08	0.12	0.10	0.03	0.07
Pb**	5.42	6.24	7.74	5.32	3.22	3.06	5.28	8.20	6.80	3.70	2.14	18.32	3.60	0.82	3.45	2.68	18.42	3.18	27.14

Th*	3.70	0.79	3.20	1.71	0.80	0.58	1.40	0.50	1.90	0.65	0.24	2.90	0.80	0.14	0.37	0.96	0.30	0.37	0.49
U*	9.46	0.89	1.37	1.67	2.22	1.09	0.73	2.42	0.56	1.04	2.27	2.38	0.64	0.36	0.80	0.63	1.03	0.56	0.65

* - determined by NAA; ** - determined by TXRF

The mean concentration of the elements in the moss samples from Dalat decreased as: K > Fe > Si > Al > S > P > Cl > Zn > Na > Mg > Ti > Mn > Rb > Cu > V > Ce > Ba > Cr > Pb > La > I > Y > Br > As > Ni > U > Th > Co > Sm > Sc > Dy > Cs > Hf > Yb > Kr > Sb > Se > Eu > Tb > Ta.

The contamination factor (CF) is the ratio of the mean concentration of each heavy metal to the average of the three lowest concentrations of the same metal. CF was calculated from (1) (Hakanson 1980; Zhou et al. 2017):

$$CF_i = \frac{C_i}{BG_i} \quad (1)$$

where C_i is the mean concentration of each element from the investigated area; and BG_i is the average value of the three sample sites with the lowest concentration of the corresponding metal from the investigated area.

According to Fernández and Carballeira (2001), the contamination factors (CF) can be used to determine the contamination levels of each element in the sample. The CF values comprise of six categories: CF < 1 (category I): no contamination, 1 < CF ≤ 2 (category II): suspected contamination, 2 < CF ≤ 3.5 (category III): slight contamination, 3.5 < CF ≤ 8: moderate contamination (category IV), 8 < CF ≤ 27: serious contamination (category V), and CF > 27: extreme contamination (category VI). Contamination factors are shown in Table 3. It can be seen from Table 3 that Tb air pollution (CF = 11.9) is very serious (category VI).

TABLE 3. The contamination factors

Element	Na	Mg	Al	Si	P	S	Cl	K	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se
CF	2.0	1.4	3.0	1.6	1.8	1.6	3.9	2.8	5.1	3.8	1.9	2.9	1.8	4.4	3.9	3.1	1.7	4.0	5.0	1.8
Category	II	II	III	II	II	II	III	III	IV	IV	II	III	II	IV	IV	III	II	IV	IV	II
El	Br	Kr	Rb	Y	Sb	I	Cs	Ba	La	Ce	Sm	Eu	Tb	Dy	Yb	Hf	Ta	Pb	Th	U
CF	1.9	5.9	4.7	5.5	3.8	2.3	3.6	3.7	5.2	5.7	4.5	6.8	11.9	5.1	4.5	3.3	4.8	3.8	5.1	1.5
Category	II	IV	IV	IV	IV	III	IV	IV	IV	IV	IV	IV	V	IV	IV	III	IV	IV	IV	II

A comparison of these results with those obtained by previous investigations of *Barbula indica* moss in Vietnam and other mosses in European countries (Barandovski et al. 2013) was carried out. The results of the comparison are listed in Table 4. Ho Chi Minh City (in the south) and Hanoi (in the north) are the biggest city and the capital of Vietnam, respectively. They have many companies and factories. Hue and Hoi An are cities in the middle of Vietnam that have many industrial parks. Doan Phan et al. (2019) used the INAA technique for analysis. It showed concentrations of only 30 elements, including: Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Sr, Cd, Sb, Cs, Ba, La, Ce, Sm, Tb, Ta, Th, and U. In another study, Khiem et al. (2020) used Proton Induced X-ray Emission to detect trace elements in *Barbula indica* moss from Hanoi; it showed the concentration of 22 elements: Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Zr, Ba, and Pb.

For Hue, Hoi An, and Ho Chi Minh City, the element concentrations are higher than in our work. For Hanoi, all element concentrations are higher than in Dalat. The element concentrations of Mg, Al, Si, S, Cl, K, Ti, Cr, Mn, Fe, Cu, As, Br, Rb, Ba, and Pb in Hanoi are higher than in Dalat by 17.2, 4.2, 8.9, 2.7, 3.7, 2.4, 5.5, 3.5, 2.3, 2.5, 2.3, 5.5, 10.5, 12.3, 132, and 32.7 times, respectively.

Concentrations of barium and lead in Hanoi are especially high compared to Dalat.

TABLE 4. Mean element concentrations due to atmospheric deposition from *Barbula indica* mosses in Dalat and other cities in Vietnam and other mosses in Europe (in mg.kg^{-1})

Element	Dalat (our work)	Doan Phan et al. 2019			Khiem et al. 2020	Barandovski et al. 2013
		Hue	Hoi An	Ho Chi Minh City	Hanoi Capital	Macedonia
Na	200	620	1310	930		
Mg	225	1550	1620	1290	3866.66	1900
Al	2395	5800	3200	4800	10591.19	1900
Si	4446				39595.76	
P	840				1100.14	1100
S	1184				3238.92	
Cl	469	1700	2100	780	1711.59	
K	5932	16000	17000	12000	14401.56	4600
Sc	0.98	1.09	0.80	1.81		
Ti	126	271	205	524	691.60	
V	9.64	12.20	5.11	8.08		3.5
Cr	7.14	11	6.80	19.90	26.73	3.5
Mn	76	74	88	77	170.95	130
Fe	2408	3720	4810	5430	6025.18	1500
Co	1.04	1.40	1.01	3.28		
Ni	2.46	4.20	2.70	9.50	4.42	3.5
Cu	12.01				27.20	3.5
Zn	245	126	254	178	397.53	20
As	2.93	2.30	3.00	4.10	16.11	
Se	0.18	1.40	0.70	0.39		
Br	3.45	10.40	7.70	12.80	36.11	
Kr	1.18					
Rb	13.42				151.17	
Y	4.21					
Sb	0.23	1.40	0.89	1.00		
I	4.69					
Cs	0.62	1.58	1.18	5.30		
Ba	11.68	58	83	101	1545.55	34
La	5.73	3.10	2.24	5.60		
Ce	8.82	6.20	4.20	11.70		
Sm	0.99	0.51	0.35	1.15		
Eu	0.14					
Tb	0.13					
Dy	0.76					
Yb	0.30					
Hf	0.37					
Ta	0.11	0.09	0.07	0.15		
Pb	7.09				231.55	4.6

Th	1.15	1.78	0.86	1.49
U	1.62	0.62	0.23	1.10

DATA PROCESSING AND STATISTICAL ANALYSIS

Factor analysis is commonly used for statistical analysis in environmental science. Data processing was performed using the Statistica-8 software. The relationship of each variable to the underlying factor is expressed though the factor loading, which ranges from -1.0 to 1.0. A factor loading close to 1 indicates a strong effect on the element concentration.

In our multivariate statistical analysis, eleven elements of interest to us were selected; namely, V, As, Fe, Zn, Se, Rb, Sb, Cs, Al, Cu, and Pb. The correlation coefficients of the selected elements in the moss samples of Dalat are presented in Table 5. Four factor loadings, F1, F2, F3, and F4, can explain more than 86% of the variance.

TABLE 5. Eigen values for the factors

Factor loading	Eigen value	Cumulative	Variability (%)	Cumulative (%)
F1	5.07	5.07	42.28	42.28
F2	2.50	7.58	20.87	63.16
F3	1.63	9.21	13.61	76.76
F4	1.16	10.37	9.63	86.39

The factor loadings and factor scores are shown in Tables 6 and 7, respectively. Earlier studies by Cucu-Man et al. (2004) and Pacyna and Pacyna (2001) have used factor score and factor loading to explain the results of moss biomonitoring studies. Factor loadings after Varimax normalized rotation and explained variance are shown in Table 6. Factor scores used to estimate factor portions at the sites are presented in Table 7. The main pollution sources in our work can be explained in the next part.

TABLE 6. Matrix of rotated factor loadings (11 selected elements)

Element	F1	F2	F3	F4
V	-0.013	0.016	**0.921**	-0.022
As	**0.836**	0.116	-0.166	-0.101
Fe	**0.865**	0.242	0.259	0.017
Zn	-0.185	**0.732**	-0.321	0.413
Se	**0.831**	-0.173	0.411	0.061
Rb	**0.692**	**0.599**	-0.304	-0.096
Sb	0.056	0.090	0.022	**0.964**
Cs	**0.9**43	-0.041	0.018	0.023
Al	0.456	0.221	**0.623**	0.045

Cu	0.244	**0.916**	0.128	0.224
Pb	-0.021	**0.859**	0.299	-0.211

TABLE 7. Factor scores for each sampling site

Sampling Site	F1	F2	F3	F4
DL01	**2.53**	-0.41	-0.7	0.52
DL02	-0.22	0.009	0.15	-0.63
DL03	**0.99**	0.46	0.41	**1.02**
DL04	**1.01**	-0.87	-0.13	-0.86
DL05	-0.15	-0.25	-0.64	-0.277
DL06	-0.78	-0.56	-0.14	-0.41
DL07	**0.72**	-0.07	-0.21	-0.59
DL08	-0.69	**1.64**	-1.58	**1.76**
DL09	**1.66**	0.37	0.42	-0.81
DL10	-0.33	-0.54	0.17	-0.65
DL11	-1.02	-0.85	-0.7	0.67
DL12	0.56	**1.61**	-0.64	-0.84
DL13	-0.46	-0.64	-0.02	0.32
DL14	-1.05	-0.92	-1.02	0.001
DL15	-0.5	-0.97	**1.54**	-0.32
DL16	0.16	-0.82	**1.79**	**2.71**
DL17	-0.63	**2**	-0.15	0.32
DL18	-0.88	-0.74	-0.9	-0.92
DL19	-0.89	**1.58**	**2.38**	-0.99

Factor 1, the strongest, explains 42.28% of the total variance. It is heavily loaded by Cs (0.943), As (0.836), Fe (0.865), Se (0.831), and Rb (0.692). These elements are found in the Earth's crust, and Fe, especially, is the fourth most abundant element in the Earth's crust. Arsenic is a naturally occurring element that is widely distributed in soils and minerals. In addition, Dalat is a major vegetable-growing region in Vietnam. Farmers use a variety of pesticides that contain As and Se to grow vegetables, so Dalat's soil may be highly polluted by As and Se. The consequence is that it is easy to find As and Se in the dust of Dalat. Therefore, Factor-1 is most likely from windblown dust. The highest F1 scores were found at sites: DL01(2.53), DL03 (0.99), DL07 (0.72), DL09 (1.66), and DL13 (1.01), which are within 2 km of a national highway and surrounded by vegetable farms.

Factor 2 is smaller than F1 and is the second strongest. It represents 20.87% of the total variance. It effects the factor loadings of Zn (0.732), Rb (0.599), Cu (0.916), and Pb (0.859). Zinc, Cu, and Pb are well known to be in emissions from brake and tire wear (Adamiec 2017; Nguyen et al. 2018). The highest F2 scores were found at sites DL08 (1.64), DL12 (1.61), DL17 (2.00), and DL19 (1.58). These sites are near a national highway and other roads. This suggests the pollution source related to the F2 factor is the traffic emissions of gasoline-burning vehicles, especially cars and motorbikes.

Factor 3 is 13.61% of the total variance. It is heavily loaded by V (0.921) and to a lesser extent by Al (0.623). It is confirmed that V is emitted from the combustion of fossil fuels and oil (Kousehlar & Windom 2019; Visschedijk et al. 2013). In Dalat, the use of fossil fuels for cooking and people's daily activities is still common. Furthermore, farmers in Dalat regularly use diesel-powered engines to irrigate coffee and other agricultural crops. These activities can be the main sources of vanadium emissions into the atmosphere in Dalat. The highest Factor 3 scores were found at sites: DL16 (1.79), DL15 (1.54), and DL19 (2.38), where there are flower and rice farms. Therefore, it may be suggested that Factor 3 is related to the combustion of fossil fuels and oil.

Factor 4 represents 9.63% of the total variance. It contains Sb for which the factor loading is 0.964. The highest Factor 4 scores were found at sites: DL03 (1.02), DL08 (1.76), DL16 (2.71). The Sb concentration is very low at all sites (maximum value is 0.64 ppm). Element Sb originates mainly from mining, especially open pit gold-antimony mines. DL03 and DL16 are located at the foothills of Elephant Mountain which has antimony ore, and DL08 is at a local antimony mining area (Hon Bo Mountain) where there was an antimony factory in 1990s. Therefore, Factor 4 should be related to antimony mining in Dalat.

CONCLUSION

For the first time, the well-known moss biomonitoring method has been applied to investigate the pollution of chemical elements in the air of Dalat, a large tourist city in Vietnam. *Barbula indica* moss samples were collected at 19 different locations in Dalat. By combining both NAA and TXRF analysis methods, the concentration of 40 chemical elements, including Na, Mg, Al, Si, P, S, Cl, K, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Kr, Rb, Y, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Yb, Hf, Ta, Pb, Th, and U were determined in the moss samples. A comparison of the concentrations of elements in the air of Dalat with other cities that we have investigated by the same method shows that the level of trace element air pollution in Dalat is lower. Contamination factors have been estimated using the concentration data. The results show that Dalat's air is suspected of being polluted by Na, Mg, Si, P, S, V, Mn, Cu, Se, Br, and U; slightly polluted by Al, Cl, Cr, Ni, S, and Hf; moderately polluted by Sc, Fe, Zn, As, Kr, Rb, Y, Sb, Cs, Ba, La, Ce, Sm, Eu, Dy, Yb, Ta, Pb, and Th; and seriously polluted by Tb. Factor analysis has been applied to the concentrations of 11 elements, including V, As, Fe, Zn, Se, Rb, Sb, Cs, Al, Cu, and Pb to find the possible sources. The analysis shows that windblown dust, emissions from vehicles, the use of pesticides, the combustion of fossil fuels, and antimony mining are the main sources of air pollution in Dalat.

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