Environmental Engineering and Management Journal

May 2021, Vol.20, No. 5, 791-800 http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu



"Gheorghe Asachi" Technical University of lasi, Romania



BIOMONITORING OF CHEMICAL ELEMENT AIR POLLUTION IN HANOI USING Barbula indica MOSS

Nguyen Huu Quyet¹, Le Hong Khiem^{2,3*}, Trinh Thi Thu My⁴, Nguyen Thi Bao My^{1,4}, Marina Frontasieva⁴, Inga Zinicovscaia^{4,5}, Nguyen An Son⁶, Tran Thien Thanh⁷, Le Dai Nam², Khuat Thi Hong², Nguyen Ngoc Mai², Trinh Dinh Trung⁸, Duong Van Thang¹, Nguyen Thi Thuy Hang²

¹Institute for Nuclear Science and Technology, 179 Hoang Quoc Viet, Hanoi, Vietnam ²Institute of Physics - Vietnam Academy of Science and Technology, 10 Dao Tan, Hanoi, Vietnam ³Graduate University of Science and Technology - Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam ⁴Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 6 Joliot-Curie, 141980 Dubna, Russia ⁵Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, 30 Reactorului Str., MG-6, Bucharest - Magurele, Romania

⁶Faculty of Nuclear Engineering, Dalat University, 1 Phu Dong Thien Vuong, Dalat, Vietnam ⁷VNUHCM - University of Science, 227 Nguyen Van Cu, Q.5, Ho Chi Minh City, Vietnam

⁸Center for High Technology Development, Vietnam Academy of Science and Technology, 179 Hoang Quoc Viet, Hanoi, Vietnam

Abstract

Atmospheric deposition of chemical elements in the Hanoi region has been investigated in this study based on moss biomonitoring. Twenty-seven *Barbula indica* moss samples were collected from the end of 2016 to the beginning of 2017, and the concentrations of 33 chemical elements in the samples were determined by instrumental neutron activation analysis. The results show that Hanoi's air is highly polluted with Zn, Ba and Ta, and slightly polluted with Al, Cl, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, As, Cd, Sb, La, Ce, Sm, Gd, Tb, Yb, Hf, Th and U. A determination of the possible pollution sources has been made for the analyzed elements; namely: coal and oil combustion are the main sources of V, Ni, Co and As; vehicle exhaust and non-exhaust sources, as well as industrial emissions, are the main sources of Mn, Co, Cd and Ba; construction dust is the source of Ca, Mg and Sb; various industries are the sources of Cr and Ni; the dust from cement kilns and ash from biomass burning is responsible for K and Cl; two-stroke motor vehicles, galvanizing factories and tire wear are the sources of Zn; and Br may be emitted from burning wastes.

Keywords: contamination factor, factor analysis, Hanoi air quality, moss biomonitoring, neutron activation analysis

Received: May, 2020; Revised final: August, 2020; Accepted: October, 2020; Published in final edited form: May, 2021

1. Introduction

Currently, Vietnam's economy is developing very fast and the speed of industrialization and urbanization is very high. A consequence of these developments is that the air in Vietnam, especially in Hanoi and Ho Chi Minh City, is badly polluted. Atmospheric pollution in Hanoi is a very serious problem nowadays, and Hanoi is ranked as the second most polluted city in Southeast Asia (Tuan et al., 2017).

Severe air pollution in Hanoi is causing serious health problems for residents who live in this region. As a result of rapid urbanization and economic development, the air quality in Hanoi is degraded. The main factors causing air pollution in Hanoi are:

^{*}Author to whom all correspondence should be addressed: e-mail: lhkhiem@iop.vast.ac.vn, Phone: +844974032932; Fax: +84437669050

- Growing numbers of motorbikes and cars on the road. In Hanoi, private motorbikes and cars are the main means of transportation. Almost every adult living in the city owns a motorbike, and public transport does not satisfy the needs of the city residents. It is expected that in 2020 the number of cars and motorcycles in Hanoi will increase to 843,000 and 6.1 million units, respectively (Dung and Kajita, 2018).

- *Growing industrial activity.* The number of industrial parks is increasing year by year in Hanoi and the surrounding regions. By the end of 2019, Hanoi owned 70 operational industrial clusters, covering a total area of more than 1,300ha, with a total of 3,100 businesses.

- A surge in construction projects. A lot of new residential areas with multistory buildings and new traffic systems are constantly being built. Many new roads in Hanoi are being constructed and the existing roads are being constantly upgraded.

However, the measures being implemented by authorities are insufficient to cope with the rapidly increasing air pollution. Therefore, continuous monitoring of air pollution is necessary to provide pollution data to the authorities and citizens so that they can find preventive measures.

At the present time, the monitoring of air quality in Vietnam is conducted mainly by using automatic monitoring stations purchased from abroad. Nevertheless, for developing countries like Vietnam, this method has some disadvantages, such as: i) the price of a monitoring station and its operational cost are very high; ii) highly qualified personnel having the ability to operate and maintain these monitoring stations are needed; iii) only places having electricity can use these stations. Furthermore, only potentially toxic gases (SO_x, NO_x, CO_x, etc.) can be monitored by these devices. Due to these disadvantages, additional methods for monitoring air quality in Vietnam are needed.

Another way of monitoring air quality is to use powerful pumps in combination with air filters. The high-powered pumps draw air into a filter and the concentration of trace elements in the filter is analyzed by various analytical techniques. However, this method requires many pumps if one wants to monitor a large region. In addition, it is impossible to extend the pumping time for long, so that the results do not represent a long period of time. To overcome the weaknesses of the above methods, a method to investigate air pollution due to chemical elements by using different biological indicators, such as lichen, moss, algae, etc., has been widely applied in Europe (Cucu-Man et al., 2002; Rühling and Tyler, 1970; Stihi et al., 2017; Vukovic et al., 2015). Among biological indicators, moss is commonly used because (Blagnyte and Paliulis, 2010; Onianwa, 2001): i) moss growth is mainly due to the uptake of nutrients from the air because moss has no real root system; ii) moss stems lack cuticles; iii) the ratio between the surface area and the mass of moss is high; iv) the moss's cation exchange capacity is high; v) moss grows everywhere, and therefore it is easy to collect. In addition, storage, carrying and preparation of moss samples are rather easy. Many previous investigations of atmospheric metal pollution using moss have been carried out worldwide (Chakrabortty and Paratkar, 2006; Fernandez and Cårballeira, 2001; Zhou et al., 2017). Unfortunately, this technique has been very rarely applied in Vietnam so far.

A project for studying air pollution in Hanoi using moss biomonitoring was carried out by us. The moss samples collected at different places in the Hanoi region were sent to the Joint Institute for Nuclear Research (JINR) in Dubna (Russia) to determine the concentration of chemical elements by instrumental neutron activation analysis (INAA) with the IBR-2 nuclear reactor. Earlier studies were performed in several regions of Vietnam (Doan Phan et al., 2019; Khiem et al., 2020; Nguyen et al., 2010). This investigation is a continuation of our project to study air pollution due to chemical elements in the Hanoi region using a moss bioindicator.

2. Material and methods

2.1. Studied area

Hanoi is the capital of Vietnam and the second biggest city in the country. Hanoi is located at latitude 20°53' - 21°23' north and longitude 105°44'-106°02' east. Hanoi is adjacent to the provinces of Thai Nguyen and Vinh Phuc to the north, Ha Nam and Hoa Binh to the south, Bac Ninh, Bac Giang and Hung Yen to the east, and Hoa Binh and Phu Tho to the west. Hanoi is one of the two leading economic centers of the country. For many reasons, the atmosphere of Hanoi is seriously polluted, especially with pollution caused by dust. Hanoi residents, from their own experiences, also see the seriousness of this air pollution source. The dust in Hanoi is created by the ongoing construction of new residential buildings, transportation systems and industrial parks. Therefore, the majority of the people living in the Hanoi region use masks as dust shields when they have to go outside.

2.2. Moss collection

In our investigation, *Barbula indica* moss was used. Sampling locations having different levels of pollution were chosen from the investigated region; namely: areas with very high population density, areas near the industrial parks, areas with high traffic flow, areas with low population density, and areas surrounded by rice fields, etc. This allows us to easily compare pollution data of areas with different features.

Moss samples were collected using plastic pickers and put in sample bags made from low-impurity materials. Each moss collection site is more than 200 meters from a highway or more than 50 meters from a local road. The mosses collected within a $2 \text{ km} \times 2 \text{ km}$ area were considered one sample.

It is noted that Hanoi has a lot of dust, and the moss growing at the sampling locations also has a lot of dust; therefore, we washed the mosses with distilled water to remove dust and other extraneous materials. Only green sections of the moss were chosen for analysis. Before analysis, the samples were dried until their weights no longer changed. Twenty-seven samples of *Barbula indica* moss were obtained in the Hanoi region from the end of 2016 to the beginning of 2017. The sampling locations are shown in Fig. 1.

2.3. Analytical method

The collected moss samples, after washing, cleaning and drying, were transferred to the Frank Laboratory of Neutron Physics of JINR in Dubna for analysis to determine the concentrations of chemical elements. The concentrations were determined by the instrumental neutron activation method using the IBR-2 nuclear reactor (Frontasyeva, 2011). The amount of dried moss in each sample was about 300 mg. The irradiation time for the short-lived elements was 3 min using channel 2 of REGATA and their gamma-ray spectra were measured for 15 min after 3-5 min of decay.

For the long-lived elements, the irradiation time was 72 h using channel 1, which is screened by Cd. After long irradiation, the gamma-ray spectra of the irradiated samples were measured two times. The first measurement was carried out for 30 minutes after 3 days of decay. The second measurement was taken 90 minutes after 20 days of decay.

For measurements of gamma-ray spectra, both Ge(Li) and HPGe detectors were used. The energy resolution at 1332 keV of ⁶⁰Co for Ge(Li) detectors is from 2.5 to 3 keV and is 1.9 keV for the HPGe detector. To determine the activities of the isotopes in question, the Genie-2000 was used. Then, using software developed at FLNP, activities were recalculated into concentrations of elements in the moss samples.

2.4. Quality control

To provide quality control for the results obtained by the comparative method, several reference materials were used, including NIST 1515 (apple leaves), NIST 1573a (tomato leaves), NIST 1547 (peach leaves), NIST 1632c (trace elements in coal), NIST 1633c (coal fly ash), 1633b (coal fly ash), NIST 2710 (Montana soil), NIST 1633c (coal fly ash) and NIST IRMM 667 (estuarine sediment). For the majority of elements, certified values were in good agreement, within 10% of the recommended values, except for Rb (17%), Ti and Ni (20%), Mo and Au (30%), Hf and W (33%) and I (39%). The average values of the relative analytical errors (written in parentheses for each element) are as follows: Na (6%), Mg (3%), Al (3%), Cl (9%), K (10%), Ca (9%), Sc (3%), Ti (10%), V (8%), Cr (6%), Mn (4%), Fe (6%), Ni (11%), Co (9%), Zn (27%), As (7%), Se (19%), Br (3%), Sr (10%), Cd (13%), Sb (8%), Ba (4%), Cs (3%), La (3%), Ce (8%), Sm (10%), Gd (10%), Tb (3%), Yb (12%), Hf (30%), Ta (32%), Th (14%) and U (5%).

2.5. Statistical analysis

Statistical analysis of our element concentration data for the moss samples, including descriptive statistics and factor analysis, was carried out using STATISTICA-8 software. Furthermore, to assess the pollution level of a given element in an investigated region, contamination factors (CF) were estimated. The contamination factor of the ith element is calculated as (Gonçalves et al., 1992) (Eq. 1):

$$CF_i = C_i / BG_i \tag{1}$$

where: C_i is the mean concentration of the *i*th element of the sample, and BG_i is the mean concentration of the *i*th element of the three samples with the smallest concentrations of that element in the survey region.



Fig. 1. Left: The moss sampling locations in the Hanoi region from the end of 2016 to the beginning of 2017. Right: the location of Hanoi on the map of Vietnam

Based on the contamination factor, the pollution level can be classified (Fernandez and Cårballeira, 2001) as: CF is smaller than 2 (C1 level): unpolluted; CF is between 1 and 2: may be polluted (C2 level); CF is between 2 and 3.5: pollution at a low level (C3 level); CF is between 3.5 and 8: moderate pollution (C4 level); CF is between 8 and 27: pollution at high level (C5 level); and CF is greater than 27: pollution level is very high (C6 level).

3. Results and discussion

3.1. Descriptive statistics

Descriptive statistics, including minimum (Min), maximum (Max), mean, median, standard deviation (SD), detection limit (DL), coefficient of variation (CV), kurtosis (Kurt) and skewness (Skew), are listed in Table 1.

From Table 1, it is found that the mean concentrations of the 33 observed elements are arranged in the following ascending order: Tb < Ta < Se < Yb < Sm < Hf < Gd < U < Cd < Cs < Sc < Th < Sb < Co < As < La < Ni < Ce < Br < V < Cr < Sr < Ba < Mn < Zn < Ti < Na < Cl < Fe < Mg < Al < K < Ca. The elements which are most abundant in the crust, Ca,

K, Al, Mg, Fe, Cl, Na and Ti, had the highest concentrations. Among 11 important metal elements detected, including Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As and Cd, the average Fe concentration is highest (4400 mg.kg⁻¹) and its concentrations vary from 1740 to 9060 mg.kg-1. The ranges of the other heavy metal elements, including Sc, Ti, V, Cr, Mn, Ni, Co, Zn, As and Cd are 0.2-2.6, 129-967, 7.54-39.1, 7.09-46.3, 63.3-147.8, 1.9-15.5, 0.35-6.68, 68.2-1900, 1.39-7.83 and 0.29-3.21 mg.kg⁻¹ with the average values of 1.16, 467.7, 17.28, 20.81, 147.8, 7.12, 1.93, 457.7, 3.19 and 0.88 mg·kg⁻¹, respectively.

As shown in Table 1, the coefficients of variation for most observed elements in the Hanoi region are at a moderate level (from 16.00% to 68.41%). For some exceptional elements, the coefficient is much higher, namely 92.69%, 135.81% and 206.09% for Zn, Ba and Ta, respectively. The elements with high variation are probably affected by several factors. In addition, the complexity of the pollution source for an element may be estimated from two other parameters in Table 1, skewness and kurtosis. The concentration distribution of a given element can be considered Gaussian if its skewness and kurtosis are within -0.8 to 0.8 and -3.0 to 3.0, respectively (Gaza and Kugara, 2018).

Table 1. Descriptive statistics for of metal concentrations in moss samples collected in the Hanoi region

El.	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)	Median (mg/kg)	SD (mg/kg)	DL (mg/kg)	CV (%)	Kurt	Skew
Na	510.0	1830	922.3	816.0	339.6	5.75	36.82	0.26	0.94
Mg	2510	8160	4417	4080	1443	115.86	32.68	0.17	0.86
Al	1340	14700	6767	5560	3439	10.52	50.83	0.13	0.97
Cl	485.0	3620	2132	2300	926.3	23.50	43.45	-1.21	-0.18
K	6450	12200	9570	9780	1560	376.22	16.30	-0.87	-0.17
Ca	13500	62600	23544	20800	9838	234.70	41.79	9.31	2.76
Sc	0.20	2.46	1.16	0.97	0.61	0.03	52.42	-0.57	0.69
Ti	129.34	967.0	467.75	428.0	229.4	129.34	49.30	-0.16	0.74
V	7.54	39.10	17.28	15.50	7.50	0.73	43.32	1.53	1.24
Cr	7.09	46.30	20.81	17.90	10.65	4.90	51.18	0.18	1.04
Mn	63.30	147.8	147.8	123.0	80.75	0.38	54.63	10.00	2.68
Fe	1740	9060	4400	4000	2058	99.87	46.78	-0.49	0.66
Ni	3.87	15.50	7.12	6.13	3.18	3.87	44.87	0.51	0.85
Co	0.35	6.68	1.93	1.57	1.24	0.08	64.09	7.65	2.33
Zn	68.20	1900	457.7	306.0	432.4	1.78	94.46	4.20	2.04
As	1.39	7.83	3.19	3.00	1.41	0.03	44.14	3.20	1.39
Se	0.23	0.68	0.32	0.30	0.11	0.23	35.00	2.51	1.36
Br	4.29	16.10	8.46	7.99	2.87	0.04	33.82	1.27	1.08
Sr	21.50	131.00	49.26	38.40	28.32	5.52	57.49	2.60	1.79
Cd	0.29	3.21	0.88	0.70	0.62	0.27	69.71	6.85	2.13
Sb	0.41	3.28	1.45	1.39	0.67	0.01	46.63	0.73	0.84
Ba	21.20	626.0	107.8	59.50	149.2	3.98	138.4	9.45	3.19
Cs	0.53	2.04	1.16	1.12	0.39	0.02	33.84	0.21	0.81
La	1.03	8.42	4.14	3.41	2.03	0.06	49.16	0.03	0.91
Ce	2.15	17.30	8.13	6.45	4.01	1.46	49.31	0.06	0.92
Sm	0.15	1.22	0.58	0.48	0.29	0.002	49.30	-0.03	0.86
Gd	0.31	1.67	0.73	0.72	0.33	0.04	45.28	1.13	1.01
Tb	0.02	0.16	0.08	0.07	0.04	0.01	47.62	-0.30	0.76
Yb	0.18	0,84	0.33	0.27	0.16	0.18	46.65	3.32	1.60
Hf	0.27	1.48	0.68	0.62	0.35	0.06	51.92	-0.48	0.78
Та	0.02	2.46	0.22	0.12	0.45	0.01	210.0	25.84	5.04
Th	0.35	2.74	1.35	1.09	0.70	0.02	51.75	-0.46	0.78
U	0.32	2.02	0.85	0.78	0.45	0.01	25.84	0.85	1.15

Skewness coefficients of all elements are positive (except for Cl and K) indicating that there are some exceptionally high concentrations in the dataset. The distributions of Ca, Mn, Co, Zn, Cd, Ba and Ta are strongly skewed. Some previous studies have shown that the high value of this coefficient reflects the presence in the study area of point pollution sources (Fernandez et al., 2007; Varela et al., 2014).

A comparison of the concentrations of the moss samples in Hanoi obtained in this work, and those previously obtained in other provinces of Vietnam, namely Thai Nguyen (Nguyen et al., 2010), Hue, Hoi An and Ho Chi Minh City (Doan Phan et al., 2019) is presented in Fig. 2. In this figure, the vertical axis is the ratio of the elements in the moss samples collected in Hanoi and the corresponding province. It can be seen from Fig. 2 that the concentrations of the majority of elements in the moss samples in Hanoi are higher than those in other provinces, except Ho Chi Minh City. This is understandable because Hanoi and Ho Chi Minh City are the two largest industrial centers, with the highest population densities and fastest urbanization rates of the country.

3.2. Contamination factor

In Table 2, the calculated contamination factors in the investigated area for all 33 observed elements, together with the pollution classification in Hanoi, are presented. From this classification, one can see that the air of Hanoi may be polluted by Na, Mg, K, Ca, Se, Br, Sr and Cs (C2 level), and is slightly polluted by Al, Cl, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, As, Cd, Sb, La, Ce, Sm, Gd, Tb, Yb, Hf, Th and U (C3 level). Furthermore, the air in the Hanoi area is highly polluted by Zn, Ba and Ta (C4 level).

3.3. Factor analysis

Factor analysis is a useful mathematical technique in environmental science because the observed data normally are multidimensional. This method is used to predict the variability of correlations using a smaller number of unobserved variables called factors. By applying this method, the dimensionality of the original dataset is reduced, and therefore, the interpretation of the original dataset becomes easier (Schaug et al., 1990).



Fig. 2. Comparison of the ratios of elemental concentrations of Hanoi to those of Thai Nguyen, Hue, Hoi An and Ho Chi Minh City. (a) Thai Nguyen/Hanoi, (b) Hue/Hanoi, (c) Hoi An/Hanoi, (d) Ho Chi Minh City/Hanoi

Element	Na	Mg	Al	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Со
CF	1.71	1.66	2.48	2.98	1.35	1.55	2.82	2.84	2.01	2.29	2.14	2.32	2.47	2.70
Rank	C2	C2	C3	C3	C2	C2	C3							
Element	Zn	As	Se	Br	Sr	Cd	Sb	Ba	Cs	La	Ce	Sm	Gd	Tb
CF	5.81	2.13	1.79	1.76	1.95	2.90	2.54	3.67	1.87	2.46	2.44	2.30	2.20	2.41
Rank	C4	C3	C2	C2	C2	C3	C3	C4	C2	C3	C3	C3	C3	C3
Element	Yb	Hf	Ta	Th	U									
CF	2.16	2.33	4.90	2.59	2.30									
Rank	C3	C3	C4	C3	C3									

Table 2. Contamination factors

STATISTICA-8 software was used in the factor analysis. The relationship of each variable to the underlying factor is expressed by the factor loading, which ranges from -1.0 to 1.0. The greater the factor loading, the stronger is its effect on the elemental concentration. Each factor may be attributed to a possible source of pollution. The factor score allows us to know the relative contribution of the factor to the elemental composition of an investigated place. A large score shows a strong effect of the factor on the local elemental composition.

In this study, we used factor analysis for attribution and characterization of various possible sources of pollution. A detailed explanation of factor analysis is given in Schaug et al., (1990). In this work, among the 33 observed elements, we are primarily interested in 24: Mg, Al, Cl, K, Ca, V, Cr, Mn, Fe, Ni, Co, Zn, As, Br, Cd, Sb, Ba, La, Ce, Gd, Tb, Yb, Hf and Th.

The elements of interest are those that are considered to indicate pollution sources in the studied region. For selecting the optimal number of factors, one of the important criteria that we have applied is that the explained variance after varimax rotation be greater than 1%. After carefully examining the options with different numbers of factors, we found that seven factors that can explain 93.15% of the total variance. The seven factors are shown in Table 3. The explained variances of F1, F2, F3, F4, F5, F6 and F7 are 58.41%, 10.72%, 6.59%, 5.37%, 5.00%, 4.12% and 2.94%, respectively. The factor loadings (F) are listed in Table 4, and the factor scores (FS) are listed in Table 5. Note that the bold type in Table 4 denotes factor loadings having values greater than or equal to 0.4. The factor loadings whose values are less than 0.4 may be due to random fluctuations.

Factor-1 is the most important one, and it explains 58.41% of the total variance. This factor has high contributions from Mg, Al, V, Fe, Ni, Co, As, La, Ce, Gd, Tb, Yb, Hf and Th with the loading factors of 0.743, 0.966, 0.847, 0.849, 0.520, 0.713, 0.781, 0.956, 0.963, 0.927, 0.957, 0.798, 0.870 and 0.970, respectively. Aluminum, Fe, Ca and Mg are among the most abundant elements in the Earth's crust, and they are considered as the main tracers of crustal elements (Alekseenko and Alekseenko, 2014). These elements, except Ca, are present with high loadings in Factor-1. The lack of Ca in the soil factor for Hanoi was found in a previous investigation by Cohen et al. (2010),

studied characterization which and source apportionment of fine particulate sources at Hanoi from 2001 to 2008. Other elements, such as La, Ce, Gd, Tb, Yb, Hf and Th, can also be found in the Earth's crust (Kim et al., 2004; Taylor, 1964; Zhao and Hopke, 2004). Regarding the presence of V, Ni, Co and As in Factor-1, coal and oil combustion are probably the main sources of these elements (Li et al., 2019). It has been shown that the air of Hanoi is heavily contaminated by soil dust mixed with anthropogenic elements (Cohen et al., 2010; Hien et al., 2004, 2005). Thus, the source for Factor-1 was identified as a mixture of soil dust and ash from coal and oil combustion. There are four high-factor-score sampling locations, including S8 (2.58), S23 (2.0), S14 (1.77) and S7 (1.24). Except for S23, which is located inside Nhu Quynh, a large town in Hung Yen province, the remaining three are located on the edge of Hanoi, where roads in residential areas are being constructed or repaired. The population and traffic density in these areas is very high, resulting in a large amount of soil dust in the air. Furthermore, the use of coal for cooking by residents is very common in these areas.

Factor-2 explains 10.72% of the total variance and shows high loadings for Mn, Co, Cd and Ba with the values of 0.820, 0.647, 0.673 and 0.805, respectively. These metals are emitted from vehicle exhaust and non-exhaust sources (brake wear, tire wear) as well as from industrial emissions (Elhadi et al., 2018). The Factor-2 maximum scores were observed at the S1 (4.47) and S9 (1.37) locations. These two locations are located in the northeast of Hanoi, close to the largest cargo warehouse in the north of Vietnam and near Bac Ninh industrial park. The number of large trucks carrying goods to and from this warehouse daily is very high. Therefore, the sources of air pollution in these areas should be related to the operation of heavy trucks and industrial activities.

Factor-3 accounts for 6.59% of the total variance, with the highest loading for Ca and moderate loadings for Mg and Sb, at 0.917, 0.413 and 0.573, respectively. Factor-3 can be identified as construction dust because Ca and Mg are the main components of cement and lime (Li et al., 2019; Wimolwattanapun et al., 2011). Two locations, S4 and S7, have high factor scores. The first location, S4, with the largest factor score (4.12), is located on the bank of West Lake.

Biomonitoring of chemical element air pollution in Hanoi using Barbula indica moss

	F1	F2	F3	F4	F5	F6	F7
Eigenvalue	14.02	2.57	1.58	1.29	1.20	0.99	0.71
Expl. Variance (%)	58.41	10.72	6.59	5.37	5.00	4.12	2.94
Cumulative (%)	58.41	69.12	75.72	81.08	86.09	90.21	93.15

Table 3. Factor analysis: explained variance and cumulative variance of the factors

Table 4. The result of factor analysis. Bold values represent factor loadings greater than 0.4

Element	F1	F2	F3	F4	F5	F6	F7
Mg	0.743	0.390	0.413	0.065	0.037	-0.129	0.105
Al	0.966	0.142	-0.001	0.124	0.020	0.017	0.021
Cl	-0.355	-0.220	-0.212	0.044	0.768	-0.095	0.035
K	0.144	-0.016	-0.059	-0.143	0.941	0.013	-0.031
Ca	0.081	0.131	0.917	0.174	-0.204	-0.095	0.024
V	0.847	0.055	0.377	0.104	0.014	-0.127	-0.081
Cr	0.252	0.203	0.151	0.896	-0.081	0.099	-0.016
Mn	0.466	0.820	-0.022	0.174	-0.048	-0.040	0.066
Fe	0.849	0.387	0.146	0.047	-0.120	-0.016	-0.179
Ni	0.520	0.224	0.410	0.609	-0.201	0.152	0.008
Со	0.713	0.647	0.089	0.196	-0.071	0.020	0.022
Zn	0.015	0.114	-0.048	0.129	-0.047	0.961	-0.060
As	0.781	0.070	0.407	0.138	-0.067	0.151	-0.001
Br	0.040	0.033	0.020	-0.011	-0.007	-0.057	0.992
Cd	0.121	0.673	0.188	0.473	0.074	0.321	-0.004
Sb	0.495	0.272	0.573	0.368	-0.100	0.405	-0.010
Ba	0.253	0.805	0.233	0.019	-0.293	0.135	-0.006
La	0.956	0.178	-0.001	0.139	-0.052	0.068	0.036
Ce	0.963	0.169	-0.035	0.136	-0.36	0.053	0.049
Gd	0.927	0.097	0.097	0.132	-0.166	0.027	0.124
Tb	0.957	0.225	0.043	0.111	-0.058	0.067	0.001
Yb	0.798	0.491	0.039	0.250	0.006	0.033	0.023
Hf	0.870	0.282	0.235	0.094	0.037	0.095	0.008
Th	0.970	0.157	0.052	0.091	-0.051	0.051	-0.002

Table 5. The factor scores

Sample	FS1	FS2	FS3	FS4	FS5	FS6	FS7
S1	0.91	4.47	0.09	0.81	0.50	-0.38	0.23
S2	-0.61	-0.30	0.02	-0.74	1.38	3.72	-0.51
S3	0.55	0.00	-0.14	-0.43	0.62	-0.09	0.18
S4	-0.09	-0.58	4.12	0.98	-0.67	-0.09	-0.13
S5	-0.48	0.21	0.06	-0.74	-0.06	0.75	0.60
S6	-0.42	-0.17	0.01	-0.35	-1.19	0.20	0.18
S 7	1.24	-0.16	1.27	-0.20	-0.16	-0.87	-0.82
S8	2.58	-1.13	0.43	-0.17	-0.32	-0.45	0.05
S9	-0.11	1.37	0.69	-1.02	-2.33	1.30	-0.21
S10	0.73	0.08	-0.37	-0.90	0.23	-0.05	-1.27
S11	0.08	-0.58	-0.67	-0.91	-1.49	-0.18	2.74
S12	0.19	-0.25	-1.13	-0.73	-1.97	0.27	-1.37
S13	-0.60	-0.46	0.20	-0.29	1.26	-0.48	0.03
S14	1.77	-0.79	-0.48	-0.17	1.13	-0.45	-1.26
S15	0.62	-0.06	-0.25	0.29	1.43	-0.22	0.82
S16	-1.28	-0.02	0.43	-1.20	0.44	-0.94	-0.48
S17	-1.10	-0.34	-0.80	2.62	-0.50	-0.66	-0.20
S18	-0.96	-0.18	0.17	-0.02	0.25	0.54	-0.29
S19	-0.52	-0.45	-0.75	1.90	-0.92	-0.42	-0.19
S20	-0.40	-0.27	-0.25	-0.06	0.52	-0.49	1.24
S21	-0.22	-0.30	-0.08	2.46	0.52	1.59	-0.37
S22	-0.69	0.04	0.57	-0.46	1.10	-0.41	2.34
S23	2.00	-0.32	-1.17	0.76	-0.26	0.96	1.22
S24	-0.98	0.24	-0.20	-0.59	0.84	-0.81	-0.46
S25	-1.02	-0.32	-0.47	-0.01	-0.79	-0.74	-0.03
S26	-0.50	-0.21	-0.34	-0.56	0.63	-0.90	-1.03
S27	-0.69	0.50	-0.96	-0.29	-0.21	-0.71	-0.99

The second location with a high factor score (1.27) is My Dinh. Both are located in the inner city of Hanoi. West Lake is the largest lake in Hanoi, with many large hotels under construction along its shores.

Factor-4 accounts for 5.37% of the total variance. Cr and Ni are responsible for this factor with loadings of 0.896 and 0.609, respectively. This factor can be attributed to industrial sources. Chromium and Ni are widely used in different industries, including metallurgy, electroplating, and leather, etc. (Dall'Osto et al., 2013). These elements are emitted into the atmosphere by different sources, among them fuel combustion (Pulles et al., 2012; Song and Gao, 2011), steel and other industries, the copper-nickel refinery and the ferro-manganese and aluminum plants (Berg et al., 1995). Three locations have high factor scores: S17 (2.62), S19 (1.90) and S21 (2.46). These locations are found in two districts of Hung Yen province that contain two large industrial parks. In both are a number of very large steel fabrication and metal refining factories that use a lot of fossil fuel to refine metals. Therefore, Factor-4 may be directly related to the metal industries in these areas.

Factor-5 explains 5.00% of the total variance. Potassium and Cl have the highest factor loadings, 0.941 and 0.768, respectively. The analysis of the chemical composition of the dust from cement kilns by several research groups has shown that its main chemical components are K and Cl (Bocheńczyk, 2019; Duchesne and Reardon, 1998). In addition, it was reported by Cohen at al. (2010) that K is emitted from burning biomass. The highest factor scores belong to the sampling points S15 (1.43), S2 (1.38), S13 (1.26), S14 (1.13) and S22 (1.10). The S2 sampling point is located in Bac Ninh province, while the remaining sampling points are in Van Giang and My Hao districts of Hung Yen province. These sampling points are located relatively close together, as the two districts of Van Giang and My Hao are located close to Bac Ninh province. About 3 km from the S2 sampling point, there is a cement factory serving the construction works of Bac Ninh province. The remaining sampling sites, S15, S13, S14, and S22, in Hung Yen province are located next to rice fields. In these areas, the burning of rice straw and postharvest crops always occurs. Thus, Factor-5 may be related to dust from cement kilns and ash from burning biomass.

Factor-6 is responsible for 4.12% of the total explained variance and only Zn is assigned for it with the factor loading of 0.961. Hopke et al. (2008), in a study of urban air quality in the Asian region, found the same factor for Zn. They explained that in Asian countries, two-stroke motor vehicles are used extensively, and this is a major source of Zn. Zinc also may be emitted from galvanizing factories (Begum and Hopke, 2019). The same situation has been found in this investigation for the Hanoi region. Furthermore, Zn is also emitted from tire wear (Blok, 2005; Longhin et al., 2016). Therefore, Factor-6 may be related to a mixture of sources that relate to two-stroke motor

vehicles, galvanizing factories and tire wear. The locations with the highest factor scores are S2 (3.72), S21 (1.59), and S9 (1.30). Zinc concentrations at these locations are 4.15, 2.93 and 2.69 times higher, respectively, than the average value in the investigated region. Location S2 is located in the Bac Ninh industrial zone, while S9 is located near the industrial park. Bac Ninh industrial park is one of the largest ones north of Hanoi with a huge number of workers. The main means of transport of these workers are motorcycles, and many of them use two-cycle engines. In this industrial park, there are various mechanical fabrication factories, metal plating workshops and factories for assembling electronic components. Likewise, the S21 sampling point is located near the large industrial zone of Hung Yen province east of Hanoi.

Factor-7 explains 2.94% of the total explained variance. Only Br with the factor loading of 0.992 is responsible for this factor. It has been found that solid waste burning is characterized by Br (Vehlow et al., 2003; Zhou et al., 2013). The sampling points with the highest factor scores are S11 (2.74), S22 (2.34), S20 (1.24) and S23 (1.22). Sampling point S11 is located in Gia Lam, which is a suburban district of Hanoi. The remaining three sampling points are located in My Hao district of Hung Yen province. In these areas, there are many companies that buy raw material waste. Materials that cannot be reused will be burned. Thus, Factor-7 may be related to waste burning activity.

4. Conclusions

In this work, the mean concentrations of 33 chemical elements have been determined by instrumental neutron activation analysis in 27 *Barbula indica* moss samples collected from the end of 2016 to early 2017. Based on the results, the following remarks can be made:

a) From the estimated contamination factors of the analyzed elements, the air pollution level in the Hanoi region is highly polluted with Zn, Ba and Ta, slightly polluted with Al, Cl, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, As, Cd, Sb, La, Ce, Sm, Gd, Tb, Yb, Hf, Th and U, and may be polluted with Na, Mg, K, Ca, Se, Br, Sr and Cs.

b) From the factor analysis, the following possible emission sources can be inferred:

- Soil dust mixed with anthropogenic elements is the main source of air pollutants in the Hanoi region.
- The next-most significant source may be transportation, including heavy trucks, vehicles and motorcycles.
- Operation of factories in industrial zones around Hanoi.
- Use of coal fuel in residential activities and the burning of rice straw and solid waste.

This study is a part of a campaign to investigate air pollution in Vietnam using the moss biomonitoring technique. Our campaign is ongoing, and other major cities in the country will be investigated.

Acknowledgements

This work was financed by the Vietnam Ministry of Science and Technology (project NDT.25.RU/17) and, in part, by Vietnam Academy of Science and Technology (grant NVCC05.02/21-21) and the International Centre of Physics at the Institute of Physics (grant ICP.2021.11). Participation of N.A.S. was supported by the Ministry of Education and Training (grant B2019-DLA-04). We would like to thank Steven Carlson for the corrected version of the manuscript.

References

- Alekseenko V., Alekseenko A., (2014), The abundances of chemical elements in urban soils, *Journal of Geochemical Exploration*, 147, 245-249.
- Begum B.A., Hopke P.K., (2019), Identification of sources from chemical characterization of fine particulate matter and assessment of ambient air quality in Dhaka, Bangladesh, *Aerosol and Air Quality Research*, **19**, 118-128.
- Berg T., Royset O., Steinnes E., Vadset M., (1995), Atmospheric trace element deposition: Principal component analysis of ICP-MS data from moss samples, *Environmental Pollution*, 88, 67-77.
- Blagnyte R., Paliulis D., (2010), Research into heavy metals pollution of atmosphere applying moss as bioindicator: A literature review, *Environmental Research*, *Engineering and Management*, 4, 26-33.
- Blok J., (2005), Environmental exposure of road borders to zinc, Science of the Total Environment, 348, 173-190.
- Bocheńczyk A.U., (2019), Chemical characteristics of dust from cement kilns, *Mineral Resources Management*, 35, 87-102.
- Chakrabortty S., Paratkar G.T., (2006), Biomonitoring of trace element air pollution using, *Aerosol and Air Quality Research*, 6, 247-258.
- Cohen D.D., Crawford J., Stelcer E., Bac V.T., (2010), Characterisation and source apportionment of fine particulate sources at Hanoi from 2001 to 2008, *Atmospheric Environment*, **44**, 320-328.
- Cucu-Man S., Mocanu R., Steinnes E., (2002), Atmospheric heavy metal survey by means of mosses: A regional study (Iasi, Romania), *Environmental Engineering and Management Journal*, **1**, 533-540.
- Dall'Osto M., Querol X., Amato F., Karanasiou A., Lucarelli F., Nava S., Calzolai G., Chiari M., (2013), Hourly elemental concentrations in PM2.5 aerosols sampled simultaneously at urban background and road site during SAPUSS-diurnal variations and PMF receptor modelling, *Atmospheric Chemistry and Physics*, **13**, 4375-4392.
- Doan Phan T.T., Trinh T.T.M., Khiem L.H., Frontasyeva M.V, Quyet N.H., (2019), Study of air pollution in Central and Southern Vietnam using moss technique and neutron activation analysis, *Asia-Pacific Journal of Atmospheric Sciences*, 55, 247-253.
- Dung T.N., Kajita Y., (2018), Traffic congestion and impact on the environment in Vietnam: Development of public transport system - Experience from actual operation of bus in Hanoi, *Journal of Civil and Environmental Engineering*, **8**, 317, doi: 10.4172/2165-784X.1000317.
- Duchesne J., Reardon E.J., (1998), Determining controls on element concentrations in cement kiln dust, *Waste Management*, 18, 339-350.
- Elhadi R.E., Abdullah A.M., Abdullah A.H., Ash'aari Z.H., Khan M.F., (2018), Seasonal variations of atmospheric particulate matter and its content of heavy metals in

Klang Valley, Malaysia, Aerosol and Air Quality Research, 18, 1148-1161.

- Fernandez J.A., Cårballeira A., (2001), Evaluation of contamination, by different elements, in terrestrial mosses, Archives of Environmental Contamination and Toxicology, 40, 461-468.
- Fernandez J.A., Aboal J.R., Real C., Carballeira A., (2007), A new moss biomonitoring method for detecting sources of small-scale pollution, *Atmospheric Environment*, **41**, 7231-7239.
- Frontasyeva M.V., (2011), Neutron activation analysis in the life sciences, *Physics of Particles and Nuclei*, **42**, 332-378.
- Gaza T., Kugara J., (2018), Study of heavy metal air pollution, using a moss (*Grimmia dissimulate*) biomonitoring technique, *Universal Journal of Chemistry*, 6, 1-13.
- Gonçalves E.P.R., Boaventura R.A.R., Mouvet C., (1992), Sediments and aquatic mosses as pollution indicators for heavy metals in the Ave River basin (Portugal), *Science of the Total Environment*, **114**, 7-24.
- Hien P.D., Bac V.T., Thinh N.T.H., (2004), PMF receptor modelling of fine and coarse PM10 in air masses governing monsoon conditions in Hanoi, northern Vietnam, *Atmospheric Environment*, **38**, 189-201.
- Hien P.D., Bac V.T., Thinh N.T.H., (2005), Investigation of sulfate and nitrate formation on mineral dust particles by receptor modelling, *Atmospheric Environment*, **39**, 7231-7239.
- Hopke P.K., Cohen D.D., Begum B.A., Biswas S.K., Ni B., Pandit G.G., Santoso M., Chung Y.S., Davy P., Markwitz A., Waheed S., Siddique N., Santos F.L., Pabroa P.C.B., Seneviratne M.C.S., Wimolwattanapun W., Bunprapob S., Vuong T.B., Hien P.D., Markowicz A., (2008), Urban air quality in the Asian region, *Science of the Total Environment*, **404**, 103-112.
- Khiem L.H., Sera K., Hosokawa T., Quyet N.H., Frontasyeva M.V., Trinh T.T.M., My N.T.B., Nghia N.T., Trung T.D., Nam L.D., Hong K.T., Mai N.N., Thang D.V., Son N.A., Thanh T.T., Tien D.P.T., (2020), Assessment of atmospheric deposition of metals in Ha Noi using the moss bio-monitoring technique and proton induced X-ray emission, *Journal* of Radioanalytical and Nuclear Chemistry, **324**, 43-54.
- Kim E., Hopke P.K., Edgerton E.S., (2004), Improving source identification of Atlanta aerosol using temperature resolve carbon factions in positive matrix factorization, *Atmospheric Environment*, **38**, 3349-3362.
- Li M., Liu Z., Chen J., Huang X., Liu J., Xie Y., Hu B., Xu Z., Zhang Y., Wang Y., (2019), Characteristics and source apportionment of metallic elements in PM2.5 at urban and suburban sites in Beijing: Implication of emission reduction, *Atmosphere*, **10**, 105, https://doi.org/10.3390/atmos10030105.
- Longhin E., Gualtieir M., Capasso L., Bengalli R., Mollerup S., Holme J.A., Ovrevik J., Casadei S., Benedetto C.D., Parenti P., Camatini M., (2016), Physico-chemical properties and biological effects of diesel and biomass particles, *Environmental Pollution*, **215**, 366-375.
- Nguyen V.H., Frontasyeva M.V., Trinh T.T.M., Gilbert D., Bernard N., (2010), Atmospheric heavy metal deposition in northern Vietnam: Hanoi and Thainguyen case study using the moss biomonitoring technique, INAA and AAS, *Environmental Science and Pollution Research*, **17**, 1045-1052.
- Onianwa P.C., (2001), Monitoring atmospheric metal pollution: A review of the use of mosses as indicators, *Environmental Monitoring and Assessment*, **71**, 13-50.

- Pulles T., Denier van der Gon H., Appelman W., Verheul M., (2012), Emission factors for heavy metals from diesel and petrol used in European vehicles, *Atmospheric Environment*, **61**, 641-651.
- Rühling Å., Tyler G., (1970), Sorption and retention of heavy metals in the woodland moss Hylocomium splendens (Hedw.) Br. et Sch, *Oikos*, 21, 92-97.
- Schaug J., Rambaek J.P., Steinnes E., Henry R.C., (1990), Multivariate analysis of trace element data from moss samples used to monitor atmospheric deposition, *Atmospheric Environment*, **24A**, 2625-2631.
- Song F., Gao Y., (2011), Size distributions of trace elements associated with ambient particular matter in the affinity of a major highway in the New Jersey–New York metropolitan area, *Atmospheric Environment*, **45**, 6714-6723.
- Stihi C., Popescu I.V., Frontasyeva M., Radulescu C., Ene A., Culicov O., Zinicovscaia I., Dulama I.D., Cucu-Man S., Todoran R., Gheboianu A.I., Bucurica A., Bancuta I., Dima G., (2017), Characterization of heavy metal air pollution in Romania using moss biomonitoring, Neutron Activation Analysis and Atomic Absorption Spectrometry, *Analytical Letters*, 50, 2851-2858.
- Taylor S.R., (1964), Abundance of chemical elements in the continental crust: A new table, *Geochimica et Cosmochimica Acta*, 28, 1273-1285.
- Tuan A.H., Chu N.X., Tran T.V., (2017), The environmental pollution in Vietnam: Sources, impact and remedies, *International Journal of Scientific and Technological Research*, 6, 249-253.

- Varela Z, Aboal J.R., Carballeira A., Real C., Fernandez J.A., (2014), Use of a moss biomonitoring method to compile emission inventories for small-scale industries, *Journal of Hazardous Materials*, 275, 72-78.
- Vehlow J., Bergfeldt B., Hunsinger H., Seifert H., Mark F.E., (2003), Bromine in waste incineration: Partitioning and influence on metal volatilisation, *Environmental Science and Pollution Research International*, **10**, 329-34.
- Vukovic G., Urosevic M.A., Tomasevic M., Samson R., Popovic A., (2015), Biomagnetic monitoring of urban air pollution using moss bags (*Sphagnum girgensohnii*), *Ecological Indicators*, 52, 40-47.
- Wimolwattanapun W., Hopke, P.K., Pongkiatkul P., (2011), Source apportionment and potential source locations of PM2.5 and PM2.5-10 at residential sites in metropolitan Bangkok, *Atmospheric Pollution Research*, 2, 172-181.
- Zhao W., Hopke P.K., (2004), Source apportionment for ambient particles in the San Gorgonio wilderness, *Atmospheric Environment*, 38, 5901-5910.
- Zhou Z., Dionisio K.L., Verissimo T.G., Kerr A.S., Coull B., Arku R.E., Koutrakis P., Spengler J.D., Hughes A.F., Vallarino J., Agyei-Mensah S., Ezzati M., (2013), Chemical composition and sources of particle pollution in affluent and poor neighborhoods of Accra, Ghana, *Environmental Research Letters*, **8**, 044025, http://dx.doi.org/10.1088/1748-9326/8/4/044025.
- Zhou X., Chen Q., Liu C., Fang Y., (2017), Using moss to assess airborne heavy metal pollution in Taizhou, China, *International Journal of Environmental Research and Public Health*, 14, 430-442.