Combination of NAA, TXRF, and ED-XRF to detect elements deposition in the moss

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1. Introduction

Mosses are effective and widely-used biomonitors of atmospheric pollution because of their bio-accumulative properties. They lack a cuticle and roots, and readily absorb contaminants from the atmosphere. Mosses are widespread, easy to collect and handle, and provide an inexpensive method of detecting atmospheric contaminants. The moss method was developed in the late 1960s by Rühling and Tyler (1968, 1969, 1970) and has been used extensively in Europe and elsewhere.

Several nuclear-related analytical techniques have been applied to measure trace element concentrations in mosses. Neutron Activation Analysis (NAA), Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Total Reflection X-ray Fluorescence (TXRF), and Proton Induced X-ray Emission (PIXE) have been used for determining heavy elements (Markert et al., 2003). The NAA technique has been used in France, India, Portugal, Ghana, Jamaica, Romania, and Russia. The ICP-MS technique has been used in France, India, Israel, and Norway. The XRF, NAA, and PIXE techniques have been used in India, Jamaica, Ghana, ... However, NAA is the main analytical tool used.

Three methods: NAA (Neutron activation analysis), TXRF (Total Reflection X-Ray Fluorescence), and ED-XRF (Energy-dispersive X-ray Fluorescence) are used in the present investigation. These three techniques are general non-destructive, multi-element techniques with high sensitivity and short analysis time. The research focused on the qualitative detection and quantitative measurement of trace elements in *Barbula indica* moss from Bao Loc, Vietnam.

2. Methods and Results

2.1 Sampling areas

Bao Loc is a city in Lam Dong Province (Vietnam) in the Central Highlands of Vietnam. It is located at 11º32'N latitude and 107º48'E longitude, covers an area of around 232.56 km², and lies about 846 m above sea level. Bao Loc's climate is classified as tropical with an average temperature of 21.2ºC. The average rainfall is about 2480 mm per year. Bao Loc normally has two seasons of six months each. The dry season begins in November and ends in May, and the rainy season lasts the rest of the year.

Barbula indica moss collection was carried out once per half month from the end of the rainy season in November, 2019 to March, 2020. Fig. 1 shows the locations of the 11 moss sample sites in Bao Loc. Sample sites were chosen where the moss was likely to have been affected by traffic, farms, or industry.

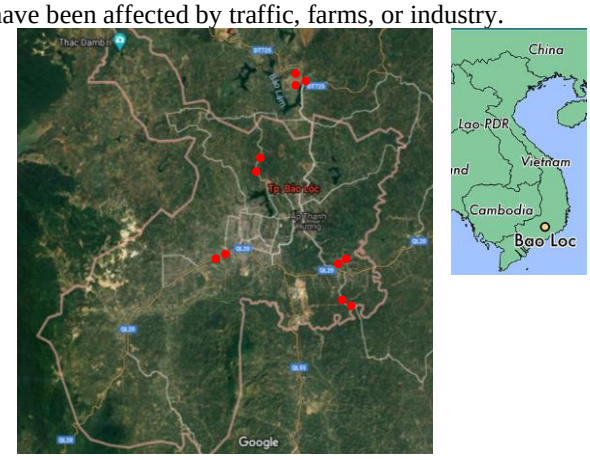

Fig. 1. Left: sampling sites in Bao Loc. Right: location of Bao Loc

2.2 Sample collection

The *Barbula indica* moss morphology and a moss powder sample are shown in Fig. 2. To minimize the influence of the substrate, the moss was collected from trees at least 1.5 m above the ground and only the top, green part was used for analysis.

Fig. 2. Left and Middle: side and overhead views of Barbula indica moss. Right: moss powder sample

2.3 Method detection

TXRF technique

A Bruker S2 PICOFOX™ spectrometer was used to collect the characteristic X-ray spectrum for each moss sample. It was operated at 50 kV high voltage with a maximum tube rating of 50 W. The characteristic

details of the TXRF spectrometer are presented by Towett et al. (2013). The S2 PICOFOX spectrometer can detect 25 elements with K-line energy (from Al to Y), and 47 elements with L-line energy (from Ru to U).

NAA technique

NAA was carried out at the 500 kW Dalat research reactor (DRR) of Vietnam. Previous work established that NAA at DRR has met the requirements of multi-element analysis for 42 elements from Al to U (Ho et al., 2016).

ED-XRF

ED-XRF was conducted on X-LabPro^5 system, at Environmental Radioactivity Assessment, KAERI.

2.1 Results

Trace element concentrations from all 11 sampling sites were analyzed using NAA, TXRF and ED-XRF techniques. All element concentration errors are smaller than 10%. In Table 1, the mean elemental concentrations in moss samples from our work.

Table 1. the mean elemental concentrations in moss samples in Baoloc area (Vietnam)

No.	Element concentration in mg/kg			
	El.	NAA	TXRF	ED-XRF
1	Na	304	--	306
2	Mg	684	--	681
3	Al	--	3,236	3,197
4	Si	--	--	6,412
5	P	--	662	654
6	S	--	1,683	1,678
7	Cl	696	682	673
8	K	914	925	918
9	Ca	--	854	856
10	Sc	1.89	--	
11	Ti	--	337	328
12	V	4.91	5.51	5.40
13	Cr	6.61	6.32	6.45
14	Mn	118	102	109
15	Fe	2,887	3,105	3,147
16	Co	2.01	1.97	1.82
17	Ni	--	3.24	3.15
18	Cu	--	16.59	16.41
19	Zn	371	413	426
20	As	5.67	--	--
21	Se	0.28	--	--
22	Br	5.14	3.43	--
23	Rb	3.27	2.91	
24	Sr	--	46	48
25	Y	--	8.24	
26	Zr			21
27	Ag	--	61	
28	Sn	--	92	
29	Sb	43.36	46.63	
30	I	7.41	--	--
31	Cs	1.13	--	1.62
32	Ba	--	45.44	46.32
33	La	6.89	--	6.78
34	Ce	14.23	--	
35	Sm	1.43	--	
36	Eu	0.24	--	
37	Tb	0.26	--	
38	Dy	1.24	--	
39	Yb	0.63	--	
40	Hf	0.69	--	
41	Ta	0.22	--	
42	Pb	--	4.14	4.57
43	Th	2.29	--	3.01
44	U	3.08	--	3.11

The three techniques detected 44 elements in the moss samples. The NAA method detected 29 elements: Na, Mg, Cl, K, Sc, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Rb, Sb, I, Cs, La, Ce, Sm, Eu, Tb, Dy, Yb, Hf, Ta, Th and U, and the TXRF method detected 24 elements: Al, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Y, Ag, Sn, Sb, Ba and Pb, and ED-ERF method detected 26 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Zr, Cs, Ba, La, Pb, Th, and U. Seven elements (Cl, K, Cr, Mn, Fe, Co, Zn) were detected by both methods. The results are consistent between the techniques.

3. Conclusions

This investigation combined NAA, TXRF, and ED-XRF techniques to identify 44 chemical elements in *Barbula indica* moss. The 29 elements identified with the NAA technique, 24 elements detected by TXRF, and 26 elements detected by ED-XRF method, just only seven elements: Cl, K, V, Cr, Mn, Fe, Co, Zn, Br, Rb and Sb were detected by three techniques.

The NAA, TXRF, and ED-XRF techniques complement each other well, increasing the number of trace elements detected in moss samples and providing more information from biomonitoring surveys. Combined, the three techniques provide a reliable method of determining atmospheric deposition in moss samples.

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