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Original Article

Air Pollution Monitoring in Hanoi Using Proton Induced X-ray Emission Analysis of Mosses on Pelletron Accelerator

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Abstract: In this work, mosses have been used as a biological indicator showing the presence of the metallic dust in the air. The Proton Induced X-ray Emission (PIXE) analysis on a Pelletron accelerator of the VNU University of Science is used for determination of concentration of the metallic dusts in air inHanoi. Depending on the observed places, dusts may contain Al, Si, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Cd or Pb metals with different concentrations. The cadmium (Cd) and lead (Pb) maximum concentrations are of 121.4 ppm and 5.5 ppm, respectively. The results have shown that Cd is presented at some sites, and Pb appears at most sites. We argue that Cd and Pb pollutions are caused by the industry and the traffic, correspondingly.

Keywords: Air pollution; Pelletron accelerator; PIXE analysis; Biomonitor; Heavy metal pollution.

1. Introduction

Air pollution is a problem in many cities around the world. Existence of heavy metals in dust particles in the air impacts negatively on human health. There are many different methods to collect dust in the air and metal concentration analysis. The usefulness of moss in determining the concentration of heavy metals in the air in different regions were discussed and demonstrated in several studies [1, 2]. Using biomonitors as air pollution indicators is an emerging trend besides direct air analysis. This is especially when monitoring large areas [3]. Research-based air pollution analysis is often limited to short sampling periods. Sampling at many locations over a long period using different equipment is very expensive. Biomonitoring is a cost effective and appropriate solution. Biomonitoring is defined as a

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method for assessing the several characteristics of the biosphere with the use of bio-organisms. Bioindicator or biological monitor [4] is used to call this organism. A biomonitors is an organism that provides quantitative information about the quality of environment [3,5]. Therefore, this method requires a suitable organism. Analyse samples can be collected over large areas or in remote sites far from laboratories.

The major advantages of bioindicators are no requirement of using expensive sampling equipment in long term, also they could be found easily. Especially, the heavy metal concentrations in organisms are higher than that in other technical monitoring systems. This can improve the accuracy of measurements. Furthermore, most organisms reflect environmental conditions in average value during certain periods of time. When pollution level rapidly changes with time, this average value is more important.

The use of mosses as biomonitors for air pollution analysis has become popular in the world such as in European countries since the early 1960 s [5], in North America in 1996. All mosses can be used as bioindicators for air pollution studies, but Sphagnum moss is the most suitable. Mosses have no cuticle and roots and obtain their nutrients directly from atmospheric wet and dry deposition [6]. Especially Sphagnum mosses have been found to be very suitable for monitoring air pollution because the shoots accumulate xenobiotics, and their large surface area and unicellular thick leaf structure allow an abundance of cation exchange sites [6].

In Wisconsin (USA), moss-bag technique was used to monitor heavy metal, sulfur and nitrogen using mesh bags containing Sphagnum moss [7]. Similar studies were done in Romania, Russia and Bulgaria using Sphagnum moss with 36 elements investigated [8]. In 1990 s, in most European countries [9], the moss species were used to obtain information about the deposition of heavy metals in the region, changes in deposition patterns, long-distance transmission of gases, and the local emission sources.

Another reason for using moss to study air pollution is that it allows for long-term air monitoring and low costs for sampling and analysis. This allows for dense sampling over a large area to study detailed pollution distribution over a large area [10]. Sphagnum mosses are characterized by the ability to efficiently absorb metals in tissues and therefore have found widespread use in moss-bag methods [11].

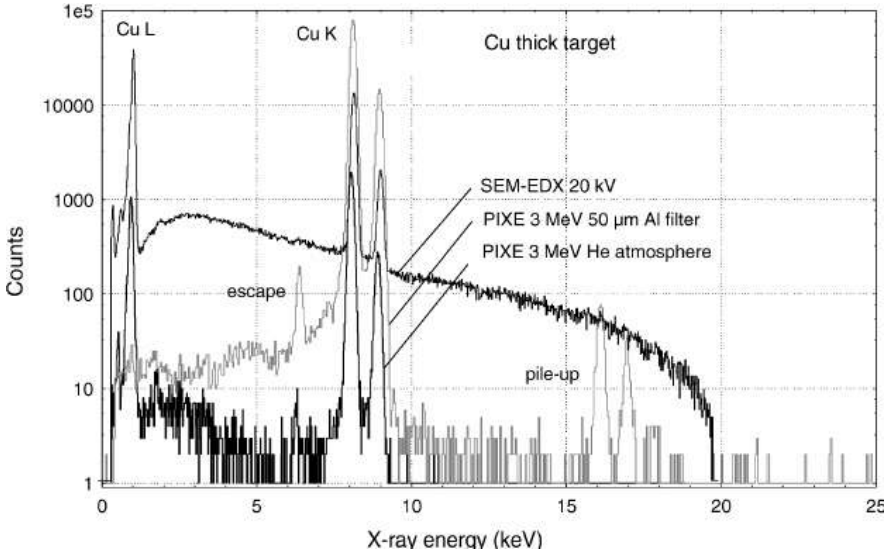

Figure 1. Comparison between PIXE and SEM-EDX spectra of a copper target obtained, respectively, with 3 MeV protons and 20 keV electrons. Note the markedly lower background of the PIXE spectra due to the much-reduced Bremsstrahlung radiation of protons [12].

The Pelletron accelerator at VNU University of Science (VNU-HUS) is equipped with a Proton Induced X-ray Emission (PIXE) analysis system. This is a modern analytical system capable of multi-elemental and non-destructive sample analysis. The amount of sample required for analysis can be very small, only a few milligrams. The analysis time for one sample ranges from just 10 to 30 minutes, depending on the sample. The ability to perform multi-elemental analysis with high sensitivity, reaching the ppm level, and without destroying the sample is a significant advantage of the PIXE analysis method. When the sample remains intact, this is very important as it allows for the preservation of the sample after analysis for potential re-examination later if any doubts arise.

Let's compare three moderns and non-destructive analytical methods: PIXE, EDX (Energy Dispersive X-ray Spectroscopy), and XRF (X-ray Fluorescence). In the case of PIXE and EDX, we have the analysis spectra as shown in Fig. 1 [12].

Comparing XRF with PIXE, Olise et al., [13] pointed out that XRF can lead to large errors if the XRF analysis results are not checked by another method. Even worse problem was due to erroneous identification of Ti K-lines as Ba-L lines of XRF.

Comparing three analytical methods: ICP-OES (Inductively Coupled Plasma- Optical Emission Spectroscopy), XRF, PIXE, Elzain et al. [14] also said that the PIXE method has more advantages because it does not require sample preparation with complex chemicals. The analytical results on plant samples of the three methods are as shown in the Table 1, below [14]:

Table 1. Elements concentrations mg/kg [14]

Element	XRF	ICP-OES	PIXE	XRF/ICP-OES	XRF/PIXE	PIXE/ICP-OES
Ca	4392.5	3740.0	4372.0	1.2	1.0	1.2
K	21325.0	18500.0	17818.0	1.2	1.2	1.0
Cr	32.3	0.5	ND	64.6	-----	-----
Cu	9.9	3.0	9.5	3.3	1.0	3.2
Fe	28.2	20.0	22.0	1.4	1.3	1.1
Mn	24.7	13.0	10.0	1.9	2.5	0.8
Ni	4.6	0.5	ND	9.1	-----	-----
Sr	23.4	22.3	25.5	1.1	0.9	1.1
Zn	5.6	6.0	4.9	0.9	1.1	0.8

The above comparisons show the advantages of PIXE over EDS, XRF and ICP-OES. It can be summarized as follows: PIXE provides higher accuracy and reliability than EDS and XRF and achieves accuracy equivalent to ICP-OES without the need for complex chemical sample preparation like ICP-OES, while the analyzed sample remains intact, but ICP-OES destroys the sample.

The aim of this work is to test the capability of the heavy metal analyzing method in mosses by PIXE analysis on Pelletron accelerator at VNU-HUS.

2. Equipment and Method

2.1. Equipment

Analysis of the samples was done on the 5SDH-2 Pelletron accelerator at VNU University of Science. This is a 1.7-million-volt tandem electrostatic accelerator.

Figure 2. 5SDH-2 Pelletron accelerator, at VNU University of Science.

2.2. Method

2.2.1. Sample Preparation and Processing

The Sphagnum mosses have been selected as suitable bioindicators for monitoring air pollution [6, 11, 15] due to the high cation exchange capacity of their cell walls, making them particularly suitable for use as indicators of heavy metal pollution [16]. The Sphagnum moss samples were collected in the mountain (higher than 1,000 m) at Ta-Cu-Ty commune belonged to Bac Ha district, Lao Cai province, Vietnam.

The reason why we have to take moss from the mountain higher than 1,000 m in Ta Cu Ty is that the moss there has not absorbed much heavy metal pollution, the air above 1,000 m in Ta-Cu-Ty is relatively unpolluted, because it is far from industrial zones, residential areas and traffic.

Moreover, on the high mountains of Ta-Cu-Ty, the air is always humid, providing ideal conditions for moss growth.

If moss is collected from Hanoi, it will contain a lot of heavy metals because the air in Hanoi is polluted with heavy metals, making analysis difficult.

Sample processing was represented (see Fig. 3 and Fig. 4):

- Washing mosses,
- Creating moss bag (2 grams of dry moss per bag),

Figure 3. Sphagnum mosses.

Figure 4. Moss bag.

2.2.2. PIXE Analysis Method

The PIXE technique is used to analyze elements in many material samples. When the X-rays are detected by a high-resolution detector, the dependence of the X-ray energy on the charge number Z, as well as the intensity of the X-ray lines, allows the determination of the elements of the target. For PIXE analyses we used a proton beam with maximal energy 2.6 MeV, and thick target was placed in the center of the reaction chamber at an angle of 32.8° relative to the incident beam. The beam transport tube of accelerator and reaction chamber was maintained in a high vacuum of 1.33×10^{-5} Pa during target irradiation.

The characteristic X-ray spectra of samples were detected using a Silicon Drift Detector (SDD), with the following main characteristics: energy resolution (FWHM) of 138 eV at X 5.9 keV line of Mn. X-ray spectra were recorded using a spectrometer system consisting of a multichannel analyzer connected to a computer and processed offline using GUPIX software.

Due to its high sensitivity and multi-elemental analysis capability, PIXE has found application in the trace elemental analysis of samples from almost every conceivable field of scientific or technical interest. Some of these fields are Biomedicine, Environment, Geology, Archaeology, Material science, Forensic studies and Industrial applications [17]. The method of PIXE analysis is now a sufficiently sophisticated technology and is highly suitable for the analysis of biological, medical, and environmental samples [18].

Methods of analysis of XRF, ICP-OES and PIXE are competitive equal for measuring Ca, K, Fe, Sr and Zn elements [14]. However, the PIXE analysis method has the advantage because it is a non-destructive analysis method and the amount of sample required is very small.

An analysis of air pollution in Hanoi, with a very small sample of PM1.0 and PM2.5 dust particles, on the filter, was analyzed by the accelerator at VNU-HUS [19].

PIXE method was applied in relative version: the concentrations of elements from samples were determined using known values of concentrations of the same elements from the standard samples.

3. Results and Discussions

In this work, we determined the concentrations of all elements in the moss samples in 30 days, 60 days, and 90 days over seven different places in Hanoi city. The results are shown in the tables and graphs below:

Table 2. Results of measurement of moss samples in the first place

Element	30 days (ppm)	60 days (ppm)	90 days (ppm)
Ti	10.93 ± 0.53	15.13 ± 0.75	22.75 ± 0.93
Fe	89.00 ± 1.56	168.65 ± 7.78	207.77 ± 3.42
Cu	0.60 ± 0.13	1.36 ± 0.29	1.39 ± 0.31
Zn	12.76 ± 0.25	20.47 ± 1.26	23.10 ± 0.66
Cd	111.74 ± 4.18	118.35 ± 4.52	121.47 ± 1.27
Pb	1.89 ± 0.10	2.85 ± 0.55	3.57 ± 1.09

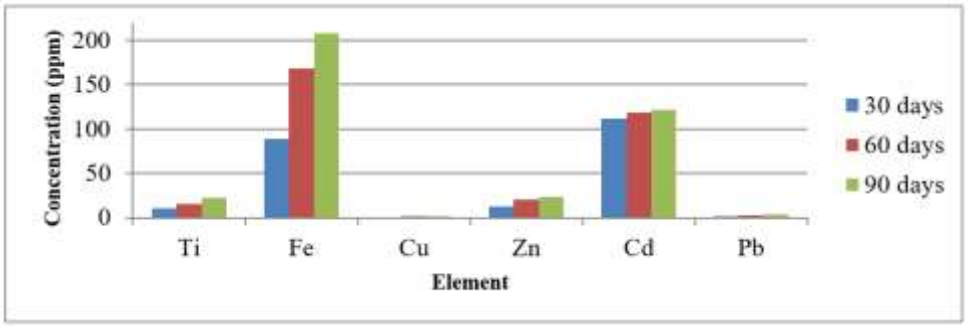

Figure 5. Concentration of metals in the samples observed for times of 30 days, 60 days and 90 days in the 1st place.

Table 3. Results of measurement of moss samples in the second place

Element	30 days (ppm)	60 days (ppm)	90 days (ppm)
Al	58.26 ± 1.52	71.43 ± 3.12	109.73 ± 5.71
Si	97.01 ± 1.58	161.87 ± 6.70	319.91 ± 10.21
Mn	16.45 ± 0.75	19.66 ± 0.89	27.48 ± 1.20
Zn	21.89 ± 0.68	22.19 ± 0.87	23.82 ± 0.97
Br	0.16 ± 0.09	0.45 ± 0.19	1.39 ± 0.59
Cd	83.24 ± 0.76	99.21 ± 6.66	111.24 ± 0.59

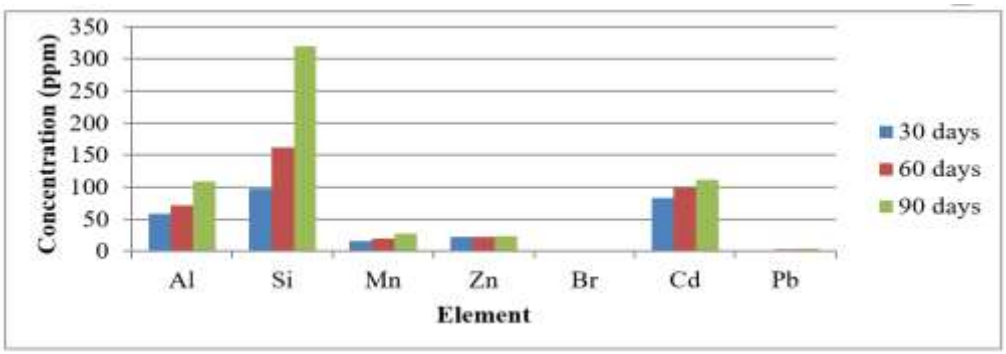

Figure 6. Concentrations of metals in the samples observed for times of 30 days, 60 days and 90 days in the second place.

Table 4. Results of measurement of moss samples in the third place

Element	30 days (ppm)	60 days (ppm)	90 days (ppm)
Ti	0.56 ± 0.04	2.44 ± 0.14	4.10 ± 0.26
Mn	12.85 ± 0.55	21.36 ± 1.09	38.30 ± 1.53
Fe	14.71 ± 0.44	37.36 ± 1.67	55.24 ± 2.40
Zn	14.39 ± 0.71	25.57 ± 0.92	26.72 ± 2.40
Pb	3.55 ± 0.61	3.95 ± 0.41	4.20 ± 0.26

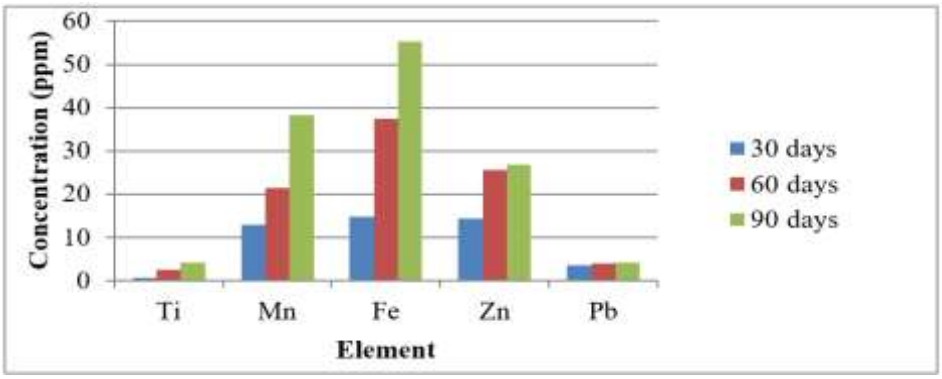

Figure 7. Concentrations of metals in the samples observed for times of 30 days, 60 days and 90 days in the third place.

Table 5. Results of measurement of moss samples in the fourth place

Element	30 days (ppm)	60 days (ppm)	90 days (ppm)
Ti	6.36 ± 0.55	12.69 ± 1.21	12.97 ± 1.23
Fe	32.82 ± 1.54	97.31 ± 5.42	115.60 ± 4.96
Cu	0.89 ± 0.18	1.06 ± 0.20	1.44 ± 0.28
Zn	12.62 ± 0.79	17.16 ± 1.06	37.46 ± 1.85
Rb	10.46 ± 0.42	13.08 ± 0.47	22.33 ± 0.70
Pb	3.80 ± 0.56	4.25 ± 0.90	4.45 ± 0.94

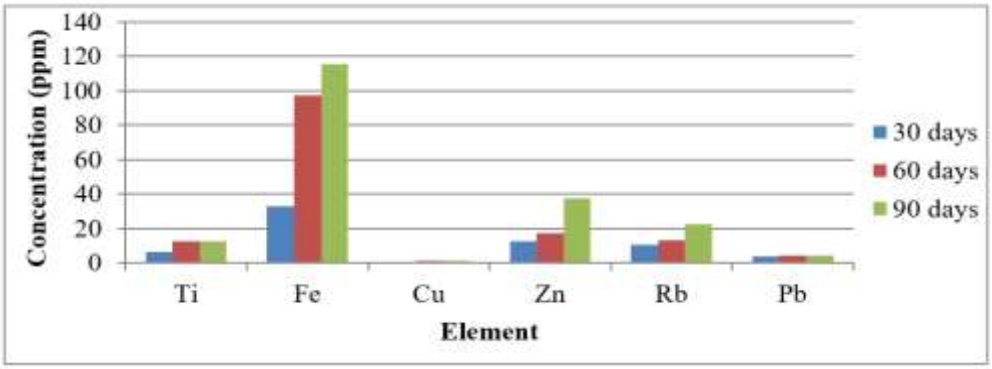

Figure 8. Concentrations of metals in the samples observed for times of 30 days, 60 days and 90 days in the fourth place.

Table 6. Results of measurement of moss samples in the fifth place

Element	30 days (ppm)	60 days (ppm)	90 days (ppm)
Mg	45.22 ± 3.28	49.51 ± 4.25	365.12 ± 27.08
Al	24.39 ± 1.06	63.31 ± 3.17	134.54 ± 7.16
Si	72.33 ± 2.43	172.12 ± 9.79	378.22 ± 19.42
Ti	5.66 ± 0.38	11.94 ± 0.55	16.56 ± 0.93
Mn	25.65 ± 1.33	27.93 ± 1.68	38.91 ± 2.01
Fe	43.91 ± 2.47	108.54 ± 6.74	141.50 ± 2.01
Ni	--	0.46 ± 0.39	0.54 ± 0.46
Cu	1.26 ± 0.27	1.12 ± 0.25	1.93 ± 0.44
Zn	13.36 ± 0.72	30.83 ± 1.71	32.71 ± 1.73
Pb	3.30 ± 0.15	3.51 ± 0.67	5.07 ± 0.50

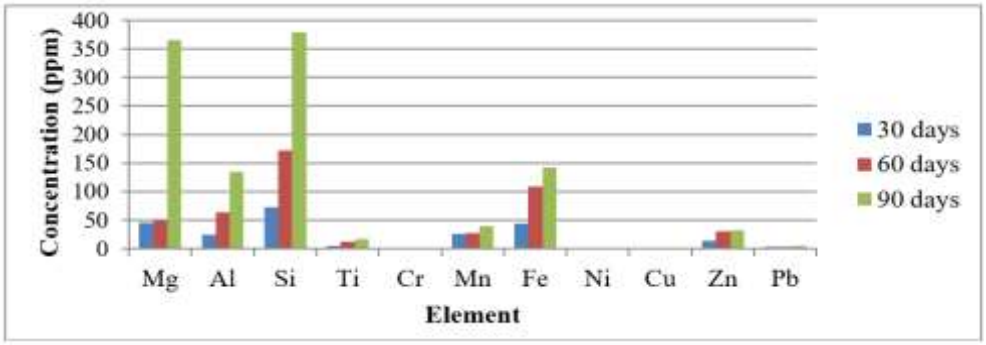

Figure 9. Concentrations of metals in the samples observed for times of 30 days, 60 days and 90 days in the fifth place.

Table 7. Results of measurement of moss samples in the sixth place

Element	30 days (ppm)	60 days (ppm)	90 days (ppm)
Ti	7.95 ± 0.69	15.00 ± 1.44	16.60 ± 1.69
Fe	70.78 ± 3.55	137.06 ± 7.77	191.98 ± 12.61
Zn	16.74 ± 1.02	26.41 ± 1.75	30.04 ± 2.22
Rb	9.94 ± 0.46	11.45 ± 0.58	27.88 ± 1.69
Pb	4.06 ± 2.09	4.39 ± 0.22	5.57 ± 0.34

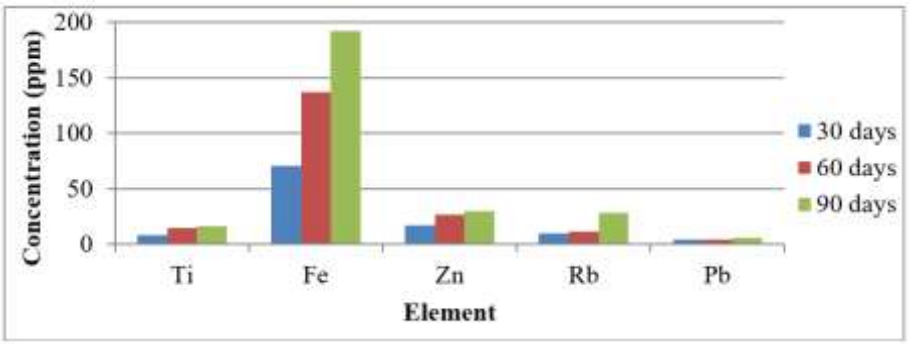

Figure 10. Concentrations of metals in the samples observed for times of 30 days, 60 days and 90 days in the sixth place.

Table 8. Results of measurement of moss samples in the seventh place

Element	30 days (ppm)	60 days (ppm)	90 days (ppm)
Mg	109.93 ± 4.13	394.68 ± 18.91	562.27 ± 77.35
Cl	120.21 ± 2.06	707.90 ± 12.96	1880.56 ± 739.38
Ca	728.15 ± 14.11	919.43 ± 5.59	2676.22 ± 926.85
Ti	11.31 ± 0.73	11.90 ± 0.57	12.60 ± 1.01
Fe	79.69 ± 3.19	86.28 ± 4.59	104.00 ± 5.92
Zn	14.99 ± 0.57	20.21 ± 1.01	33.46 ± 2.34
Cd	66.66 ± 4.07	83.68 ± 6.23	90.66 ± 8.80
Pb	3.26 ± 0.57	4.09 ± 0.63	4.30 ± 0.90

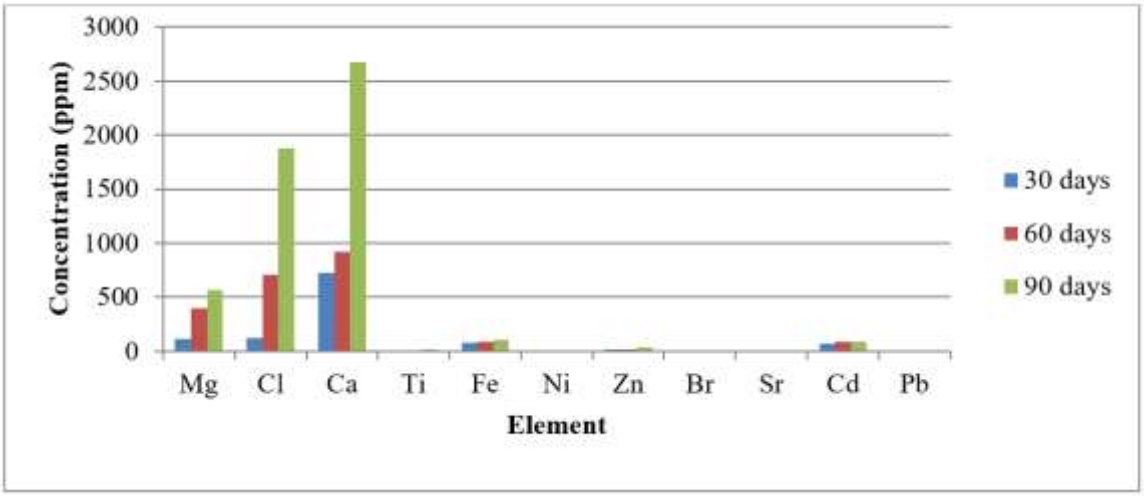

Figure 11. Concentrations of metals in the samples observed for times of 30 days, 60 days and 90 days in the seventh place.

From analyzing the experimental results for the metal contents at 7 places in Hanoi, one can see that:

- The fifth place is the area with the heaviest metals, which can be caused by the location of the sample near the area is building the railway overhead.
- The third place is the area with the lowest element content, which is caused by the location of the sample in the far distance from the road.
- The second place is the area where the content of Silicon (Si) increases sharply in the last month. The reason is due to the last month, next to the location of the suspended form a building began to start.
- Zn is present in all places, where the first place has the lowest content (23.10 ± 0.66 ppm) and the fourth place is the junction area the highest content (37.46 ± 1.85 ppm).
- Pb is present in all places, where the first place has the lowest content (3.57 ± 1.09 ppm) and the sixth place is the highest of the content (5.57 ± 0.34 ppm).

4. Conclusions

The Sphagnum mosses were taken from Ta-Cu-Ty (Lao-Cai province), the moss samples were suspended at different locations in Hanoi City. After hanging the sample for several time periods, they

were taken to Accelerator Laboratory, Faculty of Physics, VNU University of Science for analysis. The results of the PIXE analysis on 5SDH-2 Pelletron accelerator allow to conclude that

- The Sphagnum moss can be used to absorb heavy metals in the atmosphere, thereby assessing the level of heavy metal contamination in the air.
- In addition to metals, Cl and S pollution is also identified.
- The use of moss can collect sources of pollution over a long period of time, which can identify pollution sources such as traffic or industrial activity.
- If there is a denser density than the sample points, it is possible to draw a map of the contamination, thereby identifying the source of the pollution. This can help managers make decisions to minimize pollution.
- Powerful metals like Cd, Pb in the air are of concern.

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