Indication of Heavy Metal Enrichment in the Environment by Bryophytes

Zhengshang Liu, Wang Hu, Chen Long

Applied Nuclear Technology in Geosciences Key Laboratory of Sichuan Province, Chengdu University of Technology, Chengdu, China
Email: 383833294@qq.com

Abstract

With the rapid development of industrialization, the importance of detection, prevention and treatment of environmental pollutants has become increasingly prominent. As a representative biological indicator, bryophytes have an underdeveloped cuticle and a large number of cation exchange points. The dissolved mineral elements in the water and the particulate sediments in the atmosphere can be very good. Absorption can be used to monitor pollutants in the environment.

Subject Areas

Environmental Science

Keywords

Moss, Heavy Metal, Correlation

1. Introduction

More than half of the world's population lives in urban areas and is regularly exposed to higher levels of air pollutants [1]. These pollutants come from a variety of sources, chief among them from road traffic, domestic homes, industrial facilities and power plants. Traditional environmental pollutant monitoring methods are continuous monitoring at fixed sites or manual monitoring on site using portable instruments. These methods have some disadvantages such as high cost, long monitoring period, poor flexibility of use, and limited monitoring range. The results are often backward and the actual environmental changes, and it is difficult to reflect on the current situation of large-scale pollution in the region [2]. Therefore, it is difficult to conduct a comprehensive and effective assessment and analysis of the environment, which greatly increases the difficulty

of environmental governance decision-making [3]. As a representative plant for biological monitoring, moss has a strong adsorption capacity and can accumulate toxic and harmful substances in the environment [4]. It has a simple structure, a wide range of growth distribution, simple sampling, and a low technical threshold. It can be used as a long-term environmental monitoring and monitoring system. Biological indicators for assessment of pollution effects.

2. The Basic Principle of Moss for Environmental Monitoring

2.1. Basic Characteristics of Bryophytes

The structure of bryophytes is very simple (Figure 1), and most of its plants are composed of two parts: leaves and stems. Mosses have no structure equivalent to a root, only rhizoids that function similarly to roots. The rhizoid is in a hairy state, and its main function is to fix it; and it does not have the function of absorbing water and nutrients. Most mosses cannot survive on their own alone, so many mosses gather to form colonies and support each other [5]. Because moss does not have roots that can obtain nutrients from the soil, it relies on a larger area of the community to directly absorb rainwater and nutrients from the surface of leaves and stems. That is to say, the growth of moss does not necessarily depend on the soil. Rocks and tree trunks, and even man-made objects such as asphalt and cement boards, can also become the growing ground for moss plants. In addition, mosses are uniquely variable water-based, allowing them to change the water content of their cells in response to changes in surrounding humidity, a feature that allows moss to survive anywhere [6].

2.2. Monitoring Mechanism of Bryophytes on Pollutants

Bryophytes have no fibrous tube bundle structure, and the transport ability is not strong. Its leaves are only composed of one layer of cells, the cuticle is not developed, and there are a large number of cation exchange points. Strong absorption, which makes the cation exchange capacity of moss particularly outstanding; compared with other higher plants; moss can absorb heavy metal ions around its growing environment very efficiently. There are two main adsorption mechanisms of heavy metal ions in bryophytes. One is extracellular exchange adsorption, which is a fast and active physical and chemical process that does not require energy and is not affected by the physiological activities of bryophytes. Its reaction formula is:
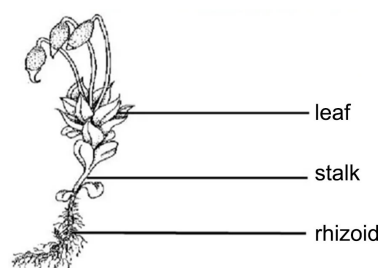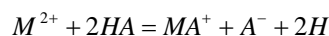

Figure 1. Basic structure of bryophytes.

$$M^{2+} + 2HA = MA^+ + A^- + 2H$$

(In the formula: M^{2+} is the metal ion enriched and absorbed by the moss; A^- is the anion functional group.)

In contrast, intracellular uptake in bryophytes is a relatively slow process, with increased adsorption over time. The adsorption rate is closely related to the physiological characteristics of the moss itself, humidity, temperature, wind and other external conditions. In general, bryophytes do not directly absorb heavy metals into cells but accumulate them outside cells through ion exchange or microparticle adsorption.

Mosses lack root systems and a well-developed cuticle, so, on the one hand, the substrate has little effect on the levels of pollutants in their tissues, and on the other, they readily absorb pollutants from the atmosphere. Mosses have high cation exchange capacity, small body size, staggered and densely distributed plants, large relative body surface area, and a high surface area-to-volume ratio. These factors are all conducive to the accumulation of a large number of pollutants.

3. Sampling and Methods

3.1. Sampling

According to the principle of comparison, around the main sampling point Chengdu University of Technology, two sampling points in Danjingshan Scenic Spot and Chengdu Shanbanqiao Park were set up to compare with each other (Figure 2).

Danjingshan is located at 31°04'42" north latitude and 103°49'37" east longitude, 50 km northwest of Chengdu. It is located in Danjingshan Town, Pengzhou City, Sichuan Province. It covers an area of 64.4 square kilometers and is 1147 m above sea level. Danjingshan is famous for its peony culture, religious culture and ancient Pengshu culture. Since the Tang Dynasty, peony has been planted on a large scale. The mountains are stretched in the territory and the ancient trees are towering. The area is lush with vegetation, far away from industrialization and urban activities, and the air quality is good all year round. The index is below 50. The site was set as a pollution-free area, which was used as a control. In this area, an area with dense moss growth was selected to collect a total of 500 g of moss samples and 200 g of soil samples.

3.2. Sample Preparation and Analysis

The moss was described and identified with reference to the "Moss Illustration", "Chinese Higher Plant Color Illustration" and other literature books, and it was determined that the collected bryophyte was the dominant species in Chengdu: Pseudomonas densifolia. In order to avoid the influence of climate change on the experimental results, the sampling time may be short, and the multi-point sampling method is selected for the collection of samples. Three small plots of one square meter are selected at the required sampling sites, and the five-point
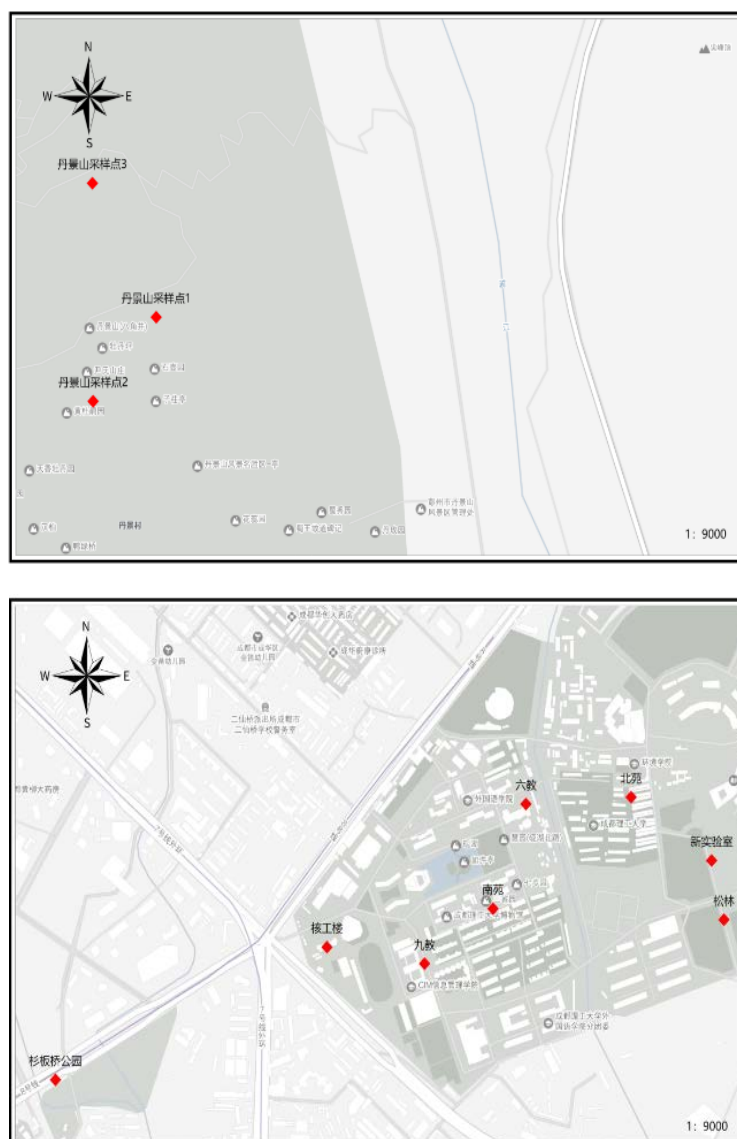
Figure 2. Sampling point distribution.

sampling method is continued in the small plots., set five 10 × 10 cm small squares, and collect the bryophytes in the small squares.

Samples brought back to the lab are removed from surface impurities such as branches, weeds, etc., and then rinsed with distilled water to remove soil adhering to the roots. Then put it into the ultrasonic cleaning machine for regular cleaning 3 times, each time for 15 minutes, until the waste liquid is transparent and clear. The cleaned samples were dried naturally, and then placed in an infrared drying oven to dry to constant weight.

The sample was ground using a vibrating mill, and then passed through a 200-mesh sieve to obtain a sample with a particle size of one to one. Finally, the powder tableting method was used, and a sample of about 3 g was taken, and the sample was pressed by the Zhonghe ZHY-401B sample pressing machine, the pressure was set to 30 tons, and the tableting pressure holding time was 8s.

This sample was measured using a portable XRF (x-ray fluorescence spectrometer) analyzer X-MET7000, which is suitable for environmental testing and consistency in various industries such as coating thickness measurement, pollutants and toxic elements in soil, handling hazardous chemicals in wood, etc. The test has the advantages of fast analysis speed, calculation of results in seconds, and non-destructive analysis. The samples were placed in an X-MET7000 handheld X-ray fluorescence analyzer for XRF analysis, and the measurement time was set to 3 min.

3.3. Data Analysis

In this experiment, six types of heavy metals such as V, Cr, Mn, Cu, Zn, and Pb with high content in the sample were analyzed. These six types of heavy metals are harmful to the environment and human body and can be combined with important cellular components, such as structural proteins, enzymes and nucleic acids, and interfere with their functions. Among them, vanadium can cause abnormal cholesterol metabolism; chromium can cause pulmonary fibrosis and lung cancer; lead can cause anemia and brain dysfunction.

According to the working principle of the X-ray fluorescence analyzer, the element content in the sample to be tested is positively correlated with the generated fluorescence count. By analyzing the count rate, the heavy metal pollution can be roughly understood in Table 1.

Bryophytes contain heavy metal elements. The count rate of Mn is the highest, reaching 387.78. The count rate of Zn and Pb is around 130. The average count rate of V, Cr, and Cu fluctuates between 20 and 50. For plants, Mn is an indispensable micronutrient that participates in many biochemical reactions especially plays an important role in photosynthesis; and manganese is widely distributed in the earth's crust, and there are a large number of manganese ore reserves in Sichuan, Cu, Zn and Pb Mainly from fossil fuel combustion and various transportation activities.

The data of Pb content has the largest dispersion degree, and the coefficient of variation is as high as 1.43. The degree of dispersion of V and Mn data is smaller, and the coefficient of variation is 0.19 and 0.22, respectively, and the coefficient of variation of Cr, Cu, and Zn is between 0.4 and 0.7. The coefficient of variation of Pb is 7 times that of V and Mn, and the coefficient of variation of Cr, Cu and Zn is 2 - 3 times that of V and Mn. It shows that the count rates of Pb, Cr, Cu, and Zn vary greatly with geographic location, which may be related to human activities; the count rates of V and Mn elements vary little with geographic location and have little relationship with human activities.

In soil, the coefficients of variation of Cr, Cu, Zn, and Pb were higher, and their coefficients of variation were 0.86, 0.55, 1.20, and 1.06, respectively. The coefficients of variation of V and Mn were lower, and their coefficients of variation were 0.19 and 0.45, respectively. The coefficient of variation of V in the soil is not much different from that in moss, indicating that its origin is less related to human activities (Table 2).

Table 1. Statistical results of heavy metals in moss.

Elements	Maximum	Minimum	Mean	SD	CV%
	(cps)	(cps)	(cps)	(cps)	
V	27.64	58.60	49.17	9.28	0.19
Cr	0.00	84.72	50.46	21.86	0.43
Mn	247.40	504.31	387.78	85.69	0.22
Cu	13.39	67.62	28.05	15.16	0.54
Zn	80.00	439.85	160.53	106.36	0.66
Pb	37.14	672.76	134.06	192.28	1.43

Table 2. Statistical results of heavy metal in soil.

Elements	Maximum	Minimum	Mean	SD	CV%
	(cps)	(cps)	(cps)	(cps)	
V	55.60	95.06	67.43	12.72	0.19
Cr	47.55	275.49	90.28	77.45	0.86
Mn	430.84	1346.54	651.42	291.21	0.45
Cu	9.62	36.71	15.87	8.74	0.55
Zn	36.10	389.27	99.14	118.96	1.20
Pb	31.56	347.88	103.07	109.35	1.06

4. Discussion

4.1. Correlation of Heavy Metals in Soil and Moss

In Figure 3, the concentrated elements of V and Cr are distributed near both sides of the straight line, indicating that their count rates in moss and soil are close. The content of these elements in moss may have a certain correlation with soil. Cu, Zn, and Elements such as Pb are mainly distributed above the straight line, and their count rate in moss is greater than that in soil, indicating that elements such as Cu, Zn, and Pb are not derived from the soil but may come from the adsorption of air pollutants by bryophytes. Mn is mainly distributed below the straight line, and its count rate in the soil is generally greater than that in moss, indicating that it does not directly adsorb Mn in soil, and this part of the element may come from soil dust and suspended particles. The three types of elements Cu, Zn, and Pb in cities are mainly generated from the combustion of fossil fuels and the wear and tear of vehicle components, and then diffuse into the atmosphere. The absorption capacity is weak, and its enrichment source mainly comes from the atmosphere.

4.2. Element Dependency Discussion

In moss samples, the content of various heavy metal elements is relatively stable. If the sources of heavy metal elements in the tissues are similar, there will be a significant correlation between their contents. If the source is not unique and the
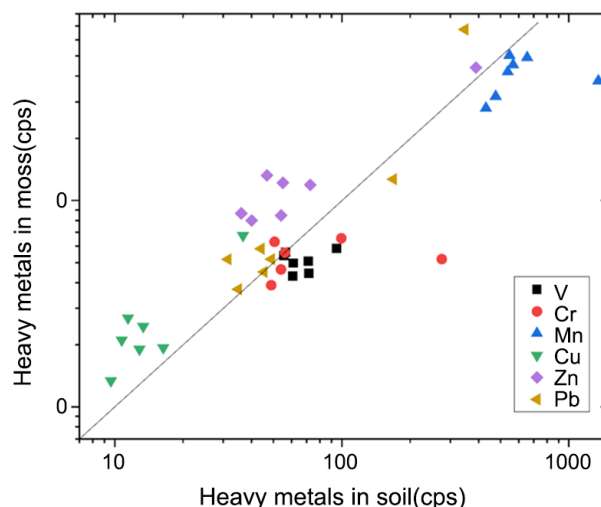
Figure 3. Correlation analysis between moss and soil.

source is more complex, there is no correlation between the heavy metal content. The Pearson product-moment correlation coefficient is used to measure the correlation (linear correlation) between two variables *X* and *Y*, and its value is a dimensionless index between −1 and 1, in natural In the scientific field, this coefficient is widely used to measure the degree of correlation between two variables. Its formula is as follows:

$$r = \frac{\sum (x - \overline{x})(y - \overline{y})}{\sqrt{\sum (x - \overline{x})^2 \sum (y - \overline{y})^2}} \qquad (4\text{-}1)$$

As can be seen from Table 3, the data show that there are three pairs of heavy metal elements that are significantly correlated, namely Cu-Zn, Cu-Pb, Zn-Pb, and the correlation coefficients are 0.978, 0.920, and 0.926, respectively, indicating that Cu, Zn, and Pb are the same. The sources of several heavy metal elements are similar or the same. The high correlation of Cu, Zn, and Pb is closely related to human activities. Cu, Zn, and Pb can be produced by the combustion of fossil fuels and the wear of vehicle components, and they are all air pollutants.

In Table 4, the six groups of heavy metal elements, Cr-Cu, Cr-Zn, Cr-Pb, Cu-Zn, Cu-Pb, and Zn-Pb, have significant correlations, and the correlation coefficients are 0.970, 0.992, and 0.879, respectively., 0.980, 0.967, 0.912. The results showed that the sources of Cr, Cu, Zn and Pb in the soil were the same or similar, and the Cr-Zn correlation reached 0.992.

5. Discussion

Through the analysis of moss and soil in the Danjingshan area, Shanbanqiao Park and the Chengdu University of Technology with different pollution levels, the following conclusions are drawn:

1) The three types of elements, Cu, Zn, and Pb in cities, come from the combustion of fossil fuels and the wear and tear of vehicle components, and they belong to air pollutants. The count rate of these three types of elements in moss is

Table 3. Correlation analysis between heavy metal elements in moss (Pearson's correlation analysis).

	V	Cr	Mn	Cu	Zn	Hg	Pb
V	1.000	0.187	0.544	−0.411	−0.393	0.376	−0.231
Cr		1.000	0.065	0.436	0.440	0.276	0.285
Mn			1.000	0.277	0.282	0.002	0.393
Cu				1.000	0.978	−0.125	0.920
Zn					1.000	−0.112	0.926
Hg						1.000	0.004
Pb							1.000

Table 4. Correlation analysis between heavy metal elements in soil (Pearson's correlation analysis).

	V	Cr	Mn	Cu	Zn	Pb
V	1.000	−0.179	−0.325	−0.208	−0.120	−0.177
Cr		1.000	0.720	0.970	0.992	0.879
Mn			1.000	0.651	0.706	0.577
Cu				1.000	0.980	0.967
Zn					1.000	0.912
Pb						1.000

higher than that in soil, so moss can enrich heavy metal pollutants in the atmosphere.

2) By comparing the data of different polluted areas, in the moss tissue, the area with a low heavy metal count rate corresponds to the uncontaminated area, and the high heavy metal count rate corresponds to the more polluted area, and its heavy metal content can be used for environmental monitoring.

3) In the discussion of element correlation, three pairs of heavy metal elements in bryophytes have significant correlation, namely Cu-Zn, Cu-Pb, Zn-Pb, and the correlation coefficient is also 0.9, indicating that Cu, Zn, Pb The sources of heavy metal elements are similar or the same. The high correlation of Cu, Zn, and Pb may be related to human activities.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest.

References

[1] Han, Y.M., Du, P.X., Cao, J.J. and Posmentier, E.S. (2006) Multivariate Analysis of Heavy Metal Contamination in Urban Dusts of Xi'an, Central China. *Science of the Total Environment*, **355**, 176-186. https://doi.org/10.1016/j.scitotenv.2005.02.026

[2] Blagnyte, R. and Paliulis, D. (2010) Research into Heavy Metals Pollution of Atmosphere Applying Moss as Bioindicator: A Literature Review. *Environmental Research, Engineering and Management*, **54**, 26-33.

[3] Cao, T., An, L., Wang, M., Lou, Y.X., Yu, Y.H., Wu, J.M., Zhu, Z.R., Qing, Y.K. and Glime, J. (2008) Spatial and Temporal Changes of Heavy Metal Concentrations in Mosses and Its Indication to the Environments in the Past 40 Years in the City of Shanghai, China. *Atmospheric Environment*, **42**, 5390-5402. https://doi.org/10.1016/j.atmosenv.2008.02.052

[4] Zhang, M.K. and Wang, H. (2009) Concentrations and Chemical Forms of Potentially Toxic Metals in Road-Deposited Sediments from Different Zones of Hangzhou, China. *Journal of Environmental Sciences*, **21**, 625-631. https://doi.org/10.1016/S1001-0742(08)62317-7

[5] Ruhling, A. and Tyler, G. (1968) An Ecological Approach to the Lead Problem. *Botaniska Notiser*, **121**, 321-342.

[6] Wolterbeek, H.Th., Kuik, P., Verburg, T.G., Herpin, U., Markert, B. and Thoni, L. (1995) Moss Interspecies Comparisons in Trace Element Concentrations. *Environmental Monitoring and Assessment*, **35**, 263-286. https://doi.org/10.1007/BF00547636