MOSS BIOMONITORING OF AIR POLLUTION IN THE VICINITY OF MINES: GEORGIA CASE STUDY

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Abstract. *During 2019-2022 moss survey in Georgia, 96 samples were collected, covering most of the country territory. To assess the trend of air pollution near two different mining area the concentrations determined in the present study were compared with the previous surveys in Georgia. The background concentrations were calculated for both surveys. The Contamination Factor was used to assess the pollution level. The data obtained can serve as baseline data for estimating the deposition of air pollutants and tracking the possible evolution of air quality in Georgia.*

Keywords: *Biomonitoring, Atmospheric deposition, Mining, Contamination Factor, Background*

Introduction

Atmospheric air quality being influenced not only by anthropogenic activity, but also by natural conditions is of primary importance for human health. According to World Health Organization, outdoor air pollution has caused approximately 4.2 million deaths from lower respiratory infections, lung cancer, chronic obstructive pulmonary disease, heart disease and stroke [1]. To assess air quality, it is necessary to carry out a complex analysis of aerosol particles to determine the concentrations of those pollutants that pose a threat to living organisms.

Over the past few decades, biomonitoring studies using living organisms as environmental pollution monitors have become a useful addition to instrumental monitoring [2]. One of the big advantages of biomonitoring over instrumental measurements is that, at high spatial resolution, it is easier and more cost effective to use widely distributed species to monitor air pollution. Mosses are recognized as good air pollution biomonitors due to their specific morphological and physiological characteristics. Mosses have a large surface area and thus facilitate nutrient uptake from wet and dry deposition, and moreover, they are relatively independent of the substrate they grow on. Mosses have been widely used in large-scale biomonitoring studies of transboundary air pollution [3–5]. Moss biomonitoring, combined with nuclear and related analytical methods, has been used regularly over the past 30 years in European countries to study atmospheric deposition of heavy metals. The first moss survey in Georgia was carried out in 2014-2017 [6–8] and the results were included in the Report of ICP Vegetation 2015–2016 [9]. During first moss survey in Georgia several hotspots associated with the extraction and processing of natural resources have been identified. Mining and processing activities often generate toxic waste, which can have adverse environmental impacts.

In the Ambrolauri district, not far from the village of Uravi, there is an arsenic deposit. When the mines were abandoned in 1992, several thousand tons of arsenic-containing waste remained on the surface [10]. High concentrations of arsenic were determined in one sampling site with an average concentration of 83.3 mg/kg. This measurement was carried out in 2016 [8]. However, all other measurements showed no anomalies.

Another hotspot was observed in Imereti, not far from the city of Chiatura, where one of the richest manganese deposits is located. Active manganese mining may explain the high concentrations of Mn at 3 sampling locations. These measurements were conducted in 2017 [8].

The elevated amounts of chemical elements may pose a significant impact on humans. Therefore, the qualitative and quantitative identification of these elements will help to assess the air quality and follow up any possible dynamics.

Materials and methods

During 2019-2022 moss survey in Georgia, 96 samples were collected, covering most of the country territory. Four species of mosses (*Hypnum cupressiforme* Hedw. (n=59), *Abietinella abietina* (Hedw.) M. Fleisch) (n=14), *Pleurozium schreberi* (Brid.) Mitt (n=13), and *Hylocomium splendens* (Hedw.) Schimp. (n=10)) were selected for the survey. To see how the situation has changed, in the vicinity of arsenic mines in Uravi, the same locations were sampled, with the addition of intermediate locations.

In case of Chiatura, where large-scale manganese mining is taking place, due to unavailability of the same sampling locations, other locations were chosen. A sample was also taken in the Zestafoni district. It should be noted that in this district Zestafoni ferro-alloy plant is located, and it processes raw manganese ore from open pit and underground mining in Chiatura.

Disposable polyethylene gloves and plastic tweezers were used to prevent contamination of the sample during its cleaning from external substances. The cleaned samples were dried to a constant weight at 105 °C for 48 h. Around 500 mg of moss was placed in a Teflon vessel and digested with 5 mL of concentrated HNO_3 and 2 mL of H_2O_2 at a temperature of 180 °C in a microwave digestion system (Mars; CEM, Matthews, NC). The solutions were quantitatively transferred into 50 ml calibrated flasks and made up to volume with bidistilled water. All of the reagents used for this study were of analytical grade: nitric acid—69%; trace pure (Merck, Darmstadt, DE); hydrogen peroxide—30%, p.a. (Merck); and bidistilled water. A total of 14 elements, namely Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, S, Sr, V, and Zn, were determined by inductively coupled plasma atomic emission spectroscopy.

Univariate and multivariate statistical analyses were implemented for data processing. Background concentration of Mn and As were calculated for current and previous moss surveys using iterative 2σ-technique. To assess the degree of air pollution Contamination Factor (CF) was calculated. The contamination factor (CF) is defined as the ratio between the content of an element in the sample and its background value. Eq. (1).

$$CF = \frac{C_m}{C_b} \tag{1}$$

where C_m is the concentration of a selected element and C_b is the background content for the same element. Contamination degrees can be categorized as follows: CF < 1–no contamination; 1–2–suspected; 2–3.5–slight; 3.5–8–moderate; 8–27–severe; and > 27–extreme [11].

Results and discussion

Different approaches have been used to assess air quality. Calculated Background concentration for some elements was rather diverse in two moss surveys. The difference in calculated background increased in the following order Mn < Zn < Cd < Ni < Sr < Pb < Fe < Co < Cu < V < Cr < Ba < Al < As and the difference was 7%, 8%, 9%, 13%, 16%, 26%, 27%, 28%, 33%, 39%, 44%, 45%, 47% and 69% respectively.

In the current moss survey, the calculated contamination factors of different elements in locations which were associated with manganese mining, showed lower contamination levels for Al, Ni, Sr, Co, Cr, Cu, V, Mn; the same contamination levels for As, Fe, Pb and higher contamination levels for Cd. The results are presented in Tab. 1.

Table 1

Elements sorted on a scale of contamination based on average CF values associated with the manganese mining site

Contamination level	**Moss Survey 2014-2017**	**Moss Survey 2019-2022**
No contamination	-	Al, Ni, S, Sr
Suspected	As, Cd, Fe, Pb, Sr, Zn	As, Co, Cr, Cu, Fe, Pb, V
Slight	Al, Co, Cr, Cu, Ni, V	Cd
Moderate	-	Mn
Severe	Mn	-
Extreme	-	-

In case of Arsenic mining site lower contamination levels were observed for Cr, the same contamination levels for Al, Cd, Co, Fe, Mn, Ni, Pb, Sr, V, As and higher contamination levels for Cu. The results are presented in Tab. 2.

Table 2

Elements sorted on a scale of contamination based on average CF values associated with the arsenic mining site

Contamination level	**Moss Survey 2014-2017**	**Moss Survey 2019-2022**
No contamination	Cu	S
Suspected	Al, Cd, Co, Fe, Mn, Ni, Pb, Sr, V	Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V
Slight	Cr	-
Moderate	-	-
Severe	-	-
Extreme	As	As

In Case of Arsenic mining place, it must be admitted, that at the most polluted sampling point in spite of 3 times lower concentration of As, that specific sampling location is still extremely contaminated. In this particular region, the average concentration of arsenic (excluding outliers) is 3.5 times higher than the national background value.

The average Mn concentration at mining location is 4.5 times lower than it was in previous survey. Such a big difference can be explained with different sampling locations in 2019-2022. It should be noted that the concentration of Mn in mosses at the sampling point associated with the Zestafoni Ferroalloy Plant was 2 times higher than at the manganese mining sites in Chiatura. At the same time, it must be admitted that biomonitoring based on terrestrial mosses is not a reliable tool for assessment of the atmospheric manganese deposition. Depending on the environment, sources and types of emissions, as well as a number of other factors, despite atmospheric inputs of manganese, its concentration in moss can still be reduced [12].

Conclusions

Moss biomonitoring is an inexpensive and effective technique to identify areas at risk of atmospheric heavy metal deposition fluxes.

Correctly calculated background makes contamination factor (CF) quite useful tool to assess the possible presence of contamination in the sample.

High levels of arsenic contamination are still noticeable in Uravi mining site.

Biomonitoring of atmospheric manganese deposition using mosses needs further research.

References

1. WHO *World Health Statistics 2022: Monitoring Health for the SDGs, Sustainable Development Goals*; Geneva, 2022.
2. Markert, B.A.; Breure, A.M.; Zechmeister, H.G. Definitions, Strategies and Principles for Bioindication/Biomonitoring of the Environment. In: *Trace Metals and other Contaminants in the Environment*; Elsevier, 2003; Vol. 6, pp. 3–39.
3. Harmens, H.; Buse, A.; Büker, P.; Norris, D.; Mills, G.; Williams, B.; Reynolds, B.; Ashenden, T.W.; Rühling, Å.; Steinnes, E. Heavy Metal Concentrations in European Mosses: 2000/2001 Survey.In: *Journal of Atmospheric Chemistry,* 2004, *49*, 425–436.
4. Harmens, H.; Norris, D.A.; Steinnes, E.; Kubin, E.; Piispanen, J.; Alber, R.; Aleksiayenak, Y.; Blum, O.; Coşkun, M.; Dam, M.; et al. Mosses as Biomonitors of Atmospheric Heavy Metal Deposition: Spatial Patterns and Temporal Trends in Europe. In: *Environmental Pollution* 2010, *158*, 3144–3156.
5. Harmens, H.; Norris, D.; Mills, G. Heavy Metals and Nitrogen in Mosses: Spatial Patterns in 2010/11 and Long-Term Temporal Trends (1990-2010) in Europe. NERC/Centre for Ecology & Hydrology, 2013.
6. Shetekauri, S.; Shetekauri, T.; Kvlividze, A.; Chaligava, O.; Kalabegishvili, T.; Kirkesali, E.I.; Frontasyeva, M. V; Chepurchenko, O.E. Preliminary Results of Atmospheric Deposition of Major and Trace Elements in the Greater and Lesser Caucasus Mountains Studied by the Moss Technique and Neutron Activation Analysis. In: *Annali di Botanica* 2015, *5*, 89–95.
7. Shetekauri, S.; Chaligava, O.; Shetekauri, T.; Kvlividze, A.; Kalabegishvili, T.; Kirkesali, E.; Frontasyeva, M.V.; Chepurchenko, O.E.; Tselmovich, V.A. Biomonitoring Air Pollution Using Moss in Georgia. In: *Polish Journal of Environmental Studies,* 2018, *27*, 2259–2266.
8. Chaligava, O.; Shetekauri, S.; Badawy, W.M.; Frontasyeva, M.V.; Zinicovscaia, I.; Shetekauri, T.; Kvlividze, A.; Vergel, K.; Yushin, N. Characterization of Trace Elements in Atmospheric Deposition Studied by Moss Biomonitoring in Georgia. In: *Archives of environmental contamination and toxicology,* 2021, *80*.
9. Frontasyeva, M.; Harmens, H.; Uzhinskiy, A.; Chaligava, O. Mosses as Biomonitors of Air Pollution: 2015/2016 Survey on Heavy Metals, Nitrogen and POPs in Europe and Beyond. In: *Report of the ICP Vegetation Moss Survey Coordination Centre*; Joint Institute for Nuclear Research Dubna, Russian Federation, 2020.
10. Gurguliani, I. Arsenic Contamination in Georgia. Environment Related Security Risks from Old Soviet Legacy. In Proceedings of the Proceedings of the 22nd OSCE Economic and Environmental Forum “Responding to Environmental Challenges with a View to Promoting Cooperation and Security in the OSCE Area”, Vienna, Austria; 2014; pp. 27–28.
11. Fernández, J.A.; Carballeira, A. Evaluation of Contamination, by Different Elements, in Terrestrial Mosses. In: *Archives of environmental contamination and toxicology,* 2001, *40*, 461–468.
12. Boquete, M.T.; Fernández, J.A.; Aboal, J.R.; Carballeira, A. Are Terrestrial Mosses Good Biomonitors of Atmospheric Deposition of Mn? In: *Atmospheric environment,* 2011, *45*, 2704–2710.