HEAVY METALS IN MOSS SAMPLES EXPOSED TO THE ATMOSPHERIC DUST AFTER ERUPTION OF EYJAFJALLAJÖKULL VOLCANO

ZAWARTOŚCI METALI CIĘŻKICH W MCHACH NARAŻONYCH NA DZIAŁANIE PYŁU ATMOSFERYCZNEGO PO ERUPCJI WULKANU EYJAFJALLAJÖKULL

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[(a)] *idea*
[(b)] *exposure experiment*
[(c)] *identification of moss species*
[(d)] *determination of metals*
[(e)] *text and references*
[(f)] *the scientific care, correction*

Abstract

Background: Volcanic ash, which is ejected during volcanic eruptions, flies in the air and spreads by the wind over large distances. It is a magmatic source and as such may contain heavy metals. The aim of the study was to carry out investigation on heavy metal content: Pb, Cd, Zn, Fe, Mn, Cu and Cr in samples of moss bags exposed to atmospheric dust containing volcanic ash in Sosnowiec (Poland) after eruption of Eyjafjallajökull volcano in Iceland.

Materials and methods: Samples have been exposed to atmospheric dust after volcanic eruption for 2 months, and were mineralised in 70% HNO_3 and 30% H_2O_2. The content of Pb and Cd was analysed by atomic absorption spectrometry with electrothermal atomization (ETAAS) and Zn, Fe, Mn, Cu, Cr by atomic absorption spectrometry with flame atomization (FAAS).

Results: During the experiment the content of lead in samples of moss increased by 54,9 μg/g, cadmium by 3,41 μg/g, manganese by 150 μg/g, iron by 6,09 mg/g, zinc by 514 μg/g, copper by 20,77 μg/g and chromium by 6,99 μg/g.

Conclusions: In Sosnowiec the comparable increase of metal content was from several to 41 times higher than in the areas not exposed to volcanic ash. It indicates that volcanic ash can be a potential source of heavy metals in the environment and, consequently, affect our health.

Key words: trace metals, environmental monitoring, moss, volcanic ash

Streszczenie

Wstęp: Pył atmosferyczny, który jest wyrzucany podczas erupcji wulkanów, długo unosi się w powietrzu i rozprzestrzenia na duże odległości przy udziale wiatru. Jest pochodzenia magmowego, więc może zawierać metale ciężkie. Celem pracy było zbadanie zawartości metali ciężkich: Pb, Cd, Zn, Fe, Mn, Cu i Cr w próbkach

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mchu narażonych na działanie pyłu wulkanicznego opadającego na ziemię.

Materiał i metody: Mchy były wystawione na działanie pyłu atmosferycznego po erupcji wulkanu przez }2 miesiące. Próby były mineralizowane kwasem azotowym i nadtlenkiem wodoru. Zawartość Pb i Cd oznaczono za pomocą absorpcyjnej spektrometrii atomowej z elektrotermiczną atomizacją, a Zn, Fe, Mn, Cu i Cr za pomocą absorpcyjnej spektrometrii atomowej z atomizacją w płomieniu.

Wyniki badań: Podczas przeprowadzenia doświadczenia zawartość ołowiu w mchach zwiększyła się o 54,9 µg/g, Cd o 3,41 µg/g, Mn o 150 µg/g, Fe o 6,09 mg/g, Zn o 514 µg/g, Cu o 20,77 µg/g oraz Cr o 6,99 µg/g.

Wnioski: W Sosnowcu stwierdzono od kilku do kilkudziestu razy wyższe przyrosty zawartości oznaczanych metali niż w porównywanych miejscach, co wskazuje, iż pył wulkaniczny może być potencjalnym źródłem metali ciężkich w środowisku, a w konsekwencji wpływać na nasze zdrowie.

Słowa kluczowe: metale ciężkie, monitoring środowiska, mchy, pył wulkaniczny

Introduction

Volcanic eruptions and associated processes such as: emission of gases, volcanic ash containing volcanic dust or lava, are natural sources of environmental pollution. Volcanic dust is a component of volcanic ash, which is ejected during volcanic eruptions. As the smallest pyroclastic material flies long in the air and spreads over large distances with the wind, and then falls onto the ground. Being a magmatic source it can contain large amounts of heavy metals. According to the literature their content can vary between: Pb 2.75–39 µg/g, Zn 39–111 µg/g, Cu 4–132 µg/g, Cd 0.36–0.71 µg/g, Cr 3–54 µg/g) [1–4].

The trace metals contained in the volcanic dust falling onto ground migrate to the soil where are absorbed with water by plants. Direct absorption of dust in the air during breathing (especially through the mouth), or consumption of water contaminated by volcanic dust can cause health problems such as kidney and liver damage, impaired development of children and allergies [1, 2, 5, 6].

Experts examining the degree of environmental exposure to heavy metals use many methods of monitoring. For the evaluation of air pollution the simplest, yet best available method, is the observation of moss (*Hylocomium splendens, Pleurozium schreberi, Scleropodium purum, Hypnum cupressiforme, Brachythecium rutabulum*), which due to a type of structure can easily absorb and accumulate harmful compounds in the environment. Content of trace elements in moss samples can be estimated in two ways; direct determination i.e. collection and study of plant fragments from a specific area, or indirect determination by exposing moss samples in the form of packets (called moss bags) to environmental exposure of a specific area and measurement of element content before and after exposure. Opportunity to study the exposure in a given period of time is the biggest advantage of this method.

The aim of the study was to assess the environmental exposure of Sosnowiec town to lead, cadmium, chromium, copper, zinc and iron using moss bags, carried out during eruption of the Icelandic volcano Eyjafjallajökull in 2010. Volcanic dust from

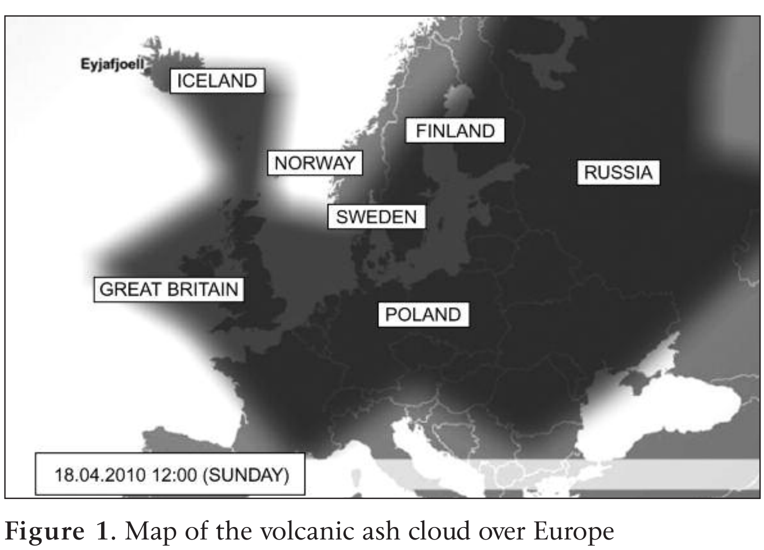

Figure 1. Map of the volcanic ash cloud over Europe
Rycina 1. Mapa chmury pyłu wulkanicznego nad Europą

the volcano Eyjafjallajökull reached considerable areas of the northern hemisphere this year, including Poland, which could be the reason for the increase of exposure to the aforementioned heavy metals.

Materials and methods

Nine samples of moss (*Brachythecium rutabulum*) were exposed to atmospheric dust from 16 April to 15 June by placing them in 3 different places outside the building of the Institute of Occupational Medicine and Environmental Health in Sosnowiec facing the adjacent park. At this time volcanic dust from the volcano Eyjafjallajökull covered large areas over of Europe, including Poland, causing considerable difficulties in air transportation. Distribution of clouds created by volcanic dust over Europe on 18.04.2010 shows Figure 1 [7].

The remaining 3 samples of moss, as control samples, were left for the same period of time in plastic bags in a non ventilated room of the Institute.

After the exposure the samples were mineralized using 69.0–70.0% nitric acid (BAKER INSTRA-ANALYZED for Trace Metals Analysis) and 30% hydrogen peroxide (BAKER ANALYZED).

Content of Fe, Mn, Zn, Cr and Cu were determined by atomic absorption spectrometry with flame atomization (FAAS) using Philips PU 9100, and contents of Pb and Cd by atomic absorption spectrometry with electro-thermal atomization (ETAAS) using ZL 4100 Perkin Elmer.

Prior to determination of metals content in mosses, the method was validated using Certified Reference Material of mixed Polish herbs (INCT-MPH-2), which are presented in Table I.

Table I. Results validation with INCT-MPH-2 [μg/g]
Tabela I. Wyniki walidacji z INCT-MPH-2 [μg/g]

	Pb	Cd	Mn	Fe	Zn	Cu	Cr
The certified value	2,16 ± 0,23	0,199 ± 0,015	191 ± 12	460*	33,5 ± 2,1	7,77 ± 0,53	1,69 ± 0,13
The measured value	2,13 ± 0,06	0,202 ± 0,003	183,8 ± 0,3	459 ± 15	33,09 ± 0,79	8,05 ± 0,21	1,75 ± 0,08

* informative value

Results

The content of heavy metals in the samples together with standard deviations are presented in Table II. This table also shows total increases and the increase per day (it was assumed that the increase each day was the same).

Samples exposed to outdoor atmospheric dust revealed higher concentration of all metals under study. The largest increase was observed in case of zinc, copper and cadmium (respectively 2.85, 2.17, 2.11-times). The smallest concentration increase was observed in case of lead and manganese (the content of these metals increased 1.80 times). All the observed changes are statistically highly significant ($p < 0.001$). Graphical comparison of the results show Figures 2–4.

Table II. Metal content in samples of moss (arithmetic mean ± SD), total increase and increase per day [μg/g]
Tabela II. Zawartości metali w mchach (średnia ar. ± SD), przyrost całkowity i dzienny [μg/g]

	Pb	Cd	Mn	Fe	Zn	Cu	Cr
Moss samples exposure to dust	123,70 ± 0,67	6,38 ± 0,07	338,71 ± 8,23	11 588 ± 491	791,66 ± 33,10	38,50 ± 1,53	14,07 ± 0,24
Control moss samples	68,78 ± 1,10	2,97 ± 0,08	188,65 ± 5,68	5498 ± 116	277,62 ± 7,62	17,73 ± 0,72	7,38 ± 0,12
The total increase	54,92	3,41	150,06	6090	514,04	20,77	6,69
Increase per day	0,915	0,057	2,50	101	8,57	0,35	0,112

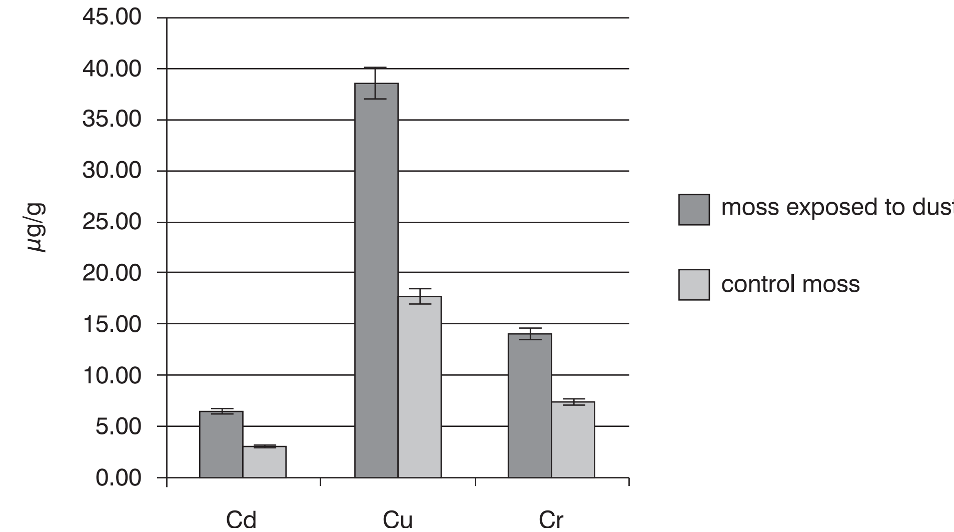

Figure 2. Content of Cd, Cu and Cr in moss samples exposed to dust and in control moss
Rycina 2. Zawartości Cd, Cu i Cr w badanych mchach

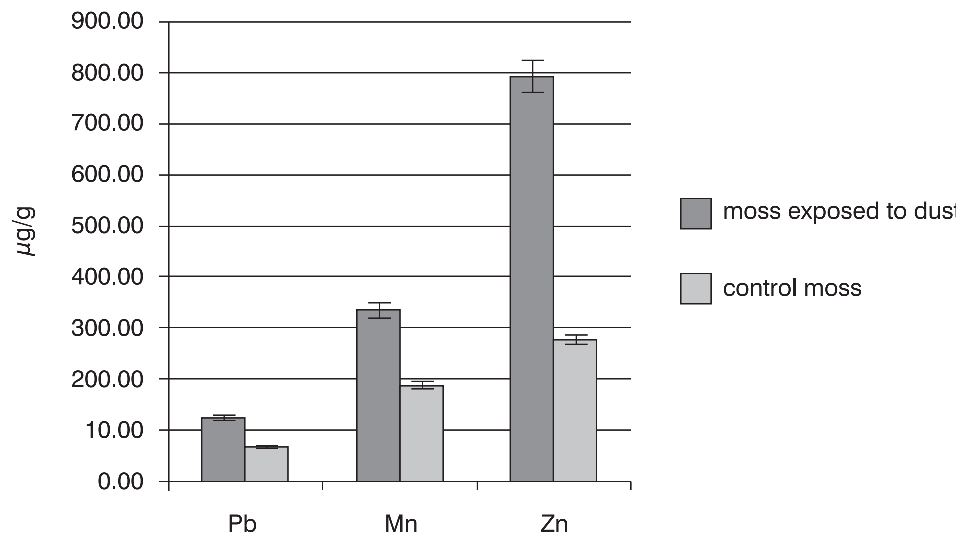

Figure 3. Content of Pb, Mn and Zn in moss samples exposed to dust and in control moss
Rycina 3. Zawartości Pb, Mn i Zn w badanych mchach

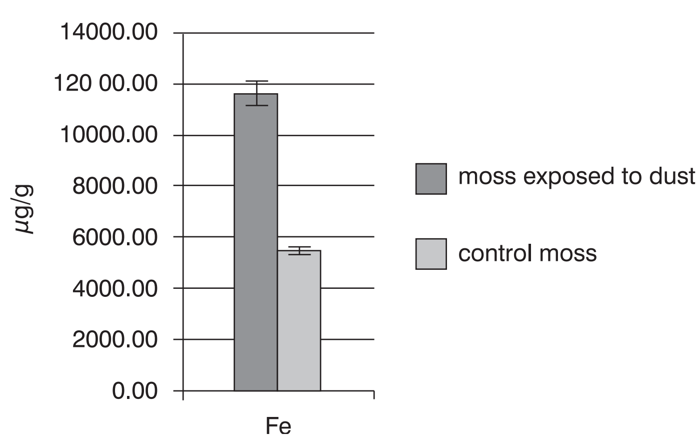

Figure 4. Content of Fe in moss samples exposed to dust and in control moss
Rycina 4. Zawartość Fe w badanych mchach

Discussion

Seismic activity at the glacier Eyjafjallajökull began in late December 2009 and manifested as thousands of tiny earthquakes of a magnitude 1–2 on the Richter scale. Ultimately the eruption of Eyjafjallajökull occurred on March 20, 2010. The second explosion occurred on April 14, which was ten to twenty times stronger in comparison to the first eruption. The emission of volcanic dust into the atmosphere caused flight disruptions across northern Europe. On April 15 Poland closed the air zone over the northern part of the country and on April 16 closed the entire Polish airspace. In early May 2010 volcanic activity gradually lessened and dust emissions decreased from 400 to 50 tons of dust per second [8].

In the PubMed database until December 2011 there were only eight articles (search using the word „Eyjafjallajökull"), of which only three are associated mainly with the characteristics of morphological and to a lesser extent chemical particles identified as a component of volcanic ash [9–11]. Analysis of atmospheric dust after eruption over Slovenia showed significant amounts of SiO_2, Al_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, and TiO_2 [10]. Researchers from the Institute of Earth Sciences, University of Iceland [12] analyzed a layer of volcanic ash and have identified the existence of oxides SiO_2, Al_2O_3, FeO, MnO respectively 57.98%, 14.87%, 9.75% and 0.24%. From analyzed heavy me-tals the presence was noted of Zn, Cu, Cr in amount of 144 ppm, 27 ppm and 25 ppm. However, in the literature one could not find any data relating to the analysis of atmospheric dust after a volcanic eruption on the determination of heavy metal content.

Sosnowiec is a typical example of a big city, where the main sources of exposure to metals are air pollutants from industry, flue gases from vehicles, power plants and coal fired power plants. The study was conducted in late spring (April–June), outside the heating season, during which the dust resulting from heating homes burning coal or wood would fall onto the ground. No literature data have been encountered concerning heavy metals content in the atmospheric dust containing volcanic dust. For comparison reasons studies on heavy metals content in the atmospheric dust were selected carried out in various European cities (Belgrade, Accera, Warsaw, Naples) in the period before the volcano's eruption [13–16].

The authors of these studies assessed concentrations of heavy metals in the „moss bags" at different time intervals. Due to lack of sufficient data on accumulation capacity of these metals in the time interval and a proved documented increase of the average metal content within the first 3 months of exposure, it was decided to compare daily increase of metals content.

In Sosnowiec, in the period from 16 April to 15 June 2010 the daily increases of metals under study were several times higher than in comparable cities – in case of lead from 1.9 to 13.5 times, for Cd from 8 to 26 times, for Mn from 1.8 to 4.9 times, for Fe from 8.2 to 19.5 times, for Zn from 5 to 41 times and for Cr from 4 to 5 times. In case of copper the increase in Sosnowiec was 3.9 times higher than in Acerra (Italy) and 0.76 times smaller than in Naples (Italy).

The greatest difference in daily increase of metals determined by us and compared with literature data (from the period before the eruption of the volcano) is observed for zinc and cadmium in Belgrade [13]. Detailed literature data from environmental monitoring carried out in various cities in Europe are shown in Table III. The above results indicate that the contents of the analyzed elements in exposed moss samples in Sosnowiec were significantly higher than in other cities in which exposure to heavy metals was measured in periods when the atmosphere was not contaminated by volcanic ash. This huge diversity of heavy metal concentration may be testimony to the presence of volcanic ash as a component of atmospheric dust in the period from 16 April to 15 June 2010 in the southern Poland.

Conclusions

Findings showed approximately two times higher concentration of the indicated elements (lead, cadmium, iron, chromium, manganese and zinc) in moss samples exposed to environmental dust in Sosnowiec after eruption of the volcano in Iceland.

The results of our study compared with environmental monitoring carried out in other countries indicate that the metal content in moss samples is higher during the exposure to volcanic ash in relation to lack of exposure.

Table III. The total increases and the increase per day of metal content in the selected cities in Europe [μg/g], in [13–16]
Tabela III. Całkowite i dzienne przyrosty zawartości metali w wybranych miastach Europy [μg/g], wg [13–16]

City	Ref.		Pb	Cd	Mn	Fe	Zn	Cu	Cr
Belgrade	[13]	The total increase	3,96	0,128	82,5	350	12,3	–	1,27
		Increase per day	0,068	0,0022	1,42	6,03	0,21	–	0,022
		R	13,46	25,91	1,76	16,83	40,81	–	5,09
Acerra	[14]	The total increase	29,1	0,31	30,6	310	74,3	5,3	1,6
		Increase per day	0,485	0,0052	0,51	5,17	1,24	0,088	0,027
		R	1,89	10,96	4,90	19,54	6,91	3,92	4,15
Warsaw	[15]	The total increase	17,4	0,60	–	–	141	–	–
		Increase per day	0,207	0,0071	–	–	1,68	–	–
		R	4,42	8,03	–	–	5,10	–	–
Naples	[16]	The total increase	9,74	–	–	1040	74,05	38,78	–
		Increase per day	0,116	–	–	12,38	0,88	0,46	–
		R	7,89	–	–	8,16	9,74	0,76	–

R – Ratio of the increase per day in Sosnowiec to the increase per day to other cities

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