Environment Protection Engineering

Vol. 7 1981 No. 2-4

JERZY KWAPULIŃSKI*, JAN SAROSIEK**,

GERMANIUM CUMULATION BY THE SELECTED SPECIES OF MOSS

In the investigations on the occurrence of germanium in the environment polluted with industrial dust a particular attention has been given to bioindication abilities of various species of moss.

It has been stated that germanium concentration in the vicinity of copper and zinc plants is many times higher than its average geochemical concentration in non-polluted soil and water. Industrial dusts contain not only germanium but also beryllium. Of 14 species examined which were characterized by the ability of germanium accumulation 4 (*Bryum argenteum*, *Ceratodon purpureus*, *Catharinea undulata*, and *Pohlia nutans*) proved to be bioindicators of germanium.

1. INTRODUCTION

Municipal wastewaters and dusts from power stations are the main sources of germanium in the environment. The concentration of this element in municipal wastewaters reaches 10 ppm [1]. Larger amounts (19 ppm), counted for dry matter, have been stated in manure [4]. In dusts from power stations the concentration of germanium, due to enrichment factor during the coal combustion process, reaches 10 ppm, being similar to the contents of other elements (Cu, As, Sn, Ag, Be). According to BERRY and WALLACE [2] the concentrations of germanium range most usually from 1.2 to 12 ppm.

From the analysis of literature data concerning the presence of germanium in natural environment it follows that, so far, no general conclusion have been formulated. The particular results are of a local importance. Thus, for instance, if the average content of germanium is estimated as beeing equal to appr. 0.75 ppm, then in soils this value may reach 10 ppm.

The rocks contain about 1.3–1.7 ppm of germanium. Its concentration in biolites may be higher due to geological processes.

* Environmental Pollution Abatement Centre, 40–832 Katowice, ul. Kossutha 6, Poland.
** Botanical Institute, University of Wrocław, 50-328 Wrocław, ul. Kanonia 6/8, Poland.

Cumulation of germanium with respect to the initial concentration resulting from biochemical and biological processes may reach the value expressed by the cumulation coefficient of order of 0.3. Thus, it seemed advisable to undertake the investigations on the presence of germanium in the environment polluted with industrial dusts. A special attention has been paid to bioindication abilities of the selected speciees of moss. The following plants have been subject to observations: heat generation and power plant, copper and zinc plants, and non-ferrous metals processing plant.

2. METHODS

Germanium and beryllium have been determined spectrographically, by means of grid spectrograph PGS-2, Carl Zeiss, Jena. In order to obtain a standard curve a matrix has been produced, the composition of minerals being similar to that of the samples examined. To the matrix prepared in this way suitable amonts of germanium or beryllium have been added. The difference in blackenings was determined with the help of a microphotometer G III (GDR) at the wavelength of 303.96 and 234.86 nm for germanium and beryllium, respectively.

The contents of both the elements in samples and standards being determined under a constant geometry of measurements, the systematic error was the least possible. The separate results referred to the mean value of six single determinations differed by about 10–18%.

The sensitivity of the method applied amounted to 4.1 ppm and 1 ppm for germanium and beryllium, the corresponding detectivity being 2 ppm and 0.5–1 ppm, respectively.

3. RESULTS AND DISCUSSION

The degree to which the natural environment may be loaded with industrial dust may be determined from the results given in tab. 1.

The following conclusions may be drawn based on the comparison of the concentrations of germanium and beryllium in the environment:

a. the main sources of pollution with germanium of the ambient air, surface waters and soil are the plants processing non-ferrous metals;

b. germanium content in industrial dusts is manifold higher than the average geochemical concentrations in soil and water reported in the literature;

c. considering the size of emission the greatest contribution to the pollution of the natural environment elements is due to the emitters of the coal combustion products;

d. the fact that the role and effect of germanium in metabolic processes is not recognized justifies the investigations on this element.

The distance-dependent changes in beryllium and germanium contents in *Bryum*

Table 1

Review of some sources responsible for the pollution of environment with beryllium and germanium

Przegląd niektórych źródeł obciążenia środowiska berylem i germanem

Kind of dust	Concentrations ppm	
	Be	Ge
Dust from zinc plant	7.2	180.4
Dust from electro-filtres in zinc plant		155.8
Dust from electro-filters in copper plant	10.0	1000-10000
Dust from non-ferrous metallurgy	100-1000	100-1000
Dust from the plants of household chemistry	100-1000	10-100
Flue dust from boiler-room of a chemical plant	100-1000	10-100
Dust from lacquer plant	100-1000	10

argenteum, *Ceratodon purpureus*, *Catharinea undulata*, and *Pohlia nutans* are presented in fig. 1.

In the case of power plant content of germanium decreased in *C. undulata* with the increasing distance from the source of pollution, an analogical dependence being stated for *P. nutans* in case of copper plant. An inverse course of the changes has been observed

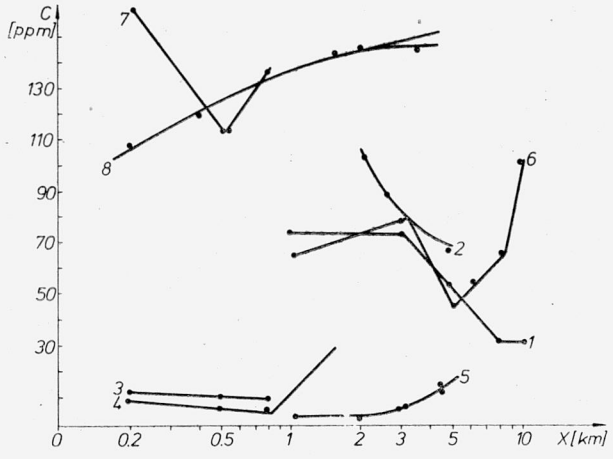

Fig. 1. Distance-dependent changes in beryllium and germanium contents

1 — *C. undulata* — Ge, *2* — *P. nutans* — Ge, *3* — *B. argenteum* — Be, *4* — *C. purpureus* — Be, *5* — *P. nutans* — Be, *6* — *C. undulata* — Be, *7* — *B. argenteum* — Ge, *8* — *C. purpureus* — Ge

3, *4*, *7*, *8* — zinc plant; *1*, *6* — electric power plant; *2*, *5* — copper plant

Rys. 1. Zmiana zawartości berylu i germanu w zależności od odległości

1 — *C. undulata* — Ge, *2* — *P. nutans* — Ge, *3* — *B. argenteum* — Be, *4* — *C. purpureus* — Be, *5* — *P. nutans* — Be, *6* — *C. undulata* — Be, *7* — *B. argenteum* — Ge, *8* — *C. purpureus* — Ge

3, *4*, *7*, *8* — huta cynku; *1*, *6* — elektrownia Turoszów; *2*, *5* — huta miedzi

for beryllium. It is characteristic that at the distance of 8–10 km the content of germanium is equal to about 50% of that observed in the direct vicinity of the emitter. For both the moss species the capacity of germanium cumulation amounts to 70 ppm, the content of germanium in *C. undulata* and *P. nutans* in the vicinity of a plant (up to 3 km) will be by 30 ppm greater than at the distance of 10 km.

The tendency of germanium content to decrease with the distance from the emitters investigated would indicate, however, that the highest percentage of germanium load is included in the coarse fractions of the industrial dusts, which are precipitated from the ambient air in the vicinity of the given plant. Such an explanation seems to be much probable, since the earlier investigations by KWAPULIŃSKI and SAROSIEK (1977) on the occurrence of beryllium in the dust fractions also allowed to state that increase in beryllium content in *C. undulata* and *P. nutans* at higher distances (about 10 km) is due to the finer dust particles the percentage of which in the beryllium load is the highest (fig. 1, curves 5 and 6).

In the surroundings of zinc plant the investigations were performed on *Bryum argenteum* and *Ceratodon purpureus*. Assuming a working hypothesis that the capacity of germanium cumulation of both the species is the function of germanium concentration, it should be stated that the technology of zinc ore processing promotes the presence of germanium in finer dust fractions since its content in *C. purpureus* increases with the distance from pollution source, being the highest of all the species of moss examined.

The problem of the occurrence of germanium at different distances from the zinc plant is illustrated also by the results listed in tab. 2. Its highest concentrations (147.6–172.6 ppm Ge) have been stated in *Bryum inclinatum*. The characteristic feature trend resulting from the data suggests that increasing cumulation of germanium is accompanied by decreasing that of beryllium.

Table 2

Determination of germanium and beryllium in the selected species of moss in the surroundings of zinc plant

Oznaczenie germanu i berylu w wybranych gatunkach mchów wokół huty cynku

Species	Element (in ppm)	Distance m						
		200	400	500	800	1500	2000	3600
Ceratodon	Ge	98.4	110.7	106.6	139.4	135.3	135.0	135.3
purpureus	Be	9.36	—	6.48	5.04	28.8	—	—
Bryum	Ge	151.7	—	102.5	127.1	—	—	—
argenteum	Be	11.5	—	9.36	9.36	—	—	—
Bryum	Ge	172.2	—	110.7	114.8	147.6	—	—
inclinatum	Be	3.6	—	4.32	—	3.6	—	—
Amblystegium	Ge	—	—	10	—	—	—	—
riparium	Be	—	—	10-100	—	—	—	—

Limitation of germanium content by beryllium is also illustrated by fig. 2, where the change in germanium/beryllium ratio in plants is presented as a function of germanium concentration. It has been stated that in five species of mosses collected in the area affected by the industrial dust emissions from three different plants, each increase in germanium concentration was followed by the decreasing amount of beryllium. The course

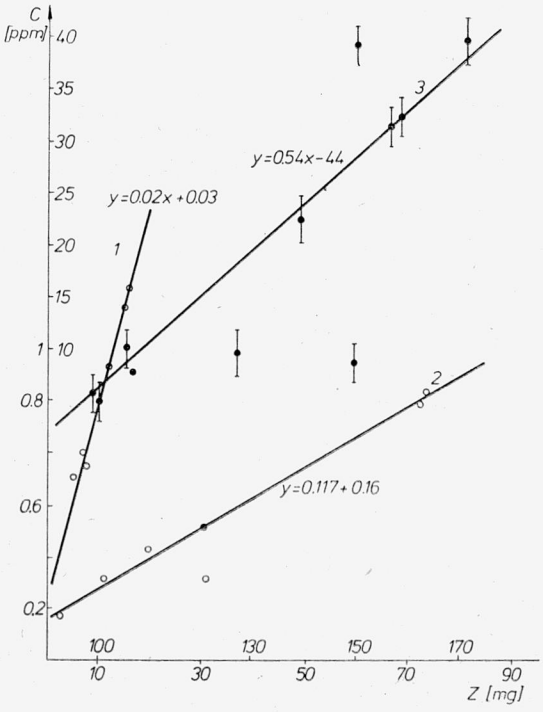

Fig. 1. Change in germanium/beryllium ratio (*C*) in plants as a function of germanium concentration (*Z*)
1 — P. nutans (10^{-10}), 2 — *C. undulata*, 3 — *C. purpureus*, *B. inclinatum*, *B. argenteum*

Rys. 1. Zmiana ilorazu zawartości germanu i berylu (*C*) w roślinach jako funkcja stężenia germanu (*Z*)
1 — P. nutans (10^{-10}), 2 — *C. undulata*, 3 — *C. purpureus*, *B. inclinatum*, *B. argenteum*

of curves gives the evidence to the competitive character of the occurrence of both the elements. The total amount of cumulated elements corresponds, however, to the selective capacities of the separate plants and depends on the total load of beryllium or germanium in the ambient air. This statement is confirmed also by the values of coefficients appearing in the equations describing co-occurrence of beryllium and germanium:

$$y = 0.02x + 0.03 \text{ for } P.\ nutans,$$
$$y = 0.117x + 0.16 \text{ for } C.\ undulata,$$
$$y = 0.54x - 44 \text{ for } C.\ purpureus,$$

where y denotes the germanium/beryllium ratio, and x denotes the concentration of germanium (in ppm); free terms are treated as the threshold content of germanium, above which a combined effect of presence of germanium and beryllium is observed. It means

that within the threshold concentrations range 0.03–0.16 units of beryllium content in *P. nutans* and *C. undulata* fall to one unit of germanium content. In case of *C. purpureus* an additional phenomenon is observed: besides a high and selective capacity of germanium cumulation at the cost of beryllium, characterized by the value of the coefficient (0.44) no discrimination effect for germanium concentration is observed up to 44 ppm. Information about the contents of germanium and beryllium in the remaining species of the total number of 14 species of mosses examined is given in tab. 3.

Table 3

Germanium and beryllium contents in the selected species of moss
Zawartość germanu i berylu w wybranych gatunkach mchów

Species	Affected area	Concentration ppm	
		Be	Ge
Catharinea undulata	electric power plant	44.0-92.7	19.5-74.5
Pohlia nutans	copper plant	69.5-107.0	2.0-17.5
Ceratodon purpureus	zinc plant	0.0-28.8	98.4-135.5
Bryum argenteum	zinc plant	9.36-11.5	102.5-151.7
Bryum inclinatum	zinc plant	0.00-4.3	110.7-172.2
Amblystegium riparium	zinc plant	10.0-100.0	10
Mnium affine	town, botanical garden	48.0	18.5
Dicranella heteromalla	non-ferrous metallurgy	10	100-1000
Barbula unguiculata	non-ferrous metallurgy	10-100	100-1000
Ceratodon purpureus	non-ferrous metallurgy	10	100-1000
Bryum argenteum	non-ferrous metallurgy	10-100	10-100
Calliergon giganteum	Grabowno town	10-100	10-100
Drepanocladus aduncus	Szczodre town	10-100	10-100

Since the amounts of beryllium cumulated by *B. argenteum*, *C. purpureus*, *C. undulata*, and *P. nutans* are relatively stable and close to the average geochemical concentrations these species of mosses may be used as germanium bioindicators and be helpful in assessing the loading of the natural environment with germanium depending on the distance from the pollution source.

4. CONCLUSIONS

1. Concentrations of germanium in industrial dusts, emitted from zinc and copper plants and resulting from coal combustion, are manifold higher than the average geochemical concentrations of this element in soils and water.

2. The content of germanium in the separate moss species increases with the decreasing that of beryllium.

3. The following moss species can be used as bioindicators of germanium: *Ceratodon purpureus*, *Catharinea undulata* and *Pohlia nutans*.

4. The competitive presence of germanium and beryllium has been proved experimentally.

5. The combined effect of the competitive occurrence of germanium and beryllium takes place at the concentrations exceeding the threshold concentrations.

6. All the 14 species examined are characterized by the ability of germanium cumulation.

REFERENCES

[1] BERROW M. K., WEBBER J., *Trace elements in sewage sludges*, J. Sci. Food. Agr., No. 23, pp. 93-99.

[2] BERRY W. I., WALLACE A., *Trace elements in the environment — their role and potential toxicity as related to fossil fuels — a preliminary study*, pp. 66, University of Calif., Los Angeles 1974.

[3] KWAPULIŃSKI J., SAROSIEK J., *Występowanie berylu w poszczególnych frakcjach pyłów elektrownianych* (typescript), 1977.

[4] MENZIES J. D., CHANNEY R. I., *Factor involved in land application of agricultural and municipal wastes*, Nat. Program Staff SWAS, pp. 19-35, Beltsville 1974, Maryland

KUMULACJA GERMANU PRZEZ WYBRANE GATUNKI MCHÓW

W badaniach nad występowaniem germanu w środowisku skażonym pyłami przemysłowymi szczególną uwagę zwrócono na zdolności bioindykacyjne różnych gatunków mchów.

Stwierdzono, że koncentracja germanu w pobliżu hut miedzi i cynku jest wielokrotnie większa od jego przeciętnych stężeń geochemicznych w nieskażonej glebie i wodzie. Obok germanu w pyłach przemysłowych występował beryl. Na 14 zbadanych gatunków, które odznaczały się zdolnością kumulowania germanu, 4 (*Bryum argenteum*, *Ceratodon purpureus*, *Catharinea undulata* i *Pohlia nutans*) są dobrymi bioindykatorami germanu.

KUMULIERUNG DES GERMANIUMS DURCH AUSGEWÄHLTE MOOSARTEN

In Untersuchungen zum Vorkommen des Germaniums in kontaminierten Industriegebieten, spezieller Augenmerk wurde dem Bioindikationsvermögen verschiedener Moosarten geschenkt.

Enorm höhere Konzentrationen von Germanium als im kontaminationsfreien Boden und Wasser, wurden in der Umgebung von Kupfer- und Zinkhütten festgestellt. Neben Germanium enthalten Industriestäube auch das Beryllium. Von den 14 untersuchten Moosarten welche Germanium anreichern, vier Arten (*Bryum argenteum*, *Ceratodon purpureus*, *Catharinea undulata* und *Pohlia nutans*) können als gute Bioindikatoren dieses Elements gelten.

КУМУЛЯЦИЯ ГЕРМАНИЯ ИЗБРАННЫМИ ВИДАМИ МХОВ

В исследованиях по распространению германия в среде, заражённой пылью, особая роль уделена биоиндикационным способностям различных видов мхов.

Отмечено, что концентрация германия вблизи медеплавильного и оловоплавильного заводов значительно больше, чем его средние геохимические концентрации в незаражённой почве и воде. Наряду с германием в промышленной пыли находился бериллий. На 14 исследованных видов, которые обладали способностью кумулировать германий, четыре из них (*Bryum argenteum*, *Ceratodon purpureus*, *Catharinea undulata* и *Pohlia nutans*) являются хорошими биоиндикаторами германия.