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Original Research

Bio-Indicative Assessment of Motorway Air Pollution Using Thermal Analysis

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Abstract

The aim of our studies was to assess the pollution resulting from burning fossil fuels and their emission lines (expressways). Quantitative and qualitative analysis of inorganic and organic pollutants, including PAHs (polycyclic aromatic hydrocarbons) adsorbed on the surfaces, or formed through thermal decomposition of used biomarkers, was based on coupled techniques such as ICP-MS (inductively coupled plasma with mass spectrometry), GC-MS (gas chromatography coupled with mass spectroscopy), and TG-FTIR (thermogravimetry coupled with Fourier transformation infrared spectroscopy).

In terms of urban areas and highways, sources of inorganic and organic pollutants are motor vehicles. Studies based on the use of the measuring apparatus do not give information on the impacts on living organisms of the pollutants such as heavy metals or PAH. Observation creates the possibility of such bioindicators. Qualitative and quantitative bioindicators exposed to environmental toxins can identify the natural environmental conditions because organisms having characteristics of bioindicators respond to changes in the biotope. They have high sensitivity to toxic substances or high degrees of tolerance against entering toxins. Bio vesicular *Pleurozium schreberi* (Willd.) Mitten is commonly used.

Keywords: biomarkers, organic pollutants, PAH (polycyclic aromatic hydrocarbons), ectohydrical nature, transplantation of moss

Introduction

Human activity contributes to the increase in atmospheric emissions of harmful substances hazardous to living organisms. In addition to gaseous pollutants of anthropogenic origin present in the atmosphere (SO_2, NO_x, CO_2, CO) there are also heavy metals. Some of them are necessary for the body (Fe, Cu, Zn, Co, Mn), while others' functions in the body are unknown and yet are among the potent toxins (Cd, Pb, Hg, As). Their toxicity is due to the ability to create easily soluble compounds, which gives the possibility of quick penetration through the membranous structures of cells and bio-accumulation. In terms of urban areas and highways their sources are emissions from motor vehicles. Studies based on the use of the measuring apparatus do not give information on the impacts on living organisms of the pollutants mentioned above. Observation creates the possibility of such bio-indindicators.

Biological tests can be used without restriction due to the prevalence in nature and low cost of research [1]. The most commonly used bio-tests next to lichens include mosses. These are good indicators of air load in heavy metals and other toxic compounds, because they consume chemicals through an ectohydrical nature, reflecting the changes of air pollution levels [2]. They stop dust and intensively accumulate heavy metals [3, 4].

The concentration of metals is a result of particulate matter retention on the plant's surface and collecting the

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Table 1. Content of heavy metals in *Pleurozium schreberi* [Brid.] Mitt., Reference sample.

R.S.	Pb	Cd	Cr	Co	Cu	Ni	Zn	Al	Fe
con.	2.8	0.1	23.5	0.3	9.9	0.0	40.3	5280.7	2956.8

concentration in μg·g^{-1} d.m.
d.m.– dry mass.

substances in ionic form. In the case of dry deposition, metals are absorbed mechanically. With high concentrations of acidifying gases in the air and the occurrence of precipitation, bioaccumulation of soluble forms of metals in ionic form increase [5]. Assessment of sanitary state of the air and the toxic heavy metals in it, using bio-indicators, has been led with great success by [1, 6-14].

Bio-test responses to environmental stimulus are revealed as dysfunctions in cells and tissues, and the effects are clearly visible as macroscopic and microscopic changes. The construction of bryophytes, in which annual increases form visible segments, makes it possible to determine the degree of contamination for the measurement period. Wide ranges of occuring mosses provide research and compare the results to large areas of research [15, 16]. In Poland, bio-indicators are increasingly included in the environment's tests, but they must meet certain requirements. A valuable and well-trusted biomarker is characterized by narrow ecological tolerance scale, responds specifically to factors of the environment, and is a common organism, occurring frequently in the area [17]. Biological material performing the functions of a bio-indicator must be genetically uniform and represent the same stage of development. These conditions are met by bryophyte *Pleurozium schreberi* [Brid.] Mitt. Contaminants, including heavy metals, are accumulated mainly from precipitation and dry deposition. It accumulates metals by simple ion exchange [18].

One of the most objective methods of using mosses to evaluate air pollution is a method of transplantation. Transplantation unifies the shooting conditions by eliminating the natural barriers such as transplant covering or failure. Transplanted moss samples are collected from clean sites and non-space research [1], and the transplant can take place in any area designated by the researcher.

The aim of the study was to assess the pollution (concentration of heavy metals and PAH) caused by the combustion of petroleum fuels and linear emissions (highways, motorways, routes).

Experimental

Materials

The moss *Pleurozium schreberi* [Brid.] Mitt. has been used as a bio-indicator. Transplants were obtained from the benchmarking clean area (Forest Borecka, NE Poland) (Fig. 1). The content of heavy metals and the concentrations of 16 of the most representative polycyclic aromatic hydrocarbons (PAH) on the surface of the used moss are presented in Tables 1 and 2.

Table 2. Content of PAH in *Pleurozium schreberi* [Brid.] Mitt., reference sample.

PAHs	Concentration [μg·g^{-1} d.m.]
Naphthalene	0.00
Acenaphthene	0.00
Acenaphthylene	0.00
Fluorene	0.00
Phenantrene	0.01
Anthracene	0.00
Fluoranthene	0.00
Pyrene	0.02
Benzo(α)anthracene	0.00
Chrysene	0.00
Benzo(b)fluoranthene	0.05
Benzo(k) fluoranthene	0.20
Benzo(a)pyrene	0.03
Indeno(1,2,3-cd)pyren	0.00
Dibenzo(a, h)anthracene	0.00
Benzo(g, h, i)perylene	0.00

Research Area

The research material was exposed in boxes with dimensions of 30×40 cm (Fig. 2), which were placed at select positions along motorway A4 Kraków-Katowice and S7 express road Kielce and Warsaw (Fig. 3). Transplant samples were arranged on each of the routes in the five points of measurement, which was determined using GPS (Table 3).

Method

The transplantation material was analyzed by microscope (Nikon SMZ 1500 using the NIS – Elements BR and Nikon microscope A2100). Qualitative and quantitative analysis of the heavy metals content was performed using a spectrometer ICP-MS/TOF Opti Mass 9500.

Thermal analyses were performed using STA 449 F1 Jupiter, by Netzsch (Germany) in the temperature range 40-1000ºC. The heating rate was 10ºC/min. The measurement was carried out under an inert gas (helium flow 40 mL/min), the weight of the sample was 10 mg, the crucible of Al_2O_3. FTIR analysis was performed using a Brucker

Table 3. Location of moss exposure points *Pleurozium schreberii*.

Exposure points	Geographical location as per GPS	
	Latitude N	Longitude E.
Motorways A4 Kraków-Katowice		
I	50º05' 57"	19º38' 42"
II	50º08'63"	19º26' 62"
III	50º05' 61"	19º34'17"
IV	50º04' 76"	19º45' 83"
V	50º06' 84"	19º52' 66"
Highways S7 Kielce-Warszawa		
VI	50º57' 37"	20º43' 03"
VII	51º31' 50"	21º05' 59"
VIII	51º31' 50"	20º56' 29"
IX	51º38' 46"	20º58' 26"
X	51º34' 17"	21º0' 02"

585 apparatus (Germany) coupled with a thermo-gravimetric analyzer.

The polycyclic aromatic hydrocarbons (PAH) adsorbed on surface bio-indicators were extracted with 50 ml of dichloromethane for 30 min. Once the extract was purified in SPE Chromabond SiOH columns (3 ml/500 mg), PAHs were determined by the GC/MS technique with the use of standard curve (Clarus 680, Clarus 600C – PerkinElmer).

Results and Discussion

Determination of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds which have received considerable attention because of the documented carcinogenicity in experimental animals of several of its members.

PAHs are fused compounds built on benzene rings. When a pair of carbon atoms is shared, then the two sharing aromatic rings are considered fused. The resulting structure is a molecule where all carbon and hydrogen atoms lie in one plane. The environmentally significant PAHs range between naphthalene ($C_{10}H_8$) and coronene ($C_{24}H_{12}$). In this range, there are a large number of PAHs differing in the number and position of aromatic rings, with varying number, positions and eventual chemistry of substituents on the basic ring system. Physical and chemical properties of PAHs vary with molecular weight. Due to their environmental concern, PAHs are included in the US EPA and in the European Union priority lists of polutants. US EPA has identified 16 unsubstituted PAHs as priority pollutants (Table 2), some of which are considered to be possible or probable human carcinogens, and hence their distribution in environment and potential risk to human health have been

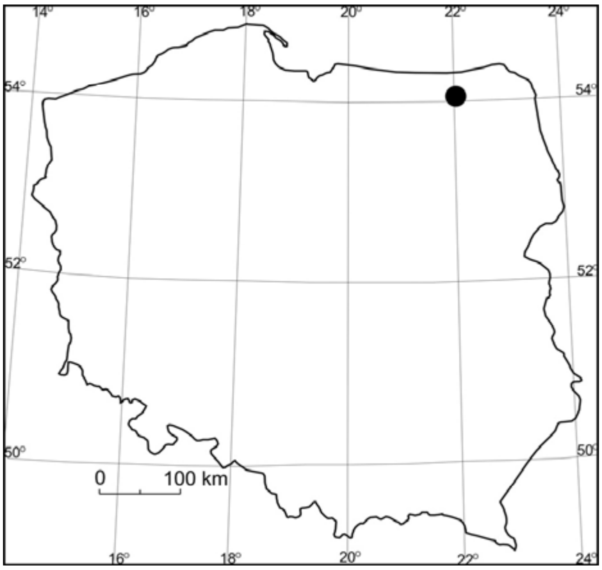

Fig. 1. Location of Borecka Forest.

Fig. 2. Transplantation of moss *Pleurozium schreberi* [Brid.] Mitt. along express routes.

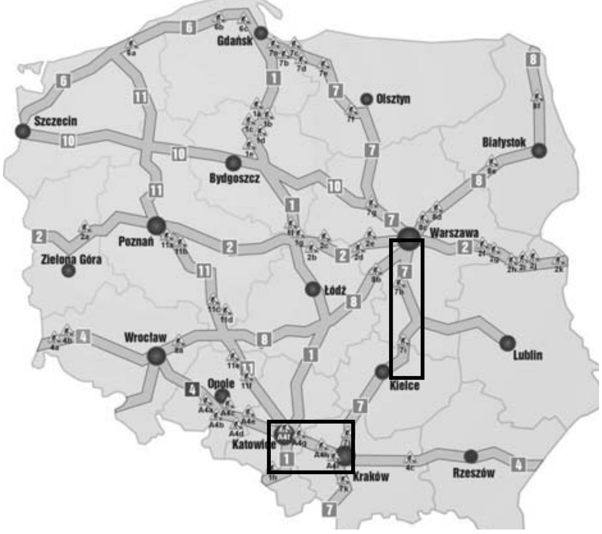

Fig. 3. Location of highways of moss exposure *Pleurozium schreberi* [Brid.] Mitt.

Table 4. Content of PAHs in *Pleurozium schreberi*. Highway A4.

PAHs	Concentration [μg·g^{-1} d.m.]
Naphthalene	0.00
Acenaphthene	0.18
Acenaphthylene	0.75
Fluorene	0.97
Phenantrene	0.32
Anthracene	0.26
Fluoranthene	0.02
Pyrene	0.02
Benzo(α)anthracene	0.24
Chrysene	0.05
Benzo(b)fluoranthene	0.05
Benzo(k) fluoranthene	0.57
Benzo(a)pyrene	0.53
Indeno(1,2,3-cd)pyren	0.25
Dibenzo(a, h)anthracene	0.00
Benzo(g, h, i)perylene	0.00

Table 5. Content of PAHs in *Pleurozium schreberi*. Expressway S7.

PAHs	Concentration [μg·g^{-1} d.m.]
Naphthalene	0.00
Acenaphthene	0.00
Acenaphthylene	0.00
Fluorene	0.00
Phenantrene	0.43
Anthracene	0.00
Fluoranthene	0.01
Pyrene	0.66
Benzo(α)anthracene	0.00
Chrysene	0.00
Benzo(b)fluoranthene	0.18
Benzo(k) fluoranthene	0.71
Benzo(a)pyrene	0.61
Indeno(1,2,3-cd)pyren	0.29
Dibenzo(a, h)anthracene	0.00
Benzo(g, h, i)perylene	0.00

the focus of much attention. The European list contains six target PAHs (Fl, B[b]Fl, B[k]Fl, B[α]Py, B[ghi]Pe, and I[1,2,3-cd]Py).

PAHs are introduced into the environment mainly via natural and anthropogenic combustion processes. As a consequence, their loadings to aquatic and terrestrial systems all have a component that is atmospheric in origin. Volcanic eruptions and forest and prairie fires are among the major natural sources of PAHs in the atmosphere. Important anthropogenic sources include combustion of fossil fuels, waste incineration, coke and asphalt production, oil refining, aluminum production and, above all, combustion of automotive fuels [19, 20].

Combustion of fuel causes high concentrations of PAHs to be determined along motorways or express roads.

The results from Tables 4 and 5 indicate that concentration, especially of the most carcinogenic PAHs that are synthesized during combustion of fuels, are relatively high.

The results of studies contained in Tables 4 and 5 show that concentrations of PAHs along motorways and expressways are practically the same.

TG-FTIR Analysis

TG curve analysis showed that the moss, regardless of its exposure, is characterized by a four-step thermal decomposition. The first taking place in the ΔT_1 = 60-100ºC is related to loss of water. In the ΔT_2 = 100-240ºC take place at the beginning of decomposition, in ΔT_3 = 240-340ºC followed by a rapid thermal decomposition of the samples, and the thermal decomposition residue is burnt in the temperature range 340-1000 $\Delta T_4 = {}^{c}$ (Figs. 4-6).

In FTIR spectrum extracted in max. absorption of the samples, signals are recorded in 1100-1,270 cm^{-1}, which may come from the groups -CH$_3$, as well as come from asymmetric vibrations of the aromatic ring. In the case of FTIR spectrum of mosses exposed near motorways A4 and S7, the FTIR spectrum are strongly marked by a signal at a wavelength of 1,179 cm^{-1}. It may provide for release, during thermal decomposition, of organic sulfur-containing compounds such as N and N-disubstituted sulfonamides.

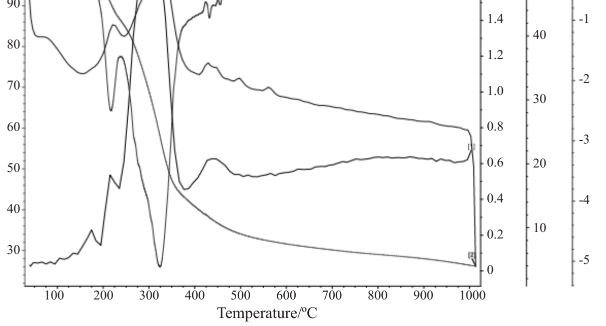

Fig. 4. Thermal curves TG, DTG test of bryophytes O I collection.

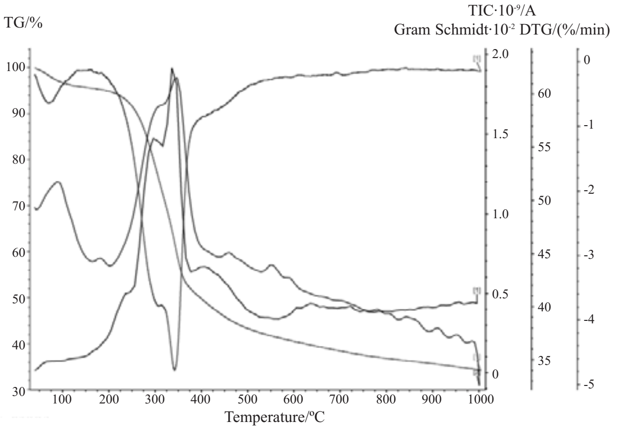

Fig. 5. Thermal curves TG, DTG test of bryophytes S7 I collection.

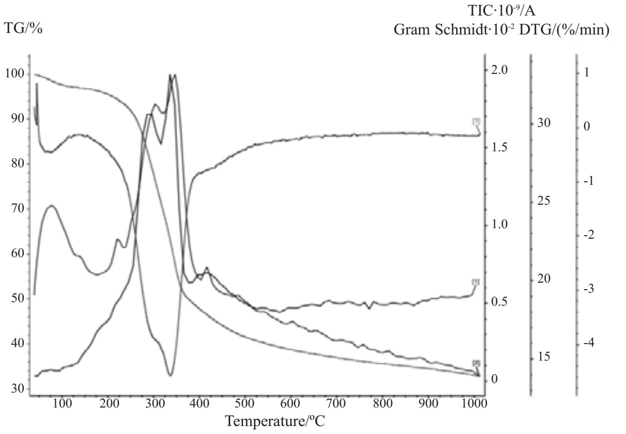

Fig. 6. Thermal curves TG, DTG test of bryophytes A4 I collection.

Signals in the range 1700-1800 cm^{-1} can be derived from unsaturated organic compounds, aromatics, and their oxidation products. Strong signals in the range of 2,300-2,350 cm^{-1} are likely to be the result of a number of emissions of CO and CO_2 in spite of carrying out the analysis in an inert atmosphere. Signals in the range 2,800 cm^{-1} due to the presence of hydroxyl groups (Figs. 7-9).

Especially noteworthy is the 3D FTIR spectrum. Spectrum made during the thermal decomposition of mosses treated prior to exposure to pollution near highways record much more intense signals in the range 1,700 and 2,300 cm^{-1}, which shows a significant degree of adsorption by the studied indicators of organic compounds, including PAHs (Figs. 10-12).

Determination Concentration of Heavy Metals

Qualitative and quantitative analysis of the content of heavy metals made in the gametophyte blades in *Pleurozium schreberi* moss exposed along the A4 showed, in order, increased concentrations of 24-fold Cr, 10-fold Ni, 8-fold Fe, 7-fold Pb, 3-fold Cd, and more than doubled compared to Co, Zn, Cu, and Al according to the control sample (Table 6).

The only metal that has been shown to decline in contaminants in spite of exposure is Mn, down from 960.1 ug·g^{-1} d.m. to 878.2 ug·g^{-1} d.m. average of five exposure places.

Accumulation of heavy metals in samples of moss creates a decreasing series Fe> Al> Mn> Cr> Zn> Cu> Pb> Ni> Co> Cd.

Qualitative and quantitative analysis of samples made of moss exposed along the S7 is shown in the following order: a 40-fold increase in the concentration of Cr, 15-fold Fe, 13-fold Ni, 4.6-fold Al., 4-fold Co, 3.6-fold Pb, 2.5-fold Zn, and 2.2-fold Cd (Table 7).

The lowest increase (1.7-fold) showed Cu. Compared to Mn, as along A4 was shown the decline of analyzed content in the test sample relative to the control sample. Quantitative analysis of accumulation of heavy metals in moss exposed along the Kielce-Warsaw route showed a decreasing series: Al> Fe, differing from the accumulation of heavy metals in moss samples exposed along the A4 motorway. The difference is the amount of accumulation of Fe, Al. It should be noted that the toxicity of the metal depends primarily on their biochemical role in plants and the proportion of synergistic or antagonistic interactions with other elements. Comparison of toxicity of analyzed metals and the resulting risk to plants and animals indicates

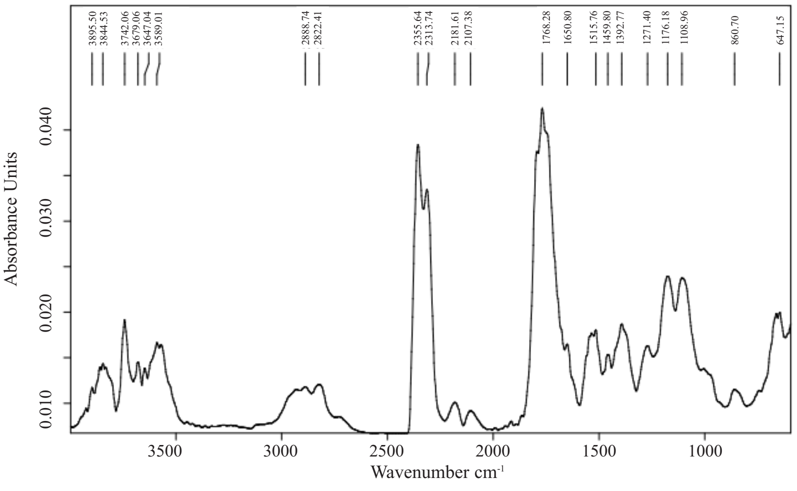

Fig. 7. FTIR spectrum recorded during thermal decomposition 0.

Table 6. Accumulation of heavy metals in moss *Pleurozium schreberi* (Brid.) Mitt. exposed along the A4.

Exposure points	Pb	Cd	Cr	Co	Cu	Mn	Ni	Zn	Al	Fe
	µg·g⁻¹ d.m.									
I	14.9	0.3	549.5	0.9	43.0	1,784.1	15.2	212.5	14,311.3	27,388.9
II	34.5	0.6	1,116.9	1.0	33.3	765.0	9.7	208.2	17,922.9	32,606.6
III	4.3	0.1	63.7	0.1	1.7	44.6	1.2	21.9	1,602.3	2,567.7
IV	35.7	0.4	1,070.8	0.8	17.0	1,368.8	7.0	194.3	13,706.0	32,934.7
V	8.3	0.2	42.3	0.8	19.8	428.5	17.0	96.4	17,653.3	23,607.3

that the least dangerous to the environment is Fe, and most dangerous are Cd and Pb [21, 22].

Microscopic Analysis

On images of analyzed microscopic changes in bryophyte were stated extensive changes of color throughout the middle part of the lamina (Fig. 3), including ribs (Fig. 14) and the lamina base (Figs. 13 and 14). Discoloration showed a varying extent and within the ranges of 250 to 400 microns of a leaf's width and 600 microns of its length. In tests carried out microscopic spots on the leaf edges were not revealed, which may result from the specific to the species of moss, spoon, gutter, and leaf shape. Naturally shaped lamina causes residual metal ion forms to be dissolved in precipitation at the bottom of gut-

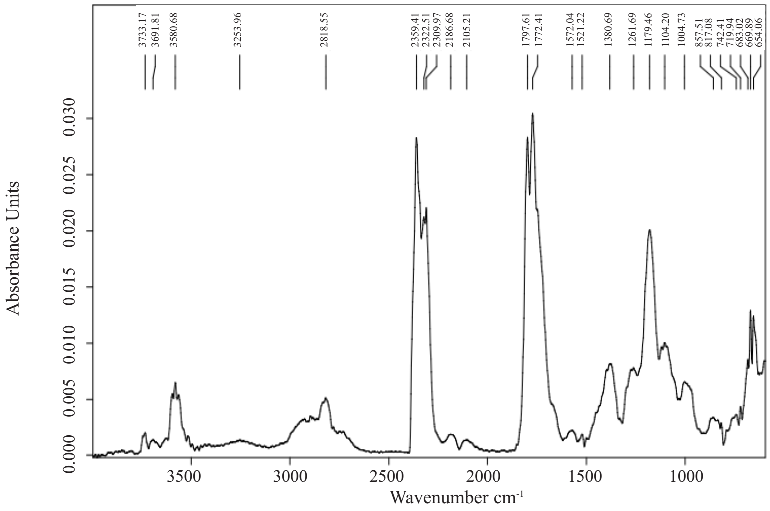

Fig. 8. FTIR spectrum recorded during pyrolysis of sample bryophytes S7 I collection.

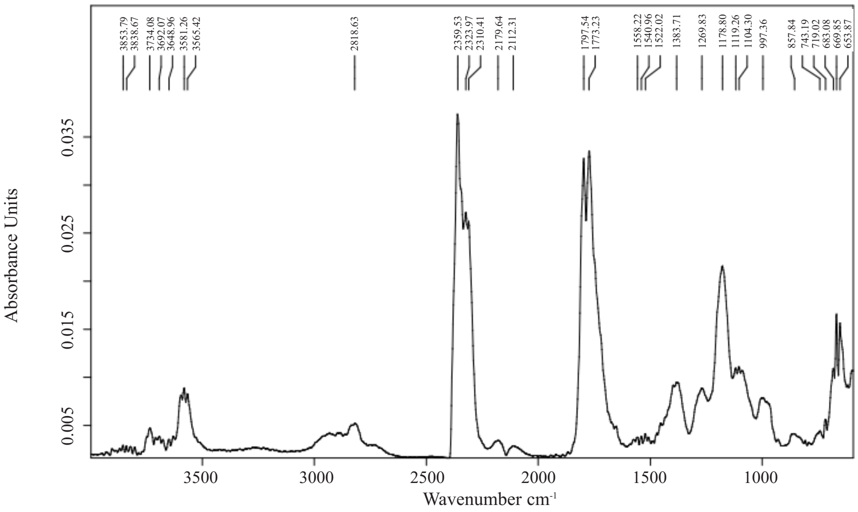

Fig. 9. FTIR spectrum recorded during pyrolysis of sample bryophytes A4 I collection.

Table 7. Accumulation of heavy metals in moss *Pleurozium schreberi* (Brid.) Mitt. exposed along the S 7.

Exposure points	Pb	Cd	Cr	Co	Cu	Mn	Ni	Zn	Al	Fe
	μg.g^{-1} d.m.									
VI	10.3	0.2	628.3	1.5	19.5	567.4	17.4	148.5	31,145.9	48,279.3
VII	8.2	0.3	1,329.3	1.0	14.8	977.7	11.7	70.3	17,672.9	39,898.4
VIII	10.7	0.2	1,119.2	1.9	18.8	560.0	16.1	94.2	39,098.3	65,061.0
IX	13.3	0.2	804.3	0.8	17.2	1,266.0	6.5	90.7	19,235.7	28,255.0
X	7.3	0.2	860.0	0.8	12.9	432.7	8.7	101.3	15,147.4	39,605.3

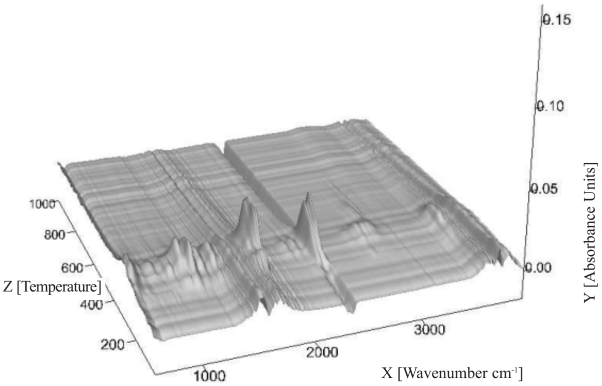

Fig. 10. Spectrum FTIR 3D recorded during thermal decomposition of sample 0.

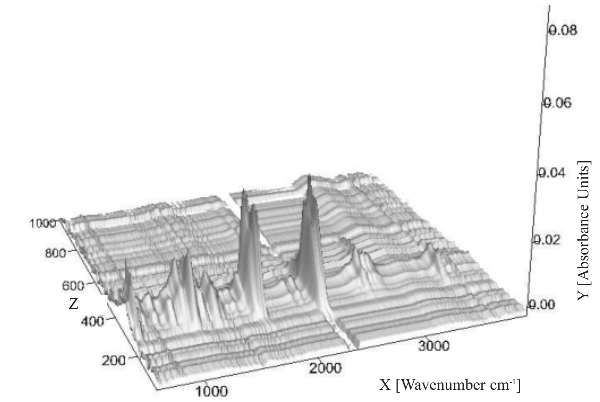

Fig. 11. Spectrum FTIR 3D recorded during thermal decomposition of mosses from S7 expressway after 6 month of exposition.

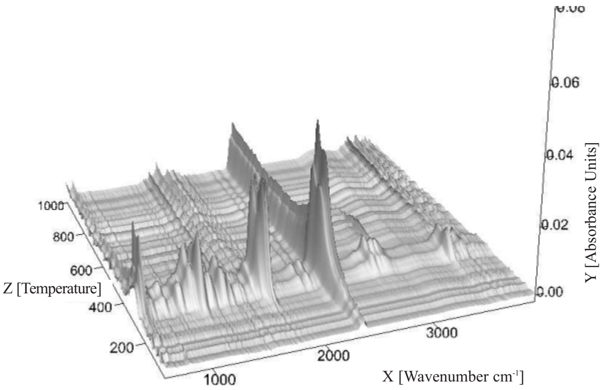

Fig. 12. Spectrum FTIR 3D recorded during thermal decomposition of sample bryophytes A4 I collection.

ters of the leaf, which favors the processes of bioaccumulation, facilitating toxin absorption in those parts of the leaf due to their anatomy because the upper surface is devoid of protective skin (lack of dermal layer).

Conclusion

Bio-indicative monitoring explores environmental pollution on the basis of biomarker response. Particularly important is the effect of abiotic factors, including environmental toxins mainly of anthropogenic origin on the natural biota (forest environment), as well as the areas covered by the economic activities – agrocenoses. The growing development of road infrastructure and the automotive environmental need to enforce control in the areas of roads and highways is due to their proximity of natural afforestation and farmland areas. The study of air pollution in forest areas using moss (*Hippophae rhamnoides P.sch.*) performed as a biomarker was made in Poland 1990-2008 [8, 17].

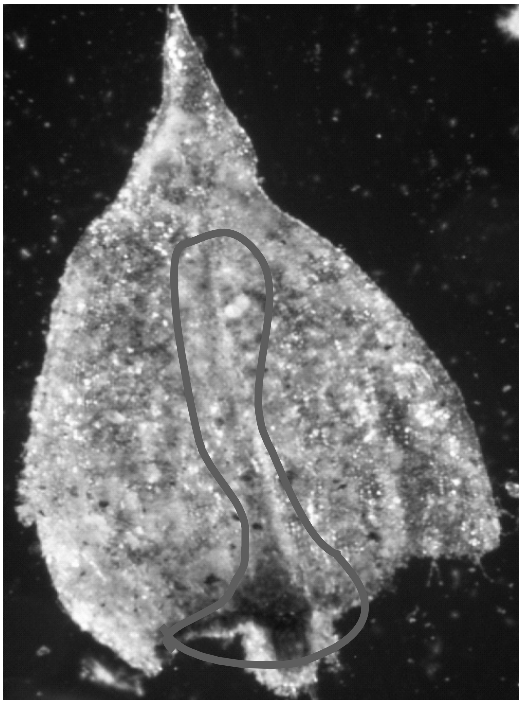

Fig. 13. Color changes in the cells of the leaf gutter. (Photo M.A. Jóźwiak).

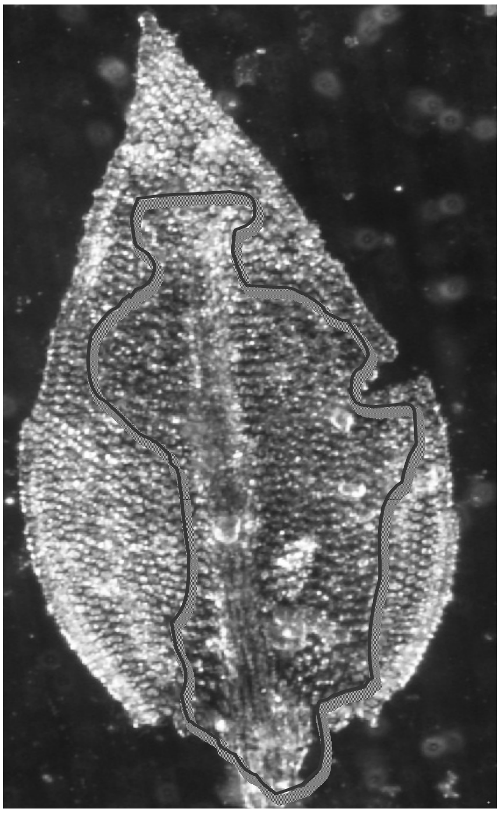

Fig. 14. Discoloration in the cells along the base of the leaf and the leaf ribs (Photo M.A.Jóźwiak).

It was found in 1990 that the moss contained 1,000 $\mu g \cdot g^{-1}$ d.m. Fe, 60 $\mu g \cdot g^{-1}$ d.m. Zn, 12 $\mu g \cdot g^{-1}$ d.m. Cu, 25 $\mu g \cdot g^{-1}$ d.m. Pb, and 0.50 $\mu g \cdot g^{-1}$ d.m. Cd and in 2000 the average metal content in moss *Pleurozium schreberi* was: 938 $\mu g \cdot g^{-1}$ d.m. Fe, 49 $\mu g \cdot g^{-1}$ d.m. Zn, 3.1 $\mu g \cdot g^{-1}$ d.m. Cr, 2.7 $\mu g \cdot g^{-1}$ d.m. Ni, 8.6 $\mu g \cdot g^{-1}$ d.m. Cu, 13.7 $\mu g \cdot g^{-1}$ d.m. Pb, and 0.49 $\mu g \cdot g^{-1}$ d.m. Cd [18]. In comparison with the data obtained as the result of the 2012 study on the A4 motorway and highway S7, concentrations of heavy metals that accumulated in the *Pleurozium schreberi* moss were much higher. This concerns mainly Zn, Fe, Cu, Cr, and Ni. This indicates a high content of heavy metals in the air that occur along the routes from road transport.

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