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A STUDY OF THE CONTENTS AND CONVERTIBILITY OF POLYCYCLIC AROMATIC HYDROCARBONS AND SULFUR IN LICHEN *HYPOGYMNIA PHYSODES* AND ITS SUBSTRATE

Abstract. The estimation of atmospheric pollution with polycyclic aromatic hydrocarbons (PAH) and sulfur on the basis of their content in lichens as air-fed organisms and their substrate, pine bark, was the main task of this research. The material was collected at Tipu and Pikasilla, Estonia, both places relatively little influenced by human activities. PAH concentrations as well as the coefficients of correlation between the concentrations of different compounds in the lichen and its substrate are nearly the same. The results of this paper suggest that benzo(a)pyrene(B(a)P) cannot be used as an indicator of carcinogenic pollution in the areas polluted during a long period.

Key words: polycyclic aromatic hydrocarbons (PAH), sulfur, lichen *Hypogymnia physodes*, pine bark.

Among environmental chemistry studies carried out in the last decades those concerned with carcinogens concentrations in the environment play an important role (Windsor, Hites, 1979; Кирсо et al., 1988). Despite the numerous research works conducted there are few data on the accumulation, migration, conversion, and degradation of carcinogens of anthropogenic origin in ecosystems (Слепян, 1981; Кирсо et al., 1988). Differences in their degradation in the environment have not allowed us to establish a universal indicator compound to estimate the carcinogenicity of environment (Слепян, 1981; Паальме et al., 1983; Кирсо et al., 1988). As the concentrations of carcinogens in the environment are relatively low as compared with those of several other xenobiotics, their tumorigenic action is difficult to determine in natural biocenosis. Therefore, most of the studies on the determination of the carcinogenicity of environment are performed using analytical methods for determining the carcinogenic compounds. As the whole spectrum of carcinogenic pollutants is difficult to study, it is important to elucidate relationships between various carcinogens and other pollutants emitted presumably together with them. One of such substances is sulfur (Brimblecombe, 1986).

As is known, the polycyclic aromatic hydrocarbons (PAH) accumulated in higher plants originate mainly from the atmosphere and only partly from the soil (Быкорез et al., 1985; Sims, Overcash, 1983). Therefore, it is difficult to find higher plants which were indicators of PAH pollution as they obtain substances from both the atmosphere and the soil at various rations. However, in lichens, which are air-fed organisms, only the atmospheric pollution with PAH and sulfur is reflected.

Therefore, a study of the contents of sulfur and PAH in the lichen *Hypogymnia physodes* and its substrate, pine bark, was undertaken.

Materials and Methods

The material, the lichen *H. Physodes* and its substrate, pine bark, was collected at Tipu and Pikasilla, South Estonia. The sites are located at a distance of 85 km from each other and are both relatively little influenced by human activities. Judging by the content of sulfur in the

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lichen and its substrate, both the places are almost similarly polluted (Леммик et al., 1990).

To identify PAH, the benzene extracts of the lichen and pine bark were previously separated by thin-layer chromatography, using a 9 : 1 mixture of benzene and acetone as the eluent. Different PAH compounds were identified by high-pressure liquid chromatography (eluent acetonitrile-water 93 : 7), using Silasorb C18 filled capillary column (0.5×300 mm) and a fluorescence detector (excitation wavelength 254 nm, detection in the range 330 ... 600 nm). The sulfur content was determined by gravimetric analysis after ashing the samples in Eschka powder.

Results and Discussion

A comparison of the results obtained (Table 1) and those available in the literature (Слепян, 1981) indicates that the compounds identified by us in different samples are distributed more uniformly. There are no differences of concentrations up to orders of magnitude. That is why the mean values of PAH concentrations are lower in our work.

Table 1

The PAH (μg/kg) and sulfur (%) contents in *H. physodes* and pine bark

Location	A	P	B(a)A	Chr	B(a)P	F	B(b)F	B(k)F	Ph	S
T_1 B	6.88	70.7	84.4	121	7.40	82.4	12.1	6.51	152	0.52
T_1 L	4.98	39.4	17.6	38.7	7.45	98.5	19.9	8.7	208	0.08
T_2 B	3.95	23.2	16.5	37.0	4.80	63.0	8.3	4.47	113	0.1
T_2 L	9.3	70.8	42.2	27.4	7.05	181.0	28.4	14.1	272	0.1
T_3 B	8.5	63.0	42.2	77.4	8.00	143	13.2	8.7	234	0.1
T_3 L	5.7	39.4	28.1	48.4	6.25	140	9.2	10.2	176	0.02
T_4 B	2.83	29.5	15.8	33.9	4.85	59.8	8.52	5.2	115	0.1
T_4 L	6.41	47.3	24.6	48.3	6.1	64.7	8.52	5.2	114	0.15
T_5 B	3.20	21.6	17.6	33.9	3.5	53.5	6.39	4.34	112	0.08
T_5 L	5.1	35.0	23.5	21.5	8.55	82.4	11.0	4.82	133	0.09
P_1 B	3.85	31.5	17.6	29.0	6.70	74.1	8.52	4.43	140	0.1
P_1 L	5.0	39.3	28.1	19.4	3.1	115.3	14.2	6.51	144	0.09
P_2 B	2.13	27.6	14.0	24.2	2.80	120	5.68	3.26	120	0.09
P_2 L	7.72	78.7	41.0	56.4	7.30	157	18.9	10.8	267	0.02
P_3 B	8.00	49.2	30.7	36.3	5.00	123.6	10.6	5.42	210	0.03
P_3 L	2.66	19.7	14.1	24.2	5.05	49.4	5.68	3.80	104	0.02
P_4 B	3.19	15.8	14.1	19.3	6.00	70.0	4.97	3.26	116	0.11
P_4 L	7.08	47.3	28.1	19.4	5.60	123	15.6	6.51	240	0.11
P_5 B	3.72	31.5	22.8	31.5	7.50	82.4	9.94	5.43	148	0.09
P_5 L	5.64	35.4	31.6	19.4	9.00	116	12.8	6.51	184	0.08
Mean										
Bark	4.62	36.5	27.6	44.3	5.65	87.2	8.78	5.1	146	0.13
Lichen	5.96	45.2	27.9	32.3	6.54	113.1	15.4	7.77	84.2	0.08

Abbreviations: A — anthracene, P — pyrene, B(a)A — benzo(a)anthracene, Chr — chrysene, B(a)P — benzo(a)pyrene, F — fluoranthene, B(b)F — benzo(b)fluoranthene, B(k)F — benzo(k)fluoranthene, Ph — phenantrene, S — sulfur; location: T_{1-5} — Tipu, P_{1-5} — Pikasilla, B — pine bark, L — lichen.

Judging by the PAH content of the lichen and its substrate it may be concluded that the origin of these compounds at Tipu and Pikasilla is almost the same. The coefficients of correlation between the PAH and sulfur contents determined in this research are presented in Table 2. The values found were compared with those obtained in our previous research

Table 2

Coefficients of correlation between the PAH and sulfur contents of *H. physodes* and pine bark

PAH	A	P	B(a)A	Chr	B(a)P	F	B(b)F	B(k)F	Ph	S
A		0.885	0.662	0.410	0.462	0.731	0.714	0.736	0.837	0.142
P			0.800	0.611	0.418	0.704	0.692	0.743	0.782	0.322
B(a)A				0.819	0.400	0.385	0.407	0.454	0.436	0.741
Chr					0.288	0.083	0.124	0.252	0.167	0.722
B(a)P						0.239	0.394	0.401	0.432	0.166
F							0.795	0.812	0.869	−0.192
B(b)F								0.956	0.827	−0.062
B(k)F									0.817	−0.079
Ph										0.166
S										

N o t e: abbreviations see Table 1.

(Trapido et al., 1988) for snow samples collected in different regions in Tallinn. The coefficients of correlation between the concentrations of different PAH except anthracene, the compound of the lowest concentration, were >0.9 in our previous work, in more than half the cases even >0.95. This may be explained by the accumulation of PAH in samples within a relatively short period of time at low temperature and in conditions comparatively similar as to their pollution characteristics in a given region.

The coefficients of correlation between the concentrations of different compounds obtained in this research are considerably lower (Table 2) and their dispersion is more noticeable than in the snow cover (Trapido et al., 1988). The reason may be the different degradability and convertibility of the PAH analysed in lichens and their substrates. On the basis of lower correlation coefficients it is possible to select more easily degradable and convertible compounds. It seems that B(a)P, in comparison with the other PAH studied, is the most easily convertible compound (Table 2). In spite of that, B(a)P was and sometimes still is used as an indicator to estimate the carcinogenicity of environment (Suess, 1976; Цыбань et al., 1985; Tiefenbacher, 1988). Based on the results of this paper it may be assumed that B(a)P may be used as an indicator to determine the carcinogenicity of recent pollution only or to determine that of exhausts *in situ*.

The use of B(a)P as an indicator in the areas polluted during a long period, may yield lower than the actual potential carcinogenicity of the environment. Therefore, we cannot agree with those authors who are still using B(a)P as a universal carcinogenicity indicator of the environment.

The higher coefficients of correlation between the concentrations of different PAH accumulated in long-lived organisms and those accumulating in comparatively stable components of the environment give evidence of their similar behaviour, higher stability and lower migration capability. Some of these relationships which may be estimated as very close are demonstrated in Figs. 1 and 2. It can be seen that the compounds depicted in the outer circles behave more similarly to one another than the B(a)P depicted in the middle of the circle (cf. Table 2). Thus, one can see from Figs. 1 and 2 that the behaviour of B(a)P is different from that of the other PAH studied by us. The behaviour of the compound in the middle cannot reveal peculiarities in the behaviour of the other PAH.

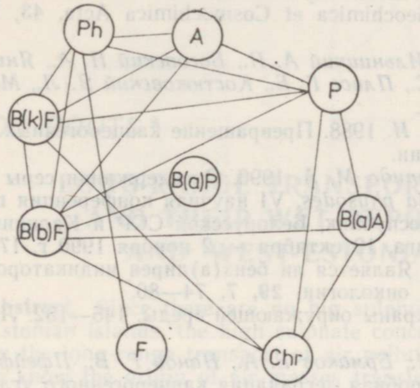

Fig. 1. Relationships between PAH concentrations in pine bark. The pairs of PAH where correlation coefficients are higher than 0.71 are connected by lines. Abbreviations see Table 1.

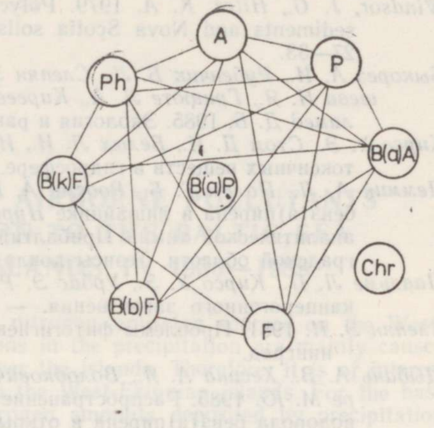

Fig. 2. Relationships between PAH concentrations in the lichen *Hypogymnia physodes*. The pairs of PAH where correlation coefficients are higher than 0.71 are connected by lines. Abbreviations see Table 1.

Proceeding also from the fact that sulfur and the components under study are distributed preferably between different aerosol fractions (Brimblecombe, 1986), the characteristics of the distribution of concentrations of the compounds under study and sulfur in air-fed organisms may serve as a model for investigating different sources of pollution in every region. The coefficients of correlation of the compounds indicate to the principal differences in the accumulation of PAH and sulfur. The results are presented in Table 2.

A comparison of PAH concentrations in the lichen and its substrate, pine bark, shows them to be nearly the same (Table 1). The coefficients of correlation between the concentrations of different compounds in the lichen and its substrate are similar, too (Figs. 1 and 2). On the basis of these results we suppose that the capacity for degradation and conversion of PAH cannot be attributed to the lichen *H. physodes* as pine bark seems to possess nearly the same capacity. It seems that, in addition to physicochemical factors, microorganisms present in the lichen and its substrate may play a certain role in the degradation and conversion of PAH in them, too.

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