Needle of Scotch Pine (*Pinus sylvestris* L.) as a Bioindicator for Atmospheric Pollution with Polycyclic Aromatic Hydrocarbons

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(Received April 13, 2007; revised August 3, 2007)

Abstract

Determination of the polycyclic aromatic hydrocarbons (PAH) accumulated in the needle of a Scotch pine (*Pinus sylvestris* L.) was for the first time carried out over the Baikal Natural Territory (BNT). It has been established, that in the industrial and urbanized territories of the BNT the level of PAH accumulation in needle amounts to as much as 1800 ng/g, whereas the background regions of BNT this value is less than 20–60 ng/g. The composition of PAH accumulated includes a priority series of organic pollutants from this class. The investigation of different age needle has demonstrated that the needle of the second year could be considered as an adequate bioindicator of atmospheric pollution. The levels of PAH accumulation in pine needle indicate a local character of atmospheric pollution over the southern part of BNT, as well as an insignificant contribution of regional transfer of the mentioned pollutants to the pollution of the Baikal lakeside comparable with the background level. The comparison of PAH content in the needle with the suppression degree of pine timber-stands allows one to assume these pollutants to exhibit a phytotoxic effect.

Keywords: *Pinus sylvestris* L. pine needle, biomonitor, atmospheric pollution, polycyclic aromatic hydrocarbons

INTRODUCTION

The application of classical monitoring methods to the studies on the distribution of polluting substances emissions on a regional scale has a number of restrictions. A direct monitoring of atmospheric air pollution with the required time intervals and sampling grid within the framework of the mentioned problems is difficult to realize in practice. A snow cover as an accumulating matrix reflects the athmospheric pollution only for the winter period of year that lasts over the territory of Pribaikalia about 100–120 days. Taking into account that an Asian anticyclone uses to stay above the Pribaikalian territory during this period when atmospheric emissions are located within the areas of the pollution sources location, the monitoring a snow cover allows one to determine, more likely, the sources of emissions rather than the zones of their distribution.

With the use of modelling the dispersion processes for polluted air masses one could estimate the potentialities of the atmosphere with respect to the processes of self-purification and repeatability of hazardous concentration values within a particular time range [1]. In the situation under consideration the inclusion of biological objects into the methodological base of monitoring allows one to determine the distribution of pollutants in the territory throughout the levels of their accumulation in biological matrices as well as to assess the results of the pollutants effect on the environment from the physiological state of living organisms.

The purpose of the present work consisted in the studies on the needle of a Scotch pine (*Pinus sylvestris* L.) as a bioindicator of atmospheric pollution with polycyclic aromatic hydrocarbons (PAH) on a regional scale; in particular, the determination of the levels of PAH accumulation in pine needle for the southern part of the Baikal Natural Territory (BNT), the studies on the dynamics of PAH accumulation in needle of different age and the comparison of PAH content in the needle with the suppression degree of pine timber stands.

The choice of Scotch pine needle as a bioindicator is caused, firstly, by its unique properties to accumulate polluting substances coming from the atmosphere; secondly, by a high sensitivity of this coniferous species to the atmospheric pollution at all the ontogenesis stages; thirdly, by a correspondence between the external damage degree of timber stands and their physiological state and, fourthly, by pine abundance as a species in Pribaikalia [2, 3]. Polycyclic aromatic hydrocarbons can be attributed to dominating components in the organic aerosol fraction in the region [4, 5] and consequently they may be considered as convenient "markers" of atmospheric pollution with stable organic pollutants.

EXPERIMENTAL

Scotch pine needle was sampled from a vast area (about 1 million ha) of the southern BNT part including industrial regions and unsettled sites of the southern Baikal lakeside, as well as from background territories such as the Mondy station for background monitoring and the northern BNT sites (Umkhey village, Kurumkhan District, Republic of Buryatia; Baikalskoe village, Irkutsk Region). On every sample area (SA) the branches of the top part of tree crown were cropped from 5–6 trees 30–40 years in age. Under laboratory conditions the needle of each year of life was separated from spears, each sample was mixed thoroughly and packed then into aluminium foil. The mass of fresh needle sample amounted to 2 to 3 kg. Before beginning the analysis the samples of needle were kept at the temperature of −5 °C. Prior to analysing, two samples of needle about 10 g in mass were taken.

In the first sample a humidity of the needle was determined through drying it up to constant mass at the temperature of 60 °C during 12–14 h. From the second sample PAH were extracted, adding 100 mL of n-hexane and 0.05 mL of a reference solution (the mixture of acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} и perylene-d_{12} in isopropyl alcohol with the concentration of each of the component amounting to 5 μg/mL). The extraction was carried out during 0.5 h at a room temperature in an ultrasonic bath, twice. The extracts joined together were concentrated, then the PAH fraction was isolated with the use of a solid-phase extraction method on a silica gel cartridge (0.5 g, Discovery ® SPE DSC-Si, Supelco) with a subsequent re-extraction of concentrated eluate from n-hexane to methanol.

The determination of PAH included in the priority series (14 compounds) as well as of benz[e]pyrene and perylene was carried out with the use of an Agilent 6890/5973N GC/MSD System (USA) under the following conditions: a DB-5MS column, 30 m × 250 μm, the temperature programming mode of the column being 95 °C during 0.5 min, then a gradient up to 310 °C, with the heating rate of 10 °C/min, and hold during 8 min at 310 °C; injector temperature at 290 °C; the volume of injected sample amounted to 2 μL in a splitless mode.

Polycyclic aromatic hydrocarbons were detected according to characteristic ions with m/z 152 (acenaphthylene), 154 (acenaphthene), 164 (acenaphthene-d_{10}), 166 (fluorene), 178 (phenanthrene, anthracene), 188 (phenanthrene-d_{10}, anthracene-d_{10}), 202 (fluoranthene, pyrene), 228 (benz[a]anthracene, chrysene), 240 (chrysene-d_{12}), 252 (benz[b]fluoranthene, benz[k]fluoranthene, benz[e]pyrene, benz[a]pyrene, perylene), 264 (perylene-d_{12}), 276 (indeno[1,2,3-c,d]pyrene, benz[g,h,i]perylene) and 278 (dibenz[a,h]pyrene). The chromatograph was calibrated against two parallel series of calibration solutions within the range of PAH concentration from 20 to 2000 μg/mL. Calibration curves were expressed in the form:

$$m_{\mathrm{PAH}}/m_{\mathrm{ref}} = k(S_{\mathrm{PAH}}/S_{\mathrm{ref}})$$

where m_{PAH} and m_{ref} are the mass of PAH and the mass of the reference within the extract sample under analysis, respectively, ng; S_{PAH} and S_{ref} are the areas of the peaks corresponding to PAH under determination and the reference, respectively, rel. units; k is the calibration factor. The correlation coefficients for calibration curves were higher than 0.985–0.998.

The mass of PAH in the needle (taking into account the humidity value) was calculated as

TABLE 1

Composition PAH, accumulated in the Scotch pine needle of the second year of life at different places of the BNT with various atmospheric pollution levels, ng/g

PAH	Sampling area													
	1	8	10	11	14	15	21	23	25	27	29	20	30	31
I	4.6	1.4	16	5.1	4.8	24	44	5.4	2.3	5.0	7.1	<0.5	<0.5	<0.5
II	4.0	3.4	1.9	16	12	<0.5	<0.5	57	3.9	7.3	2.2	<0.5	<0.5	<0.5
III	17	6.2	3.8	6.6	6.8	<0.5	1.7	42	11	6.5	6.6	<0.5	<0.5	<0.5
IV	430	40	48	670	131	160	15	220	77	51	55	35	16	12.6
V	5.4	0.5	0.98	11	<0.2	2.0	0.31	2.6	0.60	0.63	0.54	<0.2	0.46	0.42
VI	150	13	10	310	63	24	3.0	40	12	8.2	10	7.8	2.7	2.4
VII	91	6.4	7.1	190	36	12	2.0	29	4.2	5.1	5.4	3.0	1.4	1.5
VIII	8.2	0.6	0.61	36	4.2	0.30	0.36	1.5	0.5	0.31	<0.2	<0.2	<0.2	0.33
IX	55	4.0	3.1	90	34	1.5	0.73	5.4	1.2	1.9	<0.2	1.6	<0.2	1.0
X	5.7	5.4	0.94	77	29	0.35	0.44	3.9	4.7	<0.2	<0.2	9.1	<0.2	<0.2
XI	4.4	1.0	1.7	32	6.7	1.0	0.90	0.81	1.4	<0.2	<0.2	<0.2	<0.2	<0.2
XII	4.5	2.0	0.72	3.0	5.5	1.2	0.43	1.1	2.1	1.2	0.40	0.31	<0.2	<0.2
XIII	3.0	1.1	0.83	2.9	3.0	0.60	0.51	1.1	1.8	0.65	0.22	<0.2	<0.2	<0.2
XIV	0.41	0.70	1.2	6.1	1.5	0.30	0.74	0.77	0.75	<0.2	<0.2	<0.2	<0.2	<0.2
XV	1.9	1.3	0.65	37	7.3	0.81	0.61	1.1	3.7	0.90	0.57	<0.2	<0.2	<0..2
XVI	1.2	1.5	0.88	0.5	<0.2	1.1	0.61	1.7	4.5	1.3	0.81	<0.2	<0.2	<0.2
XVII	3.1	0.33	<0.2	30	5.1	<0.2	0.32	0.23	0.66	<0.2	<0.2	<0.2	<0.2	<0.2
Sum	790	89	98	1500	30	230	72	410	130	90	89	57	21	18
R	0.60	0.65	0.46	0.51	0.65	0.66	–	0.50	0.53	0.65	0.65	–	–	–

Notes. 1. PAH: I – acenaphtylene, II – acenaphtene, III – fluorene, IV – phenanthrene, V – anthracene, VI – fluoranthene, VII – pyrene, VIII – chrysene, IX – benz[a]anthracene, X – benz[b]fluoranthene, XI – benz[k]fluoranthene, XII – benz[e]pyrene, XIII – benz[a]pyrene, XIV – perylene, XV – indeno[1,2,3-c,d]pyrene, XVI – dibenz[a,h]anthracene, XVII – benz[g,h,i]perylene. 2. Sampling areas: 1 – Irkutsk city, Yunost Island, Central District; 8 – Bolshaya Rechka village; 10 – Listvyanka settlement; 11. Olkha village; 14. Kheya River; 15 – Rassokha station; 20 – Mondy station; 21 – Zun-Murino village; 23 – Slyudyanka city; 25 – Baikalsk city; 27 – Snezhnaya River; 29 – Preemnaya River; 30 – Umkhey village, Kurumkhan District, Republic of Buryatia, 31 – Baikalskoe village, Irkutsk Region.

an average value from the results of determining in two parallel tests. The variation coefficient was estimated basing on archival records as a deviation of the parallel sample analysis results from the average value, the observational accuracy was determined using a method of additions. The error of determination for individual PAH was estimated to be within the range of $\delta = 8-12$ % ($n = 2$, $P = 0.95$), the total content of PAH being about 7.4 % ($n = 2$, $P = 0.95$), the ratio value R for benzopyrenes being at 15 % ($n = 2$, $P = 0.95$). The detection limit for individual PAH amounted to 0.15–5.0 ng/g depending on individual PAH characteristics, for the mass of the sample under analysis amounting to 10 g.

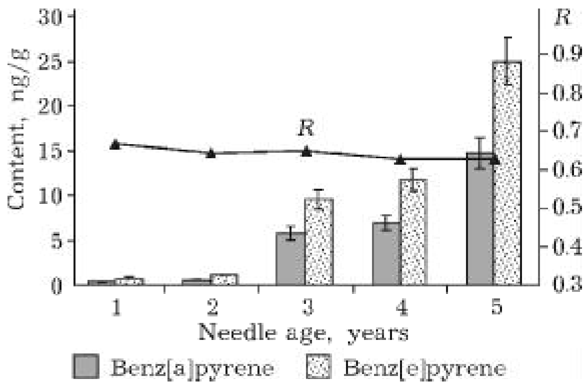

Fig. 1. Accumulation of benz[a]pyrene and benz[e]pyrene and the ratio value R ($\delta = 15$ %) in the needle of different age over the sample area with moderate atmospheric pollution (Rassokha station, Southern Pribaikalia).

RESULTS AND DISCUSSION

Qualitative composition of PAH accumulated in the needle and the identification of their sources

For the samples of the needle harvested in the regions with a high level of atmospheric pollution, the PAH species accumulated were shown to be included in the priority series of the mentioned class of organic pollutants – 15 compounds (Table 1), whereas the total content of phenanthrene, fluoranthene, pyrene and chrysene amounts to as much as 90 % from the total content of all the hydrocarbons revealed. The prevalence of the mentioned hydrocarbons in the composition of the samples is inherent in the emissions of aluminium manufacture, the objects of heat-and-power engineering working with the use of solid fuel, motor transport [9–11], as well as in the chemical composition of aerosol in this region [4, 5], which indicates a man-caused source of PAH species accumulated in the needle.

For the samples of biennial needle with a low level of PAH accumulation the number of hydrocarbons under determination is reduced down to 5–7 compounds due to minor components of the PAH fraction with 5–6 aromatic rings in the molecular structure, since their content is less than the detection limit inherent in the technique used. As the needle age increased both the level of PAH accumulation, and the number of hydrocarbons determination are observed to grow.

In order to identify the sources of the PAH accumulated in the needle, a ratio R was measured for the isomers of benzopyrenes such as benz[a]pyrene and benz[e]pyrene: R = [benz[e]-pyrene]/([benz[e]pyrene] + [benz[a]pyrene]). In contrast to its isomer, benz[e]pyrene is characterized by a higher stability under the conditions of atmospheric transfer, therefore the ratio value $R > 0.5$ one may connect with a decrease in the content of unstable benz[a]-pyrene within in a sample as the result of photochemical transformations. The source of these PAH supply could be formed by a remote atmospheric transfer as it was shown earlier for the Baikal aerosol [12]. According to the results of model studies on aerosol fields above the water area of the Baikal Lake, the benzopyrene ratio $0.65 < R < 0.75$ corresponds to the transboundary transport of air masses the distances ranging from 10 up 300 km [13].

It has been established that the ratio of isomers in the composition of accumulated PAH for 5 years of needle life exhibits a statistically insignificant deviation from the average value (Fig. 1), this fact indicates the absence of chemical and biochemical processes with the participation of benzopyrenes during their accumulation. Basing on this, a conclusion was drawn that the ratio of the isomers in the composition of accumulated PAH reflects their ratio in the composition of an aerosol prior to the accumulation in the needle occurred and thus it could be used in order to identify the sources PAH supply. Thus, the accumulation of PAH in the needle of pines growing over the area of the Shelekhov city, in the territory of the Irkutsk, Baikalsk, Slyudyanka and the Listvyanka settlement, according to the R criterion can be caused by the dispersion of the emissions of local sources, whereas at the points of the Irkutsk–Listvyanka settlement profile, as well as at unsettled places of the southern Baikal lakeside a distant atmospheric transfer could form the sources of the accumulated PAH, too.

Polycyclic aromatic hydrocarbon perylene is not included into the series of priority PAH, but according to a rather high content of this hydrocarbon in the atmospheric emissions of aluminium manufacture [11] one could identify this source. So, for example, the fraction of PAH in the needle selected from the area of an aluminium factory location, contains a significant amount of perylene (up to 6.1 ng/g). At the distance within 30 km from the factory in the direction of prevailing winds the content of perylene in needle extracts decreases: in the region of the Kheya River this value amounts to 1.5 ng/g (R = 0.65), being at 0.70 ng/g (R = 0.63) in the area of the Bolshaya Rechka settlement. In the needle from unsettled places of the southern Baikal lakeside and from the background areas of BNT perylene was not revealed (<0.2 ng/g).

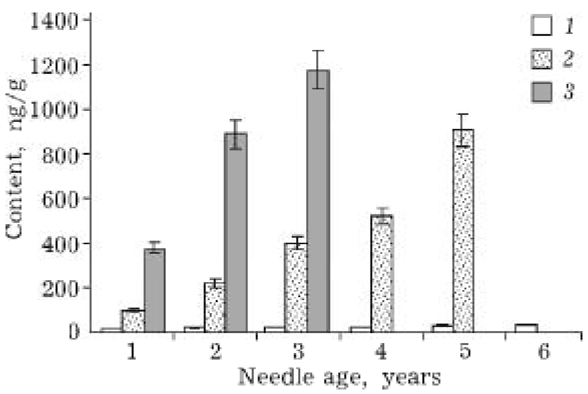

Fig. 2. PAH accumulation in the needle of different age over the sample areas with various levels of atmospheric pollution: *1* – background area (northern part of BNT, Baikalskoe village); *2* – moderate pollution (Rassokha station, Southern Pribaikalia); *3* – severe pollution (Irkutsk, Central District).

Levels of PAH accumulation in the needle

According to the data obtained in the studies on the needle of different age (Fig. 2), the dynamics of ΣPAH (the sum of PAH revealed) accumulation is determined by the level of atmospheric pollution. In the background areas the needle accumulates for six years less than 50–60 ng/g of pollutants. Under moderate atmospheric pollution the accumulation is characterized by a uniform increase of the hydrocarbons content that becomes almost an order of magnitude higher (as much as 800–1000 ng/g) during five years. The mentioned tendency is observed for healthy and slightly suppressed pine timber-stands at the needle age of 5–7 years. In the territories with a severe atmospheric pollution the pine needle remains only within 2–3 years of life, accumulating a maximal for Pribaikalia ΣPAH amount during this period (up to 1500–1800 ng/g).

Taking into account the capacity of the pine needle to accumulate maximum PAH amount within 2–3 years of life under the conditions of severe atmospheric pollution, as well as a decrease in the needle lifetime under such conditions (often three-year-old needle could not simply be revealed), the needle of the second life-year was chosen as an adequate indicator of atmospheric pollution. The determination of PAH in the needle of different age (in particular, in 5 to 7-year-old needle) for the territories with a low level of atmospheric pollution could be used in order to assess the flows of pollutants within long enough periods of time.

The revealed levels of ΣPAH accumulation in the pine needle of the second year of life for the southern BNT part are presented in Fig. 3. It can be seen that in the area of the Shelekhov city the content of ΣPAH in the needle is maximal amounting to as much as 1500–1800 ng/g (R = 0.60); at the centre of the Irkutsk this value amounts to 500–800 ng/g (R = 0.60); in the Slyudyanka city it is equal to 410 ng/g (R = 0.50). When moving away from the Irkutsk and the Shelekhov towards the Baikal Lake along the valley of the Angara River the level of ΣPAH accumulation in the needle exhibits an almost tenfold decrease amounting to 90–120 ng/g (R = 0.62–0.65), but 4 to 6 times exceeding the background level.

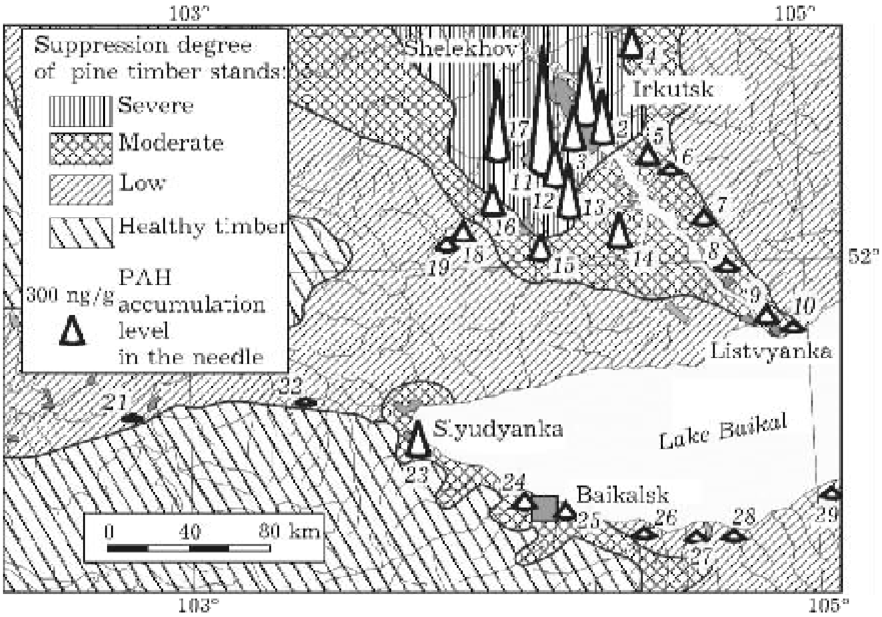

Fig. 3. Schematic map for the sampling of the Scotch pine needle over the southern part of the BNT (needle age being 2 years, August, 2006). ΣPAH accumulation in the needle (R) (δ = 7.4 %, n = 2, P = 0.95), ng/g: *1* – Irkutsk, Yunost Island, Central District – 800 (0.60); *2* – Irkutsk, Solnechny subdistrict – 320 (0.60); *3* – Irkutsk, Academgorodok – 280 (0.61); *4* – Glazunovo village – 230 (0.60); *5* – Patrony-2 village – 160 (0.52); *6* – Patrony-1 village – 76 (0.64); *7* – Burdugus village – 120 (0.62); *8* – Bolshaya Rechka village – 89 (0.65); *9* – Nikola settlement – 140 (0.59); *10* – Listvyanka settlement – 98 (0.46); *11–13* – Olkha village – 1500 (0.51), 420 (0.60), and 500 (0.60), respectively; *14* – Kheya River – 350 (0.65); *15* – Rassokha station – 230 (0.66); *16* – Chistye Klyuchi settlement – 280 (0.51); *17* – Baklashi village – 740 (0.51); *18* – Moty-1 village – 150 (0.48); *19* –Moty-2 village – 82 (0.54); *21* – Zun-Murino village – 72 (0.46); *22* – Bystraya River – 52 (0.48); *23* – Slyudyanka city – 410 (0.50); *24* – Utulik River – 160 (0.70); *25* – Baikalsk city – 130 (0.53); *26* – Khara-Murin River – 86 (0.66); *27* – Snezhnaya River – 90 (0.65); *28* – Vydrennaya River – 89 (0.64); *29* – Pereemnaya River – 89 (0.64).

TABLE 2

PAH accumulation in the snow cover, in the Scotch pine (*Pinus sylvestris* L.) needle and the estimation of physiological state for pine timber stands (2 year-old needle, 2006)

Sampling area	PAH accumulation in		Suppression degree
	snow cover, μg/m^2 [14]	needle, ng/g	of pine timber stands
Irkutsk	60–840	280–790	Severe
Zone of emissions			
Irkutsk Aluminium Smelter	1400–15 000	500–1500	«
Slyudyanka	120–420	410	Moderate
Baikalsk	15–30	130	«
Listvyanka settlement	60–120	98	«
Irkutsk–Listvyanka profile	15–230	75–160	«
Southern Baikal lakeside	10–100	85–90	Low
The Mondy station	<0.5	55–80*	Healthy timber stands
Background BNT regions	–	20–30	« «
The Great Britain, rural regions [15]	–	20–3100	–
Germany, urban regions [7]	–	310	–
Germany, industrial regions [7]	–	490	–
Sweden, background regions [7]	–	410–820	–
Sweden, industrial regions [7]	–	1000	–

* Needle age being 3 years.

At the unsettled places of the Baikal lakeside the level of ΣPAH accumulation is observed to be as much as 90 ng/g at R = 0.65.

A higher level of PAH accumulation was revealed for the needle harvested in area of the. Utulik River estuary (up to 160 ng/g, R = 0.70). To all appearance, it could be connected with the transfer of man-caused atmospheric emissions from the cities of Slyudyanka and Baikalsk of to this region. For the territory of the Slyudyanka the accumulation ΣAH in the needle is distinguished not only by a higher level (410 ng/g), but also by the ratio value R = 0.50, which indicates a local source of pollutants. For the background areas of BNT the accumulation level of PAH does not exceed 20 to 30 ng/g (the needle being 2 years old). The mentioned level of accumulation we considered as the bottom limit of ΣPAH content in the needle over the BNT. For the three-year-old needle gathered in the region of the high-mountains station for background monitoring Mondy, the content of PAH is observed to be slightly higher amounting to 55–80 ng/g.

The estimation of PAH distribution within the atmosphere of the southern BNT part, based on the pollutants accumulation levels in the needle, coincides with the results of snow cover monitoring obtained earlier [14]: the maximum atmospheric pollution and, correspondingly, the maximum PAH accumulation in natural and biological objects is observed over the areas of the local sources arrangement. However, as against the snow cover [14], the accumulation of PAH in the needle is characterized by a narrower range of the concentrations observed (from the background the extreme ones) those coincide as a whole with the levels of PAH content in the needle harvested over the background, industrial and city areas of the West Europe (Table 2).

The ΣPAH content in the needle (85–90 ng/g, R = 0.64) for unsettled places of the Baikal lakeside increased with respect to the background could apparently be connected with the dispersion of the emissions from the sources located both on the Baikal lakeside, and within the industrial zone of Priangaria. Taking into account a low level of PAH accumulation in the needle (3 to 4 times higher than for the background), the contribution of regional transfer to the pollution of the bottom atmospheric layer at the Baikal lakeside, should be, obviously, estimated as a value of little significance, comparable with the background pollution.

In addition, the schematic map (see Fig. 3) demonstrates the results of the estimation of the physiological (vital) state for pine timberstands in the BNT southern part. The estimation was carried out basing on the diagnostic scale developed that includes a set of representative structural and functional parameters [2, 3]. There are significant correlations between the measured morphophysiological characteristics of the trees and the PAH content in their needle which correlations indicate a considerable contribution of ecotoxicants of this class in the destabilization of pine forests in the region. In particular, one can observe the PAH content dependences on the timber stand defoliation level (r = 0.69, n = 31), on the needle lifetime (r = −0.47), on the length of (r = −0.30), on the needle amount the spear (r = −0.34), on the mass of a single needle (r = −0.28).

CONCLUSION

Determination of the polycyclic aromatic hydrocarbons accumulated in the needle of a Scotch pine (*Pinus sylvestris* L.) was for the first time carried out over the Baikal Natural Territory. As the result of the studies on the dynamics of PAH accumulation in the needle of different age on sample areas with a various level of atmospheric pollution it has been demonstrated that the needle of the second life year can be used as an adequate bioindicator of the atmospheric pollution. The comparative analysis of PAH accumulation levels in pine needle over the southern part of BNT indicates a local character of atmospheric pollution above the mentioned territory as well as an insignificant contribution of regional transfer of these pollutants to the pollution the Baikal lakeside comparable with the background level.

The comparison of PAH content in the needle with the physiological state estimation for pine forest stands allows one to assume these pollutants to exhibit a phytotoxic effect. Basing on the results obtained the Scotch pine needle could be included in the system of monitoring of atmospheric pollution on a regional scale as a bioindicator of stable organic pollutants.

Acknowledgement

Authors express sincere gratitude to the researcher of the Limnological Institute, SB RAS, I. I. Marinayte for the help in the preparation of samples for analysis.

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