ISSN 1028-334X, Doklady Earth Sciences, 2006, Vol. 408, No. 4, pp. 599–601. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.G. Gorshkov, T.A. Mikhailova, N.S. Berezhnaya, A.L. Vereshchagin, 2006, published in Doklady Akademii Nauk, 2006, Vol. 408, No. 2, pp. 247–249.

GEOGRAPHY

Pine Needles as a Biomonitor for Estimation of the Regional-Scale Distribution of Organic Pollutants

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Presented by Academician M.A. Grachev July 27, 2005

Received July 27, 2005

DOI: 10.1134/S1028334X06040209

Classic methods of the monitoring of pollutants to determine areas of their distribution from the sources have many limitations. The direct regular sampling of atmospheric air with a required number of sites in the study area is not an easy task. Results of modeling of the transport of polluted air masses often contradict experimental data. As a natural accumulative pattern, snow cover pollution characterizes the atmospheric state only during winter. Moreover, due to a distinct anticyclonic pattern of atmospheric circulation in winter, some areas of East Siberia are characterized by the localization of emission nearby the sources [1]. Therefore, we can use the data on snow cover pollution, primarily, to estimate the source capacity rather than the boundaries of polluted area. In this case, the application of biomonitors makes it possible to estimate atmospheric pollution based on results of the long-term communicative action of pollutants on the environment [2, 3].

The present paper is based on the first study of scotch pine (*Pinus sylvestris* L.) needles as a bioaccumulator of persistent organic pollutants (POP) in the harsh continental climate of Central Asia. As the markers of air pollution by POP, we used the priority polycyclic aromatic hydrocarbons (PAH) that are present in both gas and aerosol phases of the atmosphere. The results show that the coefficient of PAH accumulation by pine needles (k_{ac}) from the gas phase in the summer reaches $2 \cdot 10^5$. As a result of sorption of aerosol particles, the k_{ac} value drops to 10^3 in the winter. The maximum and background PAH accumulation levels in needles are equal to 1500–1800 and 60–80 ng/g, respectively. Based on the results of the simultaneous study of PAH accumulation levels and the physiological state of pine stands, we estimated the areas of POP distribution in the Baikal region.

The study was carried out in the Baikal natural reserve (Fig. 1), where the atmospheric aerosol fraction is dominated by the scotch pine among the forest-forming trees and the PAHs among the organic pollutants [4, 5]. The samples of needles were collected at 11 test sites with different degrees of pine stands inhibited by industrial atmospheric emissions during 2003–2005. Diagnostics on the state of pine stands were based on visual and morphophisiological indicators. The defoliation degree of crowns served as the most representative parameter [4]. PAH concentrations in the needle extracts were measured by chromatomass spectrometry.

The maximum net concentrations of PAH (1500–1800 ng/g) were recorded in the pine needles in the emission zone of the Irkutsk aluminum plant (the Shelikhov area) and in the Irkutsk area. The qualitative composition of the identified PAHs, 12 of which are POP (Fig. 2), indicate the anthropogenic source of the compounds. Extracts of the needles sampled near the Mondy station, a background monitoring station located >200 km from Irkutsk, contained a limited number of PAHs with phenanthrene concentration accounting for up to 60% of the total PAH content. The total PAH content in the needles did not exceed 60–80 ng/g. This concentration was taken as the background value.

In areas with strong atmospheric pollution, only the 1- to 3-yr needles remain (Fig. 3). The PAH content in young developing needles is minimal, but the content is enough for monitoring after 2 to 3 yr. Since the maximum PAH concentrations in the atmosphere are recorded during the Siberian anticyclone in the winter (the PAH concentration is related to solid particles of aerosol [1]), one can assume that the PAH mostly accumulates on the needles due to direct sorption of aerosol particles in this period when the pines are dormant. However, the efficiency of PAH accumulation during

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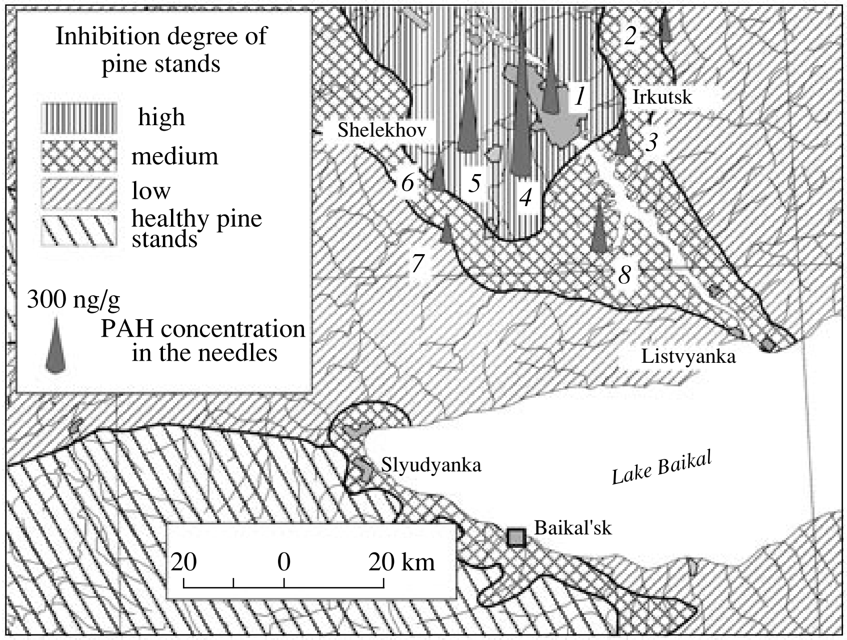

Fig. 1. Map of estimation of the inhibition degree of pine stands in the Baikal region. The PAH concentration in the scotch pine needles is shown. Test site nos. (*1*) Irkutsk (mean value for three reference sites), (*2*) 12 km from Irkutsk, (*3*) 20 km from Irkutsk, (*4*) 3 km from the aluminum plant, (*5*) 10 km from the aluminum plant, (*6*) 8 km from the aluminum plant, (*7*) 22 km from the aluminum plant, (*8*) 24 km from the aluminum plant.

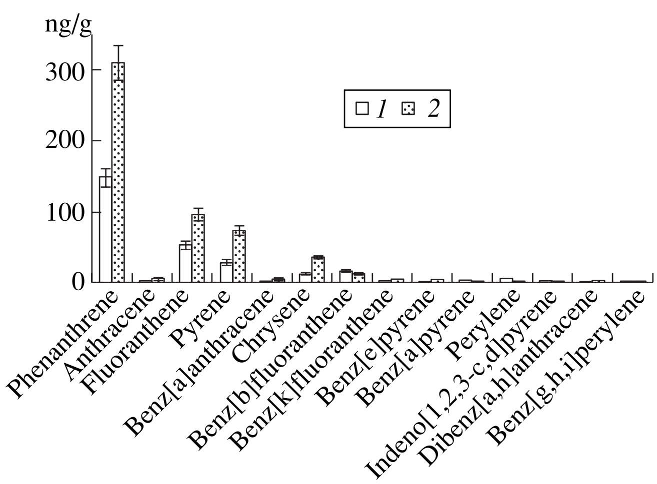

Fig. 2. PAH concentrations in the pine needles sampled in (*1*) spring and (*2*) autumn of 2004 in Irkutsk (Akademgorodok park zone).

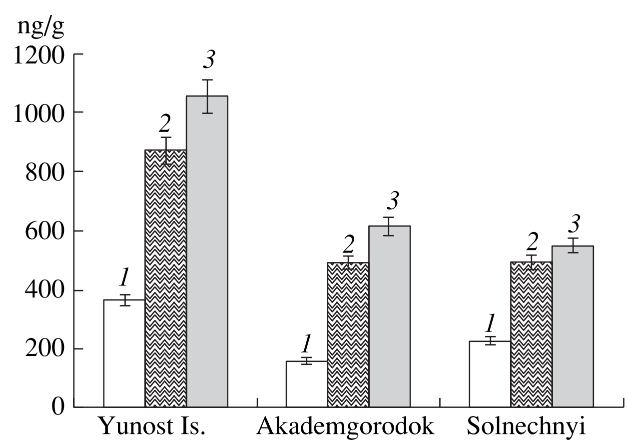

Fig. 3. Concentrations of the net priority PAHs in the different-aged pine needles in reference sectors located in various areas of Irkutsk. (*1*) 1-yr needles; (*2*) 2-yr needles; (*3*) 3-yr needles.

this period is low. The k_{ac} value does not exceed 10^3. The PAH concentration in needles in source areas with the maximal emission is only 20–25 times higher than the background value, in contrast to the concentrations 600–6000 times higher in snow cover.

According to [6], if the ambient air temperature increases, the low-molecular PAHs, such as phenanthrene, fluoranthene, pyrene, and chrysene, are partially or completely transferred from the aerosol (solid phase) to the gas phase of the atmosphere. Therefore, their concentrations in the aerosol phase in the summer are minimal. The PAH accumulate in summer primarily owing to gas exchange with low-molecular PAHs in the atmospheric gas phase. The k_{ac} value during this period is much higher ($2 \cdot 10^5$). For instance, if the mean summer PAH concentration in the surface atmosphere is $1.6 \cdot 10^{-3}$ ng/g, the PAH accumulation in needles can be as much as 290 ng/g.

The property of pine to accumulate PAH from the atmospheric gas phase is of principle importance. Spring and summer periods of the Siberian anticyclone destruction are accompanied by long-range transport of air masses, including those polluted with POP. Increase of the ambient air temperature is followed by accumulation of POP in the atmospheric gas phase. This is reflected adequately by the pine needles acting as a biomonitor.

The inhibition degree of pine stands have a positive correlation with the PAH accumulation level in the needles (Fig. 1). In test sites located 10–20 km from the industrial centers of the region (Irkutsk and Shelekhov), the PAH concentration in the needles are lower than the maximum values but are still 2–5 times higher than the background value. The pine stands in these areas are characterized by medium and low degrees of inhibition. Pine needles in sites situated in the POP source area (Irkutsk and Shelikhov) are characterized by the maximum level of PAH accumulation (20–25 times higher than the background value) and the high inhibition degree of pine stands.

Data on the accumulation of PAHs (markers of atmosphere pollution by POP) and estimates of the inhibition degree of pine stands allow us to outline sites in the Baikal region with the highest atmospheric pollution. We can also assume the absence of transport of significant volumes of polluted air masses to the southern coast of Lake Baikal (Fig. 1). The direct measurements of PAH over the lake [7] indicate that the total PAH concentration in the aerosol does not exceed 1.5 ng/m^3 (0.002 units of the admissible concentration limit in terms of benz[a]pyrene). Hence, the study region was mainly polluted by the local sources situated on the lake coast (Slyudyanka and Listvyanka areas).

PAHs were extracted from needles with 100 ml of *n*-hexane (twice in 30 min) under the ultrasound influence. The extracts were concentrated, filtered, and purified by the technique of solid-state extraction on silica gel cartridges (500 mg; Discovery SPE DSC-Si, Supelco). The extracted PAH fraction was analyzed by an Agilent GC System 6890, MSD 5973 chromatomass spectrometer in the regime of the selective ion monitoring. The PAHs were detected based on ions with the following *m/z* values: 178 (phenanthrene), 188 (phenanthrene-d_{10}), 202 (fluoranthene and pyrene), 228 (benz[a]anthracene and chrysene), 240 (chrysene-d_{12}), 252 (benz[b]fluoranthene, benz[k]fluoranthene, benz[e]pyrene, benz[a]pyrene and perylene), 264 (perylene-d_{12}), 276 (indeno[1,2,3-c,d]pyrene and benz[g,h,i]perylene), and 278 dibenz[a,h]pyrene. The contents were calculated based on the internal standard method. The PAH mass in the needles (with the consideration of water content) was calculated as a mean of two parallel measurements in each sample. The total error in the determination of the net PAH content is evaluated as $\delta_{tot} \pm 5.2\%$ ($P = 0.95$, $n = 2$).

The accumulation coefficients were calculated by the ratio of PAH concentrations in the needles to the mean PAH concentration in the atmosphere during the study period (the needles and atmosphere were sampled in the same test site): $k_{ac} = C_{PAH}$ in needles (ng/g)/C_{PAH} in atmosphere (ng/g).

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 05-05-97259) and was carried out at the Ul'tramikroanaliz Analytical Center of the Siberian Division of the Russian Academy of Sciences.

REFERENCES

1. V. K. Arguchintsev, V. L. Makukhin, Optika Atmosf. Okeana **13**, 913 (2000).
2. I. Holoubek, P. Korinek, Z. Seda, et al., *Environm. Pollution,* No. 109, 283 (2000).
3. H. Hwang, T. Wade, and J. Serincano, *Atmosph. Environment,* No. 37, 2259 (2003).
4. T. A. Mikhailova, Forest Pathology **30**, 345 (2000).
5. T. V. Khodzher, A. G. Gorshkov, V. L. Potemkin, et al., J. Aerosol Sci. **30**, Suppl. 1, S271 (1999).
6. A. R. Suzdorf, S. V. Morozov, L. I. Kuzubova, et al., Khimiya Interes. Ustoichiv. Razvit. **2**, 511 (1994).
7. A. G. Gorshkov, I. I. Marinaite, G. S. Zhamsueva, et al., J. Aerosol Sci. **35**, Suppl. 2, 1059 (2004).