UDC 504.4054+504.054(1/9)

DOI: 10.15372/CSD20180301

In memory of V. A. Koptyug

Persistent Organic Pollutants in Lake Baikal Ecosystem

S. V. MOROZOV[1], G. S. SHIRAPOVA[2], E. I. CHERNYAK[1], N. I. TKACHEVA[1], V. B. BATOEV[2], D. M. MOGNONOV[2]

[1]*N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk , Russia*

E-mail: moroz@nioch.nsc.ru

[2]*Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, Ulan-Ude, Russia*

E-mail: gshira@yandex.ru

(Received May 7, 2018)

Abstract

The paper presents the long-term investigation of biogeochemical regularities of the ingress, distribution, and accumulation of persistent organic pollutants (POPs) in the basin of Lake Baikal and the Selenga River on the territory of Russia and Mongolia. Academician V. A. Koptyug became the initiator and head of these works since 1994. The research was co-carried out by staff members of the Novosibirsk Institute of Organic Chemistry and Baikal Institute of Nature Management SB RAS within Russian and international expeditions. The GC/MS data of the qualitative and quantitative composition of POPs in environment objects and biota may be used for regional ecological-geochemical and ecological-hygienic assessments of the environmental state, effective identification of sources and areas of anthropogenic environmental impact strengthening and weakening, design of bioaccumulative POPs models for aquatic ecosystems and environmental risk assessment.

Keywords: persistent organic pollutants, chromatography-mass spectrometry, chromatographic profiles, bioaccumulative model, bioaccumulation factors, environmental risk assessment, Lake Baikal, Selenga River basin

INTRODUCTION

The unique natural object, Lake Baikal, is located almost in the centre of Asia. According to the water surface area, Baikal ranks eighth in the world and has no equal in depth. By water mass volume, Baikal is superior to all fresh water bodies of the world accommodating 20 % of the world and 80 % of Russia's fresh water reserves. Baikal annually produces about 60 km3 of unique quality water whose rare purity and other properties are due to the vital activity of the animal and vegetable world of the lake.

In 1996, Baikal received the status of a World Natural Heritage Site and was recognized by the UNESCO World Heritage Committee as an example of an outstanding aquatic ecosystem. The special status of Lake Baikal is defined by the Federal Law N 94-FZ "On protection of Lake Baikal" [1]. Preservation of this object remains one of the most important environmental issues in Russia.

Academician V. A. Koptyug paid great attention to issues of research and protection of the ecosystem and rational use of natural resources of Lake Baikal [2, 3].

By the early 1990s, with his support, the Baikal International Center for Environmental Research (BICER) was organized on the basis of the Limnological Institute of SB RAS, in which Russian and foreign scientists were able to carry out comprehensive research of Lake

Baikal. In September of 1993, at a meeting of the UN Secretary-General's Advisory Council on sustainable development, V. A. Koptyug proposed to consider Lake Baikal as a model area of world importance [4]. In September 1994, on his initiative, the first International Workshop "Baikal region as a world model of sustainable development" was held in Ulan-Ude, and many V. A. Koptyug's ideas were adduced in its solution [5]. The merit of Valentin Afanasievich in the adoption of the Federal Law of the Russian Federation regarding the protection of Lake Baikal and inclusion of the latter in the list of the Natural World Heritage Sites was great.

To develop V. A. Koptyug's ideas and to coordinate the activities of the Siberian Branch, and also to improve the efficiency of research and protection of Lake Baikal, the Scientific Council of SB RAS on problems of Lake Baikal was established by the resolution of the Presidium of SB RAS in 2002. Academician M. I. Kuzmin became the first Chairman in 2002, academician I. V. Bychkovin headed it in 2012, and Academician V. N. Parmon has been the head of the Council since 2017).

Issues of substantiation and development of integrated monitoring, analysis and prediction of the condition of the lake ecosystem attract particular attention of scientists [6–9].

Anthropogenic pollution has a significant impact on the condition of ecosystems of Lake Baikal and Baikal natural area. To take effective measures on Lake Baikal ecosystem preservation, determine regularities of the ingress, distribution, and accumulation of pollutants, reliable information on pollution levels of both Lake Baikal and surrounding areas, and also analysis of routes of entry of pollutants into the lake are required. Toxic organic substances, mainly persistent organic pollutants (POPs) that are capable of transboundary transport, long-term persistence in the environment, accumulation in food chains and harmful effects on living organisms even at low doses are particularly noteworthy.

Various groups of scientists have been carrying out research on the content and distribution of POPs in ecosystems of Lake Baikal and its basin from the late 1980s. The levels of POPs in various objects of the lake environment and its catchment area, such as the air, surface, and deep waters, soil, bottom sediments [10–16], in the body of the Baikal seal [17], in the tissues of birds [18, 19] were determined. The data on the distribution of POPs in some food chains of Lake Baikal has been acquired [20].

Nature protection concept of the Siberian Branch of the USSR Academy of Sciences was developed on the initiative and under the leadership of academician V. A. Koptyug in the late 1980s. Within the regional scientific and technical program (RSTP) "Siberia" and the Federal Centre for Collective Use (FCCU) "Environmental safety of Russia", V. A. Koptyug proposed to organize on the basis of NIOCH and BIP SB RAS joint research to explore regularities of the ingress, distribution, and accumulation of POPs in the ecosystem of Lake Baikal and Selenga River in 1993. The work was supported by expeditionary grants of SB RAS, Russian Foundation for Basic Research (RFBR) and various federal target programs (FTP).

The purpose of work was to summarize the results of long-term research on biogeochemical regularities of the ingress, distribution, and accumulation of persistent organic pollutants in the basin of Lake Baikal and Selenga River in Russia and Mongolia.

EXPERIMENTAL

Surface water samples, coastal bottom sediments, and specimens of bivalve mollusk Colletopterum, roach Rutilus, pike Esox lucius, and catfish Silurus glanic were research objects to determine POPs content levels in aqueous ecosystems of Lake Baikal and Selenga River.

Surface water specimens were conserved by the addition of conc. HCl per 1 mL of acid on 1 L of water. Samples of bottom sediments were collected from the near-surface layer in 10 cm using a dredger (Wildlife Supply Co., USA). The samples were dried at room temperature and sieved through a 0.4 mm mesh size sieve.

Sample preparation of bottom sediments (5 g) and surface water (2 L) consisted in POPs extraction with methylene chloride and treatment of the resulting extracts in a column of activated alumina. A surrogate standard was added to the samples prior to extraction.

Preparing biological samples (5 g) lied in the homogenization of soft tissues of shellfish and fish liver samples and double ultrasound extraction with a mixture of hexane and acetone (1 : 2 by volume), treatment of the resulting extracts with conc. H_2SO_4 and fractionation through a column of activated alumina. A surrogate standard was added to the samples prior to extraction. The resulting extracts were concentrated at reduced pressure and a temperature of 40–45 °C and dissolved in 1 mL of acetone.

The prepared samples were analysed using Agilent Technologies chromato-mass spectrometer (GC6890N, MSD 5975N, autosampler 7683B) in the mode of selective ion monitoring (SIM) for three individual characteristic ions of the identified compounds. The analysed components were divided using an HP-5 MS capillary quartz column, 30 m long, 0.25 mm diameter and 0.25 μm coating thickness. Chromatography conditions were as follows: detector temperature of 280 °C, ion source temperature is 230 °C, quadrupole temperature of 150 °C, helium carrier gas, and the introduced sample volume is 1 μL. There was used the following temperature mode of column thermostat: 50 °C (2 min), rise from 50 to 280 °C (10 °C/min), and 20 min at 280 °C.

Polychlorinated biphenyls (PCBs: tetra-, penta -, and hexachlorinated isomers), organochlorine pesticides (OCPs: DDT and its metabolites DDE and DDD), HCH isomers (α-HCH, β-HCH, γ-HCH, δ-HCH, HCB), polycyclic aromatic hydrocarbons (PAHs: naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-c,d)pyrene) were determined in the resulting extracts.

Standard samples of mixtures of PAHs, OCPs, and PCBs (HP No. 8500-6035 and HP No. 8500-6011, GOST 7821–2000) were used for qualitative measurements. Species 4,4'-dibromophenyl and 9,10-di(trideuteromethyl) phenanthrene were applied as surrogate standards (reference specimens).

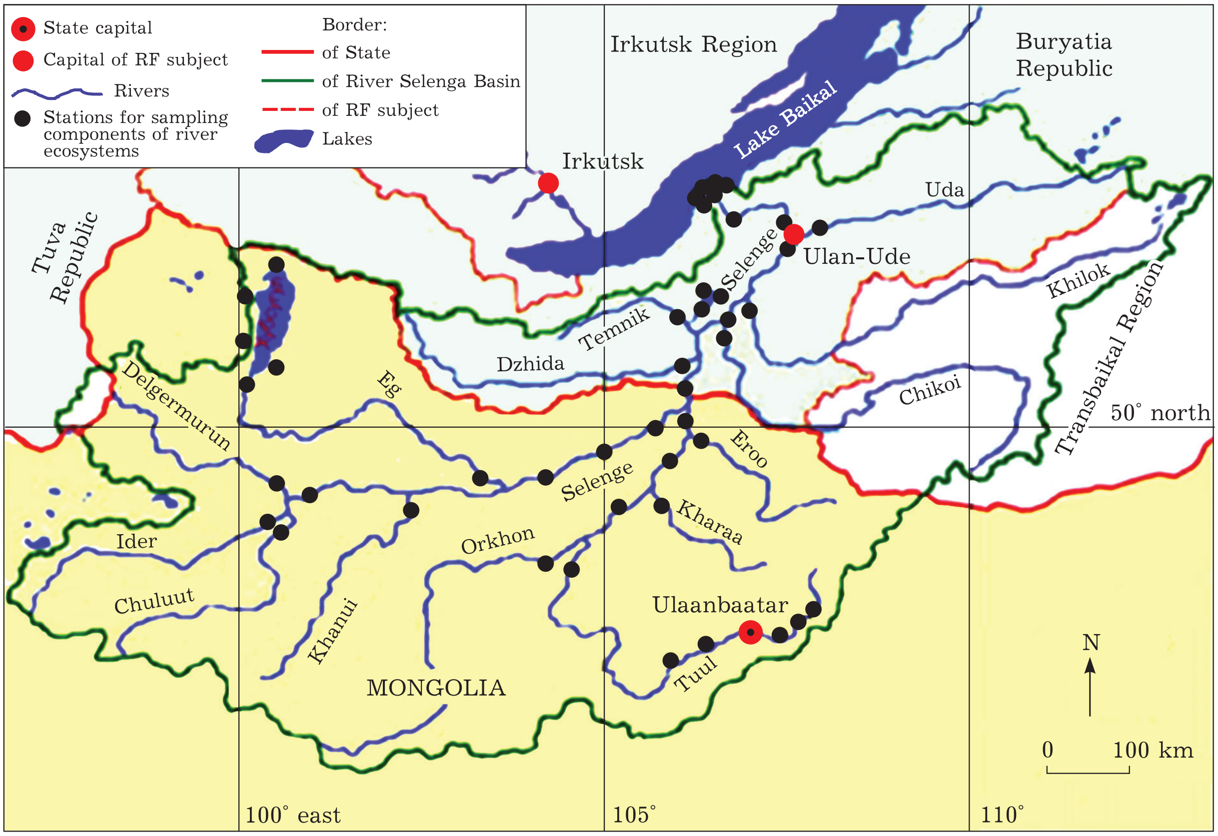

Fig. 1. Location map of sampling stations in Selenga River basin in Russia and Mongolia.

RESULTS AND DISCUSSION

A long-term detailed survey of surface and underground waters, bottom sediments and biota in the lake basin was carried out in the basin of Lake Baikal and Selenga River in Mongolia and Russia within joint Russian, Russian-Mongolian, Russian-Korean-Mongolian (2007–2010) and Russian-Mongolian-Japanese (2013–2015) expeditions (Fig. 1). The POPs content in environmental objects was determined by GCMS using detection according to individual characteristic ions and total ion current.

During the undertaken joint research on biogeochemical regularities of the ingress, distribution, and accumulation of POPs, there were acquired the following main results:

– Chromatographic profiles (fingerprint) were plotted and detailed structures and contemporary levels of POPs (OCPs, PCBs, PAHs, phenols (Ps), and oil hydrocarbons (OHCs) in surface and ground water, bottom sediments, and bioindicator organisms (bivalved mollusks Colletopterum, roach Rutilus, pike Esox lucius, catfish Silurus glanic) of the basin of Lake Baikal and Selenga River in Russia and Mongolia were determined [21–30].

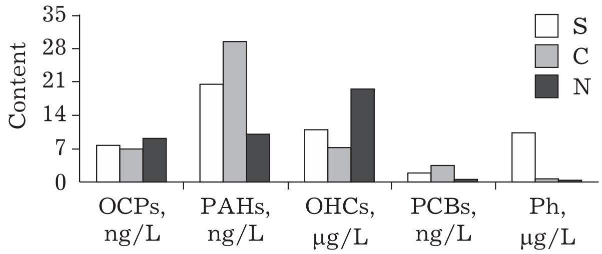

Fig. 2. Organic pollutants content in southern (S), central (C) and northern (N) parts of Lake Baikal.

– Typical pollutants for the southern, central and northern parts of Lake Baikal (Fig. 2), bioconcentration factor of OCPs, PCBs, and PAHs, the distribution of light and heavy PAHs PCBs isomers in water, sediments and the fat of the seal, were defined and characteristic profiles of aliphatic hydrocarbons determining the levels of anthropogenic and natural pollution were acquired [28, 29].

– Processes of POPs chemodynamics in the ecosystem of the basin of Selenga River and Baikal Lake were researched It is found that in the Russian part of Selenga River basin, there is an "unloading" of POPs entering from the Mongolian side (Fig. 3). The final processes

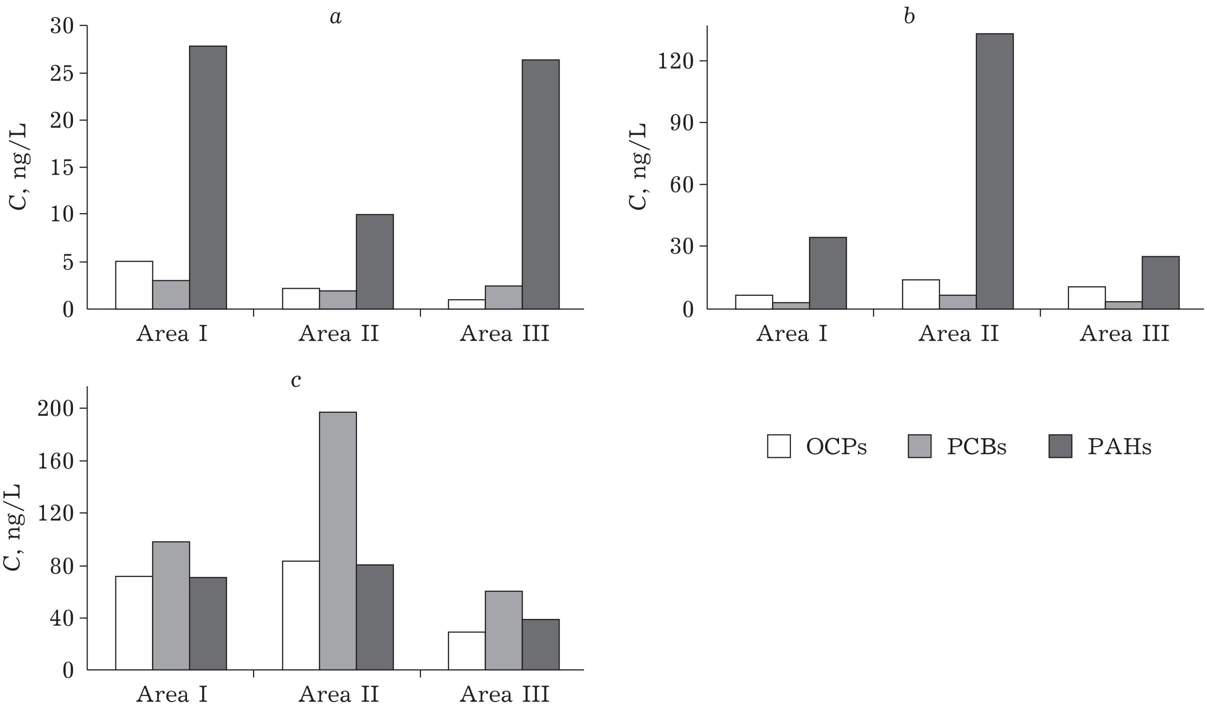

Fig. 3. Distribution of OCPs, PCBs, and PAHs in surface water (*a*), bottom sediments (*b*), and biota (*c*) in Selenga River basin in areas I (industrial regions of Mongolia), II (Selenga River in Russia), III (Selenga River Delta).

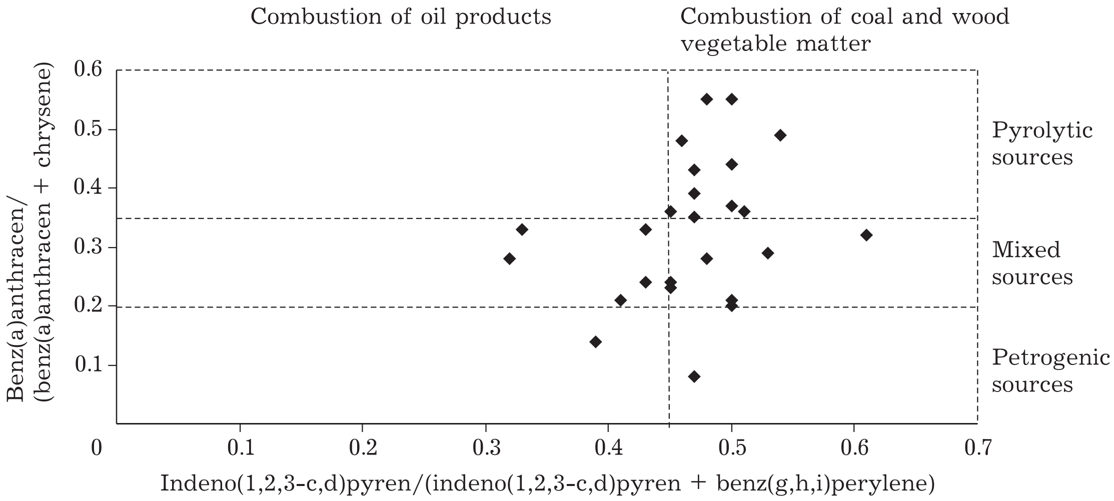

Fig. 4. PAHs ingress sources in the ecosystem of the Selenga River basin in Russia and Mongolia.

of self-purification proceed in the Selenga River Delta [24–27].

– As demonstrated by analysis of the isomeric composition of PCBs in the bottom sediments of Lake. Baikal and Selenga River basin, tetra-, penta-, and hexachlorobiphenyls are prevailing in a ratio corresponding to the technical mixture "Sovol" [22].

– It is found for the first time that the Selenga River Delta acts as a natural biogeochemical barrier during self-purification of basin ecosystem of the river itself and the Lake Baikal according to chemical, physical, and biological mechanisms for POPs and an indicator of the current environmental status of Lake Baikal [31].

– Analysis of sources of POPs in the ecosystem of Selenga River basin and Lake Baikal (bottom sediments and surface water) was carried out according to characteristic ratios of marker compounds. It is demonstrated that PAHs mainly arrive due to pyrolytic processes related to the combustion of coal, oil products, and wood (Fig. 4). The ingress of OCPs and PCBs is due to global transfer and local anthropogenic sources [28, 29].

– Comparative analysis of POPs content data in surface water and bottom sediments for the period of 2007–2015 in the Selenga River ecosystem in areas of the largest industrial centres of Mongolia (Ulan Bator, Erdenet, Zaamar, and Darkhan) was carried out. The main sources of POPs into the ecosystem were revealed [28].

– It is demonstrated that Khubsugul Lake may act as a background object to identify areas with high anthropogenic load in ecosystems of Lake Baikal and Selenga River basin in Mongolia and Russia [28].

– Ingress routes, mechanisms of distribution and accumulation of PAHs and aliphatic hydrocarbons (alkanes, hopanes, and steranes) in the Lake Baikal ecosystem in the area of natural oil outflow (Barguzin Bay) were researched.

– Analysis of the fatty acid composition of lipids of Baikal seal was carried out within research on endemics of Lake Baikal as bioindicators of its ecosystem was carried out by GC/MS. The data on the composition and ratios of the most typical fatty acids of lipids of different parts from the body of the seal caught in different parts of the Lake Baikal were acquired [28].

– A bioaccumulative model of POPs that might act as a scientific basis for the determination of universal indicators of the trophic

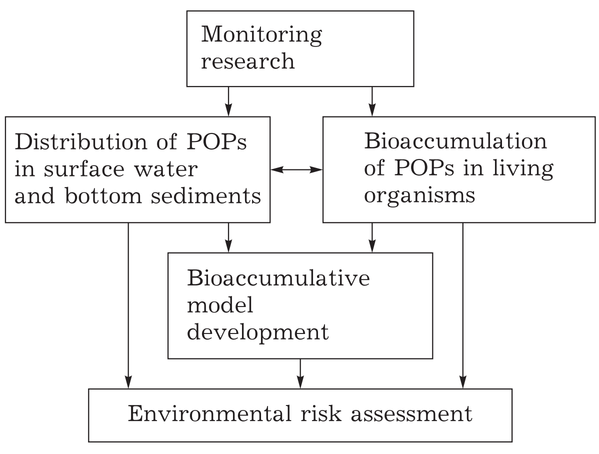

Fig. 5. Analytical research scheme for environmental risk assessment.

status of aquatic ecosystems with the purpose of integral assessment, forecasting and the modeling of their environmental status was developed for the first time for aquatic ecosystems of the basin of Selenga River and Lake Baikal in Mongolia and Buryatia [32].

– There was found the following order of accumulation of POPs on an example of the liver of bioindicator fish: PCB > HOP > PAH. The dominating role of PCBs seems to be indicative for the sustainable and intensive use of this pollutant of Selenga River basin in the past.

– Bioconcentration (BCF in biota–water), sorption (Ks in bottom sediments–water), bioaccumulation (BSAF biota–bottom sediments), and biomagnification factors (BMF in a predator–prey), *i.e.* the main criteria used in the world practice upon the assessment of environmental risk for aquatic ecosystems, were computed. The selected bioindicator organisms have a high and extremely high capacity for POPs accumulation (BCF for predatory fish is 40 000–130 000), and in the trophic chains, there is a significant transfer of POPs from the lowest to the highest level (BMF roach–pike is 4). It is demonstrated that despite the relatively low content of POPs in surface water and bottom sediments, there is the accumulation of POPs with coefficients that are higher than critical indicators in trophic chains at higher levels. The selected bioindicator organisms have extremely high bioaccumulation potential.

CONCLUSION

The findings are the first attempt of systemic research of processes of the ingress, distribution, and accumulation of persistent organic pollutants in aquatic ecosystems on an example of the unique Baikal natural area that includes Lake Baikal, Lake Hovsgol, and Selenga River basin in Mongolia and Russia.

The developed bioaccumulative model may act as a framework to determine universal indicators of the trophic status of aquatic ecosystems for the purpose of integral assessment, prediction, and their environmental status modelling.

The approach under consideration (Fig. 5) makes it possible to identify critical environmental factors, determine routes of their impact on the population, assess the risk and on this basis, manage the environmental quality with a view to ensure the public health and sustainable development in regions.

Acknowledgements

All analytical work was carried out in the Testing Analytical Centre of NIOCh SB RAS (accreditation certificate ROSS RU.0001.510483).

REFERENCES

1 Federal'nyj zakon ot 01.05.1999 No. 94-FZ (red. ot 28.06.2014) "Ob okhrane ozera Baikal" [Electronic resource]. Baza Konsul'tant-Plyus [in Russian] (Accessed 20.03.2018).
2 Ermikov V. D., World of Baikal, 2007, No. 2, P. 23–25.
3 Normy Dopustimyh Vozdejstvij na Ekosistemu Ozera Baikal: Doklad na Zasedanii Mezhvedomstvennoj Komissii po Kontrolyu za Sostoyaniem Prirodnogo Kompleksa Bassejna Ozera Baikal [In Russian], Novosibirsk: Publishing House SB RAS, 1987. 15 p.
4 Koptyug V. A., Nauka Spaset Chelovechestvo [in Russian], Novosibirsk: NIZ OIGGM SO RAN, 1997, P. 134–135.
5 Koptyug V., Uppenbrink M. (Eds.), Sustainable Development of the Lake Baikal Region: a Model Territory for the World, Berlin, etc.: Springer-Verlag, 1996.
6 Israel Yu.A., Anokhin Yu.A. (Eds.), Monitoring of Lake Baikal State, L.: Gidrometeoizdat, 1991. 261 p.
7 Grachev M. A., O Sovremennom Sostoyanii Ekologicheskoj Sistemy Ozera Bajkal [in Russian], Novosibirsk: Izd-vo SO RAN, 2002.
8 Tulochonov A. K., Plusnin A. M. (Eds.), The Selenga River Delta – Natural Biofilter and Indicator of the Condition of Lake Baikal [in Russian], Novosibirsk: Izd-vo SO RAN, 2008. 314 p.
9 Garmaev E. Zh., Khristoforov A. V., Water Resources of the Rivers of the Lake Baikal Basin: Basics of Their Use and Protection [in Russian], Novosibirsk: GEO, 2010. 231 p.
10 Samsonov D. P., Kochetkov A. I., Pasynkova E. M., Zapevalova M. A., Russ. Meteorol. Hydrol., 2017, Vol. 42, No. 5, P. 345–352.
11 Mamontov A. A., Tarasova E. N., Mamontova E. A., Kerber E. V., Ekol. Khimiya, 2015, Vol. 24, No. 3, P. 129–136.
12 Gorshkov A. G., Kustova O. V., Dzyuba E. V., Zakharova Yu. R., Shishlyannikov S. M., Khutoryansky V. A., Chem. Sust. Dev. [in Russian], 2017, Vol. 25, No. 3, P. 269–278.
13 Golobkova L. P., Filippova U. G., Marinaite I. I., Belozerova O. Yu., Gorshkov A. G., Obolkin V. A., Potemkin V. L., Khodzher T. V., Optika Atmosfery i Okeana [in Russian], 2011, Vol. 24, No. 3, P. 236–241.
14 Reznikov S. A., Adzhiev R. A., Russ. Meteorol. Hydrol., 2015, Vol. 40, No. 3, P. 207–214.
15 Nikanorov A. M., Reznikov S. A., Matveev A. A., Arakelian V. S., Irkha N., Kearse W., Palme L., Izv. RAN. Ser. Geogr. [in Russian], 2013, No. 1, P. 105–117.
16 Kuzmin M. I., Mamontova E. A., Mamontov A. A., Tarasova E. N., McLachlan M. S., Organohalogen Compd., 2011, Vol. 73, P. 13–16.
17 Nomiyama K., Hirakawa S., Eguchi A., Kanbara C.,

Imaeda D., Yoo J., Kunisue T., Kim E.-Y., Iwata H., Tanabe S., Environ. Sci. Technol., 2014, Vol. 48, No. 22, P. 13530–13539.

18 Lebedev A. T., Poliakova O. V., Karakhanova N. K., Petrosyan V. S., Renzon A., Sci. Total Environ., 1998, Vol. 212, No. 2–3, P. 153–162.

19 Kunisue T., Minh T. B., Fukuda K., Watanabe M., Tanabe S., Titenko A. M., Environ. Sci. Technol., 2002, Vol. 36, No. 7, P. 1396–1404.

20 Poliakova O. V., Lebedev A. T., Petrosyan V. S., Hanninen O., Renzoni A., Sawa D., Walker C., Toxicol. Environ. Chem., 2000, Vol. 75, No. 3–4, P. 235–243.

21 Shirapova G. S., Utyuzhnikova N. S., Rabina O. A., Vyalkov A. I., Morozov S. V., Batoev V. B., Chem. Sust. Dev. [in Russian], 2013, Vol. 21, No. 2, P. 189–195.

22 Shirapova G. S., Utyuzhnikova N. S ., Rabina O. A., Vyalkov A. I., Morozov S. V., Batoev V. B., Chem. Sust. Dev. [in Russian], 2013. Vol. 21, No. 2, P. 197–205.

23 Palitsyna S. S., Shirapova G. S., Morozov S. V., Batoev V. B., International Forum on Regional Sustainable Development of Norheast and Central Asia (Proceedings), 2011, P. 380–386.

24 Mun Y., Ko I. H., Janchivdorj L., Gomboev B. O., Lee C.-H., Kang S. J., Lee C.-H., Integrated Water Management Model on the Selenge River Basin: Status Survey and Investigation (Phase 1), Seoul: Korea Environment Institute, 2008. 423 p.

25 Chu J.-M., Lee C.-H., Janchivdorj L., Gomboev B. O., Lee C.-H., Kang S. J., Integrated Water Management Model on the Selenge River Basin: Basin Assessment and Integrates Analysis (Phase 2), Seoul: Korea Environment Institute, 2009. 356 p.

26 Tulokhonov A. K., Gomboev B. O., Mognonov D. M., Zomonova E. M., Khakhinov V. V., Zhamyanov D. Ts. D., Sanh In Kang, Jang Min Chu, Uri Moon, Chang Hee Li, Zhanchivdorzh L., Odontsetseg D., Moloytov V. S., Kolomeets O. P., Gomboeva R. I., Morozov S. V., Rabina O. A., in: Baikal Asia: Economy, Ecology, Sustainable Development (Results of International Cooperation), A. K. Tulokhonov (Ed.), Ulan-Ude: EKOS, 2009, P. 52–60.

27 Chu J.-M., Lee C.-h., Janchivdorj L., Gomboev B. O., Park S.-Y., Mun H.-J., Integrated Water Management Model on the Selenge River Basin: Development and Evaluation of the IWMM on the SRB (Phase 3), Seoul: Korea Environment Institute, 2010. 304 p.

28 Morozov S. V., Chernyak E. I., Vyalkov A. I., Tkacheva N. I., in: Chemistry of Aromatic, Heterocyclic and Natural Compounds (NIOC SB RAS 1958-2008), V. N. Parmon (Ed.), Novosibirsk, 2009. P. 737–778.

29 Morozov S. V., Chernyak E. I., Chem. Sust. Dev., 2011, Vol. 19, No. 6, P. 557–573.

30 Ok G., Shirapova G., Matafonova G., Batoev V., Le S. H., Polycycl. Aromat. Compd., 2013, Vol. 33, No. 2, P. 173–192.

31 Shirapova G. S., Morozov S. V., Batoev V. B., Bogachev M. I., Izv. SPbETU “LETI”, 2013, Vol. 7, P. 92–98.

32 Utyuzhnikova N. S., Shirapova G. S., Chernyak E. I., Vyalkov A. I., Morozov S. V., Batoev V. B, Eng. Ecol., 2011, No. 11, P. 55–61.