doi: 10.25750/1995-4301-2021-1-016-021

Phthalates – a strange delusion of ecologists

© 2021. A. A. Semenov[1] ORCID: 0000-0001-7158-884X, A. G. Enikeev[1] ORCID: 0000-0002-4111-0412,
T. A. Babenko[2] ORCID: 0000-0002-0095-5574, T. N. Shafikova[1] ORCID: 0000-0002-1099-4235,
A. G. Gorshkov[2] ORCID: 0000-0003-4833-810X,
[1]Siberian Institute Plant Physiology and Biochemistry Siberian Branch
of the Russian Academy of Sciences,
132, Lermontova St., Irkutsk, Russia, 664033,
[2]Limnological Institute Siberian Branch of the Russian Academy of Sciences,
3, Ulan-Batorskaya St., Irkutsk, Russia, 664033,
e-mail: enikeev@sifibr.irk.ru, gorchkov_ag@mail.ru

The environment is polluted with *ortho*-phthalic acid esters (phthalates). There is a steady and generally accepted opinion that the reason for this is human production activities. The global annual production of phthalic esters is estimated at 4.9 million tons. It is believed that part of this amount enters into the environment as a harmful industrial pollutant and has an adverse effect on the health of the human population. However, from a large number of publications it is clear that phthalates, as natural metabolites, are also produced in living nature: bacteria, algae, fungi, plants and other organisms. Dibutyl phthalate and di-2-ethylhexyl phthalate are the main ingredients among natural phthalic acid metabolites. The green cover of the planet simultaneously contains these substances many times more than their annual industrial production. The unicellate inhabitants of the oceans, soils, and other planetary spaces make a big contribution to the phthalates entering in the nature. The lifetime of phthalates in the environment is short and their long-term accumulation is impossible. The observed level of these pollutants in the environment is the result of a dynamic equilibrium process with the participation of natural biosynthesis and industrial production, on the one hand, and biota absorption and natural degradation, on the other. The proportion of biosynthesis and degradation in this equilibrium is seen to be predominant. Therefore, the recommended measures and efforts to limit the production and use of *ortho*-phthalic acid esters are of little use and make little sense. The observed level is supported by constant feeding from wildlife. Throughout human history, people have received and are receiving phthalates with plant foods without visible consequences. Their harmful effects on the health of the human population are exaggerated. And in the process of evolution, effective endogenous ways of detoxification have been developed.

Keywords: *ortho*-phthalic acid esters, environment, natural origin, industrial production.

УДК 504.064.2:581.192

Фталаты – странное заблуждение экологов

**© 2021. А. А. Семёнов[1], д. х. н., с. н. с., А. Г. Еникеев[1], к. б. н., в. н. с.,
Т. А. Бабенко[2], ведущий инженер, Т. Н. Шафикова[1], к. б. н., с. н. с.,
А. Г. Горшков[2], к. х. н., в. н. с.,**
[1]Сибирский институт физиологии и биохимии растений
Сибирского отделения Российской академии наук,
664033, Россия, г. Иркутск, ул. Лермонтова, д. 132,
[2]Лимнологический институт Сибирского отделения
Российской академии наук,
664033, Россия, г. Иркутск, ул. Улан-Баторская, д. 3,
e-mail: enikeev@sifibr.irk.ru, gorchkov_ag@mail.ru

Фталаты (ФТ) – сложные эфиры *орто*-фталевой кислоты, производятся химической промышленностью в объёмах, достигающих 4,9 млн т в год. Экологи традиционно рассматривают их как промышленные поллютанты-ксенобиотики, опасные для здоровья человека. Вместе с тем, эти соединения продуцируются высшими растениями, водорослями, грибами, бактериями и животными. Несмотря на то, что в настоящее время получены убедительные доказательства биосинтеза ФТ в живых организмах, вопрос об их биогенном происхождении остаётся открытым. Теоретический расчёт содержания ФТ на основе установленного среднего уровня содержания ФТ в растениях по-

казал, что единовременное содержание этих соединений в растениях превышает их годовое производство в десятки раз. Поэтому уровень ФТ в окружающей среде (ОС) является следствием конкуренции его поступления в результате техногенных и природных процессов, с одной стороны, и потреблением биотой и естественной деградацией, с другой. Подчёркивается необходимость разграничения ФТ биогенного и техногенного происхождения при оценке их содержания в объектах ОС и последующих мероприятий, необходимых для регулирования состояния экосистемы изучаемой территории.

Ключевые слова: эфиры *орто*-фталевой кислоты, окружающая среда, природное происхождение, антропогенное происхождение.

Nowadays, the problem of the effects of environmental pollution has received much attention worldwide [1]. Significant funds are allocated for the monitoring of compounds hazardous to human health in natural objects. The effectiveness of these investments largely depends on the perfection of the methodological approaches used in such studies. *Ortho*-phthalic acid esters, or phthalates (PH), are produced by the chemical industry in amounts reaching 4.9 million tons per year [2]. Phthalates are widely used as ingredients in cosmetic products, insect repellents, dielectrics. However, the bulk of the synthesized phthalates is used as plasticizers in the polymeric materials production. Since phthalates are not chemically bound to the polymer matrix, they can migrate into the environment (EN) during the operation and disposal of plastics. According to most environmentalists, the widespread detection of PH in the air, water, bottom sediments, soil is conditioned upon this fact [3–6].

However, PH were found in natural sources long before the organization of mass industrial production [7, 8]. At a later time, they were found in grapes, poppies, strawberries, tobacco, fungi, algae, and bacteria, as well as in tissues of invertebrates and fish [9–16]. Endogenous PH are found in bacterial pathogens culture collection of mammals and plants. The inhibitory effect of these compounds on the biofilm formation process is shown [17, 18]. Have PH been released to wildlife from the EN or synthesized *in vivo*? Many data speak for their natural origin. The present paper provides a critical review of the study of PH in the EN (considering them to be the result of man-made pollution) and the biosynthesis of PH in the natural world.

The purpose of the article is to conduct a comparative analysis of the volume of phthalates entering the environment from man-made and natural sources.

Phthalates: man-made pollutants or natural compounds?

The release of PH into EN with industrial emissions into the atmosphere or wastewater characterizes this class of compounds as man-made pollutants. Since PH are listed as persistent organic pollutants, a number of six compounds of this class are selected to control them in EN objects. These compounds include di-n-methyl phthalate (DMP), di-n-ethyl phthalate (DEP), di-n-butyl phthalate (DBP), benzylbutyl phthalate (BBP), di-n-ethylhexyl phthalate (DEHP), and di-n-octyl phthalate (DOP) [19–21]. Possessing hydrophobic properties (k_{ow} for a priority range from 1.60 to 8.10) [22], PH are strongly associated with particles of atmospheric aerosol and of suspended matter in water. As a result of dry sedimentation, they fall to the earth's surface with precipitation or evolve into bottom sediments of water bodies.

Phthalats content in wastewater can reach a level of 20–140 mg/L [23]. Their purification reduces the amount of PH by three orders of magnitude. In purified waters, DEP and DEHP with concentrations from 1.6 to 72.0 μg/L are usually present [24]. The release of PH into the EN during disposing of plastic materials is rather slow due to colonization of microorganisms on the plastic surface, which carry out an effective plasticizers' degradation [25]. PH from wastewater of individual dwellings also make a minimum input on the environmental pollution. In wastewater from washing machines, dishwashers, bathrooms, and after cleaning the apartments, DEHP was identified as dominant in the priority PH range from 6.2 to 100.0 μg/L [26].

Phthalates found in representatives of all the kingdoms of living organisms from bacteria to mammals. In aquatic organisms, PH undergo a relatively rapid metabolism, at the first stage of which the *ortho*-phthalic acid monoesters are formed [25]. In particular, in the tissues of fish (the Yangtze River, the delta of the East China Sea), the dominant phthalates among those found were DBP and DEHP, an average content of which was estimated at 80 μg/kg and 1900 μg/kg wet weight, respectively. The concentration of the corresponding monoesters reached 50 μg/kg wet weight in fish and 60 μg/kg wet weight in shrimps [15]. The determination of phthalic acid monoesters [14] showed that mono-butyl phthalate (75–590 μg/kg dry

weight) was the dominant monoester, while in crab tissues, ethyl phthalate, butyl phthalate (MBP), and ethylhexyl phthalate (MEHP) monoesters are found at concentration levels of 0.3–2.6, 8.7–38, 0.4–1.1 μg/kg dry weight, respectively. The content of MBP and MEHP in fish was found in the concentration range from 6.6 to 61 and from 0.2 to 1.1 μg/kg dry weight.

In the composition of 40 species of higher plants selected randomly, PH were found at a concentration level of 11 to 300 μg/g dry weight. In addition to the above, the ability to produce phthalates *de novo* by plants *in vitro* and cell cultures cultivated in media free from pollutants and environmental contact was shown [27]. DEHP was isolated in optically active form from the brown sugar [28] and the cultured *Aconitum baicalense* Turcz. ex Rapaics cells [29]. The fact of isolation of one of four possible diastereomers unambiguously indicates the natural origin of DEHP.

Special attention should be paid to the detection of phthalates in marine and freshwater algae, the primary producers of organic matter in aquatic ecosystems. DBP and DEHP were identified in the tissues of *Bangia atropurpurea*, *Phaenomenella angusta*, and *Pheidole dentate* [9]. Their content ranged from 33.0 to 62.0 mg/kg and from 6.3 to 35.0 mg/kg dry weight, respectively. According to Babu & Wu [30], the amount of phthalates in freshwater algae and cyanobacteria can reach 160 mg/kg (DBP) and 420 mg/kg dry weight (MEHP).

Convincing evidence of PH biosynthesis by algae were obtained using isotope methods. The determination of the content of the ^{14}C natural isotope in DBP isolated from the brown algae *Undaria pinnatifida*, *Laminaria japonica*, in the green alga *Ulva* sp., confirmed the biogenic pathway of PH formation. The natural content of ^{14}C in DEHP obtained from the same algae was approximately 50–80% of the standard sample, and the content of ^{14}C in DBP and DEHP industrial products was below the detection limit [12].

When monitoring PH in surface waters [5, 24, 31–38] the dominant components of this xenobiotic series are DBP and DEHP, concentrations of which were found in wide ranges: DBP from 0.01 to 180 and DEHP from 0.06 to 80 μg/L. The minimum PH content was found in the rivers of Spain, France and in Lake Baikal. Special attention should be paid to the results of the PH monitoring of the waters of Lake Baikal. This lake is notable for the purity of its waters; the presence of persistent organic pollutants, in particular, such man-made xenobiotics as polychlorinated biphenyls (PCB), is at the trace level of concentrations [39]. The number of PCB indicator congeners in the upper water layer corresponds to the range from 0.01 to 0.80 ng/L [40], whereas the concentration of phthalates is three orders of magnitude higher: DBP from 0.06 to 3.10 and DEHP from 0.03 to 0.79 μg/L [38, 41].

When identifying the sources of PH found in Lake Baikal, it is necessary to take into account the absence of man-made sources of pollutants of this class on its coast and in the Baikal region, as well as the stability of PH under long-range atmospheric transport, as in abiotic conditions (photolysis plus hydrolysis), the half-life (t½) of DEHP, in particular, ranged from 390 to 1600 days [42]. The detected amounts of PH in the upper water layer ranged from 40 to 200 tons for DEHP and from 220 to 560 tons for DBP, that correspond to the world level of man-made planet pollution with PH as a result of their potential accumulation during a year. Since phthalates are rapidly biodegraded in aquatic ecosystems (DEHP t½ is 3.2), and in bottom sediments it is 14 days [25], their residual amounts in the upper water layer should be significantly lower. For instance, global atmospheric transport is attributed to the dominant source of PCB in the aquatic ecosystem of the Baikal [40, 43], and the total amounts of PCB with maximum stability in water do not exceed 1.8–4.1 tons in the upper water layer of the lake.

Detection of an increased amount of PH in the upper photic layer of the Baikal in spring is associated with their intake from the atmosphere, accumulation in snow cover during the cold season and subsequent rapid penetration of pollutants into the lake waters. On the other hand, the same effect should occur when PH are supplied with melt waters coming from the surrounding forests because a significant amount of PH is reserved in the fallen needles and leaves [27]. It may also be related to the life cycle of the Baikal phytoplankton [38]. If the annual industrial production of phthalates (4.9 million tons) is evenly distributed over the entire area of the Earth 510 million km^2), the density of distribution can be 9.8 kg/km^2. Thus, the proportion of the water surface of Lake Baikal (31,500 km^2) accounts for up to 310 tons. In fact, according to the data, DEHP alone contains about 300 tons. Considering the rapid degradation of PH, such a number is only possible if there is a constant supply from biogenic sources, in particular, from forests.

The study of sixteen species of freshwater algae and cyanobacteria showed that some of them

are capable of producing DBP or MEHF, or both. The cultivation of cells in a medium containing $NaH^{13}CO_3$ as the sole carbon source confirmed the idea that both PH are synthesized *de novo* by the studied cells. The authors also noted that phthalic acid esters synthesized by algae are released into the environment under stress [30, 37]. This observation points to freshwater microalgae as to potential sources of phthalates in aquatic ecosystems.

Summary and conclusion

The biosynthesis of PH by higher plants should obviously be attributed to the general property of the plant world. The biosynthesis of these compounds is carried out along the shikimate pathway common to plants [44]. According to our data, the PH content in air dry biomass corresponds to an average of 80 mg/kg [27]. Considering the dry mass of the Earth's vegetation equal to 220 billion tons [45], the mass of PH contained simultaneously in the vegetation cover of the planet will correspond to 176 million tons (if not to consider PH of bacteria, fungi and algae that cannot be quantified). Despite the approximations of such a calculation, this value is up to 36 times more than industrial annual production (4.9 million tons) [2]. Therefore, the proportion of natural PH in the EN should be much higher than that from industrial sources. The afterlife of PH synthesized by higher plants is determined by their life cycle, the cycle in terrestrial ecosystems, entering the soil, groundwater and the atmosphere, for example, in case of forest fires.

Thus, the widespread opinion about PH as technogenic pollutants requires revision. Their level in the environment does not depend much on anthropogenic activity. It is a competition consequence of constant entry from wildlife and intense degradation by biota and by physical and chemical factors. The proportion of man-made pollution may be insignificant.

In this regard, it is necessary to pay attention to the fact that DEHP considered as the most toxic PH is almost always present in the living organisms studied so far as well as in the EN. Meanwhile, the toxicological studies were carried out on a synthetic, racemic product. The natural stereoisomer is not necessary to have the same physiological properties.

In the context of this article, it should be recognized that humanity has received PH with plant food throughout its existence. That fact is unlikely to have affected the population health. Therefore, the attitude to the monitoring of PH as industrial pollutants and toxicants needs to be rethought.

A work was carried out within the framework of the State Task, project No. 0345-2016-0008 (AAAA-A16-116122110065-4) and project No. 0279-2021-0005.

References

1. Declaration of the Sixth Ministerial Conference on Environment and Health. EURO/Ostrava2017/6 [Internet resource] http://www.euro.who.int/data/assets/pdf_file/0007/341944/OstravaDeclaration_SIGNED.pdf?ua=1 (Accessed: 22.05.2019).

2. Calvin E. Plasticizer market update. SPI Vinyl Produts Division 22nd Vinyl Compounding Conference July 10–13, 2011, PhD BASF Corporation [Internet resource] http://www.cpsc.gov/PageFiles/126090/spi.pdf (Accessed: 22.05.2019).

3. Xie Z., Ebinghaus R., Temme C., Lohmann R., Caba A., Ruck W. Occurrence and air-sea exchange of phthalates in the Arctic // Environ. Sci. Technol. 2007. V. 41. No. 13. P. 4555–4560. doi: 10.1021/es0630240

4. Das M.T., Ghosh P., Thahur I.S. Intake estimates of phthalate esters for South Delhi population based on exposure media assessment // Environmental Pollution. 2014. V. 189. P. 118–125. doi: 10.1016/j.envpol.2014.02.021

5. Zheng X., Zhang B.-T., Teng Y. Distribution of phthalate acid esters in lakes of Beijing and its relationship with anthropogenic activities // Sci. Total Environ. 2014. V. 476–477. P. 107–113. doi: 10.1016/j.scitotenv.2013.12.111

6. Net S., Sempéré R., Delmont A., Palusell A., Ouddane B. Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices // Environ. Sci. Technol. 2015. V. 49. No. 7. P. 4019–4035. doi: 10.1021/es505233b

7. Parry E.J. The chemistry of essential oils and artificial perfumes. V. II. London: Scott, Greenwood and Son. 1922. 365 p. [Internet resource] http://www.sciencemadness.org/library/books/the_chemistry_of_essential_oils_and_artificial_perfumes_ii.pdf (Accessed: 22.05.2019).

8. Graham P.R. Phthalate ester plasticizers-why and how they are used // Environmental Health Perspectives. 1973. V. 3. P. 3–12. doi: 10.2307/3428023

9. Lin Z-P., Ikonomou M.G., Jing H., Mackintosh C., Gobas F.A.P.C. Determination of phthalate ester congeners and mixtures by LC/ESI-MS in sediments and biota of an urbanized marine inlet // Environ. Sci. Technol. 2003. V. 37. No. 10. P. 2100–2108. doi: 10.1021/es026361r

10. Chen C.Y. Biosynthesis of di-(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DBP) from red alga – *Bangia atropurpurea* // Water Res. 2004. V. 38. No. 4. P. 1014–1018. doi: 10.1016/j.watres.2003.11.029

11. Vethaak A.D., Lahr J., Schraps S.M., Belfoid A.C., Rijs G.B.J., Gerritsen A., de Boer J., Bulder A.S., Grinwis G.C.M., Kniper R.V., Legler J., Murk I.A.J., Peijnenburg W., Verhaar H.J.M., de Voogt P. An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of the Netherlands // Chemosphere. 2005. V. 59. No. 4. P. 511–524. doi: 10.1016/j.chemosphere.2004.12.053

12. Namikoshi M., Fujiwara T., Nishikawa T., Ukai K. Natural abundance ^{14}C content of dibutyl phthalate (DBP) from three marine algae // Marine Drugs. 2006. V. 4. No. 4. P. 290–297. doi: 10.3390/md404290

13. Heudorf U., Mersch-Sundermann V., Angerer J. Phthalates: toxicology and exposure // International Journal of Hygiene and Environmental Health. 2007. V. 210. No. 5. P. 623–634. doi: 10.1016/j.ijheh.2007.07.011

14. Blair J.D., Ikonomou M.G., Kelly B.C., Surridge B., Gobas F.A.P.C. Ultra-trace determination of phthalate ester metabolites in seawater, sediments, and biota from an urbanized marine inlet by LC/ESI-MS/MS // Environ. Sci. Technol. 2009. V. 43. No. 16. P. 6262–6268. doi: 10.1021/es9013135

15. Hu X., Gu Y., Huang W., Yin D. Phthalate monoesters as markers of phthalate contamination in wild marine organisms // Environ. Pollut. 2016. V. 218. P. 410–418. doi: 10.1016/j.envpol.2016.07.020

16. Rowdhwal S.S.S., Chen J. Toxic effects of di-2-ethylhexyl phthalate: an overview // BioMed Research International. 2018. Article No. 1750368. doi: 10.1155/2018/1750368

17. Shafikova T.N., Omelichkina Y.V., Enikeev A.G., Boyarkina S.V., Gvildis D.E., Semenov A.A. *Ortho*-phthalic acid esters suppess the phytopathgen capability for biofilm formation // Doklady Biological Sciences. 2018. V. 480. No. 3. P. 107–109. doi: 10.1134/S0012496618030092

18. Shafikova T. N., Omelichkina Y.V., Boyarkina S.V., Enikeev A.G., Maksimova L.A., Semenov A.A. Detection of endogenous phthalates in bacterial pathogens of plants and animals // Doklady Biological Sciences. 2019. V. 484. No. 1. P. 13–15. doi: 10.1134/S0012496619010022

19. Kuvichkina T.N., Budina D.V., Olkova A.S., Reshetnikov A.N., Ashikhmina T.Ya. Detection di-(2-ethylhexyl)phthalate in polyvinylchloride compound of mass spectrometric and biosensor methods // Theoretical and Applied Ecology. 2015. No. 4. P. 11–15 (in Russian). doi: 10.25750/1995-4301-2015-4-011-015

20. Priority Pollutant List EPA USA [Internet resource] https://www.govinfo.gov/ content/pkg/CFR-2014-title40-vol29/pdf/CFR-2014-title40-vol29-part423-appA.pdf (Accessed: 22.05.2019).

21. Rowdhwal S.S.S., Chen J. Toxic effects of di-2-ethylhexyl phthalate: an overview // Biomed Research International. 2018. Article No. 1750368. doi: 10.1155/2018/1750368

22. Ellington J.J., Floyd T.L. Octanol/water partition coefficients for eight phthalate esters // Research and Development EPA/600/S-96/006 [Internet resource] https://p2infohouse.org/ref/03/02822.pdf (Accessed: 22.05.2019).

23. Ogunfowokan A.O., Torto N., Adenuga A.A., Okoh E.K. Survey of levels of phthalate ester plasticizers in a sewage lagoon effluent and a receiving stream // Environ. Monit. Assess. 2006. V. 118. No. 1–3. P. 457–480. doi: 10.1007/s10661-006-1500-z

24. Dargnat C., Blanchard M., Chevreuil M., Teil M.J. Occurrence of phthalate esters in the Seine River estuary (France) // Hydrological Processes. 2009. V. 23. No. 8. P. 1192–1201. doi: 10.1002/hyp.7245

25. Benjami S., Pradee S., Jos M.S., Kumar S., Masai E. A monograph on the remediation of hazardous phthalates // J. Hazard. Mater. 2015. V. 298. P. 58–72. doi: 10.1016/j.jhazmat.2015.05.004

26. Deshayes S., Eudes V., Bigourie M., Droguet C., Moilleron R. Alkylphenol and phthalate contamination of all sources of greywater from French households // Sci. Total Environ. 2017. V. 599–600. P. 883–890. doi: 10.1016/j.scitotenv.2017.05.038

27. Enikeev A.G., Semenov A.A., Permyakov A.V., Sokolova N.A., Gamburg K.Z., Dudareva L.V. Biosynthesis of *ortho*-phthalic acid in the plant and cell cultures // Applied Biochemistry and Microbiology. 2019. V. 55. No. 3. P. 294–297. doi: 10.1134/S0003683819020066

28. Chernykh E.A., Semenov A.A. Chemical structure of brown sugar. Separation *bis-2(R)*-ethylhexylphthalate // Chem. Nat. Compd. 1980. V. 2. P. 247–248 (in Russian).

29. Semenov A.A., Enikeev A.G., Snetkova L.V., Permyakov A.V., Sokolova L.A., Dudareva L.V. *Orto*-phthalic acid esters in lipophilic extract from the cell culture of *Aconitum baicalense* Turcz ex Rapaics 1907 // Doklady Biochemistry and Biophysics. 2016. V. 471. No. 1. P. 421–422. doi: 10.1134/S1607672916060120

30. Babu B., Wu J-T. Production of phthalate esters by nuisance freshwater algae and cyanobacteria // Sci. Total Environ. 2010. V. 408. No. 21. P. 4969–4975. doi: 10.1016/j.scitotenv.2010.07.032

31. Penalver A., Pocurull E., Borrull F., Marce R.M. Determination of phthalate esters in water samples by solid-phase microextraction and gas chromatography with mass spectrometric detection // J. Chromatography A. 2000. V. 872. No. 1–2. P. 191–201. doi: 10.1016/S0021-9673(99)01284-4

32. Dargnat C., Teil M.J., Chevreuil M., Blanchard M. Phthalate removal throughout wastewater treatment plant Case study of Marne Aval station (France) // Sci. Total Environ. 2009. V. 407. No. 4. P. 1235–1244. doi: 10.1016/j.scitotenv.2008.10.027

33. Vozhdaeva M.Yu., Wagner E.V., Cantor L.I., Konstantinov A.I., Perminova I.V., Cantor E.A., Trukhanova N.V., Melnitsky I.A. Effect of seasonal dtnamics and chemical treatment on the guality of dissolved organic matter in water sources and potable water of Ufa // Moscow University Chemistry Bulletin. 2012. V. 72. No. 3. P. 154–159. doi: 10.3103/S0027131416050126

34. He W., Qin N., Kong X., Liu W., He Q., Ouyang H., Yang C., Jiang Y., Wang Q., Yang B., Xu F. Spatio-temporal distributions and the ecological and health risks of phthalate esters (PAEs) in the surface water of a large, shallow Chinese lake // Sci. Total Environ. 2013. V. 461–462. P. 672–680. doi: 10.1016/j.scitotenv.2013.05.049

35. Uskov T.N. Phthalate content in water of the Novosibirsk reservoir at various hydrological periods // Water: chemistry and ecology. 2013. No. 3. P. 100–105 (in Russian).

36. Net S., Dumoulin D., El-Osmani R., Rabodonirina S., Ouddane B. Care study of PAHs, Me-PAHs, PCBs, phthalates and pesticides contamination in the Somme River water, France // International Journal of Environmental Research. 2014. V. 8. No. 4. P. 1159–1170.

37. Wu X., Hong H., Liu X., Guan W., Meng L., Ye Y., Ma Y. Graphene-dispersive solid-phase extraction of phthalate acid esters from environmental water // Sci. Total Environ. 2013. V. 444. P. 224–230. doi: 10.1016/j.scitotenv. 2012.11.060

38. Gorshkov A.G., Babenko T.A., Kustova O.N., Izosimova O.N., Shishlyannikov S.M. Priority phthalates in the Lake Baikal pelagic zone and coastal area // Chemistry for Sustainable Development. 2017. V. 25. No. 4. P. 375–383. doi: 10.15372/KhUR20170403

39. Gorshkov A.G., Kustova O.N., Izosimova O.N., Babenko T.A. POPs monitoring system in Lake Baikal – impact of time or the first need? // Limnology and Freshwater Biology. 2018. No. 1. P. 43–48. doi: 10.31951/2658-3518-2018-A-1-43

40. Gorshkov A.G., Kustova O.N., Dzyuba E.V., Zakharova Yu. Polychlorinated biphenyls in Lake Baikal ecosystem // Chemistry for Sustainable Development. 2017. V. 25. P. 269–278. doi: 10.15372/KhUR20170305

41. Baram G.I., Azarova I.N., Gorshkov A.G., Vereshchagin A.L., Lang B., Kiryukhina E.D. Determination of bis(2-ethylhexyl)phthalate in water by high-performance liquid chromatography with direct on-column preconcentration // J. Anal. Chem. 2000. V. 55. No. 8. P. 750–754. doi: 10.1007/BF02757910

42. Lertsirisopon R., Soda S., Sei K., Ike M. Abiotic degradation of four phthalic acid esters in aqueous phase under natural sunlight irradiation // Journal of Environmental Sciences. 2009. V. 21. No. 3. P. 285–290. doi: 10.1016/S1001-0742(08)62265-2

43. Samsonov D.P., Kochetkov A.I., Pasynkova E.M., Zapevalov M.A. Levels of persistent organic pollutants in the components of the Lake Baikal unique ecosystem // Russian Meteorology and Hydrology. 2015. V. 42. No. 5. P. 345–352. doi: 10.3103/S1068373917050119

44. Tian C., Ni J., Chang F., Liu S., Xu N., Sun W., Xie Y., Guo Y., Ma Y., Yang Z., Dang C., Huang Y., Tian Z., Wang Y. Bio-Source of di-n-butyl phthalate production by filamentous fungi // Scientific Reports. 2016. V. 6. Article No. 19791. doi: 10.1038/srep19791

45. Bar-OnY.M., Phllips R., Milo R. The biomass distribution on Earth // PNAS. 2018. V. 115. No. 25. P. 6506–6511. doi: 10.1073/pnas.1711842115

46. Zenkevich I.G., Rotaru K.I., Selivanov S.I., Kostikov R.R. Determination of dialkyl phthalates in different objects (problems for discussion) // Bulletin SPbSU. 2015. Ser. 4. V. 2. No. 60. P. 386–394 (in Russian).