RUDN Journal of Ecology and Life Safety
Вестник РУДН. Серия: Экология и безопасность жизнедеятельности
ISSN 2313-2310 (Print); ISSN 2408-8919 (Online)
2023 Vol. 31 No. 4 544–555
http://journals.rudn.ru/ecology

BIOLOGICAL RESOURCES

БИОЛОГИЧЕСКИЕ РЕСУРСЫ

DOI: 10.22363/2313-2310-2023-31-4-544-555
EDN: RVSPPG
УДК 628.167+628.113

Research article / Научная статья

Influence of phytoplankton on the water quality of surface water sources and drinking water

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Abstract. The problem of the appearance of odors in drinking water associated with the development of algae and cyanobacteria in reservoirs of drinking water sources is considered. The results of the analysis of information on the main types of organisms that are sources of odorants in drinking water, chemicals produced by them and a description of odors are presented. Most often, the causes of odors in drinking water are the massive development of *Aphanizomenon flos-aquae* and *Oscillatoria agardhii*, which are producers of geosmin and 2-methylisoborneol. The classification of hazard levels for water pollution by cyanobacteria and recommended measures, including the frequency of monitoring and sampling, are given. The measures implemented with a decrease in the number of cyanobacteria in reservoirs of drinking water supply sources by physical, chemical and biological methods are presented. Methods of removal of intracellular and extracellular cyanotoxins from drinking water are described. The analysis of the efficiency of removal of various substances with odorizing effect from drinking water is presented.

Keywords: drinking water, odorants, geosmin, 2-methylisoborneol phytoplankton, cyanobacteria

Acknowledgements and Funding. The research was carried out within the framework of the scientific project No. FSNM-2020-0024 “Development of scientific foundations of environmentally friendly and nature-like technologies and rational use of natural resources in the field of extraction and processing of hydrocarbon raw materials” commissioned by the Ministry of Science and Higher Education of the Russian Federation.

Authors’ contributions: *E.V. Kalinina* – literature analysis and the article text preparation; *L.V. Rudakova* – direction guidance and the article text critical analysis.

Article history: received 15.01.2023; revised 30.04.2023; accepted 15.09.2023.

For citation: Kalinina EV, Rudakova LV. Influence of phytoplankton on the water quality of surface water sources and drinking water. *RUDN Journal of Ecology and Life Safety.* 2023;31(4):544–555. http://doi.org/10.22363/2313-2310-2023-31-4-544-555

Влияние фитопланктона на качество воды поверхностных водных источников и питьевой воды

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Аннотация. Рассмотрена проблема появления запахов в питьевой воде, связанная с развитием водорослей и цианобактерий в водоемах – источниках питьевой воды. Представлены результаты анализа информации об основных видах организмов, являющихся источниками одорантов в питьевой воде, продуцируемых ими химических веществ и описание запахов. Чаще всего причинами появления запахов в питьевой воде является массовое развитие *Aphanizomenon flos-aquae* и *Oscillatoria agardhii*, являющихся продуцентами геосмина и 2-метилизоборнеола. Приведены классификация уровней опасности по загрязнению воды цианобактериями и рекомендуемые при этом мероприятия, в том числе частота мониторинга и отбора проб. Представлены мероприятия, реализуемые при снижении численности цианобактерий в водоемах – источниках питьевого водоснабжения физическими, химическими и биологическими методами. Описаны методы удаления внутриклеточных и внеклеточных цианотоксинов из питьевой воды. Приводится анализ эффективности удаления различных веществ, обладающих одорирующим эффектом из питьевой воды.

Ключевые слова: питьевая вода, одоранты, геосмин, 2-метилизоборнеол фитопланктон, цианобактерии

Благодарности и финансирование. Исследование выполнено в рамках научного проекта № FSNM-2020-0024 «Разработка научных основ экологически чистых и природоподобных технологий и рационального природопользования в области добычи и переработки углеводородного сырья» по заказу Министерства науки и высшего образования Российской Федерации.

Вклад авторов: *Е.В. Калинина* – анализ литературных источников и подготовка текста статьи; *Л.В. Рудакова* – руководство направлением и критический анализ текста статьи.

История статьи: поступила в редакцию 15.01.2023; доработана после рецензирования 30.04.2023; принята к публикации 15.09.2023.

Для цитирования: *Калинина Е.В., Рудакова Л.В.* Влияние фитопланктона на качество воды поверхностных водных источников и питьевой воды // Вестник Российского университета дружбы народов. Серия: Экология и безопасность жизнедеятельности. 2023. Т. 31. № 4. С. 544–555. http://doi.org/10.22363/2313-2310-2023-31-4-544-555

Introduction / Subhead

More than 40% of the world's population faces water scarcity. Provision of drinking water of normative quality is one of the goals of sustainable development. In regions that are quantitatively supplied with water there are problems with its quality.

Drinking water quality is determined by the quality of water in water bodies – sources of drinking water supply and depends on natural and anthropogenic factors affecting the content of mineral and organic impurities of natural and anthropogenic origin [1].

Problems of odors in drinking water have been recorded in the world and the Russian Federation: Moscow, Izhevsk, Yekaterinburg, Kachkanar, Novokuznetsk, Khabarovsk, Perm. The peculiarity of the occurrence of unpleasant odors in water is their episodic nature associated with periods of mass development of cyanobacteria [2]. The development of some species of diatoms, blue-green, green, and flagellated algae is the cause of deterioration of organoleptic properties of drinking water. Application of traditional technological scheme of water treatment (coagulation – sedimentation – filtration – disinfection) does not completely remove odorants from drinking water.

Subject area analysis

The most common odors in drinking water are soil and musty odors that are characteristic of such substances in water as geosmin and 2-methylisoborneol (MIB), which are products of actinomycetes, cyanobacteria, and many species of algae [1; 3]. The total number of species that are sources of odorants is unknown. In natural waters, geosmin and 2-methylisoborneol can occur together and separately.

Odors can be manifested in water source, appear in the process of water treatment and water distribution. It is known that in laboratory cultivation of cyanobacteria odorants are released at all stages of culture growth, but in natural water bodies the intensity of water body "blooming" is not always related to the intensity of odorants manifestation [2]. Most often odor in drinking water appears in spring and at the end of summer – beginning of autumn [3; 4].

Under normal conditions of cyanobacteria growth, the number of odorants produced by them is insignificant and does not represent a problem. When they

are exposed to stress factors (deviation from the optimal degree of illumination, temperature, pH of the medium, flow rate, content of bio-genic elements, etc.), the number of odorants produced increases [3; 5] as a result of their natural death and their destruction by heterotrophic organisms (fungi, actinomycetes and small crustaceans).

In modern conditions, due to global changes in the Earth's climate, we can expect an increase in the degree of cyanobacteria distribution in water bodies:

- increase of water temperature in water bodies, expansion of cyanobacteria habitat;
- increase in the content of nutrients in water bodies;
- increase in the frequency of droughts leading to lowering of water levels in water bodies, increase in the degree of illumination of bottom layers, formation of conditions favorable for cyanobacteria.

Observations of phytoplankton development in the Volchikhinskoe water reservoir (Sverdlovsk region) allowed us to establish [4] that odor in water appears at a sharp change of dominant species *Aphanizomenon flosaquae* and *Oscillatoria agardhii. Aphanizomenon flosaquae* and *Oscillatoria agardhii* are geosmin producers, and *Oscillatoria agardhii* is also a MIB. The co-occurrence of these species, even when one of them was dominant, did not result in odors.

The odor of water from the Izhevsk pond was characterized as the odor of "dust". During the identification of phytoplankton composition more than 250 species and intraspecific taxa were identified. Green algae were represented mainly by the genus *Scenedesmus, Pediastrum, Oocystis, Tetraedron, Monoraphidium*. Of diatom algae, representatives of genera *Aulacoseira, Asterionella, Diatoma, Stephanodiscus, Navicula, Fragilaria, Synedra, Nitzschia*. Species of blue-green algae were predominantly represented by *Aphanizomenon flosaquae, Microcystis aeruginosa, Microcystis pulverea, Merismopedia tenuissima, Oscillatoria agardhii, Anabaena flosaquae, Woronichinia compacta, Woronichinia naegeliana.* Observations have established that the "bloom" of water coincides with the mass development of the *Aphanizomenon flosaquae* [4; 5], at the same time the water contained geosmin. Appearance of odour in water of Izhevsk pond coinciding with mass development of the species was noted *Oscillatoria agardhii,* which has since become the dominant one.

Analysis of scientific and technical information [2–6] allowed us to identify the main types of planktonic organisms that are sources of odorants, priority chemical substances produced by them, and the nature of odors (Table 1).

Table 1. **Odorants produced by algae and cyanobacteria [6]**

№	Chemical substance	Odour character	TOC *, mg/dm³	Species – sources of odorant
1.	Dimethyl sulfide C_2H_6S	Cabbage, hydrogen sulphide	0.1	*Asterionella formosa; Nitzschia actinastroides; Diatoma elongate; Ochromonas danica; Ochromonas malhamensis; Chlamydomonas globose* – **1** *Anacystis nidulans; Synechococcus cedrorum; Oscillatoria chalybea; Oscillatoria tenuis; Phormidium autumnale; Plectonema boryanum* – **2**
2.	Dimethyl disulfide $C_2H_6S_2$	Septic, garlic, rot	< 0.4	*Microcystis aeruginosa; Microcystis wesenbergii* – **2**
3.	Dimethyl trisulfide $C_2H_6S_3$	Septic, garlic, rot, swamp	0.001	*Microcystis aeruginosa; Microcystis wesenbergii* – **2**
4.	Isopropyl disulfide $[(CH_3)_2CH]_2S_2$	Onions, meat, Hydrogen sulphide	–	*Microcystis flos-aquae* – **2**
5.	6-methyl-5-hepten-2-one $(CH_3)_2C=CHCH_2CH_2COCH_3$	Cabbage, fruit, ether	5.04	*Aulacoseira granulata; Cyanidium caldarium; Scenedesmus subspicatus; Syncrypta sp.; Synura sp.* – 1 *Anabaena cylindrica; Microcystis aeruginosa; Synechococcus sp.* – **2**
6.	B-cyclocitral $C_{10}H_{16}O$	Tobacco smoke, mould	1.93	*Scenedesmus subspicatus; Dinobryon cylindricum; Uroglena sp.; Ulothrix fimbriata* – **1** *Microcystis aeruginosa; Microcystis flos-aquae; Microcystis botrys; Microcystis viridis; Microcystis wesenbergii* – **2**
7.	2-methyl-isoborneol $C_{11}H_{20}O$	Earthy, musty, Camphor	0.0015	*Hyella sp.; Jaaginema geminatum (syn. Oscillatoria geminate); Leibleinia aestuarii; Oscillatoria curviceps; Oscillatoria limosa; Oscillatoria tenuis; Oscillatoria variabilis; Phormidium breve (syn. Oscillatoria brevis); Phormidium favosum; Phormidium tenue (syn. Oscillatoria tenuis); Phormidium LM689, Phormidium sp.; Planktothrix agardhii (syn. Oscillatoria agardhii); Planktothrix cryptovaginata (syn. Lyngbya cryptovaginata); Planktothrix perornata f. attenuate; Porphyrosiphon martensianus (syn. Lyngbya martensiana), Pseudanabaena articulate; Pseudanabaena catenata; Pseudanabaena limnetica (syn. Oscillatoria lill1netica); Tychonema granulatum (syn. Oscillatoria f. granulata)* – **2**
8.	Geosmin $C_{12}H_{22}O$	Earthy, musty	0.0004	*Anabaena circinalis; Anabaena crassa, Anabaena lemmermannii; Anabaena macrospora; Anabaena planctonica; Anabaena solitaria; Anabaena viguieri; Anabaena millerii; Aphanizomenon flos-aquae; Aphanizomenon gracile, Geitlerinema splendidum (syn. Oscillatoria splendida); Leibleinia subtilis (syn. Lyngbya subtilis); cf. Microcoleus sp.; Phormidium allorgei (syn. Lyngbya allorgei); Phormidium amoenum (syn. Oscillatoria amoena); Phormidium breve (syn. Oscillatoria brevis); Phormidium cortianum (syn. Oscillatoria cortiana); Phormidium formosum (syn. Oscillatoria formosa); Phormidium simplicissimum (syn. Oscillatoria simplicissima); Phormidium uncinatum; Phormidium viscosum; Phormidium sp.; Planktothrix agardhii (syn. Oscillatoria agardhii); Planktothrix prolifica (syn. Oscillatoria prolifica); Pseudanabaena catenata; Schizothrix muelleri; Symploca muscorum; Tychonema bornetii (syn. Oscillatoria bornetii); Tychonema granulatum (syn. Oscillatoria f. granulata)* – **2**
9.	B -ionone $C_{13}H_{20}O$	Violets, fruit	0.0007	*Cyanidium caldarium; Scenedesmus subspicatus; Synura sp.* – **1** *Anabaena cylindrica; Aphanizomenon gracile; Synechococcus 6911* – **2**

End of the Table 1

№	Chemical substance	Odour character	TOC *, mg/dm^3	Species – sources of odorant
10.	1,2-dihydro-1,1,6-trimethyl-naphthalene $C_{13}h_{16}$	Licorice	–	*Cyanidium caldarium* – **1**
11.	Geraniol $C_{10}H_{18}O$	Sweet, flowers, fruit, roses, wax, citrus	7.71	*Synechococcus 6911* – **2**
12.	Geranyl-acetone $C_{13}H_{22}O$	Freshness, greenery, fruit, wax, roses, trees, magnolia	0	*Cyanidium caldarium; Scenedesmus subspicatus* – **1**
13.	Nerol $C_{10}H_{18}O$	Sweet, citrus, magnolia	29.3	*Synechococcus 6911* – **2**
14.	2,4-decadienal $C_{10}H_{16}O$	Rancid, Fish	1.98	*Dinobryon divergens; Dinobryon cylindricum; Mallomonas papillosa; Synura petersenii; cf. Syncrypta sp.; Uroglena americana; Uroglena sp.; Fragilaria sp.; Cryptomonas rostratiformis; Peridinium willei* – **1**
15.	2,4,7-decatrienal $C_{10}H_{14}O$	Rancid, Fish	1.95	*Dinobryon divergens; Dinobryon cylindricum; Synura petersenii; Uroglena americana; Uroglena sp. (UTCC276)* – **1** *Microcystis papillosa; Microcystis varians* – **2**
16.	Ectocarpene $C_{11}H_{16}$	Tomato greens	–	*Amphora veneta; Gomphonema parvulum; Phaeodactylum tricornutum; Skeletonema costatum; Lithodesmium undulatum; Ectocarpus spp.* – **1**

TOC* – Threshold odour concentration; 1 – Eukaryotic algae; 2 – Cyanobacteria.

The problem of reducing the content of odorants in drinking water should be solved comprehensively and include the solution of the following tasks [5]:

1. Monitoring of the number of cyanobacteria and the content of cyanotoxins in the water source.

2. Reducing the number of cyanobacteria, content of odourants and cyanotoxins in the water source.

3. Removal of odorants and cyanotoxins from drinking water.

Most countries do not have mandatory monitoring requirements for cyanobacteria and cyanotoxins in drinking water sources. Based on the existing experience, the Global water research coalition developed the principles of monitoring the number of cyanobacteria in water bodies [7]: visual assessment of the water source condition, water sampling to study the species composition of cyanobacteria and determine their abundance, and determination of the cyanotoxin content.

To assess the danger of water source pollution by cyanobacteria [8; 9], hazard levels were identified, and their monitoring programs were proposed (Table 2).

Indirect methods of determining the level of water pollution by cyanobacteria are determination of chlorophyll α concentration in water [9] and determination of vegetation index [10]. These methods are realized, including remotely. In the European Union countries, the concentration of chlorophyll α is a regularly monitored parameter within the framework of the Water Framework Directive.

Table 2. **Hazard levels for water pollution by cyanobacteria [8; 9]**

Hazard	Level Characterisation	Recommendation
Low	500–2000 cyanobacteria cells in 1 ml of water	Regular monitoring, identification of dominant species. Water sampling once a week to determine the number of cyanobacteria cells. Visual inspection of the water body to identify signs of its «blooming»
Medium	2000–6500 cyanobacteria cells in 1 ml of water	Water sampling twice a week. Assessment of population growth and species diversity. Assessment of the need for water toxicity control and toxin monitoring
High	More 6500 cyanobacteria cells in 1 ml of water	Assessment of possible risk for human health based on the data of toxin content monitoring. Development of recommendations for consumers using untreated water. Water sampling on a daily basis. Monitoring the content of cyanotoxins in drinking water
Very high	More 65 000 cyanobacteria cells in 1 ml of water	Informing supervisory authorities. Recommendations for consumers using untreated water. Assessment of toxicity or cyanotoxin content in the water supply source and in drinking water. Water body monitoring. Use of alternative sources of drinking water supply if there is a high public health risk

Decrease in the number of cyanobacteria in water bodies

Currently, physical, chemical, and biological methods have been proposed to reduce the abundance of cyanobacteria in wo-domes [5; 7; 10–16] (Table 3).

Table 3. **Methods to reduce the number of cyanobacteria in water bodies**

Method	Actions
Physical	Artificial destratification, aeration, agitation. Bottom cleaning to remove benthic algae and nutrients. Ultrasonic treatment to slow cyanobacteria growth and kill them
Chemical	Nutrient control: hypolimnetic oxygenation, phosphorus precipitation and capturing. Control of cyanobacteria abundance: application of coagulants and substances with algicidal and algistatic action
Biological	Application of viruses and infectious bacteria. Regulation of trophic structure of aquatic ecosystem with predominant number of heterotrophs feeding on cyanobacteria or competing with them for nutrition

Elimination of cyanobacteria and cyanotoxins from drinking water

The following methods are known for reducing cyanobacteria and cyanotoxins from drinking water supplied to consumers:

1. Using of alternative sources of water supply.

2. Preventing the introduction of cyanobacteria and/or cyanotoxins during water intake from a water supply source, including changing the level of the water intake head.

3. Water treatment from cyanobacteria and/or cyanotoxins.

Characteristic of methods of water treatment from cyanobacteria and cyanotoxins produced by them is presented in Table 4.

At the first stage of water treatment it is recommended to remove cyanobacteria together with cyanotoxins and odorants contained in them by methods: pre-oxidation, coagulation, sedimentation, filtration and flotation. In the process of water treatment it is expedient to apply micro-ultrafiltration by metal

or fabric filters with different pore size. The use of nanomembranes, including those made of polymeric biodegradable materials, is known [20]. Extraction of cyanobacteria cells from water by sedimentation and flotation allows to prevent their destruction and odorants entering the water. Sedimentation extracts up to 80% of cyanobacteria, while flotation extracts up to 98% [21]. The efficiency of application of coagulants and flocculants is influenced by the species of cyanobacteria. Studies [21] have shown the advantages of polymeric coagulants in comparison with metal salts: higher efficiency, easy separation of the formed sludge, the possibility of application in a wider range of pH and temperature [19].

Table 4. **Characteristics of methods of water treatment from cyanobacteria and cyanotoxins [1; 5; 7; 19–25]**

Method	Application efficiency
Removal of intracellular cyanotoxins (intact cells)	
Pre-oxidation	May cause cell lysis and subsequent release of cyanotoxins into the water. If oxidation is used to clean up other contaminants, low doses of oxidising agents that do not cause cell lysis (potassium permanganate) should be used. If high doses are used, they should be sufficient to destroy the toxins
Coagulation, sedimentation, filtration	Used to remove intracellular toxins in cases where cells are able to aggregate into easily separable precipitates
Compartment on membranes	Little data. Presumably effective for removal of intracellular toxins. Microfiltration and ultrafiltration are not effective if cells accumulate on the membrane
Flotation	Effective in removing intracellular cyanotoxins
Removal of extracellular cyanotoxins (dissolved)	
Compartment on membranes	Depends on material, membrane pore size and water quality. Nanofiltration is effective for removal of extracellular microcystins. Reverse osmosis is used to remove extracellular microcystin and cylindrospermopsin
Potassium permanganate oxidation	Effective for the oxidation of microcystins and anatoxins
Ozonation	Effective for the oxidation of extracellular microcystin, anatoxin-α and cylindrospermopsin
Chloroaramines	Not effective
Chlorination	Effective for oxidation of extracellular cyanotoxins at pH = 8 and below. Not effective for anatoxin-α
UV irradiation	At high doses, effective in breaking down microcystin and cylindrospermopsin
Sorption by activated carbons	The effectiveness of powdered activated charcoal depends on the type and pore size. Wood activated carbon is effective for adsorption of microcystins (at doses greater than 20 mg/dm^3), not effective for removal of saxitoxins, taste and odour. Granular activated carbon is effective for removal of microcystins, less effective for removal of anatoxi-na-α and cylindrospermopsin

To reduce the intensity of odors in drinking water it is not enough to remove only cyanobacteria cells, it is necessary to clean it from cyano-toxicants. The use of sorbents for this purpose, in particular activated carbon, is the most effective and technically available method.

Powdered activated carbons (PAC) are used together with coagulants or after treatment by them. The effectiveness of their introduction in the form of suspension with a dose of 1–7 mg/dm^3 into water at the beginning of the technological process with subsequent removal in the process of purification is

shown. The advantage of PAH is the possibility of its short-term use, the disadvantage is the impossibility of its reuse.

Granulated activated carbon (GAC) is expedient to use at the final stages of water treatment. The advantage of GAC is a large adsorbing surface, allowing to use it for extraction of a wide range of organic substances from water. The disadvantage of GAC is the necessity of its regeneration and replacement.

High efficiency of cyanotoxin removal from water is achieved by using electroactive polymers [22]. For example, iron (II, III) oxide nanoparticles in polypyrrole film effectively remove microcystis and cylindrospermopsin from water. The advantages of electro-active polymers in comparison with traditional sorbents include: higher sorption capacity (238–300 μg/mg), short contact time (8–15 minutes), increased number of use cycles.

Reagent oxidation, ozonation and ultraviolet water treatment [5; 7; 23] may be accompanied by the formation of toxic by-products, such as trihalomethanes. Studies in the field of cyanotoxin oxidation allowed us to determine the efficiency of the method combining electrolysis and heterogeneous photocatalysis. Application of electrolysis method allows to reduce the concentration of microcystins by 49%, application of photocatalysis – by 41%, and their combined application – by 99% [24].

Despite the efficiency of ozonation application, its spreading is limited by the high cost of its realization. Reduction of ozonation costs is achieved by using ozone-on microbubbles generated by a low-temperature plasma reactor based on a dielectric barrier discharge with an integrated liquid oscillator [5; 25].

The effectiveness of using methods of eliminating odorants of different origin from water [6] is presented in Table 5.

Table 5. **Methods of removing odorants from water**

№	Odorant	Effective	Not effective
1.	Geosmin	O_3, UV /H_2O_2, O_3/ H_2O_2, activated charcoal, biological method	Cl_2, ClO_2, $KMnO_4$, chloramines, aeration
2.	2-methylisoborneol	O_3, UV /H_2O_2, O_3/ H_2O_2, activated charcoal, biological method	Cl_2, ClO_2, $KMnO_4$, chloramines, aeration
3.	Dimethyl disulphide, dimethyl trisulphide	Oxidation, activated carbon, biological method	Chloramines
4.	Chlorinated compounds	Activated carbon	Biological method
5.	Hydrogen sulphide	Aeration, oxidation	–
6.	Low molecular weight aromatic and aliphatic compounds	Aeration, activated carbon	Oxidation
7.	Phenol, chlorophenols	O_3, ClO_2, activated charcoal, biological method	Cl_2, chloramines, $KMnO_4$,
8.	Benthic cyanobacterial blooms	Optimisation of water levels in reservoirs	–

The use of O_3 in doses of 1–15 mgO_3/dm^3 or H_2O_2 with a concentration of 1–15 mg/dm^3 leads to a reduction in the total content of odorants (geosmin and MIB) up to 50% and a reduction in odor intensity from 4 to 3 points. The

combined application of O_3 and H_2O_2 showed greater effectiveness [3]. In general, the use of oxidizing agents for water deodorization is less effective than the use of PACs. Final chlorammonization has no practical effect on the odor level of drinking water. Secondary chlorination of treated water without ammonization can lead to chlorine odor.

Conclusion

1. Increased anthropogenic load, accompanied by the intake of nutrients from wastewater, and the Earth's climate change, which contributes to an increase in the content of cyanobacteria due to the expansion of their habitat, leads to an increase in the frequency of occurrence of odors in drinking water.

2. The most common cause of odors in drinking water is the development of odors in source water *Aphanizomenon flos-aquae; Oscillatoria agardhii; Microcystis flos-aqua; Microcystis viridis*.

3. To control the number of cyanobacteria in sources of drinking water supply it is necessary to carry out monitoring. The methods of remote sensing are included.

4. A combination of ozonation and sorption methods is appropriate for removal of most odorant species produced by cyanobacteria.

5. It is advisable to introduce powdered activated carbons at the beginning of the technological process of purification, granular activated carbons are usually used at the final stages.

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