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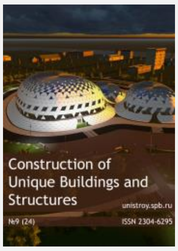

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Fluorimetric tracing of sewage effluents in the Murinsky creek

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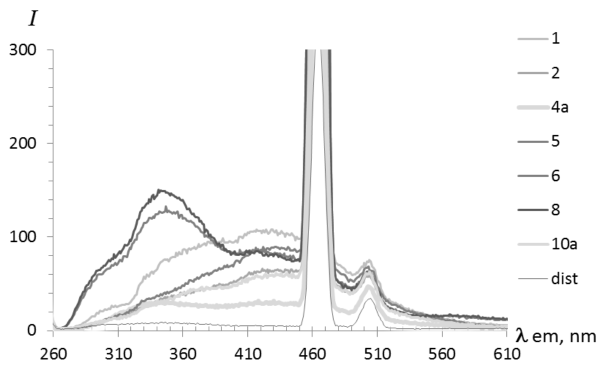
ABSTRACT



The Murinsky creek starts in a city park and takes waters from several canalization outlets of Saint-Petersburg on its way.

Fluorimetric properties and chemical parameters (electric conductivity, pH, content of total organic carbon (TOC) and total nitrogen (TN)) of the creek water samples were analyzed in order to reveal the most informative parameters for express determination of water pollution sources. The obtained results showed that electric conductivity and TOC content do not allow distinguishing between unpolluted (natural) and polluted water samples due to seasonal variation of natural background values. Fluorimetric properties at excitation wavelength 230 nm such as intensity of tyrosine-like fluorescence at 300 nm and tryptophan-like fluorescence at 340 nm proved to be informative for sewage effluents tracing in the Murinsky creek. Ratio of tyrosine-like (ex230 em300) to humic-like (ex230 em420) fluorescence for unpolluted waters was 0,06...0,27, for polluted waters – 0,25...0,81. Ratio of tryptophan-like (ex230 em340) to humic-like (ex230 em420) fluorescence for not polluted waters was within 0,14...0,94 and for polluted waters – 0,72...2,85. Significant increasing of one or both ratios was observed in waters after sewage outlets. Ratio of tyrosine-like to humic-like fluorescence showed high correlation with TN (r = 0.98), and TN/TOC (r = 0.96).

Contents

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1. Introduction

Illicit emission of untreated sewage to natural water bodies is a serious ecological issue for big cities such as St. Petersburg [1]. Emissions may happen several times per year as a volley of sewage from an industrial enterprise, a ship, a fuel station, some other objects [2]. Continuous emissions take place usually as a result of misconnection or illicit connection of sanitary sewer to drain sewer pipeline, pipes damage, etc. [1].

In many cases it is difficult to find the source of pollution because water quality control takes time and is usually done not often or when the polluted water had moved far from its source. Development of methods and devices for express on-site analysis of water quality is important to find illegal emission source and prevent such pollution in future. Fluorimetry of water samples is one of methods that can be applied for this purpose.

2. Literature review

Fluorescence spectra of natural waters and waste waters are formed as a result of organic matter fluorescence and clear difference between these kinds of waters can be observed. Fluorimetric analysis of a water sample is rather fast (one measurement takes a couple of minutes), requires minimal sample preparation for analysis (sample dilution with distilled water may be necessary), and needs no reagents [9–15, 19].

Two types of fluorescence are observed in natural and waste waters under excitation by ultraviolet and visible light – humic-like fluorescence and protein-like fluorescence. A wide peak with emission maximum 400...500 nm is named humic-like fluorescence and it is characteristic for natural organic matter and humic substances extracted from soils [3, 14, 22], natural fresh waters [3, 23], drinking waters at various stages of treatment [10–12, 21], salt waters [13, 24]. It has excitation maximums at about 220 nm and 270 nm. Protein-like fluorescence has less intensity in not polluted natural waters. Protein-like peaks resemble fluorescence of two amino acids – tyrosine and tryptophan [4]. Tyrosine-like fluorescence has emission maximum at about 300 nm (excitation at 200...240 nm) and tryptophan-like – at about 330...350 nm (excitation at 200...310 nm). Intensive protein-like fluorescence is observed in sewage and polluted waters [5, 7, 9, 15], landfills leachates [7, 8]. Spectra of oils and waters polluted by oil spills also have peaks close to protein-like and humic-like fluorescence [16–18].

Many researchers tried (with mixed success) to reveal correlations between fluorescence intensity of natural and polluted waters and chemical parameters of organic matter. Correlations were found between biochemical oxygen demand (BOD) and tryptophan-like peak (Pearson`s coefficient r = 0.77...0.98) [25–31], BOD and humic-like peak (r = 0.72...0.77) [6, 30], but some studies failed to find correlations between these parameters [32]. Correlations between chemical oxygen demand (COD) and tryptophan-like peak were reported (r = 0.42...0.96) [33-36], with total organic carbon (TOC) and humic-like peak or tryptophan-like peak with r = 0.68...0.97 (reviewed in [27]). Strong correlations(r = 0.65...0.96) were shown between protein-like fluorescence and content of not fluorescing compounds that arise from organic matter destruction and are usually present in sewage pollution such as phosphates and nitrates [29], total nitrogen and ammonium [33].

In some works relative fluorimetric parameters, for example ratio of intensity for tryptophan and humic peaks [6], tyrosine to humic and tryptophan to humic peaks [9] were determined and compared. For natural waters ratios were several times lower than for untreated sewage or polluted surface waters.

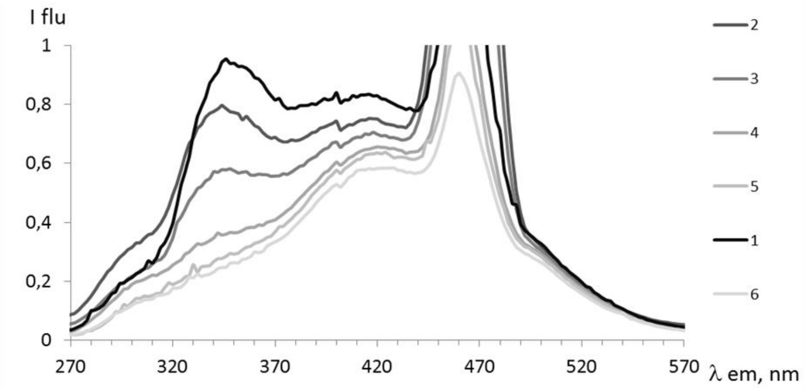

Figure 1.Fluorescence spectra of the Neva waters and its tributaries – the Okhta, the Slavyanka and the ChernayaRechka.
Spectra are corrected for excitation and emission light absorption. Samples were taken 01.09.2008 from: 1 – the Neva at the place of the Slavyanka inflow, 2 – the Okhta (20 m before inflow to the Neva), 3 – the Neva at the place of the

Okhta inflow, 4 – the Neva at inflow of the ChernayaRechka, 5 - the Neva before inflow of the ChernayaRechka, 6 - the Neva before inflow of the Okhta

In general fluorimetry proved to be informative and express method for tracing sewage pollution in surface waters. However, local characteristics such as water body parameters and proportion of wastewater in river flow rate should be taken into account while using this method. For example, fluorescence spectra of waters from River Neva and its tributaries demonstrated rather high tryptophan-like peak (see Figure 1) [9]. This data were in accordance with information about tributaries pollution by sewage. However in the Neva water samples no significant difference was observed upstream and far downstream from places of polluted tributaries inflow due to dilution effect of the Neva (and also due to sedimentation of suspended impurities) [9].

3. Problems definition

Fluorimetry of water samples is informative to determine water pollution. Ability of spectrofluorimetry toshow distinction between natural organic matter and technogenic organic pollutants is important for pollution monitoring in water objects of North-Western Russia that are rich in natural organic matter [1, 37] and can take various types of pollutants from oil spills [1, 2], municipal and industrial waste waters [1, 2, 41], municipal wastes leachates [2, 38].

However, optical properties of natural waters and waste waters vary with season and place, and this should be considered while applying this method on real objects. For example, fluorimetric analysis of the Neva river waters demonstrated that no significant difference was observed upstream and far downstream from polluted tributaries inflow. But the situation can be different in small rivers of St. Petersburg.

Construction of sewage system in St. Petersburg is still not completed. Some objects and districts of the town discard sewage directly into streams and rivers [1, 2, 39, 40]. The Murinsky creek is one of such streams and it was chosen for this investigation.

The aim of this work was to check if fluorimetry can be applied for water pollution tracing in the Murinsky creek. In order to achieve the aim the following tasks were set:

1) finding several sewer outlets and taking water samples upstream and downstream of them at the Murinsky creek;

2) determination and analysis of changing of several parameters of water quality and fluorimetric properties connected with sewage pollution.

4. Description of the research

4.1. Characteristics of object of research

The Murinsky creek has its source in the park Sosnovka, runs for 8.7 km through the Grajdanka district (in the northern part of St. Petersburg) and flows into the river Okhta that is the most polluted river of St. Petersburg [2]. Outlets of several pipes open into the Murinsky creek. These pipes carry storm waters from drain system and natural waters from springs and tributaries enclosed in pipes when the district was built up with new houses. Sewage waters are discharged to this creek as a result of cross-connection of sanitary sewer outlets from residential buildings and storm drain system [39, 41].

Reconstruction of sewers in this part of St. Petersburg is expected to be completed in 2015. Sewage waters are planned to be separated from storm waters and conveyed through a new collector to waste water treatment plant [39]. Now the Murinsky creek is a good model object of natural water body polluted with sanitary sewage.

4.2. Methods of research

Water samples of about 0.5...0.8 liters were collected into plastic bottles that were thoroughly washed and rinsed with tap water and distilled water beforehand. At the place of sampling (shown on the map at Figure 2) the bottles were rinsed with water from the creek and then filled up to the cap. Some organoleptic water characteristics (unpleasant smell, high temperature) were noted while sampling.

At the same day the filled bottles were taken to the laboratory and kept in a refrigerator at +4...+6°C to decrease biodegradation processes. However, during storage for 1–2 days no significant decreasing of total organic carbon and total nitrogen concentrations was observed even at room temperature [44]. Bottles were kept in vertical position while suspended matter was sedimenting. The upper part of water was analyzed. No samples filtration was done in order to prevent addition of fluorescing components to water.

Concentration of total carbon (TC), inorganic carbon (IC) and total nitrogen (TN) were measured on analyzer “TOC-Lvpn” and “TNM-L” (Shimadzu, Japan) without sample dilution. Measurements were done with up to 10% accuracy. Concentration of total organic carbon (TOC) was calculated by subtraction of IC from TC. Water conductivity was measured using conductometer “HI 8713” (HANNA Instruments, Austria). Water pH was measured using millivoltmeter “I-500” (Akvilon, Russia).

Water sample was put into a quartz curette and fluorescence intensity was registered at right angel to excitation light direction. Fluorescent spectra were obtained on analyzers “RF 5301 PC” (Shimadzu, Japan) and “Fluorat 02 Panorama” (Lumex, Russia) at excitation wavelength 230 nm, emission wavelength 200...650 nm. No signal correction for excitation and emission light absorption was done.

Figure 2. Sampling points at the Murinsky creek. Sewage outlets are between ##1 and 2, 5 and 6, 7 and 8

4.2. Results and discussion

The samples were divided into three groups according to their localization and degree of pollution.

1) Natural water samples from park Sosnovka were taken from a lake (##3a, 4a) and from streams in drainage ditches (## 9a, 10a, 1p, 2p, 3p, 4p, 5p). These streams form the beginning of the Murinsky creek which flows out of the pipe under a bridge and then fills a pond. Sampling point #1p is nearest to the bridge from the park side and sampling point #1 – from the pond side. Samples of the first group were presumed to be not polluted by sewage because fecal smelt was not observed near sampling places.

2) Water samples from the pond that is formed by the Murinsky creek before the dam had numbers #1, 2, 3, 4. These samples could be polluted by sewage. One sewage outlet was located in 2008 near sampling places 2 (sample 2 was taken very close to the pipe end), but in 2013 we failed to find it and sample 2 was taken in not exactly the same place. According to [41] a pipe outlet was placed under the bridge. Also two restaurants and a mini-farm were situated at the banks of the pond and could be possible sources of pollution.

3) Water samples from the narrow part of the Murinsky creek (## 5–10, 12–13) and its small tributary (#11) were supposed to be polluted by sewage. Several sewage outlets were found there and fecal smelt was felt while taking samples. Water from sample # 7 was warm on 11.09.2013 and this indicated leakage from hot water supply system.

Results of samples chemical analysis are given in table 1. They are: values of electric conductivity κ (in mkSm/cm), pH and organic matter characteristics (TC, IC, TOC, TN in mg/l and TN/TOC ratio).

Table 1. Chemical parameters of water samples from the Murinsky creek and its sources

#	Sampling date and water chemical parameters														
	28.11. 2008	10.07.2013							11.09.2013						
	κ	κ	H	TC	IC	TOC	TN	TN/TOC	κ	pH	TC	IC	TOC	TN	TN/TOC
3a	-	-	-	-	-		-		70	6,5	30	4	26	0,9	0,04
4a	-	-	-	-	-		-		60	6,4	28	4	24	0,9	0,04
9a	-	-	-	-	-		-		317	7,2	59	28	31	1,1	0,04
5p	160	-	-	-	-		-		-	-	-	-	-	-	-
#	Sampling date and water chemical parameters														
	28.11. 2008	10.07.2013							11.09.2013						
	κ	κ	H	TC	IC	TOC	TN	TN/TOC	κ	pH	TC	IC	TOC	TN	TN/TOC
4p	248	-	-	-	-		-		-	-	-	-	-	-	-
3p	256	-	-	-	-		-		-	-	-	-	-	-	-
2p	108						-		23	7,2	60	30	30	1,1	0,04
1p	110	-	-	-	-				-		-	-		-	-
1	117	1415	6,7	103	50	53	1,7	0,03	1970	6,8	170	16	153	4,0	0,03
2	980	588	6,7	70	18	52	1,1	0,02	529	7,1	66	22	44	0,9	0,02
3	-	546	6,8	67	16	52	0,9	0,02	-	-	-	-	-	-	-
4	483	539	7,2	67	15	52	0,9	0,02	-	-	-	-	-	-	-
5	490	538	8,1	64	13	51	0,9	0,02	572	6,5	82	18	64	1,0	0,02
6	900	973	7,0	97	42	54	8,2	0,15	812	7,0	128	48	81	26,9	0,33
7	900	1057	7,0	99	46	53	9,5	0,18	826	6,8	124	47	77	26,3	0,34
8	-	1075	6,9	100	47	53	8,8	0,17	848	6,7	120	46	73	24,5	0,34
9	-	1160	6,8	109	53	55	8,0	0,15	-	-	-	-	-	-	-
10	-	1151	7,1	107	52	55	8,8	0,16	-	-	-	-	-	-	-
11	-	667	7,1	49	26	23	1,5	0,07	-	-	-	-	-	-	-
12	-	1115	7,0	104	51	53	8,5	0,16	-	-	-	-	-	-	-
13	-	1126	7,1	103	51	52	8,2	0,16	-	-		-	-	-	-

Conductivity data for 28.11.2008 showed that sewage waters had higher κ values than natural (not polluted) waters. Conductivity varied from 108 to 256 mkSm/cm in streams of the park, and from 900 to 980 mkSm/cm in heavy polluted waters.

In the pond at November 2008 conductivity increased from 117 to 483 mkSm/cm with water current. However, in July and September 2013 the pond water conductivity tended to decrease downstream. This contradiction could be explained by hot weather and lack of rains in July and September that increased salts content in surface water in the park. Spring water coming from the pond bottom could dilute the surface water from the park. Nevertheless, high conductivity value in sample #1 (1415...1970 mkSm/cm) allows supposing that it was influenced by some source of pollution, maybe sewage outlet under the bridge, or water plants degradation near the bridge. Conductivity of sample #1 was the highest in two sets of samples in 2013 – higher than in heavily polluted water (in samples #6...10 conductivity varied from 812 to 1160 mkSm/cm). It also was significantly higher than in stream from the park (#9a, 2p) in contradiction to the situation in 2008. If no sewage outlet was missed in 2013 than all the data show real difficulties in distinguishing between natural and polluted waters using conductivity due to seasonal variations of natural water quality.

Values of TOC varied from 23 to 153 mg/l. Lower concentrations (23...44 mg/l) were found in unpolluted water samples from the park, the tributary (#11) and in sample #2 from the pond. However, pond and creek samples from July 2013 had close TOC values (51...55 mg/l) within margins of measurement error. In September 20313 values for pond and creek samples did not vary much (44...81 mg/l) with an exception to #1 (153 mg/l). In general it is obvious that TOC cannot be used as a parameter for distinguishing natural and polluted waters for this case (the same conclusion for COD had been done before [9]).

TN is a parameter that revealed clear difference between not polluted and polluted waters. In both sets of samples in 2013 it increased one order of magnitude after sewage inflow to the creek and kept at a high level (9...30 mg/l) for about 2 km downstream the Murinsky creek. These values correspond to the average TN values for St. Petersburg waste waters (25...38 mg/l as given in [1]). In the cases with close TOC values natural and sewage waters could be distinguished using ratio TN/TOC which is 7...15 times higher in polluted waters (comparing #5 and 6). Using this ratio we concluded that water from the troublesome sample #1 and tributary water from sample #11 were of natural origin and were not polluted by sewage.

Some examples of fluorescent spectra are given on Figures 3 and 4, where fluorescence intensity ***I*** is presented as a function of emission wavelength λ_{em}. All spectra were obtained for diluted water samples in order to decrease influence of light absorption on fluorescence signal.

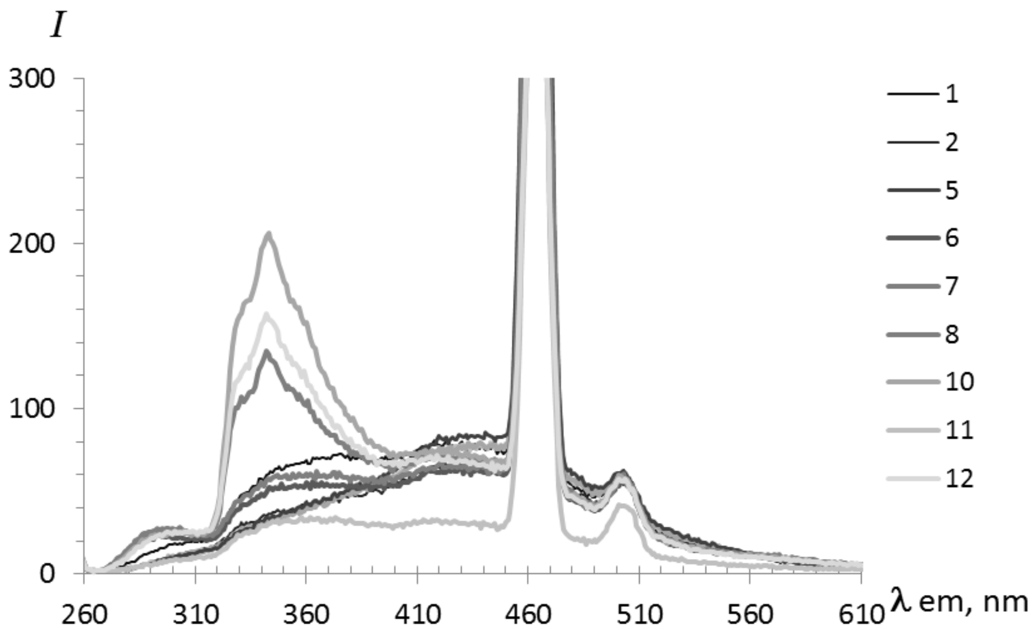

Figure 3. Fluorescence spectra of the Murinsky creek water samples (collected on July 10, 2013). Samples were diluted 10 times by distilled water

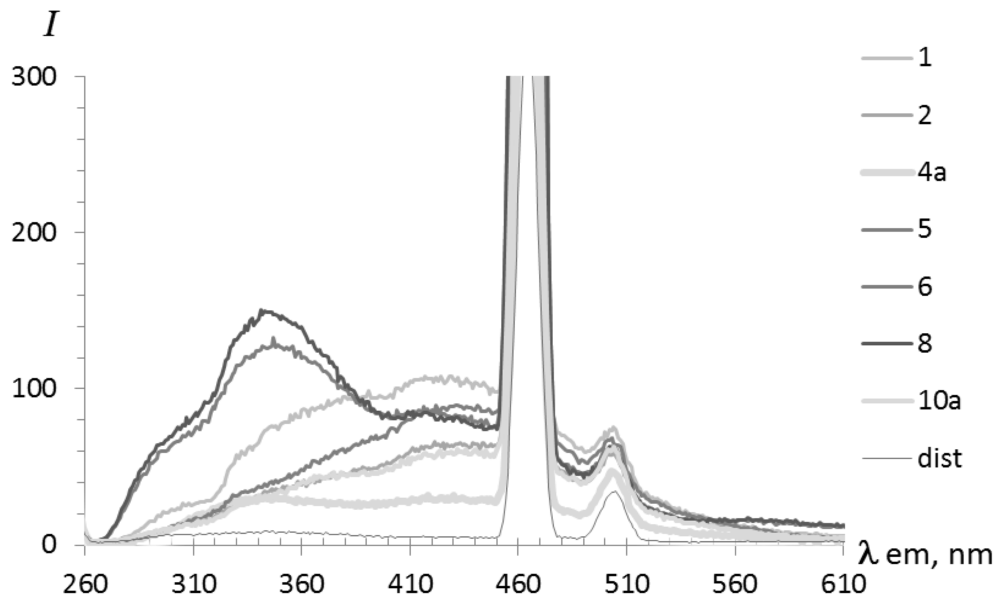

Figure 4. Fluorescence spectra of the Murinsky creek water samples (collected on September 11, 2013). Samples were diluted 10 times by distilled water

In not polluted waters humic-like fluorescence (with emission maximum at about 420...450 nm) prevailed over protein like fluorescence (with emission maximums at about 300 nm for tyrosine-like peak and 330...360 nm for tryptophan-like peak). The opposite situation was observed for polluted waters where one or both of protein-like peaks were higher than humic peak. These spectral data correspond to the results received by other researchers for humic-reach natural waters and sewage waters and also are in agreement with our data obtained for the Murinsky creek in 2007–2008 [9].

In order to give qualitative characteristic of polluted and not polluted waters ratios between fluorescence intensities of protein-like fluorescence and humic-like fluorescence can be calculated. We chose emission wavelengths 300, 340 and 420 nm that were close to the corresponding maximums. Ratios I_{300}/I_{420} and I_{340}/I_{420} are given in Table 2.

Table 2. Fluorimetric parameters of water samples from the Murinsky creek and its sources

#	Sampling date and diluted water fluorimetric parameters (excitation wavelength230 nm, no signal correction, distilled water signal was subtracted)					
	28.11.2008 dilution factor 8		10.07.2013 dilution factor 10		11.09.2013 dilution factor 10	
	I_{300}/I_{420}	I_{340}/I_{420}	I_{300}/I_{420}	I_{340}/I_{420}	I_{300}/I_{420}	I_{340}/I_{420}
3a	-	-	-	-	0,16	0,75
4a	-	-	-	-	0,19	0,94
9a	-	-	-	-	0,15	0,52
5p	0,06	0,18	-	-	-	-
3p	0,10	0,22	-	-	-	-
2p	0,06	0,14	-	-	0,09	0,4
1p	0,05	0,14	-	-	-	-
1	0,19	0,26	0,16	0,68	0,16	0,57
2	0,17	0,60	0,08	0,44	0,08	0,39
3	-	-	0,07	0,32	-	-
4	0,20	0,40	0,06	0,33	-	-
5	0,27	0,41	0,03	0,30	0,08	0,37
6	0,50	1,24	0,28	0,72	0,74	1,48
7	0,33	0,94	0,31	0,77	0,80	1,66
8	-	-	0,33	1,81	0,81	1,75
9	-	-	0,22	2,85	-	-
10	-	-	0,27	2,75	-	-
11	-	-	0,08	0,81	-	-
12	-	-	0,27	2,22	-	-
13	-	-	0,25	2,15	-	-

It can be seenfrom the figures that for unpolluted waters I_{300}/I_{420} belong to the interval 0,06...0,27 and for polluted waters – 0,25...0,81. For I_{340}/I_{420} intervals are the following: for not polluted waters 0,14...0,94 and for polluted waters 0,72...2,85. In spite intervals overlapping significant increasing of one or both ratios were observed after sewage outlets.

In order to reveal connection between these fluorimetric ratios and some chemical parameters Pearson correlation coefficients (r) were calculated. The highest coefficients were for I_{300}/I_{420} and TN (r = 0.98), and TN/TOC (r = 0.96). Correlation for another fluorimetric ratio was weaker with r = 0.64 for $I_{340}/I_{420}$and TN/TOC, r = 0.54 for $I_{340}/I_{420}$and TN. Very week correlations with r<0.4 were for fluorimetric ratios and conductivity. These results allow choosing most informative parameter for distinguishing waste waters from polluted waters.

5. Conclusions

Data of chemical and fluorimetric analysis of water samples from the Murinsky creek polluted by sewage waters allowed making the following conclusions.

1. It is difficult to use electric conductivity of water samples in distinguishing between natural and polluted waters due to seasonal variations of natural water conductivity.

2. TOC and COD values do not allow distinguishing between not polluted surface waters and waters polluted by sewage.

3. TN increased one order of magnitude after sewage inflow to the creek and kept at a high level for about 2 km downstream the Murinsky creek. Ratio TN/TOC is 7...15 times higher in sewage-polluted waters than in not pollutes waters

4. Ratio of tyrosine-like to humic-like fluorescence I_{300}/I_{420} for unpolluted waters belonged to the interval 0,06...0,27 and for polluted waters – 0,25...0,81. Ratio of tryptophan-like to humic-like fluorescence I_{340}/I_{420} for not polluted waters was within 0,14...0,94 and for polluted waters – 0,72...2,85. In spite intervals overlapping significant increasing of one or both ratios were observed in waters after sewage outlets.

5. Ratio of tyrosine-like to humic-like fluorescence I_{300}/I_{420} showed high correlation with TN (r = 0.98), and TN/TOC (r = 0.96).

6. Fluorimetric parameters mentioned above (in conclusions 4–5) proved to be informative for sewage effluents tracing in the Murinsky creek.

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Обнаружение загрязнений Муринского ручья сточными водами методом флуориметрии

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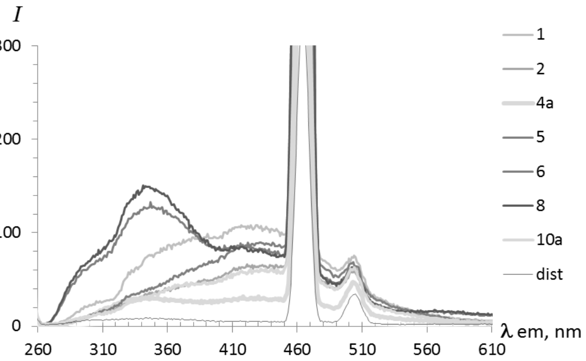
АННОТАЦИЯ



Состав воды в Муринском ручье формируется под влиянием канализационных стоков от части зданий района Гражданка города Санкт-Петербурга. Для проб воды из Муринского ручья исследовали спектры флуоресценции и химические показатели качества: удельная электропроводность, pH, содержание общего органического углерода (ООУ) и общего азота (ОА). Полученные результаты показали, что удельная электропроводность и содержание ООУ не всегда позволяют выявить загрязнение воды ручья бытовыми стоками из-за высокой сезонной вариабельности фоновых (природных) значений. В спектрах флуоресценции при длине волны возбуждения 230 нм наблюдались существенные различия между незагрязненной и загрязненной водой ручья по интенсивности флуоресценции тирозинового типа (длина волны регистрации 300 нм) и триптофанового типа (длина волны регистрации 340 нм). Отношение интенсивностей флуоресценции тирозинового и гуминового типа (при длине волны регистрации 300 и 420 нм, соответственно) составило для незагрязненной воды 0,06...0,27, для загрязненной – 0,25...0,81. Отношение интенсивностей флуоресценции триптофанового и гуминового типа (при длине волны регистрации 340 и 420 нм, соответственно) составило для незагрязненной воды 0,14...0,94, для загрязненной – 0,72...2,85. Существенное увеличение одного или обоих соотношений наблюдалось в пробах после канализационных выпусков. Первое отношение коррелирует с содержанием в воде ОА и отношением содержаний ОА к ООУ (с коэффициентами корреляции Пирсона 0,98 и 0,96, соответственно).

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