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Express-techniques in study of polluted suburban streams

Экспресс-методы в изучении загрязненных вод пригородных водотоков

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Abstract. Water samples from streams in suburban region of new builds were analyzed in order to suggest methods and parameters for pollution monitoring. Concentrations of total nitrogen (TN) varied from 0.6 to 9.0 mg/L, ammonium – from 0 to 6.8 mg/L, total organic carbon (TOC) from 8.3 to 21.1 mg/L. Electric conductivity (EC) varied from 80 to 640 mksm/cm, optical density at 254 nm – from 0.41 to 1.07. Increased concentrations of TN and ammonium at several sampling sites confirmed wastewater discharge from dwelling area. Polluted waters also showed higher values of electric conductivity and molar fractions for sodium and chloride ions, lower values of optical density (in range 230 – 420 nm) and TOC. Fluorescence intensity (I) was measured at excitation wavelength 230 and 270 nm, emission wavelengths 300-350 nm (protein-like fluorescence, present in wastewaters), 420 nm (humic-like fluorescence, present in natural and waste waters). Character of correlation between fluorescence intensity and TN (marker of pollution) and TOC depended on wavelengths, fluorescence signal correction and dilution of sample. Only I at 230 nm excitation and 350 nm emission for 10-fold diluted sample of water could be recommended for water monitoring. EC can be used as additional parameter in studied streams.

Аннотация. Пробы воды из водотоков в районе новостроек исследовали с целью предложить методики для экспресс-мониторинга загрязнений. Концентрации общего азота (TN) изменялись от 0.6 до 9.0 мг/л, иона аммония – от 0 до 6.8 мг/л, общего органического углерода (TOC) - от 8.3 до 21.1 мг/л. Электропроводность воды (ЕС) изменялась от 80 до 640 мксм/см, оптическая плотность воды при 254 нм – от 0.41 до 1.07. Повышение концентраций ионов аммония и TN в некоторых точках отбора подтверждает сброс сточных вод от жилых домов. Также в загрязненных водах отмечается: повышенные ЕС, мольные доли ионов натрия и хлоридов; пониженные TOC и оптическая плотность в диапазоне 230–420 нм. Интенсивность флуоресценции (I) измеряли при длинах волн возбуждения 230 и 270 нм, длинах волн регистрации 300–350 нм (флуоресценция белкового типа, характерная для сточных вод) и 420 нм (флуоресценция гуминового типа, регистрируемая в природных и сточных водах). Характер корреляции между I и TN (маркер загрязнения) и TOC зависел от длин волн, коррекции сигнала и разведения пробы. Только I при длинах волн возбуждения 230 нм и регистрации 350 нм для 10-кратно разведенной пробы можно рекомендовать для мониторинга загрязнений в изученных водотоках. ЕС может использоваться как дополнительный параметр.

Introduction

Surface water pollution is a great environmental problem all over the world. Pollutants from agricultural, industrial and municipal sources increase concentrations of harmful compounds in water

bodies, causes degradation of natural ecosystems in lakes and rivers, insert microbiological contamination, complicate processes of drinking water treatment.

Conditions of water in natural water objects can be esteemed from results of regular water quality monitoring and from reports of water using organizations. Regular samples collection and full chemical analysis of water are usually done several days in a year [1]. Obviously these data do not provide complete information about situation in the water objects. In annual reports from organizations volumes of wastewater effluents and concentrations of pollutants could be less than in reality.

Application of express-methods (for example, in automatic water quality monitors or on-site measurements) could make water quality control more operative. Such methods could help to find illegal sources of pollution or register the beginning of pollution process. This is important for making rapid decisions about application of water protection measures [2–4]. Also it can help to prevent wastewater discharges in future. However, informativity of express-methods depends on properties of water, such as natural background parameters. That is why investigation of particular stream is needed before recommending exact express-method.

There are several parameters possible for express monitoring of water. One of them is optical density of water at 254 nm (D_{254}), usually used in water quality control to esteem amount of dissolved organic matter [5–8]. Electric conductivity of water (EC) allows esteeming concentration of total dissolved solids and detecting pollution in fresh waters [9–11].

Fluorescence of surface water samples also can be applied for this purpose [7, 11, 12]. River waters display two main types of peaks in fluorescence spectra (see Fig. 1). Protein-like peaks are observed at excitation wavelength 210–300 nm and emission wavelengths 300 nm (tyrosine-like peak) and 350 nm (tryptophan-like peak). Humic-like peak is wider and has maximal emission between 400 and 500 nm. In not polluted river waters, humic peak is prevailing. Spectra of organic pollutants, such as light oils, sewage, landfill leachate, have noticeable protein-like peaks that can be even higher than humic-like peak [11–14].

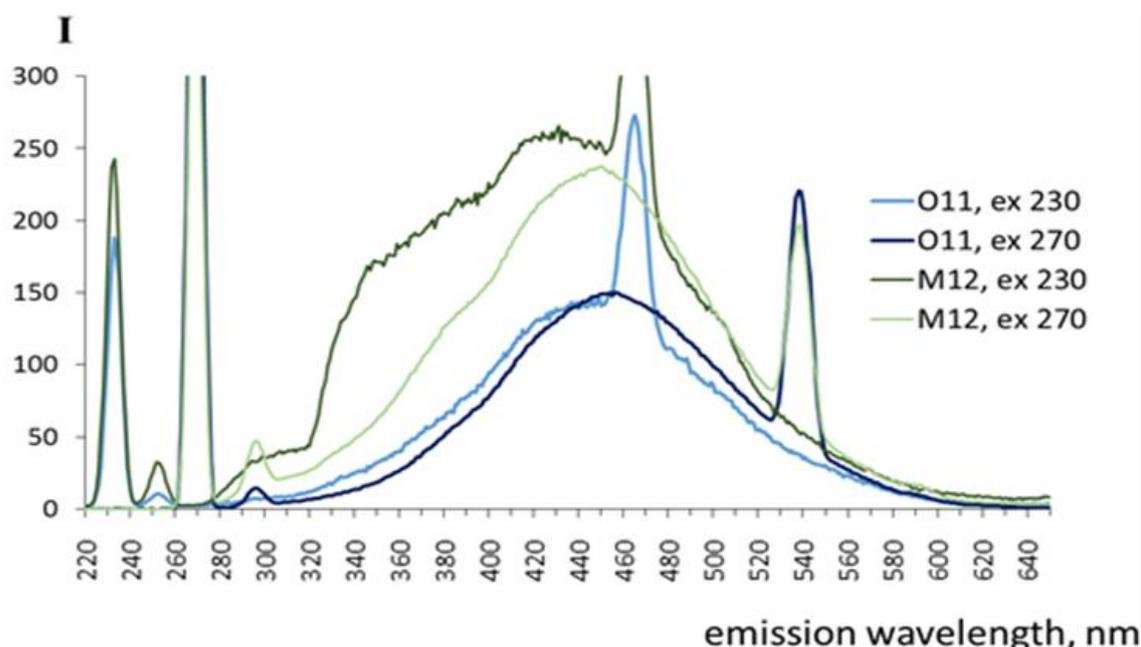


Figure 1. Examples of fluorescence spectra of studied water samples at excitation wavelengths 230 and 270 nm. I – fluorescence intensity

Correlations between fluorescence intensity ($I_{ex, em}$) at certain excitation (ex) and emission (em) wavelengths and chemical parameters of organic matter in natural, polluted waters and wastewaters were studied (reviewed in [12, 14]). Strong positive correlations were found between biochemical oxygen demand (BOD) and tryptophan-like peak (correlation coefficient $r = 0.85$ [15], $r = 0.906$ [16], $r = 0.77$ [17], $r = 0.96$ [18]), BOD and humic-like peak ($r = 0.72$ [17]), total organic carbon (TOC) and humic-like peak or tryptophan-like peak ($r = 0.876$ [16], $r = 0.96$ [18]). Strong correlations were also shown between fluorescence parameters and concentrations of inorganic (not fluorescing) compounds typical for sewage pollution (phosphates, nitrates, ammonium) [14, 15].

However, in some studies strong relationship between TOC or COD and peaks intensities were not revealed ($r = 0.1...0.51$) [7, 12, 14, 19, 20]. These results show need in more detailed study of components forming organic matter in waters. Also they show that properties of real waters should be taken into account before applying fluorescence techniques for pollution monitoring.

The aim of the present study is to check if it is possible to use several express-methods for water quality monitoring in St.Petersburg. Previously we studied the Okhta and its tributary the Murinsky creek in the boundaries of St.Petersburg. It was shown that pollution with wastewaters increased electric conductivity, changed molar fractions of ions and fluorimetric parameters [21, 22]. The present study is focused on suburban region Murino. This region recently became an area of intensive housing construction with supposed direct discharges of domestic wastewater from new buildings to local streams and the Okhta.

Objects and Methods

Characteristic of water source

The Okhta is the most polluted river of St.Petersburg due to discharge of untreated wastewaters and surface runoff [23–26]. It starts in Leningrad region and flows into the Neva which is used as source of drinking water for the city. Length of the Okhta is 93 km; 17.5 km of the river flows through the territory of St.Petersburg [27, 28].

According to reports of water using organizations about 30% of river flow at its mouth is composed by wastewaters from the city. Wastewaters of Leningrad region form about 10% of the Okhta flow at monitoring station Novoye Devyatkinno located at the boundary between St.Petersburg and Leningrad region [29]. Values higher than maximal allowable concentrations (MAC) were registered in the Okhta for such pollutants as ammonium, nitrites, iron, copper, manganese and some other metals [23, 24]. High concentrations of biodegradable organic matter were found as well; they caused decreasing of dissolved oxygen concentration [23, 24] and degradation of water plants communities [30].

Sampling sites

In the present study 11 water samples were collected in October 2016 from streams of the region Murino and near it. Murino is situated in Leningrad region near the city boundary. Sampling sites are located upstream the monitoring site Novoye Devyatkinno. They are shown at Figure 2.

Order of samples` numbers was not sequential. Five samples (# 5, 8, 10, 11, 13) were taken from the Okhta. One sample (# 12) was collected from its heavily polluted tributary the Murinsky creek, located in St.Petersburg. Five samples (# 3, 4, 2, 7, 9) were taken from Kapraliev creek which inflows into the Okhta in Murino. Samples were collected at one day. At the same day they were taken to the laboratory and stored at +4 °C in vertical position. The upper part of water was analyzed. No filtration was done to prevent addition of fluorescing components from filters to water.

Water analysis

Concentrations of total carbon (TC), inorganic carbon (IC) and total nitrogen (TN) were determined by analyzers "TOC L vpn" and "TNM-L" (Shimadzu, Japan) with measurement error $\pm 15\%$. Concentration of total organic carbon (TOC) was calculated by subtraction of IC from TC.

Chemical oxygen demand (COD) was calculated from TOC according to the formula from [31]:

$$\text{COD (mgO/L)} = \text{TOC (mg/L)} / 0.375 .$$

Concentrations of inorganic cations (NH_4^+ , K^+ , Na^+ , Mg^{2+} , Ca^{2+}) were determined at the next day after sampling. Method of capillary electrophoresis was used on device Capel 103P (Lumex, Russia). Concentrations of inorganic anions (sulfates and chlorides) were measured two days after sampling by the same device. Measurement errors were $\pm 15\%$.

Molar fraction of cation or anion among studied cations or anions were calculated according to the formula (1)

$$R(i) = (C_i \cdot 100\%) / (C_{\text{sum}}) \quad (1)$$

where C_i – molar concentration of cation or anion (mol/L), C_{sum} – sum of molar concentrations for studied cations (K^+ , Na^+ , Mg^{2+} , Ca^{2+}) or anions (Cl^- , SO_4^{2-} , HCO_3^-), correspondingly.

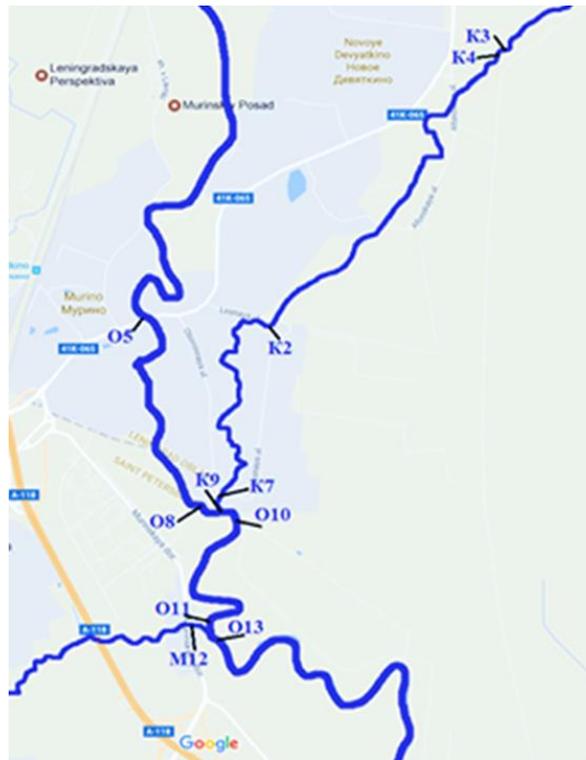


Figure 2. Scheme of sampling sites. Letter K denotes samples from Kapraliev creek, letter O – from the Okhta, letter M – from the Murinsky creek

Optical properties of samples were analyzed in collected samples of water without dilution and diluted 10-fold with distilled water. For diluted samples signal of distilled water was subtracted from signal of diluted sample.

Optic density (D) spectra were obtained by spectrophotometer “SF–56” (OKB Spectr, Russia) in 1 cm cuvette. Values at selected wavelengths were presented in this paper, for example optical density at 254 nm (D_{254}).

Fluorescence spectra were obtained by analyzer “RF 5301 PC” (Shimadzu, Japan) at two excitation wavelengths 230 nm and 270 nm near to maximums of excitation spectra for humic substances and proteins. Fluorescence was registered at emission wavelengths from 220 to 650 nm (step 1 nm, slit width 5 nm). Later basing on data from optic density spectra fluorescence intensity ($I_{ex,em}$) was corrected for the inner filters effect according to the formulas (2) [32]:

$$\begin{aligned} I_{1and2f} &= I_{ex,em} \cdot k \\ k &= 10^{0.5(D_{ex}+D_{em})} \end{aligned} \quad (2)$$

where I_{1and2f} – corrected data, $I_{ex,em}$ – measured fluorescence intensity, k – multiplying correcting factor, D_{ex} – optical density at excitation wavelength, D_{em} – optical density at emission wavelength.

Specific electric conductivity of water (EC) was measured on sampling site by “HI 8713” (HANNA Instruments) with measurement error $\pm 5\%$.

On site measurement of fluorescence intensity was done by portable fluorimeter Fluorat 02-3M (Lumex, Russia) with a set of light filters using recommendations of manufacturer.

Approximation of Fluorescence Spectra

In order to understand influence of the left part of humic peak on fluorescence intensity of protein-like peak data processing is needed. In the most detailed way it includes signal correction on inner filter effects, elimination of scattering peaks, and other actions, which require additional data and programs.

For rough estimation the following data processing was done. Humic-like peak on fluorescence spectra at excitation wavelengths 270 nm could be easily approximated by Gaussian curve without subtraction of scattering peaks.

Humic-like peak on fluorescence spectra at excitation wavelengths 270 nm was approximated by modified Gaussian curve described by the formula (3)

$$I = \frac{m}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-x_0)^2}{2\sigma^2}\right] \quad (3)$$

where I – fluorescence intensity (in arbitrary units)

m – maximal value of I for humic-like peak, multiplied by $\sigma \cdot 2\sqrt{2\pi}$,

σ – sigma, standard deviation (in nm), x – emission wavelength (in nm),

x_0 – mean value of emission wavelength for humic-like peak (in nm).

Mean value x_0 of humic-like peak was determined as wavelength at maximal I in the emission wavelength range 400-500 nm.

Sigma was found from the formula (4) connecting full width at half maximum (FWHM) for Gaussian curve [33]:

$$FWHM = \sigma \cdot 2\sqrt{2\ln 2} \approx 2.355\sigma \quad (4)$$

where $FWHM$ – interval of wavelength (in nm) at half maximum of fluorescence intensity (in arbitrary units), σ - sigma in formula (3).

Spectra at excitation wavelength 230 nm are not suitable for such approximation because of scattering peak with maximum at emission wavelength 460 nm (it is produced by diffraction grid of excitation monochromator at doubled excitation wavelength). It does not allow to localize maximal I and determine mean value of emission wavelength for humic-like peak.

Program for calculation of approximated spectra was written in R programming language using IDE RStudio1.0.44 © 2009-2016 RStudio.

Results

Chemical Parameters of Water Samples

Results of chemical analysis and D_{254} of samples are given in Tables 1-3. Clean natural waters were collected from points #3 and 4 that were located close to each other, upstream from buildings, dump site and near swampy area with source of Kapraliev creek. Sample #3 was collected near the bank where water was still while #4 was taken several meters further from a place with small noticeable current. This explains higher concentrations of ions in sample # 3 due to longer interaction of water with ground and soil waters. In general waters from #3 and 4 had low content of TOC (about 10–14mgTOC/L), low concentrations of ions and EC (80–202 mkSm/cm). Values of TN (0.6–0.8 mgTN/L) and concentrations of ammonium-ion (0–0.14 mgN_{NH4+}/L) were the lowest among studied samples.

Downstream that place sample #2 was taken. There Kapraliev creek became wider and deeper and passed through dwelled area from which wastewater discharge was supposed. In sample #2 concentration of ions, TOC, EC and D_{254} were near the ranges observed upstream (in #3 and 4). However, concentrations of TN (about 4 mgTN/L) and ammonium (2 mgN_{NH4+}/L) were increased, indicating discharge of fecal wastewaters.

Samples # 7 and 9 were collected at the end of the Kaprailev creek. Sample #9 was taken just before the inflow of the creek to the Okhta. Concentrations of ammonium and TN in samples # 7 and 9 became higher than in previous ones (5–4 mgN_{NH4+}/L and 8.5–9 mgTN/L), EC also significantly increased (to 290–480 mkSm/cm) while TOC remained approximately at the same level (15 mgTOC/L), and D_{254} decreased a little. The results show that the creek had received additional polluted waters on its way. Significant part of dissolved pollutants belonged to ions of sodium and chloride, concentrations of which seriously increased to the end of the creek (sample #9), rising molar ratio of these ions to the maximal values in the Kapraliev creek (see Table 3).

Samples #5, 8 and 10 were collected from the Okhta. Sample #8 was collected near inflow of the Kapraliev creek (#9) upstream it and sample # 10 – downstream it. Sample # 5 was taken far before the inflow of the creek. It can be seen from the data that waters of the Okhta changed most after addition of waters from the creek. They slightly increased TN (from 4 to 5 mgTN/L), noticeable increased EC (from 210 to 260 mkSm/cm) and concentration of chlorides, provided two-fold increase of ammonium (from

approximately 1 to 2 mgN_{NH4+}/L). However, TOC remained the same and D₂₅₄ showed decrease (from 1.07 to 0.86) downstream inflow of the creek.

Table 1. General parameters of water samples

#	TOC, [mg/L]	COD, [mgO/L]	TN, [mg/L]	IC, [mg/L]	EC, [mkSm/cm]	D ₂₅₄
4	13.6	36	0.6	10.5	80	0.578
3	9.8	26	0.8	14.3	202	0.498
2	13.8	37	3.7	17.3	167	0.517
5	21.1	56	3.9	13.0	208	1.030
7	15.2	41	8.5	26.0	286	0.507
8	20.9	56	4.1	12.8	213	1.067
9	15.0	40	9.0	24.7	479	0.414
10	20.1	53	5.1	15.0	263	0.863
11	20.9	56	4.3	13.0	215	1.025
12	8.3	22	5.2	30.9	640	0.265
13	16.7	44	4.7	19.2	351	0.708

Table 2. Major ions concentrations (in mg/L)

#	NH ₄ ⁺	K ⁺	Na ⁺	Mg ⁺⁺	Ca ⁺⁺	Cl ⁻	SO ₄ ⁻⁻	HCO ₃ ⁻
4	0.0	0.8	3.6	3.4	10.5	2.2	1.9	53.1
3	0.2	1.6	11.1	4.3	17.7	11.4	13.9	72.8
2	2.6	1.7	6.6	4.8	22.0	6.0	6.7	88.2
5	1.8	3.0	14.2	4.4	18.4	12.6	11.9	65.8
7	6.8	3.3	13.3	5.7	24.4	12.9	10.9	132.1
8	1.5	2.3	10.9	3.2	11.8	10.0	9.3	65.1
9	5.4	2.7	22.0	5.9	22.5	45.1	8.9	125.7
10	2.6	2.5	13.0	3.8	14.6	17.7	11.3	76.4
11	2.2	3.1	14.2	4.0	15.0	11.2	10.5	66.3
12	3.2	5.8	51.7	8.4	38.4	59.1	29.4	157.3
13	2.8	4.3	28.1	5.7	23.6	26.2	15.9	97.7

Table 3. Molar fractions for cations and anions

#	NH ₄ ⁺	K ⁺	Na ⁺	Mg ⁺⁺	Ca ⁺⁺	Cl ⁻	SO ₄ ⁻⁻	HCO ₃ ⁻
4	0.00	0.04	0.27	0.24	0.45	0.07	0.02	0.91
3	0.01	0.03	0.42	0.15	0.38	0.19	0.09	0.72
2	0.12	0.03	0.24	0.16	0.45	0.10	0.04	0.86
5	0.07	0.05	0.43	0.13	0.32	0.23	0.08	0.69
7	0.20	0.05	0.31	0.12	0.32	0.14	0.04	0.82
8	0.08	0.06	0.45	0.13	0.28	0.19	0.07	0.74
9	0.14	0.03	0.45	0.11	0.26	0.37	0.03	0.60
10	0.11	0.05	0.44	0.12	0.28	0.27	0.06	0.67
11	0.09	0.06	0.45	0.12	0.28	0.21	0.07	0.72
12	0.05	0.04	0.58	0.09	0.25	0.37	0.07	0.57
13	0.07	0.05	0.53	0.10	0.25	0.30	0.07	0.64

The Murinsky creek (sample #12) is another polluted tributary of the Okhta which inflows downstream the Kapraliev creek. The Murinsky creek also added sodium chloride to waters of the Okhta, as it can be seen from the data for samples #11 (Okhta before inflow of the Murinsky creek) and #13 (Okhta after inflow of the Murinsky creek). Also it increased EC in the Okhta. TN and ammonium had close values in samples # 11, 12 and 13 (4-5 mgTN/L and 2-3 mg N_{NH4+}/L). TOC and D₂₅₄ decreased after inflow of the creek.

In all studied samples correlation between EC and TN at $p = 0.05$ was moderate ($r = 0.59$), between EC and TN/TOC – high ($r = 0.85$). Also increasing of EC and molar fractions of sodium-ion and chloride-ion were observed as a result of pollution. EC had high positive correlation with concentrations of studied ions (except for NH_4^+); values of r were from 0.83 to 0.98. Molar fractions of sodium and chloride had high positive correlations with EC ($r = 0.70$ for Na^+ , 0.86 for Cl^-), while molar fractions for bivalent cations and hydrocarbonates had negative values of r : (-0.72) for Mg^{++} and EC; (-0.70) for Ca^{++} and EC, (-0.81) for HCO_3^- and EC. These values of r were significant at $p < 0.05$. The same effect was detected during the study of other parts of the Okhta [22].

Fluorescence Parameters of Water Samples

In order to check applicability of fluorescent detectors in revealing pollution fluorescence spectra of waters were studied. We focused on fluorescence at selected emission wavelengths (see Figs. 3, 4): 300, 320 and 350 nm characteristic for protein-like fluorescence and 420 nm – for humic-like fluorescence. In order to take into account light absorption in cuvette at excitation and emission wavelength multiplying correcting factors were calculated. For undiluted samples multiplying correcting factor for fluorescence intensity $I_{\text{ex,em}}$ was in the range 2 – 18 for excitation at 230 nm and 1.1 – 4.5 for excitation at 270 nm. These values show great aberration of signal in cuvette. In this case using of undiluted sample in fluorimetric monitoring seems not informative. Also it can lead to misinterpretation of fluorimetric signal which can rise not only because of higher amount of fluorophores from pollutants but also as a result of increasing of water transparency.

For water samples diluted 10-fold multiplying correcting factor was 1.1–1.35 for excitation at 230 nm and 1.02–1.21 for excitation at 270 nm. Therefore we suppose that these uncorrected values could be suitable for water quality monitoring without data processing.

Some common patterns in spatial changing of $I_{\text{ex,em}}$ and chemical parameters (TOC, TN, EC) can be noted from Figures 3. In order to describe general trends correlation coefficients (r) were determined between pairs of optical and chemical parameters.

Optical density D at selected wavelengths (230, 254, 270, 320, 350, 420 nm) showed positive correlation with TOC with $r = 0.92 \dots 0.82$ (significant at $p < 0.05$). However in correlations with TN values of r were negative and for the studied set of data they were not statistically significant. Resembling tendencies were observed in previous study of the Okhta and the Murinsky creek [32]: correlation of D_{254} with TOC was positive, with TN – negative.

Noticeable correlations were found with TN or TN/TOC and the intensity of protein-like fluorescence for undiluted water samples. In all cases r for TN was lower (and sometimes significantly) than for TN/TOC. For undiluted samples intensity of fluorescence (excitation at 230 or 270 nm, emission at 300, 320, 350 or 420 nm) without signal correction showed positive correlation with TN/TOC with r from 0.65 to 0.84. One exception was with $I_{230,420}$ and TN/TOC where r was +0.30 (insignificant for $p < 0.05$). TOC and uncorrected $I_{\text{ex,em}}$ for undiluted samples showed negative correlation with TOC (r from -0.52 to -0.90).

Signal correction did not change much these tendencies for protein-like fluorescence in undiluted waters at excitation on 270 nm. Positive correlations were found between $I_{270,320}$ and TN/TOC or TN (r was 0.92 or 0.77 correspondingly), $I_{270,350}$ and TN/TOC or TN (r was 0.84 or 0.73 correspondingly). Weak negative correlation (r from -0.11 to -0.20, insignificant) was found between protein-like fluorescence and TOC. Humic-like fluorescence $I_{270,420}$ showed positive correlation with TN/TOC ($r = 0.14$, insignificant) and TOC ($r = 0.60$).

However, corrected fluorescence signal at excitation 230 nm for undiluted sample showed quite another pattern: moderate or strong positive correlation with TOC (r from 0.54 to 0.77) and weak or moderate negative correlation with TN/TOC (r was from -0.08 to -0.57).

Fluorescence intensity of diluted samples without signal correction showed only one valuable example of correlation: it was strong between TN/TOC and $I_{230,350}$ ($r = 0.84$).

Moderate or strong negative correlation was found between protein-like fluorescence (without signal correction) and TOC (r from -0.61 to -0.73). Humic-like fluorescence showed weak positive correlation with insignificant values of r .

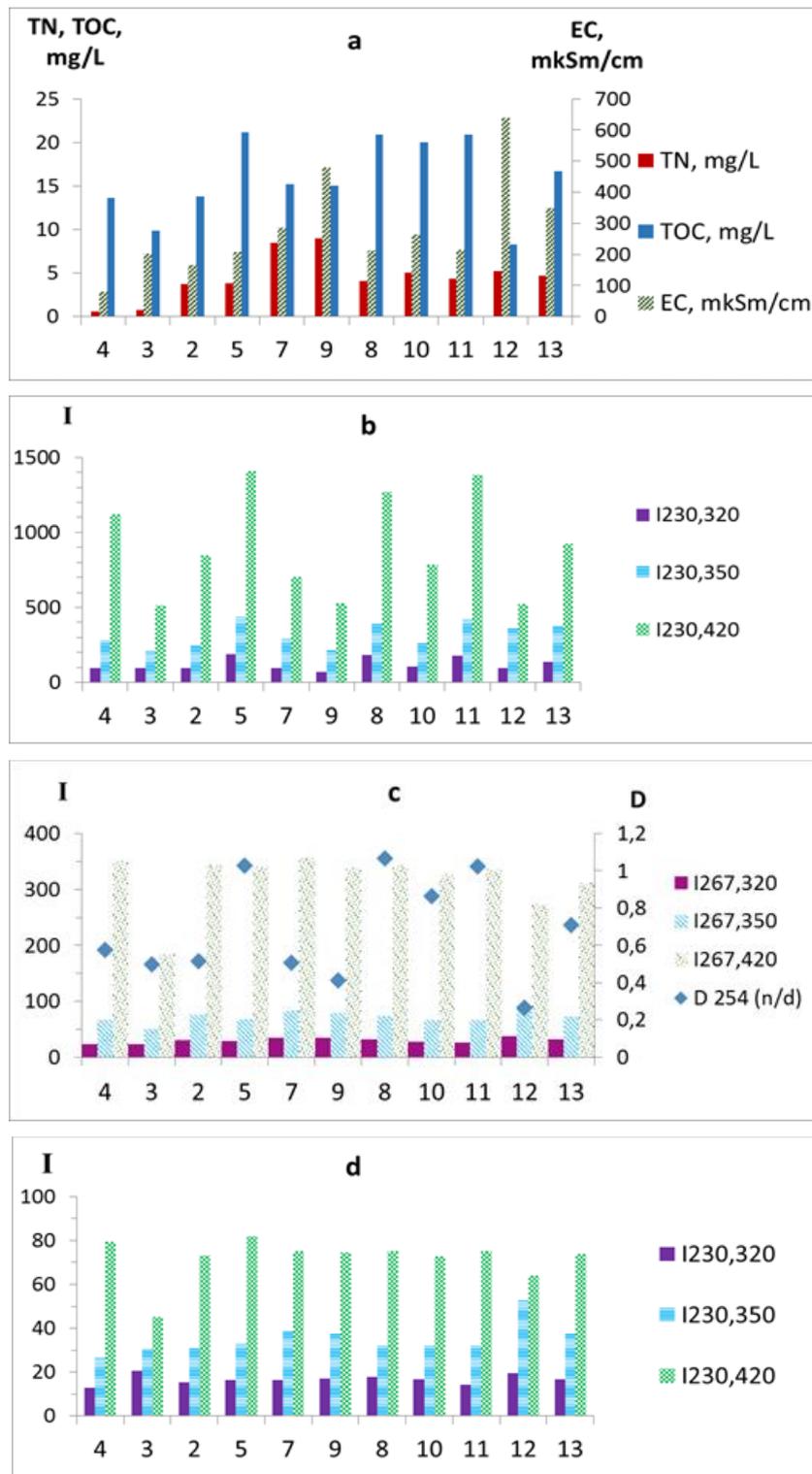


Figure 3. Chemical parameters of water samples (a). Examples of fluorescence intensities: b, c – undiluted samples without signal correction; d – diluted samples with signal correction

Fluorescence intensity of diluted samples with signal correction also showed only few examples of correlation. Positive correlation was found for the following pairs of parameters: $I_{230,350}$ and TN/TOC ($r = 0.83$), $I_{230,350}$ and TN ($r = 0.52$, insignificant at $p < 0.05$), $I_{230,420}$ and TOC ($r = 0.65$).

Such strong influence of signal correction and sample dilution on dependences between pollution and protein-like fluorescence means that concentration of fluorophores in undiluted water samples are too high and do not belong to the part where linear dependence between $I_{ex,em}$ and their concentration is observed. Moreover, increasing of uncorrected signal of protein-like fluorescence might be interpreted as

a sign of pollution while in fact it could be a result of decrease in D and not increase in concentration of fluorophores. However, wastewaters are able to decrease D of colored river waters as it was shown in [22] and in data of the present study. Thus increasing of uncorrected fluorescence signal in undiluted sample could be an indirect consequence of pollution.

These obtained results differ from tendencies found in previous study of the Oktha [22], where strong correlations were found in diluted samples between TN or TN/TOC and protein-like fluorescence (without signal correction) at all studied variants of excitation and emission wavelengths (excitation 230 or 270 nm, emission 300, 320 or 350 nm). In that study more samples were analyzed ($n = 30$), but ranges of TN, TOC and EC did not differ much from those of the present study. However $I_{ex,em}$ had varied in a wider range. For example in diluted samples (no correction) of $I_{230,350}$ had varied from 14 to 60 arbitrary units, $I_{230,4200}$ – from 26 to 93 arbitrary units, $I_{270,350}$ – from 5 to 21 arbitrary units, $I_{270,420}$ – from 13 to 48 arbitrary units [31]. In the present study the ranges are smaller: $I_{230,350}$ – from 24 to 48 arbitrary units, $I_{230,420}$ – from 40 to 70 arbitrary units, $I_{270,350}$ – from 7 to 10 arbitrary units, $I_{270,4200}$ – from 18 to 36 arbitrary units.

It can be seen from figures and tables that several values are very close to each other and the difference between them is explained by measurement error. However, tendencies of signal intensity changing with dose of pollutants are clearly observed.

Ratios of Fluorescence

On one hand wastewaters increase fluorescence intensity not only in protein wavelength range but also in the range of humic-like peak. On the other hand unpolluted waters can show high fluorescence intensity in protein-like range produced not by protein-like fluorophores (from wastewaters) but by the left part of humic-like peak of natural organic matter. In order to separate these two types of fluorescence rough estimation of humic-like fluorescence was done for uncorrected fluorescence spectra at excitation wavelengths 270 nm. Humic-like peak was approximated by Gaussian curve (see example in Fig. 4).

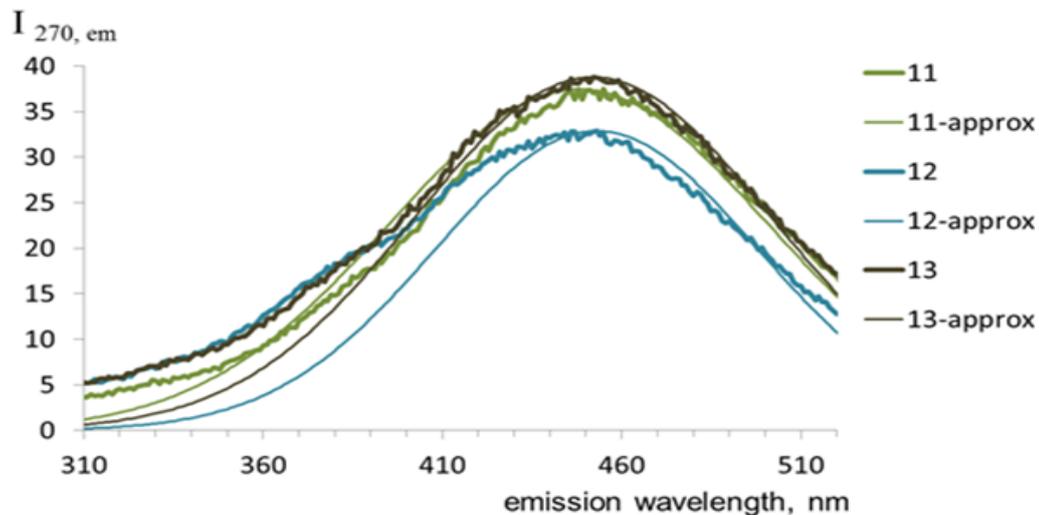


Figure 4. Example of humic-like peak approximation of by Gaussian curve for samples # 11–13. Fluorescence spectra are without correction

Results of approximation are summarized in Table 4. Differences between data from spectrum and approximated curve are shown for the studied emission wavelengths 320, 350 and 420 nm. In addition, data for 380 nm and 520 nm are shown. They are located almost symmetrical about maximums of humic-like peak (which is at 442-456 nm for undiluted spectra, 445-454 nm for diluted spectra). It is seen from the data that fluorescence of supposed left side of humic peak is rather significant.

Table 4. Results of approximation of humic peak on fluorescence spectra (uncorrected) at excitation wavelength 270 nm

emission wavelength, nm	difference, %	
	undiluted water	diluted water
320	39...80	57...93
350	10...59	11...76
380	-3...37	-10...52
420	-4...7	-10...12
520	9...17	12...19

In these circumstances ratio of protein-like to humic-like fluorescence could help to avoid misinterpretation of fluorimetric data. Fluorescence factor F showing this ratio was calculated by the formula

$$F_{ex, em1/em2} = \frac{I_{ex,em1}}{I_{ex,em2}} \quad (5)$$

where ex – 230 or 270 nm, $em1$ – 300, 320 or 350 nm, $em2$ – 420 nm.

Correlations of chemical parameters and fluorescence factors $F_{ex, em1/em2}$ were studied. Again, in contrast with the previous study of the Okhta [22], there were no significant correlations in diluted samples (with or without correction) with such markers of pollution as TN or TN/TOC.

In not diluted samples correlations between $F_{ex, em1/em2}$ (data with or without signal correction) and TN/TOC were observed with r from 0.34 (insignificant) to 0.75.

All types of $F_{ex, em1/em2}$ for undiluted and diluted samples with or without correction showed negative correlation with TOC with r from -0.19 to -0.85.

Discussion

Results in Tables 1–3 show that the Okhta and its tributaries (the Kapraliev creek and the Murinsky creek) were already polluted by wastewaters in Murino. The most significant signs of fresh pollution were increased concentrations of TN and ammonium in samples collected near buildings and houses. In these samples concentrations of ammonium were from 2.0 to 5.3 mgN_{NH4+}/L. This is higher than maximal allowable concentration (MAC) for water bodies in dwelled areas (1.5 mgN_{NH4+}/L) [34].

Typical concentrations of TN in unpolluted rivers of North-west of Russia are less than 1 mg/L, but in rare cases they could rise up to 6 mg/L [28]. Measured concentrations in samples of polluted waters were over these values and varied from 3.7 to 9.0 mgTN/L.

MAC for COD was also exceeded in most part of samples (30 mg/L in dwelled areas [35]). However COD and TOC did not increase significantly after pollution and in some places (after inflows of the Kapraliev creek and the Murinsky creek) they decreased. The same situation was with D_{254} that has high correlation with TOC. These results are in contrast to a number of studies where concentration of organic matter increased after wastewater discharge [36–37]. Lack of correlation between TN and optical density at 254 nm and other studied wavelengths (230–420 nm) demonstrate that these optical parameters could not be used to distinguish the fact of pollution.

Decrease of COD and optical density after pollution can be explained by high background concentrations of natural organic matter in the studied waters (COD can vary from 8 to 142 mgO/L in rivers of North-west of Russia [28]).

Concentrations of TN, ammonium and COD were lower than typical values for wastewaters. Average concentrations in St.Petersburg wastewaters were reported as about 30 mgTN/L, about 25 mgN_{NH4+}/L and about 300 mgO/L, correspondingly [40]. Lower values in polluted waters can be explained by partial treatment of wastewaters before discharge to rivers and surely by dilution of wastewaters in streams. Sedimentation of suspended organic matter in rivers also can significantly decrease COD because at least 50 % of COD in domestic wastewaters is present as suspended solids [38, 39].

It the present study values of EC, molar fractions of Na⁺ and Cl⁻ were higher in polluted waters of the Kapraliev creek and the Murinsky creek. The same situation was observed in our previous studies at other sampling sites of the Okhta [22, 40]. These data correspond to investigations where EC was proved

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to be a useful tool for express-monitoring of pollution of surface waters (and increase of it was followed by increase of NaCl and other pollutants) [16, 18, 36]. However, applicability of EC in monitoring should be tested on real waters because there could be some interfering factors such as high water mineralization [39], hour variation in wastewater flow rate and pollutants concentrations, seasonal changes in natural and wastewater properties.

In the present study fluorimetric data were obtained and analyzed in several variants in order to compare their informativity for water quality monitoring. Dilution of water and correction for inner-filter effects can seriously influence spectral data. Inner filter effect caused by light absorption in the sample could be negligible in some waters as in [17] therefore making sample dilution or data correction unnecessary for fluorimetric analysis. There was even a supposition that inner filter effects should be negligible in natural waters because dissolved organic matter concentrations rarely exceed 20 mgC/L in them [41]. In other studies water dilution was recommended to 1–15 mgTOC/L [12] or from 1 to 10 fold for river waters and 100 and more fold for untreated sewage and leachates [14]. In the present study water had not high concentrations of TOC from 9.8 to 21.1 mg/L and no need for sample dilution could be expected. However correlations between fluorescence signal and TN, TOC and TN/TOC in diluted (10-fold) and undiluted samples were quite different. Also strong influence of signal correction on correlations was observed. These results show that concentrations of fluorophores in undiluted water samples from Murino are too high and do not belong to the part where linear dependence between $I_{ex,em}$ and their concentration is observed. Moreover, increasing of uncorrected signal of protein-like fluorescence (marker of pollution) might be interpreted as a sign of pollution while in fact it could be a result of decrease in light absorption (and optical density) and not increase in concentration of fluorophores. However, in some cases wastewaters are able to decrease optical density of colored river waters as it was shown in [22] and in data of the present study. Thus increasing of uncorrected fluorescence signal in undiluted sample could be an indirect consequence of pollution.

In general results of the present study represent a situation where ability of fluorimetric method to reveal pollution is limited due to closeness of values to the natural variation in fluorescence spectra. We tested several possible fluorimetric parameters that showed strong correlations with concentrations of sewage pollutants, such as BOD₅, phosphates, nitrates, ammonium [7, 11, 12, 14]. In our streams only $I_{230,350}$ for 10-fold diluted sample could be recommended for pollution monitoring.

Our research group was the first who suggested studying correlations between concentration of TN or TN/TOC and $F_{ex, em1/em2}$. The last one is relative parameter showing ratio of protein-like fluorescence to humic-like fluorescence. For diluted samples correlations were not found in contrast with the previous our study of the Okhta [22].

Conclusions

Waters of suburban streams were studied in order to suggest express methods for revealing of pollution. The studied streams were supposed to be polluted with wastewaters from dwelled area.

In waters from several sampling points increased concentrations of ammonium were registered (up to 3.5 of MAC), confirming the fact of wastewater discharge. Pollution also resulted in increasing of TN, EC, decreasing of D (in the range 230–420 nm). Increasing of EC correlated with increasing of molar fraction of sodium and chloride ions in water.

Increase or decrease of TOC was registered after pollution. It can be explained by high natural background and sedimentation of part of organics from wastewater as suspended matter.

Valuable positive correlation between protein-like fluorescence and TN or TN/TOC were found only for $I_{230,350}$ in diluted water samples. In this case ability of fluorimetric method to reveal pollution is limited due to closeness of values to the natural variation in fluorescence spectra.

For water quality monitoring combination of EC and fluorimetry at excitation on 230 nm and emission on 350 nm are recommended.

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