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Changing of Cations Concentrations in Waters of Polluted Urban River

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Abstract. Water from urban river Okhta polluted with domestic and industrial wastewaters was investigated. Specific electric conductivity (k), molar concentrations of ions Na+, K+, Mg++ and Ca++, concentration of total nitrogen (TN) were measured in water samples. Increasing of k happened together with increasing of molar fraction of sodium-ion (R_{Na}) among all studied cations (and correspondingly decreasing of molar fractions of other cations). Good correlations were found between R_{Na} and TN (r = 0.67), k and TN (r = 0.84). The results support the idea of the leading role of wastewaters in changing of k and cations concentrations. Electric conductivity and R_{Na} could be used to distinguish between polluted and not polluted waters in the Okhta.

1 Introduction

Urban rivers are usually influenced by industrial and domestic wastewaters. In 2013 in St. Petersburg about 98.4% of wastewaters were accepted by city canalization system and delivered for treatment to waste water treatment plants. Amount of treated wastewaters was esteemed as 2.18 mln m^3/day [1]. However, water pollution remains possible because of untreated or poorly treated wastewaters discharged directly to rivers of the city in the frames of allowed limits. There is some evidence of underestimation of pollutants amount discharged by industrial enterprises in their annual official reports [2, 3]. Also emissions over allowed discharge limits and illicit disposal of liquid wastes from unknown sources through storm water or drainage canalization (which outlets open directly to rivers) still occur [3, 4]. Such emissions are harmful for fish and other aquatic organisms [5]. They also can influence on water quality at intakes of waterworks and demand additional treatment procedures for drinking water treatment [6 – 9].

It is important to use fast methods of water quality monitoring in order to detect pollution as soon as possible. This will help to find the source of pollution and prevent illicit discharge of wastewaters in future. However, it is difficult to control pollution of river Neva because of its high ability to dilute impurities from wastewaters. Its average flow rate is 80 km^3/year (about 220 mln m^3/day) [10]. Tributaries of the Neva are more vulnerable to pollution and can be more easily controlled because their total flow rate is rather lower (it forms about 2% of the Neva flow rate) [10].

The Okhta is a left-bank tributary of the Neva. It is considered to be the most polluted river in St.Petersburg [3] due to impurities from agricultural, municipal and industrial objects. According to

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official reports of enterprises city wastewaters contribute for about 20% of its flow rate [11]. This river was chosen for the current investigation.

In order to control water quality measurement of water specific electric conductivity (k) can be used. It takes very little time and can be done on site or by on-line monitoring devices. Electric conductivity has been investigated as marker of contamination from wastewaters discharges [12 – 16]. Specific electric conductivity is considered to be useful in providing screening of the pollution level [15, 16].

For natural surface waters in the North-Western part of Russia (to which the Okhta belongs) small or moderate concentrations of inorganic salts are usual [17]. This is explained by feeding of rivers mainly from snow and rain. Salts from the soil in their basins had been washed out during thousands of years with often rains and meltwaters. Also the significant part of rocks in that region has hardly washable crystal structure [10].

Calcium ions and hydrocarbonates are prevailing over other ions [17, 18] in this region. Sum of concentrations for the main ions responsible for electric conductivity of water (hydrocarbonates, sulfates, chlorides, nitrates, calcium, magnesium, sodium and potassium) in the Okhta vary in the range 60 –140 mg/L [17]. Concentration of dissolved solids (that include ions) in untreated domestic wastewaters is higher and is esteemed as 200 – 1000 mg/L [19, 20]. In St.Petersburg limits for total dissolved solids permitted for discharge to municipal canalization are 1000 mg/L [21]. These values suppose applying conductometry for revealing pollution with domestic wastewaters in the studied water objects.

Previous investigations of the Murinsky creek and the Okhta showed good correlation of water electric conductivity with concentrations of other pollutants characteristic for domestic wastewaters – total nitrogen, inorganic carbon, fluorimetric parameters [22, 23]. Aim of the present work was to study the role of several cations in formation of electric conductivity in polluted urban river Okhta.

2 Materials and Methods

2.1 Water Samples

Water samples were collected from the Okhta. Average flow rate of the Okhta was 5.18 m^3/s and sewerage inflow was esteemed as 1.36 m^3/s [11].

Sampling points were marked as O1 – O17. Outlets of wastewaters were localized according to map of canalization pipelines: several outlets between O10 and O11, O12 and O14. Presence of several outlets was confirmed visually during water collection (O11 and O12, O14 and O15). Scheme of sampling points is given at Fig. 1.

Water samples of about 1 liter were collected from July 2013 to March 2014. Three series of sampling were done. The bottles with the samples were stored in laboratory at +4...+6°C for several days in vertical position while suspended matter was sedimenting. The upper part of water was analyzed.

2.2 Chemical Analysis

Specific electric conductivity of water (k) was measured at the day of sampling by conductometer "HI 8713" (HANNA Instruments) at 20 °C with measurement error ± 5%. Other parameters were determined after storage of samples in the supernatant. Concentrations of inorganic carbon (IC) and total nitrogen (TN) were determined by analyzer "TOC Lvpn-TNM" (Shimadzu, Japan) with measurement error ± 10%. Concentrations of inorganic cations (potassium, sodium, magnesium, calcium) were determined by capillary electrophoresis by "Capel-103R" (Lumex, Russia) with measurement error ± 14%.

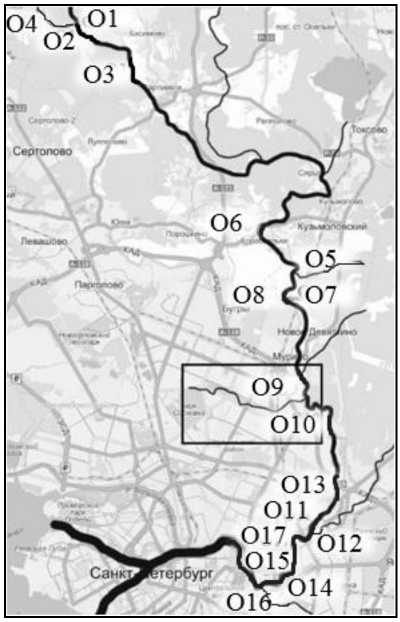

Figure 1. Scheme of sampling points at the Okhta. The Murinsky creek is shown in rectangular frame.

3 Results and Discussion

In order to esteem background values for natural (not polluted) waters of the Okhta data from [17] could be used. They include results of regular chemical analysis of water collected at various seasons from the Okhta before (upstream) St.Petersburg at observation station near village Novoye Devyatkino. Sampling point O7 of the present research is located near that station. Data in Table 1 show that during periods of low and high water flow rate concentrations of main ions changed not more than one order of magnitude [17].

Table 1. Ranges of main ions concentrations in the Okhta at various seasons in 1946-1965 [17].

Concentration	Ca^{2+}, (mg/L)	Mg^{2+}, (mg/L)	K^{+}+Na^{+}, (mg/L)	HCO_3^-, (mg/L)	Cl^-, (mg/L)	SO_4^{2-}, (mg/L)	NO_3^-, (mg/L)	NO_2^-, (mg/L)
Okhta	4.6 – 9.6	0.3 – 4.0	4.0 – 29.0	5.5 – 56.7	4.3 – 16.3	10.9 – 22.9	1.0 – 3.0	0.02 – 0.47

Table 2. Ranges of parameters of water samples from the Okhta in 2013-2014.

Concentration	Ca^{2+}, (mg/L)	Mg^{2+}, (mg/L)	K^{+}, (mg/L)	Na^{+}, (mg/L)	IC, (mg/L)	HCO_3^-, (mg/L)	TN, (mg/L)	k, (mkSm/cm)
Okhta	14 – 196	12 – 857	3 – 32	14 – 289	3 – 38	14 – 192	0.3 – 4.5	40 – 725

Chemical analysis of samples from the Okhta in the present work showed that concentrations of cations and specific electric conductivity of water (k) varied 1–2 orders of magnitude with time and place. Minimal and maximal values are given in Table 2. Maximal values in Table 2 were significantly higher than in Table 1, demonstrating influence of pollution from the city on water content. Selected data for the Okhta are shown at Fig. 2. It can be seen from Fig. 2 and other data that molar concentration of sodium was maximal among other inorganic cations.

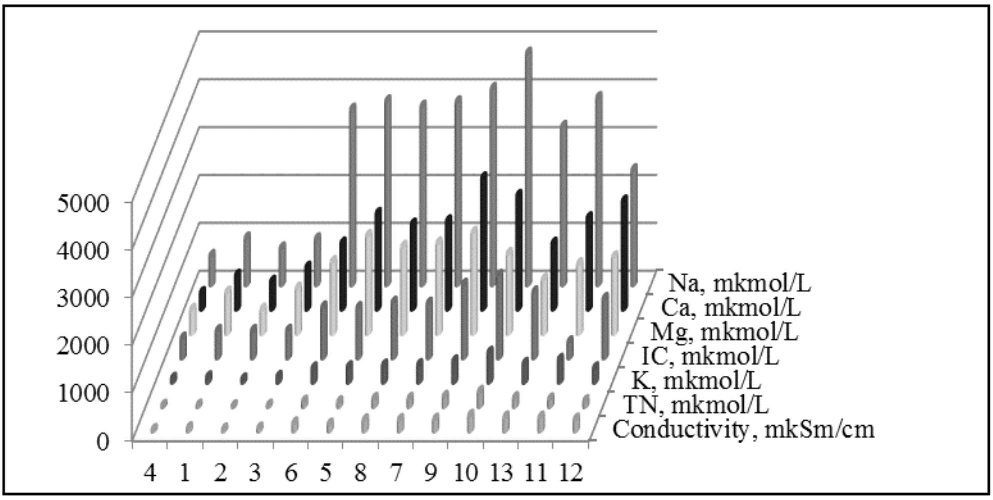

Figure 2. Parameters of the Okhta water samples from one series. Numbers of sampling points (on x axis) are placed in order of water flow.

In Table 3 molar ratios of four inorganic cations are shown for selected points of sampling. The ratios were calculated according to the formula

$$R_i = (C_i \cdot 100\%) / (C_K + C_{Na} + C_{Mg} + C_{Ca}) \quad (1)$$

where C_i - concentration of i-ion (mol/L), C_K , C_{Na} , C_{Mg} , C_{Ca} - concentrations of corresponding ions (mol/L).

Table 3. Ratios of inorganic cations (K, Na, Mg or Ca) molar concentration to sum of inorganic cations molar concentrations (in %) and specific electric conductivity k (in mkSm/cm) in water samples from the Okhta

Sample	September 2013					November 2013					March 2014				
	R_K	R_{Na}	R_{Mg}	R_{Ca}	k	R_K	R_{Na}	R_{Mg}	R_{Ca}	k	R_K	R_{Na}	R_{Mg}	R_{Ca}	k
3	4	33	33	30	68	-	-	-	-	-	3	27	37	33	54
6	4	53	22	20	175	-	-	-	-	-	4	47	24	25	141
8	5	48	24	23	238	7	41	24	29	122	-	-	-	-	-
7	5	48	24	23	244	7	41	23	29	123	-	-	-	-	-
9	5	44	23	29	252	6	33	23	38	143	4	37	25	34	186
10	7	51	18	25	334	4	58	16	22	725	4	53	18	24	263
11	6	50	19	25	296	5	39	25	32	229	4	42	21	32	252
12	5	37	24	34	254	6	46	20	28	231	4	40	25	31	239
15	-	-	-	-	-	5	44	22	29	295	5	44	24	27	281

It can be seen from Table 3 that increasing of water conductivity led to increasing of molar fraction of sodium and in most cases decreasing of molar fractions of other cations. This effect is supposed to be a result of pollution with sewage in which sodium usually prevails over other inorganic cations [24]. The most notable effect was between samples O3 and O6, O9 and O10. Sampling point O3 is placed in a forest and sampling points O6, O8, O7 – after big settlements. Sampling points O9 and O10 are situated near the boundary of St.Petersburg before and after inflow of the Murinsky creek, which is heavily polluted with domestic wastewaters. However, increasing of water conductivity could be explained also by changing of soils and ground water properties as it was done for river Volga in [25]. But for river Okhta we also observed decreasing of parameters downstream the river flow. It could be explained by dilution with less polluted water from other tributaries. In general the received data support the idea of the leading role of wastewaters in changing of water electric conductivity and cations concentrations for the studied river. Further analysis of anions concentrations could give more proof to this idea because chlorides are known to be dominating in domestic wastewaters [15].

In order to find another proof of this idea Pearson correlation coefficients (r) were calculated between parameters connected with cations concentrations and TN – a parameter characteristic for wastewaters. The values were the following: 0.84 for k and TN; 0.67 for R_{Na} and TN; 0.24 for R_K and TN; (–0.78) for R_{Mg} and TN; (–0.28) for R_{Ca} and TN. High positive values for k and R_{Na} demonstrate that electric conductivity and R_{Na} could be used to distinguish between polluted and not polluted waters in the Okhta.

4 Conclusions

Specific electric conductivity (k) and concentrations of four inorganic cations (potassium, sodium, magnesium, calcium) and total nitrogen (TN) were determined in water samples of urban river Okhta polluted with domestic and industrial wastewaters from St.Petersburg. Correlation coefficients (r) were calculated between parameters connected with cations concentrations and TN – a parameter characteristic for wastewaters.

The data obtained showed that increasing of k in samples happened together with increasing of molar fraction of sodium-ion (R_{Na}) and in most cases decreasing of molar fractions of other cations. Good correlations were found between R_{Na} and TN ($r = 0.67$), k and TN ($r = 0.84$).

In general the data support the idea of the leading role of wastewaters in changing of water electric conductivity and cations concentrations for the studied river. Electric conductivity and R_{Na} could be used to distinguish between polluted and not polluted waters in the Okhta.

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