

## COMBINED OPERATIVE INVESTIGATION OF WATER QUALITY IN THE VOLGA

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*In this paper we describe techniques for an express sampling and samples preparation for proximate chromatographic analysis of water under field conditions. Some results of measurements of the priority pollutants of water (chlorine organic pesticides, aldehydes and ketones, phenols and oil products) obtained from shipborne measurements are presented. Basic hydrochemical indices of water are determined and their quality assessed.*

Measurement of pollutants content in rivers and other water reservoirs is necessary for solving a lot of scientific and practical problems. At present, the degree of water pollution is under regular observation of a series of departmental laboratories as well as stationary posts of the State Service of Observation and Control (SSOC) located in the places of maximum anthropogenic rate. The results obtained during route measurements are very useful and interesting for collecting more data on water pollution and assessing water state from the ecological point of view.

An extensive study of quality of the Volga water had been conducted by scientists of the Scientific–Production Union (SPU) "Taifun" during the cruise Moscow–Nizhny Novgorod–Moscow, June 28 to July 8, 1993.

It should be noted that the water quality at that time featured a change from the spring flood to summer

medium level combined with rain freshet. It caused high water in the river resulted in noticeable decrease of water mineralization and, possibly, of anthropogenic pollution.

Twenty four samples of water taken in places of various anthropogenic rate (Fig. 1) have been analyzed for chlorine organic pesticides, aldehydes, and ketones by the methods developed in the SPU "Taifun". A series of hydrochemical parameters of water were analyzed by methods approved by SSOC,<sup>1</sup> whereas the content of oil products in water – by the methods improved also in the SPU "Taifun".<sup>2</sup> The scientific program included as well a quick analysis of samples of air for phenols, aldehydes, and ketones.

A quick obtaining of information was due to use of specially purposed quick methods of analysis of water samples as well as of fast–acting portable gas chromatograph.

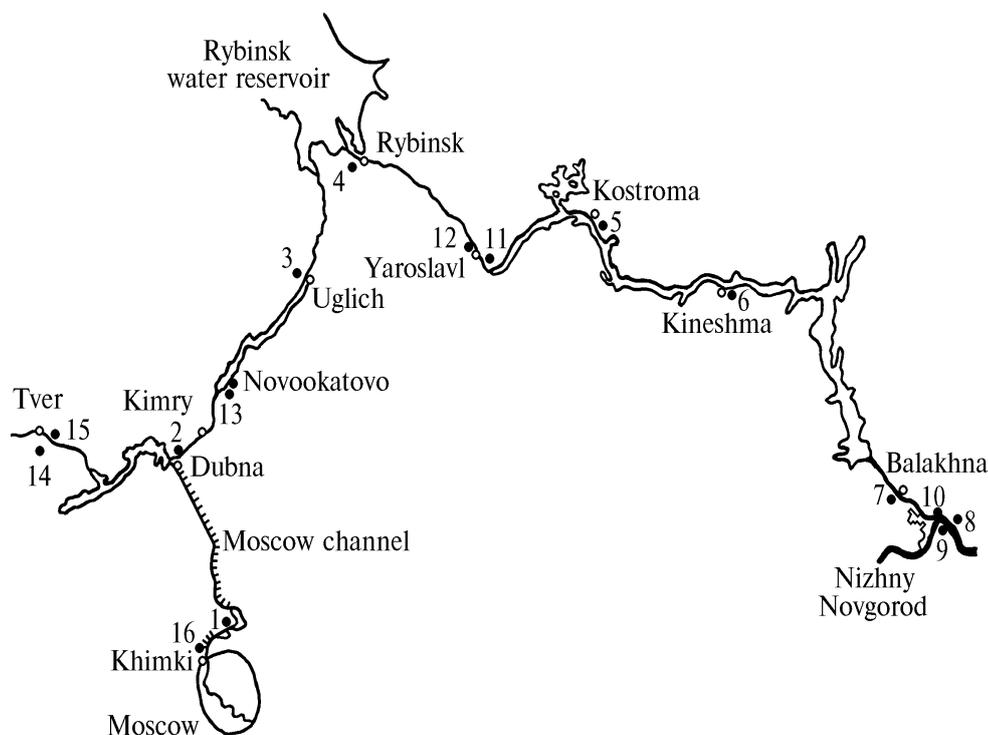


FIG. 1. Points of sampling.

## 1. INSTRUMENTATION AND EXPERIMENTAL TECHNIQUE

In order to perform a quick analysis of organic contaminants in compound subjects, a series of original methods were developed in the SPU "Taifun". They include a quick preconcentration of a sample (sorbing on extraction cartridges with chemically modified silica gel extraction), which allowed a selective concentration of pollutants under study and their subsequent analysis by the "EKHO-M" portable gas chromatograph with detector of electron capture. The constructional peculiarity of the chromatograph (polycapillary column containing about one thousand capillars, of 40  $\mu\text{m}$  i.d. and length of 120 mm coated with stationary phase SE-30) provided an efficient quick disintegration of a compound mixture in one or two minutes. An identification of individual components was performed by retention times. Concentration of pollutants in a sample was determined with reference to calibration charts made by standard solutions.

Such apparatus as device for pumping water samples through cartridges with sorbent, a field microextractor, and a container for storage and transportation of ampoules with necessary reagents were also used under field conditions during the expedition. All devices were designed in the SPU "Taifun". The use of the instrumentation enabled us to minimize the quantity of necessary operations and to automate them maximally. Preparation of samples took us about 15 minutes.

UV and IR spectroscopy methods had been used in the analysis of some pollutants. In that case, a specific prederivation (at phenols detection) or prepurification of a sample by column chromatography method (at oils detection) had been performed in order to increase selectivity of the methods.

Measurement of  $pH$  and nitrate ions was made with "Prazitronic" ionometer. Determination of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SiO}_2$  ions concentration had been also conducted during the expedition by the photometric method with "Spekol-11" spectrophotometer. Sampling of water had been performed with automatic bathometer both from the surface (5–20 cm depth) and the bottom layers.

## 2. IDENTIFICATION OF CHLORINE ORGANIC PESTICIDES IN WATER

At present the use of pesticides (the chemical means for protection of plants from pests) remains still in progress. Its consumption rate is about 50 g per hectare.<sup>3</sup>

Due to high efficiency of chlorine organic pesticides (COP) they are the most popular among the available ones. The best known representatives of COP are insecticides DDT (is not in use now) and hexachloran (a compound of hexachlorocyclohexan isomers (HCCH)). One principal source of the pesticides ingress into water is a surface effluent from the water basins, particularly in flood and raining periods. According to experimental data, the effluent coefficient of COP is equal to tenth parts of a percent.<sup>3</sup>

A half-life of the majority of COP is about 1.5 year (15 to 20 years for DDT). It means, that a large share of

DDT being produced up to the middle of 80s (about  $3 \cdot 10^6$  t) still remains invariant in the environment or presents there even in more dangerous metabolic form, for example, as hexachlorbenzene (HCB).<sup>4</sup>

The values of maximum permissible concentration (MPC) of COP in water is 0.02 mg/l for HCCH ( $\alpha$  and  $\gamma$ ), 0.05 for HCB, and 0.1 mg/l for DDT.<sup>6</sup>

To measure the COP concentration in water, a quick method was used based on preconcentration of COP on DIAPAK  $\text{C}_{16}$  extraction cartridges followed by elution of the concentrated compounds from the sorbent by hexan, and an analysis of the eluate with the portable gas chromatograph. The chromatographic analysis requires the following conditions: 175°C temperature and 100 s recording time.

The limit of COP identification with the chromatograph detector is 30 pg and  $1.1 \cdot 10^{-4}$  mg/l in a sample of water of 450 ml volume, what is significantly lower than the MPC level.

The measurement results of COP content in water (surface water) are shown in Table I. The concentration of  $\alpha$  – HCCH and HCB in water samples is seen to be not higher than the MPC level in all cases. The values of  $\gamma$  – HCCH (lindane) concentration obtained near Yaroslavl (bottom water) and Tver correspond to the MPC level. Values of DDT concentration significantly exceed the MPC level in water samples taken near Nizhny Novgorod, Rybinsk, Yaroslavl, and Kostroma cities as well as in Oka water. It may be explained by longer life time of DDT in the environment. The maximum observed concentration of DDT – 0.110 mg/l ( $\sim 6$  MPC) in water samples from Oka river (Nizhny Novgorod region) may also be associated with more area of the water basin.

## 3. DETECTION OF FORMALDEHYDE AND ACETALDEHYDE IN WATER AND AIR

Aldehydes and ketones fall in the category of the main pollutants. They are usual components of exhausts of car engines and boilers. As well they are used as intermediate products in manufacturing of plastics, rayons, and so on. A great deal of aldehydes and ketones is formed from different hydrocarbons as the result of chemical and photochemical reactions in the regions with oil and gas plants.<sup>5</sup> Many of these compounds are very toxic. The most toxic among them are formaldehyde and acetaldehyde,<sup>6</sup> the MPC value of which for water is 0.01 (formaldehyde) and 0.2 mg/l (acetaldehyde).

A field quick method of detection of aldehydes and ketones in water and air as 2,4–dinitrophenylhydrazons by means of portable gas chromatograph had been developed in the SPU "Taifun".

Identification of formaldehyde and acetaldehyde in air followed their chemisorptional preconcentration on DIAPAK–silica gel extraction cartridges impregnated by saturated solution of 2,4–dinitrophenylhydrazons in acetonitril. The air had been drawn through the extraction cartridge at the rate of 1 liter/min during 10–20 minutes. When extracting the formed aldehyde hydrazons had been eluted by 5 ml acetonitril followed by analysis of the organic phase with EKHO–M gas chromatograph.

TABLE I. COP concentration in samples of water.

N	Date, time	Distance from Moscow, km	Reference place	COP concentration mg/l				Water type
				$\alpha$ -HCCH	HCB	$\gamma$ -HCCH	DDT	
1	28.06 20.30	18	Klyazma water reservoir, Pirogov arm	n.d.*	n.d.	n.d.	n.d.	Surface
2	29.06 08.05	125	Dubna, on the beam	0.010	0.007	0.010	0.019	- > -
11	30.06 07.00	470	Yaroslavl, cargo berth	0.008	0.024	0.029	0.055	Bottom
12	30.06 09.30	482	Yaroslavl, en route	n.d.	0.026	n.d.	0.030	Surface
5	30.06 17.00	555	Kostroma, on the quay	0.008	0.035	n.d.	0.072	- > -
7	01.07 11.00	830	Balakhna, in the center of the quay	0.010	0.009	n.d.	0.050	- > -
8	01.07 13.30	861	Nizhny Novgorod, the Volga	n.d.	n.d.	n.d.	0.009	Bottom
9	02.07 10.00	861	Nizhny Novgorod, the Oka	n.d.	0.034	n.d.	0.110	Surface
10	02.07 19.15	861	Nizhny Novgorod, opposite the Strelka, the Volga	0.008	n.d.	n.d.	0.047	Surface
4	04.07 23.15	368	Rybinsk, upstream the locks	0.009	0.024	0.009	0.094	Surface
14	06.07 10.00	233	Tver, 30 m from the bank	n.d.	0.018	0.020	0.054	Bottom
15	06.07	233	Tver, middle of the Volga	0.009	0.015	0.020	0.048	Surface

Note: \* n.d. —not detected, i.e., COP content is lower the detection limit.

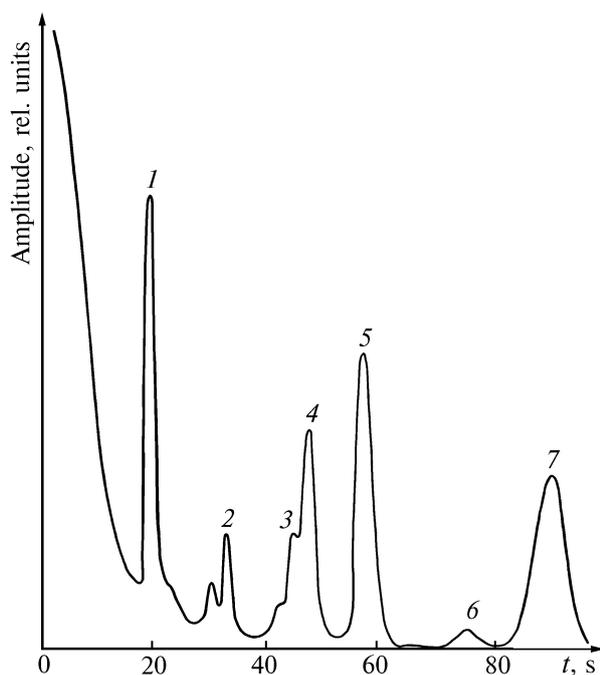


FIG. 2. Chromatogram of mixture of aldehydes and ketones hydrazones. EKHO chromatograph: 1 — formaldehyde; 2 — acetaldehyde; 3 — acetone; 4 — propionaldehyde; 5 — isobutyric aldehyde; 6 — isovaleric aldehyde; and, 7 — crotonaldehyde.

When analysing water samples the solution of 2,4-dinitrophenylhydrazine in 2M HCl had been added to 100 ml sample followed by hydrazones extracting by 2 ml toluene.

The extract was chromatographically analyzed (see Fig. 2) under the following conditions: 175°C temperature and 50 s recording time. Detection range in the chromatograph detector was from 25 to 50 pg and in water of 100 ml volume it was  $1 \cdot 10^{-4}$  mg/l (formaldehyde) and  $2 \cdot 10^{-4}$  mg/l (acetaldehyde), what was significantly lower than the MPC level.

The data on concentrations of formaldehyde and acetaldehyde are presented in Table II.

An excess of formaldehyde concentration above the MPC level (1.2–2 fold) was observed in the half of water samples and its most concentration (0.025 mg/l) had been found near Yaroslavl. Concentration of formaldehyde in bottom water was a bit higher than in the surface one. Probably, the source of it was a destruction of organic pollutants accumulated in the bottom sediments. Concentration of acetaldehyde was not higher than the MPC level in all cases.

The data on formaldehyde concentration in air are presented in Table III. As seen from the Table III, the excess above the MPC level (average daily norm is  $0.012 \text{ mg/m}^3$  for formaldehyde<sup>6</sup>) was observed practically in all cases. High concentration of formaldehyde in air can be associated with its direct ejection from anthropogenic sources or be a result of photochemical processes.<sup>7</sup> The elevated concentration of formaldehyde (19 average daily values of MPC) was most conspicuous near Yaroslavl. It may be concerned with powerful oil-refining and gas-processing plants in Yaroslavl as the east wind blew from the Yaroslavl industrial region during sampling in the dock.

TABLE II. Aldehydes concentration in samples of water, mg/l.

N	Date, time	Distance from Moscow, km	Reference place	Formaldehyde	Acetaldehyde	Water type
1	28.06 20.30	18	Klyazma water reservoir, Pirogov arm	0.004	0.001	Surface
2	29.06 8.05	125	Dubna, on the beam	n.d.*	0.002	– ” –
3	29.06 19.10	270	Uglich, on the quay	n.d	0.002	– ” –
4	30.06 10.00	378	Rybinsk, on the beam of cathedral	0.016	0.001	– ” –
5	30.06 17.00		Kostroma, on the quay	0.012	n.o.	– ” –
6	30.06 23.45	663	Kineshma, on the quay	0.009	0.005	– ” –
7	1.07	830	Balakhna, in the center of the quay	0.013	0.002	– ” –
8	1.07 13.30	861	Nizhny Novgorod, the Volga	0.002	n.o.	Bottom
9	2.07 10.00	861	Nizhny Novgorod, the Oka	0.012	0.001	Surface
10	2.07 19.15	861	Nizhny Novgorod, opposite the confluence, the Volga	0.018	0.007	Surface
11	4.07 8.20	482	Yaroslavl, cargo berth	0.025	0.001	Bottom
12	4.07 18.25	475	Yaroslavl, on the quay	0.012	0.008	Surface
13	5.07 9.30	173	Novookatovo, on the quay	0.016	0.005	– ” –
14	9.30 6.07	233	Tver, in 30 m from the bank	0.002	0.001	Bottom
15	6.07	233	Tver, in the middle of the Volga	0.005	0.01	Surface

Note : \* n.d. – not detected, the aldehydes content is lower the detection limit

TABLE III. Formaldehyde concentration in air.

N	Sampling place	Concentration, mg/m <sup>3</sup>
5	Kostroma (on the quay)	0.060
6	Kineshma (on the quay)	0.060
7	Balakhna (in the centre of town)	0.050
8	Nizhny Novgorod (on the quay)	0.002
12	Yaroslavl (on the quay)	0.220
14	Tver (30 m from the bank )	0.040

#### 4. DETERMINATION OF TOTAL CONCENTRATION OF PHENOLS IN WATER AND AIR

Determination of total concentration of phenols had been performed spectrophotometrically based on measurement of optical density of indophenol solutions, which had been formed as the result of reaction of phenols with 4-aminoantipirin in the presence of ammonium persulphate as the oxidant. The method gave a possibility to determine the total concentration of one-

atom phenols excluding a series of its paraderivatives.<sup>8</sup> In order to increase sensitivity of the method, a preconcentration of the phenols had been performed by extracting them by organic solvent from samples of water or by means of DIARAK C<sub>16</sub> extraction cartridges impregnated by alcoholic solution of lye. The method required simple instrumentation, for example, portable KFK–2 colorimeters. A quick variant of the samples preparation was also elaborated in the SPU "Taifun".

The phenols from the water samples (about 1 liter) had been selectively concentrated by butylacetate extracting them from accessory organic pollutants followed by lye reextracting. The lye reextract was added to reagent and solvent. After that an optical density of the solutions had been measured photometrically relative to a reference solution using the KFK–2 colorimeter with 490 nm colour filter (an idle experiment). The detecting limit was 0.0001 mg/l (in water the MPC value is 0.001 mg/l).

Results of phenols detection in water are presented in Table IV. As seen from Table IV, the phenols concentration in all samples is lower than the MPC level.

TABLE IV. Total concentration of phenols in samples of water.

N	Date, time	Sampling place	Concentration, mg/l	Water type
16	28.06 18.15	Khimki water reservoir	0.0002	Surface
1	28.06 20.30	Klyazma water reservoir, Pirogov arm	n.d.*	— " —
2	29.06 8.05	Dubna, on the beam	0.0007	— " —
3	29.06 19.10	Uglich	n.d.	— " —
4	30.06 1.00	Rybinsk, opposite the cathedral	0.0007	— " —
12	30.06 9.30	Yaroslavl, en route	0.0003	— " —
12	30.06 10.00	Yaroslavl, en route	0.0003	Bottom
5	30.06 17.00	Kostroma, at moorings	0.0007	Surface
6	30.06 23.45	Kineshma, opposite the town	0.0005	— " —
7	1.07 11.00	Balakhna	0.0004	— " —
8	1.07 13.30	Nizhny Novgorod, the Volga	n.d.	Bottom
9	2.07 10.00	Nizhny Novgorod, the Oka	0.0003	Surface
10	2.07 19.15	Nizhny Novgorod, opposite the confluence	n.d.	Surface
14	6.07 10.00	Tver, 30 m from the bank	0.0001	Bottom
15	6.07 18.45	Tver, in the middle of the Volga	0.0005	Surface

Note: \* n.d. — not detected, the phenols content is lower the detection limit.

When analyzing the phenols concentration in air, the sampling (and simultaneous concentrating) of the samples had been performed using the DIAPAK C<sub>16</sub> extraction cartridges impregnated by 0.1 % solution of NaOH in ethyl alcohol. The atmospheric air had been pumped through the impregnated cartridges at rate 1 liter/min during 10–20 minutes. Then the sorbates were eluted from the cartridge by ethyl alcohol. The obtained eluate was added to reagent and solvent and then measured photometrically (as it was described above).

Table V presents the measurement results of phenol concentration in air. In two cities — Tver and Yaroslavl the obtained values of concentration were lower than the average daily MPC level (average daily MPC is 0.003 mg/m<sup>3</sup>). Significant excess of phenols concentration was observed in Balakhna town. It may be explained by large cellulose plants in the town and the corresponding direction of wind.

TABLE V. Phenols concentration in air, mg/m<sup>3</sup>.

N	Date, time	Sampling place	Concentration (mg/l)
5	30.06 17.00	Kostroma (mooring)	0.012
6	30.06 23.45	Kineshma, opposite the town	0.026
7	1.07 11.00	Balakhna, opposite the town	0.055
8	2.07 10.00	Nizhny Novgorod, at moorings	0.011
12	30.06 10.00	Yaroslavl, en route	0.006
14	6.07 10.00	Tver, on the quay	0.003

## 5. TOTAL CONCENTRATION OF OIL PRODUCTS IN WATER

Total concentration of oil products in water had been determined by IR spectroscopy method under laboratory conditions. Such measurements were impossible to be performed during the cruise because of absence of the necessary mobile instrumentation.

In the course of the expedition an organic phase (5 ml tetrachlormethane) was extracted from samples of water of 0.5 liter volume and transported to the laboratory of the SPU "Taifun".

In the laboratory the organic extract after centrifuging and drying with Na<sub>2</sub>SO<sub>4</sub> was cleared from interfering components by means of column chromatography on aluminium oxide.

The oil products concentration was determined by measuring their absorption within the IR spectral range (analytical frequency of 2924 cm<sup>-1</sup>) relatively the reference solution (idle experiment) with IFS 113 BRUKER spectrometer. The detection limit was 20 µg/l.

The oil product concentration had been determined against a calibrating chart. The chart was made using a standard mixture consisted of 37.5% hexadecane, 37.5% isooctane, and 25% benzene prepared according to RE 52.107183–89.

Results of analysis show (Table VI) the total concentration of oil products in samples of water taken near river ports to be twice as large as the MPC level (in water the MPC value is 0.3 mg/l for oil products<sup>6</sup>).

TABLE VI. Oil product concentration in samples of water.

Sampling place	Concentration (mg/l)
Khimki water reservoir, surface	0.6
Uchinsk water reservoir, surface	0.3
Dubna, surface	0.5
Uglich, surface	0.7
Rybinsk, surface	1.0
Yaroslavl, surface	0.9
Yaroslavl, bottom	0.8
Kostroma, surface	0.9
Kineshma, surface	0.8
Balakhna, surface	1.0
N. Novgorod, surface	0.5
N. Novgorod, bottom	0.4
the Oka, surface	1.3
Tver, surface	2.9
Tver, bottom	0.7

## 6. HYDROCHEMICAL INDICES OF WATER QUALITY

The water of the Volga all over the length belongs to the hydrocarbonate class of the second type. Its chemical composition changes along the river length under the affect of its tributaries' water. The influence of underground waters is evidently weak because of significant excess of the Volga flow rate over them. The natural hydrochemical regime of the Upper Volga had been changed to some extent due to constructing of a series of water reservoirs.

The water of the Upper Volga is slightly mineralized (about 100 mg/l), what is characteristic of rivers and lakes of marsh type. Down the confluence of the Volga and the Selizharovka rivers the mineralization of the Volga water increases reaching 180–200 mg/l in summer time. Significant predominance of ion  $\text{HCO}_3^-$  over all others as well as comparatively low concentration of  $\text{SO}_4^{2-}$  and still lower one of  $\text{Cl}^-$  is peculiar to chemical composition of the Upper Volga water. The water is soft, its hardness is only 2–2.5 mg equiv/l. Down the Upper Volga, before its confluence with the Oka mineralization is 180–220 mg/l in summer, 300–320 mg/l in winter, and 80–100 mg/l at spring flood.<sup>9</sup>

Hydrochemical indices of the water are presented in Table VII. The table shows the total mineralization of water to change from 97 to 207 mg/l over the river length. Water is soft, its average hardness is 2.6 mg equiv/l.

Mineralisation of the Oka water is higher (324 mg/l), its water is of medium hardness (5.4 mg equiv/l).

The analysis of concentration of biogen elements, particularly, the nitrites and nitrates ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ) is of the most interest, as they are important sanitary–toxicological characteristics of water. Seasonal amplitude of the pointed ions may also be an eutrophic characteristic of water as well as to demonstrate the degree of its pollution with organic nitrogenic matters, which contain in sewages of different origin. Besides, higher concentration of ammonium ions in water indicates "fresh" pollution and the same of nitrates points out polluting in the past.<sup>1</sup>

An analysis of water samples has shown nitrate ions concentration to be lower than 0.5 mg N/l excluding the samples taken near Kalyasin (6.5 mg N/l) and from the Oka, where it was at the MPC level (9.0 mg N/l). Taking into account the fact, that presence of nitrates inside surface water is primarily connected with intrinsic processes in water reservoirs, mainly, with the nitrification process, and that the nitrates concentration is minimum at the vegetation period, their high concentrations should be associated with industrial and domestic sewages.

This suggestion may be also confirmed by high concentration of ammonium ions in the same samples (1.04 mg N/l near Kalyasin and 0.82 mg N/l in the Oka) at the MPC level of 0.39 mg N/l, and nitrite ions of 0.01 and 0.029 mg N/l, respectively, at the MPC level of 0.02 mg N/l. The nitrite ions concentration at the MPC level was also detected in a series of water samples, what indicates the water pollution and intense process of decomposition of organic residues. An elevated concentration of ammonium ions (higher than the MPC level) was detected almost in all samples of water under analysis. It may be caused, first, by processes of biochemical degradation of protein matters, second, by surface flows and precipitations, where  $\text{NH}_4^+$  ions often

TABLE VII. Indices of quality of the Volga water by main salt-forming components.

N	Sampling place	pH	Mineral form of nitrogen, mg N/l			SO <sub>4</sub> <sup>2-</sup> , mg/l	Cl <sup>-</sup> , mg/l	HCO <sub>3</sub> <sup>-</sup> , mg/l	PO <sub>4</sub> <sup>3-</sup> , mgP/l	SiO <sub>2</sub> , mgSi/l	Ca <sup>2+</sup> , mg/l	Mg <sup>2+</sup> , mg/l	Mineralization, mg/l	Oxidability, mg O <sub>2</sub> /l
			NH <sub>4</sub> <sup>+</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>									
1	Tver <sup>1</sup>	7.5	0.30	0.009	0.5	4.5	1.9	90	0.006	1.4	32	10.0	139	8.3
2	Tver <sup>2</sup>	7.5	0.45	0.004	0.5	4.3	2.2	90	0.003	1.3	32	12.0	141	—
3	Khimki water reservoir	7.8	0.34	0.015	0.5	24.0	6.3	98	0.030	1.6	32	10.0	171	8.7
4	Klyazma water reservoir	7.9	0.20	0.007	0.5	8.3	3.5	97	0.035	1.2	32	10.0	151	—
5	Dubna	7.9	0.42	0.007	0.5	8.0	3.5	105	0.013	0.9	32	7.0	156	9.1
6	Kalyasin	7.9	1.04	0.010	6.5	24.5	4.3	110	0.003	1.4	32	15.0	207	18.1
7	Uglich	7.9	0.19	0.030	0.5	9.5	3.2	97	0.019	2.3	32	12.0	154	7.5
8	Novookatovo	7.5	0.53	0.011	0.5	16.5	2.4	115	0.001	2.2	36	8.5	179	—
9	Rybinsk	8.0	0.97	0.013	0.5	9.8	3.0	90	0.004	2.4	32	10.0	146	7.4
10	Yaroslavl <sup>1</sup>	8.0	0.80	0.016	0.5	12.0	3.0	80	0.011	0.8	32	7.0	115	—
11	Yaroslavl <sup>2</sup>	7.9	0.42	0.020	0.5	17.0	3.4	85	0.015	1.0	40	2.4	148	—
12	Kostroma	7.8	0.57	0.016	0.5	13.0	3.7	90	0.013	1.0	32	10.0	149	7.2
13	Kostroma river	7.8	0.50	0.014	0.5	7.1	4.0	90	0.023	1.1	40	5.0	147	—
14	Volgorechensk	7.8	0.62	0.022	0.5	14.6	4.8	90	—	1.1	40	10.0	160	7.0
15	Ples	7.9	0.60	0.020	0.5	17.0	4.1	85	0.016	1.1	36	12.0	155	6.5
16	Kineshma	7.9	0.62	0.017	0.5	16.0	4.3	87	0.003	1.1	32	10.0	160	10.2
17	Yurievets	7.9	0.51	0.009	0.5	17.0	5.1	105	0.019	1.1	40	10.0	173	7.4
18	Chkalovsk	8.7	0.31	0.005	0.5	13.4	2.1	85	0.001	1.4	28	10.0	139	9.3
19	Balakhna	7.9	0.44	0.010	0.5	13.3	1.6	67	0.004	1.8	24	2.4	109	9.3
20	N. Novgorod the Volga <sup>1</sup>	7.3	0.68	0.020	0.5	6.0	2.7	67	—	1.7	28	0	104	10.6
21	the Volga <sup>2</sup>	7.1	0.45	0.010	0.5	7.5	2.9	60	0.013	1.6	24	2.4	97	12.8
22	the Oka	7.6	0.82	0.029	9.0	34.5	24.5	177	0.013	1.6	72	15.0	354	5.4
	MPC (fish form)	6.0–8.0	0.39	0.020	9.0	100	300	—	0.5	—	180	40	1000	7.0

Note: <sup>1</sup> – surface sampling;  
<sup>2</sup> – bottom sampling.

predominate over others, and, at last, by their presence in domestic and industrial sewages. As the expedition has worked during the period of intense surface effluents and rains, then just that very way of NH<sub>4</sub><sup>+</sup> ions ingress into water reservoirs seems to be predominant. That suggestion may be also confirmed by lower concentration of NH<sub>4</sub><sup>+</sup> ions in bottom water.

The content of oxidable organic matter in water, mainly, humic one, can be judged from the degree of permanganate oxidation (see Table VII). Oxidability of surface water changes with seasons and depends on physico-geographical location of the water reservoir. In the freshet period the oxidability increases because of ingress of organic matter from the water system round the river. So, if the average oxidability of water samples from the Volga is 8.0 mg O<sub>2</sub>/l, what can be taken as natural background, then its higher magnitude near Kalyasin, Kineshma, and Nizhny Novgorod cities points to pollutant ingress together with domestic waste.

### CONCLUSION

The following inferences may be resulted from the investigations of air and water conducted during the cruise Moscow—Nizhny Novgorod—Tver—Moscow:

1. The quick methods of sampling, sample preparation, and analysis of samples of air and water, developed in the SPU "Taifun", as well as portable analytical instrumentation enabled us to conduct complex measurements of organic pollutants concentration and indices of water quality.

2. The conducted measurements of concentration of the priority organic pollutants: chlorine organic pesticides, aldehydes, phenols, and magnitude of oil spillages in the Upper Volga have shown the water taken near Yaroslavl, Rybinsk, and Nizhny Novgorod to be the most polluted with the above mentioned ingredients.

3. According to its hydrochemical indices the Upper Volga may be classified as the polluted dirty river, not yielding the sanitary-toxicological standards by concentration of ammonium ions. The most severe anthropogenic effect was detected in the regions of Kalyasin, Rybinsk, and Nizhny Novgorod. The obtained data allow us to classify the Oka water as dirty and remarkably affecting the state of the Volga water.

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