ENVIRONMENTAL
POLICY

Alexander V. Zhulidov, Richard D. Robarts, Robert M. Holmes,
Bruce J. Peterson, Juha Kämäri, Jarmo J. Meriläinen and John V. Headley

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Zhulidov, Alexander, V., South Russian Regional Centre for Preparation and Implementation of International Projects, 200/1 Stachki av., office 301; 344104 Rostov-on-Don, Russia,

Robarts, Richard, D., UNEP GEMS/Water Programme, Environment Canada, 11 Innovation Blvd., Saskatoon, SK, S7N 3H5, Canada,

Holmes, Robert, M. and **Peterson**, Bruce, J., Holmes, Robert, M., Marine Biological Laboratory, Woods Hole, Massachusetts, USA,

Kämäri, Juha, Finnish Environment Institute, P.O. Box 140, FIN-00251 Helsinki, Finland

Meriläinen, Jarmo, J., Institute for Environmental Research, P.O. Box 35 (YAD) FIN-40014 University of Jyväskylä, Finland, and

Headley, John, V., National Water Research Institute, Environment Canada, 11 Innovation Blvd., Saskatoon, SK, S7N 3H5, Canada

Julkaisu on saatavana myös Internetistä
http://www.ymparisto.fi/palvelut/jukaisu/elektro/sy620/sy620.htm

Abstract

Monitoring of surface water quality in the former Soviet Union (FSU) and the present-day Russian Federation historically held an important place in the hierarchy of science, legal framework and relations between agencies. Sadly, the gap between the intentions, qualification of managers and effective programmes has always been sizeable. Since disintegration of the FSU this gap has become a formidable barrier for collecting reliable monitoring information and producing effective water quality management decisions in the Russian Federation.

Updating the federal system for freshwater quality monitoring in the Russian Federation is complicated by several unresolved problems. The principal issues are political, technical, institutional and financial. The existing Russian model of water chemistry data collection inherited from the FSU has proved unreliable, outdated and unrelated to modern national issues of water management. The quality of produced data is one of the greatest weaknesses of the federal monitoring system both in the Russian Federation and in other states of the FSU. A significant cause of the low reliability of the produced information is the analytical methods used in monitoring, their inappropriate use, non-compliance to laboratory practices when following expert recommendations, insufficient training level of managers and laboratory personnel and under-funding of the federal monitoring system. The growing national priorities in the field of surface water quality control and improvement conflict with the capacity of the Russian Federation to provide necessary information of guaranteed high quality.

Here we make the first attempt to present a critical analysis of the analytical methods used to assess and control surface water quality, to show the main errors arising when applying the recommended analytical methods, and to assess the degree of reliability of produced monitoring information from 1977-1978 to the present. Our overall objective is to summarize the current situation in order to facilitate implementation of future improvements.

Contents

Introduction

Modernization of surface water quality monitoring programs in the Russian Federation is a complicated task involving political, legal, institutional and technical changes at the federal and local levels. These changes are not rapid as expected by funding organisations and users of the data. The three main objectives of the modernization program are to increase (Ongley et al., 2002):

- Effectiveness: Does the program meet identified needs of users?
- Efficiency: Does the program carry out its tasks in a cost-efficient manner?
- Sustainability: Are measures taken to ensure long-term sustainability of the program?

In the Russian Federation the modernization process should be designed as a long-term project mainly impacted by (a) the necessity of lengthy consultations with stakeholders, and (b) managing decisions to propel coordinated changes (Ongley et al., 2002).

The status of surface freshwater quality monitoring in the FSU and currently in the Russian Federation has been reviewed in a series of recent publications (Zhulidov et al., 2000, 2001; Ongley et al., 2002). The general conclusions are as follows: the federal surface water quality monitoring program does not provide adequate data to the public in terms of public health, environmental protection or national water management. Its low quality is the greatest weakness of the Russian federal monitoring system (Bodo, 1998; Boeva et al., 2000; Zhulidov et al., 1998, 2000, 2000a, 2001).

The major objectives of surface water quality monitoring, i.e., to provide reliable data required by targeted users, or to address key water management issues, were not reached in the implementation of the monitoring program in the FSU, and these objectives still remain unsolved in the Russian Federation. Water quality monitoring data collection both in the FSU (under the State Service of Observation and Monitoring the Levels of Environmental Pollution, OGSNK network) and currently in the Russian Federation (currently the acronym GSN is used) was treated as an information collection activity, mostly unrelated to the actual needs of the national water economy or scientific challenges. Therefore, there is no individual institution holding responsibility for the provided information, which results in extremely low quality information.

In the present paper we perform a critical analysis of the analytical methods used to assess and control surface water quality. We intend to show the main errors arising when applying the recommended analytical methods, and to assess the degree of reliability of produced monitoring information from 1977-1978 to the present. Our overall objective is to summarize the current situation in order to facilitate implementation of future improvements.

2 History of surface water monitoring

2.1 Organization of surface water monitoring

Measurements of the chemical content of surface waters in the Russian Empire were started between 1903 and 1911. At that time these measurements were taken at irregular intervals and were aimed at specific goals. Predominantly, the studies focused on mineral waters, medicinal sediments and waters of artesian wells and of some rivers in order to assess their usefulness for drinking water supply (Alekin, 1968).

The first step in developing information on the chemical content of surface waters in the country was the establishment of stationary water chemical laboratories during the years 1936-1938. These belonged to the State Network of Hydrological Stations (SNHS) of the Head Administration of the Hydrometeorological Service (HAHS) of the Soviet of Peoples Commissioners of the Soviet Union, the main state body responsible for studies of the water resources in the FSU. The main goal of establishing these laboratories was the collection of reliable and regular data on the chemical content of surface waters in the country. These data were then distributed between relevant authorities, e.g., building, medicinal, agricultural, geological, metallurgical, and research bodies.

In 1941 the first guidelines were approved for use in SNHS "Guidelines on the chemical analyses of inland waters" (Guidelines…, 1941). The periods of water sampling followed earlier approved hydrological manuals for water bodies of the FSU: winter low water (February-March), peak of spring flood, summer low water (August-September) and under ice cover (October-December). For rivers experiencing glacial and rain generated floods additional sampling times were established (Manual…, 1938; Guidelines…, 1941). Water chemistry studies for lakes were carried out during the following periods: before ice break-out, during minimum water level (February-March, for temperate latitudes); during spring overturn (in flow-through lakes with considerable fluctuations of water level, it was at the maximum water level, i.e., usually in May); during the period of summer stratification, when the water temperature was maximal and the water level potentially at its lowest (July-August); and during the fall overturn before ice cover occurred (October-November). Less detailed water chemistry studies were to be carried out every decade between the above mentioned periods (Guidelines…, 1941).

Water samples for chemical studies were collected at predetermined HAHS sampling points on the largest and most important sources for drinking water. Samples were also collected from points which were not related to SNHS, such as in near-mouth areas of rivers subjected to wind-driven water level fluctuation, in tributaries, in places subjected to the influence of settlements, industrial and municipal ventures, harbors and other activities or structures influencing water chemistry.

The following parameters were monitored: water temperature, color and transparency, taste, odor, pH, oxygen concentration, hydrogen sulfide, dry content (sum of total dissolved solids and suspended solids), water mineral content (the sum of ions), major ions (Ca, Mg, carbonates, sulfates and chlorides; the sum of Na and K was determined by calculation), nitrogen (ammonia nitrogen, nitrite and nitrate), Fe^{+2}, Fe^{+3}, total iron, total hardness, alkalinity, permanganate oxidation and car-

bon dioxide (Guidelines…, 1941). Results of some of these studies, carried out over several decades (including the period before the beginning of large-scale hydropower construction), contain potentially valuable information for the analysis of long-term dynamics of the chemical content of several water bodies of the FSU (see, for example, Tsirkunov, 1998).

By the end of 1963 the principles of HAHS activity had changed drastically. The main tasks were changed from studies of the chemical content of ambient waters to monitoring of pollutants entering natural waters. This took place after the publication of decree No. 944 of the former USSR Soviet of Ministers (September 9, 1963). According to the decree SNHS became responsible for monitoring pollution of the country's surface waters.

Since 1964, HAHS carried out, first, preliminary, and since 1965, systematic measurements on the pollution status of the country's water bodies. The Hydrochemical Institute was responsible for scientific and methodological guidance of these. In 1963 the Hydrochemical Institute was removed from the Russian Academy of Sciences and incorporated into the structure of HAHS.

From 1964 to 1969 the number of monitoring points for pollution increased from 250 to approximately 1500. These points covered about 500 water bodies in the FSU. The majority of monitoring points were situated so that they were able to detect incoming wastewaters from the largest industrial and municipal sources. The following principles for organizing and carrying out pollution monitoring of surface waters were accepted:

- At any point, measurements were taken at several places: upstream of the pollutant source (or group of sources) that was designated as the "background river station" and downstream, at different distances from the pollution source. On wide rivers at downstream sites water was sampled at several places across a river. In deep rivers, lakes and reservoirs (with depths >5 m), water was sampled at several depths (Zhulidov et al., 2000a).
- Sampling was carried out at varying frequencies, from 2 times per year, to monthly, and taking into account the different hydrological phases.

The chemical analyses undertaken were specific to the type of wastewater entering a water body. During the first stages of monitoring the number of measured parameters did not exceed 30. To assess the potential hazard of pollution, a system of Maximum Acceptable Concentrations of Pollutants (MACP) for water bodies of either sanitary-municipal or fisheries importance, was used. The following parameters were measured most often: oxygen concentration, BOD_5, permanganate and dichromate oxidation, ammonia, nitrate, iron, extractable organic matter, sum of volatile phenols, copper, zinc, chromium, nickel, and anion-active surfactants. These results were usually accompanied by data on temperature and river discharge. As a rule, major ions were not measured since initially they were not listed in the MACP system.

As a result of the 1963 reforms the purpose of previous SNHS observation points changed fundamentally and some points were either closed or moved to other parts of rivers. By 1972 the number of measured parameters reached 200 and the number of observation points totaled approximately 3200.

In order to increase the status and increase the importance of developing an observation network, a decree No. 898 from the USSR government appeared on December 29, 1972 entitled "On reinforcement of nature preservation and improvement of use of natural resources". This allowed HAHS, with other relevant ministries, to establish the State Service of Observation and Monitoring the Levels of Environmental Pollution (known under the Russian acronym of OGSNK) (Zhuli-

dov et al., 2000). The main OGSNK goals were (Methodical Guidelines of Hydromet Service, 1977; Izrael et al., 1978; Methodical Guidelines on Principles of Organization…, 1984; Zhulidov et al., 2000):

1. Observation and monitoring of the pollution of the atmosphere, inland and marine waters, and soils using physical, chemical and biological parameters. The purpose was to reveal pathways and patterns of temporal and spatial distribution of pollutants and to assess the state of the environment and identify pollution sources.

2. Providing relevant organizations with systematic and urgent information on changes of pollutant levels and forecasts of the changes of these levels and development of prevention measures.

By the end of 1991 there were 1919 OGSNK observation points on 1274 water bodies in Russia (the former Russian Soviet Federative Socialist Republic in the USSR). In 1991, 32919 water samples were collected at these points. Water quality was assessed using 122 parameters. For the whole of the USSR there were 3295 OGSNK points on 2263 water bodies from which 55158 water samples were collected. At the end of 1997 there were 1540 observation points on 1182 water bodies in Russia (by the beginning of 1999 there were 1708 observation points at the end of 2002 there were 1716 observation points). In 1997, 22585 water samples were collected and water quality was assessed using 133 parameters. The history of the organization, working principles and main problems of OGSNK (later known under the Russian abbreviation of GSN) are analyzed by Zhulidov et al. (2000, 2001) and Ongley et al. (2002).

"Raw" results of water analyses obtained by the territorial branches of HAHS from 1935 to 1937 and from 1963 to 1975 were published in "Hydrological Yearbooks" (in the chapters "The water chemical content"). These yearbooks were published by territorial HAHS branches and were specific for the river basins included in the zone of responsibility of each HAHS branch.

From 1976 to 1983 the "raw" water chemistry data were published separately from the results of the water chemistry measurements in the quarterly "Hydrochemical bulletins". Since 1984 this data was published in report form by territorial branches of Roshydromet within the framework of the State Water Cadastre for different rivers basins under the title of "Annual data on the quality of surface inland waters". In parallel, the "Yearbooks of surface water quality on water chemistry parameters" were also published. These yearbooks contained analyzed, but not "raw", data (Zhulidov et al., 2000). Since 1975 the Hydrochemical Institute has operated a data bank on the "Quality of surface waters", that includes all the results from OGSNK/GSN from at least 1968 onwards (Zhulidov et al., 2000). However, this data bank has limited use even by relevant institutions and is inaccessible for other specialists and the public. It is important to note that the analytical methods used by HAHS–OGSNK/GSN, their transformation over the years and the validity of the data produced have not yet been analyzed in the open literature.

2.2 Data quality

Since the OGSNK was formed, the data on surface freshwater quality in the Russian Federation obtained by Roshydromet (up to 1992 data was part of the OGSNK database and covered the entire USSR; after 1992 it was part of the GSN database that covers the Russian Federation - see Zhulidov et al., 2000) are stored in the databank at the Hydrochemical Institute of Roshydromet in Rostov-on-Don. A copy of the data is sent to the All-Russia Scientific Research Institute of Hydrometeorological Information – The World Data Centre in Obninsk. Among other things, the

Hydrochemical Institute generalises the GSN information and develops the "Annual Book on surface data quality of the Russian Federation" and some other informational documents. Officially, this procedure was legalized by the Decree of the Federal Government, December 21, 1999, N 1410 "On establishing and maintaining a databank on the environmental situation and environmental pollution".

An independent critical assessment of the OGSNK/GSN database for 1985-1995 in the Lower Don region, carried out by the Centre for Preparation and Implementation of International Projects on Technical Assistance, North-Caucasus Branch (Boeva et al., 2000) in cooperation with other Russian and foreign experts under the "Environmental Management Project of the Russian Federation", indicated the presence of serious problems with data quality. The following data were reported as unreliable or erroneous:

- 25% of data for BOD_5
- 30% of data on phosphate and total dissolved-P
- 50% of data on all nitrogen species
- 70% of data on organochlorine pesticides (plus there is a problem of inadequate detection levels).

Other scientists who undertook evaluations of Russian data for other territories came to similar conclusions (Bodo, 1998; Zhulidov et al., 1998, 2000, 2000a, 2001; Holmes et al., 2000, 2001). Unfortunately, the OGSNK/GSN database was never improved as a result of these evaluations, and the problems with data quality were not commented on or officially acknowledged. Furthermore, after 1991 the deterioration of the technical infrastructure became so rapid that production of accurate data became even more problematic (Zhulidov et al., 2000, 2001).

3

Guidelines on analytical methods

3.1 First editions of guidelines

The first edition of the methods for chemical analyses of surface waters of the FSU (Guidelines…, 1941) was published in autumn of 1941, when the country was suffering from severe war losses. The guidelines were prepared by O.A. Alekin, edited by P.P. Voronkov and approved by the Head of the Hydrological Department of the USSR Hydrometeorological Service, Mr. Pushkarev, on May 19, 1941. They were aimed at water chemistry laboratories of the department of the USSR Hydrometeorological Service. As the editor's preface stated, "the objective of the guidelines, on the one hand, is to supply unified methods of water chemical analysis performed at the network of the Hydrometeorological Service of the USSR, and on the other, to incorporate modern methods of analysis, new views of chemical processes and scientific approaches to the studied chemical phenomena into the network practices" (Guidelines…, 1941).

The main goal of the guidelines was thus the unification of different water chemical methods used at earlier stages by SNHS (Volzhin, 1912; Standard methods…, 1927; Khlopin, 1930; Butyrin, 1931; Klyut, 1931; Paley, 1931; Vereschagin, 1933; Evlanov and Shtukovskaya, 1933; Lozhkin, 1933; Malinina, 1933; Priklonskiy, 1935; Rezhnikov and Mulikovskiy, 1935; The manual for chemical analyses in sea, 1938; The methods of chemical studies, 1938; Calthof and Sandal, 1938, etc.). Another goal was to implement in HAHS some modern analytical methods for detecting chemical concentrations of river and lake waters as a guarantee of their quality.

The second edition of these Guidelines dates back to 1954 (Alekin, 1954). After that separate methods and instructions for detection of certain compounds, mostly pollutants, were issued.

3.2 Guidelines of 1973

After the Decree of the USSR No. 898, December 29, 1972, a State Service of Observations and Environmental Pollution (OGSNK, after 1992 - GSN) was formed. OGSNK was meant to measure levels of pollution in air, soils, fresh surface waters and seas[1]. For these purposes the third updated edition of the Guidelines on the Chemical Analysis of Surface Waters (Alekin et al., 1973) was published in 1973. These Guidelines did not include some of the methods that by 1973 were considered outdated and ineffective, but introduced several new methods of analyzing

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[1] Establishment of the OGSNK was supervised by the Head Department of Hydrometservice at the Council of Ministers of the USSR (Glavhydrometservice). Later Glavhydrometservice was reorganized into the State Committee of the USSR on Hydrometeorology and Environmental Control, later renamed into the State Committee of the USSR on Hydrometeorology (Goskomhydromet), and still later, into the Committee for Hydrometeorology at the Cabinet of Ministers of the USSR (Goshydromet). From November 1991 (to September 1992) Goshydromet was given the name of the Committee for Hydrometeorology and Environmental Monitoring (Roscomhydromet). For several months Roscomhydromet was part of the Ministry of Ecology and Natural Resources of the Russian Federation. On September 30, 1992 Roscomhydromet was reorganized into the Federal Service of Russia on Hydrometeorology and Environmental Monitoring (Roshydromet). In April of 1998 Roshydromet was abolished and its functions were assigned to the State Committee of Environmental Protection of the Russian Federation (which in turn was disbanded on May 19, 2000 and its functions given over to the Ministry of Natural Resources). However, on September 30, 1998 Roshydromet was restored (Zhulidov et al., 2000).

chemical substances in surface waters. The new Guidelines contained relatively few methods of chemical analyses, primarily for detection of principal ions, nutrients and certain pollutants. Control of concentrations of the latter in surface waters of the FSU was meager and covered only certain rivers and lakes.

3.3 Guidelines of 1977

Rapid OGSNK development required production of new guidelines for analysing chemical substances in surface waters. These guidelines were published in 1977 (Semyonov, 1977) and for many years were obligatory for the work of OGSNK laboratories. As with previous revisions, the guidelines did not include methods that had become outdated, and introduced modern methods, some including gas chromatography and atomic-absorption spectrophotometry. For example, the method of ammonia nitrogen detection using Nessler reagent was taken out of the guidelines, since it was not sensitive and selective enough. Instead, two new methods of ammonia nitrogen detection using phenol and hypochlorite in the presence of manganese were introduced. However, both methods proved unsuccessful and were not used in OGSNK laboratories.

3.4 Amendments to the recommended methods of OGSNK laboratories

In some cases new methods of analysing pollutants in surface waters were developed and incorporated in the work of OGSNK laboratories that were described in the Guidelines of 1977 (Semyonov, 1977). For example, in 1978-1979 OGSNK laboratories received a method of detecting ammonia nitrogen with phenol and hypochlorite in the presence of sodium nitroprusside. Unfortunately, this method was used only in a few OGSNK laboratories; the majority preferred to stick to the well-established and simple method of ammonia nitrogen detection with Nessler reagent.

One of the important factors hampering the introduction of the indophenol method for ammonia nitrogen was a shortage of the necessary chemicals (hypochlorite production and phenol clean-up had to be done by laboratory personnel, but not all laboratories could do these). Besides, the indophenol method required higher professional qualifications and set additional requirements for the purity of chemicals, glassware, etc., which reduced its popularity with OGSNK laboratories. Moreover, many OGSNK laboratories believed that the results of their ammonia analyses using Nessler reagent were quite acceptable.

The 1977 Guidelines also excluded the method of iron detection using thiocyanate (although in several laboratories this method continued to be used for a while due to the difficulties related to phenanthroline procurement), and several other methods.

3.5 Methods of the Federal Roshydromet list (RD 52.24)

After 1993 all methodologies developed in the Hydrochemical Institute were published as separate documents under the code RD 52.24 (followed by the document number and the year of its development). The early 1990s (1993-1995) experience in developing and using methodologies resulted in a revision of all surface water analytical methods. The changed requirements of the State Committee on Standardisation, Metrology and Certification (Gosstandart) for the format and provision of metrological characteristics also helped bring about these revisions. By 1995 the revisions were completed and new editions of RD 52.24 appeared (76 methodologies) which were designed in compliance with the Federal Standard (Zhulidov et al., 2001).

The methodological revisions also included (Zhulidov et al., 2001):
- Many of the methodologies were extended to cover treated wastewaters;
- Metrological characteristics of the methodologies were specified;
- Analytical steps that might significantly effect a result were specified;
- Reagents, consumables, laboratory glassware and additional equipment necessary for the analyses were improved;
- New analytical apparatus was tested and recommended for use.

Following a review, methods were given new numbers and approved by Roshydromet and Gosstandart. They were then included in the Federal List of Measurement Methodologies and permitted for use in environmental surface and treated-waste water pollution monitoring (RD 52.18.595-96). This came into effect on March 13, 1998.

Federal List methodologies are obligatory for GSN laboratories and can be used by laboratories of other agencies for monitoring purposes. Other agency's methods, corresponding to Federal Standard GOST R 8.563-96 (GOST, 1996), can only be used after co-ordination with Roshydromet head institutes. In addition to the Federal List of Measurement Methodologies, other methodologies can be used to perform monitoring if Gosstandart approves them for metrological regulation of monitoring programs.

When new editions of RD 52.24 were prepared, drinking water analyses were not included. But as a result of a proposal by the Federal Centre of Sanitary and Epidemiological Control and other agencies, 17 new recommended drinking water analysis guidelines (RD 52.24) were included in Federal Standard GOST R 51232-98 (GOST, 1999). This resulted in RD 52.24 covering surface waters, treated wastewaters and drinking waters.

Even though RD 52.24 states that the Federal List of Measurement Methodologies is regularly revised, it nevertheless still includes methods that cannot be used for surface waters. An example is the method to measure ammonia concentrations and ammonium ions with Nessler reagent without distillation (Holmes et al., 2001), for some reason included in the Federal List of Measurement Methodologies. Practical application of a number of methods included in the Federal List of Measurement Methodologies was, for example, hampered by the lack of necessary instruments, consumables, pure chemicals, good laboratories and well-qualified specialists in the GSN laboratories (Zhulidov et al., 2001).

Assessment of the reliability of the analytical methods

4

4.1 Sources of error

One of the greatest drawbacks of the OGSNK/GSN database is the lack of metadata, i.e., data describing the stored water chemistry information. For example, there is no information on what methods were employed to produce the accumulated data. Quite frequently, several analytical methods were used with varying reliability of the results they produced. When, for example, the phenolate-hypochlorite method was used to detect ammonia nitrogen, the mean and median values in multi-year observation time-series are several times lower than those produced with the Nessler reagent method, but the OGSNK/GSN database made no distinction between these two methods.

Apart from the analytical methods impacting the reliability of data produced, there were other factors, such as the storage conditions and time of water sample transportation to laboratories for analysis, and the procedures of sample preparation (both in field conditions and in the laboratory). However, the OGSNK/GSN database contains no information on the transportation time and storage conditions. A particular feature of the OGSNK/GSN network has always been the long distance between sampling sites and laboratories where the samples are analysed. For about 30% of samples collected in remote areas sample transportation time often exceeded 10 days (Zhulidov et al., 2000), and in some cases as long as a month. Moreover, inadequate storage conditions for the transportation period were often used. At least 30% of water samples arrived for analysis with considerable violations of the allowable transportation time and conditions (L.V. Boeva, Hydrochemical Institute, personal communication). Under such conditions it is impossible to obtain good quality data. Changing the existing sampling system, sample preparation and transportation procedures are top priorities and the most challenging tasks for the GSN.

Other reasons for the low quality data are (Zhulidov et al., 2000):
- A general lack of well-equipped mobile laboratories;
- Insufficient (with some exceptions) qualification levels of the managers and technical staff;
- Low salaries for personnel, especially since the end of the 1980s when many qualified specialists resigned from their posts to work for other agencies;
- Scarce funds to purchase modern equipment and high quality reagents, and to maintain laboratory rooms in proper condition;
- Inadequate supervision and control that was supposed to provide scientific and methodological guidance for water chemistry works in OGSNK/GSN departments.

It is important to note that the quality of water chemistry information in different OGSNK/GSN departments has always varied considerably. The work quality of laboratories, qualifications of managers and technical staff, logistical support for the laboratories, were all largely dependent on the professionalism and persistence

of the laboratory head and personnel and, therefore, were a significant factors determining data quality. The technical level of OGSNK/GSN laboratories in different departments also greatly varied both in the FSU and now in the Russian Federation, and therefore, the quality of monitoring information is not uniform over the entire country.

It is worth mentioning that if in the mid-1970s the water chemical methods applied in the FSU were applied in line with international standards, the beginning of the 1980s was the time when methodological application began to fall behind international standards, aggravated by problems related to the growing shortage of adequate financial resources of the massive OGSNK. The lack of up-to-date instruments, consumables, chemicals of adequate quality and modern literature became very acute. While western countries used more and more modern instruments and better methods, OGSNK laboratories were not able to. For example, the content of heavy metals in water was still detected using spectral analysis with spark discharge recorded on a photographic plate, or insufficiently sensitive photometric methods. Atomic absorption spectrometry was used by OGSNK very infrequently. Water filters used were also of poor quality (for more details see Table 1). This explains why all the information on heavy metal concentrations in water obtained by OGSNK has proven unreliable. This situation has not changed and remains the case today with GSN (Zhulidov et al., 2001).

A considerable problem in the work of OGSNK and GSN water chemistry laboratories was a lack of understanding that analytical methods are merely an instrument, and the result of their application depends not only on the appropriateness of the method but also on whether the method is applied correctly. Quite often the personnel of these laboratories applied the methods:

- Without considering the operating range and detection limits of the method (i.e., limits of quantification)
- Without considering or eliminating interfering influences;
- Without a critical analysis of the appropriateness of the method selected for the task. An example of this would be the method of ammonia ion detection using Nessler reagent (Holmes et al., 2000, 2001), or detection of nitrates in surface waters using ionometry or salicylic acid instead of the required method of nitrate reduction using a cadmium reduction.

4.2 Assessment results

It is evident that the structure of the OGSNK/GSN database does not allow a critical assessment of the available information. To eliminate this shortcoming, the authors undertook a special study to assess the reliability of the available information on water chemistry, analysing the methods used and taking into account any other relevant supporting information.

Table 1 summarises information on the analytical methods used for determining chemical substances in surface waters by OGSNK/GSN laboratories from 1977 to the present. Information produced before 1977 is only of interest for a limited number of parameters (hardness, calcium, magnesium, chlorides, possibly sulphates, oxygen, carbon dioxide, hydrocarbonates, electric conductivity) as the reliability of earlier data is questionable. The information produced with the help of methods described in Table 1 covers about 95% of the data stored in the OGSNK/GSN databank. There is a possibility that in certain cases for some laboratories methods other than those described in the Table were applied, but the authors have no specific information on this.

Our assessment of the analytical methods suggests that many of them are reliable for many basic parameters, including pH, specific conductivity, oxygen, CO_2, Cl^-, SO_4, hardness and base cations (Ca, Mg, K, Na). However, most of the COD and BOD measurements and nutrient measurements, especially phosphates, dissolved phosphorus, and inorganic nitrogen (NH_4, NO_2, NO_3), the methods employed produced biased and doubtful data. Doubts also remain about the reliability of the analytical results for most metals because frequently there was no information on whether the water sample was filtered or not, and this has a significant effect on the results. For most organic pesticides the old analytical apparatus used cannot detect low concentrations and produces results that are too high.

5 Conclusions

The quality of surface water quality information in the FSU and now in the present Russian Federation depended not only on the analytical methods used, but also on the quality of field protocols and personnel, the distance between sampling sites and laboratories, the quality of laboratory equipment and facilities, the quality and level of laboratory staff training and other factors.

Although many methods were, and remain, problematical, it is important to note that a number of the methods can be considered reliable for the practical purposes of surface water monitoring. Therefore, a significant portion of the data produced, using these methods, can be used by the international community for scientific and management purposes.

While many problems have plagued the Russian water quality monitoring system and continue to do so (Zhulidov et al. 2000b; 2001), there is hope for its future redemption. In part this is because within the system there are still specialists whose level of qualifications and responsibility are worthy of the highest appreciation. While such specialists are working at the scientific institutes and regional laboratories of Roshydromet the monitoring system has the potential for a future modernization, the necessity of which has been thoroughly documented (Zhulidov et al., 2001).

Acknowledgements

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Table I. Assessment of measurement results of physical and chemical parameters produced in the OGSNK/GSN Federal water quality monitoring programme in the former USSR and present day Russian Federation.

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
			General Parameters		
Temperature	Semyonov, 1977; RD 52.24.496-95	Mercury thermometer	–	–	Data reliable
Suspended matter	Lurye, 1973 RD 52.24.468-95	Filtration, drying and weighing of the filter with suspended matter (2 mg/L)	1. Using a paper filter, which is not thick enough; losses when carrying the sample to the filter.	–	The lower the content of suspended matter, the stronger is the influence of the mentioned factors on the result.
			2. Changing the content of the suspended matter when the water sample is stored too long (from sampling to performing analysis) due to physical, chemical and biological processes.	+/–	
			3. Insufficient mixing of sample before taking aliquot for analysis.	+/–	
pH	Semyonov, 1977	Visual determination using colour scale at water object (0.2 unit pH).	1. A scale of poor quality; insufficient qualification of personnel.	+/–	Most data may be considered as reliable within the limits of visual measurement precision (0.2 unit pH).
			2. Colour or turbidity of the analysed water sample.	+/–	
	Semyonov, 1977; RD 52.24.495-95	Potentiometric measurement	1. Exceeding permissible sample transportation time (from the moment of sampling till making analysis) in cases when there is a lack of portable pH-meters	+/–	Is used less frequently than visual determination due to lack of instruments
Eh	Semyonov, 1977	Potentiometric measurement	Non-observance of the method require-ments; sample analysis is not performed at the site of collection but at the laboratory (when there is a lack of portable devices).	+ +/–	The greater part of the data is doubtful; Eh value change depends on storage conditions of water samples and the chemical composition of water.
Specific conductivity	Semyonov, 1977; RD 52.24.495-95	Measurement using the conductivity meter; limit of detection depends on the instrument	1. Water sample composition changes when stored too long.	+/–	
			2. Unsatisfactory functioning of the instrument	+/–	There is no reason to consider most data unreliable

Colour	Semyonov, 1977; RD 52.24.497-95	Visual comparison of colouring with dichromate ($Cr_2O_7^{2-}$) — cobalt or platinum-cobalt scale (5 degrees of colour)	1. A scale of poor quality; insufficient qualification of personnel.	+/−	Visual determination was mostly used. The share of doubtful or unreliable results is probably 20% at most
			2. Changing of watercolour as a result of a long transportation of water samples.	+/−	
	RD 52.24.497-95	Photometric measurement at 436 nm	1. Poor quality scale; insufficient qualification of personnel.	+/−	
Transparency	Semyonov, 1977; RD 52.24.496-95	Measuring transparency using the following method: a glass cylinder is filled with water; apiece of paper with a printed text is placed under it; the water is slowly let out of the cylinder until the letters of the text become visible; a Sechi disc was lowered into the water until it disappeared.	Water transparency changes as a result of a long transportation of water samples	+/−	Lack of necessary information to assess the data reliability
Odour	Semyonov, 1977; RD52.24.496-95	Olfactory determination of water odour at 20^0 and 60^0 C	−		−
Dissolved oxygen	Semyonov, 1977; RD52.24.419-95	Iodometric detection or Winkler method (0.5 mg/L)	1. Inadequate qualification of personnel performing the analysis on site (more than 50% of personnel on sites are not qualified for their jobs).	+ +/−	Iodometric method was preferred. For the most part the data can be considered reliable, but it is also possible that some measurement results are too high.
			2. Using reagents of poor quality or contaminating the sample in the course of analysis.	+	
			3. Not performing additional procedures to eliminate interfering influences.	+/−	
	Semyonov, 1977	Detection using electrochemical gauge	1. Interfering influence of substances adsorbed on the membrane or diffused through the membrane	+/−	
Percent oxygen saturation	Semyonov, 1977; RD 52.24.419-95	Values are attained using arithmetical calculations	The same factors as for dissolved oxygen	+/−	The data can be mostly considered reliable
Carbon dioxide (CO_2)	Semyonov, 1977	Titration with sodium carbonate (1 mg/L)	1. Inadequate qualification of personnel.	+/−	For the most part the data can be considered reliable if they agree with the data on pH, HCO_3^- concentration and ion composition.
			2. Decrease in concentration of sodium carbonate during storage due to consumption of CO_2 from air.	+	
	Semyonov, 1977	Estimation using content of hydrocarbons, pH, tempera-ture, content of principle ions	1. Correctness of estimations depends on the accuracy of detecting initial parameters, especially pH.		

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
			Principal Ions		
Chlorides	Semyonov, 1977; RD 52.24.407-95	Titration with potassium chromate (2 mg/L).	For surface waters they practically do not exist. Use in relatively clear water (up to 10.0 mg/L)		Both methods were used equally often. For the most part the data can be considered reliable.
	Semyonov, 1977; RD 52.24.402-95	Mercuric nitrate titration with diphenylcarbazone after concentrating the sample by evaporation (0.5 mg/L).	Influence of sample matrix (colour, iron, chromates, sulphides, etc.)	$+/-$	
Sulphates	Semyonov, 1977; RD 52.24.483-95	Gravimetric detection in the form of $BaSO_4$ (10 mg/L).	1. Co-precipitation of impurities, influence of high concentrations of silicates and iron.	$+$	The method that was mostly used was based on lead nitrate titration. Another one, though less popular, was the turbidimetric method, and the third one (still less frequently used) was based on barium chloride titration and the gravimetric method. In general, the data can be considered reliable. We want to stress that when the concentrations of sulphates are low (less than 40 mg/L) the probability of receiving excessively high results increases.
			2. Losses during transfer and calculation of the residue can cause considerable influence if sulphate concentrations are low.	$-$	
	Semyonov, 1977; RD 52.24.53-88 RD 52.24.401-95	Titration using lead nitrate in water after eliminating cations from the sample (10 mg/L)	1. Incorrect use of methodology when working with low sulphate concentrations.	$+$	
			2. Indistinct change in colour caused by the low quality of the indicator.	$+/-$	
	Semyonov, 1977; RD 52.24.406-95	Titration with barium chloride after eliminating cations from the sample (10 mg/L)	Incorrect use of methodology when working with low sulphate concentrations.	$+$	
	Semeyonov, 1977; RD 52.24. 57-88 RD 52.24.405-95	Turbidimetric detection with barium chloride in water —ethanol - ethylene glycol (glycerol) (2 mg/L)	1. Influence of colour or turbidity not eliminated in analysed samples.	$+$	
			2. Using an expired precipitator solution	$-$	

Hydrocarbonates	Semyonov, 1977; RD 52.24.493-95	Adding an excess of acid, eliminating CO_2, titration using sodium tetraborate with methyl red + methyl blue indicator (3 mg/L).	1. Exceeding the allowable time from the moment of sampling to analysis. 2. Presence of carbons titrated by error as hydrocarbonates. 3. Influence of the sample matrix (i.e., too high concentrations of silicates, phosphates and humic acids).	++/− + +	There is a high probability of getting unreliable results for the samples which are transported to laboratories from remote sampling sites. They make up about a quarter of the total. The influence of other factors is less probable.
	Semyonov, 1977; RD 52.24.493-95	Potentiometric titration to pH 4.5 − 4.2 (2 mg/L)	1. Exceeding of the allowable time from the moment of sampling to analysis. 2. Presence of carbons titrated by error as hydrocarbonates. 3. Influence of the sample matrix (i.e., too high concentrations of silicates, phosphates and humic acids).	++/− + +	
Hardness	Semyonov, 1977; RD 52.24.395-95	Titration with EDTA in the presence of Eriochrome Black T (0.1 mmole/L)	1. Prolonged storage of unfiltered samples which are filtered directly before the analysis	−	For the most part the data can be considered reliable
Ca	Semyonov, 1977; RD 52.24.403-95	Titration with EDTA and naphthol green (0.5 mg/L)	1. Prolonged storage of unfiltered samples which are filtered directly before the analysis 2. Indistinct colour change caused by presence of interfering substances or low quality of the indicator.	− ++/−	The majority of the data can be regarded as reliable. Appearance of doubtful results is most probable in the case of samples having a high degree of colour, alkalinity and iron content.
Mg	Semyonov, 1977;	Estimation using the differen-ce between hardness and the content (1 mg/L)	Correctness of estimations depend on the accuracy of detection of calcium and hardness.	+/−	The majority of the data can be regarded as quite reliable.
Na	Semyonov, 1977; RD 52.24.391-95	Flame and photometric detection in air-acetylene and air-propane-butane flame (0.2 mg/L)	1. Irregular functioning of the apparatus. 2. Contamination of sample at the stage of sampling or analysis	+/− +	The majority of the data must be reliable.
K	Semyonov, 1977; RD 52.24.391-95	Flame and photometric detection in air-acetylene and air-propane-butane flame (0.2 mg/L)	Irregular functioning of the apparatus.	+/−	The majority of the data must be reliable.
Na + K	Semyonov, 1977	Estimation using the con-tent of other anions and cations	Accuracy depends on the detection accuracy of all components.	+/−	The majority of the data must be reliable.
Sum of ions	Semyonov, 1977; RD52.24.514-02	Estimation based summing the concentrations of all ions	Accuracy of the estimation depends on how exact the detection of all components is	+/−	The majority of the data must be reliable.

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
			Chemical Oxygen Demand and Biological Oxygen Demand		
COD	Semyonov, 1977; RD 52.24.391-95	Oxidation with potassium dichromate in the presence of sulphur dioxide and silver sulphate with 3 hours heating (3 mg/L)	1. Sample contamination at the stage of sampling (most often), storage and analysis. 2. Insufficient oxidation of organic substances due to non-compliance with methodological requirements.	+ –	Here both positive and negative deviations are possible. Excessively high values are more probable though, especially if the COD values are low. It seems that no more than two-thirds of the results can be considered reliable
BOD$_5$	Semyonov, 1977; RD 52.24.420-95	Iodometric detection of oxygen content in the sample before incubation and after incubation for 5 days at 20^0 C (0.5 mg/L)	1. Non-observance of the conditions of sample incubation due to a lack of thermostats. 2. Inadequate qualification of personnel, performing analyses at remote sites. 3. Sample contamination at the stage of sampling and analysis	+/– + +/– +	The results are mainly excessively high. But during cold seasons BOD$_5$ results can be too low. Analytical results for samples from sites remote from laboratories are more likely to be unreliable
			Nutrients		
NH$_4$	Oradovsky, 1977 (since 1979); RD 52.24.35-87 RD 52.24.383-95	Photometric detection in the form of indophenol blue	1. Unaccounted for turbidity or colour of the water sample. 2. Performing a blank with water not clean enough. 3. Low temperature in the laboratory. 4. Non-observance of conditions and the allowable sample storage period in the process of the transportation from remote sites to laboratories.	+ – – +/– –	Before 1979 detection was performed using the Nessler method, mostly without a preliminary separation with the help of distillation (detection using distillation was no more than 2%). After 1979 a more sensitive and selective indophenol method was applied in about 20% of regions. In general, a large portion of the data is doubtful, the results often being too high due to a more frequent use of Nessler method.
	Alekin et al., 1973; RD52.24.486-95	Photometric detection with Nessler reagent without distillation and with a preliminary distillation of NH$_3$ (0.1 and 0.06 mg/L, respectively)	1. Presence of substances interfering with detection and forming a residue or colour under the influence of Nessler reagent, as well as unaccounted for turbidity or colour of the sample during detection without distillation. 2. Methodology is not sensitive enough. 3. Non-observance of the conditions and the allowable storage time for the samples in the process of their transportation from remote sites to laboratories.	+ + +/– –	

NO$_2^-$	Semyonov, 1977; RD 52.24.381-95	Photometric detection using the Griss reagent (5 μg/L)	1. Inadequate standard solution for graduation. 2. Unaccounted for turbidity or colour. 3. Non-observance of the conditions and the allowable storage time for the samples in the process of their transportation from remote sites to laboratories.	+ + −	The procedure is most likely to yield exceedingly high results. Though for some samples because of their prolonged storage the results can be too low (negative error), it is usually not obvious, as nitrite concentrations in surface waters are usually below limit of detection of the methodology
NO$_3^-$	Semyonov, 1977; RD 52.24.31-86 RD 52.24.380-95	Photometric detection using the Griss reagent after reduction to nitrite on cadmium granules treated with copper sulfate (10 μg/L)	1. Decrease of the reduction capacity of the reducer if the reducer is not controlled constantly. 2. Excessively high result of nitrite detection. 3. Performing a blank using distilled water contaminated by nitrates. 4. Non-observance of the conditions and the allowable storage time for the samples in the process of their transportation from remote sites to laboratories.	− − − + +/−	Detection was mostly performed using the method of reduction to nitrite. When this method is used, the probability of getting exceedingly low results is very high (negative error). Other methods were used much less frequently and the percentage of data they yielded is less than 10%. For these methods it is typical to get too high results (positive error). This way, both positive and negative deviations are possible. As a whole, no more than two-thirds of the data can be assessed as correct.
	RD 52.24.367-95	Direct potentiometric detection with a nitrate-selective electrode (0.2 mg/L)	1. Methodology not sensitive enough. 2. Nernsts dependence between the potential and the concentration is broken due to sorption of organic substances on the electrode surface in contaminated waters.	+ +	
	Lourye, 1973	Photometric detection in the form of nitro-derivatives (0.1mg/L)	1. Colour appears due to the influence of sulphuric acid on organic substances contained in the sample; unaccounted for colour of the analysed water sample. 2. Using sulphuric acid contaminated with nitrates. 3. Insufficient sensitivity of the methodology. 4. Non-observance of the conditions and the allowable storage time for the samples in the process of their transportation from remote sites to laboratories.	+ + + +/− + +/−	
Sum of mineral nitrogen	No reference	Sum of ammonium, nitrate and nitrite nitrogen	Accuracy of the estimation depends on the exactness of component measurements.	+/−	Both excessively high and excessively low results are possible

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
Total dissolved nitrogen	Alekin et al., 1973; (detection in a filtered water sample)	Digestion using the modified Kjeldahl method and detection with Nessler reagent (0.05 mg/L)	1. Sample contamination due to consumption of ammonia traces from the air during evaporation. 2. Filtering the sample through a loose paper filter. 3. Poor reproducibility of the method. 4. Prolonged storage of an unfiltered sample (for example, in the process of transportation to laboratories from remote sites).	+ + + +/− +/−	The amount of total nitrogen data is not large (especially before 1985). It is very difficult to assess the degree of reliability of the available data. While analysing the available results one should keep in mind that the Kjeldahl method tends to yield too high results, and the method of persulphate oxidation gives too low figures. The persulphate method is more appropriate for routine analyses, it is simpler and easier to reproduce. As a result, this method yields more reliable results. In any case, when using the available data it is necessary to compare the detection results for all nitrogen forms and take into account the peculiarities of their behaviour in surface waters of a given region of the former USSR.
	RD 52.24.364-95 (detection in a filtered water sample)	Oxidation of nitrogen-containing compounds to nitrates with potassium persulphate in an alkaline medium with heating and subsequent nitrate detection after reduction to nitrites on cadmium granules treated with copper sulfate (0.04 mg/L)	1. Incomplete oxidation of ammonia and organic substances due to non-observance of the conditions of sample degestion. 2. Filtering the sample through a loose paper filter. 3. Using inadequately clean potassium persulphate 4. Prolonged storage of an unfiltered samp-le (for example, in the process of transpor-tation to laboratories from remote sites).	− + + +/−	
Sum of dissolved and suspended nitrogen	RD 52.24.364-95 (detection in an unfiltered water sample)	Oxidation of nitrogen-containing compounds to nitrates with potassium persulphate in an alkaline medium with heating and subsequent nitrate detection after reduction to nitrites on cadmium granules treated with copper sulfate (0.04 mg/L).	1. Incomplete oxidation of ammonia and organic substances due to non-observance of the conditions of sample degestion. 2. Using inadequately clean potassium persulphate.	− +	The amount of total nitrogen data is not large. It is very difficult to assess the degree of reliability of the available data. While analysing the available results one should keep in mind that the Kjeldahl method tends to yield too high results, and the method of persulphate oxidation gives too low figures. In any case, when using the available data it is necessary to compare the detection results for all nitrogen forms and take into account the peculiarities of their behaviour in surface waters of a given region of the former USSR.
	Alekin et al., 1973; (detection in an unfiltered water sample).	Digestion using the modified Kjeldahl method and detection with Nessler reagent (0.05 mg/L).	1. Sample contamination due to consumption of ammonia traces from the air during evaporation. 2. Poor reproducibility of the method.	+ + +/−	

Organic nitrogen	Alekin et al., 1973;	Estimation was performed using the difference between concentrations of total nitrogen nitrate, nitrite and ammonium nitrogen (0.05 mg/L).	Correctness of the estimation depends on the accuracy of detection of initial values	$+/-$	
	RD 52.24.364-95	Estimation was performed using the difference between concentrations of total and mineral nitrogen (0.05 mg/l).	Correctness of the estimation depends on the accuracy of detection of initial values		
Phosphate (orthophosphate)	Semyonov, 1977; RD 52.24.382-95	Photometric detection of molybdenum blue formation (5 μg/L)	1. Using inadequate standard solution for graduation or inadequately pure sulphuric acid; sample contamination at the stage of sampling	$+$	During phosphate detection it is more probable to get exceedingly high results, especially at low concentrations. At the same time, prolonged storage of the samples (e.g., as a result of transportation) can cause a negative error.
			2. Unaccounted for colour of the sample.	$+$	
			3. Incomplete separation of the suspended fraction while detecting dissolved phosphates because a loose paper filter is used.	$+$	
			4. Non-observance of the conditions and allowed storage time (for example, in the process of transportation to laboratories from remote sites).	$+/--$	
			5. Inadequate sensitivity of the method to analyse water samples from oligotrophic water bodies	$+$	
Total dissolved phosphorus	Semyonov, 1977; RD 52.24.387-95 (detection in filtered water)	Photometric detection after transformation into orthophosphate by boiling with potassium persulphate in an acid medium (20 μg/L)	1. Using inadequate standard solution for graduation or inadequately pure sulphuric acid; sample contamination at the stage of sampling.	$+$	If samples are preserved in the field with diluted mineral acid, phosphorus should remain in solution.
			2. Incomplete separation of the suspended fraction while detecting dissolved phosphates because a loose paper filter is used.	$+$	
			3. Prolonged storage of an unfiltered sample (for example, in the process of transportation to laboratories from remote sites).	$-$	
			4. Incomplete decomposition of potassium persulphate while boiling.	$-$	
			5. Storing the samples in a plastic container.	$-$??	

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[I]	Note
Total dissolved and suspended phosphorus	Semyonov, 1977; RD 52.24.387-95 (detection in unfiltered water)	Photometric detection after transformation into orthophosphates by boiling with potassium persulphate in an acid medium (20 µg/L)	1. Using inadequate standard solution for graduation or inadequately pure sulphuric acid; sample contamination at the stage of sampling. 2. Incomplete separation of the suspended fraction while detecting dissolved phosphates because a loose paper filter is used. 3. Storing the samples in a plastic container.	+ − − ??	For the most part, the comments are the same as for orthophosphate and polyphosphate, but the probability of a negative error is higher than in the case of phosphate.
Organic phosphorus	RD 52.24.387-95	Difference between total and inorganic phosphorus concentrations (20 mg/L).	Correctness of the estimations depends on the accuracy of detection of initial values.	+/−	No comments
Silicon	Semyonov, 1977 RD 52.24.433-95	Photometric detection of monomer- dimeric forms of silicic acid and silicates in the form of yellow molybdosilicic acid (0.3 mg/L)	1. Unaccounted for colour or turbidity of the water sample. 2. Prolonged storage of an unfiltered sample (for example, in the process of transportation to laboratories from remote sites). 3. Sample conservation with sulphuric acid. 4. Considerable difference in chemical composition between calibration models and the analysed samples.	+ +/− − −	During detection both excessively high and excessively low values are possible. Too high results (positive errors) are more probable when low silicon concentrations are detected, and too low results are more typical for high silicon concentrations, especially if some time lapsed after sampling and prior to analysis.
	Semyonov, 1977 RD 52.24.432-95	The same, but after reduction of heteropolyacid to molybdenum blue (0.06 mg/L Si)	1. Unaccounted for colour or turbidity of the water sample. 2. Prolonged storage of an unfiltered sample (for example, in the process of transportation to laboratories from remote sites). 3. Sample conservation with sulphuric acid. 4. Considerable difference in chemical composition between calibration models and the analysed samples. 5. Sample contamination in the process of sampling and analysis.	+ +/− − − +	

Other Inorganic Substances

Fluorides	Semyonov, 1977 RD 52.24.360-95	Direct potentiometric detection using fluoride-selective electrode in a buffer solution at pH 5 (0.1 mg/L).	No	No	There are no obvious reasons to have serious errors while analysing surface waters, especially when the potentiometric method is used (20-25% of the data). It is now impossible to separate the data attained using photometric methods with Lanthanum-Alizarin complexone and zirconium-alizarin varnish. The former method is more exact, and it seems that it was used more often than the latter.
	Semyonov, 1977	Photometric detection with Lanthanum-Alizarin complexone in water-acetone solution at pH 5 (0.02 mg/L)	Unaccounted for colour or turbidity of the sample.	+	
	Lurye, 1973	Photometric detection with zirconium-alizarin varnish (0.05 mg/L)	1. Unaccounted for colour or turbidity of the sample. 2. Influence of the components contained in the water-sample (high content of aluminium, iron, sulphates, etc.).	– +/– –	
Hydrogen sulphide and other sulphides	Semyonov, 1977	Photometric detection in the form of methylene blue in a water solution (30 μg/L).	1. Inadequate sensitivity of the method when surface waters are analysed. 2. Standard solution of poor quality. 3. Unaccounted for colour. 4. Influence of suspended particles. 5. Operator is not qualified enough.	+ + + – –	A more sensitive method with extraction concentration of the sample has been used only during the last years (and not in all laboratories). So the data bank contains mostly results attained with the help of photometric detection method in the form of methylene blue in the water solution, which yielded excessively high results, especially at low content of sulphides in the water.
	RD 52.24.450-95	Photometric detection in the form of methylene blue after concentration by extracting into chloroform in the presence of Na-dodecylsulphate (2 μg/L).	1. Standard solution of poor quality. 2. Operator is not qualified enough.	+ –	
Borate	Methodological Guidelines… 1979	Photometric detection with 1,1- diantrimide (1,1'-dianthraquinonylamine) in sulphuric acid medium after sample evaporation (0.005-0.1 μg/L) in standard solutions, for surface waters unknown.	The method is not sensitive enough, not representative enough, and subject to many interfering influences.	+ +	It is not recommended to use data attained by this methodology.
	RD 52.24.389-95	Photometric detection with azometine—H (0.05 mg/L)	1. Unaccounted for colour or turbidity of the sample. 2. Not eliminated interference of calcium, magnesium and iron.	+ +	Few data were attained with the help of this method. At present it is difficult to assess the quality of these data. At low borate concentrations the results will probably be excessively high.

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
Cyanides (toxic or easily de-composable)	Semyonov, 1977	Photometric detection with pyridine-benzidine reagent without preliminary distillation and concentration (0.01 mg/L).	1. Influence of the sample matrix not eliminated. 2. Inadequate sensitivity for surface waters. 3. Prolonged storage of water samples conserved in alkaline.	+ + −	The method used most frequently was the one without separation and distillation so that the results are probably not always reliable. If the cyanide content in the sample is low, excessively high results are more probable (positive error).
	Semyonov, 1977	Photometric detection with pyridine-benzidine reagent with preliminary distillation and concentration (0.01 mg/L).	Prolonged storage of water samples conserved in alkaline.	−	
Thiocyanates	Semyonov, 1977	Photometric detection with pyridine-benzidine reagent after cyanide separation (0.05 mg/L).	1. Influence of the sample matrix not eliminated. 2. Inadequate sensitivity for surface waters. 3. Prolonged storage of water samples conserved in alkaline.	+ + +/− −	At low thiocyanate content reliable results are unlikely and the results will probably be exceedingly high.

Metals[2]

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
Total iron (sum of Fe^{2+} and Fe^{3+})	Semyonov, 1977; RD 52.24.358-95	Photometric detection with potassium thiocyanates after reduction to Fe^{2+} (0.03 mg/L).	1. Sample contamination at the stage of sampling, conservation and preliminary preparation. 2. Using inadequately pure distilled water for a blank.	+ −	The preferred method was the one with o-phenanthroline detection. The amount of data attained with the help of other methods did not exceed 10%. In the 1990s the number of analyses using atomic-absorption spectroscopy increased. Before 1985 the thiocyanate method was used more often. The correctness of iron detection (the same as for other metals) mostly depends on how the water sample was filtered and whether it was filtered at all (see reference [2]). The quality of reagents and glassware used at the stage of sampling, filtration and preservation is also of importance and is difficult to control.
	Alekin et al., 1973	Photometric detection with thiocyanates after oxidation of Fe^{2+} (0.05 mg/L).	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Poor reproducibility. 3. Poorly qualified personnel.	+ +/− −	
	Semyonov, 1977 RD 52.24.23-91	Detection using emission spectroscopy $(2\,\mu g/L)^3$.	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Poor reproducibility. 3. Poorly qualified personnel.	+ + +/− +/−	
	RD 52.24.81-89	Detection with atomic-absorption spectroscopy during atomisation in flame (0.03 mg/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+	

Fe^{2+}	Semyonov, 1977	Photometric detection with o-phenanthroline (0.02 mg/L).	1. Influence of colour or turbidity of the water unaccounted. 2. Prolonged storage of the samples from sampling to analysis.	+ −	While interpreting the data one should take into account a complex of factors, including the chemical composition of the sample (primarily the concentration of total iron and oxygen). It is difficult to assess the reliability of the available data.
Fe^{3+}	Semyonov, 1977	The difference between concentrations of Fe_{total} and Fe^{2+} when detected with ophenanthroline (0.03 mg/L).	Reliability depends on the detection accuracy of each component.	+/−	The same as for total iron
	Alekin, Semyonov and Skopintsev, 1973;	Photometric detection potassium thiocyanate (0.05 mg/L).	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Poor reproducibility. 3. Influence of colour of the water unaccounted for. 4. Using inadequately pure distilled water for a blank.	+ + +/− −	
Copper	Semyonov, 1977	Extraction-photometric detection with lead diethylcarbamate (2 μg/L).	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Using inadequately pure distilled water for a blank.	+ +	Photometric detection was primarily used. The amount of data attained with the emission spectroscopy method is about 15%, and approximately the same amount of data was obtained with other methods. During latter years the amount of data attained using atomic absorption increased. For the reliability of the methods see the appropriate section and reference[2].
	Semyonov, 1977 RD 52.24.23-91	Detection using emission spectroscopy (1μg/L)[3].	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Poor reproducibility. 3. Inadequate qualification of personnel. 4. Low quality of photographic plates.	+/− +/− +/− −	
	RD 52.24.81-89	Detection using atomic absorption with flame detection after concentration by evaporation or extraction as diethylcarbamate (1 μg/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+	
	RD 52.24.377-95	Detection with atomic-absorption spectroscopy with electrothermic atomisation (4 μg/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+	
	RD 52.24.371-95	Detection using a method of inversion stripping voltammetry (0.5-1 μg/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+	

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
Zinc	Semyonov, 1977	Extraction and photometric detection after copper elimination ($2\,\mu g/L$).	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Influence of iron not eliminated. 3. Using inadequately pure distilled water for a blank.	+ + + –	Photometric detection was preferred. The share of data attained with the help of other methods does not exceed 20%. More recently the amount of data received using the atomic absorption method is increasing. As for reliability - see iron and reference[2].
	RD 52.24.81-89 RD 52.24.377-95	Atomic absorption detection during atomisation in flame after concentration by evaporation ($2\,\mu g/L$).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+ +	
	RD 52.24.377-95	Atomic absorption detection ($1\,\mu g/L$).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+ +	
	RD 52.24.377-95	Detection with inversion stripping voltammetry method ($1\,\mu g/L$).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+ +	
Total chrome (sum of Cr^{6+} and Cr^{3+})	Semyonov, 1977; Lourye, 1973	Photometric detection with diphenylcarbazide after oxidation to Cr^{6+} ($5\,\mu g/L$).	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Influence of iron not eliminated. 3. Poor quality diphenylcarbazide	+ + –	See iron and reference[2].
Cr^{6+}	Semyonov, 1977; RD 52.24.100-90 RD 52.24.446-95	Photometric detection with diphenylcarbazide in water solution ($5\,\mu g/L$) or after extraction ($1\,\mu g/L$).	1. Sample contamination at the stage of sampling, conservation and preliminary preparation. 2. Influence of iron not eliminated. 3. Prolonged storage of samples between sampling and analysis. 4. Diphenylcarbazide of poor quality	+ + – –	Both high and low values are possible. It is highly probable that the majority of data are doubtful
Cr^{3+}	Semyonov, 1977	Estimation of the difference between concentrations of Cr_{total} and Cr^{6+} ($7\,\mu g/L$)	Reliability depends on the detection accuracy of each component.	+/–	See total chrome

Manganese	Semyonov, 1977	Photometric detection in the form of permanganate (0.03-0.04 mg/L).	Inadequate sensitivity and reproducibility of the method.	$+ +/-$	The methods preferred were emission spectroscopy (40-45% of all data) and photometric detection with persulphate that in recent years was replaced by the detection method with formaldoxime. The share of data received using atomic absorption is no more than 10%, but has been growing during recent years. Actual content of manganese in surface waters of the former USSR (especially in a dissolved form) often turned out to be below limit of detection of photometric methods. Most probably, the use of photometric methods resulted in excessively high values (due to the so-called boundary effect). For other methods, the high probability of excessively high values was caused by sample contamination. See also iron and reference [2].
	RD 52.24.121-92 RD 52.24.467-95	Photometric detection with formaldoxime $(CH_2=NOH)$ (0.03 mg/L).	Inadequate sensitivity of the method	$+ +/-$	
	Semyonov, 1977 RD 52.24.23-91	Detection with emission spectroscopy (0.5 mg/L)[3].	1. Sample contamination at the stage of sampling, preservation and preliminary preparation.	$+$	
			2. Inadequate qualification of personnel	$+/-$	
			3. Poor reproducibility	$+/-$	
			4. Poor quality of photographic plates	$-$	
	RD 52.24.81-89	Atomic absorption with flame ionization after concentration by evaporation (1 μg/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	$+$	
	RD 52.24.377-95	Atomic absorption detection with electrothermic atomisation (0.4 μg/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	$+$	
Mercury	Semyonov, 1977	Extraction and photometric detection (1 μg/L).	1. Sample contamination at the stage of sampling, preservation and preliminary preparation.	$+$	From 1982-1985 in OGSNK laboratories photometric methods were being replaced by atomic absorption in cold vapour. But to some extent photometric detection is still being used. When the more sensitive atomic absorption method is used, using inadequately pure tin chloride and acids causes errors. As purchasing pure reagents has always been a problem, most available data on mercury are doubtful. See also iron and reference [2].
			2. Inadequate sensitivity to analyse surface waters.	$+$	
			3. Losses of mercury occur when samples are stored too long.	$-$	
	Semyonov, 1977 RD 52.24.479-95	Detection using atomic absorption in cold vapour using Soviet industrial apparatus (0.02-0.04 μg/L, depending on sample size).	1. Sample contamination at the stage of sampling, conservation and preliminary preparation.	$+$	
			2. Losses of mercury occur when samples are stored too long.	$-$	

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
Pb	Semyonov, 1977	Extraction and photometric detection with dithizone ($2\,\mu$g/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+	Earlier emission spectroscopy was preferred (60-70% of all data) and photometric detection with dithizone. During the past few years photometric analyses have been replaced by inversion stripping voltammetry and atomic absorption almost completely (and the method of emission spectroscopy – partially). Reliability - see iron and note[2]
	Semyonov, 1977 RD 52.24.23-91	Detection with emission spectroscopy (5 mg/L)[3].	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Inadequate qualification of personnel 3. Poor quality of photographic plates	+ + +/– –	
	Unified methods..., 1983	Detection using atomic absorption and flame ionization without concentrating the sample ($100\,\mu$g/L) or with concentration (5-$10\,\mu$g/L).	1. Inadequate sensitivity without concentration 2. Sample contamination at the stage of sampling, preservation and preliminary processing when method of concentration was applied	+ +/– +	
	RD 52.24.377-95	Detection with atomic absorption ($1\,\mu$g/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+	
	RD 52.24.371-95	Detection using inversion stripping voltammetry ($1\,\mu$g/L)	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+ +	
Cadmium	Semyonov, 1977	Extraction and photometric detection ($1\,\mu$g/L).	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Inadequate reproducibility and sensitivity to analyse surface waters.	+ + +/–	In earlier years photometric detection with dithizone was preferred. The share of data attained with other methods does not exceed 20%. Between 1983-1985 atomic absorption started to be used. The amount of data received using this method has been growing and is about 40-50% of the total data available. The inversion voltammetry method was used less frequently. For reliability see iron and reference [2].
	Unified methods ..., 1983	Detection with atomic absorption using flame ionization without sample concentration ($5\,\mu$g/L) or with concentration (0.2-$0.5\,\mu$g/L).	1. Inadequate sensitivity to analyse samples without concentration. 2. Sample contamination at the stage of sampling, preservation and preliminary preparation when concentration method is used.	+ +/– +	
	RD 52.24.377-95	Detection with atomic absorption ($0.1\,\mu$g/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+	
	RD 52.24.371-95	Detection using the inversion stripping voltammetry method (0.1-$0.3\,\mu$g/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+ +	

Ni	Semyonov, 1977 RD 52.24.494.95	Extraction and photometric detection using dimethylglyoxime (3μg/L)	Sample contamination at the stage of selection, preservation and preliminary preparation.	+	Emission spectroscopy was preferred (35 -40% of all data) with photometric detection using dimethylglyoxime. Atomic absorption was used since the mid 1980s. The volume of data obtained using atomic absorption is increasing, but but currently does not exceed 10%. Reliability - see iron and note[2]
	Semyonov, 1977 RD 52.24.23.91	Detection with emission spectroscopy (0.6 mg/L)[3].	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Inadequate qualification of personnel 3. Poor quality of photographic plates	+ +/− −	
	Unified methods..., 1983	Detection using atomic absorption and flame ionization without concentrating the sample ($40\,\mu$g/L) or with concentration (2-$4\,\mu$g/L).	1. Inadequate sensitivity without concentration 2. Sample contamination at the stage of sampling, preservation and preliminary processing when method of concentration was applied	+ +/− +	
	RD 52.24.377-95	Detection with atomic absorption ($2\,\mu$g/L).	Sample contamination at the stage of selection, preservation and preliminary preparation.	+	
Cobalt	Semyonov, 1977	Extraction and photometric detection using b-nitroso-a-naphthol (1μg/L)	1. Sample contamination at the stage of selection, preservation and preliminary preparation. 2. Poor reproducibility	+ +/−	Emission spectroscopy was preferred ($>$80% of all data). Reliability - see iron and the note[2]
	Semyonov, 1977 RD 52.24.23-91.	Emission spectroscopy ($2\,\mu$g/L)	1. Poor qualification of personnel. 2. Poor quality of photographic plates 3. Sample contamination at the stage of sampling, preservation and preliminary preparation.	− + +	
	Unified methods ..., 1983	Detection using atomic absorption and flame ionization without concentrating the sample ($50\,\mu$g/L) or with concentration (2-$5\,\mu$g/L).	Inadequate sensitivity without concentration	+ +/−	
	RD 52.24.377-95	Detection using atomic absorption ($1\,\mu$g/L).	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+	

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
Aluminium	GOST 18165-81, 1984	Photometric detection method (40 μg/L).	1. Inadequate sensitivity. 2. Insufficient reproducibility. 3. Prolonged storage of sample prior to analysis. 4. Influence of fluorides is not eliminated.	+ +/– +/– – –	Method of emission spectroscopy was preferred (>80% of all data). Reliability - see iron and the note[2]
	Semyonov, 1977; RD 52.24.23-91	Emission spectroscopy method (1 μg/L)[3]	1. Sample contamination at the stage of sampling, preservation and preliminary preparation. 2. Inadequate qualification of personnel. 3. Poor quality of photographic-plates. 4. Prolonged storage of sample prior to analysis.	+ + +/– – –	
Arsenic	Semyonov, 1977	Photometric detection using reaction with silver diethylcarbamate in the presence of ephedrine after reduction to AsH$_3$ (10 μg/L)	1. Sample contamination at the stage of sampling and preservation. 2. Inadequate reproducibility, AsH$_3$ losses through loose fixtures of the device. 3. Prolonged storage of unfiltered samples prior to analysis. 4. Sample not immediately filtered after collection,	+ +/– – –	Reliability - see iron and the note[2]
Molybdenum	Semyonov, 1977; RD 52.24.23-91	Emission spectroscopy detection (1 μg/L)[3].	1. Inadequate qualification of personnel. 2. Photographic plates of poor quality.	+/– –	Method of emission spectroscopy was preferred (>95% of all data) Reliability - see iron and the note[2]
	RD 52.24.416-95	Detection using inversion stripping voltammetry (0.1-0.2 μg/L)	Sample contamination at the stage of sampling, preservation and preliminary preparation.	+	
Tin	Semyonov, 1977; RD 52.24.23-91	Emission spectroscopy detection (2 μg/L)[3].	1. Insufficient reproducibility. 2. Inadequate qualification of personnel. 3. Photographic plates of poor quality. 4. Sample contamination at the stage of sampling, preservation and preliminary preparation.	+/– +/– – +	Reliability - see iron and the note[2]
Vanadium	Unified methods ..., 1987	Extraction and photometric detection with 8- oxyquinoline (5μg/L).	1. Insufficient sensibility for surface waters. 2. Insufficient reproducibility.	+ +/– +/–	Emission spectroscopy was preferred (>95% of all data). Reliability - see iron and the note[2]
	Semyonov, 1977; RD 52.24.23-91	Emission spectroscopy (2 μg/L)[3].	1. Inadequate qualification of personnel. 2. Photographic plates of poor quality. 3. Insufficient reproducibility.	+/– – +/–	

Organic substances

Oil products (hydrocarbons)	Semyonov, 1977; RD 52.24.454-95	Extraction of oil products from water, separation using thin layer chromatography (TLC) and measurement of IR or UV absorption, or of intensity of luminescence (0.02-0.03 mg/L).	1. Sample contamination at the stage of sampling, preservation and analysis; using dirty glassware and contaminated reagents. 2. Using inadequate standard solution for calibration. 3. Using a chromatographic plate of poor quality. 4. Losses of volatile hydrocarbons in the process of evaporation. 5. Inadequate qualification of personnel. 6. Incorrect sampling.	+ + +/– + – +/– +	Detection and TLC separation of oil products was preferred. The amount of data attained using IR absorption and luminescence are approximately the same. The amount of data acquired by measuring intensity of UV ray absorption is insignificant. The column option was used very infrequently (<5% of data were acquired using this method).
	Semyonov, 1977; RD 52.24.476-95	Extraction of oil products from water, separation using a column with aluminium oxide and measurement of intensity of IR absorption (0.02 mg/L).	1. Sample contamination at the stage of sampling, preservation and analysis; using dirty glassware and contaminated reagents. 2. Using a chromatographic plate of poor quality. 3. Inadequate qualification of personnel. 4. Incorrect sampling.	+ + + +/– +	Considering the great number of factors causing serious errors during oil product detection, the share of unreliable results can be quite high. Excessively high results are more probable (positive error).
Resins and asphalt	RD 52.24.454-95	Extraction of resins and asphalt from water, separation with TLC, selection of a spot giving a yellowish brown luminescence when exposed to UV radiation, measuring intensity of luminescence (0.01mg/L)	1. Sample contamination at the stage of sampling, preservation and analysis; using dirty glassware and contaminated reagents. 2. Using inadequate standard solution for calibration. 3. Using a chromatographic plate of poor quality. 4. Losses of volatile hydrocarbons in the process of evaporation. 5. Inadequate qualification of personnel. 6. Incorrect sampling.	+ + +/– +/– +/– +/– +	Considering the great number of factors causing serious errors during detection of resins and asphalt, the proportion of unreliable results can be quite high. Excessively high results are more probable (positive error).

Parameters	Reference	Basis of methods and limit of detection (in brackets)	The main factors that influence the analytical result	Sign of probable error[1]	Note
Volatile phenols	Semyonov, 1977	Extraction and photometric detection (1μg/L).	1. Prolonged storage of samples, preserved with sodium hydroxide after sampling and prior to analysis. 2. Prolonged distillation 3. Using distilled water that is not clean enough for a blank.	++/− − −	Data reliability for volatile phenols (the so-called phenol index) is mostly distorted by the storage time between sampling and analysis, particularly for samples preserved with sodium hydroxide, as was recommended by Semyonov (1977). Usually phenol concentrations attained are too high (positive error). Later usage of sodium hydroxide as a preservative was not allowed (though in certain cases it is still being used). The problem of unacceptably long sample transportation time to laboratories from remote sampling sites is not yet resolved. In the RD 52.24.480-95 document it is recommended that extraction be performed directly at the sampling site (within 4 hours of sampling) and minimise storage time for extracts, though it is not always possible.
	RD 52.24.488-95	Extraction and photometric detection method (1μg/L).	1. Prolonged storage of samples after sampling prior to analysis. 2. Prolonged distillation 3. Using distilled water, that is not clean enough for a blank.	− − −	
	RD 52.24.480-95	Extraction and photometric method, separating volatile phenols using step-by-step operations: extraction-re-extraction-extraction (1μg/L).	1. Prolonged storage of samples prior to analysis. 2. Influence of naphthene and/or humic acids. 3. Using distilled water that is not clean enough for a blank.	− + −	
Total phenols	RD 52.24.8-84	Extraction and photometric detection (1μg/L).	A considerable influence of the sample composition, in particular, humic substances, naphthene acids, etc.	++	In fact the analythed result does not correspond with the aim of the method. For this reason the parameter was excluded from the work, and the available data should not be taken into account.
Anion surfactants	Semyonov, 1977; RD 52.24.368-95	Extraction and photometric detection using methylene blue.	1. Prolonged storage of samples prior to analysis. 2. Influence of sample composition during analysis of contaminated waters. 3. Influence of suspended particles.	− + −	Data reliability is mostly influenced by the storage time from sampling to the start of analysis. In those cases when samples are transported for a long time from remote sites to laboratories one might expect the results to be too low (negative error).

Organochlorine pesticides	Semyonov, 1977 RD 52.24.66-88; RD 52.24.412-95	Gas chromotography detection after hexane extraction, cleaning, extract and evaporation. Analysis of pesticides in an unfiltered water sample. α-HCH, γ-HCH (1 ng/L), β-HCH (4 ng/L), DDT (11 ng/L), DDE (2 ng/L), DDD (4 μg/L), Chlorethanol ($C_{14}H_9Cl_5O$) (8 ng/L), Trifluralin (3 ng/L).	1. Chromatographic column of poor quality. 2. Reagents and materials that are not clean enough. 3. Unaccounted influence of substances present in the sample or introduced during sampling, storage and analysis (sulphur-containing compounds, phthalates, and other halogen-organic substances), failing to perform additional detection using columns with phases of different polarity. 4. Using a standard of poor quality. 5. Prolonged storage of samples after sampling prior to analysis. 6. Apparatus of inadequate quality.	+/— ++/– ++ + – –	Most GSN laboratories at present have worn apparatus and cannot afford to purchase high quality spare parts and reagents. Due to these and other reasons limits of quantification specified by the guides cannot be attained. In many cases either "zero" concentrations of pesticides are recorded, or, on the contrary, excessively high concentrations (in cases when points 2-4 are not taken into account). In general, the majority of data are doubtful.

Note:

[1] "+" sign stands for positive deviation (error); "-" — for negative deviation (error). A double "+" or "-" shows that the deviation (error) is more probable.

[2] When information on metals is analysed one should take into account that though the methodologies require detection of the so-called "dissolved forms of metals" (i.e., after collection the sample should be filtered through a 0.45 μm pore-size filter, and the filtrate conserved in acid) in real life, due to a lack of capacity to filter the water samples directly at the sampling sites, quite often the water samples were not filtered, but preserved at once (filtering was done later at the laboratories) or filtered through a paper filter. So in fact, the vast majority of the data on metals are not actually dissolved metal forms, but either acid-dissolved forms that are the result of adding acid to an unfiltered sample followed by filtration, or "total forms" (sum of dissolved and suspended forms), which are the result of analysing an unfiltered sample, or the so-called "dissolved forms", attained by filtration through paper filters. In official documents all data were described as "metals in water". Some laboratories targeted detecting "total content" of metals, but after entering the federal data banks, these data were not separated from other data types. In this way, the majority of the metals data probably contains some resulting from analysis of water samples filtered through a 0.45 pore-size filter, but it is impossible to identify them. Before the end of the 1980s two methods were mainly used to detect metals — photometry and emission spectroscopy. Other methods were used very infrequently. In the 1990s the share of atomic absorption spectroscopy results began to grow, but even now photometric detection is used to analyse for iron, copper, zinc and chrome.

[3] To detect metals using emission spectroscopy, a sample is boiled with ammonium persulfate in acid to transform the metals into ion forms. Then they are extracted in the form of complexes with 8-oxyquinoline and diethyldithyocarbamate, the extract is evaporated, the residue is placed into a depression in a graphite electrode, metal atoms are excited in an arc discharge and the radiation is registered on a photographic plate. The concentration of metals is determined by the blackening of the plate.

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Documentation page

Publisher		Date
	Finnish Environment Institute	May 2003

Author(s)
Alexander Zhulidov, Richard Robarts, Robert Holmes, Bruce Peterson, Juha Kämäri, Jarmo Meriläinen and John Headley

Title of publication
Water Quality Monitoring in the former Soviet Union and the Russian Federation: Assessment of Analytical Methods

Parts of publication/ other project publications
The publication is also available in the Internet: http://www.ymparisto.fi/eng/orginfo/publica/electro/fe620/fe620.htm

Abstract
Monitoring of surface water quality in the former Soviet Union (FSU) and the present-day Russian Federation historically held an important place in the hierarchy of science, legal framework and relations between agencies. Sadly, the gap between the intentions, qualification of managers and effective programmes has always been sizeable. Since disintegration of the FSU this gap has become a formidable barrier for collecting reliable monitoring information and producing effective water quality management decisions in the Russian Federation.

Updating the federal system for freshwater quality monitoring in the Russian Federation is complicated by several unresolved problems. The principal issues are political, technical, institutional and financial. The existing Russian model of water chemistry data collection inherited from the FSU has proved unreliable, outdated and unrelated to modern national issues of water management. The quality of produced data is one of the greatest weaknesses of the federal monitoring system both in the Russian Federation and in other states of the FSU. A significant cause of the low reliability of the produced information is the analytical methods used in monitoring, their inappropriate use, non-compliance to laboratory practices when following expert recommendations, insufficient training level of managers and laboratory personnel and under-funding of the federal monitoring system. The growing national priorities in the field of surface water quality control and improvement conflict with the capacity of the Russian Federation to provide necessary information of guaranteed high quality.

Here we make the first attempt to present a critical analysis of the analytical methods used to assess and control surface water quality, to show the main errors arising when applying the recommended analytical methods, and to assess the degree of reliability of produced monitoring information from 1977-1978 and to the present. Our overall objective is to summarize the current situation in order to facilitate implementation of future improvements. |

Keywords
Monitoring, surface water quality, former Soviet Union, Russian Federation

Publication series and number
The Finnish Environment 620

Theme of publication
Environmental policy

Project name and number, if any

Financier/ commissioner
Finnish Environment Institute

Project organization

ISSN	ISBN	
1238-7312	952-11-1380-4	952-11-1381-2 (PDF)

No. of pages	Language
48	English

Restrictions	Price
Julkinen	8 EUR

For sale at/ distributor
Edita Publishing Ltd, P.O.Box 800, FIN-00043 EDITA, Finland, Phone + 358 20 450 00. Mail orders: Phone + 358 20 450 05, fax + 358 20 450 2380. Internet: www.edita.fi/netmarket.

Financier of publication
Finnish Environment Institute, P.O.Box 140, FIN-00251 Helsinki, Finland

Printing place and year
Edita Prima Ltd, Helsinki 2003

Kuvailulehti

Tiivistelmä

Pintavesien vedenlaadun seuranta entisessä Neuvostoliitossa ja nykyisessä Venäjän Federaatiossa on tieteen historian, hallinnon rakenteiden ja virastojen välisten yhteyksien näkökulmasta ollut erittäin merkittävää toimintaa. Valitettavasti tavoitteiden, tehokkaiden ja laadukkaiden seurantaohjelmien, sekä todellisuuden, henkilöstön ja analytiikan laadun, välillä on ollut huomattava ero. Neuvostoliiton hajoamisen jälkeen tämä ero on muodostunut luotettavan seurantatiedon keräämisen ja tehokkaan vedenlaadun hallintatoimen kannalta rajoittavaksi tekijäksi Venäjän Federaatiossa.

Vesistöjen seurantajärjestelmien uudenaikaistaminen on osoittautunut ongelmalliseksi ja edelleen on jäljellä useita ratkaisemattomia ongelmia. Pääongelmat ovat luonteeltaan sekä poliittis-hallinnollisia että teknis-taloudellisia. Venäjän entiseltä Neuvostoliitolta perimä ja nykyisinkin käytössä oleva käytössä oleva vedenlaatuaineiston keräämismalli on osoittautunut epäluotettavaksi ja vanhentuneeksi nykyisiä vesien tilan hallintaan liittyviin tarpeisiin nähden. Tuotetun aineiston laatu on koko seurantajärjestelmän suurin heikkous. Pääsyyt tuotetun aineiston alhaiseen luotettavuuteen liittyvät käytettyihin analyysimenetelmiin, niiden epäasianmukaiseen soveltamiseen, hyvien toimintatapojen noudattamatta jättämiseen, laboratorioiden henkilöstön heikkoon koulutustasoon sekä koko seurantatoiminnan heikkoon taloudelliseen tilanteeseen. Kasvavat kansalliset tarpeet veden laadun parantamiseen ovat ristiriidassa Venäjän Federaation kykyyn tuottaa tätä tarpeellista tietoa, jonka korkea laatu on varmistettu.

Tässä julkaisussa pyrimme ensimmäistä kertaa esittämään kattavan kriittisen analyysin entisessä Neuvostoliitossa ja nykyisessä Venäjän Federaatiossa käytössä olleista veden laadun seurannan analyysimenetelmistä. Esitämme arvion virhelähteistä suosituksen mukaisia menetelmiä käytettäessä sekä arvion havaintotiedon luotettavuudesta vuosista 1977-1978 nykypäivään. Katsauksella nykytilaan pyrimme luomaan pohjaa seurantajärjestelmän laadun kehittämiselle tulevaisuudessa.

ЛИСТ ОПИСАНИЯ ПУБЛИКАЦИИ

Резюме

Мониторинг качества поверхностных вод в бывшем СССР и ныне в Российской Федерации (РФ) занимает важное место в разработке политики и практических мероприятий по контролю качества природной среды. К сожалению, разрыв между намерениями, квалификацией персонала и эффективностью программ всегда был слишком большим. После распада СССР этот разрыв стал одним из основных препятствий для сбора достоверной информации по качеству поверхностных вод и принятия эффективных решений в области управления качеством вод в РФ.

Модернизация федеральной системы мониторинга поверхностных вод в РФ крайне сложна из-за нерешенности ряда проблем, основными из которых являются политические, финансовые и институциональные. Существующая в РФ система сбора данных по качеству вод, унаследованная от бывшего СССР, оказалась ненадежной, устаревшей и не связанной с интересами управления качеством поверхностных вод. Качество получаемых данных является одним из самых слабых мест федеральной системы мониторинга, как в РФ, так и в других государствах бывшего СССР. Ведущей причиной низкой достоверности получаемых данных являются методы, применяемые для их сбора, некачественная лабораторная практика, низкий уровень подготовки персонала и недостаточное финансирование. Растущие национальные приоритеты в области контроля качества окружающей среды явно не соответствуют возможностям федеральной системы мониторинга предоставлять необходимую информацию гарантированно высокого качества.

Авторы попытались представить критический анализ методов, применявшихся с 1977-1978 годов по настоящее время для оценки качества поверхностных вод РФ, показать основные источники ошибок, возникающих при использовании методов, допущенных для использования в контроле качества поверхностных вод, а также оценить достоверность получаемых данных. Основной целью авторов было оценить существующее состояние в области мониторинга качества пресных вод РФ для облегчения внедрения будущих обновлений.

Ключевые слова

Мониторинг, качество поверхностных вод, бывший СССР, Российская Федерация

ENVIRONMENTAL POLICY

Water Quality Monitoring in the former Soviet Union and the Russian Federation: Assessment of Analytical Methods

In this report, a first attempt is made to present a critical analysis of the analytical methods used to assess and control surface water quality in the Russian Federation, to show the main errors arising when applying the recommended analytical methods, and to assess the degree of reliability of produced monitoring information from 1977-1978 to the present. Our overall objective is to summarize the current situation in order to facilitate implementation of future improvements in the Russian Federation.