Scope and structure of diffuse pollution of the Kama reservoir

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Abstract. The natural hydrochemical regime and technogenic pollution of the upper part of the Kama reservoir are considered. It is shown that the composition of pollutants in industrial pollution is determined by the nature of the activities of enterprises engaged in the discharge of wastewater. The volume and chemical composition of discharged wastewater is taken into account through the reporting form 2-TP (water management). However, the increase in the pollutant volume in the reservoir site turns out to be ten times more than the volume of pollutant discharges from the declared sources. This discrepancy is due to diffuse pollution. The article presents a method for calculating the volume of diffuse pollution of a water body. The uneven distribution of pollution across the width and depth of the water body is shown.

1. Introduction

The formation of the chemical composition of river water is determined by both natural, climatic and soil-hydrogeological conditions, and anthropogenic factors. The natural hydrochemical regime of reservoirs is determined by the chemical composition of the rivers flowing into it. This composition in turn is in direct dependence on chemical composition of the soils and breeds composing reservoirs of these rivers. Anthropogenic pollution of a water object is defined by a type of activity of the industrial or agricultural enterprises which are on coast of this object. At the same time the volume and chemical composition of thrown off sewage is usually considered by basin management through a form of the reporting of enterprises 2-TP (water management).

However the volume and chemical composition of thrown off sewage counted in form 2-TP doesn't cover completely introduced pollution because there are many unaccounted, latent polluters, by anthropogenic origin most often. In addition, rivers, despite their potential for dilution and self-purification, cannot always fully accomplish this. Then the water body can be polluted not only by the enterprises on its banks, but also on the banks of its tributaries and even just somewhere on the catchment area. At the same time it is impossible to forget also about an underground reservoir which by the sizes often exceeds the surface and in which it is much more difficult to trace the source of pollution.

The main object of the study is the Kama reservoir, created in 1956. More precisely, it is the upper part of the reservoir, where the Solikamsk-Berezniki industrial hub is located, which is the largest source of technogenic pollution of surface waters in the basin of the Kama River. Its main streams of
pollution are bound to filtrational flows from acting and conserved slimes storages and collectors of liquid waste from the waste heaps.

Analysis of observations during the period of filling the reservoir and over the next three years in 1959 showed that “the sanitary condition of the reservoir depends on two factors: from the effluent of industrial enterprises of Solikamsk and Berezniki in the tail section and from the material of the abrasion processes on the banks of the reservoir in the central section” [1]. Incomparably smaller place is occupied by pollution from water transport in the places of its parking. Rural settlements don't play a significant role in pollution of a reservoir [1].

In connection with the peculiarities of the genesis of technogenic impacts, its influence is most pronounced in the low-flow period, characterized by the lowest values of water discharge, and with the passage of floods its influence is minimal.

The purpose of the study is to calculate the scale of pollution and consider distribution its structure across the width and depth of the stream.

2. Materials and methods

For the study of the natural hydrochemical regime and technogenic pollution the observation materials of the Federal Service for Hydrometeorology and Environmental Monitoring (hereinafter Roshydromet) of the chemical composition of the water of the Kama reservoir for the period from 1974 to 2001, the materials of the state reporting 2-TP (water management) of the Kama basin management and materials of expeditionary research in May and August 2018 were used.

The number of water samples taken by the Roshydromet for chemical analysis during the year is different for each target, but in most cases 7 times a year. On the reservoirs, samples are taken both on the surface (no more than 0.2 m depth) and at a depth near the bottom. Materials of the Roshydromet contain concentrations of pollutants in the water at the water sampling points. Comparing these concentrations by observation points from the upper reaches with those located downstream, it is easy to analyse the accumulated water pollution. Concentrations of pollutants in the upper sites show the natural hydrochemical regime of water bodies. By multiplying these concentrations by the volumes of water in these points and during these sampling periods, it is possible to determine the volumes of pollutants carried by the Kama River. Materials 2-TP (water management) gives the amount of pollutants entering the water bodies between the background and control stations. The difference between the increase in the volume of pollutants according to the observations of the Roshydromet and the volumes of 2-TP (water management) gives the volumes of latent, diffuse pollution. The proposed method is the engineering and evolution of a method for calculating the scale of the anthropogenic impact of the Solikamsk-Berezniki industrial hub on water bodies, described in [2, 3].

The Roshydromet conducts determination of pollutant concentrations at 2 points at 1 vertical in the cross section. Such observations are correct only in the case of a uniform distribution of contaminants across the width and depth of the stream. To assess the correctness of using Roshydromet data, as well as to study the distribution of contaminants (both reported and diffuse) across the width and depth of the reservoir, field measurements of concentrations were taken at a variety of points across the width, depth and length of the reservoir from the Tyulkino cross section to the control plot Ogurdino, located below the Solikamsk-Berezniki industrial hub. It should be noted that since during the field studies 187 verticals were assigned, each had from 3 to 15 points, then, naturally, samples were not taken at each point. At each point was measured conductivity of water. The measurement of specific electrical conductivity as an analogue of mineralization was proposed to be used as early as the 1960s – 1970s, in particular, in [4]. The dependence of mineralization on the electrical conductivity is determined by the chemical composition and temperature of the water, so when using this method, water samples are always taken in a given water body and under given weather conditions, the usual chemical analysis is performed for the samples.
3. Results
The background state of the upper reaches of the Kama River is characterized by an elevated content of iron and a number of other metals in the water (manganese, copper, zinc), largely due to natural soil-geochemical factors.

The impact of industrial complexes and human economic activity in general on water bodies is determined primarily by the influx of pollutants from both point concentrated and dispersed diffuse sources of pollution. The enterprises of the mining, chemical, pulp and paper, and oil refining industries with significant volumes of discharge of insufficiently treated industrial wastewater are concentrated on the territory of the Solikamsk-Berezniki industrial hub. Housing and communal services of large cities are also a source of nitrogen-containing, phenolic and organic compounds entering water bodies. The complexity of the problem is also due to the fact that the Kama river and the reservoirs located on it are the main source of centralized drinking water for the urban population.

How it all affects the chemical composition of the water of the Kama reservoir, shows table 1. It shows the average concentrations of pollutants for the available monitoring period for the Roshydromet sampling stations.

**Table 1.** Average concentrations of pollutants (mg/l) in the upper part of the Kama reservoir according to Rosgidromet.

| The name of the sampling point | Tyulkino town | below Solikamsk | below Berezniki |
|--------------------------------|---------------|-----------------|----------------|
| **Pollutant**                   | Surface       | Bottom          | Surface        | Bottom          | Surface       | Bottom          |
| Mg$^{2+}$                       | 4.69          | 3.88            | 7.72           | 4.62            | 6.42          | 6.21            |
| Cl$^-$                          | 13            | 11.9            | 93.9           | 34.4            | 99.1          | 169             |
| SO$_4^{2-}$                      | 17.1          | 15.1            | 27.7           | 16.9            | 25.1          | 21.98           |
| Mineralization                  | 143           | 124             | 296            | 164             | 305           | 398             |
| Ca$^{2+}$                       | 23.1          | 20.3            | 31.4           | 22.4            | 40.1          | 42.8            |
| NH$_4^+$                        | 0.222         | 0.192           | 0.281          | 0.224           | 0.447         | 0.434           |
| NO$_2^-$                        | 0.002         | 0.001           | 0.009          | 0.002           | 0.032         | 0.079           |
| NO$_3^-$                        | 0.095         | 0.015           | 0.19           | 0.014           | 0.376         | 0.224           |
| Fe$^+$                          | 1.081         | 0.889           | 1.076          | 0.979           | 1.058         | 0.797           |
| Cu$^{2+}$                       | 0.003         | 0.003           | 0.003          | 0.003           | 0.003         | 0.004           |
| Zn$^{2+}$                       | 0.028         | 0.008           | 0.01           | 0.007           | 0.012         | 0.009           |
| Mn$^+$                          | 0.13          | 0.099           | 0.143          | 0.1             | 0.171         | 0.101           |
| Phenols                         | 0.004         | 0.002           | 0.005          | 0.002           | 0.007         | 0.006           |
| Oil products                    | 0.266         | 0.251           | 0.26           | 0.157           | 0.164         | 0.078           |
| Synthetic Surface               | 0.021         | 0.021           | 0.033          | 0.024           | 0.034         | 0.03            |

Based on state reporting materials 2-TP (water management) of the Perm Territory, the volume of pollutants entering the water bodies between Tyulkino and Ogurdino was calculated. Also an additional pollutant introduction was calculated on the considered section of the reservoir. The results of the calculations are presented in table 2.

4. Discussion
The main sources of diffuse pollution of water resources are livestock farms, agricultural fields, residential areas, territories of small settlements, garden and cottage settlements, dumps of rocks, construction and industrial sites. [5]. However, in a large part of the territory of Russia, the main sources of diffuse pollution are agricultural facilities and residential areas, including territories of small settlements, garden and cottage settlements.
Diffuse runoff from these territories is characterized by high concentrations of all forms of mineral nitrogen (N) and phosphorus (P), oil products, heavy metals, and synthetic surfactants [6, 7]. As the pollutants move along the length of the water body, the flow of pollutants is reduced due to absorption of these substances by higher aquatic vegetation and bottom sediments, as well as self-purification processes [8]. But there are also reverse processes associated with the ingress of pollutants into water from aquatic vegetation and bottom sediments.

Table 2. Volumes of pollutants entering water bodies between Tyulkino and Ogurdino (million tons).

| Water cross section/source of pollutants | Magnesium | Chlorides | Sulfates | Mineralization | Potassium | Sodium |
|-----------------------------------------|-----------|-----------|----------|----------------|-----------|--------|
| control water cross section (Ogurdino)  | 0.214     | 5.81      | 0.864    | 13.7           | 0.093     | 0.379  |
| base water cross section (Tyulkino)     | 0.120     | 0.366     | 0.525    | 3.82           | 0.206     | 0.902  |
| introduction on the section             | 0.094     | 5.44      | 0.339    | 9.91           | 0.113     | 0.523  |
| by Materials 2-TP (water management)    | 0.006     | 0.269     | 0.020    | 0.557          | 0.039     | 0.098  |
| diffuse additive                        | 0.088     | 5.18      | 0.319    | 9.35           | 0.074     | 0.424  |
| % diffuse additive from total introduction on the section | 93.6 | 95.1 | 94.1 | 94.4 | 65.6 | 81.2 |

Other sources of diffuse pollution of water bodies are waste heaps and industrial sites of mining enterprises. They are local in nature; they occupy a not so significant place on the map of Russia as the first ones, but the scale of diffuse pollution superinduced by them is truly enormous. Diffuse runoff from industrial areas is characterized by high concentrations of those ingredients that are part of the developed fields, as well as those used by enterprises in their technological chains for processing raw materials into the final product.

According to table 1, one can also estimate the impact of technogenic pollution. According to Table 1, the magnesium content in the water below Berezniki increases by 1.5 times, chlorides by 15 times, total mineralization by 3-4 times, calcium by 2 times, ammonium nitrogen and nitrates by 2 times, and nitrites by 20 times, phenols by 2 times, synthetic surfactants 1.5 times, but the regional ingredients remain the same. Attention is drawn to the fact that the concentration of chlorides in the water below the city of Berezniki at the bottom is several times higher than on the surface.

GI Kulikov wrote in 1959 about the fact that the distribution of pollutants is not uniform in depth [9]. This fact is confirmed by expeditionary studies in 2018. Figure 1 shows the distribution of mineralization in depth along the left bank of the Kama river in the immediate vicinity of the slimes storage, called the "White Sea". Each separate graph is constructed for a separate vertical, located at a designated distance in kilometers from the highway bridge across the Kama river in the city of Berezniki. All verticals are located at a distance of 75-150 m from the coast. High values of mineralization are caused, apparently, by filtration seepage from the “White Sea”. An indirect confirmation of this hypothesis is the very high content of calcium ions in the near-bottom area, which is typical for the wastewater of the soda industry, but is quite atypical for potash brines. It should be noted that the point wastewater discharge, recorded in the state reporting, are absent here.
The results of modeling and processing of numerous field studies from 2008 to 2018 showed that, firstly, the pollution passes along the left bank from the first outlets of wastewater into the Black river to the mouth of the Yayva river below the city of Berezniki (confirmed by 2-dimensional modeling [10-12]). Alignment in width occurs only at Ogurdino village, where the reservoir makes a sharp turn to the right. Secondly, the pollutant stream does not mix with river water for a long time, and most often runs along the bottom (confirmed by 3-dimensional modeling [13, 14]). Note that the three-dimensional numerical simulation was performed using the ANSYS Fluent application software package, based on the implementation of the finite volume method. Parameters were assigned as in [15].

5. Conclusion
According to the proposed method, the volumes of pollutants discharged with wastewater at the site according to the state reporting 2-TP (water management) were compared with the values of pollutant growth according to observations at the Kama reservoir between the base and control stations.

The results in% are given in the last line of table 2. It can be observed that the increase in pollutants for all substances is substantially greater in terms of the amounts reported in the 2-TP reporting (water management). This fact can be explained only by significant volumes of diffuse seepage.

The results of modelling and processing of numerous field studies showed the presence of a significant vertical and horizontal inhomogeneity of the distribution of concentrations of pollutants inside the water flow.

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